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Synthesis and Properties of Hexakis(6-octyl-2-azulenyl)benzene as a Multielectron Redox System with Liquid Crystalline Behavior

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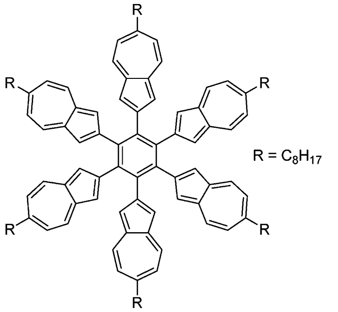

This paper describes the cyclotrimerization reaction of di(2-azulenyl)acetylenes (**2a**,**b**) catalyzed by $Co_2(CO)_8$ to produce hexa(2-azulenyl)benzene derivatives (**1a**,**b**). The cyclooligomerization of **2a** and **2b** utilizing $CpCo(CO)_2$ as a catalyst produced (η^5-cyclopentadienyl)[tetra(2-azulenyl)cyclobutadiene]cobalt complexes (**3a**,**b**). The redox behavior of hexakis(6-octyl-2-azulenyl)benzene (**1b**), bis(6-octyl-2-azulenyl)acetylene (**2b**), and the cobalt complexes **3a** and **3b** along with 6-octyl-2-phenylazulene (**19**) was examined by cyclic voltammetry (CV). The reduction of compound **1b** exhibited multiple-electron transfers in one step upon CV with a reduction potential similar to that of compound **19**. However, the CVs of compounds **2b**, **3a**, and **3b** were characterized by stepwise waves because of the reduction of each azulene ring. The mesomorphic behaviors of **1b**, **2b**, and **19** were also studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD) techniques. A new series of azulene derivatives, **1b**, **2b**, and **19**, substituted by a long alkyl chain at the 6-position shows mesomorphism with crystalline polymorphs. Compound **1b** showed a large temperature range of hexagonal columnar mesophases (Col_{ho}) from 115.5 to 199.9 °C. Compound **2b** has rectangular columnar (Col_{ro}), smectic E (S_E), and nematic (N) mesophases. Compound **19** exhibited an S_E mesophase.

Introduction

Azulene ($C_{10}H_8$) has attracted the interest of many research groups because of its unusual properties and its beautiful blue color.[1] The tendency of the system to stabilize cations as well as anions because of its remarkable polarizability is especially attractive; it could be used to construct advanced materials for electronic and photonic applications. However, to date, molecules with potentially useful electronic properties constructed from azulene derivatives are fairly scarce. In recent years, there has been growing interest in the construction of organic molecules exhibiting multiple-electron transfer for the preparation of novel polyelectrochromic materials[2] and multielectron redox catalysts.[3] We recently reported that poly(6-azulenyl)benzene derivatives exhibit multiple-

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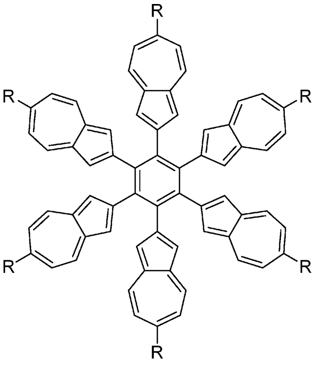
electron transfer because of the formation of the formal cyclopentadienide substructure by the electrochemical reduction of each azulene ring.[4] Although 2-azulenyl substituents do not possess the formal cyclopentadienide substructure in the electrochemically reduced form, poly(2-azulenyl)benzenes should exhibit multiple-electron transfer because of the redox reaction of azulene rings. Indeed, several poly(2-azulenyl)benzenes were shown to exhibit multielectron redox properties depending on the number of azulene rings.[5] To increase the multiplicity of the electron transfer, we examined cyclooligomerization of di(2-azulenyl)acetylene derivatives using cobalt catalysts; the isomeric di(6-azulenyl)acetylenes could not succeed in the cyclotrimerization reaction. Herein, we report the preparation and the redox behavior of hexa(2-azulenyl)benzenes (**1a**,**b**) for the design of the multielectron redox system (Chart 1).

CHART 1



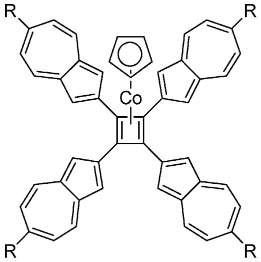
1a: R = H
1b: R = C_8H_{17}

Disklike compounds with long alkyl chains have attracted interest because of their ability to self-assemble to form the columnar mesophase.[6] The stacking behavior of discotic liquid crystals (LCs) provides opportunities for materials with one-dimensional transport processes, such as energy migration, electric conductivity, and photoconductivity.[7] Recently, we reported that hexakis(6-azulenylethynyl)benzene substituted by 12 hexyloxycarbonyl groups shows a stable columnar mesophase over a wide temperature range.[8] Because of the octyl chains substituted at the 6-position on each azulenyl group, compound **1b** would possess good solubility, fusibility, and the ability to self-organize as observed in the hexaarylbenzenes.[9] We also report, herein, the self-organization behavior of **1b**, **2b**, and **19** in which we found columnar liquid crystalline behavior.

Results and Discussion

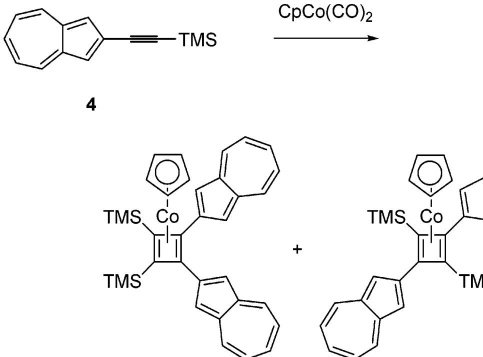
Synthesis. Attempts made toward the cyclotrimerization of di(2-azulenyl)acetylene (**2a**)[10] in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane did not yield the desired hexa(2-azulenyl)benzene (**1a**) but produced the (η^5-cyclopentadienyl)[tetra(2-azulenyl)cyclobutadiene]cobalt complex (**3a**) in a 79% yield (Chart 2).[11] The spectral features of **3a** are in agreement with the structure of the product (see Experimental Section). The formation of **3a** by the reaction of **2a** with $CpCo(CO)_2$ is similar to the results of the reaction of di(1- and 6-azulenyl)acetylenes reported in the literature.[4,12] Similarly, the reaction of 2-(trimethylsilylethynyl)azulene (**4**)[10] with $CpCo(CO)_2$ produced a mixture (16:84) of the *cis*- and *trans*-(η^5-cyclopentadienyl)[bis(1,3-diethoxycarbonyl-6-azulenyl)-bis(trimethylsilyl)cyclobutadiene]cobalt complexes (**5** and **6**) in 50% yields (Scheme 1). The major isomer **6** could be separated by recrystallization. The regiochemistry of **6** was determined to be a *trans*-cobalt complex by X-ray structure determination. The ORTEP plots and structure

CHART 2



3a: R = H
3b: R = C_8H_{17}

SCHEME 1



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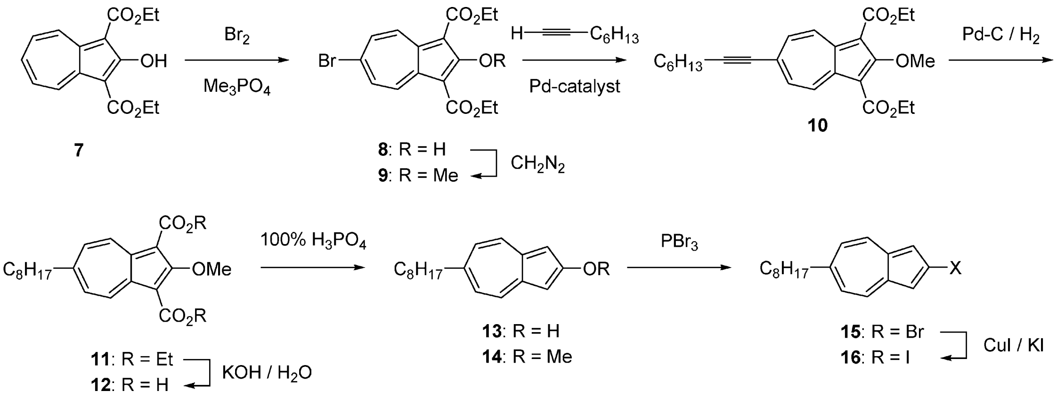
SCHEME 2



feature of the X-ray analysis of **6** are summarized in the Supporting Information.

In contrast to the exclusive formation of the cobalt complexes by the reaction with $CpCo(CO)_2$, the cyclooligomerization of **2a** with $Co_2(CO)_8$ as a catalyst produced an insoluble material in common organic solvents. The mass spectrum of the insoluble material showed the correct M^+ ion peak of **1a** at *m/z* 834, which indicated the formation of **1a**, as expected, from the reaction. However, the insolubility hampered further purification and characterization of the product. For this reason, hexa(2-azulenyl)benzene **1b** substituted by a 6-octyl substituent on each azulene ring was prepared by the cyclotrimerization reaction of the corresponding bis(6-octyl-2-azulenyl)acetylene (**2b**).

The preparation of 2-bromo- and 2-iodoazulenes (**15** and **16**, respectively) with 6-octyl chains commenced with diethyl 2-hydroxyazulene-1,3-dicarboxylate (**7**) via diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**9**);[13] it is outlined in Scheme 2. The attempt to prepare **15** or **16** commenced with diethyl 6-bromo-2-aminoazulene-1,3-dicarboxylate and was hampered by the inefficiency of the transformation of diethyl 2-aminoazulene-1,3-dicarboxylate with the 6-octyl substituent to bromide or chloride via Sandmeyer reaction, even though the reaction using the 6-unsubstituted substrate proceeds smoothly (see Supporting Information).[14] The inefficiency should be attributed to the reactivity of the 6-alkyl substituent on the azulene ring under the reaction conditions.[15]

The Pd-catalyzed cross-coupling reaction of **15** with trimethylsilylacetylene at 60 °C produced 6-octyl-2-(trimethylsilylethynyl)azulene (**17**) in a quantitative yield. Treatment of **17** with potassium fluoride in dimethylformamide (DMF) yielded 2-ethynyl-6-octylazulene (**18**). The Pd-catalyzed cross-coupling reaction of **18** with 2-iodo-6-octylazulene (**16**) produced bis(6-octyl-2-azulenyl)acetylene (**2b**) in an 86% yield (Scheme 3). The cyclooligomerization of **2b** catalyzed by $Co_2(CO)_8$ produced the expected benzene derivative, **1b**, with high solubility. The cyclooligomerization of **2b** with $CpCo(CO)_2$ produced the (η^5-cyclopentadienyl)[tetrakis(6-octyl-2-azulenyl)cyclobutadiene]cobalt complex (**3b**) in a 52% yield; the results are similar to those obtained from the reaction of the unsubstituted derivative, **2a**. For a comparison of the redox behavior, we prepared 6-octyl-2-phenylazulene (**19**) using the Pd-catalyzed reaction of **15** with phenylboronic acid in a 93% yield (Scheme 4). The spectral features of compounds **1b**, **2b**, **3b**, and **19** are in agreement with the structure of the compounds.

Hexakis(6-octyl-2-azulenyl)benzene (**1b**) possesses fair solubility in common organic solvents, such as chloroform and dichloromethane. The UV−vis spectra of **1b**, **2b**, and **19** in dichloromethane are shown in Figure 1. They show the characteristic weak absorption of the azulene system in the visible region. The bathochromic shift of the longest absorption maxima of **1b** (λ_{max} = 570 nm) in the visible region by 6 nm relative to that of **19** (λ_{max} = 564 nm) exhibits the extension of the π-system. The longest absorption maximum of **2b** (λ_{max} = 569 nm) in the visible region exhibits a slight red shift (by 5 nm) compared with

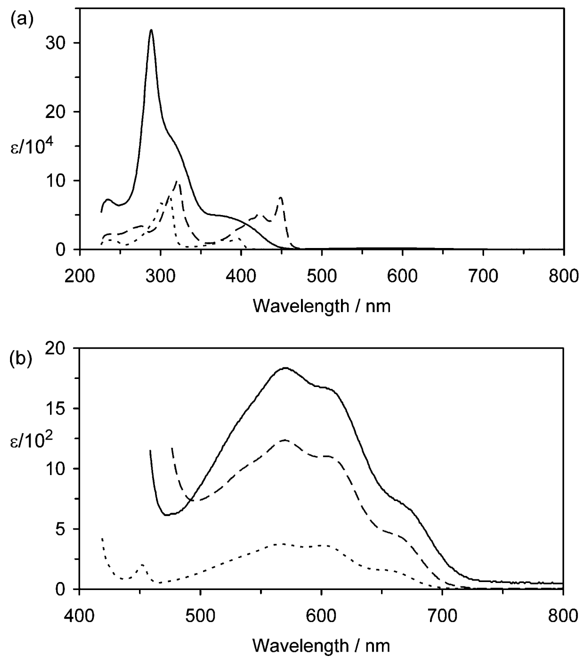


FIGURE 1. Spectra of **1b** (solid line), **2b** (broken line), and **19** (dotted line) in (a) UV−vis and (b) visible regions in dichloromethane.

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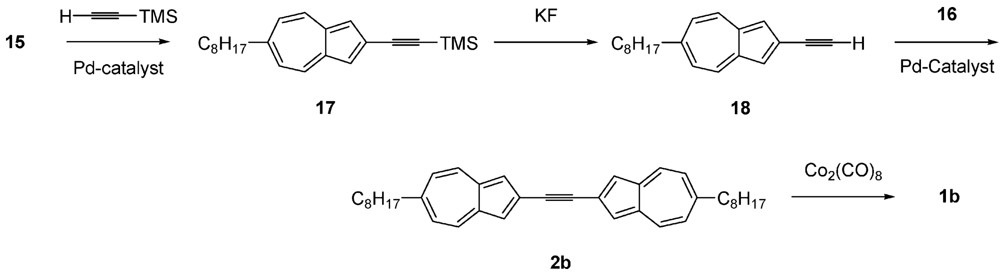
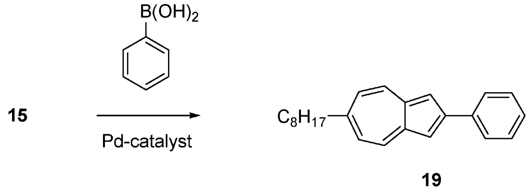
SCHEME 3



that of **19** probably because of the electron-withdrawing nature of the triple bond.[16]

Disc-type molecules have a tendency to form aggregates in solution which causes significant line broadening and shielding in their NMR spectra.[17] The concentration dependence of the ^{1}H NMR spectrum of **1b** exhibited some intermolecular aggregation in solution from the $\pi-\pi$ interactions of the aromatic cores. An increasing concentration of **1b** causes a high-field shift of the aromatic signals at H-4,8 and H-5,7 and a low-field shift of those at H-1,3 with considerable line broadening in the ^{1}H NMR spectra because the results are affected by the larger aggregates formed in solution (see Supporting Information).

SCHEME 4



Redox Behavior. The voltammetry measurements were carried out in *o*-dichlorobenzene containing *n*-Bu_4NBF_4 (0.1 M) or in benzonitrile containing Et_4NClO_4 (0.1 M) with Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing Et_4NClO_4 (0.1 M) at the scan rate of 100 mV s^{-1}. The internal reference Fc/Fc$^+$ in *o*-dichlorobenzene and benzonitrile discharges at +0.28 and +0.15 V, respectively, under these conditions. The redox potentials (V vs $Ag/AgNO_3$) of **1b**, **2b**, **3a**, **3b**, and **19** measured by cyclic voltammetry (CV) along with those of di(2-azulenyl)acetylene (**2a**) and 2-phenylazulene (**20**) (Chart 3) are summarized in Table 1. As can be seen from Table 1, compound **19** showed a reversible one-electron transfer at −1.93 V upon CV (Figure 2c). As expected, the electron-donating 6-octyl substituent on the azulenyl group slightly decreases the electron affinity of the azulene ring compared with that of **20**.[5] The 2-octyl substituent also improves the reversibility of CV because of the stabilization of the radical anionic state.

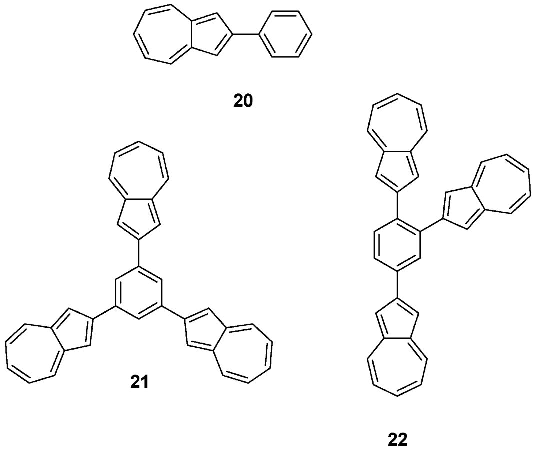
Acetylene **2b** exhibited two-electron transfer with more negative reduction potentials compared to those of **2a**[5] because of the electron-donating nature of the 6-octyl substituents (Figure 2b). The azulenyl substituents on acetylene improve the electron-accepting properties in comparison to those that are substituted on the benzene ring because of the electron-withdrawing properties of the acetylenic group. The two-step reduction of **2b** exhibits the existence of the redox interaction between the two 2-azulenyl groups. Thus, the redox system of **2b** could be considered to be that of violene similar to that of **2a**.[5]

TABLE 1. Redox Potentials of Compounds 1b, 2a, 2b, 3a, 3b, 19, and 20[a]

sample	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}	E_1^{ox}	E_2^{ox}	ref
1b	−2.01				(+0.75)	(+1.07)	
2a[b]	−1.55	(−1.91)			(+0.67)	(+1.42)	10
2b	−1.60	(−1.97)			(+1.01)	(+1.35)	
3a[b]	−1.75[c]	−1.89[c]	−2.02[c]	−2.16[c]	(+0.40)[c]	(+1.01)[c]	
3b[b]	−1.84[c]	−2.00[c]	−2.12[c]	−2.26[c]	(+0.35)[c]	(+1.06)[c]	
19	−1.91				(+0.90)	(+1.02)	
20	(−1.82)				(+1.07)	(+1.39)	5

[a] Redox potentials were measured by CV [V vs $Ag/AgNO_3$, 1 mM in *o*-dichlorobenzene containing *n*-Bu_4NBF_4 (0.1 M), Pt electrode (i.d., 1.6 mm), scan rate 100 mV s^{-1}, and Fc/Fc$^+$ = +0.28 V]. In the case of irreversible waves, which are given in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential) − 0.03 and E_{pc} (cathodic peak potential) + 0.03 V, respectively. [b] The potentials were measured in a 0.1 M Et_4NClO_4 benzonitrile solution (Fc/Fc$^+$ = +0.15 V). [c] The values are peak potentials measured by DPV.

CHART 3



Compound **1b** exhibited a reversible reduction wave at −2.01 V with a scan rate of 100 mV s^{-1} (Figure 2a). Apparently, the CV wave in Figure 2a exhibits more current compared with that of the first reduction wave of **2b** (Figure 2b) at the same concentration. Therefore, the reduction wave of **1b** could be concluded to have a multiple-electron transfer in one step (at a constant potential) to produce highly charged anionic species. However, we could not determine the exact number of

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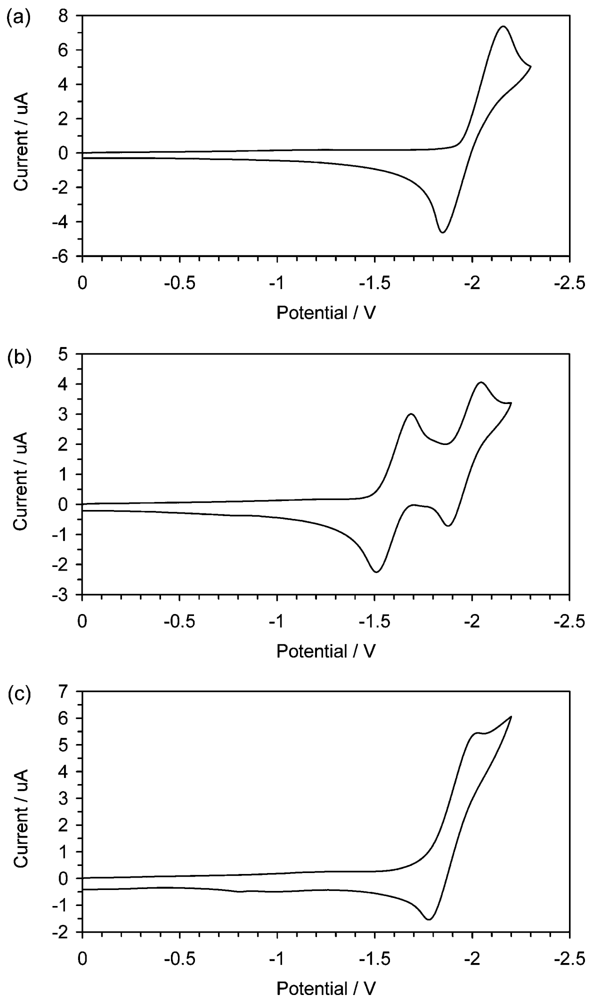

FIGURE 2. Cyclic voltammograms of (a) **1b**, (b) **2b**, and (c) **19** (1 mM) in *o*-dichlorobenzene containing *n*-Bu_4NBF_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mV s^{-1}.

transferred electrons from the analysis of the CV wave. The electrochemical reductions of 1,2,4- and 1,3,5-tri(2-azulenyl)benzenes (**21** and **22**, respectively) exhibit subsequent three-step reduction waves in a similar potential region (Chart 3).[5] No other peaks were observed up to −2.4 V in the reduction of **1b**. No separation of the reduction wave of **1b** was observed by differential pulse voltammetry (DPV). Therefore, the reduction wave of **1b** should be concluded to be a six-electron transfer in one step generating a hexaanionic species $\mathbf{1b}_{\mathrm{red}}{}^{6-}$.

The oxidation of **1b** and **19** exhibited voltammograms that were characterized by two irreversible broad waves from the oxidation of the azulene rings. The oxidation of the acetylene **2b** also exhibited an irreversible broad wave upon CV similar to the poor reversibility of the oxidation of **1b** and **19**.

The voltammogram of the cobalt complex **3a** was characterized by four reversible waves at −1.77 to −2.19 V upon CV and DPV (Figure 3). The cobalt complex **3b** exhibited a similar four-electron transfer at potentials slightly more negative than those of **3a**. The voltammetric behavior of **3a** and **3b** indicates that the ions of higher-charged anions in the cobalt complexes **3a** and **3b** are stable under the conditions for the CV measurements. The four-step reduction exhibits the existence of the redox interaction among the four 2-azulenyl groups. A similar four-electron reduction is observed upon the CV of the 6-azulenyl derivatives.[4] The electrochemical oxidation of **3a** and **3b** exhibited two irreversible waves at +0.35 and +1.26 V upon CV. The first irreversible wave of **3a** and **3b** is probably from the Co(I) oxidation, and the second one is attributable to the redox reaction of the 2-azulenyl groups, on the basis of the analogy with those of **3a** and **3b** and those of **1b**, **2b**, and **19**.

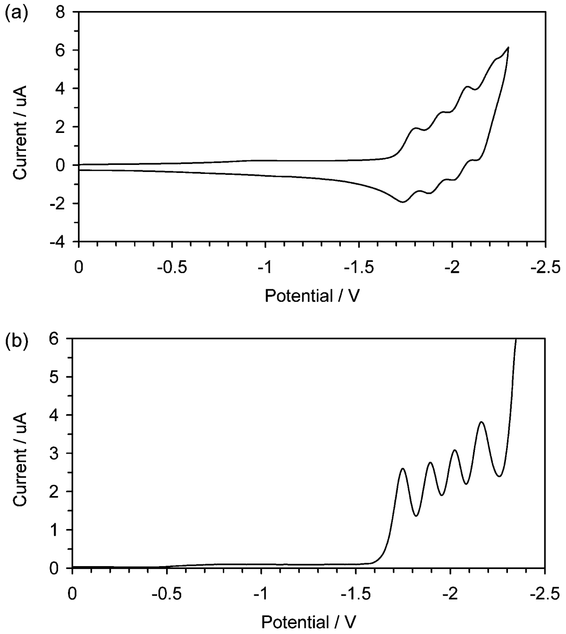

FIGURE 3. (a) Cyclic voltammogram and (b) differential pulse voltammogram of **3a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte.

Mesomorphic Properties. The phase-transition behavior of **1b**, **2b**, and **19** was examined with a polarizing microscope (POM) with a heating plate controlled by a thermoregulator and measured with a differential scanning calorimeter (DSC). X-ray diffraction powder patterns were also measured with Cu Kα radiation to distinguish between the solid polymorphs in the compounds. The X-ray diffraction powder patterns of these compounds and the assignments of X-ray reflections of each of the mesophases are summarized in the Supporting Information. In Table 2, the phase-transition temperatures and enthalpy changes for **1b**, **2b**, and **19** are summarized. The detailed thermal behaviors of these compounds are described below.

Compound **1b** exhibited mesomorphisms with crystalline polymorphs, K_1, K_2, and K_3 as summarized in Table 2. These state changes were observed in both the DSC measurements and the microscopic observations, as shown in Figures 4 and 5. Recrystallization of **1b** (hexane) produced a crystalline phase which was denoted as K_1(v) in Table 2. When the virgin crystals, K_1(v), were heated from room temperature, they exhibited subsequent solid−solid transitions at 87.8 and 108.3 °C to give the K_2 and K_3 crystals, respectively. Peaks I and II in Figure 4 correspond to the solid−solid transitions. The X-ray diffraction powder patterns revealed that the three crystalline states take a lamellar structure (see Supporting Information). When the sample was further heated to 115.5 °C, the K_3 crystals transformed into the me-

TABLE 2. Phase-Transition Temperature (*T*) and Enthalpy Changes (ΔH) of Compounds 1b, 2b, and 19[a]

sample	Phase[b] $\xrightarrow[{[\Delta H\ (\mathrm{kJ\ mol^{-1}})]}]{T\ (°\mathrm{C})}$ Phase
1b	$K_1(v) \xrightarrow[{[4.8]}]{87.8} K_2 \xrightleftharpoons{108.3} K_3 \xrightleftharpoons[{[21]}]{115.5} Col_{ho1} \xrightleftharpoons[{[0.14]}]{125.3} Col_{ho2} \xrightleftharpoons[{[0.050]}]{137.5} Col_{ho3} \xrightleftharpoons[{[0.73]}]{143.5} Col_{ho4} \xrightleftharpoons[{[0.38]}]{183.4} X \xrightleftharpoons[{[12]}]{199.9} IL$
2b	$\begin{tikzcd} K_1(v) \arrow[r, "44.0", "{[5.5]}"'] & K_3 \arrow[r, shift left, "118.8", "{[3.8]}"'] \arrow[d, shift left, "{[2.3]}"] & Col_{ro} \arrow[l, shift left] \arrow[r, shift left, "146.1", "{[5.5]}"'] & S_E \arrow[l, shift left] \arrow[r, shift left, "159.4", "{[11]}"'] & N \arrow[l, shift left] \arrow[r, shift left, "215.0", "{[0.11]}"'] & \text{IL (decomp.)} \arrow[l, shift left] \\ & K_2 \arrow[u, shift left, "63.8"] \end{tikzcd}$
19	$K_1(v) \xrightarrow[{[0.17]}]{65.9} K_2 \xrightleftharpoons[{[13]}]{109.6} S_E \xrightleftharpoons[{[22]}]{180.6} IL$

[a] Phase-transition temperature (*T*) and enthalpy change (ΔH) determined by DSC. [b] Phase nomenclature: K = crystal; Col_{ho} = hexagonal ordered columnar mesophase; Col_{ro} = rectangular ordered columnar mesophase; S_E = smectic E mesophase; N = nematic mesophase; X = unidentified mesophase; IL = isotropic liquid; (v) = fresh virgin state obtained by recrystallization from the solvent.

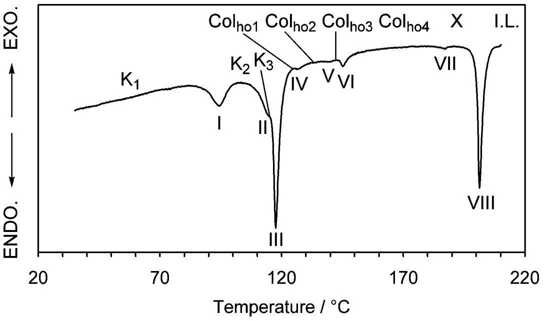

FIGURE 4. DSC thermograms of compound **1b** for a heating rate of 10 °C min^{-1}. The peaks labeled I−VIII in this figure are explained in the text.

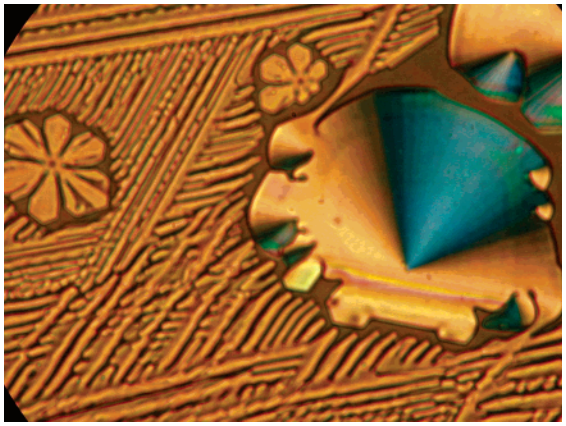

FIGURE 5. Texture of the discotic mesophase (Col_{ho}) of **1b** at 183.3 °C obtained by cooling from the isotropic liquid.

sophase, which showed a texture for the well-known developable units characteristic of columnar mesophases (peak III in Figure 4), followed by an isotropic liquid (IL) at 199.9 °C (peak VIII in Figure 4). The DSC thermogram exhibited four small endothermic peaks within the mesophase (peaks IV−VII in Figure 4). The X-ray diffraction experiments of each state exhibited a diffuse band around $2\theta = 20°$ in the wide-angle region which corresponds to the melt of the 6-octyl chains. The patterns allowed us to characterize the four lower-temperature states in the mesophase as hexagonal ordered columnar structures (Col_{ho}) with a stacking distance of 5.20−5.23 Å. In lower-temperature mesophases (Col_{ho1} and Col_{ho2}), an additional stacking distance was observed at 5.52 Å. The reflection could not be indexed into any spacing of 2D and 3D hexagonal lattices. Hence, this spacing at 5.52 Å is attributable to another stacking distance. Thus, there are two different stacking distances in the mesophases. See Figure S-18 for the presumed stacking model. It should be emphasized here that such large stacking distances (5.2 and 5.5 Å) are very unusual in the Col_{ho} mesophases. The unusually large stacking distances of the columnar mesophase could be explained by the propeller conformation of the molecule. The width of the 2-azulenyl groups corresponding to the atomic distance between 4- and 8-protons is estimated to be ca. 5.4 Å by the molecular mechanics calculations. Thus, the stacking distance indicates that the 2-azulenyl groups in the mesophase should be taking an almost perpendicular conformation to the central benzene ring (see Supporting Information).

Unequivocal analysis of the highest-temperature state within the mesophase, which was denoted as X in Figure 4, was hampered in the X-ray experiment because of the instability of compound **1b** at that temperature. The small endothermic enthalpy and no texture changes through the transitions in the mesophase indicate that the X state should be assumed to be a hexagonal columnar state (Col_h) similar to the other states in the mesophase. Thus, it should be concluded that there are no significant differences among the five states in the mesophase. The state changes should be attributed to the increase in the vacillation of the columnar structure.

The recrystallization of **2b** (toluene/methanol) produced a crystalline phase which was denoted as $K_1(v)$ in Table 2. When the virgin crystals, $K_1(v)$, were heated from room temperature, they exhibited a solid−solid transition at 44.0 °C to produce the K_3 crystals. Peak I in Figure 6 corresponds to the solid−solid transition. The X-ray diffraction data obtained are clearly different from each other. Thus, the K_1, K_2, and K_3 crystals are different crystalline polymorphs.

On further heating, the K_3 crystals melted into a columnar mesophase at 118.8 °C (ΔH = 3.8 kJ mol^{-1}) (peak II in Figure 6). The X-ray diffraction pattern of the mesophase at 133 °C showed a diffused band around

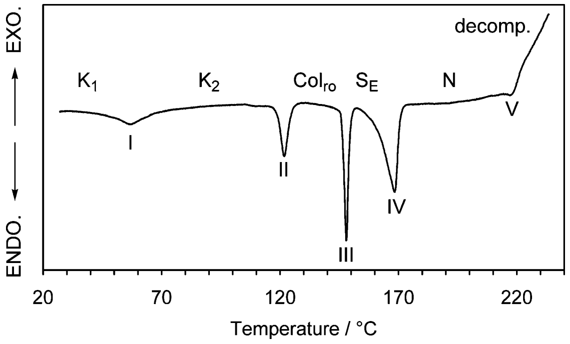

FIGURE 6. DSC thermogram of compound **2b** for a heating rate of 10 °C min^{-1}. Peaks labeled I−V in this figure are explained in the text.

$2\theta = 20°$ in the X-ray wide-angle region which corresponds to the melt of the alkyl chains (see Supporting Information). It also showed 15 narrow reflections on the X-ray diffraction pattern which correspond to the columnar structure [Col$_{\mathrm{ro}}$ ($P2_1/a$)] of the mesophase with the lattice constants in a two-dimensional rectangular lattice (a = 38.9 Å and b = 29.8 Å). By assuming a specific gravity of 1.00 g cm^{-3}, we can estimate the average number of molecules per unit cell to be 6.0 molecules with a stacking distance of 4.32 Å. Ordinarily, the average number of molecules in Col$_{\mathrm{ro}}$ ($P2_1/a$) symmetry should be two molecules per unit cell. Thus, we can assume that the three rodlike molecules of **2b** form a cluster to arrange into a columnar mesophase according to a two-dimensional rectangular lattice. The organization of **2b** may correspond to the phasmidic phases proposed for the mesomorphic properties of molecules with a rodlike rigid core ending in two half-disk shaped moieties.[18] A columnar mesophase similar to that formed by rodlike molecules is observed in the columnar mesomorphism of 1,4-bis[1,3-bis(hexyloxycarbonyl)-6-azulenylethynyl]benzene.[8] The columnar mesophase exhibited mosaic textures which became platelet textures when the sample stood at the temperature (Figure 7a,b).

Upon further heating, the rectangular columnar mesophase transformed into a smectic E (S$_\mathrm{E}$) mesophase at 146.1 °C (ΔH = 5.5 kJ mol^{-1}) (peak III in Figure 6), followed by a nematic (N) mesophase at 159.4 °C (ΔH = 11 kJ mol^{-1}) (peak IV in Figure 6). Upon further heating, the N mesophase clears to an isotropic liquid (IL) at 215.0 °C (peak V in Figure 6) accompanied by the decomposition of the compound. Compound **2b** had grandjean terrace textures for the S$_\mathrm{E}$ mesophase (Figure 7c) and schlieren textures for the N mesophase (Figure 7d). The X-ray diffraction pattern of the S$_\mathrm{E}$ mesophase at 153 °C (see Supporting Information) showed four narrow reflections in the low-angle region which correspond to the (001), (002), (003), and (004) planes; the interlayer distance was 24.2 Å. It also showed three narrow reflections in the wide-angle region which correspond to (200), (020), and (120) in a two-dimensional rectangular lattice (a = 9.35 Å and b = 8.67 Å). The stacking distance of the Col$_{\mathrm{ro}}$ phase shows that the 2-azulenyl groups in the mesophase should be tilted by ca. 37° from the plane perpendicular to the axis of the columns. Upon heating, the molecules lengthen the 6-octyl chains and align with 2D rectangular lattice to achieve the transition from the Col$_{\mathrm{ro}}$ phase to the S$_\mathrm{E}$ mesophase (see Supporting Information).

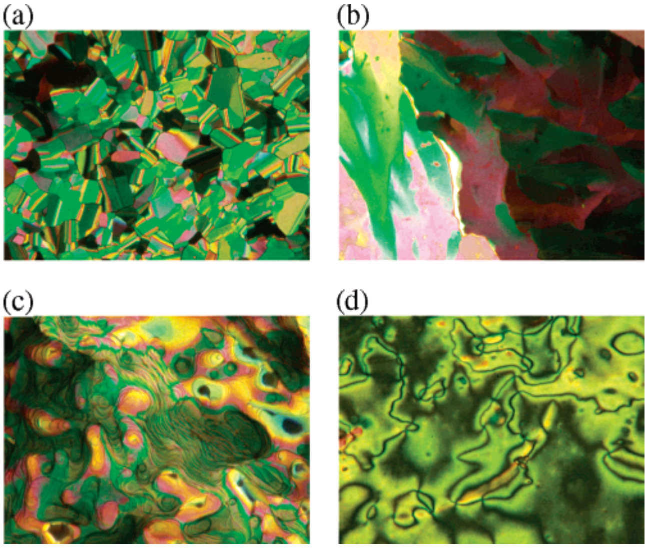

FIGURE 7. Textures of the mesophase of compound **2b**. (a) Mosaic texture of the Col$_{\mathrm{ro}}$ mesophase at 143.7 °C (upon cooling). (b) Platelet texture of the Col$_{\mathrm{ro}}$ mesophase obtained when the sample stood at 143.7 °C. (c) Grandjean terrace texture of the S$_\mathrm{E}$ mesophase at 155.9 °C. (d) Schlieren texture of the N mesophase at 161.5 °C.

Substituted azulenes linked to nematogenic alkylcyclohexanes by an ester group are reported by Praefcke and Schmidt. Smectic A and Smectic B phases are observed by Marson et al.[19,20] As far as we know, this is the first example exhibiting subsequent columnar, smectic, and nematic mesomorphism with crystalline polymorphs in a series of long-chain substituted azulene derivatives.

Compound **19** exhibited smectic mesomorphism (S$_\mathrm{E}$) with crystalline polymorphs, K$_1$ and K$_2$. Recrystallization of **19** (hexane) produced a crystalline phase which was denoted as K$_1$(v) in Table 2. The virgin crystals, K$_1$(v), exhibited a solid−solid transition at 65.9 °C (peak I in Figure 8). The diffraction data revealed the differences for each of the crystalline phases (see Supporting Information). Upon heating the sample, the K$_2$ crystals transformed into a smectic mesophase at 106.7 °C (peak II in Figure 8). The smectic phase exhibited grandjean terrace textures characteristic of the smectic E (S$_\mathrm{E}$) mesophase (Figure 9). The X-ray diffraction pattern of the mesophase at 150 °C revealed the S$_\mathrm{E}$ structure of the mesophase (see Supporting Information). It showed two narrow reflections in the low-angle region which cor-

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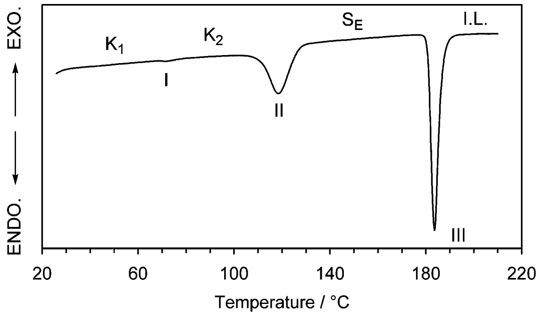

FIGURE 8. DSC thermogram of compound **19** for the heating rate of 10 °C min^{-1}. Peaks labeled I−III are explained in the text.

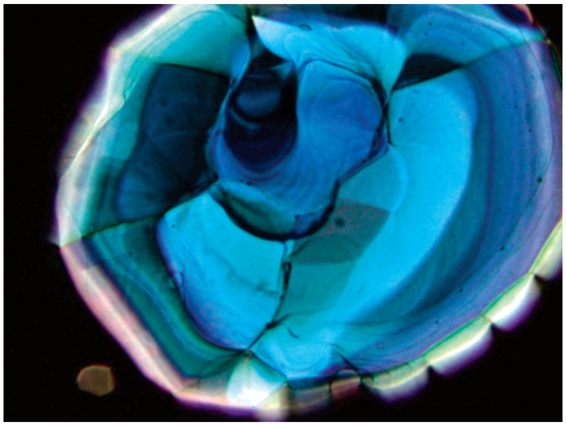

FIGURE 9. Grandjean terrace textures of the S_E mesophase of compound **19** at 175.4 °C obtained by cooling from the isotropic liquid.

respond to the (001) and (002) planes; the interlayer distance = 23.0 Å. It also had five narrow reflections in the wide-angle region which correspond to (200), (020), (120), (220), and (230) in a two-dimensional rectangular lattice (lattice constants $a = 9.33$ Å and $b = 9.22$ Å). Upon further heating, the S_E mesophase cleared to an isotropic liquid (IL) at 180.2 °C (peak III in Figure 8).

Conclusion

The cobalt-mediated cyclooligomerization of di(2-azulenyl)acetylene (**2b**) with 6-octyl substituents on each azulene ring produced a novel hexa(2-azulenyl)benzene derivative (**1b**) with high solubility. The cobalt-mediated cyclooligomerization of di(2-azulenyl)acetylenes (**2a** and **2b**) utilizing $CpCo(CO)_2$ as a catalyst produced (η^5-cyclopentadienyl)[tetra(2-azulenyl)cyclobutadiene]cobalt complexes (**3a** and **3b**). The redox behaviors examined by CV of these compounds represented the presumed multielectron redox properties under the electrochemical conditions used. Unfortunately, unequivocal analysis of the multiplicity of the electron transfer could not be established in the case of the hexa(2-azulenyl)benzene derivative (**1b**). However, the CV analysis revealed that 2-azulenyl substituents on a benzene ring increase the multiplicity of electron affinity because of the reduction of the respective azulene chromophore, similar to the reduction of 6-azulenyl derivatives. The new series of azulene derivatives, **1b**, **2b**, and **19**, substituted by long alkyl chains at the 6-position shows mesomorphism with crystalline polymorphs. Compound **1b** forms the expected hexagonal columnar mesophases with a large temperature range. Compound **2b** has three mesophases, $\mathrm{Col_{ro}}$, S_E, and N. Compound **19** exhibited an S_E mesophase. Thus, these systems could be utilized to construct advanced materials exhibiting multiple-electron transfer with liquid crystalline behavior.

Experimental Section

General. For general experimental details and instrumentation, see our earlier publication.[5] The detailed peak assignment of ^{1}H and ^{13}C NMR spectra was accomplished by NOE, CHCOSY, and/or COLOC experiments.

(η^5-Cyclopentadienyl)[tetra(2-azulenyl)cyclobutadiene]cobalt (3a). $CpCo(CO)_2$ (230 mg, 1.28 mmol) was added to a solution of **2a** (278 mg, 1.00 mmol) in 1,4-dioxane (150 mL). The mixture was refluxed for 4 days; during that time additional $CpCo(CO)_2$ (198 mg, 1.10 mmol) was added to the mixture. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to produce **3a** (267 mg, 79%): dark red powder; mp > 300 °C (toluene); MS (70 eV) *m/z* (relative intensity) 680 (M^+, 100), 402 ($M^+ - C_{10}H_7C{\equiv}CC_{10}H_7$, 41); IR (KBr disk) ν_{max} 1572, 1534, 1505, 1406, 1385, 804, 727 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.75), 302 (5.14), 403 sh (4.46), 448 (4.61), 614 sh (3.19), 670 sh (2.75); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, 8H, J = 9.5 Hz, $H_{4',8'}$), 7.71 (s, 8H, $H_{1',3'}$), 7.54 (t, 4H, J = 9.8 Hz, $H_{6'}$), 7.12 (dd, 8H, J = 9.8, 9.5 Hz, $H_{5',7'}$), 4.59 (s, 5H, Cp); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5 ($C_{2'}$), 140.6 ($C_{3'a,8'a}$), 135.2 ($C_{6'}$), 134.3 ($C_{4',8'}$), 123.9 ($C_{5',7'}$), 117.9 ($C_{1',3'}$), 83.2 (Cp), 74.6 ($C_{1,2,3,4}$). Anal. Calcd for $C_{49}H_{33}Co\cdot{}^1/_2H_2O$: C, 85.33; H, 4.97. Found: C, 85.43; H, 5.23.

(η^5-Cyclopentadienyl)[tetrakis(6-octyl-2-azulenyl)cyclobutadiene]cobalt (3b). The same procedure that was used for the preparation of **3a** was adopted. The reaction of **2b** (91 mg, 0.18 mmol) with $CpCo(CO)_2$ (80 mg, 0.44 mmol) in refluxing 1,4-dioxane (25 mL) for 2 days followed by chromatographic purification on silica gel with 20% ethyl acetate/hexane and GPC with $CHCl_3$ produced **3b** (53 mg, 52%): dark red prisms; mp 127.5−127.8 °C (hexane); MS (FAB) *m/z* (relative intensity) 1129 (M^+, 95); IR (KBr disk) ν_{max} 2924, 2855, 1578, 1509, 1412, 1399, 837 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 235 (4.74), 304 (5.23), 415 sh (4.57), 455 (4.69), 594 sh (3.50), 645 sh (3.01); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 8H, J = 10.4 Hz, $H_{4',8'}$), 7.59 (s, 8H, $H_{1',3'}$), 7.00 (d, 8H, J = 10.4 Hz, $H_{5',7'}$), 4.54 (s, 5H, Cp), 2.73 (t, 8H, J = 7.6 Hz, $H_{1''}$), 1.73 (tt, 8H, J = 7.6, 7.5 Hz, $H_{2''}$), 1.45−1.23 (m, 40H, $H_{3'',4'',5'',6'',7''}$), 0.89 (m, 12H, $H_{8''}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5 ($C_{6'}$), 147.2 ($C_{2'}$), 139.1 ($C_{3'a,8'a}$), 133.7 ($C_{4',8'}$), 125.0 ($C_{5',7'}$), 117.8 ($C_{1',3'}$), 83.0 (Cp), 74.4 ($C_{1,2,3,4}$), 42.5 ($C_{1''}$), 32.6 ($C_{2''}$), 31.9 (t), 29.5 (t), 29.4 (t), 29.3 (t), 22.7 ($C_{7''}$), 14.1 ($C_{8''}$). Anal. Calcd for $C_{81}H_{97}Co\cdot{}^1/_2H_2O$: C, 85.45; H, 8.68. Found: C, 85.60; H, 8.50.

***cis*- and *trans*-(η^5-Cyclopentadienyl)[bis(trimethylsilyl)-di(2-azulenyl)cyclobutadiene]cobalts (5 and 6, respectively).** $CpCo(CO)_2$ (595 mg, 3.30 mmol) was added to a solution of **4** (432 mg, 1.93 mmol) in 1,4-dioxane (110 mL). The mixture was refluxed for 7 days; during that time additional $CpCo(CO)_2$ (757 mg, 4.20 mmol) divided into two portions was added to the mixture. After the solvent was removed under reduced pressure, the residue was crystallized from ethyl acetate/hexane. Purification of the filtrate by column chromatography on silica gel with ethyl acetate/hexane recovered **4** (81 mg, 19%). Purification of the crystals by column chromatography on silica gel with CH_2Cl_2 produced a 16:84 mixture of **5** and **6** (273 mg, 50%). Product **6** was isolated by recrystallization from CH_2Cl_2/hexane.

6: dark red needles; mp 268.0−269.5 °C dec (CH_2Cl_2/hexane); MS (70 eV) *m/z* (relative intensity) 572 (M^+, 85), 348 ($M^+ - C_{10}H_7C{\equiv}CTMS$, 100); IR (KBr disk) ν_{max} 1534, 1501, 1406, 1248, 845, 808 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ)

274 sh (4.66), 296 (4.90), 326 sh (4.53), 450 (4.36), 577 sh (3.08), 615 sh (2.90), 673 sh (2.48); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, 4H, *J* = 9.9 Hz, $H_{4',8'}$), 7.49 (t, 2H, *J* = 9.8 Hz, $H_{6'}$), 7.25 (s, 4H, $H_{1',3'}$), 7.09 (dd, 4H, *J* = 9.9, 9.8 Hz, $H_{5',7'}$), 4.85 (s, 5H, Cp), 0.29 (s, 18H, 1,3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0 ($C_{2'}$), 140.2 ($C_{3'a,8'a}$), 134.8 ($C_{6'}$), 133.9 ($C_{4',8'}$), 123.7 ($C_{5',7'}$), 118.4 ($C_{1',3'}$), 85.0 ($C_{2,4}$), 81.0 (Cp), 71.0 ($C_{1,3}$), 1.4 (1,3-TMS). Anal. Calcd for $C_{35}H_{37}CoSi_2 \cdot {}^1/_2H_2O$: C, 72.26; H, 6.58. Found: C, 72.17; H, 6.46.

Diethyl 6-Bromo-2-hydroxyazulene-1,3-dicarboxylate (8). A solution of **7** (12.2 g, 42.3 mmol), NaOAc (3.44 g, 41.9 mmol), and Br_2 (13.4 g, 84.9 mmol) in trimethyl phosphate (300 mL) was heated at 50 °C for 8 h. The reaction mixture was poured into 10% NH_4Cl, and the precipitated crystals were collected by filtration. The filtrate was extracted with toluene, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The mixture of the crystals and residue was purified by short column chromatography on silica gel with 5% ethyl acetate/CH_2Cl_2 to produce **8** (8.12 g, 52%): yellow powder; mp 167.4−168.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H, 2-OH), 9.07 (d, 2H, *J* = 11.1 Hz, $H_{4,8}$), 7.98 (d, 2H, *J* = 11.1 Hz, $H_{5,7}$), 4.51 (q, 4H, *J* = 7.1 Hz, 1,3-CO_2Et), 1.49 (t, 6H, *J* = 7.1 Hz, 1,3-CO_2Et) (lit.[13] mp 162−163 °C).

Diethyl 2-Methoxy-6-(1-octynyl)azulene-1,3-dicarboxylate (10). $Pd(PPh_3)_4$ (57 mg, 0.049 mmol) was added to a degassed solution of **9** (381 mg, 1.00 mmol), 1-octyne (331 mg, 3.00 mmol), CuI (20 mg, 0.11 mmol), and triethylamine (10 mL) in dry toluene (25 mL). The resulting mixture was stirred at room temperature for 1.5 h under an Ar atmosphere. The reaction mixture was washed successively with a 5% NH_4Cl solution and water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 5% ethyl acetate/CH_2Cl_2 to produce **10** (405 mg, 99%): pink crystals; mp 46.5−47.2 °C (methanol); MS (70 eV) *m/z* (relative intensity) 410 (M^+, 100), 365 ($M^+ - OEt$, 23); IR (KBr disk) ν_{max} 2932, 2222 (m, C≡C), 1682 (s, C═O), 1489, 1439, 1397, 1281, 1225, 1194, 1044, 1038, 1001 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.39), 268 sh (4.12), 320 sh (4.77), 330 (4.88), 354 sh (4.15), 373 (4.20), 395 sh (3.87), 496 (2.68), 530 sh (2.55), 582 sh (1.89); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, 2H, *J* = 11.4 Hz, $H_{4,8}$), 7.73 (d, 2H, *J* = 11.4 Hz, $H_{5,7}$), 4.46 (q, 4H, *J* = 7.1 Hz, 1,3-CO_2Et), 4.14 (s, 3H, 2-OMe), 2.49 (t, 2H, *J* = 7.1 Hz, $H_{3'}$), 1.66 (tt, 2H, *J* = 7.6, 7.1 Hz, $H_{4'}$), 1.52−1.44 (m, 2H, $H_{5'}$), 1.46 (t, 6H, *J* = 7.1 Hz, 1,3-CO_2Et), 1.38−1.33 (m, 4H, $H_{6',7'}$), 0.92 (t, 3H, *J* = 7.0 Hz, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2 (C_2), 164.5 (s, 1,3-CO_2Et), 141.4 ($C_{3a,8a}$), 134.7 ($C_{4,8}$), 134.6 (C_6), 133.8 ($C_{5,7}$), 108.0 ($C_{1,3}$), 96.4 ($C_{2'}$), 84.3 ($C_{1'}$), 62.9 (t, 1,3-CO_2Et), 60.1 (2-OMe), 31.2 ($C_{6'}$), 28.6 ($C_{5'}$), 28.3 ($C_{4'}$), 22.5 ($C_{7'}$), 19.7 ($C_{3'}$), 14.4 (q, 1,3-CO_2Et), 13.9 ($C_{8'}$). Anal. Calcd for $C_{25}H_{30}O_5$: C, 73.15; H, 7.37. Found: C, 73.24; H, 7.32.

Diethyl 2-Methoxy-6-octylazulene-1,3-dicarboxylate (11). A mixture of **10** (3.03 g, 7.38 mmol) and 10% Pd-C (303 mg) in ethanol (80 mL) was stirred at room temperature for 24 h under an H_2 atmosphere. After the Pd catalyst was removed by filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with 20% ethyl acetate/hexane to produce **11** (2.94 g, 96%): orange needles; mp 40.1−40.5 °C (methanol); MS (70 eV) *m/z* (relative intensity) 414 (M^+, 100), 369 ($M^+ - OEt$, 23); IR (KBr disk) ν_{max} 2940, 2930, 1674 (s, C═O), 1493, 1429, 1418, 1397, 1277, 1184, 1038 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 236 (4.42), 270 (4.30), 306 sh (4.68), 315 (4.77), 348 sh (3.92), 355 sh (3.90), 366 sh (3.80), 464 (2.71), 491 sh (2.62), 542 sh (1.91); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, 2H, *J* = 11.1 Hz, $H_{4,8}$), 7.58 (d, 2H, *J* = 11.1 Hz, $H_{5,7}$), 4.46 (q, 4H, *J* = 7.1 Hz, 1,3-CO_2Et), 4.13 (s, 3H, 2-OMe), 2.88 (t, 2H, *J* = 7.7 Hz, $H_{1'}$), 1.72 (tt, 2H, *J* = 7.7, 6.8 Hz, $H_{2'}$), 1.46 (t, 6H, *J* = 7.1 Hz, 1,3-CO_2Et), 1.38−1.23 (m, 10H, $H_{3',4',5',6',7'}$), 0.87 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 (C_2), 164.8 (s, 1,3-CO_2Et), 155.5 (C_6), 140.9 ($C_{3a,8a}$), 136.1 ($C_{4,8}$), 132.3 ($C_{5,7}$), 107.3 ($C_{1,3}$), 62.9 (2-OMe), 60.0 (t, 1,3-CO_2Et), 41.7 ($C_{1'}$), 32.5 ($C_{2'}$), 31.8 (t), 29.4 (t), 29.2 (t, 2C), 22.6 ($C_{7'}$), 14.4 (q, 1,3-CO_2Et), 14.0 ($C_{8'}$). Anal. Calcd for $C_{25}H_{34}O_5$: C, 72.44; H, 8.27. Found: C, 72.15; H, 8.26.

2-Methoxy-6-octylazulene-1,3-dicarboxylic Acid (12). Compound **11** (6.98 g, 16.8 mmol) was dissolved in ethanol (70 mL), and 2 M KOH (50 mL) was added. The resulting mixture was refluxed for 4 h. After the reaction mixture was cooled, the mixture was acidified with 2 M HCl (40 mL). The precipitated crystals were collected by filtration, washed with water, and dried in vacuo to produce **12** (5.80 g, 96%): orange prisms; mp 129.5−130.8 °C (toluene); MS (70 eV) *m/z* (relative intensity) 314 ($M^+ - CO_2$, 11), 270 ($M^+ - 2CO_2$, 100), 171 ($M^+ - 2CO_2 - C_7H_{15}$, 53); IR (KBr disk) ν_{max} 2951, 2926, 2855, 1651 (s, C═O), 1493, 1449, 1401, 1229 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 235 (4.47), 271 (4.32), 306 sh (4.64), 313 (4.72), 344 (3.94), 368 sh (3.70), 452 (2.85), 475 sh (2.77), 515 sh (2.19); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, 2H, *J* = 11.0 Hz, $H_{4,8}$), 7.77 (d, 2H, *J* = 11.0 Hz, $H_{5,7}$), 4.40 (s, 3H, 2-OMe), 2.96 (t, 2H, *J* = 7.6 Hz, $H_{1'}$), 1.76 (tt, 2H, *J* = 7.6, 7.6 Hz, $H_{2'}$), 1.43−1.23 (m, 10H, $H_{3',4',5',6',7'}$), 0.88 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 (C_2), 166.9 (s, 1,3-CO_2H), 157.8 (C_6), 142.0 ($C_{3a,8a}$), 138.0 ($C_{4,8}$), 134.3 ($C_{5,7}$), 104.7 ($C_{1,3}$), 64.5 (2-OMe), 41.9 ($C_{1'}$), 32.6 ($C_{2'}$), 31.8 (t), 29.4 (t), 29.2 (t, 2C), 22.6 ($C_{7'}$), 14.1 ($C_{8'}$); HRMS calcd for $C_{21}H_{26}O_5 - e - CO_2$ 314.1876, found 314.1877. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.65; H, 7.57.

2-Hydroxy-6-octylazulene (13). A mixture of **12** (1.42 g, 3.96 mmol) and freshly prepared 100% phosphoric acid, which was obtained by dissolving phosphorus pentaoxide (16 g) in 85% phosphoric acid (40 g), was heated at 130 °C for 10 min with occasional stirring with a glass rod. After the reaction mixture was cooled, the mixture was poured into ice−water and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 20% ethyl acetate/hexane to produce **13** (779 mg, 77%) and 2-methoxy-6-octylazulene (**14**) (77 mg, 7%).

13: dark red crystals; mp 88.5−89.0 °C (methanol); MS (70 eV) *m/z* (relative intensity) 256 (M^+, 100), 158 ($M^+ - C_7H_{15} + 1$, 24), 157 ($M^+ - C_7H_{15}$, 49), 128 ($M^+ - C_8H_{17} - OH + 2$, 20); IR (KBr disk) ν_{max} 3033 (m, OH), 2957, 2923, 2853, 1646, 1628, 1534, 1501, 1404, 1237, 833 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 242 (4.10), 263 sh (3.95), 269 (3.96), 280 (3.97), 290 (3.97), 364 sh (4.22), 373 (4.25), 394 sh (4.08), 418 sh (3.35), 447 sh (3.09), 477 sh (2.88), 517 sh (2.53); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.49 (br s, 1H, 2-OH), 7.93 (d, 2H, *J* = 10.5 Hz, $H_{4,8}$), 7.09 (d, 2H, *J* = 10.5 Hz, $H_{5,7}$), 6.70 (s, 2H, $H_{1,3}$), 2.75 (t, 2H, *J* = 7.7 Hz, $H_{1'}$), 1.68 (tt, 2H, *J* = 7.7, 7.2 Hz, $H_{2'}$), 1.46−1.20 (m, 10H, $H_{3',4',5',6',7'}$), 0.86 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, acetone-d_6) δ 167.5 (C_2), 148.1 (C_6), 140.1 ($C_{3a,8a}$), 131.1 ($C_{4,8}$), 125.9 ($C_{5,7}$), 103.7 ($C_{1,3}$), 42.4 ($C_{1'}$), 33.7 ($C_{2'}$), 32.6 (t), 30.2 (t), 30.0 (t, 2C), 23.2 ($C_{7'}$), 14.3 ($C_{8'}$). Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.09; H, 9.59.

14: reddish purple plates; mp 52.8−53.0 °C (methanol); MS (70 eV) *m/z* (relative intensity) 270 (M^+, 100), 171 ($M^+ - C_7H_{15}$, 58); IR (KBr disk) ν_{max} 2921, 2849, 1549, 1526, 831 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 236 (4.06), 271 sh (4.42), 284 (4.82), 293 (4.92), 321 (3.86), 345 (3.70), 361 (3.84), 377 (3.85), 477 sh (2.19), 510 (2.28), 537 sh (2.22), 583 sh (1.80); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, 2H, *J* = 10.5 Hz, $H_{4,8}$), 7.10 (d, 2H, *J* = 10.5 Hz, $H_{5,7}$), 6.77 (s, 2H, $H_{1,3}$), 4.02 (s, 3H, 2-OMe), 2.76 (t, 2H, *J* = 7.7 Hz, $H_{1'}$), 1.69 (tt, 2H, *J* = 7.7, 7.2 Hz, $H_{2'}$), 1.39−1.20 (m, 10H, $H_{3',4',5',6',7'}$), 0.87 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5 (C_2), 148.6 (C_6), 138.5 ($C_{3a,8a}$), 131.5 ($C_{4,8}$), 125.5 ($C_{5,7}$), 100.9 ($C_{1,3}$), 57.5 (2-OMe), 42.0 ($C_{1'}$), 32.8 ($C_{2'}$), 31.9 (t), 29.5 (t), 29.3 (t), 29.2 (t), 22.6 (t), 14.1 ($C_{8'}$). Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.34; H, 9.72.

2-Bromo-6-octylazulene (15). PBr_3 (3.19 g, 11.8 mmol) was added to a solution of **13** (962 mg, 3.75 mmol) in dry toluene (140 mL). The resulting mixture was heated at 90−100 °C for 45 min. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 20% ethyl acetate/hexane to produce **15** (974 mg, 81%): violet crystals; mp 81.0−81.8 °C (methanol); MS (70 eV) *m/z* (relative intensity) 320 ($M^+ + 2$, 98), 318 (M^+, 100), 141 ($M^+ - C_7H_{15} - Br + 1$, 54); IR (KBr disk) ν_{max} 2921, 2853, 1582, 1402, 837 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 237 (4.08), 250 sh (3.82), 275 sh (4.50), 286 (4.85), 295 (4.84), 326 sh (3.63), 337 (3.77), 351 (3.83), 365 (3.83), 486 sh (2.47), 537 (2.63), 568 sh (2.59), 619 sh (2.20); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2H, $J = 10.5$ Hz, $H_{4,8}$), 7.25 (s, 2H, $H_{1,3}$), 7.11 (d, 2H, $J = 10.5$ Hz, $H_{5,7}$), 2.76 (t, 2H, $J = 7.7$ Hz, $H_{1'}$), 1.69 (tt, 2H, $J = 7.7$, 7.2 Hz, $H_{2'}$), 1.39−1.21 (m, 10H, $H_{3',4',5',6',7'}$), 0.87 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (C_6), 138.5 ($C_{3a,8a}$), 134.7 ($C_{4,8}$), 125.8 ($C_{5,7}$), 118.4 ($C_{1,3}$ and C_2), 42.4 ($C_{1'}$), 32.6 ($C_{2'}$), 31.8 (t), 29.4 (t), 29.3 (t), 29.2 (t), 22.6 ($C_{7'}$), 14.1 ($C_{8'}$). Anal. Calcd for $C_{18}H_{23}Br$: C, 67.71; H, 7.26; Br, 25.03. Found: C, 67.69; H, 7.25; Br, 25.18.

2-Iodo-6-octylazulene (16). A solution of **15** (439 mg, 1.37 mmol), CuI (3.14 g, 16.49 mmol), and KI (4.87 g, 29.3 mmol) in DMF (15 mL) was refluxed for 16 h. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 10% ethyl acetate/hexane to produce **16** (422 mg, 84%): violet crystals; mp 95.5−95.8 °C (methanol); MS (70 eV) *m/z* (relative intensity) 366 (M^+, 100), 141 ($M^+ - C_7H_{15} - I + 1$, 32); IR (KBr disk) ν_{max} 2924, 2853, 1582, 1399, 837 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 235 (4.10), 258 sh (4.04), 285 sh (4.57), 292 (4.80), 303 (4.87), 332 sh (3.62), 344 (3.76), 357 (3.82), 372 (3.97), 452 sh (2.30), 510 sh (2.55), 548 (2.66), 577 sh (2.62), 624 sh (2.29); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H, $J = 10.4$ Hz, $H_{4,8}$), 7.40 (s, 2H, $H_{1,3}$), 7.08 (d, 2H, $J = 10.4$ Hz, $H_{5,7}$), 2.75 (t, 2H, $J = 7.7$ Hz, $H_{1'}$), 1.69 (tt, 2H, $J = 7.7$, 7.0 Hz, $H_{2'}$), 1.39−1.20 (m, 10H, $H_{3',4',5',6',7'}$), 0.87 (m, 3H, $H_{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (C_6), 139.2 ($C_{3a,8a}$), 134.1 ($C_{4,8}$), 125.5 ($C_{5,7}$), 124.4 ($C_{1,3}$), 96.4 (C_2), 42.5 ($C_{1'}$), 32.5 ($C_{2'}$), 31.8 (t), 29.4 (t), 29.3 (t), 29.2 (t), 22.6 ($C_{7'}$), 14.1 ($C_{8'}$). Anal. Calcd for $C_{18}H_{23}I$: C, 59.02; H, 6.33; I, 34.65. Found: C, 59.17; H, 6.39; I, 34.50.

6-Octyl-2-(trimethylsilylethynyl)azulene (17). Trimethylsilylacetylene (1.08 g, 11.00 mmol) was added to a solution of **15** (646 mg, 2.02 mmol), triphenylphosphine (52 mg, 0.20 mmol), CuI (40 mg, 0.21 mmol), and *trans*-dichlorobis(triphenylphosphine)palladium(II) (70 mg, 0.10 mmol) in triethylamine (17 mL) and toluene (17 mL). The resulting mixture was stirred at 60 °C for 30 min under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane to produce **17** (681 mg, 100%): blue needles; mp 50.7−51.3 °C (methanol); MS (70 eV) *m/z* (relative intensity) 336 (M^+, 100), 321 ($M^+ - CH_3$, 31); IR (KBr disk) ν_{max} 2957, 2926, 2855, 2147 (m, C≡C), 1584, 1410, 1250, 857, 843 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.18), 246 sh (4.12), 272 (4.43), 279 (4.42), 297 (4.84), 308 (4.91), 338 sh (3.64), 353 sh (3.83), 370 (4.17), 381 sh (4.03), 389 (4.37), 526 sh (2.46), 568 (2.66), 605 sh (2.65), 655 sh (2.31); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2H, $J = 10.4$ Hz, $H_{4,8}$), 7.33 (s, 2H, $H_{1,3}$), 7.06 (d, 2H, $J = 10.4$ Hz, $H_{5,7}$), 2.76 (t, 2H, $J = 7.8$ Hz, $H_{1''}$), 1.69 (tt, 2H, $J = 7.8$, 7.2 Hz, $H_{2''}$), 1.41−1.22 (m, 10H, $H_{3'',4'',5'',6'',7''}$), 0.87 (t, 3H, $H_{8''}$), 0.29 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7 (C_6), 138.7 ($C_{3a,8a}$), 136.2 ($C_{4,8}$), 128.7 (C_2), 125.2 ($C_{5,7}$), 120.9 ($C_{1,3}$), 103.4 ($C_{1'}$), 100.2 ($C_{2'}$), 42.5 ($C_{1''}$), 32.6 ($C_{2''}$), 31.8 (t), 29.5 (t), 29.4 (t), 29.2 (t), 22.6 ($C_{7''}$), 14.1 ($C_{8''}$), 0.0 (TMS). Anal. Calcd for $C_{23}H_{32}Si$: C, 82.07; H, 9.58. Found: C, 82.07; H, 9.69.

2-Ethynyl-6-octylazulene (18). A solution of KF (132 mg, 2.27 mmol) in water (2 mL) was added to a solution of **17** (376 mg, 1.12 mmol) in DMF (10 mL). After the mixture was stirred at room temperature for 3 h, the reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 10% ethyl acetate/hexane to produce **18** (295 mg, 100%): blue needles; mp 44.8−45.2 °C (methanol); MS (70 eV) *m/z* (relative intensity) 264 (M^+, 100), 165 ($M^+ - C_7H_{15}$, 67); IR (KBr disk) ν_{max} 3316 (s, C≡CH), 2957, 2926, 2855, 2103 (w, C≡C), 1580, 1468, 1410, 839, 629, 594 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.15), 269 (4.34), 284 sh (4.55), 293 (4.83), 304 (4.86), 336 sh (3.62), 348 sh (3.76), 363 (3.97), 373 sh (3.89), 380 (4.21), 528 sh (2.49), 567 (2.66), 599 (2.66), 651 sh (2.32); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, 2H, $J = 10.5$ Hz, $H_{4,8}$), 7.36 (s, 2H, $H_{1,3}$), 7.07 (d, 2H, $J = 10.5$ Hz, $H_{5,7}$), 3.43 (s, 1H, $H_{2'}$), 2.76 (t, 2H, $J = 7.7$ Hz, $H_{1''}$), 1.69 (tt, 2H, $J = 7.7$, 7.2 Hz, $H_{2''}$), 1.40−1.21 (m, 10H, $H_{3'',4'',5'',6'',7''}$), 0.87 (m, 3H, $H_{8''}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1 (C_6), 138.6 ($C_{3a,8a}$), 136.5 ($C_{4,8}$), 127.6 (C_2), 125.3 ($C_{5,7}$), 120.9 ($C_{1,3}$), 82.2 ($C_{2'}$), 82.1 ($C_{1'}$), 42.5 ($C_{1''}$), 32.6 ($C_{2''}$), 31.9 (t), 29.5 (t), 29.3 (t), 29.2 (t), 22.7 ($C_{7''}$), 14.1 ($C_{8''}$). Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.98; H, 9.15.

Bis(6-octyl-2-azulenyl)acetylene (2b). Tetrakis(triphenylphosphine)palladium(0) (60 mg, 0.052 mmol) was added to a degassed solution of **16** (366 mg, 1.00 mmol), **18** (264 mg, 1.00 mmol), and CuI (21 mg, 0.11 mmol) in triethylamine (10 mL) and toluene (20 mL). The resulting mixture was stirred at room temperature for 70 min under an Ar atmosphere. The reaction mixture was poured into a 10% NH_4Cl solution and extracted with toluene. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to produce **2b** (431 mg, 86%): green needles; mp 159.2−168.0 °C (toluene/MeOH); MS (70 eV) *m/z* (relative intensity) 502 (M^+, 100); IR (KBr disk) ν_{max} 2923, 2851, 1578, 1410, 839 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 238 (4.35), 271 sh (4.51), 276 (4.53), 314 sh (4.92), 321 (5.01), 385 sh (4.30), 397 sh (4.48), 412 sh (4.65), 422 (4.71), 448 (4.88), 539 sh (3.01), 569 (3.09), 608 (3.04), 660 sh (2.66); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 4H, $J = 10.3$ Hz, $H_{4',8'}$), 7.46 (s, 4H, $H_{1',3'}$), 7.08 (d, 4H, $J = 10.3$ Hz, $H_{5',7'}$), 2.77 (t, 4H, $J = 7.7$ Hz, $H_{1''}$), 1.71 (tt, 4H, $J = 7.7$, 7.3 Hz, $H_{2''}$), 1.42−1.22 (m, 20H, $H_{3'',4'',5'',6'',7''}$), 0.88 (m, 6H, $H_{8''}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5 ($C_{6'}$), 139.0 ($C_{3'a,8'a}$), 136.0 ($C_{4',8'}$), 129.2 ($C_{2'}$), 125.2 ($C_{5',7'}$), 120.6 ($C_{1',3'}$), 93.9 ($C_{1,2}$), 42.5 ($C_{1''}$), 32.6 ($C_{2''}$), 31.9 (t), 29.5 (t), 29.4 (t), 29.2 (t), 22.7 ($C_{7''}$), 14.1 ($C_{8''}$). Anal. Calcd for $C_{38}H_{46}$: C, 90.78; H, 9.22. Found: C, 90.65; H, 9.48.

Hexakis(6-octyl-2-azulenyl)benzene (1b). $Co_2(CO)_8$ (24 mg, 0.070 mmol) was added to a solution of **2b** (101 mg, 0.201 mmol) in 1,4-dioxane (50 mL). The mixture was refluxed for 10 h under an Ar atmosphere. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to produce **1b** (92 mg, 91%): green needles; mp 160.9−161.3 °C (hexane); MS (FAB) *m/z* (relative intensity) 1507 (M^+, 13); IR (KBr disk) ν_{max} 2924, 2855, 1578, 1397, 837 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 236 (4.86), 289 (5.50), 310 sh (5.23), 374 sh (4.68), 543 sh (3.19), 570 (3.26), 605 sh (3.22), 661 sh (2.86); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, 12H, $J = 10.0$ Hz, $H_{4',8'}$), 6.59 (s, 12H, $H_{1',3'}$), 6.52 (d, 12H, $J = 10.0$ Hz, $H_{5',7'}$), 2.52 (t, 12H, $J = 7.7$ Hz, $H_{1''}$), 1.54 (br tt, 12H, $H_{2''}$), 1.31−1.20 (br m, 60H, $H_{3'',4'',5'',6'',7'}$), 0.86 (m, 18H, $H_{8''}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1 ($C_{6'}$), 149.9 ($C_{2'}$), 137.9 ($C_{1,2,3,4,5,6}$), 137.7 ($C_{3'a,8'a}$), 134.6 ($C_{4',8'}$), 122.9 ($C_{5',7'}$), 121.4 ($C_{1',3'}$), 42.3 ($C_{1''}$), 32.7 ($C_{2''}$), 31.9 (t), 29.5 (t, 12C), 29.3 (t), 22.7 ($C_{7''}$), 14.1 ($C_{8''}$). Anal. Calcd for $C_{114}H_{138}$: C, 90.78; H, 9.22. Found: C, 90.61; H, 9.16.

6-Octyl-2-phenylazulene (19). A solution of **15** (67 mg, 0.21 mmol), phenylboronic acid (52 mg, 0.43 mmol), $CsCO_3$ (198 mg, 0.608 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) in dioxane (5 mL) was heated at 100 °C for 2 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene to produce **19** (62 mg, 93%): blue plates; mp 179.8−181.2 °C (hexane); MS (70 eV) *m/z* (relative intensity) 316 (M^+, 7), 245 ($M^+ - C_5H_{11}$, 26), 231 ($M^+ - C_6H_{13}$, 100), 218 ($M^+ - C_7H_{15} + 1$, 100), 217 ($M^+ - C_7H_{15}$, 22), 203 ($M^+ - C_8H_{17}$, 22); IR (KBr disk) ν_{max} 2919, 2851, 837, 756, 687 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max}, nm (log ϵ) 239 (4.13), 288 sh (4.56), 301 (4.83), 311 (4.88), 344 sh (3.60), 359 sh (3.81), 378 (4.13), 397 (4.21), 447 (2.31), 523 sh (2.39), 564 (2.57), 599 (2.56), 655 sh (2.19); ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, 2H, $J = 10.4$ Hz, $H_{4,8}$), 7.94 (dd, 2H, $J = 8.2$, 1.2 Hz, $H_{2',6'}$), 7.60 (s, 2H, $H_{1,3}$), 7.45 (t, 2H, $J = 8.2$, 7.4 Hz, $H_{3',5'}$), 7.32 (t, 1H, $J = 7.4$, 1.2 Hz, $H_{4'}$), 7.06 (d, 2H, $J = 10.4$ Hz, $H_{5,7}$), 2.77 (t, 2H, $J = 7.7$ Hz, $H_{1''}$), 1.71 (tt, 2H, $J = 7.7$, 7.7 Hz, $H_{2''}$), 1.40−1.21 (m, 10H, $H_{3'',4'',5'',6'',7''}$), 0.88 (t, 3H, $J = 6.9$ Hz, $H_{8''}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1 (C_6), 148.6 (C_2), 139.9 ($C_{3a,8a}$), 136.7 ($C_{1'}$), 135.4 ($C_{4,8}$), 128.8 ($C_{3',5'}$), 127.9 ($C_{4'}$), 127.5 ($C_{2',6'}$), 125.0 ($C_{5,7}$), 114.2 ($C_{1,3}$), 42.4 ($C_{1''}$), 32.6 ($C_{2''}$), 31.9 (t), 29.5 (t), 29.3 (t), 29.2 (t), 22.6 (t), 14.1 ($C_{8''}$); HRMS calcd for $C_{24}H_{28} - e$ 316.2186, found 316.2196. Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.27; H, 9.00.

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Supporting Information Available: Description of the attempt to prepare 2-haloazulenes starting from diethyl 6-bromo-2-aminoazulene-1,3-dicarboxylate, ORTEP plots and structure features of the X-ray analysis of **6**, concentration dependence of the ^1H NMR spectrum of **1b**, CV and DPV data for **1b**, **2b**, and **19**, X-ray diffraction powder patterns and diffraction data for **1b**, **2b**, and **19**, and proposed phase structure models for **1b** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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