Synthesis of Transition Metal Substituted Pentacene Derivatives and Their Application

(遷移金属を置換基にもつペンタセン誘導体の合成及び応用研究)

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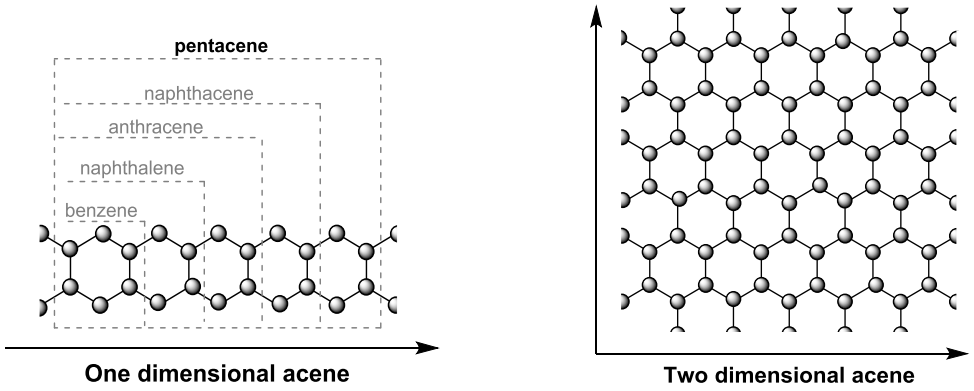
Contents

Abbreviations

°C	degrees centigrade
brs	broad singlet
Bu	butyl
calcd.	calculated
cm	centimeter
δ	chemical shift in parts per million downfield from tetramethylsilane (^{1}H and ^{13}C NMR)
d	doublet
d	day(s)
dd	doublet of doublets
DDQ	2,3-dichloro-5,6-dicyano -1,4-benzoquinone
DMAD	dimethyl acetylenedicarboxylate
dt	doublet of triplets
Eq	equition
equiv	equivalents
Et	ethyl
g	gram(s)
h	hour(s)
HRMS	high resolution mass spectrometry
Hz	hertz
J	coupling constant (in NMR)
L	liter(s)
M	moles per liter
mg	milligram(s)
mL	milliliter
mmol	millimole(s)
N	equivalent concentration
OAc	acetate
Pr	propyl
ppm	parts per million
q	quartet
r.t.	room temperature
s	singlet
t	triplet
THF	tetrahydrofuran
TLC	thin-layer chromatography
μL	microlite

Chapter 1. General Introduction to Synthetic Methods for Acenes and Two-Dimensional Acenes

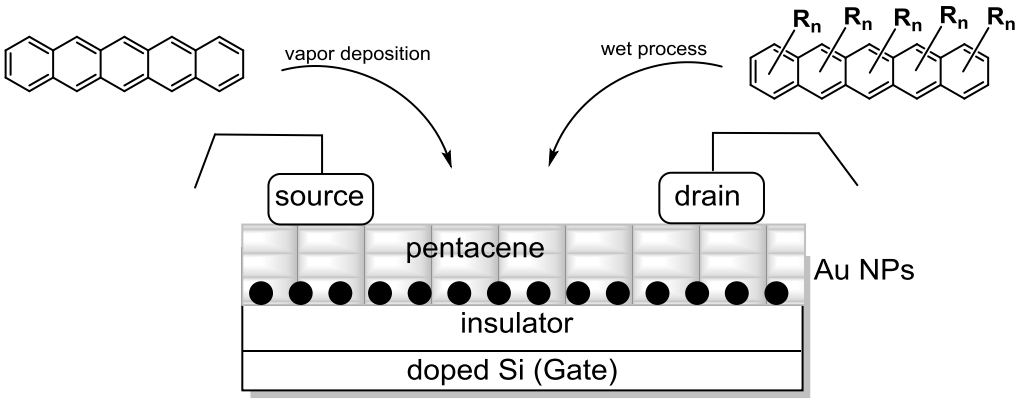
Acenes or polyacenes are simple organic molecules consisting of linearly fused benzene rings. These molecules are very electron rich and have various interesting electronic properties. Typical examples are anthracene (three benzene rings) and pentacene (five benzene rings). Linearly fused benzene rings are one-dimensional acenes, and those fused in a planar arrangement are two-dimensional acenes. The most famous example of a two-dimensional acene is graphene.



1-1. Substituted acenes

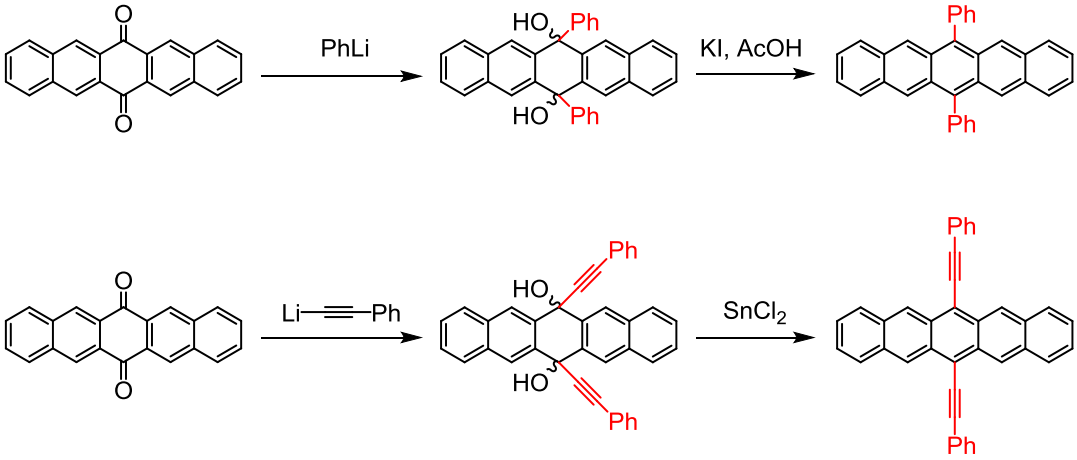
1-1-1. Organic-group-substituted acenes

Pentacene consists of five linearly fused benzene rings. In 1997, pentacene was reported to show the highest charge mobility among organic compounds, comparable to that of inorganic amorphous silicon.[1] However, pentacene has a serious limitation, namely poor solubility in organic solvents. The fabrication of pentacene thin films is therefore expensive; inconvenient vapor deposition methods are needed, because the common wet process (printing) method cannot be used. How can this problem be resolved? One method is the introduction of substituents into pentacene.



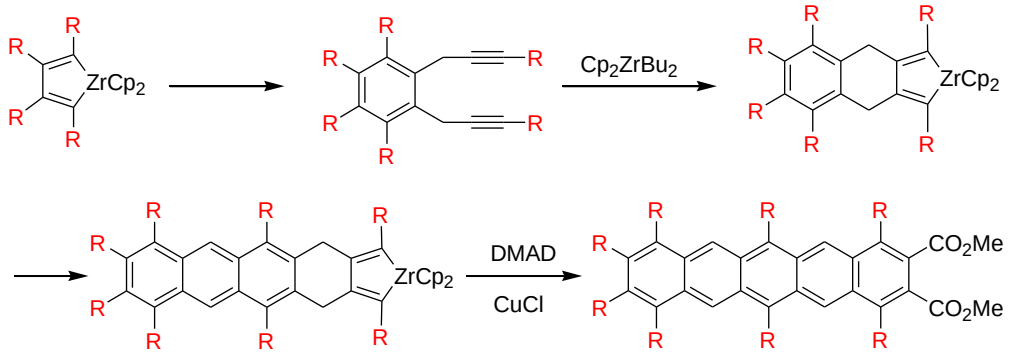
Some examples of substituted pentacenes were reported before 1997, but they are not for the organic materials. The first organic-substituted pentacene derivative, 6,13-diphenylpentacene, was reported in 1942.[2] It was obtained through the reaction of 6,13-pentacenequinone with phenyllithium. No further research was reported until Maulding *et al.* reported the formation of a 6,13-bis(alkynyl)pentacene derivative in 1969. However, the method was the same as that previously used, and involved the reaction between pentacenequinone and an alkynylmetal (Scheme 1).[3]

Scheme 1. Synthesis of substituted pentacenes



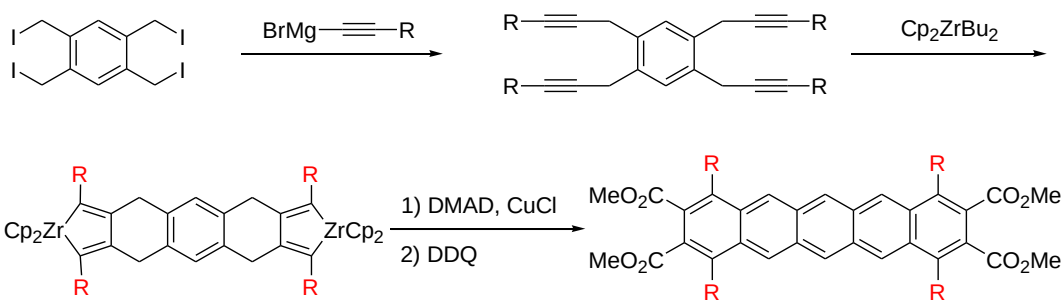
To the best of our knowledge, apart from these occasional reports, no systematic methods for the preparation of substituted pentacene derivatives were published before 1997. In 2000, Takahashi's group reported a novel zirconium-mediated homologation method for the formation of multi-alkyl-substituted pentacene derivatives. The method is shown in Scheme 2. This was the first reported systematic method for the preparation of substituted pentacenes.[4] These substituted pentacenes have good solubilities in common organic solvents.

Scheme 2. Preparation of substituted pentacenes by homologation method



The homologation method extends the aromatic ring system in one direction by diyne cyclization. A more efficient method for the formation of symmetrical pentacene derivatives, i.e., double homologation, was reported by Takahashi's group in 2009.[5] This method extends the aromatic ring system in two directions by tetrayne cyclization (Scheme 3).

Scheme 3. Preparation of substituted pentacenes by double homologation method

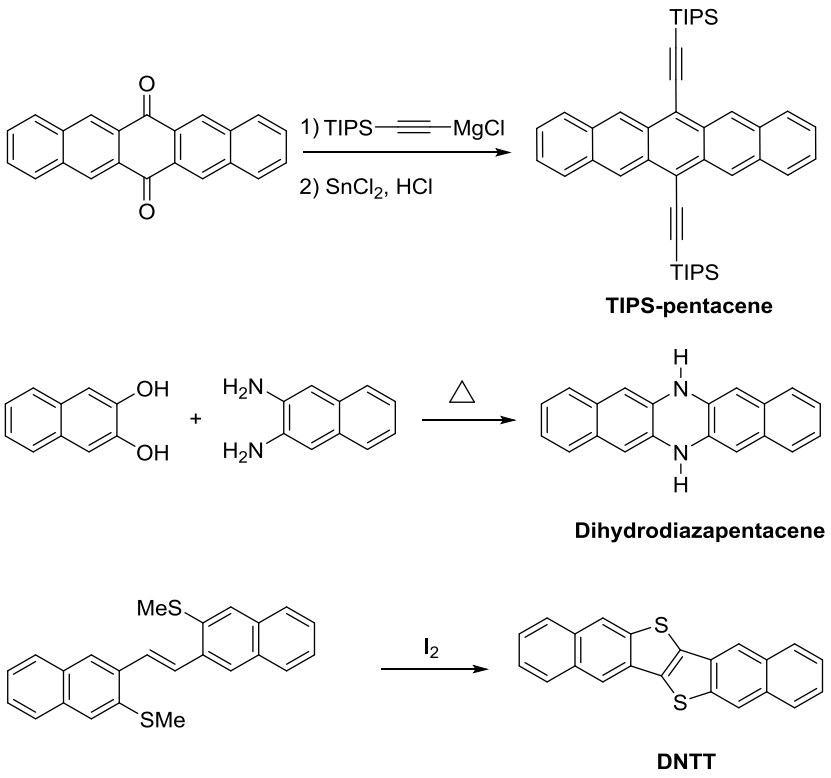


This area then attracted much attention, and many papers on the preparation of substituted pentacenes and analogous compounds have been published (Scheme 4). One example is 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), which was reported by Anthony *et al.* in 2001.[6a] In the pentacenequinone method, the addition of triisopropylsilylethynylmagnesium chloride to 6,13-pentacenedione produces a diol intermediate. Subsequent treatment with a solution of HCl and $SnCl_2$ gives TIPS-pentacene in high yield. The bulky triisopropylsilylethynyl groups on the central ring give TIPS-pentacene significant environmental stability.

Heteroacenes have attracted considerable interest in recent years. Dihydrodiazapentacene was reported by Nuckolls *et al.* in 2003.[6b] Dihydrodiazapentacene has the same molecular shape as pentacene, but nitrogen atoms replace two of the carbon atoms in pentacene. This compound was readily prepared by simple condensation between 2,3-naphthalenediol and 2,3-naphthalenediamine. It has much better environmental stability than that of unsubstituted pentacene. Another highly π-extended heteroacene, DNTT, was reported by

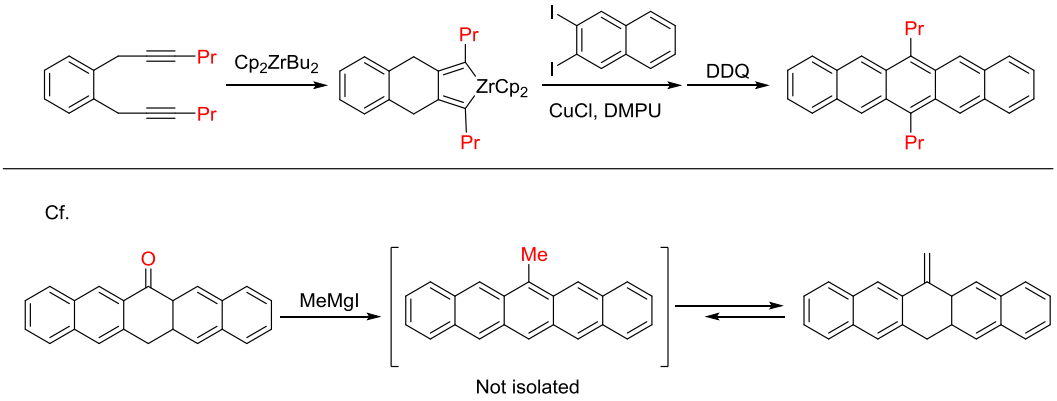
Takimiya *et al.* in 2007.[6c] DNTT has six fused aromatic rings and is air stable. It could be used for high-performance semiconductors.

Scheme 4. Other methods for preparation of substituted pentacenes and analogs



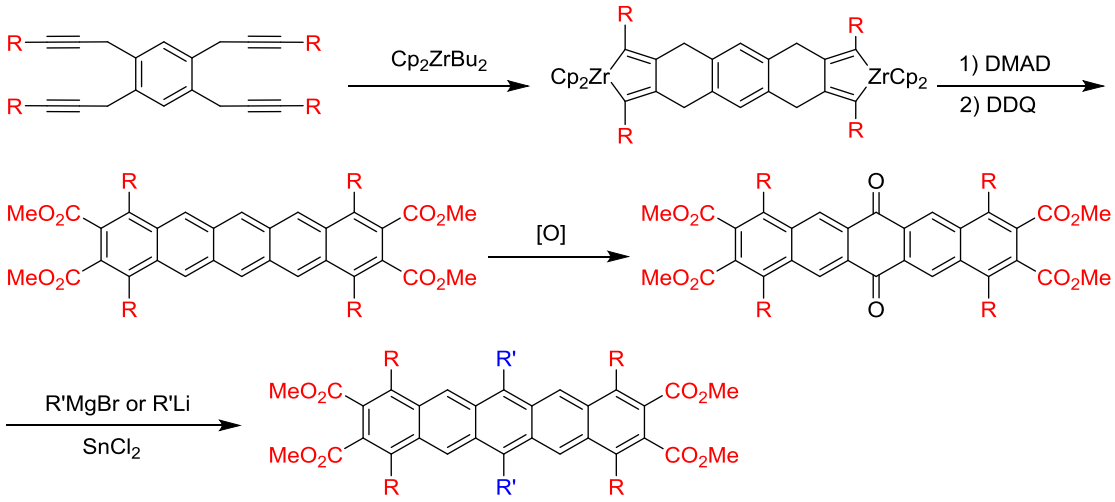
It should be noted that the pentacenequinone method can be used to introduce aryl, alkynyl, or fluorine substituents into pentacene.[7] The introduction of alkyl groups into pentacene using this method is difficult. The reaction of a propyl Grignard reagent with pentacenequinone gave a mixture of unidentified species. Although Clar *et al.* reported the formation of 6-methylpentacene, the isolation was not successful, and a more stable isomer, i.e., 6-methylene-6,13-dihydropentacene, was obtained instead.[8] Tautomerization makes the synthesis of alkylpentacenes very challenging. To overcome this, Takahashi's group developed a zirconocene-mediated coupling method. As shown in Scheme 5, compound 6,13-dipropylpentacene was prepared and isolated successfully. [9]

Scheme 5. Preparation of substituted pentacenes by coupling method



In 2010, Takahashi's group used a combination of the double homologation and pentacenequinone methods to synthesize multi-substituted pentacene derivatives.[10] As shown in Scheme 6, octasubstituted pentacene derivatives were first prepared using the zirconium-mediated double homologation method. Subsequent oxidation of the octasubstituted pentacene derivatives with H_5IO_6 and DDQ gave octasubstituted pentacenequinone derivatives. Finally, the corresponding decasubstituted pentacene derivatives were prepared using the pentacenequinone method.

Scheme 6. Combination of double homologation and pentacenequinone methods for preparation of substituted pentacenes

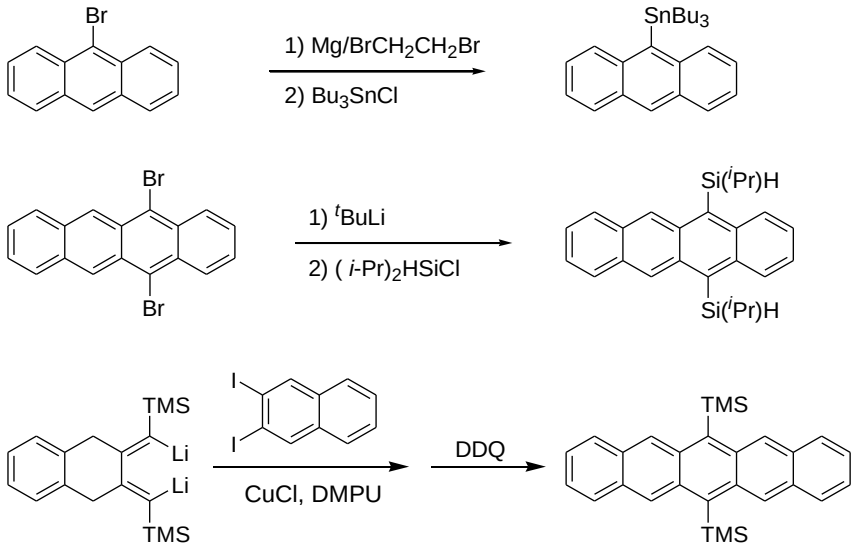


1-1-2. Main-group-metal-substituted acenes

There are many examples of pentacene derivatives substituted with functional groups. Acenes substituted with main-group metals have also have been reported. Several examples are shown in Scheme 7. 9-Tri-*n*-butylstannylanthracene was prepared via the reaction of anthracene bromide with tributyltin chloride.[11a] The first example of a silyl-substituted

naphthacene, 5,12-bis(diisopropylsilyl)naphthacene, was reported in 2006.[11b] The pentacene derivative 6,13-bis(trimethylsilyl)pentacene was reported by Takahashi *et al.* in 2011.[11c] It was formed by the reaction of dilithiobutadiene with diiodonaphthalene, and aromatization.

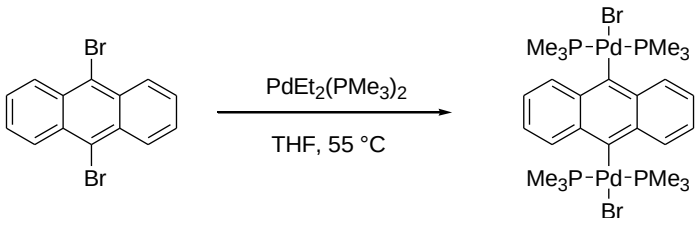
Scheme 7. Main-group-metal-substituted acenes



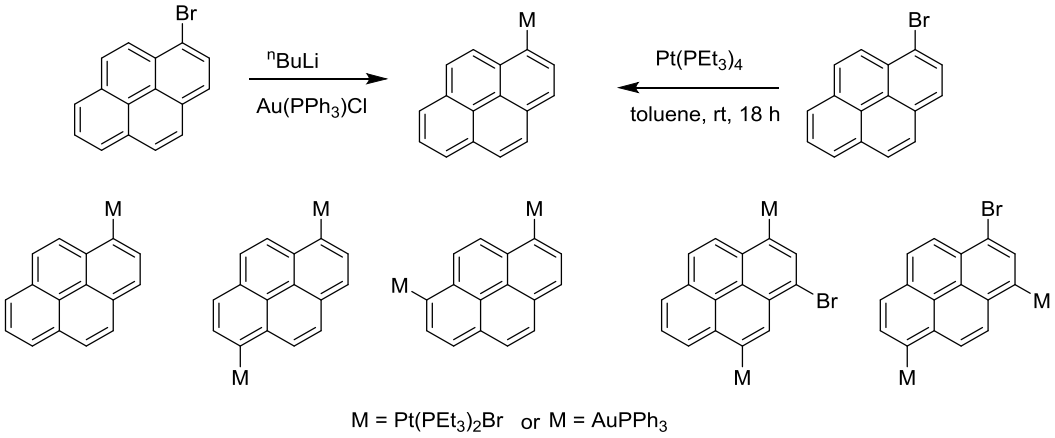
1-1-3. Transition-metal-substituted acenes

Transition-metal-substituted aromatic compounds are well known intermediates in transition-metal-catalyzed or -mediated organic syntheses.[12] They are also important precursors of supramolecules.[13] These complexes can be prepared by oxidative addition or transmetalation reactions.[14] For acenes with transition-metal σ-bonded substituents, the introduction of gold or platinum into anthracene, pyrene, or tetracene has been reported. The electronic absorption and emission spectra and reactivities of acenes are significantly affected by metals.[15] Dipalladated anthracene has been prepared by the oxidative addition of 9,10-dibromoanthracene to *trans*-[$PdEt_2(PMe_3)_2$] in THF at 55 °C (Scheme 8).[16]

Scheme 8. Transition-metal-substituted anthracene



Scheme 9. Transition-metal-substituted pyrenes

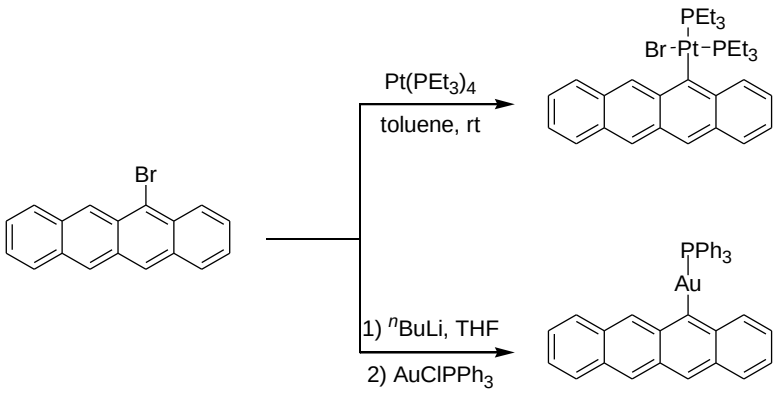


In another study, a series of metalated pyrene complexes were prepared (Scheme 9), and the effects of the metal on the electronic properties of the pyrenyl ring were studied. Oxidative addition of bromopyrene to excess $Pt(PEt_3)_4$ in toluene gave monoplatinated or diplatinated pyrene in good yields. However, the triplatinated pyrene complex was not observed, even with excess $Pt(PEt_3)_4$.

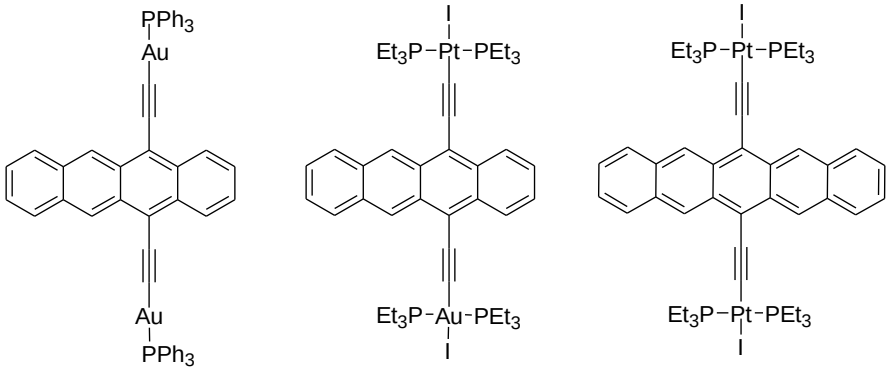
Lithiation of bromopyrene with ^{n}BuLi followed by addition of $Au(PPh_3)Cl$ afforded monoaurated and diaurated pyrene complexes in good yields. Spectroscopic studies showed that the absorption bands of the metalated pyrene complexes were all red-shifted from those of the corresponding pyrenes.[15a]

Recently, Yip *et al.* prepared platinum-substituted or gold-substituted naphthacene derivatives and determined their structures using X-ray analysis (Scheme 10).[15b] They reported that platination of tetracene changes the photophysical properties of the organic chromophore. Significant red-shifts of the absorption and emission spectra of platinated tetracene were observed. However, the platinum- or gold-substituted naphthacenes were unstable in solvents under air. They decomposed within 2 d, via cleavage of the metal–carbon bonds, to give naphthacene.

Scheme 10. Transition-metal-substituted tetracenes



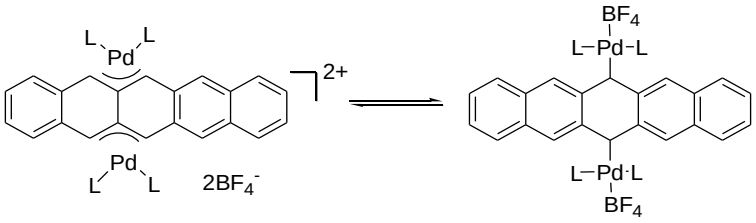
Scheme 11. Gold and platinum complexes of diethynyltetracene and diethynylpentacene



Platinum and gold complexes of diethynyltetracene and diethynylpentacene were reported by Yip *et al.* (Scheme 11),[17] but the platinum and gold atoms were not directly attached to the tetracene and pentacene rings.

To the best of my knowledge, no example of a transition-metal-substituted pentacene derivative has yet been reported. Pentacene derivatives are more unstable than naphthacenes, therefore I thought that transition-metal-substituted pentacenes might be very unstable. Coordination of one double bond to the palladium atom of dihydropentacenepalladium was recently reported by Murahashi *et al*. (Scheme 12)[18] In this case, the palladium–pentacene π-complex is equivalent to a palladated dihydropentacene.

Scheme 12. Palladium–pentacene complex



1-1-4. Summary

Many examples of pentacene derivatives with organic substituents have been reported. Several examples of main-group-metal-substituted anthracenes, tetracenes, and pentacenes have also been reported, and transition-metal-substituted benzenes, anthracenes, pyrenes, and tetracenes have been reported. However, to the best of our knowledge, no example of a pentacene with a σ-bonded transition-metal substituent has been reported. This may be because such pentacene complexes are unstable.

1-2. Two-dimensional acenes: Graphene and graphene ribbon

Recently, graphene has attracted much attention,[19] because it conducts heat and electricity with great efficiency.[20]

Graphene consists of a two-dimensional sheet. It can also be described as a one-atom-thick layer of graphite. It was first isolated from graphite by Geim and Noveselov in 2004.[21] In 2010, they won the Nobel Prize in Physics for their work on this new two-dimensional material.

Graphene is a zero bandgap material. It can be obtained by mechanical cleavage of graphite, for example, using adhesive tape. However, this method produces a mixture of mono- and multi-layer graphenes. Graphene can also be produced by depositing one layer of carbon onto another material.

Graphene ribbons are strips of graphene. Graphene ribbons have a finite bandgap, and are better than graphene for practical applications. The bandgap of a graphene ribbon can be controlled by the width of the graphene ribbon. The charge mobilities of graphene ribbons are related to their band gaps. The properties and performances of graphene ribbons can therefore be controlled. Graphene ribbons are expected to give much better performances than Si and GaAs, and they are attracting much attention as next-generation semiconductor materials.[22]

Figure 1. Relationship between semiconductor charge mobility and bandgap

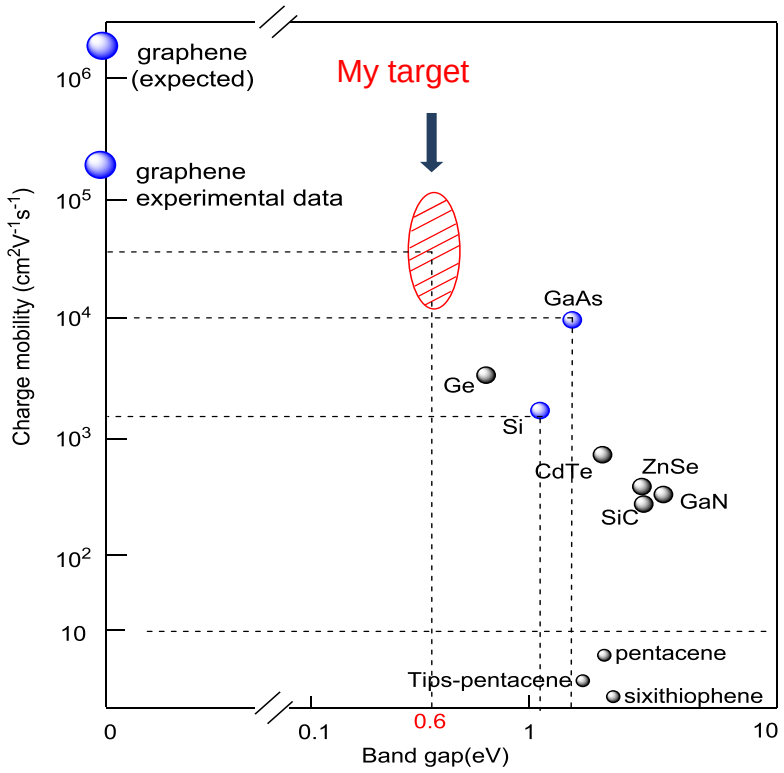


Figure 1 and 2 are taken from a report on science and technology trends.[23] Figure 1 shows the relationship between semiconductor charge mobility and bandgap. It can be seen that the charge mobility of Si is about 1000 $cm^2\ V^{-1}\ s^{-1}$, and the bandgap of Si is about 1.1 eV. The charge mobility of GaAs is about 10 000 $cm^2\ V^{-1}\ s^{-1}$, and the bandgap of GaAs is about 1.4 eV.

The charge mobilities of organic semiconductor such as pentacene,[24a] TIPS-pentacene,[24b] and sexathiophene[24c] are lower than 10 $cm^2\ V^{-1}\ s^{-1}$. Surprisingly, graphene has a zero bandgap, therefore the charge mobility of graphene is expected to be 10^6 $cm^2\ V^{-1}\ s^{-1}$. The charge mobility of graphene is 1000 times higher than that of Si, and 100 times higher than that of GaAs. This is very attractive, but not of practical use in this research.

My target was to achieve a charge mobility higher than those of Si and GaAs. Figure 1 shows that this target corresponds to a graphene ribbon bandgap of about 0.6 eV. Figure 2 shows the relationship between bandgap and graphene ribbon width; it can be seen that a 0.6 eV bandgap requires a graphene ribbon of width about 1.3 nm, and we therefore needed to prepare graphene ribbon of this width.

Figure 2. Relationship between bandgap and width of graphene ribbon

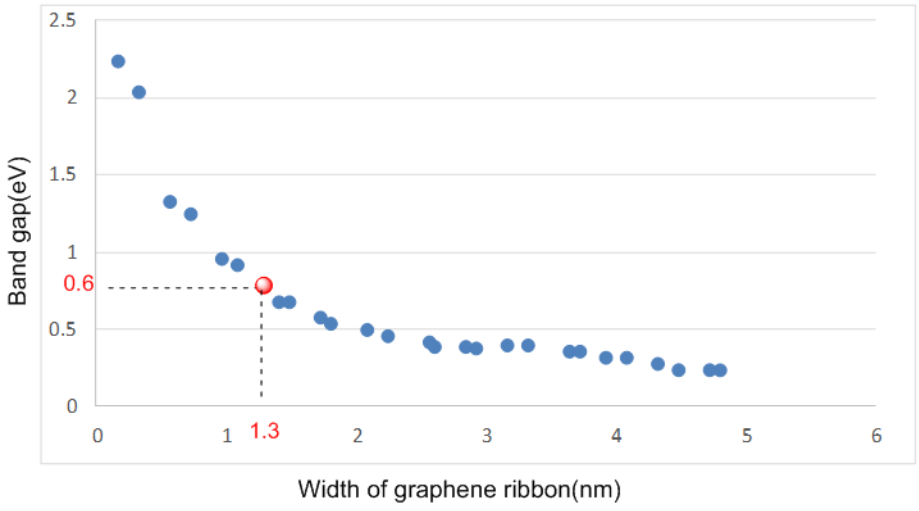
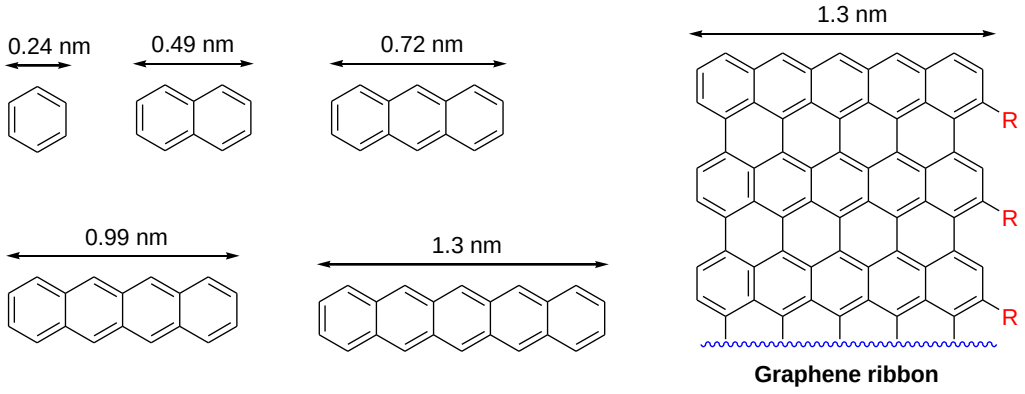


Figure 3. Pentacene-based graphene ribbon



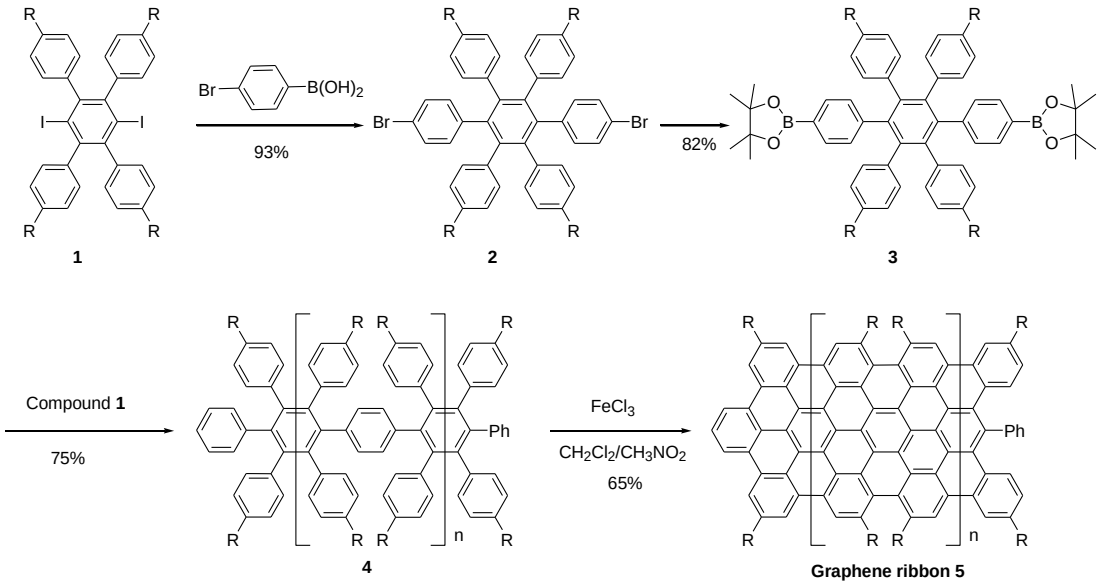
The molecular lengths of benzene to five fused benzene rings range from 0.24 to 1.3 nm (Figure 3); the length of five fused benzene rings, i.e., pentacene, is around 1.3 nm. Pentacene-based graphene ribbons were therefore my target.

Figure 2 shows that as the width of the graphene ribbon increases, the graphene bandgap decreases. Graphene ribbons based on longer acenes such as hexacene, heptacene, and octacene should therefore perform better than pentacene-based ones. However, longer acenes such as hexacene and heptacene are very unstable,[25a,b] and difficult to handle. Unsubstituted octacene and nonacene have only been detected in an argon matrix.[25c] A pentacene-based graphene ribbon is therefore the best choice.

There are two major methods for producing graphene ribbons, i.e., mechanical exfoliation and organic synthesis. Graphene ribbons can be easily obtained using physical methods, but the graphene ribbon width cannot be controlled, and the edges are not smooth. Another problem is functionalization. However, these problems can be solved by using organic synthetic methods. The width of the graphene ribbon can be controlled, and substituents can be selectively introduced to alter the properties.

1-2-1. Preparation of graphene ribbon

Scheme 13. Preparation of graphene ribbon **5**

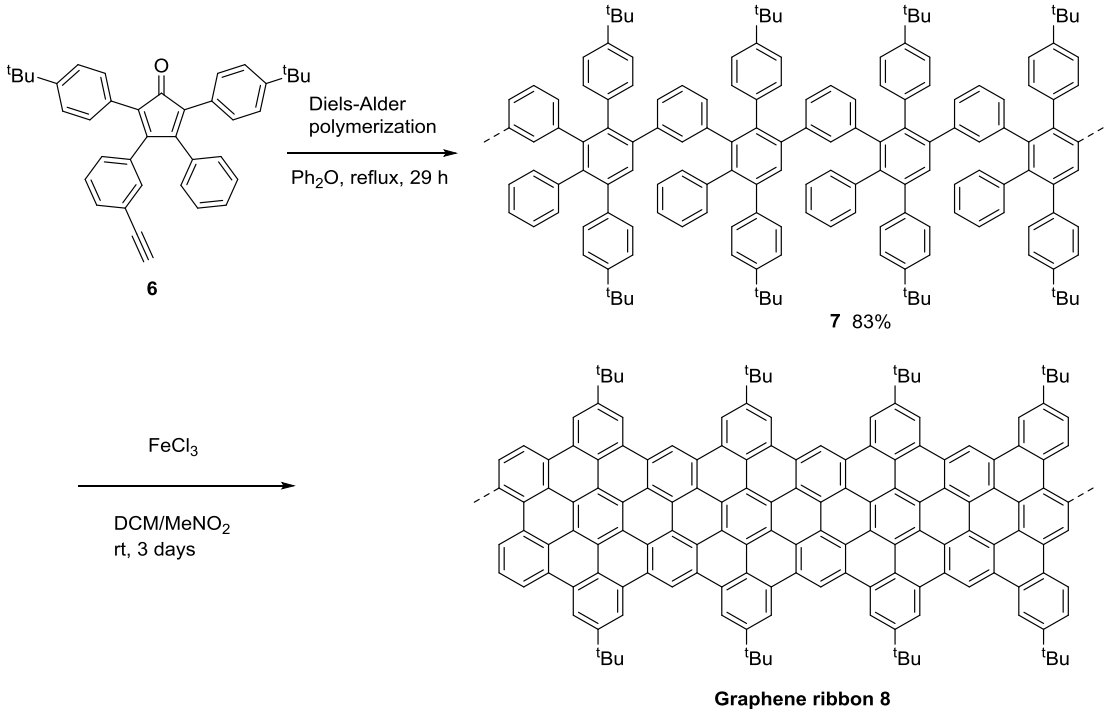


Several papers have reported the preparation of graphene ribbons. An example is shown in Scheme 13. Suzuki coupling of diiodobenzene **1** with 4-bromophenylboronic acid gave hexaphenylbenzene derivative **2**. Lithiation of **2** with ^{n}BuLi, followed by addition of a boron reagent, afforded the bisboronic ester **3**. Polymerization of **3** with diiodobenzene **1** at 120 °C

for 3 d gave polymer **4**. Cyclodehydrogenation of **4** with $FeCl_3$ provided graphene ribbon **5**. The UV-vis spectrum of **5** was obtained (λ_{max} = 485 nm).[26]

Another method, reported by the same group, is shown in Scheme 14. Diels–Alder polymerization of **6** gave polymer **7**, and cyclodehydrogenation of **7** with $FeCl_3$ produced graphene ribbon **8** in high yield. The optical bandgap of graphene ribbon **8** is 1.88 eV. The UV-vis spectrum of graphene ribbon **8** was also obtained (λ_{max} = 550 nm).[27]

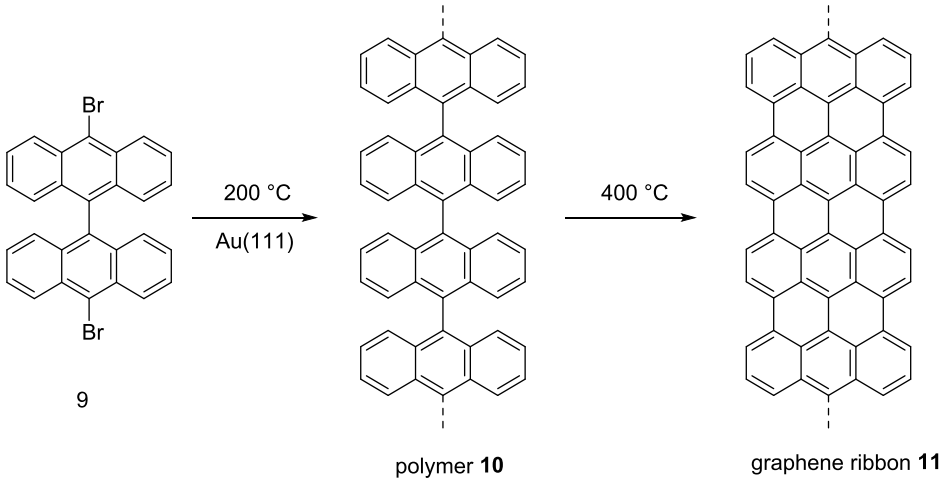
Scheme 14. Preparation of graphene ribbon **8**



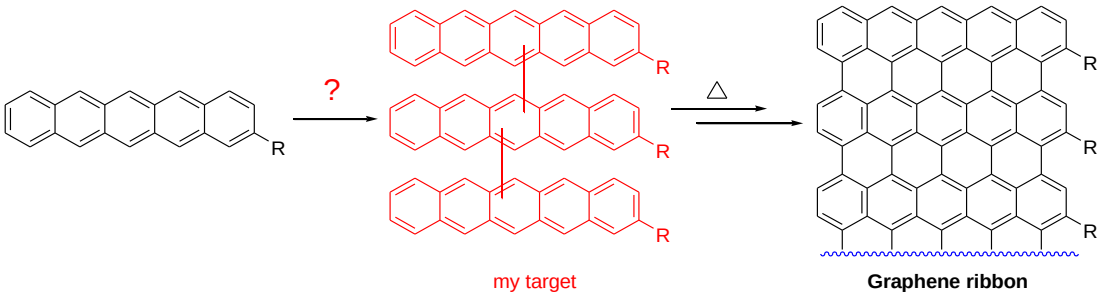
In addition to oxidative coupling, thermal sublimation is a common method for fabricating large-area π materials. Thermal sublimation of 10,10'-dibromo-9,9'-bianthryl monomer **9** onto a Au(111) surface gave linear polymer **10**. Intramolecular cyclodehydrogenation of **10** by annealing at 400 °C produced graphene ribbon **11** (Scheme 15).[28]

It should be noted that in this reaction the graphene ribbon was obtained by C–C bond formation among acenes. Such compounds can be regarded as two-dimensional acenes. The key step is the formation of the first C–C bond. However, the reported thermal conditions are quite harsh and the molecular weight is not controllable. The selective formation of acene oligomers is more attractive than polymerization, but has not yet been widely studied.

Scheme 15. Preparation of graphene ribbon **11**



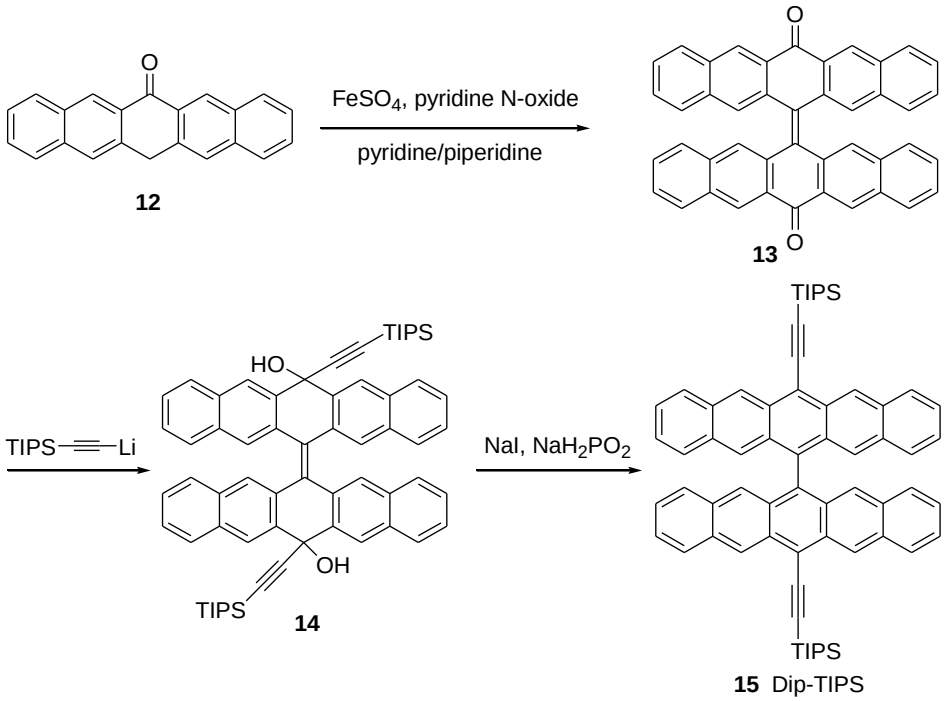
To the best of our knowledge, the synthesis of pentacene-based graphene ribbons has not yet been reported Pentacene oligomers are important precursors for the preparation of pentacene-based graphene ribbons. However, there is no systematic method for the preparation of pentacene oligomers, and only a few papers have reported the formation of pentacene dimers. The selective preparation of pentacene oligomers with substituents in the same direction was therefore my target.



1-2-2. Methods for preparation of pentacene dimers

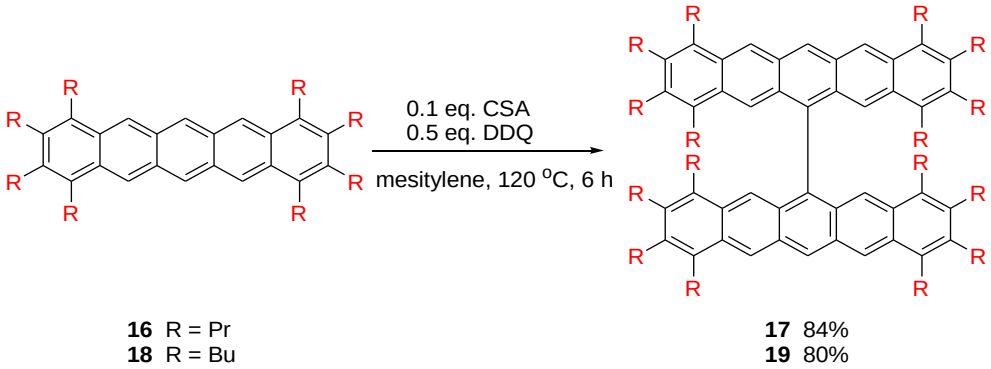
Several methods have been reported for the preparation of pentacene dimers. In 2010, Wu *et al.* reported the synthesis of Dip-TIPS **15**, shown in Scheme 16. Pentacenone **12** was treated with $FeSO_4$ and pyridine *N*-oxide in a mixture of pyridine and piperidine to give 6,6'-bispentacenequinone **13**. Treatment of **13** with triisopropylsilylethynyllithium gave diol **14**. Reduction of **14** with sodium iodide and sodium hypophosphite provided the central-ring pentacene dimer **15** in 74% yield.[29] However, pentacene oligomers such as pentacene trimers cannot be prepared using this method.

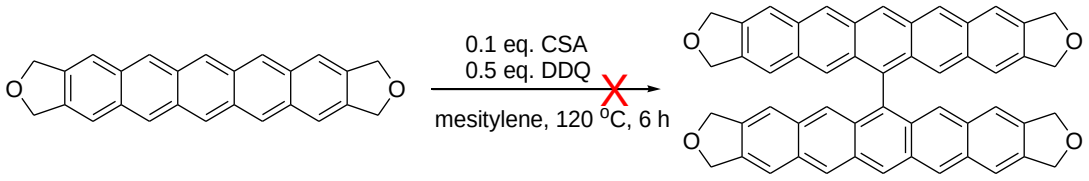
Scheme 16. Preparation of pentacene dimer **15**



In 2011, Takahashi's group reported a novel method for formation of the central-ring pentacene dimers **17** and **19**.[30] Substituted pentacene **16** or **18** was treated with 0.1 equiv of camphorsulfonic acid (CSA) and 0.5 equiv of DDQ in mesitylene to give the corresponding pentacene dimers in high yields. In this method, multi-electron-donating groups are necessary for the dimerization reaction at the central ring of the pentacene derivative, otherwise such side dimers of pentacene cannot be formed; for example, the central-ring pentacene dimer **21** was not formed by this method, because pentacene **20** does not have a sufficient number of electron-donating groups. This method is therefore limited (Scheme 17).

Scheme 17. Previous pentacene dimerizations reported by our group

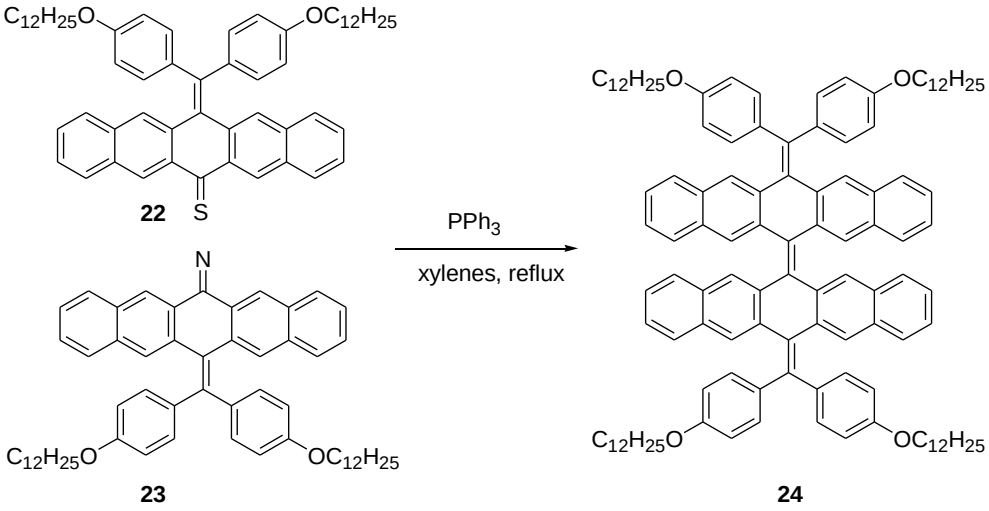




20 **21 Not formed**

In 2013, Nuckolls *et al.* reported the synthesis of the pentacene dimer derivative **24** by the reaction of pentacene fragments **22** and **23** in the presence of PPh_3 (Scheme 18).[31] However, this type of pentacene trimer or oligomer has not yet been reported.

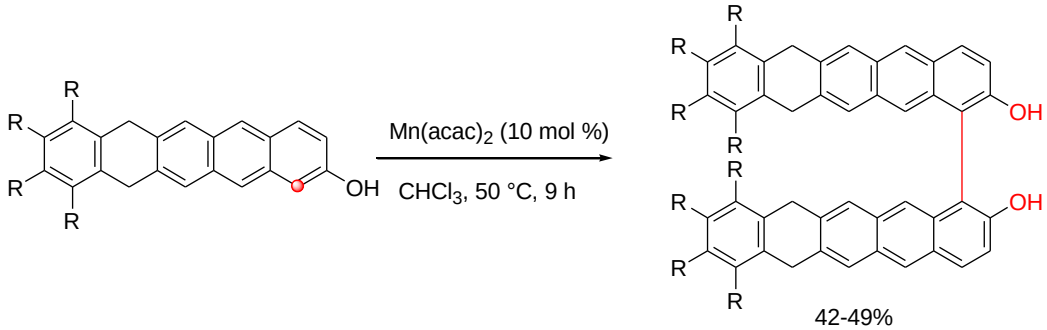
Scheme 18. Preparation of pentacene dimer derivative **24**



22 **23** **24**

In 2014, Dr. Zhang, a member of Takahashi's group, developed an oxidative coupling method for pentacene dimer formation using a manganese catalyst (Scheme 19).[32] A series of first-ring-side dimers of pentacene derivatives were prepared successfully. However, pentacene trimers or oligomers cannot be prepared using this method.

Scheme 19. Preparation of pentacene dimers



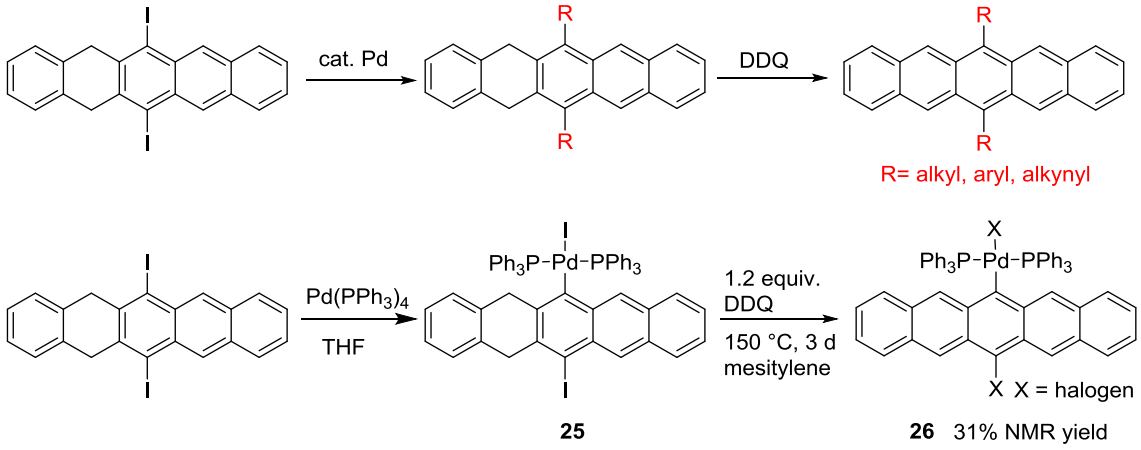
1-2-3. Summary

Several papers have reported for the formation of graphene ribbons. However, as far as we know, there has been no report of the synthesis of pentacene-based graphene ribbons. Pentacene oligomers are important precursors of pentacene-based graphene ribbons. Although several methods have been reported for the formation of pentacene dimers, there is no systematic method for the preparation of pentacene oligomers. In this thesis, C–C formation using transition metals was developed as a general method for the preparation of pentacene oligomers with substituents in the same direction.

1-3. This work

Very recently, Dr. Jia, a member of Takahashi's group, developed a palladium-catalyzed cross-coupling method for the introduction of substituents into pentacene. She also isolated the palladated dihydropentacene intermediate **25** (Scheme 20).[33] Surprisingly, it was a stable complex. However, after aromatization of complex **25** with DDQ, the iodine atom was exchanged with another halogen. The iodine may have exchanged with chlorine, with DDQ as the chlorine source.

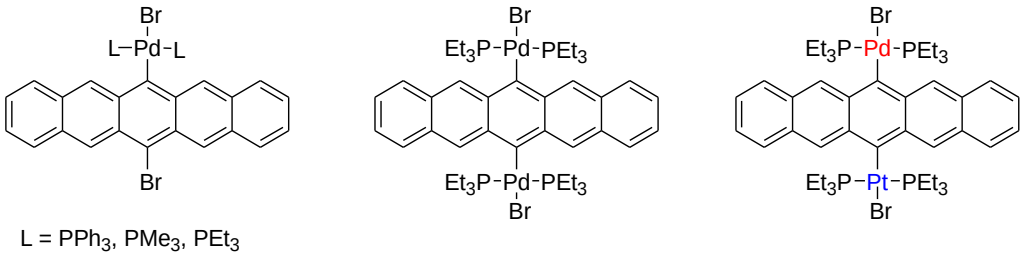
Scheme 20. Previous work of Takahashi's group



Iodine is too active in this reaction, and was exchanged during aromatization. Therefore, in my work I used bromine instead of iodine. 6,13-Dibromo-5,14-dihydropentacene was used as the substrate; a series of transition-metal-substituted pentacene derivatives were successfully prepared. This type of palladated dihydropentacene complex could also be useful for further reactions and construction of pentacene oligomers.

The work described in this thesis can be separated into four parts.

Part I Synthesis and Characterization of Palladated Pentacene Derivatives

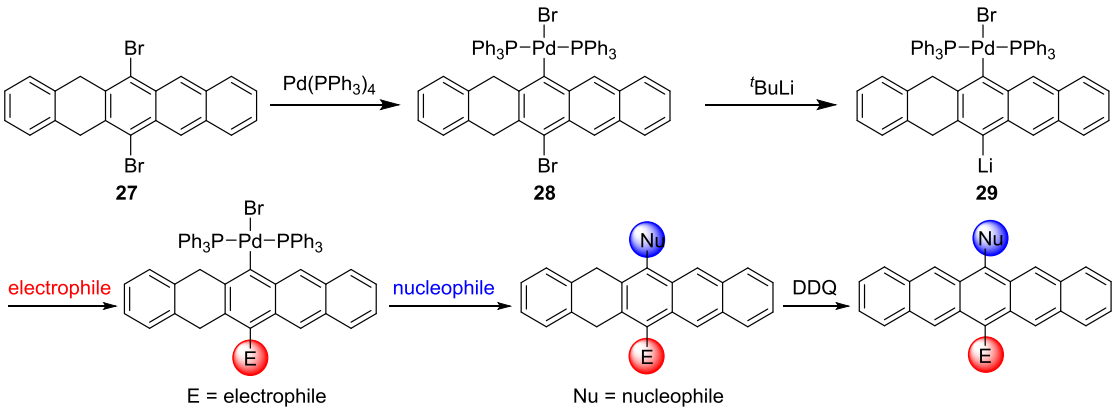


Oxidative addition of 6,13-dibromo-5,14-dihydropentacene to $Pd(PPh_3)_4$ was followed by aromatization. The corresponding central-ring-palladated pentacene was obtained as an unexpectedly stable complex, even in a solvent under air. PPh_3 was exchanged with PMe_3 or PEt_3 by ligand exchange. Aromatization gave the corresponding palladated pentacene containing PMe_3 or PEt_3.

The reaction of 6,13-dibromo-5,14-dihydropentacene with 1.2 equiv of $Pd(PPh_3)_4$ gave the monopalladated dihydropentacene in good yield. Formation of the dipalladium-substituted dihydropentacene derivative was not observed, even when the amount of $Pd(PPh_3)_4$ was increased to 4 equiv. The PPh_3 ligands of the central-ring- and second-ring-palladated pentacenes were exchanged for the electron-donating PMe_3 or PEt_3 ligand. The reactivity of bromine at the opposite side increased. Oxidative addition of monopalladated dihydropentacene bromide to $Pd(PPh_3)_4$ proceeded smoothly to give the dipalladated pentacene complex. This method was used to prepare a series of dipalladated pentacene complexes, and mixed transition-metal-substituted pentacene complexes were prepared successfully. The structures of some palladated pentacene derivatives were verified by X-ray analysis. UV-vis absorption and emission spectra of these palladated pentacene derivatives were also obtained.

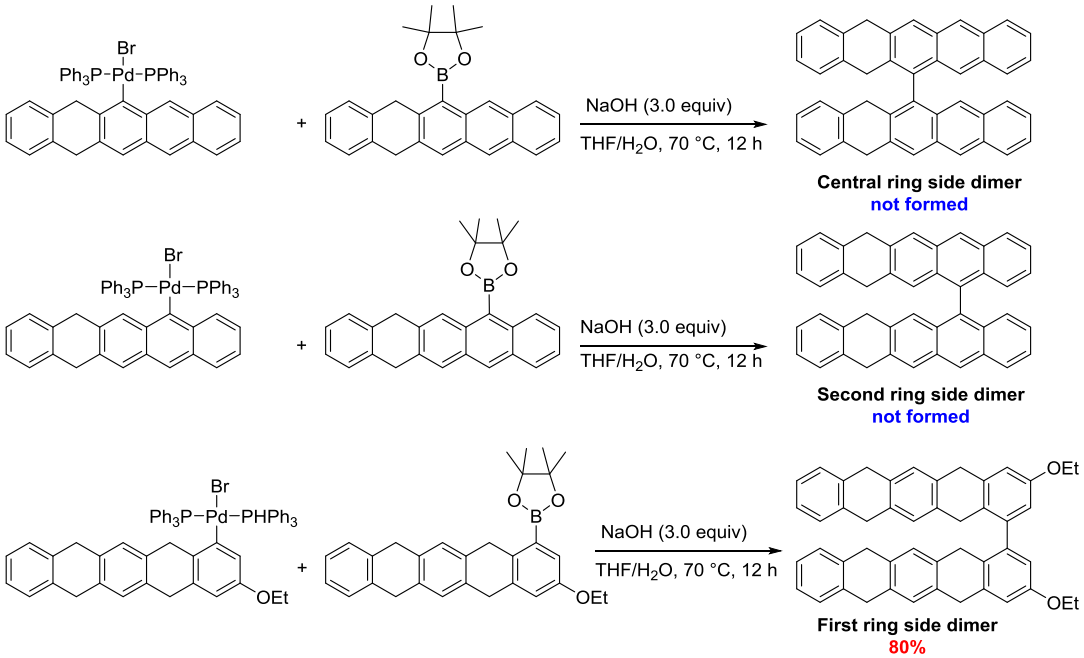
Part II Introduction of Substituents from Electrophiles and Nucleophiles into Pentacene using Palladated Pentacene

Many methods for the formation of substituted pentacene derivatives have been reported. In our homologation and coupling methods, the substituents on pentacene come from the starting alkynes. In the pentacenequinone and cross-coupling methods, all the substituents on pentacene come from nucleophiles. In this part, I report the introduction of substituents using electrophiles and nucleophiles successively. The advantage of my method is that the substituents on these pentacene derivatives come from both nucleophiles and electrophiles.



Lithiation of 6,13-dibromo-5,14-dihydropentacene **27** with BuLi was not selective. 6-Bromo-5,14-dihydropentacene was obtained in very low yield. However, lithiation of central-ring-monopalladated pentacene complex **28** with ^{t}BuLi in THF/toluene afforded lithiated palladium reagent **29** in high yield. This important intermediate **29** was used to perform reactions with electrophiles. A series of substituents were introduced into pentacene from electrophiles. The palladium part then reacted successfully with nucleophiles to give pentacene substituents.

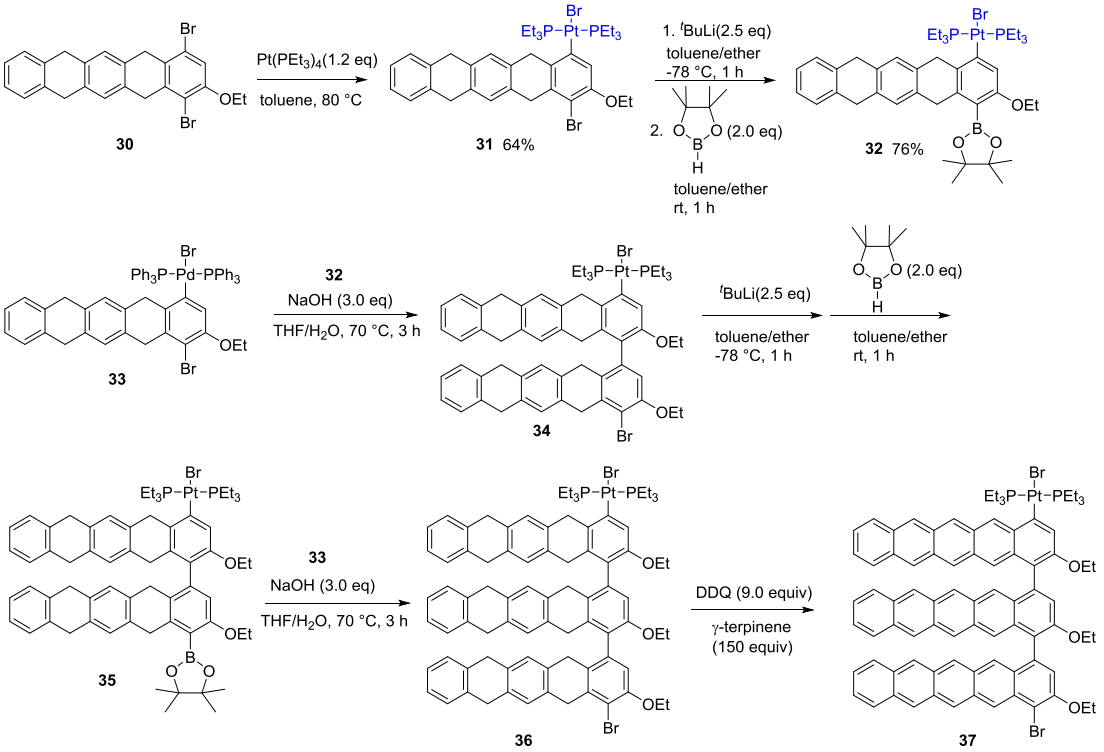
Part III Synthesis of Pentacene Dimers using Palladated Pentacene



With the central-ring-palladated dihydropentacene in hand, its dimerization was studied. However, the central-ring-side dimer of pentacene was not obtained by the cross-coupling reaction, probably because the steric hindrance of the central ring was too high. Pentacene derivatives with palladated second and terminal rings were then prepared and used for dimerization reactions. However, the second-ring dimer of pentacene was not obtained, because of the bulkiness of the two pentacene derivatives. The terminal-ring-palladated pentacene is less

bulky than the central- and second-ring-palladated pentacenes. The first-ring-side dimer of pentacene was obtained in high yield under the same reaction conditions.

Part IV Selective Oligomerization of Pentacene Derivatives using Platinum



Pentacene oligomers are important precursors of pentacene-based graphene ribbons. However, to date there has been no report of the synthesis of pentacene oligomers. In the work described in this section, I successfully developed a selective oligomerization of platinum pentacene derivatives. In the previous section, the preparation of terminal-ring dimers of pentacene was described. However, this dimer does not have two substituents in the same direction. This is because the *meta* positions of the ethoxy groups of two pentacene derivatives were coupled during cross-coupling. In order to align the substituents in the same direction, the *meta* position of the ethoxy group on one pentacene should be coupled with the *ortho* position of the ethoxy group of another pentacene, therefore activation of the *ortho* position of the ethoxy group is necessary.

Oxidative addition of dibromotetrahydropentacene **30** to $Pt(PEt_3)_4$ occurred selectively at the *meta* ethoxy group. Because the reactivity of the platinum complex is lower than that of the palladium complex, so the *meta* position of the ethoxy group was protected by Pt(II). Activation of the *ortho* ethoxy group through introduction of a boronic ester group gave complex **32**. Complex **33**, in which palladium is introduced at the *meta* ethoxy group, is described in Chapter 4. Coupling of **32** with **33** was performed. The desired product **34**, with substituents in the same direction, was obtained. This homologation method was successfully used to prepare pentacene

trimer **37** with substituents in the same direction.

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Chapter 2. Synthesis and Characterization of Palladated Pentacene Derivatives

Abstract

A series of monopalladated pentacene derivatives were synthesized by oxidative addition of dibromodihydropentacene to $Pd(PPh_3)_4$ and then aromatization. From 6,13-dibromo-5,14-dihydropentacene, palladated pentacenes at the central ring were prepared. Central ring palladated pentacene with PPh_3 ligands was unexpectedly stable even in the solvent under air. Moreover, a series of dipalladium and mixed transition metals substituted pentacene derivatives were prepared by two steps one pot reaction successfully. The UV-vis absorption spectra of these complexes had remarkable red-shifted compared with pentacene.

2-1. Introduction

Pentacene has received much attention in relevance to organic materials. Pentacene is not soluble in organic solvent. Therefore, many substituted pentacene derivatives have been prepared with various organic groups to improve the solubility.[1-2] As for main metal substituted pentacenes, there are some limited numbers of examples.[3] To date, transition metals-substituted benzene, anthracene, pyrene and tetracene have been reported (Figure 1).[4] However, to the best of our knowledge, there is no example for transition metal substituted pentacene derivatives.

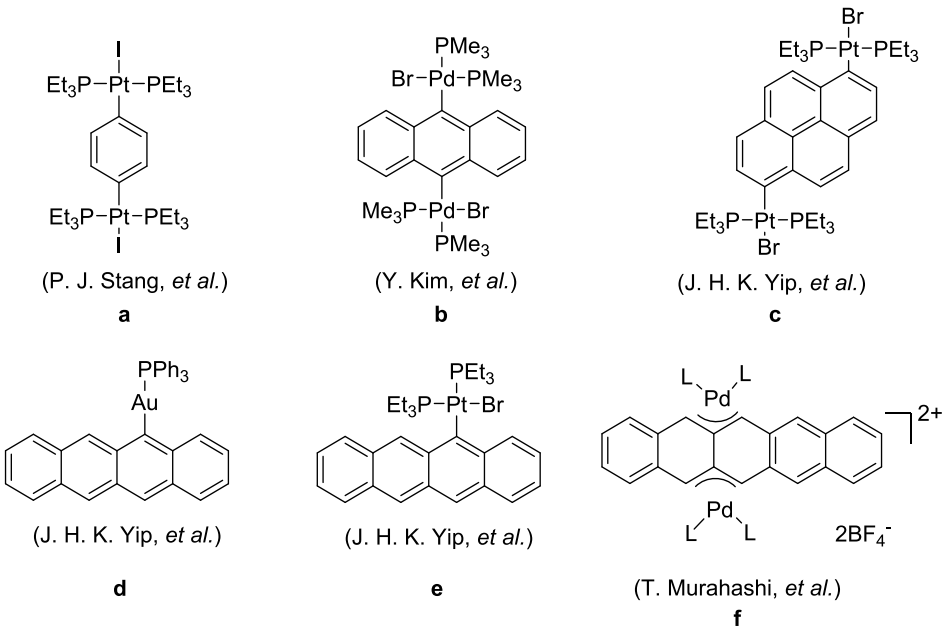


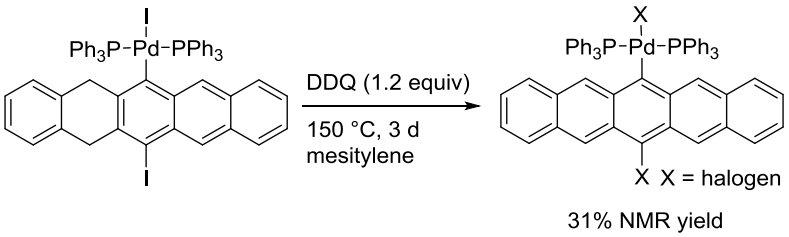
Figure 1. Some examples of transition metals substituted compounds

One of the major reasons is suggestion of instability of such pentacene derivatives. It is known that palladated anthracene derivative **b** has been prepared and it is stable.[4c] But as for naphthacene derivatives, it was quite different. Recently, Yip *et al* prepared gold substituted naphthacene **d** or platinum substituted naphthacene **e** and determined their structures by X-ray analysis. They reported that those platinum substituted and gold substituted naphthacenes were unstable in solvents under air. They decomposed within 2 days by the cleavage of the metal-carbon bonds to give naphthacene.[4d]

In general, pentacene derivatives are more unstable than naphthacenes. Therefore, I thought that transition metal substituted pentacenes might be very unstable. A dihydropentacene palladium π–complex **f** was recently reported by Murahashi *et al*.[5] Very recently, a former Takahashi's group member Dr. Jia has reported cross-coupling reaction for the introduction of organic substituents into pentacene.[6] She also isolated the palladated

dihydropentacene intermediate. After aromatization of the palladated dihydropentacene, the iodine was changed to other halogen (Scheme 1). That because the iodine was too active in this reaction.

Scheme 1.



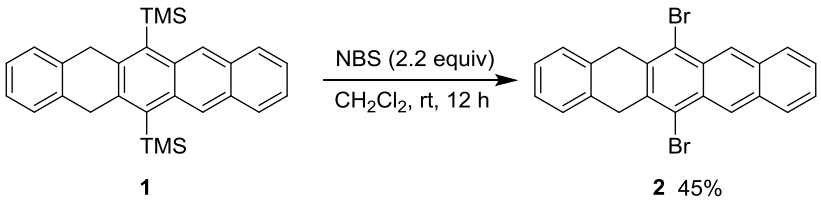
So here, I changed the iodine to bromine. 6,13-Dibromo-5,14-dihydropentacene was used as substrate. Oxidative addition of 6,13-dibromo-5,14-dihydropentacene to $Pd(PPh_3)_4$ was followed by aromatizaiton. Fortunately, the corresponding central ring palladated pentacene was obtained as an air-stable complex. By the ligands exchanged reaction, the PPh_3 ligands could be changed to PMe_3 or PEt_3. After aromatization, the corresponding palladated pentacenes were prepared successfully. Moreover, a series of dipalladated pentacene derivatives were prepared by one-pot reaction. The structures of some palladated pentacene derivatives were verified by X-ray analysis.

2-2. Results and Discussion

2-2-1. Synthesis of central ring monopalladated pentacene derivatives

Previously Takahashi's group reported the synthesis of 6,13-bis(trimethylsilyl)-5,14-dihydropentacene **1**,[7] which could be readily converted to dibromodihydropentacene **2**. The synthetic method is shown in Scheme 2.

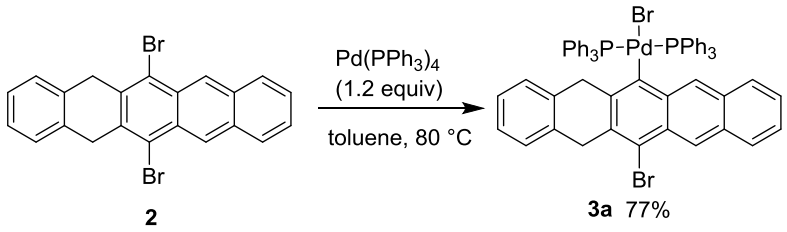
Scheme 2. Synthesis of 6,13-dibromo-5,14-dihydropentacene **2**



Dibromo-*o*-xylene was converted to a diyne. Reaction of the diyne with Cp_2ZrBu_2 gave zirconacyclopentadiene. The iodinated product of the zirconacycle was lithionated. And dilithiobutadiene was coupled with 2,3-diiodonaphthalene in the presence of CuCl and DMPU to afford bis(trimethylsilyl)dihydropentacene **1** in 40% yield. Compound **1** was treated with NBS in dichloromethane to give dibromodihydropentacene **2** in 45% yield. This product was

characterized by NMR spectra and HRMS.

Scheme 3. Synthesis of central ring palladated dihydropentacene **3a**



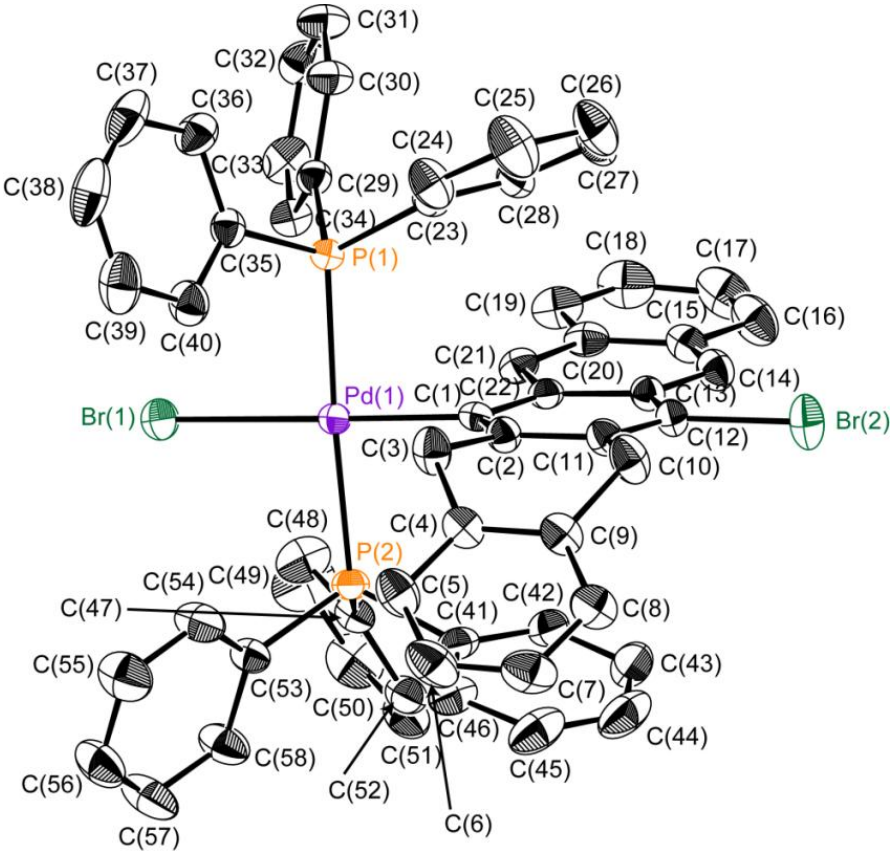
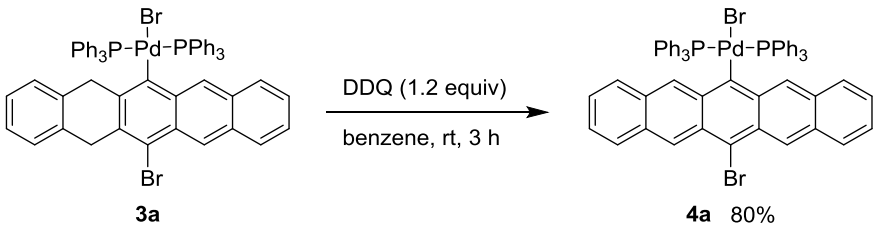


Figure 2. X-ray structure of complex **3a**

Dibromodihydropentacene **2** was treated with $Pd(PPh_3)_4$ to afford palladated dihydropentacene **3a** in 77% isolated yield (Scheme 3). Green crystals of complex **3a** were grown by slow diffusion of hexane into chloroform solution at room temperature. The structure of **3a** was determined by X-ray crystallographic analysis (Figure 2). We could see the palladium with PPh_3 ligands attached to the central ring of dihydropentacene clearly. The skeleton of dihydropentacene bent at the second ring.

Scheme 4. Aromatization of central ring palladated dihydropentacene **3a**



Aromatization of complexes **3a** was carried out by using DDQ (Scheme 4). Treatment of **3a** with 1.2 equiv DDQ afforded palladated pentacene **4a** in 80% isolated yield. The reaction underwent in benzene at room temperature for 3 h. Isolation and purification were carried out by silica gel column chromatography. Fortunately, blue single crystals of **4a** were obtained from a mixture solution of benzene and hexane. The X-ray structure of **4a** is shown in Figure 3. It is quite clear that the flat pentacene skeleton is attached with Pd moiety though σ-bond.

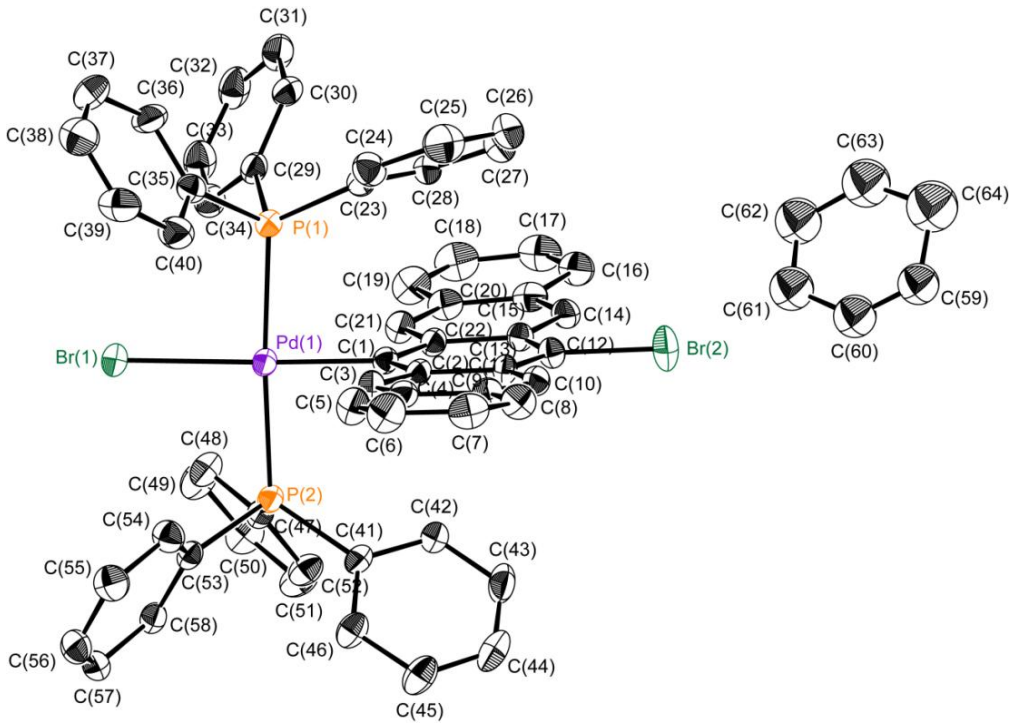
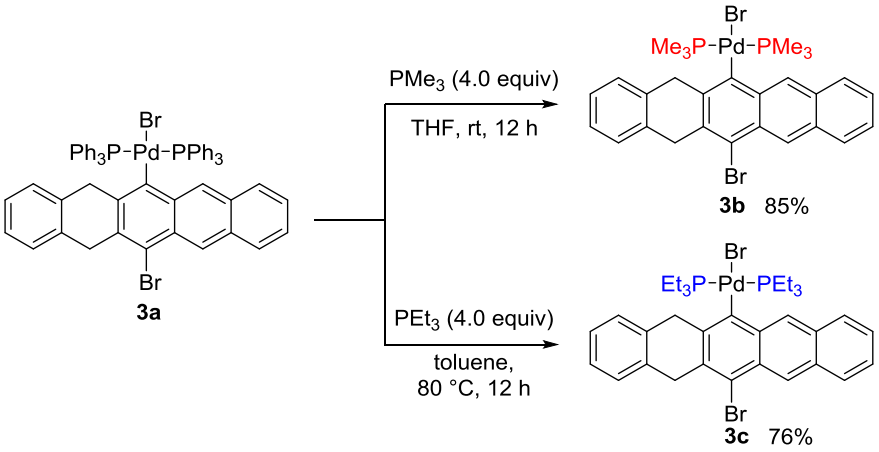


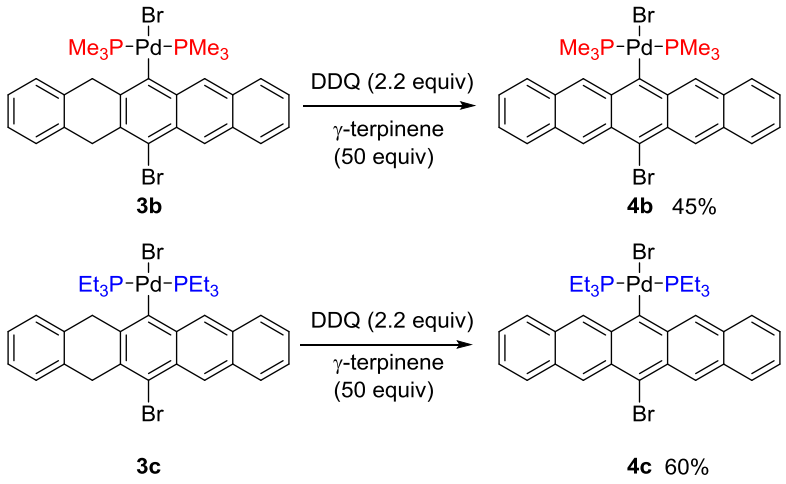
Figure 3. X-ray structure of complex **4a**

Scheme 5. Synthesis of central ring palladated dihydropentacene **3b** and **3c**



The ligands of complex **3a** could be changed to PMe_3 and PEt_3, respectively. Complex **3a** was treated with 4.0 equiv of PMe_3 in THF at room temperature for 12 h, complex **3b** was obtained in 85% yield. When complex **3a** reacted with 4.0 equiv of PEt_3 in toluene at 80 °C for 12 h, complex **3c** was formed in 76% yield (Scheme 5).

Scheme 6. Aromatization of central ring palladated dihydropentacene **3b** and **3c**



Aromatization of complex **3b** with 1.2 equiv of DDQ at room temperature for 1 h gave a mixture of starting material and DDQ adduct. I then optimized the reaction conditions. Firstly, complex **3b** reacted with 2.2 equiv DDQ to give DDQ adduct cleanly. The adduct was treated with 50 equiv of γ-terpinene at 80 °C for 3 h to provide palladated pentacene **4b** in 45% yield. By the same procedure, the palladated pentacene **4c** was obtained in 60% yield (Scheme 6). The X-ray structure of **4b** and **4c** are shown in Figure 4 and Figure 5, respectively.

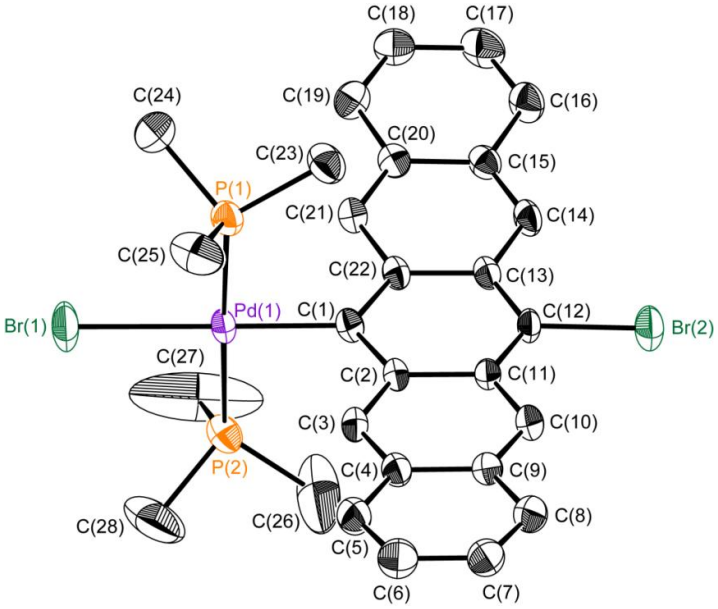


Figure 4. X-ray structure of complex **4b**

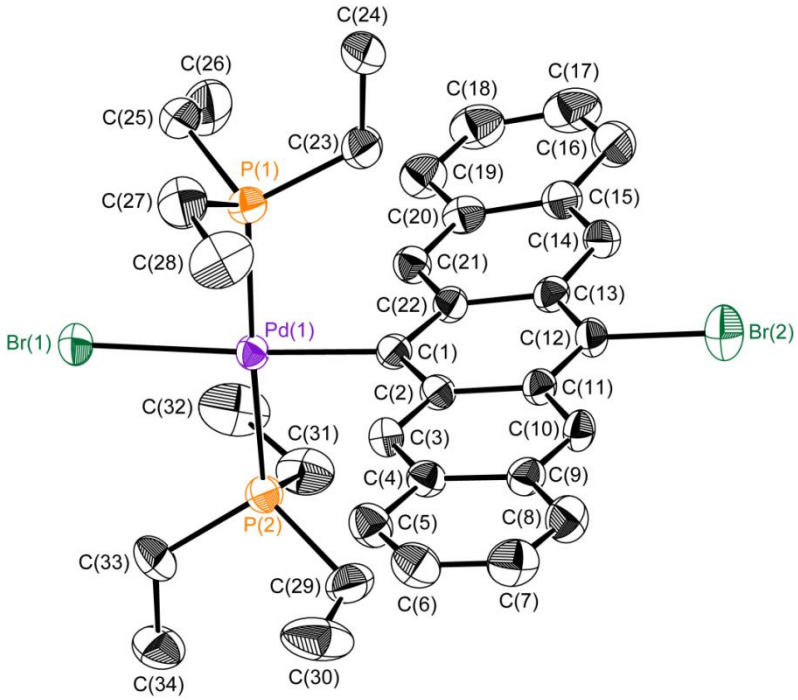


Figure 5. X-ray structure of complex **4c**

As mentioned above, platinum or gold naphthacene derivatives were very unstable. It decomposed within 2 days in organic solvent under air according to the literature. However, surprisingly, complex **4a** was stable in benzene under air. After 2 days, 100% of the complex remained unchanged. After 10 days, a little decomposition of **4a** was observed. But it is notable that the metal-carbon bond was not cleaved under the conditions. The central ring is the most reactive ring of the pentacene skeleton. Bulky palladium moiety blocking the central ring is probably one major factor for the unusual stability of **4a**.

UV-vis spectra of **4a** showed strong resonance at 664 nm (Figure 6). They had remarkable red-shift compared with pentacene (λ_{max} = 577 nm),[8] 6,13-diphenylpentacene (λ_{max} = 604 nm),[9] 6,13-ditrimethylsilylpentacene (λ_{max} = 607 nm), and 6,13-triisopropylsilylethynylpentacene (λ_{max} = 643 nm).[10]

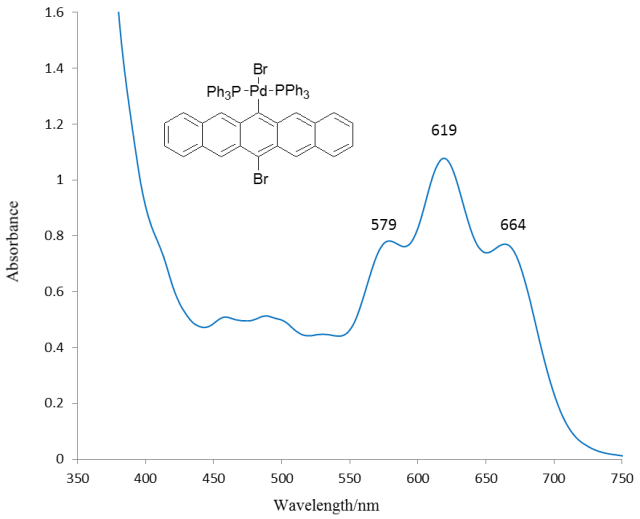
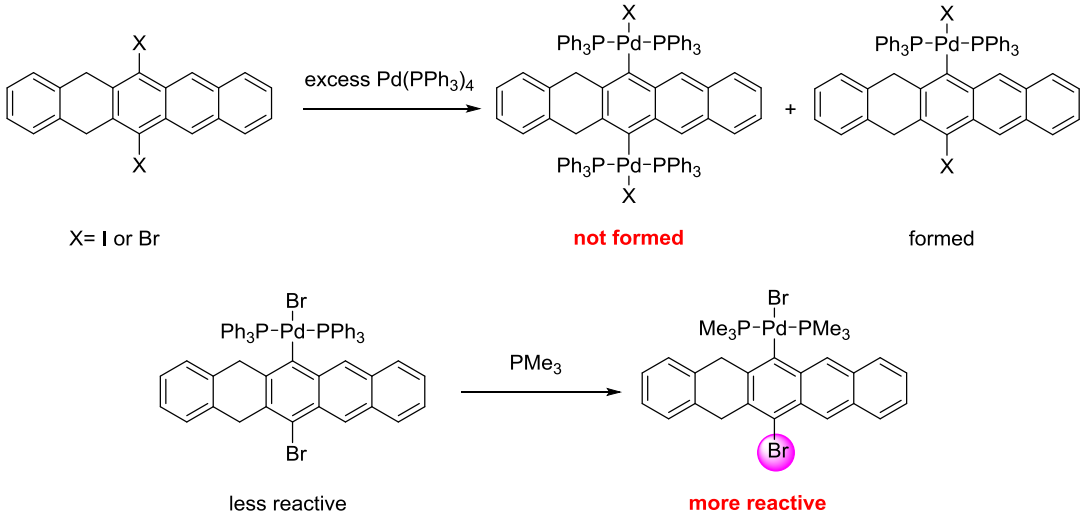


Figure 6. Absorption spectrum of palladated pentacene **4a** in $CHCl_3$ at rt.

2-2-2. Synthesis of dipalladated pentacene complexes

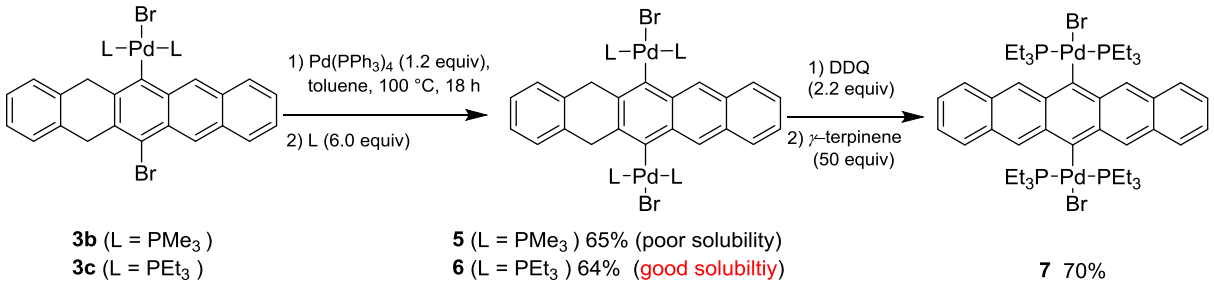
I found that even excess amounts of $Pd(PPh_3)_4$ was used, the dipalladium substituted dihydropentacene derivative was not observed. Only the monopalladated dihydropentacene was formed (Scheme 7). Probably the palladium with PPh_3 lead to the opposite bromine less reactive. Because PPh_3 was electron-withdrawing ligand, if the PPh_3 ligand was changed to electron-donating PMe_3 ligand, the opposite bromine would be more reactive.

Scheme 7. Oxidative addition of $Pd(PPh_3)_4$ to dihydropentacene halide



For this purpose, complex **3b** with PMe_3 ligands was treated with 1.2 equiv $Pd(PPh_3)_4$ in toluene at 100 °C for 18 h. Proton NMR spectrum of the mixture showed that complex **3b** disappeared. At the same time a set of complicated peaks was observed. Without isolation, after the solution was cooled to room temperature, 6.0 equivalent of PMe_3 was added. The mixture was stirred at room temperature for 12 h, one set of clearly peaks was observed. After purification by silica gel column chromatography, the central ring dipalladated dihydropentacene complex **5** was obtained in 65% yield. However, because of poor solubility of complex **5** in benzene or toluene, aromatization of complex **5** was failed.

Scheme 8. Synthesis of central ring bimetallic pentacene complexes



Complex **3c** was treated with 1.2 equiv $Pd(PPh_3)_4$ in toluene at 100 °C for 12 h. After starting material **3c** disappeared (monitored by TLC), the solution was cooled to room temperature. To the reaction mixture 6.0 equivalent of PEt_3 was added. The mixture was stirred at 80 °C for 12 h. Dipalladated dihydropentacene complex **6** was obtained in 64% yield. The structure of complex **6** was verified by X-ray analysis as shown in Figure 7. Complex **6** with PEt_3 ligands has better solubility than complex **5**. Aromatization of complex **6** with 2.2 equivalent of DDQ and 50 equivalent of γ-terpinene gave the corresponding central ring dipalladated pentacene **7** in 70% yield.

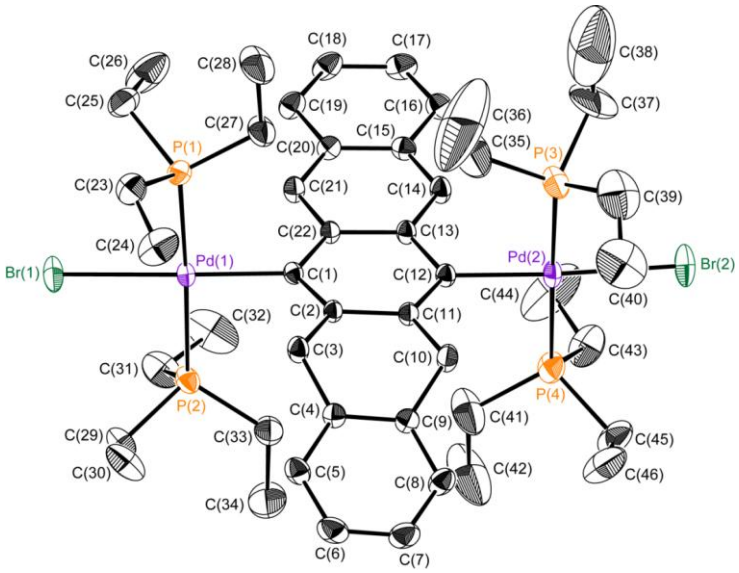


Figure 7. X-ray structure of complex **6**

The UV-vis spectrum of **7** was measured in chloroform at room temperature. The maximum absorption of complex **7** appears at 672 nm (Figure 8). It is red-shifted about 29 nm compared with 6,13-triisopropylsilylethynylpentacene (λ_{max} = 643nm). Dipalladated pentacene **7** is also very stable under air. It dissolved in C_6D_6 under air for 3 days, 100% of **7** remained. After 4 days, 97% of **7** remained. The structure of complex **7** also was verified by X-ray analysis (Figure 9). I can see that two palladium with PEt_3 ligands attached to the central ring of pentacene flat skeleton clearly.

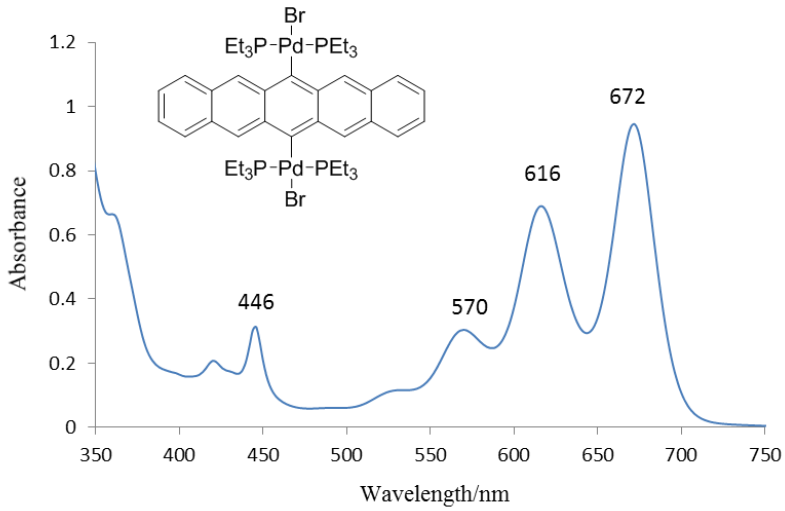


Figure 8. Absorption spectrum of central ring dipalladated pentacene **7** in $CHCl_3$ at rt

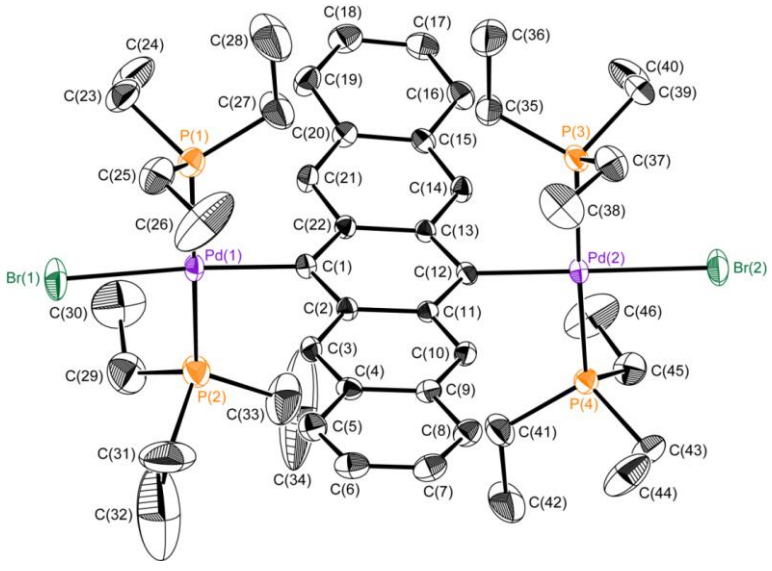
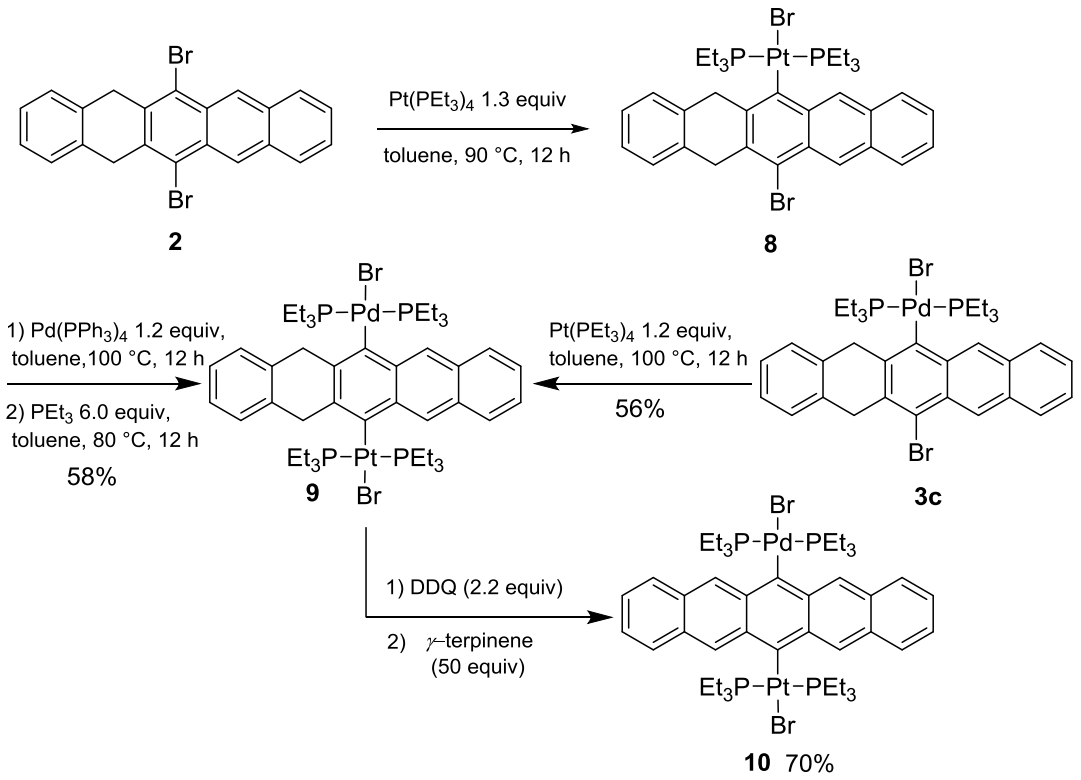


Figure 9. X-ray structure of complex **7**

2-2-3. Synthesis of central ring mixed metals substituted pentacene complexes

Scheme 9. Synthesis of central ring mixed metals substituted pentacene complexes



Platinated dihydropentacene **8** was prepared by oxidative addition of 6,13-dibromo-5,14-dihydropentacene to $Pt(PEt_3)_4$. Treatment of complex **8** with 1.2 equivalent of $Pd(PPh_3)_4$ was followed by addition of 6.0 equivalent of PEt_3 gave a mixed-transition metals-substituted dihydropentacene **9** in 58% yield. The complex **9** could be also prepared by the reaction of complex **3c** with $Pt(PEt_3)_4$ directly. Aromatization of complex **9** with 2.2 equiv DDQ and 50 equivalent of γ-terpinene gave the corresponding central ring mixed transition metals substituted pentacene **10** in 70% yield (Scheme 9).

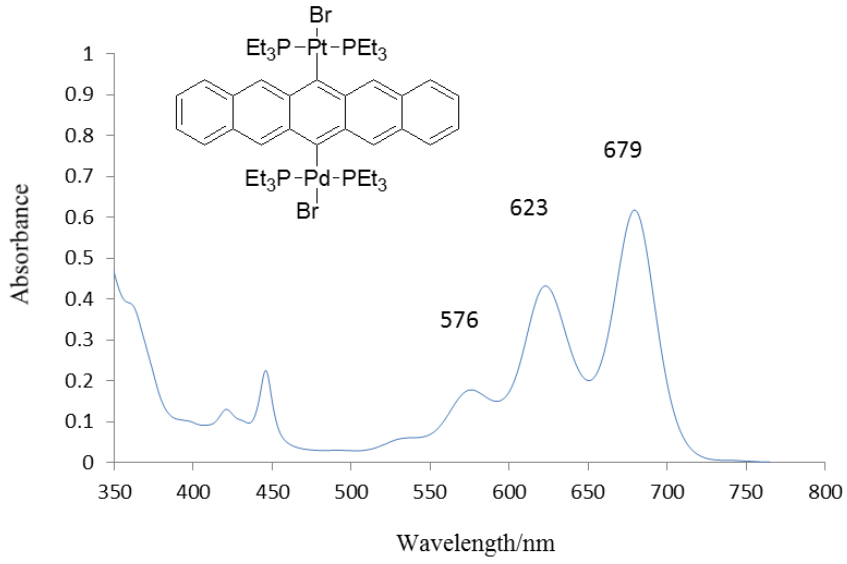


Figure 10. Absorption spectrum of pentacene derivative **10** in $CHCl_3$ at rt.

The UV-vis spectrum of **10** was measured in chloroform at room temperature. The maximum absorption of complex **10** appears at 679 nm (Figure 10). It is red-shifted about 36 nm compared with 6,13-triisopropylsilylethynylpentacene (λ_{max} = 643 nm).

2-3. Summary

In summary, central ring monopalladated and dipalladated pentacene derivatives were synthesized successfully. The central ring palladated pentacenes **4a** was unexpectedly stable in the solvent under air. Complex **4a** was dissolved in C_6D_6 under air to check its stability. After 8 days, 100% of complex **4a** remained. The λ_{max} of central ring monopalladated pentacene **4a** is 664 nm. Dipalladated pentacene **7** dissolved in C_6D_6 under air. After 3 days, 100% of **7** remained. The maximum absorption of complex **7** is 672 nm. The λ_{max} of central ring mixed metals substituted pentacene **10** is up to 679 nm. Compared to pentacene (λ_{max} = 577nm), a large red-shift was observed.

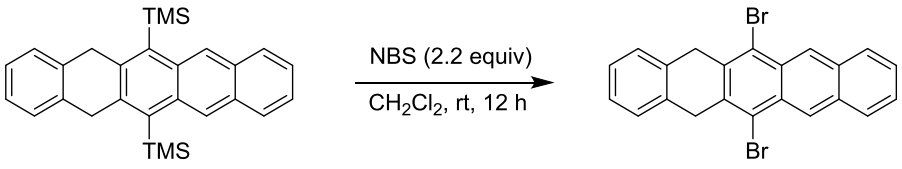
2-4. Experimental Section

General Experimental Method.

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. The reaction temperature recorded here refers to the bath temperature. Tetrahydrofuran (THF), toluene, benzene, and hexane were refluxed and distilled from sodium benzophenone ketyl under nitrogen atmosphere. All starting materials were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded for C_6D_6 or $CDCl_3$ solution on JEOL JNM-ECX400 and JEOL JNM-ECX600. Chemical shifts (δ) were quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) were quoted in Hz. NMR yields were determined using mesitylene, dichloromethane or dioxane as internal standard, 6,13-Bis-trimethylsilanyl-5,14-dihydro-pentacene **1.**[7] All the other reagents were commercially available and used as received. Mass spectra were obtained on JEOL JMS-T100GCv spectrometer.

Column chromatography was conducted with silica gel 60N (spherical, neutral, 100 – 210 μm. KANTO CHEMICAL, Co. INC). Some compounds were purified by Model LC-9201R/U Recycling Preparative HPLC (GPC) (Japan Analytical Industry, Co. Ltd).

Preparation of 6,13-dibromo-5,14-dihydropentacene 2 from 1.

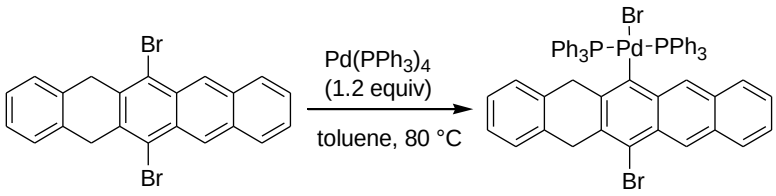


1 **2**

In a 50 mL Schlenk tube, under nitrogen atmosphere, 6,13-bis-trimethylsilanyl-5,14-dihydro-pentacene **1** (783 mg, 1.84 mmol) and NBS (722 mg, 4.06 mmol) were dissolved in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 12 h at room temperature. The mixture was quenched with H_2O at 0 °C and extracted with $CHCl_3$. The organic phase was separated and washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound **2** (363 mg, 45% isolated yield) as a solid.

2: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.44 (s, 4 H), 7.27-7.29 (m, 2 H), 7.41-7.43 (m, 2 H), 7.52-7.55 (m, 2 H), 8.07-8.10 (m, 2 H), 8.92 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 38.2, 122.7, 126.5, 126.8, 127.1, 127.5, 128.3, 129.9, 132.3, 135.3, 135.4. HRMS (EI) calcd for $C_{22}H_{14}Br_2$: 435.9462. Found: 435.9460.

Preparation of palladated dihydropentacene 3a from 2.

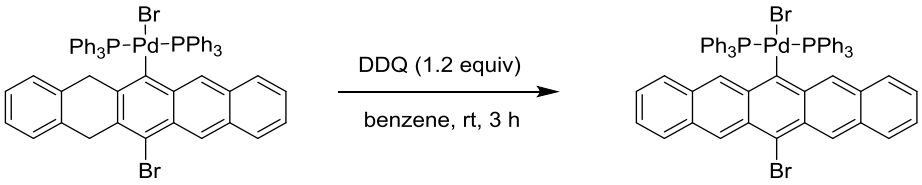


2 **3a** 77%

In a 20 mL Schlenk tube, 6,13-dibromo-5,14-dihydropentacene **2** (16 mg, 0.0365 mmol) and $Pd(PPh_3)_4$ (51 mg, 0.0438 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 80 °C. The solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 3:1 as eluent) to afford the title compound **3a** (30 mg, 77% isolated yield) as a green solid.

3a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.62 (s, 2 H), 4.08 (s, 2 H), 6.68 (d, J = 7.8 Hz, 1 H), 6.97 (t, J = 7.8 Hz, 1 H), 6.96-7.10 (m, 12 H), 7.09 (t, J = 7.8 Hz, 1 H), 7.17-7.20 (m, 7 H), 7.32-7.39 (m, 14 H), 7.67 (d, J = 8.4 Hz, 1 H), 7.89 (d, J = 7.8 Hz, 1 H), 8.33 (s, 1 H), 9.40 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 37.9, 41.4, 118.6, 124.7, 124.9, 125.4, 125.8, 125.9, 126.5, 126.9, 127.5, 127.9, 129.7, 129.9, 130.2 130.5, 130.7, 130.9, 131.2, 134.4, 134.9, 136.0, 136.4, 136.9, 137.0, 159.1. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 24.15. HRMS (FAB) calcd for $C_{58}H_{44}Br_2P_2Pd$: 1068.0322. Found: 1068.0358.

Preparation of palladated pentacene 4a from 3a.



3a **4a** 80%

In a 20 mL Schlenk tube, palladated dihydropentacene **3a** (23.5 mg, 0.022 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (6 mg, 0.026 mmol) were dissolved in degassed benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 3 h at room temperature. The solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **4a** (18.7 mg, 80% isolated yield) as a blue solid.

4a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.91 (t, J = 7.2 Hz, 12 H), 7.10 (t, J = 7.2 Hz, 6 H), 7.24-7.28 (m, 4 H), 7.32-7.33 (m, 12 H), 7.73 (d, J = 7.8 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 8.56 (s, 2 H), 9.66 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 117.6, 124.5, 125.4, 125.7, 127.5, 128.1, 128.4, 129.1, 129.8, 130.0, 130.4, 130.6, 130.8, 131.6, 132.0, 134.2, 134.7, 169.3. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 24.24. HRMS (FAB) calcd for $C_{58}H_{42}Br_2P_2Pd$: 1066.0165. Found: 1066.0132.

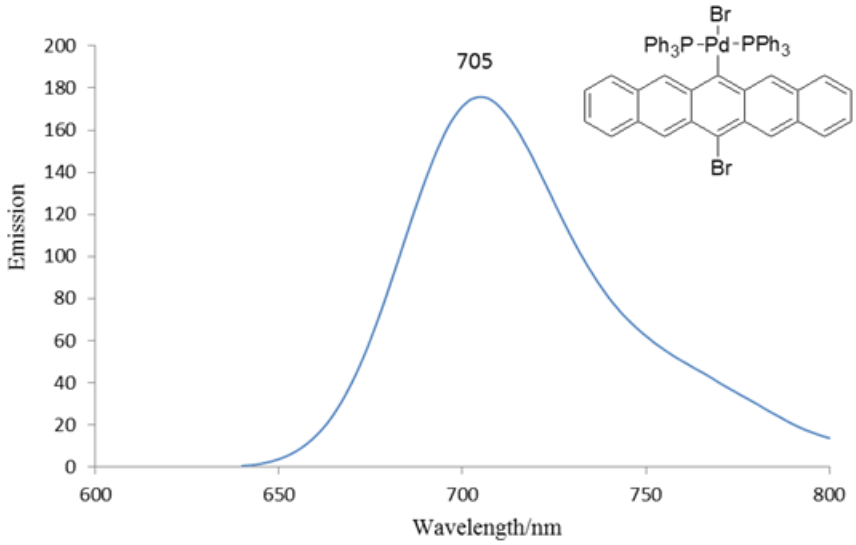
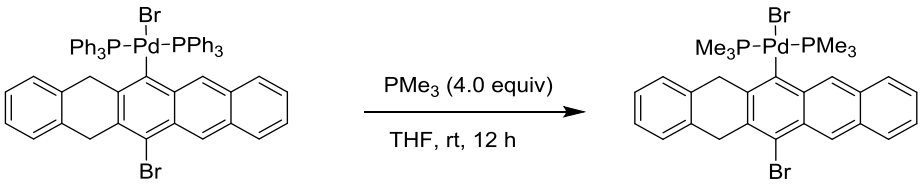


Figure 11. Emission spectrum of palladated pentacene **4a** in $CHCl_3$ at rt (λ_{ex} = 619 nm).

Preparation of palladated dihydropentacene 3b from 3a



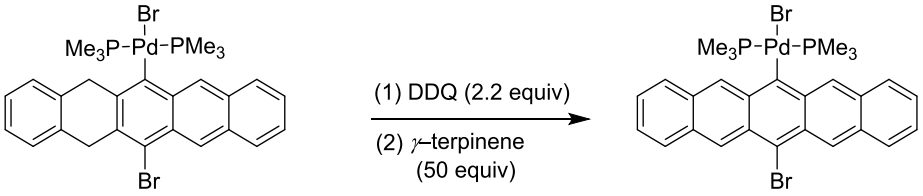
3a **3b** 85%

In a 20 mL Schlenk tube, palladated dihydropentacene **3a** (60 mg, 0.056 mmol) was

dissolved in THF (4 mL). To which PMe_3 (0.22mL, 0.225 mmol) was added at 0 °C. Then remove the cooling bath, under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **3b** (33 mg, 85% isolated yield) as a green solid.

3b: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.09 (t, J = 3.6 Hz, 9 H), 4.35 (s, 2 H), 4.47 (s, 2 H), 7.24-7.25 (m, 2 H), 7.34-7.36 (m, 1 H), 7.41-7.42 (m, 1 H), 7.47-7.49 (m, 2 H), 8.00-8.02 (m, 1 H), 8.06-8.08 (m, 1 H), 8.81 (s, 1 H), 9.21 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.9, 38.3, 41.9, 118.8, 125.4, 125.5, 126.4, 126.4, 126.5, 126.6, 127.6, 127.8, 128.4, 129.9, 130.5, 131.0, 131.8, 134.9, 136.7, 137.3, 137.4, 137.7, 154.5. HRMS (FAB) calcd for $C_{28}H_{32}Br_2P_2Pd$: 695.9373. Found: 695.9395.

Preparation of palladated pentacene 4b from 3b.



3b 77% **4b** 45%

In a 20 mL Schlenk tube, palladated dihydropentacene **3b** (20 mg, 0.0288 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (15 mg, 0.063 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 3 h at room temperature. The pentacene-DDQ adduct was formed firstly. Without isolation of pentacene-DDQ adduct, γ-terpinene (0.23 mL, 1.44 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 3 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **4b** (9 mg, 45% isolated yield) as a blue solid.

4b: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J = 3.6Hz, 18 H), 7.35-7.41 (m, 4 H), 7.99 (d, J = 8 Hz, 2 H), 8.03 (d, J = 8 Hz, 2 H), 9.12 (s, 2 H), 9.50 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.8, 117.3, 125.2, 126.2, 126.6, 128.5, 128.7, 129.2, 130.7, 132.4, 132.7, 135.9, 135.9, 167.6. ^{31}P NMR ($CDCl_3$, Me_4Si) δ -15.47. HRMS (FAB) calcd for $C_{28}H_{30}Br_2P_2Pd$: 693.9217. Found: 693.9228.

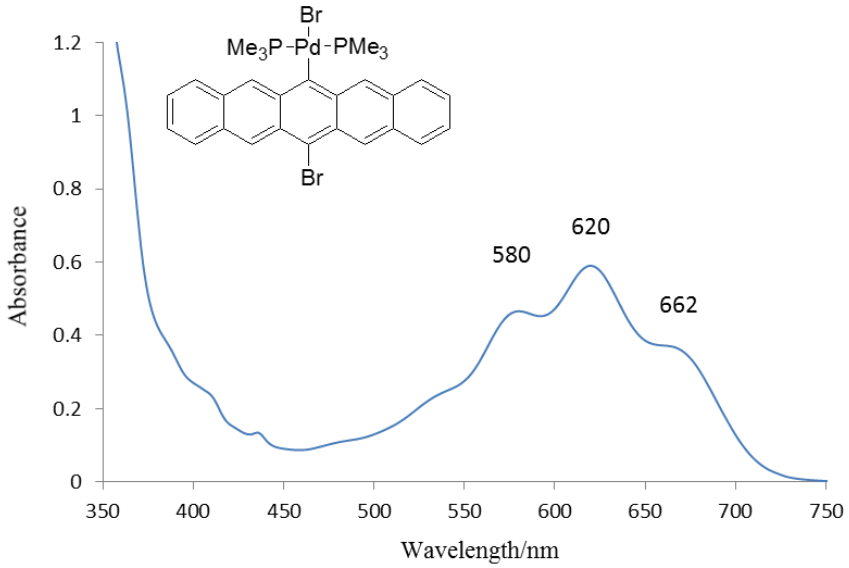


Figure 12. Absorption spectrum of palladated pentacene **4b** in $CHCl_3$ at rt.

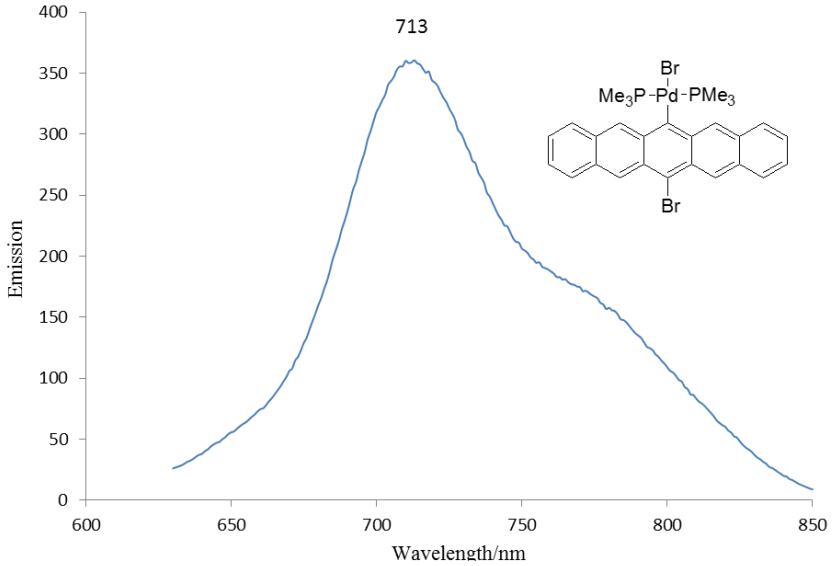
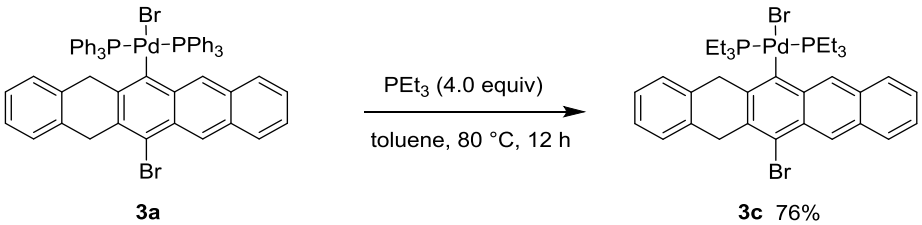


Figure 13. Emission spectrum of pentacene derivative **4b** in $CHCl_3$ at rt (λ_{ex} = 600 nm).

Preparation of palladated dihydropentacene 3c from 3a.



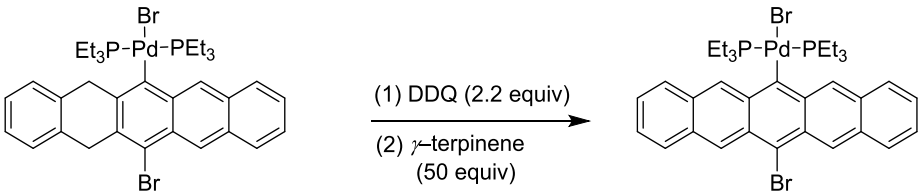
3a **3c** 76%

In a 20 mL Schlenk tube, palladated dihydropentacene **3a** (91 mg, 0.085 mmol) was dissolved in toluene (5 mL), and PEt_3 (0.36mL, 0.34 mmol) was added at room temperature. Under nitrogen atmosphere, the mixture was stirred at 80 °C for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane:

ethyl acetate = 5:1 as eluent) to afford the title compound **3c** (50mg, 76% isolated yield) as a green solid.

3c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.94-1.02 (m, 18 H), 1.35-1.53 (m, 12 H), 4.34 (s, 2 H), 4.49 (s, 2 H), 7.23-7.25 (m, 2 H), 7.32-7.35 (m, 1 H), 7.41-7.44 (m, 1 H), 7.45-7.50 (m, 2 H), 7.93 (d, *J* = 7.2Hz, 1 H), 8.07 (d, *J* = 7.2 Hz, 1 H), 8.80 (s, 1 H), 9.37 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.4, 15.6, 38.3, 42.3, 118.9, 125.4, 125.4, 126.0, 126.4, 126.4, 126.6, 127.5, 127.6, 128.4, 130.3, 130.4, 131.4, 131.8, 134.4, 136.4, 137.2, 137.2, 137.5, 153.9. HRMS (FAB) calcd for $C_{34}H_{44}Br_2P_2Pd$: 780.0314. Found: 780.0302.

Preparation of palladated pentacene 4c from 3c



3c 77% **4c** 60%

4c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.87-0.93 (m, 18 H), 1.28-1.29 (m, 12 H), 7.26-7.36 (m, 2 H), 7.38-7.41 (m, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 8.04 (d, *J* = 8.4 Hz, 2 H), 9.11 (s, 2 H), 9.64 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.31, 15.32, 117.12, 125.08, 126.11, 128.30, 128.70, 129.05, 129.97, 132.76, 133.99, 135.76, 168.47. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.69. HRMS (FAB) calcd for $C_{34}H_{42}Br_2P_2Pd$: 778.0158. Found: 778.0142.

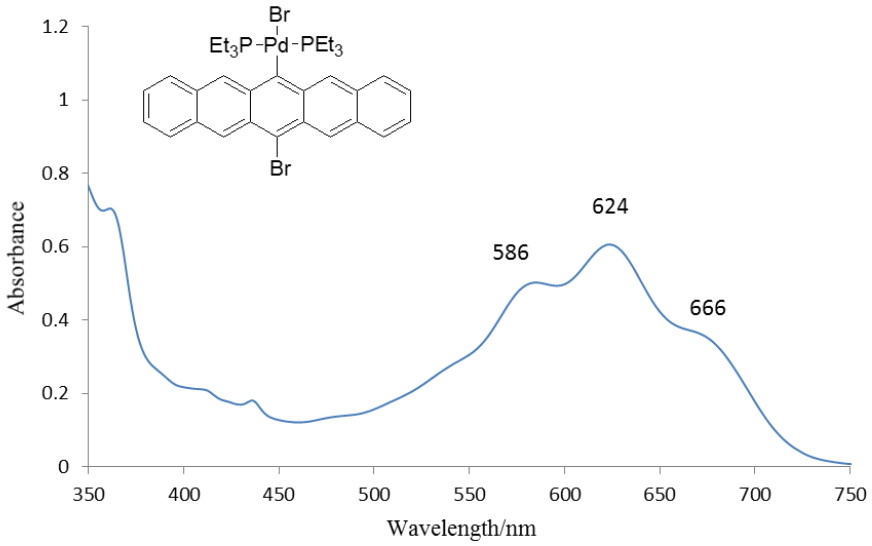


Figure 14. Absorption spectrum of pentacene derivative **4c** in $CHCl_3$ at rt.

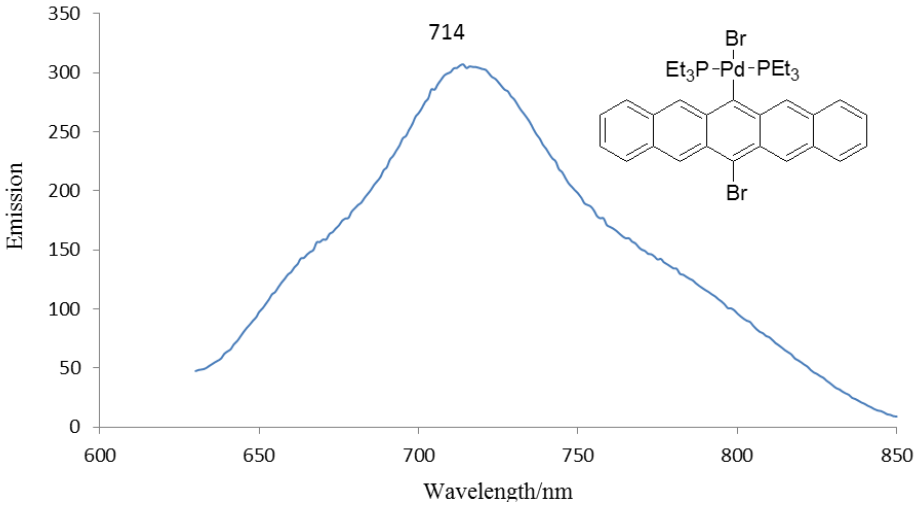


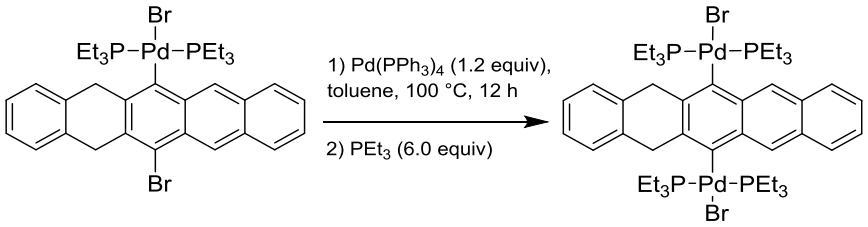
Figure 15. Emission spectrum of pentacene derivative **4c** in $CHCl_3$ at rt (λ_{ex} = 600 nm).

Preparation of central ring dipalladated dihydropentacene 5

3b **5** 65%

In a 20 mL Schlenk tube, palladated dihydropentacene **3b** (19 mg, 0.0273 mmol) and $Pd(PPh_3)_4$ (38 mg, 0.0328 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 18 h at 100 °C. After cooling to room temperature, PMe_3 (0.164mL, 01638mmol) was added to the mixture, then it was stirred at room temperature for 12h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound **5** (17mg, 65% isolated yield) as a green solid. **5:** ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.09 (t, *J* = 3.6 Hz, 36 H), 4.40 (s, 4 H), 7.20-7.22 (m, 2 H), 7.33-7.34 (m, 2 H), 7.40-7.42 (m, 2 H), 7.97-7.99 (m, 2 H), 9.08 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 15.3, 42.1, 124.6, 126.4, 126.8, 128.2, 129.1, 130.8, 138.1, 138.4, 139.2, 147.1. ^{31}P NMR ($CDCl_3$, Me_4Si) δ -16.25. HRMS (FAB) calcd for $C_{34}H_{50}Br_2P_4Pd_2$: 955.9299. Found: 955.9297.

Preparation of central ring dipalladated dihydropentacene 6

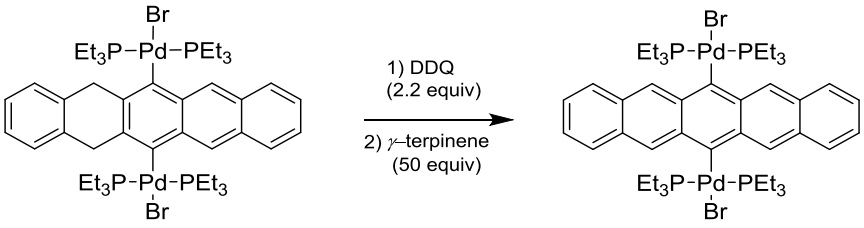


3c **6** 64%

In a 20 mL Schlenk tube, palladated dihydropentacene **3c** (20 mg, 0.0256 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.031 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 °C. After cooling to room temperature, PEt_3 (0.16mL, 0.154 mmol) was added to the mixture, then it was stirred at 80 °C for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **6** (18.4 mg, 64% isolated yield) as a green solid.

6: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.01-1.06 (m, 36 H), 1.37-1.51 (m, 24 H), 4.41 (s, 4 H), 7.20-7.21 (m, 2 H), 7.32-7.33 (m, 2 H), 7.38-7.40 (m, 2 H), 7.90-7.92 (m, 2 H), 9.21 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.6, 15.4, 42.4, 124.2, 126.0, 126.7, 127.9, 130.0, 130.0, 137.1, 138.1, 138.5, 147.2. HRMS (FAB) calcd for $C_{46}H_{74}Br_2P_4Pd_2$: 1124.1182. Found: 1124.1178.

Preparation of central ring dipalladated pentacene 7



6 **7** 70%

In a 20 mL Schlenk tube, palladated dihydropentacene **6** (18.3 mg, 0.0163 mmol) and DDQ (8.1 mg, 0.0358 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 1 h at room temperature. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, γ-terpinene (0.131 mL, 0.815 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ and 2% Et_3N as eluent) under nitrogen to afford the title compound **7** (12.8mg, 70% isolated yield) as a green solid.

7: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.96 (t, J = 8 Hz 36 H), 1.26-1.30 (m, 24 H), 7.26-7.29 (m, 4 H), 7.86-7.89 (m, 4 H), 9.47(s, 4 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 8.3, 14.9, 124.2, 128.4, 129.9, 132.3, 136.3, 156.3. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.48. HRMS (FAB) calcd for $C_{46}H_{72}Br_2P_4Pd_2$: 1122.1026. Found: 1122.1017.

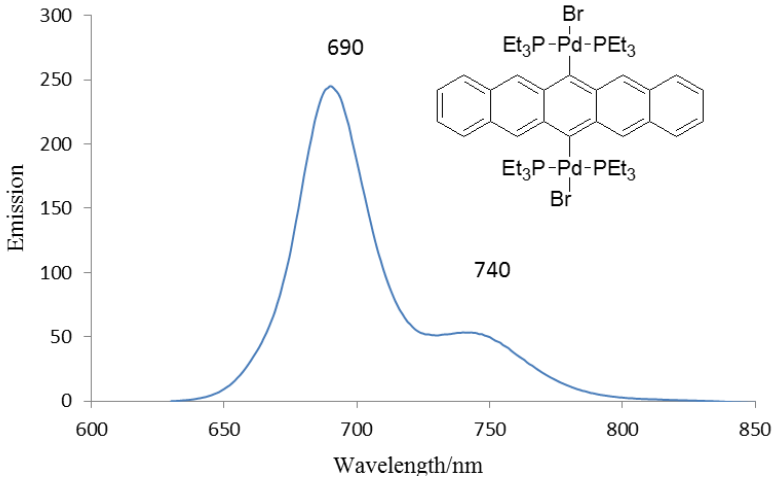
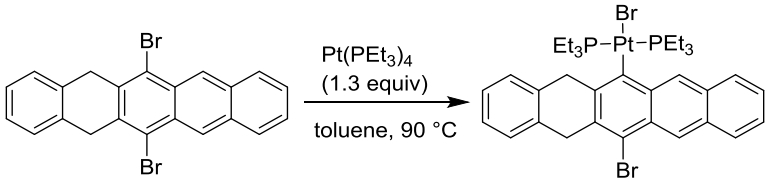


Figure 16. Emission spectrum of **7** in $CHCl_3$ at rt (λ_{ex} = 600 nm).

Preparation of platinated dihydropentacene 8

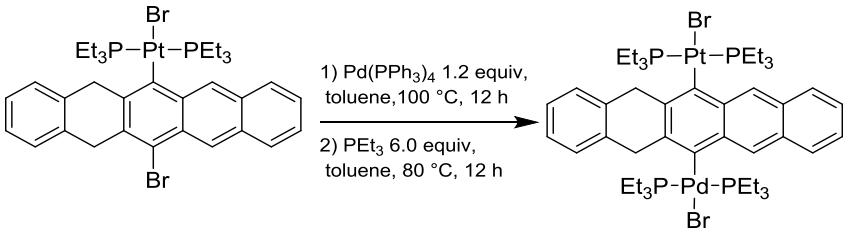


2 **8** 63%

In a 20 mL Schlenk tube, $Pt(PEt_3)_4$ (151 mg, 0.226 mmol) and 6,13-dibromo-5,14-dihydro-pentacene **2** (76 mg, 0.17 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 hours at 90 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform = 10:1:1 as eluent) to afford the title compound **8** (95 mg, 63% isolated yield) as a green solid.

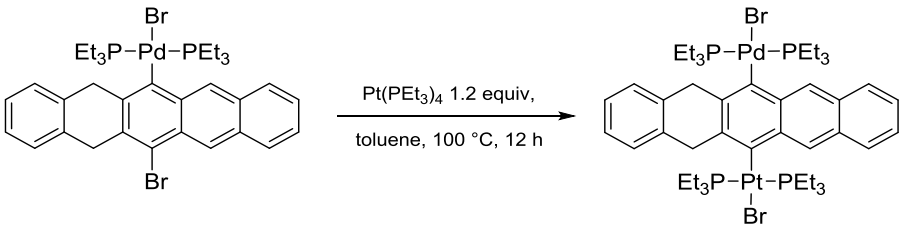
8: ^{1}H NMR ($CDCl_3$, Me_4Si, 600 M) δ 0.96-1.01 (m, 18 H), 1.47-1.53 (m, 6 H), 1.56-1.62 (m, 6 H), 4.37 (s, 2 H), 4.51 (s, 2 H),7.22-7.24 (m, 2 H), 7.32 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 6.6 Hz, 1H), 7.43-7.46 (m, 2 H), 7.89 (d, J = 9 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 8.82 (s, 1 H), 9.65 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600 M) δ 8.2, 15.5, 38.9, 43.0, 118.0, 125.6, 125.9, 125.9, 126.7, 126.8, 127.1, 127.8, 128.3, 128.8, 130.9, 131.2, 132.8, 133.0, 136.0, 137.5, 138.0, 138.6, 139.5, 142.3. HRMS (FAB) calcd for $C_{34}H_{44}Br_2P_2Pt$: 870.0916. Found: 870.0891.

Preparation of central ring mixed transition metals substituted dihydropentacene 9



8 **9** 58%

Method a: In a 20 mL Schlenk tube, platinated dihydropentacene **8** (18.5 mg, 0.0213 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.0255 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 ℃. After cooling to room temperature, PEt_3 (0.14mL, 0.128mmol) was added to the mixture and stirred at 80 ℃ for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: $CHCl_3$ = 5:1:1 as eluent) to afford the title compound **9** (15 mg, 58% isolated yield) as a green solid.

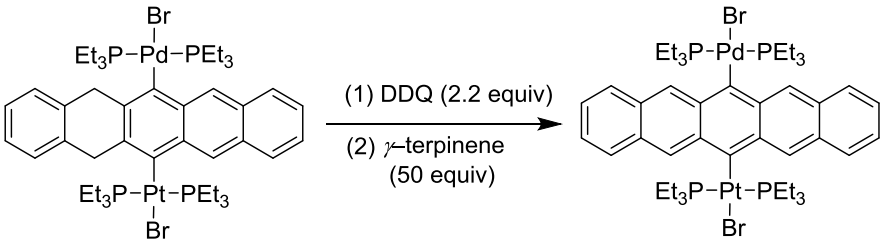


3c **9** 56%

Method b: In a 20 mL Schlenk tube, palladated dihydropentacene **3c** (94 mg, 0.12 mmol) and $Pt(PEt_3)_4$ (107 mg, 0.16 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 ℃. After cooling to room temperature, the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: $CHCl_3$ = 5:1:1 as eluent) to afford the title compound **9** (81mg, 56% isolated yield) as a green solid.

9: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.00-1.06 (m, 36 H), 1.37-1.63 (m, 24 H), 4.42 (s, 2 H), 4.44 (s, 2 H), 7.19-7.20 (m, 2 H), 7.30-7.33 (m, 2 H), 7.36-7.39 (m, 2 H), 7.87-7.91 (m, 2 H), 9.23 (s, 1 H), 9.47 (s, 1 H); ^{31}P NMR (C_6D_6, Me_4Si) δ: 10.54, 12.41. ^{13}C NMR (C_6D_6, Me_4Si, 600M) δ 8.4, 8.8, 15.0, 15.8, 124.5, 124.8, 126.3, 126.3, 126.9, 127.0, 130.0, 130.3, 130.8, 131.1, 137.1, 138.0, 139.0, 139.1, 140.0, 146.6. HRMS (ESI) calcd for $C_{46}H_{74}Br_2P_4PdPt$: 1212.1753. Found: 1212.1743.

Preparation of central ring mixed transition metals substituted pentacene 10



9 **10** 70%

In a 20 mL Schlenk tube, palladated dihydropentacene **9** (16.5 mg, 0.0136 mmol) and DDQ (6.8 mg, 0.03 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 1 h at room temperature. The pentacene-DDQ adduct was formed firstly, without

isolation of pentacene-DDQ adduct, γ-terpinene (0.109 mL, 0.68 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were washed by methanol under air to afford the title compound **10** (13mg, 79% isolated yield) as a green solid.

10: ^{1}H NMR (C_6D_6, Me_4Si, 600M) δ 0.84-0.92 (m, 36 H), 1.23-1.27 (m, 12 H), 1.33-1.37 (m, 12 H), 7.10-7.12 (m, 2 H), 7.16-7.18 (m, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 8.06 (d, *J* = 8.4 Hz, 2 H), 9.85 (s, 2 H), 9.95 (s, 2 H). ^{31}P NMR (C_6D_6, Me_4Si, 600M) *δ* 11.16, 12.45. HRMS (ESI) calcd for $C_{46}H_{72}Br_2P_4PdPt$: 1210.1640. Found: 1210.1599.

X-ray analysis data for compound 3a

Table 1. Crystallographic data and experimental details for compound **3a**

Compound	**3a**
Formula	C_{58} H_{44} Br_2 P_2 Pd
M	1069.09
Crystal system	monoclinic
Space group	P 1 21/c 1
a, (Å)	11.581(3)
b, (Å)	18.509(4)
c, (Å)	22.700(5)
α, (°)	90.00
β, (°)	100.345(11)
γ, (°)	90.00
V, (Å^3)	4787(2)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	brown
Crystal size, (mm^3)	0.60 x 0.30 x 0.10
D_{calcd}, (g cm^{-3})	1.483
Transm factor	0.3570-0.8128
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-15≤ h ≤ 15
	-24≤ k ≤ 24
	-29≤ l ≤ 29
No. of reflection measd	10898
No. of reflection obsd [I>2σ(I)]	8373
No. of parameters refined	744
R	0.0495

R_ω	0.1218
S, goodness of fit	1.020
Largest diff peak, (e Å^{-3})	1.393
Largest diff hole, (e Å^{-3})	-0.982

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 2. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.030(3)	Pd1 P1 2.3297(9)
Pd1 P2 2.3464(10)	Pd1 Br1 2.5074(8)
Br2 C12 1.911(4)	P1 C35 1.819(4)
P1 C29 1.824(4)	P1 C23 1.826(4)
P2 C41 1.824(4)	P2 C53 1.828(4)
P2 C47 1.835(4)	C1 C2 1.362(5)
C1 C22 1.422(4)	C2 C11 1.434(5)
C2 C3 1.509(5)	C3 C4 1.497(6)
C3 H1 0.95(5)	C3 H2 0.97(4)
C4 C9 1.389(6)	C4 C5 1.394(6)
C5 C6 1.374(8)	C5 H3 0.86(6)
C6 C7 1.368(9)	C6 H4 0.88(6)
C7 C8 1.374(7)	C7 H5 0.96(6)
C8 C9 1.386(6)	C8 H6 0.92(5)
C9 C10 1.520(6)	C10 C11 1.506(6)
C10 H7 1.00(6)	C10 H8 1.06(6)
C11 C12 1.356(5)	C12 C13 1.425(5)
C13 C14 1.409(5)	C13 C22 1.439(5)
C14 C15 1.390(6)	C14 H9 0.89(5)
C15 C20 1.416(6)	C15 C16 1.433(6)
C16 C17 1.339(8)	C16 H10 0.81(6)
C17 C18 1.386(9)	C17 H11 0.81(5)
C18 C19 1.367(7)	C18 H12 0.91(6)
C19 C20 1.428(6)	C19 H13 0.97(6)
C20 C21 1.392(5)	C21 C22 1.402(5)
C21 H14 0.83(5)	C23 C24 1.382(6)
C23 C28 1.393(5)	C24 C25 1.392(7)
C24 H15 0.97(5)	C25 C26 1.374(8)
C25 H16 0.94(7)	C26 C27 1.341(8)
C26 H17 0.86(6)	C27 C28 1.385(6)
C27 H18 0.84(5)	C28 H19 0.94(4)
C29 C34 1.386(5)	C29 C30 1.398(5)
C30 C31 1.377(6)	C30 H20 0.95(5)
C31 C32 1.354(7)	C31 H21 0.80(5)
C32 C33 1.364(7)	C32 H22 0.96(6)
C33 C34 1.383(6)	C33 H23 0.80(5)
C34 H24 0.93(4)	C35 C40 1.380(6)
C35 C36 1.386(6)	C36 C37 1.402(7)
C36 H25 0.97(5)	C37 C38 1.349(9)
C37 H26 0.97(6)	C38 C39 1.342(9)
C38 H27 1.00(7)	C39 C40 1.390(7)
C39 H28 0.87(9)	C40 H29 0.90(5)
C41 C46 1.385(6)	C41 C42 1.394(6)
C42 C43 1.392(7)	C42 H30 1.03(5)
C43 C44 1.374(10)	C43 H31 0.90(5)
C44 C45 1.354(10)	C44 H32 0.87(7)
C45 C46 1.381(7)	C45 H33 0.99(7)
C46 H34 1.06(5)	C47 C48 1.374(7)
C47 C52 1.391(6)	C48 C49 1.385(7)
C48 H35 0.97(5)	C49 C50 1.358(9)
C49 H36 1.01(7)	C50 C51 1.354(9)
C50 H37 0.85(7)	C51 C52 1.371(7)
C51 H38 0.95(5)	C52 H39 0.85(5)
C53 C58 1.374(6)	C53 C54 1.382(6)
C54 C55 1.382(7)	C54 H40 0.87(5)
C55 C56 1.368(8)	C55 H41 0.93(5)
C56 C57 1.353(8)	C56 H42 0.86(5)
C57 C58 1.370(7)	C57 H43 0.77(6)

C58 H44 0.81(6)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P1 87.86(9)	C1 Pd1 P2 88.90(9)
P1 Pd1 P2 176.73(3)	C1 Pd1 Br1 178.92(9)
P1 Pd1 Br1 91.68(3)	P2 Pd1 Br1 91.57(3)
C35 P1 C29 108.71(17)	C35 P1 C23 102.02(17)
C29 P1 C23 102.41(16)	C35 P1 Pd1 112.04(12)
C29 P1 Pd1 112.24(12)	C23 P1 Pd1 118.42(12)
C41 P2 C53 103.48(18)	C41 P2 C47 103.99(19)
C53 P2 C47 105.46(17)	C41 P2 Pd1 115.45(12)
C53 P2 Pd1 111.74(12)	C47 P2 Pd1 115.49(13)
C2 C1 C22 121.2(3)	C2 C1 Pd1 121.5(2)
C22 C1 Pd1 117.3(2)	C1 C2 C11 120.4(3)
C1 C2 C3 122.9(3)	C11 C2 C3 116.7(3)
C4 C3 C2 113.1(4)	C4 C3 H1 115(3)
C2 C3 H1 101(3)	C4 C3 H2 112(2)
C2 C3 H2 108(2)	H1 C3 H2 107(4)
C9 C4 C5 119.6(4)	C9 C4 C3 118.1(4)
C5 C4 C3 122.3(4)	C6 C5 C4 119.3(5)
C6 C5 H3 124(4)	C4 C5 H3 117(4)
C7 C6 C5 121.3(5)	C7 C6 H4 122(4)
C5 C6 H4 116(4)	C6 C7 C8 119.7(5)
C6 C7 H5 125(3)	C8 C7 H5 115(3)
C7 C8 C9 120.4(5)	C7 C8 H6 118(3)
C9 C8 H6 121(3)	C8 C9 C4 119.6(4)
C8 C9 C10 122.5(4)	C4 C9 C10 117.9(4)
C11 C10 C9 112.0(3)	C11 C10 H7 107(3)
C9 C10 H7 113(3)	C11 C10 H8 113(3)
C9 C10 H8 106(3)	H7 C10 H8 105(4)
C12 C11 C2 118.8(3)	C12 C11 C10 123.7(4)
C2 C11 C10 117.4(3)	C11 C12 C13 123.4(3)
C11 C12 Br2 119.2(3)	C13 C12 Br2 117.4(3)
C14 C13 C12 124.9(4)	C14 C13 C22 118.4(3)
C12 C13 C22 116.8(3)	C15 C14 C13 122.1(4)
C15 C14 H9 122(3)	C13 C14 H9 115(3)
C14 C15 C20 119.5(3)	C14 C15 C16 122.8(4)
C20 C15 C16 117.8(4)	C17 C16 C15 120.8(6)
C17 C16 H10 124(5)	C15 C16 H10 115(5)
C16 C17 C18 121.7(5)	C16 C17 H11 122(4)
C18 C17 H11 116(4)	C19 C18 C17 120.4(5)
C19 C18 H12 114(3)	C17 C18 H12 126(3)
C18 C19 C20 119.9(5)	C18 C19 H13 119(4)
C20 C19 H13 121(4)	C21 C20 C15 119.1(4)
C21 C20 C19 121.7(4)	C15 C20 C19 119.3(4)
C20 C21 C22 122.4(4)	C20 C21 H14 120(3)
C22 C21 H14 118(3)	C21 C22 C1 122.1(3)
C21 C22 C13 118.5(3)	C1 C22 C13 119.3(3)
C24 C23 C28 118.1(4)	C24 C23 P1 122.0(3)
C28 C23 P1 119.8(3)	C23 C24 C25 120.7(5)
C23 C24 H15 115(3)	C25 C24 H15 124(3)
C26 C25 C24 119.8(5)	C26 C25 H16 115(4)
C24 C25 H16 123(4)	C27 C26 C25 120.2(5)
C27 C26 H17 123(4)	C25 C26 H17 117(4)
C26 C27 C28 121.2(5)	C26 C27 H18 123(3)
C28 C27 H18 115(3)	C27 C28 C23 120.1(4)
C27 C28 H19 122(2)	C23 C28 H19 118(2)
C34 C29 C30 118.0(4)	C34 C29 P1 120.6(3)
C30 C29 P1 121.4(3)	C31 C30 C29 120.0(4)
C31 C30 H20 117(3)	C29 C30 H20 122(3)
C32 C31 C30 121.3(4)	C32 C31 H21 122(4)
C30 C31 H21 116(4)	C31 C32 C33 119.8(4)
C31 C32 H22 120(4)	C33 C32 H22 120(4)
C32 C33 C34 120.4(5)	C32 C33 H23 116(4)
C34 C33 H23 123(4)	C33 C34 C29 120.6(4)
C33 C34 H24 119(3)	C29 C34 H24 119(3)
C40 C35 C36 118.9(4)	C40 C35 P1 118.7(3)
C36 C35 P1 122.2(3)	C35 C36 C37 119.0(5)

C35 C36 H25 119(3)	C37 C36 H25 122(3)
C38 C37 C36 121.3(5)	C38 C37 H26 125(4)
C36 C37 H26 113(4)	C39 C38 C37 119.4(5)
C39 C38 H27 113(4)	C37 C38 H27 127(4)
C38 C39 C40 121.7(6)	C38 C39 H28 123(6)
C40 C39 H28 115(6)	C35 C40 C39 119.6(5)
C35 C40 H29 119(3)	C39 C40 H29 121(3)
C46 C41 C42 119.7(4)	C46 C41 P2 120.6(3)
C42 C41 P2 119.4(3)	C43 C42 C41 119.2(5)
C43 C42 H30 122(3)	C41 C42 H30 118(3)
C44 C43 C42 119.9(6)	C44 C43 H31 128(3)
C42 C43 H31 112(4)	C45 C44 C43 120.8(6)
C45 C44 H32 124(5)	C43 C44 H32 114(5)
C44 C45 C46 120.5(6)	C44 C45 H33 122(4)
C46 C45 H33 118(4)	C45 C46 C41 119.8(5)
C45 C46 H34 119(3)	C41 C46 H34 121(3)
C48 C47 C52 118.5(4)	C48 C47 P2 119.5(3)
C52 C47 P2 121.9(3)	C47 C48 C49 120.2(5)
C47 C48 H35 120(3)	C49 C48 H35 120(3)
C50 C49 C48 120.4(6)	C50 C49 H36 125(3)
C48 C49 H36 115(3)	C51 C50 C49 119.9(5)
C51 C50 H37 120(4)	C49 C50 H37 120(5)
C50 C51 C52 120.8(5)	C50 C51 H38 122(3)
C52 C51 H38 117(3)	C51 C52 C47 120.2(5)
C51 C52 H39 121(3)	C47 C52 H39 119(3)
C58 C53 C54 117.9(4)	C58 C53 P2 122.0(3)
C54 C53 P2 120.1(3)	C53 C54 C55 120.7(4)
C53 C54 H40 119(4)	C55 C54 H40 120(4)
C56 C55 C54 120.0(5)	C56 C55 H41 121(3)
C54 C55 H41 118(3)	C57 C56 C55 119.5(5)
C57 C56 H42 120(3)	C55 C56 H42 120(3)
C56 C57 C58 120.9(5)	C56 C57 H43 119(5)
C58 C57 H43 119(5)	C57 C58 C53 121.0(5)
C57 C58 H44 112(4)	C53 C58 H44 127(4)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

X-ray analysis data for compound 4a

Table 4. Crystallographic data and experimental details for compound **4a**

Compound	**4a**
Formula	C_{58} H_{42} Br_2 P_2 Pd
M	1066.02
Crystal system	triclinic
Space group	P -1
a, (Å)	11.394(4)
b, (Å)	12.801(4)
c, (Å)	20.325(8)
α, (°)	74.476(13)
β, (°)	86.292(15)
γ, (°)	70.216(12)
V, (Å^3)	2686.7(17)
Z	2
Temperature T, (K)	298
Crystal habit	prism
Crystal color	brown
Crystal size, (mm^3)	0.20 x 0.15 x 0.05

D_{calcd}, (g cm^{-3})	1.367
Transm factor	0.6990- 0.9097
λ (Mo Kα), ($Å^3$)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-14≤ h ≤ 14
	-16≤ k ≤ 16
	-26≤ l ≤ 26
No. of reflection measd	26044
No. of reflection obsd [I>2σ(I)]	5832
No. of parameters refined	592
R	0.0632
R_ω	0.1602
S, goodness of fit	0.944
Largest diff peak, (e $Å^{-3}$)	0.731
Largest diff hole, (e $Å^{-3}$)	-0.732

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 5. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.022(6)	Pd1 P1 2.3416(18)
Pd1 P2 2.3429(18)	Pd1 Br1 2.5063(12)
Br2 C12 1.908(6)	P1 C29 1.814(7)
P1 C23 1.820(7)	P1 C35 1.828(6)
P2 C53 1.812(6)	P2 C47 1.826(7)
P2 C41 1.834(7)	C1 C2 1.370(8)
C1 C22 1.414(7)	C2 C3 1.413(8)
C2 C11 1.456(8)	C3 C4 1.367(9)
C3 H3 0.9300	C4 C9 1.413(9)
C4 C5 1.437(8)	C5 C6 1.346(12)
C5 H5 0.9300	C6 C7 1.383(12)
C6 H6 0.9300 .	C7 C8 1.360(10)
C7 H7 0.9300	C8 C9 1.414(10)
C8 H8 0.9300	C9 C10 1.383(8)
C10 C11 1.406(9)	C10 H10 0.9300
C11 C12 1.391(8)	C12 C13 1.389(9)
C13 C22 1.456(8)	C13 C14 1.457(8)
C14 C15 1.363(10)	C14 H14 0.9300
C15 C20 1.423(11)	C15 C16 1.445(9)
C16 C17 1.336(13)	C16 H16 0.9300
C17 C18 1.400(13)	C17 H17 0.9300
C18 C19 1.340(10)	C18 H18 0.9300
C19 C20 1.413(11)	C19 H19 0.9300
C20 C21 1.371(8)	C21 C22 1.410(9)
C21 H21 0.9300	C23 C24 1.389(10)
C23 C28 1.394(9)	C24 C25 1.406(12)
C24 H24 0.9300	C25 C26 1.400(14)
C25 H25 0.9300	C26 C27 1.340(14)
C26 H26 0.9300	C27 C28 1.370(11)
C27 H27 0.9300	C28 H28 0.9300
C29 C34 1.381(10)	C29 C30 1.411(9)
C30 C31 1.389(11)	C30 H30 0.9300
C31 C32 1.363(13)	C31 H31 0.9300
C32 C33 1.357(12)	C32 H32 0.9300
C33 C34 1.386(11)	C33 H33 0.9300
C34 H34 0.9300	C35 C36 1.371(9)

C35 C40 1.382(10)	C36 C37 1.438(10)
C36 H36 0.9300	C37 C38 1.369(13)
C37 H37 0.9300	C38 C39 1.336(13)
C38 H38 0.9300	C39 C40 1.400(10)
C39 H39 0.9300	C40 H40 0.9300
C41 C42 1.376(8)	C41 C46 1.394(9)
C42 C43 1.400(11)	C42 H42 0.9300
C43 C44 1.357(12)	C43 H43 0.9300
C44 C45 1.344(11)	C44 H44 0.9300
C45 C46 1.396(10)	C45 H45 0.9300
C46 H46 0.9300	C47 C48 1.377(10)
C47 C52 1.383(9)	C48 C49 1.368(11)
C48 H48 0.9300	C49 C50 1.355(11)
C49 H49 0.9300	C50 C51 1.364(12)
C50 H50 0.9300	C51 C52 1.375(10)
C51 H51 0.9300	C52 H52 0.9300
C53 C58 1.373(9)	C53 C54 1.380(9)
C54 C55 1.398(9)	C54 H54 0.9300
C55 C56 1.368(11)	C55 H55 0.9300
C56 C57 1.373(10)	C56 H56 0.9300
C57 C58 1.413(8)	C57 H57 0.9300
C58 H58 0.9300	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 6. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P1 86.58(16)	C1 Pd1 P2 89.82(16)
P1 Pd1 P2 174.09(6)	C1 Pd1 Br1 177.14(17)
P1 Pd1 Br1 91.41(5)	P2 Pd1 Br1 92.34(5)
C29 P1 C23 104.4(3)	C29 P1 C35 105.9(3)
C23 P1 C35 103.5(3)	C29 P1 Pd1 111.5(2)
C23 P1 Pd1 117.2(2)	C35 P1 Pd1 113.2(2)
C53 P2 C47 106.3(3)	C53 P2 C41 101.9(3)
C47 P2 C41 103.6(3)	C53 P2 Pd1 112.1(2)
C47 P2 Pd1 110.8(2)	C41 P2 Pd1 120.8(2)
C2 C1 C22 121.5(5)	C2 C1 Pd1 119.4(4)
C22 C1 Pd1 118.9(5)	C1 C2 C3 122.8(6)
C1 C2 C11 120.5(5)	C3 C2 C11 116.6(6)
C4 C3 C2 123.8(6)	C4 C3 H3 118.1
C2 C3 H3 118.1	C3 C4 C9 119.2(6)
C3 C4 C5 121.7(7)	C9 C4 C5 119.0(7)
C6 C5 C4 119.9(8)	C6 C5 H5 120.1
C4 C5 H5 120.1	C5 C6 C7 121.4(8)
C5 C6 H6 119.3	C7 C6 H6 119.3
C8 C7 C6 120.5(8)	C8 C7 H7 119.8
C6 C7 H7 119.8	C7 C8 C9 121.3(8)
C7 C8 H8 119.4	C9 C8 H8 119.4
C10 C9 C4 119.5(6)	C10 C9 C8 122.5(7)
C4 C9 C8 118.0(6)	C9 C10 C11 122.3(6)
C9 C10 H10 118.8	C11 C10 H10 118.8
C12 C11 C10 124.2(6)	C12 C11 C2 117.3(6)
C10 C11 C2 118.5(5)	C13 C12 C11 123.8(6)
C13 C12 Br2 117.3(4)	C11 C12 Br2 118.9(5)
C12 C13 C22 118.0(5)	C12 C13 C14 126.0(6)
C22 C13 C14 116.1(6)	C15 C14 C13 122.5(6)
C15 C14 H14 118.8	C13 C14 H14 118.8
C14 C15 C20 120.3(6)	C14 C15 C16 121.1(8)
C20 C15 C16 118.6(8)	C17 C16 C15 119.8(8)
C17 C16 H16 120.1	C15 C16 H16 120.1
C16 C17 C18 121.7(8)	C16 C17 H17 119.2
C18 C17 H17 119.2	C19 C18 C17 120.2(9)
C19 C18 H18 119.9	C17 C18 H18 119.9
C18 C19 C20 121.9(9)	C18 C19 H19 119.1
C20 C19 H19 119.1	C21 C20 C19 122.9(7)
C21 C20 C15 119.2(7)	C19 C20 C15 117.9(6)
C20 C21 C22 123.0(7)	C20 C21 H21 118.5
C22 C21 H21 118.5	C21 C22 C1 122.2(6)
C21 C22 C13 118.9(5)	C1 C22 C13 118.8(6)
C24 C23 C28 118.4(7)	C24 C23 P1 121.5(5)
C28 C23 P1 119.9(6)	C23 C24 C25 119.4(8)

C23 C24 H24 120.3	C25 C24 H24 120.3
C26 C25 C24 120.0(10)	C26 C25 H25 120.0
C24 C25 H25 120.0	C27 C26 C25 119.9(9)
C27 C26 H26 120.1	C25 C26 H26 120.1
C26 C27 C28 120.9(9)	C26 C27 H27 119.6
C28 C27 H27 119.6	C27 C28 C23 121.5(8)
C27 C28 H28 119.3	C23 C28 H28 119.3
C34 C29 C30 117.7(7)	C34 C29 P1 120.7(5)
C30 C29 P1 121.6(6)	C31 C30 C29 119.9(8)
C31 C30 H30 120.1	C29 C30 H30 120.1
C32 C31 C30 119.9(8)	C32 C31 H31 120.0
C30 C31 H31 120.0	C33 C32 C31 121.6(8)
C33 C32 H32 119.2	C31 C32 H32 119.2
C32 C33 C34 119.1(9)	C32 C33 H33 120.5
C34 C33 H33 120.5	C29 C34 C33 121.8(7)
C29 C34 H34 119.1	C33 C34 H34 119.1
C36 C35 C40 119.7(6)	C36 C35 P1 122.0(5)
C40 C35 P1 118.4(6)	C35 C36 C37 119.2(8)
C35 C36 H36 120.4	C37 C36 H36 120.4
C38 C37 C36 119.9(9)	C38 C37 H37 120.0
C36 C37 H37 120.0	C39 C38 C37 119.6(8)
C39 C38 H38 120.2	C37 C38 H38 120.2
C38 C39 C40 122.1(8)	C38 C39 H39 119.0
C40 C39 H39 119.0	C35 C40 C39 119.5(8)
C35 C40 H40 120.3	C39 C40 H40 120.3
C42 C41 C46 116.7(6)	C42 C41 P2 121.4(5)
C46 C41 P2 121.9(5)	C41 C42 C43 121.1(8)
C41 C42 H42 119.4	C43 C42 H42 119.4
C44 C43 C42 120.8(7)	C44 C43 H43 119.6
C42 C43 H43 119.6	C45 C44 C43 119.4(8)
C45 C44 H44 120.3	C43 C44 H44 120.3
C44 C45 C46 120.8(8)	C44 C45 H45 119.6
C46 C45 H45 119.6	C41 C46 C45 121.1(7)
C41 C46 H46 119.4	C45 C46 H46 119.4
C48 C47 C52 117.6(7)	C48 C47 P2 120.6(5)
C52 C47 P2 121.8(5)	C49 C48 C47 120.9(7)
C49 C48 H48 119.5	C47 C48 H48 119.5
C50 C49 C48 120.2(8)	C50 C49 H49 119.9
C48 C49 H49 119.9	C49 C50 C51 120.8(8)
C49 C50 H50 119.6	C51 C50 H50 119.6
C50 C51 C52 118.8(7)	C50 C51 H51 120.6
C52 C51 H51 120.6	C51 C52 C47 121.6(7)
C51 C52 H52 119.2	C47 C52 H52 119.2
C58 C53 C54 119.9(6)	C58 C53 P2 121.7(5)
C54 C53 P2 118.3(5)	C53 C54 C55 119.9(7)
C53 C54 H54 120.1	C55 C54 H54 120.1
C56 C55 C54 120.4(7)	C56 C55 H55 119.8
C54 C55 H55 119.8	C55 C56 C57 120.3(6)
C55 C56 H56 119.9	C57 C56 H56 119.9
C56 C57 C58 119.5(7)	C56 C57 H57 120.2
C58 C57 H57 120.2	C53 C58 C57 120.0(6)
C53 C58 H58 120.0	C57 C58 H58 120.0

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

X-ray analysis data for compound 4b

Table 7. Crystallographic data and experimental details for compound **4b**

Compound	**4b**
Formula	C_{28} H_{30} Br_2 P_2 Pd
M	694.68
Crystal system	triclinic
Space group	P -1
a, (Å)	8.937(4)
b, (Å)	10.867(5)

c, (Å)	15.024(8)
α, (°)	97.183(19)
β, (°)	102.54(2)
γ, (°)	100.928(15)
V, (Å^3)	1377.3(11)
Z	2
Temperature T, (K)	298
Crystal habit	prism
Crystal color	brown
Crystal size, (mm^3)	0.50 x 0.10 x 0.02
D_{calcd}, (g cm^{-3})	1.675
Transm factor	0.2587- 0.9296
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-11≤ h ≤ 10
	-14≤ k ≤ 14
	-19≤ l ≤ 19
No. of reflection measd	6164
No. of reflection obsd [I>2σ(I)]	4330
No. of parameters refined	298
R	0.0533
R_ω	0.1438
S, goodness of fit	1.055
Largest diff peak, (e Å^{-3})	1.026
Largest diff hole, (e Å^{-3})	-1.237

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 8. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.006(5)	Pd1 P1 2.3028(19)
Pd1 P2 2.3039(19)	Pd1 Br1 2.5136(12)
Br2 C12 1.908(4)	P1 C25 1.817(8)
P1 C24 1.818(8)	P1 C23 1.822(7)
P2 C27 1.738(12)	P2 C28 1.772(10)
P2 C26 1.781(12)	C1 C2 1.417(7)
C1 C22 1.430(7)	C2 C3 1.406(7)
C2 C11 1.456(6)	C3 C4 1.376(8)
C3 H3 0.9300	C4 C5 1.425(8)
C4 C9 1.443(7)	C5 C6 1.356(9)
C5 H5 0.9300	C6 C7 1.399(9)
C6 H6 0.9300	C7 C8 1.365(9)
C7 H7 0.9300	C8 C9 1.421(8)
C8 H8 0.9300	C9 C10 1.380(8)
C10 C11 1.420(8)	C10 H10 0.9300
C11 C12 1.396(7)	C12 C13 1.389(7)
C13 C14 1.417(7)	C13 C22 1.443(6)
C14 C15 1.378(8)	C14 H14 0.9300

C15 C20 1.438(7)	C15 C16 1.448(8)
C16 C17 1.332(9)	C16 H16 0.9300
C17 C18 1.408(10)	C17 H17 0.9300
C18 C19 1.335(9)	C18 H18 0.9300
C19 C20 1.427(8)	C19 H19 0.9300
C20 C21 1.378(7)	C21 C22 1.424(7)
C21 H21 0.9300	C23 H23A 0.9600
C23 H23B 0.9600	C23 H23C 0.9600
C24 H24A 0.9600	C24 H24B 0.9600
C24 H24C 0.9600	C25 H25A 0.9600
C25 H25B 0.9600	C25 H25C 0.9600
C26 H26A 0.9600	C26 H26B 0.9600
C26 H26C 0.9600	C27 H27A 0.9600
C27 H27B 0.9600	C27 H27C 0.9600
C28 H28A 0.9600	C28 H28B 0.9600
C28 H28C 0.9600	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 9. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P1 88.86(16)	C1 Pd1 P2 89.36(16)
P1 Pd1 P2 178.19(5)	C1 Pd1 Br1 179.12(15)
P1 Pd1 Br1 90.35(6)	P2 Pd1 Br1 91.44(6)
C25 P1 C24 104.3(4)	C25 P1 C23 103.4(4)
C24 P1 C23 102.7(4)	C25 P1 Pd1 112.2(3)
C24 P1 Pd1 114.0(3)	C23 P1 Pd1 118.7(2)
C27 P2 C28 102.3(9)	C27 P2 C26 106.9(10)
C28 P2 C26 97.5(7)	C27 P2 Pd1 111.0(5)
C28 P2 Pd1 118.3(4)	C26 P2 Pd1 118.8(4)
C2 C1 C22 118.0(4)	C2 C1 Pd1 120.1(4)
C22 C1 Pd1 121.9(3)	C3 C2 C1 121.2(4)
C3 C2 C11 117.8(4)	C1 C2 C11 120.9(5)
C4 C3 C2 123.5(4)	C4 C3 H3 118.2
C2 C3 H3 118.2	C3 C4 C5 123.1(5)
C3 C4 C9 118.8(5)	C5 C4 C9 118.1(5)
C6 C5 C4 121.0(6)	C6 C5 H5 119.5
C4 C5 H5 119.5	C5 C6 C7 120.7(6)
C5 C6 H6 119.7	C7 C6 H6 119.7
C8 C7 C6 121.3(6)	C8 C7 H7 119.3
C6 C7 H7 119.3	C7 C8 C9 120.0(5)
C7 C8 H8 120.0	C9 C8 H8 120.0
C10 C9 C8 122.0(5)	C10 C9 C4 119.0(5)
C8 C9 C4 118.9(5)	C9 C10 C11 122.8(5)
C9 C10 H10 118.6	C11 C10 H10 118.6
C12 C11 C10 124.0(4)	C12 C11 C2 118.2(4)
C10 C11 C2 117.9(5)	C13 C12 C11 123.2(4)
C13 C12 Br2 118.8(4)	C11 C12 Br2 117.9(4)
C12 C13 C14 124.3(4)	C12 C13 C22 118.1(4)
C14 C13 C22 117.6(4)	C15 C14 C13 123.2(4)
C15 C14 H14 118.4	C13 C14 H14 118.4
C14 C15 C20 119.1(5)	C14 C15 C16 123.1(5)
C20 C15 C16 117.8(5)	C17 C16 C15 121.3(6)
C17 C16 H16 119.4	C15 C16 H16 119.4
C16 C17 C18 120.6(6)	C16 C17 H17 119.7
C18 C17 H17 119.7	C19 C18 C17 121.0(6)
C19 C18 H18 119.5	C17 C18 H18 119.5
C18 C19 C20 121.9(6)	C18 C19 H19 119.0
C20 C19 H19 119.0	C21 C20 C19 123.5(5)
C21 C20 C15 118.9(5)	C19 C20 C15 117.5(5)
C20 C21 C22 122.6(5)	C20 C21 H21 118.7
C22 C21 H21 118.7	C21 C22 C1 120.0(4)
C21 C22 C13 118.4(4)	C1 C22 C13 121.4(4)
P1 C23 H23A 109.5	P1 C23 H23B 109.5
H23A C23 H23B 109.5	P1 C23 H23C 109.5
H23A C23 H23C 109.5	H23B C23 H23C 109.5
P1 C24 H24A 109.5	P1 C24 H24B 109.5
H24A C24 H24B 109.5	P1 C24 H24C 109.5
H24A C24 H24C 109.5	H24B C24 H24C 109.5
P1 C25 H25A 109.5	P1 C25 H25B 109.5
H25A C25 H25B 109.5	P1 C25 H25C 109.5

H25A C25 H25C 109.5	H25B C25 H25C 109.5
P2 C26 H26A 109.5	P2 C26 H26B 109.5
H26A C26 H26B 109.5	P2 C26 H26C 109.5
H26A C26 H26C 109.5	H26B C26 H26C 109.5
P2 C27 H27A 109.5	P2 C27 H27B 109.5
H27A C27 H27B 109.5	P2 C27 H27C 109.5
H27A C27 H27C 109.5	H27B C27 H27C 109.5
P2 C28 H28A 109.5	P2 C28 H28B 109.5
H28A C28 H28B 109.5	P2 C28 H28C 109.5
H28A C28 H28C 109.5	H28B C28 H28C 109.5

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

X-ray analysis data for compound 7

Table 10. Crystallographic data and experimental details for compound **7**

Compound	**7**
Formula	$C_{46}\ H_{72}\ Br_2\ P_4\ Pd_2$
M	1122.10
Crystal system	monoclinic
Space group	P 1 21/n 1
a, (Å)	14.882(2)
b, (Å)	15.600(3)
c, (Å)	22.041(4)
α, (°)	90.00
β, (°)	96.233(8)
γ, (°)	90.00
V, (Å^3)	5086.9(16)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	green
Crystal size, (mm^3)	0.30 x 0.20 x 0.10
D_{calcd}, (g cm^{-3})	1.464
Transm factor	0.5290- 0.7930
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-19≤ h ≤ 19
	-20≤ k ≤ 20
	-28≤ l ≤ 28
No. of reflection measd	11589
No. of reflection obsd [I>2σ(I)]	8826
No. of parameters refined	487
R	0.0452
R_ω	0.1140

S, goodness of fit	1.030
Largest diff peak, (e Å^{-3})	1.001
Largest diff hole, (e Å^{-3})	-1.115

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(\text{m-n})]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 11. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.019(3)	Pd1 P1 2.3106(14)
Pd1 P2 2.3149(15)	Pd1 Br1 2.5193(6)
Pd2 C12 2.023(3)	Pd2 P4 2.3171(12)
Pd2 P3 2.3271(12)	Pd2 Br2 2.5083(6)
P1 C27 1.822(6)	P1 C25 1.836(6)
P1 C23 1.847(5)	P2 C29 1.780(7)
P2 C33 1.813(7)	P2 C31 2.129(14)
P3 C35 1.812(5)	P3 C37 1.819(5)
P3 C39 1.825(5)	P4 C41 1.824(5)
P4 C45 1.827(5)	P4 C43 1.832(5)
C1 C22 1.400(5)	C1 C2 1.414(5)
C2 C3 1.418(5)	C2 C11 1.456(5)
C3 C4 1.382(5)	C3 H3 0.9300
C4 C5 1.428(5)	C4 C9 1.436(5)
C5 C6 1.356(6)	C5 H5 0.9300
C6 C7 1.411(7)	C6 H6 0.9300
C7 C8 1.349(6)	C7 H7 0.9300
C8 C9 1.440(5)	C8 H8 0.9300
C9 C10 1.383(5)	C10 C11 1.416(5)
C10 H10 0.9300	C11 C12 1.407(5)
C12 C13 1.416(5)	C13 C14 1.417(5)
C13 C22 1.450(5)	C14 C15 1.393(5)
C14 H14 0.9300	C15 C20 1.427(5)
C15 C16 1.431(5)	C16 C17 1.354(6)
C16 H16 0.9300	C17 C18 1.400(7)
C17 H17 0.9300	C18 C19 1.350(7)
C18 H18 0.9300	C19 C20 1.432(5)
C19 H19 0.9300	C20 C21 1.395(5)
C21 C22 1.420(5)	C21 H21 0.9300
C23 C24 1.518(9)	C23 H23A 0.9700
C23 H23B 0.9700	C24 H24A 0.9600
C24 H24B 0.9600	C24 H24C 0.9600
C25 C26 1.490(9)	C25 H25A 0.9700
C25 H25B 0.9700	C26 H26A 0.9600
C26 H26B 0.9600	C26 H26C 0.9600
C27 C28 1.525(9)	C27 H27A 0.9700
C27 H27B 0.9700	C28 H28A 0.9600
C28 H28B 0.9600	C28 H28C 0.9600
C29 C30 1.477(11)	C29 H29A 0.9700
C29 H29B 0.9700	C30 H30A 0.9600
C30 H30B 0.9600	C30 H30C 0.9600
C31 C32 1.377(16)	C31 H31A 0.9700
C31 H31B 0.9700	C32 H32A 0.9600
C32 H32B 0.9600	C32 H32C 0.9600
C33 C34 1.269(11)	C33 H33A 0.9700
C33 H33B 0.9700	C34 H34A 0.9600
C34 H34B 0.9600	C34 H34C 0.9600
C35 C36 1.511(8)	C35 H35A 0.9700
C35 H35B 0.9700	C36 H36A 0.9600
C36 H36B 0.9600	C36 H36C 0.9600
C37 C38 1.523(8)	C37 H37A 0.9700
C37 H37B 0.9700	C38 H38A 0.9600
C38 H38B 0.9600	C38 H38C 0.9600
C39 C40 1.507(8)	C39 H39A 0.9700
C39 H39B 0.9700	C40 H40A 0.9600
C40 H40B 0.9600	C40 H40C 0.9600
C41 C42 1.533(8)	C41 H41A 0.9700
C41 H41B 0.9700	C42 H42A 0.9600
C42 H42B 0.9600	C42 H42C 0.9600

C43 C44 1.507(8)	C43 H43A 0.9700
C43 H43B 0.9700	C44 H44A 0.9600
C44 H44B 0.9600	C44 H44C 0.9600
C45 C46 1.499(8)	C45 H45A 0.9700
C45 H45B 0.9700	C46 H46A 0.9600
C46 H46B 0.9600	C46 H46C 0.9600

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 12. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P1 91.96(11)	C1 Pd1 P2 88.35(11)
P1 Pd1 P2 178.42(5)	C1 Pd1 Br1 175.28(10)
P1 Pd1 Br1 89.81(4)	P2 Pd1 Br1 90.00(4)
C12 Pd2 P4 92.57(10)	C12 Pd2 P3 89.64(10)
P4 Pd2 P3 177.12(4)	C12 Pd2 Br2 178.36(10)
P4 Pd2 Br2 88.58(3)	P3 Pd2 Br2 89.26(3)
C27 P1 C25 104.8(3)	C27 P1 C23 105.5(4)
C25 P1 C23 100.4(3)	C27 P1 Pd1 118.0(2)
C25 P1 Pd1 115.2(2)	C23 P1 Pd1 111.1(2)
C29 P2 C33 108.7(4)	C29 P2 C31 105.4(4)
C33 P2 C31 105.8(5)	C29 P2 Pd1 114.8(3)
C33 P2 Pd1 118.5(3)	C31 P2 Pd1 102.2(3)
C35 P3 C37 104.7(3)	C35 P3 C39 104.3(3)
C37 P3 C39 100.6(3)	C35 P3 Pd2 118.61(16)
C37 P3 Pd2 113.5(2)	C39 P3 Pd2 113.25(19)
C41 P4 C45 105.8(3)	C41 P4 C43 105.2(3)
C45 P4 C43 99.9(2)	C41 P4 Pd2 117.25(18)
C45 P4 Pd2 112.04(18)	C43 P4 Pd2 114.94(19)
C22 C1 C2 117.7(3)	C22 C1 Pd1 122.9(3)
C2 C1 Pd1 119.4(3)	C1 C2 C3 120.8(3)
C1 C2 C11 120.9(3)	C3 C2 C11 118.3(3)
C4 C3 C2 122.9(3)	C4 C3 H3 118.6
C2 C3 H3 118.6	C3 C4 C5 122.6(4)
C3 C4 C9 118.7(3)	C5 C4 C9 118.7(4)
C6 C5 C4 121.0(4)	C6 C5 H5 119.5
C4 C5 H5 119.5	C5 C6 C7 120.2(4)
C5 C6 H6 119.9	C7 C6 H6 119.9
C8 C7 C6 121.5(4)	C8 C7 H7 119.2
C6 C7 H7 119.2	C7 C8 C9 120.5(4)
C7 C8 H8 119.7	C9 C8 H8 119.7
C10 C9 C4 119.8(3)	C10 C9 C8 122.2(4)
C9 C10 C11 122.7(3)	C9 C10 H10 118.7
C11 C10 H10 118.7	C12 C11 C10 121.2(3)
C12 C11 C2 121.1(3)	C10 C11 C2 117.7(3)
C11 C12 C13 117.7(3)	C11 C12 Pd2 121.2(2)
C13 C12 Pd2 120.8(2)	C12 C13 C14 120.7(3)
C12 C13 C22 120.8(3)	C14 C13 C22 118.5(3)
C15 C14 C13 122.4(3)	C15 C14 H14 118.8
C13 C14 H14 118.8	C14 C15 C20 119.3(3)
C14 C15 C16 122.0(4)	C20 C15 C16 118.7(3)
C17 C16 C15 120.2(4)	C17 C16 H16 119.9
C15 C16 H16 119.9	C16 C17 C18 121.1(4)
C16 C17 H17 119.5	C18 C17 H17 119.5
C19 C18 C17 121.1(4)	C19 C18 H18 119.4
C17 C18 H18 119.4	C18 C19 C20 120.4(4)
C18 C19 H19 119.8	C20 C19 H19 119.8
C21 C20 C15 119.2(3)	C21 C20 C19 122.3(4)
C15 C20 C19 118.5(4)	C20 C21 C22 122.6(3)
C20 C21 H21 118.7	C22 C21 H21 118.7
C1 C22 C21 120.4(3)	C1 C22 C13 121.7(3)
C21 C22 C13 117.8(3)	C24 C23 P1 113.7(4)
C24 C23 H23A 108.8	P1 C23 H23A 108.8
C24 C23 H23B 108.8	P1 C23 H23B 108.8
H23A C23 H23B 107.7	C23 C24 H24A 109.5
C23 C24 H24B 109.5	H24A C24 H24B 109.5
C23 C24 H24C 109.5	H24A C24 H24C 109.5
H24B C24 H24C 109.5	C26 C25 P1 116.0(5)
C26 C25 H25A 108.3	P1 C25 H25A 108.3
C26 C25 H25B 108.3	P1 C25 H25B 108.3
H25A C25 H25B 107.4	C25 C26 H26A 109.5

C25 C26 H26B 109.5	H26A C26 H26B 109.5
C25 C26 H26C 109.5	H26A C26 H26C 109.5
H26B C26 H26C 109.5	C28 C27 P1 116.0(5)
C28 C27 H27A 108.3	P1 C27 H27A 108.3
C28 C27 H27B 108.3	P1 C27 H27B 108.3
H27A C27 H27B 107.4	C27 C28 H28A 109.5
C27 C28 H28B 109.5	H28A C28 H28B 109.5
C27 C28 H28C 109.5	H28A C28 H28C 109.5
H28B C28 H28C 109.5	C30 C29 P2 115.1(6)
C30 C29 H29A 108.5	P2 C29 H29A 108.5
C30 C29 H29B 108.5	P2 C29 H29B 108.5
H29A C29 H29B 107.5	C29 C30 H30A 109.5
C29 C30 H30B 109.5	H30A C30 H30B 109.5
C29 C30 H30C 109.5	H30A C30 H30C 109.5
H30B C30 H30C 109.5	C32 C31 P2 97.7(13)
C32 C31 H31A 112.2	P2 C31 H31A 112.2
C32 C31 H31B 112.2	P2 C31 H31B 112.2
H31A C31 H31B 109.8	C31 C32 H32A 109.5
C31 C32 H32B 109.5	H32A C32 H32B 109.5
C31 C32 H32C 109.5	H32A C32 H32C 109.5
H32B C32 H32C 109.5	C34 C33 P2 128.0(8)
C34 C33 H33A 105.3 .	P2 C33 H33A 105.3
C34 C33 H33B 105.3	P2 C33 H33B 105.3
H33A C33 H33B 106.0	C33 C34 H34A 109.5
C33 C34 H34B 109.5	H34A C34 H34B 109.5
C33 C34 H34C 109.5	H34A C34 H34C 109.5
H34B C34 H34C 109.5	C36 C35 P3 117.3(4)
C36 C35 H35A 108.0	P3 C35 H35A 108.0
C36 C35 H35B 108.0	P3 C35 H35B 108.0
H35A C35 H35B 107.2	C35 C36 H36A 109.5
C35 C36 H36B 109.5	H36A C36 H36B 109.5
C35 C36 H36C 109.5	H36A C36 H36C 109.5
H36B C36 H36C 109.5	C38 C37 P3 114.7(4)
C38 C37 H37A 108.6	P3 C37 H37A 108.6
C38 C37 H37B 108.6	P3 C37 H37B 108.6
H37A C37 H37B 107.6	C37 C38 H38A 109.5
C37 C38 H38B 109.5	H38A C38 H38B 109.5
C37 C38 H38C 109.5	H38A C38 H38C 109.5
H38B C38 H38C 109.5	C40 C39 P3 114.5(4)
C40 C39 H39A 108.6	P3 C39 H39A 108.6
C40 C39 H39B 108.6	P3 C39 H39B 108.6
H39A C39 H39B 107.6	C39 C40 H40A 109.5
C39 C40 H40B 109.5	H40A C40 H40B 109.5
C39 C40 H40C 109.5	H40A C40 H40C 109.5
H40B C40 H40C 109.5	C42 C41 P4 115.8(4)
C42 C41 H41A 108.3	P4 C41 H41A 108.3
C42 C41 H41B 108.3	P4 C41 H41B 108.3
H41A C41 H41B 107.4	C41 C42 H42A 109.5
C41 C42 H42B 109.5	H42A C42 H42B 109.5
C41 C42 H42C 109.5	H42A C42 H42C 109.5
H42B C42 H42C 109.5	C44 C43 P4 114.0(4)
C44 C43 H43A 108.7	P4 C43 H43A 108.7
C44 C43 H43B 108.7	P4 C43 H43B 108.7
H43A C43 H43B 107.6	C43 C44 H44A 109.5
C43 C44 H44B 109.5	H44A C44 H44B 109.5
C43 C44 H44C 109.5	C46 C45 P4 115.6(4)
C46 C45 H45A 108.4	P4 C45 H45A 108.4
C46 C45 H45B 108.4	P4 C45 H45B 108.4
H45A C45 H45B 107.5	C45 C46 H46A 109.5
C45 C46 H46B 109.5	H46A C46 H46B 109.5
C45 C46 H46C 109.5	H46A C46 H46C 109.5
H46B C46 H46C 109.5	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

2-5. References and Notes

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Chapter 3. Introduction of Substituents into Pentacene using Palladated Pentacene from Electrophiles and Nucleophiles

Abstract

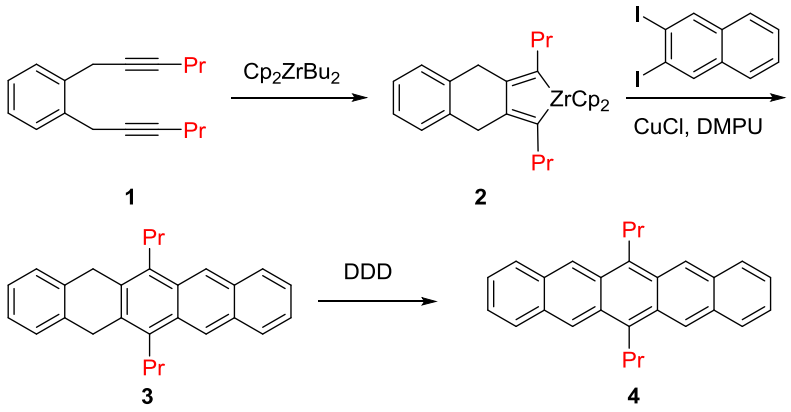
Introduction of substituents onto pentacene skeleton is an important research issue in pentacene chemistry. The substituents can be introduced before or after the pentacene skeleton formation. In Takahashi group's homologation method and coupling method, the substituents of pentacene come from starting material alkynes. On the other hand, in pentacenequinone method and cross-coupling method, the substituents come from nucleophiles. In this work, I will report a conceptually new methodology. Substituents of pentacene were from not only nucleophiles but also electrophiles.

Lithiation of 6,13-dibromo-5,14-dihydropentacene with one equivalent of BuLi was not regio-selective. 6-Bromo-5,14-dihydropentacene was obtained in very low yield. Fortunately, lithiation of central monopalladated pentacene complex with ^{t}BuLi in THF/toluene afforded lithiated palladium reagent in high yield. Subsequently, the reactions of this intermediate with electrophiles and nucleophiles in successive afforded substituted pentacene in good yields.

3-1. Introduction

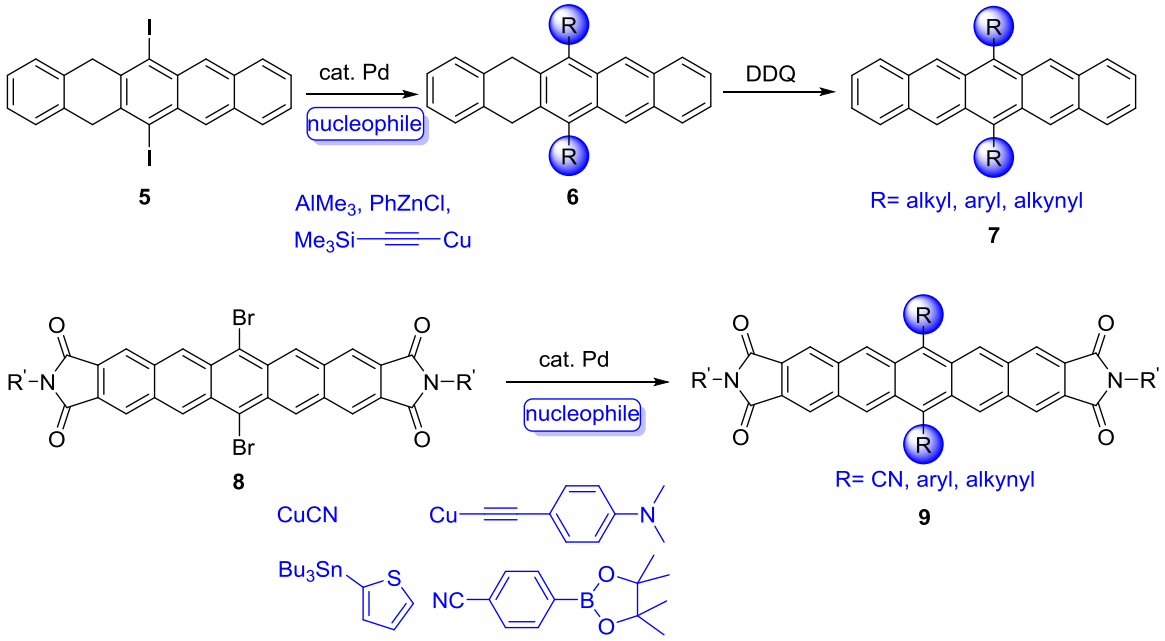
Pentacene has received much attention in relevance to organic materials. Introduction of substituents into pentacene has been attractive, because its properties could be controlled by the substituents. For introduction of substituents into pentacene, some methods have been reported. Takahashi's group has reported zirconacene-mediated coupling method to introduce substituents into pentacene, the substituents of pentacene come from starting material alkynes (Scheme 1).[1] The diyne **1** was treated with Cp_2ZrBu_2 (Negishi reagent) followed by the reaction with diiodonaphthalene in the presence of CuCl and DMPU to afford 6,13-dipropyl-5,14-dihydropentacene **3**. Aromatization of **3** with DDQ gave 6,13-dipropylpentacene **4**. The propyl group of pentacene **4** come from the starting material diyne **1**.

Scheme 1. Coupling method for preparation of substituted pentacene derivatives



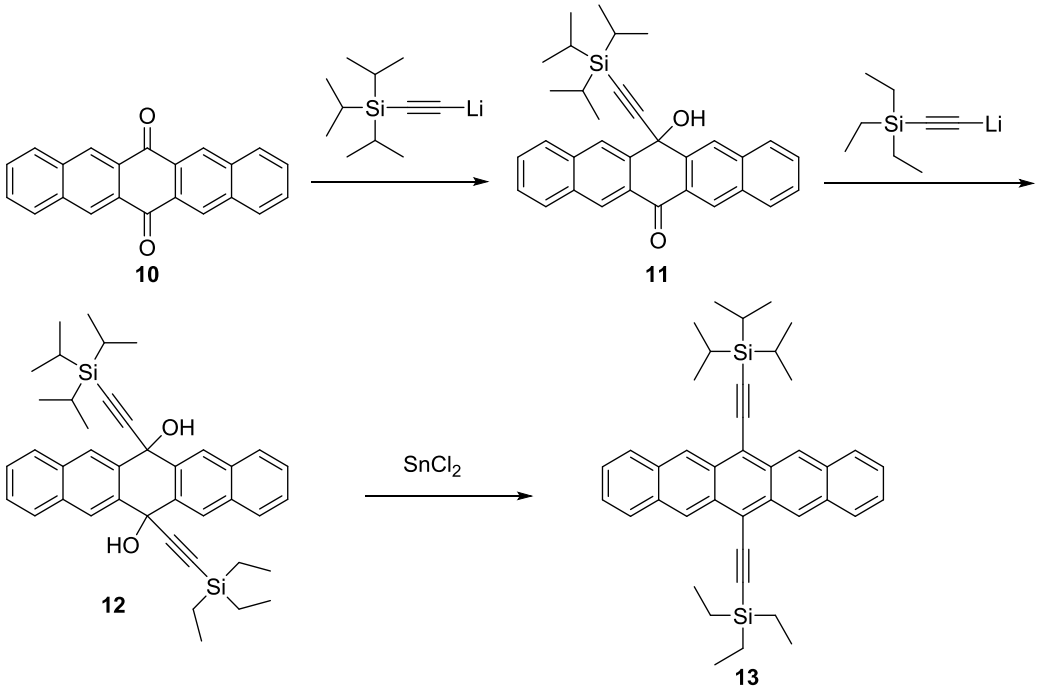
Recently, Takahashi's group and others also reported cross-coupling reaction for the introduction of organic substituents into the central ring of pentacene derivatives by using palladium catalyst. A series of symmetric 6,13-disubstituted pentacene derivatives were obtained (Scheme 2).[2] 6,13-Diiodo-5,14-dihydropentacene **5** reacted with nucleophiles such as $AlMe_3$, PhZnCl or trimethylsilyl ethynyl copper reagent in the presence of palladium catalyst to give the corresponding disubstituted dihydropentacene **6**. After aromatization, disubstituted pentacene **7** was obtained. The alkyl, aryl or alkynyl group of pentacene **7** come from nucleophiles, respectively. Palladium catalyzed coupling reaction of 6,13-dibromopentacene **8** with nucleophiles such as CuCN, 4-dimethylaminophenylacetylene copper reagent, tributyl(thiophen-2-yl)stannane or 4-cyanophenylboronic ester afforded the corresponding disubstituted pentacene **9** in good yield. The cyano, alkynyl or aryl group of pentacene **9** also come from nucleophiles.

Scheme 2. Introduction of substituents into pentacene by cross-coupling method



Another important method is pentacenequinone method. Pentacenequinone was treated with aryl or alkynyl metal reagent to give a diol intermediate. Then, reduction of the diol with $SnCl_2$ afforded the 6,13-disubstituted pentacene derivative successfully.

Scheme 3. Synthesis of asymmetric pentacene derivative

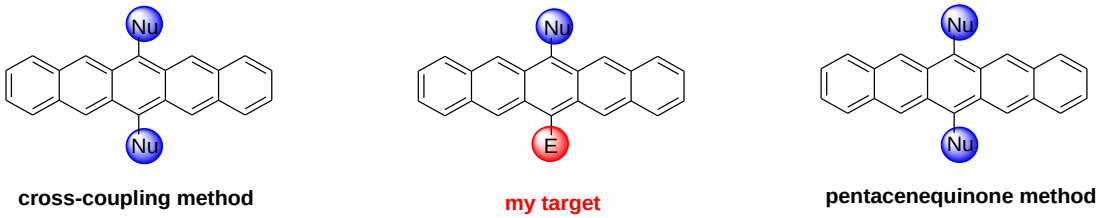


Unsymmetric pentacene derivative **12** was synthesized by addition of lithiated triisopropylsilylacetylene and triethylsilylacetylene to pentacenequinone in two steps

(Scheme 3).[3] After aromatization, asymmetric pentacene **13** with TIPSCC and TESCC at the central ring was obtained in good yield. We can see both substituents of this pentacene also come from nucleophiles.

In cross-coupling reaction, the halogenated pentacene reacts with nucleophiles in the presence of Pd. In pentacenequinone method, the carbonyl moiety was attacked by nucleophiles. In both cases, the pentacene substrate has positively polarized carbons. They can react with nucleophiles. If pentacene had negatively polarized carbon, the coupling partner could be electrophiles. However, such species had been unknown. In this regard, I started a project of introduction of substituents into pentacene from nucleophile as well as electrophile (Figure 1).

Figure 1. Methods for introduction of substituents into pentacene



3-2. Results and Discussion

3-2-1. Lithiation of dihydropentacene derivatives and the coupling reactions

To introduce substituents into pentacene from both electrophile and nucleophile, a pentacene framework with both negatively and positively charged carbons is needed. Therefore, in the primary stage, I attempted to lithiate 6,13-dibromo-5,14-dihydropentacene **14** with BuLi to give monolithium reagent **15** selectively. Then **15** attempted to react with electrophile firstly (Scheme 4). However, lithiation of 6,13-dibromo-5,14-dihydropentacene **14** was not regio-selective.

Scheme 4. Attempts to introduce substituents into pentacene from electrophile

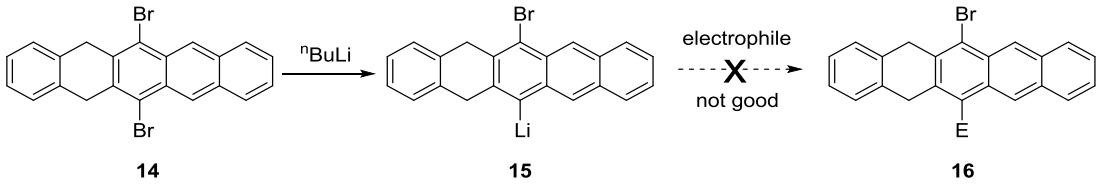
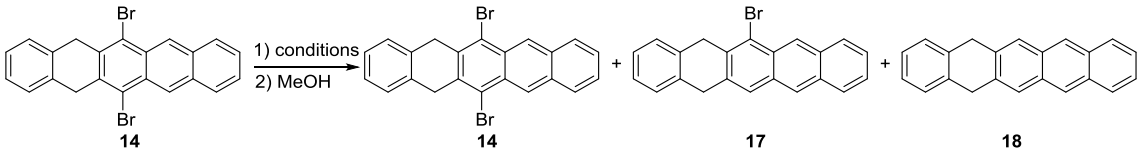


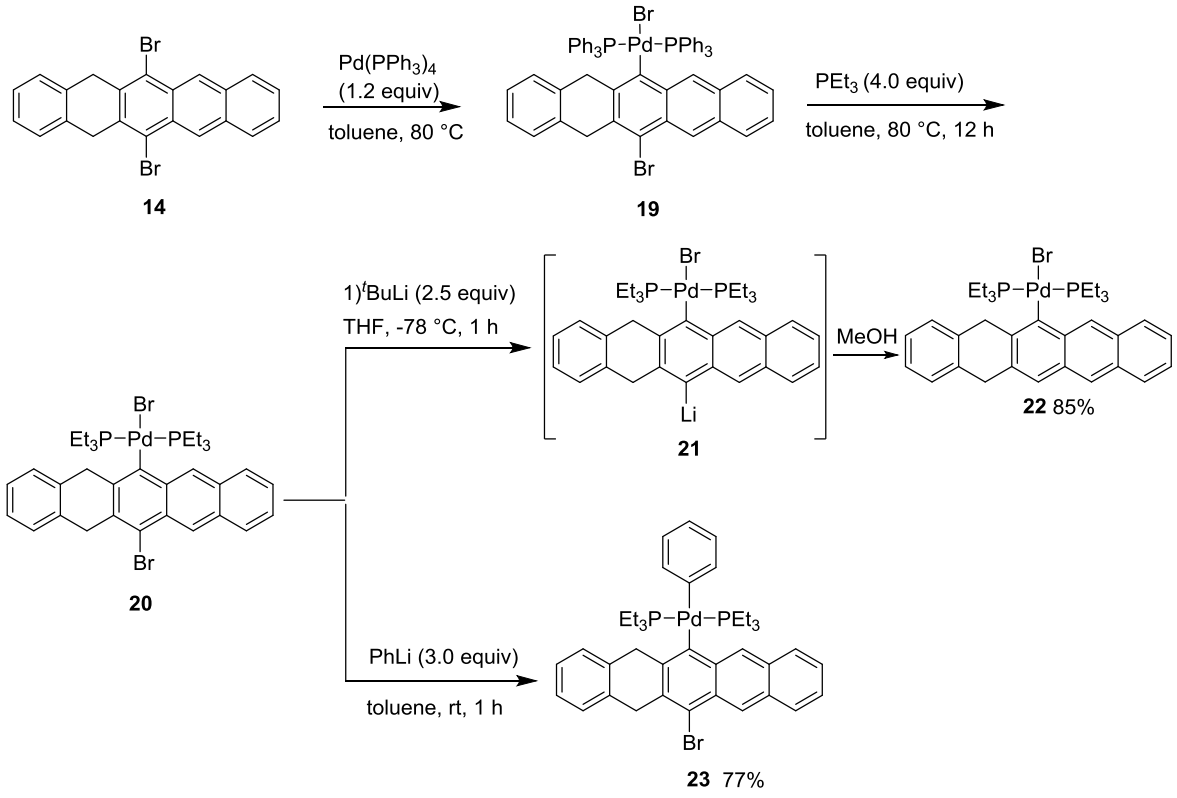
Table 1. Lithiation of 6,13-dibromo-5,14-dihydropentacene **14**



conditions		yield	
^{n}BuLi (1.2 equiv), THF, -78 °C, 1 h	21%	7%	5%
^{n}BuLi (1.2 equiv), Et_2O, -78 °C, 1 h	32%	14%	
^{t}BuLi (2.5 equiv), toluene/ether, -78 °C, 1 h	9%	23%	8%

Lithiation of 6,13-dibromo-5,14-dihydropentacene **14** with ^{n}BuLi or ^{t}BuLi always gave a mixture of 6,13-dibromo-5,14-dihydropentacene **14**, 6-bromo-5,14-dihydropentacene **17** and 5,14-dihydropentacene **18**. The yield of 6-bromo-5,14-dihydropentacene **17** was very low (Table 1).

Scheme 5. Lithiation of central ring palladated dihydropentacene **20**



I then changed the strategy. In Chapter 2, it was demonstrated that oxidative addition of 6,13-dibromo-5,14-dihydropentacene **14** to $Pd(PPh_3)_4$ gave monopalladated

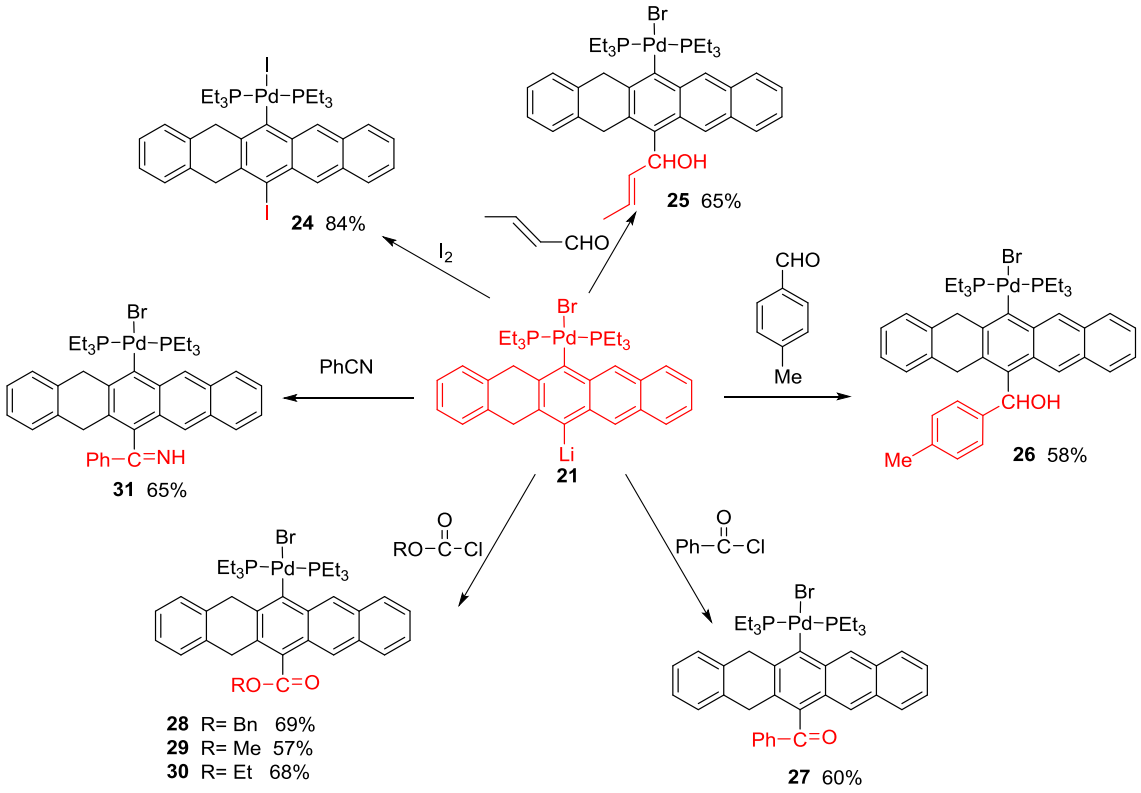
dihydropentacene **19** selectively. So I expected that the lithiation of the bromine atom of palladated dihydropentacene **19** should be selective. For this purpose, lithiation of palladated dihydropetacene **20** was carried out firstly. Because complex **20** with PEt_3 ligands has good solubility compared to complex **19**. Palladated dihydropentacene **20** was treated with 2.5 equivalent of ^{t}BuLi to give lithiated palladium intermediate **21** in high yield. Protonolysis of the lithium reagent **21** by methanol afforded complex **22** in 85% yield. In contrast, complex **20** was treated with phenyllithium to give complex **23** in 77% isolated yield selectively. The bromine atom connected to palladium was changed to phenyl. However, the other bromine was intact (Scheme 5).

With this lithiated palladium intermediate **21** in hand, a series of reactions with electrophiles were carried out. It was encouraging to see this lithiated palladium reagent could react with a variety of electrophiles, such as iodine, aldehyde, acid chloride, chloroformate and benzonitrile *et al* (Scheme 6). The corresponding products were obtained in good yields.

Lithiation of palladated dihydropentacene **20** with ^{t}BuLi in THF gave the intermediate. The palladium-lithium pentacene intermediate reacted with iodine at room temperature for 12 h to give complex **24** in 84% yield. The bromine atom attached to palladium was changed to iodine during the reaction process. By the same method, products **25** and **31** were obtained in 65% and 65% yields, respectively.

When the lithiated palladium complex **21** was treated with chloroformate or acid chloride in THF, the corresponding product was obtained in very low yield. I then changed the solvent to toluene. However, lithiation of palladated dihydropentacene with ^{t}BuLi was very slow. When diethyl ether was used as a solvent, lithiation of palladated dihydropentacene also was not good. Since the solubility of palladated dihydropentacene in diethyl ether was not good. Finally, I found that a mixed solvent of toluene and diethyl ether (3:1) gave good results. The corresponding products **26**, **27**, **28**, **29** and **30** were obtained in good yields.

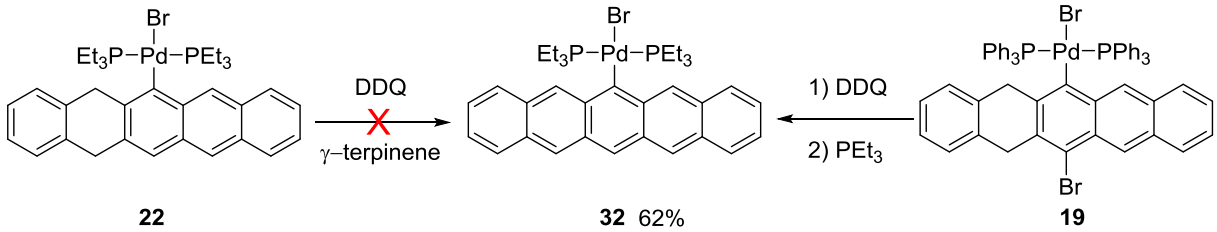
Scheme 6. Reaction of palladated dihydropentacene complex **21** with electrophiles



3-2-2. Aromatization of the dihydropentacene derivatives

Aromatization of complex **22** with DDQ and γ-terpinene did not afford complex **32** directly. An unidentified mixture was observed. However, complex **19** firstly reacted with 1.2 equivalent of DDQ at room temperature for 3 h. After that, the reaction mixture was added 4.0 equivalent of PEt_3 and heated at 80 °C for 12 h. The desired product **32** was obtained in 62% yield (Scheme 7). The X-ray structure of **32** is shown in Figure 2. It clearly shows that one bromine has disappeared.

Scheme 7. Preparation of palladated pentacene **32**



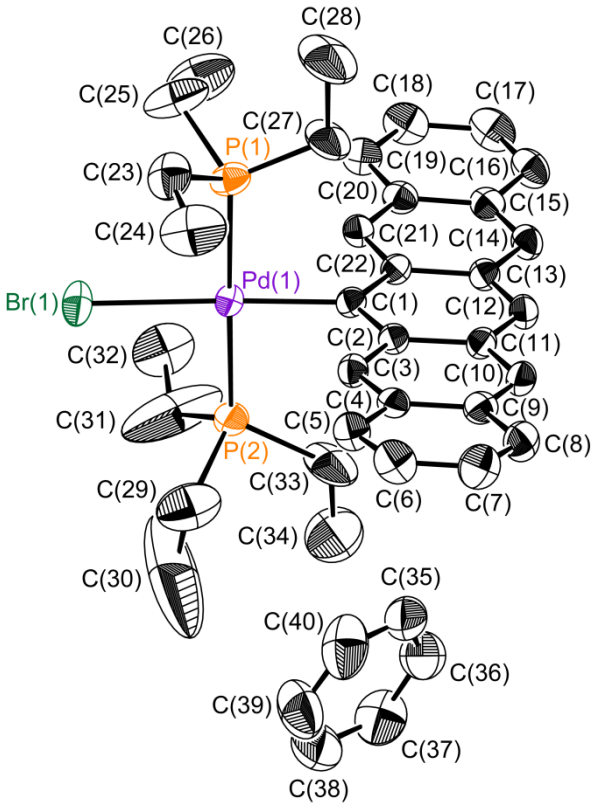
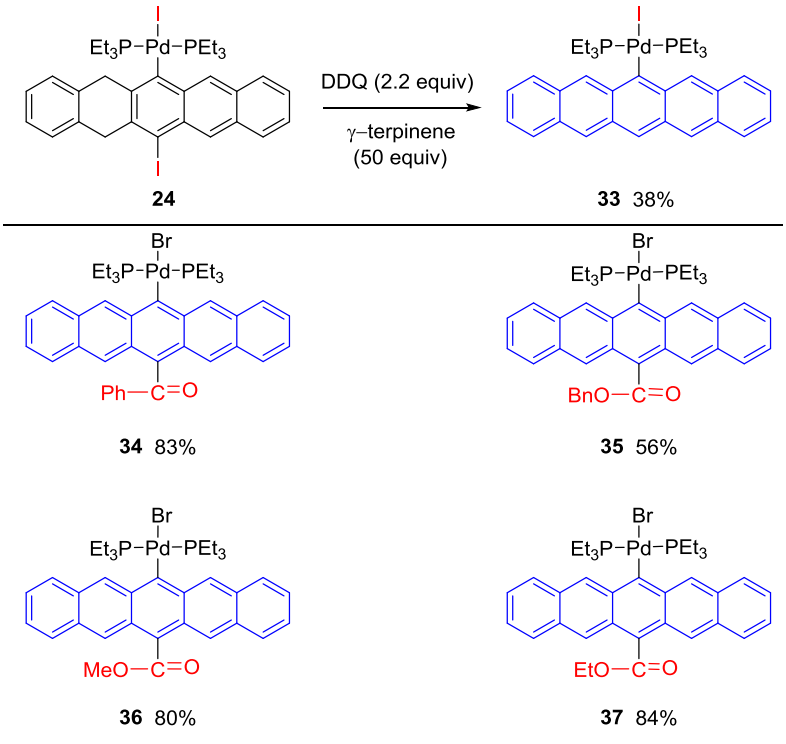


Figure 2. X-ray structure of complex **32**

Table 2. Aromatization of palladated dihydropentaene complexes



Aromatization of complex **6** with DDQ and γ-terpinene afforded complex **33** in 38%

isolated yield. Because the iodine was very active, one iodine atom of complex **33** was removed during the reaction process (Table 2).

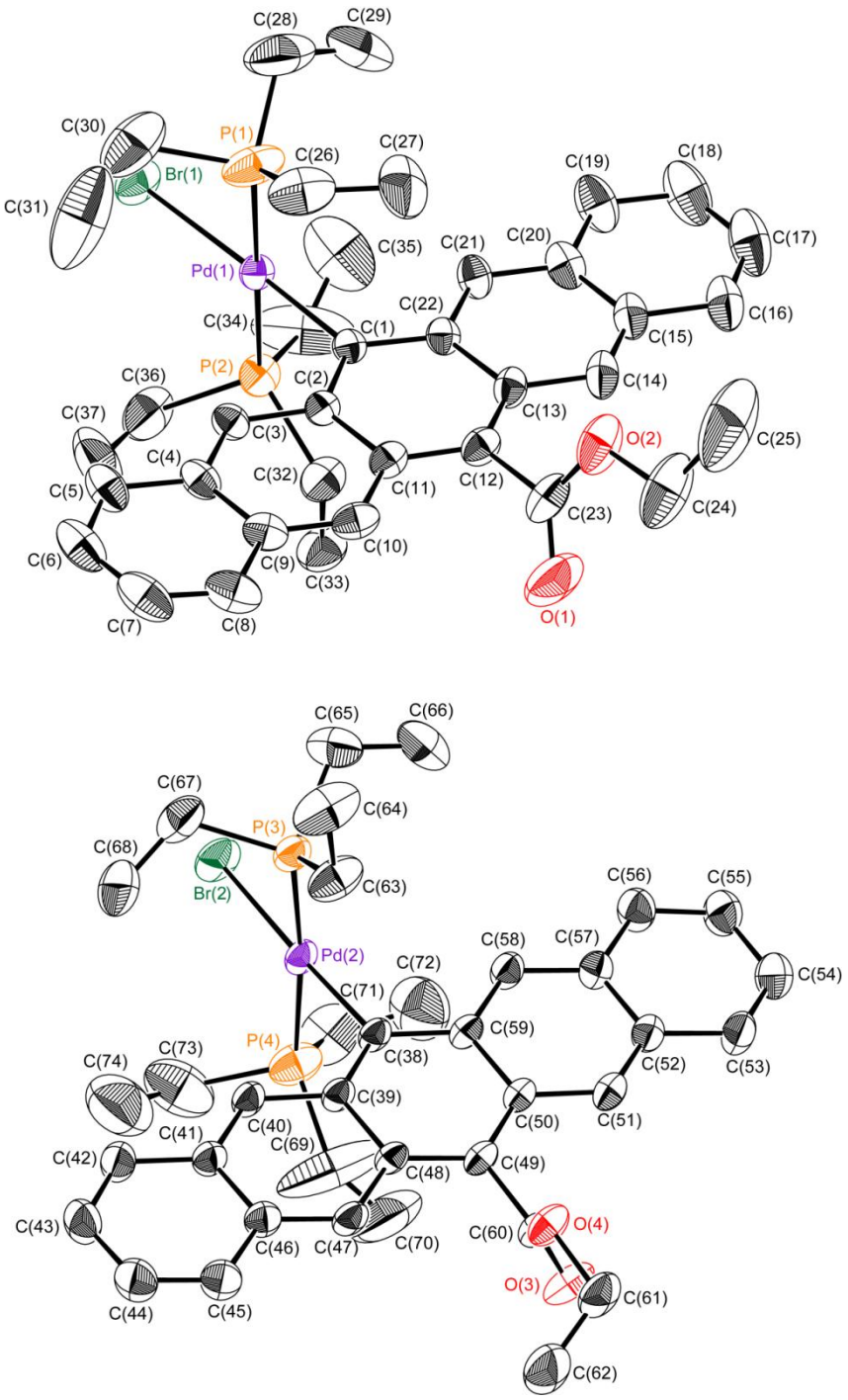


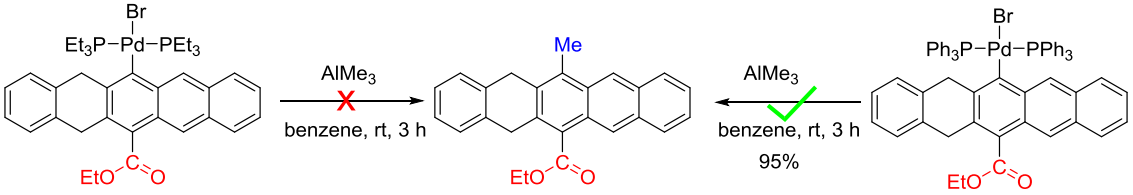
Figure 3 X-ray structure of complex **37**

Aromatizaiton of palladated dihydropentacenes **27**, **28**, **29** and **30** with DDQ and γ-terpinene afforded the corresponding palladated pentacenes **34**, **35**, **36** and **37** in high yields. The X-ray structure of **37** is shown in Figure 3. It clearly shows that the ester group attached to the central

ring of pentacene's flat skeleton. Unfortunately, maybe due to the effect of hydroxy group or imine, aromatization of palladated dihydropentacenes **25**, **26** and **31** with DDQ and γ-terpinene were failed.

3-2-3. Coupling reaction of the dihydropentacene derivatives

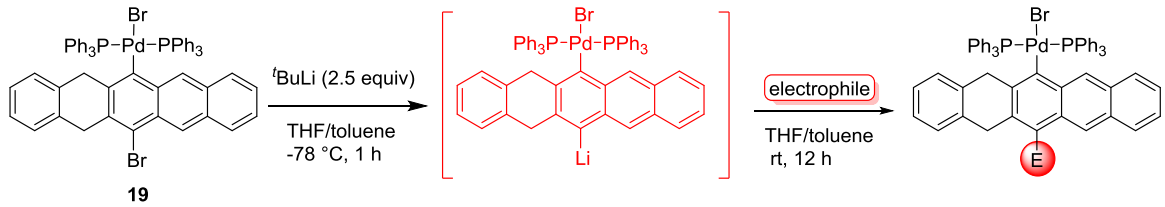
Scheme 8.

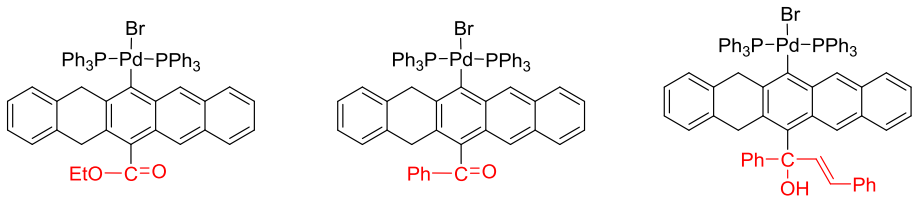


30 **42** **38**

For the further coupling reaction, palladium with PPh_3 ligands is better than PEt_3. Because when complex **30** was treated with $AlMe_3$ in benzene at room temperature, there was no reaction observed. However, when complex **38** was treated with $AlMe_3$ in benzene at room temperature for 3 h, the corresponding coupling product **42** was obtained in high yield (Scheme 8).

Table 3. Reaction of palladated dihydropentacene complex with electrophiles





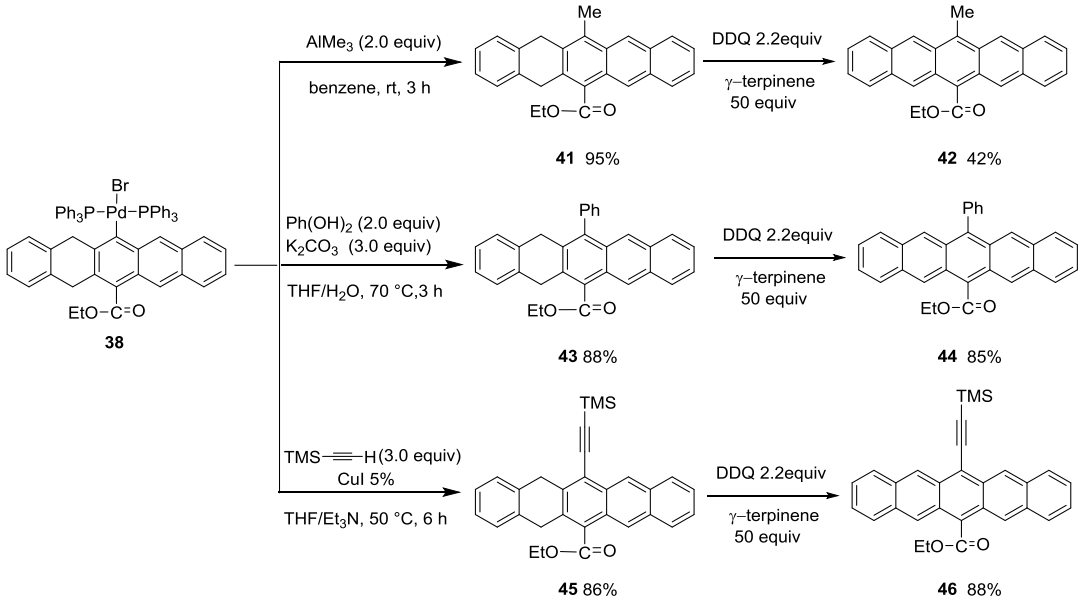
38 57% **39** 62% **40** 66%

For this purpose, lithiation of complex **19** with ^{t}BuLi in a mixed solution of THF and toluene (3:1) was carried out. Because the poor solubility of complex **19** in a mixed solution of diethyl ether and toluene, so here, diethyl ether was changed to THF. After lithiation reaction, the mixture was treated with electrophiles such as ethyl chloroformate or benzoyl chloride, the corresponding products **38** and **39** were obtained in good yields. Palladium-lithium reagent reacted with (*E*)-chalcone in THF to give 1,2-addition product **40** selectively in 66% yield

(Table 3).

After introduction of substituents into pentacene from electrophiles, introduction of substituents into pentacene by cross-coupling reaction was investigated (Scheme 9). With complex **38** in hand, by Negishi coupling, Suzuki coupling and Sonogashira coupling reactions, methyl, phenyl and trimethylsilylethynyl groups were introduced into pentacene. The unsymmetrical substituted dihydropentacenes **41**, **43**, and **45** were obtained in high yields. Aromatization of these compounds with DDQ and γ-terpinene afforded the corresponding unsymmetrical substituted pentacenes **42**, **44**, and **46** in good yields.

Scheme 9. Introduction of substituents into pentacene from nucleophiles



3-3. Summary

In summary, a new method was developed for introduction of substituents into pentacene from electrophiles and nucleophiles. Lithiation of monopalladated dihydropentacene complex **2** and **3** with ^{t}BuLi was selective. After lithiation, palladium-lithium intermediate could react with some kinds of electrophiles to give corresponding product in good yield. After that, by cross-coupling reaction, another substituent was introduced into pentacene from nucleophile. Additional aromatization, afforded disubstituted pentacene derivatives. Two substituents of these pentacene frameworks come from not only electrophile but also nucleophile.

3-4. Experimental Section

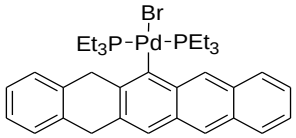
General information

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk

line techniques. The reaction temperature recorded here refers to the bath temperature. Tetrahydrofuran (THF), toluene, benzene, and hexane were refluxed and distilled from sodium benzophenone ketyl under nitrogen atmosphere. All starting materials were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded for C_6D_6 or $CDCl_3$ solution on JEOL JNM-ECX400 and JEOL JNM-ECX600. Chemical shifts (δ) were quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) were quoted in Hz. NMR yields were determined using mesitylene, dichloromethane or dioxane as internal standard. Mass spectra were obtained on JEOL JMS-T100GCv spectrometer.

Column chromatography was conducted with silica gel 60N (spherical, neutral, 100 – 210 μm. KANTO CHEMICAL, Co. INC). Some compounds were purified by Model LC-9201R/U Recycling Preparative HPLC (GPC) (Japan Analytical Industry, Co. Ltd).

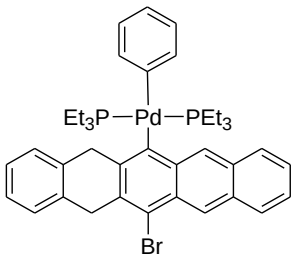
Preparation of palladated dihydropentacene 22 from 20



In a 20 mL Schlenk tube, palladated dihydropentacene **20** (60 mg, 0.0768 mmol) was dissolved in THF (2 mL). To the mixture was added ^{t}BuLi (0.109 mL, 0.192 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. After being quenched by methanol, the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **22** (46 mg, 85% isolated yield).

22: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.95-1.00 (m, 18 H), 1.37-1.50 (m, 12 H), 4.08 (s, 2 H), 4.44 (s, 2 H), 7.21-7.23 (m, 2 H), 7.33-7.36 (m, 2 H), 7.37-7.43 (m, 2 H), 7.61 (s, 1 H), 7.92 (d, *J* = 7.8Hz, 1 H), 7.97 (d, *J* = 7.8 Hz, 1 H), 8.25 (s, 1 H), 9.28 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.5, 15.8, 38.1, 41.8, 121.3, 124.5, 124.9, 125.1, 126.3, 126.3, 127.0, 127.1, 127.9, 128.3, 130.4, 130.8, 131.3, 132.3, 135.3, 137.1, 137.6, 137.9, 153.1. HRMS (ESI) calcd for $C_{34}H_{45}BrP_2Pd$: 702.1219. Found: 702.1204.

Preparation of palladated dihydropentacene 23 from 20

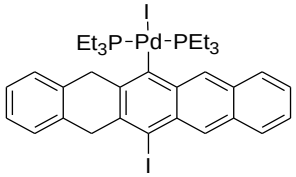


In a 20 mL Schlenk tube, palladated dihydropentacene **20** (16 mg, 0.02 mmol) was dissolved in toluene (2 mL). After the solution was cooled to -78 °C, phenyllithium (0.042 mL, 0.08

mmol) was added dropwise. Then remove the cooling bath, the mixture was stirred for 1 h at room temperature. After that the mixture was quenched by methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **23** (12 mg, 77% isolated yield).

23: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.90 (t, J = 7.8 Hz, 18 H), 1.00-1.05 (m, 6 H), 1.14-1.20 (m, 6 H), 4.08 (s, 2 H), 4.40 (s, 2 H), 4.52 (s, 2 H), 6.99 (t, J = 7.2 Hz, 2 H), 7.12-7.17 (m, 4 H), 7.22-7.24 (m, 4 H), 7.37-7.44 (m, 8 H), 7.76 (d, J = 7.2 Hz, 2 H),7.79 (d, J = 7.2 Hz, 2 H),7.96 (d, J = 7.8 Hz, 2 H), 8.08(d, J = 7.8 Hz, 2 H), 8.79 (s, 2 H), 9.44 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.2, 38.7, 43.0, 118.5, 122.1, 124.4, 124.7, 125.4, 126.0, 126.1, 126.7, 126.8, 126.9, 127.6, 127.8, 128.6, 129.9, 130.7, 131.5, 133.1, 133.7, 137.3, 138.6, 138.7, 138.8, 139.7, 141.4, 168.0, 169.4. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 10.13. HRMS (ESI) calcd for $C_{40}H_{49}BrP_2Pd$: 776.1528. Found: 776.1523.

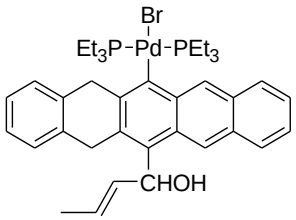
Preparation of palladated dihydropentacene 24 from 20



In a 20 mL Schlenk tube, to a THF (2 mL) solution of palladated dihydropentacene **20** (68 mg, 0.087 mmol) cooled to -78 °C was added ^{t}BuLi (0.123 mL, 0.22 mmol). The mixture was stirred at -78 °C for 1 h, then iodine (67 mg, 0.262 mmol) was added to the mixture solution at -78 °C, then remove the cooling bath. Under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. The reaction solution was quenched by saturated aqueous $Na_2S_2O_3$ solution at 0 °C, extracted with ethyl acetate. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **24** (64 mg, 84% isolated yield).

24: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93-0.98 (m, 18 H), 1.43-1.49 (m, 6 H), 1.54-1.61 (m, 6 H), 4.39 (s, 2 H), 4.45 (s, 2 H), 7.23-7.25 (m, 2 H), 7.32-7.33 (m, 1 H), 7.42-7.49 (m, 3 H), 7.91 (d, J = 7.8 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 8.75 (s, 1 H), 9.27 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 8.5, 16.8, 41.9, 44.9, 100.8, 125.4, 125.5, 126.4, 126.4, 126.5, 127.4, 128.3, 130.4, 131.0, 131.4, 132.1, 132.9, 136.8, 137.3, 137.4, 137.8, 139.2, 157.6. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 10.68. HRMS (ESI) calcd for $C_{34}H_{44}I_2P_2PdNa$: 892.9956[M + Na]+. Found: 892.9951[M + Na]+.

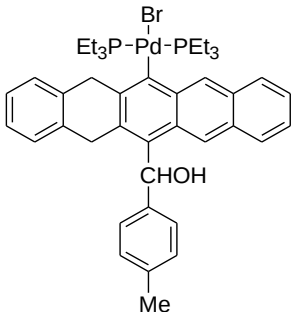
Preparation of palladated dihydropentacene 25 from 20



In a 20 mL Schlenk tube, palladated dihydropentacene **20** (22 mg, 0.028 mmol) was dissolved in THF (2 mL). To the mixture was added ^{t}BuLi (0.04 mL, 0.07 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. After that, crotonaldehyde (0.005 mL, 0.056 mmol) was added to the mixture solution at -78 °C. Remove the cooling bath, under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. The solution was quenched by methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =2:1 as eluent) to afford the title compound **25** (14 mg, 65% isolated yield).

25: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.93-1.00 (m, 18 H), 1.38-1.51 (m, 12 H), 1.69-1.7 (m, 3 H), 2.21 (s, 1 H), 4.16 (d, J = 16.8 Hz, 1 H), 4.34 (d, J = 16.8 Hz, 1 H), 4.39 (d, J = 16.2 Hz, 1 H), 4.59 (d, J = 16.2 Hz, 1 H), 5.60-5.64 (m, 1 H), 6.17-6.20 (m, 1 H), 6.46 (m, 1 H), 7.21-7.23 (m, 2 H), 7.33-7.35 (m, 2 H), 7.40-7.43 (m, 2 H), 7.89 (d, J = 9 Hz, 1 H), 7.99 (d, J = 9 Hz, 1 H), 8.86 (s, 1 H), 9.40 (s, 1 H). ^{13}C NMR (C_6D_6, Me_4Si, 600M) δ 8.5, 16.1, 17.8, 35.1, 42.8, 70.9, 123.7, 125.2, 125.3, 125.7, 126.5, 126.6, 126.8, 127.5, 129.1, 130.0, 130.4, 130.5, 131.7, 132.1, 134.4, 134.6, 138.1, 138.3, 138.8, 155.1 ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.37. HRMS (FAB) calcd for $C_{38}H_{51}BrOP_2Pd$: 772.1635. Found: 772.1616.

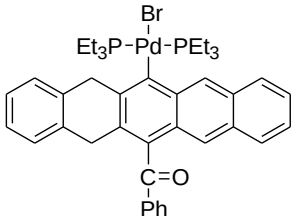
Preparation of palladated dihydropentacene 26 from 20



In a 20 mL Schlenk tube, palladated dihydropentacene **20** (21 mg, 0.027 mmol) was dissolved in diethyl ether : toluene (0.5 : 1.5) mL. To the mixture was added ^{t}BuLi (0.038 mL, 0.068 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. p-tolualdehyde (0.006 mL, 0.054 mmol) was added to the mixture solution at -78 °C. Remove the cooling bath, under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. After that the solution was quenched by methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =3:1 as eluent) to afford the title compound **26** (12.2 mg, 58% isolated yield).

26: ^{1}H NMR (C_6D_6, Me_4Si, 600M) δ 0.83-0.89 (m, 18 H), 1.29-1.44 (m, 12 H), 2.03 (br, 1 H), 2.13 (s, 3 H), 4.06 (d, J = 16.8 Hz, 1 H), 4.22 (d, J = 16.8 Hz, 1 H), 4.54 (d, J = 16.2 Hz, 1 H), 4.66 (d, J = 16.2 Hz, 1 H), 7.00 (s, 1 H), 7.07-7.10 (m, 3 H), 7.12-7.15 (m, 3 H), 7.25-7.28 (m, 1 H), 7.42 (d, J = 7.2 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 1 H),8.05 (d, J = 8.4 Hz, 1 H), 8.94 (s, 1 H), 9.71 (s, 1 H). ^{13}C NMR (C_6D_6, Me_4Si, 600M) δ 8.6, 16.3, 21.1, 35.1, 42.8, 70.7, 124.0, 125.3, 125.4, 126.2, 126.5, 126.6, 126.7, 127.5, 129.2, 129.2, 130.5, 130.8, 130.9, 131.9, 132.1, 135.4, 136.0, 138.1, 138.2, 138.7, 142.4, 156.0. ^{31}P NMR (C_6D_6, 600M) δ 12.54. HRMS (ESI) calcd for $C_{42}H_{53}BrONaP_2Pd$: 845.1686. Found: 845.1690.

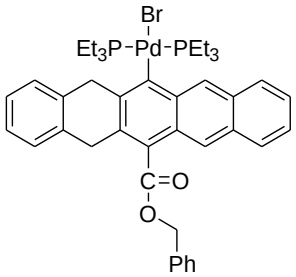
Preparation of palladated dihydropentacene 27 from 20



By the same method as described for compound **26** from palladated dihydropentacene **20**. Just benzoyl chloride was used instead of p-tolualdehyde. The title compound **27** in 60% isolated yield

27: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.00-1.05 (m, 18 H), 1.46-1.48 (m, 6 H), 1.54-1.56 (m, 6 H), 3.83 (s, 2 H), 4.52 (s, 2 H),7.03(d, J = 7.2 Hz, 1 H), 7.14 (t, J = 7.2 Hz, 1 H), 7.20(t, J = 7.2 Hz, 1 H),7.33-7.42 (m, 5 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.78-7.79 (m, 3 H), 7.91(d, J = 8.4 Hz, 1 H), 8.00 (s, 1 H), 9.41 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.5, 15.8, 35.2, 41.8, 123.6, 125.1, 125.3, 126.3, 126.7, 127.1, 127.8, 128.1, 128.7, 128.8, 129.7, 130.0, 130.3, 131.4, 131.9, 133.7, 136.3, 136.5, 137.4, 138.3, 156.8, 200.8. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.62; HRMS (ESI) calcd for $C_{41}H_{49}BrOP_2PdNa$: 829.1373[M + Na]+. Found: 829.1384[M + Na]+.

Preparation of palladated dihydropentacene 28 from 20

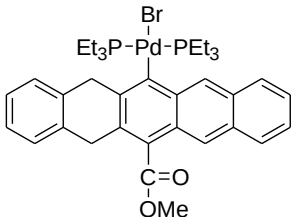


In a 20 mL Schlenk tube, Under nitrogen atmosphere, palladated dihydropentacene **20** (17.6 mg, 0.0225 mmol) was dissolved in Et_2O: toluene (0.5 : 1.5) mL. To the mixture was added ^{t}BuLi (0.032 mL, 0.056 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then benzyl chloroformate (0.004 mL, 0.027 mmol) was added to the mixture solution at -78 °C. The solution was warmed to room temperature and stirred for 12 h. The solvent was evaporated, and

the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =5:1 as eluent) to afford the title compound **28** (13 mg, 69% isolated yield) as a solid.

28: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.95-1.00 (m, 18 H), 1.36-1.40 (m, 6 H), 1.45-1.49 (m, 6 H), 4.00 (s, 2 H), 4.46 (s, 2 H), 5.65 (s, 2 H), 7.16-7.21 (m, 3 H), 7.30-7.31 (m, 1 H), 7.41-7.50 (m, 5 H), 7.64-7.65 (m, 2 H), 7.82-7.83 (m, 1 H), 7.88-7.90 (m, 1 H), 8.26 (s, 1 H), 9.36 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.6, 35.4, 41.8, 67.1, 123.1, 124.3, 125.1, 125.3, 126.3, 126.6, 127.2, 127.7, 127.9, 128.2, 128.6, 128.8, 129.2, 130.2, 131.3, 131.5, 133.1, 136.0, 136.1, 136.3, 136.4, 137.3, 158.7, 170.3. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.42. HRMS (ESI) calcd for $C_{42}H_{52}BrOP_2Pd$: 837.1640[M + H]+, Found: 837.1630[M + H]+.

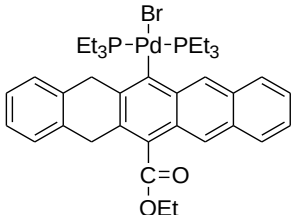
Preparation of palladated dihydropentacene 29 from 20



Compound **29** was synthesized by the same way as described for **28** from palladated dihydropentacene **20**. In this reaction methyl chloroformate was used. The title compound **29** was obtained in 57% isolated yield.

29: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.98 (t, J = 7.8 Hz, 18 H), 1.37-1.42 (m, 6 H), 1.46-1.50 (m, 6 H), 4.08 (s, 2 H), 4.17 (s, 3 H), 4.49 (s, 2 H), 7.22-7.23 (m, 2 H), 7.33-7.34 (m, 2 H), 7.42-7.46 (m, 2 H), 7.90-7.91 (m, 1 H), 7.97-7.98 (m, 1 H), 8.32 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 15.6, 35.6, 41.8, 52.3, 123.1, 124.6, 125.1, 125.4, 126.3, 126.4, 126.6, 127.3, 127.8, 127.9, 128.2, 130.2, 131.4, 131.6, 133.1, 136.2, 136.3, 136.4, 137.3, 158.7, 171.0. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.44. HRMS (ESI) calcd for $C_{36}H_{47}BrO_2P_2PdNa$: 783.1166[M + Na]+. Found: 783.1171[M + Na]+.

Preparation of palladated dihydropentacene 30 from 20

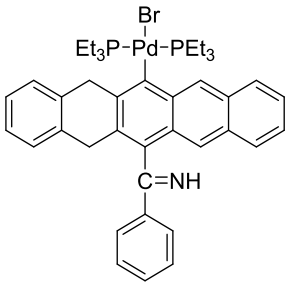


This compound was prepared by same method as described for **28** from complex **20**. Here, electrophilic reagent ethyl chloroformate was used in this reaction. Compound **30** was obtained in 68% isolated yield.

30: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.96-1.01 (m, 18 H), 1.36-1.42 (m, 6 H), 1.45-1.51 (m, 6 H), 1.58 (t, J = 7.2 Hz, 3 H), 4.10 (s, 2 H), 4.48 (s, 2 H), 4.68 (q, J = 7.2 Hz, 2 H), 7.22-7.24 (m,

2 H), 7.32-7.33 (m, 2 H), 7.41-7.45 (m, 2 H), 7.91 (d, *J* = 6.6 Hz, 1 H), 7.96 (d, *J* = 6.6 Hz, 1 H), 8.36 (s, 1 H), 9.38 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 14.6, 15.6, 35.4, 41.8, 61.3, 123.1, 124.8, 125.1, 125.3, 126.3, 126.3, 126.6, 127.3, 127.8, 127.9, 128.2, 130.2, 131.4, 131.6, 132.9, 136.2, 136.3, 136.5, 137.3, 158.3, 170.5. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.45. HRMS (ESI) calcd for $C_{37}H_{49}BrO_2P_2PdNa$: 797.1322[M + Na]+. Found: 797.1325[M + Na]+.

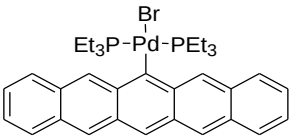
Preparation of palladated dihydropentacene 31 from 20



In a 20 mL Schlenk tube, palladated dihydropentacene **20** (22 mg, 0.028 mmol) was dissolved in THF 2 mL. To the mixture was added ^{t}BuLi (0.039 mL, 0.069 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then benzonitrile (0.006 mL, 0.055 mmol) was added to the mixture solution at -78 °C and stirred for 2 h. After being quenched by methanol, the solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =3:1 as eluent) to afford the title compound **31** (11 mg, 50% isolated yield).

31: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.96-0.1.07 (m, 18 H), 1.43-1.58 (m, 12 H), 3.74-3.96 (m, 2 H), 4.50-4.51 (m, 2 H), 7.09 (d, *J* = 7.2 Hz, 1 H), 7.15 (t, *J* = 7.2 Hz, 1 H), 7.21 (t, *J* = 7.2 Hz, 1 H), 7.30-7.34 (m, 3H), 7.36-7.44 (m, 3 H), 7.72-7.73 (m, 2 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 8.09 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.4, 8.5, 15.8 (q, *J* = 13 Hz), 35.2, 41.9, 123.8, 125.1, 125.2, 126.3, 126.6, 127.1, 127.8, 127.8, 128.1, 128.6, 128.9, 130.2, 131.1, 131.3, 131.4, 136.5, 136.6, 137.5, 138.6, 155.0, 178.3. ^{31}P NMR ($CDCl_3$, 600M) δ 12.65.

Preparation of palladated pentacene 32 from 19



In a 20 mL Schlenk tube, palladated dihydropentacene **19** (33 mg, 0.03087 mmol) and DDQ (8.4 mg, 0.037 mmol) were dissolved in benzene (2 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 3 h. After that PEt_3 (0.197 mL, 0.185 mmol) was added to the above solution at room temperature. The mixture was stirred at 80 °C for 12 h. The solvent was removed in vacuo, and the resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **32** (13mg, 62% isolated

yield) as a blue solid.

32: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.85-0.93 (m, 18 H), 1.24-1.32 (m, 12 H), 7.27-7.34 (m, 4 H), 7.87-7.94 (m, 4 H), 8.58 (s, 2 H), 8.65 (s, 1 H), 9.52 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.3, 15.3, 121.6, 124.4, 125.3, 126.3, 128.2, 128.8, 130.1, 130.9, 131.6, 132.9, 135.4, 165.3. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 13.05. HRMS (FAB) calcd for $C_{34}H_{43}BrP_2Pd$: 698.1058. Found: 698.1065.

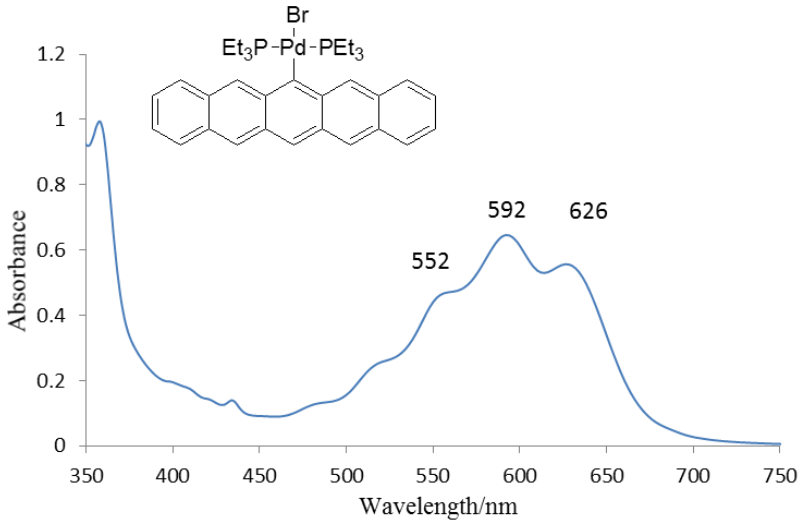


Figure 4. Absorption spectrum of pentacene derivative **32** in $CHCl_3$ at rt

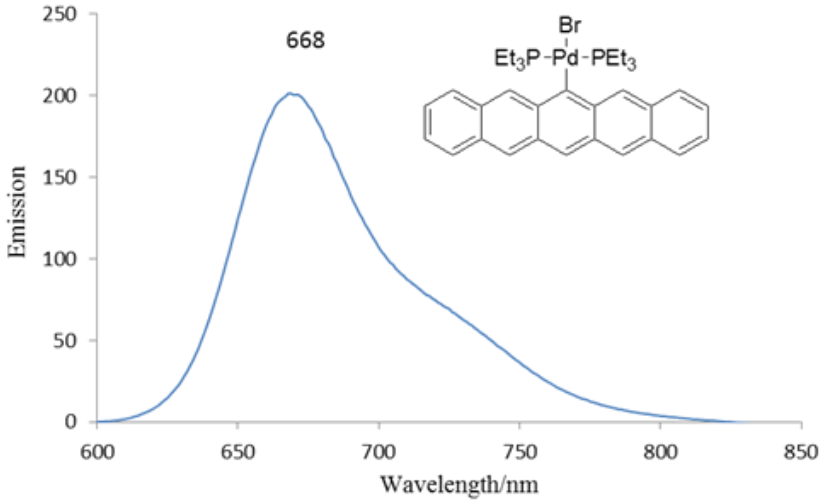
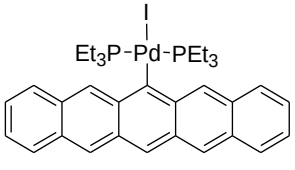


Figure 5. Emission spectrum of pentacene derivative **32** in $CHCl_3$ at rt (λ_{ex} = 592 nm)

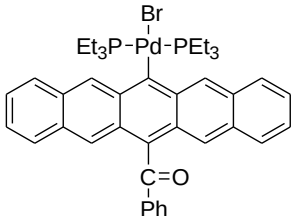
Preparation of palladated pentacene 33 from 24



In a 20 mL Schlenk tube, palladated dihydropentacene **24** (15.4 mg, 0.0176 mmol) and DDQ (9 mg, 0.039 mmol) were dissolved in benzene (2 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 1 h. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, *γ*-terpinene (0.14 mL, 0.88 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford compound **33** (5 mg, 38% isolated yield) as a blue solid.

33: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.83-0.93 (m, 18 H), 1.32-1.37 (m, 12 H), 7.27-7.34 (m, 4 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.93 (d, J = 8.0 Hz, 2 H), 8.59 (s, 2 H), 8.68 (s, 1 H), 9.44 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 8.3, 16.3, 121.7, 124.3, 125.1, 126.2, 128.1, 128.6, 129.9, 130.8, 131.4, 132.2, 135.41, 167.0. ^{31}P NMR ($CDCl_3$, Me_4Si). δ 11.55. HRMS (FAB) calcd for $C_{34}H_{43}IP_2Pd$:746.0933. Found: 746.0935.

Preparation of palladated pentacene 34



In a 20 mL Schlenk tube, palladated dihydropentacene **27** (14.4 mg, 0.0179 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (9 mg, 0.039 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 2 h at room temperature. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, *γ*-terpinene (0.14 mL, 0.9 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **34** (12mg, 83% isolated yield) as a blue solid.

34: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.92-0.98 (m, 18 H), 1.34-1.39 (m, 12 H), 7.26-7.30 (m, 4 H), 7.35(t, J = 7.8 Hz, 2 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 7.2 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H), 8.30 (s, 2 H), 9.66 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.3, 15.3, 123.7, 124.7, 125.8, 127.2, 128.3, 128.7, 129.7, 130.0, 132.0, 133.6, 134.5, 138.9, 171.4, 201.6. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.98. HRMS (FAB) calcd for $C_{41}H_{47}BrOP_2Pd$: 804.1323. Found: 804.1339.

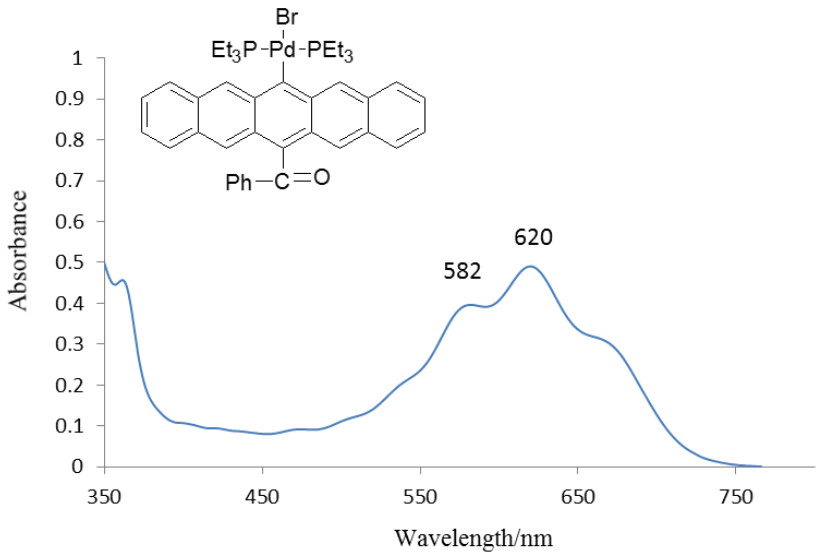
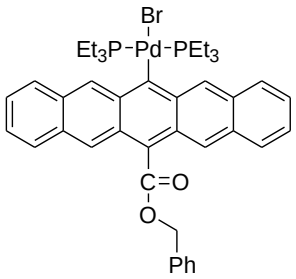


Figure 6. Absorption spectrum of pentacene derivative **34** in $CHCl_3$ at rt

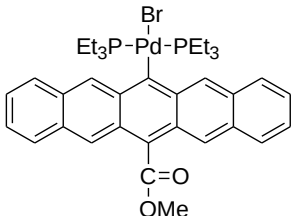
Preparation of palladated pentacene 35



By the same method as described for **34**, the title compound **35** was obtained in 65% isolated yield as a blue solid.

35: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.90 (t, J = 7.8 Hz, 18 H), 1.27-1.28 (m, 12 H), 5.80 (s, 2 H), 7.30-7.34 (m, 4 H), 7.48-7.53 (m, 3 H), 7.72 (d, J = 7.8 Hz, 2 H), 7.77 (d, J = 7.8Hz, 2 H), 7.86 (d, J = 7.8 Hz, 2 H), 8.60 (s, 2 H), 9.63 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.2, 15.1, 67.4, 121.2, 123.5, 124.8, 125.9, 127.0, 128.2, 128.4, 128.7, 128.8, 129.4, 129.6, 132.3, 133.7, 134.5, 136.2, 170.9, 174.4. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.70. HRMS (FAB) calcd for $C_{42}H_{49}BrO_2P_2Pd$: 834.1429. Found: 834.1432.

Preparation of palladated pentacene 36



By the same method as described for **34**, the title compound **36** was obtained in 80% isolated yield as a blue solid.

36: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.88-0.93 (m, 18 H), 1.27-1.32 (m, 12 H), 4.31 (s, 3 H), 7.32-7.37 (m, 4 H), 7.88 (d, J = 8.4Hz, 2 H), 7.94 (d, J = 8.4Hz, 2 H), 8.67 (s, 2 H), 9.66 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.2, 15.2, 52.6, 121.5, 123.4, 124.8, 126.0, 127.0, 128.3, 128.5, 129.7, 132.5, 133.8, 134.5, 171.5, 174.4. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.71. HRMS (FAB) calcd for $C_{36}H_{45}BrO_2P_2Pd$: 758.1114. Found: 758.1140

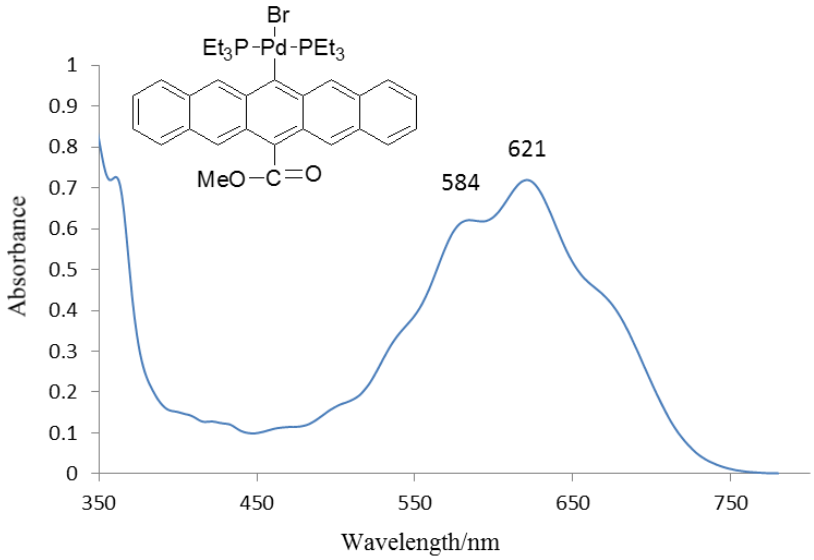
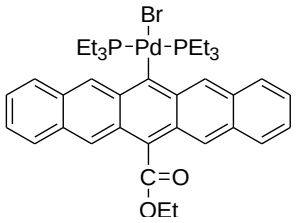


Figure 7. Absorption spectrum of pentacene derivative **36** in $CHCl_3$ at rt

Preparation of palladated pentacene 37



By the same method as described for **34**, the title compound **37** was obtained in 84% isolated yield as a blue solid.

37: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.88-0.94 (m, 18 H), 1.27-1.32 (m, 12 H), 1.65 (t, J = 7.2 Hz, 3 H), 4.83 (q, J = 7.2 Hz, 2 H), 7.31-7.37 (m, 4 H), 7.88 (d, J = 7.8 Hz, 2 H), 7.93 (d, J = 8.4 Hz, 2 H), 8.72 (s, 2 H), 9.65 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.1, 14.7, 15.1, 61.6, 121.9, 123.4, 124.8, 125.9, 127.0, 128.3, 128.4, 129.7, 132.4, 133.7, 134.5, 171.1, 173.9. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.73. HRMS (FAB) calcd for $C_{37}H_{47}BrO_2P_2Pd$: 772.1271. Found: 772.1276.

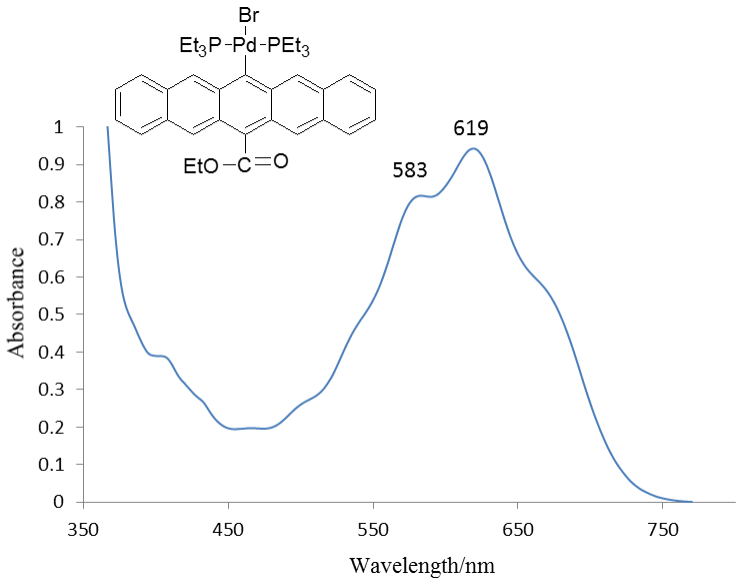
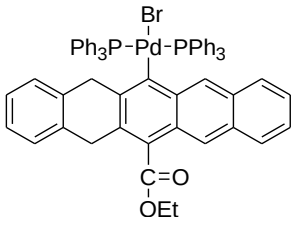


Figure 8. Absorption spectrum of pentacene derivative **37** in $CHCl_3$ at rt

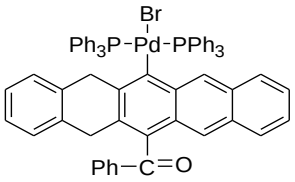
Preparation of palladated dihydropentacene 38



In a 20 mL Schlenk tube, under nitrogen atmosphere, palladated dihydropentacene **19** (25 mg, 0.023 mmol) was dissolved in THF : toluene (0.5 : 1.5) mL. To the mixture was added ^{t}BuLi (0.033 mL, 0.058 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then ethyl chloroformate (0.004 mL, 0.046 mmol) was added to the mixture solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform =5:1:1 as eluent) to afford the title compound **38** (14 mg, 57% isolated yield) as a pale yellow solid.

38: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.51 (t, J = 7.2 Hz, 3 H), 3.32 (s, 2 H), 4.03 (s, 2 H), 4.55 (q, J = 7.2 Hz, 2 H), 6.64 (d, J = 7.6 Hz, 1 H), 6.94-7.08 (m, 16 H), 7.18-7.22 (m, 6 H), 7.29-7.37 (m, 13 H), 7.64 (d, J = 6.8 Hz, 1 H), 7.78 (d, J = 6.8 Hz, 1 H), 7.88 (s, 1 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.5, 35.2, 40.8, 60.7, 122.4, 124.3, 124.8, 125.8, 125.9, 126.6, 126.6, 127.6, 127.7, 127.8, 129.7, 129.8, 130.4, 130.6, 130.9, 131.0, 132.9, 134.3, 135.4, 136.1, 137.1, 164.0, 170.1. ^{31}P NMR ($CDCl_3$, 400M) δ 24.3. HRMS (ESI) calcd for $C_{61}H_{49}BrO_2P_2Pd$: 1062.1406. Found: 1062.1410.

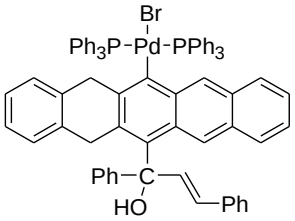
Preparation of palladated dihydropentacene 39



By the same method as described for **38**, the title compound **39** was obtained in 62% isolated yield as a pale yellow solid.

39: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 3.08 (s, 2 H), 4.15 (s, 2 H), 6.69 (d, J = 7.2 Hz,1 H), 6.75 (d, J = 7.2 Hz, 1 H), 6.95 (t, J = 7.2 Hz, 1 H), 6.98 (t, J = 7.2 Hz,1 H), 7.11-7.13 (m, 12 H), 7.23-7.28 (m, 10 H), 7.42-7.46 (m, 12 H), 7.57 (s, 1 H), 7.59-7.60 (m, 2 H),7.63 (d, J = 7.8 Hz, 1 H), 7.74-7.76 (m, 2 H), 9.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 35.1, 41.2, 123.1, 124.3, 124.6, 125.7, 125.8, 126.4, 126.6, 127.8, 128.4, 128.9, 129.7, 130.0, 130.8, 132.7, 133.5, 134.4, 135.7, 135.8, 136.2, 137.5, 138.3, 159.3, 200.2. ^{31}P NMR ($CDCl_3$, 600M) δ 24.6. HRMS (FAB) calcd for $C_{65}H_{49}BrOP_2Pd$: 1094.1487. Found: 1094.1504.

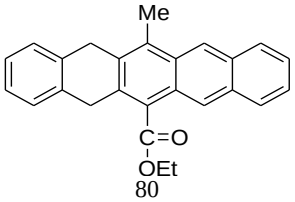
Preparation of palladated dihydropentacene 40



In a 20 mL Schlenk tube, under nitrogen atmosphere, palladated dihydropentacene **19** (62 mg, 0.058 mmol) was dissolved in THF (4 mL). To the mixture was added ^{t}BuLi (0.082 mL, 0.145 mmol) at -78 °C, and it was stirred for 1 h. (E)-chalcone (14 mg, 0.07 mmol) was added to the mixture solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. It was quenched with methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform =3:1:1 as eluent) to afford the title compound **40** (46 mg, 66% isolated yield) as a yellow solid.

40: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 2.27 (s, 1 H), 3.35 (d, J = 15.6 Hz, 1 H), 3.62 (d, J = 15.6 Hz, 1 H), 4.13 (d, J = 15.6 Hz, 1 H), 4.42 (d, J = 15.6 Hz, 1 H), 6.03 (d, J = 15.6 Hz, 1 H), 6.48 (d, J = 7.2 Hz, 1 H), 6.60 (d, J = 7.8 Hz, 1 H), 6.70 (d, J = 15.6 Hz, 1 H), 6.85 (t, J = 7.2 Hz, 1 H), 6.91 (t, J = 7.8 Hz, 1 H), 7.06-7.11 (m, 12 H), 7.18-7.52 (m, 31 H), 7.68 (d, J = 8.4 Hz, 1 H), 8.41 (s, 1 H), 9.58 (s, 1 H). ^{31}P NMR ($CDCl_3$, 600M) δ 24.3. HRMS (FAB) calcd for $C_{73}H_{57}BrOP_2Pd$: 1198.2116. Found: 1198.2139.

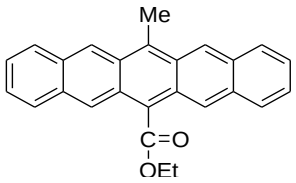
Preparation of palladated dihydropentacene 41



In a 20 mL Schlenk tube, palladated dihydropentacene **38** (30 mg, 0.0282 mmol) was dissolved in benzene 2 mL. To the mixture was added $AlMe_3$ (0.052 mL, 0.056 mmol) at room temperature, and it was stirred for 3 h at room temperature. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **41** (9.9 mg, 96% isolated yield).

41: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.56 (t, J = 7.2 Hz, 3 H), 2.91 (s, 3 H), 4.11 (s, 2 H), 4.20 (s, 2 H), 4.68 (q, J = 7.2 Hz, 2 H), 7.23-7.25 (m, 2 H), 7.33 (t, J = 4.2 Hz, 1 H), 7.38 (t, J = 4.2 Hz, 1 H), 7.45-7.47 (m, 2 H), 7.96-7.97 (m, 1 H), 8.01-8.03 (m, 1 H), 8.34 (s, 1 H), 8.62 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 14.5, 15.3, 33.9, 35.1, 61.5, 123.1, 123.6, 125.5, 125.6, 126.5, 126.6, 126.9, 127.2, 127.2, 127.3, 128.1, 128.4, 130.0, 131.4, 131.4, 132.0, 133.0, 136.1, 136.6, 170.1. HRMS (EI) calcd for $C_{26}H_{22}O_2$: 366.1620. Found: 366.1614.

Preparation of palladated pentacene 42



In a 20 mL Schlenk tube, palladated dihydropentacene **41** (9.9 mg, 0.027 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (13.5 mg, 0.059 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 2 h at 50 °C. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, γ-terpinene (0.22 mL, 1.35 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 6 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **42** (4.1mg, 42% isolated yield) as a blue solid.

42: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.64 (t, J = 7.2 Hz, 3 H), 3.48 (s, 3 H), 4.85 (q, J = 7.2 Hz, 2 H), 7.26-7.39 (m, 4 H), 7.90-7.92 (m, 2 H), 7.96-7.98 (m, 2 H), 8.66 (s, 2 H), 8.96 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.6, 15.4, 61.9, 123.8, 123.9, 125.5, 125.9, 126.3, 127.8, 128.3, 128.7, 131.1, 131.8, 133.8, 170.7. HRMS (EI) calcd for $C_{26}H_{20}O_2$: 364.1463. Found: 364.1468

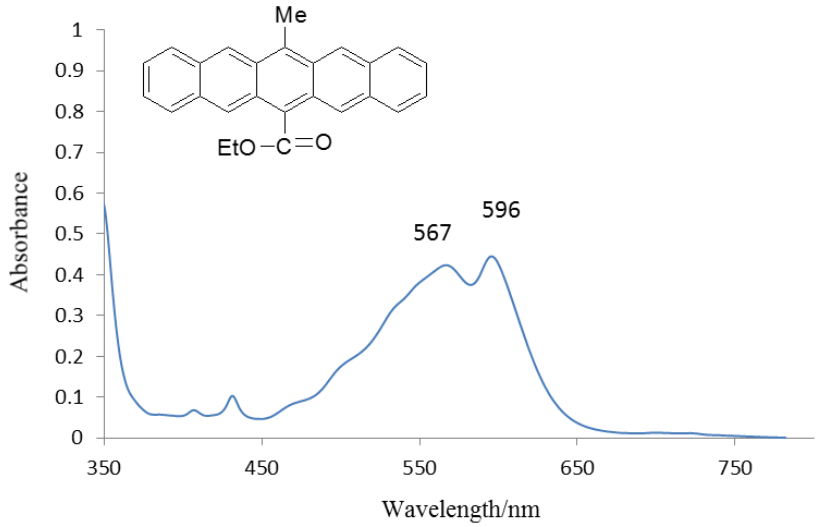
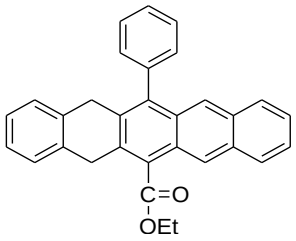


Figure 9. Absorption spectrum of pentacene derivative **42** in CH_2Cl_2 at rt

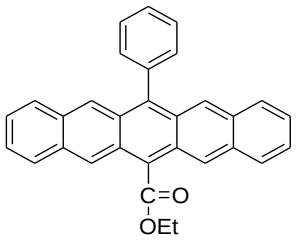
Preparation of palladated dihydropentacene 43



In a 20 mL Schlenk tube, palladated dihydropentacene **38** (43 mg, 0.04 mmol), phenylboronic acid (10 mg, 0.08 mmol) and potassium carbonate (17 mg, 0.12 mmol) were dissolved in mixed solution of THF and H_2O (10:1) 2 mL. The solution was degassed by three times of freeze-pump-thaw cycles and heated at 70 °C for 3 h. The solvent was evaporated, and the resulting solids were purified by column chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **43** (15 mg, 88% isolated yield) as solid.

43: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.59 (t, J = 7.6 Hz, 3 H), 3.81 (s, 2 H), 4.17 (s, 2 H), 4.73 (q, J = 7.6 Hz, 2 H), 7.11-7.24 (m, 3 H), 7.33-7.45 (m, 5 H), 7.56-7.64 (m, 3 H), 7.78 (d, J = 8.4 Hz, 1 H), 7.94 (s, 2 H), 7.97 (d, J = 8.4 Hz, 1 H), 8.42 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.6, 34.9, 35.2, 61.6, 123.1, 125.4, 125.7, 125.8, 126.5, 126.8, 127.1, 127.2, 127.7, 128.1, 128.4, 128.7, 130.2, 131.3, 131.5, 132.5, 133.3, 136.1, 136.9, 138.2, 139.0, 169.9. HRMS (EI) calcd for $C_{31}H_{24}O_2$: 428.1776. Found: 428.1773.

Preparation of palladated pentacene 44



By the same aromatic method as described for pentacene **42**, the title compound **44** was obtained in 85% isolated yield as a blue solid.

44: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.67 (t, J = 7.2 Hz, 3 H), 4.89 (q, J = 7.2 Hz, 2 H), 7.25-7.29 (m, 2 H), 7.33-7.37 (m, 2 H), 7.55-7.57 (m, 2 H), 7.68-7.74 (m, 5 H), 7.92 (d, J = 8.8 Hz, 2 H), 8.29 (s, 2 H), 8.70 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 14.6, 62.1, 123.3, 125.4, 126.1, 126.2, 126.3, 127.5, 128.0, 128.2, 128.3, 128.6, 128.7, 131.1, 131.4, 132.0, 138.9, 140.1, 170.5. HRMS (EI) calcd for $C_{31}H_{22}O_2$: 426.1620. Found: 426.1625.

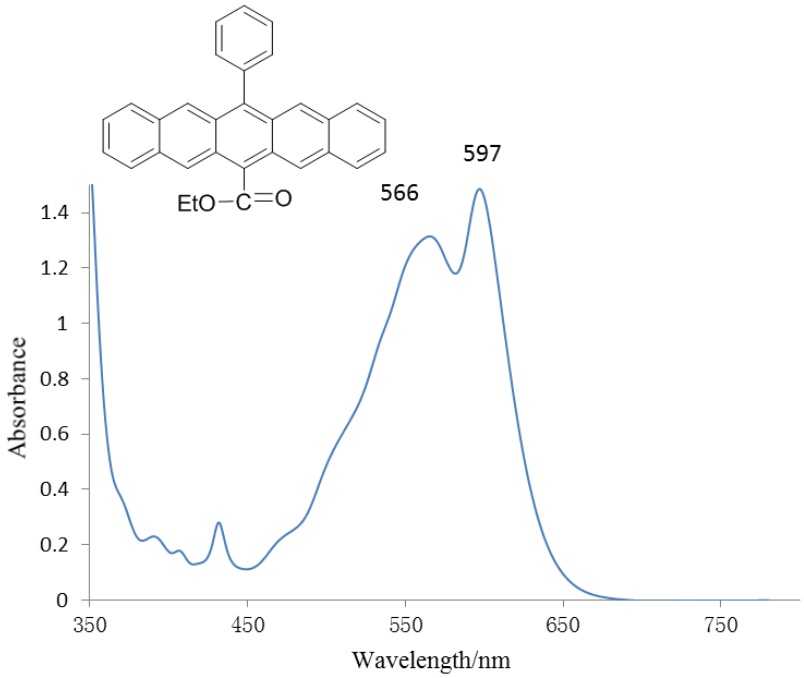
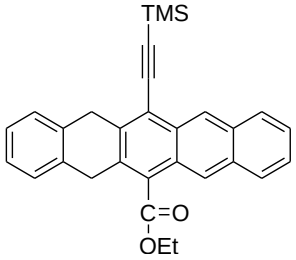


Figure 10. Absorption spectrum of pentacene derivative **44** in $CHCl_3$ at rt

Preparation of palladated dihydropentacene 45

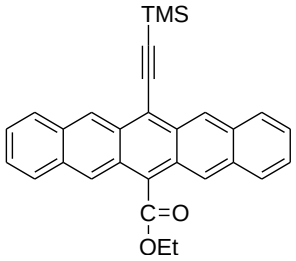


In a 20 mL Schlenk tube, palladated dihydropentacene **38** (13.7 mg, 0.0129 mmol) and CuI (3

mg, 0.016 mmol) were dissolved in mixed solution of (THF : Et_3N = 1 : 1) 2 mL. The mixture was degassed by three times of freeze-pump thaw cycle. To the mixture was added trimethylsilylacetylene (0.005 mL, 0.039 mmol) at room temperature, and it was stirred for 6 h at 50 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **45** (5mg, 86% isolated yield) as a solid.

45: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.47 (s, 9 H), 1.57 (t, J = 7.2 Hz, 3 H), 4.11 (s, 2 H), 4.41 (s, 2 H), 4.69 (q, J = 7.2 Hz, 2 H), 7.23-7.28 (m, 2 H), 7.33 (d, J = 7.2 Hz, 1 H), 7.40 (d, J = 7.2 Hz, 1 H), 7.47-7.51 (m, 2 H), 7.98 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.38 (s, 1 H), 8.92 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 0.2, 14.5, 34.7, 35.7, 61.7, 101.4, 106.4, 119.5, 123.7, 125.4, 125.9, 126.4, 126.6, 126.7, 127.3, 127.5, 128.3, 128.4, 129.0, 129.7, 131.8, 131.9, 132.8, 135.6, 136.0, 138.8, 169.4. HRMS (EI) calcd for $C_{30}H_{28}O_2Si$: 448.1859. Found: 448.1862.

Preparation of palladated pentacene 46



In a 20 mL Schlenk tube, palladated dihydropentacene **45** (6.2 mg, 0.0138 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (7 mg, 0.0304 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 1 h at room temperature. The pentacene-DDQ adduct was formed firstly, without isolation of pentacene-DDQ adduct, γ-terpinene (0.11 mL, 0.69 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 1 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **46** (4.7 mg, 85% isolated yield) as a blue solid.

46: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.55 (s, 9 H), 1.64 (t, J = 7.2Hz, 3 H), 4.86 (t, J = 7.2Hz, 2 H), 7.38-7.42 (m, 4 H), 7.93-7.94 (m, 2 H), 8.01-8.03 (m, 2 H), 8.65 (s, 2 H), 9.24 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 0.3, 14.6, 62.2, 102.4, 110.4, 119.7, 124.1, 126.0, 126.1, 126.1, 126.2, 128.5, 128.7, 130.2, 132.0, 132.3, 169.9. HRMS (EI) calcd for $C_{30}H_{26}O_2Si$: 446.1702. Found: 446.1697.

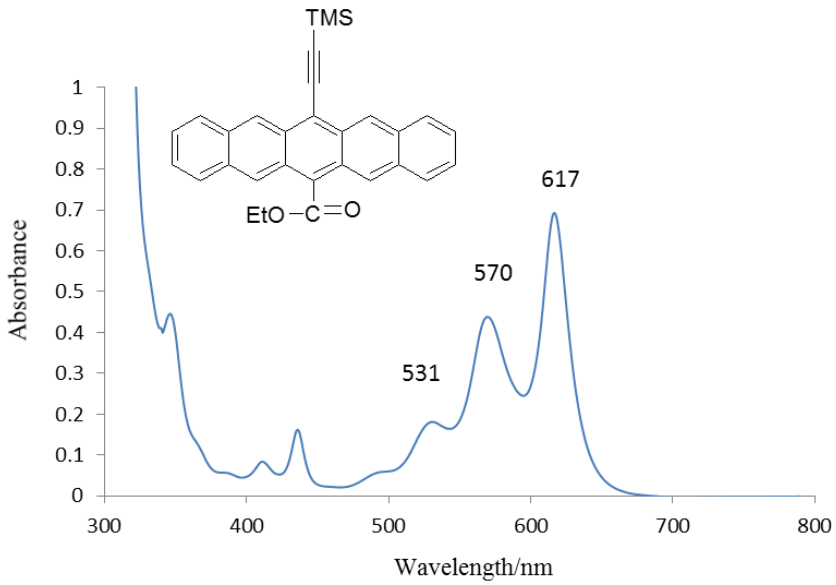


Figure 11. Absorption spectrum of pentacene derivative **46** in $CHCl_3$ at rt

X-ray analysis data for compound 37

Table 4. Crystallographic data and experimental details for compound **37**

Compound	**37**
Formula	$C_{37}\ H_{47}\ Br\ O_2P_2\ Pd$
M	772.13
Crystal system	triclinic
Space group	P -1
a, (Å)	12.581(4)
b, (Å)	14.672(5)
c, (Å)	21.170(5)
α, (°)	104.748(11)
β, (°)	98.673(11)
γ, (°)	100.210(12)
V, ($Å^3$)	3639.5(19)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	brown
Crystal size, (mm^3)	0.35 x 0.35 x 0.35
D_{calcd}, (g cm^{-3})	1.409
Transm factor	0.5834- 0.5834
λ (Mo Kα), ($Å^3$)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-16≤ h ≤ 15

	-18≤ k ≤ 19
	-27≤ l ≤ 27
No. of reflection measd	16432
No. of reflection obsd [I>2σ(I)]	11297
No. of parameters refined	775
R	0.0474
R_ω	0.1382
S, goodness of fit	1.058
Largest diff peak, (e Å^{-3})	0.749
Largest diff hole, (e Å^{-3})	-0.790

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 5. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.015(3)	Pd1 P2 2.3113(13)
Pd1 P1 2.3146(16)	Pd1 Br1 2.5154(7)
Pd2 C38 2.026(3)	Pd2 P3 2.3158(13)
Pd2 P4 2.3189(16)	Pd2 Br2 2.5107(8)
P1 C28 1.771(10)	P1 C26 1.840(7)
P1 C30 1.898(10)	P2 C34 1.798(8)
P2 C36 1.813(7)	P2 C32 1.821(5)
P3 C63 1.784(5)	P3 C67 1.836(6)
P3 C65 1.838(6)	P4 C69 1.768(8)
P4 C71 1.795(8)	P4 C73 1.907(11)
O1 C23 1.212(7)	O2 C23 1.322(7)
O2 C24 1.468(7)	O3 C60 1.195(5)
O4 C60 1.336(5)	O4 C61 1.468(5)
C1 C2 1.406(5)	C1 C22 1.417(5)
C2 C3 1.406(5)	C2 C11 1.450(5)
C3 C4 1.379(5)	C3 H1 0.9300
C4 C9 1.421(6)	C4 C5 1.431(6)
C5 C6 1.363(7)	C5 H2 0.9300
C6 C7 1.394(9)	C6 H3 0.9300
C7 C8 1.333(8)	C7 H4 0.9300
C8 C9 1.452(6)	C8 H5 0.9300
C9 C10 1.368(6)	C10 C11 1.423(6)
C10 H6 0.9300	C11 C12 1.397(6)
C12 C13 1.401(6)	C12 C23 1.494(6)
C13 C14 1.406(5)	C13 C22 1.467(5)
C14 C15 1.369(7)	C14 H7 0.9300
C15 C20 1.433(7)	C15 C16 1.440(6)
C16 C17 1.334(9)	C16 H8 0.9300
C17 C18 1.378(10)	C17 H9 0.9300
C18 C19 1.369(8)	C18 H10 0.9300
C19 C20 1.421(7)	C19 H11 0.9300
C20 C21 1.382(5)	C21 C22 1.403(5)
C21 H12 0.9300	C24 C25 1.418(14)
C24 H13 0.9700	C24 H14 0.9700
C25 H15 0.9600	C25 H16 0.9600
C25 H17 0.9600	C26 C27 1.494(9)
C26 H18 0.9700	C26 H19 0.9700
C27 H20 0.9600	C27 H21 0.9600
C27 H22 0.9600	C28 C29 1.513(14)
C28 H23 0.9700	C28 H24 0.9700
C29 H25 0.9600	C29 H26 0.9600
C29 H27 0.9600	C30 C31 1.388(17)
C30 H28 0.9700	C30 H29 0.9700
C31 H30 0.9600	C31 H31 0.9600
C31 H32 0.9600	C32 C33 1.502(7)
C32 H33 0.9700	C32 H34 0.9700
C33 H35 0.9600	C33 H36 0.9600

C33 H37 0.9600	C34 C35 1.270(11)
C34 H38 0.9700	C34 H39 0.9700
C35 H40 0.9600	C35 H41 0.9600
C35 H42 0.9600	C36 C37 1.452(13)
C36 H43 0.9700	C36 H44 0.9700
C37 H45 0.9600	C37 H46 0.9600
C37 H47 0.9600	C38 C39 1.397(5)
C38 C59 1.423(5)	C39 C40 1.409(5)
C39 C48 1.455(5)	C40 C41 1.381(5)
C40 H48 0.9300	C41 C46 1.424(5)
C41 C42 1.432(6)	C42 C43 1.355(6)
C42 H49 0.9300	C43 C44 1.409(8)
C43 H50 0.9300	C44 C45 1.327(7)
C44 H51 0.9300	C45 C46 1.443(6)
C45 H52 0.9300	C46 C47 1.371(6)
C47 C48 1.408(5)	C47 H53 0.9300
C48 C49 1.403(5)	C49 C50 1.400(5)
C49 C60 1.492(5)	C50 C51 1.414(5)
C50 C59 1.442(5)	C51 C52 1.360(6)
C51 H54 0.9300	C52 C53 1.429(6)
C52 C57 1.434(6)	C53 C54 1.337(7)
C53 H55 0.9300	C54 C55 1.410(8)
C54 H56 0.9300	C55 C56 1.356(7)
C55 H57 0.9300	C56 C57 1.423(6)
C56 H58 0.9300	C57 C58 1.389(6)
C58 C59 1.412(5)	C58 H59 0.9300
C61 C62 1.426(8)	C61 H60 0.9700
C61 H61 0.9700	C62 H62 0.9600
C62 H63 0.9600	C62 H64 0.9600
C63 C64 1.557(8)	C63 H65 0.9700
C63 H66 0.9700	C64 H67 0.9600
C64 H68 0.9600	C64 H69 0.9600
C65 C66 1.411(10)	C65 H70 0.9700
C65 H71 0.9700	C66 H72 0.9600
C66 H73 0.9600	C66 H74 0.9600
C67 C68 1.453(9)	C67 H75 0.9700
C67 H76 0.9700	C68 H77 0.9600
C68 H78 0.9600	C68 H79 0.9600
C69 C70 1.149(11)	C69 H80 0.9700
C69 H81 0.9700	C70 H82 0.9600
C70 H83 0.9600	C70 H84 0.9600
C71 C72 1.463(11)	C71 H85 0.9700
C71 H86 0.9700	C72 H87 0.9600
C72 H88 0.9600	C72 H89 0.9600
C73 C74 1.392(14)	C73 H90 0.9700
C73 H91 0.9700	C74 H92 0.9600
C74 H93 0.9600	C74 H94 0.9600

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 6. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P2 90.14(10)	C1 Pd1 P1 91.15(10)
P2 Pd1 P1 178.48(5)	C1 Pd1 Br1 178.31(10)
P2 Pd1 Br1 89.92(3)	P1 Pd1 Br1 88.81(4)
C38 Pd2 P3 91.96(11)	C38 Pd2 P4 89.81(11)
P3 Pd2 P4 174.19(6)	C38 Pd2 Br2 176.37(10)
P3 Pd2 Br2 89.60(3)	P4 Pd2 Br2 88.96(4)
C28 P1 C26 112.3(4)	C28 P1 C30 98.4(5)
C26 P1 C30 97.1(4)	C28 P1 Pd1 113.3(4)
C26 P1 Pd1 120.8(2)	C30 P1 Pd1 111.1(3)
C34 P2 C36 102.0(6)	C34 P2 C32 104.9(4)
C36 P2 C32 104.2(3)	C34 P2 Pd1 113.9(3)
C36 P2 Pd1 113.3(2)	C32 P2 Pd1 116.92(16)
C63 P3 C67 105.7(3)	C63 P3 C65 107.3(3)
C67 P3 C65 97.0(3)	C63 P3 Pd2 118.28(18)
C67 P3 Pd2 112.0(2)	C65 P3 Pd2 114.2(2)
C69 P4 C71 110.6(5)	C69 P4 C73 100.5(7)
C71 P4 C73 94.9(5)	C69 P4 Pd2 118.9(3)
C71 P4 Pd2 116.9(3)	C73 P4 Pd2 110.9(3)
C23 O2 C24 115.4(6)	C60 O4 C61 116.1(4)

C2 C1 C22 118.4(3)
C22 C1 Pd1 120.9(3)
C3 C2 C11 117.2(3)
C4 C3 C2 123.9(4)
C2 C3 H1 118.0
C3 C4 C5 122.7(4)
C6 C5 C4 120.2(5)
C4 C5 H2 119.9
C5 C6 H3 119.5
C8 C7 C6 121.6(5)
C6 C7 H4 119.2
C7 C8 H5 119.8
C10 C9 C4 119.3(4)
C4 C9 C8 118.3(4)
C9 C10 H6 118.4
C12 C11 C10 122.7(4)
C10 C11 C2 117.7(3)
C11 C12 C23 118.8(4)
C12 C13 C14 123.4(4)
C14 C13 C22 117.6(4)
C15 C14 H7 118.5
C14 C15 C20 120.0(4)
C20 C15 C16 117.8(5)
C17 C16 H8 119.9
C16 C17 C18 122.3(6)
C18 C17 H9 118.9
C19 C18 H10 119.6
C18 C19 C20 119.7(6)
C20 C19 H11 120.1
C21 C20 C15 118.3(4)
C20 C21 C22 123.3(4)
C22 C21 H12 118.3
C21 C22 C13 117.9(3)
O1 C23 O2 122.7(5)
O2 C23 C12 112.4(5)
C25 C24 H13 110.0
C25 C24 H14 110.0
H13 C24 H14 108.4
C24 C25 H16 109.5
C24 C25 H17 109.5
H16 C25 H17 109.5
C27 C26 H18 109.1
C27 C26 H19 109.1
H18 C26 H19 107.9
C26 C27 H21 109.5
C26 C27 H22 109.5
H21 C27 H22 109.5
C29 C28 H23 108.6
C29 C28 H24 108.6
H23 C28 H24 107.6
C28 C29 H26 109.5
C28 C29 H27 109.5
H26 C29 H27 109.5
C31 C30 H28 107.7
C31 C30 H29 107.7
H28 C30 H29 107.1
C30 C31 H31 109.5
C30 C31 H32 109.5
H31 C31 H32 109.5
C33 C32 H33 107.9
C33 C32 H34 107.9
H33 C32 H34 107.2
C32 C33 H36 109.5
C32 C33 H37 109.5
H36 C33 H37 109.5
C35 C34 H38 104.8
C35 C34 H39 104.8
H38 C34 H39 105.8
C34 C35 H41 109.5
C34 C35 H42 109.5
H41 C35 H42 109.5
C37 C36 H43 108.6
C37 C36 H44 108.6
H43 C36 H44 107.5
C36 C37 H46 109.5
C36 C37 H47 109.5
H46 C37 H47 109.5
C2 C1 Pd1 120.6(2)
C3 C2 C1 121.6(3)
C1 C2 C11 121.2(3)
C4 C3 H1 118.0
C3 C4 C9 118.7(4)
C9 C4 C5 118.6(4)
C6 C5 H2 119.9
C5 C6 C7 121.0(5)
C7 C6 H3 119.5
C8 C7 H4 119.2
C7 C8 C9 120.3(6)
C9 C8 H5 119.8
C10 C9 C8 122.3(5)
C9 C10 C11 123.1(4)
C11 C10 H6 118.4
C12 C11 C2 119.6(3)
C11 C12 C13 121.0(3)
C13 C12 C23 120.2(4)
C12 C13 C22 119.0(3)
C15 C14 C13 123.0(4)
C13 C14 H7 118.5
C14 C15 C16 122.3(5)
C17 C16 C15 120.2(6)
C15 C16 H8 119.9
C16 C17 H9 118.9
C19 C18 C17 120.9(6)
C17 C18 H10 119.6
C18 C19 H11 120.1
C21 C20 C19 122.6(5)
C19 C20 C15 119.0(4)
C20 C21 H12 118.3
C21 C22 C1 121.4(3)
C1 C22 C13 120.7(3)
O1 C23 C12 124.8(6)
C25 C24 O2 108.5(9)
O2 C24 H13 110.0
O2 C24 H14 110.0
C24 C25 H15 109.5
H15 C25 H16 109.5
H15 C25 H17 109.5
C27 C26 P1 112.4(6)
P1 C26 H18 109.1
P1 C26 H19 109.1
C26 C27 H20 109.5
H20 C27 H21 109.5
H20 C27 H22 109.5
C29 C28 P1 114.8(6)
P1 C28 H23 108.6
P1 C28 H24 108.6
C28 C29 H25 109.5
H25 C29 H26 109.5
H25 C29 H27 109.5
C31 C30 P1 118.4(9)
P1 C30 H28 107.7
P1 C30 H29 107.7
C30 C31 H30 109.5
H30 C31 H31 109.5
H30 C31 H32 109.5
C33 C32 P2 117.6(4)
P2 C32 H33 107.9
P2 C32 H34 107.9
C32 C33 H35 109.5
H35 C33 H36 109.5
H35 C33 H37 109.5
C35 C34 P2 130.1(6)
P2 C34 H38 104.8
P2 C34 H39 104.8
C34 C35 H40 109.5
H40 C35 H41 109.5
H40 C35 H42 109.5
C37 C36 P2 114.9(6)
P2 C36 H43 108.6
P2 C36 H44 108.6
C36 C37 H45 109.5
H45 C37 H46 109.5
H45 C37 H47 109.5
C39 C38 C59 119.2(3)

C39 C38 Pd2 121.6(3)
C38 C39 C40 121.7(3)
C40 C39 C48 117.5(3)
C41 C40 H48 118.3
C40 C41 C46 118.5(4)
C46 C41 C42 118.9(4)
C43 C42 H49 119.7
C42 C43 C44 120.0(5)
C44 C43 H50 120.0
C45 C44 H51 119.1
C44 C45 C46 121.0(5)
C46 C45 H52 119.5
C47 C46 C45 122.7(4)
C46 C47 C48 123.0(3)
C48 C47 H53 118.5
C49 C48 C39 118.8(3)
C50 C49 C48 121.3(3)
C48 C49 C60 120.7(3)
C49 C50 C59 119.3(3)
C52 C51 C50 123.2(4)
C50 C51 H54 118.4
C51 C52 C57 119.3(4)
C54 C53 C52 121.6(5)
C52 C53 H55 119.2
C53 C54 H56 119.7
C56 C55 C54 120.7(5)
C54 C55 H57 119.7
C55 C56 H58 119.7
C58 C57 C56 122.4(4)
C56 C57 C52 118.8(4)
C57 C58 H59 118.6
C58 C59 C38 121.8(3)
C38 C59 C50 120.3(3)
O3 C60 C49 124.6(4)
C62 C61 O4 110.6(5)
O4 C61 H60 109.5
O4 C61 H61 109.5
C61 C62 H62 109.5
H62 C62 H63 109.5
H62 C62 H64 109.5
C64 C63 P3 117.1(4)
P3 C63 H65 108.0
P3 C63 H66 108.0
C63 C64 H67 109.5
H67 C64 H68 109.5
H67 C64 H69 109.5
C66 C65 P3 115.4(6)
P3 C65 H70 108.4
P3 C65 H71 108.4
C65 C66 H72 109.5
H72 C66 H73 109.5
H72 C66 H74 109.5
C68 C67 P3 115.8(4)
P3 C67 H75 108.3
P3 C67 H76 108.3
C67 C68 H77 109.5
H77 C68 H78 109.5
H77 C68 H79 109.5
C70 C69 P4 139.9(14)
P4 C69 H80 102.1
P4 C69 H81 102.1
C69 C70 H82 109.5
H82 C70 H83 109.5
H82 C70 H84 109.5
C72 C71 P4 112.8(7)
P4 C71 H85 109.0
P4 C71 H86 109.0
C71 C72 H87 109.5
H87 C72 H88 109.5
H87 C72 H89 109.5
C74 C73 P4 118.5(8)
P4 C73 H90 107.7
P4 C73 H91 107.7
C73 C74 H92 109.5
H92 C74 H93 109.5
H92 C74 H94 109.5
C59 C38 Pd2 119.1(3)
C38 C39 C48 120.7(3)
C41 C40 C39 123.4(3)
C39 C40 H48 118.3
C40 C41 C42 122.6(4)
C43 C42 C41 120.6(4)
C41 C42 H49 119.7
C42 C43 H50 120.0
C45 C44 C43 121.8(5)
C43 C44 H51 119.1
C44 C45 H52 119.5
C47 C46 C41 119.7(4)
C41 C46 C45 117.7(4)
C46 C47 H53 118.5
C49 C48 C47 123.3(3)
C47 C48 C39 117.8(3)
C50 C49 C60 117.8(3)
C49 C50 C51 122.5(3)
C51 C50 C59 118.2(4)
C52 C51 H54 118.4
C51 C52 C53 123.0(4)
C53 C52 C57 117.7(4)
C54 C53 H55 119.2
C53 C54 C55 120.6(5)
C55 C54 H56 119.7
C56 C55 H57 119.7
C55 C56 C57 120.6(5)
C57 C56 H58 119.7
C58 C57 C52 118.8(4)
C57 C58 C59 122.7(4)
C59 C58 H59 118.6
C58 C59 C50 117.7(3)
O3 C60 O4 123.2(4)
O4 C60 C49 112.2(3)
C62 C61 H60 109.5
C62 C61 H61 109.5
H60 C61 H61 108.1
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C61 C62 H64 109.5
H63 C62 H64 109.5
C64 C63 H65 108.0
C64 C63 H66 108.0
H65 C63 H66 107.3
C63 C64 H68 109.5
C63 C64 H69 109.5
H68 C64 H69 109.5
C66 C65 H70 108.4
C66 C65 H71 108.4
H70 C65 H71 107.5
C65 C66 H73 109.5
C65 C66 H74 109.5
H73 C66 H74 109.5
C68 C67 H75 108.3
C68 C67 H76 108.3
H75 C67 H76 107.4
C67 C68 H78 109.5
C67 C68 H79 109.5
H78 C68 H79 109.5
C70 C69 H80 102.1
C70 C69 H81 102.1
H80 C69 H81 104.8
C69 C70 H83 109.5
C69 C70 H84 109.5
H83 C70 H84 109.5
C72 C71 H85 109.0
C72 C71 H86 109.0
H85 C71 H86 107.8
C71 C72 H88 109.5
C71 C72 H89 109.5
H88 C72 H89 109.5
C74 C73 H90 107.7
C74 C73 H91 107.7
H90 C73 H91 107.1
C73 C74 H93 109.5
C73 C74 H94 109.5
H93 C74 H94 109.5

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

3-5. References

[1] Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc*. **2007**, *129*, 15752-15753.

[2] (a) Jia, Z.; Li, S.; Nakajima, K.; Kanno, K.; Song, Z.; Takahashi, T. *Heterocycles* **2012**, *86*, 1495-1506. (b) Qu, H.; Cui, W.; Li, J.; Shao, J.; Chi, C. *Org. Lett.* **2011**, *13*, 924-927.

[3] Combe, C. M. S.; James, D. T.; Wade, J.; White, A. J. P.; Kim, J. S.; McCulloch, I. *Tetrahedron Letters* **2013**, *54*, 6814-6818.

Chapter 4. Synthesis of Pentacene Dimer by using Palladated Pentacene Complex

Abstract

Dimerization of various palladated pentacene derivatives was studied. Because of the steric effect of two pentacenes, central ring and second ring pentacene dimers were not obtained under coupling reaction conditions. In contrast, first ring side dimer of pentacene was obtained in high yield under the same reaction conditions. It is obvious that the first ring of pentacene has less steric effect compared to central ring and second ring of pentacene. These results clearly indicated that combining carbon-carbon bond at the first ring of pentacene is key point for constructing pentacene oligomers.

4-1. Introduction

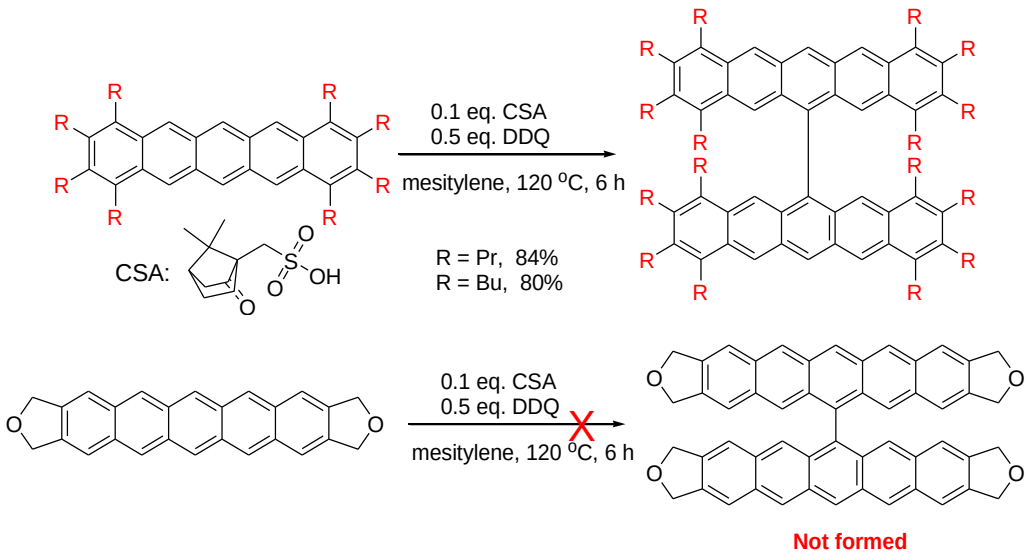
Pentacene has attracted much attention as organic semiconductors. Promoted by this π-conjugated molecule, people started to explore larger π-conjugated molecules. The larger π-conjugated system should have better performance than pentacene due to the smaller bandgap of them.

Extension of π-conjugated system in one direction will give longer acenes. However, hexacene and heptacene are very unstable.[1a,b] They are difficult to handle. Furthermore, non-substituted octacene and nonacene have not been isolated by far. They had only been detected in an argon matrix.[1c] Therefore, further extension of π-conjugation in one direction became difficult.

Two-dimensional extension of acene rings from both lateral and vertical directions is more possible and efficient. Recently, two-dimensional acenes, such as pentacene dimer attract much attention. Such compounds are expected to have better performance as organic field effect transistors.

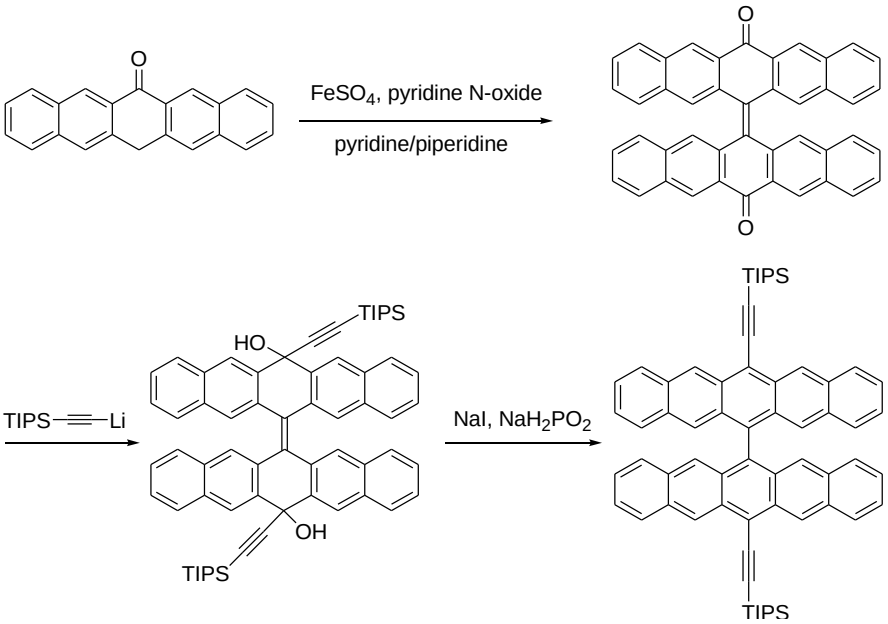
Takahashi's group started a project of C-C bond formation between two pentacenes. The central ring side dimer of pentacene has been reported by Takahashi's group as the first example (Scheme 1).[2] In this method, the multi-electron donating groups were needed for the dimerization reaction at the central ring of pentacene derivatives. Otherwise such side dimer could not be formed. Therefore, this method is a limited method.

Scheme 1. Previous dimerization of pentacene Takahashi's group reported



Another available method now is quinone method. The dimer could be formed via 6,6'-bispentacenequinone from 6-pentacenone. In this method, the starting material 6-pentacenone was prepared via partial reduction of 6,13-pentacenone. The yield of the reaction was not good. (Scheme 2).[3]

Scheme 2. Preparation of pentacene dimer from pentacenone



For preparation of pentacene dimer, the C-C bond formation reaction using transition metals should be a general method (Figure 1). For this purpose, with central ring palladated pentacene derivatives in hand, the dimerization of central ring palladated pentacene was studied firstly.

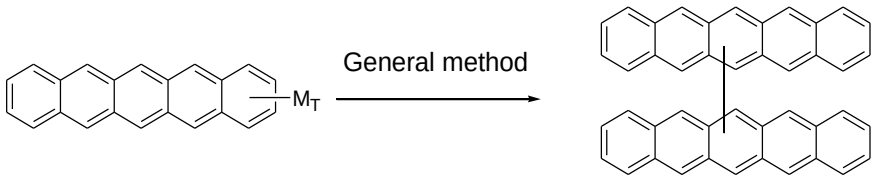


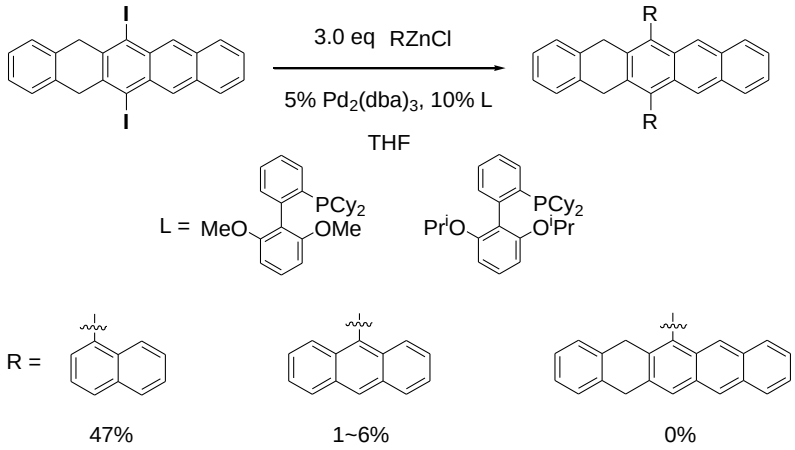
Figure 1. Strategy for preparation of pentacene dimer

4-2. Results and Discussion

Former group member Dr. Jia studied the coupling reaction of 6,13-diiododihydropentacene with naphthalene, anthracene and dihydropentacene. The results are summarized in Scheme 3. As the number of benzene rings increases, the yield of the corresponding coupling product decreases. Naphtalene was introduced into the central ring of dihydropentacene in 47% yield. In anthracene case, only trace amount of coupling product was obtained. Moreover, pentacene dimer was not observed at all.

The possible reason is the steric effect. After that, I took over this project by using the well-defined palladated dihydropentacene complexes to study the dimerization of pentacene.

Scheme 3.

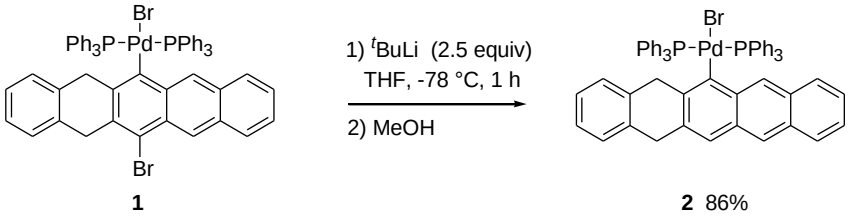


4-2-1. Dimerization of central ring palladated pentacene

1）Synthesis of central ring palladated pentacene **2**

Central ring palladated dihydropentacene **1** has been reported in Chapter 2. Complex **1** was treated with 2.5 equivalent of ^{t}BuLi in THF at –78 °C. The reaction was monitored by TLC. The reaction finished within 1 h. Upon quenching with methanol, palladated dihydropentacene derivative **2** was obtained in 86% isolated yield.

Scheme 4.

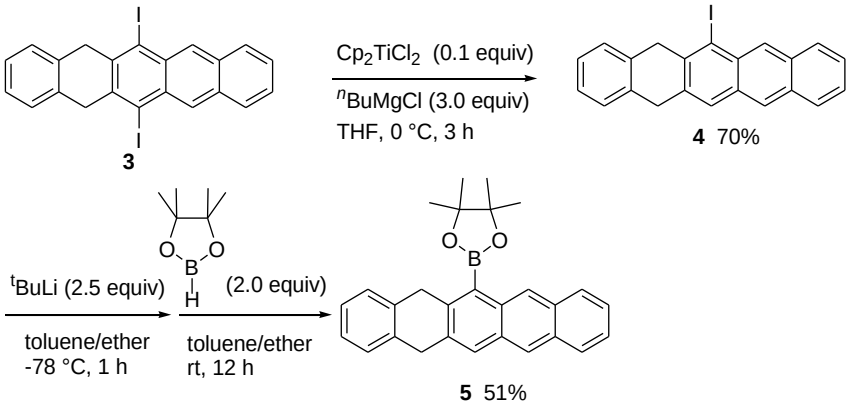


1 **2** 86%

2）Synthesis of central ring pentacene boronic ester reagent **5**

To prepare pentacene boronic ester reagent, lithiation of bromodihydropentacene was studied in chapter 3. Lithiation of 6,13-dibromo-5,14-dihydropentacene was not selective. And 6-bromo-5,14-dihydropentacene was obtained in very low yield. Fortunately, 6,13-diiodo-5,14-dihydropentacene **3** was treated with 0.1 equivalent of Cp_2TiCl_2 and 3.0 equivalent of ^{n}BuMgCl in THF to give 6-iodo-5,14-dihydropentacene **4** selectively.[2b] Lithiation of compound **4** followed by addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane was carried out. Central ring boronic ester reagent **5** was obtained in 51% isolated yield (Scheme 5).

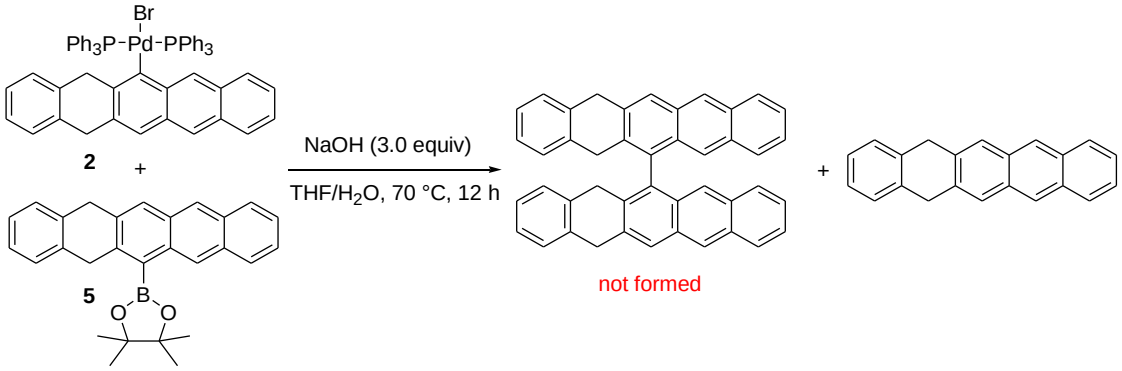
Scheme 5.



3）Coupling reaction of **2** and **5**

Coupling reaction of palladated dihydropentacene **2** with boronic ester reagent **5** was carried out. The mixture of **2** and **5** was treated with NaOH under N_2 atmosphere. However, unfortunately, central ring side dimer of pentacene was not formed. Only 5,14-dihydropentacene was obtained (Scheme 6).

Scheme 6.



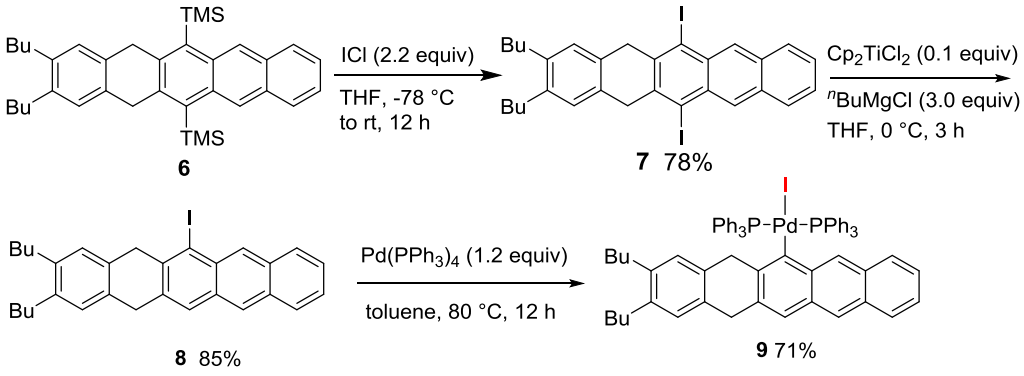
4-2-2. Dimerization of functional central ring palladated pentacene

1) Synthesis of palladated dihydropentacene derivative **9**

In Scheme 6, the central ring side dimer of pentacene was not formed. I then tried to introduce electron donating groups into pentacene derivative, and changed the bromine to iodine to activate the central ring palladated dihydropentacene derivative **9** (Scheme 7).

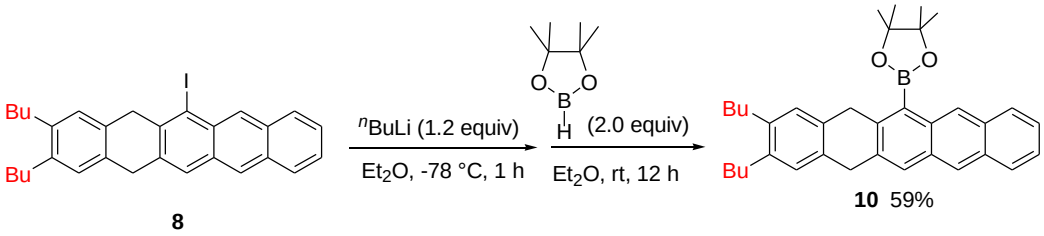
By Takahashi's group reported method,[4] compound **6** was obtained. Compound **6** was treated with ICl to give diiododihydropentacene **7** in 78% yield. Compound **7** was treated with Cp_2TiCl_2 and ^{n}BuMgCl in THF to give monoiododihydropentacene **8** in 85% yield. Oxidative addition of $Pd(PPh_3)_4$ to compound **8** afforded palladated dihydropentacene **9** in 71% yield.

Scheme 7.



2）Synthesis of central ring pentacene boronic ester reagent **10**

Scheme 8.

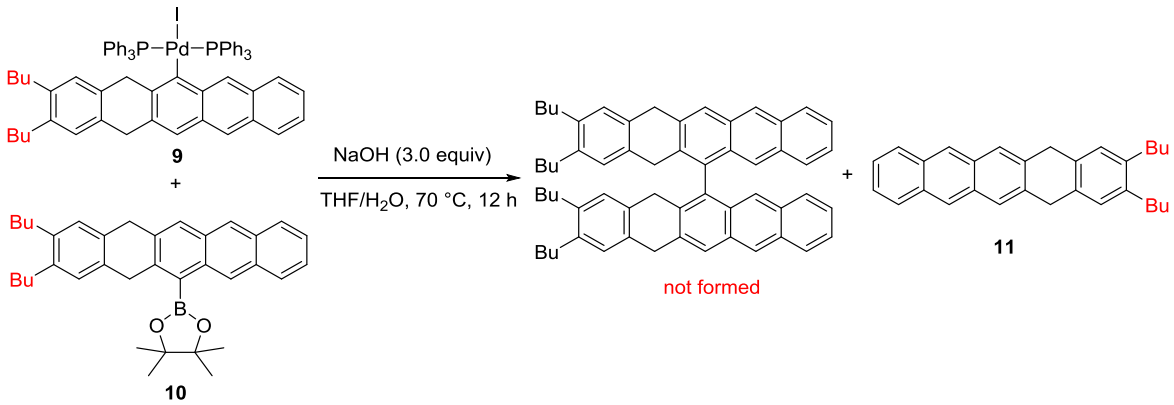


Lithiation of compound **8** with ^{n}BuLi in diethyl ether followed by addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded central ring boronic ester reagent **10** in 59% yield.

3）Coupling reaction of **9** and **10**

Suzuki coupling reaction of **9** with **10** was carried out under the same reaction conditions. Again, such central ring side dimer of pentacene was not formed. Only dihydropentacene derivative **11** was observed.

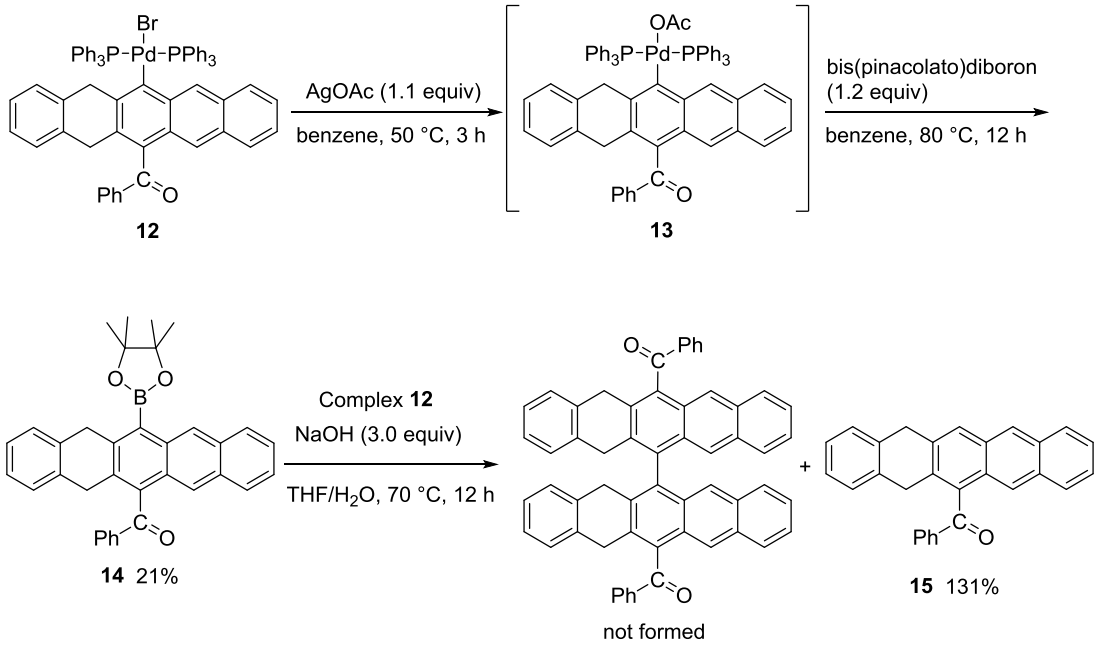
Scheme 9.



4-2-3. Dimerization of central ring palladated pentacene with electron-withdrawing group

Central ring side dimer of pentacene with electron-donating group was not obtained by cross-coupling method. So how about the dimerization of central ring palladated pentacene derivatives with electron-withdrawing group? For this purpose, coupling reaction of **12** and **14** was carried out. Complex **12** with electron-withdrawing group has been reported in Chapter 3. By cross-coupling method,[5] boronate pentacene **14** was prepared.

Scheme 10.



Complex **12** reacted with sliver acetate in benzene firstly to give intermediate complex **13**. After that, the by-product sliver bromide was filtered off to give a clear solution. Then bis(pinacolato)diboron was added into the above filtrate and stirred at 80 °C for 12 h. Central ring boronic ester reagent **14** was obtained in 21% isolated yield.

If the sliver bromide was kept in the reaction solution, the desired product **14** was formed in trace. The major byproduct **15** was obtained.

Suzuki coupling reaction of **12** and **14** under the same reaction condition was carried out. Unfortunately, such central ring side dimer of pentacene also was not formed. Only dihydropentacene derivative **15** was obtained (Scheme 10).

Central ring side dimer of pentacene was not formed by cross-coupling method. Probably, the major reason is the steric effect of two pentacene skeleton. Then, how about the dimerization of second ring palladated pentacene derivative?

4-2-4. Synthesis of second ring monopalladated pentacene derivatives

The synthesis is shown in Scheme 11. 5,14-Dihydropentacene **17** was prepared via desilylation of 6,13-bis(trimethylsilyl)-5,14-dihydropentacene **16**. Bromination of dihydropentacene **17** with Br_2 in CCl_4 provided 5,14-dibromo-7,12-dihydropentacene **18** in 76% yield. The structure of **18** was verified by X-ray analysis. Two bromine atoms were attached to the second ring of dihydropentacene as shown in Figure 2. Oxidative addition of **18** to $Pd(PPh_3)_4$ gave second ring palladated dihydropentacene **19a** in 79% yield. Finally, aromatization of **19a** with DDQ and γ-terpinene afforded palladated pentacene **20a** in 40% yield. Blue crystals of **20a** were obtained from a mixture solution of benzene and hexane. The X-ray structure is shown in Figure 3. Palladium with PPh_3 ligands is attaching on the second ring of pentacene's flat skeleton.

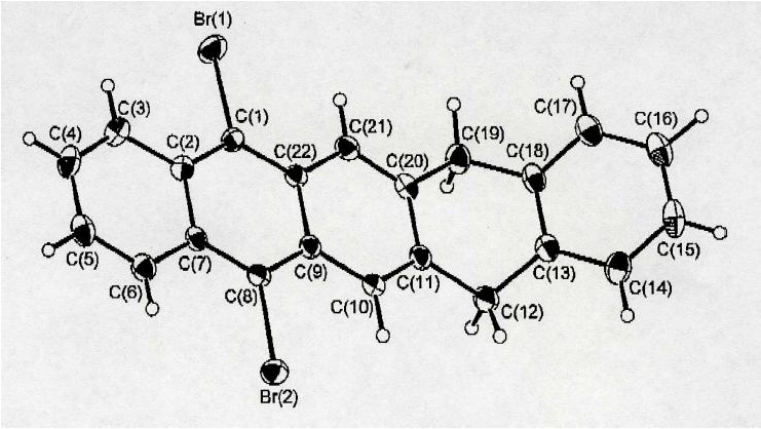
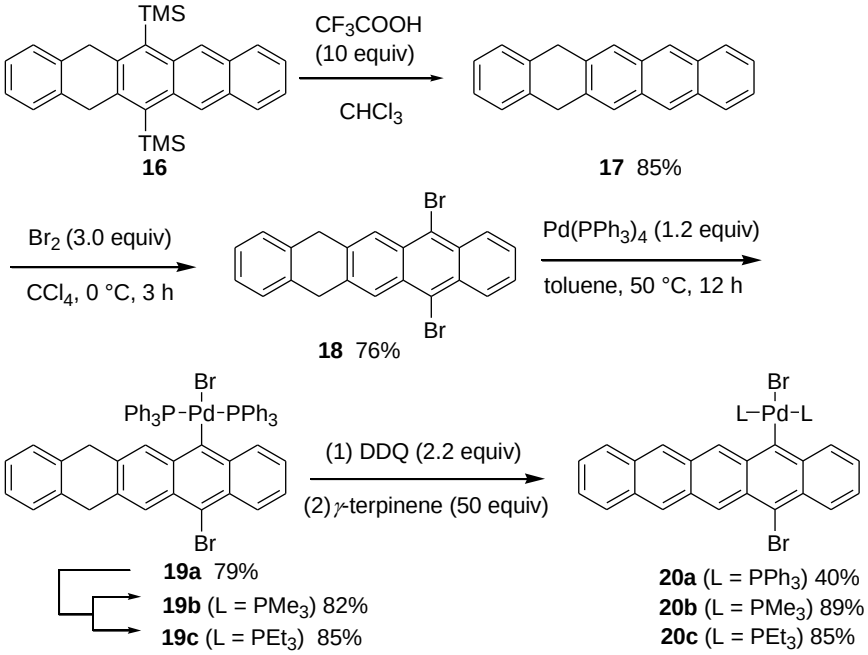


Figure 2. X-ray structure of complex **18**

Scheme 11. Synthesis of second ring palladated pentacene derivatives



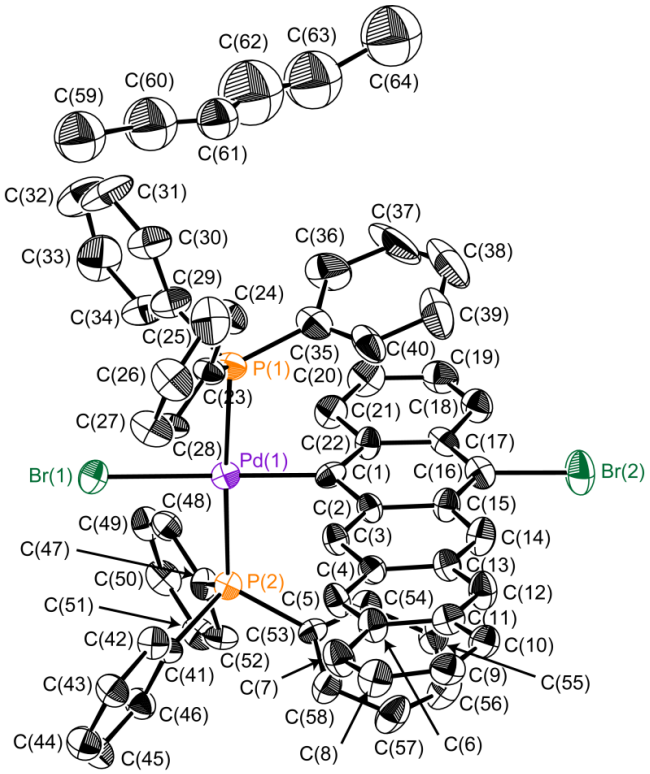


Figure 3. X-ray structure of complex **20a**

By the same ligands exchanged reaction, complex **19b** and **19c** were obtained in 82% and 85% yields, respectively. The X-ray structure of **19b** is shown in Figure 4. Finally, by the same aromatic method as described for **20a**, the second ring palladated pentacene derivatives **20b** and **20c** were obtained in 89% and 85% yields, respectively. The X-ray structure of **20b** is shown in Figure 5.

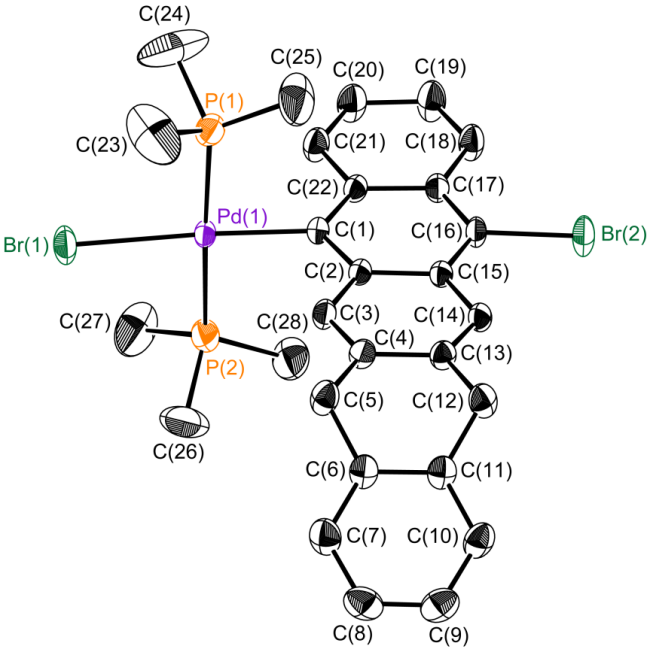


Figure 4. X-ray structure of complex **19b**

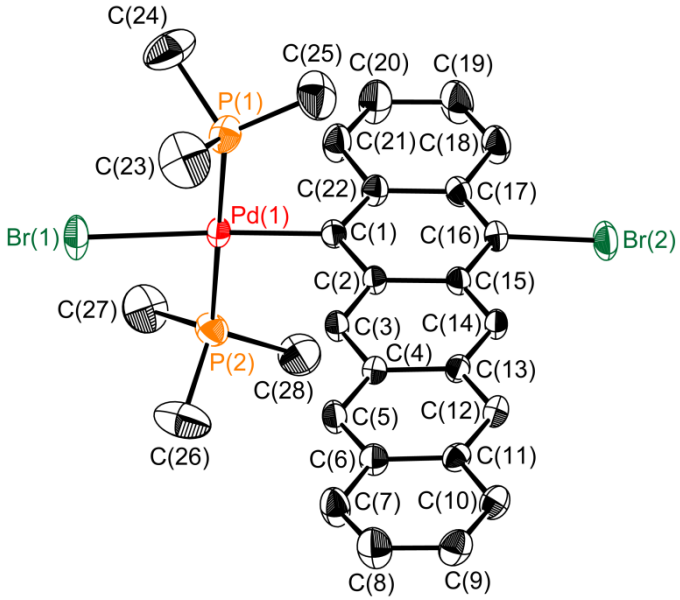


Figure 5. X-ray structure of complex **20b**

Under air, complex **20a** was dissolved in benzene to check the stability. After 2 days, 80% of **20a** remained. It is clear that the stability of **20a** is lower than that of the corresponding central ring palladated pentacene.

UV-vis spectra of **20a** showed strong resonance at 639 nm (Figure 6). It had remarkable red-shift compared with pentacene (λ_{max} = 577 nm), 6,13-diphenylpentacene (λ_{max} = 604 nm), 6,13-ditrimethylsilylpentacene (λ_{max} = 607 nm).

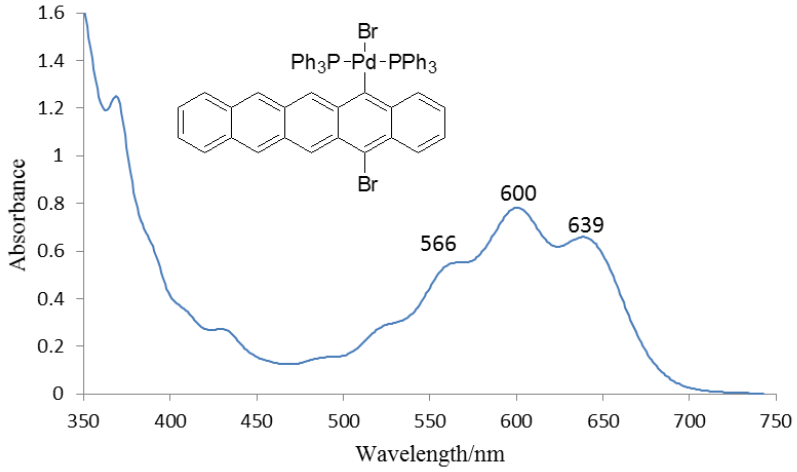
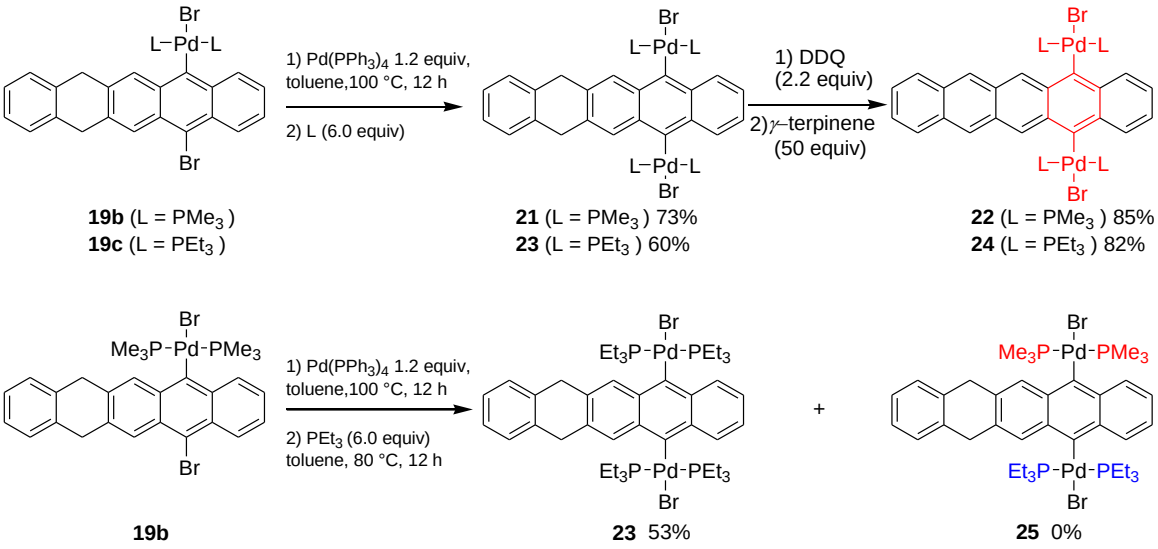


Figure 6. Absorption spectrum of second ring palladated pentacene **20a** in $CHCl_3$ at rt.

4-2-5. Synthesis of second ring dipalladated pentacene complexes

By the same method as described in chapter 2, second ring dipalladated dihydropentacene **21** was obtained in 73% yield (Scheme 12). Aromatization of complex **21** with DDQ and γ-terpinene gave the corresponding second ring dipalladated pentacene **22** in 85% yield.

Scheme 12. Synthesis of second ring dipalladated pentacene complexes



By the same method, second ring dipalladated dihydropentacene **23** was obtained in 60% yield. After aromatization, second ring dipalladated pentacene **24** was obtained in 82% yield. When complex **19b** was treated with 1.2 equivalent of $Pd(PPh_3)_4$ in toluene at 100 °C for 12 h, the mixture was treated with 6.0 equivalent of PEt_3 in toluene at 100 °C for 12 h. The mixed ligands complex **25** was not observed. Complex **23** was obtained in 53% yield. That means PMe_3 ligands could be changed to PEt_3 ligands.

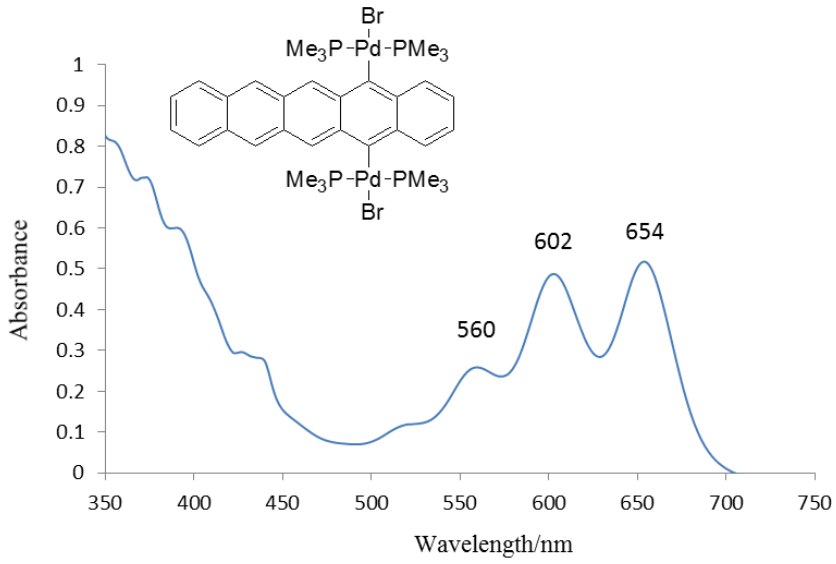


Figure 7. Absorption spectrum of second ring dipalladated pentacene **22** in $CHCl_3$ at rt

The UV-vis spectra of **22** and **24** were measured in chloroform at room temperature. The λ_{max} of complex **22** is 654 nm (Figure 7). The λ_{max} of complex **24** is 663 nm (Figure 8). Second ring dipalladated pentacene **23** dissolved in C_6D_6 under air for 6 h, 90% of **23** remained. The stability of second ring dipalladated pentacene **23** is lower than that of the corresponding central ring dipalladated pentacene.

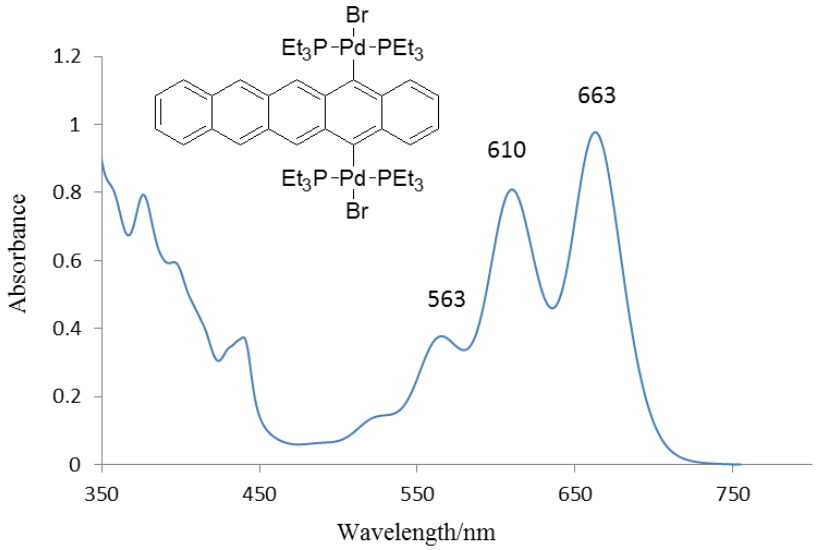


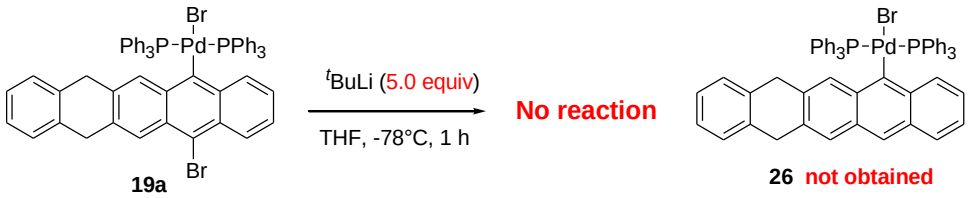
Figure 8. Absorption spectrum of second ring dipalladated pentacene **24** in $CHCl_3$ at rt

4-2-6. Dimerization of second ring palladated pentacene

1） Synthesis of palladated dihydropentacene **26**

Second ring palladated dihydropentacene **19a** was treated with up to 5.0 equivalent of ^{t}BuLi. However, no reaction occurred. Palladated dihydropentacene **26** could not be obtained by this method (Scheme 13).

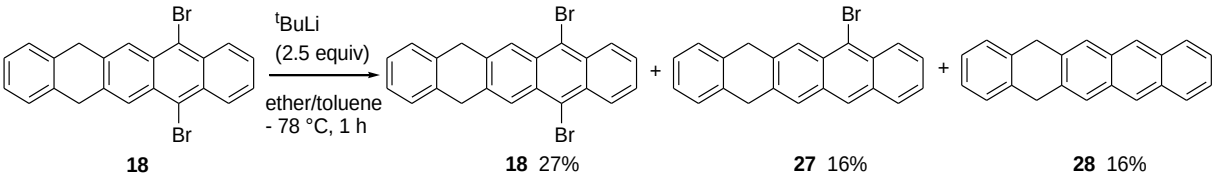
Scheme 13.



Then I changed my method. My plan was partially debromonation of dibromodihydropentacene **18** and then oxidative addition of it to $Pd(PPh_3)_4$. However, lithiation of dibromodihydropentacene **18** with ^{t}BuLi was not selective. A mixture of staring material **18**,

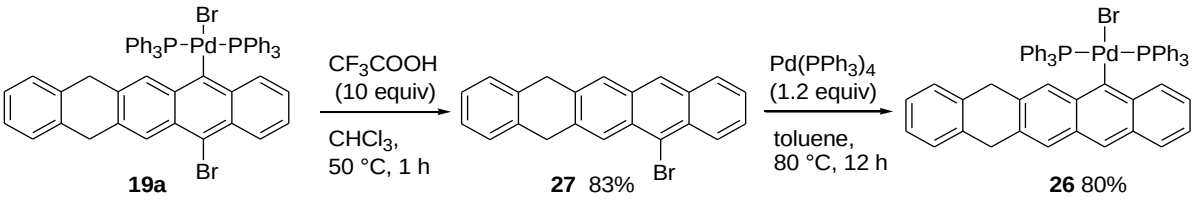
monobromodihydropentacene **27** and dihydropentacene **28** was obtained (Scheme 14).

Scheme 14.



Fortunately, second ring palladated dihydropentacene **19a** was treated with trifluoroacetic acid in chloroform to give monobromodihydropentacene **27** in 83% yield. Oxidative addition of compound **27** to $Pd(PPh_3)_4$ afforded desired product **26** in 80% yield (Scheme 15).

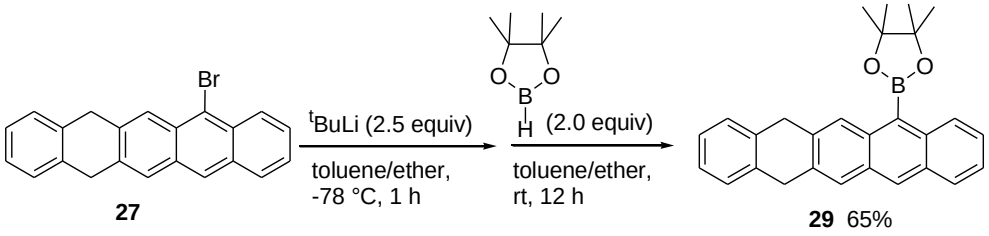
Scheme 15.



2) Synthesis of second ring boronic ester reagent **29**

Lithiation of monobromodihydropentacene **27** with ^{t}BuLi gave the corresponding lithiated intermediate. Subsequent addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave second ring boronic ester reagent **29** in 65% yield (Scheme 16).

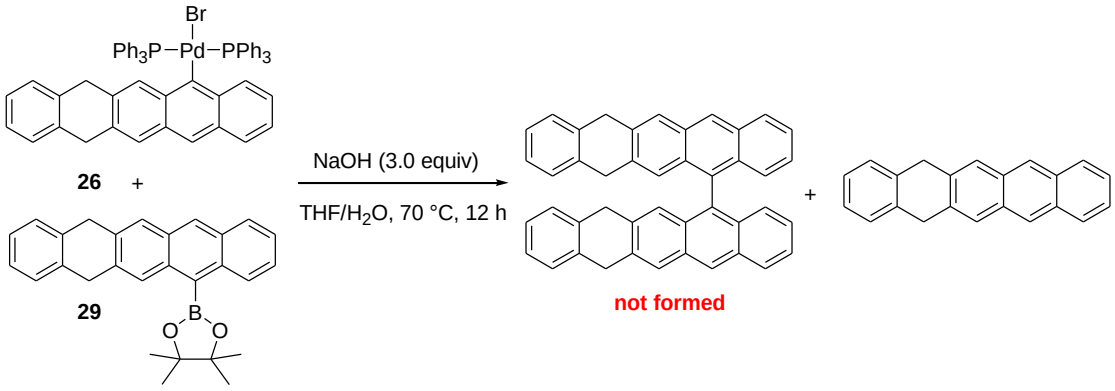
Scheme 16.



3) Coupling reaction of **26** and **29**

With complex **26** and compound **29** in hand, Suzuki coupling reaction of them was carried out under the same reaction conditions. Unfortunately, the second ring side dimer of pentacene also was not obtained (Scheme 17).

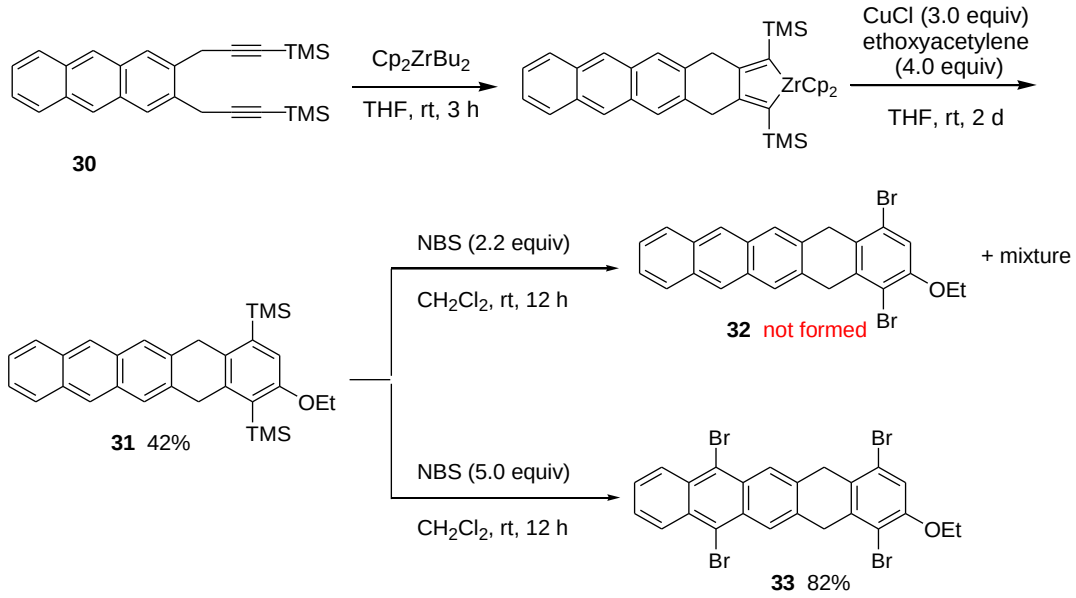
Scheme 17.



4-2-7. Synthesis of first ring palladated pentacene

The central ring and second ring side dimers of pentacene were not formed by coupling reaction method. I thought the major reason should be the steric effect of two pentacenes. It looks like that the first ring of pentacene has less steric effect compared to central ring and second ring of pentacenes. Probably, the first ring side dimer of pentacene could be prepared by cross-coupling method.

Scheme 18. Attempt to prepare first ring dibromodihyropentacene **32**



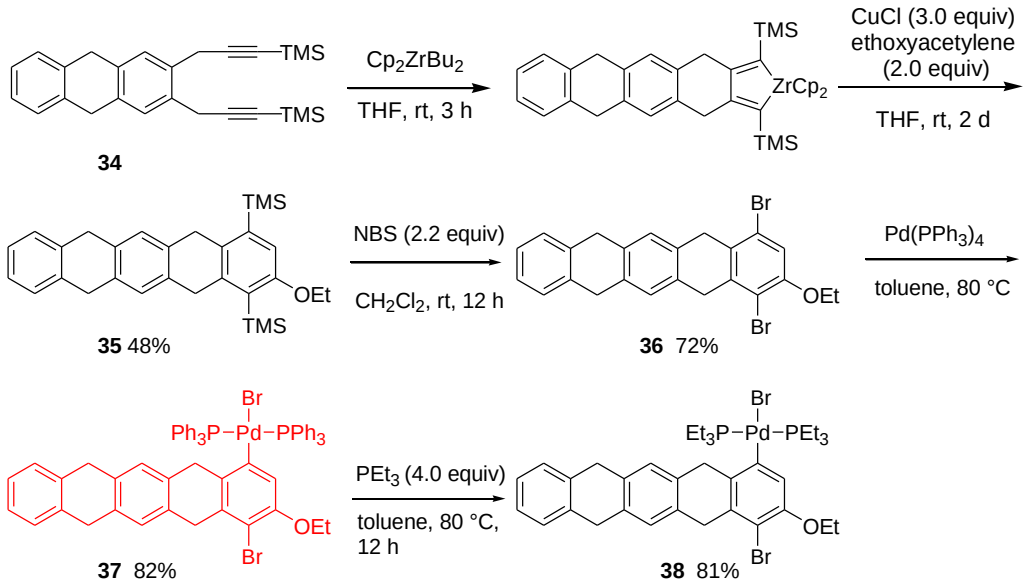
Diyne **30** was treated with Cp_2ZrBu_2 (Negishi reagent) to give a zirconacycle intermediate. Addition of ethoxyacetylene in the presence of CuCl gave dihydropentacene derivative **31** in 42% yield. Bromination of compound **31** with 2.2 equiv NBS, however, gave a mixture. The desired product **32** was not obtained as a single product. Proton NMR spectrum of these

mixtures showed that TMS groups still remained. Therefore, excess of NBS was added. Until the amount of NBS increased to 5.0 equivalent, a single product **33** was obtained in 82% yield. This result indicated that bromination of compound **31** was not selective. Bromination was occurred at the central ring of anthracene part of compound **31** at the same time (Scheme 18).

I then changed the method. In Scheme 19, another diyne **34** was used as a starting material instead of diyne **30**. By the same method, tetrahydropentacene derivative **35** was obtained in 48% yield. Bromination of compound **35** with 2.2 equivalent of NBS afforded first ring dibromotetrahydropentacene **36** in 72% yield. Oxidative addition of compound **36** to $Pd(PPh_3)_4$ gave palladated tetrahydropentacene **37** in 82% yield. Complex **37** was obtained selectively.

It should be noted that due to the steric effect of ethoxy group, oxidative addition occurred at the meta-position of ethoxy group selectively. Furthermore, complex **38** was obtained in 81% yield. The structure of complex **38** was verified by X-ray analysis. I can clearly see the palladium atom with PEt_3 ligands attached to the meta-position of ethoxy group.

Scheme 19. Synthesis of first ring palladated pentacene derivatives



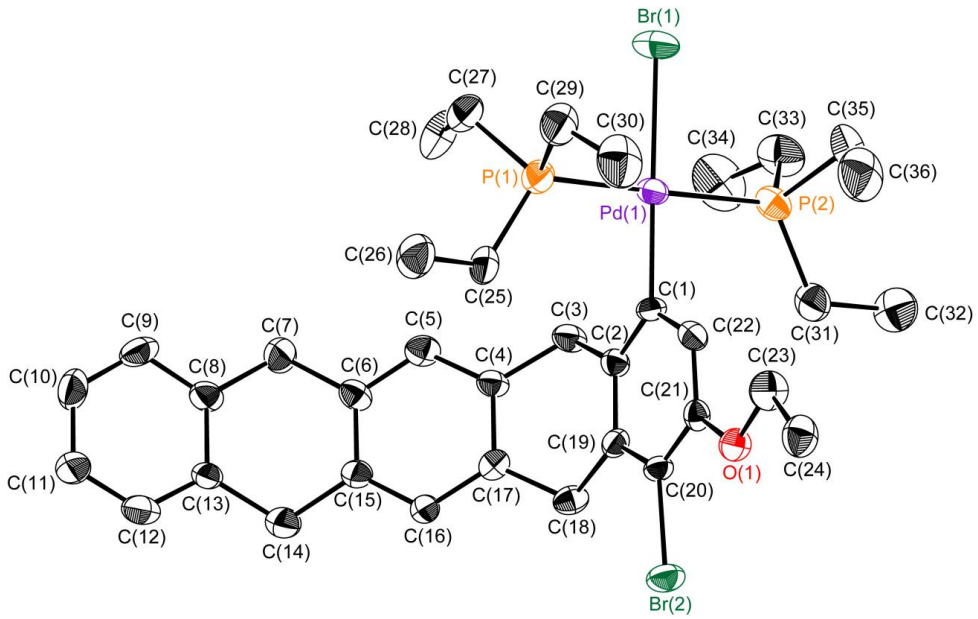


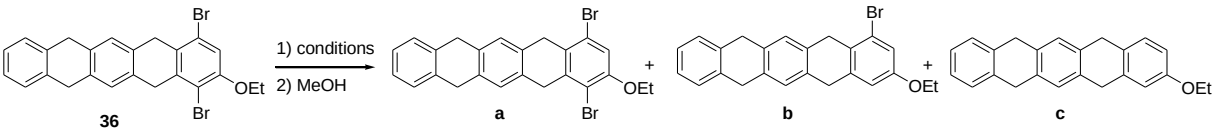
Figure 9. X-ray structure of complex **38**

4-2-8. Dimerization of first ring palladated pentacene

1) Synthesis of first ring boronic ester reagent

Attempt to prepare first ring boronic ester reagent via lithiation of compound **36** had been carried out. Lithiation of compound **36** with ^{t}BuLi was not selective. The results are shown in Table 1.

Table 1. Lithiation of compound **36**



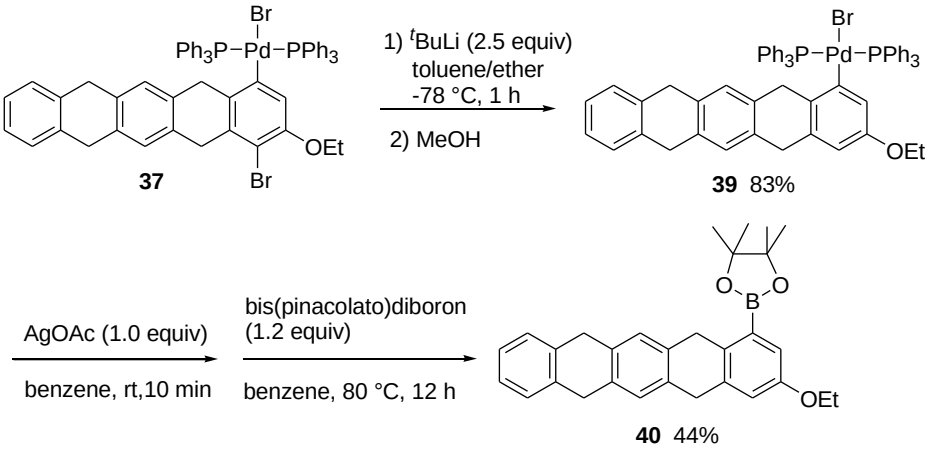
Entry	Conditions	Yield/%		
		a	**b**	**c**
1	^{t}BuLi (2.5 equiv), Et_2O, -78 °C, 1 h	32	26	32
2	^{t}BuLi (2.5 equiv), toluene/ether, -78 °C, 1 h	0	68	25
3	^{t}BuLi (2.0 equiv), toluene/ether, -78 °C, 1 h	18	63	18

In entry 1, compound **36** was treated with 2.5 equivalent of ^{t}BuLi in diethyl ether to give a mixture. Monobromide **b** and tetrahydropentacene **c** were obtained in 26% yield and 32% yield, respectively. Staring material **36** was recovered in 32%. Entry 2, when the solvent was changed to a mixture of toluene and diethyl ether, monobromotetrahydropentacene **b** and tetrahydropentacene **c** were obtained in 68% and 25%, respectively. In entry 3, the amount of ^{t}BuLi was reduced to 2.0 equivalent to avoid formation of tetrahydropentacene **c**. However,

under these reaction conditions, starting material **36** was remained in 18% yield. The reaction conditions of entry 2 looked better. However, separation of compound **b** and **c** by silica gel column chromatography was difficult. Therefore, preparation of first ring boronic ester reagent by lithiation method was not good.

I then turned to coupling method. First ring palladated tetrahydropentacene **37** was treated with ^{t}BuLi in toluene/diethyl ether at -78 °C for 1 h. Subsequent addition of methanol gave palladated complex **39** in 83% yield. Complex **39** was treated with 1.0 equiv silver acetate in benzene at room temperature for 10 mins and then filtered off silver bromide. Bis(pinacolato)diboron was added to the above filtrate and reacted at 80 °C for 12 h to give first ring boronic ester reagent **40** in 44% yield successfully (Scheme 20).

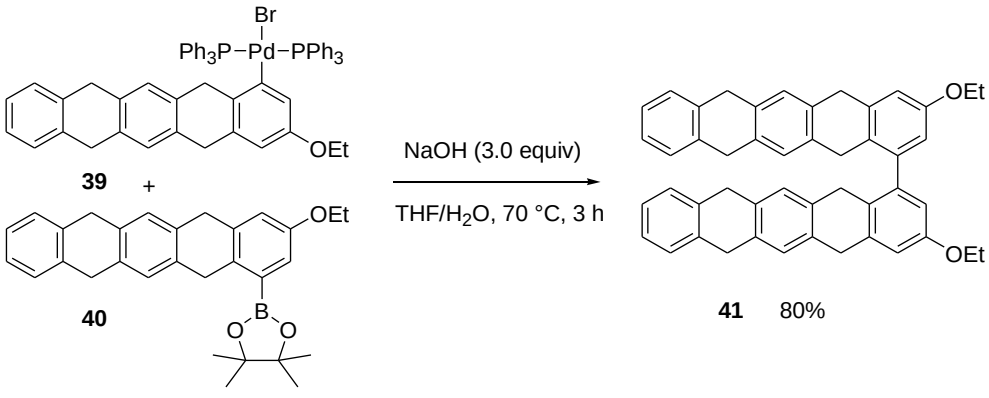
Scheme 20. Synthesis of first ring boron reagent



2) Coupling reaction of **39** and **40**

With complex **39** and compound **40** in hand, Suzuki coupling reaction of them was carried out under the same reaction conditions. As the result, the first ring pentacene side dimer **41** was obtained in high yield.

Scheme 21. Dimerization of first ring palladated pentacene derivative



The ^{1}H NMR spectrum of dimer **41** shows that the peak of methyl is triplet. The peak of methylene is multiplet rather than quartet. Because the hydrogen effect of two tetrahydropentacene, the split peaks of two dihydro ring' hydrogens were observed. The HRMS of dimer **41** was measured. The molecular weight 650.3185 was found as 650.3162. This data clearly indicated the formation of dimer **41**.

4-3. Summary

In summary, the central ring side dimer of pentacene could not be prepared by cross-coupling reaction. When electron-donating group or electron-withdrawing group was introduced into pentacene, such central ring side dimer of pentacene was still not formed. The steric effect of two pentacene maybe the major reason. I then turned to the dimerization of second ring palladated pentacene. A series of second ring palladated pentacene derivatives were prepared. However, second ring side dimer of pentacene also was not obtained by cross-coupling reaction. Moreover, the first ring palladated pentacene was investigated. The first ring pentacene has less steric effect compared to central ring and second ring of pentacene. Finally, the first ring side dimer of pentacene was obtained in high yield under the same reaction conditions.

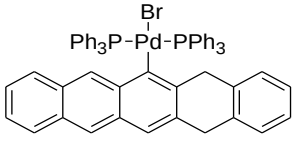
4-4. Experimental Section

General information

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. The reaction temperature recorded here refers to the bath temperature. Tetrahydrofuran (THF), toluene, benzene, and hexane were refluxed and distilled from sodium benzophenone ketyl under nitrogen atmosphere. All starting materials were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded for C_6D_6 or $CDCl_3$ solution on JEOL JNM-ECX400 and JEOL JNM-ECX600. Chemical shifts (δ) were quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) were quoted in Hz. NMR yields were determined using mesitylene, dichloromethane or dioxane as internal standard. Mass spectra were obtained on JEOL JMS-T100GCv spectrometer.

Column chromatography was conducted with silica gel 60N (spherical, neutral, 100 – 210 μm. KANTO CHEMICAL, Co. INC). Some compounds were purified by Model LC-9201R/U Recycling Preparative HPLC (GPC) (Japan Analytical Industry, Co. Ltd).

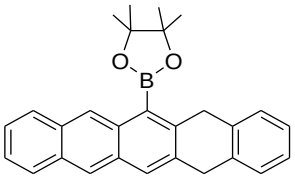
Preparation of palladated dihydropentacene 2 from 1



In a 20 mL Schlenk tube, palladated dihydropentacene **1** (23 mg, 0.021 mmol) was dissolved in a mixture solution of toluene and diethyl ether (3:1, 2 mL). To the mixture was added ^{t}BuLi (0.03 mL, 0.052 mmol) at -78 °C, and it was stirred at -78 °C for 1 h. After being quenched by methanol, the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to afford the title compound **2** (18 mg, 83% isolated yield).

2: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 3.40 (s, 2 H), 4.09 (s, 2 H), 6.75 (t, J = 7.6 Hz, 1 H), 7.04 (s, 1 H), 7.09-7.14 (m, 12 H), 7.16-7.19 (m, 1 H), 7.25-7.28 (m, 6 H), 7.33-7.38 (m, 2 H), 7.46-7.48 (m, 12H), 7.74-7.82 (m, 3 H), 7.85-7.86 (m, 2 H), 9.39 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 37.7, 40.8, 123.6, 124.2, 125.6, 126.3, 126.8, 127.3, 127.5, 128.0, 129.7, 130.0, 130.6, 130.8, 131.0, 131.2, 131.9, 134.4, 135.3, 136.3, 136.4, 137.2, 137.5, 159.9. ^{31}P NMR ($CDCl_3$, Me_4Si, 400M) δ 24.98. HRMS (ESI) calcd for $C_{58}H_{45}BrP_2PdNa$: 1013.1117[M + Na]+, Found: 1013.1142[M + Na]+,

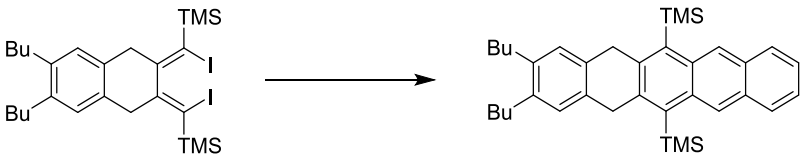
Preparation of central ring boronic ester reagent 5



In a 20 mL Schlenk tube, under nitrogen atmosphere, monoiododihydropentacene **4** (90 mg, 0.22 mmol) was dissolved in diethyl ether : toluene (1:3, 4 mL). To the mixture was added ^{t}BuLi (0.31mL, 0.55mmol) at -78 °C, and it was stirred at -78 °C for 1 h. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.063mL, 0.44mmol) was added to the mixture solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =10:1 as eluent) to afford the title compound **5** (46 mg, 51% isolated yield).

5: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.62 (s, 12 H), 4.10 (s, 2 H), 4.31 (s, 2 H), 7.21-7.24 (m, 2 H), 7.31-7.36 (m, 2 H), 7.40-7.43 (m, 2 H), 7.94 (s, 1 H), 7.95-7.97 (m, 2H), 8.32 (s, 1 H), 8.75 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 25.2, 37.2, 37.5, 84.3, 124.7, 124.9, 125.6, 126.2, 126.3, 126.8, 127.1, 127.2, 127.8, 128.6, 130.6, 131.1, 131.5, 133.6, 135.1, 137.3, 137.6, 142.4. HRMS (EI) calcd for $C_{28}H_{27}BO_2$: 406.2104. Found: 406.2096.

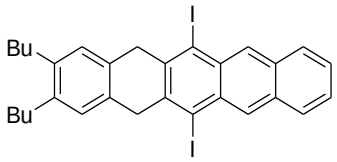
Preparation of 2,3-dibutyl-6,13-bis(trimethylsilyl)-5,14-dihydropentacene 6



In a 50 mL Schlenk tube, 1,4-diiodobutadiene (2.75 mg, 4.14 mmol) was dissolved in THF (20 mL). ^{t}BuLi (9.4 mL, 16.55 mmol) was slowly added to the above solution at -78 °C, and the mixture was stirred for 20 min. The solution was warmed to -40 °C for 20 min and then warm to room temperature for 20 min. After that the solution was cooled to -78 °C, CuCl (820 mg, 8.28 mmol) and DMPU (1.5 mL, 12.42 mmol) were added to the solution, and the mixture was stirred for 20 min at -78 °C. The solution was warmed to -40 °C for another 20 min and then warm to room temperature for 20 min. After that 2,3-diiodonaphthalene (3 g, 8 mmol) was added to the mixture, and heated to 50 °C for 12 h. The solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: triethylamine = 50:1:1 as eluent) to afford the title compound **6** (845 mg, 38% isolated yield) as a solid.

6: ^{1}H NMR ($CDCl_3$, Me_4Si, 400 M) δ 0.69 (s, 18 H), 0.95 (t, J = 7.6 Hz, 6 H), 1.36-1.45 (m, 4 H), 1.51-1.58 (m, 4 H), 2.56-2.60 (m, 4 H), 4.14 (s, 4 H), 7.08 (s, 2 H), 7.39-7.42 (m, 2 H), 7.90-7.93 (m, 2 H), 8.65 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400 M) δ 4.1, 14.0, 22.9, 32.2, 33.8, 38.6, 124.8, 126.7, 127.1, 127.9, 129.8, 134.5, 135.0, 135.2, 138.7, 144.1. HRMS (EI) calcd for $C_{36}H_{48}Si_2$: 536.3295, Found: 536.3298.

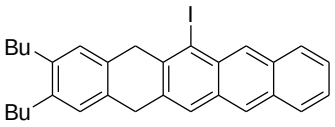
Preparation of 6,13-diiodo-2,3-dibutyl-5,14-dihydropentacene 7



In a 20 mL Schlenk tube, under nitrogen atmosphere, 2,3-dibutyl-6,13-bis(trimethylsilyl)-5,14-dihydro-pentacene **6** (475 mg, 0.88 mmol) was dissolved in THF (10 mL). ICl (2.65 mL, 2.65 mmol) was added to the above solution at -78 °C. The mixture was stirred for 12 h from -78 °C to room temperature. The mixture was quenched with saturated NH_4Cl solution and extracted with chloroform three times. The combined organic phase was washed with water and brine. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound **7** (445 mg, 78% isolated yield) as a solid.

7: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.97 (t, J = 7.2 Hz, 6 H), 1.39-1.48 (m, 4 H), 1.57-1.63 (m, 4 H), 2.61-2.65 (m, 4 H), 4.42 (s, 4 H), 7.21 (s, 2 H), 7.52-7.54 (m, 2 H), 8.09-8.11 (m, 2 H), 8.84 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.0, 22.9, 32.2, 33.8, 45.0, 106.9, 126.4, 127.9, 128.0, 131.9, 132.5, 132.8, 133.3, 139.3, 140.0. HRMS (EI) calcd for $C_{30}H_{30}I_2$: 644.0437. Found: 644.0422.

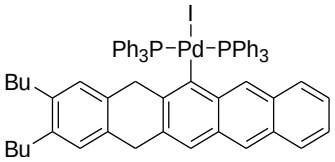
Preparation of 6-iodo-2,3-dibutyl-5,14-dihydropentacene 8



In a 20 mL Schlenk tube, under nitrogen atmosphere, 6,13-Diiodo-2,3-dibutyl-5,14-dihydropentacene **7** (202 mg, 0.31 mmol) and Cp_2TiCl_2 (8 mg, 0.031 mmol) were dissolved in THF (10 mL). ^{n}BuMgCl (1 mL, 0.94 mmol) was added to the above solution at 0 °C, the mixture was stirred for 3 h at 0 °C. The mixture was quenched with HCl (3 mol/L), extracted with ethyl acetate three times. The combined organic phase was washed with water and brine. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 20:1 as eluent) to afford the title compound **8** (137 mg, 85% isolated yield) as a solid.

8: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.94-0.98 (m, 6 H), 1.37-1.48 (m, 4 H), 1.54-1.63 (m, 4 H), 2.60-2.63 (m, 4 H), 4.10 (s, 2 H), 4.35 (s, 2 H), 7.15 (s, 1 H), 7.21 (s, 1 H), 7.46-7.50 (m, 2 H), 7.85 (s, 1 H), 7.98-8.01 (m, 1 H), 8.08-8.10 (m, 1 H), 8.30 (s, 1 H), 8.79 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.0, 22.9, 22.9, 32.2, 33.8, 33.8, 37.4, 43.9, 104.4, 125.5, 125.8, 125.9, 126.0, 127.5, 128.4, 128.6, 131.1, 131.7, 132.0, 132.3, 133.7, 133.8, 135.8, 138.9, 139.0, 140.8. HRMS (EI) calcd for $C_{30}H_{31}I$: 518.1470. Found: 518.1458.

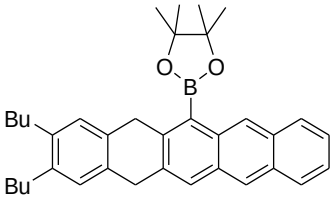
Preparation of palladated dihydropentacene 9



In a 20 mL Schlenk tube, 6-iodo-2,3-dibutyl-5,14-dihydro-pentacene **8** (44 mg, 0.085 mmol) and $Pd(PPh_3)_4$ (118 mg, 0.1 mmol) were dissolved in toluene (3 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 80 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to afford the title compound **9** (69 mg, 71% isolated yield) as a solid.

9: ^{1}H NMR ($CDCl_3$, Me_4Si, 600 M) δ 0.93-0.98 (m, 6 H), 1.37-1.54 (m, 8 H), 2.44-2.56 (m, 4 H), 3.24 (s, 1 H), 4.00 (s, 1 H), 6.61 (s, 1 H), 6.87 (s, 1 H), 6.91 (s, 1 H), 7.01 (brs, 12 H), 7.17 (brs, 6 H), 7.30-7.31 (m, 2 H), 7.38 (brs, 12 H), 7.74-7.78 (m, 3 H), 9.33 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600 M) δ 14.0, 14.1, 22.8, 23.1, 32.1, 32.1, 33.9, 33.9, 37.3, 40.1, 120.5, 123.7, 124.1, 124.2, 127.3, 127.7, 127.9, 128.5, 129.7, 130.0, 130.2, 130.6, 131.5, 131.7, 131.8, 132.1, 134.3, 134.6, 135.2, 135.9, 136.5, 136.7, 137.7, 137.8, 162.7. ^{31}P NMR ($CDCl_3$, Me_4Si, 600 M) δ 24.34; HRMS (ESI) calcd for $C_{66}H_{61}IPdP_2Na$: 1171.2226[M + Na]+, Found: 1171.2268[M + Na]+.

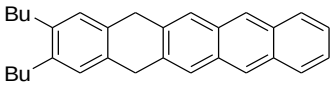
Preparation of central ring boron reagent 10



In a 20 mL Schlenk tube, under nitrogen atmosphere, 6-iodo-2,3-dibutyl-5,14-dihydropentacene **8** (61 mg, 0.12 mmol) was dissolved in Et_2O (2 mL). ^{n}BuLi (0.087 mL, 0.14 mmol) was added to the above solution at -78 °C, the mixture was stirred for 1 h at -78 °C. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.034 mL, 0.236 mmol) was added to the above mixture at -78 °C. The mixture was stirred at room temperature for 12 hours. The mixture was quenched with methanol, the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to afford the title compound **10** (36 mg, 59% isolated yield).

10: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.93-0.98 (m, 6 H), 1.36-1.47 (m, 4 H), 1.53-1.58 (m, 4 H), 1.61 (s, 12 H), 2.58-2.62 (m, 4 H), 4.03 (s, 2 H), 4.24 (s, 2 H), 7.05 (s, 1 H), 7.12 (s, 1 H), 7.39-7.41 (m, 2 H), 7.91 (s, 1 H), 7.93-7.96 (m, 2 H), 8.31 (s, 1 H), 8.73 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.0, 22.9, 22.9, 25.2, 32.1, 32.3, 33.8, 33.9, 36.8, 37.1, 84.2, 124.6, 124.8, 125.5, 126.1, 127.0, 127.6, 127.7, 128.0, 128.6, 130.6, 131.0, 131.4, 133.6, 134.4, 134.6, 135.5, 138.5, 142.8. HRMS (EI) calcd for $C_{36}H_{43}BO_2$: 518.3356. Found: 518.3349.

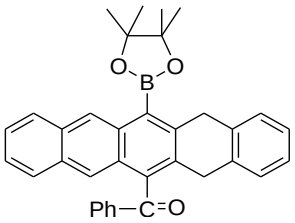
Preparation of dihydropentacene derivative 11



In a 20 mL Schlenk tube, palladated dihydropentacene **9** (18 mg, 0.016 mmol) and boronic ester **10** (36 mg, 0.031 mmol) were dissolved in THF : H_2O (10:1, 2.2 mL), under nitrogen atmosphere, the mixture was added NaOH (1.92 mg, 0.048 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and heated at 70 °C for about 12 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to give the compound **11.**

11: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.96 (t, J = 7.6 Hz, 6 H), 1.37-1.47 (m, 4 H), 1.53-1.61 (m, 4 H), 2.59-2.63 (m, 4 H), 4.08 (s, 4 H), 7.14 (s, 2 H), 7.40-7.44 (m, 2 H), 7.90 (s, 2 H), 7.96-7.99 (m, 2 H), 8.35 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.0, 22.9, 32.1, 33.8, 36.7, 124.7, 124.9, 125.2, 128.0, 128.1, 131.0, 131.4, 134.2, 136.1, 138.6. HRMS (EI) calcd for $C_{30}H_{32}$: 392.2504. Found: 392.2493.

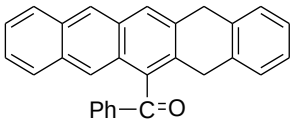
Preparation of boronic ester reagent 14



In a 20 mL Schlenk tube, palladated dihydropentacene **12** (123 mg, 0.112 mmol) and sliver acetate (21 mg, 0.124 mmol) were dissolved in benzene (10 mL). Under nitrogen atmosphere, the mixture was stirred at 50 °C for 3 h, then removed the AgBr by filtered method. The clear solution was added bis(pinacolato)diboron (34 mg, 0.135 mmol) and stirred at 80 °C for 12 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to afford the title compound **14** (12 mg, 21% isolated yield) as a yellow solid.

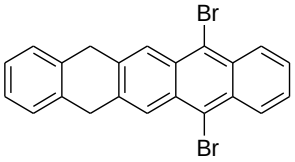
14: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.64 (s, 12 H), 3.79-3.89 (m, 2 H), 4.29-4.37 (m, 2 H), 7.01 (d, J = 7.8 Hz, 1 H), 7.13 (t, J = 7.8 Hz, 1 H), 7.20 (t, J = 7.8 Hz, 1 H), 7.32 (d, J = 7.2 Hz, 1 H), 7.35-7.42 (m, 4 H), 7.58 (t, J = 7.8 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.85-7.87(m, 2 H), 7.94 (d, J = 8.4 Hz, 1 H), 8.05(s, 1 H), 8.77 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 25.2, 34.8, 37.3, 84.6, 124.0, 125.3, 125.4, 126.4, 126.4, 126.7, 126.9, 126.9, 127.4, 128.1, 128.3, 128.9, 129.9, 131.2, 131.4, 131.9, 132.9, 134.0, 135.5, 136.1, 137.2, 137.5, 141.4, 200.1. HRMS (EI) calcd for $C_{35}H_{31}BO_3$: 510.2366. Found: 510.2356.

Preparation of dihydropentacene derivative 15



15: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 3.89 (s, 2 H), 4.18 (s, 2 H), 7.05 (d, J = 7.6 Hz, 1 H), 7.15 (t, J = 7.6 Hz, 1 H), 7.23 (t, J = 7.6 Hz, 1 H), 7.36-7.46 (m, 5 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.90-7.92 (m, 2 H), 7.97 (d, J = 8.4 Hz, 1 H), 8.04 (s, 1 H), 8.08 (s, 1 H), 8.42 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 34.5, 37.1, 123.8, 125.4, 125.6, 125.9, 126.3, 126.4, 126.6, 127.0, 127.3, 127.8, 128.0, 128.4, 129.0, 129.9, 130.4, 131.5, 131.6, 132.8, 133.9, 134.0, 135.1, 136.0, 136.8, 137.6, 200.0. HRMS (EI) calcd for $C_{29}H_{20}O$: 384.1514, Found: 384.1517.

Preparation of 7,12-dibromo-5,14-dihydropentacene 18

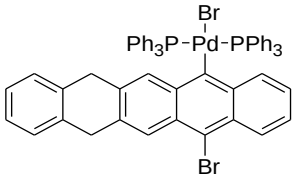


In a 20 mL Schlenk tube, 5,14-dihydropentacene **17** (229 mg, 0.82 mmol) was dissolved in

CCl_4 (5 mL). To the mixture was added Br_2 (2.45ml, 2.45mmol) at 0 °C, and it was stirred at 0 °C for 1 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound **18** (273 mg, 76% isolated yield).

18: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.22 (s, 4 H), 7.24-7.25 (m, 2 H), 7.38-7.40 (m, 2 H), 7.59-7.62 (m, 2 H), 8.51 (s, 2 H), 8.55-8.57 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 36.9, 122.5, 125.1, 126.6, 127.1, 127.3, 128.2, 130.3, 130.7, 136.4, 138.2. HRMS (EI) calcd for $C_{22}H_{14}Br_2$: 435.9462. Found: 435.9470.

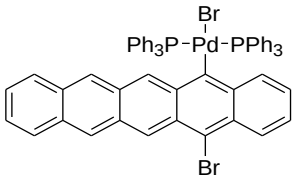
Preparation of palladated dihydropentacene 19a



In a 20 mL Schlenk tube, 7,12-dibromo-5,14-dihydropentacene **18** (22 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 50 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 3:1 as eluent) to remove PPh_3 firstly, then use chloroform as eluent to afford the title compound **19a** (42 mg, 79% isolated yield) as a yellow solid.

19a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.76 (s, 2 H), 4.01 (s, 2 H), 6.99 (t, J = 7.6 Hz, 12 H), 7.02-7.09 (m, 2 H), 7.15 (t, J = 7.6 Hz, 6 H), 7.21-7.27 (m, 4 H), 7.30-7.34 (m, 12 H), 7.79 (d, J = 8 Hz, 1 H), 7.88 (s, 1 H), 8.72 (d, J = 8 Hz, 1 H), 8.88 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si,) δ 36.3, 37.0, 117.8, 122.9, 124.0, 125.5, 126.3, 126.3, 127.3, 127.3, 127.4, 127.5, 129.9, 130.4, 130.6, 130.7, 130.9, 132.1, 132.9, 134.3, 135.6, 136.0, 136.2, 137.2, 137.3, 163.4. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 23.84. HRMS (FAB) calcd for $C_{58}H_{44}Br_2P_2Pd$: 1068.0321. Found: 1068.0332.

Preparation of second ring palladated pentacene 20a



In a 20 mL Schlenk tube, palladated dihydropentacene **19a** (20 mg, 0.0187 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (9.3 mg, 0.041 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 3 h at room temperature. The pentacene-DDQ adduct was formed firstly. Without isolation of pentacene-DDQ adduct, γ-terpinene (0.15 mL, 0.935 mmol) was added to the reaction solution. The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 3 h. After

cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **20a** (8 mg, 40% isolated yield) as a blue solid.

20a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 6.97 (t, J = 7.2 Hz, 12 H), 7.04-7.06 (m, 2 H), 7.14 (t, J = 7.2 Hz, 6 H), 7.32-7.37 (m, 14 H), 7.83 (d, J = 9 Hz, 1 H), 7.91 (d, J = 9 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 8.36 (s, 1 H), 8.59 (s, 1 H), 8.78 (d, J = 8.4 Hz, 1 H), 8.90 (s, 1 H), 10.01 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 118.1, 122.7, 125.0, 125.2, 125.8, 126.0, 126.3, 127.6, 128.6, 128.6, 128.8, 129.4, 130.0, 130.4, 130.5, 130.7, 130.9, 131.2, 131.7, 131.9, 132.7, 134.3, 135.4, 135.5, 167.7. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 24.06. HRMS (FAB) calcd for $C_{58}H_{42}Br_2P_2Pd$: 1066.0165. Found: 1066.0167.

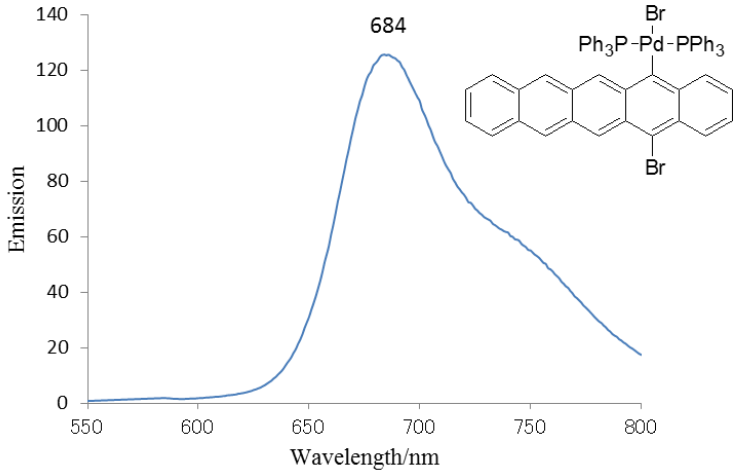
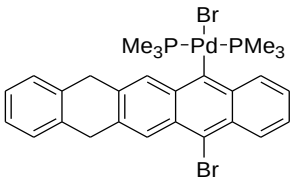


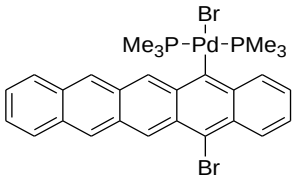
Figure 10. Emission spectrum of **20a** in $CHCl_3$ at rt (λ_{ex} = 560 nm).

Preparation of second ring palladated dihydropentacene 19b



19b: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J = 3.6 Hz,18 H), 4.16 (s, 2 H), 4.20 (s, 2 H), 7.25-7.27 (m, 2 H), 7.39-7.43 (m, 3 H), 7.48-7.50 (m, 2 H), 8.38 (s, 1 H), 8.42 (d, J = 9 Hz, 1 H), 8.70 (s, 1 H), 8.79 (d, J = 9 Hz, 1 H). ^{13}C NMR (C_6D_6, Me_4Si) δ 14.3, 36.7, 37.1, 117.5, 123.9, 125.4, 126.6, 126.7, 126.9, 127.4, 127.7, 128.4, 130.2, 130.4, 130.9, 133.9, 134.8, 137.2, 137.2, 137.6, 137.9, 138.1, 164.3. HRMS (FAB) calcd for $C_{28}H_{32}Br_2P_2Pd$: 695.9373. Found: 69.9365.

Preparation of second ring palladated pentacene 20b



20b: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.02 (t, J = 3.6 Hz, 18 H), 7.31-7.43 (m, 4 H), 7.96-7.99 (m, 2 H), 8.39 (d, J = 8.8 Hz, 1 H), 8.73-8.78 (m, 3 H), 9.44 (s, 1 H), 9.83 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.7, 117.6, 123.4, 125.3, 125.5, 126.3, 126.5, 126.8, 127.1, 128.0, 128.4, 128.4, 129.4, 129.5, 130.2, 130.7, 131.6, 132.1, 132.4, 133.9, 136.4, 136.4, 165.6. HRMS (FAB) calcd for $C_{28}H_{30}Br_2P_2Pd$: 693.9217. Found: 693.9224.

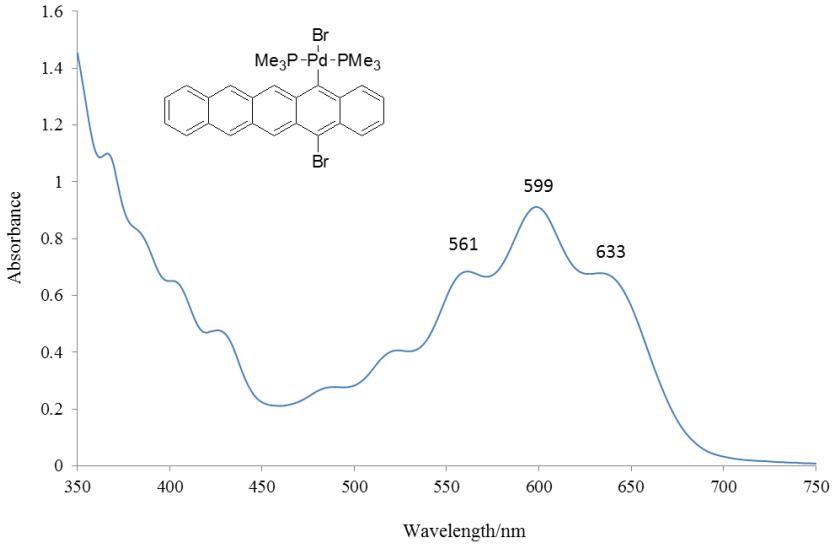


Figure 11. Absorption spectrum of **20b** in $CHCl_3$ at rt

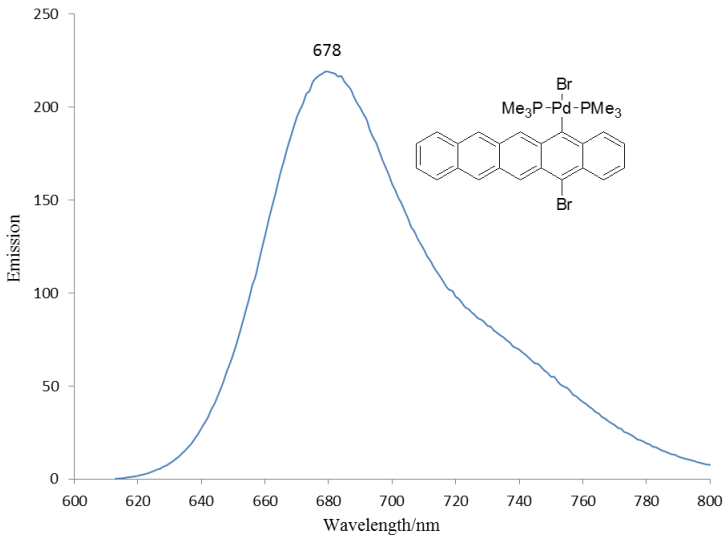
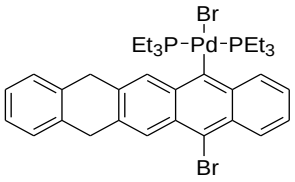


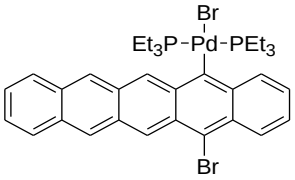
Figure 12. Emission spectrum of **20b** in $CHCl_3$ at rt (λ_{ex} = 599 nm).

Preparation of second ring palladated dihydropentacene 19c



19c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.87-0.94 (m, 18 H), 1.26-1.32 (m, 12 H), 4.09 (s, 2 H), 4.21 (s, 2 H), 7.24-7.27 (m, 2 H), 7.33-7.35 (m, 1 H), 7.38-7.42 (m, 2 H), 7.47-7.51 (m, 1 H), 8.36 (s, 1 H), 8.41 (d, *J* = 8 Hz, 1 H), 8.83 (d, *J* = 8 Hz, 1 H), 8.87 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) *δ* 8.1, 15.1, 36.5, 37.1, 117.2, 122.9, 124.4, 126.4, 126.4, 127.2, 127.4, 127.5, 129.4, 130.1, 131.5, 133.3, 134.6, 136.4, 136.9, 137.0, 137.0, 137.1, 161.8. HRMS (FAB) calcd for $C_{34}H_{44}Br_2P_2Pd$: 780.0314. Found: 780.0299.

Preparation of second ring palladated pentacene 20c



8c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89-0.95 (m, 18 H), 1.28-1.40 (m, 12 H), 7.30-7.33 (m, 1 H), 7.35-7.4 (m, 2 H), 7.41-7.43 (m, 1 H), 7.96-7.98 (m, 2 H), 8.39 (d, *J* = 9 Hz, 1 H), 8.62 (s, 1 H), 8.78-8.80 (m, 2 H), 9.42 (s, 1 H), 9.99 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si) *δ* 8.1, 15.2, 117.6, 122.5, 125.2, 125.4, 125.9, 126.3, 126.6, 127.2, 127.8, 128.4, 128.5, 128.9, 129.3, 129.9, 130.7, 131.5, 132.1, 133.8, 135.2, 136.2, 136.3, 166.0. HRMS (FAB) calcd for $C_{34}H_{42}Br_2P_2Pd$: 778.0158. Found: 778.0146.

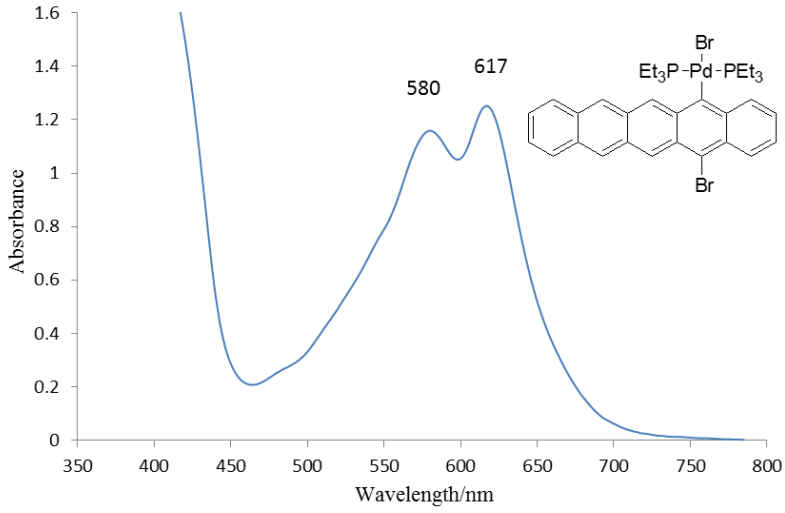


Figure 13. Absorption spectrum of **20c** in $CHCl_3$ at rt

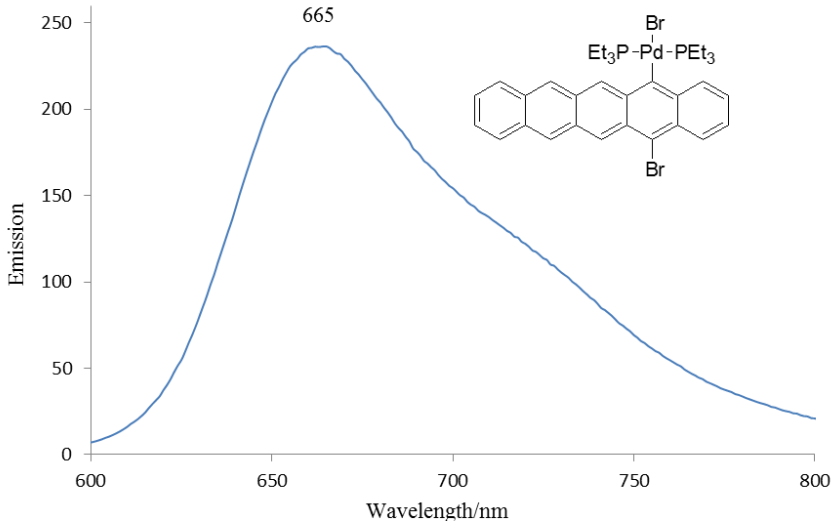
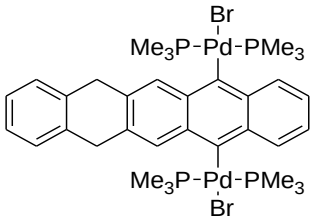


Figure 14. Emission spectrum of **20c** in $CHCl_3$ at rt (λ_{ex} = 560 nm).

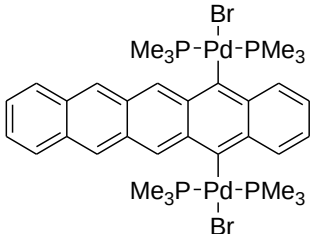
Preparation of second ring dipalladated dihydropentacene 21



In a 20 mL Schlenk tube, palladated dihydropentacene **19b** (65 mg, 0.0936 mmol) and $Pd(PPh_3)_4$ (130 mg, 0.1123 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 °C. After cooling to room temperature, PMe_3 (0.56 mL, 0.56 mmol) was added to the mixture and stirred for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: $CHCl_3$ = 3:1:1 as eluent) to afford the title compound **21** (65mg, 73% isolated yield) as a yellow solid.

21: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.98 (t, J = 3.6 Hz, 36 H), 4.14 (s, 4 H), 7.26-7.31 (m, 4 H), 7.39-7.42 (m, 2 H), 8.56 (s, 2 H), 8.63-8.65 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ: 15.0, 37.0, 123.3, 126.4, 127.6, 129.4, 133.0, 133.6, 137.2, 137.7, 137.8, 151.6. ^{31}P NMR ($CDCl_3$, Me_4Si) δ: -16.42.

Preparation of second ring dipalladated pentacene 22



22: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.01 (t, J = 3.6 Hz, 36 H), 7.22-7.24 (m, 2 H), 7.26-7.32 (m, 2 H), 7.93-7.95 (m, 2 H), 8.61-8.63 (m, 2 H), 8.69 (s, 2 H), 9.69 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ: 15.0, 123.6, 125.1, 126.2, 128.5, 129.7, 131.0, 131.3, 133.5, 137.3, 137.8, 154.2. ^{31}P NMR ($CDCl_3$, Me_4Si) δ -16.23. HRMS (FAB) calcd for $C_{34}H_{48}Br_2P_4Pd_2$: 953.9143. Found: 953.9158.

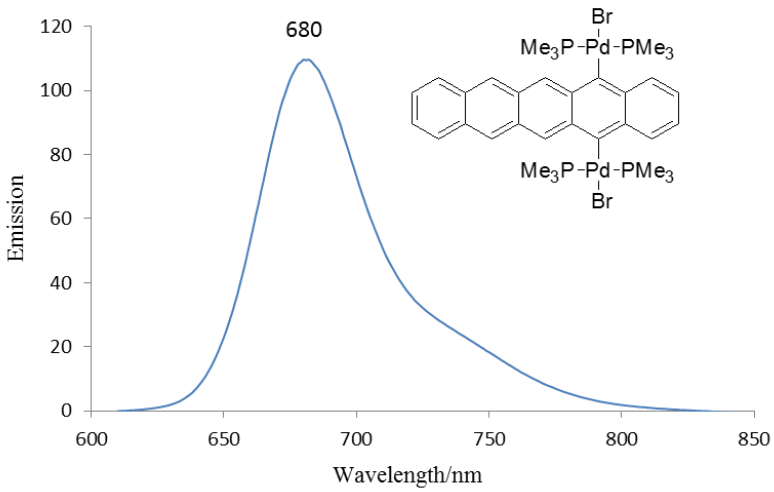
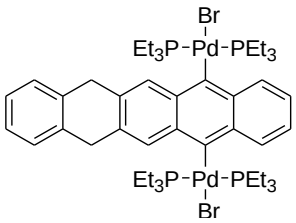


Figure 15. Emission spectrum of **22** in $CHCl_3$ at rt (λ_{ex} = 602 nm).

Preparation of second ring dipalladated dihydropentacene 23



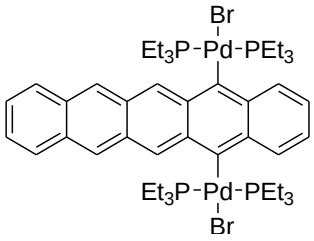
Method a: In a 20 mL Schlenk tube, palladated dihydropentacene **19b** (20 mg, 0.028 mmol) and $Pd(PPh_3)_4$ (39 mg, 0.034 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 °C. After cooling to room temperature, PEt_3 (0.18 mL, 0.17 mmol) was added to the mixture, then it was stirred at 80 °C for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform = 5:1:1 as eluent) to afford the title compound **23** (17mg, 53% isolated yield) as a yellow solid.

Method b: In a 20 mL Schlenk tube, palladated dihydropentacene **19c** (58 mg, 0.074 mmol) and $Pd(PPh_3)_4$ (103 mg, 0.089 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 100 °C. After cooling to room temperature, PEt_3 (0.33 mL, 0.44 mmol) was added to the mixture. The mixture was stirred at 80 °C for 12 h. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **23** (50 mg, 60% isolated

yield) as a yellow solid.

23: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.93-1.01 (m, 36 H), 1.28-1.32 (m, 24 H), 4.09 (s, 4 H), 7.24-7.28 (m, 4 H), 7.35-7.37 (m, 2 H), 8.65-8.67 (m, 4 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 8.5, 15.1, 36.7, 122.4, 126.3, 127.5, 130.8, 132.3, 134.1, 136.5, 137.4, 137.7, 152.2. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 11.91. HRMS (FAB) calcd for $C_{46}H_{74}Br_2P_4Pd_2$: 1124.1182. Found: 1124.1189.

Preparation of second ring dipalladated pentacene 24



24: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.95-1.00 (m, 36 H), 1.28-1.42 (m, 24 H), 7.20-7.22 (m, 2 H), 7.29-7.31 (m, 2 H), 7.92-7.94 (m, 2 H), 8.58 (s, 2 H), 8.63-8.65 (m, 2 H), 9.81 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.5, 15.2, 122.7, 124.9, 126.0, 128.6, 129.1, 131.3, 132.1, 134.7, 136.8, 137.4, 154.9. ^{31}P NMR ($CDCl_3$, Me_4Si) δ 12.01. HRMS (FAB) calcd for $C_{46}H_{72}Br_2P_4Pd_2$: 1122.1026. Found: 1122.1017.

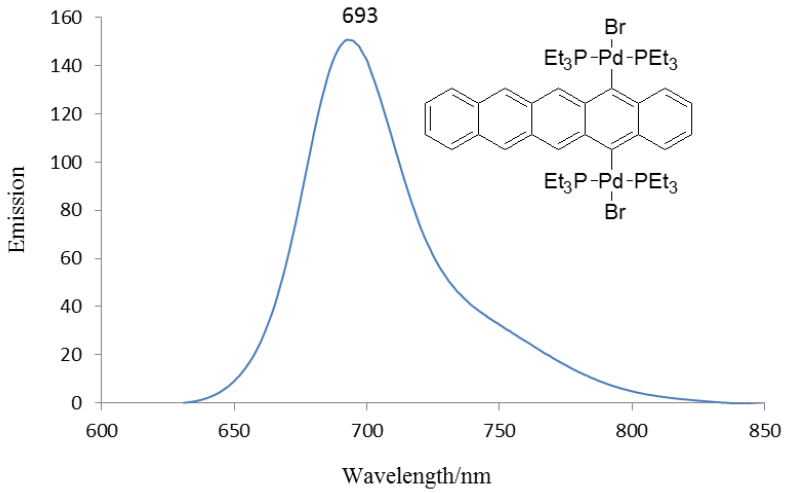
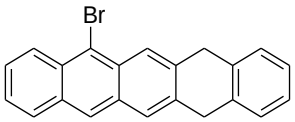


Figure 16. Emission spectrum of **24** in $CHCl_3$ at rt (λ_{ex} = 610 nm).

Preparation of 7-bromo-5,14-dihydropentacene 27

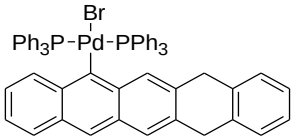


In a 20 mL Schlenk tube, under nitrogen atmosphere, second ring palladated dihydropentacene **19a** (362 mg, 0.339 mmol) was dissolved in $CHCl_3$ (3 mL). The mixture was added CF_3COOH (0.26 mL, 3.39 mmol) at room temperature. The mixture was heated at 50 °C

for about 1 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to afford the title compound **27** (101mg, 83% isolated yield) as a solid.

27: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 4.15 (s, 2 H), 4.20 (s, 2 H), 7.24-7.25 (m, 2 H), 7.36-7.39 (m, 2 H), 7.46-7.48 (m, 1 H), 7.56-7.58 (m, 1 H), 7.90 (s, 1 H), 7.97 (d, J = 8.4 Hz, 1 H), 8.37 (s, 1 H), 8.43 (s, 1 H), 8.49 (d, J = 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 36.7, 37.4, 121.3, 124.4, 125.2, 125.2, 126.2, 126.4, 126.5, 126.8, 127.2, 127.3, 127.5, 128.5, 129.8, 130.3, 131.4, 132.0, 136.1, 136.7, 136.8, 137.8. HRMS (ESI) calcd for $C_{22}H_{15}Br$: 358.0357, Found: 358.0353.

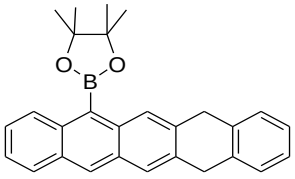
Preparation of second ring palladated dihydropentacene 26



In a 20 mL Schlenk tube, 7-bromo-5,14-dihydropentacene **27** (34 mg, 0.095 mmol) and $Pd(PPh_3)_4$ (132 mg, 0.114 mmol) were dissolved in toluene (3 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 80 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to afford the title compound **26** (75 mg, 80% isolated yield) as a solid.

26: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 3.69 (s, 2 H), 3.87 (s, 2 H), 6.85-6.87 (m, 1 H), 6.89-6.95 (m, 13 H), 7.06-7.08 (m, 6 H), 7.13-7.21 (m, 13 H), 7.23-7.28 (m, 5 H), 7.32 (s, 1 H), 8.56 (d, J = 8.1 Hz, 1 H), 8.71 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 36.6, 36.7, 121.2, 122.5, 123.4, 124.2, 126.0, 126.1, 127.1, 127.1, 127.2, 127.3, 127.3, 127.3, 127.4, 127.9, 129.5, 130.8, 130.9, 131.1 131.1, 131.4, 131.9, 132.3, 133.8, 134.1, 134.1, 134.2, 134.2, 134.9, 135.2, 137.5, 162.5. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 24.70. HRMS (ESI) calcd for $C_{58}H_{45}BrP_2PdNa$: 1013.1092[M + Na]+, Found: 1013.1106[M + Na]+.

Preparation of 2-(7,12-dihydro-pentacen-5-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 29

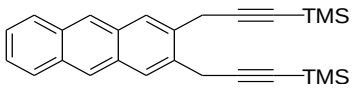


In a 20 mL Schlenk tube, under nitrogen atmosphere, 7-bromo-5,14-dihydropentacene **27** (39 mg, 0.11 mmol) was dissolved in diethyl ether : toluene (1:3, 2 mL). To the mixture was added ^{t}BuLi (0.15mL, 0.27mmol) at -78 °C and stirred for 1 h. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (0.063mL, 0.44mmol) was added to the above solution at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvent was

evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate =10:1 as eluent) to afford the title compound **29** (35 mg, 65% isolated yield).

29: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.61 (s, 12 H), 4.12 (s, 2 H), 4.13 (s, 2 H), 7.21-7.24 (m, 2 H), 7.35-7.39 (m, 2 H), 7.40-7.47 (m, 2 H), 7.89 (s, 1 H), 7.95-7.97 (m, 1H), 8.37 (s, 1 H), 8.41-8.43 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 25.2, 36.9, 37.6, 84.3, 124.5, 125.1, 125.3, 125.4, 126.2, 127.1, 127.2, 128.2, 128.6, 128.7, 130.4, 130.9, 135.0, 135.3, 135.7, 135.9, 137.1, 137.1. HRMS (EI) calcd for $C_{28}H_{27}BO_2$: 406.2104. Found: 406.2096.

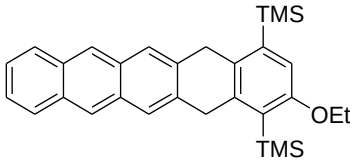
Preparation of diyne 30



In a 500 ml two-neck flask, trimethylsilylacetylene (5.02 mL, 35.54 mmol) was dissolved in 50 ml THF. The ethylmagnesium bromide (36.64 mL, 35.54 mmol) was added to the above solution. The mixture was heated at 40 °C for 1 hour. CuCl (440 mg, 4.44 mmol) and 2,3-bis(iodomethyl)anthracene (4.07 g, 8.88 mmol) were added to the mixture at room temperature, the mixture was heated to 70 °C for overnight. After cooling to room temperature, the mixture was quenched with aqueous saturated NH_4Cl and extracted with ethyl acetate. The combined organic phase was washed with water, brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel chromatography (hexane: ethyl acetate: chloroform = 50:1:1 as eluent) to afford **30** (2.69 g, 76% yield).

30: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.24 (s, 18 H), 3.83 (s, 4 H), 7.45-7.47 (m, 2 H), 7.99-8.02 (m, 2 H), 8.08 (s, 2 H), 8.34 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 0.1, 24.3, 88.2, 103.4, 125.2, 125.6, 127.3, 128.1, 130.9, 131.7, 132.2. HRMS (EI) calcd for $C_{26}H_{30}Si_2$: 398.1886. Found: 398.1881

Preparation of 2-ethoxy-1,4-bis-trimethylsilanyl-5,14-dihydropentacene 31

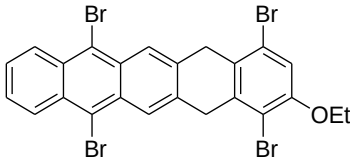


Cp_2ZrCl_2 (1.10 g, 3.75 mmol) was dissolved in 15 mL of THF. The solution was cooled to -78 °C. ^{n}BuLi (1.60 M hexane solution, 4.7 mL, 7.5 mmol) was added dropwise to the solution and stirred for 1 h. To the mixture was added diyne **30** (741 mg, 3 mmol), and it was warmed to room temperature. After stirring for 3 hours, CuCl (891 mg, 9 mmol) and ethoxyacetylene (2.8 mL, 12 mmol) were added to the mixture at 0 °C, and it was stirred at room temperature for 24 hours. The mixture was quenched with HCl solution (3 mol/L) and extracted with ethyl acetate three times. The combined organic phase was washed with water, $NaHCO_3$ and brine. The solution was dried over $MgSO_4$. The solvent was evaporated, and the resulting oil was purified

by a flash chromatography (silica gel, hexane: ethyl acetate: chloroform=10:1:1 as eluent) to afford the title compound **31** as a yellow solid (485 mg, 34% yield).

31: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 0.45 (s, 9 H), 0.50 (s, 9 H), 1.41 (t, J = 7.2 Hz, 3 H), 4.01 (q, J = 7.2 Hz, 2 H), 4.13 (s, 2 H), 4.21 (s, 2 H), 6.84 (s, 1 H), 7.41-7.43 (m, 2 H), 7.86 (s, 1 H), 7.87 (s, 1 H), 7.97-7.98 (m, 2 H), 8.36 (s, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 0.2, 3.1, 14.9, 37.5, 37.8, 63.4, 113.9, 123.4, 124.0, 124.8, 124.9, 125.3, 125.3, 126.1, 128.0, 128.1, 131.1, 131.1, 131.4, 131.4, 135.4, 136.8, 137.0, 139.1, 144.7, 161.7. HRMS (EI) calcd for $C_{30}H_{36}Si_2O$: 468.2305. Found: 468.2300.

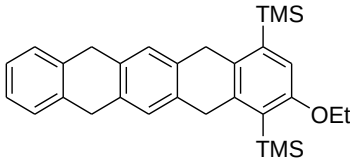
Preparation of 1,4,7,12-tetrabromo-2-ethoxy-5,14-dihydropentacene 33



In a 50 ml Schlenk tube, 2-ethoxy-1,4-bis-trimethylsilanyl-5,14-dihydropentacene **31** (312 mg, 0.67 mmol) and NBS (596 mg, 3.35 mmol) were dissolved in CH_2Cl_2 (20 mL) at room temperature. Under nitrogen atmosphere, the mixture was stirred for 12 h at room temperature. The solvent was evaporated, and the resulting solids were washed by methanol and chloroform to afford the title compound **33** (350 mg, 82% isolated yield) as a pale green solid.

33: ^{1}H NMR ($C_2D_2Cl_4$, Me_4Si, 600M, 110 °C) δ 1.53 (t, J = 10.8 Hz, 3 H), 4.18 (q, J = 10.8 Hz, 2 H), 4.42 (s, 2 H), 4.52 (s, 2 H), 7.17 (s, 1 H), 7.65-7.67 (m, 2 H), 8.60-8.61 (m, 4 H). ^{13}C NMR ($C_2D_2Cl_4$, Me_4Si, 600M, 110 °C) δ 15.7, 37.2, 38.2, 67.0, 114.9, 117.5, 123.4, 123.7, 123.7, 126.7, 126.8, 128.3, 129.2, 129.2, 130.3, 131.6, 131.6, 132.1, 132.1, 137.3, 137.6, 139.4, 155.8. HRMS (EI) calcd for $C_{24}H_{16}Br_4O$: 639.7894. Found: 639.7879.

Preparation of 2-ethoxy-1,4-bis-trimethylsilanyl-5,7,12,14-tetrahydropentacene 35

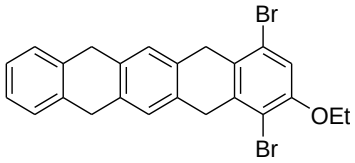


Cp_2ZrCl_2 (1.10 g, 3.75 mmol) was dissolved in 15 mL of THF. The solution was cooled to -78 °C. ^{n}BuLi (1.60 M hexane solution, 4.7 mL, 7.5 mmol) was added dropwise to the solution and stirred for 1 h. To the mixture was added diyne **34** (747 mg, 3 mmol), and it was warmed to room temperature. After stirring for 3 h, CuCl (891 mg, 9 mmol) and ethoxyacetylene (2.8 mL, 12 mmol) were added to the mixture at 0 °C, and it was stirred at room temperature for 24 hours. The mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate three times. The combined organic phase was washed with water and brine. The solution was dried over $MgSO_4$. The solvent was evaporated, and the resulting oil was purified by a flash

chromatography (silica gel, hexane as eluent) to afford the title compound **35** as a yellow solid (587 mg, 42% yield).

35: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 0.40 (s, 9 H), 0.44 (s, 9 H), 1.40 (t, J = 6.8 Hz, 3 H), 3.91 (s, 2 H), 3.93 (s, 4 H), 3.98 (s, 2 H), 4.00 (q, J = 6.8 Hz, 2 H), 7.17-7.19 (m, 2 H), 7.21-7.21 (m, 2 H), 7.27-7.30 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 0.2, 3.1, 14.9, 35.9, 36.8, 37.2, 63.4, 113.8, 125.2, 125.6, 126.0, 126.1, 127.3, 134.3, 134.4, 135.5, 136.0, 136.2, 136.9, 139.0, 144.8, 161.5. HRMS (EI) calcd for $C_{30}H_{38}Si_2O$: 470.2461. Found: 470.2448.

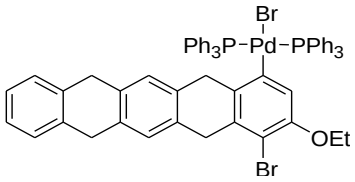
Preparation of 1,4-dibromo-2-ethoxy-5,7,12,14-tetrahydropentacene 36



In a 50 mL Schlenk tube, under nitrogen atmosphere, 2-ethoxy-1,4-bis-trimethylsilanyl-5,7,12,14-tetrahydropentacene **35** (587 mg, 1.25 mmol) and NBS (488 mg, 2.74 mmol) were dissolved in CH_2Cl_2 (10 mL) at room temperature, the mixture was stirred for 12 h at room temperature. After that the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to afford the title compound **36** (436 mg, 72% isolated yield) as a yellow solid.

36: ^{1}H NMR ($CDCl_3$, Me_4Si, 400 M) δ 1.48 (t, J = 7.2 Hz, 3 H), 3.93 (s, 4 H), 4.04 (s, 2 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.13 (s, 2 H), 7.04 (s, 1 H), 7.18-7.20 (m, 2 H), 7.26-7.31 (m, 4 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400 M) δ 14.7, 35.3, 35.8, 36.4, 65.3, 113.2, 115.0, 122.6, 126.1, 126.5, 126.5, 127.4, 129.2, 132.3, 132.6, 135.0, 135.1, 136.7, 138.6, 153.9. HRMS (EI) calcd for $C_{24}H_{20}Br_2O$: 481.9881. Found: 481.9867.

Preparation of palladated tetrahydropentacene 37

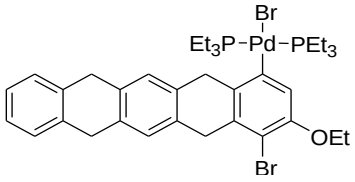


In a 20 mL Schlenk tube, 1,4-dibromo-2-ethoxy-5,7,12,14-tetrahydro-pentacene **36** (20 mg, 0.04 mmol) and $Pd(PPh_3)_4$ (57 mg, 0.05 mmol) were dissolved in toluene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 12 h at 80 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to afford the title compound **37** (37 mg, 82% isolated yield) as a pale yellow solid.

37: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.11 (t, J = 7.2 Hz, 3 H), 3.26 (q, J = 7.2 Hz, 2 H), 3.39 (s, 2 H), 3.42 (s, 2 H), 3.76 (s, 2 H), 3.86 (s, 2 H), 6.18 (s, 1 H), 6.49 (s, 1 H), 7.02 (s, 1 H), 7.16-7.21 (m, 14 H), 7.25-7.31 (m, 7 H), 7.38-7.45 (m, 13 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M)

δ 14.6, 35.7, 35.7, 36.4, 39.3, 64.5, 108.9, 118.6, 125.7, 126.0, 127.2, 127.3, 127.8, 129.9, 130.4, 130.6, 130.7, 133.1, 133.6, 133.7, 134.5, 134.6, 135.2, 137.0, 137.4, 151.2, 155.4. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 23.47. HRMS (ESI) calcd for $C_{60}H_{50}Br_2OP_2PdNa$: 1137.0616[M + Na]+, Found: 1137.0624[M + Na]+.

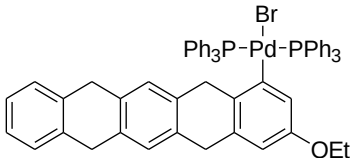
Preparation of palladated tetrahydropentacene 38



In a 20 mL Schlenk tube, palladated tetrahydropentacene **37** (58 mg, 0.052 mmol) was dissolved in toluene (2 mL). PEt_3 (0.22mL, 0.21 mmol) was added to the solution at room temperature. Under nitrogen atmosphere, the mixture was stirred at 80 °C for 12 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **38** (35 mg, 81% isolated yield) as a yellow solid.

38: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.03-1.09 (m, 18 H), 1.46 (t, J = 7.2 Hz, 3 H), 1.51-1.63 (m, 12 H), 3.92 (s, 2 H), 3.94 (s, 2 H), 3.99 (q, J = 7.2 Hz, 2 H), 4.04 (s, 2 H), 4.11 (s, 2 H), 6.81 (s, 1 H), 7.14 (s, 1 H), 7.19-7.20 (m, 2 H), 7.27 (s, 1 H), 7.30-7.31 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.3, 14.8, 14.9, 14.9, 15.0, 35.8, 36.21, 40.4, 65.0, 108.9, 118.9, 125.8, 126.0, 126.1, 126.6, 127.4, 133.5, 133.7, 134.4, 134.4, 135.4, 136.8, 151.9, 153.7. ^{31}P NMR ($CDCl_3$, Me_4Si, 600 M) δ 13.03. HRMS (ESI) calcd for $C_{36}H_{50}Br_2P_2OPdNa$: 849.0616[M + Na]+, Found: 849.0615[M + Na]+.

Preparation of palladated tetrahydropentacene 39

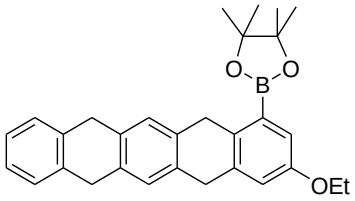


In a 20 mL Schlenk tube, palladated tetrahydropentacene **37** (23 mg, 0.021 mmol) was dissolved in a mixed solution of toluene and diethyl ether (3:1, 2 mL). To the mixture was added ^{t}BuLi (0.03 mL, 0.052 mmol) at -78 °C and stirred for 1 h. After being quenched by methanol, the solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to afford the title compound **39** (18 mg, 83% isolated yield).

39: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.10 (t, J = 7.2 3 H), 3.15 (s, 2 H), 3.34 (q, J = 7.2 2 H), 3.38 (s, 2 H), 3.75 (s, 2 H), 3.84 (s, 2 H), 6.03 (s, 1 H), 6.18-6.19 (m, 1 H), 6.47 (s, 1 H), 6.94 (s, 1 H), 7.15-7.20 (m, 15H), 7.22-7.30(m, 7 H), 7.41-7.44 (m, 12 H). ^{13}C NMR ($CDCl_3$, Me_4Si,

600M) δ 14.8, 35.7, 37.0, 38.9, 62.9, 109.0, 118.7, 125.2, 125.9, 127.3, 127.7, 129.7, 130.8, 130.9, 131.1, 132.6, 133.2, 133.3, 134.2, 134.7, 135.3, 137.0, 137.1, 138.0, 155.1, 157.6. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 24.17. HRMS (ESI) calcd for $C_{60}H_{51}BrOP_2PdNa$: 1059.1511[M + Na]+, Found: 1059.1530[M + Na]+,

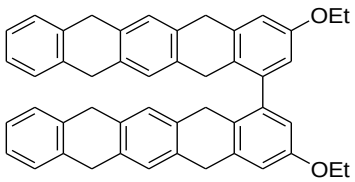
Preparation of first ring boronic ester reagent 40



In a 20 mL Schlenk tube, palladated tetrahydropentacene **39** (104 mg, 0.1 mmol) and sliver acetate (17 mg, 0.1 mmol) were dissolved in benzene (3 mL). Under nitrogen atmosphere, the mixture was stirred at room temperature for 30 min. Then removed the AgBr by filter method. The clear solution was added bis(pinacolato)diboron (30 mg, 0.12 mmol). The mixture was stirred at 80 °C for 12 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 10:1 as eluent) to afford the title compound **32** (20 mg, 44% isolated yield).

40: ^{1}H NMR ($CDCl_3$, Me_4Si, 600 M) δ 1.40-1.42 (m, 15 H), 3.89 (s, 2 H), 3.93 (s, 2 H), 3.94 (s, 2 H), 4.07 (q, J = 6.6 Hz, 2 H), 4.22 (s, 2 H), 6.94 (d, J = 3.0 Hz, 1 H), 7.18-7.19 (m, 2 H), 7.22 (s, 1 H), 7.25 (d, J = 3.0 Hz, 1 H), 7.27 (s, 1 H), 7.29-7.30 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600 M) δ 14.9, 24.9, 34.1, 35.8, 36.6, 63.5, 83.6, 116.9, 119.0, 125.8, 125.9, 126.5, 127.3, 127.3, 134.0, 134.2, 134.4, 135.7, 135.8, 136.9, 138.3, 156.4. HRMS (ESI) calcd for $C_{30}H_{33}NaBO_3$: 474.2451[M + Na]+. Found: 474.2461[M + Na]+.

Preparation of pentacene dimer derivative 41



In a 20 mL Schlenk tube, palladated tetrahydropentacene **39** (118 mg, 0.11 mmol) and boronic ester reagent **40** (77 mg, 0.17 mmol) were dissolved in THF : H_2O (10:1, 3.3 mL). Under nitrogen atmosphere, the mixture was added NaOH (7.2 mg, 0.18 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and heated at 70 °C for about 3 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, chloroform as eluent) to give the crude product, then it was purified by a flash chromatography (silica gel, hexane: ethyl acetate: = 5:1) to remove the byproduct firstly, at last use the chloroform to afford the title compound **41** (57 mg, 80% isolated yield) as

a pale yellow solid.

41: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.41 (t, J = 7.2 Hz, 3 H), 3.51 (s, 2 H), 3.77-3.84 (m, 2 H), 3.93 (s, 2 H), 3.97-4.00 (m, 2 H), 4.02-4.06 (m, 2 H), 6.63 (d, J = 2.4 Hz, 1 H), 6.92 (d, J = 2.4 Hz, 1 H), 6.95 (s, 1 H), 7.16-7.21 (m, 3 H), 7.27-7.29 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si. 600 M) δ 14.9, 32.4, 35.8, 35.8, 36.7, 63.5, 113.0, 113.2, 126.0, 126.0, 126.5, 127.0, 127.3, 127.4, 134.3, 134.4, 134.5, 134.9, 136.8, 138.5, 140.7, 156.8. HRMS (EI) calcd for $C_{48}H_{42}O_2$: 650.3185, Found: 650.3162.

X-ray analysis data for compound 20a

Table 2. Crystallographic data and experimental details for compound **20a**

Compound	**20a**
Formula	C_{58} H_{42} Br_2 P_2 Pd
M	1066.02
Crystal system	triclinic
Space group	P -1
a, (Å)	11.277(5)
b, (Å)	12.726(5)
c, (Å)	19.559(8)
α, (°)	81.269(14)
β, (°)	86.892(16)
γ, (°)	72.801(15)
V, (Å^3)	2650(2)
Z	2
Temperature T, (K)	298
Crystal habit	prism
Crystal color	dark
Crystal size, (mm^3)	0.15 x 0.10 x 0.03
D_{calcd}, (g cm^{-3})	1.445
Transm factor	0.7577- 0.9436
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku R-AXIS RAPID
Scan mode	ω
Reflections measd	-14≤ h ≤ 14
	-16≤ k ≤ 16
	-25≤ l ≤ 22
No. of reflection measd	11789
No. of reflection obsd [I>2σ(I)]	4245
No. of parameters refined	592
R	0.0808
R_ω	0.1775
S, goodness of fit	0.923

Largest diff peak, (e Å^{-3})	0.644
Largest diff hole, (e Å^{-3})	-0.877

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 3. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 1.998(9)	Pd1 P1 2.323(3)
Pd1 P2 2.324(3)	Pd1 Br1 2.5152(14)
Br2 C16 1.895(9)	P1 C29 1.787(12)
P1 C35 1.803(13)	P1 C23 1.814(11)
P2 C47 1.813(9)	P2 C53 1.832(8)
P2 C41 1.851(10)	C1 C2 1.409(12)
C1 C22 1.416(13)	C2 C3 1.394(13)
C2 C15 1.460(12)	C3 C4 1.395(12)
C3 H3 0.9300	C4 C5 1.411(14)
C4 C13 1.429(12)	C5 C6 1.372(13)
C5 H5 0.9300	C6 C11 1.444(14)
C6 C7 1.447(15)	C7 C8 1.324(14)
C7 H7 0.9300	C8 C9 1.387(15)
C8 H8 0.9300	C9 C10 1.369(16)
C9 H9 0.9300	C10 C11 1.401(14)
C10 H10 0.9300	C11 C12 1.374(15)
C12 C13 1.408(13)	C12 H12 0.9300
C13 C14 1.387(14)	C14 C15 1.409(14)
C14 H14 0.9300	C15 C16 1.406(14)
C16 C17 1.364(14)	C17 C18 1.433(15)
C17 C22 1.443(12)	C18 C19 1.327(15)
C18 H18 0.9300	C19 C20 1.403(15)
C19 H19 0.9300	C20 C21 1.383(15)
C20 H20 0.9300	C21 C22 1.410(13)
C21 H21 0.9300	C23 C28 1.361(14)
C23 C24 1.411(14)	C24 C25 1.393(17)
C24 H24 0.9300	C25 C26 1.408(19)
C25 H25 0.9300	C26 C27 1.314(16)
C26 H26 0.9300	C27 C28 1.363(15)
C27 H27 0.9300	C28 H28 0.9300
C29 C34 1.383(17)	C29 C30 1.393(16)
C30 C31 1.384(19)	C30 H30 0.9300
C31 C32 1.28(2)	C31 H31 0.9300
C32 C33 1.42(3)	C32 H32 0.9300
C33 C34 1.442(18)	C33 H33 0.9300
C34 H34 0.9300	C35 C40 1.392(18)
C35 C36 1.400(18)	C36 C37 1.37(2)
C36 H36 0.9300	C37 C38 1.37(4)
C37 H37 0.9300	C38 C39 1.40(3)
C38 H38 0.9300	C39 C40 1.423(19)
C39 H39 0.9300	C40 H40 0.9300
C41 C46 1.348(13)	C41 C42 1.385(13)
C42 C43 1.363(14)	C42 H42 0.9300
C43 C44 1.330(15)	C43 H43 0.9300
C44 C45 1.387(16)	C44 H44 0.9300
C45 C46 1.397(15)	C45 H45 0.9300
C46 H46 0.9300	C47 C52 1.389(12)
C47 C48 1.396(13)	C48 C49 1.386(13)
C48 H48 0.9300	C49 C50 1.383(14)
C49 H49 0.9300	C50 C51 1.343(14)
C50 H50 0.9300	C51 C52 1.386(13)
C51 H51 0.9300	C52 H52 0.9300
C53 C54 1.388(13)	C53 C58 1.397(13)
C54 C55 1.396(13)	C54 H54 0.9300
C55 C56 1.369(16)	C55 H55 0.9300
C56 C57 1.350(17)	C56 H56 0.9300
C57 C58 1.362(13)	C57 H57 0.9300
C58 H58 0.9300	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in

parentheses.

Table 4. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P1 87.9(3)	C1 Pd1 P2 88.9(3)
P1 Pd1 P2 176.66(9)	C1 Pd1 Br1 179.7(3)
P1 Pd1 Br1 92.34(7)	P2 Pd1 Br1 90.90(7)
C29 P1 C35 103.6(7)	C29 P1 C23 105.1(5)
C35 P1 C23 104.6(6)	C29 P1 Pd1 114.9(5)
C35 P1 Pd1 115.3(4)	C23 P1 Pd1 112.2(4)
C47 P2 C53 102.5(4)	C47 P2 C41 105.3(4)
C53 P2 C41 103.3(4)	C47 P2 Pd1 113.5(3)
C53 P2 Pd1 116.8(3)	C41 P2 Pd1 114.0(3)
C2 C1 C22 118.2(8)	C2 C1 Pd1 121.2(7)
C22 C1 Pd1 120.6(6)	C3 C2 C1 120.6(8)
C3 C2 C15 118.8(8)	C1 C2 C15 120.4(9)
C2 C3 C4 122.8(8)	C2 C3 H3 118.6
C4 C3 H3 118.6	C3 C4 C5 122.2(9)
C3 C4 C13 119.4(10)	C5 C4 C13 118.2(9)
C6 C5 C4 122.0(9)	C6 C5 H5 119.0
C4 C5 H5 119.0	C5 C6 C11 120.0(10)
C5 C6 C7 123.7(9)	C11 C6 C7 116.3(9)
C8 C7 C6 121.8(10)	C8 C7 H7 119.1
C6 C7 H7 119.1	C7 C8 C9 121.1(12)
C7 C8 H8 119.5	C9 C8 H8 119.5
C10 C9 C8 121.0(10)	C10 C9 H9 119.5
C8 C9 H9 119.5	C9 C10 C11 120.2(10)
C9 C10 H10 119.9	C11 C10 H10 119.9
C12 C11 C10 122.4(10)	C12 C11 C6 118.0(10)
C10 C11 C6 119.5(11)	C11 C12 C13 122.7(9)
C11 C12 H12 118.6	C13 C12 H12 118.6
C14 C13 C12 123.5(9)	C14 C13 C4 117.6(9)
C12 C13 C4 118.9(10)	C13 C14 C15 124.6(9)
C13 C14 H14 117.7	C15 C14 H14 117.7
C16 C15 C14 125.2(9)	C16 C15 C2 118.3(9)
C14 C15 C2 116.5(9)	C17 C16 C15 122.4(9)
C17 C16 Br2 119.9(8)	C15 C16 Br2 117.7(8)
C16 C17 C18 123.4(9)	C16 C17 C22 119.1(9)
C18 C17 C22 117.5(10)	C19 C18 C17 122.2(11)
C19 C18 H18 118.9	C17 C18 H18 118.9
C18 C19 C20 121.0(12)	C18 C19 H19 119.5
C20 C19 H19 119.5	C21 C20 C19 119.7(11)
C21 C20 H20 120.1	C19 C20 H20 120.1
C20 C21 C22 121.2(10)	C20 C21 H21 119.4
C22 C21 H21 119.4	C21 C22 C1 120.4(8)
C21 C22 C17 118.3(9)	C1 C22 C17 121.4(9)
C28 C23 C24 118.3(10)	C28 C23 P1 121.2(8)
C24 C23 P1 120.5(9)	C25 C24 C23 119.4(13)
C25 C24 H24 120.3	C23 C24 H24 120.3
C24 C25 C26 118.1(13)	C24 C25 H25 121.0
C26 C25 H25 121.0	C27 C26 C25 121.8(14)
C27 C26 H26 119.1	C25 C26 H26 119.1
C26 C27 C28 120.0(13)	C26 C27 H27 120.0
C28 C27 H27 120.0	C23 C28 C27 122.3(11)
C23 C28 H28 118.9	C27 C28 H28 118.9
C34 C29 C30 116.2(12)	C34 C29 P1 120.1(10)
C30 C29 P1 123.7(10)	C31 C30 C29 120.5(15)
C31 C30 H30 119.8	C29 C30 H30 119.8
C32 C31 C30 125.5(19)	C32 C31 H31 117.3
C30 C31 H31 117.3	C31 C32 C33 117.9(18)
C31 C32 H32 121.0	C33 C32 H32 121.0
C32 C33 C34 118.2(19)	C32 C33 H33 120.9
C34 C33 H33 120.9	C29 C34 C33 121.7(15)
C29 C34 H34 119.2	C33 C34 H34 119.2
C40 C35 C36 118.8(13)	C40 C35 P1 120.4(11)
C36 C35 P1 120.7(13)	C37 C36 C35 120(2)
C37 C36 H36 119.9	C35 C36 H36 119.9
C38 C37 C36 121(3)	C38 C37 H37 119.4
C36 C37 H37 119.4	C37 C38 C39 121(2)
C37 C38 H38 119.6	C39 C38 H38 119.6
C38 C39 C40 118(2)	C38 C39 H39 121.1
C40 C39 H39 121.1	C35 C40 C39 121.0(18)
C35 C40 H40 119.5	C39 C40 H40 119.5
C46 C41 C42 120.4(10)	C46 C41 P2 121.6(8)

C42 C41 P2 118.0(8)	C43 C42 C41 121.2(11)
C43 C42 H42 119.4	C41 C42 H42 119.4
C44 C43 C42 119.2(11)	C44 C43 H43 120.4
C42 C43 H43 120.4	C43 C44 C45 121.0(12)
C43 C44 H44 119.5	C45 C44 H44 119.5
C44 C45 C46 120.1(12)	C44 C45 H45 119.9
C46 C45 H45 119.9	C41 C46 C45 118.1(11)
C41 C46 H46 120.9	C45 C46 H46 120.9
C52 C47 C48 118.9(9)	C52 C47 P2 123.1(7)
C48 C47 P2 118.0(8)	C49 C48 C47 119.4(10)
C49 C48 H48 120.3	C47 C48 H48 120.3
C50 C49 C48 120.8(10)	C50 C49 H49 119.6
C48 C49 H49 119.6	C51 C50 C49 119.5(10)
C51 C50 H50 120.3	C49 C50 H50 120.3
C50 C51 C52 121.5(10)	C50 C51 H51 119.3
C52 C51 H51 119.3	C51 C52 C47 119.9(9)
C51 C52 H52 120.0	C47 C52 H52 120.0
C54 C53 C58 119.0(9)	C54 C53 P2 119.6(7)
C58 C53 P2 121.1(8)	C53 C54 C55 119.8(10)
C53 C54 H54 120.1	C55 C54 H54 120.1
C56 C55 C54 118.7(11)	C56 C55 H55 120.7
C54 C55 H55 120.7	C57 C56 C55 122.2(11)
C57 C56 H56 118.9	C55 C56 H56 118.9
C56 C57 C58 119.9(11)	C56 C57 H57 120.1
C58 C57 H57 120.1	C57 C58 C53 120.4(11)
C57 C58 H58 119.8	C53 C58 H58 119.8

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

X-ray analysis data for compound 38

Table 5. Crystallographic data and experimental details for compound **38**

Compound	**38**
Formula	C_{36} H_{50} Br_2 OP_2 Pd
M	824.07
Crystal system	monoclinic
Space group	P 1 21/a 1
a, (Å)	14.9611(16)
b, (Å)	13.3085(14)
c, (Å)	19.584(2)
α, (°)	90.00
β, (°)	94.055(2)
γ, (°)	90.00
V, (Å^3)	3889.6(7)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	colorless
Crystal size, (mm^3)	0.20 x 0.20 x 0.10
D_{calcd}, (g cm^{-3})	1.439
Transm factor	0.6202 - 0.7781
λ (Mo Kα), (Å^3)	0.71075
Diffractometer	Rigaku SCX mini

Scan mode	ω
Reflections measd	-19≤ h ≤ 19
	-17≤ k ≤ 17
	-25≤ l ≤ 25
No. of reflection measd	8902
No. of reflection obsd [I>2σ(I)]	3591
No. of parameters refined	387
R	0.0793
R_ω	0.1716
S, goodness of fit	1.018
Largest diff peak, (e Å^{-3})	0.769
Largest diff hole, (e Å^{-3})	-0.617

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 6. Intramolecular distances involving the non-hydrogen atoms

Pd1 C1 2.032(6)	Pd1 P2 2.318(3)
Pd1 P1 2.320(3)	Pd1 Br1 2.5188(12)
Br2 C20 1.906(7)	P1 C29 1.818(10)
P1 C27 1.821(9)	P1 C25 1.830(9)
P2 C31 1.821(9)	P2 C33 1.826(10)
P2 C35 1.834(10)	O1 C21 1.371(8)
O1 C23 1.415(10)	C1 C2 1.362(9)
C1 C22 1.407(10)	C2 C19 1.394(10)
C2 C3 1.534(10)	C3 C4 1.521(10)
C3 H1 0.9700	C3 H2 0.9700
C4 C5 1.391(10)	C4 C17 1.412(10)
C5 C6 1.378(10)	C5 H3 0.9300
C6 C15 1.369(10)	C6 C7 1.535(11)
C7 C8 1.543(11)	C7 H4 0.9700
C7 H5 0.9700	C8 C13 1.377(10)
C8 C9 1.405(11)	C9 C10 1.414(12)
C9 H6 0.9300	C10 C11 1.360(12)
C10 H7 0.9300	C11 C12 1.389(12)
C11 H8 0.9300	C12 C13 1.380(11)
C12 H9 0.9300	C13 C14 1.546(11)
C14 C15 1.517(10)	C14 H10 0.9700
C14 H11 0.9700	C15 C16 1.390(10)
C16 C17 1.406(10)	C16 H12 0.9300
C17 C18 1.508(10)	C18 C19 1.526(10)
C18 H13 0.9700	C18 H14 0.9700
C19 C20 1.407(10)	C20 C21 1.396(10)
C21 C22 1.388(10)	C22 H15 0.9300
C23 C24 1.531(12)	C23 H16 0.9700
C23 H17 0.9700	C24 H18 0.9600
C24 H19 0.9600	C24 H20 0.9600
C25 C26 1.518(12)	C25 H21 0.9700
C25 H22 0.9700	C26 H23 0.9600
C26 H24 0.9600	C26 H25 0.9600
C27 C28 1.477(13)	C27 H26 0.9700
C27 H27 0.9700	C28 H28 0.9600
C28 H29 0.9600	C28 H30 0.9600
C29 C30 1.476(13)	C29 H31 0.9700
C29 H32 0.9700	C30 H33 0.9600
C30 H34 0.9600	C30 H35 0.9600
C31 C32 1.512(12)	C31 H36 0.9700
C31 H37 0.9700	C32 H38 0.9600
C32 H39 0.9600	C32 H40 0.9600
C33 C34 1.517(13)	C33 H41 0.9700

C33 H42 0.9700	C34 H43 0.9600
C34 H44 0.9600	C34 H45 0.9600
C35 C36 1.505(14)	C35 H46 0.9700
C35 H47 0.9700	C36 H48 0.9600
C36 H49 0.9600	C36 H50 0.9600

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7. Intramolecular angles involving the non-hydrogen atoms

C1 Pd1 P2 90.0(2)	C1 Pd1 P1 90.3(2)
P2 Pd1 P1 174.73(9)	C1 Pd1 Br1 178.8(2)
P2 Pd1 Br1 89.80(7)	P1 Pd1 Br1 89.77(7)
C29 P1 C27 101.8(5)	C29 P1 C25 105.5(5)
C27 P1 C25 105.2(5)	C29 P1 Pd1 109.8(4)
C27 P1 Pd1 114.3(4)	C25 P1 Pd1 118.6(3)
C31 P2 C33 106.2(5)	C31 P2 C35 106.0(5)
C33 P2 C35 100.0(5)	C31 P2 Pd1 117.5(3)
C33 P2 Pd1 115.4(4)	C35 P2 Pd1 110.0(4)
C21 O1 C23 118.0(6)	C2 C1 C22 119.0(7)
C2 C1 Pd1 124.3(6)	C22 C1 Pd1 116.6(5)
C1 C2 C19 121.9(7)	C1 C2 C3 121.9(7)
C19 C2 C3 116.2(6)	C4 C3 C2 111.3(6)
C4 C3 H1 109.4	C2 C3 H1 109.4
C4 C3 H2 109.4	C2 C3 H2 109.4
H1 C3 H2 108.0	C5 C4 C17 118.4(7)
C5 C4 C3 124.0(7)	C17 C4 C3 117.6(7)
C6 C5 C4 121.9(8)	C6 C5 H3 119.0
C4 C5 H3 119.0	C15 C6 C5 119.9(8)
C15 C6 C7 120.8(7)	C5 C6 C7 119.3(8)
C6 C7 C8 111.1(7)	C6 C7 H4 109.4
C8 C7 H4 109.4	C6 C7 H5 109.4
C8 C7 H5 109.4	H4 C7 H5 108.0
C13 C8 C9 119.5(8)	C13 C8 C7 120.7(8)
C9 C8 C7 119.7(8)	C8 C9 C10 119.3(9)
C8 C9 H6 120.3	C10 C9 H6 120.3
C11 C10 C9 121.2(9)	C11 C10 H7 119.4
C9 C10 H7 119.4	C10 C11 C12 117.8(9)
C10 C11 H8 121.1	C12 C11 H8 121.1
C13 C12 C11 123.1(9)	C13 C12 H9 118.5
C11 C12 H9 118.5	C8 C13 C12 119.1(8)
C8 C13 C14 118.5(8)	C12 C13 C14 122.4(8)
C15 C14 C13 112.7(7)	C15 C14 H10 109.1
C13 C14 H10 109.1	C15 C14 H11 109.1
C13 C14 H11 109.1	H10 C14 H11 107.8
C6 C15 C16 120.3(7)	C6 C15 C14 119.4(7)
C16 C15 C14 120.2(7)	C15 C16 C17 120.3(7)
C15 C16 H12 119.8	C17 C16 H12 119.8
C16 C17 C4 119.1(7)	C16 C17 C18 123.0(7)
C4 C17 C18 117.9(7)	C17 C18 C19 111.1(6)
C17 C18 H13 109.4	C19 C18 H13 109.4
C17 C18 H14 109.4	C19 C18 H14 109.4
H13 C18 H14 108.0	C2 C19 C20 118.1(7)
C2 C19 C18 119.6(6)	C20 C19 C18 122.3(7)
C21 C20 C19 121.4(7)	C21 C20 Br2 118.6(5)
C19 C20 Br2 120.1(6)	O1 C21 C22 124.2(7)
O1 C21 C20 117.6(7)	C22 C21 C20 118.1(7)
C21 C22 C1 121.4(7)	C21 C22 H15 119.3
C1 C22 H15 119.3	O1 C23 C24 108.7(8)
O1 C23 H16 110.0	C24 C23 H16 110.0
O1 C23 H17 110.0	C24 C23 H17 110.0
H16 C23 H17 108.3	C23 C24 H18 109.5
C23 C24 H19 109.5	H18 C24 H19 109.5
C23 C24 H20 109.5	H18 C24 H20 109.5
H19 C24 H20 109.5	C26 C25 P1 118.4(7)
C26 C25 H21 107.7	P1 C25 H21 107.7
C26 C25 H22 107.7	P1 C25 H22 107.7
H21 C25 H22 107.1	C25 C26 H23 109.5
C25 C26 H24 109.5	H23 C26 H24 109.5
C25 C26 H25 109.5	H23 C26 H25 109.5
H24 C26 H25 109.5	C28 C27 P1 116.7(7)

C28 C27 H26 108.1	P1 C27 H26 108.1
C28 C27 H27 108.1	P1 C27 H27 108.1
H26 C27 H27 107.3	C27 C28 H28 109.5
C27 C28 H29 109.5	H28 C28 H29 109.5
C27 C28 H30 109.5	H28 C28 H30 109.5
H29 C28 H30 109.5	C30 C29 P1 114.8(8)
C30 C29 H31 108.6	P1 C29 H31 108.6
C30 C29 H32 108.6	P1 C29 H32 108.6
H31 C29 H32 107.5	C29 C30 H33 109.5
C29 C30 H34 109.5	H33 C30 H34 109.5
C29 C30 H35 109.5	H33 C30 H35 109.5
H34 C30 H35 109.5	C32 C31 P2 117.6(7)
C32 C31 H36 107.9	P2 C31 H36 107.9
C32 C31 H37 107.9	P2 C31 H37 107.9
H36 C31 H37 107.2	C31 C32 H38 109.5
C31 C32 H39 109.5	H38 C32 H39 109.5
C31 C32 H40 109.5	H38 C32 H40 109.5
H39 C32 H40 109.5	C34 C33 P2 113.2(7)
C34 C33 H41 108.9	P2 C33 H41 108.9
C34 C33 H42 108.9	P2 C33 H42 108.9
H41 C33 H42 107.7	C33 C34 H43 109.5
C33 C34 H44 109.5	H43 C34 H44 109.5
C33 C34 H45 109.5	H43 C34 H45 109.5
H44 C34 H45 109.5	C36 C35 P2 114.9(8)
C36 C35 H46 108.5	P2 C35 H46 108.5
C36 C35 H47 108.5	P2 C35 H47 108.5
H46 C35 H47 107.5	C35 C36 H48 109.5
C35 C36 H49 109.5	H48 C36 H49 109.5
C35 C36 H50 109.5	H48 C36 H50 109.5
H49 C36 H50 109.5	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

4-5. References

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Chapter 5. Selective Oligomerization of Pentacene Derivatives using Platinum

Abstract

A selective oligomerization of pentacene derivatives using platinum pentacene derivatives was developed. The first elemental reaction is the formation of pentacene dimer. In the Chapter 4, the first ring side dimer of a pentacene derivative was prepared successfully. The pentacene substrate had an ethoxyl group at the 2-position of side ring. The cross-coupling occurred at 4-position of two pentacenes. As the result, two substituents were in the different direction on the dimer product. In this section, a new dimer with two substituents in the same direction was obtained. The coupling occurred between the 1-position of one pentacene and the 4-position of the other pentacene. This difference was made by the use of a platinated pentacene derivative.

It should be noted that this method could be developed into a selective oligomerization of pentacene derivatives. Based on this dimer formation method, a pentacene trimer was prepared readily. The substituents of three pentacene moieties were in the same direction.

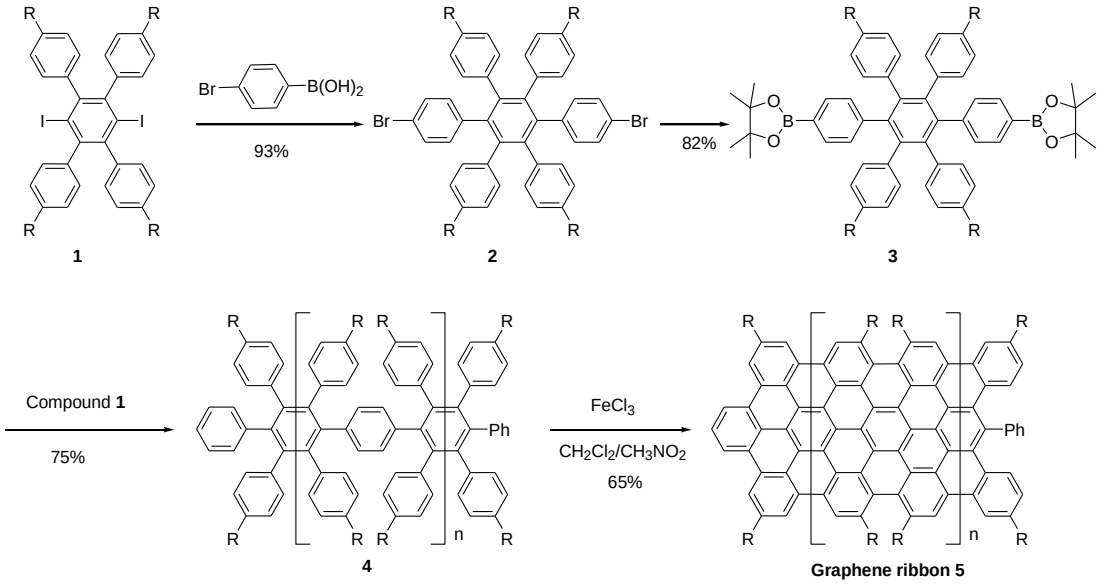
5-1. Introduction

Graphene is a two-dimensional organic material with zero bandgad. Graphene ribbons are strips of graphene. Graphene ribbons with a finite bandgap are more practical. The bandgap of graphene ribbon could be controlled through designing the width.

The charge mobility of graphene ribbons related to the bandgap of them. So the properties and performance of graphene ribbons can be controlled. Recently, graphene ribbons are attracting much attention because of their promising high performance.[1]

For preparation of graphene ribbons by organic synthetic method, several examples have been reported.[2] An representative method is shown in Scheme 1. Suzuki-Miyaura polymerization of diiodobenzene **1** with bis-boronic ester **3** gave polymer **4**. Cyclodehydrogenation of polymer **4** with $FeCl_3$ provided graphene ribbon **5**.

Scheme 1. Preparation of graphene ribbon **5**

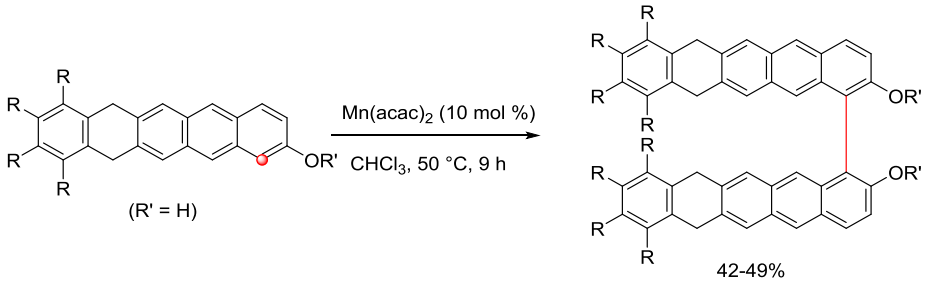


As mentioned in Chapter 1, the width of pentacene-based graphene ribbon is about 1.3 nm. The charge mobility of pentacene-based graphene ribbon is expected to be higher than Si and GaAs. However, there is no report on the synthesis of pentacene based grapheme ribbons, to our best knowledge. To get pentacene based graphene ribbons, the synthesis of oligomers of pentacene is important. And the dimer formation is the most critical step. Although several methods have been reported for the formation of pentacene dimers,[3] those methods could not be used for oligomer formation. So far, there is no selective and systematic preparation method for the pentacene oligomers.

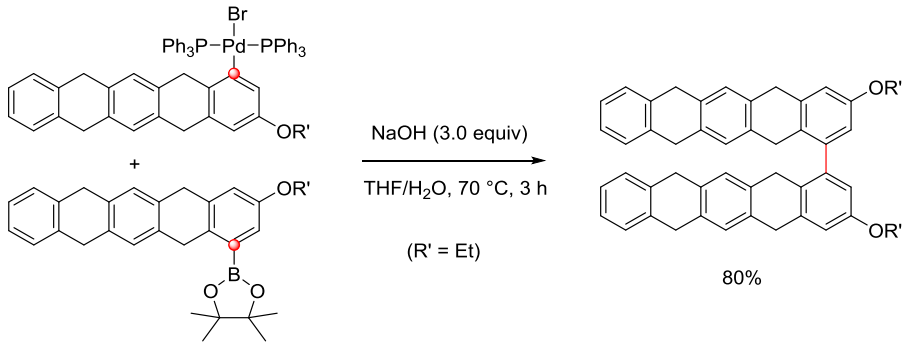
For formation of pentacene dimer, our group has developed an oxidative coupling method by using manganese catalyst (Scheme 2). The carbon-carbon bond formation occurred at the ortho-position of hydroxy group. The functional hydroxy groups of pentacene dimer derivatives

are inside.

Scheme 2. Dimerization of pentacene by oxidative coupling method[3d]



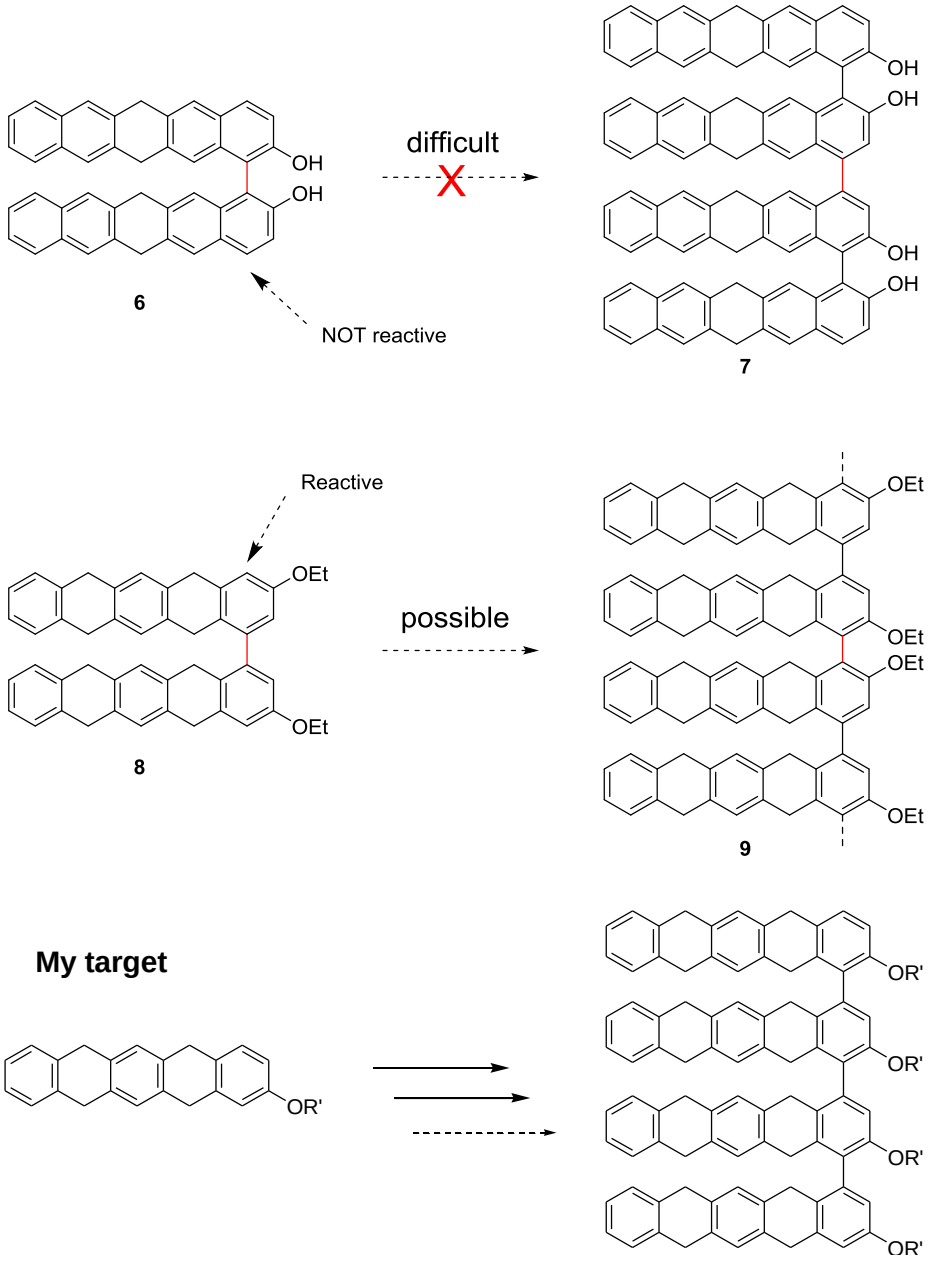
Scheme 3. Dimerization of pentacene by cross-coupling method



In my case, the carbon-carbon bond formation occurred at the meta-position of ethoxyl group by cross coupling reaction (Scheme 3). The functional ethoxyl groups of pentacene dimer derivatives are outside.

However, both could not be used for the further oligomerization of pentacene (Scheme 4). If starting from dimer **6**, tetramer **7** was very difficult to be obtained. Because hydroxy group is an ortho and para positional directing group. It can't activate the meta-position. On the other hand, if starting from dimer **8**, the new C-C bond formation was possible by oxidative coupling reaction. However, the substituents of tetramer **9** were not in the same direction. This kind of pentacene oligomers was not my target. In my target, the substituents of pentacene oligomer are all in the same direction. In this section, I developed selective oligomerization of pentacene derivatives using platinum pentacene derivatives.

Scheme 4. Attempt to prepare pentacene oligomers



5-2. Results and Discussion

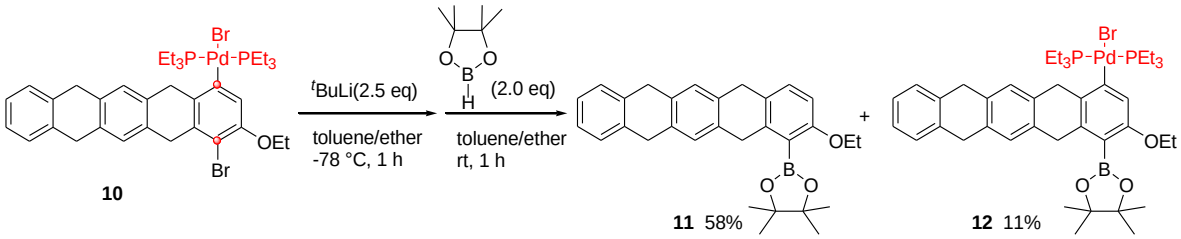
5-2-1. Preparation of pentacene dimer 20 by using platinum

In the previous section, the dimer of pentacene using first ring palladated pentacene derivatives was prepared (Scheme 3). However, this dimer does not have two substituents in the same direction. This because the meta-position of ethoxyl group of two pentacene derivatives was coupled in the cross-coupling. In order to align the substituents in the same direction, the meta-position of ethoxyl group of one pentacene derivative should be coupled with the ortho-position of ethoxyl group of the other pentacene derivative. For this purpose, activation of

the ortho-position of ethoxyl group was needed.

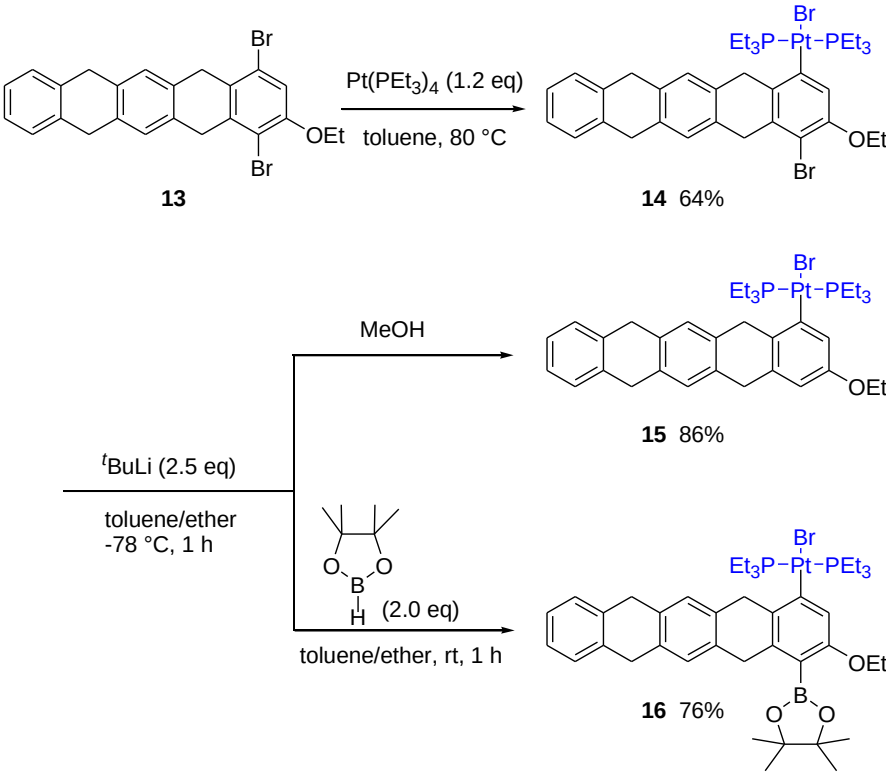
At the beginning, I used complex **10** as starting material to activate the bromine atom located at the ortho-position of ethoxyl group (Scheme 5). Lithiation of complex **10** was followed by addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane. However, the desired product **12** was obtained only in 11% yield. Because the Pd-C bond was very active, and Pd-C bond was cleaved during the reaction process to give byproduct **11** in 58% yield.

Scheme 5. Boronation of palladated tetrahydropentacene complex **10**



I then changed the palladium atom to more stable platinum atom. Oxidative addition of dibromotetrahydropentacene **13** to $Pt(PEt_3)_4$ was selective (Scheme 6). Because the steric effect of ethoxyl group, oxidative addition reaction occurred at the meta-position of ethoxyl group selectively.

Scheme 6. Boronation of platinated tetrahydropentacene complex **14**



Lithiation of complex **14** followed by addition of methanol to give complex **15** in 86% yield.

The structure of complex **15** was verified by X-ray analysis (Figure 1). It shows that platinum attached to the meta position of ethoxy group clearly. This result indicated that the bromine atom at the ortho-position of ethoxyl group was activated. After lithiation, addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded product **16** in 76% yield. In the structure of **16**, the meta-position of ethoxyl group was protected by platinum. Next step coupling reaction would not occur at platinum part. At the same time, the ortho-position of ethoxyl group was activated by introduction of boronic ester.

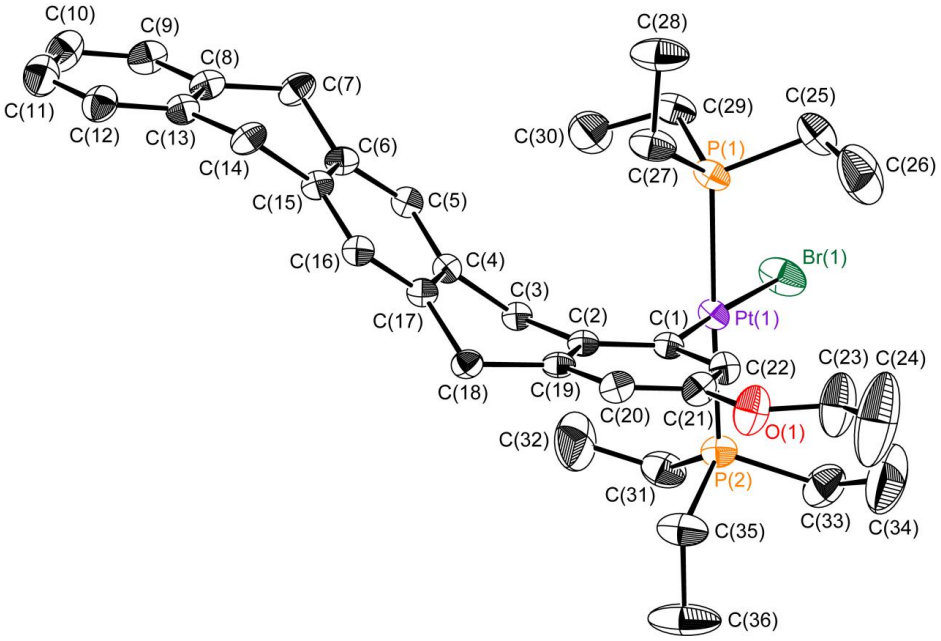
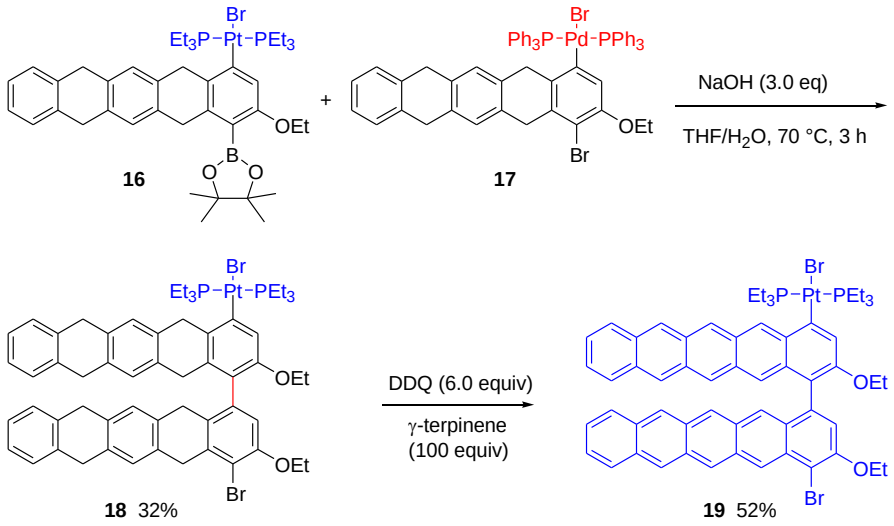


Figure 1. X-ray structure of complex **15**

Scheme 7. Preparation of platinated pentacene dimer **19**



Complex **17** has been synthesized in Chapter 4. With complex **16** in hand, coupling reaction

of **16** with palladated tetrahydropentacene **17** was carried out (Scheme 7). The desired product dimer **18** was obtained in 32% yield. In this reaction, the carbon-carbon bond formation occurred between the meta-position and ortho-position of ethoxyl group selectively. As the result, substituents of pentacene dimer **18** are in the same direction. Aromatization of **18** with DDQ and γ-terpinene gave platinated pentacene dimer **19** in 52% yield. Pentacene dimer **19** can be purified by silica gel column chromatography under nitrogen.

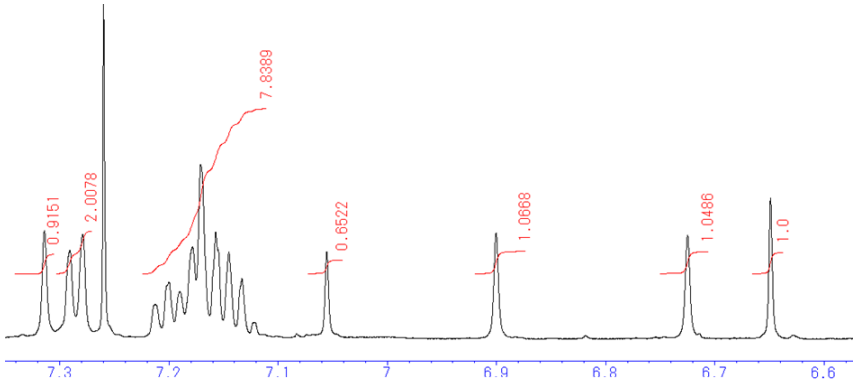


Figure 2. ^{1}H NMR spectrum of **18** in $CDCl_3$

From the ^{1}H NMR of **18**, we can see clearly a set of peaks (Figure 2). Five singlet peaks were observed clearly. The sixth single peak overlapped with multiplet. Integration of peaks in low field is constant with the number of aromatic ring's hydrogens. Moreover, the HRMS of dimer **18** was measured. The molecular weight of **18** was found as 1263.2774[M + Na]+. From ^{1}H NMR, dimer **18** was a single product. It was not a mixture of isomers. The coupling reaction of **16** with **17** was very selective.

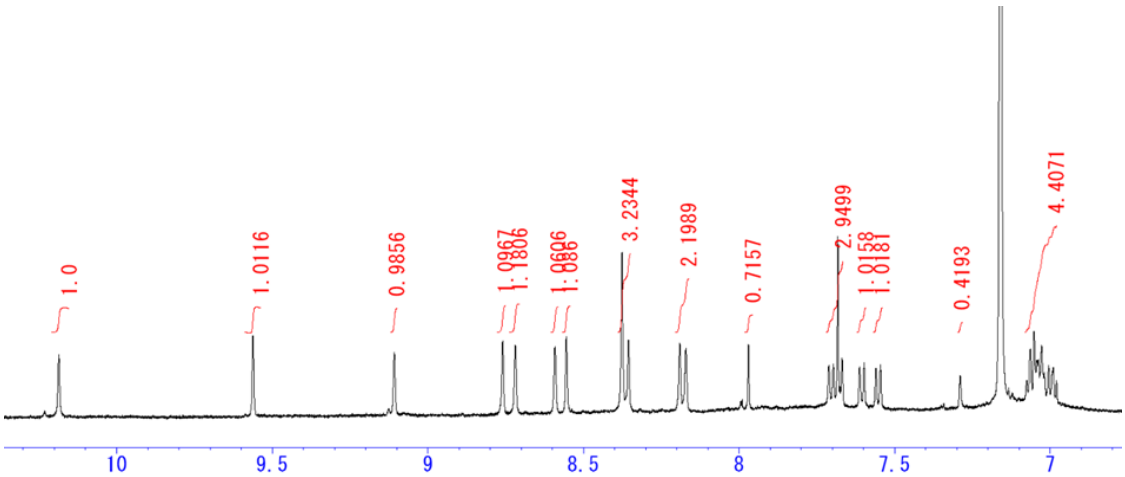


Figure 3. ^{1}H NMR spectrum of complex **19** in C_6D_6

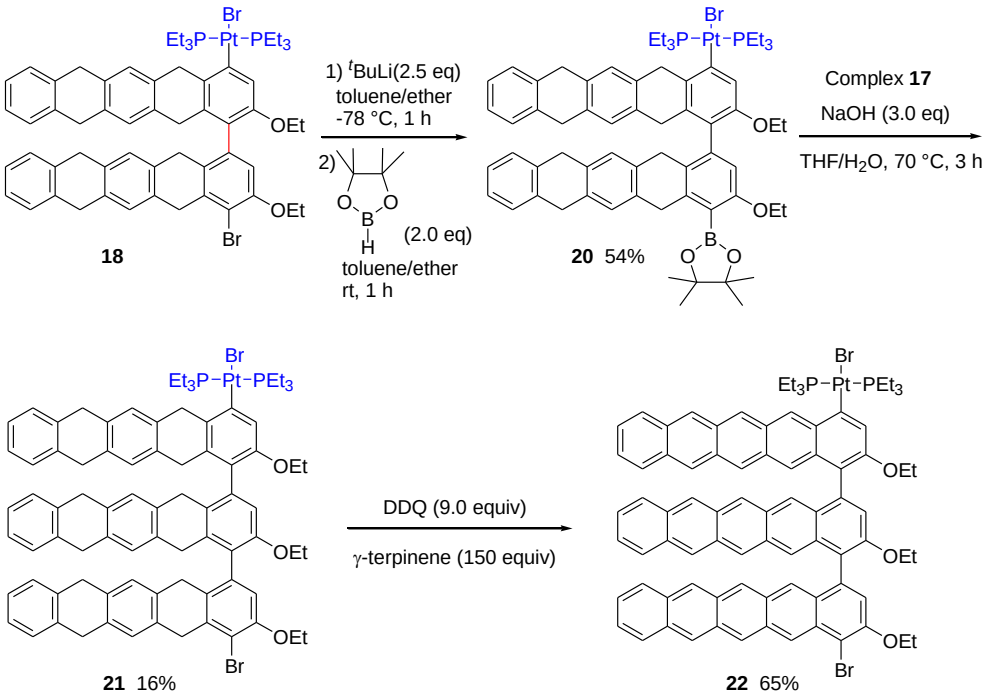
The ^{1}H NMR of **19** also suggests a single product (Figure 3). Fourteen single peaks were observed. Integration of peaks in low field is 22. It is just the number of aromatic protons.

Dimer **19** could be isolated under nitrogen by silica gel column chromatography. However, the blue-green solution of dimer **19** was sealed in NMR tube under nitrogen for one night, the color was changed to pale green. So the ^{13}C NMR data of dimer **19** was not obtained at this moment.

5-2-2. Preparation of pentacene trimer 22 by using platinum

Pentacene dimer **18** still has functional groups platinum atom and bromine atom. Further boronation of **18** was possible by the same way as for **14** (Scheme 8). Under the same reaction conditions, pentacene dimer boronic ester reagent **20** was obtained in 54% yield. Further coupling reaction of **20** with palladated tetrahydropentacene **19** was carried out under the same reaction conditions. Product pentacene trimer **21** was obtained in 16% yield. The low yield of dimer **18** and trimer **21** maybe due to the steric effect of ethoxyl group. Aromatization of **21** with 9.0 equivalent of DDQ and 150 equivalent of γ-terpinene gave platinated pentacene trimer **22** in 65% yield. Pentacene trimer **22** can be isolated by silica gel column chromatography under nitrogen.

Scheme 8. Selective oligomerization of pentacene derivatives using platinum



Compound **20** was prepared from **18**. From the ^{1}H NMR of **20**, I also can see it was a single product (Figure 4). Four singlet peaks were observed clearly. Other two singlet peaks were overlapped with multiplet peaks. The integration of peaks in low field is 14. It is the number of aromatic protons. Moreover, the molecular weight of **20** was measured by HRMS. The structure of **20** was characterized.

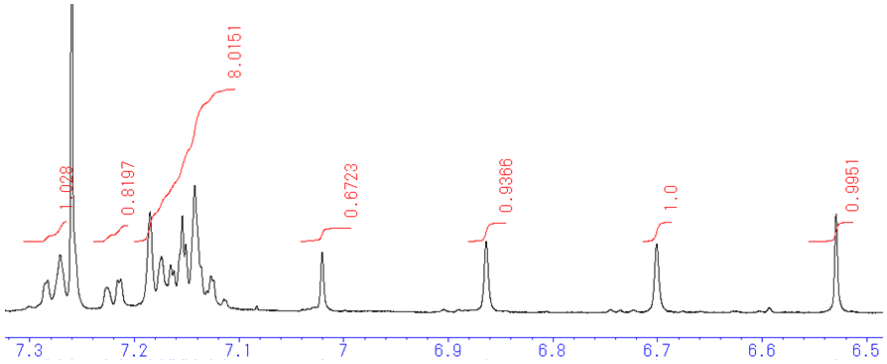


Figure 4. ^{1}H NMR spectrum of **20** in $CDCl_3$

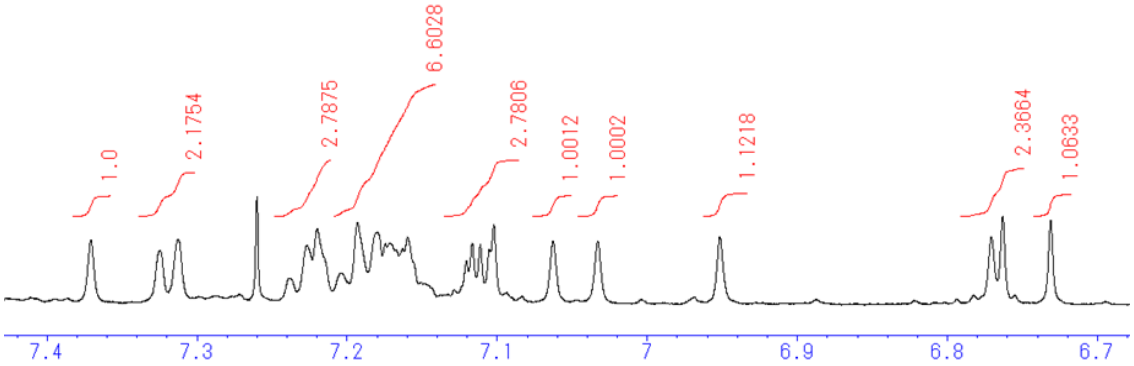


Figure 5. ^{1}H NMR spectrum of **21** in $CDCl_3$

The ^{1}H NMR chart of **21** is shown in Figure 5. It shows cleanly one set of peaks. Although the chart of **21** was a little complicated, integration of peaks in low field can be attributed to the number of aromatic hydrogens. It was clear that trimer derivative **21** was a single product. It was not a mixture of isomers. The coupling reaction of **18** with **20** was selective.

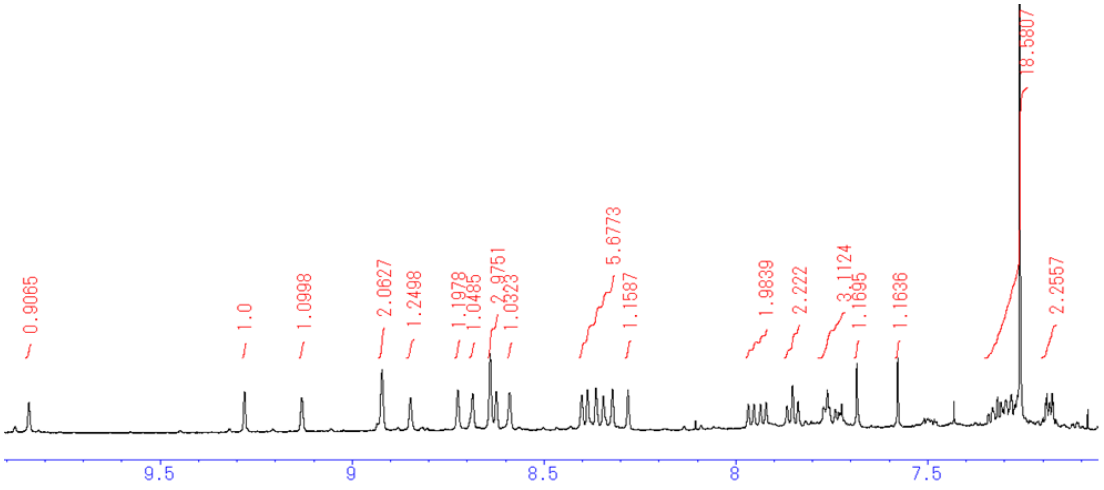


Figure 6. ^{1}H NMR spectrum of complex **22** in $CDCl_3$

From the ^{1}H NMR of **22**, we can find a set of peaks (Figure 6). Sixteen single peaks were

observed clearly. Other five single peaks overlapped. The integration of peaks in low field is 33. It is constant with the number of aromatic protons.

5-3. Summary

In this section, a pentacene dimer was synthesized successfully. The pentacene substrate had an ethoxyl group at the 2-position. The coupling occurred at the 1-position of one pentacene and the 4-position of the other. Two ethoxyl groups were in the same direction at the dimer product. This selectivity was made by the use of a platinated pentacene derivative. In general, the 4-position of the 2-ethoxylpentacene was more active for coupling than the 1-position because of the steric hindrance. Introduction of the Pt moiety can occupy the 4-position firstly. Coupling reaction then occurred at the 1-position.

More importantly, this method could be developed into a selective oligomerization of pentacene derivatives. For example, based on this dimer formation method, a pentacene trimer was prepared successfully. The substituents of three pentacene moieties were aligned in the same direction.

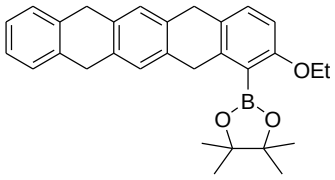
5-4. Experimental Section

General comment

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. The reaction temperature recorded here refers to the bath temperature. Tetrahydrofuran (THF) toluene, benzene, and hexane were refluxed and distilled from sodium benzophenone ketyl under nitrogen atmosphere. All starting materials were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded for C_6D_6 or $CDCl_3$ solution on JEOL JNM-ECX400 and JEOL JNM-ECX600. Chemical shifts (δ) were quoted in ppm downfield of tetramethylsilane. Coupling constants (*J*) were quoted in Hz. NMR yields were determined using mesitylene, dichloromethane or dioxane as internal standard, Mass spectra were obtained on JEOL JMS-T100GCv spectrometer.

Column chromatography was conducted with silica gel 60N (spherical, neutral, 100 – 210 μm. KANTO CHEMICAL, Co. INC).Some compounds were purified by Model LC-9201R/U Recycling Preparative HPLC (GPC)(Japan Analytical Industry, Co. Ltd).

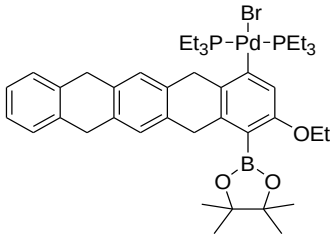
Preparation of boronic ester 11



In a 20 mL Schlenk tube, under nitrogen atmosphere, complex **10** (32 mg, 0.039 mmol) was dissolved in toluene/Et_2O (3:1, 2 mL). ^{t}BuLi (0.055 mL, 0.097 mmol) was added to the above solution at -78 °C and stirred for 1 h. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.017 mL, 0.12 mmol) was added to the above mixture at -78 °C. The mixture was stirred at room temperature for 1 h. After being quenched by methanol, the solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **11** (10 mg, 58% isolated yield).

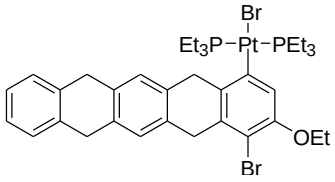
11: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.37 (t, J = 7.2 Hz, 3 H), 1.46 (s, 12 H), 3.83 (s, 2 H), 3.92 (brs, 6 H), 3.98 (q, J = 7.2 Hz, 2 H), 1.37 (d, J = 8.4 Hz, 1 H), 7.16-7.20 (m, 6 H), 7.27-7.29 (m, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 14.9, 24.9, 35.2, 35.7, 35.8, 63.9, 83.8, 108.7, 125.9, 126.1, 126.4, 127.3, 127.4, 128.5, 129.3, 134.1, 134.2, 134.4, 134.8, 136.9, 136.9, 141.3, 160.8. HRMS (ESI) calcd for $C_{30}H_{33}NaBO_3$: 474.2451[M + Na]+. Found: 474.2459[M + Na]+.

Preparation of complex 12



12: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.02-1.08 (m, 18 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.46 (s, 12 H), 1.48-1.53 (m, 6 H), 1.57-1.62 (m, 6 H), 3.88-3.91 (m, 6 H), 3.93 (s, 2 H), 4.03 (s, 2 H), 6.71 (s, 1 H), 7.13 (s, 1 H), 7.14 (s, 1 H), 7.18-7.19 (m, 2 H), 7.27-7.30 (m, 2 H).

Preparation of platinated tetrahydropentacene 14

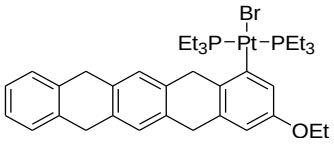


In a 20 mL Schlenk tube, 1,4-dibromo-2-ethoxy-5,7,12,14-tetrahydropentacene **13** (80 mg, 0.165 mmol) and $Pt(PEt_3)_4$ (143 mg, 0.215 mmol) were dissolved in toluene (3 mL). Under nitrogen atmosphere, the mixture was stirred for 6 h at 80 °C. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **14** (97 mg, 64% isolated yield) as a pale yellow solid.

14: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.04-1.09 (m, 18 H), 1.46 (t, J = 7.2 Hz, 3 H), 1.59-1.63 (m, 6 H), 1.69-1.74 (m, 6 H), 3.91 (s, 2 H), 3.94 (s, 2 H), 3.99 (q, J = 7.2 Hz, 2 H), 4.03 (s, 2 H), 4.13 (s, 2 H), 6.96 (s, 1 H), 7.13 (s, 1 H), 7.19-7.20 (m, 2 H), 7.27 (s, 1 H), 7.29-7.31 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.0, 14.1 (t, J = **1**7.1 Hz), 15.0, 35.8, 35.8, 36.3, 40.3, 64.8,

108.1, 119.8, 125.7, 126.0, 126.0, 126.4, 127.4, 127.4, 133.9, 134.2, 134.3, 134.7, 135.4, 136.9, 136.9, 139.7, 152.3. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 12.37. HRMS (ESI) calcd for $C_{36}H_{50}Br_2OP_2PtNa$: 939.1187[M + Na]+. Found: 939.1219[M + Na]+.

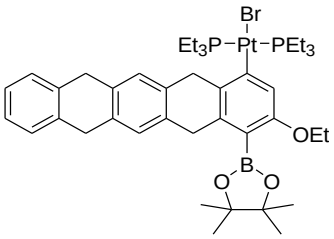
Preparation of platinated tetrahydropentacene 15



In a 20 mL Schlenk tube, platinated tetrahydropentacene **14** (25 mg, 0.027 mmol) was dissolved in a mixed solution of toluene and ethyl ether (3:1, 2 mL). To the mixture was added ^{t}BuLi (0.038 mL, 0.068 mmol) at -78 °C and stirred for 1 h. After being quenched by methanol, the solvent was evaporated. The resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **15** (19 mg, 86% isolated yield).

15: ^{1}H NMR ($CDCl_3$, Me_4Si, 400 M) δ 1.02-1.10 (m, 18 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.54-1.76 (m, 12 H), 3.80 (s, 2 H), 3.91-3.98 (m, 6 H), 4.06 (s, 2 H), 6.43 (s, 1 H), 6.87-6.88 (m, 1 H), 7.14 (s, 1 H), 7.18-7.20 (m, 3 H), 7.28-7.31 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 400M) δ 8.0, 14.2, 15.1, 35.8, 35.8, 36.8, 39.9, 63.2, 108.2, 120.0, 126.0, 127.4, 132.3, 133.8, 133.9, 134.9, 135.8, 136.1, 136.9, 137.0, 140.6, 156.4. ^{31}P NMR ($CDCl_3$, Me_4Si, 400M) δ 12.79. HRMS (ESI) calcd for $C_{36}H_{51}BrOP_2PtNa$: 859.2102[M + Na]+. Found: 859.2133[M + Na]+.

Preparation of compound 16

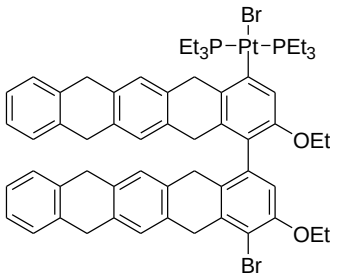


In a 20 mL Schlenk tube, under nitrogen atmosphere, complex **14** (100 mg, 0.11 mmol) was dissolved in toluene/Et_2O (3:1, 4 mL). Reagent ^{t}BuLi (0.154 mL, 0.27 mmol) was added to the above solution at -78 °C, the mixture was stirred for 1 h at -78 °C. Then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.024 mL, 0.16 mmol) was added to the above mixture at -78 °C. The mixture was stirred at room temperature for 1 h. The mixture was quenched with methanol. The solvent was evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **16** (80 mg, 76% isolated yield).

16: ^{1}H NMR ($CDCl_3$, Me_4Si, 400M) δ 1.00-1.08 (m, 18 H), 1.25 (t, J = 7.2 Hz, 3 H), 1.46 (s, 12 H), 1.56-1.61 (m, 6 H), 1.67-1.74 (m, 6 H), 3.87-3.93 (m, 8 H), 4.05 (s, 2 H), 6.84 (s, 1 H), 7.11 (s, 1 H), 7.14 (s, 1 H), 7.17-7.19 (m, 2 H), 7.28-7.30 (m, 2 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M)

δ 8.0, 14.0 (t, J = **1**7.1 Hz), 15.1, 24.9, 35.8, 35.8, 36.5, 40.3, 63.6, 83.5, 117.3, 125.7, 125.9, 125.9, 126.0, 127.4, 127.4, 132.0, 133.6, 133.7, 135.2, 135.7, 137.0, 137.0, 139.8, 143.5, 159.9. ^{31}P NMR ($CDCl_3$, Me_4Si, 400M) δ 12.78. HRMS (ESI) calcd for $C_{42}H_{62}BBrO_3P_2PtNa$: 985.2955[M + Na]+. Found: 985.2988[M + Na]+.

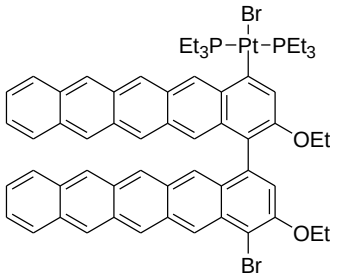
Preparation of platinated octohydropentacene dimer 18



In a 20 mL Schlenk tube, palladated tetrahydropentacene **16** (70 mg, 0.063 mmol) and compound **17** (77 mg, 0.08 mmol) were dissolved in THF: H_2O (10:1, 3.3 mL). Under nitrogen atmosphere, the mixture was added NaOH (8 mg, 0.19 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and heated at 70 °C for about 3 h. After that the solvent was removed evaporated, and the resulting solids were purified by a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **18** (25 mg, 32% isolated yield) as a pale yellow solid.

18: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.07 (t, J = 7.2 Hz, 3 H), 1.13-1.22 (m, 18 H), 1.47 (t, J = 7.2 Hz, 3 H), 1.64-1.74 (m, 6 H), 1.75-1.81 (m, 6 H), 3.28 (d, J = 18 Hz, 1 H), 3.40 (d, J = 18.6 Hz, 1 H), 3.46 (d, J = 18 Hz, 1 H), 3.50 (d, J = 18.6 Hz, 1 H), 3.77-3.82 (m, 5 H), 3.85-3.93 (m, 5 H), 4.09-4.13 (m, 3 H), 4.18 (d, J = 16.8 Hz, 1 H), 4.24 (d, J = 17.4 Hz, 1 H), 4.30 (d, J = 19.2 Hz, 1 H), 6.65 (s, 1 H), 6.73 (s, 1 H), 6.90 (s, 1 H), 7.06 (s, 1 H), 7.12-7.21 (m, 7 H), 7.28-7.29 (m, 2 H), 7.31 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.0, 8.2, 13.7-14.2(m, 2 C), 14.9, 15.0, 32.7, 33.8, 35.7, 35.8, 35.8, 35.9, 36.3, 40.8, 64.1, 65.1, 112.3, 113.8, 119.4, 122.4, 125.6, 125.9, 125.9, 125.9, 126.0, 126.0, 126.1, 126.6, 127.3, 127.3, 127.4, 127.4, 129.4, 133.0, 133.6, 133.8, 134.0, 134.1, 134.2, 134.4, 134.4, 135.0, 135.8, 136.5, 136.7, 136.8, 136.9, 136.9, 153.0, 153.2. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 14.75, 14.86. HRMS (ESI) calcd for $C_{60}H_{70}Br_2NaOP_2Pt$: 1263.2701[M + Na]+. Found: 1263.2774[M + Na]+.

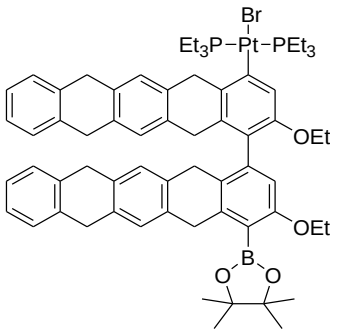
Preparation of platinated pentacene dimer 29



In a 20 mL Schlenk tube, pentacene dimer derivative **18** (19 mg, 0.015 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (21 mg, 0.092 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 2 h at room temperature. The pentacene-DDQ adduct was formed firstly. Without isolation, pentacene-DDQ adduct was treated with γ-terpinene (0.25 mL, 1.53 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and heated at 80 °C for about 6 h. After cooling to room temperature, the solvent was removed in vacuo. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **19** (10 mg, 52% isolated yield) as a blue solid.

19: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.05 (t, J = 7.2 Hz, 3 H), 1.16-1.25 (m, 9 H), 1.27-1.54 (m, 9 H), 1.58 (t, J = 7.2 Hz, 3 H), 1.73-1.85 (m, 6 H), 1.93-2.05 (m, 6 H), 4.00-4.06 (m, 1 H), 4.09-4.14 (m, 1 H), 4.39-4.43 (m, 2 H), 7.21-7.30 (m, 4 H), 7.41 (s, 1 H), 7.66 (s, 1 H), 7.78-7.81 (m, 2 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 8.03 (s, 1 H), 8.19 (s, 1 H), 8.36 (s, 1 H), 8.38 (s, 1 H), 8.40 (s, 1 H), 8.54 (s, 1 H), 8.60 (s, 1 H), 8.64 (s, 1 H), 8.83 (s, 1 H), 9.04 (s, 1 H), 9.18 (s, 1 H), 9.75 (s, 1 H). ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 12.83, 13.03. HRMS (ESI) calcd for $C_{60}H_{62}Br_2O_2P_2Pt$: 1232.2178. Found:1232.2251.

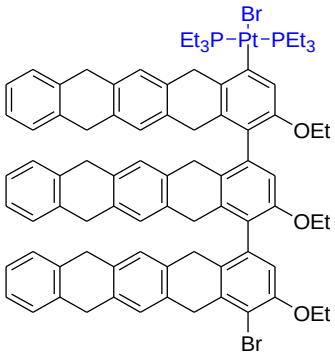
Preparation of complex 20



By the same method as described for compound **16**, the title compound **20** was obtained in 54% isolated yield.

20: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.04 (t, J = 7.2 Hz, 3 H), 1.11-1.20 (m, 18 H), 1.37 (t, J = 7.2 Hz, 3 H), 1.52 (s, 12 H), 1.69-1.85 (m, 12 H), 3.25 (d, J = 18 Hz, 1 H), 3.33 (d, J = 17.4 Hz, 1 H), 3.40-3.46 (m, 2 H), 3.72-3.85 (m, 6 H), 3.89 (s, 2 H), 3.92 (s, 2 H), 3.97-4.03 (m, 4 H), 4.17 (s, 2 H), 6.53 (s, 1 H), 6.70 (s, 1 H), 6.86 (s, 1 H), 7.02 (s, 1 H), 7.12-7.19 (m, 8 H), 7.21-7.23 (m, 1 H), 7.27-7.28 (m, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.1, 8.3, 14.2-14.5 (m, 2 C), 15.0, 15.1, 24.9, 25.0, 32.3, 33.6, 35.7, 35.8, 35.8, 35.9, 36.3, 40.5, 63.8, 64.4, 83.9, 111.2, 119.4, 123.8, 125.6, 125.9, 125.9, 126.2, 127.3, 127.3, 127.4, 132.7, 133.7, 133.8, 133.8, 133.9, 134.5, 134.8, 135.1, 135.2, 135.7, 136.8, 136.9, 137.0, 137.0, 138.9, 139.0, 140.9, 153.4, 160.2. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 12.84, 12.99. HRMS (ESI) calcd for $C_{66}H_{82}BBrNaO_4P_2Pt$: 1309.4469[M + Na]+. Found: 1309.4560[M + Na]+.

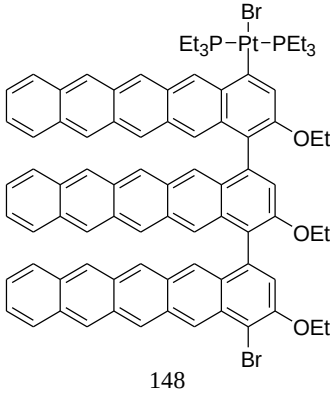
Preparation of platinated dodecahydropentacene trimer 21



In a 20 mL Schlenk tube, palladated tetrahydropentacene **17** (45 mg, 0.04 mmol) and platinum substituted pentacene dimer boron reagent **20** (52 mg, 0.04 mmol) were dissolved in THF : H_2O (10:1, 3.3 mL). Under nitrogen atmosphere, the mixture was added NaOH (4.8 mg, 0.12 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and heated at 70 °C for about 3 h. After cooling to room temperature, the solvent was removed. The residue was purified on a flash chromatography (silica gel, hexane: ethyl acetate = 5:1 as eluent) to afford the title compound **21** (10 mg, 16% isolated yield) as a pale yellow solid.

21: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.10 (t, J = 7.2 Hz, 3 H), 1.14-1.24 (m, 21 H), 1.50 (t, J = 7.2 Hz, 3 H), 1.73-1.81 (m, 6 H), 1.85-1.88 (m, 6 H), 3.46 (d, J = 19.2 Hz, 1 H), 3.52 (d, J = 16.8 Hz, 1 H), 3.56 (d, J = 17.4 Hz, 1 H), 3.61-3.72 (m, 4 H), 3.76-3.77 (m, 4 H), 3.88-3.98 (m, 13 H), 4.14 (q, J = 7.2 Hz, 2 H), 4.20 (d, J = 16.8 Hz, 1 H), 4.24-4.25 (m, 2 H), 4.35 (d, J = 19.2 Hz, 1 H), 6.73 (s, 1 H), 6.76 (s, 1 H), 6.77 (s, 1 H), 6.95 (s, 1 H), 7.03 (s, 1 H), 7.06 (s, 1 H), 7.10-7.12 (m, 3 H), 7.16-7.24 (m, 9 H), 7.31 (s, 1 H), 7.33 (s, 1 H), 7.37 (s, 1 H). ^{13}C NMR ($CDCl_3$, Me_4Si, 600M) δ 8.1, 8.3, 14.3-14.7 (m, 2 C), 14.8, 14.9, 15.1, 29.7, 32.8, 32.9, 34.0, 34.1, 35.7, 35.9, 35.9, 36.4, 40.7, 64.0, 64.2, 65.1, 125.8, 125.8, 125.9, 126.0, 126.0, 126.1, 126.2, 126.3, 126.4, 126.6, 126.6, 127.2, 127.3, 127.4, 127.4, 128.4, 129.5, 133.6, 133.8, 134.0, 134.1, 134.3, 134.5, 134.8, 135.2, 135.2, 135.8, 135.8, 136.0, 136.7, 136.8, 136.8, 136.9, 136.9, 137.0, 137.1, 153.1, 153.5, 153.7. ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 12.84, 12.97. HRMS (ESI) calcd for $C_{84}H_{90}Br_2NaO_3P_2Pt$: 1587.4215[M + Na]+. Found:1587.4265[M + Na]+.

Preparation of platinated pentacene trimer 22



In a 20 mL Schlenk tube, platinum substituted pentacene dimer derivative **21** (6 mg, 0.0038 mmol) and DDQ (7.8 mg, 0.035 mmol) were dissolved in benzene (2 mL). Under nitrogen atmosphere, the mixture was stirred for 2 h at room temperature. The pentacene-DDQ adduct was formed firstly. Without isolation, pentacene-DDQ adduct solution was added with *γ*-terpinene (0.093 mL, 0.57 mmol). The mixture was degassed by three times of freeze-pump thaw cycle and then heated at 80 °C for about 6 h. After cooling to room temperature, the solvent was removed *in vacuo*. The resulting solids were purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) under nitrogen to afford the title compound **22** (3.8 mg, 65% isolated yield) as a blue solid.

22: ^{1}H NMR ($CDCl_3$, Me_4Si, 600M) δ 1.14 (t, J = 7.2 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 1.22-1.36 (m, 18 H), 1.63 (t, J = 7.2 Hz, 3 H), 1.79-1.88 (m, 6 H), 2.00-2.09 (m, 6 H), 4.18-4.26 (m, 4 H), 4.45-4.49 (m, 2 H), 7.18-7.19 (m, 2 H), 7.28-7.34 (m, 4 H), 7.58 (s, 1 H), 7.69 (s, 1 H), 7.72-7.76 (m, 3 H), 7.84-7.87 (m, 2 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 8.28 (s, 1 H), 8.32 (s, 1 H), 8.35 (s, 1 H), 8.36 (s, 1 H), 8.39 (s, 1 H), 8.40 (s, 1 H), 8.59 (s, 1 H), 8.63 (s, 1 H), 8.64 (s, 2 H), 8.69 (s, 1 H), 8.72 (s, 1 H), 8.85 (s, 1 H), 8.92 (s, 2 H), 9.13 (s, 1 H), 9.28 (s, 1 H), 9.84 (s, 1 H). ^{31}P NMR ($CDCl_3$, Me_4Si, 600M) δ 12.71, 13.18. HRMS (ESI) calcd for $C_{84}H_{78}Br_2O_3P_2Pt$: 1552.3379. Found:1552.3449.

X-ray analysis data for complex 15

Table 1. Crystallographic data and experimental details for complex **15**

Compound	**15**
Formula	$C_{36}H_{51}BrOP_2Pt$
M	836.71
Crystal system	monoclinic
Space group	P 1 21/c 1
a, (Å)	17.4520(3)
b, (Å)	9.5316(2)
c, (Å)	23.0649(4)
α, (°)	90.00
β, (°)	107.0610(10)
γ, (°)	90.00
V, (Å^3)	3667.90(12)
Z	4
Temperature T, (K)	298
Crystal habit	prism
Crystal color	colorless
Crystal size, (mm^3)	0.60 x 0.40 x 0.20
D_{calcd}, (g cm^{-3})	1.515
Transm factor	0.1524 - 0.4330
λ (Mo Kα), (Å^3)	0.71075

Diffractometer	Rigaku SCX mini
Scan mode	ω
Reflections measd	-22≤ h ≤22
	-12≤ k ≤12
	-29≤ l ≤29
No. of reflection measd	8405
No. of reflection obsd [I>2σ (I)]	7091
No. of parameters refined	370
R	0.0518
R_ω	0.1279
S, goodness of fit	1.091
Largest diff peak, (e Å^{-3})	4.109
Largest diff hole, (e Å^{-3})	-2.113

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$,

$R_\omega=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$, $\omega=[\sigma^2(F_o)+0.00063(F_o)^2]^{-1}$.

$S=[\Sigma\omega(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, (m=no. of used reflections, n=no. of refined parameters)

Table 2. Intramolecular distances involving the non-hydrogen atoms

Pt1 C1 2.013(4)	Pt1 P2 2.3063(15)
Pt1 P1 2.3095(15)	Pt1 Br1 2.5269(6)
P1 C27 1.816(6)	P1 C29 1.819(6)
P1 C25 1.839(6)	P2 C31 1.811(7)
P2 C35 1.814(6)	P2 C33 1.840(7)
O1 C21 1.382(6)	O1 C23 1.406(9)
C1 C22 1.406(7)	C1 C2 1.423(6)
C2 C19 1.394(6)	C2 C3 1.523(6)
C3 C4 1.523(6)	C3 H1 0.9700
C3 H2 0.9700	C4 C5 1.390(6)
C4 C17 1.405(6)	C5 C6 1.393(7)
C5 H3 0.9300	C6 C15 1.384(7)
C6 C7 1.519(7)	C7 C8 1.505(7)
C7 H4 0.9700	C7 H5 0.9700
C8 C13 1.387(7)	C8 C9 1.410(7)
C9 C10 1.405(9)	C9 H6 0.9300
C10 C11 1.391(10)	C10 H7 0.9300
C11 C12 1.363(9)	C11 H8 0.9300
C12 C13 1.387(7)	C12 H9 0.9300
C13 C14 1.519(7)	C14 C15 1.515(7)
C14 H10 0.9700	C14 H11 0.9700
C15 C16 1.394(7)	C16 C17 1.384(7)
C16 H12 0.9300	C17 C18 1.512(7)
C18 C19 1.515(6)	C18 H13 0.9700
C18 H14 0.9700	C19 C20 1.399(7)
C20 C21 1.367(8)	C20 H15 0.9300
C21 C22 1.385(7)	C22 H16 0.9300
C23 C24 1.465(12)	C23 H17 0.9700
C23 H18 0.9700	C24 H19 0.9600
C24 H20 0.9600	C24 H21 0.9600
C25 C26 1.496(12)	C25 H22 0.9700
C25 H23 0.9700	C26 H24 0.9600
C26 H25 0.9600	C26 H26 0.9600
C27 C28 1.523(9)	C27 H27 0.9700
C27 H28 0.9700	C28 H29 0.9600
C28 H30 0.9600	C28 H31 0.9600
C29 C30 1.497(9)	C29 H32 0.9700
C29 H33 0.9700	C30 H34 0.9600
C30 H35 0.9600	C30 H36 0.9600
C31 C32 1.496(11)	C31 H37 0.9700
C31 H38 0.9700	C32 H39 0.9600
C32 H40 0.9600	C32 H41 0.9600

C33 C34 1.506(14)	C33 H42 0.9700
C33 H43 0.9700	C34 H44 0.9600
C34 H45 0.9600	C34 H46 0.9600
C35 C36 1.526(9)	C35 H47 0.9700
C35 H48 0.9700	C36 H49 0.9600
C36 H50 0.9600	C36 H51 0.9600

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Intramolecular angles involving the non-hydrogen atoms

C1 Pt1 P2 92.19(13)	C1 Pt1 P1 91.56(14)
P2 Pt1 P1 176.25(5)	C1 Pt1 Br1 175.29(13)
P2 Pt1 Br1 87.75(4)	P1 Pt1 Br1 88.52(4)
C27 P1 C29 105.5(3)	C27 P1 C25 105.7(4)
C29 P1 C25 102.0(3)	C27 P1 Pt1 117.0(2)
C29 P1 Pt1 113.6(2)	C25 P1 Pt1 111.7(3)
C31 P2 C35 106.1(4)	C31 P2 C33 101.4(4)
C35 P2 C33 104.4(4)	C31 P2 Pt1 112.7(3)
C35 P2 Pt1 117.5(2)	C33 P2 Pt1 113.1(3)
C21 O1 C23 119.0(5)	C22 C1 C2 116.5(4)
C22 C1 Pt1 118.3(3)	C2 C1 Pt1 125.2(3)
C19 C2 C1 120.5(4)	C19 C2 C3 118.4(4)
C1 C2 C3 121.1(4)	C2 C3 C4 111.9(4)
C2 C3 H1 109.2	C4 C3 H1 109.2
C2 C3 H2 109.2	C4 C3 H2 109.2
H1 C3 H2 107.9	C5 C4 C17 118.8(4)
C5 C4 C3 122.5(4)	C17 C4 C3 118.7(4)
C4 C5 C6 121.5(4)	C4 C5 H3 119.3
C6 C5 H3 119.3	C15 C6 C5 119.4(4)
C15 C6 C7 119.1(5)	C5 C6 C7 121.5(4)
C8 C7 C6 111.9(4)	C8 C7 H4 109.2
C6 C7 H4 109.2	C8 C7 H5 109.2
C6 C7 H5 109.2	H4 C7 H5 107.9
C13 C8 C9 119.5(5)	C13 C8 C7 120.5(4)
C9 C8 C7 119.9(5)	C10 C9 C8 119.1(5)
C10 C9 H6 120.5	C8 C9 H6 120.5
C11 C10 C9 120.1(5)	C11 C10 H7 119.9
C9 C10 H7 119.9	C12 C11 C10 119.9(6)
C12 C11 H8 120.1	C10 C11 H8 120.1
C11 C12 C13 121.3(6)	C11 C12 H9 119.4
C13 C12 H9 119.4	C12 C13 C8 120.0(5)
C12 C13 C14 121.6(5)	C8 C13 C14 118.3(4)
C15 C14 C13 111.6(4)	C15 C14 H10 109.3
C13 C14 H10 109.3	C15 C14 H11 109.3
C13 C14 H11 109.3	H10 C14 H11 108.0
C6 C15 C16 119.6(4)	C6 C15 C14 119.6(4)
C16 C15 C14 120.7(4)	C17 C16 C15 121.1(4)
C17 C16 H12 119.4	C15 C16 H12 119.4
C16 C17 C4 119.5(4)	C16 C17 C18 122.0(4)
C4 C17 C18 118.4(4)	C17 C18 C19 111.8(4)
C17 C18 H13 109.2	C19 C18 H13 109.2
C17 C18 H14 109.2	C19 C18 H14 109.2
H13 C18 H14 107.9	C2 C19 C20 120.8(4)
C2 C19 C18 119.2(4)	C20 C19 C18 120.1(4)
C21 C20 C19 119.3(5)	C21 C20 H15 120.3
C19 C20 H15 120.3	C20 C21 O1 114.5(5)
C20 C21 C22 120.7(4)	O1 C21 C22 124.8(5)
C21 C22 C1 122.2(4)	C21 C22 H16 118.9
C1 C22 H16 118.9	O1 C23 C24 107.0(7)
O1 C23 H17 110.3	C24 C23 H17 110.3
O1 C23 H18 110.3	C24 C23 H18 110.3
H17 C23 H18 108.6	C23 C24 H19 109.5
C23 C24 H20 109.5	H19 C24 H20 109.5
C23 C24 H21 109.5	H19 C24 H21 109.5
H20 C24 H21 109.5	C26 C25 P1 112.9(5)
C26 C25 H22 109.0	P1 C25 H22 109.0
C26 C25 H23 109.0	P1 C25 H23 109.0
H22 C25 H23 107.8	C25 C26 H24 109.5
C25 C26 H25 109.5	H24 C26 H25 109.5
C25 C26 H26 109.5	H24 C26 H26 109.5

H25 C26 H26 109.5	C28 C27 P1 116.8(5)
C28 C27 H27 108.1	P1 C27 H27 108.1
C28 C27 H28 108.1	P1 C27 H28 108.1
H27 C27 H28 107.3	C27 C28 H29 109.5
C27 C28 H30 109.5	H29 C28 H30 109.5
C27 C28 H31 109.5	H29 C28 H31 109.5
H30 C28 H31 109.5	C30 C29 P1 114.5(4)
C30 C29 H32 108.6	P1 C29 H32 108.6
C30 C29 H33 108.6	P1 C29 H33 108.6
H32 C29 H33 107.6	C29 C30 H34 109.5
C29 C30 H35 109.5	H34 C30 H35 109.5
C29 C30 H36 109.5	H34 C30 H36 109.5
H35 C30 H36 109.5	C32 C31 P2 113.9(5)
C32 C31 H37 108.8	P2 C31 H37 108.8
C32 C31 H38 108.8	P2 C31 H38 108.8
H37 C31 H38 107.7	C31 C32 H39 109.5
C31 C32 H40 109.5	H39 C32 H40 109.5
C31 C32 H41 109.5	H39 C32 H41 109.5
H40 C32 H41 109.5	C34 C33 P2 114.6(7)
C34 C33 H42 108.6	P2 C33 H42 108.6
C34 C33 H43 108.6	P2 C33 H43 108.6
H42 C33 H43 107.6	C33 C34 H44 109.5
C33 C34 H45 109.5	H44 C34 H45 109.5
C33 C34 H46 109.5	H44 C34 H46 109.5
H45 C34 H46 109.5	C36 C35 P2 116.6(5)
C36 C35 H47 108.1	P2 C35 H47 108.1
C36 C35 H48 108.1	P2 C35 H48 108.1
H47 C35 H48 107.3	C35 C36 H49 109.5
C35 C36 H50 109.5	H49 C36 H50 109.5
C35 C36 H51 109.5	H49 C36 H51 109.5
H50 C36 H51 109.5	

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

5-5. References

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