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Lateral Extension of π Conjugation along the Bay Regions of Bisanthene through a Diels–Alder Cycloaddition Reaction

Jinling Li,[a] Chongjun Jiao,[a] Kuo-Wei Huang,[b] and Jishan Wu*[a]

Abstract: Diels–Alder cycloaddition reactions at the bay regions of bisanthene (**1**) with dienophiles such as 1,4-naphthoquinone have been investigated. The products were submitted to nucleophilic addition followed by reductive aromatization reactions to afford the laterally extended bisanthene derivatives **2** and **3**. Attempted synthesis of a larger expanded bisanthene **4** revealed an unexpected hydrogenation reaction at the last reductive aromatization step. Unusual Michael addition was observed on quinone **14**, which was obtained by Diels–Alder reaction between **1** and 1,4-anthraquinone. Compounds **1**–**3** exhibited near-infrared (NIR) absorption and emission with high-to-moderate fluorescent quantum yields. Their structures and absorption spectra were studied by density function theory and non-planar twisted structures were calculated for **2** and **3**. All compounds showed amphoteric redox behavior with multiple oxidation/reduction waves. Oxidative titration with $SbCl_5$ gave stable radical cations, and the process was followed by UV/Vis/NIR spectroscopic measurements. Their photostability was measured and correlated to their different geometries and electronic structures.

Keywords: cycloaddition · dyes/pigments · hyperconjugation · Michael addition · polycycles

Introduction

Polycyclic aromatic hydrocarbons (PAHs) with large, extended π conjugation and small band gaps have promising applications as organic semiconductors[1] for electronic devices and as organic dyes[2] for solar cells and bio-imaging. The physical properties and chemical reactivity of PAHs are largely determined by the arrangement of the benzenoid rings in the π system and by the extent of π conjugation. Linear fusion of benzene rings leads to oligoacenes, among which both the band gap and stability quickly decrease with increasing numbers of benzene rings.[3] Anthracene,[4] tetracene,[5] and pentacene derivatives[6] have been successfully applied in organic field effect transistors (OFETs) and organic light-emitting diodes (OLEDs). Higher order acenes (larger than pentacene) with low band gaps turned out to be extremely unstable, and appropriate substitution by aryl, alkyne, or arylthio groups and/or electronegative halogen atoms is required to obtain relatively stable hexacene,[7] heptacene,[7d,8] and nonacene.[9] Alternative approaches to stabilize oligoacenes and to extend π conjugation is benzannulation around the acene framework, and various benzannulated pentacene and higher order homologues have been reported.[10] Introduction of phenyl rings in these benzannulated acene fragments usually results in puckering of the molecules, for example, twisting, and gives a family of contorted molecules termed “twistacenes”.[11] Another type of interesting PAH molecule is rylene, in which two or more naphthalene units are *peri*-condensed together in a top-on-top mode. Similar to oligoacenes, rylene molecules show a convergence of band gap with increasing numbers of naphthalene units from perylene to terrylene, quaterrylene, pentarylene, and hexarylene.[12] Rylene derivatives have been studied in detail because they are important dyes for many practical applications.[13]

The third type of interesting PAH molecules is called periacene, in which two acene units (anthracene, tetracene, or pentacene) are *peri*-condensed together in a similar mode to that for perylene; the molecules are called bisanthene, peritetracene, and peripentacene, respectively.[14] Periacene molecules have been predicted theoretically to have very small band gaps with a significant singlet biradical character, and they are expected to be highly reactive due to their high-lying HOMO energy levels.[14] So far, syntheses of peritetracene and peripentacene derivatives have never been successful, although our group recently made some attempts.[15] Even the smallest member of the periacene family (i.e., bisanthene) is very sensitive to oxygen and light.[16] We recently developed a number of approaches[17] to prepare a series

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[a] J. Li, C. Jiao, Prof. J. Wu
Department of Chemistry
National University of Singapore
3 Science Drive 3, 117543 (Singapore)
Fax: (+65) 6779-1691
E-mail: chmwuj@nus.edu.sg

[b] Prof. K.-W. Huang
KAUST Catalysis Center and
Division of Chemical and
Life Sciences and Engineering
4700 King Abdullah University
of Science and Technology
Thuwal 23955-6900 (Kingdom of Saudi Arabia)

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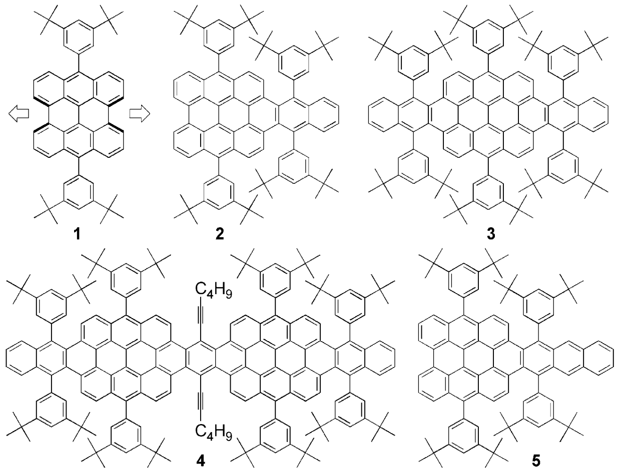
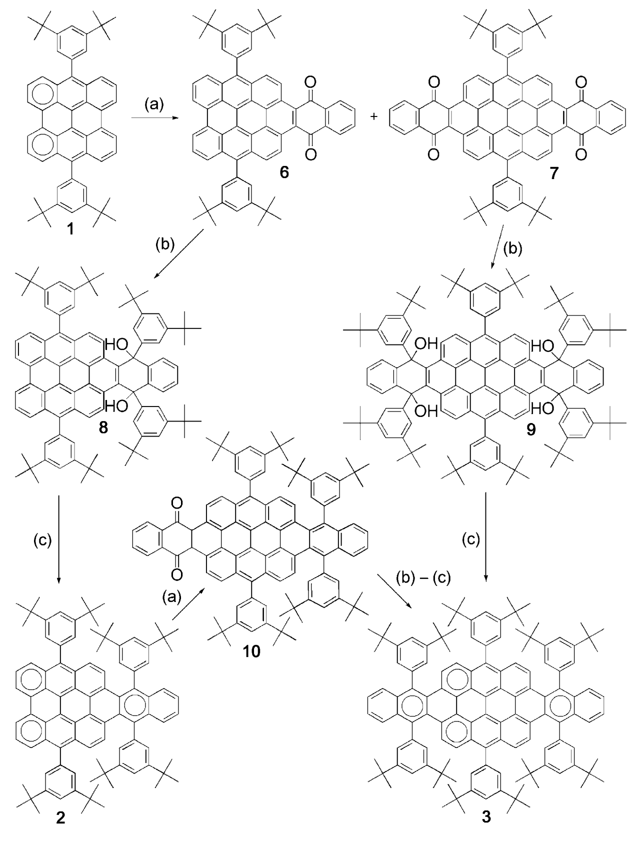
of soluble and stable bisanthene-based near-infrared (NIR) dyes with structural features that included: 1) substitution by electron-withdrawing dicarboxylic imide groups at the zig-zag edges; 2) quinoidization along the short-axis, and 3) substitution by aryl or alkyne groups at the most reactive *meso*-positions. Similar to perylene, the bay regions of bisanthene have a diene character as shown in compound **1** (Scheme 1) and this raises the opportunity to introduce further functionalization through Diels–Alder cycloaddition reaction at the bay positions of bisanthene. Clar et al. reported that Diels–Alder cycloaddition of parent bisanthene with maleic anhydride gave ovalene dianhydride, which was then successfully converted into ovalene by decarboxylation.[18] Liquid crystalline ovalene tetraesters were also prepared by esterification of ovalene dianhydride.[19] Recently, Scott et al. reported that nitroethylene could be used as a masked acetylene, and this compound underwent Diels–Alder reaction at the bay regions of bisanthene to give ovalene derivatives.[20] This result implied that it was possible to synthesize single-chirality carbon nanotubes by using a metal-free approach from a suitable cylindrical template. Diels–Alder reaction between a diene and a dienophile such as 1,4-benzoquinone, 1,4-naphthoquinone, and 1,4-anthraquinone have been frequently used to construct extended acenequinones and higher order acenes.[3] In this work, we report the cycloaddition reactions between bisanthene and these quinones, and subsequent synthesis of a series of aryl-annulated bisanthene compounds with laterally extended π conjugation (e.g., compounds **2**–**5**; Scheme 1). In all target molecules **2**–**5**, bulky 3,5-di-*tert*-butylphenyl groups are attached to the zig-zag edges to increase their stability and solubility. These molecules were expected to have a contorted structure due to steric congestion induced by the phenyl substituents, and can also be regarded as anthryl-annulated twistacenes. Herein, the synthetic chemistry, structure, photophysical properties, electrochemical properties, and photostability of these laterally expanded bisanthene compounds are fully investigated, and attempts have been made to understand their fundamental structure–property relationships.



Scheme 1. Structures of compounds **1**–**5**.

Results and Discussion

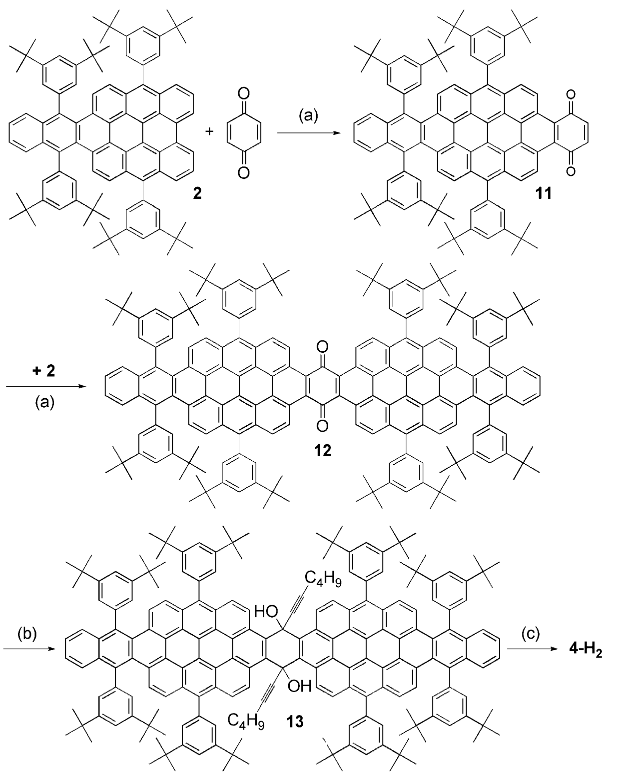
Synthesis: The synthesis of **2** and **3** is depicted in Scheme 2. The 3,5-di-*tert*-butylphenyl-substituted bisanthene **1** was first prepared according to our previous report.[17c] Diels–Alder reaction between **1** and a large excess of 1,4-naphthaquinone (20 equiv) in nitrobenzene heated to reflux (240 °C) afforded the mono-addition product **6** and bis-addition product **7**; the ratio of **6**/**7** was dependent on the reaction time. Compound **6** was obtained as a dominant product after heating the reaction to reflux temperature for 24 h, but compound **7** was generated as a major product after extending the period of reflux to two days. The nitrobenzene served as a high-boiling-point solvent as well as an oxidant to convert the Diels–Alder product into the dehydrogenated final products **6** and **7**. Compound **6** reacted with the Grignard reagent of 3,5-di-*tert*-butyl-1-bromobenzene in an anhydrous mixture of tetrahydrofuran (THF) and toluene to give diol **8** in 52 % yield, which was followed by dehydroxylation and reductive aromatization with NaI/NaH_2PO_2 to afford the target compound **2** in nearly quantitative yield. Subsequent



Scheme 2. Synthesis of **2** and **3**. Reagents and conditions: a) 1,4-naphthoquinone (20 equiv), nitrobenzene, reflux, 1 d (**6** as major product) or 2 d (**7** as major product); b) 3,5-di-*tert*-butyl-phenyl magnesium bromide, THF/toluene, RT; c) $NaH_2PO_2{\cdot}H_2O$, NaI, acetic acid, reflux, 2 h.

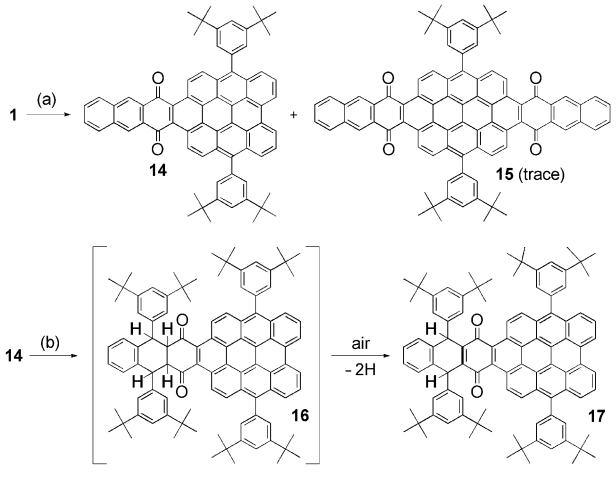
Diels–Alder reaction of the latter with 1,4-naphthaquinone (20 equiv) gave **10** in 85 % yield, which underwent a similar nucleophilic addition reaction with 3,5-di-*tert*-butyl-phenyl magnesium bromide, dehydroxylation, and reductive aromatization, to yield the target compound **3** in 76 % yield. Alternatively, the latter compound could also be prepared from quinone **7**; thus, addition reaction of 3,5-di-*tert*-butyl-phenyl magnesium bromide to **7** gave tetraol **9**, and subsequent dehydroxylation/reductive aromatization afforded the final compound **3** in moderate yield.

Scheme 3 outlines the synthetic route to the highly extended π-conjugated system of **4**. Diels–Alder reaction took place between compound **2** and an excess of 1,4-benzoquinone in nitrobenzene at reflux temperature, to give **11** in 85 % yield. A second Diels–Alder cycloaddition reaction between **2** and **11** produced quinone **12** in 40 % yield. We also attempted a one-step Diels–Alder reaction between two equivalents of **2** and one equivalent of 1,4-benzoquinone, however, no desired product **12** was formed. The nucleophilic addition of **12** with triisopropylsilyl (TIPS) acetylene Grignard reagent turned out to be challenging; there was no addition product detected even under heating in THF, presumably due to the steric hindrance between the TIPS groups and the core. Thus, the less bulky hexynyl group was used; in this case, addition of **12** with hexynylmagnesium bromide in anhydrous THF/toluene proceeded smoothly and afforded the intermediate compound **13**. The resulting diol **13** was used for subsequent dehydroxylation and reductive aromatization with the aim of preparing the target compound **4**. Surprisingly, a hydrogenated product **4-H$_2$** was obtained instead of **4**, which was confirmed by high resolution MALDI-TOF mass spectrometry. A peak at $m/z = 2685.6657$ ([M^+]; calculated exact mass for $C_{206}H_{212}$: 2685.6589) was observed, which is 2 Da higher than expected for **4** (calculated exact mass for $C_{206}H_{210}$: 2683.6433). The product **4-H$_2$** is red in color, with the longest absorption maximum at 595 nm (see Figure S1 in the Supporting Information), which is much shorter than that for **2** and **3** (both at 700 nm, see below) as well as **12** (674 nm, see Figure S1 in the Supporting Information). This indicates that the π conjugation in **4** was broken by dihydrogenation. This unexpected hydrogenation may be caused by the greatly extended π delocalization and strongly twisted structure of **4**, which makes the lateral acene fragment very reactive, leading to dihydrogenation under the reductive conditions (NaH_2PO_2/NaI, acetic acid). However, the exact structure of **4-H$_2$** was not confirmed because of the complexity of the ^{1}H NMR spectrum and because of the lack of crystals suitable for crystallographic analysis.



Scheme 3. Synthetic route towards **4**. Reagents and conditions: a) nitrobenzene, reflux, 2 d; b) n-C_4H_9-C≡C-MgBr, THF/toluene, 60 °C, overnight; c) $NaH_2PO_2{\cdot}H_2O$, NaI, acetic acid, reflux, 2 h.

To achieve further lateral extension of π conjugation along the bisanthene core, a similar Diels–Alder cycloaddition reaction between compound **2** and a large excess of 1,4-anthraquinone (20 equiv) was performed; under these conditions, mono-addition-product **14** was obtained together with a trace amount of **15** when the reaction was heated to reflux for 1 day in nitrobenzene (Scheme 4). Extended reaction time did not help to generate more **15**, presumably due to the relatively low reactivity and low solubility of **14** for further Diels–Alder reaction. Nucleophilic addition of compound **14** with excess Grignard reagent derived from 1-bromo-3,5-di-*tert*-butylbenzene in anhydrous THF/toluene was then tested. Interestingly, a diaryl-substituted compound **17** was obtained in 54 % yield after standard acidification



Scheme 4. Reagents and conditions: a) 1,4-anthraquinone (20 equiv), nitrobenzene, reflux, 1 d; b) 3,5-di-*tert*-butyl-phenyl magnesium bromide, THF/toluene, RT, 2 d; then quenched with water.

workup and column chromatography in air, suggesting that the aryl Grignard reagent attacked the benzene rings instead of the carbonyl groups in **14**. The structure of **17** was unambiguously confirmed by NMR spectroscopy and by high-resolution mass spectrometry (see the Supporting Information). Such an unusual addition reaction is similar to the 1,4-Michael addition of α,β-unsaturated ketones.[21] Similar Michael addition reactions have been observed with a fused bispentacenequinone, as recently reported in our group.[15b] Herein, Michael addition reactions take place on the benzene rings adjacent to the ketone groups and subsequent acidification should give the intermediate compound **16**, which undergoes simultaneous dehydrogenation in air to afford product **17** (Scheme 4). Only two, instead of four, hydrogen atoms were removed during the dehydrogenation process, giving a partially dehydrogenated product. We also attempted to perform further dehydrogenation of **17** with *p*-chloranil in toluene heated to reflux, however, no reaction took place.

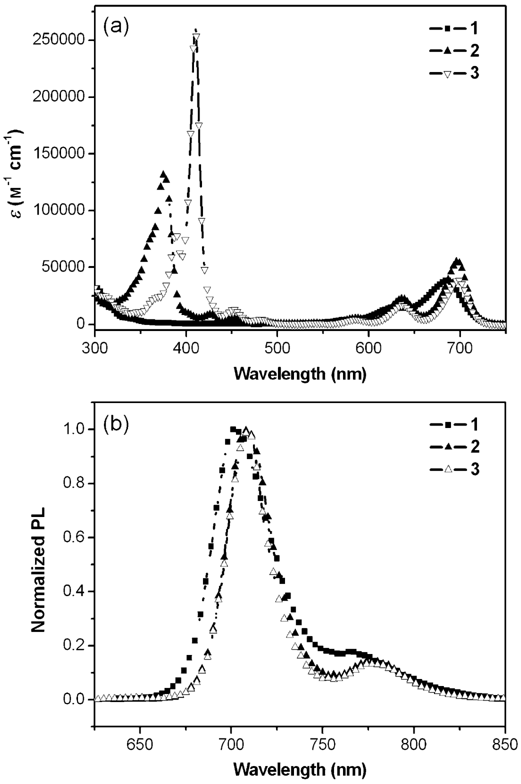


Figure 1. a) UV/Vis/NIR absorption, and b) fluorescence spectra of compounds **1**, **2**, and **3** in dilute toluene solutions (concentration = 1×10^{-5} M for absorption spectra and 1×10^{-7} M for emission spectra).

Photophysical properties: The attachment of 3,5-di-*tert*-butylphenyl groups makes the final products and most intermediate compounds readily soluble in common organic solvents. The UV/Vis/NIR absorption and fluorescence spectra of compounds **1**, **2**, and **3** recorded in toluene are shown in Figure 1(a), and the data are collected in Table 1. The optical spectra of **2** and **3** in toluene show two major absorption bands, one at 300–500 nm (β band) and a second at 550–750 nm (p band). The absorption maximum of **3** (409 nm) displays a clear bathochromic shift with respect to **2** (375 nm) as a result of annulation of an additional naphthalene unit at the bay regions. The long-wavelength absorption bands of **1**–**3** have similar shapes, and the maxima are located at 687, 697, and 697 nm, respectively. Such a small shift of the absorption band can be explained by Clar's aromatic rule.[22] Molecules **2** and **3**, although larger in size, possess more Clar's aromatic sextet rings than **1** (i.e., three for **2**, four for **3**, and two for **1**; labeled as circle rings in Scheme 2). In addition, compounds **2** and **3** are expected to show contorted structures (see below), and deviation from planarity could also result in a blue shift of the absorption spectrum. Compounds **2** and **3** show fluorescence, with the emission maximum at 708 nm (Figure 1(b) and Table 1), which is a 7 nm bathochromic shift with respect to compound **1**. The photoluminescence quantum yields (*Φ*) were determined according to an optical dilute method (optical density $A<0.05$) by using cardiogreen dye (λ_{abs} (max) = 780 nm, $\Phi=0.13$ in DMSO) as a standard.[23] The *Φ* values of 0.45 and 0.38, obtained for **2** and **3**, respectively, are lower than for compound **1** (0.81) presumably due to the twisted structures. The UV/Vis/NIR absorption spectra of **11**, **12**, **4-H$_2$**, and **17** were also recorded in toluene (see Figure S1 in the Supporting Information). Compounds **11**, **12**, and **17** all showed typical intramolecular charge-transfer bands at 684, 674, and 648 nm, respectively, due to the existence of electron-withdrawing quinone units. Compound **4-H$_2$** exhibits a p band at much shorter wavelength (450–620 nm) because of interruption of π conjugation in **4**.

Table 1. Photophysical and electrochemical data of compounds **1**–**3**.[a]

Compd	λ_{abs} [nm]	λ_{em} [nm]	QY	E^1_{ox} [V]	E^2_{ox} [V]	E^3_{ox} [V]	E^1_{red} [V]	E^2_{red} [V]	HOMO [eV]	LUMO [eV]	E^{EC}_g [eV]	E^{Opt}_g [eV]
1	582, 628, 687	701	0.81	−0.02	0.58	–	−1.68	−2.10	−4.71	−3.20	1.51	1.73
2	375, 427, 453, 586, 637, 697	708, 778	0.45	−0.04	0.57	–	−1.72	–	−4.69	−3.14	1.55	1.72
3	388, 409, 451, 586, 637, 697	708, 778	0.38	−0.04	0.49	1.20	−1.80	–	−4.69	−3.07	1.62	1.72

[a] The redox potentials are calibrated by Fc/Fc$^+$. HOMO and LUMO energy levels were deduced from the onset potentials of the first oxidation (E^{onset}_{ox}) and the first reduction wave (E^{onset}_{red}), according to the following equations: HOMO = $-(4.8+E^{onset}_{ox})$ and LUMO = $-(4.8+E^{onset}_{red})$, in which the potentials are calibrated to $E_{Fc+/Fc}$. E^{EC}_g as the electrochemical band gap deduced from the LUMO−HOMO. E^{Opt}_g is optical band gap estimated from the lowest energy absorption onset.

Theoretical calculations: The geometries and electronic structures of molecules **2** and **3** were studied by density function theory (DFT) calculations at the B3LYP/6-31G* level. The optimized structures and the frontier molecular orbital profiles of **2** and **3** are shown in Figure 2. As predicted, molecules **2** and **3** both have non-planar, twisted structures due to steric congestion, and the center-to-end distortion angle is around 41° for both. In both cases, the HOMO and LUMO are mainly delocalized in the bisanthene unit, and are partially delocalized along the naphthalene units, although there is significant twist between the bisanthene and the naphthalene moieties. Time-dependent DFT (TD-DFT) calculations also predict that both molecules have two major absorption bands with maxima at 372 and 748 nm for **2**, and 410 and 758 nm for **3** (see the Supporting Information). These two bands can be correlated to the β band and p band, respectively, and the redshift trend agrees well with the experimental observations.

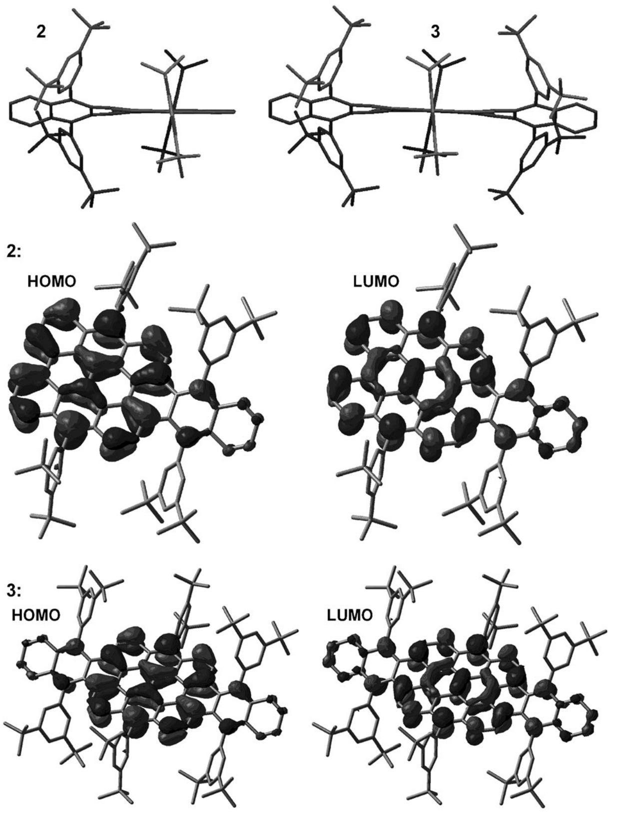


Figure 2. Optimized geometric structure and frontier molecular orbital profiles of **2**–**3**. Hydrogen atoms are omitted for clarity.

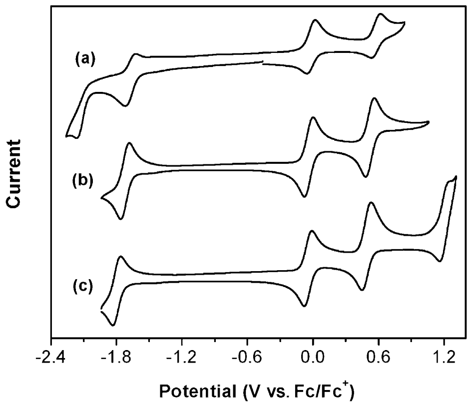


Figure 3. Cyclic voltammograms of a) **1**, b) **2**, and c) **3** in dichloromethane (1 mM) with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and a scan rate of 50 mV s^{-1}.

Electrochemical properties: The electrochemical properties of compounds **2** and **3** were investigated by cyclic voltammetry (CV) in anhydrous dichloromethane and compared to **1** (Figure 3 and Table 1). The cyclic voltammograms of **1** and **2** exhibited two reversible oxidation waves with half-wave potentials (E_{ox}^{n}) at −0.02 and 0.58 V for **1** and −0.04 and 0.57 V for **2**, whereas three oxidative waves were observed for **3**, with E_{ox}^{n} at −0.04, 0.49, and 1.20 V (vs. Fc/Fc$^+$). Compound **1** also showed two quasi-reversible reduction waves with the half-wave potential of the first reductive waves (E_{red}^{1}) at −1.68 V, whereas compounds **2** and **3** exhibited one reversible reduction wave with the half-wave potential (E_{red}^{1}) at −1.72 and −1.80 V, respectively. Such amphoteric redox behavior suggests that compounds **1**, **2**, and **3** can be reversibly oxidized to the respective cationic species (e.g., radical cations and dications) and reduced to the corresponding anionic species (e.g., radical anion and dianion), and the charged species can be stabilized by the large delocalized π system. The electrochemical properties of compounds **11** and **12** were also studied by CV in anhydrous dichloromethane (see Figure S2 and Table S1 in the Supporting Information). The cyclic voltammograms of **11** exhibited two reversible oxidation waves with half-wave potentials (E_{ox}^{n}) at 0.25 and 0.71 V, whereas three oxidative waves were observed for **12**, with E_{ox}^{n} at 0.22, 0.27, and 0.70 V (vs. Fc/Fc$^+$). Compound **11** also showed three quasi-reversible reduction waves with the half-wave potential of the first reductive waves (E_{red}^{1}) at −1.13 V, whereas compound **12** exhibited four reversible reduction wave with the half-wave potential of the first reductive wave (E_{red}^{1}) at −1.43 V.

The HOMO and LUMO energy levels were deduced from the onset potentials of the first oxidation ($E_{\mathrm{ox}}^{\mathrm{onset}}$) and the first reduction wave ($E_{\mathrm{red}}^{\mathrm{onset}}$), according to the following equations: $\mathrm{HOMO} = -(4.8 + E_{\mathrm{ox}}^{\mathrm{onset}})$ and $\mathrm{LUMO} = -(4.8 + E_{\mathrm{red}}^{\mathrm{onset}})$, in which the potentials are calibrated to $E_{\mathrm{Fc+/Fc}}$.[24] Compared with the precursor **1**, compounds **2** and **3** have slightly higher HOMO and LUMO energy levels. In agreement with the small optical band gap (E_{g}^{Opt}) determined from the absorption spectra, the electrochemical band gaps are also small due to a convergence of the HOMO and LUMO energy levels. Compounds **11** and **12** have similar HOMO energy levels, whereas a higher LUMO energy level was observed for **12** than for **11**.

Chemical oxidation titrations of **2** and **3** were conducted in dichloromethane by using $SbCl_5$ as an oxidant, and the process was followed by UV/Vis/NIR absorption spectroscopy. Like compound **1**,[17c] these two compounds can be reversibly oxidized by $SbCl_5$ to generate stable radical cations, with the appearance of two new characteristic absorption bands at shorter and longer wavelength (Figure 4). Such a phenomenon is common due to the redistribution of frontier molecular orbital energy in the energy gap, and one-electron transition at the higher energy and one-electron transition at lower energy are allowed in the new energy diagram. The longest absorption maximum for the radical cation exhibited a clear bathochromic shift from **1** (782 nm)[17c] to **2** (1276 nm) and **3** (1324 nm). The oxidized species can also be reversibly reduced to the neutral state by adding Zn dust to the solution containing oxidized species. Similar reversible processes could be observed for **2** and **3** when iodine was used as an oxidant and Zn as a reductant.

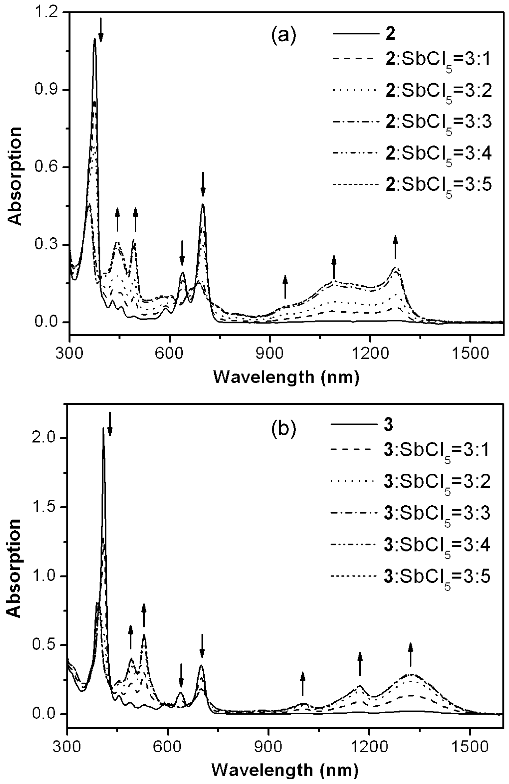


Figure 4. UV/Vis/NIR absorption spectra of **2** and **3** during titration with $SbCl_5$ in anhydrous dichloromethane. The arrows show the changes of the spectra during the titration.

Photostability: In contrast to the very unstable parent bisanthene, solutions of **1**–**3** in toluene are relatively stable under ambient conditions. The photostabilities of these three compounds were also tested by irradiation with a white-light bulb (60 W) and a UV lamp (254 nm, 4 W). Upon irradiation with white light, the solutions gradually decomposed, with a decrease of the optical intensity at the longest absorption band and the appearance of new absorption bands at shorter wavelengths, as depicted by arrows in Figure 5. The times required for 10 % decomposition were approximately 244, 70, and 38 min for **1**, **2**, and **3**, respectively; this was determined by plotting the optical density at the longest absorption λ_{max} against the irradiation time (Figure 5). Upon irradiation with a UV lamp (4 W), the decomposition process became faster, and the compounds displayed times of approximately 67, 9, and 24 min for 10 % decomposition, respectively (see Figure S3 in the Supporting Information). These results revealed that the photostabilities of compounds **2** and **3** are both lower than for compound **1**, and this difference can be explained by the strongly twisted structures of **2** and **3** as well as by the slightly higher-lying HOMO energy levels, which increases the sensitivity towards light and oxygen. The structure of the obtained products after UV irradiation was investigated by MALDI-TOF mass spectrometry, and the major components were found to be addition products with one or two oxygen molecules, which is common for many acene-related compounds.

Conclusion

We have investigated the synthesis of laterally expanded bisanthene compounds through Diels–Alder cycloaddition reaction at the bay regions of bisanthene. The naphthalene-annulated bisanthenes **2** and **3** have been successfully prepared, but synthetic efforts towards the creation of more extended π systems, such as **4** and **5**, met with unexpected hydrogenation or Michael addition reactions. Nevertheless, compounds **2** and **3** represent new members of greatly extended PAHs with small band gaps and NIR absorption/emission, which could be suitable for NIR OLEDs. Our detailed studies on the geometric and electronic structures, photophysical and electrochemical properties, and photostabilities revealed that the twisted structures, the extent of π conjugation, and the number of Clar's sextet rings all played important roles in the physical properties and chemical reactivities. Synthesis of larger-sized, expanded bisanthenes with planar geometry is underway in our laboratories; such compounds could potentially be employed in organic electronic devices such as OFETs.

Experimental Section

General: All reagents and starting materials were obtained from commercial suppliers and were used without further purification. THF and toluene were purified by routine procedures and distilled over sodium under nitrogen before use. Column chromatography was performed on silica gel 60 (Merck 40–60 nm, 230–400 mesh). All NMR spectra were recorded with Bruker AMX500 or AMX300 spectrometers at RT. All chemical shifts are quoted in ppm, relative to tetramethylsilane, by using the residual solvent peak as a reference standard. MALDI-TOF MS spectra were measured with a Bruker Autoflex MALDI-TOF instrument, with 1,8,9-trihydroxyanthracene as a matrix. UV/Vis/NIR absorption spectra were measured with a Shimadzu UV-1700 or a Lambda 750 spectrometer. Fluorescence spectra were recorded with a RF-5301 fluorometer. Cyclic voltammetry measurements of compounds **2** and **3** in dichloromethane (1 M) were performed with a CHI 620C electrochemical analyzer

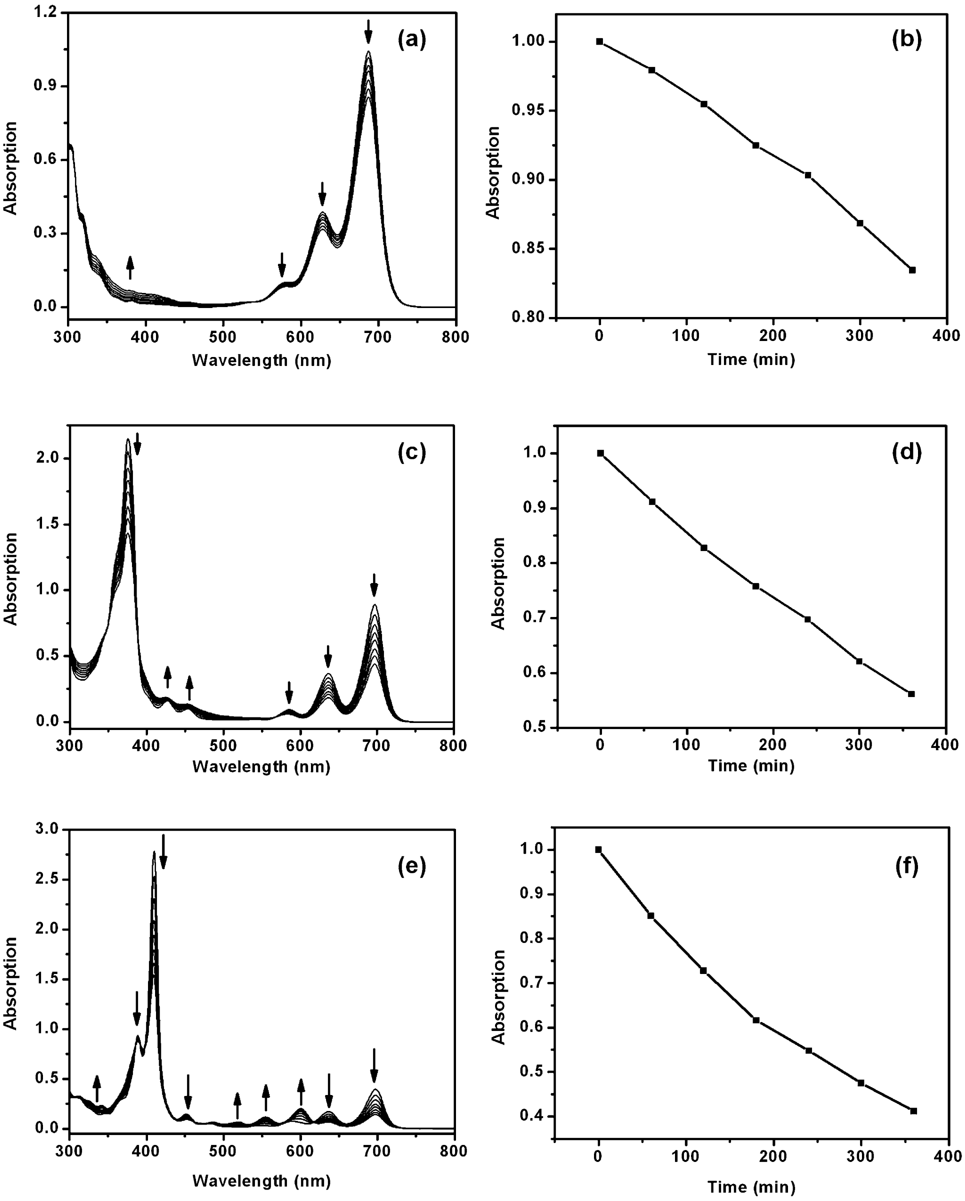


Figure 5. Photostability test of compounds **1**–**3** in toluene upon irradiation with a 60 W white-light bulb. Left: UV/Vis/NIR absorption spectra of a) **1**, c) **2**, and e) **3** in toluene recorded during the irradiation. The arrows indicate the change in the spectra. Right: change of optical density of b) **1**, d) **2**, and f) **3** at the longest absorption maximum wavelength with the irradiation time. The original optical density before irradiation was normalized at the absorption maximum.

with a three-electrode cell, by using 0.1 м Bu_4NPF_6 as supporting electrolyte, $AgNO_3$/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and a scan rate of 50 mV s^{-1}.

Synthesis of compounds 6 and 7: Compound **1** (100 mg, 0.14 mmol) was heated to reflux (240 °C) with 1,4-naphthoquinone (435 mg, 2.75 mmol) in deoxygenated nitrobenzene (50 mL); the color slowly changed from deep-blue to black-brown. Methanol was added to the cooled solution and the green precipitate was filtered off, washed with acetone, and dried under vacuum to yield a mixture of compounds **6** and **7**. When the reaction time was 24 h, the major product was **6**, together with a trace amount of **7**. When the reaction was conducted for 2 d, the major product was **7** together with a trace amount of **6**. The mixture was used directly for the next step.

Synthesis of compound 8: Magnesium (3 mg, 0.13 mmol) and a piece of iodine crystal were placed in anhydrous THF (1 mL). To the mixture, 1-bromo-3,5-di-*tert*-butylbenzene (305.5 mg, 1.13 mmol) in anhydrous THF (4 mL) was added dropwise and the mixture was stirred at RT for 2 h to generate the Grignard reagent. The prepared Grignard reagent was transferred into a suspension of crude compound **6** (100 mg) in anhydrous toluene (20 mL) and the mixture was stirred at RT for 2 d. The reaction was quenched with water (100 mL) and extracted with hexane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was further purified by column chromatography on silica gel ($CHCl_3$/hexane = 2:1 *v*/*v*) to afford compound **8** (72 mg, 52 %) as a black-purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.11$ (s, 36 H; *t*Bu), 1.41 (s, 18 H; *t*Bu), 1.45 (s, 18 H; *t*Bu), 3.27 (s, 2 H; OH), 7.12 (s, 2 H; Ph), 7.23 (dd, $^3J = 6.09$ Hz, $^4J = 3.3$ Hz, 2 H; Ph), 7.35 (s, 2 H; Ph), 7.43 (s, 4 H; Ph), 7.47 (s, 2 H; Ph), 7.60 (m, 4 H; Ar), 7.70 (m, 2 H; Ar), 7.90 (t, $J = 8.0$ Hz, 2 H; Ar), 8.09 (d, $J = 8.4$ Hz, 2 H; Ar), 8.88 (d, $J = 10.0$ Hz, 2 H; Ar), 9.02 ppm (d, $J = 7.2$ Hz, 2 H; Ar). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.1$, 32.3, 32.4, 35.5, 35.7, 35.8, 120.1, 120.9, 121.3, 121.8, 123.2, 124.5, 125.5, 125.8, 126.3, 126.6, 126.7, 127.3, 128.3, 128.7, 129.1, 129.2, 129.4, 132.3, 132.4, 135.5, 137.8, 138.6, 140.1, 149.8, 150.9 ppm. HRMS (FAB): *m*/*z* calcd for $C_{94}H_{100}O_2$: 1260.77178; found: 1260.77196 [M^+] (error = 0.14 ppm).

Synthesis of 2: In absence of light, a mixture of **8** (100 mg, 0.079 mmol), NaI (119 mg, 0.79 mmol), $NaH_2PO_2 \cdot H_2O$ (152.8 mg, 1.185 mmol), and acetic acid (20 mL) was heated to reflux for 2 h. After cooling to RT, the precipitate was collected by filtration, washed with water, and purified by column chromatography with hexane as eluent to afford **2** quantitatively as a deep-blue solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.29$ (s, 36 H; *t*Bu), 1.42 (s, 36 H; *t*Bu), 7.23 (m, 2 H; Ar), 7.37 (d, $J = 1.65$ Hz, 4 H; Ph), 7.46 (d, $J = 1.62$ Hz, 4 H; Ph), 7.53 (s, 2 H; Ph), 7.57 (s, 2 H; Ar), 7.60 (m, 4 H; Ar), 7.72 (m, 4 H; Ar), 7.93 (m, $J = 8.55$ Hz, 2 H; Ar), 8.36 (m, 2 H; Ar), 8.76 ppm (d, $J = 7.41$ Hz, 2 H; Ar). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 32.2$, 32.3, 35.6, 35.8, 120.7, 121.37, 121.41, 123.9, 124.5, 125.7, 125.8, 126.0, 126.2, 126.8, 127.0, 127.3, 127.4, 127.5, 128.4, 128.8, 129.9, 130.0, 130.3, 132.4, 132.9, 136.5, 137.3, 138.6, 141.7, 151.4, 152.0 ppm. HRMS (FAB): *m*/*z* calcd for $C_{94}H_{98}$: 1226.7663; found: 1226.7640 [M^+] (error = −1.88 ppm).

Synthesis of 10: Compound **2** (100 mg, 0.08 mmol) was heated at reflux for 2 d with 1,4-naphthoquinone (253 mg, 1.6 mmol) in deoxygenated nitrobenzene (30 mL); a slow color change from green to black-green was observed. Nitrobenzene was distilled off under vacuum, and the remaining green solid was washed with acetone and further purified by column chromatography on silica gel ($CHCl_3$/hexane = 2:1 *v*/*v*) to afford **10**

(96 mg, 85 %) as a black-green solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 1.29 (s, 36 H; *t*Bu), 1.52 (s, 36 H; *t*Bu), 7.56 (s, 4 H; Ph), 7.61 (s, 2 H; Ph), 7.62 (br, 2 H; Ar), 7.67 (d, $J=1.5$ Hz, 4 H; Ph), 7.72 (m, 2 H; Ar), 7.75 (s, 2 H; Ph), 8.18 (d, $J=9.5$ Hz, 2 H; Ar), 8.20 (br, 2 H; Ar), 8.48 (m, 2 H; Ar), 8.61 (d, $J=9.5$ Hz, 2 H), 8.71 (d, $J=9.5$ Hz, 2 H; Ar), 10.04 ppm (d, $J=10$ Hz, 2 H; Ar). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=32.2$, 32.4, 35.7, 35.9, 121.3, 121.7, 121.9, 122.8, 123.7, 124.4, 124.7, 126.5, 126.69, 126.73, 127.05, 127.14, 127.3, 127.6, 127.7, 128.6, 128.7, 128.9, 128.9, 129.5, 130.0, 130.7, 130.9, 133.5, 135.5, 137.3, 138.4, 138.6, 141.7, 151.5, 152.4, 188.1 ppm. HRMS (MALDI-TOF, positive): *m*/*z* calcd for $C_{104}H_{100}O_2$: 1380.7718; found: 1380.7691 [M^+] (error $=-1.98$ ppm).

Synthesis of 3: Magnesium (19.3 mg, 0.80 mmol) and a piece of iodine crystal were placed in anhydrous THF (1 mL). To the mixture, 1-bromo-3,5-di-*tert*-butylbenzene (194.7 mg, 0.72 mmol) in anhydrous THF (4 mL) was added dropwise and the mixture was stirred at RT for 2 h to generate the Grignard reagent. The prepared Grignard reagent was transferred into a suspension of **10** (100 mg, 0.07 mmol) in anhydrous toluene (20 mL) and the mixture was stirred at RT for 2 d. The reaction was quenched with water (100 mL) and extracted with hexane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation and the residue was dried under vacuum. In the absence of light, a mixture of the crude product diol (123 mg, 0.07 mmol), NaI (105 mg, 0.7 mmol), $NaH_2PO_2{\cdot}H_2O$ (135.4 mg, 1.05 mmol), and acetic acid (20 mL) was heated to reflux for 2 h. After cooling to RT, the deep-green precipitate was collected by filtration, washed with water and acetone, and purified by column chromatography on silica gel ($CHCl_3$/hexane $=1{:}5$ *v*/*v*) to afford **3** (92 mg, 76 %) as a green solid. Alternatively, compound **3** can be prepared from qunione **7** by a similar approach via intermediate compound **9**. ^{1}H NMR (500 MHz, [D$_6$]benzene): $\delta=1.27$ (s, 72 H; *t*Bu), 1.54 (s, 36 H; *t*Bu), 7.45 (m, 4 H; Ar), 7.74 (s, 4 H; Ph), 7.75 (s, 8 H; Ph), 7.84 (s, 2 H; Ph), 7.96 (s, 4 H; Ph), 8.34 (d, $J=9.5$ Hz, 4 H; Ar), 8.56 (d, $J=9.5$ Hz, 4 H; Ar), 8.66 ppm (m, 4 H; Ar). ^{13}C NMR (125 MHz, [D$_6$]benzene): $\delta=32.3$, 32.6, 35.7, 36.1, 121.5, 121.6, 124.3, 124.4, 125.7, 126.3, 126.5, 128.0, 128.1, 128.6, 129.0, 129.5, 129.8, 130.3, 131.3, 136.8, 137.1, 139.6, 142.9, 151.5, 152.6 ppm. HRMS (MALDI-TOF, positive): *m*/*z* calcd for $C_{132}H_{142}$: 1727.1106; found: 1727.1037 [M^+] (error $=-4.00$ ppm).

Synthesis of 11: Compound **2** (100 mg, 0.08 mmol) was heated at reflux for 2 d with benzoquinone (173 mg, 1.6 mmol) in deoxygenated nitrobenzene (30 mL); a slow color change from green to black-green was observed. Nitrobenzene was distilled off under vacuum, and the remaining green solid was washed with acetone and further purified by column chromatography on silica gel ($CHCl_3$/hexane $=1{:}1$ *v*/*v*) to afford **11** (90 mg, 85 %) as a black-green solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=$ 1.30 (s, 36 H; *t*Bu), 1.51 (s, 36 H; *t*Bu), 6.72 (s, 2 H; quinone), 7.57 (d, $J=$ 1 Hz, 4 H; Ph), 7.62 (s, 2 H; Ph), 7.65 (s, 4 H; Ph), 7.72 (m, 2 H; Ar), 7.74 (s, 2 H; Ph), 8.17 (d, $J=9.5$ Hz, 2 H; Ar), 8.48 (m, 2 H; Ar), 8.61 (d, $J=$ 9.5 Hz, 2 H), 8.65 (d, $J=9$ Hz, 2 H; Ar), 9.86 ppm (d, $J=10$ Hz, 2 H; Ar). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=32.2$, 32.4, 35.7, 35.9, 121.2, 121.7, 122.0, 122.9, 123.7, 124.5, 124.7, 124.9, 126.2, 126.5, 126.6, 127.3, 127.5, 127.8, 128.5, 128.6, 128.9, 129.1, 129.6, 130.1, 131.1, 131.3, 137.5, 138.4, 138.9, 139.4, 141.7, 151.5, 152.5, 189.7 ppm. HRMS (FAB): *m*/*z* calcd for $C_{100}H_{98}O_2$: 1330.75613; found: 1330.75594 [M^+] (error $=-0.15$ ppm).

Synthesis of 12: Compound **11** (100 mg, 0.07 mmol) was heated at reflux for 2 d with **2** (184 mg, 0.15 mmol) in deoxygenated nitrobenzene (30 mL); a slow color change from green to black-green was observed. Nitrobenzene was distilled off under vacuum, and the remaining green solid was washed with acetone and further purified by column chromatography on silica gel ($CHCl_3$/hexane $=3{:}1$ *v*/*v*) to afford **12** (142 mg, 40 %) as a black-green solid. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.29$ (s, 72 H; *t*Bu), 1.54 (s, 72 H; *t*Bu), 7.56 (d, $J=1.5$ Hz, 8 H; Ph), 7.61 (t, $J=$ 2 Hz, 4 H; Ph), 7.68 (d, $J=2$ Hz, 8 H; Ph), 7.72 (m, 4 H; Ar), 7.77 (t, $J=$ 2 Hz, 4 H; Ph), 8.19 (d, $J=9.5$ Hz, 4 H; Ar), 8.49 (m, 4 H; Ar), 8.62 (d, $J=9.5$ Hz, 4 H), 8.83 (d, $J=9.5$ Hz, 4 H; Ar), 10.05 ppm (d, $J=9.5$ Hz, 4 H; Ar). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=32.2$, 32.4, 35.7, 35.9, 121.7, 121.9, 122.0, 123.0, 123.9, 124.3, 124.8, 126.47, 126.49, 126.6, 127.1, 127.3, 127.5, 127.7, 128.8, 129.0, 129.1, 129.5, 130.0, 130.4, 130.8, 130.9, 137.2, 138.5, 138.6, 141.7, 151.6, 152.4, 193.4 ppm. HRMS (MALDI-TOF, positive): *m*/*z* calcd for $C_{194}H_{192}O_2$: 2553.4917; found: 2553.4978 [M^+] (error $=2.39$ ppm).

Synthesis of 4-H$_2$: Ethylmagnesium bromide (3 M in ether, 0.13 mL, 0.39 mmol) was added dropwise to a solution of 1-hexyne (32 mg, 0.39 mmol) in anhydrous THF (1 mL) at RT with stirring, and this mixture was maintained at 60 °C for 2 h. Compound **12** (100 mg, 0.039 mmol) was dissolved under nitrogen in anhydrous toluene (10 mL) and then added dropwise to the prepared Grignard reagent and the mixture was stirred at 60 °C overnight. The reaction was quenched with water (100 mL) and extracted with hexane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation and the residue was dried under vacuum. In the absence of light, a mixture of the crude diol **13** (62 mg, 0.39 mmol), NaI (105 mg, 0.7 mmol), $NaH_2PO_2{\cdot}H_2O$ (68 mg, 0.78 mmol), and acetic acid (20 mL) was heated to reflux for 2 h. After cooling to RT, the dark-purple precipitate was collected by filtration, washed with water and acetone, and purified by column chromatography on silica gel ($CHCl_3$/hexane $=1{:}4$ *v*/*v*) to afford **4-H$_2$** (a hydrogenated form of **4**). HRMS (MALDI-TOF, positive): *m*/*z* calcd for $C_{206}H_{212}$: 2685.6584; found: 2685.6657 [M^+] (error $=$ 2.73 ppm).

Synthesis of 14: Compound **1** (100 mg, 0.14 mmol) was heated at reflux for 2 d with 1,4-anthraquinone (573 mg, 2.75 mmol) in deoxygenated nitrobenzene (50 mL); a slow color change from deep-blue to black-brown was observed. Methanol was added into the cooled solution, and the green precipitate was filtered off, washed with acetone, and dried under vacuum to yield **15** with a trace amount of **16** (as confirmed by MALDI-TOF mass spectrometry). The mixture was used directly for the next step.

Synthesis of 17: Magnesium (3 mg, 0.13 mmol) and a piece of iodine crystal were placed in anhydrous THF (1 mL). To the mixture, 1-bromo-3,5-di-*tert*-butylbenzene (305.5 mg, 1.13 mmol) in anhydrous THF (4 mL) was added dropwise and the mixture was stirred at RT for 2 h to generate the Grignard reagent. The prepared Grignard reagent was transferred into a suspension of crude compound **14** (100 mg, 0.11 mmol) in anhydrous toluene (20 mL) and the mixture was stirred at RT for 2 d. The reaction was quenched with water (100 mL) and extracted with hexane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After removal of solvent, the residue was further purified by column chromatography on silica gel ($CHCl_3$/hexane $=1{:}8$ *v*/*v*) to afford **17** (77 mg, 54 %) as a black-purple solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.24$ (s, 36 H; *t*Bu), 1.47 (s, 36 H; *t*Bu), 5.70 (s, 2 H; CH), 7.13 (m, 2 H; Ar), 7.24 (m, 8 H; Ar, Ph), 7.48 (m, 4 H; Ph), 7.69 (t, $J=2$ Hz, 2 H; Ph), 7.94 (d, $J=10$ Hz, 2 H; Ar), 8.03 (t, $J=7.5$ Hz, 2 H; Ar), 8.2 (d, $J=$ 8.5 Hz, 2 H; Ar), 9.04 (d, $J=10$ Hz, 2 H; Ar), 9.16 ppm (d, $J=7.5$ Hz, 2 H; Ar). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=35.5$, 35.8, 46.0, 121.1, 122.0, 122.2, 122.9, 123.9, 125.1, 125.5, 126.5, 126.7, 126.9, 127.2, 127.45, 127.53, 128.2, 129.2, 129.5, 130.0, 130.8, 132.2, 132.8, 137.1, 138.3, 139.6, 144.1, 147.0, 151.5, 151.7, 151.8, 189.7 ppm. HRMS (MALDI-TOF, positive): *m*/*z* calcd for $C_{98}H_{100}O_2$: 1308.7668; found: 1308.7718 [M^+] (error $=$ -3.81 ppm).

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