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COMMUNICATION

Splitting and Reorientation of π-Conjugation by an Unprecedented Photo-Rearrangement Reaction†

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A dodecahexaene analogue cross-conjugated with four carbonyl groups was prepared from an aliphatic tetraketone. Exposure to LED light (>420 nm) led to the splitting of the dodecahexaene conjugation into the two hexatriene subunits, connected through a stereogenic carbon atom. The two triene subunits exhibited excitonic coupling in the UV-Vis absorption and CD spectra.

Retinal, also known as a vitamin A, is produced by oxidative cleavage of β-carotene.[1] Such redistributions of π-conjugation during splitting reactions are important processes for modulating the optical properties of π-systems. Considering the recent upsurge in the synthesis of large π-conjugated organic compounds,[2] such reactions are also considered to have extensive applicability to existing π-systems. However, compared with extension of π-systems, regioselective π-splitting reactions (Fig. 1) remain limited[3] because they require dissociation of stable C–C or C=C covalent bonds. As a representative example, Osuka and co-workers reported a thermal splitting reaction of expanded porphyrins into two contracted porphyrinoids (Fig. 1b)[4]. Recently, Yamago *et al.* reported strain-induced cleavage of cycloparaphenylenes into linear oligophenylene analogues.[5] Focusing on the fragments of π-splitting reactions, two resultant chromophores that have identical or similar excitation energies are expected to show remarkable interchromophore interactions when they are arranged in appropriate orientations.[6] Interchromophore interaction such as excitonic coupling is also an interesting phenomenon that cannot be seen for discrete, single chromophores.

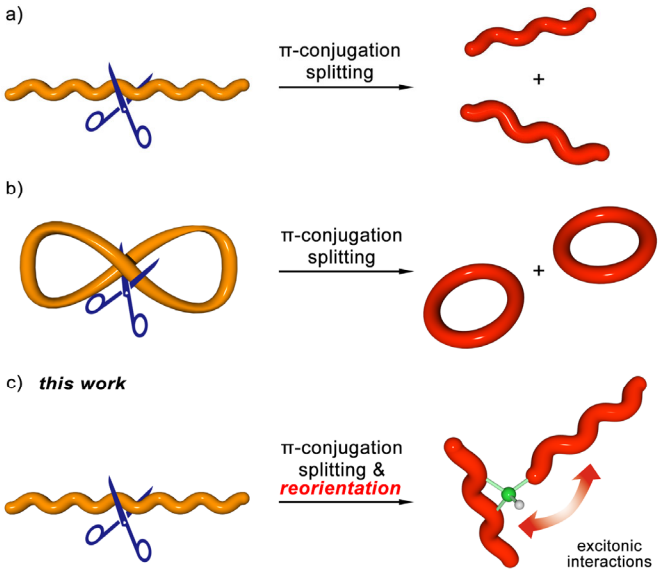

Fig. 1 Schematic diagrams of π-conjugation splitting reactions: a) from a single linear to two linear molecules, b) from macrocyclic to smaller cyclic molecules, and c) splitting and reorientation of a polyene system (this work).

Here we report regioselective π-conjugation splitting reaction of a planar dodecahexaene analogue into an orthogonally arranged bis(triene) with the use of an unprecedented photo-induced rearrangement reaction (Fig. 1c).Starting from 2,5-dihydropentalene-1,4-dione as a stable triene subunit, its conjugated dimer (dodecahexaene) splits into two triene subunits in high yield upon visible light irradiation. Notably, the two triene chromophores were orthogonally arranged in a close proximity by a stereogenic carbon center that was generated in the photo-rearrangement. Therefore, excitonic coupling interactions were clearly observed in the absorption spectrum. Furthermore, because this photo-rearrangement reaction afforded chiral chromophores from achiral hexaene, circular dichroism (CD) signals were observed after optical resolution of enantiomers.

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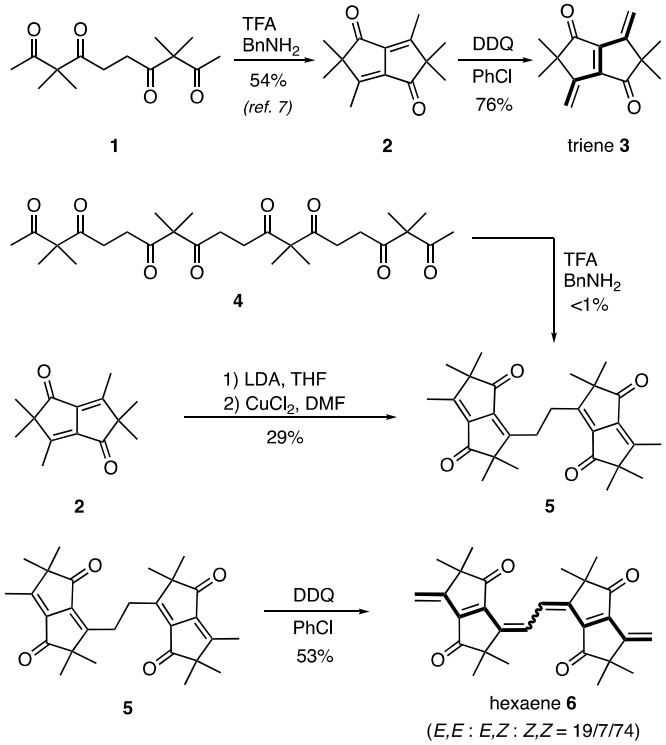
In this work, we focused on a pentalene-based bicyclic carbon skeleton as a stable hexatriene component. Previously, we have reported an efficient synthesis of 2,2,3,5,5,6-hexamethyl-2,5-dihydropentalene-1,4-dione (**2**) from an aliphatic tetraketone precursor **1**.[7] Upon oxidation using 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), two allylic methyl positions of **2** were oxidized to give hexatriene analogue **3** bearing two cross-conjugated carbonyl groups in 76% yield (Scheme 1) as a yellow solid. Single crystal X-ray analysis revealed the bond length alternation of **3** (from-end-to-end 1.330, 1.455, 1.352, 1.455, and 1.330 Å; Fig. 2a), which clearly indicated hexatriene-like π-conjugation of the planar pentalene-based bicyclic system.



Scheme 1 Synthesis of hexatriene **3** and dodecahexaene **6** derivatives.

The parent compound **2** is colorless; however, a dichloromethane solution of triene **3** is yellow because the absorption edge of **3** extended up to 380 nm (Fig. 3). Despite the intense absorption band at 300–380 nm, compound **3** did not show *Z* ↔ *E* photoisomerization at the central double bond, because of the rigid bicyclic skeleton. Because this oxidation reaction warrants that compound **2** can be used as a synthon of hexatriene, we attempted to synthesize a dodecahexaene by connecting the pentalene-based subunits. When octaketone **4**[8] was treated under the reaction conditions similar to the synthesis of **2** from tetraketone **1**, a complex mixture containing ethylene-linked pentalene dimer **5** (< 1%) was formed. Because the yield of **5** could not be improved despite many efforts, we alternatively synthesized dimer **5** by an oxidative homo-coupling reaction of monomer **2**. Oxidation of the dienolate species of **2**, generated by the treatment with lithium diisopropylamide (LDA), with $CuCl_2$ afforded dimer **5** in 29% yield after chromatographic separation. Formation of C–C bond at the allylic position of monomer **2** was confirmed by the single crystal X-ray analysis (see ESI).

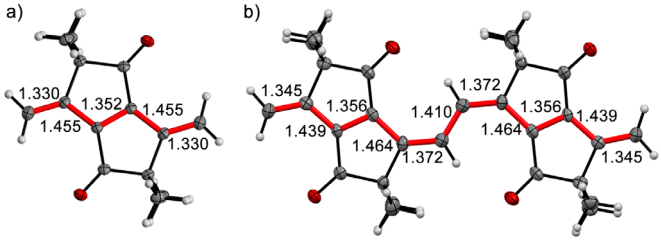


Fig. 2 X-ray crystal structures of a) **3** and b) **6**. Thermal ellipsoids are set at the 50% probability level. Selected distances (in Å) are shown for C–C or C=C bonds highlighted in red.

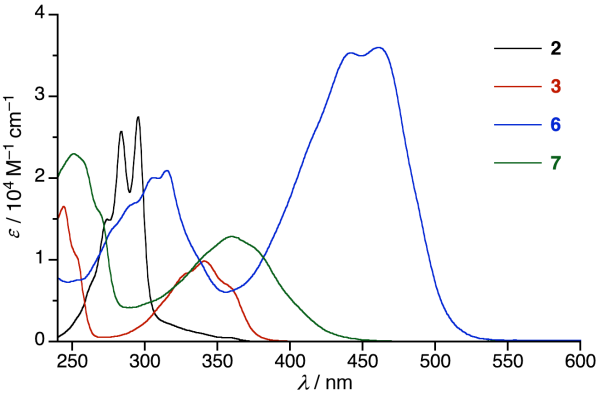


Fig. 3 UV-Vis absorption spectra of compounds **2**, **3**, (*Z*,*Z*)-**6**, and **7** in CH_2Cl_2.

Dimer **5** also underwent DDQ-mediated oxidation to give a dodecahexaene moiety **6** bearing four cross-conjugated carbonyl groups in 53% yield as an orange solid. The as-obtained **6** contained *E*,*E*, *E*,*Z*, and *Z*,*Z* isomers in a 19/7/74 ratio, chromatographic separation on silica gel was unsuccessful because of overlap and rapid photoisomerization even under room light. Repeated recrystallization allowed isolation of the major product (*Z*,*Z*)-**6** as single crystals. X-ray diffraction analysis revealed the planar structure of (*Z*,*Z*)-**6** and its bond length alternation (Fig. 2b), which is typical of the crystal structures of carotenoids.[9] (*Z*,*Z*)-**6** can be classified as a (3*E*,5*Z*,7*Z*,9*E*)-dodecahexaene analogue, in which central two C=C double bonds are able to undergo *Z* ↔ *E* photoisomerization.

Dodecahexaene **6** exhibited an intense visible absorption band at 456 nm in dichloromethane with a molar extinction coefficient of 3.8×10^4 M^{-1} cm^{-1} (Fig. 3). When a $CDCl_3$ solution of as-synthesized **6** was exposed to room light, intensities of proton signals assignable to (*E*,*E*)-**6** and (*E*,*Z*)-**6** gradually increased in the ^1H NMR spectra with concomitant decrease in those for (*Z*,*Z*)-**6**. After 10 h, the system reached a pseudo photo-stationary state with an *E*,*E* : *E*,*Z* : *Z*,*Z* ratio of 41/11/48 (see ESI). DFT calculations indicated that the total energies decreased in the order of (*E*,*Z*)-**6**, (*E*,*E*)-**6**, and (*Z*,*Z*)-**6**, which roughly matched with the observed distribution of diastereomers.

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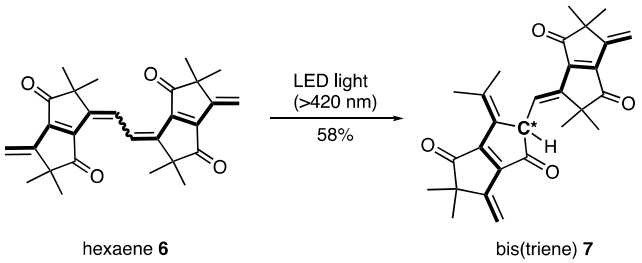
Prolonged visible light irradiation (>420 nm) of dodecahexaene **6** in degassed chloroform by a LED light caused splitting of the π-conjugated system and rearrangement of pentalene-based carbon skeleton (Scheme 2). Upon visible irradiation, the orange color of the solution was gradually degraded over 10 h. The ^{1}H NMR spectroscopy showed the formation of non-symmetric product **7** in 80% yield based on an internal standard (isolated yield: 58%). It should be noted that other peaks assignable to other diastereomers of **7** were not found in ^{1}H NMR spectra during the reaction. The Atmospheric Pressure Chemical Ionization (APCI)-TOF mass analysis of **7** indicated the chemical formula to be $C_{28}H_{30}O_4$, which is exactly the same as that of **6**. Whereas the starting material **6** has six vinylic protons, only five were observed in the ^{1}H NMR spectrum of **7**. A methine proton was observed at 4.47 ppm in $CDCl_3$ as a doublet which coupled to a vinyl proton at 6.21 ppm with a coupling constant of 10.6 Hz. In the HMQC spectrum, the methine proton showed correlation with sp^3-hybridized carbon at 58.4 ppm. Furthermore, two of the eight methyl groups were shifted down-field to 2.36 and 1.87 ppm, indicating the formation of an isopropylidene group.



Scheme 2 Photo-induced rearrangement of hexaene **6** into bis(triene) **7**.

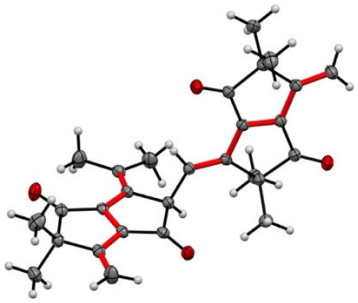


Fig. 4 Crystal structure of photo-rearranged product **7**. Two hexatriene moieties are highlighted in red. Only the R-form in racemic crystal is shown.

Single crystal X-ray analysis of **7** unambiguously confirmed the splitting and redistribution of the hexaene π-conjugation of **6** into two triene moieties arranged in an orthogonal fashion. Photo-product **7** crystallized in a centrosymmetric space group $P2_1/c$ in its racemic form. One of two pentalene-based subunits was identical to that in **6**; however, the other contained a stereogenic sp^3-carbon center and an isopropylidene group. Nonetheless, a hexatriene-like π-conjugation with the two cross-conjugated carbonyl groups was preserved. The center-to-center distance of the two triene subunits was 6.21 Å, and the dihedral angle of the mean planes of two pentalene-based subunits was 79.7°. The through-bond π-conjugation between the two triene moieties was cleaved at the bridging sp^3-carbon atom; however, the observed orientation is advantageous for inducing interchromophore interactions.

Although the detailed mechanism is unclear, this photo-induced rearrangement reaction can be explained by a Norrish type I-like α-cleavage reaction at an internal carbonyl group (see ESI). As observed for 5,5-dimethylcyclopent-2-en-1-one,[10] a substructure of **6**, a ketene intermediate can be generated by photo-induced α-cleavage at the quaternary sp^3-carbon side. Single bond rotation and a subsequent ring closing reaction form a stereogenic sp^3-carbon-embedded five-membered ring bearing the isopropylidene group. As the crystal structure and NMR spectrum of **7** indicated that the *E*-isomer with respect to the double bond attached with chiral carbon was exclusibely obtained under the given conditions, the visible light-induced photo-rearrangement reaction occurred on (*E*,*Z*)-**6**, or (*E*,*E*)-**6** that were generated by photoisomerization of (*Z*,*Z*)-**6**. Notably, the regioselective transformation of **6** into **7** was observed only under visible light (>420 nm) irradiation. UV irradiation of dichloromethane solution of **6** produced a complex mixture of photo-products, presumably due to further photo-reactions of **7** by UV-excitation.

The π-splitting reaction of **6** led to drastic changes in optical properties of the chromophores. Because the π-conjugation length is shortened, UV-Vis absorption spectrum of rearranged product **7** hypsochromically shifted compared with **6** (Fig. 3). While hexaene (*Z*,*Z*)-**6** and its *E*/*Z* mixture (*E*,*E* : *E*,*Z*, : *Z*,*Z* = 19/7/74) showed visible fluorescence emission at 567 nm (quantum yield: 5%; lifetime 2.2 ns) and 568 nm (quantum yield: 3%; lifetime 2.1 ns), respectively, rearranged product **7** was virtually non-fluorescent as well as its component chromophore **3**. These observations matched well with the TD-DFT calculation results: while the lowest energy transition for **6** corresponded to the allowed transition of the dodecahexaene moiety, those of **7** and **3** were forbidden transitions.

Due to the rearrangement reaction, the triene chromophores in compound **7** were positioned in close proximity influencing its UV-Vis absorption spectrum (Fig. 3) through excitonic interaction. Although the conjugation length of **7** is similar to that of monomer **3**, the absorption bands of **7** were markedly red-shifted and slightly broadened. In spite of having an additional effect of the terminal methyl groups at one triene segment in the overall absorption spectrum of **7**, the presence of excitonic coupling between two chromophores was also indicated from the spectral shape.[6] We analysed the spectrum using molecular exciton theory with the Holstein-type vibronic Hamiltonian[11] (See ESI). The total excitonic coupling was estimated to be 540 cm^{-1}. The coupling likely originated from Dexter-type interaction rather than Förster-type interaction, which is consistent with the well-established theory of excitonic interactions.[12]

Because compound **7** is chiral, we further evaluated the excitonic interactions between two hexatriene species using CD spectroscopy. The two enantiomers of **7** were successfully resolved by HPLC with a cellulose-based chiral column. The racemic **7** was CD silent; however, the first fraction eluted at

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13.1 min exhibited positive CD signals at 415 nm and 347 nm (Fig. 5). The mirror-image spectrum was observed for the second fraction eluted at a retention time of 17.0 min. TD-DFT calculation results at the B3LYP/6-31G(d,p) level suggested that the stereochemistry of the first and second fractions were *R* and *S*, respectively. These observations clearly showed that the photo-rearrangement reaction converted the achiral dodecahexaene derivative into two π-conjugated fragments having a chiral orientation, which induces excitonic coupling interactions.

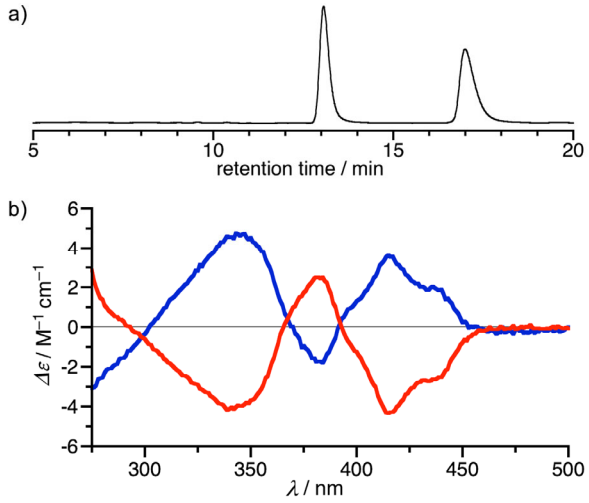

Fig. 5 a) Chiral HPLC chromatogram for optical resolution of racemic compound **7** (detection by absorption at 254 nm). b) CD spectra of the first (blue) and the second (red) fractions in dichloromethane.

In summary, we have demonstrated a photo-induced π-conjugation splitting and reorientation of a pentalene-based dodecahexaene system as a novel approach for π-conjugation redistribution. Because the two resultant chromophores were held in a chiral orientation by a stereogenic sp^3-carbon atom, excitonic interactions were observed in the UV-vis absorption and CD spectra. As a result, drastic structural and optical property changes were achieved by the π-conjugation redistribution reaction. Because π-conjugated carbon materials such as polyenes and nanographenes have been extensively synthesized by organometallic means, our π-splitting and reorientation strategy will contribute to the reconstruction of existing π-conjugated systems. In this sense, the introduction of cross-conjugated carbonyl groups to a conjugated carbon skeleton may play an important role in regioselectively cleave the conjugation.

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Conflicts of interest

There are no conflicts to declare.

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