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Synthesis and Two-Electron Redox Behavior of Diazuleno[2,1-*a*:1,2-*c*]naphthalenes

Shunji Ito,*,† Akiko Nomura,† Noboru Morita,† Chizuko Kabuto,† Hirokazu Kobayashi,‡
Seiko Maejima,‡ Kunihide Fujimori,‡ and Masafumi Yasunami§

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan,
Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390-8621, Japan, and
Department of Materials Science and Engineering, College of Engineering, Nihon University,
Koriyama 963-1165, Japan

ito@funorg.chem.tohoku.ac.jp

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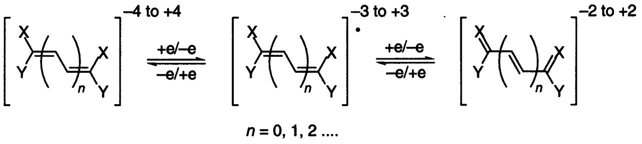
The Diels–Alder reaction of di-2-azulenylacetylene with tetraphenylcyclopentadienone afforded 7,8,9,10-tetraphenyldiazuleno[2,1-*a*:1,2-*c*]naphthalene in one pot via autoxidation of the presumed 1,2-di-2-azulenylbenzene derivative. In contrast, a similar reaction of bis(1-methoxycarbonyl-2-azulenyl)acetylene with tetraphenylcyclopentadienone gave the 1,2-di-2-azulenylbenzene derivative. The following cyclodehydrogenation reaction of the benzene derivative with iron(III) chloride afforded diazuleno[2,1-*a*:1,2-*c*]naphthalene 6,11-bismethoxycarbonyl derivative. The redox behavior of these novel diazuleno[2,1-*a*:1,2-*c*]naphthalenes was examined by cyclic voltammetry (CV). These compounds exhibited two-step oxidation waves at +0.22 to +0.71 V upon CV, which revealed the formation of a radical cation and dication stabilized by the fused two azulene rings under the electrochemical oxidation conditions. Since the 1,2-di-2-azulenylbenzene derivative was oxidized at higher oxidation potentials (+0.83 and +1.86 V), the fusion of the two azulene rings to naphthalene increased electron-donating properties because of the formation of a closed-shell dicationic structure. Formation of the radical cation was characterized by UV–vis spectroscopy under the electrochemical oxidation conditions, although no evidence was obtained for the presumed dication under the conditions of the UV–vis spectroscopy measurement.

Introduction

Azulene ($C_{10}H_8$) has attracted the interest of many research groups due to its unusual properties as well as its beautiful blue color.[1] Especially, the system has a tendency to stabilize cations, as well as anions, owing to its remarkable polarizability. However, to date, molecules with potentially useful electronic properties constructed by azulene derivatives are fairly scarce. Recently, Hünig et al. have proposed the concept of a violene/cyanine hybrid as stabilized organic electrochromics.[2] The hybrid contains the moieties X═C–Y, which represent a "cyanine"-type structure in fully reduced or oxidized form, as end groups of a violene. The system provides a highly colored closed-shell form as a cyanine dye by an overall two-electron transfer as illustrated by the general structure in Scheme 1.

SCHEME 1



We have recently proposed that hexa-6-azulenylbenzene (**1**) is considered a candidate for such a system (Chart 1).[3] The redox system of **1** could be assumed as a hybrid in which the stabilized closed-shell cyanine-type structure is generated by the two-electron reduction. Polycyclic aromatic hydrocarbon **2**, which could be prepared by cyclodehydrogenation reaction of hexa-2-azulenylbenzene, could be considered another type of hybrid, because compound **2** will provide delocalized closed-shell dication $\mathbf{2}_{ox}^{+2}$ by two-electron oxidation and could be expected to show significant changes in absorption spectra in the different oxidation states. The presumed cyanine-type structure formed by two-electron oxidation

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* To whom correspondence should be addressed. Telephone: +81-22-217-7714. Fax: +81-22-217-7714.

† Tohoku University.

‡ Shinshu University.

§ Nihon University.

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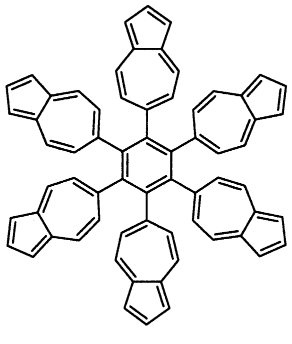
CHART 1



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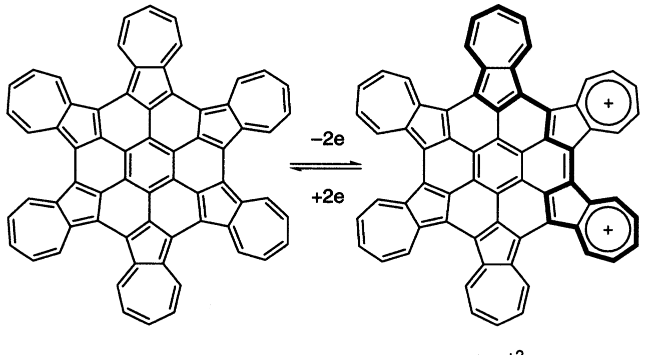
SCHEME 2



2 2_{OX}^{+2}

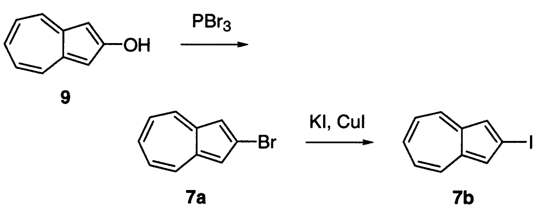
is represented by the bold line in Scheme 2. These systems could be utilized to construct advanced materials for electrochromic applications.[4]

Diazuleno[2,1-*a*:1,2-*c*]naphthalenes (**3a**,**b**) would be a model compound for the formation of such a closed-shell dicationic species by the two-electron oxidation. The system would afford a colored radical cation by the electrochemical oxidation similar to the redox system of violene.[5] Herein we report a preparation of novel diazuleno[2,1-*a*:1,2-*c*]naphthalene derivatives toward the synthesis of **2** and their two-electron redox behavior examined by cyclic voltammetry (CV).

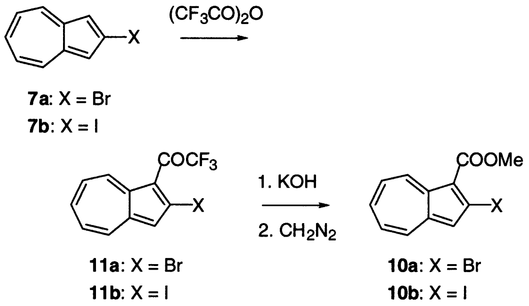
Results and Discussion

Synthesis. Di-2-azulenylacetylenes (**4a**,**b**) would be a key intermediate for the synthesis of **3a**,**b**. The Diels−Alder reaction of **4a**,**b** with tetraphenylcyclopentadienone (**5**) will afford 1,2-di-2-azulenylbenzene derivatives (**6a**,**b**), which could be transformed into the desired **3a**,**b** by cyclodehydrogenation reaction.[6] Recently, ethynylation of azulene at the 2-position utilizing Pd-catalyzed cross-coupling reaction of 2-iodoazulene (**7b**) with trimethylsilylacetylene (**8**) is reported by Hafner et al.[7] Thus, 2-haloazulenes are an efficient starting material for the preparation of **4a**,**b**. Recently, we have developed a simple route to 2-hydroxyazulene (**9**) starting from commercially available cycloheptatriene.[8] We found that the treatment of **9** with phosphorus tribromide afforded the desired 2-bromoazulene (**7a**)[9] in 78% yield. Following the treatment of **7a** with a mixture of potassium iodide and copper(I) iodide in refluxing dimethyl formamide (DMF), 2-iodoazulene (**7b**)[10] was obtained in 95% yield (Scheme 3). Methyl 2-bromo- and 2-iodoazulene-1-carboxylates (**10a**,**b**[11]) are readily prepared in high yield starting from **7a**,**b**, respectively, according to the three-step strategy via trifluoroacetylation reported by McDonald et al. as outlined in Scheme 4.[11]

SCHEME 3



SCHEME 4



We found that 2-bromoazulenes (**7a** and **10a**) reacted with **8** under Sonogashira−Hagihara conditions[12] to afford 2-(trimethylsilylethynyl)azulenes (**12a**[7] and **12b**) in almost quantitative yields, respectively. It is noteworthy that the ethynylation of azulenes at the 2-position readily proceeded using bromides. Treatment of **12a**,**b** with potassium fluoride in DMF furnished 2-ethynylazulenes (**13a**[7] and **13b**) in 100 and 98% yields, respectively (Scheme 5).

Cross-coupling reaction of **13a** with **7a** using $Pd(PPh_3)_4$ as a catalyst afforded di-6-azulenylacetylene (**4a**) and di-6-azulenyldiacetylene (**14a**) in 64 and 17% yields, respectively. Likewise, the reaction of **13b** with **10a** also afforded a mixture (3.9:1) of di-6-azulenylacetylene (**4b**) and di-6-azulenyldiacetylene (**14b**) in 82 and 30% yields, respectively, together with the recovered **10a** (23%). Many difficulties arose in the separation of these compounds. Formation of diacetylenes **14a**,**b** is presumably

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(4) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: Weinheim, Germany, 1995.

(5) Deuchert, K.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 875−886.

(6) See, e.g.: (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267−1300. (b) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785.

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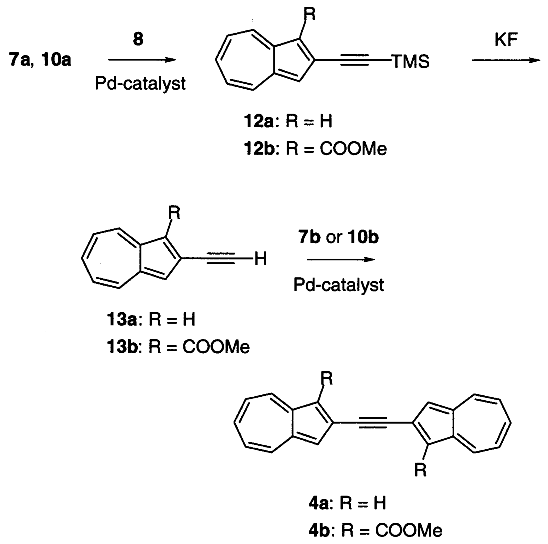
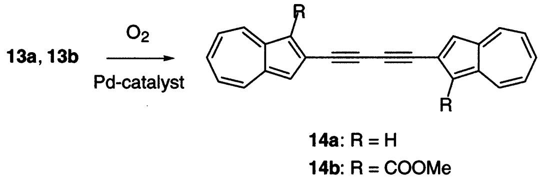
(12) (a) Sonogashira, K. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 3, Chapter 2.4, pp 521−529. (b) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630. (c) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

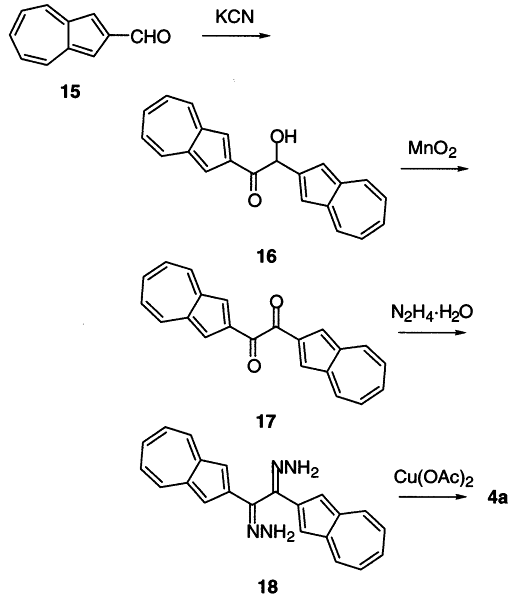
SCHEME 5



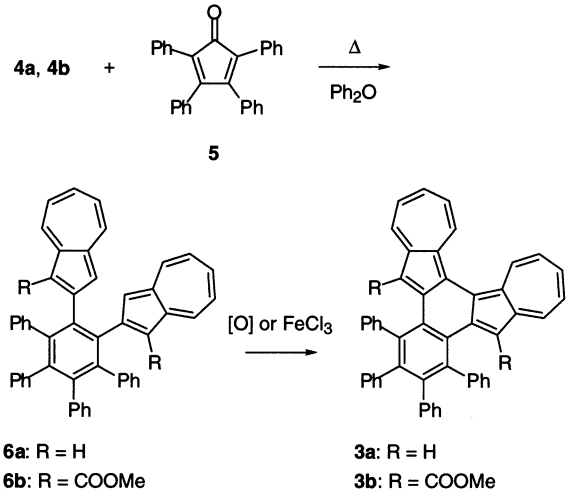
SCHEME 6



SCHEME 7



SCHEME 8



attributed to the low reactivity of 2-bromoazulenes (**7a** and **10a**) under the cross-coupling conditions. To improve the preparation of **4a**,**b**, 2-iodoazulenes (**7b** and **10b**) were used for the Pd-catalyzed cross-coupling reaction. Indeed, the reaction of **7b** and **10b** with **13a** or **13b** under the Pd-catalyzed conditions exclusively afforded the desired **4a**,**b** in 96 and 83% yields, respectively (Scheme 5). Diacetylenes **14a**,**b** were characterized by the selective synthesis using Pd-catalyzed oxidative coupling of **13a**,**b** in 69 and 76% yields, respectively (Scheme 6).[13]

Di-2-azulenylacetylene could also be prepared selectively from azulene-2-carbaldehyde (**15**)[14] via dihydrazone **18** as illustrated in Scheme 7. Benzoin condensation reaction of **15** in the presence of potassium cyanide and subsequent oxidation reaction with activated manganese(IV) oxide afforded di-2-azulenylethanedione (**17**) in 77% overall yield. The reaction of **17** with hydrazine monohydrate in refluxing ethanol for 3 days afforded the dihydrazone **18** in 92% yield. Treatment of **18** with copper(II) acetate in a mixture of methanol and dichloromethane afforded the desired **4a** in 76% yield.

Diels–Alder reaction of **4a** with a large excess of **5** in diphenyl ether at 160 °C for 20 h and subsequent chromatographic purification of the reaction mixture on silica gel afforded the desired **3a** in one pot in 47% yield.[6,15] Direct formation of **3a** by the Diels–Alder reaction of **4a** with **5** is ascribed to the autoxidation of the presumed 1,2-di-2-azulenylbenzene derivative **6a** under the reaction conditions. In contrast, a similar reaction of **4b** with **5** afforded 1,2-di-2-azulenylbenzene derivative **6b** in 51% yield. Cyclodehydrogenation reaction of **6b** with iron(III) chloride[16] and subsequent column chromatographic purification afforded the desired **3b** in 78% yield (Scheme 8). These novel azulene-fused naphthalene derivatives **3a**,**b** are stable, showing no decomposition even after several weeks at room temperature. The spectral features of **3a**,**b** are in agreement with the structure of these products.

Spectroscopic Properties. UV–vis spectra of **3a**,**b** and that of the precursor **6b** in dichloromethane are shown in Figure 1. The absorption maxima in the visible region were significantly influenced by the ring closure at the 1,1′-positions of the two azulene rings. The azulene-fused naphthalene derivatives **3a**,**b** exhibited the longest wavelength absorption up to 942 ($\log \epsilon$ 2.50) and 844 nm ($\log \epsilon$ 2.76), respectively. Comparison of the longest-wavelength absorption maximum of **3b** with that

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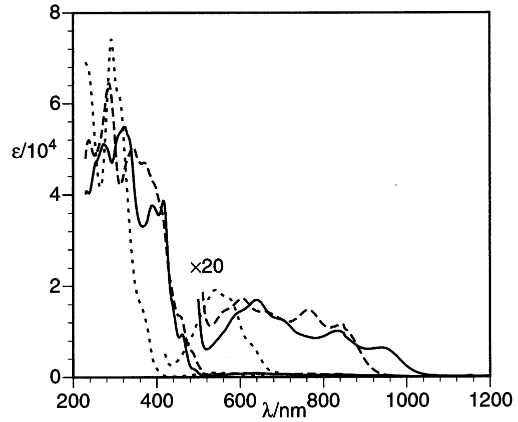
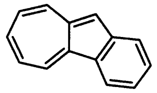


FIGURE 1. UV-vis spectra of **3a** (solid line), **3b** (broken line), and **6b** (dotted line) in dichloromethane.

CHART 2



19

of **6b** (539 nm (log ϵ 2.98)) showed a bathochromic shift by more than 300 nm. These results suggest that an apparent conjugation between the two azulene rings exists in **3a**,**b**, although the typical distortions could be expected for the two azulene rings.

The vicinal coupling constants on ^{1}H NMR allow us to estimate the degree of bond alternation of azulenes in a seven-membered ring.[17] The coupling constants of **3a**,**b** vary between 9.3−9.5 Hz across the formal C−C bonds and 9.9−10.3 Hz across the formal C═C bonds. These values indicate the existence of some bond alternation in the seven-membered ring of **3a**,**b**. However, the difference in the values between those for short and long bonds of **3a**,**b** is much smaller than those of benz[*a*]-azulene (**19**) in which the values in the seven-membered ring were reported as 10.9 and 11.1 Hz for the long bonds and 8.3 and 8.5 Hz for the short ones (Chart 2).[17b] These results could be concluded by less localization of the double bonds in **3a**,**b** compared with those in **19**.

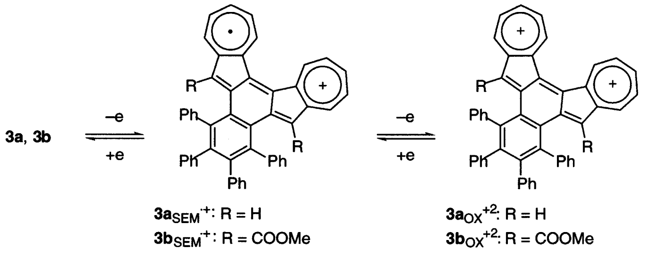
X-ray Structure Analysis. The crystal structure of **3a** was examined by X-ray crystallographic analysis. The ORTEP drawing of the molecular structure is shown in Supporting Information. The measurement was accomplished at −123 °C. The crystals of **3a** for the X-ray structure determination were prepared by slow evaporation of a solution in dichloromethane/hexane. The product **3a** crystallized in an orthorhombic cell with dichloromethane in a ratio of 1:1, space group *Pbcn*, and $Z = 8$. The final *R* was 0.11 for 2298 reflections. We presumed that the large *R* value is attributable to the fragility of the crystal resulting from the evolution of the incorporated dichloromethane molecules. Thus, a detailed discussion of the molecular geometry may be meaningless. However, the analysis revealed a large distortion between the two azulene rings. The dihedral angle between the two seven-membered rings in **3a** was 32.1°. In consideration of the large estimated standard deviations (esd), the two azulene rings in **3a** show an apparent alternating pattern of the bond lengths around the seven-membered rings. These results exhibit the tendency toward a localized heptafulvene substructure in the π-system of **3a** as expected from the vicinal coupling constants on ^{1}H NMR measurement.

TABLE 1. Redox Potentials[a] of the Compounds 3a,b, 6b, and 20a,b

sample	E_1^{ox}	E_2^{ox}	E_3^{ox}	E_1^{red}	E_2^{red}
3a	+0.22	+0.63	(+1.62)	(−1.62)	(−2.10)
3b	+0.46	+0.71	(+1.60)	(−1.45)	(−1.89)
6b	(+0.83)	(+1.86)		(−1.80)	(−1.92)
20a	(+0.30)	(+0.62)		(−1.88)	(−2.16)
20b	(+0.61)	(+0.87)		(−1.61)	(−1.83)

[a] The redox potentials were measured by CV (0.1 M Et_4NClO_4 in benzonitrile, Pt electrode, scan rate = 100 mV s^{-1}, and Fc/Fc$^+$ = +0.15 V). In the case of irreversible waves, which are shown 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.

SCHEME 9



Redox Properties. Redox potentials (V vs Ag/Ag$^+$) of the azulene-fused naphthalenes **3a**,**b** and the precursor **6b** measured by CV are summarized in Table 1. The compound **3a** showed a reversible two-step oxidation wave at the half-wave potentials of +0.22 and +0.63 V upon CV, which suggests a redox interaction between the two azulene rings (Figure 2a). The compound **3b** also showed a similar two-electron transfer at the potentials of +0.46 and +0.71 V (Figure 2b). These waves correspond to the formation of a radical cation and a closed-shell dication. The more positive oxidation potentials of **3b** compared with those of **3a** are attributable to the destabilization of the cations by the methoxycarbonyl groups substituted in the five-membered ring. Consequently, the redox system of **3a**,**b** could be depicted to be a violene and should exhibit a color change in different oxidation states, as illustrated in Scheme 9.

In contrast to the oxidation of **3a**,**b**, the benzene derivative **6b** exhibited an irreversible two-step oxidation wave at higher oxidation potentials by 0.37 V compared with the first one of **3b**. Therefore, the fusion of the two 2-azulenyl substituents on a benzene ring at the 1,1′-positions increased electron-donating properties because of the formation of a closed-shell dicationic structure $\mathbf{3}_{ox}^{+2}$.

The redox pattern of **3a**,**b** could be identical to those of 1,1′-biazulenes **20a**,**b** (Scheme 10).[18] To examine the effect of the ring fusion, **20a**,**b** were prepared by the modified procedure reported by Morita et al.[19] starting from methyl 3-iodoazulene-1-carboxylate,[20] as described

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[17] (a) Lu, Y.; Lemal, D. M.; Jasinski, J. P. *J. Am. Chem. Soc.* **2000**, *122*, 2440−2445. (b) Bühl, M.; Koźmiński, W.; Linden, A.; Nanz, D.; Sperandio, D.; Hansen, H.-J. *Helv. Chim. Acta* **1996**, *79*, 837−854. (c) Bertelli D. J.; Crews, P. *Tetrahedron* **1970**, *26*, 4717−4728.

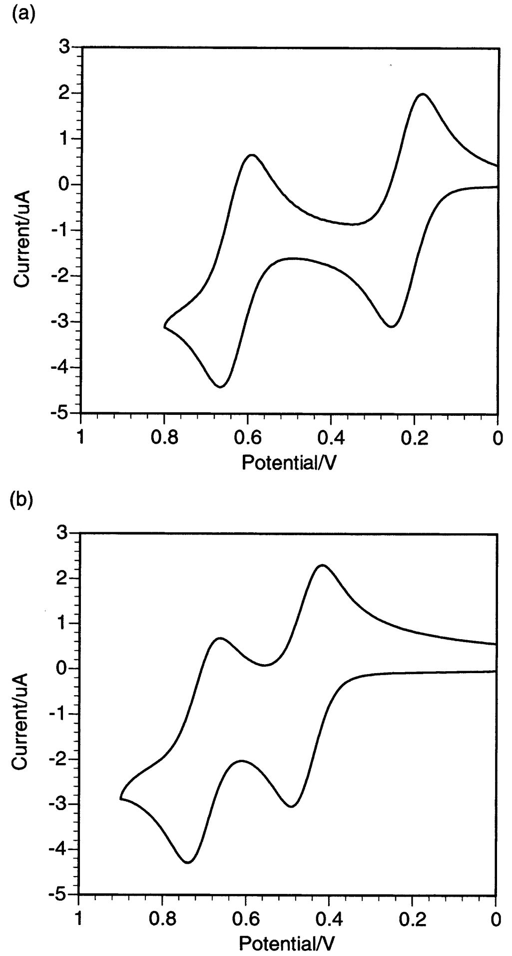
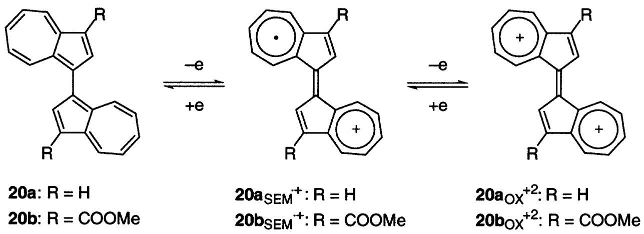


FIGURE 2. Cyclic voltammograms of (a) **3a** and (b) **3b** in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

SCHEME 10



in detail in the Supporting Information. The redox potentials of **20a**,**b** were measured under the same conditions for the measurement of **3a**,**b** (Table 1). The first oxidation potentials of **20a**,**b** were more positive by 0.08 and 0.15 V compared with the first ones of **3a**,**b**, respectively. Oxidation waves of **20a**,**b** exhibited poor reversibility except for the first oxidation wave of **20b**, although those of **3a**,**b** showed good reversibility upon CV. Thus, the fusion of the two azulene rings to naphthalene not only increases the electron-donating properties but also improves the stability of the cationic species in the electrochemical oxidation.

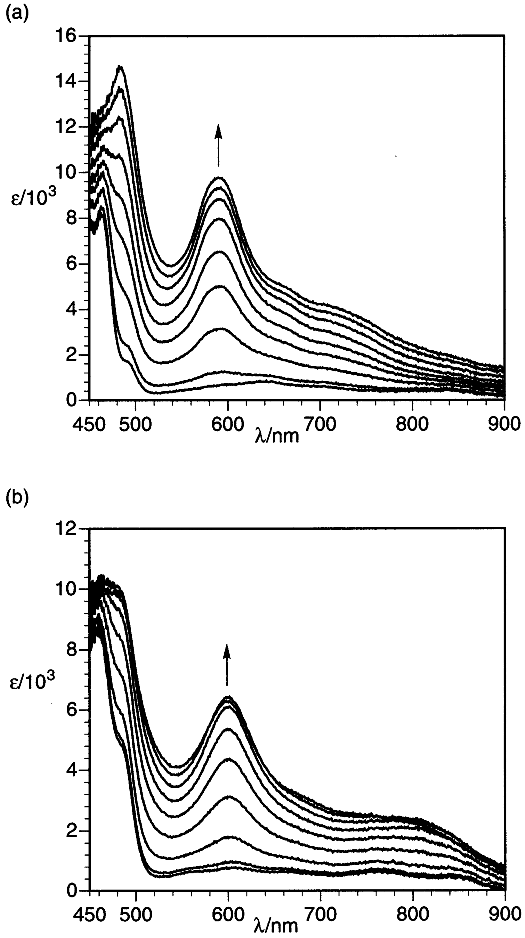


FIGURE 3. Continuous change in visible spectrum of (a) **3a** (2 mL; 1.0 × 10^{-3} M) and (b) **3b** (2 mL; 1.0 × 10^{-3} M) in benzonitrile containing Et_4NClO_4 (0.1 M) upon constant-current electrochemical reduction (100 uA) at 30 s interval.

The reduction of **3a**,**b** exhibited voltammograms that were characterized by two irreversible waves due to the reduction of two azulene rings to generate a dianionic species. The less negative reduction potentials of **3b** compared with those of **3a** are attributable to the methoxycarbonyl groups substituted in the five-membered ring. Similar to the poor reversibility of the reduction of **3a**,**b**, the reduction of the precursor **6b** also exhibited two irreversible waves upon CV. However, the first reduction potential of **6b** is apparently more negative by 0.35 V compared with that of **3b**. Thus, the fusion also increased the electron-accepting ability of the azulene rings.

Electrochromic Behavior. Electrochemical oxidation of **3a**,**b** was examined to clarify the formation of colored species arisen from radical cations **3a**$_{SEM}^{\bullet+}$ and **3b**$_{SEM}^{\bullet+}$ by UV−vis spectroscopy under the electrochemical oxidation conditions. When the visible spectra of **3a**,**b** were measured under the electrochemical oxidation conditions in benzonitrile containing Et_4NClO_4 (0.1 M) at room temperature, a new absorption in the visible region (**3a**, 591 nm; **3b**, 599 nm) was gradually developed as shown in Figure 3. The color of the solutions of **3a**,**b** gradually

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(18) Redox behavior of 1,1′-biazulenes, see: (a) Kurihara, T.; Suzuki, T.; Wakabayashi, H.; Ishikawa, S.; Shindo, K.; Shimada, Y.; Chiba, H.; Miyashi, T.; Yasunami, M.; Nozoe, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2003−2008. (b) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1959−1971. (c) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1936−1951.

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changed from green to deep green during the electrochemical oxidation. This change is accompanied with an increase of broad bands over 900 nm. From these bands, the observed spectral change could be attributed to a radical cationic species during the stepwise oxidation of **3a**,**b** under electrochemical oxidation as suggested by the CV measurement. The reverse reduction of the colored solution regenerated the UV−vis spectra of the neutral **3a**,**b**. The UV−vis measurement suggests the formation of a stable radical cationic species in solution. On further oxidation the new bands in the visible region gradually decreased accompanied with a decrement of the bands in the UV region. The color of the solutions of **3a**,**b** changed to brown and reddish-brown, respectively. Absence of the reversibility for the further oxidation suggests the instability of the dicationic species under the conditions of the UV−vis measurement, although good reversibility was observed upon CV.

Conclusion

We have demonstrated the Pd-catalyzed ethynylation of azulenes at the 2-position using 2-bromoazulenes (**7a** and **10a**). The novel azulene-fused naphthalene derivatives **3a**,**b** were prepared by Diels−Alder reaction of **4a**,**b** with **5** following the cyclodehydrogenation reaction via 1,2-di-2-azulenylbenzenes (**6a**,**b**). The redox behavior of **3a**,**b** examined by CV represented the presumed two-electron redox properties under the electrochemical oxidation conditions. Unfortunately, measurement of the UV−vis spectroscopy of **3a**,**b** under electrochemical oxidation conditions did not afford any evidence of the formation of the presumed dication **3a**$_{ox}^{+2}$ and **3b**$_{ox}^{+2}$ due to the instability of these species. However, we were able to reveal the formation of the colored radical cationic species **3a**$_{SEM}^{\bullet+}$ and **3b**$_{SEM}^{\bullet+}$ under the conditions of the UV−vis measurement.

Experimental Section

2-Bromoazulene (7a). A mixture of **9** (2.71 g, 18.8 mmol) and PBr_3 (2.8 mL, 29 mmol) in dry toluene (850 mL) was stirred at 90 °C for 2 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 20% ethyl acetate/hexane to afford **7a** (3.05 g, 78%) as violet plates: mp 106.8−107.2 °C (hexane) [lit.[9] mp 104.2−104.8 °C].

2-Iodoazulene (7b). A solution of **7a** (414 mg, 2.00 mmol), CuI (6.45 g, 33.9 mmol), and KI (11.6 g, 69.9 mmol) in DMF (20 mL) was refluxed for 16 h. After workup, the residue was purified by column chromatography on silica gel with 10% ethyl acetate/hexane to afford **7b** (482 mg, 95%) as violet plates: mp 122.0−122.5 °C (hexane) [lit.[10] mp 125−126 °C].

Methyl 2-Bromoazulene-1-carboxylate (10a). A mixture of **11a** (275 mg, 0.907 mmol) in 0.6 M NaOH in 50% aqueous ethanol (6 mL) was refluxed for 50 min. The reaction mixture was poured into water. The aqueous layer was washed with ether, acidified with 2 N HCl, and extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to afford 2-bromoazulene-1-carboxylic acid.[11] Treatment of the acid with excess diazomethane ethereal solution (15 mL) and purification by column chromatography on silica gel with 20% ethyl acetate/hexane afforded **10a** (238 mg, 99%) as purple needles: mp 70.3−70.8 °C (hexane); MS (70 eV; *m*/*z* (relative intensity)) 264 (M^+, 76), 233 ($M^+ - OCH_3$, 100), 126 ($M^+ - Br - CO_2CH_3$, 83); IR (KBr disk) ν_{max} 1694 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 238 (4.30), 297 (4.72), 308 (4.76), 354 (3.84), 520 (2.75) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, $J = 10.1$ Hz, 1H, H_8), 8.33 (d, $J = 9.8$ Hz, 1H, H_4), 7.81 (dd, $J = 10.1$, 9.6 Hz, 1H, H_6), 7.56 (dd, $J = 10.1$, 10.1 Hz, 1H, H_7), 7.47 (dd, $J = 9.8$, 9.6 Hz, 1H, H_5), 7.38 (s, 1H, H_3), 4.01 (s, 3H, 1-COOMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9 (s, 1-COOMe), 142.2 (C_{3a}), 140.8 (C_{8a}), 139.0 (C_6), 137.1 (C_8), 136.7 (C_4), 130.2 (C_2), 128.7 (C_7), 128.1 (C_5), 121.5 (C_3), 115.0 (C_1), 51.2 (q, 1-COOMe). Anal. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42, Br, 30.14. Found: C, 54.36; H, 3.61; Br, 30.04.

Methyl 2-(Trimethylsilylethynyl)azulene-1-carboxylate (12b). Trimethylsilylacetylene (**8**) (645 mg, 6.57 mmol) was added to a solution of **10a** (535 mg, 2.02 mmol), PPh_3 (54 mg, 0.21 mmol), CuI (48 mg, 0.25 mmol), and $PdCl_2(PPh_3)_2$ (71 mg, 0.10 mmol) in triethylamine (10 mL) and toluene (10 mL). The resulting mixture was stirred at room temperature for 2 h under an Ar atmosphere. After workup, the residue was purified by column chromatography on silica gel with 10% ethyl acetate/hexane to afford **12b** (571 mg, 100%) as violet needles: mp 86.0−86.1 °C (hexane); MS (70 eV; *m*/*z* (relative intensity)) 282 (M^+, 100), 267 ($M^+ - CH_3$, 49), 237 ($M^+ - 3CH_3$, 62); IR (KBr disk) ν_{max} 2151 (w, C≡C), 1676 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 239 (4.17), 256 (4.25), 269 (4.24), 311 (4.71), 322 (4.75), 355 (3.94), 372 (3.96), 384 (3.83), 576 (2.85) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, $J = 10.1$ Hz, 1H, $H_{8'}$), 8.32 (d, $J = 9.6$ Hz, 1H, $H_{4'}$), 7.73 (dd, $J = 9.9$, 9.9 Hz, 1H, $H_{6'}$), 7.53 (dd, $J = 10.1$, 9.9 Hz, 1H, $H_{7'}$), 7.42 (s, 1H, $H_{3'}$), 7.41 (dd, $J = 9.9$, 9.6 Hz, 1H, $H_{5'}$), 3.98 (s, 3H, 1′-COOMe), 0.33 (s, 9H, 1-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4 (s, 1′-COOMe), 143.0 ($C_{3'a}$), 141.4 ($C_{8'a}$), 139.3 ($C_{6'}$), 138.2 ($C_{8'}$), 138.0 ($C_{4'}$), 132.1 ($C_{2'}$), 128.6 ($C_{7'}$), 127.4 ($C_{5'}$), 123.2 ($C_{3'}$), 117.3 ($C_{1'}$), 105.4 (C_1), 102.5 (C_2), 50.9 (q, 1′-COOMe), 0.0 (1-TMS). Anal. Calcd for $C_{17}H_{18}O_2Si$: C, 72.30; H, 6.42. Found: C, 71.79; H, 6.43.

Methyl 2-Ethynylazulene-1-carboxylate (13b). A solution of KF (129 mg, 2.22 mmol) in water (2 mL) was added to a solution of **12b** (291 mg, 1.03 mmol) in DMF (10 mL). After the mixture was stirred at room temperature for 1.5 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 20% ethyl acetate/hexane to afford **13b** (213 mg, 98%) as violet plates: mp 98.5−99.0 °C (hexane); MS (70 eV; *m*/*z* (relative intensity)) 210 (M^+, 95), 179 ($M^+ - OCH_3$, 100), 151 ($M^+ - CO_2CH_3$, 21); IR (KBr disk) ν_{max} 3278, 3266 (s, C≡CH), 1686 (s, C=O) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 251 (4.27), 265 (4.20), 305 (4.71), 317 (4.77), 350 (3.88), 366 (3.94), 573 (2.84) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 9.55 (d, $J = 9.9$ Hz, 1H, H_8), 8.36 (d, $J = 9.6$ Hz, 1H, H_4), 7.77 (dd, $J = 10.1$, 9.7 Hz, 1H, H_6), 7.55 (dd, $J = 10.1$, 9.9 Hz, 1H, H_7), 7.46 (s, 1H, H_3), 7.44 (dd, $J = 9.7$, 9.6 Hz, 1H, H_5), 4.00 (s, 3H, 1-COOMe), 3.74 (s, 1H, 2-C≡CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2 (s, 1-COOMe), 142.9 (C_{3a}), 140.9 (C_{8a}), 139.6 (C_6), 138.5 (C_8), 138.3 (C_4), 131.4 (C_2), 128.5 (C_7), 127.5 (C_5), 123.6 (C_3), 117.5 (C_1), 86.7 (d, 2-C≡CH), 81.1 (s, 2-C≡CH), 51.2 (q, 1-COOMe). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.25; H, 4.84.

1,2-Di-2-azulenyl-2-hydroxyethanone (16). To a solution of **15** (500 mg, 3.20 mmol) in ethanol (100 mL) was added KCN (30 mg, 0.46 mmol) in water (15 mL). After the resulting mixture was stirred at room temperature for 1.5 h, the reaction mixture was diluted with water. Precipitated green crystals were collected by filteration with Celite and were dissolved in CH_2Cl_2. The dried organic layer was concentrated, and the residue was purified by column chromatography on silica gel with $CHCl_3$ to afford **16** (423 mg, 85%) as bluish green plates: mp 150−152 °C; MS (70 eV; *m*/*z* (relative intensity)) 312 (M^+, 2.6), 155 ($C_{10}H_7CO^+$, 100); IR (KBr disk) ν_{max} 1671 (C=O) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 4.59 (d, $J = 6.4$ Hz, 1H, 2-OH), 6.49 (d, $J = 6.4$ Hz, 1H, H_2), 7.12 (dd, $J = 9.6$, 9.6 Hz, 4H,

$H_{5',7'}$ and $H_{5'',7''}$), 7.39 (s, 2H, $H_{1',3'}$), 7.54 (dd, $J = 9.6$, 9.6 Hz, 2H, $H_{6'}$ and $H_{6''}$), 7.77 (s, 2H, $H_{1',3'}$), 8.23 (d, $J = 9.6$ Hz, 2H, $H_{4',8'}$), 8.36 (d, $J = 9.6$ Hz, 2H, $H_{4'',8''}$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 197.1, 149.6, 141.8, 141.6, 141.2, 140.7, 140.3, 137.5, 137.1, 124.3, 123.6, 118.8, 116.5, 74.3. Anal. Calcd for $C_{22}H_{16}O_2$; C, 84.59; H, 5.16. Found: C, 84.89; H, 5.32.

Di-2-azulenylethanedione (17). A mixture of **16** (81 mg, 0.26 mmol) and activated MnO_2 (113 mg, 1.30 mmol) in benzene (80 mL) was stirred at room temperature for 18 h. From the reaction mixture, excess MnO_2 was removed by filtration. The organic layer was concentrated and the residue was purified by column chromatography on silica gel with benzene to give **17** (73 mg, 91%) as green plates: mp 209−210 °C; MS (70 eV; *m*/*z* (relative intensity)) 310 (M^+, 9), 155 ($M^+/2$, 100), 127 ($C_{10}H_7^+$, 54); IR (KBr disk) ν_{max} 1652 ($C=O$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, $J = 9.8$ Hz, 4H, $H_{4',8'}$), 7.89 (s, 4H, $H_{1',3'}$), 7.68 (dd, $J = 9.8$, 9.8 Hz, 2H, $H_{6'}$), 7.19 (dd, $J = 9.8$, 9.8 Hz, 4H, $H_{5',7'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3 ($C_{1,2}$), 142.5 ($C_{4',8'}$), 141.8 ($C_{6'}$), 140.6 ($C_{3'a,8'a}$), 140.2 ($C_{2'}$), 124.5 ($C_{5',7'}$), 119.7 ($C_{1',3'}$). Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.32; H, 4.53.

Di-2-azulenylethanedione Dihydrazone (18). The ethanedione **17** (210 mg, 0.677 mmol) and 80% hydrazine monohydrate (340 mg, 5.4 mmol) in ethanol (16 mL) was refluxed for 3 days. After workup, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **18** (211 mg, 92%) as green plates: mp 202 °C dec.; MS (70 eV; *m*/*z* (relative intensity)) 338 (M^+, 60), 278 ($M^+ - N_4H_4$, 81), 127 ($C_{10}H_7^+$, 100); IR (KBr disk) ν_{max} 3380, 3320, 3265, 3170 (NNH_2) cm^{-1}. NMR data could not be obtained due to the low solubility. Anal. Calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36. Found: C, 78.25; H, 5.35.

Di-2-azulenylacetylene (4a), Method 1. To a degassed solution of **13a** (760 mg, 4.99 mmol), **7b** (1.27 g, 5.00 mmol), and CuI (96 mg, 0.50 mmol) in triethylamine (50 mL) and toluene (100 mL) was added $Pd(PPh_3)_4$ (288 mg, 0.249 mmol). The resulting mixture was stirred at room temperature for 1.5 h under an Ar atmosphere. After workup, the residue was purified by recrystallization from toluene to afford **4a** (1.34 g, 96%) as green needles.

Di-2-azulenylacetylene (4a), Method 2. The dihydrazone **18** (135 mg, 0.399 mmol) and copper(II) acetate monohydrate (319 mg, 1.60 mmol) in methanol (84 mL) and CH_2Cl_2 (35 mL) was stirred at room temperature for 20 h. After workup, the residue was purified by column chromatography on silica gel with toluene to afford **4a** (84 mg, 76%).

Compound 4a. Mp 252.0−257.0 °C dec.; MS (70 eV; *m*/*z* (relative intensity)) 278 (M^+, 100); Raman (Ar laser, 5145 Å) 2190 ($C\equiv C$) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 263 (4.51), 318 (4.97), 413 (4.62), 438 (4.78), 584 (3.02), 625 (2.99) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, $J = 9.5$ Hz, 4H, $H_{4',8'}$), 7.55 (t, $J = 9.9$ Hz, 2H, $H_{6'}$), 7.55 (s, 4H, $H_{1',3'}$), 7.19 (dd, $J = 9.9$, 9.5 Hz, 4H, $H_{5',7'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 ($C_{3'a,8'a}$), 137.6 ($C_{6'}$), 136.7 ($C_{4',8'}$), 130.5 ($C_{2'}$), 124.0 ($C_{5',7'}$), 120.8 ($C_{1',3'}$), 94.3 ($C_{1,2}$). Anal. Calcd for $C_{22}H_{14}$•0.5toluene: C, 94.41; H, 5.59. Found: C, 94.11; H, 5.18.

Bis(1-methoxycarbonyl-2-azulenyl)acetylene (4b). The same procedure used for the preparation of **4a** was adopted. The reaction of **13b** (106 mg, 0.504 mmol) with **10b** (157 mg, 0.503 mmol), CuI (13 mg, 0.068 mmol), and $Pd(PPh_3)_4$ (28 mg, 0.024 mmol) in triethylamine (5 mL) and toluene (10 mL) at 50 °C for 1 h followed by recrystallization from toluene afforded **4b** (165 mg, 83%) as green prisms: mp 234.0−234.3 °C; MS (70 eV; *m*/*z* (relative intensity)) 394 (M^+, 100), 363 ($M^+ - OCH_3$, 62), 348 ($M^+ - OCH_3 - CH_3$, 60); IR (KBr disk) ν_{max} 1682 (s, $C=O$) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 257 (4.43), 279 (4.25), 329 (4.85), 415 (4.54), 439 (4.70), 584 (3.37) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, $J = 10.1$ Hz, 2H, $H_{8'}$), 8.39 (d, $J = 9.6$ Hz, 2H, $H_{4'}$), 7.76 (dd, $J = 9.9$, 9.8 Hz, 2H, $H_{6'}$), 7.58 (s, 2H, $H_{3'}$), 7.57 (dd, $J = 10.1$, 9.8 Hz, 2H, $H_{7'}$), 7.45 (dd, $J = 9.9$, 9.6 Hz, 2H, $H_{5'}$), 4.07 (s, 6H, 1′-COOMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5 (s, 1′-COOMe), 143.2 ($C_{3'a}$), 141.6 ($C_{8'a}$), 139.3 ($C_{6'}$), 138.2 ($C_{8'}$), 138.1 ($C_{4'}$), 132.7 ($C_{2'}$), 128.6 ($C_{7'}$), 127.5 ($C_{5'}$), 123.2 ($C_{3'}$), 117.1 ($C_{1'}$), 97.6 ($C_{1,2}$), 51.3 (q, 1′-COOMe). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.47; H, 4.90.

Di-2-azulenyldiacetylene (14a). A solution of **13a** (51 mg, 0.34 mmol), $PdCl_2(PPh_3)_2$ (8.2 mg, 0.012 mmol), CuI (2.0 mg, 0.011 mmol), and triethylamine (1.5 mL) in toluene (3 mL) was stirred at room temperature for 1 h under an O_2 atmosphere. After workup, the residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford **14a** (35 mg, 69%) as green needles: mp 222.0−223.0 °C dec. (ethyl acetate/hexane); MS (70 eV; *m*/*z* (relative intensity)) 302 (M^+, 100); IR (KBr disk) ν_{max} 2186 (w, $C\equiv C$) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 266 (4.65), 317 (4.95), 407 (4.70), 443 (4.76), 587 (3.05), 629 (3.04) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, $J = 9.5$ Hz, 4H, $H_{4',8'}$), 7.56 (t, $J = 9.9$ Hz, 2H, $H_{6'}$), 7.50 (s, 4H, $H_{1',3'}$), 7.20 (dd, $J = 9.9$, 9.5 Hz, 4H, $H_{5',7'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 ($C_{3'a,8'a}$), 138.3 ($C_{6'}$), 137.2 ($C_{4',8'}$), 128.5 ($C_{2'}$), 124.3 ($C_{5',7'}$), 121.6 ($C_{1',3'}$), 82.4 ($C_{1,4}$), 80.2 ($C_{2,3}$). Anal. Calcd for $C_{24}H_{14}$•0.5toluene: C, 94.76; H, 5.21. Found: C, 94.67; H, 4.98.

Bis(1-methoxycarbonyl-2-azulenyl)diacetylene (14b). The same procedure used for the preparation of **14a** was adopted. The oxidation of **13b** (106 mg, 0.504 mmol) in the presence of $PdCl_2(PPh_3)_2$ (11 mg, 0.016 mmol), CuI (3.1 mg, 0.016 mmol), and triethylamine (2.5 mL) in toluene (5 mL) for 1.5 h followed by column chromatography on silica gel with 10% ethyl acetate/CH_2Cl_2 afforded **14b** (80 mg, 76%) as dark green prisms: mp 205.0−205.3 °C (toluene); MS (70 eV; *m*/*z* (relative intensity)) 418 (M^+, 100), 403 ($M^+ - CH_3$, 31), 178 (($M^+ - 2OCH_3$)/2, 24); IR (KBr disk) ν_{max} 1692 (s, $C=O$) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 270 (4.19), 335 (4.56), 383 (4.06), 409 (4.30), 446 (4.38), 553 (3.39), 584 (3.41) nm; ^1H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, $J = 9.9$ Hz, 2H, $H_{8'}$), 8.37 (d, 2H, $J = 9.3$ Hz, $H_{4'}$), 7.77 (dd, 2H, $J = 10.0$, 9.7 Hz, $H_{6'}$), 7.57 (dd, $J = 9.9$, 9.7 Hz, 2H, $H_{7'}$), 7.53 (s, 2H, $H_{3'}$), 7.45 (dd, $J = 10.0$, 9.3 Hz, 2H, $H_{5'}$), 4.05 (s, 6H, 1′-COOMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1 (s, 1′-COOMe), 143.1 ($C_{3'a}$), 141.4 ($C_{8'a}$), 139.9 ($C_{6'}$), 138.6 ($C_{8'}$), 138.5 ($C_{4'}$), 130.8 ($C_{2'}$), 128.8 ($C_{7'}$), 127.7 ($C_{5'}$), 124.1 ($C_{3'}$), 117.9 ($C_{1'}$), 83.8 ($C_{2,3}$), 83.1 ($C_{1,4}$), 51.4 (q, 1′-COOMe). Anal. Calcd for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34. Found: C, 80.55; H, 4.45.

7,8,9,10-Tetraphenyldiazuleno[2,1-*a*:1,2-*c*]naphthalene (3a). A solution of **4a** (418 mg, 1.50 mmol) and **5** (4.03 g, 10.5 mmol) in diphenyl ether (33 mL) was stirred at 160 °C for 20 h under an Ar atmosphere. The reaction mixture was purified by column chromatography on silica gel with hexane and 50% CH_2Cl_2/hexane and GPC with $CHCl_3$ to afford the recovered **4a** (69 mg, 17%) and **3a** (373 mg, 47%) as ocher needles: mp 293.9−295.0 °C dec. (toluene); MS (70 eV; *m*/*z* (relative intensity)) 632 (M^+, 100); UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 273 (4.71), 323 (4.74), 388 (4.58), 416 (4.59), 461 (3.97), 639 (2.93), 831 (2.70), 942 (2.50) nm; ^1H NMR (600 MHz, $CDCl_3 + Et_3N$) δ 9.28 (d, $J = 9.3$ Hz, 2H, $H_{8'}$), 7.96 (d, $J = 9.9$ Hz, 2H, $H_{4'}$), 7.49 (dd, $J = 10.2$, 9.3 Hz, 2H, $H_{6'}$), 7.31−7.28 (m, 10H, $H_{2'',3'',4'',5''}$), 7.10 (dd, $J = 10.2$, 9.3 Hz, 2H, $H_{7'}$), 6.98 (dd, $J = 9.9$, 9.3 Hz, 2H, $H_{5'}$), 6.91−6.88 (m, 6H, $H_{3''',4''',5'''}$), 6.83−6.82 (m, 4H, $H_{2''',6'''}$), 6.41 (s, 2H, $H_{3'}$); ^{13}C NMR (150 MHz, $CDCl_3 + Et_3N$) δ 142.6 ($C_{3,6}$ or $C_{1''}$), 140.9 ($C_{2'}$), 140.8 ($C_{1'''}$), 140.4 ($C_{4,5}$), 139.5 ($C_{1''}$ or $C_{3,6}$), 137.7 ($C_{4'}$), 137.5 ($C_{3'a}$), 137.4 ($C_{6'}$), 134.3 ($C_{8'a}$), 134.1 ($C_{8'}$), 131.8 ($C_{2'',6''}$), 131.5 ($C_{2''',6'''}$), 129.1 ($C_{1,2}$), 128.2 ($C_{3'',5''}$), 126.8 ($C_{4''}$), 126.6 ($C_{3''',5'''}$), 125.3 ($C_{4'''}$), 123.4 ($C_{1'}$), 122.3 ($C_{5'}$ and $C_{7'}$), 118.3 ($C_{3'}$). Anal. Calcd for $C_{50}H_{32}$: C, 94.90; H, 5.10. Found: C, 94.60; H, 5.26.

1,2-Bis(1-methoxycarbonyl-2-azulenyl)-3,4,5,6-tetraphenylbenzene (6b). The same procedure used for the preparation of **3a** was adopted. The reaction of **4b** (198 mg, 0.502 mmol) with **5** (1.36 g, 3.54 mmol) in diphenyl ether (11 mL) for 2 days followed by column chromatography on silica gel with hexane and CH_2Cl_2 and GPC with $CHCl_3$ afforded **6b** (192 mg, 51%) as purple prisms: mp 161.0−161.7 °C (ethyl acetate); MS (FAB; *m*/*z* (relative intensity)) 750 (M^+, 100), 719

($M^+ - OCH_3$, 42), 691 ($M^+ - CO_2CH_3$, 36), 632 ($M^+ - 2CO_2CH_3$, 62), 630 ($M^+ - 2CO_2CH_3$, 23); IR (KBr disk) ν_{max} 1694 (s, C═O) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 231 (4.84), 292 (4.87), 539 (2.98) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, $J = 10.0$ Hz, 2H, $H_{8'}$), 7.94 (d, $J = 9.5$ Hz, 2H, $H_{4'}$), 7.43 (dd, $J = 9.9$, 9.7 Hz, 2H, $H_{6'}$), 7.15 (dd, $J = 10.0$, 9.9 Hz, 2H, $H_{7'}$), 7.08 (dd, $J = 9.7$, 9.5 Hz, 2H, $H_{5'}$), 6.94 (s, 2H, $H_{3'}$), 6.88−6.81 (m, 12H, $H_{6''}$ and $H_{2'''-6'''}$), 6.77 (d, $J = 7.6$ Hz, 2H, $H_{2''}$), 6.74 (ddd, $J = 7.7$, 7.4, 1.1 Hz, 2H, $H_{5''}$), 6.70 (ddt, $J = 7.4$, 7.3, 1.3 Hz, 2H, $H_{4''}$), 6.65 (ddd, $J = 7.6$, 7.3, 1.1 Hz, 2H, $H_{3''}$), 3.83 (s, 6H, 1′-COOMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7 (s, 1′-COOMe), 154.6 ($C_{2'}$), 141.7 ($C_{3'a}$), 140.8 (s), 140.5 (s), 139.9 ($C_{8'a}$), 139.6 (s), 139.1 (s), 137.2 ($C_{6'}$), 136.8 ($C_{4'}$), 136.6 ($C_{1,2}$), 136.3 ($C_{8'}$), 131.8 (d), 131.6 (d), 131.0 (d), 130.8 ($C_{2''}$), 126.8 ($C_{7'}$), 126.5 (d), 126.3 ($C_{5''}$), 126.1 ($C_{3''}$), 126.0 ($C_{5'}$), 125.2 ($C_{4''}$), 125.0 (d), 122.0 ($C_{3'}$), 116.9 ($C_{1'}$), 50.7 (q, 1′-COOMe). Anal. Calcd for $C_{54}H_{38}O_4{\cdot}0.5H_2O$: C, 85.35; H, 5.17. Found: C, 85.62; H, 5.17.

6,11-Bis(methoxycarbonyl)-7,8,9,10-tetraphenyldiazuleno[2,1-*a*:1,2-*c*]naphthalene (3b). To a solution of **6b** (95 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was added a solution of $FeCl_3$ (219 mg, 1.35 mmol) in nitromethane (2 mL). The resulting mixture was stirred at room temperature for 35 min. After an addition of methanol and water to the reaction mixture, the resulting mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to afford a mixture (16:1) of **3b** and the recovered **6b** (75 mg, 78 and 5%, respectively). The naphthalene **3b** (47 mg, 52%) was isolated by recrystallization from CH_2Cl_2/ethyl acetate as green needles: mp > 300 °C; MS (FAB; *m*/*z* (relative intensity)) 748 (M^+, 100), 717 ($M^+ - OCH_3$, 21); IR (KBr disk) ν_{max} 1705 (s, C═O) cm^{-1}; UV−vis (CH_2Cl_2; λ_{max} (log ϵ)) 237 (4.71), 286 (4.81), 343 (4.70), 369 (4.67), 604 (2.94), 764 (2.87), 844 (2.76) nm; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.43 (d, $J = 9.5$ Hz, 2H, $H_{8'}$), 8.76 (d, $J = 10.3$ Hz, 2H, $H_{4'}$), 7.70 (dd, $J = 10.1$, 9.4 Hz, 2H, $H_{6'}$), 7.37 (dd, $J = 10.1$, 9.5 Hz, 2H, $H_{7'}$), 7.32 (dd, $J = 10.3$, 9.4 Hz, 2H, $H_{5'}$), 7.08 (tt, $J = 7.1$, 1.4 Hz, 2H, $H_{4''}$ or $H_{4'''}$), 7.03−6.95 (m, 14H, Ph), 6.73 (dd, $J = 7.1$, 1.4 Hz, 4H, $H_{2''',6'''}$ or $H_{2'',6''}$), 3.61 (s, 6H, 3′-COOMe); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8 (s, 3′-COOMe), 141.9 ($C_{2'}$), 140.5 (s), 140.3 (s), 139.6 (s), 138.5 ($C_{6'}$), 138.4 (s), 138.3 ($C_{3'a}$), 136.3 ($C_{8'a}$), 135.9 ($C_{4'}$), 135.2 ($C_{8'}$), 134.7 ($C_{2'',6''}$ or $C_{2''',6'''}$), 131.6 ($C_{2''',6'''}$ or $C_{2'',6''}$), 130.6 ($C_{1,2}$), 126.9 ($C_{3'',5''}$ and $C_{3''',5'''}$), 126.4 ($C_{5'}$ and $C_{4''}$ or $C_{4'''}$), 125.6 ($C_{4'''}$ or $C_{4''}$), 125.0 ($C_{7'}$), 122.5 ($C_{1'}$), 117.9 ($C_{3'}$), 51.5 (q, 3′-COOMe). Anal. Calcd for $C_{54}H_{36}O_4{\cdot}0.5H_2O$: C, 85.58; H, 4.92. Found: C,85.75; H, 5.05.

Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of **3b**, **6b**, **12b**, **13b**, and **14a** and CV data of **4a**,**b** and **14a**,**b**, tables listing single-crystal X-ray data for **3a**, and text describing experimental details and characterization data for **10b**, **11a**,**b**, **12a**, **13a**, and **20a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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