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Doctoral Dissertation

Challenges toward the World Record of the Longest C-C Bond: Expandability of the Ultimate Covalent Bond and its Application to the C-O Bond

（世界最長の炭素－炭素結合への挑戦：究極的共有結合の伸長性と炭素－酸素結合への展開）

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General Introduction

Chapter 1

Preparation of Unsymmetrical Substituted 1,1,2,2-Tetraarylpyracene by a Flow Microreactor Method : Substituent Effects on the Ultralong C-C Bond Length

Chapter 2

Expandability of Ultralong C-C Bond in Hexaphenylethane-type Compounds with a 1*H*-Benzo[*cd*]indol-2-one Skeleton

Chapter 3

Missing Isomer of Hexaphenylethane: Unprecedented α,*o*-Dimer Formation on a 1*H*-Cyclobuta[*de*]naphthalene Skeleton

Chapter 4

Expansion of C-O Bond Length by "Scissor Effects" in Naphtho[1,8-*bc*] furan Derivatives

General Introduction

0-1. The C-C Single Bond in Chemistry

A better understanding of the nature of covalent bonds is important because covalent bonding is a fundamental concept in chemistry. The structural parameter in a specific bond, such as bond length or angle, is substantially constant value in almost of all organic compounds, but the compounds with an unusual value[1] have been ever slightly observed. Deviation from the standard value gives us a good opportunity to gain further insight into covalent bonds. There have been ever many studies[2-8] based on this idea, especially on the C-C single bond, which is the most important and universal in organic chemistry. Thus, the investigation of its properties should provide significant information on covalent bonds. A C-C single bond has a high bond energy (ca. 100 kcal/mol), a standard bond length (1.54 Å) and bond angle (109.5 °).[9] Compounds with unusual C-C bond lengths or C-C-C bond angles have been synthesized to investigate whether they exhibit special properties or reactivities. For example, propellanes are known to have a C-C bond with unusual bond angles. The resulting strain causes high reactivity of such compounds. In terms of bond length, Sekiguchi reported a very short C-C single bond [1.436(3) Å] in a tetrahedranyltetrahedrane derivative.[10] This bond shortening was attributed to the high *s* character of the bonding orbitals.

Although it is unclear how far a C-C single bond can be stretched, based on a database study, Zavitsas predicted that the limit of a maximum C-C bond length is 1.748 Å by assuming a negative-sloped linear correlation between bond dissociation energy (BDE) and the bond length (Figure 0-1 (a)).[11] Additionally, Nakai recently reported that the longest theoretically possible C-C bond length is 1.803 Å by DFT calculation using diamond-like nanostructured alkanes (Figure 0-1 (b)).[12]

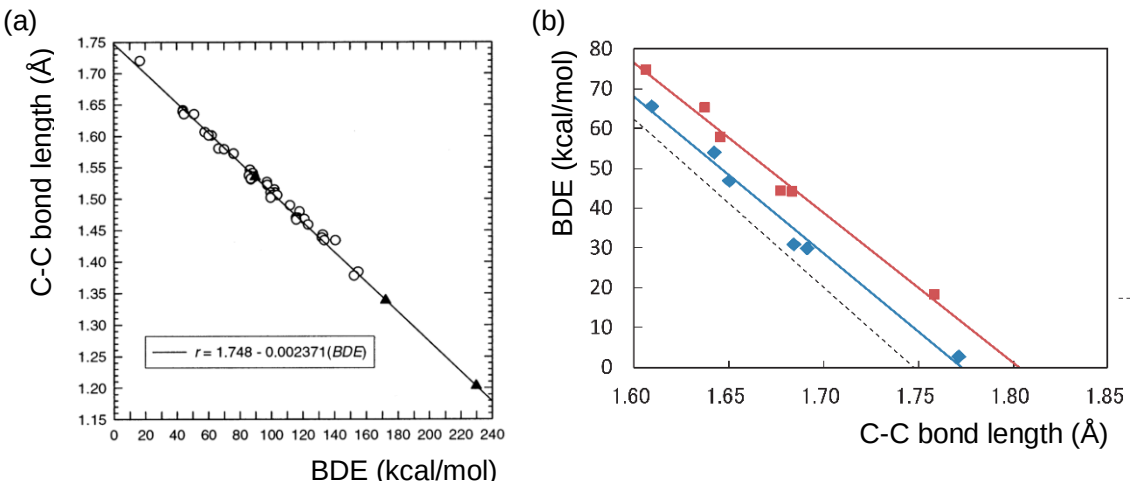
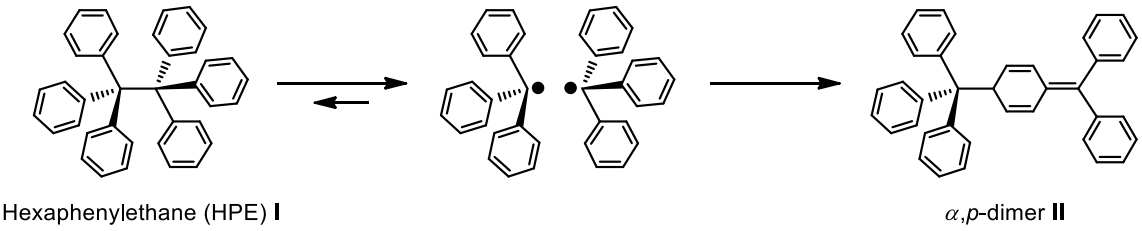


Figure 0-1. (a) C-C bond lengths vs bond dissociation energy (BDE) proposed by Zavitsas. (b) C-C bond lengths vs BDE proposed by Nakai.

This result seems to be consistent with the fact reported by Adcock that the shortest non-bonded C…C contact was 1.80(2) Å, which suggests that the C-C bond length might have a limit of around 1.8 Å.[13] However, when we consider that the bond length of a covalent bond is determined by the balance between the stabilization energy obtained by the sharing of electrons and the repulsive force generated by two positively charged atomic nuclei, the Lennard-Jones potential may be more appropriate than a simple linear correlation. Thus, the change in BDE with an increase in the length of prestrained C-C bonds (1.6-1.7 Å) should be smaller than the energy required to lengthen a normal C-C bond (1.54 Å) to the same degree. Therefore, it is highly possible that we can find a C-C bond longer than that described Zavitsas and Nakai before the bond is degraded.

0-2. Example of Compounds with a Long C-C Bond

As a representative example of the compound with a much longer C-C single bond, a hexaphenylethane (HPE) derivative should be mentioned. The parent HPE **I** undergoes C-C bond fission into two triphenylmethyl radicals to isomerize thermodynamically more stable *α*,*p*-dimer **II** (Scheme 0-1).[2] *α*,*p*-Dimerization can be suppressed by the introduction of *t*-Bu groups at the 3,5-positions of the phenyl groups. The length of the central C-C bond of the resulting stabilized HPE derivative was determined to be 1.67(3) Å by an X-ray analyses, but with a large estimated standard deviation (esd) due to structural disorder (Figure 0-2, left).[3] Although an anthracene photodimer with a caged molecular framework was once reported to have a much longer C-C bond [1.77(3) Å],[4] this value was later proven to be an artifact due to structural disorder caused by the coexistence of the ring-opened isomer in the crystal lattice.[5]



Scheme 0-1. Bond-dissociation equilibrium in hexaphenylethane (HPE) and the formation of *α*,*p*-dimer

Both Toda[6] and Herges[7] have demonstrated an actual C-C bond length of greater than 1.70 Å. With high accuracy, they showed that tetraphenylbenzocyclobutene derivatives have ultralong C-C bonds whose length is greater than 1.7 Å. The benzene ring of benzocyclobutene, which can be regarded as the shared part for the two benzene rings of the HPE framework, clamps the two

diphenylmethylene units to suppress dissociation. The two exo carbons with two phenyl groups on each are fixed nearly on the same plane by the rigidity and planarity of the benzocyclobutene scaffold. Toda synthesized a series of tetraarylnaphthocyclobutenes by thermal cyclization of 1,2-bis (diarylallenyl)benzenes in solid state. X-ray analyses revealed that the central C-C bond is longer than 1.7 Å. Especially, the length of the C1-C2 bond observed in the diiodo derivative [1.734(5) Å] reported in 2001 (Figure 0-2, right) established the record for the longest C-C bond ever reported.[6c, 8]

Herges prepared caged hydrocarbon (Figure 0-2, center) with a benzocylcobutene scaffold by reacting highly reactive tetradehydroanthracene dimer and benzyne. According to the results of X-ray analyses, the C1-C2 bond was elongated to 1.713(2) Å. DFT calculations and studies on the related compounds revealed that this bond elongation was due to ring strain in a cyclobutene ring and steric repulsion among four aromatic units. Raman spectrum measurement revealed that the stretching vibration of the long C-C bond was red-shifted ($\Delta\nu$ = ca. 300 cm^{-1}), which corresponds to a decrease in the force constant of the C-C bond to less than one-third of that in a standard C-C bond. This measurement is an example of the physical properties of C-C bonds with an unusual bond length.

Schreiner recently described that the preparation of diadamantylethane-type molecules with a long C-C bond by Wurtz coupling of the corresponding bromides.[14] The C-C bond length of 1.71 Å observed in the cross-dimer of [121]tetramantane and diamantane set up new record for the longest C-C bond in alkanes. These molecules were stable enough to isolate, even though they were not "clamped". They suggested that van der Waals attraction through the intramolecular CH···HC contact surfaces around the long C−C bond stabilized the elongated bond despite the steric repulsion between two caged-alkane units contributed to the elongation of C-C bond.

Ever since compounds with ultralong C-C bonds were first described, there has been a discussion on the origin of bond elongation especially on the HPE derivatives. Although through-bond interaction between a π orbital of aryl substituents and a σ orbital of an elongated C-C bond[15] is an attractive explanation to account for this phenomenon, detailed experimental and theoretical examinations have indicated that steric repulsion between aryl substituents is the dominant factor in bond elongation.[16]

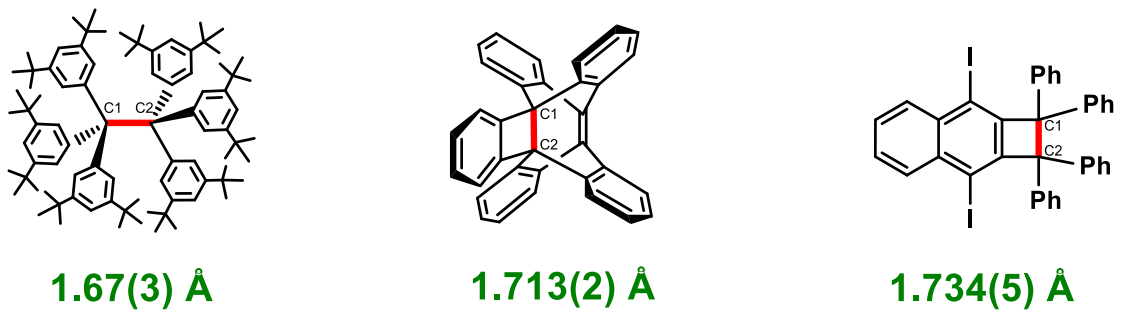
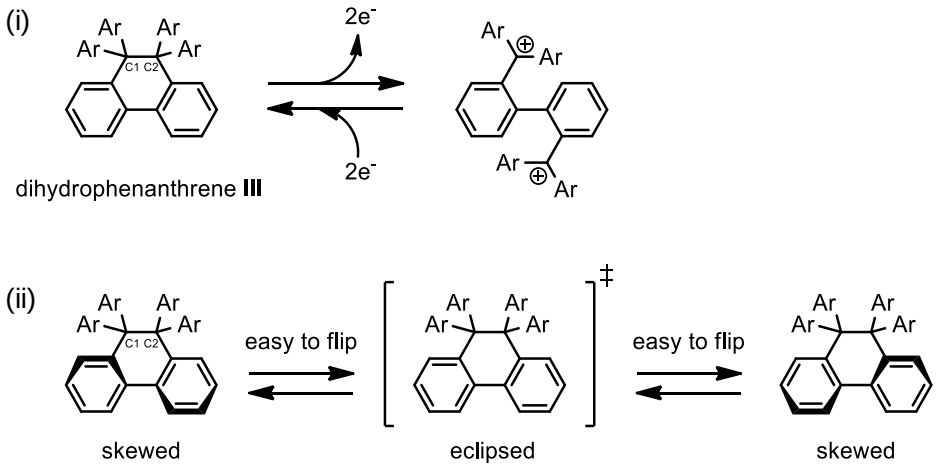


Figure 0-2. Compounds with a long C-C bond and their bond lengths determined by X-ray analyses.

0-3. Molecular Design for an Ultralong C-C Bond

In the author's laboratory, electrochromic system have been studied based on oxidative fission and the reductive reformation of a long C-C bond of clumped HPE derivatives.[18] 9,9,10,10-Tetraphenyl-9,10-dihyrophenanthrene (**III,** Ar = Ph) is a stable molecule whose central C-C bond is longer than the other "clamped" HPE derivatives. Dr. Jun-ichi Nishida has found that a series of tetraaryldihydrophenanthrenes **III** have a long C1-C2 bond [1.656(6) -1.614(2) Å]. The central C1-C2 bond of dihydrophenanthrene is cleaved upon oxidation to afford the corresponding dication. Upon reduction of the dication, the central C-C bond is reformed to regenerate dihydrophenanthrene (Scheme 0-2, (i)). However, in the phenanthrene framework, the aryl substituents are arranged in a non-eclipsed geometry around the long C-C ethane bond, since the skeleton is flexible enough to adopt a skewed conformation (Scheme 0-2, (ii)). The fact that the central six membered ring undergoes ring-flip in solution with an energy barrier of 12 kcal/mol indicates that the eclipsed conformer (transition state) is much higher in energy than the skewed geometry.



Scheme 0-2. Dyrex reaction and conformational change of dihydrophenanthrene.

Dr. Takashi Takeda designed tetraarylacenaphthene in anticipation of a longer C1-C2 bond (Figure 0-3). An acenaphthene framework was used to suppress skewing deformation around the cross-clamping part and to arrange four aryl substituents in a much closer proximity. The *peri*-position of naphthalene has been used to arrange two substituents in close proximity.[19] Thus, one can expect greater steric repulsion around the ethane bond in **IV** than in **III**. A naphthalene group also participates in cross-clamping to suppress dissociation of the bond to form diradical species. As expected, low-temparature X-ray analyses of a series of **IV** revealed that the central C1-C2 bonds are highly extended [1.708(4)-1.670(3) Å], but acenapthene framework is not rigid enough to arrange aryl substituents in a complete eclipsed conformation.

To incorporate additional factors for bond elongation, tetraarylpyracene **V** which has additional etheno-clamping at another *peri*-position to **IV** was also designed by Takeda. The parent pyracene has a longer C1-C2 bond (1.59 Å) than acenaphthene (1.56 Å).[20] The additional five-membered ring should provide greater rigidity to the pyracene scaffold in **V** than to the acenaphthene scaffold in **IV**. X-ray analyses of a series of tetraarylpyracene derivatives elucidated that the central C1-C2 bonds are extremely extended [1.761(4)-1.717(4) Å]. Notably, pyracene derivative **DSAP** with two methylacridan group shows the longest C-C bond value [1.771(3) Å at 93 K, 1.791(3) Å at 413 K] in the uncharged organic compounds to have been determined with high accuracy (Figure 0-4).[21] This results indicated that the eclipsed conformation becomes more predominant, because the more rigid pyracene framework makes skewing deformation energetically more unfavorable.

The C1-C2 bond length in **DSAP** is greater than the limiting value, nevertheless Zavitsas expected that the BDE of C-C single bond become zero at 1.75 Å. This results indicated that the supposed linear correlation between the bond length and BDE is invalid in very long bonds whose length exceeds a certain value. Thus, boundary between C-C single bond and two carbon radicals as well as the limit of C-C covalent bond length are still unclear. Although many studies on a C-C covalent bond have been performed for many years, these problems are still remained unsolved to prevent through understanding of the nature of chemical bonding.

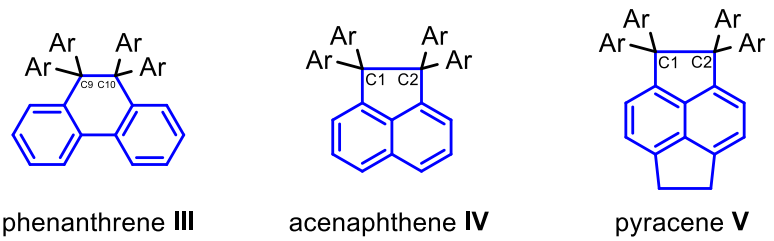


Figure 0-3. Clamping skeletons adopted in the previous work.

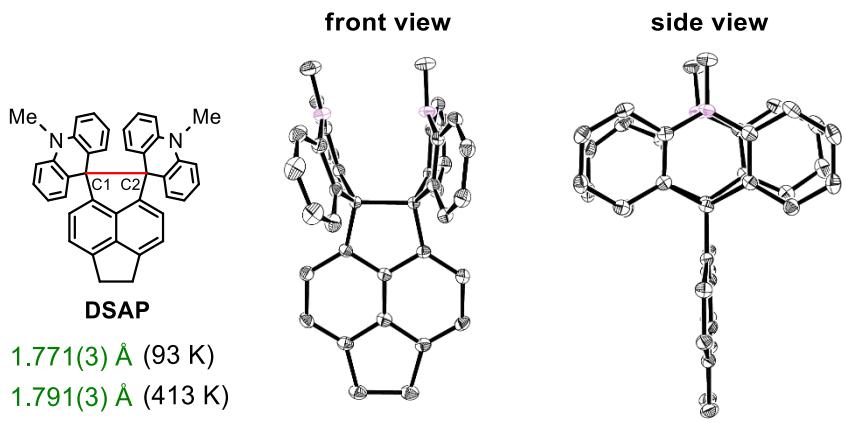


Figure 0-4. X-ray structures of Dispiro[(10-methylacridan)-9,1'-pyracene-2',9''-(10-methylacridan)].

0-4. Contents of This Thesis

In this thesis, the author has challenged the following four themes to elucidate the boundary of the ultralong C-C covalent bond and the short non-bond with examining the phenomena in the extreme situation of the C-C bond through the synthetic study of the compound with the much longer C-C bond, and to confirm the utility of his strategy for bond elongation by application to the C-O bond.

In Chapter 1, the influence of electronic factor on the elongation of the C-C bond was investigated. Unsymmetrically 1,1,2,2-tetraarylpyracenes with a variety of substituents on the aryl group were prepared using a flow microreactor method. X-ray analyses demonstrated that the electronic nature of substituents does not contribute to the elongation of bond, whereas intermolecular perturbation such as crystal packing is largely effected. In addition, it have been found that 1,1-bis(4-fluorophenyl)-2,2-bis(4-methoxyphenyl)pyracene forms a series of pseudopolymorphs by incorporating a variety of solvent in the crystal, and the ultralong C-C single bonds beyond 1.70 Å easily change by the difference of the solvent molecules.

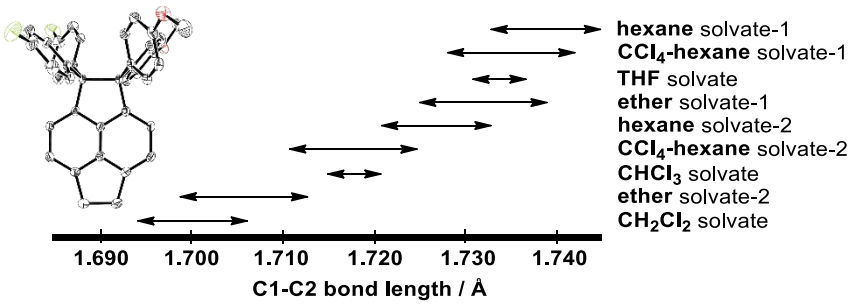
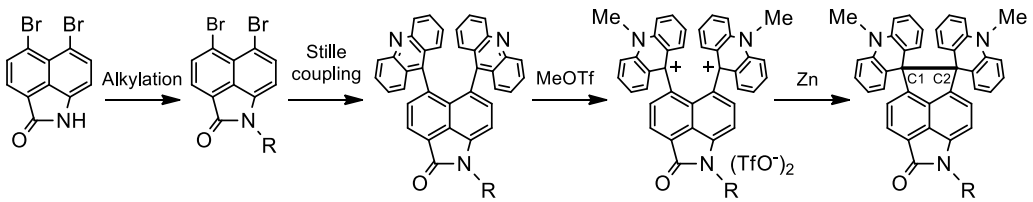


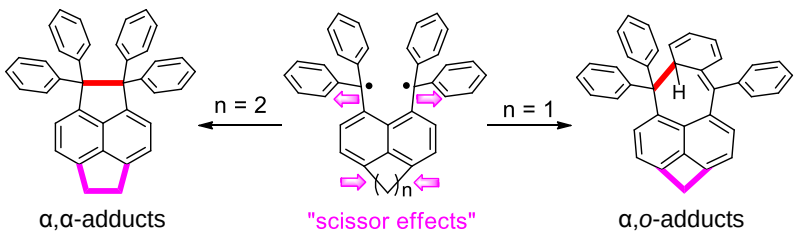
Figure 0-5. Considerable variation of bond length found in pseudopolymorphs.

In Chapter 2, the preparation of the world-record setting compounds with the longest C-C covalent bond was described. The newly designed HPEs framed in the 1*H*-benzo[*cd*]indol-2-one skeleton were prepared (Scheme 0-3). From their X-ray structure analyses at various temperatures for these compounds, it has been found that the C-C bond are greatly elongated by application of heat. *N*-*p*-fluorobenzyl derivative has the extraordinary C-C bond with the world-record bond length, which is beyond the value for the non-bond C…C contact of 1.80 Å. Thus, ever reported, there is no longer the untouched blank area between “bond” and “non-bond”.



Scheme 0-3. Preparation of HPEs with a 1*H*-Benzo[*cd*]indol-2-one Skeleton.

In Chapter 3, the generation of the missing isomer of HPE was described. The author expected that it would be able to obtain the missing isomer of HPE, namely the α,*o*-isomer, by suppressing both of the α,*p*- and α,α-coupling pathways. Actually, these pathways were suppressed by adopting “arylenediyl approach” and "scissor effects". By attaching an annulated cyclobutane ring at the opposite *peri*-position of the naphthalene-1,8-diyl core, the distance between the C_α carbon atoms was elongated beyond the limit of σ-bond formation through "scissor effects". As a result, the author has succeeded in generating the α,*o*-adducts for the first time after the discovery of triphenylmethyl by Gomberg in 1900 (Scheme 0-4).



Scheme 0-4. Suppression of α,α-coupling by “Scissor effects”.

In Chapter 4, the author’s knowledge on the longer C-C bond was applied to realize a longer C-O bond. The author expected that the elongation of a C-O bond would be made possible by application of "scissor effects" for a 2*H*-naphtho[1,8-*bc*]furan skeleton (Figure 0-6). X-ray analyses of these compounds revealed that the derivatives fused with a five-membered ring at the *peri*-position of naphthalene have a longer C-O bond than non-bridge compound due to the “Scissor effects”.

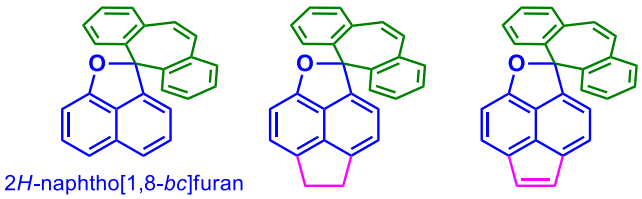


Figure 0-6. Naphtho[1,8-*bc*]furan derivatives synthesized in this chapter.

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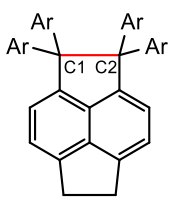
Chapter 1

Preparation of Unsymmetrical Substituted 1,1,2,2-Tetraarylpyracene by a Flow Microreactor Method : Substituent Effects on the Ultralong C-C Bond Length

1-1. Introduction

A series of symmetrically substituted 1,1,2,2-tetraarylpyracenes **1** were prepared by Takeda, which were proven to have an extremely long C-C bond, and the considerable variation in the C1-C2 bond length (*d*) comes with the substituents at the 4-position of aryl groups (Figure 1-1).[1] The bond lengths in those compounds do not correlate with the radical stabilizing/destabilizing parameter $\sigma^{\bullet}$[2] which represents the thermodynamic stability of the benzyl radical with substituents. This result gives clear evidence for the absence of diradical species which is generated by bond cleavage. Although the major factor to expand the C1-C2 bond should be the steric repulsion among the four aryl groups at C1 and C2, it is unlikely that the direct spatial interaction between the substituents at the 4-position produces the difference in steric congestion. Thus, it is still unclear how the substituent on the aryl rings, which does not directly affect the increase or decrease of steric hindrance, causes variation [Δd : 0.044 Å, 1.761(4)-1.717(4) Å] on *d*. Thus, in this chapter, the author has planned to shed light on the ambiguous substituent effects on expanding the prestrained bond. Unsymmetrically substituted derivatives of **1** were designed in anticipation that *d* in the unsymmetric compounds would exhibit the intermediary value of those in two symmetric counterparts if the electronic effects of the substituents are working as the major factor in changing *d*.



1

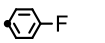
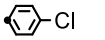
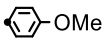
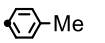
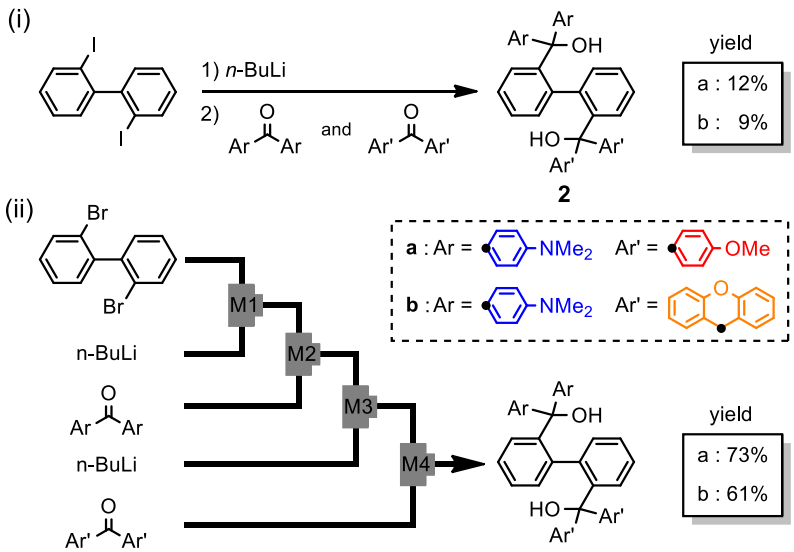
Ar	$\sigma^{\bullet}$	*d* (Å)
	-0.011	1.761(4)
	0.000	1.754(2)
	0.017	1.730(2)
	0.034	1.726(3)
	0.015	1.717(4)

Figure 1-1. Comparison of bond length in symmetrically substituted tetraarylpyracenes.

Symmetrically substituted derivatives **1** are available from the dicationic precursor, which in turn were obtained from symmetric pyrans with the same aryl groups on C1 and C2. As shown in the previous work,[1] they were easily obtained from 5,6-dibromoacenaphthene by the successive treatment with *n*-BuLi (2.5 equiv.) and the diarylketone (2.5 equiv.) followed by treatment with TFA,

and isolated in respective yields of 52-80% with no need of chromatography for separation.

However, this would not be the case of unsymmetric tetraarylpyranes with two different aryl group on each of C1 and C2 as suggested by the previous study on “dynamic redox system” in the author’s laboratory. The problem in the synthesis is difficulty to prepare unsymmetric compounds under the conventional macro batch conditions because selective monolithiation of arylenedihlide is ineffective. In the macro batch conditions, Nishida found that the desired unsymmetric diols were obtained as a mixture containing two symmetric diols and other byproducts, however troublesome chromatographic separation only afforded pure **2a** and **2b** in respective yield of 12% and 9% (Scheme 1-1 (i)).[3] Further attempts to improve the yield were unfruitful even when dihalobiphenyl was treated sequentially with *n*-BuLi (1.0 equiv.), $Ar_2C{=}O$ (1.0 equiv.), *n*-BuLi (1.0 equiv.), and $Ar'_2C{=}O$ (1.0 equiv.).

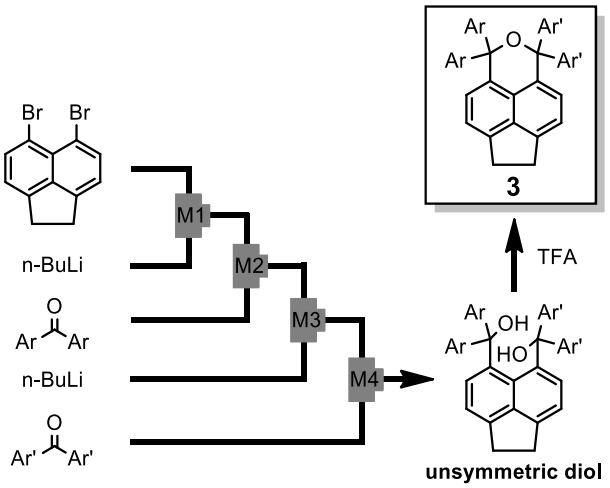


Scheme 1-1. Preparation of unsymmetric compounds (i) The macro batch conditions, (ii) The flow microreactor conditions

On the other hand, Prof. Jun-ichi Yoshida at Kyoto University recently have demonstrated that monolithiation of arylenedibromide can be successfully conducted under the flow microreactor conditions.[4] By taking advantage of this process, Dr. Yusuke Ishigaki succeeded in the sequential introduction of two diarylmethanol units on the 2,2’-positions of dibromobiphenyl by reaction integration using flow microreactors.[5] He obtained pure **2a** and **2b** in respective yield of 72% and 61% (Scheme 1-1 (ii)).[6]

1-2. Preparation of Unsymmetrically Substituted Pyrans 3a-3g

The author expected that the similar protocol could be applied not only to the biphenyl skeleton but also to the acenaphthene skeleton. Even under the careful execution by sequential addition of *n*-BuLi (1.0 equiv.), $Ar_2C{=}O$ (1.0 equiv.), *n*-BuLi (1.2 equiv.), and $Ar'_2C{=}O$ (1.2 equiv.), the yield of **3a** was only 49% after chromatographic separation. On the other hand, the author found that the flow method works effectively in selective production of unsymmetric pyrans **3a**-**3g**. Thus, 0.1 M 5,6-dibromoacenaphthene in THF (flow rate 6.0 mL/min) was reacted with 0.5 M *n*-BuLi in hexane (1.2 mL/min) at 24 °C to generate 5-bromo-6-lithioacenaphthene, which was sequentially reacted with 4,4'-dimethoxybenzophenone (0.2 M in THF, 3.0 mL/min), *n*-BuLi (0.5 M in hexane, 1.44 mL/min), and 4,4'-dimethylbenzophenone (0.2 M in THF, 3.6 mL/min). After treatment with TFA, **3a** was obtained as a sole product without contamination of the symmetric pyracenes and isolated in 68% yield. Similarly, by using a series of diarylketones as an electrophile, pyrans **3b**-**3g** were also obtained in 51-71% yields (Scheme 1-2), thus demonstrating the validity of a flow microreactor synthesis in this series of compounds.

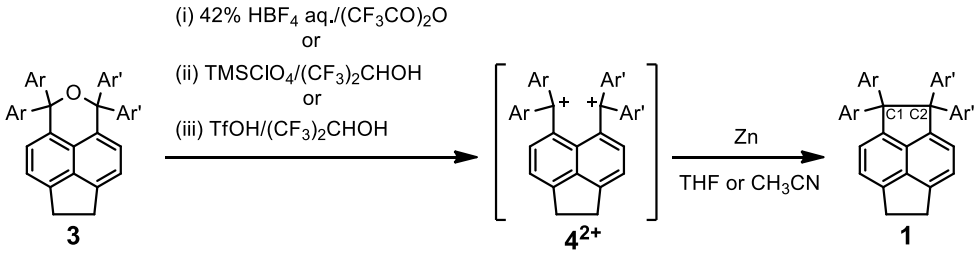


Substituents			yield of **3**
a : Ar = OMe	Ar' = Me		**68%**
b : Ar = OMe	Ar' =		**69%**
c : Ar = OMe	Ar' = Cl		**71%**
d : Ar = OMe	Ar' = F		**56%**
e : Ar = Me	Ar' = F		**62%**
f : Ar =	Ar' = F		**55%**
g : Ar = Cl	Ar' = F		**51%**

Scheme 1-2. An integrated flow microreactor system for the sequential introduction of two different diarylmethanol units at the 5,6-position of acenaphthene.

1-3. Preparation of Unsymmetrically Substituted Pyracenes 1a-1g

As shown in the previous study of symmetric analogues, the largely congested molecules **1a**-**1g** would be obtained from the less hindered dicationic precursors **4a**$^{2+}$-**4g**$^{2+}$ upon two-electron reduction,[7] which in turn would be generated from pyrans **3a**-**3g** under the acidic dehydrating conditions. With pyrans **3a**-**3g** in hand, new members of tetraarylpyracenes **1a**-**1g** were prepared according to Scheme 1-3. In the case of **1a** with four electron-donating aryl groups, the precursor dication **4a**$^{2+}$ was generated by using 42% HBF_4 aq./$(CF_3CO)_2O$ and isolated as stable BF_4^- salts. Dications **4b**$^{2+}$-**4d**$^{2+}$ generated with $TMSClO_4$[8] were not isolated due to expected explosive nature but directly reduced with Zn dust to furnish **1b**-**1d**. The stronger acidic treatment [TfOH/$(CF_3)_2CHOH$] is necessary on **3e**-**3g** for dehydration. Despite the different acidic conditions applied on **3a**-**3g**, the target compounds **1a**-**1g** were isolated in high yields (y. 72%, 81%, 75%, 86%, 99%, 91% and 95%, respectively, based on **3a**-**3g**) as stable pale yellow crystalline materials.



Substituents	condition	yield of **1**
a : Ar = OMe Ar' = Me	(i)	72%
b : Ar = OMe Ar' =	(ii)	81%
c : Ar = OMe Ar' = Cl	(ii)	75%
d : Ar = OMe Ar' = F	(ii)	86%
e : Ar = Me Ar' = F	(iii)	99%
f : Ar = Ar' = F	(iii)	91%
g : Ar = Cl Ar' = F	(iii)	95%

Scheme 1-3. Preparation of unsymmetrically substituted pyracenes **1a**-**1g**

1-4. X-ray Structures of Pyracenes 1a-1c, 1e-1g

By the vapor diffusion method (CH_2Cl_2-hexane or $CHCl_3$-hexane), single-crystalline specimen of high quality of tetraarylpyracenes **1a-1g** and **1b**·CH_2Cl_2 (1:1 solvate) were obtained for precise determination of the *d* value. Low-temperature X-ray analyses at 153 K showed that all of them have an extremely long C1-C2 bond with a greater bond length greater than 1.70 Å (Table 1-1). Only the *d* value with a large estimated standard deviation (esd) was obtained [1.712(8) Å] for **1c**. Probably due to the similar spatial requirement of MeO and Cl groups, two kinds of aryls groups occupy the same positions in the crystals of unsolvated **1c** which is not included significantly in the following discussion. No structural disorder was found except **1c**. Thus the bond lengths were determined with high accuracy [esd : 0.002-0.004 Å]. As shown in Figure 1-2, the ORTEP drawings exhibit no anomalies in the thermal ellipsoids of the long C1-C2 bond or the electron density maps for all cases.

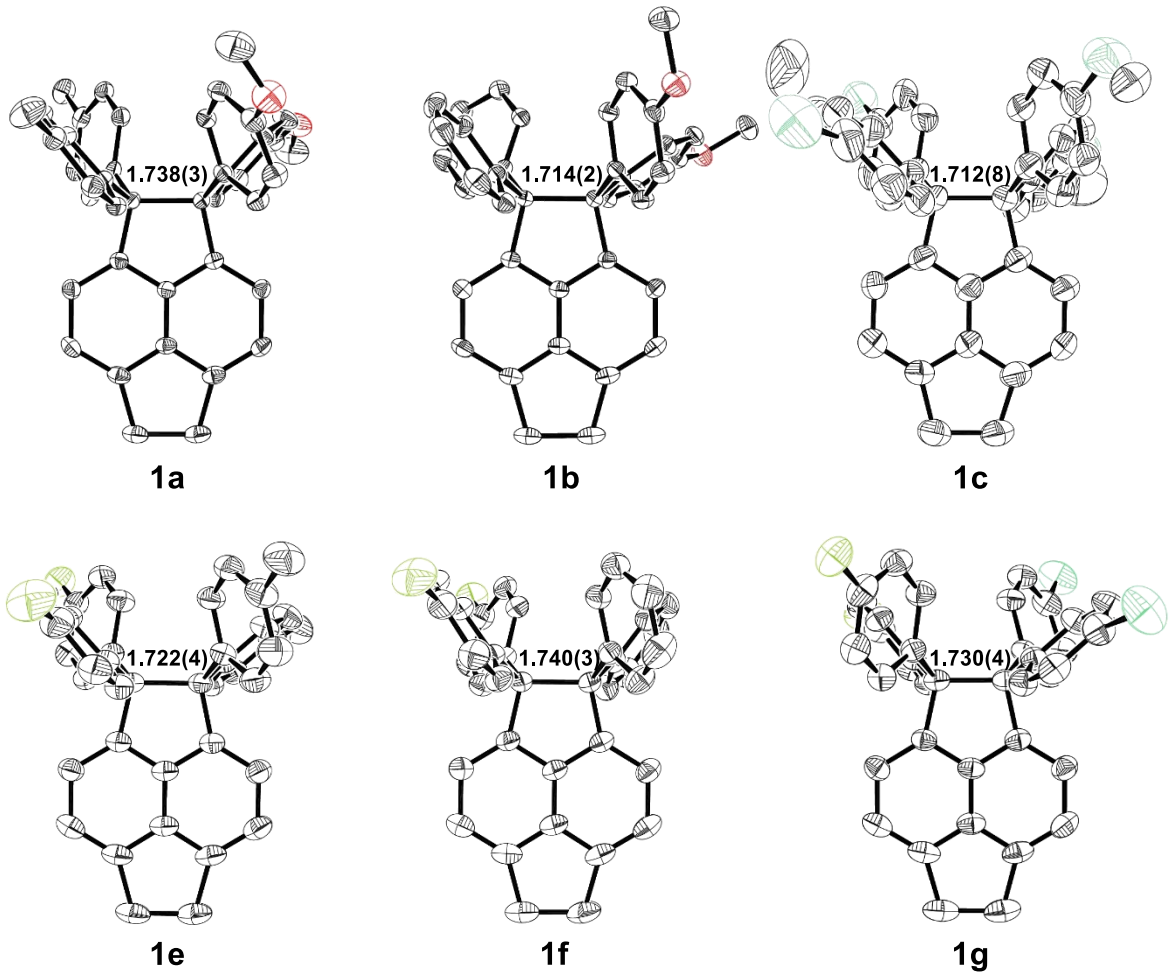
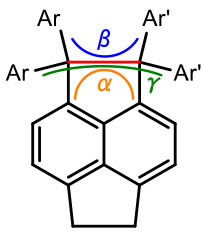


Figure 1-2. ORTEP drawings of tetraarylpyracenes **1a-1c**, **1e-1g**

The significant finding is that the *d* value in the unsymmetric derivative **1a** (Ar = 4-methoxyphenyl, Ar' = 4-methylphenyl) [1.738(3) Å] is greater than either of those in two symmetric counterparts: **1MeO$_4$** (Ar = Ar' = 4-methoxyphenyl) [1.726(3) Å] and **1Me$_4$** (Ar = Ar' = 4-methylphenyl) [1.717(4) Å]. Furthermore, in another unsymmetric derivative **1b** (Ar = 4-methoxyphenyl, Ar' = phenyl), the bond length [1.714(2) Å] is smaller than in both of the corresponding symmetric counterparts: **1MeO$_4$** (Ar = Ar' = 4-methoxyphenyl) [1.726(3) Å] and **1H$_4$** (Ar = Ar' = phenyl) [1.754(2) Å]. Similarly, in another family with 4-fluorophenyl groups, the *d* values in the unsymmetric derivative are quite different from the arranged values of those in the corresponding symmetric derivatives. Therefore, it can be concluded that the electronic nature of substituents is not the major determinant of the *d* values in the crystals of **1** despite the fact that the large variation of bond length [Δ*d* : 0.047 Å, 1.761(4)-1.714(2) Å], which cannot be ascribed to the intramolecular factors, was observed for a series of **1** with different aryl groups.

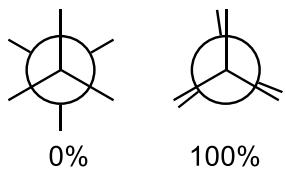
Table 1-1. Structural date of **1a**-**1c**, **1d**-**1g** determined by X-ray analyses.

	substituents Ar	substituents Ar'	C1-C2 bond length *d* (Å)	torsion angles(°) α	β	γ	sum of torsions Σ(°)	eclipseness χ (%)
	F	F	1.761(4)	3.1(2)	2.3(3)	0.6(3)	6.0(8)	96.7
			1.754(2)	2.27(15)	2.69(18)	2.69(18)	7.65(51)	95.8
1f	F		1.740(3)	2.36(16)	2.58(14)	3.3(2)	8.24(50)	95.4
1a	OMe	Me	1.738(3)	0.87(17)	5.87(17)	6.17(17)	12.91(51)	92.8
	Cl	Cl	1.730(2)	0.98(19)	6.31(18)	6.55(18)	13.87(55)	92.3
1g	F	Cl	1.730(4)	1.1(3)	9.1(3)	9.2(3)	19.4(9)	89.2
	OMe	OMe	1.726(3)	1.04(18)	8.7(2)	9.4(2)	19.14(58)	89.4
1e	F	Me	1.722(4)	0.74(19)	8.86(19)	8.91(19)	18.51(57)	89.7
	Me	Me	1.717(4)	0.6(3)	7.6(3)	8.3(3)	16.5(9)	90.8
1b	OMe		1.714(2)	1.32(13)	5.05(13)	9.4(3)	15.77(56)	91.2
(**1c**	OMe	Cl	1.712(8)	1.3(5)	9.4(7)	9.8(7)	20.5(19)	88.6)



$$\chi\,(\%) = \left(1 - \frac{\Sigma}{180}\right) \times 100$$

Σ : sum of torsions



On the other hand, the *d* values rather seem to exhibit a monotonic correlation with the eclipsing degree (χ) of C1-C2 (Figure 1-3), showing that the *d* value becomes greater by larger steric repulsion among aryl groups as the C1-C2 bond becomes closer to the perfect eclipsed conformation (χ = 100). The eclipsing degree (χ) was calculated from the sum of three torsion angles around C1-C2 unit (Table 1-1). The χ value in **1** is difficult to predict. It is still ambiguous what factor of the substituents determines the preference for the more or less eclipsed conformation since it is largely affected by the intermolecular contacts among aryl groups in a certain crystal packing.

Another important finding is that the *d* value of **1b** in the unsolvated crystal [1.714(2) Å] and that in CH_2Cl_2 solvate [1.739(4) Å] differ considerably even though there are no special interaction with the solvent and aryls groups in **1b**·CH_2Cl_2, showing that the expansion of C1-C2 (Δ*d* : 0.025 Å) can be induced only by the small energy supplied from the different crystal packing. Due to the small BDE for the extremely long C1-C2, change in BDE upon further expansion of the prestrained bond would be only marginal, which results in wide variation of *d* in response to the small perturbation ("bond expandability"). Because of that newly found idea of "expandability", the author got interested in **1d** in anticipation of variation of bond length in pseudopolymorphs. The author made a lot of efforts to obtain a single crystalline sample containing a variety of solvent. The results on these crystals will be discussed in the next section.

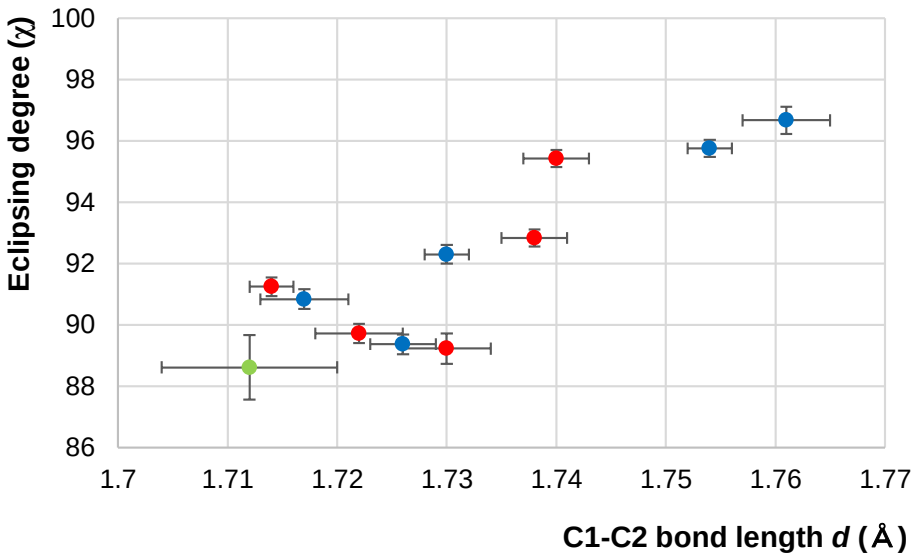


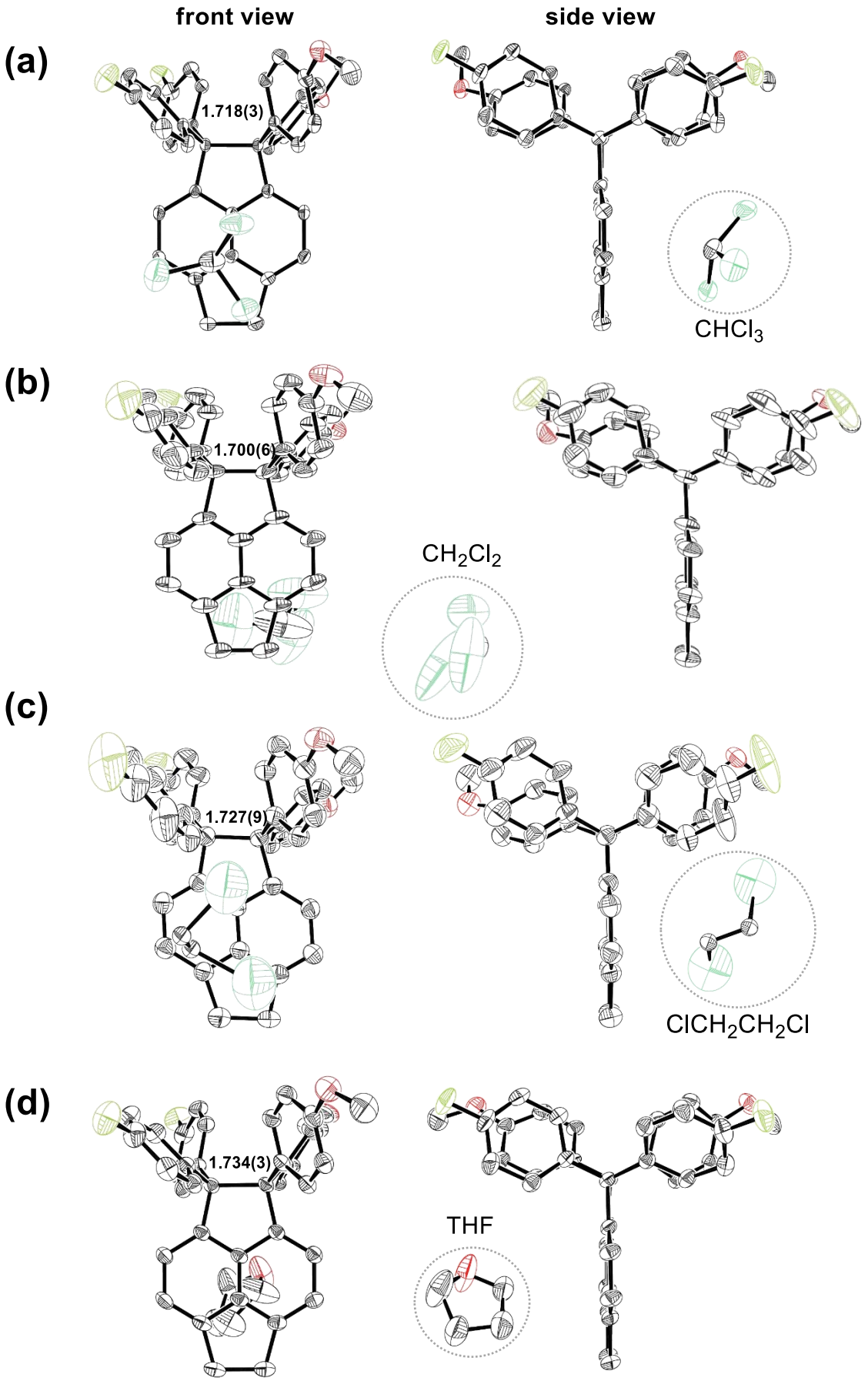
Figure 1-3. Scattering plot of *d* versus the eclipsing degree (χ) of C1-C2 for symmetrically substituted pyracenes and **1a**-**1c**, **1e**-**1g** determined by X-ray analyses. Error bar represents estimated standard deviation (esd). Blue point : symmetrically substituted compounds. Red point : **1a**, **1b**, **1e**-**1g**. Green point : **1c**

1-5. X-ray Structures of Pseudopolymorphs of 1d

To confirm the idea that the crystallographically determined *d* value is largely affected by the intermolecular perturbation (e.g. crystal packing force), the author planned to conduct X-ray analyses of the polymorphs/pseudopolymorphs of a certain derivative of **1**, in which only the intermolecular factors are responsible to account for the Δ*d* value, if observed. As a result, different from **1a**, **1c**, **1e**-**1g** forming unsolvated crystals, **1d** was crystallized but with including solvent molecules in the unit cell [**1d**·$CHCl_3$, **1d**·CH_2Cl_2 and **1d**·$ClCH_2CH_2Cl$; isomorphous, $P2_1/c$, $Z = 4$]. Not only halogenated solvents but also ether and hexane were found to be incorporated in the crystal lattice [(**1d**)$_2$·ether and (**1d**)$_2$·hexane; isomorphous, *C*c, $Z = 4$, two independent molecules of **1d**]. The **1d**·THF solvate crystal adopts another space group [$P\bar{1}$, $Z = 2$], whose packing arrangement is similar to (**1d**)$_2$·CCl_4·(hexane)$_{0.5}$ [$P\bar{1}$, $Z = 2$, two independent molecules of **1d**; hexane on the center of symmetry] but not to others (Table 1-2). Differences in the molecular ratio and the space group indicate that the inclusion lattices formed by **1d** in crystal have several variations. Despite facile formation of pseudopolymorphs as above, single crystals of unsolvated **1d** were not obtained.

Table 1-2. Crystal date of peseudopolymorphs of **1d** and the bond length determined by X-ray analyses.

Solvent	$CHCl_3$	CH_2Cl_2	$ClCH_2CH_2Cl$	THF	CCl_4 & hexane	ether	hexane
Ratio (**1d** : solvent)	1 : 1	1 : 1	1 : 1	1 : 1	2 : 1 (CCl_4) 2 : 0.5 (hexane)	2 : 1	2 : 1
C1-C2 bond length (Å)	1.718(3)	1.700(6)	1.727(9)	1.734(3)	1.735(7) 1.718(7)	1.732(7) 1.706(7)	1.739(6) 1.727(6)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Cc	Cc
a (Å)	12.624(2)	12.562(11)	12.030(8)	11.819(4)	11.976(5)	19.255(9)	19.157(11)
b (Å)	22.527(4)	22.28(2)	21.49(2)	12.132(3)	12.469(4)	15.420(7)	15.524(8)
c (Å)	12.030(2)	12.062(10)	12.714(9)	12.210(4)	24.139(9)	22.907(11)	23.456(13)
α (°)	90	90	90	78.759(12)	71.90(3)	90	90
β (°)	102.014(2)	102.39(2)	102.69(2)	83.352(12)	79.04(3)	109.521(7)	108.802(6)
γ (°)	90	90	90	75.349(10)	78.22(3)	90	90
V (Å^3)	3346.1(10)	3297(5)	3206(4)	1657.3(8)	3323(3)	6410(5)	6603(6)
Z	4	4	4	2	2	4	4


front view
side view
(a)
1.718(3)
CHCl3
(b)
1.700(6)
CH2Cl2
(c)
1.727(9)
ClCH2CH2Cl
(d)
1.734(3)
THF

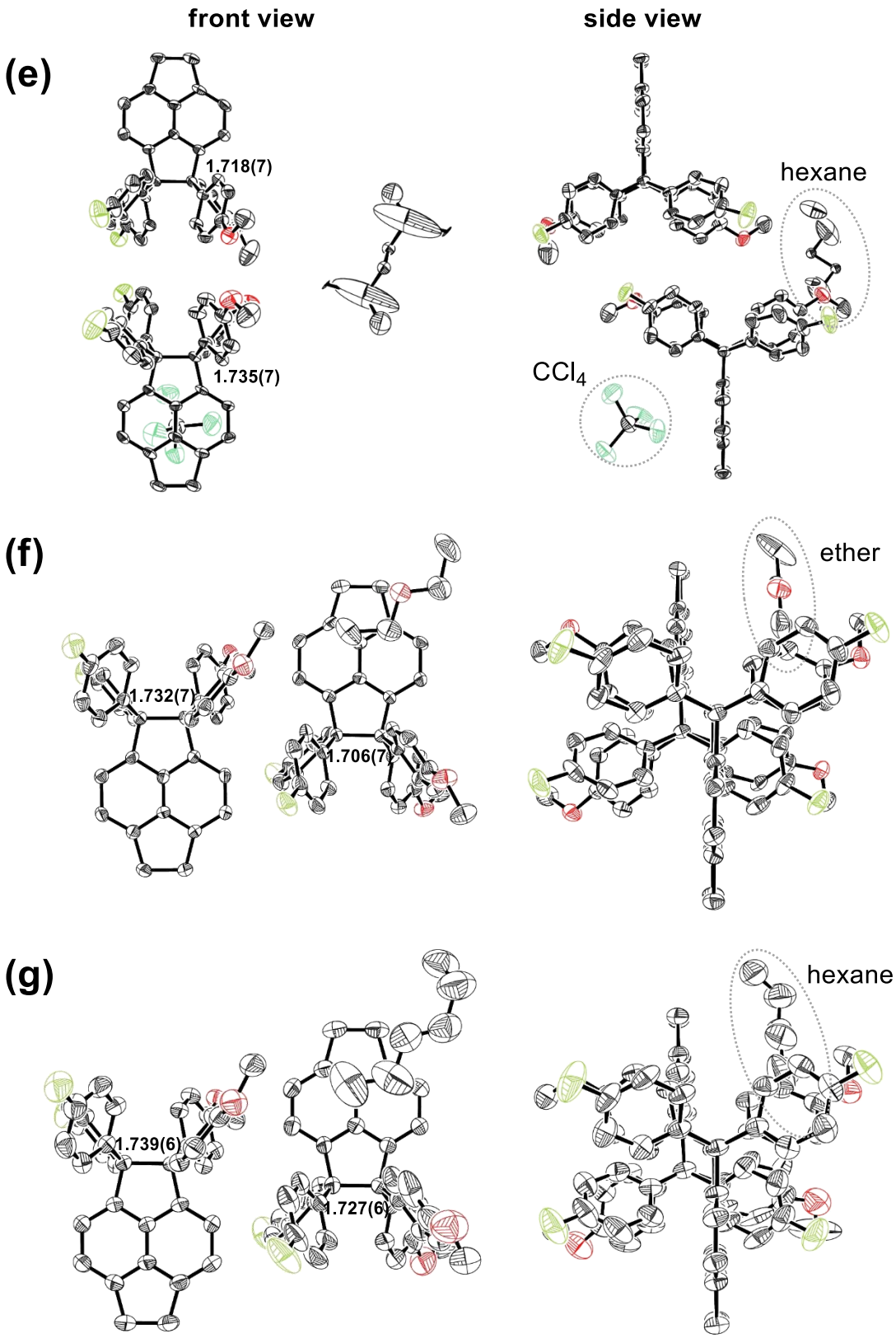


Figure 1-4. ORTEP drawings of pseudopolymorphs of **1d** in (a) $CHCl_3$, (b) CH_2Cl_2, (c) $ClCH_2CH_2Cl$, (d) THF, (e) CCl_4 & hexane, (f) ether, and (g) hexane solvate crystals. One chlorine atom in (b) suffers from positional disorder.

In accord with the assumption of "bond expandability" that the prestrained bond can be elongated/shortened very easily, structural refinement of the above seven pseudopolymorphs of **1d** has revealed a considerable variation of C1-C2 bond length [Δd : 0.039 Å, 1.739(6)-1.700(6)] although there are no direct/short contacts between solvent molecules and the C1/C2 atom of **1d**. The four crystals including the solvent molecule in a 1:1 ratio (THF, $ClCH_2CH_2Cl$, $CHCl_3$, CH_2Cl_2) have the *d* value of 1.734(3), 1.727(9), 1.718(3), and 1.700(6) Å, respectively (Figure 1-4). It is interesting to note that $CHCl_3$ solvate, CH_2Cl_2 solvate and $ClCH_2CH_2Cl$ solvate are isomorphous, yet the packing force afforded different degree of perturbation on **1d** to adopt different *d* values. This is also the case for another isomorphs of (**1d**)$_2$・ether [*d* : 1.732(7), 1.706(7) Å] and (**1d**)$_2$・hexane [1.739(6), 1.727(6) Å] (Table 2-2). Moreover, the two crystallographically independent molecules in (**1d**)$_2$・ether have the quite different bond lengths (Δd : 0.026 Å) despite being packed in the same crystal.

All the above experimental results demonstrate high susceptibility of the *d* value to the intermolecular perturbation. In general, the covalent bond length is the parameter with a high uniformity since the slight change in length causes considerable loss of BDE. In the case of prestrained bond with a much smaller BDE, further expansion/contraction of the bond would occur with only slight loss of BDE, which accounts for the "expandability" in the ultralong covalent bond such as the C1-C2 bond of **1**.

1-6. Theoretical Rationale for the “Expandability”

To obtain theoretical support for the "expandability", structural optimization (B3LYP/6-31G*) of tetraphenylpyracene (**1H$_4$**: Ar = Ar’ = phenyl) was conducted under the full-optimization and constrained conditions. The *d* value in the fully optimized **1H$_4$** was estimated to be 1.763 Å, which is close to the experimental value [1.754(2) Å]. When the geometrical optimization processes were reconducted by constraining *d* at the 13 different values between 1.700 - 1.820 Å, the scattering plot of the relative energy vs *d* suggests a parabolic relationship (Figure 1-5), and the characteristic feature is the very shallow potential curve with the energy difference of 0.35 kcal/mol. Such a small amount of energy loss upon increasing/decreasing the *d* value from that of the optimized structure can be compensated easily by the different crystal packing force among polymorphs/pseudopolymorphs,[9] which rationalizes the observation of a variety of *d* values in the pseudopolymorphs of **1d**.

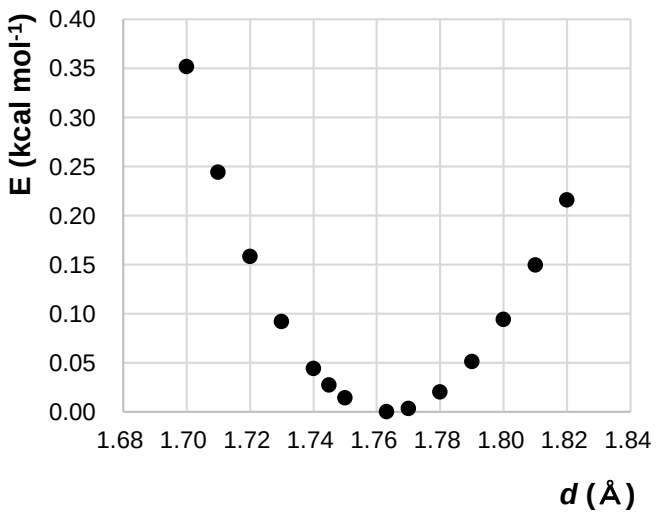


Figure 1-5. Scattering plot of relative energy (E) of tetraphenylpyracene vs *d* estimated by DFT calculations (B3LYP/6-31G*).

1-7. Raman Spectroscopy

For further validation of the *d* value determined crystallographically on the ultralong C-C bonds, Raman spectroscopy which gives the direct information of the force constant of the bond was applied on the crystalline samples of **1f** (Ar = 4-fluorophenyl, Ar' = phenyl) and tetrafluoro (**1F4**) derivatives. The Raman frequencies for the stretching vibration of the long C1-C2 bond were compared with that of unsubstituted compound **1H4** studied before.[1] The values are 643 (**1f**), 640 (**1H4**), and 638 cm^{-1} (**1F4**) (Figure 1-6), which are largely shifted compared with that of ethane itself (995 cm^{-1}). Thus, the C1-C2 bond in **1** has a much smaller force constant than the ordinary C-C bonds. The absorption with the highest intensity (expt. 640 cm^{-1}) in **1H4** corresponds to the normal mode having the largest amplitude along the trajectory of the stretching vibration as verified by DFT calculation (calcd. 650 cm^{-1}). Although the difference in the Raman frequency is not large among **1f**, **1H4**, and **1F4**, the observed values decrease in the increasing order of the experimental *d* values [1.740(3), 1.754(2), 1.761(4) Å, respectively], suggesting that the crystallographically determined bond lengths on the ultralong C-C bond are actually related to the properties of the C-C bond in question (e.g. stretching vibration / force constant).

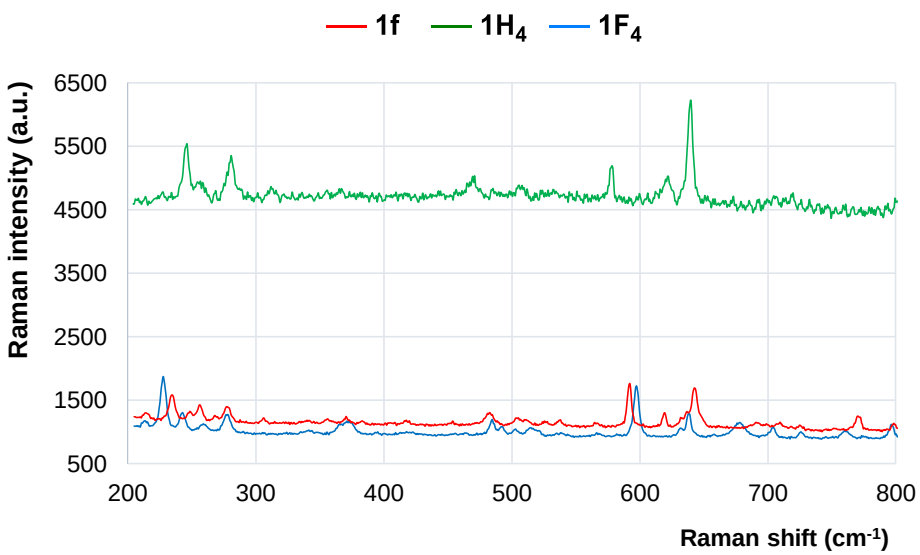


Figure 1-6. Raman spectra of **1f**, **1H4** and **1F4**

1-8. Conclusion

Based on space integration using a flow microreactor system, unsymmetrically substituted pyracenes **1a**-**1g** with an extremely long C-C bond [1.714(2)-1.739(4) Å] are readily accessible, whose structures demonstrate nonadditive substituent effects on expanding the polyarylated C1-C2 bond in crystal. The bond lengths rather exhibit correlation with the eclipsing degree of the C_{sp3}-C_{sp3} bond, which is more affected by the intermolecular factors such as crystal packing. Moreover, the low-temperature X-ray analyses on the seven pseudopolymorphs (solvate crystals) of **1d** revealed that the C1-C2 bond length of the highly congested unsymmetrically substituted pyracenes can adopt quite different values [1.739(6) - 1.700(6) Å]. Such an unusual observation indicates that the ultralong covalent bond is endowed with "expandability", thus the prestrained bond can be elongated/shortened very easily accompanied by only a minute change in energy, which can be compensated by intermolecular perturbation in crystal.

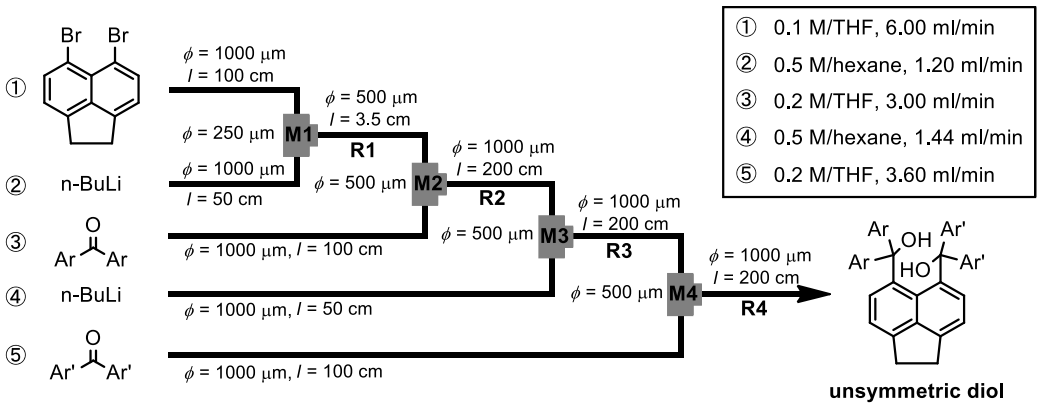
Therefore, the expandability of the extremely long C-C bond would be the key to future developing novel function (e.g. chromism), since the enough energy for changing the bond length would be easily supplied by external stimuli. At the same time, by further increment of steric repulsion with keeping the eclipsed conformation, there is high possibility to discover much longer C-C bond, whose length is greater than the value for the shortest nonbonded C⋯C contact (1.80 Å).

Experimental Section

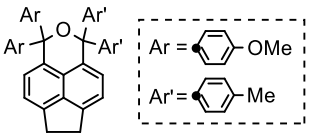
General Procedures

All reactions were carried out under an argon atmosphere unless otherwise indicated. All commercially available compounds were used without further purification. Dry MeCN was obtained by distillation from CaH_2 prior to use. Column chromatography was performed on silica gel I-6-40 (YMC) of particle size 40-63 μm and aluminium oxide 90 standardized (Merck 63-200 μm). ^{1}H and ^{13}C NMR spectra were recorded on JOEL AL300 (^{1}H/300MHz and ^{13}C/75MHz) and BRUKER Ascend™ 400 (^{13}C/100MHz) spectrometers, respectively. IR spectra were taken on a JEOL JIR-WINSPEC100FT/IR spectrophotometer. IR spectra were measured as a KBr pellet on a JEOL JIR-WINSPEC100FT/IR spectrophotometer. Mass spectra were recorded on JMS-AX500, JMS-SX102A, or JEOL JMS-T100GCV spectrometers in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Melting points were measures on a Yamato MP-21 melting point apparatus and reported uncorrected. Element analyses were taken on a J-Science micro corder JM10 or a Yanaco CHN corder MT-6 at the Center for Instrumental Analysis of Hokkaido University. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer.

Scheme 1-4. An integrated flow microreactor system for the sequential introduction of two different diarylmethanol units at the 5,6-position of acenaphthene



Preparation of 1,1-Bis(4-methoxyphenyl)-3,3-bis(4-methylphenyl)-1,3,6,7-tetrahydro indeno[6,7,1-*def*]isochromene 3a



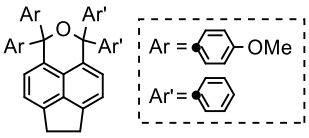
3a

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bath (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethoxybenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-dimethylbenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 180 s and was stirred for 3 h at 25 °C. Then the mixture was treated with BuLi (1.62 M) in hexane (9.0 mL) to consume excess ketones at -78°C. The resultant solution was further stirred for 2 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (30 mL), and trifluoroacetic acid (70 μL, 0.94 mmol) was added at 25 °C, and then the mixture was stirred for 14 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **3a** (722 mg, 68%) as a yellow solid.

M.p. 249-251 °C ; ^{1}H NMR ($CDCl_3$) δ 7.17 (d, J = 7.1 Hz, 2H), 7.02-6.93 (m, 8H), 6.88-6.78 (m, 6H), 6.52 (d, J = 8.8 Hz, 4H), 3.72 (s, 6H), 3.43 (s, 4H), 2.23 (s, 6H) ; IR (KBr) 3025, 2995, 2907, 2832, 1608, 1587, 1508, 1464, 1304, 1249, 1181, 1173, 1040, 1026, 1009, 847, 835, 813, 783, 576 cm^{-1} ; LR-MS (FD) *m/z* (%): 588 (M^+, bp), 589 (48), 590 (14) ; Anal. Calcd (%) for $C_{42}H_{36}O_3$: C 85.68, H 6.16, Found : C 85.53, H 6.32.

Preparation of 1,1-Bis(4-methoxyphenyl)-3,3-bisphenyl-1,3,6,7-tetrahydroindeno [6,7,1-*def*]isochromene 3b



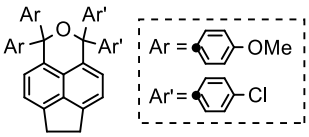
3b

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethoxybenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of benzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 210 s and was stirred for 4 h at 23 °C. Then the mixture was treated with BuLi (1.62 M) in hexane (10.0 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 1.5 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (30 mL), and trifluoroacetic acid (100 μL, 1.35 mmol) was added at 23 °C, and then the mixture was stirred for 17 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **3b** (814 mg, 69%) as a pale yellow solid.

M.p. 239-241 °C ; ^{1}H NMR ($CDCl_3$) δ 7.18 (d, J = 7.2 Hz, 2H), 7.12-6.97 (m, 14H), 6.87 (d, J = 7.2 Hz, 1H), 6.84 (d, J = 7.2 Hz, 1H), 6.53 (d, J = 8.8 Hz, 4H), 3.72 (s, 6H), 3.43 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 158.14, 146.89, 144.26, 144.23, 138.85, 138.54, 133.59, 132.67, 130.66, 129.38, 127.33, 127.05, 126.89, 126.46, 124.42, 118.65, 112.44, 84.18, 83.68, 55.15, 30.54 ; IR (KBr) 3034, 3003, 2930, 2832, 1607, 1589, 1508, 1492, 1463, 1443, 1300, 1248, 1173, 1038, 1015, 1006, 1001, 845, 832, 824, 762, 734, 700, 589 cm^{-1} ; LR-MS (FD) *m/z* (%): 560 (M^+, bp), 561 (45), 562 (12) ; HR-MS (FD) Calcd. for $C_{40}H_{32}O_3$: 560.2351, Found : 560.2325.

Preparation of 1,1-Bis(4-chlorophenyl)-3,3-bis(4-methoxyphenyl)-1,3,6,7-tetrahydro indeno[6,7,1-*def*]isochromene 3c



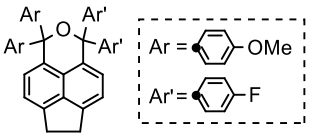
3c

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethoxybenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-dichlorobenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 240 s and was stirred for 3.5 h at 23 °C. Then the mixture was treated with BuLi (1.62 M) in hexane (12.0 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 1.5 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (30 mL), and trifluoroacetic acid (100 μL, 1.35 mmol) was added at 23 °C, and then the mixture was stirred for 14 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **3c** (1.07 g, 71%) as a pale yellow solid.

M.p. 222-224 °C ; ^{1}H NMR ($CDCl_3$) δ 7.19 (d, J = 7.3 Hz, 2H), 7.00 (s, 8H), 6.95 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 7.3 Hz, 1H), 6.81 (d, J = 7.3 Hz, 1H), 6.56 (d, J = 8.8 Hz, 4H), 3.75 (s, 6H), 3.44 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 158.46, 145.09, 144.88, 144.43, 138.57, 138.40, 133.29, 132.55, 131.73, 130.62, 127.27, 127.09, 127.01, 124.23, 118.92, 118.67, 112.52, 83.96, 83.24, 55.22, 30.52 ; IR (KBr) 3033, 2930, 2835, 1608, 1586, 1508, 1488, 1464, 1441, 1396, 1306, 1249, 1178, 1092, 1038, 1015, 1000, 831, 812, 747, 609, 525 cm^{-1} ; LR-MS (FD) m/z (%): 628 (M^+, bp), 629 (48), 630 (76), 631 (36), 632 (19) ; HR-MS (FD) Calcd. for $C_{40}H_{30}Cl_2O_3$: 628.1572, Found : 628.1564.

Preparation of 1,1-Bis(4-fluorophenyl)-3,3-bis(4-methoxyphenyl)-1,3,6,7-tetrahydro indeno[6,7,1-*def*]isochromene 3d



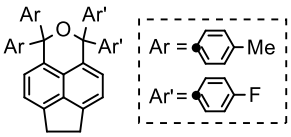
3d

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethoxybenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-difluorobenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 270 s and was stirred for 3.5 h at 24 °C. Then the mixture was treated with BuLi (1.59 M) in hexane (13.5 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 2 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (30 mL), and trifluoroacetic acid (130 μL, 1.75 mmol) was added at 23 °C, and then the mixture was stirred for 17 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 35) to give **3d** (896 mg, 56%) as a pale yellow solid.

M.p. 233-234 °C ; ^{1}H NMR ($CDCl_3$) δ 7.19 (d, J = 7.1 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 4H), 6.84 (d, J =7.2 Hz, 1H), 6.81 (d, J =7.2 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 9.0 Hz, 4H), 3.73 (s, 6H), 3.44 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 162.77, 160.32, 158.38, 144.75, 144.40, 142.55, 142.52, 138.67, 138.60, 133.37, 132.47, 131.03, 130.95, 130.63, 127.16, 127.04, 124.27, 118.90, 118.67, 114.00, 113.89, 112.57, 83.93, 83.30, 55.24, 30.58 ; IR (KBr) 3034, 2988, 2928, 2832, 1607, 1462, 1303, 1253, 1225, 1172, 1158, 1039, 1015, 1001, 836, 826, 581, 574 cm^{-1} ; LR-MS (FD) *m/z* (%): 596 (M^+, bp), 597 (50), 598 (12) ; HR-MS (FD) Calcd. for $C_{40}H_{30}F_2O_3$: 596.2163, Found : 596.2166.

Preparation of 1,1-Bis(4-fluorophenyl)-3,3-bis(4-methylphenyl)-1,3,6,7-tetrahydro indeno[6,7,1-*def*]isochromene 3e



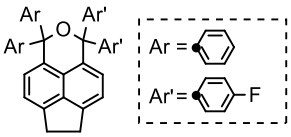
3e

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethylbenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-difluorobenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 165 s and was stirred for 4 h at 21 °C. Then the mixture was treated with BuLi (1.59 M) in hexane (9.0 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 2 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (30 mL), and trifluoroacetic acid (70 μL, 0.95 mmol) was added at 23 °C, and then the mixture was stirred for 13.5 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **3e** (475 mg, 62%) as a pale yellow solid.

M.p. 230-232 °C ; ^{1}H NMR ($CDCl_3$) δ 7.19 (d, J = 7.3 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 8.5 Hz, 4H), 6.88-6.79 (m, 6H), 6.70 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 3.44 (s, 4H), 2.25 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 162.87, 160.43, 144.74, 144.32, 143.50, 142.38, 142.35, 138.58, 136.42, 133.00, 132.49, 131.03, 130.95, 129.37, 127.83, 127.26, 126.91, 124.27, 118.93, 118.60, 113.89, 113.68, 84.23, 83.26, 30.55, 20.91 ; IR (KBr) 3030, 2921, 2870, 1603, 1505, 1227, 1159, 1004, 834, 811, 785, 574 cm^{-1} ; LR-MS (FD) m/z (%): 564 (M^+, bp), 565 (45), 566 (11) ; HR-MS (FD) Calcd. for $C_{40}H_{30}F_2O$: 564.2265, Found : 564.2266.

Preparation of 1,1-Bis(4-fluorophenyl)-3,3-bisphenyl-1,3,6,7-tetrahydroindeno[6,7,1-*def*]isochromene 3f



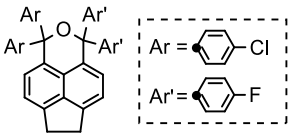
3f

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of benzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-difluorobenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 130 s and was stirred for 4 h at 22 °C. Then the mixture was treated with BuLi (1.59 M) in hexane (6.8 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 2 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (15 mL), and trifluoroacetic acid (50 μL, 0.67 mmol) was added at 20 °C, and then the mixture was stirred for 15 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 60) to give **3f** (397 mg, 55%) as a pale yellow solid.

M.p. 228-230 °C ; ^{1}H NMR ($CDCl_3$) δ 7.20 (d, J = 7.1 Hz, 2H), 7.10-7.01 (m, 14H), 6.88 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 7.1 Hz, 1H), 6.81 (d, J = 7.1 Hz, 1H), 6.70 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 3.44 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 162.82, 160.37, 146.39, 144.82, 144.52, 142.18, 142.15, 138.60, 132.40, 131.08, 131.00, 129.40, 127.52, 127.19, 127.00, 126.79, 124.21, 118.93, 118.68, 114.00, 113.79, 84.46, 83.35, 30.56 ; IR (KBr) 3058, 3030, 2924, 1604, 1505, 1444, 1227, 1157, 1011, 834, 759, 701, 582 cm^{-1} ; LR-MS (FD) m/z (%): 536 (M^+, bp), 537 (52), 538 (11) ; HR-MS (FD) Calcd. for $C_{38}H_{26}F_2O$: 536.1952, Found : 536.1963.

Preparation of 1,1-Bis(4-chlorophenyl)-3,3-bis(4-fluorophenyl)-1,3,6,7-tetrahydro indeno[6,7,1-*def*]isochromene 3g



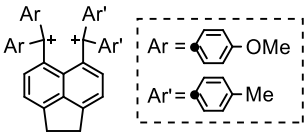
3g

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four microtube reactors (R1, R2, R3 and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μm, length l = 100 cm), P2 (ϕ = 1000 μm, l = 50 cm), P3 (ϕ = 1000 μm, l = 100 cm), P4 (ϕ = 1000 μm, l = 50 cm), P5 (ϕ = 1000 μm, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bass (24 ℃). A solution of 5,6-dibromoacenaphthene (0.10 M) in THF (flow rate = 6.00 mL min^{-1}) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min^{-1}) were introduced to M1 (ϕ = 250 μm). The resulting solution was passed through R1 (ϕ = 500 μm, l = 3.5 cm) and was mixed with a solution of 4,4'-dichlorobenzophenone (0.20 M) in THF (flow rate = 3.00 mL min^{-1}) in M2 (ϕ = 500 μm). The resulting solution was passed through R2 (ϕ = 1000 μm, l = 200 cm) and was introduced to M3 (ϕ = 500 μm) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min^{-1}). The resulting solution was passed through R3 (ϕ = 1000 μm, l = 200 cm) and was introduced to M4 (ϕ = 500 μm) where the solution was mixed with a solution of 4,4'-difluorobenzophenone (0.20 M) in THF (flow rate = 3.60 mL min^{-1}). The resulting solution was passed through R4 (ϕ = 1000 μm, l = 200 cm). After a steady state was reached, the product solution was collected for 120 s and was stirred for 4 h at 23 °C. Then the mixture was treated with BuLi (1.65 M) in hexane (6.0 mL) to consume excess ketones at -78 °C. The resultant solution was further stirred for 2 h, and was treated with water.

After diluted with water, the whole mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, solvent was concentrated under reduced pressure. The resulting residue was dissolved in dry CH_2Cl_2 (10 mL), and trifluoroacetic acid (50 μL, 0.67 mmol) was added at 24 °C, and then the mixture was stirred for 13.5 h, After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 30) to give **3g** (496 mg, 53%) as a pale yellow solid.

M.p. 245-247 °C ; ^{1}H NMR ($CDCl_3$) δ 7.21 (d, J = 7.1 Hz, 2H), 7.05-6.96 (m, 12H), 6.82 (d, J = 7.1 Hz, 1H), 6.81 (d, J = 7.1 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 3.45 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 163.06, 160.61, 145.14, 144.61, 141.85, 141.82, 138.66, 133.05, 132.08, 131.43, 131.05, 130.97, 130.81, 130.63, 127.45, 127.28, 127.23, 124.03, 118.98, 114.18, 113.97, 83.62, 83.55, 30.59 ; IR (KBr) 3044, 2925, 1603, 1505, 1505, 1489, 1397, 1227, 1157, 1092, 1015, 1007, 834, 585, 571, 523 cm^{-1} ; LR-MS (FD) *m/z* (%): 604 (M^+, bp), 605 (45), 606 (78), 607(32), 608(19) ; HR-MS (FD) Calcd. for $C_{38}H_{24}Cl_2F_2O$: 604.1172, Found : 604.1196.

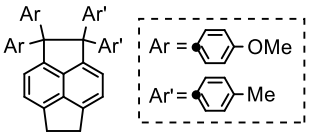
Preparation of Acenaphthene-5-yl-[bis(4-methoxyphenyl)methylium]-6-yl-[bis(4-methylphenyl)methylium] bis(tetrafluoroborate) $4a^{2+}(BF_4^-)_2$



$4a^{2+}$

To a solution of pyran **1a** (492 mg, 836 μmol) in CH_2Cl_2 (4 mL) was added trifluoroacetic anhydride (2 mL) followed by aqueous HBF_4 (42%, 500 μL, 3.32 mmol), and the mixture was stirred for 1 h at 24 °C. The mixture was diluted with dry ether, and the resulting precipitates were filtered and washed with ether to give **$4a^{2+}$**$(BF_4^-)_2$ (591 mg, 95%) as a dark red-purple solid. M.p. 115-118 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.81 (brd, *J* = 7.0 Hz, 2H), 7.77 (brd, *J* = 7.7 Hz, 2H), 7.52-7.28 (m, 8H), 7.00 (brd, *J* = 8.8 Hz, 4H), 6.78 (brs, 4H), 4.02 (brs, 6H), 3.77 (brs, 4H), 2.52 (brs, 6H) ; IR (KBr) 3029, 2932, 2849, 1589, 1578, 1508, 1494, 1450, 1438, 1363, 1316, 1279, 1184, 1164, 1124, 1084, 1062, 1010, 920, 852, 533, 521 cm^{-1}

Preparation of 1,1-Bis(4-methoxyphenyl)-2,2-bis(4-methylphenyl)pyracene 1a

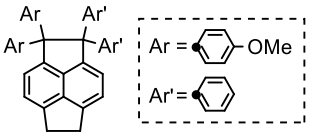


1a

Dicationic salt **$4a^{2+}$**$(BF_4^-)_2$ and Zn powder (2.05 g, 31.4 mmol) were suspended in dry THF (30 mL), and the mixture was stirred for 21 h at 21 °C. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **1a** (341 mg, 76%) as a yellow solid.

M.p. 259-260 °C ; ^{1}H NMR ($CDCl_3$) δ 7.31 (d, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 4H), 6.82 (d, *J* = 8.2 Hz, 4H), 6.69 (d, *J* = 8.2 Hz, 4H), 6.42 (d, *J* = 9.0 Hz, 4H), 3.66 (s, 6H), 3.52 (s, 4H), 2.16 (s, 6H) ; IR (KBr) 3022, 2997, 2920, 2833, 1606, 1577, 1508, 1463, 1441, 1429, 1293, 1254, 1181, 1038, 844, 831, 817, 799, 771, 588 cm^{-1} ; LR-MS (FD) *m/z* (%): 572(M^+, bp), 573 (47), 574 (12) ; Anal. Calcd (%) for $C_{42}H_{36}O_2$: C 88.08, H 6.34, Found : C 87.98, H 6.47.

Preparation of 1,1-Bis(4-methoxyphenyl)-2,2-diphenylpyracene 1b

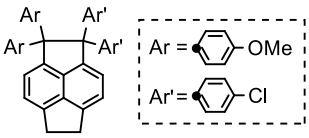


1b

To a suspension of pyran **3b** (104 mg, 185 μmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added $TMSClO_4$ in toluene (0.79 M, 0.94 mL, 743 μmol) at 26 °C. The mixture was stirred for 2 h, and then solvent was evaporated. To the residue were added Zn powder (488 mg, 7.47 mmol) and dry THF (15 mL). After stirring for 18.5 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **1b** (81.4 mg, 81%) as a white solid.

M.p. 220-221 °C ; ^{1}H NMR ($CDCl_3$) δ 7.33 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.10 (dd, *J* = 7.0, 1.8 Hz, 2H), 6.99-6.87 (m, 10H), 6.84 (d, *J* = 8.9 Hz, 4H), 6.41 (d, *J* = 8.9 Hz, 4H), 3.66 (s, 6H), 3.53 (s, 4H) ; IR (KBr) 3035, 2929, 2835, 1605, 1577, 1508, 1463, 1447, 1443, 1299, 1253, 1182, 1036, 834, 816, 754, 700, 644, 597 cm^{-1} ; LR-MS (FD) *m/z* (%): 544(M^+, bp), 545 (45), 546 (12) ; Anal. Calcd (%) for $C_{40}H_{32}O_2$: C 88.20, H 5.92, Found : C 88.28, H 6.03.

Preparation of 1,1-Bis(4-chlorophenyl)-2,2-bis(4-methoxyphenyl)pyracene 1c

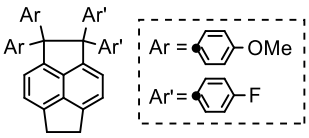


1c

To a suspension of pyran **3c** (201 mg, 319 μmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (3 mL) was added $TMSClO_4$ in toluene (0.79 M, 1.62 mL, 1.28 mmol) at 24 °C. The mixture was stirred for 1 h, and then solvent was evaporated. To the residue were added Zn powder (835 mg, 12.8 mmol) and dry THF (15 mL). After stirring for 22.5 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 30) to give **1c** (147 mg, 75%) as a pale yellow solid.

M.p. 246-248 °C ; ^{1}H NMR ($CDCl_3$) δ 7.35 (d, *J* = 6.2 Hz, 1H), 7.32 (d, *J* = 6.2 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.90-6.76 (m, 12H), 6.45 (d, *J* = 9.0 Hz, 4H), 3.68 (s, 6H), 3.54 (s, 4H) ; IR (KBr) 3035, 2998, 2928, 2834, 1607, 1577, 1509, 1491, 1462, 1441, 1289, 1250, 1183, 1095, 1038, 1012, 845, 832, 815, 793, 775, 525 cm^{-1} ; LR-MS (FD) *m/z* (%): 612 (M^+, bp), 613 (46), 614 (76), 615 (32), 616 (17) ; Anal. Calcd (%) for $C_{40}H_{30}Cl_2O_2$: C 78.30, H 4.93, Found : C 78.30, H 5.11.

Preparation of 1,1-Bis(4-fluorophenyl)-2,2-bis(4-methoxyphenyl)pyracene 1d

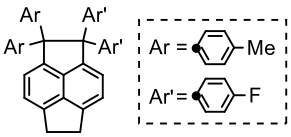


1d

To a suspension of pyran **3d** (203 mg, 340 μmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (3 mL) was added $TMSClO_4$ in toluene (0.79 M, 1.62 mL, 1.28 mmol) at 24 °C. The mixture was stirred for 1.5 h, and then solvent was evaporated. To the residue were added Zn powder (881 mg, 13.5 mmol) and dry THF (15 mL). After stirring for 21 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 35) to give **1d** (171 mg, 87%) as a pale yellow solid.

M.p. 205-206 °C ; ^{1}H NMR ($CDCl_3$) δ 7.34 (d, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.60 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 8.8 Hz, 4H), 3.67 (s, 6H), 3.54 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 161.87, 159.43, 157.26, 145.29, 145.09, 142.45, 142.17, 140.64, 140.61, 138.46, 136.86, 135.55, 132.24, 132.16, 131.77, 124.81, 124.62, 121.31, 121.13, 113.41, 113.20, 112.04, 77.86, 77.58, 55.14, 31.79 ; IR (KBr) 3041, 2929, 2836, 1605, 1505, 1465, 1442, 1298, 1251, 1232, 1183, 1162, 1038, 846, 834, 822, 805, 776, 587 cm^{-1} ; LR-MS (FD) *m/z* (%): 580 (M^+, bp), 581 (46), 582 (12) ; HR-MS (FD) Calcd. for $C_{40}H_{30}Cl_2F_2O_2$: 580.2214, Found : 580.2215.

Preparation of 1,1-Bis(4-fluorophenyl)-2,2-bis(4-methylphenyl)pyracene 1e

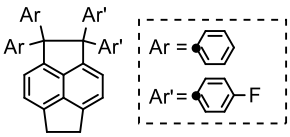


1e

To a suspension of pyran **3e** (96.3 mg, 171 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (150 μL, 1.71 mmol) at 26 °C. The mixture was stirred for 4 h, and then solvent was evaporated. To the residue were added Zn powder (1.74 g, 26.6 mmol) and dry MeCN (10 mL). After stirring for 17.5 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 30) to give **1e** (93.6 mg, 99%) as a pale yellow solid.

M.p. 294-296 °C ; ^{1}H NMR ($CDCl_3$) δ 7.33 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 4H), 6.71 (d, *J* = 8.3 Hz, 4H), 6.58 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 9.0 Hz, 2H), 3.54 (s, 4H), 2.17 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 159.43, 145.13, 145.10, 142.43, 142.10, 141.58, 140.76, 140.73, 138.44, 135.59, 135.02, 132.17, 132.09, 130.61, 127.40, 124.75, 124.39, 121.31, 121.07, 113.34, 113.13, 78.15, 77.21, 31.77 ; IR (KBr) 3024, 2915, 1604, 1504, 1232, 1193, 1162, 844, 822, 813, 774, 761, 584, 530 cm^{-1} ; LR-MS (FD) *m/z* (%): 548 (M^+, bp), 549 (44), 550 (11) ; HR-MS (FD) Calcd. for $C_{40}H_{30}F_2$: 548.2316, Found : 548.2323.

Preparation of 1,1-Bis(4-fluorophenyl)-2,2-bisphenylpyracene 1f

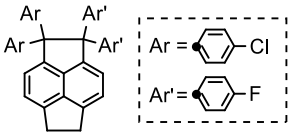


1f

To a suspension of pyran **3f** (98.5 mg, 184 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (160 μL, 1.82 mmol) at 25 °C. The mixture was stirred for 5 h, and then solvent was evaporated. To the residue were added Zn powder (1.81 g, 27.7 mmol) and dry MeCN (10 mL). After stirring for 15.5 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 30) to give **1f** (87.4 mg, 91%) as a pale yellow solid.

M.p. 245-246 °C ; ^{1}H NMR ($CDCl_3$) δ 7.35 (d, *J* =7.0 Hz, 2H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 6.96-6.85 (m, 14H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.55 (s, 4H) ; IR (KBr) 3061, 3024, 2922, 1601, 1504, 1233, 1162, 840, 822, 770, 754, 698 cm^{-1} ; LR-MS (FD) *m/z* (%): 520 (M^+, bp), 521 (41), 522 (8) ; Anal. Calcd (%) for $C_{38}H_{26}F_2$: C 87.67, H 5.03, Found : C 87.45, H 5.26.

Preparation of 1,1-Bis(4-fluorophenyl)-2,2-bis(4-methylphenyl)pyracene 1g



1g

To a suspension of pyran **3g** (114 mg, 188 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (170 μL, 1.94 mmol) at 26 °C. The mixture was stirred for 4 h, and then solvent was evaporated. To the residue were added Zn powder (1.91 g, 29.3 mmol) and dry MeCN (10 mL). After stirring for 16 h, the mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 50) to give **1g** (105 mg, 95%) as a pale yellow solid.

M.p. 294-296 °C ; ^{1}H NMR ($CDCl_3$) δ 7.36 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.92-6.80 (m, 12H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 3.55 (s, 4H) ; IR (KBr) 3036, 2922, 1603, 1505, 1492, 1235, 1162, 1097, 1013, 835, 822, 777 cm^{-1} ; LR-MS (FD) *m/z* (%): 588 (M^+, bp), 589 (44), 590 (74), 591(28), 592(18) ; Anal. Calcd (%) for $C_{38}H_{24}Cl_2F_2$: C 77.42, H 4.10, Found : C 77.40, H 4.38.

X-ray analyses

Data collection was conducted with a Rigaku Mercury 70 diffractometer (Mo-Kα radiation, λ = 0.71075 Å). The structure was solved by the direct method (SIR2004) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding.

Crystal date for 1a

Crystals were obtained by recrystallizing from CH_2Cl_2/hexane. MF : $C_{42}H_{36}O_2$, FW : 572.75, pale yellow prism, 0.20 × 0.20 × 0.20 mm^3, triclinic $P\bar{1}$, a = 9.030(2) Å, b = 12.375(2) Å, c = 14.665(2) Å, α = 70.856(6)°, β = 84.816(8)°, γ = 77.393(7)°, V = 1510.4(4) Å^3, ρ (Z = 2) = 1.259 g/cm^3. A total 6876 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.753 cm^{-1}). The final *R1* and *wR2* values are 0.092 (I > 2σI) and 0.256 (all data) for 6876 reflections and 397 parameters. Estimated standard deviations are 0.002-0.004 Å for bond lengths and 0.12-0.3° for bond angles, respectively. CCDC 870491

Crystal date for 1b

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{40}H_{32}O_2$, FW : 544.69, yellow prism, 0.50 × 0.20 × 0.20 mm^3, monoclinic $C2/c$, a = 32.999(6) Å, b = 8.968(1) Å, c = 23.998(5) Å, α = 90°, β = 126.937(3)°, γ = 90°, V = 5677(2) Å^3, ρ (Z = 8) = 1.275 g/cm^3. A total 6869 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.77 cm^{-1}). The final *R1* and *wR2* values are 0.085 (I > 2σI) and 0.205 (all data) for 6866 reflections and 379 parameters. Estimated standard deviations are 0.0016-0.004 Å for bond lengths and 0.10-0.3° for bond angles, respectively. CCDC 870493

Crystal date for 1b·CH_2Cl_2

Crystals were obtained by recrystallizing from CH_2Cl_2/hexane. MF : $C_{41}H_{34}Cl_2O_2$, FW : 629.62, yellow pletelet, 0.20 × 0.20 × 0.20 mm^3, triclinic $P\bar{1}$, a = 11.627(3) Å, b = 11.757(3) Å, c = 12.437(3) Å, α = 73.325(7)°, β = 78.633(9)°, γ = 85.120(9)°, V = 1596.1(6) Å^3, ρ (Z = 2) = 1.310 g/cm^3. A total 7282 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.40 cm^{-1}). The final *R1* and *wR2* values are 0.098 (I > 2σI) and 0.283 (all data) for 7282 reflections and 406 parameters. Estimated standard deviations are 0.004-0.007 Å for bond lengths and 0.17-0.4° for bond angles, respectively. CCDC 870492

Crystal date for 1c

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{40}H_{30}Cl_2O_2$, FW : 613.58, pale yellow pletelet, 0.10 × 0.05 × 0.05 mm^3, triclinic $P\bar{1}$, a = 11.246(13) Å, b = 11.916(13) Å, c = 13.297(14) Å, α = 103.784(3)°, β = 95.53(3)°, γ = 116.99(2)°, V = 1498(3) $Å^3$, ρ (Z = 2) = 1.360 g/cm^3. A total 7062 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.532 cm^{-1}). The final *R1* and *wR2* values are 0.175 (I > 2σI) and 0.422 (all data) for 7062 reflections and 415 parameters. Estimated standard deviations are 0.006-0.05 Å for bond lengths and 0.4-4° for bond angles, respectively. The positions of Cl and O are completely disordered, which is the reason for the low accuracy of the structural parameters as well as the high residual values of *R1* and *wR2*.

Crystal date for 1d·CH_2Cl_2

Crystals were obtained by recrystallizing from CH_2Cl_2/hexane. MF : $C_{42}H_{36}O_2$, FW : 572.75, colorless pletelet, 0.40 × 0.20 × 0.05 mm^3, monoclinic $P2_1$/c, a = 12.562(11) Å, b = 22.28(2) Å, c = 12.062(10) Å, α = 90°, β = 102.39(2)°, γ = 90°, V = 3297(5) $Å^3$, ρ (Z = 4) = 1.313 g/cm^3. A total 7529 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.427 cm^{-1}). The final *R1* and *wR2* values are 0.186 (I > 2σI) and 0.452 (all data) for 7529 reflections and 433 parameters. Estimated standard deviations are 0.006-0.03 Å for bond lengths and 0.4-1.5° for bond angles, respectively. CCDC 962024

Crystal date for 1d·$CHCl_3$

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{41}H_{31}Cl_3F_2O_2$, FW : 700.05, colorless prism, 0.20 × 0.20 × 0.20 mm^3, monoclinic $P2_1$/c, a = 12.624(2) Å, b = 22.527(4) Å, c = 12.030(2) Å, α = 90°, β = 102.014(2)°, γ = 90°, V = 3346.1(10) $Å^3$, ρ (Z = 4) = 1.390 g/cm^3. A total 8014 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 3.214 cm^{-1}). The final *R1* and *wR2* values are 0.104 (I > 2σI) and 0.270 (all data) for 8014 reflections and 433 parameters. Estimated standard deviations are 0.003-0.004 Å for bond lengths and 0.14-0.3° for bond angles, respectively. CCDC 962023

Crystal date for 1d·$ClCH_2CH_2Cl$

Crystals were obtained by recrystallizing from $ClCH_2CH_2Cl$/hexane. MF : $C_{42}H_{34}Cl_2F_2O_2$, FW : 679.63, colorless prism, 0.20 × 0.20 × 0.20 mm^3, monoclinic $P2_1/c$, a = 12.030(8) Å, b = 21.49 (2) Å, c = 12.714(9) Å, α = 90°, β = 102.69(2)°, γ = 90°, V = 3206(4) Å^3, ρ (Z = 4) = 1.408 g/cm^3. A total 7688 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.527 cm^{-1}). The final *R1* and *wR2* values are 0.268 (I > 2σI) and 0.620 (all data) for 7688 reflections and 413 parameters. Estimated standard deviations are 0.009-0.03 Å for bond lengths and 0.6-1.7° for bond angles, respectively.

Crystal date for 1d·THF

Crystals were obtained by recrystallizing from THF/hexane. MF : $C_{44}H_{38}F_2O_3$, FW : 652.78, colorless block, 0.40 × 0.20 × 0.20 mm^3, triclinic $P\bar{1}$, a = 11.819(4) Å, b = 12.132(3) Å, c = 12.210(4) Å, α = 78.759(12)°, β = 83.352(12)°, γ = 75.349(10)°, V = 1657.3(8) Å^3, ρ (Z = 2) = 1.308 g/cm^3. A total 7544 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.880 cm^{-1}). The final *R1* and *wR2* values are 0.098 (I > 2σI) and 0.269 (all data) for 7544 reflections and 442 parameters. Estimated standard deviations are 0.003-0.008 Å for bond lengths and 0.14-0.4° for bond angles, respectively. CCDC 962022

Crystal date for 1d·CCl_4 and hexane

Crystals were obtained by recrystallizing from CCl_4/hexane. MF : $C_{42}H_{33.5}Cl_2F_2O_2$, FW : 679.13, colorless platelet, 0.20 × 0.20 × 0.05 mm^3, triclinic $P\bar{1}$, a = 11.976(5) Å, b = 12.469(4) Å, c = 24.139(9) Å, α = 71.90(3)°, β = 79.04(3)°, γ = 78.22(3)°, V = 3323(3) Å^3, ρ (Z = 4) = 1.358 g/cm^3. A total 12835 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.438 cm^{-1}). The final *R1* and *wR2* values are 0.155 (I > 2σI) and 0.393 (all data) for 12835 reflections and 862 parameters. Estimated standard deviations are 0.007-0.014 Å for bond lengths and 0.14-0.4° for bond angles, respectively. CCDC 962026

Crystal date for 1d·ether

Crystals were obtained by recrystallizing from ether/hexane. MF : $C_{40}H_{30}F_2O_2$, FW : 580.67, colorless block, 0.20 × 0.20 × 0.20 mm^3, monoclinic Cc, a = 19.255(9) Å, b = 15.420(7) Å, c = 22.907(11) Å, α = 90°, β = 109.521(7)°, γ = 90°, V = 3323(3) Å^3, ρ (Z = 8) = 1.203 g/cm^3. A total 10964 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.806 cm^{-1}). The final *R1* and *wR2* values are 0.109 (I > 2σI) and 0.311 (all data) for 10964 reflections and 838 parameters. Estimated standard deviations are 0.007-0.02 Å for bond lengths and 0.4-0.9° for bond angles, respectively. CCDC 962027

Crystal date for 1d·hexane

Crystals were obtained by recrystallizing from Benzene/hexane. MF : $C_{43}H_{37}F_2O_2$, FW : 623.76, colorless prism, 0.40 × 0.20 × 0.20 mm^3, monoclinic *Cc*, a = 19.157(11) Å, b = 15.524(8) Å, c = 23.456(13) Å, α = 90°, β = 108.802(6)°, γ = 90°, V = 6603(6) Å^3, ρ (Z = 8) = 1.255 g/cm^3. A total 8021 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.830 cm^{-1}). The final *R1* and *wR2* values are 0.088 (I > 2σI) and 0.246 (all data) for 8021 reflections and 848 parameters. Estimated standard deviations are 0.005-0.03 Å for bond lengths and 0.3-1.3° for bond angles, respectively. CCDC 962025

Crystal date for 1e

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{40}H_{30}F_2$, FW : 548.67, colorless prism, 0.40 × 0.40 × 0.40 mm^3, triclinic $P\bar{1}$, a = 8.994(8) Å, b = 11.976(10) Å, c = 14.203(13) Å, α = 75.60(4)°, β = 84.81(5)°, γ = 73.00(4)°, V = 1417(3) Å^3, ρ (Z = 2) = 1.286 g/cm^3. A total 5272 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.820 cm^{-1}). The final *R1* and *wR2* values are 0.098 (I > 2σI) and 0.274 (all data) for 5272 reflections and 380 parameters. Estimated standard deviations are 0.003-0.005 Å for bond lengths and 0.16-0.3° for bond angles, respectively. CCDC 962030

Crystal date for 1f

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{38}H_{26}F_2$, FW : 520.62, colorless platelet, 0.40 × 0.30 × 0.20 mm^3, triclinic $P\bar{1}$, a = 9.082(4) Å, b = 12.822(5) Å, c = 13.274(5) Å, α = 104.1181(12)°, β = 101.859(4)°, γ = 110.534(6)°, V = 1329.8(9) Å^3, ρ (Z = 2) = 1.300 g/cm^3. A total 6062 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 0.836 cm^{-1}). The final *R1* and *wR2* values are 0.091 (I > 2σI) and 0.269 (all data) for 6062 reflections and 362 parameters. Estimated standard deviations are 0.003-0.005 Å for bond lengths and 0.13-0.3° for bond angles, respectively. CCDC 962028

Crystal date for 1g

Crystals were obtained by recrystallizing from $CHCl_3$/hexane. MF : $C_{38}H_{24}Cl_2F_2$, FW : 589.51, yellow platelet, 0.20 × 0.20 × 0.15 mm^3, triclinic $P\bar{1}$, a = 9.055(4) Å, b = 11.980(4) Å, c = 14.215(6) Å, α = 75.34(2)°, β = 84.08(2)°, γ = 72.91(2)°, V = 1425.3(9) Å^3, ρ (Z = 2) = 1.374 g/cm^3. A total 6329 unique data ($2\theta_{max}$ = 55°) were measured at T = 153 K. Numerical absorption correction was applied (μ = 2.678 cm^{-1}). The final *R1* and *wR2* values are 0.091 (I > 2σI) and 0.269 (all data) for 6329 reflections and 380 parameters. Estimated standard deviations are 0.003-0.006 Å for bond lengths and 0.18-0.4° for bond angles, respectively. CCDC 962029

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Chapter 2

Expandability of Ultralong C-C Bond in Hexaphenylethane-type Compounds with a 1*H*-Benzo[*cd*]indol-2-one Skeleton

2-1. Introduction

In the author's laboratory, a number of hexaphenylethane(HPE)-type compounds with a long C-C bond were studied using an "arylenediyl approach", which is the method for facilitating α,α-coupling by connecting or annulating two phenyl groups.[1] Among them, di(spiroacridan)pyracene has the longest C-C bond length of 1.791(3) Å.[1a-c] On the other hand, the value for the shortest non-bonded C···C contact is 1.80(2) Å.[2] In terms of the C-C atomic separation, the untouched blank area still exists between 1.79 and 1.80 Å. Thus, in this chapter, the author has planned to fill in the unknown area between "bond" and "non-bond" through the synthetic study of the world-record's compound with the longest C-C covalent bond. Based on the knowledge obtained in the previous studies, the author proposes the design concept for the novel skeleton as detailed below.

[A] Introduction of more rigid cross-link than the previous ones: Steric repulsion between the bulky aryl substituents would be reduced by the skewing deformation of the arylene moiety or the elongation of C-C bond. Thus, by suppressing the skeletal deformation, the further elongation of the bond should be induced.

[B] Addition of prestrain to the skeleton by using "Scissor effects": The angle strain induced by ring annulation at the *peri*-position of the naphthalene core would enlarge the separation of the opposite *peri*-position. This prestrain could contribute to further bond elongation in conjunction with steric repulsion between the bulky aryl groups.

[C] Structural variation by substituents: As mentioned chapter 1, the ultralong covalent bond can be very easily changed by the difference of the substituents on the aryl group and the incorporation of solvents in the crystal. Thus, the molecular skeleton with an atom to attach various substituents is ideal.

First, the author focused his attention on the bond length of the bridge, and envisaged that C-N bond (1.46 Å) shorter than C-C bond (1.54 Å) can enhance the separation of the *peri*-position of naphthalene. Next, the author paid attention on the planarity of the amide structure, and expected that the amide bond can increase planarity and rigidity of skeleton due to its partial double-bond character. By using the cross-link containing a nitrogen atom, it becomes easy to attach a variety of substituents to design a series of compound. Based on these ideas, the author newly designed HPEs framed in the 1*H*-benzo[*cd*]indol-2-one skeleton fused with a γ-lactam ring at the *peri*-position of naphthalene.

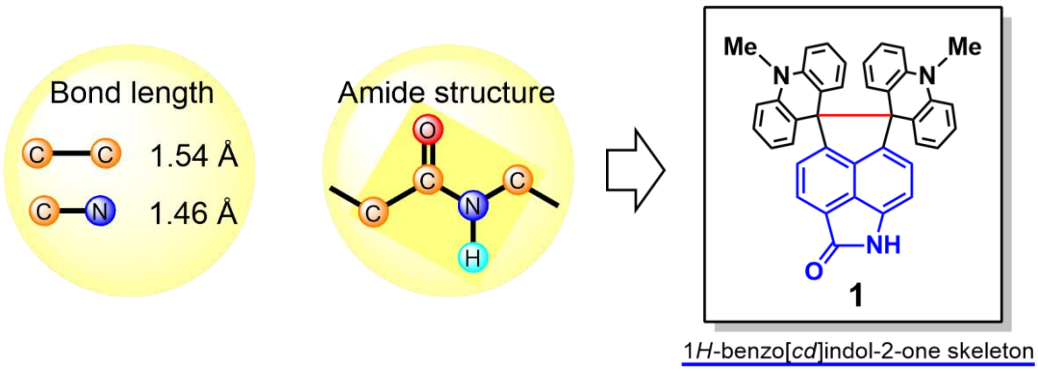


Figure 2-1. Newly designed HPEs framed in the 1*H*-benzo[*cd*]indol-2-one skeleton.

In fact, a DFT calculation for the 5,6-dihydroindeno[6,7,1-*cde*]indol-2(1*H*)-one predicted that the target skeleton has a longer bond (1.589 Å) than pyracene (1.586 Å) and acenaphthene (1.569 Å). This result supports that the addition of prestrain to the skeleton induces the elongation of C-C bond in **1**. Additionally, the full optimization of **1** revealed that 1*H*-benzo[*cd*]indol-2-one skeleton is planar, and the central C-C bond length is 1.795 Å, which is greater than that for the longest C-C bond length ever reported. Thus, the synthetic studies of the target compound were conducted.

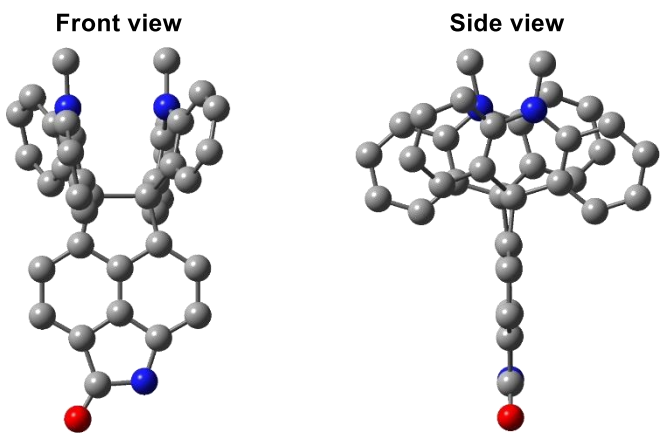
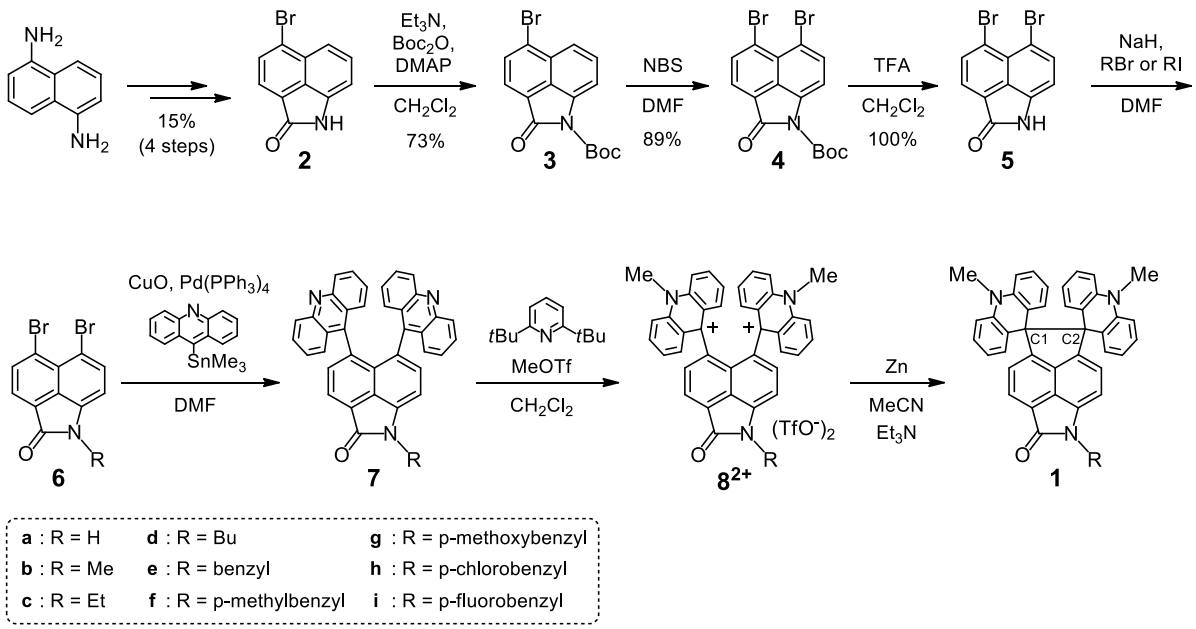


Figure 2-2. Optimized structures of **1** determined by DFT calculations (B3LYP/6-31G*).

2-2. Preparation of HPEs with a 1*H*-Benzo[*cd*]indol-2-one Skeleton 1a-1i

5-Bromo-1*H*-benzo[*cd*]indol-2-one **2** was prepared in 4 steps from commercially available 1,5-diaminonaphthalene following the published procedures,[3] and *tert*-butoxycarbonyl (Boc) group was introduced to suppress electron-donating ability of nitrogen (Scheme 2-1). Bromination of **3** with NBS followed by treatment of **4** with TFA gave 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5**. At this stage, various substituents (**b**-**i**) were introduced to the nitrogen atom of **5**. The Stille reaction of dibromo compound **6a** and 9-trimethylstannylacridine, using $Pd(PPh_3)_4$ (0.3 equiv.) and CuO (2 equiv.) in DMF at 140°C,[4] gave **7a** in a yield of 41% as slightly soluble yellow crystals (Scheme 2-2). Under similar conditions, the Stille reactions of a series of *N*-alkylated compound **6b**-**6i** with 9-trimethylstannylacridine gave a series of diacridine compounds **7b**-**7i** with higher solubility in moderate yields (y. 34%, 61%, 63%, 59%, 41%, 48%, 54% and 56%, respectively). Upon treatment with a large excess of MeOTf in the presence of a bulky base (2,6-di-tert-butylpyridine) in CH_2Cl_2 at room temperature, compounds **7b**-**7i** were transformed into orange crystals of $\mathbf{8b^{2+}}$-$\mathbf{8i^{2+}}(TfO^-)_2$ salts in high yields (y. 97%, 88%, 94%, 85%, 80%, 90%, 92% and 85%, respectively). In the case of **7a**, even with a large excess of MeOTf, the double quaternization reaction did not proceed, and only the corresponding monocation salt was deposited due to low solubility. Finally, treatment of dications with Zn powder in Et_3N/THF (3:10) gave HPE-type compounds **1b**-**1g** and **1i**, which was isolated as yellow ocher or olive-colored crystals in good yields (y. 46%, 81%, 78%, 84%, 83%, 72% and 54%, respectively). As for **1h**, the author has not so far succeeded in its purification from the by-products.



Scheme 2-2. Preparation of HPEs with a 1*H*-benzo[*cd*]indol-2-one Skeleton **1a-1i**.

2-3. X-ray Structures of HPEs with a 1*H*-Benzo[*cd*]indol-2-one Skeleton 1b-1i

After a great deal of examination on the vapor diffusion method using a variety of solvent, single crystals of high quality of HPEs with a 1*H*-benzo[*cd*]indol-2-one skeleton **1c**-**1e** and **1i** were successfully obtained, although crystals of good quality were difficult to grow for other members of **1**. X-ray analyses at 150 K showed that the C1-C2 bond length (*d*) varies depending on the substituent on the nitrogen atom since they exhibit a different degree of skewing deformation of dispirocyclopentane moiety in the crystal. As expected, 1*H*-benzo[*cd*]indol-2-one skeleton moiety was planar. It is noteworthy that the value of **1e** [1.789(10) Å] and **1i** [1.781(4) Å] have a much longer C-C bond than **1c** [1.736(5) Å] or **1d** [1.734(7) Å], and the former values are comparable to the longest C-C bond length [1.791(3) Å] (Figure 2-3). Thus, to perform further investigation of **1e** and **1i**, X-ray analyses at elevated temperatures were conducted.

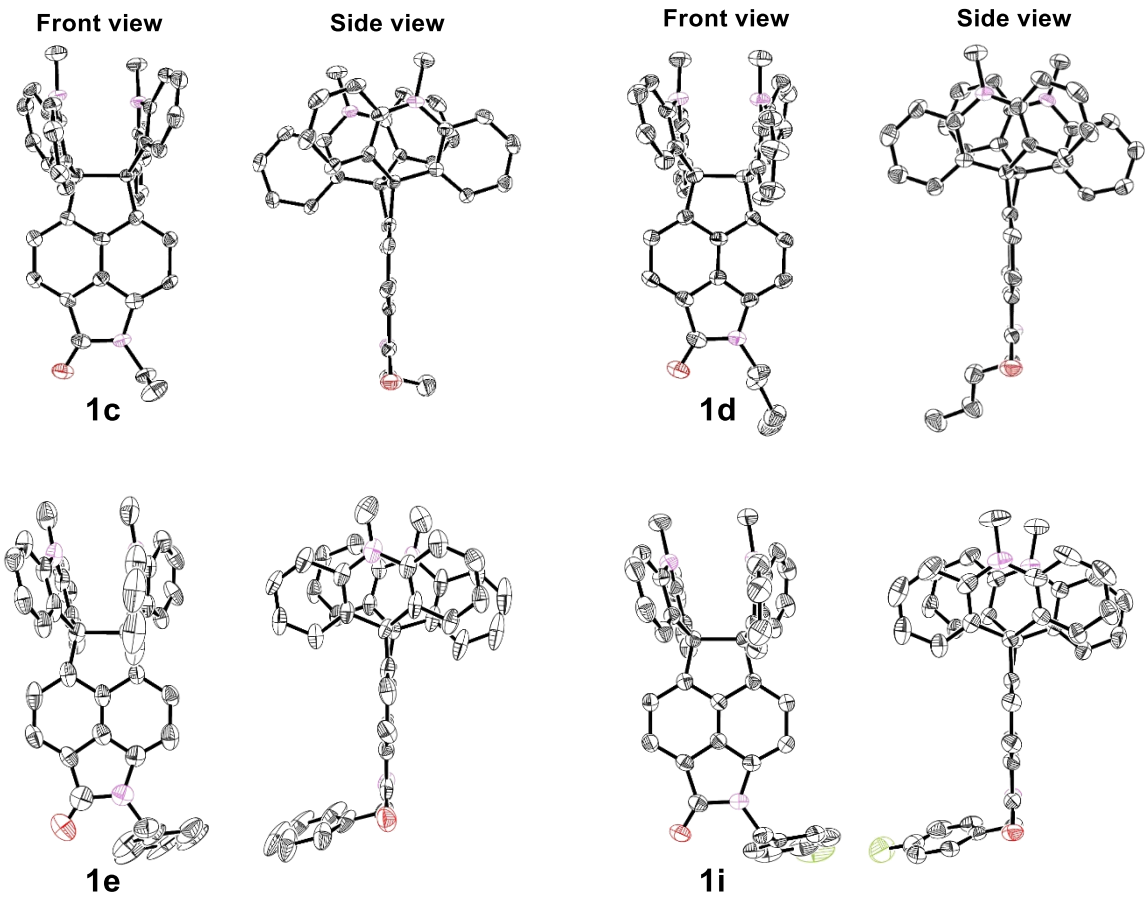
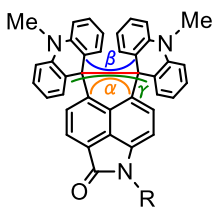


Figure 2-3. ORTEP drawings of HPEs **1c-1e**, **1i** at 150 K.

Surprisingly, the C1-C2 bond lengths of **1e** and **1i** become greater continuously with the increase in the measurement temperature. In all temperature region, the bond lengths of *N-p*-fluorobenzyl derivative **1i** were determined with high accuracy. Eventually, it has been found that **1i** has the new-record C-C bond length of 1.877(6) Å at 400 K, which overwhelmingly surpasses the value for the shortest non-bonded C···C contact [1.80(2) Å] (Table 2-1). No sign of decomposition or deterioration was observed when the crystal was measured at high temperature. These unprecedented results show that the C-C covalent bond can be elongated upon heating, which may be related to the "expandability" of the ultralong bond. There is no example of the compound that indicates such a wide range of change in bond length. In the case of **1e**, the estimated standard deviation (esd) of the *d* value in the high-temperature region was small, whereas the large esd value was determined in the low-temperature region, due to a solid-state phase transition that occurs between 200 K and 230 K (Table 2-2). In fact, the thermal ellipsoids of **1e** were subglobular at 230 K, whereas they were oblong at 150 K.

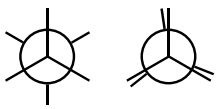
Table 2-1. Structural date of **1i** (the upper side) and **1e** (the under side) determined by X-ray analyses at various temperature.

measured temperature	C1-C2 bond length *d* (Å)	torsion angles(°) α	β	γ	sum of torsions Σ(°)	eclipseness χ (%)
120 K	1.782(4)	11.24(18)	17.0(3)	13.6(3)	41.84(78)	76.8
150 K	1.781(4)	10.89(19)	17.5(3)	13.7(3)	42.09(79)	76.6
200 K	1.787(4)	11.1(3)	17.1(3)	13.4(3)	41.6(9)	76.9
230 K	1.801(4)	10.7(3)	17.2(3)	13.4(3)	41.3(9)	77.1
273 K	1.807(4)	10.8(3)	16.5(3)	13.6(3)	40.9(9)	77.3
320 K	1.819(4)	10.7(3)	16.3(3)	12.9(3)	39.9(9)	77.8
360 K	1.857(5)	9.9(3)	16.8(4)	12.2(4)	38.9(11)	78.4
400 K	1.877(6)	9.9(3)	15.8(4)	12.3(4)	38.0(11)	78.9
measured temperature	C1-C2 bond length *d* (Å)	torsion angles(°) α	β	γ	sum of torsions Σ(°)	eclipseness χ (%)
120 K	1.786(11)	15.1(6)	20.3(9)	17.9(10)	53.3(25)	70.4
150 K	1.789(10)	15.0(6)	20.0(8)	18.4(9)	53.4(23)	70.3
200 K	1.790(8)	15.1(5)	20.3(6)	17.3(6)	52.7(17)	70.7
230 K	1.792(5)	14.4(3)	20.6(4)	17.3(4)	51.6(11)	71.3
273 K	1.802(5)	14.0(3)	20.4(3)	17.2(4)	51.6(10)	71.3
320 K	1.822(5)	13.3(3)	20.2(3)	17.2(3)	50.7(9)	71.8
360 K	1.841(5)	13.7(3)	20.4(4)	15.8(4)	49.9(11)	72.3
400 K	1.868(6)	13.2(3)	19.2(4)	16.3(4)	48.7(11)	72.9



$$\chi\,(\%) = \left(1 - \frac{\Sigma}{180}\right) \times 100$$

Σ : sum of torsions



0% 100%

As is the case with 1,1,2,2-tetraarylpyracenes in chapter 1, the *d* values of **1** exhibit a linear correlation with the eclipsing degree (χ) of C1-C2 (Table 2-1, 2-2, and Figure 2-4 (a)). With a rise in temperature, the expansion of the volume of unit cell as well as C1-C2 bond length were observed (Figure 2-4 (b, c)). Therefore, it is considered that the excitation of molecular vibration by heating causes the increase of the substantive steric repulsion, which results in the elongation of the ultralong C-C bond. Additionally, in association with the elongation of C1-C2 bond, slight increase in sp^2 character of C1 and C2 carbons is expected (Figure 2-4 (d)). The degree of sp^3 (φ) was calculated from the following formula φ (%) ={1－{(X－328.5)°/31.5°}×100 (X : The sum of three bond angles at the C1 or C2 atom). The φ value of the perfect sp^3 carbon is 100.

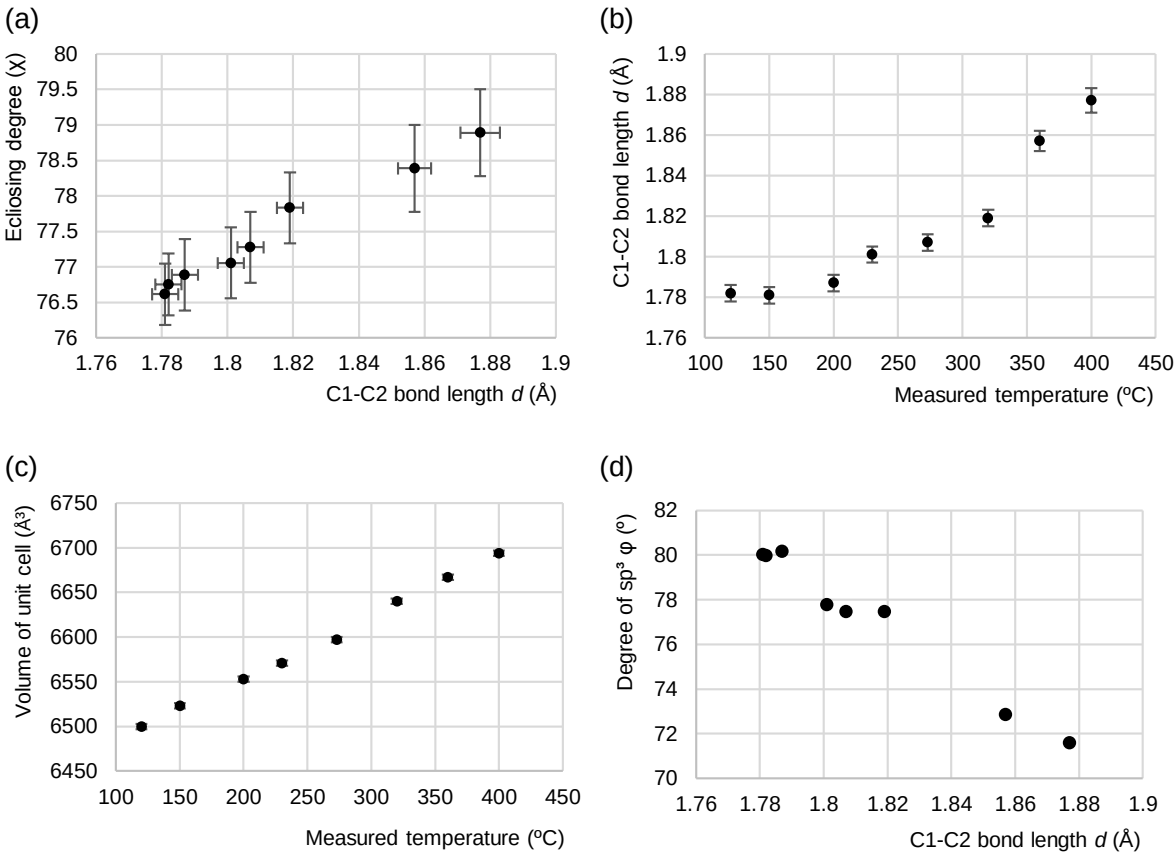


Figure 2-4. Scattering plot of the structural parameters of **1i**. (a) The C1-C2 bond length *d* versus the eclipsing degree (χ) at various temperature. (b) The C1-C2 bond length *d* versus measured temperature of X-ray analyses. (c) The volume of unit cell versus measured temperature of X-ray analyses. (d) The average value of the sp^3 degree of C1 and C2 carbon (φ) versus The C1-C2 bond length *d*.

Moreover, X-ray analyses at 150 K revealed that *N*-*p*-methoxybenzyl derivative **1g** has the C-C bond length of 1.815(13) Å, with exhibiting an almost complete eclipsed conformation in the crystal [sum of torsions Σ (◦)= 12.0(25), eclipseness χ = 93.3], although the sufficient X-ray diffraction date could not be obtained due to the small size of the single crystal. This result strongly suggests that, depending on the substituents on the nitrogen atom, there is a great possibility of observing the further elongation of the C-C bond. On the other hand, the ^{1}H NMR spectra of **1** in CD_2Cl_2 at ambient temperature shows broad signals for the resonances of aromatic hydrogen atoms, and upon a progressive cooling, sharp signals was observed. Therefore, for some portion of **1**, the elongated C-C bond is cleaved in solution to generate diradical species.

2-4. DFT Calculation

The *d* value and sum of torsions Σ in the fully optimized **1** was estimated to be 1.795 Å and 60.5°, which is close to the experimental value of **1e** at 150 K [1.789(10) Å and 53.4 (23)°, respectively]. When the geometrical optimization processes were reconducted by constraining *d* at the 11 different values between 1.730 - 1.870 Å, the scattering plot of the relative energy vs *d* suggests a parabolic relationship (Figure 2-5), and the characteristic feature is the very shallow potential curve with the energy difference of 0.25 kcal/mol, which is shallower than the potential curve estimated for the 1,1,2,2-tetraarylpyracenes in chapter 1. DFT calculations also indicate that the difference in energy between the optimized structure and the structure with C1-C2 bond length of 1.877 Å is only 0.21 kcal/mol. The observed elongation of C1-C2 bond length can be explained in terms of the estimated small energy difference. DFT calculations were performed with the Gaussian 09 program package.[5] The geometries of the compounds were optimized using the B3LYP method with the 6-31G* basis set. The natures of the stationary points were assessed by means of vibration frequency analysis.

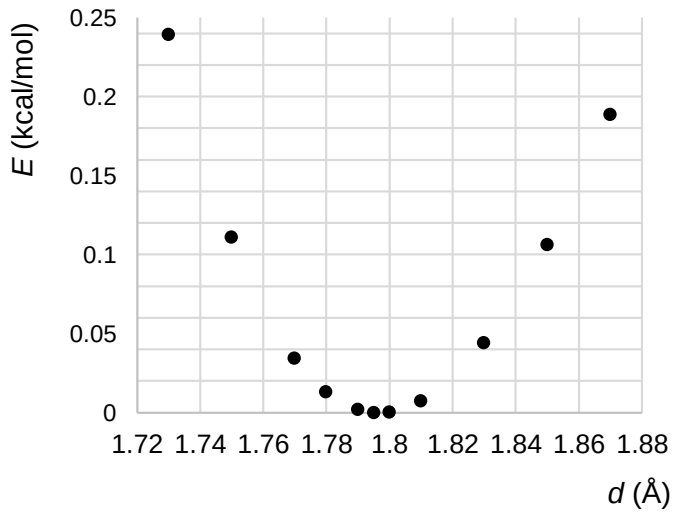


Figure 2-5. Scattering plot of relative energy (*E*) of **1** vs *d* estimated by DFT calculations (B3LYP/6-31G*).

2-5. Conclusion

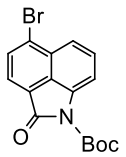
The author has succeeded in preparing the newly designed HPEs **1** framed in the 1*H*-benzo[*cd*]indol-2-one skeleton fused with a γ-lactam ring at the *peri*-position of naphthalene. X-ray analyses of **1** showed that the substituents on the amide *N* largely affect the C1-C2 bond length. Moreover, X-ray analyses at various temperature of *N*-benzyl (**1e**) and *N*-*p*-fluorobenzyl (**1i**) derivatives revealed the temperature-dependent structural change, in which the C1-C2 bond greatly elongate upon heating. It should be noted that *N*-*p*-fluorobenzyl derivative **1i** has the C-C bond with the world-record bond length ever reported [1.877(6) Å at 400 K]. With this result, the unexplored separation range of the C-C atomic distance no longer exists. This unique phenomenon of the extraordinarily long bond may become a springboard for the discovery of novel chemical species, which has a C-C separation between the ordinary “bond” and “non-bond”.

Experimental Section

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise indicated. All commercially available compounds were used without further purification. Dry MeCN was obtained by distillation from CaH_2 prior to use. Column chromatography was performed on silica gel I-6-40 (YMC) of particle size 40-63 µm and aluminium oxide 90 standardized (Merck 63-200 µm). ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER Ascend™ 400 (^{1}H/400MHz and ^{13}C/100MHz) spectrometer. IR spectra were measured as a KBr pellet on a JEOL JIR-WINSPEC100FT/IR spectrophotometer. Mass spectra were recorded on JMS-AX500, JMS-SX102A, or JEOL JMS-T100GCV spectrometers in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Melting points were measures on a Yamato MP-21 melting point apparatus and reported uncorrected. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer.

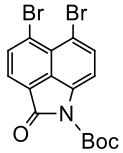
Preparation of *N-tert*-butoxycarbonyl-5-bromo-1*H*-benzo[*cd*]indol-2-one 3



To a suspension of 5-bromo-1*H*-benzo[*cd*]indol-2-one (201 mg, 810 µmol) in dry CH_2Cl_2 (30 mL) was added triethylamine (115 µL, 830 µmol), di-*tert*-butyl dicarboxylate (225 µL, 929 µmol) and *N*,*N*-dimethyl-4-aminopyridine (12.2 mg, 100 µmol), then the mixture was stirred for 15 min for 0°C and then 1 h at 23 °C. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ EtOAc = 15) to give *N*-*tert*-butoxycarbonyl-5-bromo-1*H*-benzo[*cd*]indol-2-one **3** (261 mg, 92%) as a pale yellow solid.

M. p. 120-121 °C ; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.66 (dd, *J* = 8.2, 7.4 Hz, 1H), 1.71 (s, 9H) ; ^{13}C NMR ($CDCl_3$) δ 164.70, 149.49, 135.79, 132.23, 130.13, 129.45, 128.08, 126.64, 125.19, 124.41, 121.20, 112.97, 84.42, 28.20 ; IR (KBr) 2977, 2931, 1784, 1752, 1728, 1487, 1462, 1434, 1395, 1371, 1315, 1287, 1251, 1162, 1079, 1026, 844, 769 cm^{-1} ; LR-MS (FD) *m/z* (%): 347 (M^+, bp), 348 (18), 349 (99), 350 (19), 351 (2) ; HR-MS (FD) Calcd. for $C_{16}H_{14}BrNO_3$: 347.0157, Found : 347.0170.

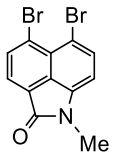
Preparation of *N-tert*-butoxycarbonyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 4



To a solution of (*N-tert*-butoxycarbonyl)-5-bromo-1*H*-benzo[*cd*]indol-2-one **3** (819 mg, 2.35 mmol) in dry DMF (15 mL) was transferred NBS (848 mg, 4.76 mmol) in dry DMF (20 mL) with a cannula in the dark, and the mixture was stirred for 15 h at 50 °C. The mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ EtOAc = 10) to give *N-tert*-butoxycarbonyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **4** (1.00 g, 100%) as a pale yellow solid.

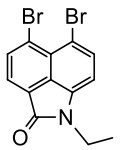
M. p. 146-147 °C ; ^{1}H NMR ($CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 1.69 (s, 9H) ; ^{13}C NMR ($CDCl_3$) δ 163.91, 149.15, 136.76, 136.39, 135.89, 128.03, 126.95, 126.36, 125.61, 125.27, 114.06, 113.92, 84.85, 28.16 ; IR (KBr) 3127, 2979, 2931, 1787, 1747, 1736, 1720, 1620, 1579, 1485, 1425, 1359, 1343, 1308, 1248, 1160, 1056, 1044, 836 cm^{-1} ; LR-MS (FD) *m/z* (%): 425 (51), 426 (10), 427 (M^+, bp), 428 (19), 429 (51), 430 (9) ; HR-MS (FD) Calcd. for $C_{16}H_{13}Br_2NO_3$: 424.9262, Found : 424.9267.

Preparation of *N*-methyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6b



To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (211 mg, 645 μmol) in dry DMF (20 mL) was cooled at 0°C, and then 60% NaH in oil (43.3 mg, 1.08 mmol) was added. After stirring for 15 min, iodomethane (120 μL, 1.93 mmol) was added at 0°C, and the mixture was stirred for 1 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, *N*-methyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6b** (220 mg, 100%) was given as a yellow solid.

Preparation of *N*-ethyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6c

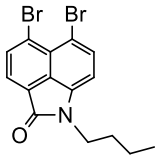


To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (502 mg, 1.54 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (100 mg, 2.50 mmol) was added. After stirring for 15 min, iodoethane (480 μL, 4.66 mmol) was added at 0°C, and the mixture was stirred for 5 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ EtOAc = 3) to give *N*-ethyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6c** (503 mg, 92%) as a yellow solid.

M. p. 176-177 °C ; ^{1}H NMR ($CDCl_3$) δ 8.08 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$) δ 166.33, 139.37, 136.59, 135.76, 127.44, 127.09, 126.36, 125.66, 125.26, 111.97,

106.53, 34.98, 13.80 ; IR (KBr) 3091, 2980, 2939, 1716, 1624, 1491, 1423, 1378, 1358, 1236, 989, 817, 731 cm^{-1} ; LR-MS (FD) *m/z* (%): 353 (52), 354 (8), 355 (M^+, bp), 356 (15), 357 (50), 358 (7) ; HR-MS (FD) Calcd. for $C_{13}H_9Br_2NO$: 352.9051, Found :352.9062.

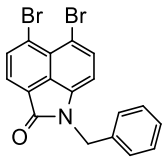
Preparation of *N*-butyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6d



To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (508 mg, 1.55 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (104 mg, 2.60 mmol) was added. After stirring for 15 min, 1-bromobutane (500 µL, 4.67 mmol) was added at 0°C, and the mixture was stirred for 6 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ EtOAc = 10) to give *N*-butyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6d** (559 mg, 94%) as a yellow solid.

M. p. 102-103 °C ; ^{1}H NMR ($CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 3.86 (t, *J* = 7.3 Hz, 2H), 1.74 (quin, *J* = 7.3 Hz, 2H), 1.41 (sext, *J* = 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR ($CDCl_3$) δ 166.62, 139.79, 136.56, 135.75, 127.36, 126.99, 126.30, 125.64, 125.27, 111.91, 106.69, 40.03, 30.62, 20.17, 13.74 ; IR (KBr) 3058, 2951, 2929, 2870, 1713, 1625, 1489, 1423, 1375, 1223, 1105, 1055, 847, 811, 796, 729 cm^{-1} ; LR-MS (FD) *m/z* (%): 381 (52), 382 (9), 383 (M^+, bp), 384 (17), 385 (50), 386 (9) ; HR-MS (FD) Calcd. for $C_{15}H_{13}Br_2NO$: 380.9364, Found : 380.9385.

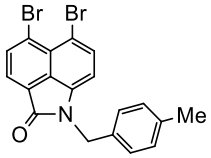
Preparation of *N*-benzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6e



To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (503 mg, 1.54 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (97.3 mg, 2.43 mmol) was added. After stirring for 15 min, benzylbromide (550 µL, 4.63 mmol) was added at 0°C, and the mixture was stirred for 3 h at 24°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 only) to give *N*-benzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6e** (599 mg, 93%) as a yellow solid.

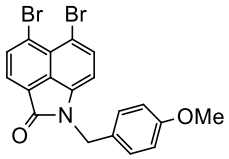
M. p. 169-170 °C ; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.33-7.27 (m, 5H), 6.62 (d, *J* = 7.7 Hz, 1H), 5.10 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 166.65, 139.23, 136.63, 136.02, 135.78, 128.89, 127.86, 127.49, 127.41, 126.65, 126.34, 125.99, 125.55, 112.27, 107.60, 43.93 ; IR (KBr) 3085, 3061, 2923, 1716, 1624, 1488, 1423, 1378, 1348, 1274, 1226, 1108, 1058, 977, 941, 811, 728, 703 cm^{-1} ; LR-MS (FD) *m/z* (%): 415 (50), 416 (11), 417 (M^+, bp), 418 (20), 419 (52), 420 (10) ; HR-MS (FD) Calcd. for $C_{18}H_{11}Br_2NO$: 414.9207, Found : 414.9199.

Preparation of *N-p*-methylbenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6f



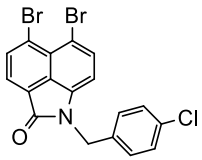
To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (509 mg, 1.56 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (97.8 mg, 2.45 mmol) was added. After stirring for 15 min, p-methylbenzylbromide (856 mg, 4.63 mmol) was added at 0°C, and the mixture was stirred for 3 h at 24°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 only) to give *N*-p-methylbenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6f** (653 mg, 97%) as a yellow solid.

Preparation of *N-p*-methoxybenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6g



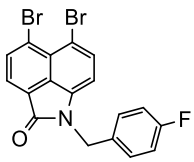
To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (508 mg, 1.55 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (97.4 mg, 2.44 mmol) was added. After stirring for 15 min, p-methoxybenzylbromide (700 µL, 4.80 mmol) was added at 0°C, and the mixture was stirred for 2 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 only) to give *N*-p-methoxybenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6g** (582 mg, 84%) as a yellow solid.

Preparation of *N-p*-chlorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6h



To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (504 mg, 1.54 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (103 mg, 2.58 mmol) was added. After stirring for 15 min, p-chlorobenzylbromide (938 mg, 4.56 mmol) was added at 0°C, and the mixture was stirred for 1.5 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 only) to give *N*-p-chlorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6h** (669 mg, 96%) as a yellow solid.

Preparation of *N-p*-fluorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one 6i

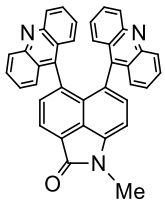


To a solution of 5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **5** (507 mg, 1.55 mmol) in dry DMF (40 mL) was cooled at 0°C, and then 60% NaH in oil (103 mg, 2.58 mmol) was added. After stirring for 15 min, p-fluorobenzylbromide (580 µL, 4.65 mmol) was added at 0°C, and the mixture was stirred for 2 h at 23°C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with

brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 only) to give *N*-p-fluorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6i** (672 mg, 100%) as a yellow solid.

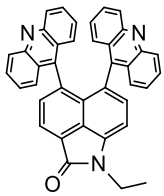
M. p. 145-146 °C ; ^{1}H NMR ($CDCl_3$) δ 8.11 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 5.06 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 166.60, 162.33 ($J_{C\text{-}F}$ = 245 Hz), 139.02, 136.70, 135.73, 131.83 ($J_{C\text{-}F}$ = 3.5 Hz), 129.17 ($J_{C\text{-}F}$ = 8.0 Hz), 127.48, 126.54, 126.39, 126.12, 125.62, 115.84 ($J_{C\text{-}F}$ = 21.7 Hz), 112.44, 107.43, 43.25 ; IR (KBr) 3054, 2928, 1708, 1623, 1605, 1509, 1490, 1424, 1381, 1296, 1273, 1222, 1158, 1092, 824, 811, 728, 619 cm^{-1} ; LR-MS (FD) *m/z* (%): 433 (51), 434 (10), 435 (M^+, bp), 436 (20), 437 (51), 438 (10) ; HR-MS (FD) Calcd. for $C_{18}H_{10}Br_2FNO$: 432.9113, Found : 432.9131.

Preparation of 9,9'-(*N*-methyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7b



To *N*-methyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6b** (220 mg, 645 μmol), CuO (108 mg, 1.36 mmol) and $Pd(PPh_3)_4$ (227 mg, 196 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (888 mg, 2.60 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 15 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-methyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7b**(118 mg, 34%) as a yellow ocher solid.

Preparation of 9,9'-(*N*-ethyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7c

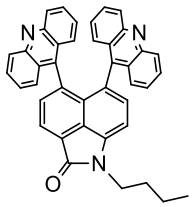


To *N*-ethyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6c** (213 mg, 600 μmol), CuO (99.8 mg, 1.25 mmol) and $Pd(PPh_3)_4$ (214 mg, 185 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (826 mg, 2.42 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 19 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-ethyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7c** (203 mg, 61%) as a yellow solid.

M. p. > 300 °C ; ^{1}H NMR ($CDCl_3$) δ 8.33 (d, *J* = 7.1 Hz, 1H), 7.72 (brd, *J* = 8.6 Hz, 4H), 7.57

(d, J = 7.1 Hz, 1H), 7.36 (ddd, J = 8.6, 6.5, 1.2 Hz, 4H), 7.32 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.02 (brd, J = 8.6 Hz, 2H), 6.87 (brd, J = 8.6 Hz, 2H), 6.74 (dt, J = 1.2, 6.5 Hz, 2H), 6.72 (dt, J = 1.2, 6.5 Hz, 2H), 4.21 (q, J = 7.2 Hz, 2H), 1.59 (t, J = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$) δ 167.33, 146.76, 146.60, 144.07, 143.47, 140.27, 138.95, 132.63, 132.31, 129.84, 129.12, 129.08, 129.02, 128.97, 127.87, 127.16, 126.31, 126.01, 125.71, 125.19, 124.93, 124.86, 124.32, 124.13, 105.07, 35.29, 14.19 ; IR (KBr) 3059, 2971, 2934, 1707, 1619, 1516, 1502, 1461, 1410, 1351, 1066, 752, 645, 604 cm^{-1} ; LR-MS (FD) *m/z* (%): 551 (M^+, bp), 552 (43), 553 (10) ; HR-MS (FD) Calcd. for $C_{39}H_{25}N_3O$: 551.1998, Found : 551.1991.

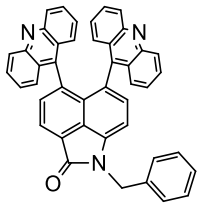
Preparation of 9,9'-(*N*-butyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7d



To *N*-butyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6d** (296 mg, 773 μmol), CuO (125 mg, 1.57 mmol) and $Pd(PPh_3)_4$ (273 mg, 236 μmol) was added degassed dry DMF (10 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (1.07 g, 3.14 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 18 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-butyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7d** (283 mg, 63%) as a yellow solid.

M. p. 275-277 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 8.33 (d, J = 7.1 Hz, 1H), 7.72 (brd, J = 8.6 Hz, 4H), 7.57 (d, J = 7.1 Hz, 1H), 7.36 (dt, J = 1.2, 7.4 Hz, 4H), 7.31 (d, J = 7.2 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.02 (brd, J = 8.1 Hz, 2H), 6.88 (brd, J = 8.1 Hz, 2H), 6.75 (dt, J = 1.2, 6.5 Hz, 2H), 6.73 (dt, J = 1.2, 6.5 Hz, 2H), 4.14 (t, J = 7.3 Hz, 2H), 1.98 (quin, J = 7.3 Hz, 2H), 1.63 (sext, J = 7.3 Hz, 2H), 1.11 (t, J = 7.3 Hz, 3H) ; ^{13}C NMR ($CDCl_3$) δ 167.63, 146.74, 146.58, 144.14, 143.53, 140.71, 138.92, 132.64, 132.32, 129.77, 129.10, 129.05, 129.00, 127.80, 127.10, 126.25, 126.03, 125.74, 125.20, 124.95, 124.87, 124.34, 124.14, 105.20, 40.39, 31.04, 20.44, 13.93 ; IR (KBr) 3060, 2957, 2931, 2871, 1709, 1621, 1518, 1503, 1462, 1410, 1389, 754, 646, 605 cm^{-1} ; LR-MS (FD) *m/z* (%): 579 (M^+, bp), 580 (46), 581 (11) ; HR-MS (FD) Calcd. for $C_{41}H_{29}N_3O$: 579.2311, Found : 579.2315.

Preparation of 9,9'-(*N*-benzyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7e

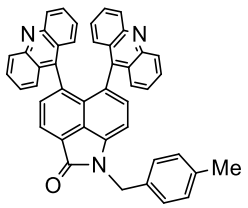


To *N*-benzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6e** (230 mg, 551 μmol), CuO (93.7 mg, 1.18 mmol) and $Pd(PPh_3)_4$ (193 mg, 167 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (767 mg, 2.24 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 19 h with stirring.

After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-benzyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7e** (198 mg, 59%) as a yellow solid.

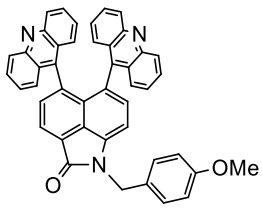
M. p. > 300 °C ; ^{1}H NMR ($CDCl_3$) δ 8.38 (d, *J* = 7.0 Hz, 1H), 7.72 (brd, *J* = 8.6 Hz, 4H), 7.61 (brd, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.47 (brd, *J* = 7.1 Hz, 1H), 7.45 (brd, *J* = 7.7 Hz, 1H), 7.41-7.33 (m, 5H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.97 (brd, *J* = 8.1 Hz, 2H), 6.86 (brd, *J* = 8.1 Hz, 2H), 6.73 (dt, *J* = 1.1, 6.5 Hz, 2H), 6.71 (dt, *J* = 1.1, 6.5 Hz, 2H), 5.34 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 167.64, 146.62, 146.52, 144.10, 143.46, 140.20, 139.18, 136.65, 132.69, 132.33, 129.77, 129.10, 129.06, 129.00, 128.95, 128.02, 127.99, 127.45, 127.35, 126.39, 126.00, 125.70, 125.25, 124.98, 124.82, 124.60, 124.10, 105.95, 44.40 ; IR (KBr) 3061, 2926, 1710, 1653, 1621, 1559, 1517, 1502, 1461, 1436, 1410, 1387, 1351, 753, 646 cm^{-1} ; LR-MS (FD) *m/z* (%): 613 (M^+, bp), 614 (50), 615 (13) ; HR-MS (FD) Calcd. for $C_{44}H_{27}N_3O$: 613.2154, Found : 613.2163.

Preparation of 9,9'-(*N-p*-methylbenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7f



To (*N*-p-methylbenzyl)-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6f** (220 mg, 510 μmol), CuO (84.1 mg, 1.06 mmol) and $Pd(PPh_3)_4$ (179 mg, 155 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (705 mg, 2.06 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 19 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-p-methylbenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7f** (130 mg, 41%) as a yellow ocher solid.

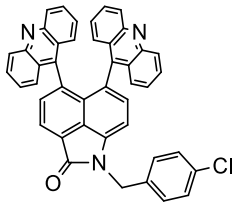
Preparation of 9,9'-(*N-p*-methoxybenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7g



To *N*-methoxybenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6g** (267 mg, 597 μmol), CuO (97.2 mg, 1.22 mmol) and $Pd(PPh_3)_4$ (215 mg, 186 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (822 mg, 2.40 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 16 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting

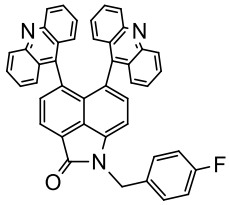
residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-p-methoxybenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7g** (184 mg, 48%) as a yellow ocher solid.

Preparation of 9,9'-(*N-p*-chlorobenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7h



To (*N*-p-chlorobenzyl)-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6h** (260 mg, 576 μmol), CuO (94.3 mg, 1.19 mmol) and $Pd(PPh_3)_4$ (203 mg, 176 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (798 mg, 2.33 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 17 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-p-chlorobenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7h** (202 mg, 54%) as a yellow ocher solid.

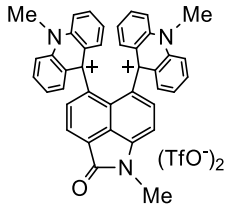
Preparation of 9,9'-(*N-p*-fluorobenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine 7i



To *N*-p-fluorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one **6i** (252 mg, 579 μmol), CuO (97.3 mg, 1.22 mmol) and $Pd(PPh_3)_4$ (204 mg, 177 μmol) was added degassed dry DMF (8 mL). The mixture was heated at 140°C for 5 min. Then, a solution of 9-trimethylstannylacridine (806 mg, 2.36 mmol) in degassed dry DMF (10 mL) was added to the mixture, and heated at 140°C for 18 h with stirring. After cooling to room temperature, the mixture was diluted with 5% aqueous ammonium hydroxide, and extracted with $CHCl_3$. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 ($CHCl_3/Et_3N$=100) to give 9,9'-(*N*-p-fluorobenzyl-1*H*-benzo[*cd*]indol-2-one)diacridine **7i** (206 mg, 56%) as a yellow solid.

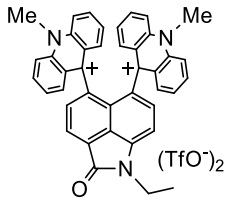
M. p. > 300 °C ; ^{1}H NMR ($CDCl_3$) δ 8.38 (d, *J* = 7.1 Hz, 1H), 7.71 (dd, *J* = 8.7, 3.2 Hz, 4H), 7.61-7.56 (m, 3H), 7.36 (ddd, *J* = 6.4, 3.4, 1.4 Hz, 2H), 7.34 (ddd, *J* = 6.4, 3.4, 1.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.96 (brd, *J* = 8.7 Hz, 2H), 6.86 (brd, *J* = 8.7 Hz, 2H), 6.73 (dt, *J* = 1.1, 6.5 Hz, 2H), 6.71 (dt, *J* = 1.1, 6.5 Hz, 2H), 5.30 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 167.60, 162.47 (J_{C-F} = 245 Hz), 146.67, 146.54, 143.93, 143.36, 139.98, 139.31, 132.76, 132.44 (J_{C-F} = 3.3 Hz), 132.28, 129.75 (J_{C-F} = 8.6 Hz), 129.09, 129.04, 129.01, 127.53, 127.33, 126.38, 125.95, 125.67, 125.25, 125.00, 124.80, 124.68, 124.08, 115.94 (J_{C-F} = 21.7 Hz), 105.81, 43.70 ; IR (KBr) 3061, 2928, 1709, 1622, 1510, 1462, 1438, 1410, 1389, 1223, 754, 743 cm^{-1} ; LR-MS (FD) *m/z* (%): 631 (M^+, bp), 632 (52), 633 (13) ; HR-MS (FD) Calcd. for $C_{44}H_{26}FN_3O$: 631.2060, Found : 631.2060.

Preparation of 9,9'-(*N*-methyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methylacridinium) 8b^{2+} (TfO$^-$)$_2$



To a solution of 9,9'-(*N*-methyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7b** (53.3 mg, 99.1 μmol) and 2,6-di-tert-butylpyridine (30 μL, 139 μmol) in dry CH_2Cl_2 (3 mL) was added methyl triflate (110 μL, 1.00 mmol). After the mixture was stirred for 20 h at 24 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8b**$^{2+}$(TfO$^-$)$_2$ (83.0 mg, 97%) as an orange solid.

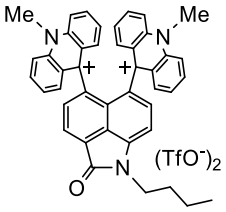
Preparation of 9,9'-(*N*-ethyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methylacridinium) bis(trifluoromethanesulfonate) 8c^{2+} (TfO$^-$)$_2$



To a solution of 9,9'-(*N*-ethyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7c** (50.1 mg, 90.8 μmol) and 2,6-di-tert-butylpyridine (26 μL, 120 μmol) in dry CH_2Cl_2 (2.5 mL) was added methyl triflate (100 μL, 912 μmol). After the mixture was stirred for 24 h at 24 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8c**$^{2+}$(TfO$^-$)$_2$ (70.6 mg, 88%) as an orange solid.

M. p. > 300 °C ; ^{1}H NMR (CD_3CN) δ 8.44 (d, *J* = 7.1 Hz, 1H), 8.19 (brd, *J* = 4.0 Hz, 2H), 8.16 (d, *J* = 4.0 Hz, 2H), 8.10 (ddd, *J* = 6.7, 2.6, 1.5 Hz, 2H), 8.08 (ddd, *J* = 6.7, 2.6, 1.5 Hz, 2H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.52 (brd, *J* = 0.6 Hz, 2H), 7.49 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.29 (brd, *J* = 6.7 Hz, 2H), 7.28 (brd, *J* = 6.7 Hz, 2H), 4.52 (s, 3H), 4.51 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.56 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR (CD_3CN) δ 167.21, 159.95, 158.88, 143.01, 139.97, 139.84, 139.79, 134.68, 133.87, 133.77, 130.48, 130.25, 130.03, 128.99, 128.76, 128.37, 127.02, 126.51, 125.88, 124.91, 123.29, 122.28, 120.10, 118.05, 117.99, 106.27, 39.22, 39.10, 35.82, 13.84 ; IR (KBr) 3086, 2980, 2941, 1713, 1622, 1608, 1579, 1550, 1501, 1373, 1275, 1224, 1154, 1031, 764, 637 cm^{-1} ; LR-MS (FD) *m/z* (%): 566 (80), 567 (37), 568 (9), 581 (M$^+$, bp), 582 (48), 583 (11), 730 (94), 731 (46), 732 (15), 733 (5) ; HR-MS (FD) Calcd. for $C_{41}H_{31}N_3O$: 581.2467, Found : 581.2442.

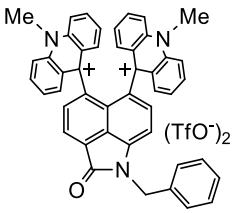
Preparation of 9,9'-(*N*-butyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methylacridinium) bis(trifluoromethanesulfonate) 8d^{2+} (TfO$^-$)$_2$



To a solution of 9,9'-(*N*-butyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7d** (52.1 mg, 89.9 μmol) and 2,6-di-tert-butylpyridine (25 μL, 116 μmol) in dry CH_2Cl_2 (2.5 mL) was added methyl triflate (100 μL, 912 μmol). After the mixture was stirred for 24 h at 24 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8d**$^{2+}$(TfO$^-$)$_2$ (76.9 mg, 94%) as an orange solid.

M. p. 154-156 °C (decomp.) ; ^{1}H NMR (CD_3CN) δ 8.43 (d, *J* = 7.1 Hz, 1H), 8.20 (brd, *J* = 4.0 Hz, 2H), 8.18 (d, *J* = 4.0 Hz, 2H), 8.10 (ddd, *J* = 6.7, 2.6, 1.5 Hz, 2H), 8.08 (ddd, *J* = 6.7, 2.6, 1.5 Hz, 2H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.51 (brs, 2H), 7.49 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.30 (brd, *J* = 6.7 Hz, 2H), 7.28 (brd, *J* = 6.7 Hz, 2H), 4.54 (s, 3H), 4.53 (s, 3H), 4.19 (t, *J* = 7.3 Hz, 2H), 1.98 (quin, *J* = 7.3 Hz, 2H), 1.62 (sext, *J* = 7.3 Hz, 2H), 1.11 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR (CD_3CN) δ 167.54, 159.95, 159.89, 143.40, 139.96, 139.84, 139.80, 134.65, 133.88, 133.77, 130.49, 130.26, 129.92, 128.99, 128.75, 128.34, 126.96, 126.51, 125.88, 124.91, 123.25, 122.28, 120.06, 118.07, 118.01, 106.43, 40.66, 39.22, 39.10, 31.06, 20.47, 13.71 ; IR (KBr) 3086, 2961, 2935, 2873, 1709, 1622, 1608, 1579, 1550, 1501, 1461, 1373, 1275, 1225, 1156, 1031, 763, 637 cm^{-1} ; LR-MS (FD) *m/z* (%): 594 (bp), 595 (49), 596 (12), 609 (M$^+$, 99), 610 (49), 611 (12), 758 (57), 759 (29), 760 (11) ; HR-MS (FD) Calcd. for $C_{43}H_{35}N_3O$: 609.2780, Found : 609.2771.

Preparation of 9,9'-(*N*-benzyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methylacridinium) bis(trifluoromethanesulfonate) 8e^{2+} (TfO$^-$)$_2$

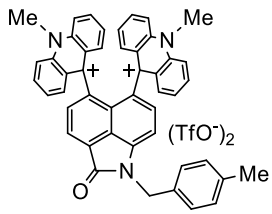


To a solution of 9,9'-(*N*-benzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7e** (50.6 mg, 82.5 μmol) and 2,6-di-tert-butylpyridine (25 μL, 116 μmol) in dry CH_2Cl_2 (3 mL) was added methyl triflate (90 μL, 820 μmol). After the mixture was stirred for 20 h at 22 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8e**$^{2+}$(TfO$^-$)$_2$ (66.2 mg, 85%) as an orange solid.

M. p. 159-161 °C (decomp.) ; ^{1}H NMR (CD_3CN) δ 8.49 (d, *J* = 7.1 Hz, 1H), 8.18 (brd, *J* = 6.6 Hz, 2H), 8.15 (brd, *J* = 6.6 Hz, 2H), 8.09 (dt, *J* = 1.5, 6.0 Hz, 2H), 8.07 (dt, *J* = 1.5, 6.0 Hz, 2H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.65 (brd, *J* = 7.5 Hz, 2H), 7.57 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.49 (brd, *J* = 7.5 Hz, 4H), 7.45-7.42 (m, 3H), 7.31-7.24 (m, 4H), 5.39 (s, 2H), 4.52 (s, 3H), 4.51 (s, 3H) ; ^{13}C NMR (CD_3CN) δ 167.57, 159.74, 158.74, 142.94, 139.96, 139.83, 139.81, 139.77, 137.49, 134.51, 134.13, 133.87, 130.45, 130.25, 129.62, 129.54, 128.98, 128.75, 128.47, 128.35, 127.07, 126.43, 125.84, 125.25,

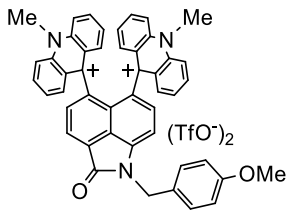
123.25, 122.64, 120.07, 118.05, 117.98, 106.72, 44.39, 39.21, 39.09 ; IR (KBr) 3108, 1710, 1623, 1608, 1579, 1550, 1498, 1374, 1275, 1225, 1154, 1031, 762, 637 cm^{-1} ; LR-MS (FD) *m/z* (%): 321 (60), 322 (35), 323 (10), 628 (57), 629 (29), 630 (8), 643 (M^+, 46), 644 (25), 645 (7), 792 (bp), 793 (59), 794 (22), 795 (6) ; HR-MS (FD) Calcd. for $C_{44}H_{33}N_3O$: 643.2624, Found : 643.2607.

Preparation of 9,9'-(*N*-*p*-methylbenzyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methyl acridinium) bis(trifluoromethanesulfonate) 8f^{2+} (TfO$^-$)$_2$



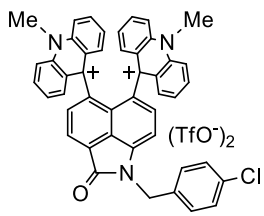
To a solution of 9,9'-(*N*-p-methylbenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7f** (32.5 mg, 51.8 μmol) and 2,6-di-tert-butylpyridine (15 μL, 69.4 μmol) in dry CH_2Cl_2 (2 mL) was added methyl triflate (60 μL, 547 μmol). After the mixture was stirred for 23 h at 23 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8f**$^{2+}$(TfO$^-$)$_2$ (44.7 mg, 90%) as an orange solid.

Preparation of 9,9'-(*N*-*p*-methoxybenzyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methyl acridinium) bis(trifluoromethanesulfonate) 8g^{2+} (TfO$^-$)$_2$



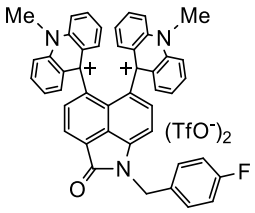
To a solution of 9,9'-(*N*-p-methoxybenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7g** (47.8 mg, 74.3 μmol) and 2,6-di-tert-butylpyridine (20 μL, 92.5 μmol) in dry CH_2Cl_2 (3 mL) was added methyl triflate (80 μL, 729 μmol). After the mixture was stirred for 20 h at 23 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8g**$^{2+}$(TfO$^-$)$_2$ (57.7 mg, 80%) as an orange solid.

Preparation of 9,9'-(*N*-*p*-chrolobenzyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methyl acridinium) bis(trifluoromethanesulfonate) 8h^{2+} (TfO$^-$)$_2$



To a solution of 9,9'-(*N*-p-chlorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7h** (51.8 mg, 79.9 μmol) and 2,6-di-tert-butylpyridine (25 μL, 116 μmol) in dry CH_2Cl_2 (3 mL) was added methyl triflate (90 μL, 820 μmol). After the mixture was stirred for 23 h at 23 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8h**$^{2+}$(TfO$^-$)$_2$ (71.5 mg, 92%) as an orange solid.

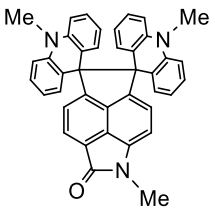
Preparation of 9,9'-(*N*-*p*-fluorobenzyl-1*H*-benzo[*cd*]indol-2-one)bis(10-methyl acridinium) bis(trifluoromethanesulfonate) 8i^{2+} (TfO$^-$)$_2$



To a solution of 9,9'-(*N*-p-fluorobenzyl-5,6-dibromo-1*H*-benzo[*cd*]indol-2-one)diacridine **7i** (118 mg, 187 μmol) and 2,6-di-tert-butylpyridine (50 μL, 231 μmol) in dry CH_2Cl_2 (6 mL) was added methyl triflate (205 μL, 1.87 mmol). After the mixture was stirred for 24 h at 22 °C, the mixture was diluted with dry ether. After removal of the supernatant liquid with a pipette, the resulting precipitates were purified by reprecipitation with dry MeCN and dry ether to give dicationic salt **8i**$^{2+}$(TfO$^-$)$_2$ (161 mg, 90%) as an orange solid.

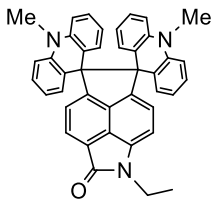
M. p. 292-293 °C (decomp.) ; ^{1}H NMR (CD_3CN) δ 8.49 (d, *J* = 7.2 Hz, 1H), 8.18 (brd, *J* = 6.1 Hz, 2H), 8.16 (brd, *J* = 6.1 Hz, 2H), 8.10 (dt, *J* = 1.5, 5.8 Hz, 2H), 8.07 (d, *J* = 1.5, 5.8 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.49 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.45 (d, *J* = 1.0 Hz, 2H), 7.31-7.22 (m, 6H), 5.37 (s, 2H), 4.52 (s, 3H), 4.51 (s, 3H) ; ^{13}C NMR (CD_3CN) δ 167.56, 162.87 (J_{C-F} = 242 Hz), 159.73, 158.73, 142.79, 139.97, 139.84, 139.79, 134.52, 134.17, 133.89, 133.63 (J_{C-F} = 3.1 Hz), 130.46 (J_{C-F} = 8.2 Hz), 130.44, 130.24, 129.59, 129.00, 128.77, 128.39, 127.10, 126.45, 125.86, 125.28, 123.26, 122.72, 120.07, 118.07, 118.00, 116.20 (J_{C-F} = 21.9 Hz), 106.73, 43.71, 39.23, 39.10 ; IR (KBr) 3082, 1713, 1623, 1608, 1579, 1550, 1510, 1373, 1274, 1225, 1159, 1031, 762, 637 cm^{-1} ; LR-MS (FD) *m/z* (%): 646 (bp), 647 (51), 648 (13), 661 (M$^+$, 85), 662 (45), 663 (12), 810 (50), 811 (28), 812 (10), 813 (3) ; HR-MS (FD) Calcd. for $C_{46}H_{32}FN_3O$: 661.2529, Found : 661.2523.

Preparation of Dispiro[(10-methylacridan)-9',5-*N*-methyl-5,6-dihydroindeno[6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1b



To a suspension of Zn powder (623 mg, 9.53 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8b**$^{2+}$(TfO$^-$)$_2$ (81.9 mg, 94.5 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 23 °C under argon, and the mixture was stirred for 21 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1b** (24.7 mg, 46%) as a yellow ocher solid.

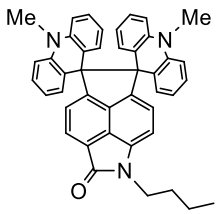
Preparation of Dispiro[(10-methylacridan)-9',5-*N*-ethyl-5,6-dihydroindeno[6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1c



To a suspension of Zn powder (527 mg, 8.06 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8c**$^{2+}$(TfO^-)$_2$ (68.9 mg, 78.3 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 24 °C under argon, and the mixture was stirred for 20 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1c** (37.1 mg, 81%) as a yellow ocher solid.

M. p. > 300 °C ; ^{1}H NMR (CD_2Cl_2, 193 K) δ 8.22 (brd, *J* = 7.1 Hz, 1H), 7.33 (brd, *J* = 7.1 Hz, 1H), 7.20 (brd, *J* = 6.9 Hz, 1H), 7.10 (brd, *J* = 6.9 Hz, 1H), 6.92 (brt, *J* = 7.5 Hz, 4H), 6.57 (brd, *J* = 7.8 Hz, 2H), 6.56 (brd, *J* = 7.8 Hz, 2H), 6.31 (brt, *J* = 7.8 Hz, 2H), 6.29 (brt, *J* = 7.8 Hz, 2H), 6.05 (brd, *J* = 7.5 Hz, 2H), 5.85 (brd, *J* = 7.5 Hz, 2H), 4.08 (brq, *J* = 6.6 Hz, 2H), 3.05 (brs, 6H), 1.42 (brt, *J* = 6.6 Hz, 3H) ; ^{13}C NMR (CD_2Cl_2, 193 K) δ 168.36, 150.98, 140.96, 140.88, 139.69, 137.07, 136.43, 129.17, 127.84, 127.10, 127.03, 126.59, 125.84, 125.75, 125.24, 124.00, 122.71, 118.58, 110.80, 110.75, 108.31, 75.82, 75.17, 35.85, 33.36, 14.78 ; IR (KBr) 3076, 3036, 2975, 2931, 2873, 2818, 1713, 1697, 1590, 1501, 1470, 1357, 1298, 1272, 745 cm^{-1} ; LR-MS (FD) *m/z* (%): 581 (M$^+$, bp), 582 (46), 583 (2) ; HR-MS (FD) Calcd. for $C_{41}H_{31}N_3O$: 581.2467, Found : 581.2487.

Preparation of Dispiro[(10-methylacridan)-9',5-*N*-butyl-5,6-dihydroindeno[6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1d

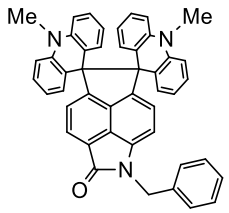


To a suspension of Zn powder (462 mg, 7.07 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8d**$^{2+}$(TfO^-)$_2$ (62.3 mg, 68.6 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 23 °C under argon, and the mixture was stirred for 20 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1d** (32.6 mg, 78%) as a yellow ocher solid.

M. p. 212-214 °C (decomp.) ; ^{1}H NMR (CD_2Cl_2, 233 K) δ 8.22 (d, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.94 (dt, *J* = 1.5, 7.7 Hz, 4H), 6.59 (brd, *J* = 7.6 Hz, 2H), 6.58 (brd, *J* = 7.6 Hz, 2H), 6.37-6.29 (m, 4H), 6.09 (dd, *J* = 7.7, 1.5 Hz, 2H), 5.89 (dd, *J* = 7.7, 1.5 Hz, 2H), 4.05 (t, *J* = 7.3 Hz, 2H), 3.10 (s, 3H), 3.09 (s, 3H), 1.87 (quin, *J* = 7.3 Hz, 2H), 1.52 (sext, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H) ; ^{13}C NMR (CD_2Cl_2, 193 K) δ 168.67, 150.97, 140.95, 140.88, 139.67, 137.02, 136.90, 129.18, 129.15, 127.81, 127.09, 127.01, 126.56,

125.80, 125.76, 125.25, 123.93, 122.65, 118.58, 110.79, 110.74, 108.44, 75.84, 75.19, 40.89, 33.33, 31.45, 20.63, 14.31 ; IR (KBr) 3036, 2958, 2929, 2872, 1697, 1636, 1608, 1591, 1501, 1471, 1359, 1299, 1273, 1054, 745 cm^{-1} ; LR-MS (FD) *m/z* (%): 609 (M^+, bp), 610 (49), 611 (13), 612 (3) ; HR-MS (FD) Calcd. for $C_{43}H_{35}N_3O$: 609.2780, Found : 609.2801.

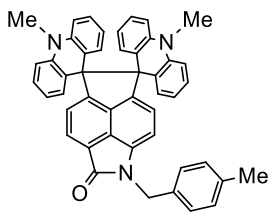
Preparation of Dispiro[(10-methylacridan)-9',5-*N*-benzyl-5,6-dihydroindeno[6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1e



To a suspension of Zn powder (463 mg, 7.08 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8e**$^{2+}$(TfO^-)$_2$ (65.1 mg, 69.1 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 23 °C under argon, and the mixture was stirred for 21 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1e** (37.3 mg, 84%) as an olive solid.

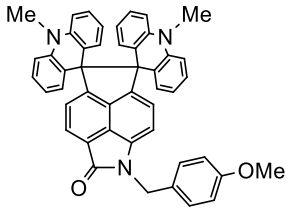
M. p. 276-278 °C (decomp.) ; ^{1}H NMR (CD_2Cl_2, 233 K) δ 8.28 (brd, *J* = 7.0 Hz, 1H), 7.56 (brd, *J* = 7.0 Hz, 2H), 7.42 (brt, *J* = 7.6 Hz, 2H), 7.39-7.33 (m, 2H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.96-6.90 (m, 4H), 6.57 (brt, *J* = 7.6 Hz, 4H), 6.31 (dt, *J* = 3.0, 7.6 Hz, 4H), 6.05 (dd, *J* = 7.6, 1.5 Hz, 2H), 5.88 (dd, *J* = 7.6, 1.5 Hz, 2H), 5.25 (s, 2H), 3.09 (s, 3H), 3.08 (s, 3H) ; ^{13}C NMR (CD_2Cl_2, 193 K) δ 168.63, 151.32, 140.91, 140.85, 140.08, 137.66, 137.05, 136.31, 129.21, 129.02, 128.22, 127.98, 127.12, 127.04, 126.75, 125.79, 125.68, 125.19, 123.54, 122.84, 118.64, 118.58, 110.74, 110.70, 108.70, 75.89, 75.24, 44.52, 33.32 ; IR (KBr) 3062, 3034, 2875, 2819, 1693, 1591, 1501, 1471, 1358, 1273, 745 cm^{-1} ; LR-MS (FD) *m/z* (%): 643 (M^+, bp), 644 (54), 645 (14), 646 (3) ; HR-MS (FD) Calcd. for $C_{46}H_{33}N_3O$: 643.2624, Found : 643.2645.

Preparation of Dispiro[(10-methylacridan)-9',5-*N*-*p*-methylbenzyl-5,6-dihydroindeno [6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1f



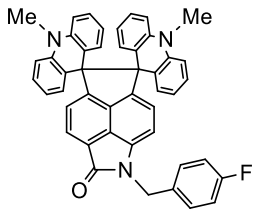
To a suspension of Zn powder (360 mg, 5.51 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8f**$^{2+}$(TfO^-)$_2$ (44.1 mg, 46.1 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 23 °C under argon, and the mixture was stirred for 14 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1f** (21.8 mg, 72%) as a yellow ocher solid.

Preparation of Dispiro[(10-methylacridan)-9',5-*N*-*p*-methoxybenzyl-5,6-dihydroindeno [6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1g



To a suspension of Zn powder (397 mg, 6.07 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8g**$^{2+}$(TfO^-)$_2$ (56.6 mg, 58.2 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 23 °C under argon, and the mixture was stirred for 19 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1g** (32.7 mg, 83%) as a yellow ocher solid.

Preparation of Dispiro[(10-methylacridan)-9',5-*N*-*p*-fluorobenzyl-5,6-dihydroindeno [6,7,1-*cde*]indol-2(1*H*)-one-6,9''(10-methylacridan)] 1i



To a suspension of Zn powder (382 mg, 5.84 mmol) in degassed dry MeCN/ Et_3N (10:3, 5 mL) was transferred a solution of the as-prepared dication salt **8i**$^{2+}$(TfO^-)$_2$ (52.4 mg, 54.6 μmol) in degassed dry MeCN/ Et_3N (10:3, 10 mL) with a cannula at 22 °C under argon, and the mixture was stirred for 21 h. The mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by reprecipitation with EtOAc and hexane to give **1i** (19.4 mg, 54%) as an olive solid.

M. p. 214-216 °C (decomp.) ; ^{1}H NMR (CD_2Cl_2, 233 K) δ 8.28 (d, J = 7.2 Hz, 1H), 7.56 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 7.13 (d, J = 8.6 Hz, 1H), 7.06 (brs, 2H), 6.97-6.90 (m, 4H), 6.58 (brt, J = 7.7 Hz, 4H), 6.32 (dt, J = 3.8, 7.7 Hz, 4H), 6.05 (dd, J = 7.7, 1.4 Hz, 2H), 5.84 (dd, J = 7.7, 1.4 Hz, 2H), 5.22 (s, 2H), 3.09 (s, 3H), 3.08 (s, 3H) ; ^{13}C NMR (CD_2Cl_2, 193 K) δ 168.60, 162.01 ($J_{C\text{-}F}$ = 244 Hz), 151.38, 140.91, 140.86, 140.17, 137.06, 136.16, 133.58 ($J_{C\text{-}F}$ = 2.6 Hz), 130.01 ($J_{C\text{-}F}$ = 8.0 Hz), 129.22, 128.26, 127.16, 127.09, 126.82, 125.80, 125.67, 125.18, 123.45, 122.84, 118.65, 118.60, 115.82 ($J_{C\text{-}F}$ = 21.1 Hz), 110.81, 110.77, 108.71, 75.90, 75.25, 43.84, 33.31 ; IR (KBr) 3065, 3037, 2965, 2889, 2820, 1711, 1697, 1608, 1591, 1510, 1473, 1359, 1298, 1273, 1224, 744 cm^{-1} ; LR-MS (FD) *m/z* (%): 661 (M^+, bp), 662 (52), 663 (14), 664 (3) ; HR-MS (FD) Calcd. for $C_{46}H_{32}FN_3O$: 661.2529, Found : 661.2548.

X-ray analyses

Data collection was conducted with a Rigaku Mercury 70 diffractometer (Mo-Kα radiation, λ = 0.71075 Å). The structure was solved by the direct method (SIR2004) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding.

Crystal date for 1c

MF : $C_{41}H_{31}N_3O$, FW : 581.72, yellow platelet, 0.20 × 0.15 × 0.05 mm, monoclinic $P2_1/c$, a = 8.089(3) Å, b = 17.736(8) Å, c = 20.063(9) Å, α = 90°, β = 92.094(7)°, γ = 90°, V = 2876(3) Å^3, ρ (Z = 4) = 1.343 g/cm^3. A total 5036 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.809 cm^{-1}). The final *R1* and *wR2* values are 0.0846 (I > 2σI) and 0.1810 (all data) for 5036 reflections and 406 parameters. Estimated standard deviations are 0.005-0.008 Å for bond lengths and 0.3-0.5° for bond angles, respectively.

Crystal date for 1d

MF : $C_{43}H_{35}N_3O$, FW : 609.77, yellow platelet, 0.20 × 0.10 × 0.01 mm, monoclinic $P2_1/c$, a = 8.124(3) Å, b = 18.145(7) Å, c = 20.945(9) Å, α = 90°, β = 95.895(7)°, γ = 90°, V = 3071(2) Å^3, ρ (Z = 4) = 1.319 g/cm^3. A total 5932 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.791 cm^{-1}). The final *R1* and *wR2* values are 0.0797 (I > 2σI) and 0.2270 (all data) for 5932 reflections and 424 parameters. Estimated standard deviations are 0.007-0.009 Å for bond lengths and 0.4-0.6° for bond angles, respectively.

Crystal date for 1e at 120K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.712(5) Å, b = 15.631(5) Å, c = 27.337(9) Å, α = 90°, β = 90°, γ = 90°, V = 6287(4) Å^3, ρ (Z = 8) = 1.360 g/cm^3. A total 6038 unique data ($2\theta_{max}$ = 55°) were measured at T = 120 K. Numerical absorption correction was applied (μ = 0.815 cm^{-1}). The final *R1* and *wR2* values are 0.1784 (I > 2σI) and 0.3379 (all data) for 6038 reflections and 451 parameters. Estimated standard deviations are 0.011-0.03 Å for bond lengths and 0.6-1.5° for bond angles, respectively.

Crystal date for 1e at 150K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.728(5) Å, b = 15.655(5) Å, c = 27.369(8) Å, α = 90°, β = 90°, γ = 90°, V = 6310(4) Å^3, ρ (Z = 8) = 1.355 g/cm^3. A total 6033 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.812 cm^{-1}). The final *R1* and *wR2* values are 0.1676 (I > 2σI) and 0.3234 (all data) for 6033 reflections and 451 parameters. Estimated standard deviations are 0.01-0.03 Å for bond lengths and 0.6-1.5° for bond angles, respectively.

Crystal date for 1e at 200K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.761(5) Å, b = 15.683(5) Å, c = 27.442(8) Å, α = 90°, β = 90°, γ = 90°, V = 6353(4) Å^3, ρ (Z = 8) = 1.346 g/cm^3. A total 6101 unique data ($2\theta_{max}$ = 55°) were measured at T = 200 K. Numerical absorption correction was applied (μ = 0.806 cm^{-1}). The final *R1* and *wR2* values are 0.1281 (I > 2σI) and 0.2338 (all data) for 6101 reflections and 451 parameters. Estimated standard deviations are 0.008-0.02 Å for bond lengths and 0.4-1.1° for bond angles, respectively.

Crystal date for 1e at 230K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.782(4) Å, b = 15.707(4) Å, c = 27.503(7) Å, α = 90°, β = 90°, γ = 90°, V = 6386(3) Å^3, ρ (Z = 8) = 1.339 g/cm^3. A total 5552 unique data ($2\theta_{max}$ = 55°) were measured at T = 230 K. Numerical absorption correction was applied (μ = 0.802 cm^{-1}). The final *R1* and *wR2* values are 0.0874 (I > 2σI) and 0.2228 (all data) for 5552 reflections and 451 parameters. Estimated standard deviations are 0.005-0.016 Å for bond lengths and 0.3-0.8° for bond angles, respectively.

Crystal date for 1e at 273K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.857(4) Å, b = 15.772(4) Å, c = 27.596(7) Å, α = 90°, β = 90°, γ = 90°, V = 6466(3) Å^3, ρ (Z = 8) = 1.322 g/cm^3. A total 6338 unique data ($2\theta_{max}$ = 55°) were measured at T = 273 K. Numerical absorption correction was applied (μ = 0.792 cm^{-1}). The final *R1* and *wR2* values are 0.0833 (I > 2σI) and 0.1942 (all data) for 6338 reflections and 451 parameters. Estimated standard deviations are 0.004-0.014 Å for bond lengths and 0.3-0.7° for bond angles, respectively.

Crystal date for 1e at 320K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.859(3) Å, b = 15.794(3) Å, c = 27.672(6) Å, α = 90°, β = 90°, γ = 90°, V = 6494(3) Å^3, ρ (Z = 8) = 1.317 g/cm^3. A total 6365 unique data ($2\theta_{max}$ = 55°) were measured at T = 320 K. Numerical absorption correction was applied (μ = 0.789 cm^{-1}). The final *R1* and *wR2* values are 0.0740 (I > 2σI) and 0.2297 (all data) for 6365 reflections and 451 parameters. Estimated standard deviations are 0.004-0.016 Å for bond lengths and 0.3-0.8° for bond angles, respectively.

Crystal date for 1e at 360K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.883(3) Å, b = 15.826(3) Å, c = 27.727(6) Å, α = 90°, β = 90°, γ = 90°, V = 6531(3) Å^3, ρ (Z = 8) = 1.309 g/cm^3. A total 6387 unique data ($2\theta_{max}$ = 55°) were measured at T = 360 K. Numerical absorption correction was applied (μ = 0.784 cm^{-1}). The final *R1* and *wR2* values are 0.0940 (I > 2σI) and 0.2475 (all data) for 6387 reflections and 451 parameters. Estimated standard deviations are 0.005-0.03 Å for bond lengths and 0.3-1.2° for bond angles, respectively.

Crystal date for 1e at 400K

MF : $C_{46}H_{33}N_3O$, FW : 643.79, green platelet, 0.30 × 0.20 × 0.05 mm, orthorhombic *Pbca*, a = 14.890(3) Å, b = 15.851(3) Å, c = 27.784(6) Å, α = 90°, β = 90°, γ = 90°, V = 6558(3) Å^3, ρ (Z = 8) = 1.304 g/cm^3. A total 6412 unique data ($2\theta_{max}$ = 55°) were measured at T = 400 K. Numerical absorption correction was applied (μ = 0.781 cm^{-1}). The final *R1* and *wR2* values are 0.0969 (I > 2σI) and 0.2930 (all data) for 6412 reflections and 451 parameters. Estimated standard deviations are 0.006-0.03 Å for bond lengths and 0.3-1.4° for bond angles, respectively.

Crystal date for 1i at 120K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 14.988(3) Å, b = 15.779(3) Å, c = 27.486(5) Å, α = 90°, β = 90°, γ = 90°, V = 6500(3) Å^3, ρ (Z = 8) = 1.352 g/cm^3. A total 7430 unique data ($2\theta_{max}$ = 55°) were measured at T = 120 K. Numerical absorption correction was applied (μ = 0.851 cm^{-1}). The final *R1* and *wR2* values are 0.0608 (I > 2σI) and 0.1865 (all data) for 7430 reflections and 462 parameters. Estimated standard deviations are 0.003-0.006 Å for bond lengths and 0.17-0.4° for bond angles, respectively.

Crystal date for 1i at 150K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.005(2) Å, b = 15.791(3) Å, c = 27.531(4) Å, α = 90°, β = 90°, γ = 90°, V = 6523(2) Å^3, ρ (Z = 8) = 1.348 g/cm^3. A total 7471 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.848 cm^{-1}). The final *R1* and *wR2* values are 0.0631 (I > 2σI) and 0.1897 (all data) for 7471 reflections and 462 parameters. Estimated standard deviations are 0.003-0.007 Å for bond lengths and 0.17-0.5° for bond angles, respectively.

Crystal date for 1i at 200K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.010(3) Å, b = 15.812(3) Å, c = 27.610(6) Å, α = 90°, β = 90°, γ = 90°, V = 6553(3) Å^3, ρ (Z = 8) = 1.341 g/cm^3. A total 7475 unique data ($2\theta_{max}$ = 55°) were measured at T = 200 K. Numerical absorption correction was applied (μ = 0.844 cm^{-1}). The final *R1* and *wR2* values are 0.0712 (I > 2σI) and 0.2000 (all data) for 7475 reflections and 460 parameters. Estimated standard deviations are 0.004-0.008 Å for bond lengths and 0.19-0.5° for bond angles, respectively.

Crystal date for 1i at 230K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.018(3) Å, b = 15.822(3) Å, c = 27.656(5) Å, α = 90°, β = 90°, γ = 90°, V = 6571(3) Å^3, ρ (Z = 8) = 1.338 g/cm^3. A total 7508 unique data ($2\theta_{max}$ = 55°) were measured at T = 230 K. Numerical absorption correction was applied (μ = 0.841 cm^{-1}). The final *R1* and *wR2* values are 0.0676 (I > 2σI) and 0.2168 (all data) for 7508 reflections and 460 parameters. Estimated standard deviations are 0.004-0.009 Å for bond lengths and 0.19-0.6° for bond angles, respectively.

Crystal date for 1i at 273K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.035(3) Å, b = 15.827(3) Å, c = 27.722(5) Å, α = 90°, β = 90°, γ = 90°, V = 6597(3) Å^3, ρ (Z = 8) = 1.333 g/cm^3. A total 7536 unique data ($2\theta_{max}$ = 55°) were measured at T = 273 K. Numerical absorption correction was applied (μ = 0.838 cm^{-1}). The final *R1* and *wR2* values are 0.0683 (I > 2σI) and 0.2225 (all data) for 7536 reflections and 460 parameters. Estimated standard deviations are 0.004-0.011 Å for bond lengths and 0.2-0.7° for bond angles, respectively.

Crystal date for 1i at 320K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.054(3) Å, b = 15.853(3) Å, c = 27.823(5) Å, α = 90°, β = 90°, γ = 90°, V = 6640(3) Å^3, ρ (Z = 8) = 1.324 g/cm^3. A total 7494 unique data ($2\theta_{max}$ = 55°) were measured at T = 320 K. Numerical absorption correction was applied (μ = 0.833 cm^{-1}). The final *R1* and *wR2* values are 0.0733 (I > 2σI) and 0.2459 (all data) for 7494 reflections and 462 parameters. Estimated standard deviations are 0.004-0.013 Å for bond lengths and 0.2-0.8° for bond angles, respectively.

Crystal date for 1i at 360K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.061(3) Å, b = 15.868(3) Å, c = 27.898(6) Å, α = 90°, β = 90°, γ = 90°, V = 6667(3) Å^3, ρ (Z = 8) = 1.318 g/cm^3. A total 7600 unique data ($2\theta_{max}$ = 55°) were measured at T = 360 K. Numerical absorption correction was applied (μ = 0.829 cm^{-1}). The final *R1* and *wR2* values are 0.0766 (I > 2σI) and 0.2405 (all data) for 7600 reflections and 460 parameters. Estimated standard deviations are 0.005-0.015 Å for bond lengths and 0.3-1.0° for bond angles, respectively.

Crystal date for 1i at 400K

MF : $C_{46}H_{32}FN_3O$, FW : 661.78, green block, 0.30 × 0.10 × 0.10 mm, orthorhombic *Pbca*, a = 15.075(3) Å, b = 15.887(4) Å, c = 27.952(6) Å, α = 90°, β = 90°, γ = 90°, V = 6694(3) Å^3, ρ (Z = 8) = 1.313 g/cm^3. A total 7558 unique data ($2\theta_{max}$ = 55°) were measured at T = 400 K. Numerical absorption correction was applied (μ = 0.826 cm^{-1}). The final *R1* and *wR2* values are 0.0856 (I > 2σI) and 0.2471 (all data) for 7558 reflections and 460 parameters. Estimated standard deviations are 0.005-0.017 Å for bond lengths and 0.3-1.1° for bond angles, respectively.

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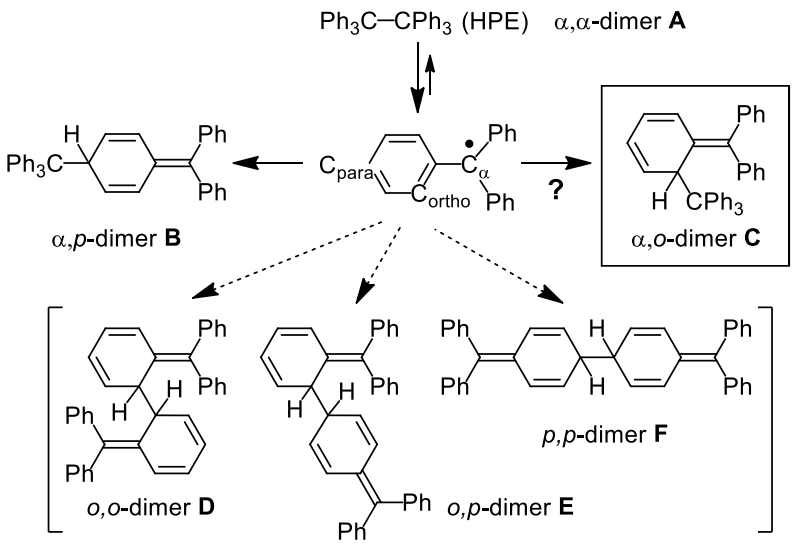
Chapter 3

Missing Isomer of Hexaphenylethane: Unprecedented α,*o*-Dimer Formation on a 1*H*-Cyclobuta[*de*]naphthalene Skeleton

3-1. Introduction

Hexaphenylethane (HPE, **A**) is a molecule with many riddles.[1] The trityl radical ($Ph_3C^{\bullet}$) dimerizes to form 3-diphenylmethylene-6-triphenylmethyl-1,4-cyclohexadiene (α,*p*-dimer, **B**),[2] as **B** is thermodynamically more stable than **A** (α,α-dimer), and the central C-C bond of **A** is easily cleaved to regenerate two radicals (Scheme 3-1). When the formation of the α,*p*-dimer is prevented by the attachment of bulky substituents on the aryl moieties, HPE derivatives (α,α-dimers) can be generated,[3] which also gain stability by dispersion forces.[4] Other coupling modes for a trityl radical, such as *o*,*o*-, *o*,*p*-, and *p*,*p*-dimerization,[5] are energetically disfavored because a greater number of aromatic sextets[6] are lost in the resulting dimers (**D**-**F**) than in **A** or **B**. In this context, the α,*o*-dimer (**C**), which has the same number of aromatic sextets as **B**, is especially interesting. Considering that **B** and **C** have nearly the same steric energy (ΔE=6.63 kcal/mol) as estimated by calculations employing the OPLS force field (Figure 3-1), there should be no reason for the absence of α,*o*-adducts, although such derivatives have never been described in the literature. As HPE derivatives (α,α-adducts) become accessible when the α,*p*-coupling is suppressed, the α,*o*-adducts should be generated when the formation of the corresponding α,*p*- and α,α-adducts is prevented.



Scheme 3-1. Dimerization modes of the trityl radical.

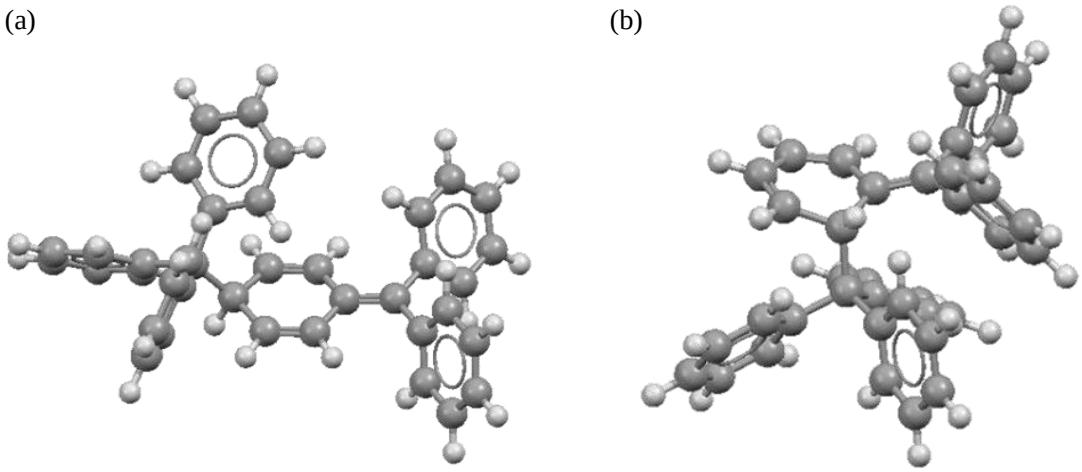
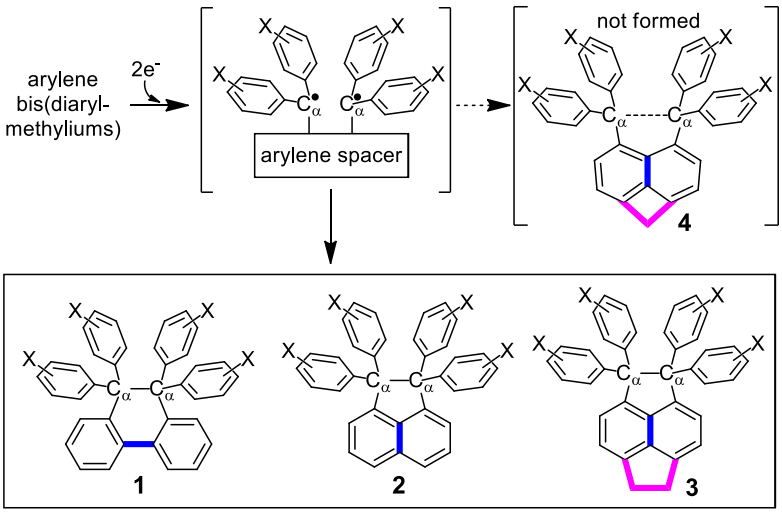


Figure 3-1. Energy-minimized structures for (a) α,*p*-dimer **B** (rel. 0 kcal/mol) and (b) α,*o*-dimer **C** (+ 6.63 kcal/mol) obtained by a conformational search with Macro Model software (v9.9 Monte Carlo Multiple Minimum method, OPLS_2005, non-solvated, 10000 steps).

So, the author has planned to suppress the α,*p*-coupling by adopting the "arylenediyl approach" using a naphthalene-1,8-diyl skeleton as in **2**. The "arylenediyl approach" is another method for facilitating α,α-coupling. By connecting or annulating two phenyl groups between the two radicals, the C_α carbon atoms are spatially arranged in close proximity, and the formation of a C_α-C_α bond becomes a favored intramolecular process (Scheme 3-2). Thus, a series of 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes **1**[7] or 1,1,2,2-tetraarylacenaphthenes **2**[8] were prepared as stable α,α-adducts[9] despite their elongated C_α-C_α bond with a length of up to 1.761(4) Å.[10]



Scheme 3-2. Arylenediyl approach for facilitating α,α-couplings.

Furthermore, the author considered to discourage the α,α-coupling by using "Scissor effects" through ring annulation at the opposite *peri*-position of the naphthalene core (Figure 3-2). The C_α and C_{ortho} carbon atoms of each radical unit are thus brought into close contact in addition to the two C_α atoms. The angle strain induced by annulation of a five-membered ring, as in 1,1,2,2-tetraarylpyracenes **3**, would result in a smaller $\theta 1$ angle and a larger $\theta 2$ angle so that the interatomic distance $d2$ becomes much greater than $d1$. In 4,4,5,5-tetraaryl-1*H*-cyclobuta[*fg*]acenaphthenes **4**, these effects would be more prominent and prevent C_α-C_α bonding because the interatomic distance $d3$ is much greater in the precursor diradicals for **4** than in those for **3**. Thus, it is highly likely that in 1*H*-cyclobuta[*de*]naphthalene-4,5-diyl diradicals, both the α,*p*- and α,α-coupling pathways would be suppressed so that α,*o*-adducts can be obtained for the first time. In this chapter, the author report the successful generation and isolation of α,*o*-adducts **5** along with their unique properties and X-ray structures.

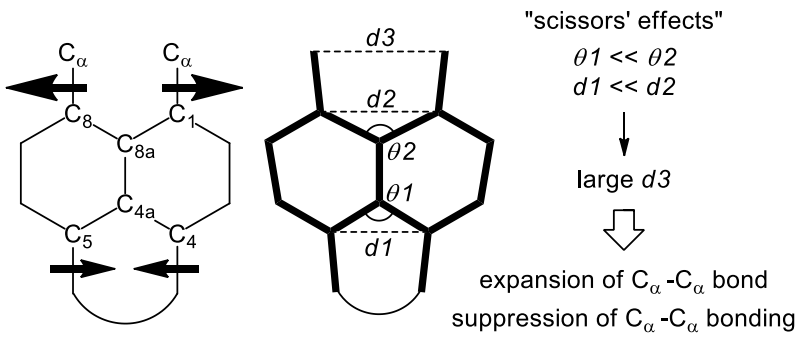
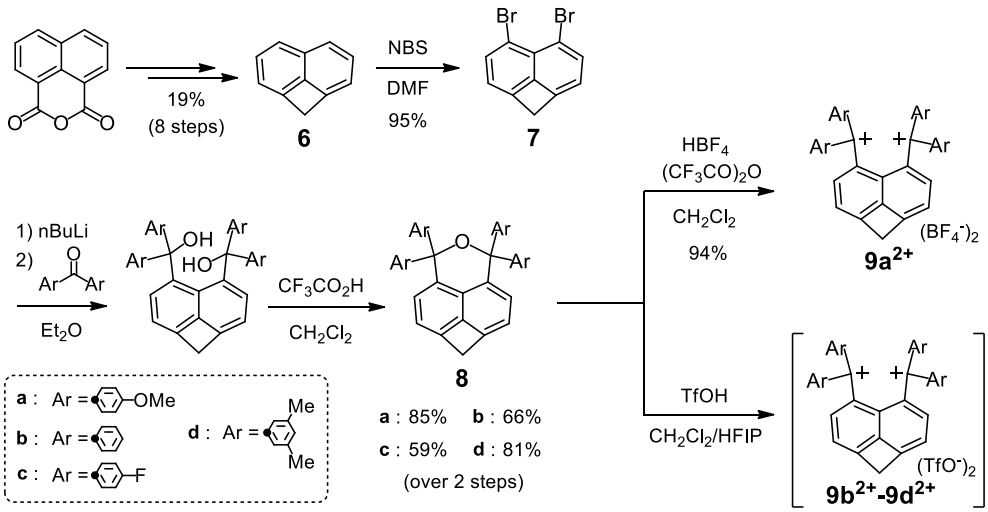


Figure 3-2. Scissor effects in a naphthalene core fused to another ring system at the opposite *peri*-position.

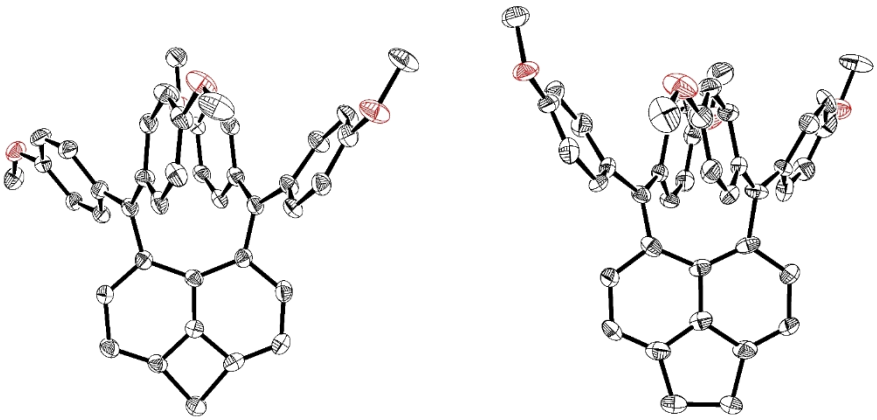
3-2. Preparation and X-ray Structure of Precursor Dication 9^{2+}

1*H*-Cyclobuta[*de*]naphthalene **6** was prepared in 8 steps from commercially available 1,8-naphthalic anhydride following the published procedures.[11] Bromination of **6** into 4,5-dibromide **7** was conducted in a stepwise manner,[12] however the author could make it more easily by using NBS (4 equiv.) in DMF (50°C, 20 h, y. 95%). The reaction of **7** with *n*-BuLi in diethyl ether followed by the addition of benzophenone gave pyran **8b** (y. 66%) after acidic workup with trifluoroacetic acid (Scheme 3-2). The 4-methoxy, 4-fluoro-, and 3,5-dimethyl-substituted derivatives (**8a**, **8c**-**8d**) were similarly obtained in yields of 59, 81, and 85%, respectively. Upon treatment of pyrans **8b**-**8d** with TfOH in a mixture of $(CF_3)_2CHOH$ and CH_2Cl_2, the dications **9b**$^{2+}$-**9d**$^{2+}$ were generated, and their crude $(TfO^-)_2$ salts were directly used for the next step after removal of the solvents in vacuo. For a substrate with electron-donating methoxy groups, namely pyran **8a**, the dication was more easily generated with HBF_4 in a mixture of trifluoroacetic anhydride and CH_2Cl_2, and **9a**$^{2+}$-$(BF_4^-)_2$ was isolated in 94% yield as stable red crystals, which were suitable for X-ray crystallography.



Scheme 3-2. Preparation of precursor dications **9a**$^{2+}$-**9d**$^{2+}$.

The geometrical parameters that were determined by X-ray analysis at 150 K clearly show that scissor effects are prominent in the cyclobutanaphthalene skeleton of **9a**$^{2+}$ (Figure 3-3). Therefore, the difference between the angles $\theta 1$ and $\theta 2$ is more than 40°, and $d2$ is greater than $d1$ by 0.62 Å. Whereas a similar in-plane deformation was also observed in the crystal structure of acenaphthene-5,6-diylbis(diarylmethylium) salt **10a**$^{2+}$-$(BF_4^-)_2$, the effects are much less pronounced in this five-membered-ring analogue (Table 3-1). Consequently, the non-bonded C_α-C_α separation in **9a**$^{2+}$ [$d3$= 3.396(7) Å] is much longer than in **10a**$^{2+}$ [3.143(16), 3.177(16) Å]. The increase in $d3$ by more than 0.2 Å would be enough to suppress the C_α-C_α coupling pathway in the diradicals derived from **9**$^{2+}$ whereas the reduction of **10**$^{2+}$ was shown to be a reliable method for the synthesis of compounds **3**, which feature a long C_α-C_α bond.[10] On the other hand, because of the C_α-C_{ortho} distances of 3.251(7) and 3.282(7) Å in **9a**$^{2+}$, we hypothesized that a new C-C bond-forming process between these two carbon atoms should be possible upon reduction of **9**$^{2+}$.



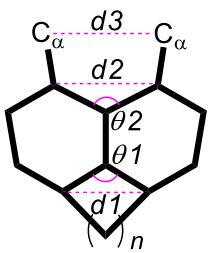
9a^{2+} **10a**$^{2+}$

Figure 3-3. ORTEP drawings of precursor dication **9a**$^{2+}$ and **10a**$^{2+}$.

Table 3-1. Geometrical parameters related to the scissor effects determined by X-ray analysis.

parameters	**9a**$^{2+}$[a]	**10a**$^{2+}$(A)[b]	**10a**$^{2+}$(B)[b]
$\theta 1$ / °	96.6(4)	112.0(7)	112.2(7)
$\theta 2$ / °	137.9(4)	128.6(7)	128.6(7)
$d1$ / Å	2.071(7)	2.348(18)	2.239(18)
$d2$ / Å	2.695(6)	2.608(17)	2.595(16)
$d3$ / Å	3.396(7)	3.143(16)	3.177(16)

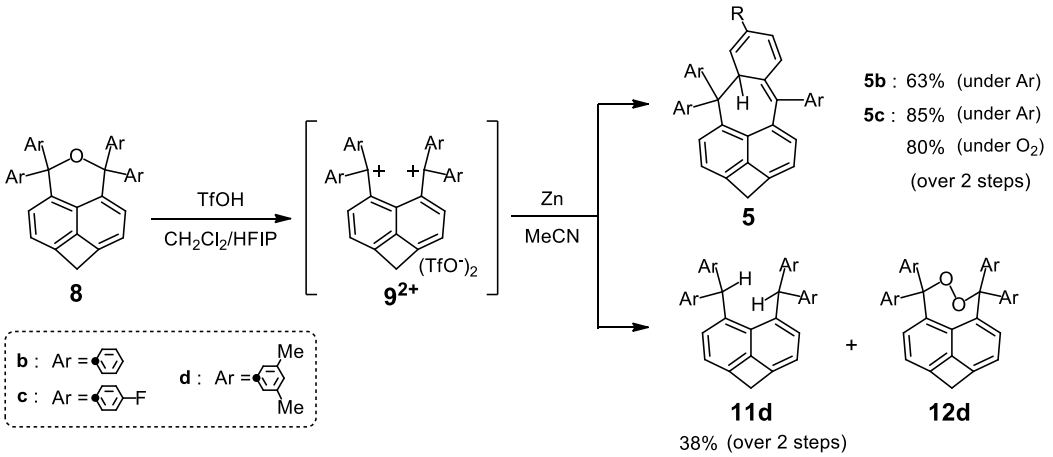
[a] In **9a**$^{2+}$-$(BF4^-)_2$. [b] In **10a**$^{2+}$-$(BF4^-)_2$-CH_2Cl_2 with two crystallographically independent molecules A and B.



9a^{2+}: n = 1, **10a**$^{2+}$: n = 2

3-3. Generation and X-ray Structure of α,*o*-Dimer 5

Finally, the author has succeeded in generating the first α,*o*-adducts **5**. When a MeCN solution of **9b**$^{2+}$-(TfO$^-$)$_2$ was treated with Zn dust under argon atmosphere, yellow crystals with a molecular formula of $C_{37}H_{26}$ were obtained as the sole product (63% yield over two steps). ^{1}H and ^{13}C NMR spectra indicated the presence of a methine and a conjugated triene unit, suggesting the successful formation of α,o-adduct **5b** (Scheme 3-3). Similarly, reduction of 4-fluorophenyl derivative **9c**$^{2+}$-(TfO$^-$)$_2$ gave yellow crystals of **5c** (85% yield over two steps) ; its structural identity was unambiguously confirmed by X-ray analysis (Figure 3-4). The cyclobutanaphthalene unit also exhibits an in-plane deformation owing to "scissor effects" as in **9a**$^{2+}$. With the formation of a new bond between the C_α and C_{ortho} atoms [1.6155(14) Å], one of the four fluorophenyl groups was transformed into a 5-methylene-1,3-hexadiene unit with a remarkable bond alternation.



Scheme 3-3. Reduction of precursor dications **9**$^{2+}$-(TfO$^-$)$_2$.

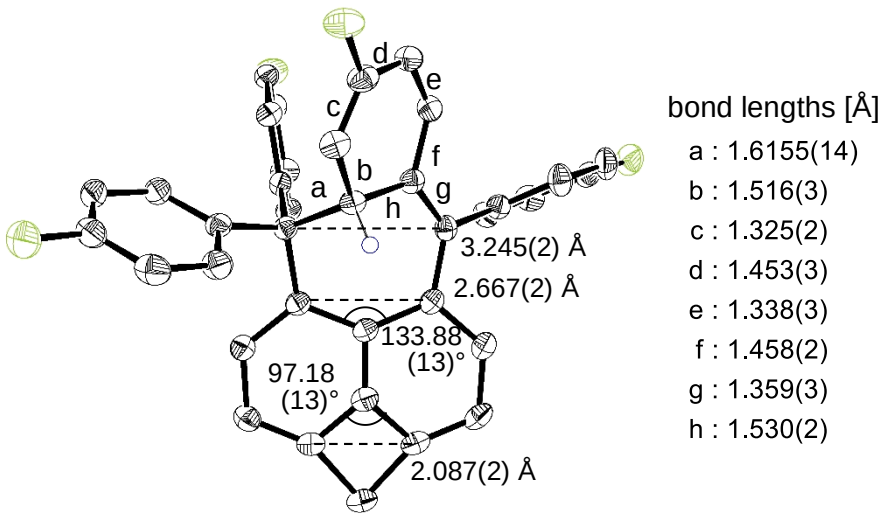
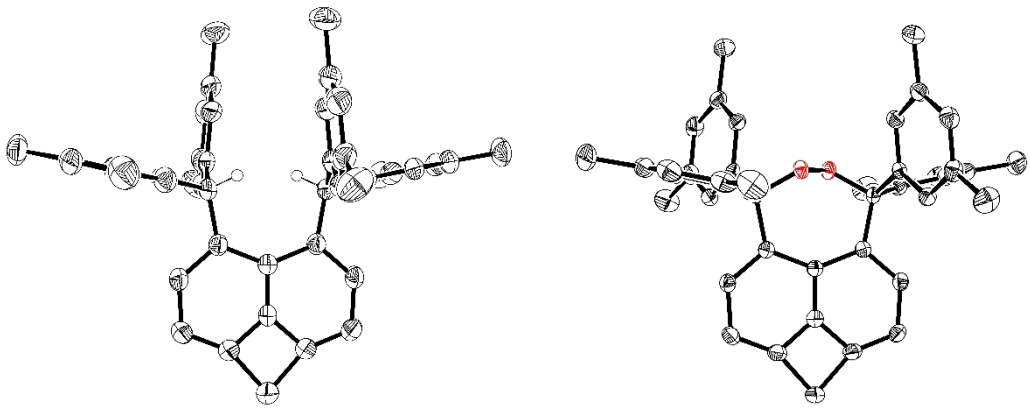


Figure 3-4. Molecular structure of α,*o*-adduct **5c** determined by X-ray analysis at 150 K.

When substituents were attached next to the C_{ortho} carbon atoms, the α,*o*-coupling was suppressed. Upon reduction of 3,5-dimethylphenyl derivative **9d**$^{2+}$-$(TfO^-)_2$, hydrogenated compound **11d**, rather than α,*o*-adduct **5d**, was obtained in 38% yield over two steps (Scheme 3-3). In the presence of O_2, peroxide **12d** was also obtained as a side product. Therefore, diradical **9**$^{2\bullet}$ undergoes intermolecular reactions when the α,*p*-, α,α-, and α,*o*-coupling pathways are suppressed. X-ray analysis showed that the C_α-C_α distances in **11d** and **12d** [*d*3=3.258(4) and 3.316(2) Å, respectively] are close to the values determined for dication **9a**$^{2+}$, showing that the scissor effects place the two C_α carbon atoms of **9**$^{2\bullet}$ far enough apart to accommodate two atoms (-H, H- or -O-O-) between them (Figure 3-5, Table 3-2).

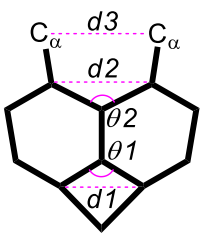


11d **12d**

Figure 3-5. ORTEP drawings of **11d** and **12d** determined by X-ray analysis.

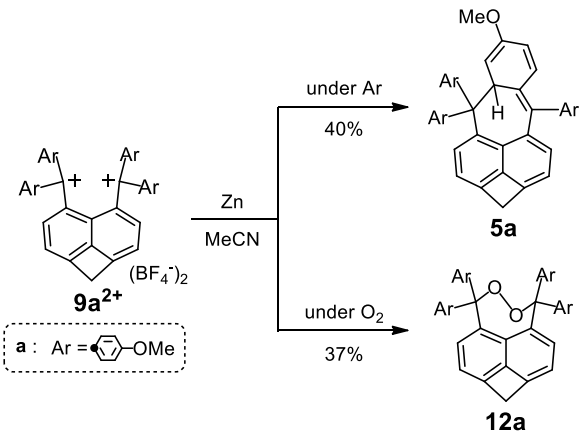
Table 3-2. Selected geometrical parameters determined by Low-temperature X-ray analyses.

parameters	**5c**	**11d**	**12d**	**12a**
θ1 / °	97.18(13)	97.4(3)	97.20(14)	96.9(4)
θ2 / °	135.88(13)	136.4(3)	137.75(15)	136.9(4)
d1 / Å	2.087(2)	2.092(4)	2.089(2)	2.090(7)
d2 / Å	2.667(2)	2.687(4)	2.692(2)	2.684(6)
d3 / Å	3.245(2)	3.258(4)	3.316(2)	3.310(3)



Upon reduction of 4-methoxyphenyl derivative **9a**$^{2+}$-$(BF_4^-)_2$ under argon atmosphere, α,*o*-adduct **5a** was obtained (40% yield) whereas under oxygen atmosphere, peroxide **12a** was the major product (37% yield) (Scheme 3-4). Its solid-state geometry [*d*3=3.310(6) Å] was determined to be very similar to that of **12d** (Figure 3-6, Table 3-2). This observation is in sharp contrast to the exclusive formation of α,*o*-adduct **5c** (80% yield over two steps) under oxygen atmosphere upon reduction of 4-fluorophenyl derivative **9c**$^{2+}$-$(TfO^-)_2$ (Scheme 3-3). This difference in intermolecular reactivity between diradicals **9c**$^{2\bullet}$ and **9a**$^{2\bullet}$ can be rationalized by effects induced by the substituents at the 4-position of the aryl groups. In general, 4-substituted benzyl radicals are stabilized by a methoxy group ($\sigma_\alpha^\bullet$=0.034)[13] but destabilized by a fluorine substituent ($\sigma_\alpha^\bullet$= -0.011). Therefore, **9c**$^{2\bullet}$ must be so short-lived that it undergoes rapid intramolecular α,*o*-coupling to give **5a** exclusively, whereas **9a**$^{2\bullet}$ would have a longer lifetime to be involved in the intermolecular reaction with O_2. Thus, for the high-yield formation of α,*o*-adduct **5**, the attachment of a radical-destabilizing group is preferred in the present system.

The α,*o*-adducts **5** are stable entities. No sign of decomposition or transformation into the aromatized isomer was observed when a toluene solution of **5b** was heated at reflux for four hours. Thermal isomerization of **5** is a symmetry-forbidden reaction, and some arylated 5-methylene-1,3-cyclohexadienes have been reported to have a long lifetime.[14] Attempts to induced an isomerization via the excited state were unfruitful as photoirradiation of **5a** and **5c** (end absorption: 500 nm) in $CDCl_3$ or C_6D_6 with a 300W Xe lamp with a glass filter (λ>400 nm) gave only complex mixtures.



Scheme 3-4. Reduction of **9a**$^{2+}$-$(BF_4^-)_2$.

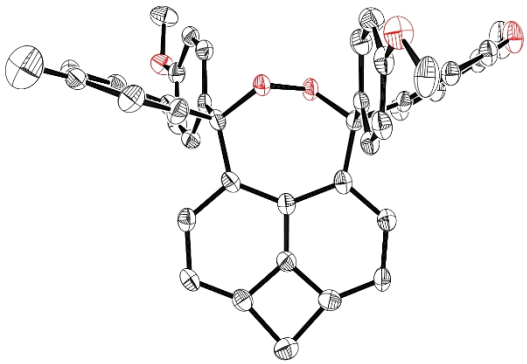


Figure 3-6. ORTEP drawing of **12a**.

3-4. DFT Calculation

The structure obtained by DFT calculation for **5b** well-reproduced the X-ray structure (Figure 3-7 (b)). Additionally, it was predicted that the α,α-adduct **4b** has a C_α-C_α bond length of 1.813 Å, which is much greater than the distance reported for the shortest nonbonded contact 1.80 Å.[15] The preferred formation of α,*o*-adduct **5b** over α,α-adduct **4b** can also be explained in terms of the estimated energy difference of 8.18 kcal/mol in favor of **5b**. DFT calculations also indicate that with little or no influence from scissor effects, the α,α-adducts **3b** and **2b** are more stable than the corresponding α,*o*-adducts by 9.01 and 19.23 kcal/mol, respectively (Figure 3-7). All of the above DFT calculations were performed with the Gaussian 09 program package.[16] The geometries of the compounds were optimized using the B3LYP method with the 6-31G* basis set. The natures of the stationary points were assessed by means of vibration frequency analysis.

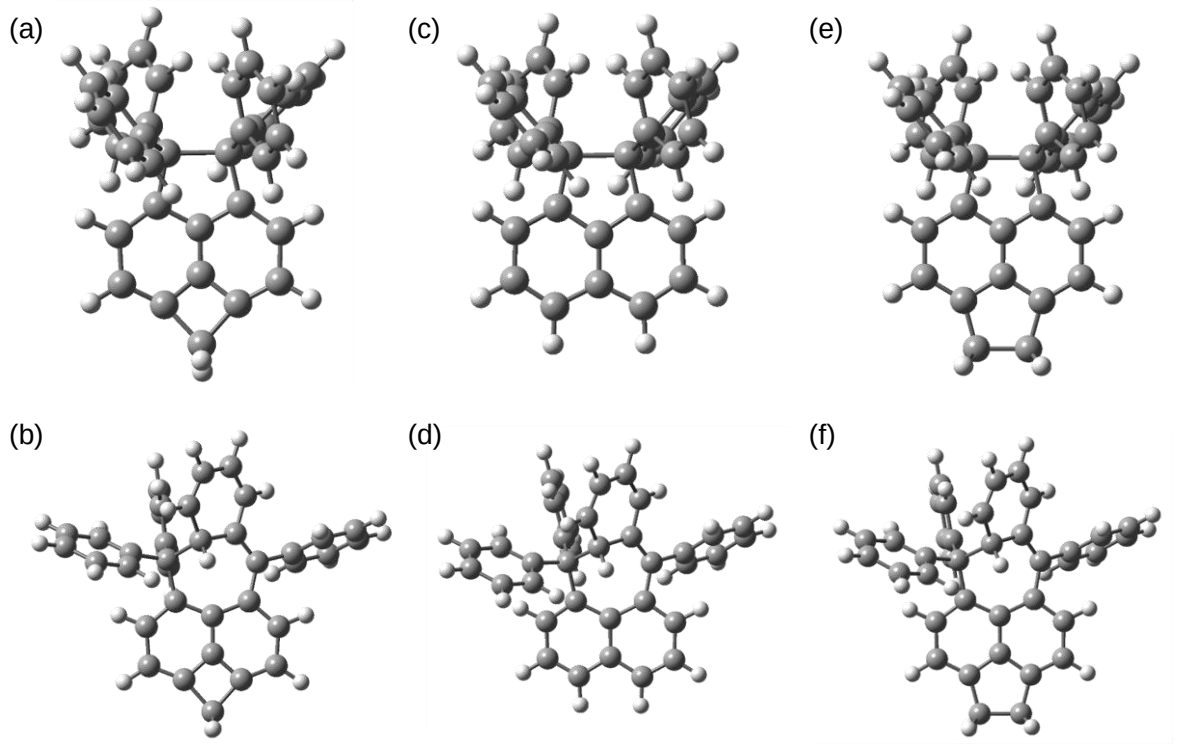
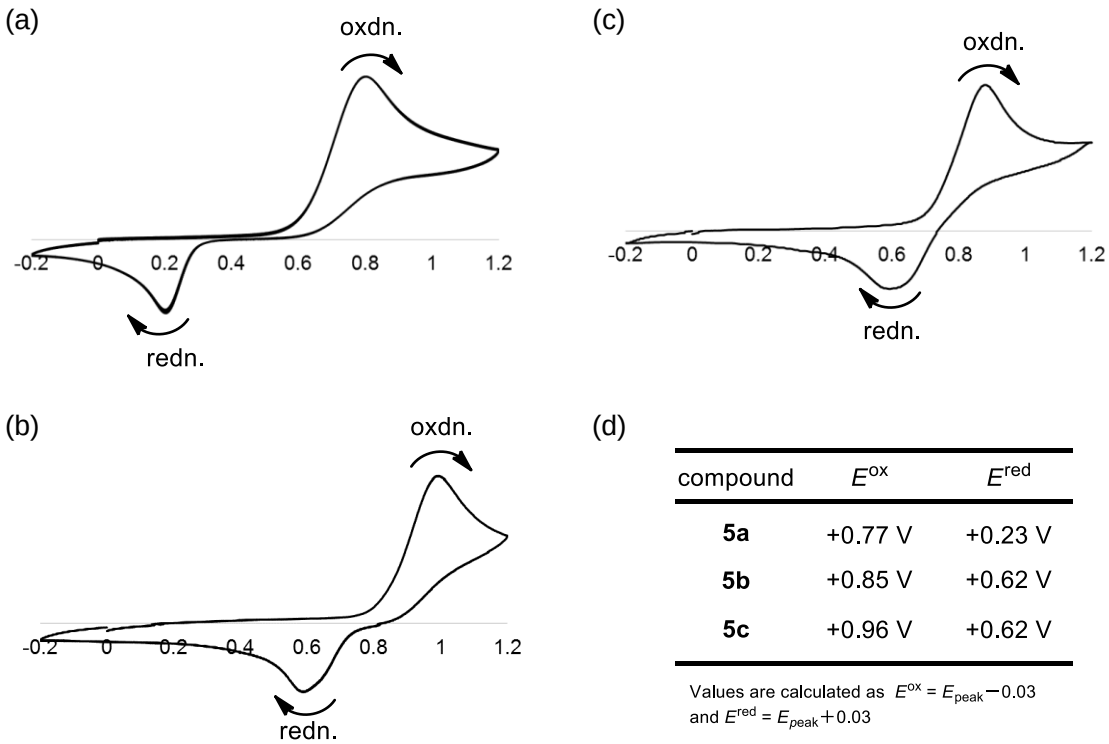


Figure 3-7. Optimized structures of (a) **4b** (+ 8.18 kcal mol^{-1}), (b) **5b** (rel. 0 kcal mol^{-1}), (c) **2b** (rel. 0 kcal mol^{-1}), (d) **2b'**(α,*o*-isomer of **2b**) (+ 19.23 kcal mol^{-1}), (e) **3b** (rel. 0 kcal mol^{-1}) and (f) **3b'**(α,*o*-isomer of **3b**) (+ 9.01 kcal mol^{-1}) determined by DFT calculations (B3LYP/6-31G*).

3-5. Redox Properties of α,*o*-Dimer 5

The author investigated the unique reactivity of α,o-adducts **5** involved the cleavage of the newly formed C_{α}-C_{ortho} bond. According to a voltammetric analysis (Figure 3-8), **5a** undergoes facile two-electron oxidation owing to the presence of the electron-donating methoxy groups (E^{ox} = + 0.77 V vs. Fc/Fc^{+} in CH_2Cl_2). The oxidation process is irreversible in the sense that the return peak was observed in the far cathodic region, which corresponds to the reduction of dication **9a^{2+}** (E^{red} = + 0.23 V). The separation of the redox peaks is a characteristic feature of dyrex (dynamic redox) systems undergoing reversible C-C bond formation/cleavage upon electron transfer.[30] In fact, when **5a** was treated with two equivalents of $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^{-}$, **9a^{2+}**-$(SbCl_6^{-})_2$ was isolated in 80% yield. As shown in Figure 3-8, the voltammograms of **5b** (E^{ox} = + 0.87 V vs. Fc/Fc^{+}) and **5c** (+ 0.96 V) resemble that of **5a** in shape, indicating that the C_{α}-C_{ortho} bond in **5b** and **5c** would also be cleaved upon oxidation.



compound	E^{ox}	E^{red}
5a	+0.77 V	+0.23 V
5b	+0.85 V	+0.62 V
5c	+0.96 V	+0.62 V

Values are calculated as $E^{ox} = E_{peak} - 0.03$ and $E^{red} = E_{peak} + 0.03$

Figure 3-8. Cyclic voltammograms of **5** in CH_2Cl_2 (*E*/V vs. SCE, 0.1 M Bu_4NBF_4, Pt electrode, scan rate 100 mVs^{-1}). (a) Cyclic voltammogram of **5a**, (b) Cyclic voltammogram of **5b**, (c) Cyclic voltammogram of **5c**, (d) Redox potentials of **5a**-**5c**.

3-6. Electrochromic Behavior of α,*o*-Dimer 5

During the electrochemical transformation of **5a** into **9a**$^{2+}$, a continuous change in the UV/Vis spectrum with several isosbestic points was observed accompanied by a vivid color change from yellow to deep red (Figure 3-9). The strongest absorption in the visible region is identical to that of the isolated salt of **9a**$^{2+}$ (λ_{max} 483 nm) in MeCN.

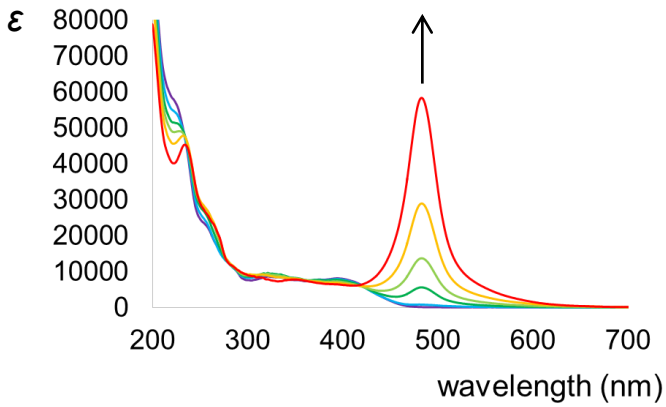


Figure 3-9. A continuous change in the UV-vis spectrum of α,o-adduct **5a** (2×10^{-5}M) in MeCN containing 0.05 M Et_4NClO_4 upon constant-current electrochemical oxidation (70 μA, every 3 min).

3-7. Conclusion

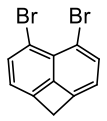
The author have succeeded in generating the first α,o-adduct **5** by combining two trityl radicals into the 1*H*-cyclobuta[*de*]naphthalene skeleton. Upon reduction of a 1*H*-cyclobuta[*de*]naphthalene-4,5-diylbis(diarylmethylium) species, a new C-C bond is formed between the C_α and C_{ortho} atoms of the two chromophores, which presents an unprecedented coupling pattern for the dimerization of two trityl units. By attaching an annulated cyclobutane ring at the opposite *peri*-position of the naphthalene core, the distance between the C_α carbon atoms was elongated beyond the limit of σ-bond formation through "scissor effects". The suppression of C_α-C_α bond formation, which would lead to hexaphenylethane-type compounds, is key to the first successful isolation of the α,o-adducts. The 5-diarylmethylene-6-triarylmethyl-1,3-cyclohexadiene unit in the α,o-adducts **5** is stable, and isomerization of the cyclohexadiene unit into an aromatic system was not observed. The newly formed C_α-C_{ortho} bond was cleaved upon two-electron oxidation to regenerate the dicationic dye.

Experimental Section

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise indicated. All commercially available compounds were used without further purification. Dry MeCN was obtained by distillation from CaH_2 prior to use. Column chromatography was performed on silica gel I-6-40 (YMC) of particle size 40-63 µm and aluminium oxide 90 standardized (Merck 63-200 µm). ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER Ascend™ 400 (^{1}H/400MHz and ^{13}C/100MHz) spectrometer. IR spectra were measured as a KBr pellet on a JEOL JIR-WINSPEC100FT/IR spectrophotometer. Mass spectra were recorded on JMS-AX500, JMS-SX102A, or JEOL JMS-T100GCV spectrometers in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Melting points were measures on a Yamato MP-21 melting point apparatus and reported uncorrected. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer.

Improved preparation of 4,5-Dibromo-1*H*-cyclobuta[*de*]naphthalene 7



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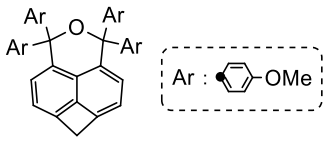
To a solution of 1*H*-cyclobuta[*de*]naphthalene (320 mg, 2.28 mmol) in dry DMF (10 mL) was transferred NBS (1.62 g, 9.10 mmol) in dry DMF (20 mL) with a cannula in the dark, and the mixture was stirred for 20 h at 50 °C. The mixture was diluted with water and extracted with hexane : EtOAc = 4 : 1. The organic layer was washed with water and brine, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane only) to give 4,5-dibromo-1*H*-cyclobuta[*de*]naphthalene **7** (646 mg, 95%) as a pale yellow solid.

Preparation of 1,1,3,3-Tetrakis(4-methoxyphenyl)-3,6-dihydro-1*H*-cyclobuta[4,5] naphtho[1,8-*cd*]pyran 8a



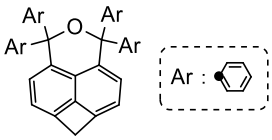
8a

To a suspension of 4,5-dibromo-1*H*-cyclobuta[*de*]acenaphthene **7** (307 mg, 1.03 mmol) in dry ether (20 mL) was added *n*-BuLi in *n*-hexane (1.60 M, 1.4 mL, 2.24 mmol) at 22 °C. After 15 min, 4,4'-dimethoxybenzophenone (543 mg, 2.24 mmol) was added. After stirring for 2 h, *n*-BuLi in *n*-hexane (1.60 M, 0.7 mL, 1.12 mmol) was added to consume excess ketone. The resultant solution was further stirred for 1 h, and was quenched with water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was dissolved in dry CH_2Cl_2 (20 mL), and trifluoroacetic acid (80 µL, 1.08 mmol) was added at 22 °C. After stirring for 16 h, the mixture was diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was

purified by column chromatography on silica gel (hexane/ EtOAc = 10) to give **8a** (531 mg, 85%) as a pale yellow solid.

M.p. 208-209 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.03 (d, *J* = 6.5 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 8H), 6.84 (d, *J* = 6.5 Hz, 2H), 6.56 (d, *J* = 8.9 Hz, 8H), 4.97 (s, 2H), 3.72 (s, 12H) ; ^{13}C NMR ($CDCl_3$) δ 158.20, 144.88, 139.09, 138.40, 135.41, 130.38, 127.51, 119.31, 117.75, 112.53, 84.32, 55.13, 50.19 ; IR (KBr) 3036, 2998, 2952, 2930, 2834, 1607, 1584, 1509, 1463, 1442, 1299, 1251, 1174, 1037, 965, 827, 621, 586 cm^{-1} ; LR-MS (FD) *m/z* (%): 606 (M^+, bp), 607 (46), 608 (12), 609 (2) ; HR-MS (FD) Calcd. for $C_{41}H_{34}O_5$: 606.2406, Found : 606.2421.

Preparation of 1,1,3,3-Tetrakisphenyl-3,6-dihydro-1*H*-cyclobuta[4,5]naphtho[1,8-*cd*] pyran 8b

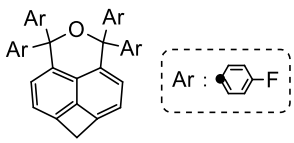


8b

To a suspension of 4,5-dibromo-1*H*-cyclobuta[*de*]acenaphthene **7** (405 mg, 1.36 mmol) in dry ether (30 mL) was added *n*-BuLi in *n*-hexane (1.55 M, 1.9 mL, 2.95 mmol) at 24 °C. After 15 min, benzophenone (540 mg, 2.97 mmol) was added. After stirring for 4 h, *n*-BuLi in *n*-hexane (1.55 M, 0.9 mL, 1.40 mmol) was added to consume excess ketone. The resultant solution was further stirred for 1 h, and was quenched with water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was dissolved in dry CH_2Cl_2 (50 mL). Trifluoroacetic acid (100 µL, 1.35 mmol) was added at 24 °C, and then the mixture was stirred for 14.5 h. After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 50) to give **8b** (433 mg, 66%) as a pale yellow solid.

M.p. 239-241 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.16-7.12 (m, 8H), 7.06-7.01 (m, 14H), 6.89 (d, *J* = 6.6 Hz, 2H), 4.97 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 145.79, 144.88, 139.27, 134.38, 129.18, 127.89, 127.17, 126.79, 119.17, 117.83, 84.90, 50.21 ; IR (KBr) 3086, 3058, 3033, 2927, 1601, 1492, 1444, 1177, 971, 832, 774, 767, 739, 696, 661, 616 cm^{-1} ; LR-MS (FD) *m/z* (%): 486 (M^+, bp), 487 (41), 488 (9) ; HR-MS (FD) Calcd. for $C_{37}H_{26}O$: 486.1984, Found : 486.1963.

Preparation of 1,1,3,3-Tetrakis(4-fluorophenyl)-3,6-dihydro-1*H*-cyclobuta[4,5] naphtho[1,8-*cd*]pyran 8c



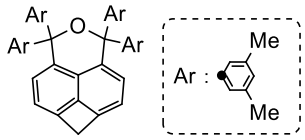
8c

To a suspension of 4,5-dibromo-1*H*-cyclobuta[*de*]acenaphthene **7** (170 mg, 570 µmol) in dry ether (10 mL) was added *n*-BuLi in *n*-hexane (1.60 M, 0.8 mL, 1.28 mmol) at 23 °C. After 1 h, 4,4'-difluorobenzophenone (278 mg, 1.27 mmol) was added. After stirring for 5 h, *n*-BuLi in *n*-hexane (1.60 M, 0.4 mL, 640 µmol) was added to consume excess ketone. The resultant solution was further stirred for 1 h, and was quenched with water. The mixture was extracted

with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was dissolved in dry CH_2Cl_2 (10 mL). Trifluoroacetic acid (50 µL, 673 µmol) was added at 23 °C, and then the mixture was stirred for 13 h. After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 50) to give **8c** (187 mg, 59%) as a pale yellow solid.

M.p. 227-229 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.07 (d, *J* = 8.8 Hz, 4H), 7.06 (d, *J* = 6.6 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 4H), 6.83 (d, *J* = 6.6 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 4H), 6.74 (d, *J* = 8.8 Hz, 4H), 4.99 (s, 2H) ; ^{13}C NMR ($CDCl_3$) δ 161.80 ($J_{C\text{-}F}$= 245 Hz), 144.86, 141.30 ($J_{C\text{-}F}$= 3.5 Hz), 139.76, 133.88, 130.78 ($J_{C\text{-}F}$= 8.0 Hz), 127.87, 118.80, 118.13, 114.15 ($J_{C\text{-}F}$= 21.1 Hz), 84.20, 50.38 ; IR (KBr) 3061, 2931, 1604, 1506, 1406, 1299, 1230, 1186, 1158, 1015, 976, 918, 828, 620, 578 cm^{-1} ; LR-MS (FD) *m/z* (%): 558 (M^+, bp), 559 (43), 560 (9) ; HR-MS (FD) Calcd. for $C_{37}H_{22}F_4O$: 558.1607, Found : 558.1626.

Preparation of 1,1,3,3-Tetrakis(3,5-dimethylphenyl)-3,6-dihydro-1*H*-cyclobuta[4,5] naphtho[1,8-*cd*]pyran 8d

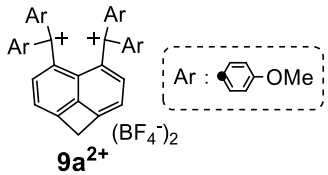


8d

To a suspension of 4,5-dibromo-1*H*-cyclobuta[*de*]acenaphthene **7** (198 mg, 666 µmol) in dry ether (15 mL) was added *n*-BuLi in *n*-hexane (1.60 M, 0.88 mL, 1.36 mmol) at 21 °C. After 20 min, 3,3',5,5'-tetramethylbenzophenone (352 mg, 1.48 mmol) was added. After stirring for 3 h, *n*-BuLi in *n*-hexane (1.60 M, 0.42 mL, 672 µmol) was added to consume excess ketone. The resultant solution was further stirred for 1 h, and was quenched with water. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was dissolved in dry CH_2Cl_2 (15 mL), and trifluoroacetic acid (70 µL, 942 µmol) was added at 21 °C. The reaction mixture was stirred for 13 h, and then diluted with MeOH. The resulting precipitates were collected by filtration, and washed with MeOH to give **8d** (322 mg, 81%) as a white solid.

M.p. 284-286 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.04 (d, *J* = 6.6 Hz, 2H), 6.90 (d, *J* = 6.6 Hz, 2H), 6.76 (brs, 8H), 6.67 (brs, 4H), 4.98 (s, 2H), 2.11 (s, 24H) ; ^{13}C NMR ($CDCl_3$) δ 145.93, 144.83, 138.93, 136.06, 134.96, 128.30, 127.59, 127.08, 119.26, 117.70, 84.80, 50.14, 21.40 ; IR (KBr) 3035, 3003, 2917, 2862, 1600, 1468, 1173, 1160, 978, 926, 852, 840, 792, 740, 712 cm^{-1} ; LR-MS (FD) *m/z* (%):598 (M^+, bp), 599 (51), 600 (13), 601 (2) ; HR-MS (FD) Calcd. for $C_{45}H_{42}O$: 598.3236, Found : 598.3248.

Preparation of 1*H*-Cyclobuta[*de*]naphthalene-4,5-diyl-bis(4-methoxyphenyl) methylium bis(tetrafluoroborate) 9a^{2+} (BF$_4^-$)$_2$

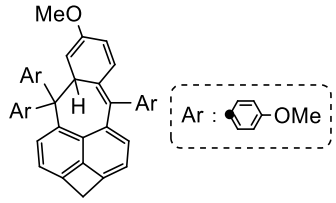


9a^{2+}

To a solution of pyran **8a** (168 mg, 278 μmol) in dry CH_2Cl_2 (1.5 mL) were added trifluoroacetic anhydride (1.5 mL) followed by aqueous HBF_4 (42%, 170 μL, 1.13 mmol), and the mixture was stirred for 1 h at 23 °C under argon. The mixture was diluted with dry ether, and the resulting precipitates were filtered and washed with ether to give dicationic salt **9a**$^{2+}$(BF_4^-)$_2$ (199 mg, 94%) as a red solid.

M.p. 101-104 °C (decomp.) ; ^{1}H NMR (CD_3CN) δ 7.64 (d, *J* = 6.7 Hz, 2H), 7.51 (brd, *J* = 6.7 Hz, 6H), 7.11 (brs, 12H), 5.11 (s, 2H), 4.05 (s, 12H) ; ^{13}C NMR (CD_3CN) δ 191.23, 173.00, 152.57, 146.52, 145.44, 132.88, 131.20, 128.22, 121.10, 117.93, 58.14, 47.50 ; IR (KBr) 3059, 2943, 2845, 1605, 1580, 1508, 1453, 1373, 1281, 1165, 1124, 1084, 1004, 915, 854, 691, 603, 533 cm^{-1} ; LR-MS (FD) *m/z* (%): 590 (M$^+$, 35), 591 (21), 592 (6) ; HR-MS (FD) Calcd. for $C_{41}H_{34}O_4$: 590.2457, Found : 590.2464.

Preparation of 6-Methoxy-4,4,9-tris(4-methoxyphenyl)-4,4a-dihydro-1*H*-cyclobuta[*cd*] pleiadene 5a

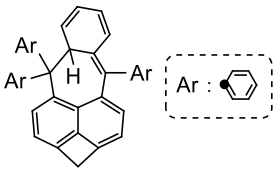


5a

To a suspension of Zn powder (852 mg, 13.0 mmol) in dry degassed MeCN (5 mL) was transferred a solution of the as-prepared dicationic salt **9a**$^{2+}$(BF_4^-)$_2$ (88.2 mg, 115 μmol) in degassed dry MeCN (10 mL) with a cannula at 24 °C under argon, and the mixture was stirred for 2 h. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 10) to give **5a** (30.5 mg, 40%) as a yellow solid.

M.p. 150-153 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.24 (dd, *J* = 6.0, 2.2 Hz, 1H), 7.21 (dd, *J* = 6.0, 2.2 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.06 (d, *J* = 6.7 Hz, 1H), 7.02 (d, *J* = 6.7 Hz, 1H), 6.96-6.70 (m, 5H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 6.7 Hz, 1H), 6.59 (d, *J* = 8.8 Hz, 2H), 6.38 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.58 (d, *J* = 10.1 Hz, 1H), 5.36 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.90 (dd, *J* = 5.5, 1.8 Hz, 1H), 4.77 (d, *J* = 14.3 Hz, 1H), 4.72 (d, *J* = 5.5 Hz, 1H), 4.61 (d, *J* = 14.3 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.71 (s, 3H), 3.28 (s, 3H) ; ^{13}C NMR ($CDCl_3$) δ 158.42, 157.89, 157.56, 152.71, 146.28, 146.10, 141.03, 140.85, 140.64, 139.85, 136.06, 135.71, 135.00, 134.78, 134.73, 132.99, 132.85, 132.77, 131.43, 130.97, 130.85, 130.40, 124.56, 120.44, 117.46, 116.58, 114.82, 114.25, 112.64, 112.14, 110.29, 97.56, 65.27, 55.24, 55.10, 54.07, 50.62, 44.49 ; IR (KBr) 3059, 2997, 2952, 2929, 2834, 1654, 1607, 1508, 1463, 1288, 1247, 1221, 1178, 1036, 829, 808, 621, 591 cm^{-1} ; LR-MS (FD) *m/z* (%): 590 (M$^+$, bp), 591 (48), 592 (15), 593 (3) ; HR-MS (FD) Calcd. for $C_{41}H_{34}O_4$: 590.2457, Found :590.2481.

Preparation of 4,4,9-Trisphenyl-4,4a-dihydro-1*H*-cyclobuta[*cd*]pleiadene 5b

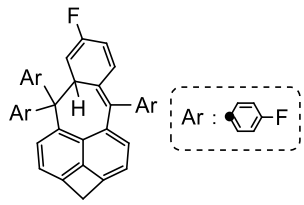


5b

To a solution of pyran **8b** (89.7 mg, 184 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (160 μL, 1.82 mmol) at 24 °C under argon. The mixture was stirred for 1 h, and then solvent was evaporated. To a suspension of Zn powder (1.86 g, 28.4 mmol) in degassed dry MeCN (5 mL) was transferred a solution of the as-prepared dication salt in degassed dry MeCN (10 mL) with a cannula at 24 °C under argon, and the mixture was stirred for 2 h. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 5) to give **5b** (54.6 mg, 63% over 2 steps) as a yellow solid.

M.p. 227-230 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.40-7.31 (m, 5H), 7.30-7.21 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12-7.02 (m, 5H), 6.99 (d, *J* = 6.7 Hz, 1H), 6.90 (d, *J* = 6.7 Hz, 1H), 6.59 (d, *J* = 6.7 Hz, 1H), 6.38 (d, *J* = 7.4 Hz, 1H), 6.09 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.98-5.92 (m, 1H), 5.50 (d, *J* = 2.9 Hz, 2H), 4.76 (d, *J* = 14.3 Hz, 1H), 4.73 (brs, 1H), 4.59 (d, *J* = 14.3 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ 147.60, 146.20, 145.86, 143.71, 142.76, 141.28, 140.66, 140.05, 136.18, 134.62, 134.36, 132.77, 132.37, 131.67, 131.02, 130.24, 129.91, 129.52, 129.08, 128.60, 127.99, 127.53, 127.02, 126.95, 126.57, 126.22, 124.66, 124.15, 121.25, 117.59, 116.51, 66.34, 51.03, 44.52 cm^{-1} ; LR-MS (FD) *m/z* (%): 470 (M^+, bp), 471 (41), 472 (9), 473 (1) ; HR-MS (FD) Calcd. for $C_{37}H_{26}$: 470.2035, Found : 470.2051.

Preparation of 6-Fluoro-4,4,9-tris(4-fluoroxyphenyl)-4,4a-dihydro-1*H*-cyclobuta[*cd*] pleiadene 5c



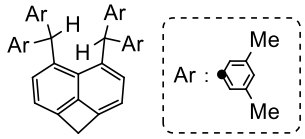
5c

To a solution of pyran **8c** (66.7 mg, 119 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (105 μL, 1.20 mmol) at 24 °C under argon. The mixture was stirred for 2 h, and then solvent was evaporated. To a suspension of Zn powder (2.24 g, 34.3 mmol) in degassed dry MeCN (10 mL) was transferred a solution of the as-prepared dication salt in degassed dry MeCN (15 mL) with a cannula at 24 °C under argon, and the mixture was stirred for 2 h. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ CH_2Cl_2 = 5) to give **5c** (55.2 mg, 85% over 2 steps) as a yellow solid.

M.p. 206-209 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.31-7.26 (m, 1H), 7.23-7.14 (m, 2H), 7.12-

7.06 (m, 4H), 7.01-6.90 (m, 5H), 6.79 (d, J = 8.6 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.57 (d, J = 6.7 Hz, 1H), 6.42-6.37 (m, 1H), 5.60-5.54 (m, 1H), 5.49-5.41 (m, 2H), 4.79 (brs, 1H), 4.78 (d, J = 14.4 Hz, 1H), 4.63 (d, J = 14.4 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ 162.00 ($J_{C\text{-}F}$ = 245 Hz), 161.72 ($J_{C\text{-}F}$ = 244 Hz), 161.32 ($J_{C\text{-}F}$ = 245 Hz), 157.66 ($J_{C\text{-}F}$ = 245 Hz), 146.05, 145.01, 142.95 ($J_{C\text{-}F}$ = 3.5 Hz), 142.14, 141.84, 140.52, 139.01 ($J_{C\text{-}F}$ = 3.1 Hz), 137.93 ($J_{C\text{-}F}$ = 3.7 Hz), 135.51, 134.31, 133.54, 133.18 ($J_{C\text{-}F}$ = 8.0 Hz), 133.06, 133.02 ($J_{C\text{-}F}$ = 7.7 Hz), 132.31 ($J_{C\text{-}F}$ = 8.8 Hz), 131.64 ($J_{C\text{-}F}$ = 7.8 Hz), 131.16 ($J_{C\text{-}F}$ = 7.8 Hz), 130.80 ($J_{C\text{-}F}$ = 7.5 Hz), 124.18, 117.87, 116.90, 116.78 ($J_{C\text{-}F}$ = 35.3 Hz), 115.96 ($J_{C\text{-}F}$ = 21.7 Hz), 115.91 ($J_{C\text{-}F}$ = 21.1 Hz), 114.65 ($J_{C\text{-}F}$ = 21.0 Hz), 114.16 ($J_{C\text{-}F}$ = 21.0 Hz), 114.01 ($J_{C\text{-}F}$ = 21.0 Hz), 113.29 ($J_{C\text{-}F}$ = 20.2 Hz), 104.56 ($J_{C\text{-}F}$ = 19.1 Hz), 65.12 ($J_{C\text{-}F}$ = 2.6 Hz), 50.75 ($J_{C\text{-}F}$ = 6.6 Hz), 44.64 ; IR (KBr) 3064, 2963, 2929, 1671, 1603, 1506, 1424, 1225, 1178, 1163, 1014, 875, 837, 826, 787, 615, 585, 534 cm^{-1} ; LR-MS (FD) *m/z* (%): 542 (M^+, bp), 543 (44), 544 (10) ; HR-MS (FD) Calcd. for $C_{37}H_{22}F_4$: 542.1658, Found : 542.1653.

Preparation of hydrogen adduct 11d

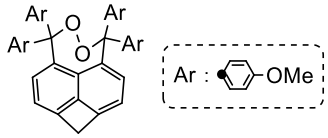


11d

To a solution of pyran **8d** (44.1 mg, 73.6 μmol) in dry CH_2Cl_2 (2 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added trifluoromethanesulfonic acid (65 μL, 741 μmol) at 22 °C under argon. The mixture was stirred for 1 h, and then solvent was evaporated. To a suspension of Zn powder (734 mg, 11.2 mmol) in degassed dry MeCN (5 mL) was transferred a solution of the as-prepared dication salt in degassed dry MeCN (10 mL) with a cannula at 22 °C under argon, and the mixture was stirred for 24 h. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc= 50) to give **11d** (16.1 mg, 38% over 2 steps) as a colorless solid.

M.p. 288-290 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 6.99 (d, J = 6.6 Hz, 2H), 6.94 (d, J = 6.6 Hz, 2H), 6.83 (s, 4H), 6.47 (s, 8H), 5.95 (s, 2H), 4.59 (s, 2H), 2.20 (s, 24H) ; ^{13}C NMR ($CDCl_3$) δ 147.03, 144.87, 139.81, 137.50, 137.34, 132.71, 127.74, 127.60, 124.54, 117.14, 52.98, 43.68, 21.38 ; IR (KBr) 3013, 2922, 2858, 1724, 1599, 1468, 1376, 1038, 851, 788, 701 cm^{-1} ; LR-MS (FD) *m/z* (%): 584 (M^+, bp), 585 (51), 586 (12) ; HR-MS (FD) Calcd. for $C_{45}H_{44}$: 584.3443, Found : 584.3463.

Preparation of 1,1,4,4-Tetrakis(4-methoxyphenyl)-4,7-dihydro-1*H*-cyclobuta[4,5] naphtho[1,8-*de*][1,2]dioxepine 12a



12a

To a Zn powder (1.65 g, 25.3 mmol) in oxygen-saturated dry MeCN (15 mL) was transferred dicationic salt **9a**$^{2+}$(BF_4^-)$_2$ (350 mg, 578 μmol) in oxygen-saturated dry MeCN (20 mL) with a cannula at 24 °C, and the mixture was stirred under O_2 for 22 h. The mixture was diluted with CH_2Cl_2 and water, filtered, and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc = 9) to give **12a** (115 mg, 37%) as a pale yellow solid.

M.p. 252-253 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 7.37 (d, *J* = 8.9 Hz, 4H), 7.02 (d, *J* = 6.5 Hz, 2H), 6.90 (d, *J* = 6.5 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 4H), 6.76 (d, *J* = 8.9 Hz, 4H), 6.62 (d, *J* = 8.9 Hz, 4H), 4.66 (s, 2H), 3.84 (s, 6H), 3.70 (s, 6H) ; ^{13}C NMR ($CDCl_3$) δ 158.84, 158.79, 146.52, 140.33, 139.41, 136.66, 134.90, 133.48, 130.72, 129.58, 122.02, 116.37, 113.01, 112.84, 95.80, 55.26, 55.16, 44.27 ; IR (KBr) 3061, 3036, 2999, 2953, 2929, 2835, 1607, 1582, 1509, 1463, 1442, 1307, 1299, 1253, 1176, 1037, 827, 600 cm^{-1} ; LR-MS (FD) *m/z* (%): 622 (M^+, bp), 623 (47), 624 (12), 625 (2) ; HR-MS (FD) Calcd. for $C_{41}H_{34}O_6$: 622.2355, Found : 622.2368.

X-ray analyses

Data collection was conducted with a Rigaku Mercury 70 diffractometer (Mo-Kα radiation, λ = 0.71075 Å). The structure was solved by the direct method (SIR2004) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding.

Crystal date for 5c

MF : $C_{37}H_{22}F_4$, FW : 572.75, yellow prism, 0.30 × 0.20 × 0.20 mm, triclinic $P\bar{1}$, a = 9.209(2) Å, b = 10.783(3) Å, c = 14.198(4) Å, α = 98.069(3)°, β = 106.357(2)°, γ = 104.647(3)°, V = 1274.4(6) Å^3, ρ (Z = 2) = 1.414 g/cm^3. A total 5609 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 1.011 cm^{-1}). The final *R1* and *wR2* values are 0.0471 (I > 2σI) and 0.1862 (all data) for 5609 reflections and 370 parameters. Estimated standard deviations are 0.0014-0.003 Å for bond lengths and 0.10-0.17° for bond angles, respectively. CCDC 1041335

Crystal date for 9a^{2+}

MF : $C_{41}H_{34}B_2F_8O_4$, FW : 764.32, red needle, 0.50 × 0.02 × 0.02 mm, monoclinic *Pc*, a = 8.427(4) Å, b = 13.850(6) Å, c = 15.515(7) Å, α = 90°, β = 105.076(5)°, γ = 90°, V = 1748(2) Å^3, ρ (Z = 2) = 1.452 g/cm^3. A total 5811 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 1.197 cm^{-1}). The final *R1* and *wR2* values are 0.0674 (I > 2σI) and 0.2134 (all data) for 5811 reflections and 496 parameters. Estimated standard deviations are 0.005-0.013 Å for bond lengths and 0.3-1.3° for bond angles, respectively. CCDC 1041336

Crystal date for 10a^{2+}

MF : $C_{43}H_{38}B_2Cl_2F_8O_4$, FW : 863.28, violet needle, 0.60 × 0.05 × 0.05 mm, monoclinic *Cc*, a = 33.570(9) Å, b = 12.616(3) Å, c = 23.192(6) Å, α = 90°, β = 126.515(3)°, γ = 90°, V = 7894(4) Å^3, ρ (Z = 8) = 1.453 g/cm^3. A total 9560 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 2.458 cm^{-1}). The final *R1* and *wR2* values are 0.0891 (I > 2σI) and 0.2802 (all data) for 9560 reflections and 1063 parameters. Estimated standard deviations are 0.010-0.02 Å for bond lengths and 0.7-1.2° for bond angles, respectively. CCDC 1041338

Crystal date for 11d

MF : $C_{45}H_{44}$, FW : 584.84, colorless prism, 0.20 × 0.20 × 0.20 mm, monoclinic *C*2/*c*, a = 14.13(2) Å, b = 15.09(2) Å, c = 16.32(2) Å, α = 90°, β = 101.308(13)°, γ = 90°, V = 3412(6) Å^3, ρ (Z = 4) = 1.138 g/cm^3. A total 3884 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.638 cm^{-1}). The final *R1* and *wR2* values are 0.0772 (I > 2σI) and 0.1282 (all data) for 3884 reflections and 213 parameters. Estimated standard deviations are 0.003-0.005 Å for bond lengths and 0.14-0.3° for bond angles, respectively. CCDC 1041340

Crystal date for 12a

MF : $C_{41}H_{34}O_6$, FW : 622.72, colorless platelet, 0.20 × 0.20 × 0.050 mm, triclinic $P\bar{1}$, a = 9.698(3) Å, b = 11.191(4) Å, c = 15.379(5) Å, α = 81.71(2)°, β = 72.892(13)°, γ = 80.23(2)°, V = 1564.2(9) Å^3, ρ (Z = 2) = 1.322 g/cm^3. A total 5239 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.878 cm^{-1}). The final *R1* and *wR2* values are 0.0792 (I > 2σI) and 0.2045 (all data) for 5239 reflections and 424 parameters. Estimated standard deviations are 0.004-0.008 Å for bond lengths and 0.3-0.5° for bond angles, respectively. CCDC 1041339

Crystal date for 12d

MF : $C_{45}H_{42}O_2$, FW : 614.83, colorless block, 0.40 × 0.20 × 0.20 mm, monoclinic *C*2/*c*, a = 13.585(4) Å, b = 15.276(4) Å, c = 17.783(5) Å, α = 90°, β = 109.499(4)°, γ = 90°, V = 3479(2) Å^3, ρ (Z = 4) = 1.174 g/cm^3. A total 3767 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.699 cm^{-1}). The final *R1* and *wR2* values are 0.0501 (I > 2σI) and 0.1476 (all data) for 3767 reflections and 222 parameters. Estimated standard deviations are 0.0011-0.003 Å for bond lengths and 0.08-0.16° for bond angles, respectively. CCDC 1041337

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Chapter 4

Expansion of C-O Bond Length by "Scissor Effects" in Naphtho[1,8-*bc*] furan Derivatives

4-1. Introduction

The C-O bond length is generally 1.43 Å in non-ionic bond and 1.49 Å in electrically charged bond, respectively, although it has been known that the elongation of the C-O bond was induced by intramolecular steric strain and electronic effects.[1-4] The representative examples of a long C-O$^+$ bond include 2-ethoxy-3,4,4a,5,6,7,8,8a-octahydro-1-benzopyrylium **I** [1.538(8) Å] reported by Childs[1] and 1-oxonia-adamantane **II** [1.520(4) Å] reported by Olah (Figure4-1).[2] In particular, oxatriquinane (OTQ) prepared by Mascal has an unusual C-O$^+$ bond length of 1.537(3) Å due to ring strain of the trefoil structure fused with three five-membered ring.[3a] They expected that the further elongation of C-O bond can be observed by using this tricyclic skeleton. In fact, the C-O$^+$ bond was elongated to 1.6221(10) Å by the substitution of alkyl groups to α-position of OTQ system (Figure4-1, **III**).[3b] They suggested that steric strain of substituents and hyperconjugation from adjacent C-H and C-C bonds to σ^*(C−O$^+$) orbitals contribute to elongation of the C-O bond. Additionally, it has been recently demonstrated that α-hydroxy OTQ established the record for the longest C-O bond [1.658(2) Å], which is attributable to direct electron donation of nonbonding electrons on oxygen into the adjacent σ^*(C-O$^+$) orbital (Figure4-1, **IV**).[3c] Thus, the oxonium compounds with a long C-O$^+$ bond have been often reported, whereas the non-ionic compounds with a long C-O bond have hardly ever been reported due to cleavage of C-O bond by β-elimination.

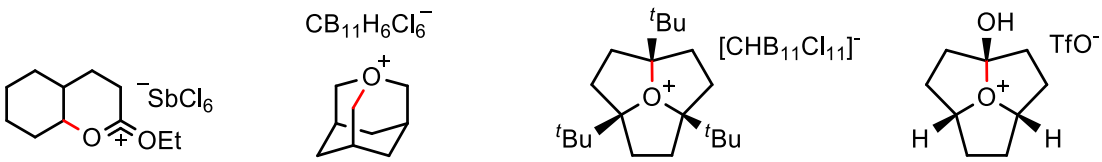


Figure 4-1. Compounds with a long C-O bond and their bond lengths determined by X-ray analyses.

In the previous work on the hexaphenylethane-type compounds with an extremely long C-C bond (> 1.7 Å), it has been found that the distance between the *peri*-position carbons of naphthalene increased elongated by introduction of cross-linkage at the opposite *peri*-position. So, the author expected that this "Scissor effects" can be also applicable to design of compounds with a long non-ionic C-O bond. The precedented investigation revealed that naphtho[1,8-*bc*]furan **1** with spiro-substitution of dibenzocycloheptene at the 2-position could be generated as a stable entity, although its X-ray structure was not determined (Figure 4-2).[5] In this chapter, the preparation and structural analyses of a series of naphtho[1,8-*bc*]furan derivatives **1**-**3** with spiro-substitution of dibenzocycloheptene were performed. The derivatives **2**, **3** installed with the cross-linkage of C-C single bond and double bond, respectively.

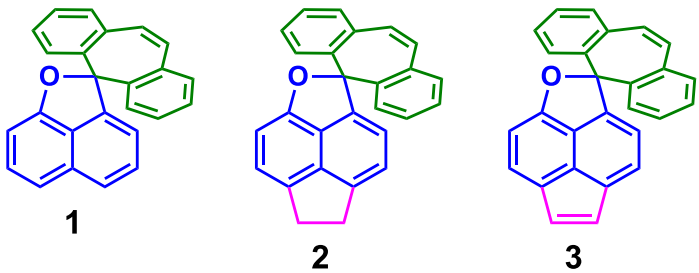
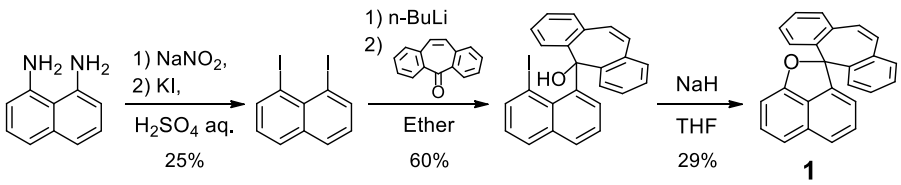


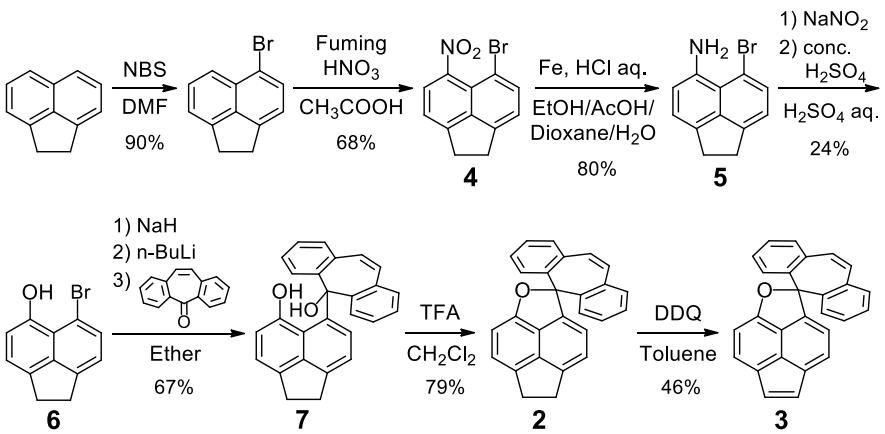
Figure 4-2. The known naphtho[1,8-*bc*]furan derivative **1** and newly designed naphtho[1,8-*bc*]furan derivatives **2**, **3**.

4-2. Preparation of Naphtho[1,8-*bc*]furan Derivatives 1-3

Naphtho[1,8-*bc*]furan **1** was prepared in 3 steps from commercially available 1,8-diaminonaphthalene following the reported procedures (Scheme 4-1).[5] The author attempted to synthesize naphthofuran derivative **2** in a route similar to **1**, but the intramolecular aromatic nucleophilic substitution reaction was found to be difficult. So, compound **2** was synthesized in another route (Scheme 4-2). Monobromination of acenaphthene with NBS followed by treatment with fuming HNO_3 gave 5-bromo-6-nitroacenaphthene **4**.[6] Upon reduction of nitro group of **4** with iron, amine **5** was obtained (y. 80%). The Sandmeyer reaction of amine **5** gave naphthol **6** (y. 24%). After deprotonation of **6** with NaH, the reaction of the resulting naphthoxide with *n*-BuLi in diethyl ether followed by the addition of dibenzosuberenone gave diol **7** (y. 67%). Finally, by dehydration of **7** with TFA in CH_2Cl_2 at room temperature, compound **2** was isolated as colorless crystals in good yields (y. 79%). Then, upon treatment with DDQ in toluene at 80°C, compounds **2** was transformed into yellow crystals of naphthofuran derivative **3** in moderate yield (y. 46%).



Scheme 4-1. Preparation of Naphtho[1,8-*bc*]furan **1**.



Scheme 2-2. Preparation of Naphtho[1,8-*bc*]furan derivatives **2** and **3**.

4-3. X-ray Structures of Naphtho[1,8-*bc*]furan Derivatives 1-3

Single-crystalline samples of high quality of naphthofuran derivatives **1**, **1**·CH_2Cl_2, **2**·CH_2Cl_2, **2**·THF, **3**·CH_2Cl_2 and $\mathbf{3_2}$·Ether were obtained by the vapor diffusion method using a variety of solvent. X-ray analyses at 150 K revealed that all of naphthofuran derivatives **1**-**3** have a C-O bond longer than non-ionic standard C-O bond (1.43 Å). The C-O bond length (*d*3) of naphthofuran derivatives **1**-**3** was compared for a series of CH_2Cl_2 solvated crystals, because the precise geometry for unsolvated crystal was obtained only for **1**. As a result, it was found that the C-O bond length of **2** [1.491(2) Å] and **3** [1.493(3) Å] are much greater than that of **1** [1.477(3) Å] (Figure 4-3), and the former values are comparable to the standard C-O^+ bond length (1.49 Å). Furthermore, when the interatomic distances of compound **1** and compound **2** with a cross-link at the *peri*-position were compared, the value of *d*2 in **2** is larger than that in **1**, whereas the value of *d*1 in **2** is much smaller than that in **1** due to angle strain induced by ring annulation (Table 4-1). Thus, it can be concluded that "Scissor effects" contribute greatly to the expansion of the C-O bond. On the other hand, the conversion of the cross-link from a C-C single bond to a C-C double bond has only marginal effects in C-O bond expansion.

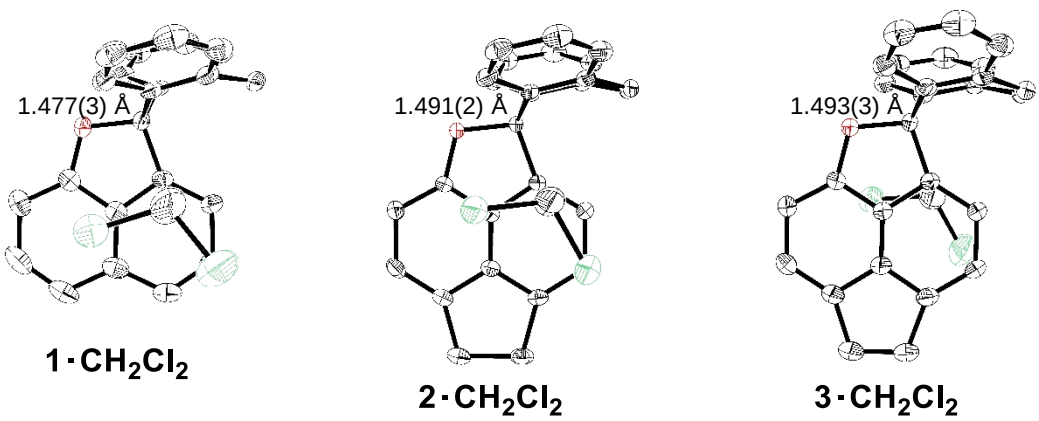
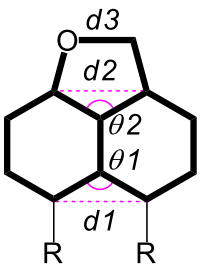


Figure 4-3. ORTEP drawings of naphthofuran derivatives **1**-**3** include CH_2Cl_2 at 150 K.

Table 4-1. Selected geometrical parameters of **1**-**3** in CH_2Cl_2 solvated crystal.

parameters	**1**·CH_2Cl_2	**2**·CH_2Cl_2	**3**·CH_2Cl_2
$\theta 1$ / °	129.6(4)	117.12(16)	114.90(17)
$\theta 2$ / °	110.7(3)	114.34(15)	114.62(17)
d1 / Å	2.564(5)	2.387(2)	2.355(3)
d2 / Å	2.314(4)	2.332(2)	2.335(3)
d3 / Å	1.477(3)	1.491(2)	1.493(3)



As is the case with 1,1,2,2-tetraarylpyracenes in chapter 1, the difference in C-O bond length of **1** in the unsolvated crystal [1.473(2) Å] and that in CH_2Cl_2 solvate [1.477(3) Å] was observed, but the difference falls within the experimental errors (Figure 4-4). This is also the case for another isomorphs of **2**·CH_2Cl_2 [1.491(2) Å] and **2**·THF [1.489(2) Å]. On the other hand, the two crystallographically independent molecules in $\mathbf{3_2}$·Ether have the quite different bond lengths (Δd : 0.031 Å) despite being packed in the same crystal. One of the two values is close to that of **3**·CH_2Cl_2, whereas the other is much greater than any of naphthofuran derivatives [1.495(7) Å, 1.526 (6) Å respectively]. X-ray analyses also showed that the molecule with a longer C-O bond in $\mathbf{3_2}$·Ether has the large $d2$, $\theta2$ and the small $d1$, $\theta1$ compared to another naphthofuran derivatives (Table 4-2). Further investigation is necessary with analyzing the structures with smaller esds to confirm it the crystallographically independent molecules could adopt quite different $d3$ values.

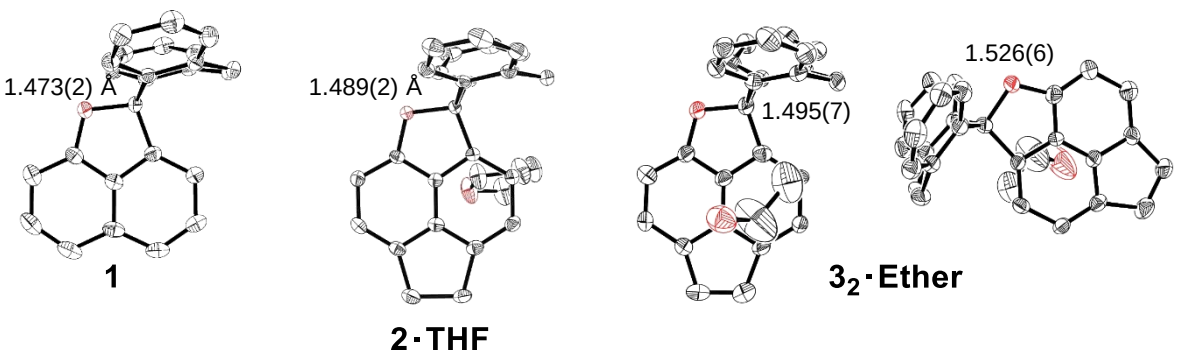
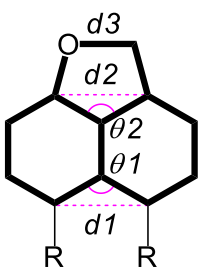


Figure 4-4. ORTEP drawings of naphthofuran derivatives **1**, **2**·THF, $\mathbf{3_2}$·Ether at 150 K.

Table 4-2. Selected geometrical parameters of **1**, **2**·THF, $\mathbf{3_2}$·Ether.

parameters	**1**	**2·THF**	**3·Ether**	
$\theta1$ / °	129.80(18)	117.52(15)	115.9(5)	114.7(5)
$\theta2$ / °	110.94(16)	114.30(15)	114.2(5)	116.0(5)
$d1$ / Å	2.571(3)	2.384(2)	2.363(8)	2.358(8)
$d2$ / Å	2.299(3)	2.328(2)	2.321(8)	2.356(8)
$d3$ / Å	1.473(2)	1.489(2)	1.495(7)	1.526(6)



4-4. DFT Calculation

The C-O bond lengths estimated by DFT calculation for **1**-**3** were 1.475 Å, 1.492 Å and 1.498 Å respectively. These values are very close to the experimental values of **1**-**3** within 0.005 Å (Figure 4-4 (a-c)). Additionally, it was found that these calculated values are much larger than these of their parent skeletons without the spiro unit (2*H*-naphtho[1,8-*bc*]furan: 1.461 Å, 5,6-dihydro-2*H*-acenaphtho[5,6-*bc*]furan: 1.477 Å, 2*H*-acenaphtho[5,6-*bc*]furan: 1.481 Å), although the steric repulsion of the substituent is not likely to have a contribution to the expansion of the C-O bond (Figure 4-4 (d-f)). Thus, through-space interaction, electronic effects and angle strain can be considered as plausible factors to account for the differences. All of the above DFT calculations were performed with the Gaussian 09 program package.[6] The geometries of the compounds were optimized using the B3LYP method with the 6-31G* basis set. The natures of the stationary points were assessed by means of vibration frequency analysis.

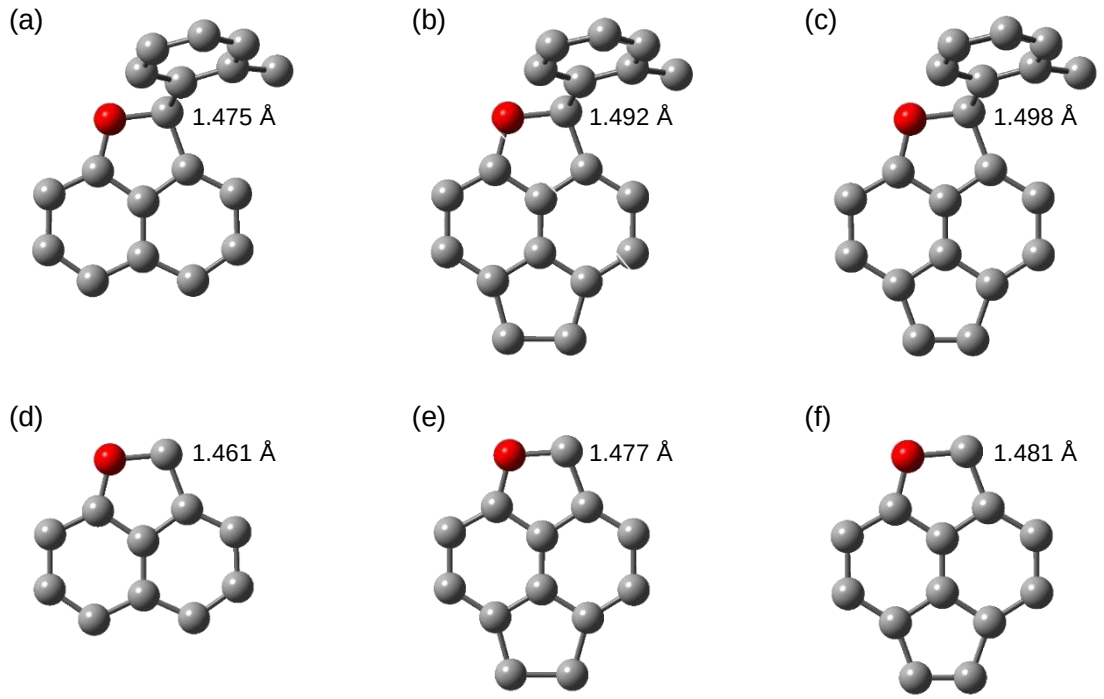


Figure 4-4. Optimized structures of (a) **1**, (b) **2**, and (c) **3** determined by DFT calculations along with those for the parent skeleton without the spiro unit (B3LYP/6-31G*).

4-5. Conclusion

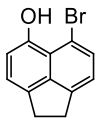
The author has planned to expand a non-ionic C-O bond by application of “Scissor effects” for a 2*H*-naphtho[1,8-*bc*]furan skeleton of **2**, and has succeeded in preparing the derivatives **2** and **3** with a additional bridge on the opposite *peri*-positions of naphtho[1,8-*bc*]furan skeleton. X-ray analyses of these compounds revealed that all of them have a longer C-O bond than non-ionic standard bond length (1.43 Å), and the derivatives **2** and **3** fused with a five-membered ring at the *peri*-position of naphthalene have a longer C-O bond than compound **1**. Thus, it has been confirmed that "Scissor effects" is greatly contributed to the extension of the C-O bond. On the other hand, it has been suggested that the factors except for steric strain such as “Scissor effects” and intermolecular factors such as crystal packing would possibly some contribution to the bond elongation.

Experimental Section

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise indicated. All commercially available compounds were used without further purification. Dry MeCN was obtained by distillation from CaH_2 prior to use. Column chromatography was performed on silica gel I-6-40 (YMC) of particle size 40-63 µm and aluminium oxide 90 standardized (Merck 63-200 µm). ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER Ascend™ 400 (^{1}H/400MHz and ^{13}C/100MHz) spectrometer. IR spectra were measured as a KBr pellet on a JEOL JIR-WINSPEC100FT/IR spectrophotometer. Mass spectra were recorded on JMS-AX500, JMS-SX102A, or JEOL JMS-T100GCV spectrometers in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Melting points were measures on a Yamato MP-21 melting point apparatus and reported uncorrected. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer.

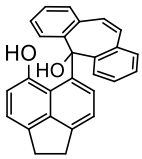
Preparation of 6-Bromo-acenaphthen-5-ol 6



To a suspension of 5-amino-6-bromoacenaphthene **5** (1.69 g, 6.80 mmol) in 1M H_2SO_4 aq. (10 mL) was added a solution of $NaNO_2$ (590 mg, 8.55 mmol) in water (2 mL) dropwise over 15 min for 0°C under air, and the mixture was stirred for 15 min at 0°C. To the suspension was added conc. H_2SO_4 (4 mL) at 0°C, and the mixture was warmed up to 100°C and stirred for 1 h. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ CH_2Cl_2 = 3) to give 6-bromo-acenaphthen-5-ol **6** (414 mg, 24%) as a pale yellow solid.

M. p. 110-111 °C ; ^{1}H NMR ($CDCl_3$) δ 7.61 (s, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 4.43 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 149.43, 146.90, 142.02, 137.81, 131.78, 121.15, 120.07, 119.11, 114.14, 110.26, 30.48, 29.76 ; IR (KBr) 3472, 3068, 2924, 2836, 1584, 1460, 1385, 1349, 1254, 1217, 1193, 1184, 841 cm^{-1} ; LR-MS (FD) *m/z* (%): 248 (M^+, bp), 249 (14), 250 (98), 251 (13) ; HR-MS (FD) Calcd. for $C_{12}H_9BrO$: 247.9837, Found : 247.9845.

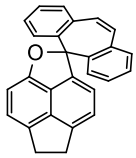
Preparation of 5-(6-hydroxy-1,2-dihydroacenaphthylene-5-yl)-5*H*-dibenzo[a,d] cyclopenten-5-ol 7



To a solution of 6-bromo-acenaphthen-5-ol **6** (372 mg, 1.49 mmol) in dry ether (30 mL) was added 60% NaH in oil (79.3 mg, 1.98 mmol). After stirring for 30 min at 22 °C, *n*-BuLi in hexane (1.54 M, 1.1 mL, 1.65 mmol) was added, and the mixture was stirred for 1 h at 22 °C. Then, dibenzosuberenon (378 mg, 1.83 mmol) was added, and the mixture was stirred for 16 h at 22 °C. The mixture was quenched with water, and extracted with EtOAc. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (CH_2Cl_2 / hexane = 2) to give **7** (375 mg, 67%) as a white solid.

M. p. 205-208 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 8.29 (s, 1H), 8.14 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.50 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.48 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.18 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.58 (s, 2H), 3.86 (s, 1H), 3.23 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 148.80, 147.67, 142.07, 141.35, 137.04, 133.26, 131.02, 130.21, 128.86, 128.02, 127.98, 126.36, 123.18, 120.62, 120.25, 116.57, 114.23, 79.75, 30.19, 29.52 ; IR (KBr) 3517, 3279, 3059, 3020, 2924, 2843, 1454, 1429, 1343, 1232, 1156, 1014, 848, 793, 769, 745 cm^{-1} ; LR-MS (FD) *m/z* (%): 376 (M^+, bp), 377 (30), 378 (5) ; HR-MS (FD) Calcd. for $C_{27}H_{20}O_2$: 376.1463, Found : 376.1482.

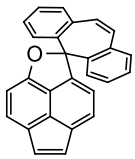
Preparation of 5,6-Dihydrospiro(dibenzo[*a*,*d*]cyclopentene-5,2'-acenaphtho[5,6-*bc*] furan) 2



To a solution of **7** (46.3 mg, 123 μmol) in dry CH_2Cl_2 (10 mL) was added trifluoroacetic acid (90 μL, 1.21 mmol), and then the mixture was stirred for 30 min at 23 °C. After solvent was concentrated under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ EtOAc = 10) to give **2** (34.7 mg, 79%) as a white solid.

M. p. 183-186 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 8.04 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.33-7.26 (m, 4H), 7.24 (s, 2H), 7.12 (dd, *J* = 7.2, 1.5 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 1H), 3.41-3.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 155.70, 143.54, 139.82, 139.50, 139.21, 134.30, 132.84, 132.74, 130.06, 128.75, 127.39, 125.27, 124.95, 121.68, 121.29, 120.88, 101.80, 100.33, 32.51, 31.53 ; IR (KBr) 3066, 3027, 2922, 2832, 1573, 1498, 1476, 1426, 1211, 1148, 989, 902, 831, 806, 771, 748 cm^{-1} ; LR-MS (FD) *m/z* (%): 358 (M^+, bp), 359 (29), 360 (5) ; HR-MS (FD) Calcd. for $C_{27}H_{18}O$: 358.1358, Found : 358.1351.

Preparation of Spiro(dibenzo[*a*,*d*]cyclopentene-5,2'-acenaphtho[5,6-*bc*]furan) 3



To a solution of **2** (28.7 mg, 80.0 μmol) in dry toluene (10 mL) was added DDQ (29.3 mg, 129 μmol), and the mixture was stirred for 1 h at 80 °C. After filtration, the solvent was concentrated under reduced pressure, the resulting residue was purified by column chromatography on SiO_2 (hexane/ CH_2Cl_2 = 3) to give **3** (13.2 mg, 46%) as a yellow solid.

M. p. 197-200 °C (decomp.) ; ^{1}H NMR ($CDCl_3$) δ 8.05-8.01 (m, 3H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 5.7 Hz, 1H), 7.46 (d, *J* = 5.7 Hz, 1H), 7.31-7.28 (m, 6H), 7.10 (d, *J* = 4.8 Hz, 1H), 6.99 (d, *J* = 4.8 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ 161.11, 143.60, 137.93, 137.48, 133.73, 132.76, 130.15, 130.04, 129.58, 128.79, 127.99, 127.84, 126.57, 125.33, 124.72, 123.17, 121.91, 102.52, 102.10 ; IR (KBr) 3053, 1643, 1485, 1414, 1234, 1153, 1077, 997, 896, 833, 808, 799, 753 cm^{-1} ; LR-MS (FD) *m/z* (%): 356 (M^+, bp), 357 (30), 358 (19), 359 (5) ; HR-MS (FD) Calcd. for $C_{27}H_{16}O$: 356.1201, Found : 356.1200.

X-ray analyses

Data collection was conducted with a Rigaku Mercury 70 diffractometer (Mo-Kα radiation, λ = 0.71075 Å). The structure was solved by the direct method (SIR2004) and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding.

Crystal date for 1

MF : $C_{25}H_{16}O$, FW : 332.40, colorless platelet, 0.30 × 0.20 × 0.05 mm, monoclinic $P2_1$/n, a = 8.960(2) Å, b = 8.128(2) Å, c = 23.410(5) Å, α = 90°, β = 90.740(3)°, γ = 90°, V = 1704.7(7) Å^3, ρ (Z = 4) = 1.295 g/cm^3. A total 3862 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.773 cm^{-1}). The final *R1* and *wR2* values are 0.0533 (I > 2σI) and 0.1515 (all data) for 3862 reflections and 235 parameters. Estimated standard deviations are 0.002-0.004 Å for bond lengths and 0.13-0.19° for bond angles, respectively.

Crystal date for 1·CH_2Cl_2

MF : $C_{26}H_{18}Cl_2O$, FW : 417.33, colorless platelet, 0.50 × 0.25 × 0.10 mm, monoclinic $P2_1$, a = 8.920(2) Å, b = 8.349(2) Å, c = 13.932(4) Å, α = 90°, β = 104.646(3)°, γ = 90°, V = 1003.9(5) Å^3, ρ (Z = 2) = 1.381 g/cm^3. A total 4004 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 3.379 cm^{-1}). The final *R1* and *wR2* values are 0.0560 (I > 2σI) and 0.1564 (all data) for 4004 reflections and 262 parameters. Estimated standard deviations are 0.003-0.007 Å for bond lengths and 0.19-0.4° for bond angles, respectively.

Crystal date for 2·CH_2Cl_2

MF : $C_{28}H_{20}Cl_2O$, FW : 443.37, colorless platelet, 0.50 × 0.40 × 0.15 mm, monoclinic $P2_1/n$, a = 8.9937(4) Å, b = 8.4986(5) Å, c = 27.6131(12) Å, α = 90°, β = 94.606(3)°, γ = 90°, V = 2103.8(2) Å^3, ρ (Z = 4) = 1.400 g/cm^3. A total 4508 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 3.271 cm^{-1}). The final *R1* and *wR2* values are 0.0483 (I > 2σI) and 0.1225 (all data) for 4508 reflections and 280 parameters. Estimated standard deviations are 0.002-0.003 Å for bond lengths and 0.12-0.18° for bond angles, respectively.

Crystal date for 2·THF

MF : $C_{31}H_{26}O_2$, FW : 430.55, colorless platelet, 0.20 × 0.05 × 0.05 mm, orthorhombic $P2_12_12_1$, a = 8.414(2) Å, b = 14.466(3) Å, c = 17.819(4) Å, α = 90°, β = 90°, γ = 90°, V = 2168.9(8) Å^3, ρ (Z = 4) = 1.318 g/cm^3. A total 3559 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.806 cm^{-1}). The final *R1* and *wR2* values are 0.0324 (I > 2σI) and 0.0828 (all data) for 3559 reflections and 298 parameters. Estimated standard deviations are 0.0019-0.004 Å for bond lengths and 0.12-0.2° for bond angles, respectively.

Crystal date for 3·CH_2Cl_2

MF : $C_{28}H_{18}Cl_2O$, FW : 441.36, yellow platelet, 0.40 × 0.10 × 0.05 mm, monoclinic $P2_1/n$, a = 8.888(2) Å, b = 8.5623(11) Å, c = 27.745(5) Å, α = 90°, β = 95.850(2)°, γ = 90°, V = 2100.4(6) Å^3, ρ (Z = 4) = 1.396 g/cm^3. A total 4552 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 3.274 cm^{-1}). The final *R1* and *wR2* values are 0.0573 (I > 2σI) and 0.1653 (all data) for 4552 reflections and 280 parameters. Estimated standard deviations are 0.003-0.004 Å for bond lengths and 0.13-0.2° for bond angles, respectively.

Crystal date for 3·Ether

MF : $C_{29}H_{21}O_{1.5}$, FW : 393.48, yellow platelet, 0.20 × 0.20 × 0.05 mm, monoclinic $C2$, a = 12.223(7) Å, b = 12.044(7) Å, c = 27.73(2) Å, α = 90°, β = 98.846(7)°, γ = 90°, V = 4034(5) Å^3, ρ (Z = 8) = 1.296 g/cm^3. A total 7144 unique data ($2\theta_{max}$ = 55°) were measured at T = 150 K. Numerical absorption correction was applied (μ = 0.783 cm^{-1}). The final *R1* and *wR2* values are 0.0841 (I > 2σI) and 0.2462 (all data) for 7144 reflections and 551 parameters. Estimated standard deviations are 0.006-0.015 Å for bond lengths and 0.4-1.1° for bond angles, respectively.

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