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Efficient synthesis and redox behavior of a series of 6-alkyl-2-phenylazulenes

Shunji Ito *, Mao Ueda, Ryuta Sekiguchi, Jun Kawakami

Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

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ABSTRACT

Three new members of 6-alkyl-2-phenylazulene (*n*PA with *n* being the number of carbon atoms in the 6-alkyl chain) homologous series, **3a** (*n*=4), **3b** (*n*=6), and **3d** (*n*=10), expected to show smectic E (SmE) phase as a mesophase below fusion, has been synthesized by $Pd(PPh_3)_4$ catalyzed Suzuki–Miyaura cross-coupling reaction of the corresponding 6-alkyl-2-bromoazulenes. The redox behavior of **3a**, **3b**, and **3d** including that of their 6-octyl and 6-hexadecyl derivatives **3c** (*n*=8) and **3e** (*n*=16), the synthesis was reported previously, was studied in detail by voltammetric and electrochromic analyses. As the results, amphoteric redox properties with a significant color change were revealed by the *n*PA homologous series **3a**–**e**, which would be attracted to the application for the device fabrication of the molecular materials.

1. 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] Amphoteric redox properties of the azulene derivatives are especially attractive to construct advanced materials for electronic applications. However, to date, molecules with potentially useful electronic properties constructed from azulene derivatives are fairly scarce. Spontaneous or controllable alignment of molecules on a substrate is an important factor for device fabrication of molecular materials.[2] Smectic mesophases, such as smectic E, B, and H (SmE, SmB, and SmH) have positional order, and show no fluidity in contrast to the liquid crystal phase, such as nematic mesophase. Some liquid crystalline semiconductors utilizing the ordered smectic mesophase are recently found to show very fast carrier mobility.[3] Thus, the stacking behavior of the liquid crystal phases may provide opportunities for materials with one-dimensional transport processes, such as energy migration, electric conductivity, and photoconductivity.[4]

The SmE phase has a layered structure with a 'herring bone' ordering of the molecules. One of the mesogenic series showing the SmE phase is a series of 4-alkyl-4′-isothiocyanatobiphenyls (*n*TCB with *n* being the number of carbon atoms in the 4-alkyl chain).[5] However, the highly ordered SmE phase is restricted to a few classes of substances.

Substituted azulene derivatives linked to nematogenic alkylcyclohexanes by an ester function have been reported in the literature to show nematic or smectic mesomorphisms.[6] Recently, we have also reported the synthesis of the first azulene derivatives (**1**, **2a**, and **2b**) exhibiting discotic liquid crystalline behavior (Fig. 1).[7] Novel hexakis(6-octyl-2-azulenyl)benzene (**2a**) surrounding six octyl groups exhibits the columnar mesophases, Col_{ho}, with unusually large staking distances (*h*=5.20–5.52 Å), probably due to the propeller conformation of the molecule.[8] Spontaneous uniform hometropic alignment on non-treated glass substrate is established in the Col_{hd} phase by the elongation of the six alkyl chains surrounding, hexakis(6-hexadecyl-2-azulenyl)benzene (**2b**), so far.[9]

During the way to explore the azulene derivatives with liquid crystalline behavior, we have recently reported the 6-alkyl-2-phenylazulene (abbreviated as *n*PA in this paper with *n* being the number of carbon atoms in the 6-alkyl chain) homologous series (*8*PA **3c** and *16*PA **3e**) showed only SmE phase as a mesophase below fusion (Fig. 2).[8,9] The *n*PA molecules have simple structures composed of azulene core, phenyl group, and alkyl chain. The molecular difference of the *n*PA series from *n*TCB series is in polar groups. The phase behavior of all hydrocarbon derivatives, *n*PA series, will open the possibility to study the nature of SmE phase in detail over a wide temperature range. Details of the investigation of the SmE phase in *8*PA **3c** have been reported, recently.[10]

Herein, we report efficient synthetic procedure of the three new members of 6-alkyl-2-phenylazulene homologous series [*n*PAs **3a** (*n*=4), **3b** (*n*=6), and **3d** (*n*=10)], which are expected to show SmE mesomorphism, to investigate the influence of the peripheral side chains in length, to better understand the SmE phase and the electrochemical properties in the *n*PA homologous series.[11] The redox properties of *8*PA **3c** have been examined by cyclic

* Corresponding author. Tel.: +81 172 39 3568; fax: +81 172 39 3541; e-mail address: itsnj@cc.hirosaki-u.ac.jp (S. Ito).

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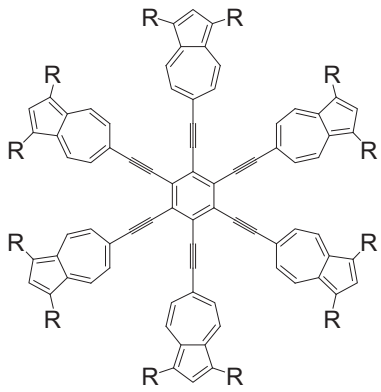
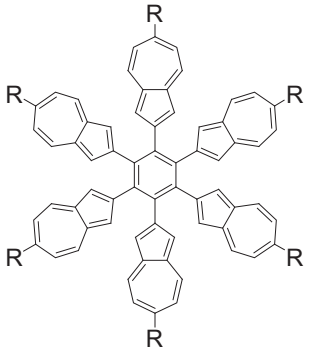
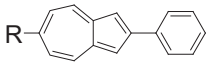


1: R = $COOC_6H_{13}$



2a: R = C_8H_{17}
2b: R = $C_{16}H_{33}$

Fig. 1. Azulene derivatives (**1**, **2a**, and **2b**) exhibiting discotic liquid crystalline behaviors.



3a: R = C_4H_9
3b: R = C_6H_{13}
3c: R = C_8H_{17}
3d: R = $C_{10}H_{21}$
3e: R = $C_{16}H_{33}$

Fig. 2. 6-Alkyl-2-phenylazulenes (*n*PAs **3a**–**e**).

voltammetry (CV) in *o*-dichlorobenzene containing Et_4NClO_4 (0.1 M) as a supporting electrolyte, however, the comparative study should clarify the redox behavior of these *n*PA homologous series **3a**–**e**. We also report, herein, the details of the redox behavior of these *n*PA homologous series **3a**–**e** examined by voltammetric and electrochromic analyses.

2. Results and discussion

2.1. Synthesis

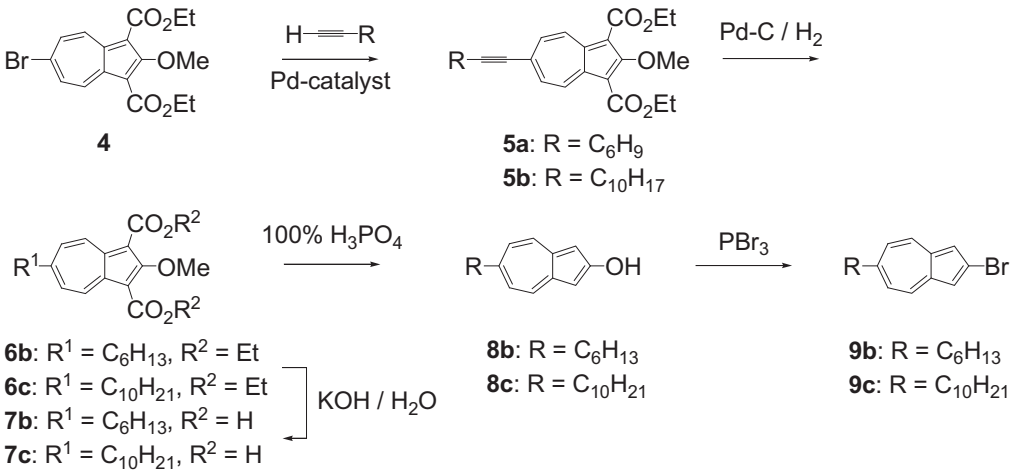
Preparation of the 6-hexyl and 6-decyl derivatives *6*PA **3b** and *10*PA **3d** was easily established by the application of the synthetic procedure similar to that of 6-octyl and 6-hexadecyl derivatives *8*PA **3c** and *16*PA **3e**, reported, previously.[8,9] Preparation of *6*PA **3b** and *10*PA **3d** via **9b** and **9c**, respectively, commenced with diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**);[8,12] it is outlined in Schemes 1 and 2. Pd-catalyzed cross-coupling reaction of **4** with 1-hexyne and 1-decyne under Sonogashira–Hagihara conditions afforded diethyl 6-hexynyl- and 6-decynyl-2-methoxyazulene-1,3-dicarboxylates (**5a** and **5b**) in 85% and 87% yields, respectively. Catalytic hydrogenation of **5a** and **5b** utilizing Pd–C catalyst produced reduced products **6b** and **6c** in 90% and 94% yields, respectively. Two ethyl ester parts of **6b** and **6c** were hydrolyzed under basic conditions to give **7b** and **7c**, following the treatment of **7b** and **7c** with 100% H_3PO_4, which was freshly prepared by dissolving phosphorous(V) oxide in 85% phosphoric acid, afforded 2-hydroxy derivatives **8b** and **8c** in 49% and 58% yields in two steps, respectively. The products **8b** and **8c** were transformed into 2-bromo derivatives **9b** and **9c** by the treatment with PBr_3 in 73% and 58% yields, respectively.

6-Hexyl- and 6-decyl-2-phenylazulenes (**3b** and **3d**) were prepared by the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of **9b** and **9c** with phenyl boronic acid in 76% and 68% yields, respectively (Scheme 2). The spectral features of *6*PA **3b** and *10*PA **3d** are in agreement with the structure of these products as summarized in the Experimental section.

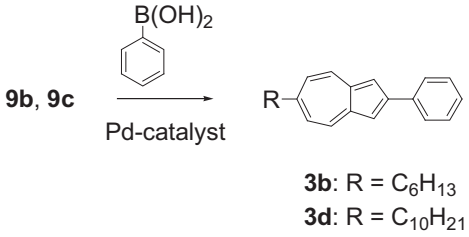
Extension of the procedure to the preparation of 6-butyl-2-phenylazulene (**3a**) requires 1-butyne (bp=8 °C) as a reagent for the starting Sonogashira–Hagihara cross-coupling reaction with bromide **4**. However, we found the Pd-catalyzed cross-coupling reaction of **4** with butylzinc bromide at 50 °C for 30 min under Negishi cross-coupling conditions to afford diethyl 6-butyl-2-methoxyazulene-1,3-dicarboxylate (**6a**) in 71% yield, directly, although it is well known that 2-methoxyazulene derivatives with 1,3-diester functions readily react with organometallic reagents, such as Grignard and lithium reagents, to afford 2-alkyl azulene derivatives (Scheme 3).[13] The procedure produces the desired 6-alkyl derivative **6a**, efficiently, but the reaction provides a small amount of undesired diethyl 6-butyl-2-butoxyazulene-1,3-dicarboxylate (**10**) in 14% yield. However, the procedure may have advantage over the Sonogashira–Hagihara cross-coupling route for the preparation as illustrated in Scheme 1, because the present procedure reduces the catalytic hydrogenation step to obtain the 6-alkyl derivative **6a**.

Formation of the OMe–OBu exchange product **10** by the Pd-catalyzed Negishi cross-coupling reaction of **4** roused our curiosity, although the desired product **6a** was obtained in satisfactory yield for further transformation. To obtain the aspect for the exchange reaction we have firstly examined the effect of the amount of the butylzinc reagent employed. As the results, by increasing the amount of butylzinc reagent up to 4.4 equiv the reaction at 55 °C for 1 h yielded the exchange product **10** in 46% yield, along with **6a** in 32% yield. The starting material **4** was pure enough to exclude the contamination of the hydroxy compound, diethyl 6-bromo-2-hydroxyazulene-1,3-dicarboxylate, which may act as the precursor for the exchange product **10**. Thus, the formation of **10** implies the cleavage of the O–Me bond of **4** under the reaction conditions in any way.

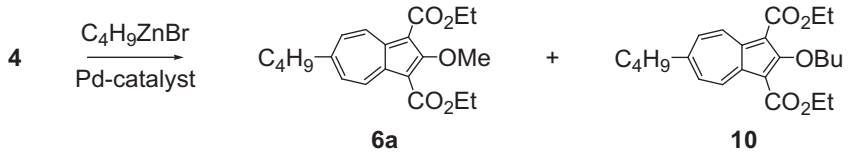
Although the secondary and tertiary alkylzinc reagents are known to exhibit isomerization during the Negishi cross-coupling reaction, we anticipated the reaction with the higher zinc reagents might produce O–Me bond cleaved products instead of the exchange product owing to the steric reasons. However, the Pd-catalyzed cross-coupling reaction of **4** with the secondary alkylzinc reagent, 1-propylbutylzinc bromide, under the Negishi cross-coupling conditions to afford only an inseparable 77:23 mixture of diethyl 6-(1-propylbutyl)-2-methoxyazulene-1,3-dicarboxylate (**11**) and diethyl 6-(1-ethylpentyl)-2-methoxyazulene-1,3-dicarboxylate (**12**) in 79% yield (Scheme 4). Contrary to the



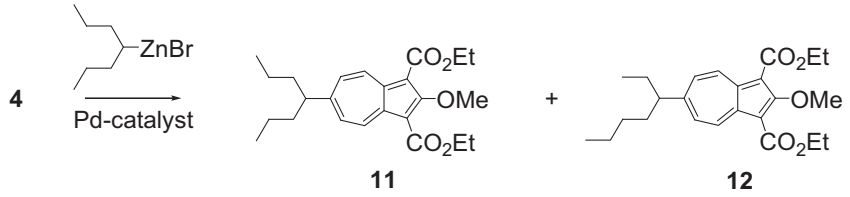
Scheme 1. Preparation of 6-hexyl- and 6-decyl-2-bromoazulenes (**9b** and **9c**).



Scheme 2. Preparation of 6-hexyl- and 6-decyl-2-phenylazulenes (**3b** and **3d**).



Scheme 3. Negishi cross-coupling reaction of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) with butylzinc bromide.



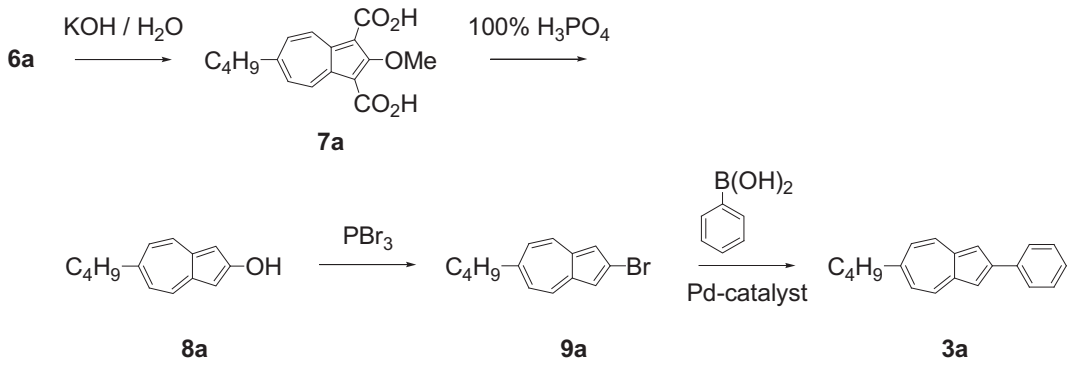
Scheme 4. Negishi cross-coupling reaction of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) with 1-propylbutylzinc bromide.

expectation the O–Me bond cleaved products and also the corresponding exchange product were not obtained in this case at all. Thus, formation of the OMe–OBu exchange product **10** would be concluded to the participation of some transition-metal catalyzed reaction. The azulene nuclei with two ester groups may operate as a good electron-withdrawing group for the Pd-catalyzed oxidative addition reaction. Thus, there is a possibility that the azulene functional group will act as an effective functional group for the transition-metal-catalyzed reaction.

Two ethyl ester parts of **6a** was hydrolyzed under basic conditions to give **7a**, following the treatment of **7a** with freshly prepared 100% H_3PO_4 afforded 2-hydroxy derivative **8a** in 64% yield in two steps (Scheme 5). The product **8a** was also transformed into 2-bromo derivative **9a** by the treatment with PBr_3 in 70% yield. 6-Butyl-2-phenylazulene (**3a**) was obtained by the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of **9a** with phenyl boronic acid in 79% yield. The spectral features of *4*PA **3a** are also in agreement with the structure of the compound as summarized in the Experimental section.

2.2. Spectroscopic properties

Mass spectrum of *n*PAs **3a** (n=4), **3b** (n=6), and **3d** (n=10) measured by ESI-TOF conditions showed correct $M+H^+$ ion peaks, which afford a criterion of the structure of these compounds. The typical examples of UV and visible spectra of **3d**, **8c**, and **9c** in



Scheme 5. Preparation of 6-butyl-2-phenylazulene (**3a**).

dichloromethane are shown in Fig. 3, the rest is summarized in the Supplementary data. The absorption spectra of the newly prepared compounds are quite similar with those of their 6-octyl and 6-hexadecyl derivatives. *n*PAs **3a** (n=4), **3b** (n=6), and **3d** (n=10) showed the characteristic weak absorption of the azulene system in the visible region at 562 nm (log ε 2.58), 562 nm (log ε 2.62), and 562 nm (log ε 2.56), respectively. The longest absorption maximum of *n*PAs **3a** (n=4), **3b** (n=6), and **3d** (n=10) in the visible region exhibits a slight red shift by 23 nm, 25 nm, and 25 nm, respectively, relative to those of 2-bromo derivatives **9a** (λ_{max}=539 nm), **9b** (λ_{max}=537 nm), and **9c** (λ_{max}=537 nm) probably because of the electron-withdrawing nature of the substituted halogen atom. The absorption spectra of 2-hydroxy derivatives **8a**, **8b**, and **8c** in dichloromethane are quite different from azulene derivatives because of the keto–enol tautomerisms in solution depending on the solvent polarity.[14] The NMR spectra of **8c** in $CDCl_3$ represent the existence of their keto forms (keto–enol ratio=92:8) in the solvent, whereas in acetone-d_6 the equilibrium changed to their enol forms as shown the spectra in the Supplementary data. Therefore, the difference in the absorption spectra of the hydroxyl derivatives is supposed by their tautomerisms depending on the solvent polarities. We found that the keto–enol ratios of these compounds **8a** (3:97), **8b** (18:82), and **8c** (18:82) depends on the length of 6-alkyl chain substituted in acetone-d_6. These changes should be caused by the effect of the substituted alkyl chains.

2.3. Redox properties

To clarify the electrochemical property, the redox behavior of *n*PAs **3a**–**e** was examined by CV and differential pulse voltammetry (DPV) in benzonitrile containing tetraethylammonium perchlorate (0.1 M) as a supporting electrolyte. Measurements were made by using a standard three electrode configuration as platinum wire auxiliary and disk working electrodes. All measurements were carried out an argon atmosphere and potentials were related to a standard $Ag/AgNO_3$ reference electrode. Half-wave potential of ferrocene–ferrocenium couple (Fc/Fc^+) under the conditions using this reference electrode is observed at +0.15 V on CV.

Redox potentials (in volts vs $Ag/AgNO_3$) of *n*PAs **3a**–**e** are summarized in Table 1. The typical CV waves of *n*PA **3d** are shown in Fig. 4 and the other data for the *n*PAs **3a**–**e** are summarized in the Supplementary data. The redox properties essentially did not depend on the length of the 6-alkyl chain substituted. These compounds exhibited a reversible reduction wave on CV at −1.91 V to −1.94 V. The E_1^{red} wave should correspond to the one-electron injection forming a radical anionic species. The reversibility on the CV wave should be attributed to the stabilization of the radical anionic species by the 2-azulenyl substituent.

The oxidation of *n*PAs **3a**–**e** showed an irreversible oxidation wave on CV at 0.72 V–0.76 V. The irreversibility should be ascribed to the electron removal from the 2-azulenyl group forming a radical cationic species with high reactivity. The DPV analysis revealed the existence of two further oxidation waves that should correspond to the formation of higher electronic states as summarized in Table 1.

2.4. Electrochromic analysis

To obtain the aspect for the redox species, the electrochemical reduction and oxidation of *n*PAs **3a**–**e** was conducted by visible spectral monitoring. Constant-current reduction and oxidation were applied to the solutions of *n*PAs **3a**–**e** with a platinum mesh as

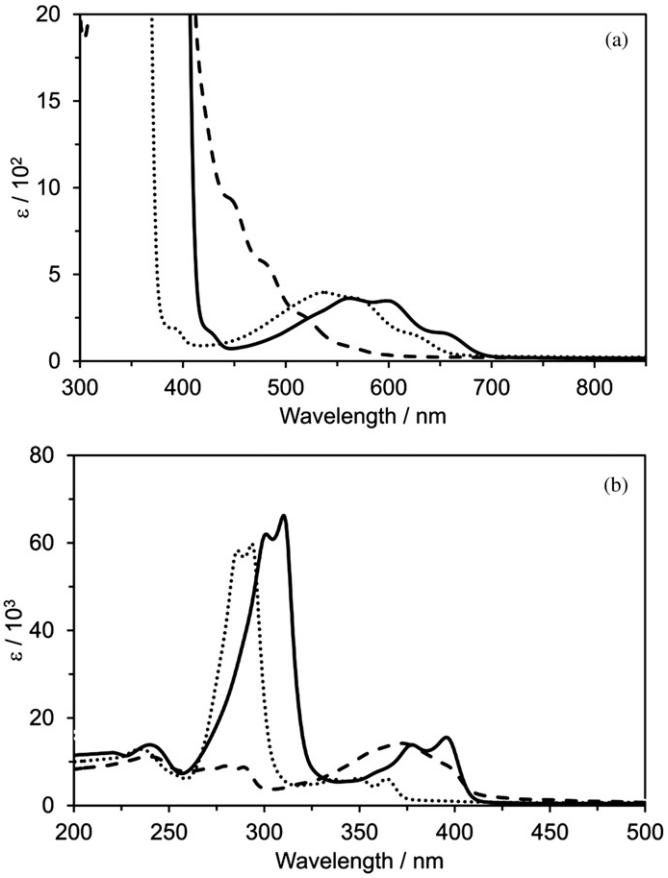


Fig. 3. UV/vis spectra of *10*PA **3d** (solid line), **8c** (broken line), and **9c** (dotted line) in dichloromethane: (a) visible and (b) UV–vis regions.

Table 1
Redox potentials of the *n*PA homologous series **3a**–**e** measured by CV and DPV[a]

Sample	E_1^{red} [V]	E_1^{ox} [V]	E_2^{ox} [V]	E_3^{ox} [V]
*4*PA **3a**	−1.92	(+0.75)		
DPV[b]	*−1.90*	*+0.64*	*+0.84*	*+1.78*
*6*PA **3b**	−1.93	(+0.72)		
DPV[b]	*−1.90*	*+0.63*	*+0.83*	*+1.77*
*8*PA **3c**	−1.91	(+0.76)		
DPV[b]	*−1.90*	*+0.65*	*+0.82*	*+1.79*
*10*PA **3d**	−1.94	(+0.72)		
DPV[b]	*−1.91*	*+0.64*	*+0.82*	*+1.76*
*16*PA **3e**	−1.92	(+0.74)		
DPV[b]	*−1.91*	*+0.67*	*+0.81*	*+1.79*

[a] The redox potentials were measured by CV and DPV [V versus $Ag/AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (i.d., 1.6 mm), scan rate 100 mV s^{-1} and Fc/Fc^+=+0.15 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 V and E_{pc} (cathodic peak potential)+0.03 V, respectively.
[b] The values are peak potentials measured by DPV.

the working electrode and a wire counter electrode, and visible spectra were measured in benzonitrile containing Et_4NCO_4 (0.1 M) as a supporting electrolyte at room temperature under the electrochemical redox conditions. The visible spectral changes of *10*PA **3d** under electrochemical redox conditions are shown in Fig. 5. The other data for the visible spectral changes of *n*PAs **3a**–**e** are summarized in the Supplementary data. The blue color of the solution of *10*PA **3d** gradually changed to yellow during the electrochemical reduction. Accordingly, a new absorption band in the visible region gradually developed during the electrochemical reduction (Fig. 5a). Observed color change should be ascribed to the formation of

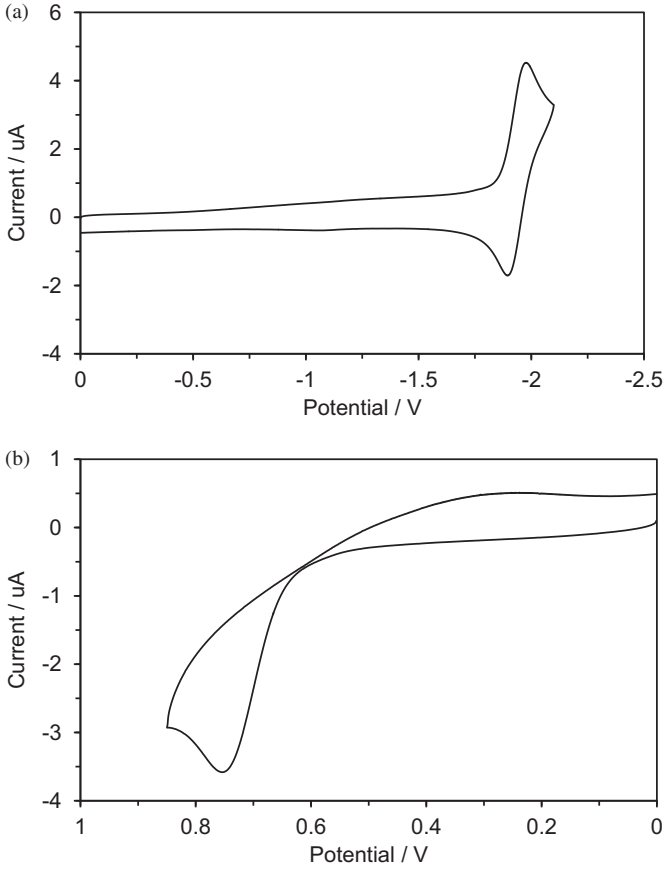


Fig. 4. CV waves of *10*PA **3d** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte: (a) reduction wave and (b) oxidation wave.

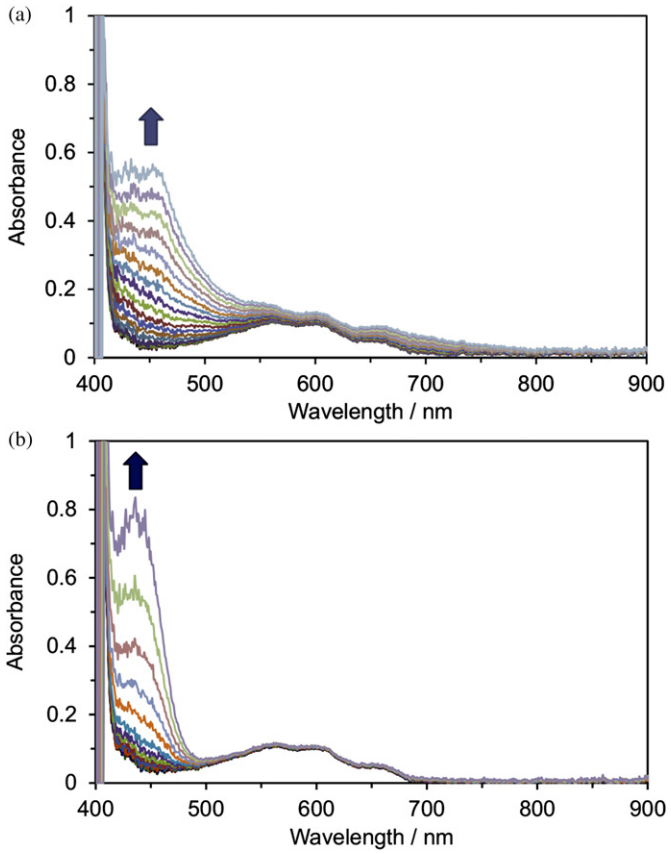


Fig. 5. Continuous change in visible spectra of *10*PA **3d**: (a) constant-current electrochemical reduction (100 μA, 1 min intervals) and (b) constant-current electrochemical oxidation (100 μA, 1 min intervals) in benzonitrile (2 mL; 2.9×10^{-3} M) containing Et_4NClO_4 (0.1 M).

a radical anionic species in one-electron reduction. Reverse oxidation of the intermediary yellow colored solution regenerated the spectrum of *10*PA **3d** with good reversibility as suggested by the reversibility upon CV under the electrochemical reduction conditions.

When the visible spectra of *10*PA **3d** were measured under electrochemical oxidation conditions, a new absorption band also gradually developed in the visible region (Fig. 5b). The blue color of the solution also changed to yellow during the electrochemical oxidation. Reverse reduction of the intermediary yellow colored solution regenerated the spectrum of *10*PA **3d** with good reversibility in contrast to the expectation. The radical cationic species produced by the electrochemical oxidation should be unstable under the condition of the spectral measurements as suggested by the irreversible CV wave under the oxidation conditions. The reversibility for the spectral measurements may be ascribed to the reproduction of the neutral species by the electrochemical reaction of the oxidized species.

2.5. Theoretical calculations

To better understand the electronic properties of the 6-alkyl-2-phenylazulene homologous series [*n*PA, **3a** (*n*=4), **3b** (*n*=6), **3c** (*n*=8), **3d** (*n*=10), and **3e** (*n*=16)], we have also performed time-dependent density functional theory (TDDFT/TDA) calculations at the B3LYP/6-31G** level[15] of 2-phenylazulene along with its radical cationic and anionic species. The results on the calculations are summarized in the Supplementary data. As shown in the Supplementary data, the HOMOs, SOMO, and LUMOs of these

compounds showed symmetrical orbitals with respect to the symmetrical structure of these species. Judging from a comparison between the experimental and the theoretical UV/vis spectra, the longest wavelength absorption maxima of the neutral species could be assigned to HOMO→LUMO transition as characteristics for azulene derivatives.

Density potential analysis of the radical ionic species represented to the localization of the most of charges on the azulene part. Therefore, the amphoteric redox behaviors of these 6-alkyl-2-phenylazulene homologous series are responsible to the stabilization by the substituted 2-azulenyl group. Spin density distributes on the whole molecule in the radical anionic state, whereas that of the radical cationic state localizes on the azulene moiety. In addition, the radical anion had been characterized by ESR spectroscopy, previously, although the radical cation has never examined spectroscopically.[16] Therefore, the spectral changes under electrochemical conditions to develop the new absorption band in the visible region are presumably due to the generation of these radical ionic states, although the experimental absorption maxima of these species could not be reproduced by the TDDFT/TDA calculations at the B3LYP/6-31G** level.

3. Conclusions

Three new members of 6-alkyl-2-phenylazulene homologous series [*n*PA, **3a** (*n*=4), **3b** (*n*=6), and **3d** (*n*=10)] have been successfully synthesized by $Pd(PPh_3)_4$ catalyzed Suzuki–Miyaura cross-coupling reaction of 6-alkyl-2-bromoazulenes (**9a**, **9b**, and **9c**). The efficient preparation of the 6-alkyl-2-bromoazulene homologous (**9a**, **9b**, and **9c**) are established by the introduction of 6-alkyl substituent via Sonogashira–Hagihara and Negishi cross-coupling reactions. The spectroscopic properties of *n*PA series **3a** (*n*=4), **3b** (*n*=6), and **3d** (*n*=10) have been clarified and were compared with those of 6-octyl and 6-hexadecyl derivatives **3c** (*n*=8) and **3e** (*n*=12). Amphoteric redox behavior of **3a**–**e** with a significant color change under electrochemical conditions was revealed by voltammetric and electrochromic analyses. The number of carbon atoms in the peripheral side chain does not affect significantly the redox behaviors of **3a**–**e**. Introduction of 6-alkyl chain in 2-phenylazulene should induce SmE mesomorphism that is closest to an ordered crystal among orthorhombic structures exhibited by the calamitic mesogens. Therefore, the present compounds might exhibit excellent paths for charge carrier transportation and may become an intrinsic candidate for the future applications to a semiconductor owing the amphoteric redox properties of the azulene derivatives.[11]

4. Experimental section

4.1. General

Melting points were determined on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. Mass spectra were obtained with a Hitachi NanoFrontier LD instrument. IR and UV/vis spectra were measured on a JUSCO FT/IR-6100 infrared spectrophotometer, and a JUSCO V-670 spectrophotometer, respectively. ^{1}H NMR spectra (^{13}C NMR spectra) were recorded on a JEOL ECA500 at 500 MHz (125 MHz). ^{1}H NMR chemical shifts in $CDCl_3$ and DMSO-d_6 are reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR chemical shifts in $CDCl_3$ are referred by the solvent signals as 77.0 ppm. The peak assignment of ^{1}H and ^{13}C NMR spectra reported was accomplished by HH COSY, DEPT, HMQC, and HMBC experiments. Gel permeation chromatography (GPC) was performed on a TOSOH TSKgel G2000H_6 with $CHCl_3$ as an eluent. Spectroelectrogram measurements were accomplished in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte using a quarts cell (1×10×35 mm) equipped with a Pt mesh and a wire as the working and counter electrodes, respectively, which were separated by a glass filter. A constant-current reduction and oxidation were applied to the sample solution. The electrical current was monitored by a microampere meter. The potential values are automatically increased by the resistance of the sample solution from 0 V up to ±12 V by our constant-current apparatus. Spectroelectrograms were monitored on an Ocean Optics USB2000 spectrophotometer.

*4.1.1. 6-Butyl-2-phenylazulene (**3a**).* A solution of 2-bromo-6-butylazulene (**9a**) (467 mg, 1.77 mmol), phenyl boronic acid (401 mg, 3.29 mmol), $CsCO_3$ (1.55 g, 4.76 mmol), $Pd(PPh_3)_4$ (91 mg, 0.079 mmol) in dioxane (39 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 afford **3a** (367 mg, 79%). Blue plates; mp 191.8–192.7 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.17 (d, $^3J_{H,H}$=10.4 Hz, 2H, 4,8-H), 7.93 (d, $^3J_{H,H}$=8.2 Hz, 2H, 2′,6′-H), 7.59 (s, 2H, 1,3-H), 7.44 (dd, $^3J_{H,H}$=8.2, 7.3 Hz, 2H, 3′,5′-H), 7.32 (tt, $^3J_{H,H}$=7.3 Hz, 1H, 4′-H), 7.05 (d, $^3J_{H,H}$=10.4 Hz, 2H, 5,7-H), 2.77 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1″-H), 1.69 (tt, $^3J_{H,H}$=7.8, 7.5 Hz, 2H, 2″-H), 1.40 (tq, $^3J_{H,H}$=7.5, 7.4 Hz, 2H, 3″-H), 0.95 (t, $^3J_{H,H}$=7.4 Hz, 3H, 4″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.03 (C-6), 148.58 (C-2), 139.93 (C-3a,8a), 136.72 (C-1′), 135.41 (C-4,8), 128.85 (C-3′,5′), 127.88 (C-4′), 127.45 (C-2′,6′), 124.96 (C-5,7), 114.26 (C-1,3), 42.07 (C-1″), 34.74 (C-2″), 22.40 (C-3″), 13.96 (C-4″); IR (KBr disk): ν_{max}=2970 (w), 2927 (m), 2857 (w), 1577 (m), 1546 (w), 1464 (m), 1440 (m), 1413 (m), 1381 (w), 1335 (w), 1297 (w), 1232 (w), 1023 (w), 965 (w), 908 (w), 834 (s), 760 (s), 687 (m), 640 (w), 497 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=240 (4.15), 287 sh (4.55), 301 (4.82), 311 (4.86), 343 sh (3.71), 359 sh (3.89), 378 (4.16), 396 (4.22), 525 sh (2.44), 562 (2.58), 601 (2.57), 660 sh (2.21) nm; HRMS (ESI positive): calcd for $C_{20}H_{20}$+H$^+$ 261.1638; found 261.1640. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74; found: C, 92.58; H, 7.47.

*4.1.2. 6-Hexyl-2-phenylazulene (**3b**).* A solution of 2-bromo-6-hexylazulene (**9b**) (196 mg, 0.673 mmol), phenyl boronic acid (153 mg, 1.25 mmol), $CsCO_3$ (575 mg, 1.76 mmol), $Pd(PPh_3)_4$ (34 mg, 0.029 mmol) in dioxane (12 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 afford **3b** (148 mg, 76%). Blue plates; mp 180.6–181.3 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.17 (d, $^3J_{H,H}$=10.4 Hz, 2H, 4,8-H), 7.94 (d, $^3J_{H,H}$=8.1 Hz, 2H, 2′,6′-H), 7.60 (s, 2H, 1,3-H), 7.45 (dd, $^3J_{H,H}$=8.1, 7.3 Hz, 2H, 3′,5′-H), 7.32 (t, $^3J_{H,H}$=7.3 Hz, 1H, 4′-H), 7.05 (d, $^3J_{H,H}$=10.4 Hz, 2H, 5,7-H), 2.76 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1″-H), 1.70 (tt, $^3J_{H,H}$=7.8, 7.4 Hz, 2H, 2″-H), 1.40–1.27 (m, 6H, 3″,4″,5″-H), 0.89 (t, $^3J_{H,H}$=7.1 Hz, 3H, 6″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.09 (C-6), 148.54 (C-2), 139.90 (C-3a,8a), 136.69 (C-1′), 135.42 (C-4,8), 128.84 (C-3′,5′), 127.88 (C-4′), 127.44 (C-2′,6′), 124.97 (C-5,7), 114.23 (C-1,3), 42.38 (C-1″), 32.59 (C-2″), 31.72 (C-4″), 28.99 (C-3″), 22.58 (C-5″), 14.08 (C-6″); IR (KBr disk): ν_{max}=2954 (w), 2927 (m), 2855 (m), 1577 (m), 1465 (m), 1443 (w), 1418 (w), 836 (m), 757 (s), 688 (m), 508 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=240 (4.17), 280 sh (4.40), 301 (4.81), 310 (4.84), 343 sh (3.76), 360 sh (3.92), 378 (4.16), 396 (4.21), 447 (2.32), 527 sh (2.50), 562 (2.62), 598 (2.60), 659 sh (2.26) nm; HRMS (ESI positive): calcd for $C_{22}H_{24}$+H$^+$ 289.1951; found 289.1947. Anal. Calcd for $C_{22}H_{24}\cdot 1/6H_2O$: C, 90.67; H, 8.42; found: C, 90.93; H, 8.66.

*4.1.3. 6-Decyl-2-phenylazulene (**3d**).* A solution of 2-bromo-6-decylazulene (**9c**) (441 mg, 1.27 mmol), phenyl boronic acid

(324 mg, 2.66 mmol), $CsCO_3$ (1.21 g, 3.71 mmol), $Pd(PPh_3)_4$ (56 mg, 0.048 mmol) in dioxane (31 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 afford **3d** (297 mg, 68%). Blue plates; mp 171.2–172.3 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.17 (d, $^3J_{H,H}$=10.3 Hz, 2H, 4,8-H), 7.94 (d, $^3J_{H,H}$=8.1 Hz, 2H, 2′,6′-H), 7.60 (s, 2H, 1,3-H), 7.45 (dd, $^3J_{H,H}$=8.1, 7.4 Hz, 2H, 3′,5′-H), 7.32 (t, $^3J_{H,H}$=7.4 Hz, 1H, 4′-H), 7.05 (d, $^3J_{H,H}$=10.3 Hz, 2H, 5,7-H), 2.76 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1″-H), 1.70 (tt, $^3J_{H,H}$=7.8, 7.3 Hz, 2H, 2″-H), 1.40–1.26 (m, 14H, 3″–9″-H), 0.88 (t, $^3J_{H,H}$=7.0 Hz, 3H, 10″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.10 (C-6), 148.55 (C-2), 139.92 (C-3a,8a), 136.71 (C-1′), 135.42 (C-4,8), 128.84 (C-3′,5′), 127.87 (C-4′), 127.45 (C-2′,6′), 124.97 (C-5,7), 114.23 (C-1,3), 42.39 (C-1″), 32.63 (C-2″), 31.88 (t), 29.60 (t), 29.56 (t), 29.52 (t), 29.33 (t), 29.31 (t), 22.67 (t), 14.11 (C-10″); IR (KBr disk): ν_{max}=3045 (w), 2917 (s), 2849 (s), 1577 (m), 1548 (w), 1468 (m), 1440 (m), 1414 (m), 1295 (w), 1127 (w), 1024 (w), 966 (w), 907 (w), 834 (s), 757 (s), 720 (w), 687 (m), 653 (w), 497 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=240 (4.14), 301 (4.79), 310 (4.82), 345 sh (3.74), 360 sh (3.89), 378 (4.14), 396 (4.19), 429 sh (2.19), 523 sh (2.40), 562 (2.56), 598 (2.54), 655 sh (2.20) nm; HRMS (ESI positive): calcd for $C_{26}H_{32}$+H$^+$ 345.2577; found 345.2566. Anal. Calcd for $C_{26}H_{32}$: C, 90.64; H, 9.36; found: C, 90.86; H, 9.46.

*4.1.4. Diethyl 6-(1-hexynyl)-2-methoxyazulene-1,3-dicarboxylate (**5a**).* To a degassed solution of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) (1.96 g, 5.14 mmol), 1-hexyne (1.30 g, 15.8 mmol), CuI (113 mg, 0.590 mmol), triethylamine (130 mL) in dry toluene (130 mL) was added $Pd(PPh_3)_4$ (315 mg, 0.273 mmol). The resulting mixture was stirred at room temperature for 2.5 h under an Ar atmosphere. The reaction mixture was washed successively with 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 afford **5a** (1.67 g, 85%). Reddish purple crystals; mp 50.2–51.2 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.31 (d, $^3J_{H,H}$=11.4 Hz, 2H, 4,8-H), 7.73 (d, $^3J_{H,H}$=11.4 Hz, 2H, 5,7-H), 4.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt), 4.14 (s, 3H, 2-OMe), 2.50 (t, $^3J_{H,H}$=7.1 Hz, 2H, 3′-H), 1.65 (tt, $^3J_{H,H}$=7.5, 7.1 Hz, 2H, 4′-H), 1.51 (tq, $^3J_{H,H}$=7.5, 7.3 Hz, 2H, 5′-H), 1.46 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt), 0.98 (t, $^3J_{H,H}$=7.3 Hz, 3H, 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.28 (C-2), 164.65 (1,3-COOEt), 141.46 (C-3a,8a), 134.83 (C-4,8), 134.67 (C-6), 133.96 (C-5,7), 108.06 (C-1,3), 96.41 (C-2′), 84.28 (C-1′), 62.99 (2-OMe), 60.22 (1,3-COOEt), 30.48 (C-4′), 22.06 (C-5′), 19.43 (C-3′), 14.43 (1,3-COOEt), 13.60 (C-6′); IR (KBr disk): ν_{max}=2935 (m), 2864 (w), 2219 (w, C≡C), 1674 (s, C=O), 1580 (w), 1568 (m), 1534 (w), 1485 (s), 1433 (s), 1390 (m), 1330 (w), 1285 (m), 1249 (m), 1223 (m), 1197 (m), 1126 (w), 1109 (w), 1077 (w), 1036 (m), 996 (m), 877 (w), 852 (w), 794 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=239 (4.27), 270 (4.00), 318 sh (4.64), 329 (4.75), 372 (4.07), 397 sh (3.69), 466 sh (2.49), 494 (2.58), 534 sh (2.42), 588 sh (1.67) nm; HRMS (ESI positive): calcd for $C_{23}H_{26}O_5$+Na$^+$ 405.1672; found 405.1651. HRMS (ESI positive): calcd for $C_{23}H_{26}O_5$+H$^+$ 383.1853; found 383.1833. Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85; found: C, 72.12; H, 6.76.

*4.1.5. Diethyl 6-(1-decynyl)-2-methoxyazulene-1,3-dicarboxylate (**5b**).* To a degassed solution of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) (2.88 g, 7.55 mmol), 1-decyne (3.14 g, 22.7 mmol), CuI (159 mg, 0.835 mmol), triethylamine (80 mL) in dry toluene (190 mL) was added $Pd(PPh_3)_4$ (352 mg, 0.305 mmol). The resulting mixture was stirred at room temperature for 2.5 h under an Ar atmosphere. The reaction mixture was washed successively with 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 afford **5b** (2.87 g, 87%). Red crystals; mp 49.2–50.9 °C (H_2O/methanol); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.31 (d, $^3J_{H,H}$=11.2 Hz, 2H, 4,8-H), 7.73 (d, $^3J_{H,H}$=11.2 Hz, 2H, 5,7-H), 4.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt), 4.14 (s, 3H, 2-OMe), 2.49 (t, $^3J_{H,H}$=7.1 Hz, 2H, 3′-H), 1.66 (tt, $^3J_{H,H}$=7.6, 7.1 Hz, 2H, 4′-H), 1.47 (m, 2H, 5′-H), 1.46 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt), 1.35–1.30 (m, 8H, 6′–9′-H), 0.89 (t, $^3J_{H,H}$=6.9 Hz, 3H, 10′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.29 (C-2), 164.65 (1,3-COOEt), 141.47 (C-3a,8a), 134.83 (C-4,8), 134.69 (C-6), 133.97 (C-5,7), 108.07 (C-1,3), 96.51 (C-2′), 84.30 (C-1′), 63.00 (2-OMe), 60.22 (1,3-COOEt), 31.81 (t), 29.16 (t), 29.07 (t), 28.98 (t), 28.43 (C-4′), 22.63 (t), 19.75 (C-3′), 14.44 (1,3-COOEt), 14.09 (C-10′); IR (KBr disk): ν_{max}=2990 (m), 2979 (m), 2935 (m), 2913 (m), 2855 (m), 2224 (w, C≡C), 1682 (s, C=O), 1587 (w), 1567 (m), 1541 (m), 1490 (s), 1469 (m), 1438 (s), 1394 (m), 1383 (m), 1354 (w), 1333 (w), 1278 (s), 1224 (m), 1195 (s), 1116 (m), 1107 (m), 1078 (m), 1038 (m), 1003 (m), 851 (m), 794 (w), 716 (w), 704 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=239 (4.39), 271 sh (4.13), 318 sh (4.72), 329 (4.82), 372 (4.19), 383 sh (4.06), 398 sh (3.83), 467 sh (2.65), 494 (2.71), 534 sh (2.57), 593 sh (2.01) nm; HRMS (ESI positive): calcd for $C_{27}H_{34}O_5$+Na$^+$ 461.2298; found 461.2301. HRMS (ESI positive): calcd for $C_{27}H_{34}O_5$+H$^+$ 439.2479; found 439.2477. Anal. Calcd for $C_{27}H_{34}O_5$: C, 73.94; H, 7.81; found: C, 73.83; H, 7.75.

*4.1.6. Diethyl 6-butyl-2-methoxyazulene-1,3-dicarboxylate (**6a**).* To a degassed solution of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) (2.12 g, 5.56 mmol) and butylzinc bromide (0.5 M, 33 mL) in dry THF (18 mL) was added $PdCl_2$[dppf]·CH_2Cl_2 (186 mg, 0.228 mmol). The resulting mixture was stirred at 50 °C for 30 min under an Ar atmosphere. The reaction mixture was washed successively with 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 20% ethyl acetate/hexane to afford **6a** (1.41 g, 71%) and diethyl 2-butoxy-6-butylazulene-1,3-dicarboxylate (**10**) (303 mg, 14%).

Compound **6a**: Orange prisms; mp 59.0–60.5 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.42 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.59 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt), 4.13 (s, 3H, 2-OMe), 2.89 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 1.71 (tt, $^3J_{H,H}$=7.7, 7.6 Hz, 2H, 2′-H), 1.46 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt), 1.39 (tq, $^3J_{H,H}$=7.6, 7.3 Hz, 2H, 3′-H), 0.95 (t, $^3J_{H,H}$=7.3 Hz, 3H, 4′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=169.77 (C-2), 164.83 (1,3-COOEt), 155.43 (C-6), 140.88 (C-3a,8a), 136.13 (C-4,8), 132.30 (C-5,7), 107.34 (C-1,3), 62.96 (2-OMe), 60.04 (1,3-COOEt), 41.39 (C-1′), 34.64 (C-2′), 22.26 (C-3′), 14.46 (1,3-COOEt), 13.86 (C-4′); IR (KBr disk): ν_{max}=2936 (m), 1673 (s, C=O), 1577 (w), 1545 (w), 1482 (m), 1427 (s), 1389 (m), 1278 (m), 1232 (m), 1187 (s), 1102 (m), 1034 (m), 994 (m), 869 (w), 807 (w), 707 (w), 563 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=235 (4.48), 263 sh (4.30), 270 (4.36), 304 sh (4.70), 314 (4.80), 348 (3.98), 358 sh (3.94), 374 sh (3.71), 444 sh (2.67), 462 (2.73), 494 sh (2.61), 545 sh (1.85) nm; HRMS (ESI positive): calcd for $C_{21}H_{26}O_5$+K$^+$ 397.1412; found 397.1438. HRMS (ESI positive): calcd for $C_{21}H_{26}O_5$+Na$^+$ 381.1672; found 381.1693. HRMS (ESI positive): calcd for $C_{21}H_{26}O_5$+H$^+$ 359.1853; found 359.1869. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31; found: C, 70.33; H, 7.24.

Compound **10**: Red oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.40 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.57 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.45 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt), 4.28 (t, $^3J_{H,H}$=6.6 Hz, 2H, 1′-H), 2.88 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1″-H), 1.88 (tt, $^3J_{H,H}$=7.7, 6.6 Hz, 2H, 2′-H), 1.70 (tt, $^3J_{H,H}$=7.7, 7.6 Hz, 2H, 2″-H), 1.54 (tq, $^3J_{H,H}$=7.7, 7.4 Hz, 2H, 3′-H), 1.45 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt), 1.39 (tq, $^3J_{H,H}$=7.4, 7.4 Hz, 2H, 3″-H), 0.99 (t, $^3J_{H,H}$=7.4 Hz, 3H, 4′-H), 0.94 (t, $^3J_{H,H}$=7.4 Hz, 3H, 4″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=168.88 (C-2), 164.99 (1,3-COOEt), 155.03 (C-6), 141.05 (C-3a,8a), 135.76 (C-4,8), 132.23 (C-5,7), 107.29 (C-1,3), 76.18 (C-1′), 59.98 (1,3-COOEt), 41.34 (C-1″), 34.62 (C-2″), 32.44

(C-2′), 22.23 (C-3″), 19.14 (C-3′), 14.50 (1,3-COOEt), 13.93 (C-4′), 13.84 (C-4″); IR (KBr disk): ν_{max}=2958 (s), 2933 (s), 2872 (m), 1683 (s, C=O), 1578 (m), 1545 (m), 1478 (s), 1458 (s), 1431 (s), 1383 (s), 1274 (s), 1235 (s), 1180 (s), 1102 (m), 1063 (m), 1032 (s), 994 (m), 962 (m), 932 (w), 896 (w), 847 (m), 813 (w), 797 (w), 717 (w), 684 (w), 647 (w), 611 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=236 (4.40), 269 (4.28), 305 sh (4.64), 315 (4.73), 348 (3.93), 368 sh (3.83), 460 (2.69), 495 (2.54), 547 (1.75) nm; HRMS (ESI positive): calcd for $C_{24}H_{32}O_5$+Na^+ 423.2142; found 423.2164. HRMS (ESI positive): calcd for $C_{24}H_{32}O_5$+H^+ 401.2323; found 401.2340.

*4.1.7. Diethyl 2-methoxy-6-(1-propylbutyl)azulene-1,3-dicarboxylate (**11**).* To a degassed solution of diethyl 6-bromo-2-methoxyazulene-1,3-dicarboxylate (**4**) (509 mg, 1.34 mmol) and 1-propylbutylzinc bromide (0.5 M, 8 mL) in dry THF (15 mL) was added $PdCl_2$[dppf]·CH_2Cl_2 (57 mg, 0.070 mmol). The resulting mixture was stirred at 50 °C for 1 h under an Ar atmosphere. The reaction mixture was washed successively with 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 20% ethyl acetate/hexane to afford a 77:23 mixture of **11** and diethyl 6-(1-ethylpentyl)-2-methoxyazulene-1,3-dicarboxylate (**12**) (421 mg, 79%). Red oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.44 (d, $^3J_{H,H}$=11.2 Hz, 2H, minor-4,8-H), 9.43 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.563 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 7.559 (d, $^3J_{H,H}$=11.2 Hz, 2H, minor-5,7-H), 4.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt and 4H, minor-1,3-COOEt), 4.133 (s, 3H, minor-2-OMe), 4.131 (s, 3H, 2-OMe), 2.80 (dddd, $^3J_{H,H}$=9.8, 9.8, 4.9, 4.9 Hz, 1H, 1′-H), 2.67 (dddd, $^3J_{H,H}$=9.8, 9.8, 4.9, 4.9 Hz, 1H, minor-1′-H), 1.86–1.62 (m, 4H, 2′-H and 4H, minor-2′-H and -1″-H), 1.47 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt and 6H, minor-1,3-COOEt), 1.31–1.00 (m, 4H, 3′-H and 4H, minor-3′-H and -4′-H), 0.85 (t, $^3J_{H,H}$=7.3 Hz, 6H, 4′-H), 0.81 (t, $^3J_{H,H}$=7.2 Hz, 3H, minor-5′-H), 0.78 (t, $^3J_{H,H}$=7.3 Hz, 3H, minor-2″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=169.87 (C-2 and minor-C-2), 164.83 (minor-1,3-COOEt), 164.82 (1,3-COOEt), 158.77 (C-6), 158.57 (minor-C-6), 140.89 (minor-C-3a,8a), 140.86 (C-3a,8a), 136.07 (C-4,8 and minor-C-4,8), 131.52 (minor-C-5,7), 131.46 (C-5,7), 107.25 (C-1,3 and minor-C1,3), 62.95 (2-OMe and minor-2-OMe), 60.05 (1,3-COOEt and minor-1,3-COOEt), 52.91 (minor-C-1′), 50.54 (C-1′), 39.61 (C-2′), 36.81 (minor-C-2′), 30.30 (minor-C-1″), 29.84 (minor-C-3′), 22.69 (minor-C-4′), 20.74 (C-3′), 14.47 (1,3-COOEt and minor-1,3-COOEt), 14.04 (C-4′), 13.88 (minor-C-5′), 12.21 (minor-C-2″); IR (neat): ν_{max}=2957 (m), 2930 (m), 2871 (m), 1682 (s, C=O), 1579 (m), 1544 (m), 1487 (s), 1433 (s), 1390 (s), 1276 (s), 1238 (s), 1185 (s), 1107 (m), 1090 (m), 1070 (m), 1033 (s), 1000 (s), 925 (w), 850 (m), 796 (w), 714 (w), 572 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=229 sh (4.40), 236 (4.45), 264 sh (4.28), 270 (4.33), 304 sh (4.68), 314 (4.79), 348 (3.96), 358 sh (3.92), 374 sh (3.68), 438 sh (2.63), 463 (2.73), 491 sh (2.63), 537 sh (1.99) nm; HRMS (ESI positive): calcd for $C_{24}H_{32}O_5$+K^+ 439.1881; found 439.1875. HRMS (ESI positive): calcd for $C_{24}H_{32}O_5$+Na^+ 423.2142; found 423.2122. HRMS (ESI positive): calcd for $C_{24}H_{32}O_5$+H^+ 401.2323; found 401.2321.

*4.1.8. Diethyl 6-hexyl-2-methoxyazulene-1,3-dicarboxylate (**6b**).* A mixture of diethyl 6-(1-hexynyl)-2-methoxyazulene-1,3-dicarboxylate (**5a**) (1.67 g, 4.37 mmol), 10% Pd–C (466 mg) in ethanol (255 mL) was stirred at room temperature for 1 day 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 afford **6b** (1.52 g, 90%). Orange prisms; mp 45.3–47.5 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.42 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.59 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.46 (q, $^3J_{H,H}$=7.2 Hz, 4H, 1,3-COOEt), 4.13 (s, 3H, 2-OMe), 2.88 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 1.72 (tt, $^3J_{H,H}$=7.7, 7.4 Hz, 2H, 2′-H), 1.46 (t, $^3J_{H,H}$=7.2 Hz, 6H, 1,3-COOEt), 1.38–1.29 (m, 6H, 3′,4′,5′-H), 0.88 (t, $^3J_{H,H}$=7.1 Hz, 3H, 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=169.78 (C-2), 164.85 (1,3-COOEt), 155.48 (C-6), 140.90 (C-3a,8a), 136.14 (C-4,8), 132.31 (C-5,7), 107.34 (C-1,3), 62.97 (2-OMe), 60.06 (1,3-COOEt), 41.70 (C-1′), 32.52 (C-2′), 31.61 (C-4′), 28.83 (C-3′), 22.51 (C-5′), 14.47 (1,3-COOEt), 14.02 (C-6′); IR (KBr disk): ν_{max}=2943 (w), 2923 (m), 2875 (w), 2852 (w), 1677 (s, C=O), 1580 (w), 1545 (w), 1491 (s), 1430 (s), 1415 (s), 1391 (s), 1335 (w), 1276 (s), 1240 (m), 1203 (s), 1156 (m), 1109 (m), 1038 (s), 1001 (m), 923 (w), 898 (w), 838 (m), 735 (w), 710 (w), 568 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=236 (4.43), 263 sh (4.26), 270 (4.31), 304 sh (4.65), 314 (4.74), 347 (3.98), 359 sh (3.93), 374 sh (3.74), 438 sh (2.60), 464 (2.70), 496 sh (2.56), 545 sh (1.80) nm; HRMS (ESI positive): calcd for $C_{23}H_{30}O_5$+Na^+ 409.1985; found 409.2032. HRMS (ESI positive): calcd for $C_{23}H_{30}O_5$+H^+ 387.2166; found 387.2213. Anal. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82; found: C, 71.39; H, 7.76.

*4.1.9. Diethyl 6-decyl-2-methoxyazulene-1,3-dicarboxylate (**6c**).* A mixture of diethyl 6-(1-decynyl)-2-methoxyazulene-1,3-dicarboxylate (**5b**) (2.87 g, 6.54 mmol), 10% Pd–C (691 mg) in ethanol (305 mL) was stirred at room temperature for 1 day 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 afford **6c** (2.71 g, 94%). Red oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.42 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.59 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.46 (q, $^3J_{H,H}$=7.1 Hz, 4H, 1,3-COOEt), 4.13 (s, 3H, 2-OMe), 2.88 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 1.72 (tt, $^3J_{H,H}$=7.7, 7.3 Hz, 2H, 2′-H), 1.46 (t, $^3J_{H,H}$=7.1 Hz, 6H, 1,3-COOEt), 1.38–1.25 (m, 14H, 3′–9′-H), 0.87 (t, $^3J_{H,H}$=7.0 Hz, 3H, 10′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=169.77 (C-2), 164.84 (1,3-COOEt), 155.49 (C-6), 140.89 (C-3a,8a), 136.14 (C-4,8), 132.32 (C-5,7), 107.34 (C-1,3), 62.97 (2-OMe), 60.05 (1,3-COOEt), 41.70 (C-1′), 32.57 (C-2′), 31.84 (t), 29.53 (t), 29.48 (t), 29.42 (t), 29.27 (t), 29.17 (t), 22.64 (t), 14.47 (1,3-COOEt), 14.08 (C-10′); IR (KBr disk): ν_{max}=2920 (s), 2851 (m), 1683 (s, C=O), 1580 (w), 1546 (w), 1493 (s), 1484 (m), 1431 (s), 1415 (s), 1392 (s), 1277 (s), 1241 (m), 1203 (s), 1153 (m), 1109 (m), 1034 (s), 1001 (m), 857 (w), 823 (w), 718 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=236 (4.46), 270 (4.34), 304 sh (4.68), 314 (4.77), 348 (4.00), 359 sh (3.95), 373 sh (3.78), 440 sh (2.69), 464 (2.75), 496 sh (2.63), 544 sh (2.08) nm; HRMS (ESI positive): calcd for $C_{27}H_{38}O_5$+Na^+ 465.2611; found 465.2604. HRMS (ESI positive): calcd for $C_{27}H_{38}O_5$+H^+ 443.2792; found 443.2784.

*4.1.10. 6-Butyl-2-hydroxyazulene (**8a**).* To a solution of diethyl 6-butyl-2-methoxyazulene-1,3-dicarboxylate (**6a**) (426 mg, 1.19 mmol) was dissolved in ethanol (6 mL) was added 2 M KOH (4 mL). The resulting mixture was refluxed for 4 h. After cooling the reaction mixture, the mixture was acidified with 2 M HCl (7 mL). The precipitated crystals were collected by filtration, washed with water, and dried in vacuo to afford 6-butyl-2-methoxyazulene-1,3-dicarboxylic acid (**7a**) (357 mg, 99%), which was utilized to the next reaction without further purification.

A mixture of **7a** (1.10 g, 3.64 mmol) and freshly prepared 100% phosphoric acid, which was prepared by 85% phosphoric acid (64.0 g) and phosphorous(V) oxide (25.4 g), was heated at 130 °C for 20 min with occasional stirring with a glass rod. After cooling the reaction mixture, 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 afford **8a** (476 mg, 65%).

Compound **7a**: Yellow crystals; mp 148.2–149.3 °C (hexane); ^{1}H NMR (500 MHz, DMSO-d_6): δ=12.57 (s, 2H, 1,3-COOH), 9.33 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.75 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.06 (s, 3H, 2-OMe), 2.89 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 1.67 (tt, $^3J_{H,H}$=7.7, 7.5 Hz, 2H, 2′-H), 1.34 (tq, $^3J_{H,H}$=7.5, 7.3 Hz, 2H, 3′-H), 0.91 (t, $^3J_{H,H}$=7.3 Hz,

3H, 4′-H); ^{13}C NMR (125 MHz, DMSO-d_6=39.5 ppm): δ=169.08 (C-2), 165.43 (1,3-COOH), 155.16 (C-6), 139.76 (C-3a,8a), 135.45 (C-4,8), 132.12 (C-5,7), 107.12 (C-1,3), 62.26 (2-OMe), 40.30 (C-1′), 34.10 (C-2′), 21.73 (C-3′), 13.75 (C-4′); IR (KBr disk): ν_{max}=2956 (m), 2868 (w), 1658 (s, C=O), 1577 (m), 1547 (w), 1493 (s), 1444 (s), 1401 (m), 1271 (w), 1226 (m), 1104 (w), 1004 (w), 843 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=235 (4.50), 263 sh (4.24), 271 (4.34), 302 sh (4.63), 312 (4.74), 342 (3.99), 371 sh (3.72), 426 sh (2.78), 450 (2.87), 477 sh (2.78), 521 sh (2.18) nm; HRMS (ESI positive): calcd for $C_{17}H_{18}O_5$+H$^+$ 303.1227; found 303.1234.

Compound **8a**: Red needles; mp 75.7–76.6 °C (hexane); ^{1}H NMR (500 MHz, acetone-d_6=2.04 ppm) of major tautomer: δ=9.49 (s, 1H, 2-OH), 7.93 (d, $^3J_{H,H}$=10.5 Hz, 2H, 4,8-H), 7.09 (d, $^3J_{H,H}$=10.5 Hz, 2H, 5,7-H), 6.70 (s, 2H, 1,3-H), 2.75 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1′-H), 1.66 (tt, $^3J_{H,H}$=7.8, 7.5 Hz, 2H, 2′-H), 1.37 (tq, $^3J_{H,H}$=7.5, 7.4 Hz, 2H, 3′-H), 0.92 (t, $^3J_{H,H}$=7.4 Hz, 3H, 4′-H); ^{13}C NMR (125 MHz, acetone-d_6=29.8 ppm) of major tautomer: δ=167.51 (C-2), 148.02 (C-6), 140.09 (C-3a,8a), 131.08 (C-4,8), 125.94 (C-5,7), 103.73 (C-1,3), 42.07 (C-1′), 35.85 (C-2′), 22.98 (C-3′), 14.20 (C-4′); IR (KBr disk): ν_{max}=2966 (m), 2928 (m), 1644 (s), 1627 (s), 1580 (m), 1531 (s), 1498 (s), 1436 (m), 1403 (m), 1260 (m), 1234 (m), 1158 (m), 1142 (w), 841 (m), 786 (w), 759 (w), 716 (w), 667 (w), 597 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=237 (4.12), 243 sh (4.11), 269 (3.98), 281 (3.99), 290 (3.99), 319 (3.67), 357 sh (4.19), 372 (4.25), 397 sh (4.04), 448 sh (3.07), 481 sh (2.85), 520 (2.48), 570 (1.87) nm; HRMS (ESI positive): calcd for $C_{14}H_{16}O$+K$^+$ 239.0833; found 239.0917. HRMS (ESI positive): calcd for $C_{14}H_{16}O$+Na$^+$ 223.1093; found 223.1093. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05; found: C, 83.95; H, 7.97.

*4.1.11. 6-Hexyl-2-hydroxyazulene (**8b**).* To a solution of diethyl 6-hexyl-2-methoxyazulene-1,3-dicarboxylate (**6b**) (1.50 g, 3.88 mmol) was dissolved in ethanol (20 mL) was added 2 M KOH (14 mL). The resulting mixture was refluxed for 4 h. After cooling the reaction mixture, the mixture was acidified with 2 M HCl (23 mL). The precipitated crystals were collected by filtration, washed with water, and dried in vacuo to afford 6-hexyl-2-methoxyazulene-1,3-dicarboxylic acid (**7b**) (1.23 g, 96%), which was utilized to the next reaction without further purification.

A mixture of **7b** (1.13 g, 3.42 mmol) and freshly prepared 100% phosphoric acid, which was prepared by 85% phosphoric acid (59.7 g) and phosphorous(V) oxide (24.4 g), was heated at 130 °C for 20 min with occasional stirring with a glass rod. After cooling the reaction mixture, 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 afford **8b** (401 mg, 51%).

Compound **7b**: Yellow crystals; mp 136.4–137.4 °C (hexane); ^{1}H NMR (500 MHz, DMSO-d_6): δ=12.58 (s, 2H, 1,3-COOEt), 9.34 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.75 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.08 (s, 3H, 2-OMe), 2.88 (t, $^3J_{H,H}$=7.6 Hz, 2H, 1′-H), 1.67 (tt, $^3J_{H,H}$=7.6, 7.1 Hz, 2H, 2′-H), 1.31–1.25 (m, 6H, 3′,4′,5′-H), 0.84 (t, $^3J_{H,H}$=7.0 Hz, 3H, 6′-H); ^{13}C NMR (125 MHz, DMSO-d_6=39.5 ppm): δ=169.11 (C-2), 165.44 (1,3-COOH), 155.17 (C-6), 139.78 (C-3a,8a), 135.47 (C-4,8), 132.12 (C-5,7), 107.14 (C-1,3), 62.27 (2-OMe), 40.60 (C-1′), 31.95 (C-2′), 31.07 (C-4′), 28.25 (C-3′), 22.00 (C-5′), 13.91 (C-6′); IR (KBr disk): ν_{max}=2928 (s), 2864 (m), 2580 (m), 1653 (s, C=O), 1576 (m), 1545 (m), 1491 (s), 1449 (s), 1399 (s), 1281 (m), 1227 (s), 1126 (w), 1097 (w), 1006 (m), 926 (w), 892 (w), 860 (w), 736 (w), 676 (w), 420 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=236 (4.31), 263 sh (4.07), 271 (4.17), 302 sh (4.43), 312 (4.55), 345 sh (3.89), 370 sh (3.66), 426 sh (2.71), 450 (2.78), 476 sh (2.70), 521 sh (2.20) nm; HRMS (ESI positive): calcd for $C_{19}H_{22}O_5$+Na$^+$ 353.1359; found 353.1351. HRMS (ESI positive): calcd for $C_{19}H_{22}O_5$+H$^+$ 331.1540; found 331.1529.

Compound **8b**: Red needles; mp 90.8–91.2 °C (hexane); ^{1}H NMR (500 MHz, acetone-d_6=2.04 ppm) of keto–enol ratio=18:82: δ=9.51 (s, 1H, 2-OH), 7.93 (d, $^3J_{H,H}$=10.6 Hz, 2H, 4,8-H), 7.09 (d, $^3J_{H,H}$=10.6 Hz, 2H, 5,7-H), 6.85 (d, $^3J_{H,H}$=11.9 Hz, 1H, mior-8-H), 6.70 (s, 2H, 1,3-H), 6.51 (dd, $^3J_{H,H}$=11.9 Hz, $^4J_{H,H}$=1.2 Hz, 1H, minor-7-H), 6.37 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,H}$=1.2 Hz, 1H, minor-5-H), 6.30 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,H}$=1.2 Hz, 1H, minor-4-H), 5.65 (d, $^4J_{H,H}$=1.2 Hz, 1H, minor-1-H), 2.97 (s, 2H, minor-3-H), 2.75 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 2.26 (t, $^3J_{H,H}$=7.7 Hz, 2H, minor-1′-H), 1.67 (tt, $^3J_{H,H}$=7.7, 7.4 Hz, 2H, 2′-H), 1.50 (tt, $^3J_{H,H}$=7.7, 7.3 Hz, 2H, minor-2′-H), 1.40–1.26 (m, 6H, 3′,4′,5′-H and 6H, minor-3′,4′,5′-H), 0.87 (t, $^3J_{H,H}$=7.0 Hz, 3H, minor-6′-H), 0.86 (t, $^3J_{H,H}$=7.1 Hz, 3H, 6′-H); ^{13}C NMR (125 MHz, acetone-d_6=29.8 ppm) of major tautomer: δ=167.51 (C-2), 148.05 (C-6), 140.09 (C-3a,8a), 131.08 (C-4,8), 125.94 (C-5,7), 103.73 (C-1,3), 42.37 (C-1′), 33.65 (C-2′), 32.43 (C-4′), 29.66 (C-3′), 23.23 (C-5′), 14.30 (C-6′); IR (KBr disk): ν_{max}=2955 (m), 2927 (m), 2854 (m), 1646 (m), 1631 (m), 1580 (w), 1534 (s), 1499 (s), 1437 (m), 1404 (m), 1261 (w), 1236 (m), 1158 (w), 1136 (w), 841 (w), 832 (w), 787 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=241 (4.07), 268 (3.93), 280 (3.93), 289 (3.92), 318 sh (3.62), 357 sh (4.15), 373 (4.21), 397 sh (4.01), 425 sh (3.27), 448 sh (3.05), 480 sh (2.84), 519 sh (2.49), 569 sh (1.96) nm; HRMS (ESI positive): calcd for $C_{16}H_{20}O$+H$^+$ 229.1587; found 229.1585. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83; found: C, 84.10; H, 8.79.

*4.1.12. 6-Decyl-2-hydroxyazulene (**8c**).* To a solution of diethyl 6-decyl-2-methoxyazulene-1,3-dicarboxylate (**6c**) (2.65 g, 5.99 mmol) was dissolved in ethanol (32 mL) was added 2 M KOH (24 mL). The resulting mixture was refluxed for 4 h. After cooling the reaction mixture, the mixture was acidified with 2 M HCl (39 mL). The precipitated crystals were collected by filtration, washed with water, and dried in vacuo to afford 6-decyl-2-methoxyazulene-1,3-dicarboxylic acid (**7c**) (2.23 g, 96%), which was utilized to the next reaction without further purification.

A mixture of **7c** (260 mg, 0.673 mmol) and freshly prepared 100% phosphoric acid, which was prepared by 85% phosphoric acid (11.9 g) and phosphorous(V) oxide (4.86 g), was heated at 130 °C for 20 min with occasional stirring with a glass rod. After cooling the reaction mixture, 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 afford **8c** (114 mg, 60%).

Compound **7c**: Yellow crystals; mp 124.3–126.9 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=11.84 (br, 2H, 1,3-COOH), 9.75 (d, $^3J_{H,H}$=11.1 Hz, 2H, 4,8-H), 7.78 (d, $^3J_{H,H}$=11.1 Hz, 2H, 5,7-H), 4.40 (s, 3H, 2-OMe), 2.96 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 1.76 (tt, $^3J_{H,H}$=7.7, 7.3 Hz, 2H, 2′-H), 1.41–1.26 (m, 14H, 3′–9′-H), 0.88 (t, $^3J_{H,H}$=6.9 Hz, 3H, 10′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=169.02 (C-2), 166.95 (1,3-COOH), 157.90 (C-6), 141.99 (C-3a,8a), 138.03 (C-4,8), 134.37 (C-5,7), 104.67 (C-1,3), 64.48 (2-OMe), 41.85 (C-1′), 32.56 (C-2′), 31.85 (t), 29.54 (t), 29.48 (t), 29.40 (t), 29.27 (t), 29.18 (t), 22.65 (t), 14.09 (C-10′); IR (KBr disk): ν_{max}=2925 (s), 2854 (m), 1645 (s, C=O), 1575 (m), 1545 (w), 1492 (s), 1449 (s), 1398 (m), 1284 (m), 1226 (s), 1008 (m), 677 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=236 (4.45), 271 (4.32), 303 sh (4.60), 312 (4.69), 346 sh (3.98), 371 sh (3.71), 426 sh (2.82), 450 (2.89), 496 sh (2.58), 544 sh (1.95) nm; HRMS (ESI positive): calcd for $C_{23}H_{30}O_5$+H$^+$ 387.2166; found 387.2151. Anal. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82; found: C, 71.83; H, 7.62.

Compound **8c**: Red plates; mp 90.4–91.3 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) of keto–enol ratio=92:8: δ=9.02 (br, 1H, minor-2-OH), 7.93 (d, $^3J_{H,H}$=10.5 Hz, 2H, minor-4,8-H), 7.05 (d, $^3J_{H,H}$=10.5 Hz, 2H, minor-5,7-H), 6.78 (d, $^3J_{H,H}$=11.8 Hz, 1H, 8-H), 6.75 (s, 2H, minor-1,3-H), 6.45 (dd, $^3J_{H,H}$=11.8 Hz, $^4J_{H,H}$=1.1 Hz, 1H, 7-H), 6.32 (dd, $^3J_{H,H}$=8.5 Hz, $^4J_{H,H}$=1.1 Hz, 1H, 5-H), 6.28 (dd, $^3J_{H,H}$=8.5 Hz, $^4J_{H,H}$=1.1 Hz, 1H, 4-H), 5.75 (d, $^4J_{H,H}$=1.1 Hz, 1H, 1-H), 3.06 (s, 2H, 3-H), 2.74 (t, $^3J_{H,H}$=7.7 Hz, 2H, minor-1′-H), 2.26 (t, $^3J_{H,H}$=7.6 Hz, 2H, 1′-H), 1.67 (tt, $^3J_{H,H}$=7.7, 7.3 Hz, 2H, minor-2′-H),

1.50 (tt, $^3J_{H,H}$=7.6, 7.0 Hz, 2H, 2′-H), 1.30–1.26 (m, 14H, 3′–9′-H and 14H, minor-3′–9′-H), 0.88 (t, $^3J_{H,H}$=7.0 Hz, 3H, 10′-H), 0.87 (t, $^3J_{H,H}$=7.0 Hz, 3H, minor-10′-H); ^{13}C NMR (125 MHz, $CDCl_3$) of keto–enol ratio=92:8: δ=202.49 (C-2), 167.86 (C-8a), 165.94 (minor-C-2), 147.88 (C-3a), 147.67 (minor-C-6), 145.62 (C-6), 139.23 (C-7), 138.93 (minor-C-3a,8a), 131.27 (C-5), 130.60 (minor-C-4,8), 130.33 (C-8), 125.60 (C-4), 125.22 (minor-C-5,7), 122.03 (C-1), 102.87 (minor-C-1,3), 43.85 (C-3), 41.92 (minor-C-1′), 40.32 (C-1′), 32.86 (minor-C-2′), 31.85 (C-2′), 30.26 (t), 29.57 (t), 29.54 (t), 29.51 (t), 29.49 (t), 29.39 (t), 29.29 (t, 2C-minor), 29.27 (t), 28.98 (t), 22.64 (t), 14.07 (C-10′ and minor-C-10′); ^{1}H NMR (500 MHz, acetone-d_6=2.04 ppm) of keto–enol ratio=18:82: δ=9.49 (s, 1H, 2-OH), 7.93 (d, $^3J_{H,H}$=10.5 Hz, 2H, 4,8-H), 7.10 (d, $^3J_{H,H}$=10.5 Hz, 2H, 5,7-H), 6.84 (d, $^3J_{H,H}$=11.9 Hz, 1H, minor-8-H), 6.69 (s, 2H, 1,3-H), 6.50 (dd, $^3J_{H,H}$=11.9 Hz, $^4J_{H,H}$=1.4 Hz, 1H, minor-7-H), 6.32 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,H}$=1.0 Hz, 1H, minor-5-H), 6.30 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,H}$=1.0 Hz, 1H, minor-4-H), 5.65 (d, $^4J_{H,H}$=1.0 Hz, 1H, minor-1-H), 2.99 (s, 2H, minor-3-H), 2.75 (t, $^3J_{H,H}$=7.7 Hz, 2H, 1′-H), 2.27 (t, $^3J_{H,H}$=7.6 Hz, 2H, minor-1′-H), 1.68 (tt, $^3J_{H,H}$=7.7, 7.2 Hz, 2H, 2′-H), 1.50 (tt, $^3J_{H,H}$=7.6, 7.1 Hz, 2H, minor-2′-H), 1.40–1.26 (m, 14H, 3′–9′-H and 14H, minor-3′–9′-H), 0.87 (t, $^3J_{H,H}$=7.0 Hz, 3H, minor-10′-H), 0.86 (t, $^3J_{H,H}$=7.0 Hz, 3H, 10′-H); ^{13}C NMR (125 MHz, acetone-d_6=29.8 ppm) of major tautomer: δ=167.52 (C-2), 148.06 (C-6), 140.10 (C-3a,8a), 131.08 (C-4,8), 125.94 (C-5,7), 103.73 (C-1,3), 42.38 (C-1′), 33.69 (C-2′), 32.59 (t), 30.29 (t, 3C), 30.21 (t), 30.02 (t), 29.98 (t), 29.34 (t), 23.29 (t), 14.32 (C-10′); IR (KBr disk): ν_{max}=2921 (s), 2851 (s), 1645 (m), 1629 (m), 1583 (w), 1535 (s), 1500 (s), 1465 (m), 1439 (m), 1404 (m), 1261 (w), 1236 (m), 1139 (w), 876 (w), 831 (m), 787 (w), 719 (w), 650 (w), 411 (w) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=239 (4.05), 271 (3.92), 280 (3.95), 289 (3.94), 319 (3.70), 356 sh (4.09), 372 (4.15), 398 sh (3.93), 424 sh (3.26), 448 sh (2.97), 481 sh (2.75), 519 sh (2.41), 570 sh (1.84) nm; HRMS (ESI positive): calcd for $C_{20}H_{28}O$+H$^+$ 285.2213; found 285.2228. Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92; found: C, 84.76; H, 9.75.

*4.1.13. 2-Bromo-6-butylazulene (**9a**).* To a solution of 6-butyl-2-hydroxyazulene (**8a**) (615 mg, 3.07 mmol) in dry toluene (115 mL) was added PBr_3 (2.26 g, 8.35 mmol). The resulting mixture was heated at 100 °C for 1 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 **9a** (562 mg, 70%). Violet plates; mp 103.2–103.9 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.13 (d, $^3J_{H,H}$=10.5 Hz, 2H, 4,8-H), 7.26 (s, 2H, 1,3-H), 7.12 (d, $^3J_{H,H}$=10.5 Hz, 2H, 5,7-H), 2.77 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1′-H), 1.68 (tt, $^3J_{H,H}$=7.8, 7.5 Hz, 2H, 2′-H), 1.39 (tq, $^3J_{H,H}$=7.5, 7.4 Hz, 2H, 3′-H), 0.94 (t, $^3J_{H,H}$=7.4 Hz, 3H, 4′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=154.13 (C-6), 138.53 (C-3a,8a), 134.66 (C-4,8), 125.77 (C-5,7), 125.76 (C-2), 118.41 (C-1,3), 42.11 (C-1′), 34.67 (C-2′), 22.38 (C-3′), 13.93 (C-4′); IR (KBr disk): ν_{max}=2954 (m), 2920 (m), 2855 (m), 1579 (m), 1464 (m), 1438 (m), 1401 (m), 1284 (w), 1232 (m), 1102 (w), 1068 (w), 1027 (w), 980 (w), 916 (m), 859 (m), 834 (s), 788 (m), 722 (w), 693 (w), 596 (m, C–Br) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=233 (4.16), 256 sh (3.82), 275 sh (4.52), 285 (4.82), 293 (4.81), 325 sh (3.65), 336 (3.76), 350 (3.81), 364 (3.81), 497 sh (2.45), 539 (2.61), 574 sh (2.56), 631 sh (2.12) nm; HRMS (ESI positive): calcd for $C_{14}H_{15}Br$+H$^+$ 263.0430; found 263.0461. Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74; found: C, 64.03; H, 5.85.

*4.1.14. 2-Bromo-6-hexylazulene (**9b**).* To a solution of 6-hexyl-2-hydroxyazulene (**8b**) (308 mg, 1.35 mmol) in dry toluene (50 mL) was added PBr_3 (2.02 g, 7.46 mmol). The resulting mixture was heated at 100 °C for 1 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 **9b** (286 mg, 73%). Violet plates; mp 87.8–89.0 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.13 (d, $^3J_{H,H}$=10.4 Hz, 2H, 4,8-H), 7.26 (s, 2H, 1,3-H), 7.12 (d, $^3J_{H,H}$=10.4 Hz, 2H, 5,7-H), 2.77 (t, $^3J_{H,H}$=7.8 Hz, 2H, 1′-H), 1.69 (tt, $^3J_{H,H}$=7.8, 7.3 Hz, 2H, 2′-H), 1.39–1.28 (m, 6H, 3′,4′,5′-H), 0.88 (t, $^3J_{H,H}$=7.1 Hz, 3H, 6′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=154.18 (C-6), 138.52 (C-3a,8a), 134.67 (C-4,8), 125.77 (C-5,7), 125.74 (C-2), 118.40 (C-1,3), 42.42 (C-1′), 32.52 (C-2′), 31.67 (C-4′), 28.96 (C-3′), 22.55 (C-5′), 14.06 (C-6′); IR (KBr disk): ν_{max}=2961 (m), 2927 (s), 2855 (m), 1581 (m), 1557 (w), 1545 (w), 1465 (w), 1438 (m), 1402 (s), 1286 (w), 1232 (w), 1072 (w), 973 (w), 917 (w), 861 (w), 838 (s), 791 (m), 596 (m, C–Br) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=234 (4.23), 286 (4.87), 293 (4.87), 325 sh (3.76), 337 (3.86), 350 (3.90), 364 (3.88), 502 sh (2.58), 537 (2.71), 575 sh (2.65), 629 sh (2.26) nm; HRMS (ESI positive): calcd for $C_{16}H_{19}Br$+H$^+$ 291.0743; found 291.0744. Anal. Calcd for $C_{16}H_{19}Br$: C, 65.99; H, 6.58; found: C, 66.37; H, 6.54.

*4.1.15. 2-Bromo-6-decylazulene (**9c**).* To a solution of 6-decyl-2-hydroxyazulene (**8c**) (776 mg, 2.73 mmol) in dry toluene (100 mL) was added PBr_3 (2.44 g, 9.01 mmol). The resulting mixture was heated at 100 °C for 1 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 **9c** (550 mg, 58%). Violet plates; mp 76.1–77.1 °C (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.13 (d, $^3J_{H,H}$=10.5 Hz, 2H, 4,8-H), 7.26 (s, 2H, 1,3-H), 7.12 (d, $^3J_{H,H}$=10.5 Hz, 2H, 5,7-H), 2.77 (t, $^3J_{H,H}$=7.0 Hz, 2H, 1′-H), 1.69 (tt, $^3J_{H,H}$=8.1, 7.0 Hz, 2H, 2′-H), 1.39–1.25 (m, 14H, 3′–9′-H), 0.87 (t, $^3J_{H,H}$=7.0 Hz, 3H, 10′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=154.18 (C-6), 138.54 (C-3a,8a), 134.66 (C-4,8), 125.77 (C-5,7 and C-2), 118.41 (C-1,3), 42.42 (C-1′), 32.56 (C-2′), 31.87 (t), 29.57 (t), 29.52 (t), 29.47 (t), 29.29 (t, 2C), 22.66 (t), 14.10 (C-10′); IR (KBr disk): ν_{max}=2917 (s), 2850 (s), 1582 (m), 1532 (w), 1467 (m), 1440 (w), 1402 (m), 1290 (w), 1234 (w), 1218 (w), 1156 (w), 1070 (w), 1031 (w), 969 (w), 916 (w), 862 (w), 831 (m), 787 (w), 768 (w), 720 (w), 594 (m, C–Br) cm^{-1}; UV–vis (CH_2Cl_2): λ_{max} (log ε)=235 (4.11), 255 sh (3.82), 286 (4.77), 294 (4.78), 325 sh (3.69), 337 (3.78), 350 (3.80), 364 (3.78), 395 sh (2.26), 503 sh (2.48), 537 (2.60), 573 sh (2.55), 627 sh (2.17) nm; HRMS (ESI positive): calcd for $C_{20}H_{27}Br$+H$^+$ 347.1369; found 347.1353. Anal. Calcd for $C_{20}H_{27}Br$: C, 69.16; H, 7.84; found: C, 69.47; H, 7.77.

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Supplementary data

General and experimental details for the electrochemical measurements; cyclic voltammograms of *n*PAs **3a**–**e**; spectroelectrograms of *n*PAs **3a**–**e**; UV/vis spectra of *4*PA **3a**, *6*PA **3b**, and *10*PA **3d** and related compounds; Copies of ^{1}H and ^{13}C NMR spectra of the reported compounds; DFT calculation results based on B3LYP/6-31G** method. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.084. These data include MOL files and InChiKeys of the most important compounds described in this article.

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