Electrochromic Application of an Enediyne Scaffolding as a Redox-Active Chromophore − Synthesis and Redox Behavior of 9,10-Bis[3-(6-azulenyl)-1-(6-azulenylethynyl)-2-propynylidene]-9,10-dihydroanthracenes

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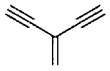
A bis(enediyne) system utilizing anthraquinodimethane as a platform for a redox-active substructure that bears azulenes as π-electron-accepting groups at the periphery has been prepared by a simple one-pot reaction involving repeated Pd-catalyzed alkynylation of 6-bromoazulenes with the bis-(enediyne). The novel bis(enediyne)s exhibited two, one-step two-electron redox properties under electrochemical reduction conditions together with a significant color change owing to the generation of a closed-shell cyanine-type substructure by the two-electron reduction.

Introduction

Electrochromism is observed in reversible redox systems that exhibit significant color changes in different oxidation states.[1] The construction of organic molecules that contain multiple redox-active chromophores[2] is fairly important for the preparation of polyelectrochromic materials that respond to different potentials with a variety of colors.[3] The enediyne unit **1** is a molecular scaffold designed for molecular architectures that contain one- and two-dimensional carbon networks.[4] Interest in conjugated enediynes has grown because of their wide range of applications, for example in molecular wires, non-linear optics (NLO), and molecular switches.



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We are interested in exploring the preparation of novel polyelectrochromic systems based on the use of the enediyne unit. Electrochemical studies of the enediyne system have so far revealed its strong electron-accepting properties and an ability to undergo multi-electron reduction under cyclic voltammetric conditions.[5] Therefore, we tried to further enhance the electron affinity and stability of the charged states of the enediyne systems by introducing π-electron-accepting groups into the periphery. We have recently reported the construction of a redox system utilizing poly(ethynyl)benzene as a platform that bears azulene as multiple redox centers.[6] Anthraquinodimethane is a well-established, redox-active substructure. The redox properties of the sterically hindered acceptor 11,11,12,12-tetracyanoanthraquinodimethane and the donor 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives are well know.[7] The extension of the anthraquinodimethane substructure by ethynyl groups should afford a bis(enediyne) system with substantial redox stability. In this paper, we report the synthesis and electrochromic behavior of 9,10-bis[3-(6-azulenyl)-1-(6-azulenylethynyl)-2-propynylidene]-9,10-dihydroanthracenes **2a** and **2b** (Scheme 1).

Results and Discussion

Compounds **2a** and **2b** were prepared by a simple one-pot reaction involving repeated Pd-catalyzed alkynylation of 6-bromoazulenes **5a** and **5b** with the enediyne scaffolding **4** prepared in solution via 9,10-bis[3-trimethylsilyl-1-(trimethylsilylethynyl)-2-propynylidene]-9,10-dihydroanthracene (**3**)[8] under Sonogashira−Hagihara conditions (Scheme 2). A solution of **3** in tetrahydrofuran was treated with methanolic potassium carbonate solution to generate the enediyne **4**. The yellow solid of **4** polymerized at room temperature, but was stable enough in solution to be employed for further transformation. The cross-coupling reaction of **5a** with the enediyne **4** using [$Pd(PPh_3)_4$] as a catalyst, and subsequent chromatographic purification of the reaction

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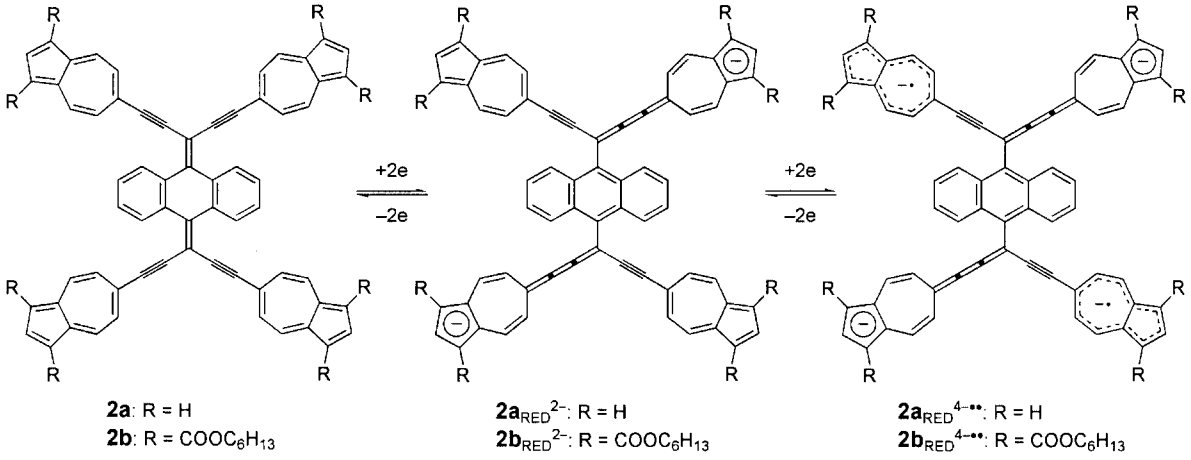
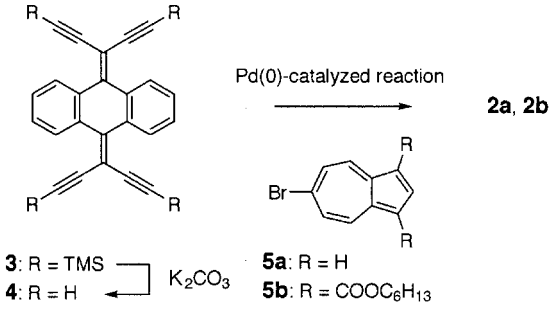


Scheme 1. Redox-system of azulene-substituted enediynes **2a** and **2b**



Scheme 2. Synthesis of azulene-substituted bis(enediyne)s **2a** and **2b**

mixture on silica gel, afforded the desired **2a** in 57% yield. Likewise, the reaction of **5b** with **4** afforded **2b** in 75% yield.

Compounds **2a** and **2b** were fully characterized by their spectroscopic data (see Exp. Sect.). The mass spectra of **2a** and **2b** ionized by FAB show the correct [M^+] ion peak along with the [$M^+ - OC_6H_{13}$] ion peak in the case of **2b**. The UV/Vis spectra of **2a** and **2b** in chloroform are shown in Figure 1. In the electronic spectrum **2a** exhibits a weak absorption in the visible region characteristic of azulene [λ (log ε) = 620 sh (3.27), 691 sh (3.10), and 777 sh (2.50) nm]. However, **2b** exhibits no clear absorption in the longest wavelength region owing to the existence of a neighboring absorption band [**2a**:λ (log ε) = 493 (4.68) nm; **2b**:λ (log ε) = 504 (4.72) nm]. Compounds **2a** and **2b** do not display any fluorescence emission in chloroform.

The redox potentials (in V vs. Ag/Ag^+) of **2a** and **2b** measured by cyclic voltammetry (CV) are summarized in Table 1. The voltammograms of **2a** and **2b** are characterized by two one-step, two-electron reduction waves (Figure 2). The first cathodic peaks of **2a** and **2b** correspond to the reduction of **2a** and **2b** to generate the closed-shell dianions $\mathbf{2a}_{RED}^{2-}$ and $\mathbf{2b}_{RED}^{2-}$, respectively. The second peaks are attributable to the formation of a tetraanionic species (Scheme 1). The cyclic scan shows that the anodic peaks

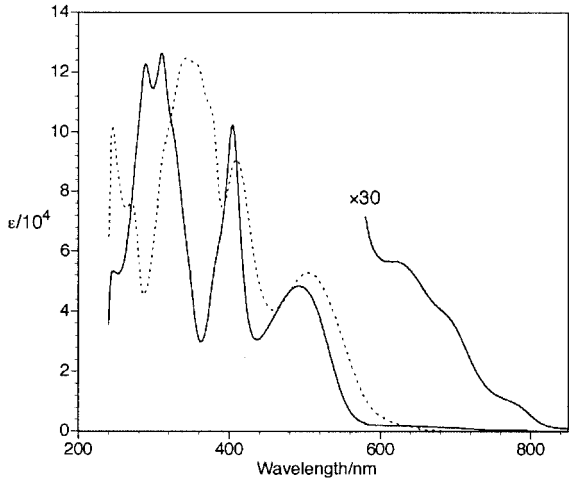


Figure 1. UV/Vis spectra of **2a** (solid line) and **2b** (broken line) in chloroform

Table 1. Reduction potentials of compounds **2a**, **2b**, **6a**, and **6b**

Sample[a]		E_1^{red}	E_2^{red}	E_3^{red}
2a	E_{pc}	−1.12 (2e)	−1.79 (2e)	
	E_{pc}	−0.89 (2e)	−1.64 (2e)	
	E_{DPV} [b]	−1.03	−1.70	
2b	E_{pa}	−0.95 (2e)	−1.40 (2e)	
	E_{pc}	−0.37 (2e)	−1.25 (2e)	
	E_{DPV} [b]	−0.86	−1.32	
6a	E_{pa}	−1.29	−1.42	−1.82
	E_{pc}	−1.16	−1.29	−1.71
	E_{DPV} [b]	−1.21	−1.36	−1.75
6b	E_{pc}	−1.05	−1.18	−1.46
	E_{pc}	−0.95	−1.09	−1.35
	E_{DPV}[b]	−1.00	−1.13	−1.40

[a] The redox potentials [E_{pa} (anodic peak potential) and E_{pc} (cathodic peak potential)] were measured by CV (0.1 M Bu_4NBF_4 in *o*-dichlorobenzene, Pt electrode, scan rate 100 $mV \cdot s^{-1}$, and Fc^+/Fc = 0.27 V). [b] The values are peak potentials measured by DPV.

corresponding to the oxidation of $\mathbf{2a}^{2-}_{RED}$ and $\mathbf{2b}^{2-}_{RED}$ are positively shifted by 0.23 and 0.57 V, respectively, from the first cathodic peaks.[9] The positive shift of the anodic peak in the first redox couple is consistent with the formation of the closed-shell dianions $\mathbf{2a}^{2-}_{RED}$ and $\mathbf{2b}^{2-}_{RED}$, where **2a** and **2b** are considered to be in a twisted dianionic structure. Some extra energy would be required upon oxidation of the twisted dianions back to the planer neutral **2a** and **2b**. The less negative reduction potentials of **2b** compared with those of **2a** are attributable to the stabilization of the charged species by hexyloxycarbonyl substituents. The two-electron reduction of **2a** and **2b** could be explained by the stabilization of the dianions $\mathbf{2a}^{2-}_{RED}$ and $\mathbf{2b}^{2-}_{RED}$ owing to the formation of a cyanine-type substructure in addition to a gain in aromatization energy in the dianionic form similar to the two-electron transfer of the acceptor 11,11,12,12-tetracyanoanthraquinodimethane and the donor 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives.[7]

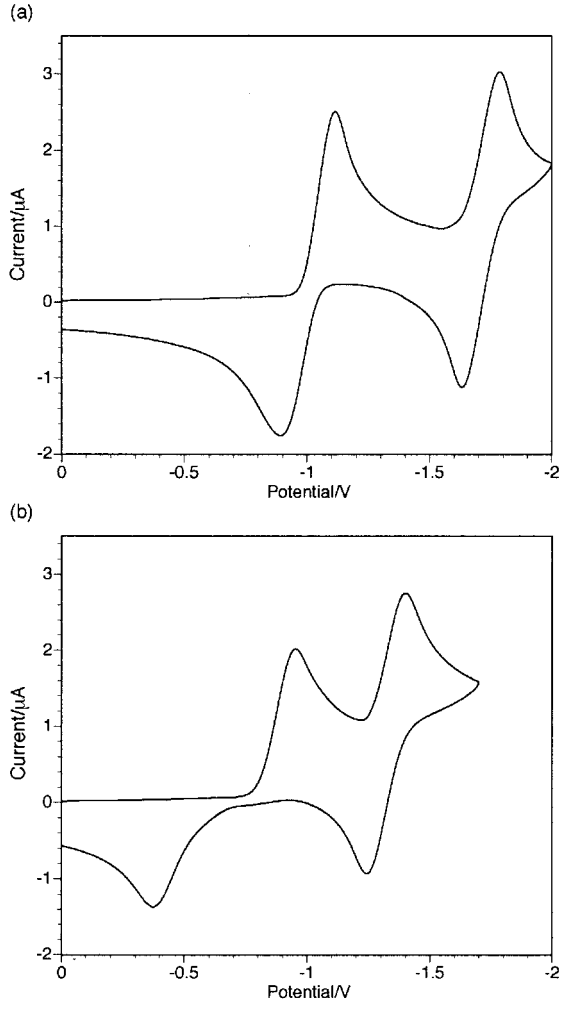
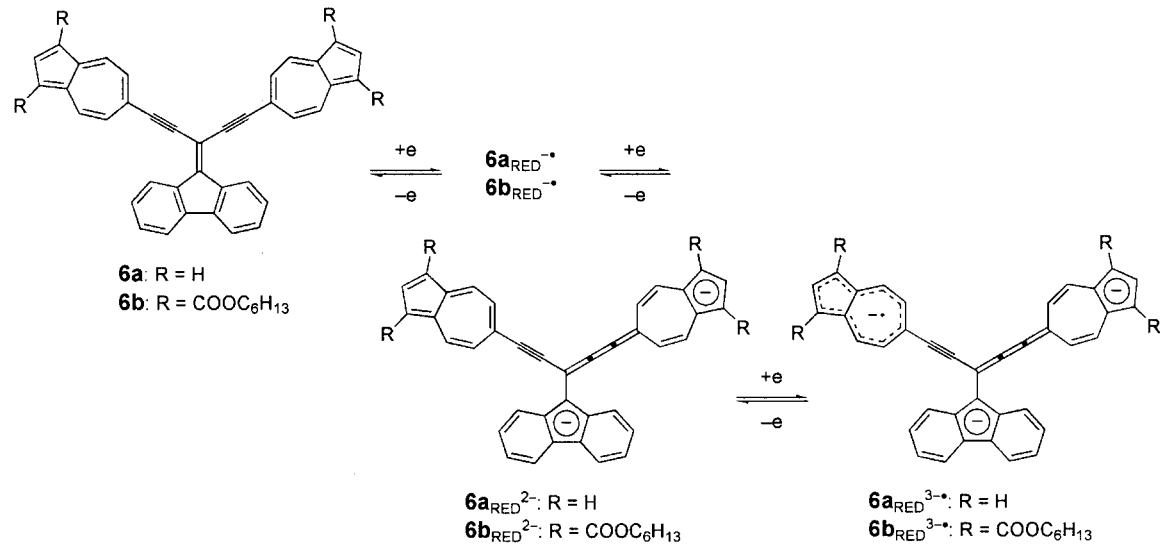


Figure 2. Cyclic voltammograms of (a) **2a** and (b) **2b** (1 mM) in *o*-dichlorobenzene containing Bu_4NBF_4 (0.1 M) as a supporting electrolyte

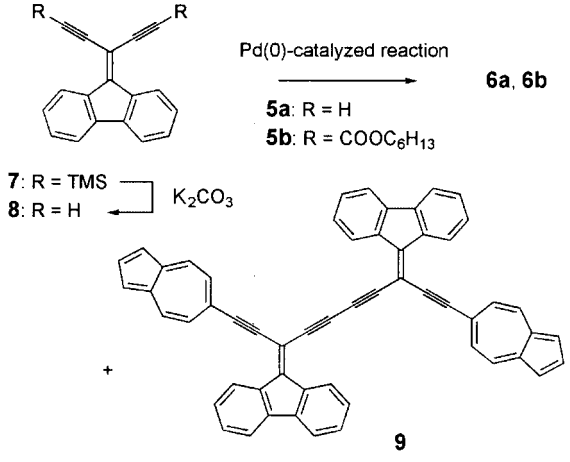
To confirm the four-electron reduction of **2a** and **2b** in two steps, we prepared the mono(enediyne)s attached to fluorene (**6a** and **6b**) using a similar procedure to that employed for the synthesis of **2a** and **2b** (Scheme 3). In addition to the redox activity of the enediyne system with azulene end-groups, the redox activity of the fulvene substructure in **6a** and **6b** should exhibit a three-electron transfer, with high redox stability, at reduction potentials similar to those of **2a** and **2b**. Comparison of the redox properties of **2a** and **2b** with those of **6a** and **6b** should afford evidence for the four-electron reduction of **2a** and **2b**. The reaction of 9-bis(ethynyl)methylene-9*H*-fluorene (**8**), prepared by the desilylation of 9-[bis(trimethylsilylethynyl)methylene]-9*H*-fluorene (**7**)[7] with 6-bromoazulenes **5a** and **5b**, afforded the desired **6a** and **6b** along with 9,9′-[1,6-bis(6-azulenylethynyl)-2,4-hexadiyne-1,6-diylidene]bis(9*H*-fluorene) (**9**) in the case of the reaction with **5a** (Scheme 4). The redox potentials (in V vs. Ag/Ag^+) of **6a** and **6b** measured by CV are summarized in Table 1. The reduction waves of **6a** and **6b** are shown in Figure 3. The electrochemical reduction of **6a** and **6b** exhibits three-step reversible redox waves, which should correspond to three single-electron transfers to generate a trianionic species. The potential region of the three-step reduction of **6a** and **6b** corresponds to those of the two-step reduction of **2a** and **2b**. Accordingly, these observations provide evidence for the four-electron reduction of **2a** and **2b** in two steps. The geometrical changes of **6a** and **6b** during the redox reaction should be smaller than those of **2a** and **2b** as the peak separation of the anodic and cathodic peaks is less than for **2a** and **2b**. This can be attributed to the lower steric hindrance between the central ring and the ethynylazulene substructures in **6a** and **6b**.

The electrochemical reduction of **2a** and **2b** was examined spectroscopically to clarify the formation of colored species due to the dianions $\mathbf{2a}^{2-}_{RED}$ and $\mathbf{2b}^{2-}_{RED}$. When the visible spectra of **2a** and **2b** were measured under the electrochemical reduction conditions in benzonitrile containing Et_4NClO_4 (0.1 M), at room temperature, a new absorption ($\mathbf{2a}^{2-}_{RED}$: λ = 844 nm; $\mathbf{2b}^{2-}_{RED}$: λ = 885 nm) gradually developed in the near-IR region as shown in Figure 4 (a). Accordingly, the color of the solutions of **2a** (orange) and **2b** (red) gradually changed to deep green during the electrochemical reduction. The observed color change can be attributed to the formation of a cyanine-type structure in the two-electron reduction. The reverse oxidation of these deeply colored solutions caused bleaching of the deep color and regenerated the UV/Vis spectra of the neutral **2a** and **2b**.

On further reduction of the deeply colored solution of $\mathbf{2a}^{2-}_{RED}$ the new band in the near infrared region gradually decreased accompanied by the growth of a new absorption at λ = 752 nm [Figure 4 (b)]. The deep green color of the solution changed to light blue. The incompleteness of the reversibility of the second reduction step suggests the instability of the tetraanionic species under the conditions of the UV/Vis measurement, although good reversibility was observed in the CV.



Scheme 3. Presumed electrochemical behavior of **6a** and **6b**



Scheme 4. Synthesis of azulene-substituted mono(enediyne)s **6a** and **6b**

Conclusion

A bis(enediyne) system utilizing anthraquinodimethane as a platform for a redox-active substructure that bears π-electron-accepting groups at the periphery (**2a** and **2b**) has been synthesized. Compounds **2a** and **2b** exhibited two one-step two-electron redox reactions with significant color change under electrochemical reduction conditions. This system could be assumed as a violene−cyanine hybrid,[10] whose concept was recently proposed by Hünig et al. for the design of a stabilized organic electrochromic system, from the viewpoint of the generation of a closed-shell, cyanine-type structure by two-electron reduction. Construction of stabilized polyelectrochromic systems utilizing the enediyne scaffolding to respond multiply depending on the electric potential will be a focus of future work.

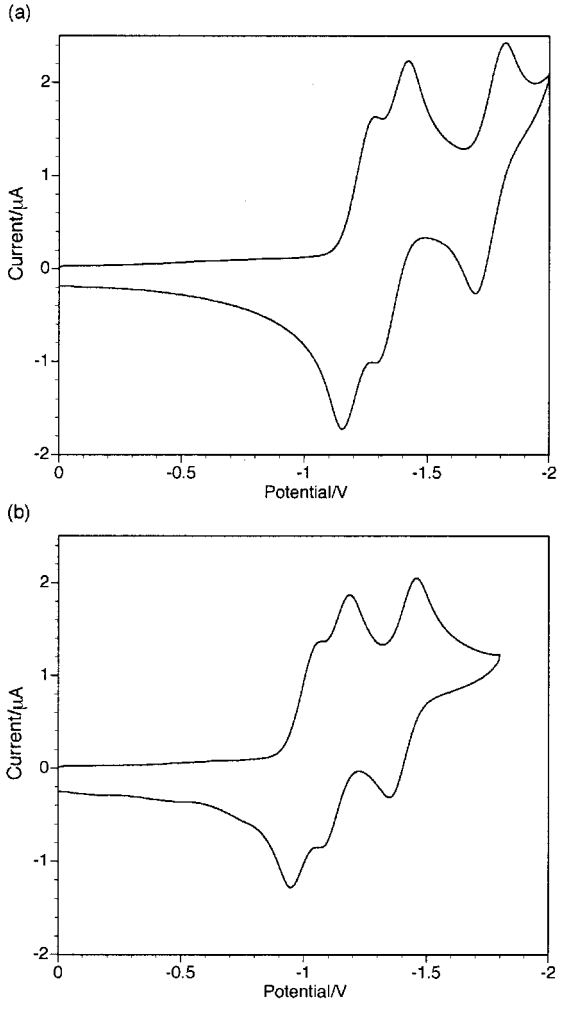


Figure 3. Cyclic voltammograms of (a) **6a** and (b) **6b** (1 mM) in *o*-dichlorobenzene containing Bu_4NBF_4 (0.1 M) as a supporting electrolyte

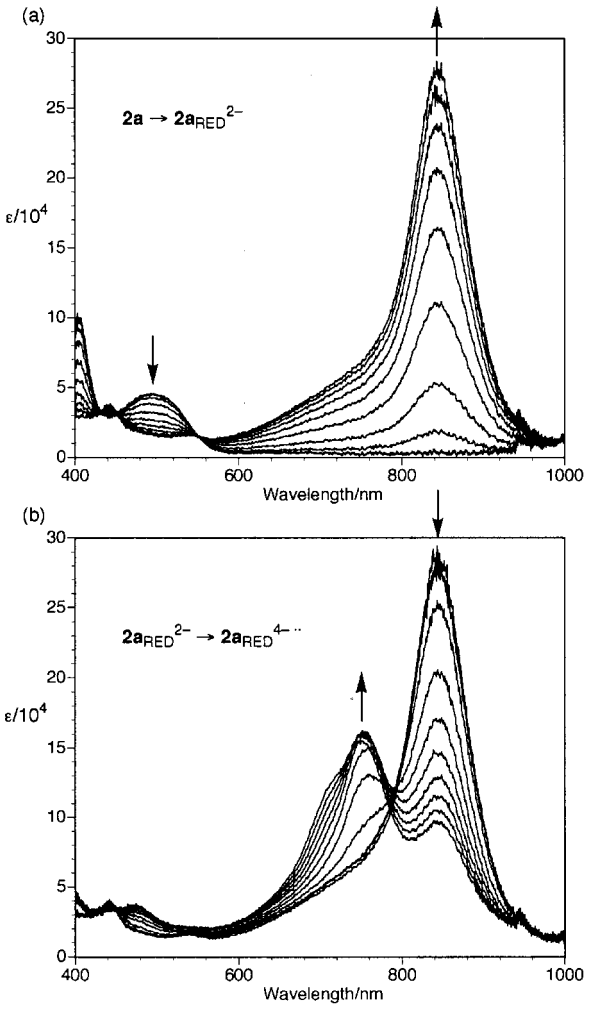


Figure 4. Continuous change in the visible spectrum of **2a** (2 mL; 0.5×10^{-4} M) in benzonitrile containing Et_4NClO_4 (0.1 M) upon constant-current electrochemical reduction (100 μA) at (a) 1 min (**2a** → $\mathbf{2a}_{RED}^{2-}$) and (b) 5 min ($\mathbf{2a}_{RED}^{2-}$ → $\mathbf{2a}_{RED}^{4-}$) interval

Experimental Section

General Remarks: Melting points were determined with a Yanagimoto micro melting apparatus MP-S3 and are uncorrected. Mass spectra were obtained with a JEOL HX-110, a Hitachi M-2500, or a Bruker APEX II instrument, usually at 70 eV. IR and UV/Vis spectra were measured with a Shimadzu FTIR-8100M and a Hitachi U-3410 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded with a JEOL GSX 400 at 400 MHz (100 MHz), a JEOL JNM A500 at 500 MHz (125 MHz), or a Bruker AM 600 spectrometer at 600 MHz (150 MHz). Gel permeation chromatography (GPC) purification was performed on a TSKgel G2000H$_6$. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes, and a reference electrode formed from Ag/AgNO$_3$ (0.01 M) in a tetrabutylammonium perchlorate (0.1 M)/acetonitrile solution. Elemental analyses were performed at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University.

9,10-Bis[bis(6-azulenylethynyl)methylene]-9,10-dihydroanthracene (2a): Potassium carbonate (10 mg, 0.072 mmol) was added to a solution of **3** (50 mg, 0.085 mmol) in water (0.1 mL), THF (5 mL), and methanol (15 mL). The resulting mixture was stirred at room temperature for 2 h. After addition of diethyl ether and water to the reaction mixture, the organic layer was separated, dried with MgSO$_4$, and concentrated under reduced pressure to 5 mL. Compound **5a** (89 mg, 0.43 mmol), CuI (2 mg, 0.01 mmol), triethylamine (1 mL), and THF (5 mL) were added to the solution of **4**. After addition of [Pd(PPh$_3$)$_4$] (5 mg, 0.004 mmol) to the degassed mixture, it was stirred at room temperature for 2.5 h. The reaction mixture was diluted with CH$_2$Cl$_2$, washed successively with 10% NH$_4$Cl and brine, dried with MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene and GPC with CHCl$_3$ to afford **2a** (39 mg, 57%). Brown crystals, m.p. > 300 °C (toluene). MS (FAB): *m*/*z* = 804 [M$^+$]. IR (KBr disk): $\tilde{\nu}$ = 2190 (w, C≡C) cm^{-1}. UV/Vis (CHCl$_3$): $\lambda_{max.}$ (log ε) = 289 (5.09), 310 (5.10), 329 sh (4.98), 346 sh (4.75), 383 sh (4.78), 404 (5.01), 493 (4.68), 620 sh (3.27), 691 sh (3.10), 777 sh (2.50) nm. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.41 [d, $^3J_{H,H}$ = 3.7 Hz, 8 H, C(1′′,3")-H], 7.42 [d, $^3J_{H,H}$ = 10.4 Hz, 8 H, C(5′′,7")-H], 7.57 [m, 4 H, C(2,3,6,7)-H)], 7.91 [t, $^3J_{H,H}$ = 3.7 Hz, 4 H, C(2")-H], 8.29 [d, $^3J_{H,H}$ = 10.4 Hz, 8 H, C(4′′,8")-H], 8.56 [m, 4 H, C(1,4,5,8)-H] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 91.4 (C-11,12 or -1′), 98.4 (C-2′), 100.9 (C-11,12 or -1′), 119.2 (C-1′′,3"), 125.8 (C-5′′,7"), 127.6 (C-1,4,5,8), 127.8 (C-2,3,6,7), 131.7 (C-6"), 134.5 (C-4a,8a,9a,10a), 135.0 (C-4′′,8"), 138.1 (C-2"), 139.9 (C-3"a,8"a), 147.4 (C-9,10) ppm. $C_{64}H_{36}$·1/2H$_2$O (814.00): calcd. C 94.44, H 4.58; found C 94.42, H 4.80.

9,10-Bis{bis[1,3-bis(hexyloxycarbonyl)-6-azulenylethynyl]-methylene}-9,10-dihydroanthracene (2b): The same procedure as was used for the preparation of **2a** was adopted. The solution of **4** was prepared by the reaction of **3** (54 mg, 0.092 mmol) with potassium carbonate (10 mg, 0.072 mmol) in water (0.1 mL), THF (5 mL), and methanol (15 mL). The reaction of **4** with **5b** (196 mg, 0.423 mmol) in the presence of CuI (18 mg, 0.095 mmol), triethylamine (15 mL), and Pd(PPh$_3$)$_4$ (8 mg, 0.007 mmol) in THF (10 mL) at room temperature for 2.5 h, followed by chromatographic purification on silica gel with CH$_2$Cl$_2$ and 5% ethyl acetate/CH$_2$Cl$_2$ afforded **2b** (126 mg, 75%). Purple crystals, m.p. > 300 °C (ethyl acetate/toluene). MS (FAB): *m*/*z* = 1829 [M$^+$], 1728 [M$^+$ − OC$_6$H$_{13}$]. IR (KBr disk): $\tilde{\nu}$ = 2188 (w, C≡C), 1698 (s, C=O) cm^{-1}. UV/Vis (CHCl$_3$): $\lambda_{max.}$ (log ε) = 271 (4.88), 312 sh (4.96), 344 (5.10), 357 sh (5.09), 377 sh (5.03), 409 (4.96), 504 (4.72), 654 sh (2.77) nm. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.92 [m, 24 H, C(6"′)-H], 1.42−1.33 [m, 32 H, C(4"′,5"′)-H], 1.50 [m, 16 H, C(3"′)-H], 1.83 [tt, $^3J_{H,H}$ = 7.6, 6.8 Hz, 16 H, C(2"′)-H], 4.38 [t, $^3J_{H,H}$ = 6.8 Hz, 16 H, C(1"′)-H], 7.65 [m, 4 H, C(2,3,6,7)-H], 7.90 [d, $^3J_{H,H}$ = 11.1 Hz, 8 H, C(5′′,7")-H], 8.55 [m, 4 H, C(1,4,5,8)-H], 8.80 [s, 4 H, C(2")-H], 9.71 [d, $^3J_{H,H}$ = 11.1 Hz, 8 H, C(4′′,8")-H] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 14.0 (C-6"′), 22.6 (C-5"′), 25.8 (C-3"′), 28.9 (C-2"′), 31.5 (C-4"′), 64.4 (C-1"′), 93.8 (C-11,12 or -1′), 97.4 (C-2′), 100.3 (C-11,12 or -1′), 117.4 (C-1′′,3"), 127.7 (C-1,4,5,8), 128.6 (C-2,3,6,7), 132.9 (C-5′′,7"), 134.1 (C-4a,8a,9a,10a), 135.4 (C-6"), 137.6 (C-4′′,8"), 143.4 (C-3"a,8"a), 144.0 (C-2"), 149.6 (C-9,10), 164.9 (C=O) ppm. $C_{120}H_{132}O_{16}$ (1830.36): calcd. C 78.75, H 7.27; found C 78.60, H 7.39.

9,10-Bis[bis(ethynyl)methylene]-9,10-dihydroanthracene (4): Potassium carbonate (29 mg, 0.21 mmol) was added to a solution of **3** (20 mg, 0.034 mmol) in water (0.3 mL), THF (10 mL), and methanol (30 mL). The resulting mixture was stirred at room temperature for 3 h. After addition of diethyl ether and water to the reac-

tion mixture, the organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure to afford **4** (10 mg, 98%) as an unstable yellow crystalline solid. MS (70 eV): *m/z* (%) = 300 (100) [M^+], 299 (40), 298 (96). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26 (s, 4 H, 11,12-C≡CH), 7.37−7.32 [m, 4 H, C(2,3,6,7)-H], 8.26−8.21 [m, 4 H, C(1,4,5,8)-H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.1 (11,12-*C*≡CH), 82.4 (11,12-C≡*C*H), 98.7 (C-11,12), 127.3 (C-1,4,5,8), 127.7 (C-2,3,6,7), 133.7 (C-4a,8a,9a,10a), 148.8 (C-9,10) ppm. HRMS calcd. for $C_{24}H_{12}$ 300.0938, found 300.0935.

9-[Bis(6-azulenylethynyl)methylene]-9*H*-fluorene (6a): Potassium carbonate (37 mg, 0.27 mmol) was added to a degassed solution of **7** (108 mg, 0.291 mmol) in water (0.3 mL), THF (15 mL), and methanol (45 mL). The resulting mixture was stirred at room temperature for 2 h. After addition of diethyl ether and water to the reaction mixture, the organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure to 20 mL. Compound **5a** (167 mg, 0.81 mmol), CuI (10 mg, 0.053 mmol), triethylamine (20 mL), and THF (20 mL) were added to this solution of **8**. After addition of $[Pd(PPh_3)_4]$ (17 mg, 0.015 mmol) to the degassed mixture, the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with 5% NH_4Cl and brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and GPC with $CHCl_3$ to afford **6a** (85 mg, 61%), **9** (12 mg, 12%), and recovered **5a** (73 mg, 44%).

6a: Brown micro needles, m.p. 248.0−249.2 °C (toluene/hexane). MS (70 eV): *m/z* (%) = 478 (100) [M^+]. IR (KBr disk): $\tilde{\nu}$ = 1572 (s), 1397 (s), 831 (s), 720 (s) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 241 (4.65), 281 (4.93), 308 (4.74), 328 (4.72), 352 sh (4.44), 374 sh (4.45), 394 (4.71), 439 (4.63), 458 sh (4.55), 590 sh (2.84), 632 (2.91), 693 sh (2.78), 782 sh (2.17) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 [dd, $^3J_{H,H}$ = 7.7, 7.4 Hz, 2 H, C(2,7)-H], 7.41 [dd, $^3J_{H,H}$ = 7.4, 7.3 Hz, 2 H, C(3,6)-H], 7.45 [d, $^3J_{H,H}$ = 3.7 Hz, 4 H, C(1′′,3")-H], 7.54 [d, $^3J_{H,H}$ = 10.3 Hz, 4 H, C(5′′,7")-H], 7.69 [d, $^3J_{H,H}$ = 7.3 Hz, 2 H, C(4,5)-H], 7.95 [t, $^3J_{H,H}$ = 3.7 Hz, 2 H, C(2")-H], 8.34 [d, $^3J_{H,H}$ = 10.3 Hz, 4 H, C(4′′,8")-H], 8.72 [d, $^3J_{H,H}$ = 7.7 Hz, 2 H, C(1,8)-H] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 90.7 (C-10, -1′, or -2′), 100.5 (C-10, -1′, or -2′), 102.1 (C-10, -1′, or -2′), 119.5 (C-1′′,3"), 119.8 (C-4,5), 125.7 (C-1,8), 125.9 (C-5′′,7"), 127.7 (C-2,7), 130.1 (C-3,6), 131.4 (s), 135.0 (C-4′′,8"), 137.4 (s), 138.4 (C-2"), 140.0 (C-3"a,8"a), 140.6 (s), 146.9 (s) ppm. $C_{38}H_{22}$ (478.59): calcd. C 95.37, H 4.63; found C 95.25, H 4.86.

9: Brown crystals, m.p. > 300 °C (toluene/hexane). MS (FAB): *m/z* = 703 [M^+ + H]. IR (KBr disk): $\tilde{\nu}$ = 1572 (s), 1443 (s), 1397 (s), 835 (s), 725 (s), 718 (s) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 240 (4.85), 279 (5.03), 294 sh (4.87), 322 (4.72), 353 sh (4.58), 366 (4.60), 392 sh (4.73), 421 (4.82), 449 sh (4.74), 481 sh (4.47), 590 (2.97), 699 sh (2.89), 739 sh (2.52) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 [dd, $^3J_{H,H}$ = 7.9, 7.6 Hz, 2 H, C(2′ or 7′)-H], 7.39 [dd, $^3J_{H,H}$ = 7.6, 7.6 Hz, 2 H, C(2′ or 7′)-H], 7.43 [dd, $^3J_{H,H}$ = 7.6, 7.5 Hz, 2 H, C(3′ or 6′)-H], 7.44 [dd, $^3J_{H,H}$ = 7.6, 7.5 Hz, 2 H, C(3′ or 6′)-H], 7.45 [d, $^3J_{H,H}$ = 3.9 Hz, 4 H, C(1′′,3")-H], 7.55 [d, $^3J_{H,H}$ = 10.1 Hz, 4 H, C(5′′,7")-H], 7.69 [d, $^3J_{H,H}$ = 7.5 Hz, 4 H, C(4′,5′)-H], 7.95 [t, $^3J_{H,H}$ = 3.9 Hz, 2 H, C(2")-H], 8.35 [d, $^3J_{H,H}$ = 10.1 Hz, 4 H, C(4′′,8")-H], 8.67 [d, $^3J_{H,H}$ = 7.6 Hz, 2 H, C(1′ or 8′)-H], 8.69 [d, $^3J_{H,H}$ = 7.9 Hz, 2 H, C(1′ or 8′)-H] ppm. $C_{56}H_{30}$·4/3H_2O (726.87): calcd. C 92.54, H 4.53; found C 92.68, H 4.45.

9-{Bis[1,3-bis(hexyloxycarbonyl)-6-azulenylethynyl]methylene}-9*H*-fluorene (6b): The same procedure as was used for the preparation of **6a** was adopted. The solution of **8** was prepared by the reaction of **7** (101 mg, 0.273 mmol) with potassium carbonate (33 mg, 0.24 mmol) in water (0.3 mL), THF (15 mL), and methanol (45 mL). The reaction of **8** with **5b** (378 mg, 0.816 mmol) in the presence of CuI (7 mg, 0.04 mmol), triethylamine (20 mL), and $[Pd(PPh_3)_4]$ (20 mg, 0.017 mmol) in THF (20 mL) at room temperature for 2 h followed by chromatographic purification on silica gel with toluene and CH_2Cl_2 afforded **6b** (231 mg, 86%) and the recovered **5b** (142 mg, 38%). Brown crystals, m.p. 154.2−155.8 °C ($CHCl_3$/EtOH). MS (FAB): *m/z* (%) = 990 (8) [M^+], 889 (100) [M^+ − OC_6H_{13}]. IR (KBr disk): $\tilde{\nu}$ = 1698 (s, C=O) cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 238 (4.90), 271 (4.72), 278 sh (4.67), 312 (4.65), 338 sh (4.76), 359 (4.80), 376 sh (4.78), 399 (4.70), 444 (4.65), 468 sh (4.58), 554 sh (3.28), 600 sh (3.09), 658 sh (2.45) nm. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.94 [m, 12 H, C(6"′)-H], 1.42−1.37 [m, 16 H, C(4"′,5"′)-H], 1.51 [m, 8 H, C(3"′)-H], 1.85 [tt, $^3J_{H,H}$ = 7.6, 6.8 Hz, 8 H, C(2"′)-H], 4.39 [t, $^3J_{H,H}$ = 6.8 Hz, 8 H, C(1"′)-H], 7.32 [dd, $^3J_{H,H}$ = 7.7, 7.3 Hz, 2 H, C(2,7)-H], 7.38 [dd, $^3J_{H,H}$ = 7.5, 7.3 Hz, 2 H, C(3,6)-H], 7.56 [d, $^3J_{H,H}$ = 7.5 Hz, 2 H, C(4,5)-H], 7.93 [d, $^3J_{H,H}$ = 11.0 Hz, 4 H, C(5′′,7")-H], 8.56 [d, $^3J_{H,H}$ = 7.7 Hz, 2 H, C(1,8)-H], 8.76 [s, 2 H, C(2")-H], 9.66 [d, $^3J_{H,H}$ = 11.0 Hz, 4 H, C(4′′,8")-H] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.0 (C-6"′), 22.6 (C-5"′), 25.8 (C-3"′), 28.9 (C-2"′), 31.5 (C-4"′), 64.5 (C-1"′), 93.2 (C-10 or -1′), 98.9 (C-10 or -1′), 100.5 (C-2′), 117.5 (C-1′′,3"), 120.0 (C-4,5), 125.8 (C-1,8), 127.8 (C-2,7), 130.8 (C-3,6), 132.9 (C-5′′,7"), 135.0 (s), 137.0 (s), 137.5 (C-4′′,8"), 140.9 (C-3"a,8"a), 143.4 (s), 144.2 (C-2"), 149.3 (s), 164.8 (C=O) ppm. $C_{66}H_{70}O_8$ (991.28): calcd. C 79.97, H 7.12; found C 79.73 H, 7.10.

9-[Bis(ethynyl)methylene]-9*H*-fluorene (8): Potassium carbonate (35 mg, 0.25 mmol) was added to a solution of **7** (20 mg, 0.054 mmol) in water (0.3 mL), THF (10 mL), and methanol (30 mL). The resulting mixture was stirred at room temperature for 2 h. After addition of diethyl ether and water to the reaction mixture, the organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated under reduced pressure to afford **8** (12 mg, 98%) as an unstable yellow crystalline solid. MS (70 eV): *m/z* (%) = 226 (100) [M^+], 224 (30). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 2 H, 10-C≡CH), 7.27 [dd, $^3J_{H,H}$ = 7.8, 7.5 Hz, 2 H, C(2,7)-H], 7.37 [dd, $^3J_{H,H}$ = 7.5, 7.5 Hz, 2 H, C(3,6)-H], 7.63 [d, $^3J_{H,H}$ = 7.5 Hz, 2 H, C(4,5)-H], 8.63 [d, $^3J_{H,H}$ = 7.8 Hz, 2 H, C(1,8)-H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.2 (10-*C*≡CH), 86.5 (10-C≡*C*H), 98.3 (C-10), 119.5 (C-4,5), 125.8 (C-1,8), 127.6 (C-2,7), 130.2 (C-3,6), 136.9 (C-4a,4b, -8a,9a, or -9), 140.5 (C-4a,4b, -8a,9a, or -9), 148.2 (C-4a,4b, -8a,9a, or -9) ppm. HRMS calcd. for $C_{18}H_{10}$ 226.0782, found 226.0786.

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