Azulene-Substituted Donor-Acceptor Polymethines and 1,6′-Bi-, 1,6′;3,6′′-Ter-, and Quinqueazulenes via Zincke Salts: Synthesis, and Structural, Optical, and Electrochemical Properties

Taku Shoji,*[a, b] Akari Yamazaki,[a] Yukino Ariga,[a] Mayumi Uda,[a] Daichi Ando,[b] Nichika Sasahara,[b] Naohito Kai,[c] and Shunji Ito[c]

Dedicated to the late Professor Klaus Hafner for his long-termed contribution to azulene chemistry.

Azulene-substituted donor-acceptor polymethines, bi-, ter-, and quinqueazulenes composed of the 1,6′-biazulene unit have been successfully prepared from corresponding Zincke salts. The synthesis of polymethines through the reaction of Zincke salts with several amines, followed by a Knoevenagel reaction with malononitrile, was accomplished in moderate to high yields (40–92%). Meanwhile, the reaction of Zincke salts with secondary amines and the subsequent sequential condensation-cyclization with cyclopentadienide ions, so-called Ziegler-Hafner method, produced the corresponding 1,6′-biazulenes, 1,6′;3,6′′-terazulenes, and quinqueazulene, respectively. The structural, optical, and electrochemical properties of the azulene-substituted donor-acceptor polymethines, bi-, ter-, and quinqueazulenes were revealed by single-crystal X-ray structure analysis, UV/vis spectroscopy, voltammetry analysis, spectroelectrochemistry, and theoretical calculations. These results suggested that the substituents on the azulene ring and their substitution positions directly affect their reactivities, optical and electrochemical properties.

Introduction

Since the discovery of Zincke salts in 1904, the salts which could be obtained by the reaction of pyridine derivatives with 2,4-dinitrochlorobenzene[1] are widely used as natural product synthesis,[2] substructures of pharmaceuticals,[3] organic materials,[4] and precursors for polymethine dyes.[5] The polymethine dyes, which are bonded donor and acceptor units to both terminals, can be prepared via the ring-opening reaction of the Zincke salts with amines. The dyes are an important class of compounds to elucidate the correlation between the donor-acceptor chromophores and their electronic and optical properties.[6] Hence, there has been a large volume of literature on the synthesis and characterization of the polymethine dyes with donor and acceptor moieties by this method.[5,6,7] Meanwhile, in the chemistry of azulene, the Zincke salt was applied to the synthesis of azulenes by Ziegler and Hafner et al., in which the Zincke salt is treated with amines or anilines, by following the sequential nucleophilic-cyclization reactions with cyclopentadienide ion.[8] Nowadays, this methodology is well known as Ziegler-Hafner's azulene synthesis, which has been approved as the best way to synthesize the parent azulene.[9]

In recent years, several synthetic methods for 1-pyridyl- or 1,3-di(pyridyl)azulene derivatives have been developed.[10] Our group has also established the efficient synthesis of 1-(4-pyridyl)- and 1,3-di(4-pyridyl)azulenes by the subsequent electrophilic substitution and aromatization reactions.[11] Although the pyridine derivative is a promising building block for the construction of polymethine dyes and azulenes, the reactivity of 1-(4-pyridyl)- and 1,3-di(4-pyridyl)azulenes has been hardly explored, excluding the N-alkylation reaction of the pyridine moiety. Since many applications have been found in azulene derivatives with extended π-conjugated systems, such as photovoltaics, semiconductors, and stimuli-responsive and electrochromic materials, the development of the new synthetic methods for the polymethines and the azulene ring assemblies starting from the 1-(4-pyridyl)- and 1,3-di(4-pyridyl)azulenes as precursors and characterization of their properties should contribute to the field of organic electronics.

In this paper, we report the synthesis of azulene-substituted polymethines, 1,6′-biazulenes, 1,6′;3,6′′-terazulenes and a quinqueazulene, utilizing the azulene-substituted Zincke salts as precursors, which are prepared from 1-(4-pyridyl)- and 1,3-di(4-pyridyl)azulenes.[12] The structure of some products was revealed by single-crystal X-ray analysis. The optical and electro-

[a] Prof. Dr. T. Shoji, A. Yamazaki, Y. Ariga, M. Uda
Department of Material Science
Graduate School of Science and Technology
Shinshu University
Matsumoto 390-8621,
Nagano (Japan)
E-mail: tshoji@shinshu-u.ac.jp
[b] Prof. Dr. T. Shoji, D. Ando, N. Sasahara
Department of Chemistry
Faculty of Science
Shinshu University
Matsumoto 390-8621,
Nagano (Japan)
[c] N. Kai, Prof. Dr. S. Ito
Graduate School of Science and Technology,
Hirosaki University
Hirosaki 036-8561,
Aomori (Japan)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cplu.202100174

chemical properties of the azulene-substituted polymethines, 1,6′-biazulenes and 1,6′;3,6′′-terazulenes were clarified by UV/vis spectroscopy, voltammetry analysis, spectroelectrochemistry, and theoretical calculations.

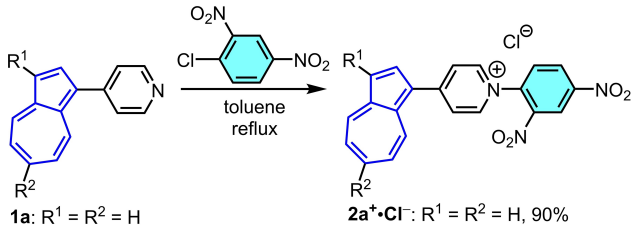
Results and Discussion

Synthesis of azulene-substituted polymethines

As mentioned above, pyridine derivatives are well-known for the derivation into pyridinium salts and the subsequent reactions with amines induced into the polymethines through the ring-opening reactions.[1–6] Thus, for the synthesis of azulene-substituted polymethines, we have employed 1-(4-pyridyl)- and 1,3-di(4-pyridyl)azulenes as starting materials, which can be efficiently prepared by our method reported previously.

The conversion of the 1-(4-pyridyl)- and 1,3-di(4-pyridyl) azulenes to the corresponding pyridinium salts, which become efficient precursors for the polymethines, was accomplished by the reaction with 1-chloro-2,4-dinitrobenzene as previously reported in the synthesis of the parent azulene by Hafner et al.[8,9] The reaction of **1a**[11a] with 1- chloro-2,4-dinitrobenzene in toluene at refluxing temperature afforded Zincke salt **2a**$^+$·Cl$^-$[12a] in 90% yield (Scheme 1). Since the Zincke salt **2a**$^+$·Cl$^-$ was insoluble toward the reaction solvent, the product was precipitated during the reaction, which could be easily isolated by simple filtration. The Zincke salts **2b**$^+$·Cl$^-$ [12b] and **2c**$^+$·Cl$^-$ were also prepared from 1-(4-pyridyl)azulenes **1b**[11c] and **1c**[11d] in a similar manner (Scheme 1).

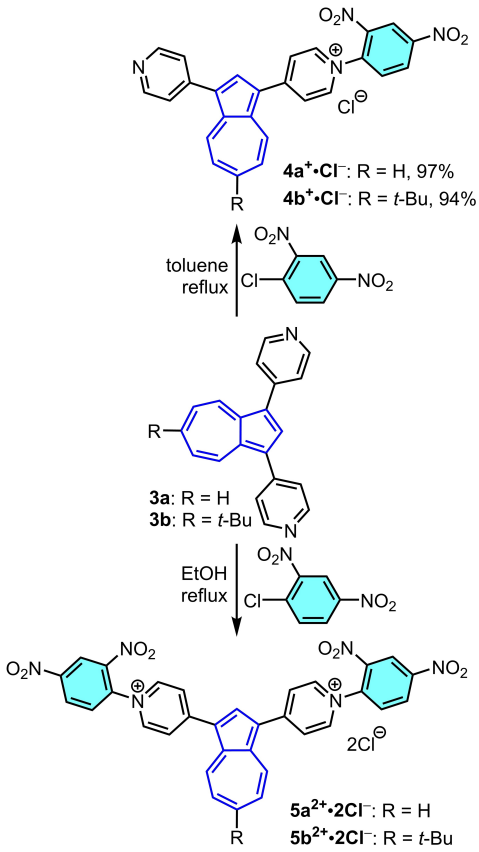
Subsequently, the preparation of the Zincke salts with two pyridinium groups at the 1,3-positions of the azulene ring was examined according to the similar procedure described above. However, the reaction of 1,3-(4-pyridyl)azulenes **3a** and **3b** with 1-chloro-2,4-dinitrobenzene in refluxing toluene produced Zincke salts **4a**$^+$·Cl$^-$[12b] and **4b**$^+$·Cl$^-$, [12b] which were retained an unreacted pyridine ring, in 94% and 97% yields, respectively (Scheme 2). This incompleteness of the reaction should be attributed to the precipitation of the products **4a**$^+$·Cl$^-$ and **4b**$^+$·Cl$^-$ in the reaction solvent. Therefore, to avoid the precipitation of the products, ethanol was selected as the solvent that facilitated the dissolution of the pyridinium salts. As a result, the reaction in ethanol was found to give Zincke salts **5a**$^{2+}$·2Cl$^-$[12b] and **5b**$^{2+}$·2Cl$^-$[12b] with the two-pyridinium units in 99% and 99% yields, respectively, from **3a** and **3b** (Scheme 2). However, because of the difficulty in purifying the dicationic products, **5a**$^{2+}$·2Cl$^-$ and **5b**$^{2+}$·2Cl$^-$ were employed in the next reaction without further purification.



1a: $R^1 = R^2$ = H
1b: R^1 = H, R^2 = *t*-Bu
1c: $R^1 = R^2$ = *t*-Bu

2a$^+$•**Cl**$^-$: $R^1 = R^2$ = H, 90%
2b$^+$•**Cl**$^-$: R^1 = H, R^2 = *t*-Bu, 97%
2c$^+$•**Cl**$^-$: $R^1 = R^2$ = *t*-Bu, 99%

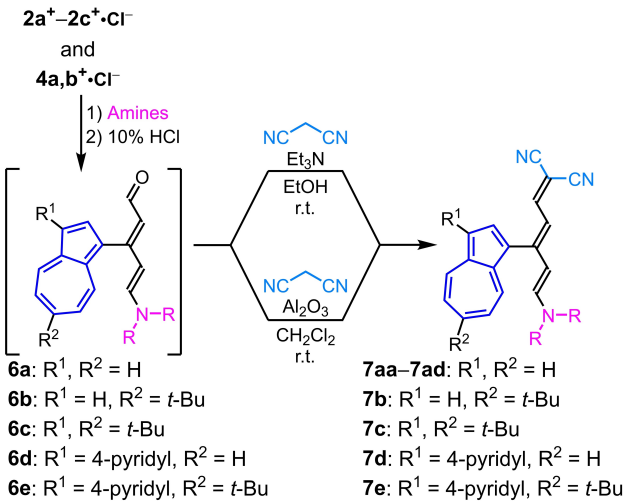
Scheme 1. Synthesis of azulene-substituted pyridinium salts **2a–c**$^+$·Cl$^-$.



Scheme 2. Synthesis of azulene-substituted pyridinium salts **4a,b**$^+$·Cl$^-$ and **5a,b**$^{2+}$·2Cl$^-$.

The ring-opening of the pyridinium salts **2a–c**$^+$·Cl$^-$ was conducted by the reaction with several secondary amines, so-called Zincke reaction (Scheme 3).[13] The Zincke reaction of **2a**$^+$·Cl$^-$ with diethylamine, by following the hydrolysis with 10% HCl, produced the Zincke aldehyde **6a**. However, the aldehyde **6a** was unstable to show significant decomposition during the purification by silica gel chromatography. Therefore, the aldehyde **6a** was transformed to **7aa**[12a] by Knoevenagel reaction with malononitrile without further purification in 57% as a two-step yield from **2a**$^+$·Cl$^-$ (Table 1, Entry 1). The similar ring-opening of **2a**$^+$·Cl$^-$ was also found in the reaction with morpholine, piperidine, and pyrrolidine, and the subsequent amine-induced Knoevenagel reaction with malononitrile produced the corresponding polymethines **7ab–7ad**[12a] in moderate to good yields (Table 1, Entries 3, 5 and 7).

In 1982, Texier-Boullet and Foucaud reported the Knoevenagel reaction of various carbonyl compounds with active methylene compounds using alumina as a catalyst.[14] Since their preparation method is simple to operate and the product yields are good to excellent, their methodology is adopted for the synthesis of various donor-acceptor type molecules.[15] We also evaluated the Knoevenagel reaction using alumina as a catalyst



Scheme 3. Synthesis of azulene-substituted polymethines **7a–e**. For the R groups on the amine moiety, see Table 1.

Table 1. Synthesis of azulene-substituted polymethines **7a–e**.

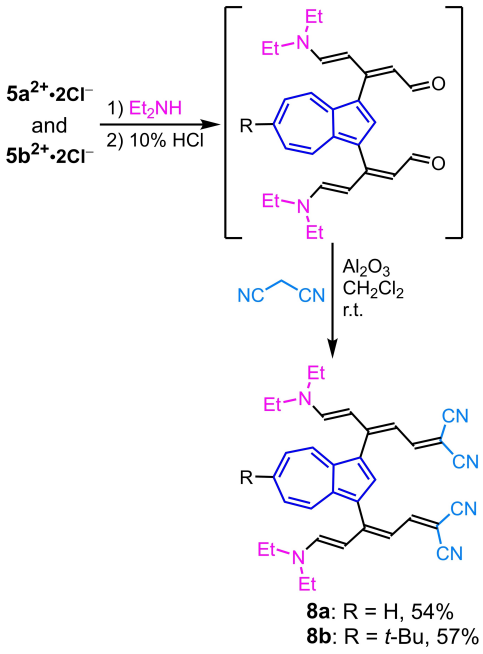
Entry	Ring-opening reaction substrate	amine	Knoevenagel reaction additive	product, yield [%][a]
1	**2a**$^+$·Cl$^-$	Et_2NH	Et_3N	**7aa**, 57
2	**2a**$^+$·Cl$^-$	Et_2NH	alumina	**7aa**, 64
3	**2a**$^+$·Cl$^-$	morpholine	Et_3N	**7ab**, 75
4	**2a**$^+$·Cl$^-$	morpholine	alumina	**7ab**, 89
5	**2a**$^+$·Cl$^-$	piperidine	Et_3N	**7ac**, 40
6	**2a**$^+$·Cl$^-$	piperidine	alumina	**7ac**, 81
7	**2a**$^+$·Cl$^-$	pyrrolidine	Et_3N	**7ad**, 52
8	**2a**$^+$·Cl$^-$	pyrrolidine	alumina	**7ad**, 66
9	**2b**$^+$·Cl$^-$	diethylamine	Et_3N	**7b**, 80
10	**2b**$^+$·Cl$^-$	diethylamine	alumina	**7b**, 76
11	**2c**$^+$·Cl$^-$	diethylamine	alumina	**7c**, 92
12	**4a**$^+$·Cl$^-$	diethylamine	alumina	**7d**, 84
13	**4b**$^+$·Cl$^-$	diethylamine	alumina	**7e**, 87

[a] two-step yield from the pyridinium salts **2a**$^+$·Cl$^-$–**2c**$^+$·Cl$^-$ and **4a,b**$^+$·Cl$^-$.

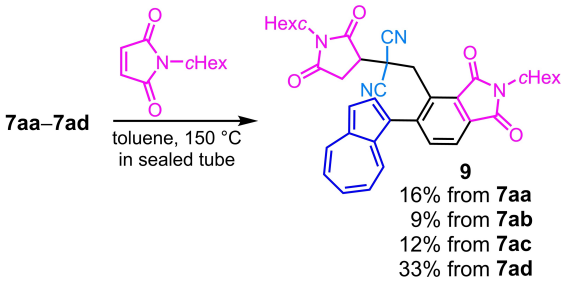
as another condition for the preparation of **7aa–ad** because this might become more useful conditions than those of the base-catalyzed reaction. As a result, the alumina-catalyzed Knoevenagel reaction of the Zincke aldehydes with malononitrile provided the desired polymethines **7aa–ad** in higher yields than those under the basic conditions (Table 1, Entries 2, 3, 6, and 8). Furthermore, the alumina catalyst could be easily removed by filtration at the workup process. The above results suggest that the alumina-catalyzed Knoevenagel reaction is a better selection for the preparation of the donor-acceptor type polymethines. Thus, the ring-opening reaction of the pyridinium salts **2b,c**$^+$·Cl$^-$ and **4a,b**$^+$·Cl$^-$ with diethylamine, by following the alumina-catalyzed Knoevenagel reaction with malononitrile also afforded the corresponding polymethines **7b–e** in good to excellent yields without the isolation of **6b–e** (Table 1, Entries 9–13).

Azulene derivatives **8a,b** with two polymethine units were also obtained by the same method. The Zincke salts **5a**$^{2+}$·2Cl$^-$ and **5b**$^{2+}$·2Cl$^-$ with two pyridinium groups were treated with diethylamine to produce the corresponding aldehydes, which were difficult to isolate. The alumina-catalyzed Knoevenagel reaction of the aldehydes with malononitrile gave **8a** and **8b** in 54% and 57% yields, respectively (Scheme 4).

In general, electron-rich dienes undergo [4+2] cycloaddition with electron-deficient alkenes, known as Diels-Alder reaction, to form the corresponding six-membered ring products. Since the obtained polymethines have a triene moiety, the Diels-Alder reaction with olefins may proceed to afford cycloaddition products. Since the polymethines possess both an amine moiety, which has an electron-donating ability, and a dicyanovinyl group, which shows an electron-withdrawing nature, at both termini, the reactivity and reaction site of the triene with olefins is of great interest. Therefore, the [4+2] cycloaddition of the polymethines **7aa–ad** with maleimide, which is known as one of the reactive olefins, was examined for the evaluation of their reactivity (Scheme 5). As a result, the reaction of **7aa–ad** with *N*-cyclohexyl maleimide in toluene at 150 °C yielded the azulene-substituted phthalimide **9**, which is obtained by the elimination of the amino group from the presumed cycloadduct and further addition of the second maleimide to the dicyanovinyl moiety, instead of the formation



Scheme 4. Synthesis of azulene-substituted polymethines **8a,b**.



Scheme 5. [4+2] cycloaddition of **7aa–ad** with *N*-cyclohexylmaleimide.

of the usual simple [4+2] cycloadduct. The structure of **9** is supported by single-crystal X-ray structure analysis as appeared later (Figure 2).

The presumed reaction mechanism for the formation of **9** is shown in Scheme 6. Initially, the usual [4+2] cycloaddition of maleimide to the polymethine moiety takes place to give the intermediate **A**. Subsequently, the amine is eliminated from **A** to form the diene **B**. Additionally, the carbanion **C** stabilized by the dicyanomethylene unit is formed by the deprotonation under the basic conditions, which undergoes conjugate addition to another maleimide to afford intermediate **D**. Finally, the aromatization occurs at the cyclohexadienylidene moiety by the allyl rearrangement of **D** to form **9**. Since the intermediates illustrated in Scheme 6 have never been isolated, there might be still room for argument about the mechanism for the formation of **9**.

Spectroscopic properties of azulene-substituted polymethines

These new compounds were fully characterized based on their spectral data, as summarized in the Experimental Section. The NMR spectroscopic assignment of the reported compounds was confirmed by the COSY experiment (Supporting Information Figures S1–S48). High-resolution mass spectra showed the correct molecular ion peaks. The characteristic stretching vibration band of the C≡N moieties of **7**, **8**, and **9** was observed at ν_{max} = 2188–2201 cm^{-1} in their IR spectra. These results are consistent with the structures of these products.

Since single crystals suitable for the X-ray structure analysis were obtained, the structures of **7aa** and **9** were clarified by the single-crystal X-ray structure analysis (Figures 1 and 2).[16] The triene moiety of **7aa** containing diethylamine and dicyanomethylene takes all-trans and almost planar structure. The crystal structure analysis of **7aa** also revealed a twisted conformation between the azulene and polymethine planes, in which the dihedral angle was 63.42° (Figure 1). The single bond in the triene moiety of **7aa** was shorter than the general bond length, while the double bond showed a longer bond distance compared to that of the normal double bond. This supports the push-pull resonance effect between the amine and the dicyanomethylene moieties as represented by the resonance structures shown in Scheme 7.

To elucidate the optical properties of the azulene-substituted polymethines, the UV/Vis spectra of the series of **7** and **8** were measured in CH_2Cl_2 and 10% CF_3CO_2H (TFA)/CH_2Cl_2. The

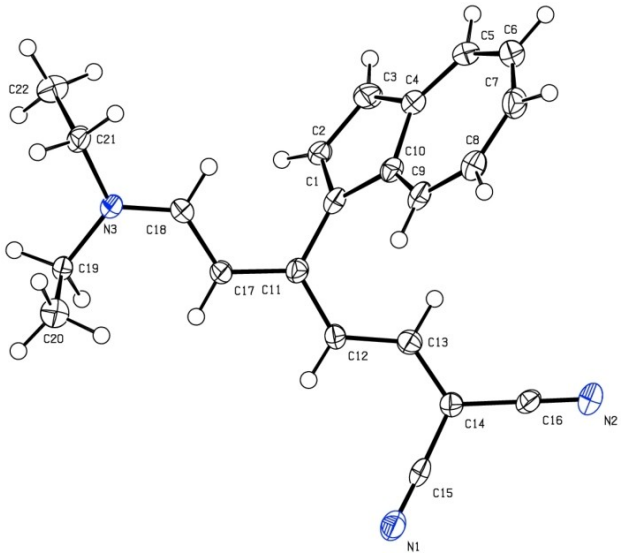


Figure 1. ORTEP representation of **7aa** (Deposition Number 1838801 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures) recrystalized from a mixed solvent of CH_2Cl_2/MeOH; ellipsoids are shown at the 50% probability level. orthorhombic, $Pca2_1$ (#29), a = 10.1071(4) Å, b = 15.4777(6) Å, c = 11.3725(5) Å, V = 1779.05(13) $Å^3$, Z = 4, D_{calc} = 1.222 g/cm^3, $\mu(MoK_\alpha)$ = 0.730 cm^{-1}, R1 (I > 2.00σ) = 0.0604, R (All reflections) = 0.0747, wR2 (All reflections) = 0.1421.

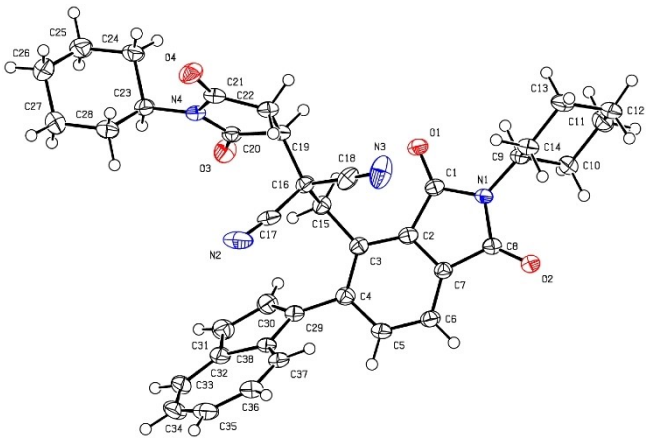
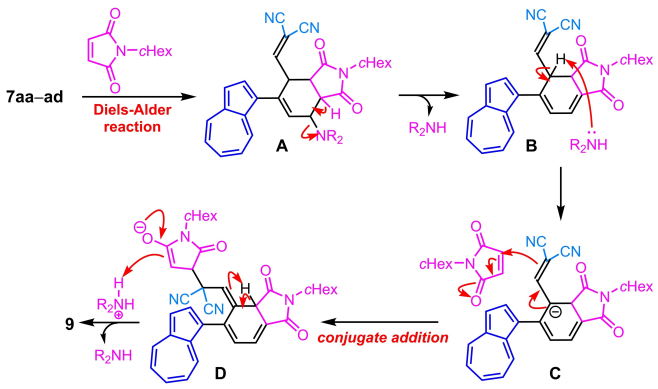
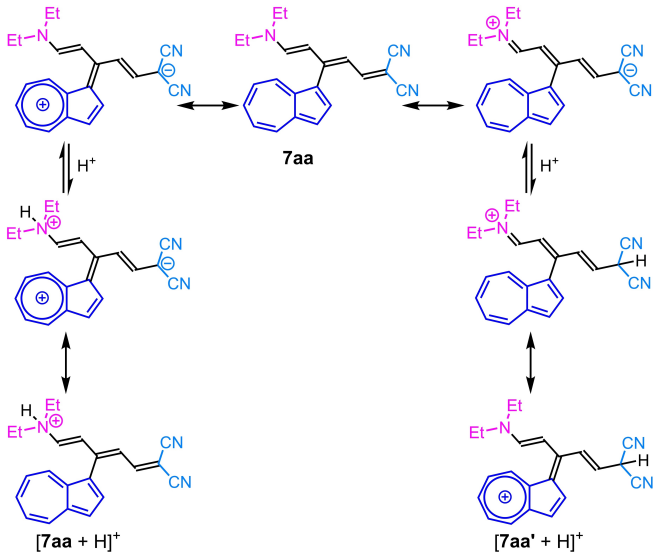


Figure 2. ORTEP representation of **9** (Deposition Number 1922390 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures) recrystalized from mixed solvent of $CHCl_3$/MeOH; ellipsoids are shown at the 50% probability level. orthorhombic, $Pca2_1$ (#29), a = 33.5514(17) Å, b = 6.3927(3) Å, c = 31.6001(16) Å, β = 110.124(6)°, V = 6363.9(6) $Å^3$, Z = 4, D_{calc} = 1.279 g/cm^3, $\mu(MoK_\alpha)$ = 0.839 cm^{-1}, R1 (I > 2.00σ) = 0.0765, R (All reflections) = 0.1339, wR2 (All reflections) = 0.2081.



Scheme 6. Presumed reaction mechanism for the formation of **9**.



Scheme 7. Resonance structure and protonation behavior of **7aa**.

UV/Vis spectra of **7aa**–**ad** in CH_2Cl_2 showed a strong and broad absorption band in the visible region, but their absorption maxima were almost the same from each other (Figure 3). The absorption maximum of **7aa** was observed at $\lambda_{max} = 505$ nm in CH_2Cl_2. This strong absorption band should be explained by the push-pull effect on both the azulene and amine moieties to the dicyanomethylene unit as illustrated in Scheme 7. Similarly, **7ab**, **7ac**, and **7ad** showed the maximum absorption wavelengths at $\lambda_{max} = 509$ nm, 506 nm, and 509 nm, respectively, but **7ab** showed a slight decrease in molar absorption coefficient, although the reason is unclear.

When the solvent was changed to 10% TFA/CH_2Cl_2 from CH_2Cl_2, a remarkable decrease in the molar absorption coefficient was observed for the maximum absorption band of **7aa**. In the acidic medium, by the protonation of either the amine moiety or the dicyanomethylene unit, $[\mathbf{7aa}+H]^+$ and $[\mathbf{7aa'}+H]^+$ should be generated. Since the donor nature of the amine moiety disappears by the protonation, the electron donation is allowed only from the azulene ring, which should contribute to the absorption band of $[\mathbf{7aa}+H]^+$ with the lower molar absorption coefficient.

Compounds **7b** and **7c** with *t*Bu groups on the azulene ring exhibited a slight red-shift compared to that of **7aa**, but the shift values were almost negligible. These results also imply that the push-pull effect from the amine moiety to the dicyanomethylene moiety contributes more effectively than that from the azulene ring. The absorption maxima of **8a** and **8b**, which have two polymethine units at the 1,3-positions of azulene, are almost identical to those of **7aa** and **7b**, while the molar absorption coefficients tend to increase with the number of polymethine units (Figure 4). These phenomena are originated from the overlap of the absorption bands arising from the push-pull effect within the two polymethines and the resonance effect between the central 1,3-azulen-di-yl core and the two dicyanomethylene moieties as represented by the resonance structures shown in Scheme 7.

To clarify the origin of the absorption band of **7aa** in the UV/Vis spectra from a theoretical aspect, the electronic transition of the absorption band and HOMO and LUMO energies were investigated by time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G** level.[17] Since the absorption spectra for the series of **7** and **8** were similar to each other, **7aa** was evaluated as a model compound. The electronic transitions of **7aa** derived from the calculations are summarized in Table 2. The frontier Kohn–Sham orbitals and their energy levels are represented in Figure 5.

Theoretical calculations revealed that the strong absorption band at 505 nm of **7aa** is mainly composed of π-π^* transitions from azulene to triene (H−1→L+1), triene moiety itself (H→L+1), and triene to azulene (H→L+2). TD-DFT calculations also suggest that several transitions are involved in the end absorption, but their contribution to the absorption band is negligibly small from the viewpoint of the oscillator strength. These results support the existence of the push-pull effect both

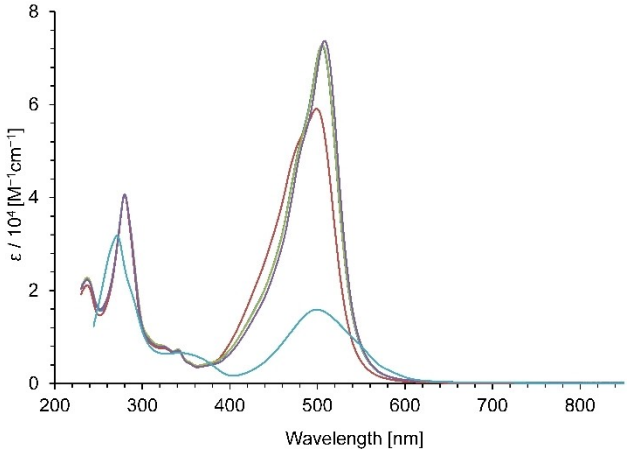


Figure 3. UV/Vis spectra of the polymethines **7aa** (blue line), **7ab** (red line), **7ac** (light-green line), and **7ad** (purple line) in CH_2Cl_2 and **7aa** (light-blue line) in 10% TFA/CH_2Cl_2.

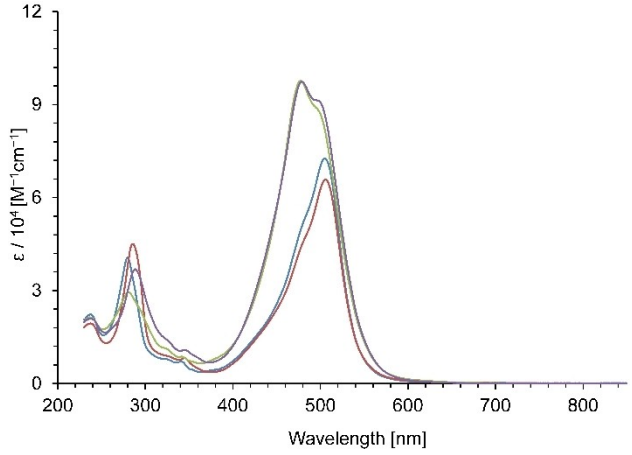


Figure 4. UV/Vis spectra of the polymethines **7aa** (blue line), **7b** (red line), **8a** (light-green line) and **8b** (purple line) in CH_2Cl_2.

Table 2. The electronic transitions of **7aa** derived from the computed values based on the TD-DFT calculations at the B3LYP/6-31G** level.

Sample	Experimental λ_{max} [log ε]	Computed values λ_{max} [Oscillator Strength]	Composition of band [contribution]
7aa	505 (4.86)	552 (0.0049)	H–1→L (0.0486) H→L (0.8497) H→L+1 (0.0846)
		488 (0.0035)	H–1→L (0.8765)
		421 (0.1381)	H–1→L+1 (0.7682) H→L+1 (0.0741)
		394 (0.1750)	H→L+1 (0.2459 H→L+2 (0.6882)

H = HOMO, L = LUMO.

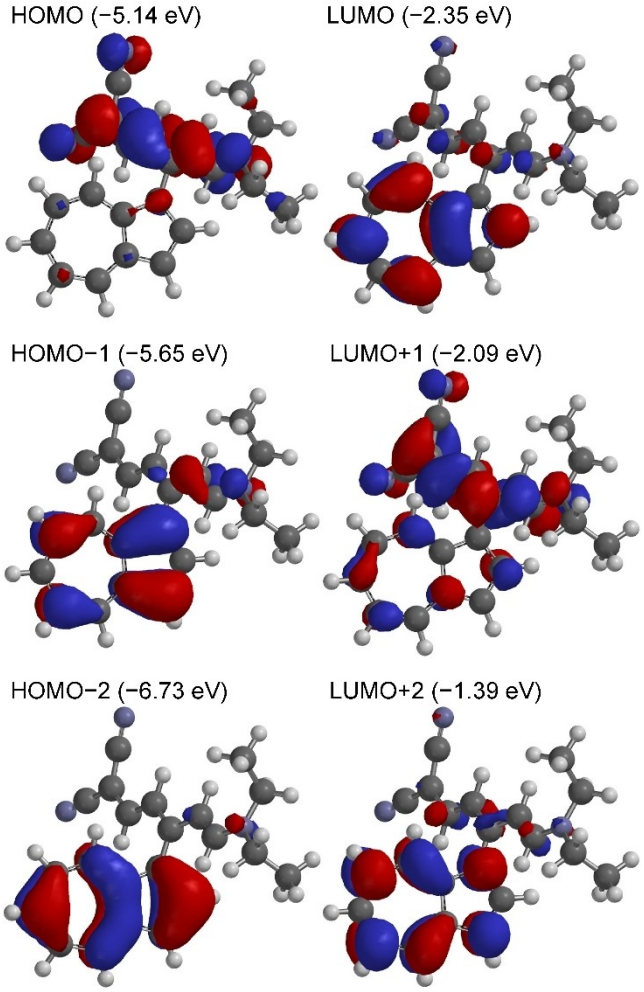


Figure 5. Frontier Kohn−Sham orbitals of **7aa** at the B3LYP/6-31G** level.

in the triene unit and in both azulene and triene moieties in **7aa**.

To clarify the electrochemical behavior of **7a**–**e** and **8a**,**b**, redox potentials of these products were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox potentials measured by DPV are summarized in Table 3. Cyclic and differential pulse voltammograms are appeared in Supporting Information (Figures 123–132).

Most of **7a**–**e** and **8a**,**b** were revealed to show irreversible redox waves by the CV measurements. The irreversibility could be derived from either the instability of the radical species generated or structural changes during the electrochemical redox reaction. The first oxidation and reduction potentials of these compounds were almost the same, meaning that the amine moiety on the trienes **7aa**–**ad** has no noticeable effect on the electronic properties. On the other hand, the *t*Bu groups at the 1- or 6-positions of the azulene ring increase both the first oxidation and reduction potentials. As a result, $\Delta E_1^{ox}-E_1^{red}$ values of **7b** and **7c** become almost equal to those of **7aa**–**ad**. These findings are consistent with the fact that the similarity in the maximum absorption wavelengths observed in the UV/Vis spectra of **7aa**–**ad**, **7b**, and **7c** because the $\Delta E_1^{ox}-E_1^{red}$ values should be correlated to the HOMO-LUMO gap. Pyridine-substituted adducts **7d**,**e**, and bis-adducts **8a**,**b** displayed slightly smaller $\Delta E_1^{ox}-E_1^{red}$ values than those of **7aa**–**ad**, **7b**, and **7c**, corresponding to the narrower HOMO-LUMO gap due to the extension of the π-conjugation.

Spectroelectrochemical measurements of **7aa**, **7b**–**e**, and **8a**,**b** were performed to verify the electrochromic behavior. In the spectroscopic electrochemical measurements, **7aa**, **7b**–**e**, except for **7c**, and **8a**,**b** exhibited relatively high reversibility in the redox cycles, meaning that the irreversibility in CV could be ascribed to the structural changes by the electrochemical reaction rather than the decomposition of the radical species produced

When the spectral changes of **7aa** were measured under the electrochemical reduction conditions, generation of broad absorption bands at around λ_{max} = 450 nm and 550 nm was observed along with the disappearance of the original absorption band at around 500 nm. Reverse oxidation of the reduced species of **7aa** recovered the original spectrum, but incompletely (regeneration 78%). Compound **7b** (regeneration 81%) also displayed similar spectral changes to **7aa**. However, the regeneration ratio of the original spectrum by the reverse oxidation of the reduced species of **7c** was rather low (regeneration 36%). This outcome suggests that the electron-donating nature of the *t*Bu group at the 1-position of the azulene ring might significantly destabilize the anionic species produced by the electrochemical reduction. The spectral change of **7d** was also developed new absorption bands centered at 480 nm and 580 nm under the electrochemical

Table 3. Redox potentials of the azulene-substituted polymethines **7a–7e** and **8a,b** measured by DPV.[a]

Sample	E_1^{ox} [V]	E_2^{ox} [V]	E_1^{red} [V]	E_2^{red} [V]	$\Delta E_1^{ox} - E_1^{red}$
7aa	+0.42	+1.01	−1.59	–	2.01
7ab	+0.43	+0.99	−1.53	–	1.96
7ac	+0.42	+0.99	−1.56	–	1.98
7ad	+0.43	+1.00	−1.53	–	1.96
7b	+0.34	+0.94	−1.62	−1.92	1.96
7c	+0.36	+0.87	−1.62	−1.93	1.98
7d	+0.40	+1.16	−1.51	–	1.91
7e	+0.39	–	−1.55	–	1.94
8a	+0.38	+1.24	−1.46	−1.76[b]	1.84
8b	+0.38	+1.21	−1.53	−1.92	1.91

[a] 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 20 mVs^{-1}, and external standard $Fc/Fc^+ = +0.15$ V. [b] E_3^{red} was also observed at −1.92 V.

reduction conditions. In contrast, the electrochemical reduction of **7e** at −1.80 V generated the broad absorption band spreading into 750 nm. Reverse oxidation of the reduced species regenerated the original spectra of **7d** (regeneration 64%) and **7e** (regeneration 79%) to some extent. Di-substituted products **8a** and **8b** also displayed pronounced spectral changes under the electrochemical reduction conditions, but the spectral recovery to the neutral species upon the reverse oxidation was also rather high, but incomplete (regeneration **8a**: 67% and **8b**: 94%).

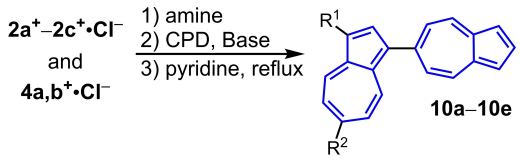
In general, cyanine dyes exhibit electrochromism with low reversibility due to the thermodynamic instability of the radical species generated by the electrochemical redox reactions.[18] However, **7aa**, **7b–e**, and **8a,b** showed relatively good reversibility in the spectroelectrochemistry, except for **7c**, which might indicate the stabilization of the generated radical species by the azulene ring on the cyanine moiety through the delocalization on the whole molecule.

Synthesis of bi-, ter-, and quinqueazulenes

An efficient synthesis of the parent azulene was achieved by Ziegler and Hafner et al. via condensation of the Zincke salt with cyclopentadienide ion by the subsequent intramolecular cyclization reaction. Numerous azulene derivatives have been prepared by this method because this method is suitable for the synthesis of azulenes having no substituting groups on the five-membered ring.[19] This method was applied to the synthesis of 5,5′-[20] and 6,6′-biazulenes[21] by Hanke and Jutz. After that, there are no reports on the preparation of biazulenes by the Ziegler-Hafner method. Recently, terazulenes composed of 2,6′-biazulene core have been revealed the potential as high-performance n-type organic field-effect transistors,[22] so the development of the synthetic methods for biazulenes and terazulenes has attracted much attention in terms of the development of organic materials. Therefore, we addressed the synthesis of 1,6′-biazulene, 1,6′:3,6″-terazulene derivatives, and a quinqueazulene by the Ziegler-Hafner method using the azulene-substituted Zincke salts as promising starting materials.

The synthesis of 1,6′-biazulenes **10a–e** was conducted by the same procedure for the preparation of the parent azulene reported by Hafner et al. using the pyridinium salts **2a–c**$^+$·Cl^- and **4a,b**$^+$·Cl^- as starting materials (Table 4). The reaction of **2a–c**$^+$·Cl^- and **4a,b**$^+$·Cl^- with diethylamine or pyrrolidine in EtOH at room temperature afforded the corresponding iminium salts as brown oils, which were used in the following reactions without further purification. Recently, Langhals and Eberspächer have demonstrated that pyrrolidine is the most favorable amine for the ring-opening reaction of the pyridinium salt in the preparation of the parent azulene.[23] Hence, pyrrolidine was used as an amine for the ring-opening reaction of the

Table 4. Synthesis of 1,6′-biazulenes **10a–e**.



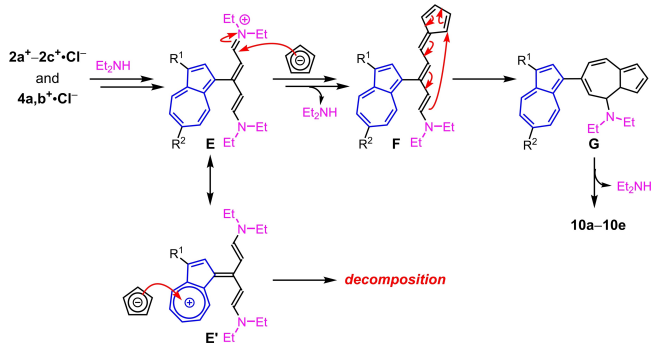
Entry	substrate	R^1	R^2	amine	Base	Product, yield [%][a]
1	**2a**$^+$·Cl^-	H	H	Et_2NH	NaOMe	**10a**, 56[12b]
2	**2b**$^+$·Cl^-	H	*t*Bu	Et_2NH	NaOMe	**10b**, 91[12b]
3	**2c**$^+$·Cl^-	*t*Bu	*t*Bu	pyrrolidine	*t*BuOK	**10c**, 90
4	**4a**$^+$·Cl^-	4-pyridyl	H	pyrrolidine	*t*BuOK	**10d**, 47
5	**4b**$^+$·Cl^-	4-pyridyl	*t*Bu	pyrrolidine	*t*BuOK	**10e**, 92

[a] isolated yield.

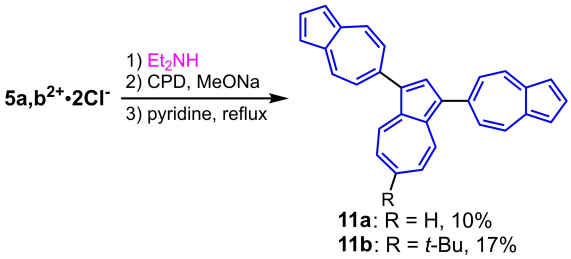
pyridinium salts **2c**$^+$·Cl$^-$ and **4a,b**$^+$·Cl$^-$. Condensation of the Zincke salts with cyclopentadiene (CPD) in the presence of sodium methoxide (NaOMe) or potassium *tert*-butoxide (KO*t*Bu) afforded the corresponding 1,6′-biazulenes **10a–e** in moderate to good yields in two steps from **2a–c**$^+$·Cl$^-$ and **4a,b**$^+$·Cl$^-$, respectively. Overall, **2b**$^+$·Cl$^-$, **2c**$^+$·Cl$^-$ and **4b**$^+$·Cl$^-$, which have a *t*Bu group at the 6-position of the azulene ring, tended to give 1,6′-biazulenes in higher yields rather than those from **2a**$^+$·Cl$^-$ and **4a**$^+$·Cl$^-$.

A plausible reaction mechanism for the formation of the 1,6′-biazulenes **10a–e** is shown in Scheme 8. Essentially, this reaction should be proceeded by the same mechanism as the formation of the parent azulene reported by Ziegler and Hafner. First, the ring-opening of the pyridinium salts **2a–c**$^+$·Cl$^-$ and **4a,b**$^+$·Cl$^-$ takes place and the subsequent condensation with diethylamine results in iminium salt **E**. The following condensation reaction of the iminium salt **E** with cyclopentadienide ion provides pentafulvene intermediate **F** accompanying the elimination of diethylamine. Finally, the formation of the hydroazulene intermediate **G** by the electrocyclic reaction of the fulvene intermediate **F** and the subsequent aromatization by deamination to produce 1,6′-biazulenes.

The difference in the yields for the 1,6′-biazulenes could be explained by the steric bulkiness of the *t*Bu group at the 6-position of the azulene ring. The iminium intermediate **E** has a contribution of the resonance structure **E′** where the azulene ring has a tropylium ion substructure. Therefore, the nucleophilic addition of cyclopentadienide ion to the azulene moiety at the seven-membered ring should take place to lead to the undesired decomposition in the reaction of **2a**$^+$·Cl$^-$ and **4a**$^+$·Cl$^-$ resulting in the low product yields. Whereas the derivatives



Scheme 8. Plausible reaction mechanism for the formation of 1,6′-biazulenes **10a–e** by Ziegler-Hafner's method.



Scheme 9. Synthesis of 1,6′;3,6″-terazulenes **11a,b**.

with a *t*Bu group at the 6-position may prevent the attack of the nucleophile to the seven-membered ring owing to the steric hindrance of **E′** by the substituent. Thus, **2b,c**$^+$·Cl$^-$, and **4b**$^+$·Cl$^-$ have probably been obtained in higher product yields compared to those of **2a**$^+$·Cl$^-$ and **4a**$^+$·Cl$^-$.

Likewise, the preparation of 1,6′-biazulenes **10a–e**, the synthesis of 1,6′;3,6″-terazulenes **11a,b**[12b] was also investigated using the corresponding bis-pyridinium derivatives **5a,b**$^{2+}$·2Cl$^-$ as starting materials (Scheme 9). The ring-opening reaction of **5a**$^{2+}$·2Cl$^-$ with diethylamine, by following the reaction with cyclopentadienide ion afforded the desired 1,6′;3,6″-terazulene (**11a**), but in low yield (10%). The 6-*tert*-butyl derivative **11b** was also obtained from **5b**$^{2+}$·2Cl$^-$ by the same method in 17% yield. The product yields were both low in these cases, but **5b**$^{2+}$·2Cl$^-$ having a *t*Bu group at the 6-position of the azulene ring gave a slightly higher product yield as predicted.

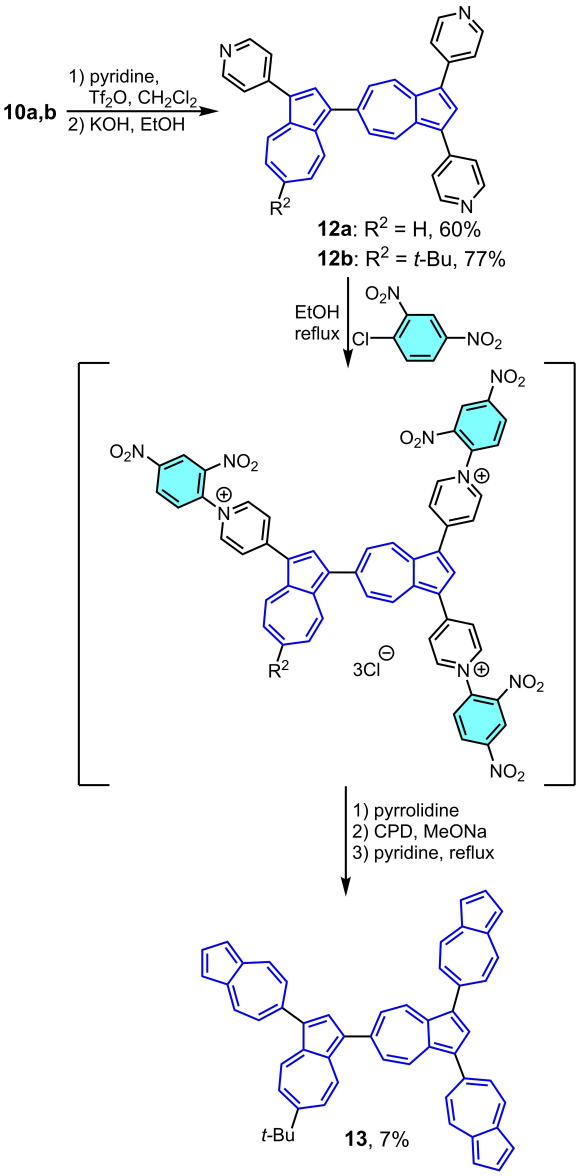
Next, the synthesis of a quinqueazulene was investigated to extend the scope of the synthetic methodology (Scheme 10). For the synthesis of the quinqueazulene, it is required to prepare the azulene derivatives with pyridine substituents as a precursor. Thus, the pyridinylation of **10a,b** was examined by the method reported by us, previously.[11] The reaction of **10a,b** with pyridine in the presence of trifluoromethanesulfonic anhydride (Tf_2O) by following the base-induced aromatization of the dihydropyridine intermediates with KOH afforded the tri(4-pyridyl) derivatives **12a** and **12b** in 60% and 77%, respectively, as two-step yields. Although **12a** could not convert to the quinqueazulene by the Ziegler-Hafner method due to the decomposition of the compound, the reaction of **12b** under the same conditions gave **13** in 7% yield.

To extend the applicability of this methodology, the preparation of unsymmetrically substituted 1,6′;3,6″-terazulene **15** was also investigated (Scheme 11). The electrophilic substitution reaction of **10d** with *N*-iodosuccinimide gave a diiodo derivative, which was insoluble in common organic solvents. Thus, the crude product was employed in the next Suzuki-Miyaura cross-coupling reaction with 4-*tert*-butylphenylboronic acid without further purification. The Suzuki-Miyaura cross-coupling reaction catalyzed by Pd(dppf)Cl_2 provided **14** in 44% yield, which could be converted to 1,6′;3,6″-terazulene **15** in 19% yield by the Ziegler-Hafner method.

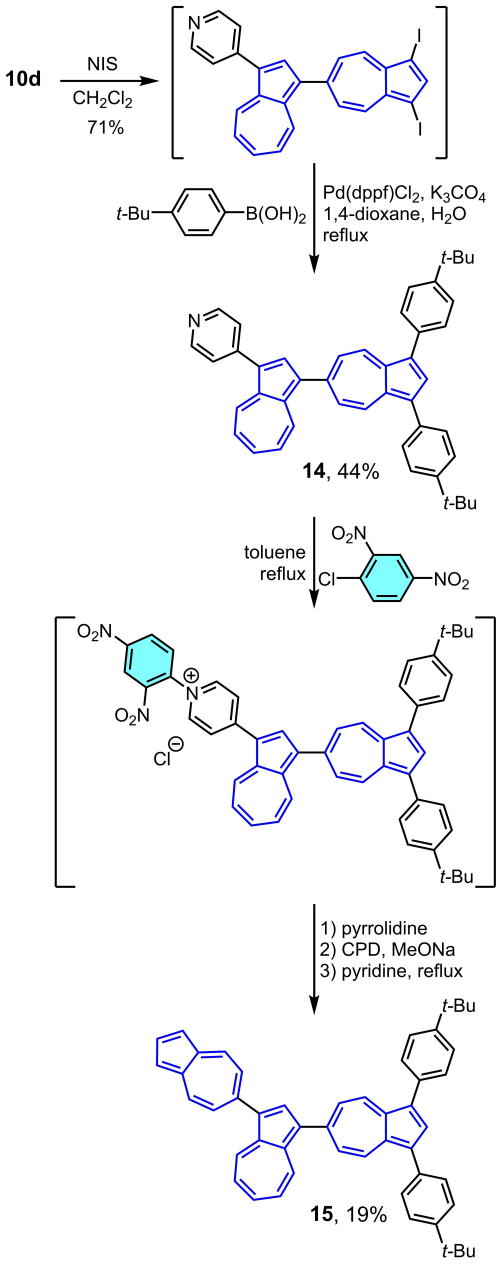
Spectroscopic properties of bi-, ter-, and quinqueazulenes

The new compounds were fully characterized based on their spectral data, as summarized in the Experimental Section. The NMR spectroscopic assignment of the reported compounds was confirmed by the COSY experiment (Supporting Information Figures S49–S83). High-resolution mass spectra showed the correct molecular ion peaks.

To elucidate the optical properties of a series of 1,6′-biazulenes, 1,6′;3,6″-terazulenes and a quinqueazulene prepared by this study, measurements of the UV/Vis spectra of these compounds were investigated (Supporting Information Figures S84–S121). The absorption maxima (λ_{max}) of the series of **10–15** in CH_2Cl_2 and 30% TFA/CH_2Cl_2 are summarized in Table 5.



Scheme 10. Synthesis of quinqueazulene **13**.



Scheme 11. Synthesis of unsymmetrical 1,6′;3,6″-terazulene **15**.

UV/Vis spectra of 1,6′-biazulenes, 1,6′;3,6″-terazulenes and the quinqueazulene in CH_2Cl_2 showed a characteristic weak absorption band in the range of 500–600 nm originating from the π-π* transition of the azulene rings, along with the strong absorption band at around 430 nm. Although the molar absorption coefficient increased with the number of azulene rings in the molecule, the substitution of the *t*Bu group at the 6-position of the azulene ring resulted in a slight blue-shift in the longest absorption wavelength (Table 5, Figure 6). For example, the longest absorption wavelength of **10a** (λ_{max} = 583 nm) displayed a blue-shift by 11 nm compared to that of **10b** (λ_{max} = 572 nm). This phenomenon can be explained by Plattner's rule, which states that the alkyl groups substituted at the even-numbered positions of the azulene ring (2-, 4-, 6- and 8-positions) represent a blue-shift of the absorption maxima in the visible region.[24] The longest absorption wavelengths of

Table 5. Absorption maxima and their coefficients (log ε) of **10**–**15** in CH_2Cl_2 and 30% TFA/CH_2Cl_2.

Sample	λ_{max} [log ε] in CH_2Cl_2[a]	λ_{max} [log ε] in 30% TFA/CH_2Cl_2[a]
10a	430 (4.32), 583 (2.95)	581 (4.56)
10b	439 (4.33), 572 (3.03)	601 (4.61)
10c	458 (4.22), 586 (3.04)	421 (3.87), 629 (4.46)
10d	419 (4.35), 587 (2.94)	412 (4.30), 552 (4.48)
10e	433 (4.24), 578 (3.08)	421 (4.42), 569 (4.47)
11a	436 (4.54), 579 (3.20)	575 (4.66)
11b	446 (4.57), 576 (3.24)	593 (4.74)
12a	456 (4.26), 590 (3.03)	427 (4.69)
12b	466 (4.39), 571 (3.23)	424 (4.59)
13	456 (4.84)	585 (4.96)
14	421 (4.52), 577 (2.97)	415 (4.34), 555 (4.52)
15	443 (4.58), 592 (3.17)	579 (4.70)

[a] Shoulder peaks are omitted for clarity.

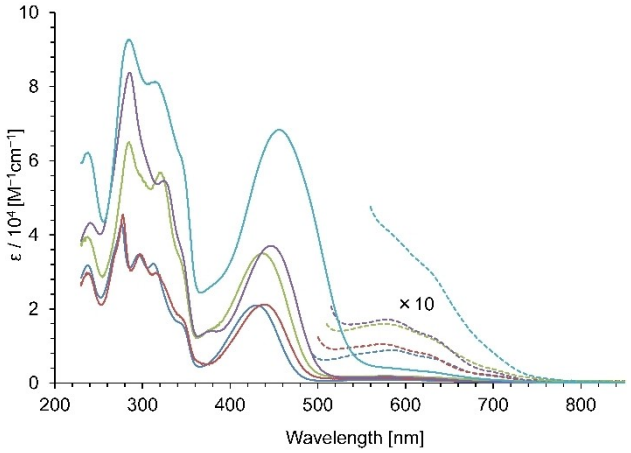


Figure 6. UV/Vis spectra of polymethines **10a** (blue line), **10b** (red line), **11a** (light-green line), **11b** (purple line) and **13** (light-blue line) in CH_2Cl_2; the dotted lines represent those of 10× magnification.

1,6′-biazulenes **10d** (λ_{max} = 587 nm), **10e** (λ_{max} = 578 nm), **12a** (λ_{max} = 590 nm), **12b** (λ_{max} = 571 nm) and **14** (λ_{max} = 577 nm) did not exhibit any significant difference from those of **10a,b**, suggesting that the pyridine substituents hardly contribute to the expansion of the π-conjugation. Contrary to the longest wavelength absorption band, the absorption band at around 430 nm exhibited a red-shift by the substitution of the *t*Bu group at the 6-position. Quinqueazulene **13** showed a strong and broad absorption band at λ_{max} = 456 nm, which spreads into the near-infrared region.

To examine the theoretical aspects of the spectroscopic properties, molecular orbital calculations were performed on **10a–c** by using B3LYP/6-31G** density functional theory.[17] The frontier Kohn-Sham orbitals of **10b** are shown in Figure 7. The theoretical calculations suggest that the strong absorption band of **10a** observed at λ_{max} = 430 nm can be explained by the transition from HOMO-1 to LUMO + 1, i.e., the π-π* transition from 1-azulenyl group to 6-azulenyl group (Table 6). Similar to **10a**, the strong absorption band of the compounds **10b** and

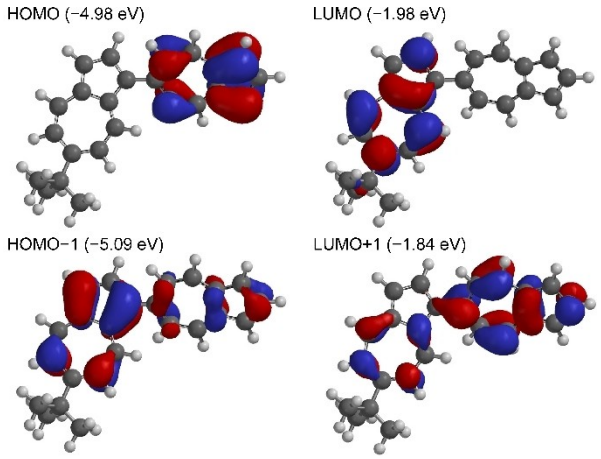


Figure 7. Frontier Kohn−Sham orbitals of **10b** at the B3LYP/6-31G** level.

Table 6. Their electronic transitions of **10a–c** derived from the computed values based on the TD-DFT calculations at the B3LYP/6-31G** level.

Sample	Experimental λ_{max}	Computed values λ_{max} [Oscillator Strength]	Composition of band (contribution)
10a[12b]	583 (2.95)	531 (0.0078)	H–1→L (0.9386)
		519 (0.0086)	H→L + 1 (0.9044)
		497 (0.0001)	H→L (0.9819)
	430 (4.32)	403 (0.4482)	H–1→L + 1 (0.8849)
10b	572 (3.03)	529 (0.0082)	H–1→L (0.9241)
		518 (0.0083)	H→L (0.0460)
			H→L + 1 (0.8750)
		486 (0.0001)	H→L (0.9495)
			H→L + 1 (0.0453)
	439 (4.33),	407 (0.5168)	H–1→L + 1 (0.8827)
10c	586 (3.04)	548 (0.0073)	H–1→L (0.6699)
			H→L (0.2596)
		518 (0.0079)	H–1→L + 1 (0.2369)
			H→L + 1 (0.6450)
		480 (0.0001)	H–1→L (0.2584)
			H→L (0.6961)
	458 (4.22)	421 (0.4904)	H–1→L + 1 (0.6360)
			H→L + 1 (0.2474)

H = HOMO, L = LUMO.

10c could also be regarded as the transition from the 1-azulenyl group to the 6-azulenyl group.

The theoretical calculations of the compounds **10a–c** reproduced the absorption maxima according to Plattner's rule. As shown in Table 6, the relatively weak absorption band of **10a** at λ_{max} = 583 nm originates from the overlap of several π-π* transitions involving HOMO and HOMO − 1 to LUMO and LUMO + 1. The energy levels of HOMO and LUMO of **10b** (HOMO: −4.98 eV; LUMO: −1.98 eV) are higher than those of **10a** (HOMO: −5.04 eV; LUMO: −2.10 eV). This is probably due to the *t*Bu group on the seven-membered ring of azulene, which raises both the HOMO and LUMO energy levels, but has a much pronounced effect on the LUMO level, resulting in a hypsochromic shift of the longest wavelength absorption band of **10b** compared to that of **10a**. According to Plattner's rule, the substitution of the electron-donating group at the 1-position of the azulene ring leads to a bathochromic shift of the longest wavelength absorption band, so that the absorption band of **10c** was observed in the longest wavelength side among those of **10a–c** despite the substitution of the *t*Bu group at the 6-position.

Among azulene derivatives, some of them are known to show a remarkable color change, so-called halochromism, in acidic solutions.[25] Recently, we have also reported that azulene derivatives with extended π-conjugated systems by substitution or fusion of aromatic rings exhibit pronounced halochromism in TFA/CH_2Cl_2 mixed solvents.[26] Therefore, the halochromic behavior of the series of **10–15** was investigated by UV/Vis spectroscopy in acidic solutions. UV/Vis spectra of **10a**, **10c**, **10d**, and **11a** in CH_2Cl_2 and 30% TFA/CH_2Cl_2 are shown in Figure 8.

All compounds exhibited a noticeable color change when TFA was added to the CH_2Cl_2 solution (Figure 9). The reverse neutralization of the acidic solutions with triethylamine (Et_3N)

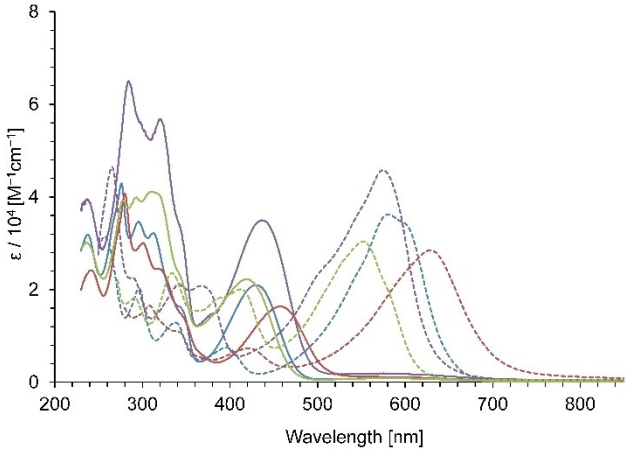


Figure 8. UV/Vis spectra of polymethines **10a** (blue line), **10c** (red line), **10d** (light-green line) and **11a** (purple line) in CH_2Cl_2 and **10a** (blue dot-line), **10c** (red dot-line), **10d** (light-green dot-line) and **11a** (purple dot-line) in 30% TFA/CH_2Cl_2.

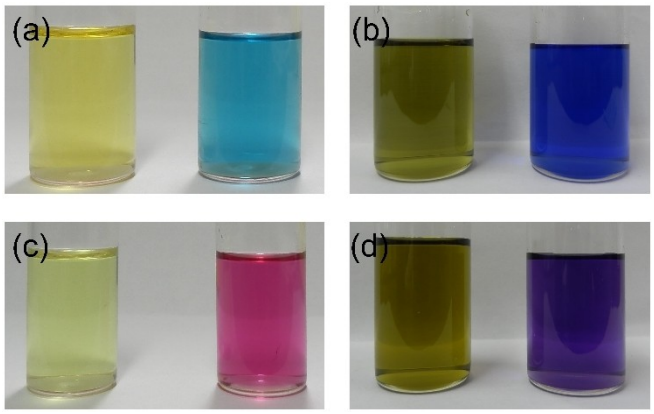
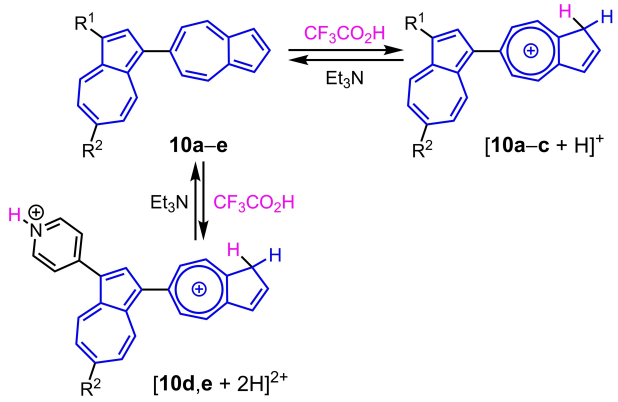


Figure 9. Photo of colour change of (a) **10a**, (b) **10c**, (c) **10d** (d) **11a** in CH_2Cl_2 (left) and in 30% TFA/CH_2Cl_2 (right).

recovered the original color. The maximum absorption wavelengths of **10a** and **11a** in 30% TFA/CH_2Cl_2 were observed at λ_{max} = 581 nm and 575 nm, respectively, in their UV/Vis spectra. Compound **10c** (λ_{max} = 629 nm) revealed the absorption band in the longest wavelength region among those of **10a**–**10e**. On the other hand, the longest wavelength absorption bands of **10d** (λ_{max} = 552 nm) and **10e** (λ_{max} = 569 nm) with 4-pyridyl group exhibited a blue-shift compared to those of **10a** and **10b** (λ_{max} = 601 nm) with their partial structures of **10e** and **10d**.

These differences in the absorption wavelengths can be explained by the protonation as illustrated in Scheme 12. The 6-azulenyl group of 1,6′-biazulenes **10a**–**c** should be protonated by TFA to form [**10a**–**c** + H]$^+$, in which the 6-azulenyl group forms a tropylium ion substructure, resulting in a strong electron-withdrawing group. As a result, a strong charge-transfer absorption band between the electron-donating 1-azulenyl group and the protonated 6-azulenyl group is observed in the visible region. In the cases of **10b** and **10c**, the electron-donating *t*Bu group on the azulene ring increases the HOMO energy level, resulting in the decrease of the HOMO-



Scheme 12. Protonation behavior of 1,6′-biazulenes **10a**–**e**.

LUMO energy gap. Thus, these derivatives exhibited a red-shift of the absorption band. On the other hand, the 4-pyridyl group of **10d** and **10e** is also protonated to produce an electron-withdrawing pyridinium ion to decrease the HOMO level, resulting in a blue-shift in the absorption band compared to those of **10a** and **10b**.

Measurements of ^{1}H NMR of **10b** in $CDCl_3$ and in 30% $CF_3CO_2D/CDCl_3$ were also conducted to obtain further information on the protonated chemical species (Figure 10). In the ^{1}H NMR spectra in 30% $CF_3CO_2D/CDCl_3$, protons at the 1-, 1′-, and 3′-positions disappeared owing to the proton-deuterium exchange with CF_3CO_2D. In 30% $CF_3CO_2D/CDCl_3$ compared to in $CDCl_3$, most of the proton signals of **10b** exhibited a down-field shift of the chemical shifts in the spectrum, but the shift values were larger for the 6-azulenyl group than for the 1-azulenyl group. Furthermore, the proton signal at the 2′-position was observed in the olefin region in the 30% $CF_3CO_2D/CDCl_3$ mixed solvent. These facts should support the correctness of the structure of the protonated species in acidic media represented in Scheme 12.

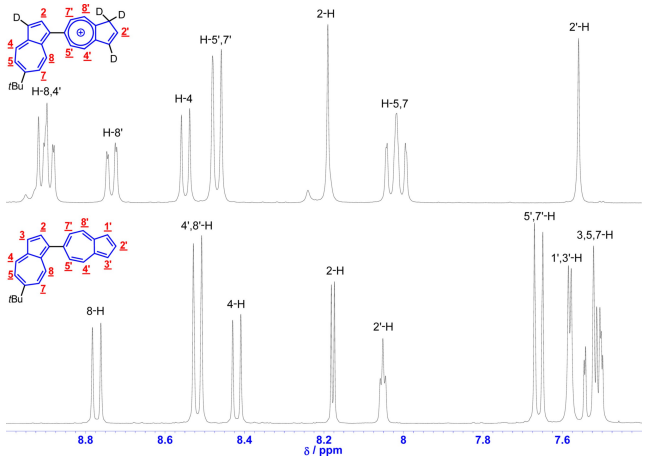


Figure 10. ^{1}H NMR (500 MHz) of **10b** in $CDCl_3$ (bottom) and in 30% $CF_3CO_2D/CDCl_3$ (top).

Since some azulene derivatives are known to exhibit luminescence in acidic media, the measurement of fluorescence spectra of 1,6′-biazulenes, 1,6′;3,6″-terazulenes and a quinqueazulene was examined. However, these derivatives did not show any emission as well as the usual azulene derivatives.

To clarify the electrochemical behavior of 1,6′-biazulenes **10a–e**, **11a,b**, **14**, and **15**, redox potentials of these products were measured by CV and DPV. The redox potentials measured by DPV are summarized in Table 7. Cyclic and differential pulse voltammograms are shown in Supporting Information (Figures 133–141).

Most of the 1,6′-biazulenes showed irreversible redox waves on the CV, which means the generation of unstable cationic and anionic species from these derivatives under both electrochemical oxidation and reduction conditions. Even though **14** represented a quasi-reversible oxidation wave, exceptionally (Figure 11), 1,6-biazulenes were extremely unstable toward the electrochemical oxidation reaction, and insoluble decomposition products were deposited on the electrode after the reaction. Since the first oxidation potential of **10c** (+0.45 V) exhibited a more anodic shift than those of **10a** (+0.51 V) and **10b** (+0.50), the *t*Bu group on the azulene ring should raise the HOMO level of the molecule. Lower first oxidation potentials were observed in terazulenes **11a** and **11b** compared to those of **10a** and **10b**; these facts imply that the extension of the π-conjugated system effectively increases the HOMO level. The increase of the HOMO levels is also supported by the results of the theoretical calculations as described above. The lower first oxidation potential of 1,6-biazulene **14** (+0.43 V) than that of **10d** (+0.63 V) indicates that the aryl group on the 1,3-positions of the 6-azulenyl group also contributes to the extension of the π-conjugated system. The first oxidation potential of **15** was slightly shifted to the lower potential side from that of **11a**. On the other hand, the substitution of the pyridinyl group (e.g., **10d** and **10e**) led to an increase in the oxidation potential despite the extension of the π-conjugated system. This phenomenon should be attributed to the decrease in the HOMO level due to the electron-withdrawing nature of the substituted pyridinyl group.

The first reduction potentials of **10b** (−1.83 V), **10e** (−1.74 V) and **11b** (−1.71 V) with a *t*Bu group at the 6-position exhibited a cathodic shift from those of **10a** (−1.74 V), **10d** (−1.63 V), and **11a** (−1.68 V), which represented the increment of the LUMO level due to the electron-donating nature of the *t*Bu group. Since there was no significant difference between the first reduction potentials of **10b** and **10c** (−1.84 V), the *t*Bu group at the 6-position should have a much pronounced effect on the LUMO energy level than that at the 1-position. The lower first reduction potentials of **14** (−1.61 V) and **15** (−1.60 V) than those of **11a** and **11b** are probably due to the decrease in the HOMO-LUMO gap caused by the extension of the π-conjugated system by the substituted aryl groups.

We have investigated the preparation of the extended π-conjugated molecules substituted with 6-azulenyl groups, as well as their electrochromic behavior.[28] As a result, these compounds have been identified to behave as electrochromic molecules that show significant spectral changes under the electrochemical redox conditions. The electrochromic behavior of **10a–e**, **11a,b**, **14**, and **15** was deduced by the spectroelectrochemical measurements because 1,6′-biazulenes prepared by this study may also show large spectral changes under the redox conditions.

On the basis of our previous studies, we expected that compounds **10a–e**, **11a,b**, **14**, and **15** should exhibit significant color changes in their absorption spectra in the visible region. However, the spectral changes of these compounds in the visible region were not completely reversible, as reflected by the results on the CV measurements. For example, when the visible spectrum of **10a** was monitored under the electrochemical reduction conditions at room temperature, a new strong absorption band centered at λ_{max} = 600 nm was appeared accompanying an isosbestic point at λ = 575 nm. This obvious spectral change implies the formation of radical anionic or anionic species from **10a** by electrochemical reduction. However, the reverse oxidation of the reduced species of **10a** did not reconstitute the original spectrum, completely, even though the newly formed absorption band was decreased (Figure 12).

We have also evaluated the electrochromic properties of **10b–e**, **11a,b**, **14**, and **15**. As similar to the case of **10a**, the

Table 7. Redox potentials of 1,6′-biazulenes **10a–e**, **11a,b**, **14** and **15** measured by DPV.[a]

Sample[27]	E_1^{ox} [V]	E_2^{ox} [V]	E_1^{red} [V]	E_2^{red} [V]
10a	+0.51	+1.08	−1.74	–
10b	+0.50	+0.91	−1.83	–
10c	+0.45	+0.80	−1.84	–
10d	+0.63	+1.04	−1.63	−1.95
10e	+0.62	+0.94	−1.74	–
11a	+0.43	+1.21	−1.68	–
11b	+0.42	+1.08	−1.71	−1.95
14	+0.43	+1.24	−1.61	−1.94
15	+0.41	+0.76	−1.60	−1.96

[a] 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 20 mVs^{-1}, and external standard Fc/Fc^+ = +0.15 V.

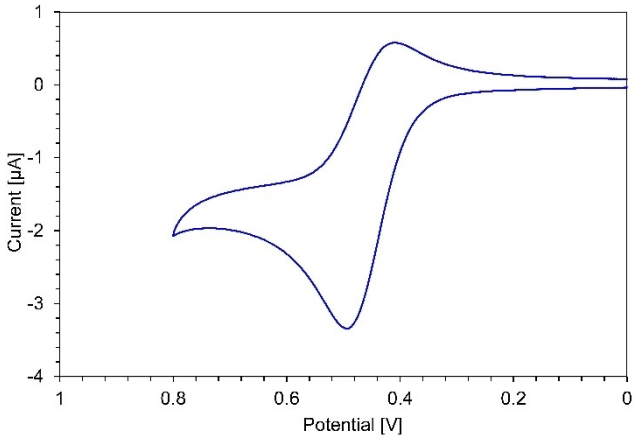


Figure 11. Cyclic voltammograms for the oxidation of **14** in benzonitrile (1 mM) containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; V vs. Ag/$AgNO_3$ and external standard Fc/Fc^+ = +0.15 V.

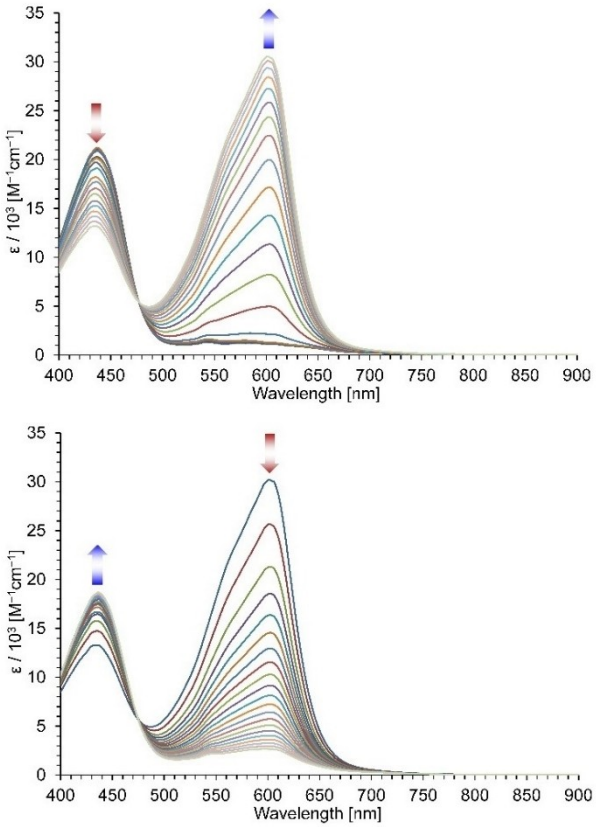


Figure 12. Continuous change in the visible spectrum of **10a**: constant voltage electrochemical reduction at –1.90 V (top) and reverse oxidation of the reduced species at ±0 V (bottom) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 s intervals.

large spectral changes of **10b–e**, **11a,b**, **14**, and **15** in the visible region were observed under the reduction conditions, but again the spectra did not return to the original states, completely, upon the reverse oxidation of the reduced species. The spectra obtained by the reverse oxidation of the reduced species of **10a–e**, **11a,b**, **14**, and **15** exhibited higher absorption coefficients than those of the original ones, suggesting that the polymerization reaction might proceed to some extent during the reduction or reverse oxidation process, although the generated species could not be isolated.

Conclusion

In conclusion, we have described herein an efficient and practical procedure for the synthesis of azulene-substituted donor-acceptor type polymethines and 1,6′-biazulenes, 1,6′;3,6″-terazulenes and a quinqueazulene starting from the azulene substituted Zincke salts.

Azulene-substituted Zincke salts reacted with several amines, and subsequent Knoevenagel reaction with malononitrile afforded azulene-substituted donor-acceptor type polymethines in moderate to excellent yields. In the Knoevenagel reaction, alumina was revealed as a good catalyst to give the desired products in higher yields than the basic conditions using triethylamine as a catalyst. The Diels-Alder reaction of polymethines **7aa–7ad** with maleimides did not give the expected [4+2] cycloadduct but yielded phthalimide **9**, whose structure was determined by single-crystal X-ray analysis.

The conversion of the Zincke salts to 1,6′-biazulenes, 1,6′;3,6″-terazulenes and a quinqueazulene was also investigated. The reaction of the Zinke salts with secondary amines by following the successive condensation-cyclization reactions with cyclopentadienide ion, so-called Ziegler-Hafner method, afforded the corresponding 1,6′-biazulenes, 1,6′;3,6″-terazulenes and quinqueazulene. In these series of reactions, Zincke salts with a *t*Bu group at the 6-position of the azulene ring resulted in higher yields of the desired products. The rationale for this was identified in terms of the reaction mechanism.

The optical and electrochemical properties of azulene-substituted polymethines, 1,6′-biazulenes, 1,6′;3,6″-terazulenes and a quinqueazulene obtained by this study were investigated by UV/Vis spectroscopy, voltammetry analysis, spectroelectrochemistry, and theoretical calculations. These results suggested that the substituents on the azulene ring and their substitution positions directly affect their reactivities and optical and electrochemical properties. The present outcomes provide an efficient method for the preparation of new azulene derivatives, which are difficult to obtain, and should contribute to the development of organic electronic materials with azulene skeletons.

Experimental Section

General: Melting points were determined with a Yanagimoto MPS3 micromelting apparatus. The HRMS data were obtained with a Bruker autoflex III TOF/TOF or JEOL JMS-700 spectrometer. IR and UV/Vis spectra were recorded with JASCO FTIR-4100 and Shimadzu UV-2550 spectrophotometers, respectively. ^1H and ^{13}C NMR spectra were recorded with a JEOL ECA500 spectrometer at 500 MHz and 125 MHz, respectively. The voltammetry measurements were performed with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M).

Compound 2a$^+$·Cl$^-$: To a solution of 1-(4-pyridinyl)azulene (**1a**) (1.03 g, 5.02 mmol) in toluene (20 mL) was added 1-chloro-2,4-dinitrobenzene (2.02 g, 10.0 mmol). The resulting solution was stirred and heated at reflux temperature for 24 h. The reaction mixture was cooled and the precipitated product was collected by vacuum filtration to afford **2a**$^+$·Cl$^-$ as a reddish brown solid (1.83 g, 90% yield). Mp 277–278 °C; IR (ATR): ν_{max} = 3108 (w), 3063 (w), 3009 (w), 1628 (s), 1612 (s), 1536 (s), 1513 (s), 1492 (m), 1390 (s), 1343 (s), 1305 (w), 1286 (w), 1229 (w), 1215 (s), 1070 (m), 917 (w), 903 (w), 862 (m), 835 (m), 802 (s), 752 (m), 740 (w), 707 (w), 682 (w) cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ_H = 9.24 (d, *J* = 2.0 Hz, 1H, 3-H of benzene), 9.09 (d, *J* = 10.0 Hz, 1H, 8-H of azulene), 8.91 (d, *J* = 7.5 Hz, 2H, 2,6-H of pyridine), 8.89 (dd, *J* = 9.0, 2.0 Hz, 1H, 5-H of benzene), 8.67 (d, *J* = 10.0 Hz, 1H, 4-H of azulene), 8.50–8.48 (m, 3H, 2-H of azulene, 3,5-H of pyridine), 8.32 (d, *J* = 9.0 Hz, 1H, 6-H of benzene), 8.03 (t, *J* = 10.0 Hz, 1H, 6-H of azulene), 7.77 (t, *J* = 10.0 Hz, 1H, 7-H of azulene), 7.65 (t, *J* = 10.0 Hz, 1H, 5-H of azulene), 7.60 (d, *J* = 4.0 Hz, 1H, 3-H of azulene) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ_C = 154.52, 149.45, 147.97, 143.76, 143.59, 141.00, 139.74,

139.55, 139.10, 138.99, 136.11, 131.51, 129.74, 129.71, 129.44, 123.93, 122.92, 121.91, 121.49 ppm; HRMS (FAB-MS, positive): Calcd for $C_{21}H_{14}N_3O_4^+$ $[M]^+$ 372.0984, found: 372.0990.

Compound 2b$^+$·Cl$^-$: To a solution of **1b** (1.05 g, 4.00 mmol) in toluene (60 mL) was added 1-chloro-2,4-dinitrobenzene (1.62 g, 7.99 mmol). The resulting solution was stirred and heated at reflux temperature for 14.5 h. The reaction mixture was cooled and the precipitated product was collected by vacuum filtration to afford pure **2b$^+$·Cl$^-$** (1.80 g, 97% yield) as a reddish brown solid. M.p. 253–255 °C (decomp.); IR (AT–IR): ν_{max} = 2970 (w), 1631 (s), 1614 (s), 1586 (m), 1541 (m), 1523 (m), 1509 (m), 1479 (m), 1442 (m), 1397 (s), 1342 (s), 1309 (m), 1289 (m), 1232 (m), 1218 (s), 1124 (w), 1068 (m), 1010 (w), 915 (m), 849 (m), 835 (m), 822 (w), 783 (m), 764 (w), 741 (w), 711 (w), 683 (w) cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ_H = 9.25 (d, J = 2.3 Hz, 1H), 9.10 (d, J = 10.9 Hz, 1H), 8.89 (dd, J = 8.6, 2.3 Hz, 1H), 8.83 (d, J = 6.9 Hz, 2H), 8.64 (d, J = 10.3 Hz, 1H), 8.48 (d, J = 6.9 Hz, 2H), 8.44 (d, J = 4.6 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 8.03 (dd, J = 10.9, 1.7 Hz, 1H), 7.96 (dd, J = 10.6, 2.0 Hz, 1H), 7.54 (d, J = 4.0 Hz, 1H), 1.54 (s, 9H) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ_C = 166.29, 154.34, 149.43, 147.24, 143.84, 143.26, 139.05, 139.01, 138.61, 138.26, 135.33, 131.40, 129.64, 128.35, 128.20, 123.26, 122.51, 121.92, 121.26, 38.74, 30.70 ppm; HRMS (FAB-MS, positive): Calcd for $C_{25}H_{22}N_3O_4^+$ $[M]^+$ 428.1600, found: 428.1621.

Compound 2c$^+$·Cl$^-$: To a solution of **1c** (473 mg, 1.49 mmol) in toluene (24 mL) was added 1-chloro-2,4-dinitrobenzene (910 mg, 4.49 mmol). The resulting solution was stirred and heated at reflux temperature for 24 h. The reaction mixture was cooled and the precipitated product was collected by vacuum filtration to afford **2c$^+$·Cl$^-$** (772 mg, 99% yield) as a reddish brown solid. M.p. 210–212 °C; IR (AT-IR): ν_{max} = 3358 (w), 3034 (w), 2962 (w), 1626 (s), 1602 (m), 1575 (m), 1542 (s), 1519 (s), 1474 (m), 1429 (s), 1371 (s), 1343 (s), 1317 (w), 1279 (w), 1249 (m), 1209 (s), 1079 (w), 1065 (w), 1026 (w), 966 (w), 944 (w), 916 (w), 899 (w), 875 (w), 857 (m), 846 (m), 831 (m), 798 (w), 765 (w), 745 (w), 730 (w), 712 (w), 685 (w) cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ_H = 9.23 (d, J = 2.6 Hz, 1H, 3-H of benzene), 9.02 (d, J = 11.0 Hz, 1H, 4-H of azulene), 9.00 (d, J = 11.0 Hz, 1H, 8-H of azulene), 8.88 (dd, J = 8.6, 2.6 Hz, 1H, 5-H of benzene), 8.77 (d, J = 7.2 Hz, 2H, 2,6-H of pyridinium), 8.42 (d, J = 7.2 Hz, 2H, 3,5-H of pyridinium), 8.31 (s, 1H, 2-H of azulene), 8.28 (d, J = 8.6 Hz, 1H, 6-H of benzene), 7.92–7.96 (m, 2H, 5,7-H of azulene), 1.64 (s, 9H, *t*Bu), 1.53 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ_C = 166.02, 153.79, 149.37, 143.87, 142.91, 142.82, 142.77, 140.92, 139.09, 137.74, 136.15, 134.85, 131.42, 129.65, 128.59, 128.20, 127.88, 126.76, 123.23, 121.93, 120.63, 38.53, 32.90, 30.65, 30.57 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{29}H_{30}N_3O_4^+$ $[M]^+$ 484.2231, found: 484.2245.

Compound 4a$^+$·Cl$^-$: To a solution of **3a** (282 mg, 1.00 mmol) in toluene (15 mL) was added 1-chloro-2,4-dinitrobenzene (609 mg, 3.01 mmol). The resulting solution was stirred and heated at reflux temperature for 24 h. The reaction mixture was cooled and the precipitated product was collected by filtration to afford **4a$^+$·Cl$^-$** (469 mg, 97% yield) as a reddish brown solid. M.p. 218–220 °C; IR (AT-IR): ν_{max} = 3108 (w), 2964 (w), 2926 (w), 1627 (s), 1607 (s), 1596 (m), 1577 (m), 1541 (s), 1514 (s), 1475 (w), 1434 (s), 1388 (w), 1373 (m), 1341 (s), 1323 (w), 1283 (w), 1252 (w), 1219 (s), 1191 (w), 1160 (w), 1143 (w), 1078 (w), 1067 (w), 1027 (w), 1007 (w), 989 (w), 946 (w), 909 (w), 892 (w), 867 (m), 851 (w), 837 (m), 823 (s), 768 (w), 736 (m), 715 (w), 675 (w), 653 (w) cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ_H = 9.27 (d, J = 2.6 Hz, 1H, 3-H of benzene), 9.19 (d, J = 9.8 Hz, 1H, 4-H of azulene), 9.03 (d, J = 7.2 Hz, 2H, 2,6-H of pyridinium), 8.88–8.93 (m, 2H, 5-H of benzene, 8-H of azulene), 8.76 (s, 1H, 2-H of azulene), 8.68 (d, J = 6.0 Hz, 2H, 2,6-H of pyridine), 8.61 (d, J = 6.9 Hz, 2H, 3,5-H of pyridinium), 8.34 (d, J = 8.6 Hz, 1H, 6-H of benzene), 8.14 (t, J = 9.8 Hz, 1H, 6-H of azulene), 7.86 (t, J = 9.8 Hz, 1H, 5-H of azulene), 7.77–7.81 (m, 3H, 7-H of azulene, 3,5-H of pyridine) ppm; ^{13}C NMR (125 MHz, CD_3OD): δ_C = 154.52, 149.57, 149.07, 144.72, 144.02, 143.71, 142.52, 142.33, 141.04, 139.19, 138.94, 137.81, 137.13, 131.45, 130.62, 130.47, 129.98, 129.74, 124.76, 124.62, 122.72, 121.96 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{26}H_{17}N_4O_4^+$ $[M]^+$ 449.1244, found: 449.1236.

Compound 4b$^+$·Cl$^-$: To a solution of **3b** (439 mg, 1.30 mmol) in toluene (15 mL) was added 1-chloro-2,4-dinitrobenzene (786 mg, 3.88 mmol). The mixture solution was stirred and heated at reflux temperature for 24 h. The reaction mixture was cooled and the precipitated product was collected by filtration to afford **4b$^+$·Cl$^-$** (661 mg, 94% yield) as a reddish brown solid. M.p. 246–249 °C; IR (AT–IR): ν_{max} = 2963 (w), 2926 (w), 2876 (w), 1627 (m), 1607 (s), 1596 (m), 1577 (m), 1540 (s), 1514 (s), 1475 (m), 1434 (s), 1388 (m), 1373 (m), 1341 (m), 1323 (w), 1283 (m), 1253 (w), 1219 (s), 1192 (w), 1143 (w), 1079 (w), 1007 (w), 990 (w), 946 (m), 910 (w), 892 (w), 867 (m), 837 (m), 823 (m), 768 (w), 736 (m), 715 (w), 689 (w), 677 (w), 652 (w), 634 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.25 (d, J = 2.3 Hz, 1H, 3-H of benzene), 9.17 (d, J = 10.9 Hz, 1H, 4-H of azulene), 8.96 (d, J = 6.9 Hz, 2H, 2,6-H of pyridinium), 8.90 (dd, J = 8.6, 2.3 Hz, 1H, 5-H of benzene), 8.85 (d, J = 10.6 Hz, 1H, 8-H of azulene), 8.68 (s, 1H, 2-H of azulene), 8.66 (d, J = 6.0 Hz, 2H, 2,6-H of pyridine), 8.58 (d, J = 6.9 Hz, 2H, 3,5-H of pyridinium), 8.33 (d, J = 8.6 Hz, 1H, 6-H of benzene), 8.10 (dd, J = 10.7, 1.6 Hz, 1H, 5-H of azulene), 8.04 (dd, J = 10.9, 1.7 Hz, 1H, 7-H of azulene), 7.78 (d, J = 6.0 Hz, 2H, 3,5-H of pyridine), 1.55 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 167.76, 154.31, 149.52, 149.22, 144.53, 143.75, 141.72, 140.18, 138.98, 138.24, 136.82, 136.27, 131.51, 129.86, 129.74, 129.18, 124.37, 124.16, 122.26, 121.94, 38.89, 30.64 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{30}H_{25}N_4O_4^+$ $[M]^+$ 505.1870, found: 505.1870.

Compound 5a^{2+}·2Cl$^-$: To a solution of **3a** (149 mg, 0.53 mmol) in ethanol (10 mL) was added 1-chloro-2,4-dinitrobenzene (312 mg, 1.54 mmol). The resulting solution was stirred and heated at reflux temperature for 24 h. The solvent was removed under reduced pressure and added toluene. The reaction mixture was cooled and the precipitated product was collected by vacuum filtration to afford **5a^{2+}·2Cl$^-$** (360 mg, 99% yield) as a reddish-brown solid. The crude product was used in the next reaction without further purification.

Compound 5b^{2+}·2Cl$^-$: To a solution of **3b** (331 mg, 0.98 mmol) in ethanol (20 mL) was added 1-chloro-2,4-dinitrobenzene (810 mg, 4.00 mmol). The mixture solution was stirred and heated at reflux temperature for 24 h. The solvent was removed under reduced pressure and added toluene. The reaction mixture was cooled to room temperature and the precipitated product was collected by filtration to afford **5b^{2+}·2Cl$^-$** (723 mg, 99% yield) as a reddish-brown solid. The crude product was used in the next reaction without further purification.

Compound 7aa: ***Preparation by triethylamine-catalyzed Knoevenagel reaction***: Diethylamine (5 mL) was added to a solution of **2a$^+$·Cl$^-$** (404 mg, 0.99 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Triethylamine (2 mL) was added to a solution of the crude Zincke aldehyde (204 mg, 0.73 mmol) and malononitrile (96 mg, 1.46 mmol) in dichloromethane (5 mL). The resulting solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1 : 1) to give **7aa** (184 mg, 57% as two-step yield from **2a$^+$·Cl$^-$**) as a deep red solid.

Preparation by alumina-catalyzed Knoevenagel reaction: Diethylamine (1 mL) was added to a solution of **2a$^+$·Cl$^-$** (306 mg,

0.75 mmol) in ethanol (5 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (568 mg) was added to a solution of the crude Zincke aldehyde (156 mg, 0.56 mmol) and malononitrile (88 mg, 1.33 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7aa** (158 mg, 64% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid. M.p. 181–182 °C; IR (AT–IR): ν_{max} = 2982 (w), 2938 (w), 2878 (w), 2194 (s), 1614 (m), 1508 (s), 1488 (s), 1457 (s), 1424 (m), 1397 (w), 1357 (s), 1309 (m), 1287 (m), 1221 (s), 1187 (s), 1176 (s), 1148 (m), 1115 (s), 1078 (m), 1066 (m), 990 (w), 965 (m), 952 (m), 869 (m), 782 (w), 773 (w), 749 (w), 671 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.35), 280 (4.61), 324 sh (3.90), 340 sh (3.85), 480 sh (4.71), 505 (4.86) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.40 (d, *J* = 10.0 Hz, 1H, 4-H of azulene), 8.40 (d, *J* = 10.0 Hz, 1H, 8-H of azulene), 7.78 (d, *J* = 4.0 Hz, 1H, 2-H of azulene), 7.67 (t, *J* = 9.5 Hz, 1H, 6-H of azulene), 7.43 (d, *J* = 4.0 Hz, 1H, 3-H of azulene), 7.28 (t, *J* = 10.0 Hz, 1H, 5-H of azulene), 7.21 (d, *J* = 10.0 Hz, 1H, 7-H of azulene), 6.80 (d, *J* = 13.0 Hz, 1H, H of triene), 6.65 (d, *J* = 13.0 Hz, 1H, H of triene), 6.80 (d, *J* = 13.0 Hz, 1H, H of triene), 6.48 (d, *J* = 15.0 Hz, 1H, H of triene), 5.79 (d, *J* = 15.0 Hz, 1H, H of triene), 3.21 (br s, 4H, Et), 1.15 (br s, 6H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 160.70, 157.09, 152.50, 142.11, 138.98, 138.85, 138.20, 137.95, 135.82, 124.58, 124.33, 124.09, 118.03, 117.59, 117.07, 115.99, 104.00, 64.52, 50.97, 43.21, 14.81, 12.23 ppm; HRMS (FAB-MS, positive): Calcd for $C_{22}H_{21}N_3^+$ $[M]^+$ 327.1735, found: 327.1731.

Compound 7ab: ***Preparation by triethylamine-catalyzed Knoevenagel reaction***: Morpholine (2 mL) was added to a solution of **2a**$^+$·Cl^- (240 mg, 0.59 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Triethylamine (0.5 mL) was added to a solution of the crude Zincke aldehyde (135 mg, 0.46 mmol) and malononitrile (82 mg, 1.24 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7ab** (149 mg, 75% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid.

Preparation by alumina-catalyzed Knoevenagel reaction: Morpholine (1 mL) was added to a solution of **2a**$^+$·Cl^- (29 mg, 0.072 mmol) in ethanol (1 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (86 mg) was added to a solution of the crude Zincke aldehyde (24 mg, 0.082 mmol) and malononitrile (16 mg, 0.24 mmol) in dichloromethane (2 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7ab** (22 mg, 89% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid. M.p. 94–97 °C; IR (AT–IR): ν_{max} = 2966 (w), 2917 (w), 2860 (w), 2200 (m), 2187 (m), 1617 (m), 1577 (w), 1487 (s), 1428 (s), 1396 (w), 1364 (m), 1331 (w), 1311 (w), 1287 (w), 1213 (s), 1174 (s), 1153 (s), 1115 (m), 1068 (w), 1020 (m), 960 (w), 943 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.29), 280 (4.57), 325 sh (3.85), 341 (3.81), 477 sh (4.67), 499 (4.74) nm; ^{1}H NMR (500 MHz, $CDCl_3$):δ_H = 8.42 (d, *J* = 9.5 Hz, 1H, 4-H of azulene), 8.16 (d, *J* = 9.7 Hz, 1H, 8-H of azulene), 7.78 (d, *J* = 4.0 Hz, 1H, 2-H of azulene), 7.69 (t, *J* = 9.9 Hz, 1H, 6-H of azulene), 7.43 (d, *J* = 3.7 Hz, 1H, 3-H of azulene), 7.30 (t, *J* = 9.7 Hz, 1H, 5-H of azulene), 7.22 (d, *J* = 9.7 Hz, 1H, 7-H of azulene), 6.83 (d, *J* = 12.6 Hz, 1H, H of triene), 6.67 (d, *J* = 12.9 Hz, 1H, H of triene), 6.38 (d, *J* = 12.6 Hz, 1H, H of triene), 5.84 (d, *J* = 12.9 Hz, 1H, H of triene), 3.67 (br s, 4H, morpholine), 3.23 (br s, 4H, morpholine) ppm; ^{13}C NMR (125 MHz, $CDCl_3$):δ_C = 160.04, 157.44, 152.20, 142.04, 139.02, 138.70, 138.14, 138.00, 135.67, 124.67, 124.46, 123.84, 118.04, 117.79, 117.63, 117.27, 115.22, 104.29, 77.35, 77.10, 76.84, 67.23, 66.12, 29.68 ppm; HRMS (FAB-MS, positive): Calcd for $C_{22}H_{19}N_3O$ $[M]^+$ 341.1528, found: 341.1530.

Compound 7ac: ***Preparation by triethylamine-catalyzed Knoevenagel reaction***: Piperidine (2 mL) was added to a solution of **2a**$^+$·Cl^- (202 mg, 0.50 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Triethylamine (0.5 mL) was added to a solution of the crude Zincke aldehyde (129 mg, 0.44 mmol) and malononitrile (68 mg, 1.03 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7ac** (67 mg, 40% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid.

Preparation by alumina-catalyzed Knoevenagel reaction: Pyrrolidine (2 mL) was added to a solution of **2a**$^+$·Cl^- (96 mg, 0.23 mmol) in ethanol (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (234 mg) was added to a solution of the crude Zincke aldehyde (66 mg, 0.23 mmol) and malononitrile (36 mg, 0.55 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7ac** (65 mg, 0.19 mmol, 81% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid. M.p. 85–87 °C; IR (AT–IR): ν_{max} = 2938 (w), 2857 (w), 2199 (m), 1616 (w), 1505 (s), 1458 (m), 1444 (m), 1396 (w), 1361 (m), 1311 (w), 1207 (s), 1186 (s), 1125 (m), 1106 (w), 1021 (w), 999 (w), 942 (w), 853 (w), 782 (w), 748 (w), 673 (w), 664 (w), 637 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 235 (4.24), 280 (4.49), 323 sh (3.80), 341 (3.75), 481 sh (4.60), 506 (4.75) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.41 (d, *J* = 9.5 Hz, 1H, 4-H of azulene), 8.18 (d, *J* = 9.7 Hz, 1H, 8-H of azulene), 7.78 (d, *J* = 3.7 Hz, 1H, 2-H of azulene), 7.69 (t, *J* = 9.9 Hz, 1H, 6-H of azulene), 7.43 (d, *J* = 3.7 Hz, 1H, 3-H of azulene), 7.30 (t, *J* = 9.7 Hz, 1H, 5-H of azulene), 7.22 (d, *J* = 9.7 Hz, 1H, 7-H of azulene), 6.78 (d, *J* = 12.9 Hz, 1H, H of triene), 6.63 (d, *J* = 12.9 Hz, 1H, H of triene), 6.44 (d, *J* = 12.6 Hz, 1H), 5.84 (d, *J* = 12.6 Hz, 1H, H of triene), 3.31 (br s, 4H, piperidine), 1.64 (br s, 6H, piperidine) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ_C = 161.07, 156.69, 153.21, 141.92, 138.86, 138.71, 138.04, 137.85, 135.68, 124.47, 124.26, 124.04, 118.15, 117.48, 116.67, 116.02, 103.66, 63.49, 55.55, 46.48, 26.38, 25.19, 23.76 ppm; HRMS (FAB-MS, positive): Calcd for $C_{23}H_{21}N_3^+$ $[M]^+$ 339.1735, found: 339.1737.

Compound 7ad: ***Preparation by triethylamine-catalyzed Knoevenagel reaction***: Pyrrolidine (2 mL) was added to a solution of **2a**$^+$·Cl^- (206 mg, 0.50 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Triethylamine (0.5 mL) was added to a solution of the crude Zincke aldehyde (101 mg, 0.36 mmol) and malononitrile (66 mg, 1.00 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7ad** (84 mg, 52% as two-step yield from **2a**$^+$·Cl^-) as a deep red solid.

Preparation by alumina-catalyzed Knoevenagel reaction: Pyrrolidine (2 mL) was added to a solution of **2a**$^+$·Cl$^-$ (80 mg, 0.20 mmol) in ethanol (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (146 mg) was added to a solution of the crude Zincke aldehyde (39 mg, 0.14 mmol) and malononitrile (17 mg, 0.25 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1: 1) to give **7ad** (42 mg, 66% as two-step yield from **2a**$^+$·Cl$^-$) as a deep red solid. M.p. 102–105 °C; IR (AT–IR): ν_{max} = 3011 (w), 2975 (w), 2873 (w), 2200 (m), 1614 (w), 1577 (w), 1499 (s), 1473 (m), 1451 (m), 1412 (w), 1396 (w), 1361 (m), 1338 (w), 1313 (m), 1265 (w), 1207 (s), 1194 (s), 1170 (s), 1109 (w), 1033 (w), 944 (w), 864 (w), 780 (w), 750 (m), 668 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.32), 280 (4.58), 323 sh (3.87), 341 (3.82), 482 sh (4.68), 509 (4.84) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.40 (d, *J* = 9.5 Hz, 1H, 4-H of azulene), 8.18 (d, *J* = 9.7 Hz, 1H, 8-H of azulene), 7.78 (d, *J* = 3.7 Hz, 1H, 2-H of azulene), 7.66 (t, *J* = 9.9 Hz, 1H, 6-H of azulene), 7.42 (d, *J* = 3.7 Hz, 1H, 3-H of azulene), 7.29 (d, *J* = 9.5 Hz, 1H, 5-H of azulene), 7.20 (t, *J* = 9.7 Hz, 1H, 7-H of azulene), 6.77 (d, *J* = 12.9 Hz, 1H, H of triene), 6.64 (d, *J* = 12.9 Hz, 2H, H of triene), 5.72 (d, *J* = 11.5 Hz, 1H, H of triene), 3.27 (br s, 4H, pyrrolidine), 1.83–2.00 (m, 4H, pyrrolidine) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ_C = 160.61, 156.59, 150.46, 141.81, 138.80, 138.66, 138.00, 137.79, 135.63, 124.38, 124.20, 123.96, 118.14, 117.76, 117.40, 116.88, 116.04, 105.53, 63.29, 52.83, 47.36, 24.92 ppm; HRMS (FAB-MS, positive): Calcd for $C_{22}H_{19}N_3^+$ [M]$^+$ 325.1579, found: 325.1571.

Compound 7b: ***Preparation by triethylamine catalyzed Knoevenagel reaction***: Diethylamine (2 mL) was added to a solution of **2b**$^+$ (230 mg, 0.50 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Triethylamine (0.5 mL) was added to a solution of the crude Zincke aldehyde (158 mg, 0.47 mmol) and malononitrile (62 mg, 0.94 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7b** (155 mg, 80% as two-step yield from **2b**$^+$·Cl$^-$) as a deep red solid.

Preparation by alumina-catalyzed Knoevenagel reaction: Diethylamine (2 mL) was added to a solution of **2b**$^+$·Cl$^-$ (172 mg, 0.37 mmol) in ethanol (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (146 mg) was added to a solution of the crude Zincke aldehyde (114 mg, 0.34 mmol) and malononitrile (47 mg, 0.71 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 hours at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7b** (161 mg, 86% as two-step yield from **2b**$^+$·Cl$^-$) as a deep red solid. M.p. 96–98 °C; IR (AT–IR): ν_{max} = 2966 (w), 2879 (w), 2201 (m), 1616 (m), 1509 (s), 1460 (m), 1402 (w), 1360 (m), 1311 (w), 1217 (s), 1198 (s), 1118 (m), 1077 (w), 945 (w), 843 (w), 771 (w), 669 (w), 634 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.29), 286 (4.65), 345 (3.92), 478 sh (4.64), 506 (4.82) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.36 (d, *J* = 10.4 Hz, 1H, 4-H of azulene), 8.14 (d, *J* = 10.8 Hz, 1H, 8-H of azulene), 7.69 (d, *J* = 4.0 Hz, 1H, 2-H of azulene), 7.48 (dd, *J* = 10.4, 1.9 Hz, 1H, 5-H of azulene), 7.41 (dd, *J* = 10.8, 1.9 Hz, 1H, 7-H of azulene), 7.34 (d, *J* = 3.7 Hz, 1H, 3-H of azulene), 6.84 (d, *J* = 12.9 Hz, 1H, H of triene), 6.63 (d, *J* = 12.9 Hz, 1H, H of triene), 6.53 (s, 1H, H of triene), 5.78 (d, *J* = 12.3 Hz, 1H, H of triene), 3.36 (s, 2H, Et), 3.09 (s, 2H, Et), 1.47 (s, 9H, *t*Bu), 1.25 (s, 3H, Et), 1.06 (s, 3H, Et) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ_C = 163.34, 160.96, 157.36, 152.42, 152.35, 140.89, 138.01, 137.14, 136.99, 134.87, 123.54, 122.74, 118.16, 117.03, 116.09, 104.01, 77.34, 77.09, 76.83, 64.45, 50.91, 43.16, 38.93, 31.96, 14.86, 12.27 ppm; HRMS (FAB-MS, positive): Calcd for $C_{26}H_{29}N_3^+$ [M]$^+$ 383.2361, found: 383.2351.

Compound 7c: Diethylamine (5 mL) was added to a solution of **2c**$^+$·Cl$^-$ (322 mg, 0.62 mmol) in ethanol (5 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (611 mg) was added to a solution of the crude Zincke aldehyde (235 mg, 0.60 mmol) and malononitrile (81 mg, 1.22 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7c** (251 mg, 92% as two-step yield from **2c**$^+$·Cl$^-$) as a deep red solid. M.p. 96–98 °C; IR (AT–IR): ν_{max} = 2966 (w), 2879 (w), 2201 (m), 1616 (m), 1509 (s), 1460 (m), 1402 (w), 1360 (m), 1311 (w), 1217 (s), 1198 (s), 1118 (m), 1077 (w), 945 (w), 843 (w), 771 (w), 669 (w), 634 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.29), 286 (4.65), 345 (3.92), 478 sh (4.64), 506 (4.82) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.36 (d, *J* = 10.4 Hz, 1H, 4-H of azulene), 8.14 (d, *J* = 10.7 Hz, 1H, 8-H of azulene), 7.69 (d, *J* = 4.0 Hz, 1H, 2-H of azulene), 7.48 (dd, *J* = 10.4, 1.9 Hz, 1H, 5-H of azulene), 7.41 (d, *J* = 10.7, 1.9 Hz, 1H, 7-H of azulene), 7.34 (d, *J* = 3.7 Hz, 1H, 3-H of azulene), 6.84 (d, *J* = 12.9 Hz, 1H, H of triene), 6.63 (d, *J* = 12.9 Hz, 1H, H of triene), 6.53 (s, 1H, H of triene), 5.78 (d, *J* = 12.3 Hz, 1H, H of triene), 3.36 (br s, 2H, Et), 3.09 (br s, 1H, Et), 1.47 (s, 9H, *t*Bu), 1.25 (br s, 3H, Et), 1.06 (br s, 3H, Et) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ_C = 163.34, 160.96, 157.36, 152.42, 152.35, 140.89, 138.01, 137.14, 136.99, 134.87, 123.54, 122.74, 118.16, 117.03, 116.09, 104.01, 77.34, 77.09, 76.83, 64.45, 50.91, 43.16, 38.93, 31.96, 14.86, 12.27 ppm; HRMS (FAB-MS, positive): Calcd for $C_{26}H_{29}N_3^+$ [M]$^+$ 383.2361, found: 383.2351.

Compound 7d: Diethylamine (3 mL) was added to a solution of **2d**$^+$·Cl$^-$ (272 mg, 0.56 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (507 mg) was added to a solution of the crude Zincke aldehyde (182 mg, 0.51 mmol) and malononitrile (71 mg, 1.08 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7d** (190 mg, 84% as two-step yield from **2d**$^+$·Cl$^-$) as a deep red solid. M.p. 125–127 °C; IR (AT–IR): ν_{max} = 2975 (w), 2200 (m), 1616 (w), 1595 (m), 1577 (w), 1507 (s), 1460 (m), 1361 (m), 1311 (w), 1291 (w), 1215 (s), 1200 (s), 1119 (s), 1077 (m), 992 (w), 945 (w), 864 (w), 824 (w), 774 (w), 751 (w), 696 (w), 676 (w), 652 (w), 633 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.36), 278 sh (4.37), 304 (4.48), 374 (4.03), 480 sh (4.69), 504 (4.81) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.72 (dd, *J* = 4.6, 1.6 Hz, 2H, 2,6-H of pyridine), 8.69 (d, *J* = 9.7 Hz, 1H, 4-H of azulene), 8.24 (d, *J* = 9.7 Hz, 1H, 8-H of azulene), 7.94 (s, 1H, 2-H of azulene), 7.77 (t, *J* = 9.9 Hz, 1H, 6-H of azulene), 7.56 (dd, *J* = 4.6, 1.6 Hz, 2H, 3,5-H of pyridine), 7.39 (t, *J* = 9.9 Hz, 1H, 5-H of azulene), 7.30 (t, *J* = 9.9 Hz, 1H, 7-H of azulene), 6.81 (d, *J* = 12.8 Hz, 1H, H of triene), 6.68 (d, *J* = 12.8 Hz, 1H, H of triene), 6.49 (br s, 1H, H of triene), 5.83 (d, *J* = 10.6 Hz, 1H, H of triene), 3.37 (br s, 2H, Et), 3.09 (br s, 2H, Et), 1.27 (br s, 3H, Et), 1.06 (br s, 3H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 159.48, 156.84, 152.03, 150.23, 144.16, 140.42, 140.35, 138.29, 137.39, 137.06, 136.60, 127.31, 126.06,

125.61, 124.31, 117.75, 117.43, 115.67, 104.11, 65.72, 51.09, 43.25, 14.86, 12.27 ppm. One signal is overlapped with other signal. HRMS (MALDI-TOF, positive): Calcd for $C_{27}H_{24}N_4+H^+$ $[M+H]^+$ 405.2074, found: 405.2071.

Compound 7e: Diethylamine (3 mL) was added to a solution of **2e**$^{+}$·Cl^{-} (255 mg, 0.47 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (466 mg) was added to a solution of the crude Zincke aldehyde (182 mg, 0.44 mmol) and malononitrile (63 mg, 0.95 mmol) in dichloromethane (3 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **7e** (189 mg, 87% as two-step yield from **2e**$^{+}$·Cl^{-}) as a deep red solid. M.p. 178–180 °C; IR (AT–IR): ν_{max} = 2969 (w), 2201 (m), 1615 (m), 1597 (m), 1580 (m), 1509 (s), 1461 (m), 1428 (m), 1361 (m), 1312 (m), 1217 (s), 1201 (s), 1120 (m), 1077 (m), 993 (w), 948 (m), 859 (m), 823 (m), 775 (m), 737 (w), 668 (w), 654 (m), 643 (w), 633 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (4.40), 310 (4.50), 324 sh (4.41), 378 (4.04), 480 sh (4.66), 505 (4.79) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.70 (dd, *J* = 4.4, 1.6 Hz, 2H, 2,6-H of pyridine), 8.65 (d, *J* = 10.9 Hz, 1H, 4-H of azulene), 8.18 (d, *J* = 10.7 Hz, 1H, 8-H of azulene), 7.85 (s, 1H, 2-H of azulene), 7.55–7.59 (m, 3H, 5-H of azulene and 3,5-H of pyridine), 7.48 (dd, *J* = 10.7, 1.9 Hz, 1H, 7-H of azulene), 6.84 (d, *J* = 12.8 Hz, 1H, H of triene), 6.66 (d, *J* = 12.8 Hz, 1H, H of triene), 6.53 (br s, 1H, H of triene), 5.82 (d, *J* = 11.5 Hz, 1H, H of triene), 3.36 (s, 2H, Et), 3.10 (s, 2H, Et), 1.48 (s, 9H, *t*Bu), 1.27 (s, 3H, Et), 1.06 (s, 3H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.15, 159.87, 157.02, 152.06, 150.10, 144.40, 139.34, 137.31, 136.09, 135.63, 126.76, 124.44, 124.10, 123.94, 117.92, 115.80, 104.17, 65.36, 51.07, 43.23, 39.09, 31.88, 14.88, 12.26 ppm. Three signals are overlapped with other signals. HRMS (MALDI-TOF, positive): Calcd for $C_{31}H_{32}N_4+H^+$ $[M+H]^+$ 461.2700, found: 461.2713.

Compound 8a: Diethylamine (2 mL) was added to a solution of **5a**$^{2+}$·2Cl^{-} (111 mg, 0.16 mmol) in ethanol (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (110 mg) was added to a solution of the crude Zincke aldehyde (43 mg, 0.10 mmol) and malononitrile (16 mg, 0.24 mmol) in dichloromethane (5 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **8a** (46 mg, 54% as two-step yield from **5a**$^{2+}$·2Cl^{-}) as a deep red solid. M.p. 278–279 °C; IR (AT–IR): ν_{max} = 2974 (w), 2931 (w), 2198 (m), 2188 (w), 1617 (w), 1508 (s), 1468 (m), 1441 (m), 1422 (w), 1359 (m), 1345 (w), 1311 (m), 1282 (w), 1222 (s), 1200 (s), 1118 (m), 1077 (m), 993 (w), 953 (w), 942 (w), 869 (w), 834 (w), 775 (w), 751 (w), 716 (w), 687 (w), 666 (w), 650 (w), 640 (w), 627 (w), 617 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 233 (4.17), 281 (4.32), 326 sh (3.89), 342 sh (3.79), 477 (4.84), 500 sh (4.79) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.26 (d, *J* = 9.8 Hz, 2H, 4,8-H of azulene), 7.80 (t, *J* = 9.8 Hz, 1H, 6-H of azulene), 7.69 (s, 1H, 2-H of azulene), 7.35 (t, *J* = 9.8 Hz, 2H, 5,7-H of azulene), 6.69 (br s, 4H, H of triene), 6.50 (br s, 2H, H of triene), 5.83 (d, *J* = 12.0 Hz, 2H, H of triene), 3.32 (br s, 8H, Et), 1.22 (br s, 12H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 159.63, 156.18, 152.34, 140.81, 139.84, 139.57, 137.39, 125.96, 117.87, 115.42, 104.12, 65.34, 51.70, 43.52, 14.47, 12.41 ppm; HRMS (FAB-MS, positive): Calcd for $C_{34}H_{34}N_6^+$ $[M]^+$ 526.2845, found: 526.2853.

Compound 8b: Diethylamine (2 mL) was added to a solution of **5b**$^{2+}$·2Cl^{-} (82 mg, 0.11 mmol) in ethanol (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was poured into 2 M NaOH and extracted with dichloromethane, dried with Na_2SO_4, and concentrated under reduced pressure. Alumina (103 mg) was added to a solution of the crude Zincke aldehyde (44 mg, 0.09 mmol) and malononitrile (14 mg, 0.21 mmol) in dichloromethane (5 mL). The resulting solution was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc/hexane (1:1) to give **8b** (61 mg, 57% as two-step yield from **5b**$^{2+}$·2Cl^{-}) as a deep red solid. M.p. 288–290 °C; IR (AT–IR): ν_{max} = 2975 (w), 2931 (w), 2201 (w), 1618 (w), 1517 (s), 1466 (m), 1449 (w), 1426 (w), 1361 (w), 1311 (w), 1228 (s), 1202 (s), 1122 (w), 1097 (w), 1078 (w), 994 (w), 955 (w), 940 (w), 877 (w), 831 (w), 775 (w), 745 (w), 687 (w), 671 (w), 651 (w), 638 (w), 615 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.33), 289 (4.57), 324 sh (4.16), 346 (4.04), 479 (4.99), 499 (4.96) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.20 (d, *J* = 10.3 Hz, 2H, 4,8-H of azulene), 7.53–7.59 (m, 3H, 2,5,7-H of azulene), 6.70 (br s, 4H, H of triene), 6.54 (br s, 2H, H of triene), 5.82 (d, *J* = 12.0 Hz, 2H, H of triene), 3.30 (br s, 8H, Et), 1.50 (s, 9H, *t*Bu), 1.22 (br s, 12H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.87, 160.06, 156.35, 152.40, 138.96, 138.42, 136.36, 124.33, 123.49, 118.09, 116.99, 115.58, 104.13, 64.85, 51.56, 39.29, 31.93, 29.79, 14.62, 12.59 ppm; HRMS (FAB-MS, positive): Calcd for $C_{38}H_{42}N_6^+$ $[M]^+$ 582.3471, found: 582.3464.

Compound 9: ***Preparation from 7aa***: A solution of **7aa** (103 mg, 0.31 mmol) in *N*-cyclohexylmaleimide (154 mg, 0.86 mmol) in toluene was stirred at 150 °C for 46 h under an Ar atmosphere. After the reaction, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to afford **9** (32 mg, 16% yield) as a green solid.

Preparation from 7ab: A solution of **7ab** (70 mg, 0.21 mmol) in *N*-cyclohexylmaleimide (114 mg, 0.64 mmol) in toluene was stirred at 150 °C for 23.5 h under an Ar atmosphere. After the reaction, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to afford **9** (37 mg, 9% yield) as a green solid.

Preparation from 7ac: A solution of **7ac** (116 mg, 0.34 mmol) in *N*-cyclohexylmaleimide (186 mg, 1.03 mmol) in toluene was stirred at 150 °C for 15.5 h under an Ar atmosphere. After the reaction, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to afford **9** (76 mg, 12% yield) as a green solid.

Preparation from 7ad: A solution of **7ad** (120 mg, 0.37 mmol) in *N*-cyclohexylmaleimide (197 mg, 1.10 mmol) in toluene was stirred at 150 °C for 16 h under an Ar atmosphere. After the reaction, solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to afford **9** (74 mg, 33% yield) as a green solid. M.p. 229–231 °C; IR (AT–IR): ν_{max} = 2930 (w), 2852 (w), 2204 (w), 1765 (m), 1699 (s), 1618 (w), 1579 (w), 1530 (m), 1474 (m), 1451 (m), 1423 (m), 1398 (m), 1373 (s), 1347 (m), 1294 (w), 1258 (w), 1230 (m), 1196 (m), 1171 (m), 1145 (m), 1117 (w), 1101 (m), 1077 (w), 1024 (w), 984 (w), 937 (w), 911 (w), 896 (w), 851 (m), 786 (m), 750 (s), 714 (m), 693 (w), 662 (w), 638 (m), 620 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.45 (d, *J* = 9.5 Hz, 1H, 8-H of azulene), 7.95–8.04 (m, 2H, 4-H of azulene, Bz), 7.92 (d, *J* = 7.7 Hz, 1H, Bz), 7.76 (dd, *J* = 3.7, 3.6 Hz, 1H, 2-H of azulene), 7.70 (q, *J* = 9.7 Hz, 1H, 6-H of azulene), 7.52 (dd, *J* = 3.7, 3.6 Hz, 1H, 1-H of azulene), 7.31 (dd, *J* = 9.7 Hz, 1H, 7-H of azulene), 7.23 (dd, *J* = 9.7 Hz, 1H, 5-H of azulene), 4.35 (dd, *J* = 13.5, 4.6 Hz, 1H, *c*Hex), 3.97-4.17 (m, 2H, CH_2), 3.82 (t, *J* = 12.3 Hz, 1H, CH), 3.22 (m, 1H, *c*Hex), 2.53-2.70 (m, 2H, CH_2), 2.18-2.26 (m, 2H, *c*Hex), 1.56-1.97 (m, 10H, *c*Hex), 1.10–1.44 (m, 8H, *c*Hex) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 172.67, 172.15, 169.70, 167.59, 145.34, 141.91, 138.85, 138.34, 138.15, 138.11, 137.95, 137.51, 136.94,

135.13, 135.00, 131.44, 131.24, 131.16, 130.54, 130.20, 125.72, 125.60, 124.72, 124.68, 124.50, 123.37, 118.14, 118.04, 112.88, 112.64, 112.53, 112.22, 52.54, 51.33, 45.41, 45.26, 39.60, 39.48, 32.03, 31.94, 31.67, 29.89, 28.50, 28.46, 26.09, 25.72, 25.19, 24.92 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{38}H_{36}N_4O_4+H^+$ $[M+H]^+$ 612.2857, found: 612.2878.

Compound (10a): Diethylamine (16 mL) was added to a solution of **2a**$^+$·Cl^- (1.71 g, 4.20 mmol) in ethanol (36 mL). The resulting solution was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (333 mg, 5.0 mmol), 2.5 M NaOMe (2 mL), and pyridine (50 mL) and the mixture was refluxed for 24 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give **10a** (593 mg, 56%) as green crystals. M.p. 135–137 °C; IR (AT-IR): ν_{max} = 3084 (w), 3022 (w), 1571 (s), 1546 (m), 1492 (w), 1471 (w), 1452 (w), 1391 (s), 1293 (w), 1230 (w), 1199 (w), 1150 (w), 1050 (w), 985 (w), 944 (w), 913 (w), 898 (w), 842 (s), 788 (s), 738 (s), 687 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.50), 276 (4.63), 295 (4.54), 313 (4.51), 343 sh (4.21), 430 (4.32), 540 sh (2.88), 583 (2.95), 635 sh (2.81), 705 sh (2.25) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 257 (4.50), 296 (4.31), 338 (4.11), 396 (3.87), 581 (4.56), 600 sh (4.54) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.66 (d, *J* = 10.0 Hz, 1H, 8-H), 8.41 (d, *J* = 10.5 Hz, 2H, 4′,8′-H), 8.40 (d, *J* = 10.0 Hz, 1H, 4-H), 8.13 (d, *J* = 4.0 Hz, 1H, 2-H), 7.88 (t, *J* = 3.5 Hz, 1H, 2′-H), 7.65 (t, *J* = 10.0 Hz, 1H, 6-H), 7.51 (d, *J* = 10.5 Hz, 2H, 5′,7′-H), 7.47 (d, *J* = 4.0 Hz, 1H, 3-H), 7.41 (d, *J* = 3.5 Hz, 2H, 1′,3′-H), 7.23 (t, *J* = 10.5 Hz, 2H, 5,7-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 147.10 (C-3a′,8a′), 142.51 (C-8a), 138.60 (C-6), 138.44 (C-2), 138.00 (C-4), 137.70 (C-3a), 136.06 (C-8), 135.93 (C-2′), 135.86 (C-6′), 135.64 (C-4′,8′), 134.79 (C-1), 125.55 (C-5′,7′), 124.34 (C-5 or C-7), 123.99 (C-5 or C-7), 118.12 (C-1′,3′), 117.89 (C-3) ppm; HRMS (FAB-MS, positive): Calcd for $C_{20}H_{14}^+$ $[M]^+$ 254.1096, found: 254.1105.

Compound (10b): Pyrrolidine (12 mL) was added to a solution of **2b**$^+$·Cl^- (1.46 g, 3.14 mmol) in ethanol (27 mL). The resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (284 mg, 4.30 mmol), KO*t*Bu (423 mg, 3.77 mmol), and pyridine (45 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 19 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/EtOAc as an eluent to give **10b** (970 mg, 99% yield) as green oil. IR (AT-IR): ν_{max} = 3078 (w), 2964 (w), 2904 (w), 2868 (w), 1568 (s), 1546 (m), 1468 (w), 1444 (w), 1435 (w), 1395 (s), 1362 (w), 1299 (w), 1264 (w), 1242 (w), 1192 (w), 1054 (w), 1014 (w), 982 (w), 915 (w), 873 (w), 840 (s), 825 (m), 751 (m), 738 (m), 715 (w), 666 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.48), 268 sh (4.54), 278 (4.66), 298 (4.55), 314 (4.48), 345 sh (4.25), 439 (4.33), 572 (3.03), 625 sh (2.89), 700 sh (2.33) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 257 (4.48), 303 (4.36), 340 (4.15), 408 (3.82), 575 sh (4.52), 601 (4.61) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.77 (d, *J* = 11.0 Hz, 1H, 8-H), 8.51 (d, *J* = 10.5 Hz, 2H, 4′,8′-H), 8.42 (d, *J* = 11.0 Hz, 1H, 4-H), 8.18 (d, *J* = 3.5 Hz, 1H, 2-H), 8.05 (t, *J* = 3.5 Hz, 1H, 2′-H), 7.66 (d, *J* = 10.5 Hz, 2H, 5′,7′-H), 7.58 (d, *J* = 3.5 Hz, 2H, 1′,3′-H), 7.55–7.50 (m, 3H, 3,5,7-H), 1.61 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 162.51 (C-6), 147.24 (C-6′), 141.31 (C-8a), 138.23 (C-3a′,8a′), 137.03 (C-2), 136.69 (C-4), 135.65 (C-2′), 135.58 (C-4′,8′), 134.87 (C-8), 134.53 (C-3a), 134.20 (C-1), 125.32 (C-5′,7′), 122.65 (C-5 or C-7), 122.01 (C-5 or C-7), 117.97 (C-1′,3′), 117.44 (C-3), 38.49 (*t*Bu), 31.75 (*t*Bu) ppm; HRMS (FAB-MS, positive): Calcd for $C_{24}H_{22}^+$ $[M]^+$ 310.1721, found: 310.1719.

Compound (10c): Pyrrolidine (3 mL) was added to a solution of **2c**$^+$ (352 mg, 0.68 mmol) in ethanol (6 mL). The resulting solution was stirred at room temperature for 3.5 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (57 mg, 0.86 mmol), KO*t*Bu (93 mg, 0.83 mmol), and pyridine (10 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 17.5 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give **10c** (223 mg, 90% yield) as green oil. M.p. 110–113 °C; IR (AT–IR): ν_{max} = 2963 (w), 2904 (w), 2868 (w), 1573 (m), 1548 (w), 1474 (w), 1459 (w), 1424 (w), 1395 (m), 1362 (w), 1235 (w), 1218 (w), 1091 (w), 1055 (w), 952 (w), 878 (w), 850 (m), 837 (m), 822 (w), 752 (s), 682 (w), 667 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 241 (4.39), 280 (4.61), 301 (4.48), 319 (4.39), 346 sh (4.16), 368 sh (3.79), 458 (4.22), 586 (3.04), 636 sh (2.91), 695 sh (2.56), 751 sh (2.31) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 280 (4.58), 299 (4.47), 318 sh (4.39), 346 sh (4.18), 367 sh (3.93), 457 (4.21), 723 (3.39) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 308 (4.22), 339 sh (4.04), 370 sh (3.72), 421 (3.87), 629 (4.46) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.78 (d, *J* = 10.6 Hz, 1H, 8-H), 8.65 (d, *J* = 10.6 Hz, 1H, 4-H), 8.46 (d, *J* = 10.3 Hz, 2H, 4′,8′-H), 8.07 (s, 1H, 2-H), 7.94 (t, *J* = 3.7 Hz, 1H, 2′-H), 7.60 (d, *J* = 10.3 Hz, 2H, 5′,7′-H), 7.48 (d, *J* = 3.7 Hz, 2H, 1′,3′-H), 7.45–7.36 (m, 2H, 5,7-H), 1.76 (s, 9H, *t*Bu), 1.55 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 162.38, 147.61, 138.98, 138.37, 136.34, 135.93, 135.82, 135.67, 134.77, 132.25, 125.61, 122.19, 120.27, 118.02, 38.45, 33.37, 32.22, 31.85 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{28}H_{30}^+$ $[M]^+$ 367.2420, found: 367.2417.

Compound (10d): Pyrrolidine (8 mL) was added to a solution of **4a**$^+$·Cl^- (968 mg, 1.99 mmol) in ethanol (18 mL). The resulting solution was stirred at room temperature for 19.5 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (159 mg, 2.40 mmol), KO*t*Bu (274 mg, 2.44 mmol), and pyridine (30 mL) and the mixture was stirred at room temperature and refluxed for 24 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$/EtOAc as an eluent to give **10d** (308 mg, 47% yield) as a green solid. M.p. 210–211 °C; IR (AT–IR): ν_{max} = 3084 (w), 3041 (w), 1594 (m), 1574 (m), 1547 (m), 1521 (w), 1490 (w), 1472 (w), 1451 (w), 1424 (m), 1406 (m), 1378 (w), 1359 (w), 1319 (w), 1306 (w), 1269 (w), 1245 (w), 1211 (w), 1195 (w), 1154 (w), 1136 (w), 1091 (w), 1050 (w), 1018 (w), 991 (w), 972 (w), 931 (w), 874 (w), 860 (w), 849 (m), 836 (m), 811 (w), 753 (s), 691 (w), 670 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 237 (4.48), 278 (4.60), 293 (4.60), 310 (4.61), 320 sh (4.60), 346 sh (4.33), 419 (4.35), 587 (2.94), 635 sh (2.83), 710 sh (2.26) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 276 (4.59), 292 (4.54), 320 (4.58), 343 sh (4.40), 415 (4.41), 584 (3.02) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 291 (4.26), 334 (4.37), 384 sh (4.25), 412 (4.30), 526 sh (4.40), 552 (4.48), 581 sh (4.29) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.73 (dd, *J* = 4.4, 1.6 Hz, 2H, 2,6-H of pyridine), 8.69 (d, *J* = 10.0 Hz, 1H, 8-H), 8.65 (d, *J* = 10.0 Hz, 1H, 4-H), 8.43 (d, *J* = 10.6 Hz, 2H, 4′,8′-H), 8.25 (s, 1H, 2-H), 7.91 (t, *J* = 3.7 Hz, 1H, 2′-H), 7.73 (t, *J* = 9.7 Hz, 1H, 6-H), 7.59 (dd, *J* = 4.4, 1.6 Hz, 2H, 3,5-H of pyridine), 7.51 (d, *J* = 10.6 Hz, 2H, 5′,7′-H), 7.44 (d, *J* = 3.7 Hz, 2H, 1′,3′-H), 7.31 (m, 2H, 5,7-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 150.19, 146.23, 144.58, 140.00, 138.74, 138.19, 137.89, 137.74, 137.17, 136.70, 136.28, 135.73, 134.73, 127.51, 125.58, 125.55, 125.52, 124.37, 118.54 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{25}H_{17}N+H^+$ $[M+H]^+$ 332.1434, found:332.1419

Compound (10e): Pyrrolidine (22 mL) was added to a solution of **4b**$^+$·Cl^- (2.95 g, 5.46 mmol) in ethanol (50 mL). The resulting solution was stirred at room temperature for 15.5 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (433 mg, 6.55 mmol), KO*t*Bu (736 mg, 6.55 mmol), and pyridine (75 mL) and the mixture was stirred at

room temperature for 1 h and refluxed for 14 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/EtOAc as an eluent to give **10e** (1.94 g, 92% yield) as a green solid. M.p. 181–182 °C; IR (AT–IR): ν_{max} = 3024 (w), 2969 (w), 1567 (s), 1545 (m), 1516 (w), 1491 (w), 1473 (w), 1435 (s), 1396 (s), 1379 (m), 1361 (w), 1318 (w), 1268 (w), 1233 (w), 1211 (w), 1194 (w), 1138 (w), 1052 (w), 989 (w), 967 (w), 932 (w), 906 (w), 850 (s), 822 (m), 806 (s), 781 (w), 758 (m), 714 (w), 964 (w), 682 (w), 667 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 241 (4.44), 278 (4.53), 293 sh (4.57), 313 (4.65), 322 sh (4.63), 372 sh (4.08), 433 (4.24), 548 sh (4.05), 578 (3.08), 624 sh (3.01), 690 sh (2.75) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 277 (4.56), 295 (4.50), 328 (4.56), 341 sh (4.47), 421 (4.42), 569 (4.47) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 294 (4.26), 340 (4.44), 402 sh (4.30), 413 (4.31), 522 sh (4.28), 569 (4.47) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.70 (dd, *J* = 4.4, 1.6 Hz, 2H, 2,6-H of pyridine), 8.66 (d, *J* = 10.9 Hz, 1H, 8-H), 8.62 (d, *J* = 10.9 Hz, 1H, 4-H), 8.42 (d, *J* = 10.3 Hz, 2H, 4′,8′-H), 8.18 (s, 1H, 2-H), 7.89 (t, *J* = 3.7 Hz, 1H, 2′-H), 7.61 (dd, *J* = 4.4, 1.6 Hz, 2H, 3,5-H of pyridine), 7.49–7.53 (m, 4H, 5,7,5′,7′-H), 7.43 (d, *J* = 3.7 Hz, 2H, 1′,3′-H), 1.49 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 164.59, 149.65, 146.44, 145.16, 138.69, 137.21, 136.91, 136.71, 136.46, 136.31, 135.74, 135.37, 134.45, 126.89, 125.44, 124.22, 124.08, 123.99, 118.45, 38.90, 31.85 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{29}H_{25}N^+$ $[M]^+$ 388.2060, found: 388.2077.

Compound (11a): Diethylamine (20 mL) was added to a solution of **5a**$^{2+}$ (3.44 g, 5.00 mmol) in ethanol (50 mL). The resulting solution was stirred at room temperature for 17 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (397 mg, 6.00 mmol), KO*t*Bu (673 mg, 6.00 mmol), and pyridine (70 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 10 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/EtOAc as an eluent to give **10e** (190 mg, 10% yield) as a green solid. M.p. 278–280 °C; IR (AT–IR) ν_{max} = 3078 (w), 3022 (w), 1569 (s), 1543 (m), 1507 (w), 1471 (w), 1445 (w), 1423 (w), 1395 (s), 1346 (w), 1302 (w), 1267 (w), 1240 (w), 1195 (w), 1041 (w), 993 (w), 847 (s), 831 (m), 759 (m), 739 (s), 673 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.59), 285 (4.81), 321 (4.75), 345 sh (4.50), 436 (4.54), 579 (3.20), 633 sh (3.05), 705 sh (2.49) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 266 (4.67), 288 (4.35), 342 (4.32), 368 (4.32), 498 sh (4.36), 575 (4.66) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.68 (d, *J* = 10.0 Hz, 2H, 4,8-H), 8.44 (d, *J* = 10.5 Hz, 4H, 4′,8′,4″,8″-H), 8.33 (s, 1H, 2-H), 7.90 (t, *J* = 3.5 Hz, 2H, 2′,2″-H), 7.70 (t, *J* = 10.0 Hz, 1H, 6-H), 7.54 (d, *J* = 10.5 Hz, 4H, 5′,7′,5″,7″-H), 7.41 (d, *J* = 3.5 Hz, 4H, 1′,3′,1″,3″-H), 7.27 (t, *J* = 10.5 Hz, 2H, 5,7-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 146.37 (C-6′,6″), 139.75 (C-6), 138.69 (C-3a′,8a′,3a″,8a″), 138.61 (C-2), 137.94 (C-3a,8a), 136.96 (C-4,8), 136.45 (C-2′,2″), 135.63 (C-4′,8′,4″,8″), 134.37 (C-1,3), 125.53 (C-5′,7′,5″,7″), 125.27 (C-5,7), 118.36 (C-1′,3′,1″,3″) ppm; HRMS (FAB-MS, positive): Calcd for $C_{30}H_{20}^+$ $[M]^+$ 380.1565, found: 380.1574.

Compound (11b): Diethylamine (15 mL) was added to a solution of **5b**$^{2+}$ (3.35 g, 4.50 mmol) in ethanol (45 mL). The resulting solution was stirred at room temperature for 15 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (331 mg, 5.00 mmol), KO*t*Bu (561 mg, 5.00 mmol), and pyridine (60 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 12 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene/EtOAc as an eluent to give **10e** (334 mg, 17% yield) as a green solid. M.p. 274–275 °C; IR (AT–IR) ν_{max} = 3089 (w), 2963 (w), 1568 (s), 1546 (m), 1473 (w), 1429 (m), 1396 (s), 1349 (w), 1302 (w), 1267 (w), 1235 (w), 1192 (w), 1118 (w), 1054 (w), 1028 (w), 982 (w), 921 (w), 877 (w), 846 (s), 827 (m), 799 (w), 745 (s), 704 (w), 672 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.64), 286 (4.92), 325 (4.74), 345 sh (4.55), 373 sh (4.14), 446 (4.57), 576 (3.24), 632 sh (3.09), 707 sh (2.43) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 265 (4.68), 297 (4.42), 342 (4.40), 376 (4.26), 508 sh (4.41), 593 (4.74) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.65 (d, *J* = 11.0 Hz, 2H, 4,8-H), 8.43 (d, *J* = 10.5 Hz, 4H, 4′,8′,4″,8″-H), 8.23 (s, 1H, 2-H), 7.88 (t, *J* = 3.5 Hz, 2H, 2′,2″-H), 7.56 (d, *J* = 10.5 Hz, 4H, 5′,7′,5″,7″-H), 7.46 (d, *J* = 11.0 Hz, 2H, 5,7-H), 7.42 (d, *J* = 3.5 Hz, 4H, 1′,3′,1″,3″-H), 1.48 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 164.16 (C-6), 146.61 (C-6′,6″), 138.50 (C-3a′,8a′,3a″,8a″), 137.76 (C-2), 136.83 (C-3a,8a), 136.16 (C-2′,2″), 136.04 (C-4,8), 135.65 (C-4′,8′,4″,8″), 134.03 (C-1,3), 125.43 (C-5′,7′,5″,7″), 123.65 (C-5,7), 118.22 (C-1′,3′,1″,3″), 38.76 (*t*Bu), 31.78 (*t*Bu) ppm; HRMS (FAB-MS, positive): Calcd for $C_{34}H_{28}^+$ $[M]^+$ 436.2191, found: 436.2185.

Compound (12a): To a solution of **10a** (608 mg, 1.95 mmol) and pyridine (3.08 g, 38.9 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of Tf_2O (2.21 g, 7.84 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 1 h at room temperature and the solvent was removed under the reduced pressure. The reaction mixture was passed through silica gel with toluene and the solvent was removed by evaporation. KOH (500 mg, 8.91 mmol) was added to a solution of the obtained green-solid in EtOH (30 mL). The resulting mixture was refluxed for 16.5 h. The reaction mixture was poured into ice water and the generated precipitate was collected by filtration to afford **12a** (568 mg, 60% yield from **10a**) as a brown solid. M.p. 290–292 °C; IR (AT-IR) : ν_{max} = 3033 (w), 2959 (w), 1593 (m), 1569 (s), 1504 (w), 1491 (w), 1428 (m), 1395 (w), 1371 (w), 1338 (w), 1311 (w), 1250 (w), 1220 (w), 1092 (w), 1061 (w), 992 (w), 947 (w), 892 (w), 854 (w), 813 (m), 760 (m), 734 (m), 697 (w), 682 (w), 661 (m), 632 (m), 616 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 (4.55), 309 (4.56), 330 (4.55), 387 sh (4.31), 456 (4.26), 590 (3.03), 650 sh (2.87), 723 (2.22) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 255 (4.44), 280 (4.32), 321 (4.32), 346 (4.38), 427 (4.69), 484 sh (4.46), 585 sh (3.59) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.66–8.75 (m, 10H, 4,4′,8,8′-H, 2,2′,2″,6,6′,6″-H of pyridine), 8.27 (s, 1H, 2-H), 8.15 (s, 1H, 2′-H), 7.78 (t, *J* = 9.7 Hz, 1H, 6-H), 7.66 (d, *J* = 10.6 Hz, 2H, 5′,7′-H), 7.61 (dd, *J* = 4.4, 1.6 Hz, 4H, 3′,3″,5′,5″-H of pyridine), 7.57 (dd, *J* = 4.4, 1.6 Hz, 2H, 3,5-H of pyridine), 7.37 (t, *J* = 9.7 Hz, 2H, 5,7-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 150.25, 150.22, 149.32, 144.46, 144.27, 140.42, 138.36, 138.31, 137.87, 136.94, 136.65, 136.22, 136.10, 135.43, 133.35, 128.24, 128.15, 128.07, 126.22, 124.34, 124.26 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{35}H_{23}N_3 + H^+$ $[M+H]^+$ 486.1970, found:486.1991.

Compound (12b): To a solution of **10b** (466 mg, 1.50 mmol) and pyridine (2.37 g, 30.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of Tf_2O (1.69 g, 6.00 mmol) in CH_2Cl_2 (10 mL). The resulting solution was stirred for 1 h at room temperature and the solvent was removed under the reduced pressure. The reaction mixture was passed through silica gel with toluene and the solvent was removed by evaporation. KOH (842 mg, 15.0 mmol) was added to a solution of the obtained green-solid in EtOH (30 mL). The resulting mixture was refluxed for 15 h. The reaction mixture was poured into ice water and the generated precipitate was collected by filtration to afford **12b** (626 mg, 77% yield from **10b**) as a brown solid. M.p. 295–297 °C; IR (AT–IR): ν_{max} = 3027 (w), 2965 (w), 2868 (w), 1588 (s), 1567 (s), 1550 (w), 1518 (w), 1502 (w), 1487 (w), 1429 (s), 1389 (w), 1383 (w), 1368 (m), 1308 (w), 1245 (w), 1217 (w), 1139 (w), 1110 (w), 1071 (w), 1062 (w), 991 (w), 948 (w), 933 (w), 880 (w), 858 (w), 841 (w), 817 (s), 734 (w), 718 (w), 696 (w), 679 (w), 658 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.64), 302 sh (4.66), 316 (4.71), 330 sh (4.67), 360 sh (4.48), 381 sh (4.43), 466 (4.39), 571 (3.23), 629 sh (3.09) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 284 sh (4.42), 321 sh (4.58), 344 (4.62), 424 (4.59), 465 sh (4.47), 578 sh (3.53) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 288

(4.45), 321 (4.41), 352 (4.50), 429 (4.76), 479 sh (4.62), 543 sh (4.07), 571 sh (3.81) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.70–8.74 (m, 9H, 4,4′,8′-H, 2,2′,2″,6,6′,6″-H of pyridine), 8.65 (d, J = 10.9 Hz, 1H, 8-H), 8.22 (s, 1H, 2-H), 8.15 (s, 1H, 2′-H), 7.72 (d, J = 10.9 Hz, 2H, 5′,7′-H), 7.65 (dd, J = 4.6, 1.7 Hz, 4H, 3′,3″,5′,5″-H of pyridine), 7.61 (dd, J = 4.6, 1.4 Hz, 2H, 3,5-H of pyridine), 7.59 (d, J = 10.6 Hz, 2H, 5,7-H), 1.50 (s, 9H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.33, 149.80, 149.68, 149.62, 145.09, 144.91, 137.52, 137.44, 136.93, 136.45, 136.11, 135.92, 135.82, 135.51, 132.99, 128.37, 128.09, 127.59, 124.93, 124.85, 124.31, 124.22, 39.05, 31.85 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{39}H_{31}N_3^+$ [M]$^+$ 542.2591, found: 542.2611.

Compound (13): To a solution of **12b** (294 mg, 0.54 mmol) in EtOH (10 mL) was added 1-chloro-2,4-dinitrobenzene (659 mg, 3.25 mmol), then the resulting solution was refluxed for 22.5 h. The precipitate was collected by filtration to afford pyridinium salt intermediate as a reddish brown solid. Pyrrolidine (2 mL) was added to a solution of the pyridinium salt in EtOH (5 mL). The resulting mixture was stirred at room temperature for 3 h and the solvent was removed under reduced pressure. To the residue was added cyclopentadiene (160 mg, 2.42 mmol), KO*t*Bu (252 mg, 2.24 mmol), and pyridine (8 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 17 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **13** (25 mg, 7% yield) as a brown solid. M.p. > 300 °C; IR (AT–IR): ν_{max} = 3079 (w), 2965 (w), 1943 (w), 1795 (w), 1716 (w), 1566 (s), 1545 (w), 1498 (w), 1474 (w), 1427 (s), 1397 (s), 1377 (m), 1345 (w), 1303 (w), 1267 (w), 1243 (w), 1200 (w), 1107 (w), 1051 (w), 985 (w), 919 (w), 905 (w), 878 (w), 843 (s), 800 (w), 784 (w), 748 (m), 705 (w), 680 (w), 664 (w), 652 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.80), 285 (4.97), 314 (4.91), 343 sh (4.79), 378 sh (4.43), 456 (4.84), 583 sh (3.61), 621 sh (3.51), 690 sh (3.03) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 300 (4.57), 344 (4.62), 373 sh (4.46), 411 sh (4.23), 585 (4.96), 610 sh (4.91) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.75 (dd, J = 10.7, 5.9 Hz, 3H, 4,4′′′,8′′′-H), 8.67 (d, J = 10.3 Hz, 1H, 8-H), 8.47 (d, J = 10.6 Hz, 4H, 4″,4‴,8″,8‴-H), 8.43 (d, J = 10.6 Hz, 2H, 4′,8′-H), 8.29 (s, 2H, 2,2′-H), 7.90 (t, J = 3.7 Hz, 3H, 2″,2‴,2′′′′-H), 7.67 (d, J = 10.9 Hz, 2H, 5′′′′,7′′′′-H), 7.63 (d, J = 10.3 Hz, 4H, 5″,5‴,7″,7′′′′-H), 7.50–7.56 (m, 4H, 1′′′′,3′′′′,5′,7′-H), 7.44 (m, 6H, 1″, 1‴,3″, 3″,5,7,–H), 1.49 (s, 9H, *t*Bu) ppm. Measurement of ^{13}C NMR was hampered by the insolubility of the compound. HRMS (MALDI-TOF, positive): Calcd for $C_{54}H_{40}+H^+$ [M + H]$^+$ 689.3203, found: 689.3190.

Compound (14): NIS (357 mg, 1.40 mmol) was added to a solution of **10d** (155 mg, 0.47 mmol) in CH_2Cl_2 (10 mL) and Et_3N (3 drops). The resulting solution was stirred at 0 °C for 1 h. The reaction mixture was concentrated under reduced pressure. The residue was passed through short column chromatography on alumina with $CHCl_3$ as an eluent to give the crude diiodo derivative (194 mg, 71% yield) as a brown solid. To a solution of the diiodo derivative (194 mg, 0.33 mmol), 4-*tert*-butylphenylboronic acid (177 mg, 0.994 mmol), and K_3PO_4 (426 mg, 2.00 mmol) in 1,4-dioxane (5 mL) and H_2O (0.5 mL) was added $PdCl_2$(dppf) (12 mg, 0.016 mmol). The resulting mixture was refluxed for 15.5 h under an Ar atmosphere. The reaction mixture was poured into aq. NaOH (10%) and extracted with toluene. The organic layer was washed with sat. NH_4Cl and brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on alumina with $CHCl_3$/hexane as an eluent to give **14** (87 mg, 44% yield) as a green solid. M.p. 183–185 °C; IR (AT–IR): ν_{max} = 3024 (w), 2959 (w), 2902 (w), 5865 (w), 1596 (m), 1568 (s), 1543 (w), 1519 (w), 1492 (w), 1460 (w), 1429 (m), 1366 (m), 1317 (w), 1303 (w), 1269 (w), 1223 (w), 1204 (w), 1113 (w), 1017 (w), 992 (w), 939 (w), 874 (w), 830 (s), 777 (w), 741 (m), 723 (w), 701 (w), 688 (w), 680 (w), 667 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 234 (4.58), 278 (4.65), 300 sh (4.54), 335 (4.63), 387 (4.60), 421 (4.52), 543 sh (2.92), 577 (2.97), 631 sh (2.91), 697 sh (2.64) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 277 (4.68), 335 (4.67), 386 (4.62), 419 (4.52) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 285 sh (4.40), 331 (4.42), 370 (4.36), 415 (4.34), 534 sh (4.50), 555 (4.52), 587 sh (4.37) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.72–8.73 (m, 3H, 4-H, 2,6-H of pyridine), 8.60–8.63 (m, 3H, 8-H, 4′,8′-H), 8.23 (s, 1H, 2-H), 8.10 (s, 1H, 2′-H), 7.70 (t, J = 9.7 Hz, 1H, 6-H), 7.65 (d, J = 8.3 Hz, 4H, 4-*t*BuPh), 7.55–7.58 (m, 6H, 4-*t*BuPh, 3,5-H of pyridine), 7.38 (d, J = 10.6 Hz, 2H, 5′,7′-H), 7.28 (dd, J = 9.9, 1.7 Hz, 2H, 5,7-H), 1.44 (s, 18H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 150.17, 149.40, 147.63, 144.52, 140.00, 138.21, 137.89, 137.71, 137.14, 136.73, 136.25, 135.33, 135.08, 134.42, 134.40, 131.13, 129.51, 127.58, 125.73, 125.57, 124.33, 34.67, 31.54 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{45}H_{41}N+H^+$ [M + H]$^+$ 596.3312, found: 596.3329.

Compound (15): To a solution of **14** (159 mg, 0.27 mmol) in toluene (10 mL) was added 1-chloro-2,4-dinitrobenzene (109 mg, 0.54 mmol) and the solution was reflux for 24 h. The precipitate was collected by filtration to afford the pyridinium salt (213 mg, 100% yield) as a reddish brown solid. Pyrrolidine (1 mL) was added to a solution of the pyridinium salt (213 mg, 0.266 mmol) in ethanol (3 mL). The resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure. To the residue was added cyclopentadiene (24 mg, 0.36 mmol), KO*t*Bu (35 mg, 0.311 mmol), and pyridine (4 mL) and the mixture was stirred at room temperature for 1 h and refluxed for 18 h. The precipitate was separated by filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as an eluent to give **15** (32 mg, 19% yield) as a green solid. M.p. > 300 °C; IR (AT–IR): ν_{max} = 3022 (w), 2959 (w), 2867 (w), 1573 (s), 1548 (w), 1491 (w), 1472 (w), 1429 (m), 1397 (m), 1370 (m), 1350 (w), 1304 (w), 1269 (w), 1230 (w), 1197 (w), 1147 (w), 1113 (w), 1050 (w), 1017 (w), 988 (w), 964 (w), 941 (w), 851 (m), 841 (s), 828 (m), 814 (w), 790 (w), 763 (m), 752 (w), 737 (s), 722 (w), 706 (w), 679 (w), 664 (w), 654 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 239 (4.65), 283 (4.81), 335 (4.74), 386 sh (4.50), 443 (4.58), 592 (3.17), 633 sh (3.12), 699 sh (2.80) nm; UV/Vis (30% CH_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 284 (4.80), 336 (4.75), 374 sh (4.56), 395 sh (4.51), 442 (4.57), 709 (3.50) nm; UV/Vis (30% CF_3CO_2H/CH_2Cl_2): λ_{max} (log ε) = 291 sh (4.51), 343 sh (4.47), 369 (4.50), 500 sh (4.45), 547 sh (4.61), 579 (4.70) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.73 (d, J = 9.7 Hz, 1H, 4-H), 8.68 (d, J = 9.7 Hz, 1H, 8-H), 8.62 (d, J = 10.6 Hz, 2H, 4′,8′-H), 8.43 (d, J = 10.3 Hz, 2H, 4″,8″-H), 8.32 (s, 1H, 2-H), 8.10 (s, 1H, 2′-H), 7.91 (t, J = 3.7 Hz, 1H, 2″-H), 7.70 (d, J = 9.7 Hz, 1H, 6-H), 7.66 (d, J = 8.3 Hz, 4H, 4-*t*BuPh), 7.57 (d, J = 8.3 Hz, 4H, 4-*t*BuPh), 7.53 (d, J = 10.6 Hz, 2H, 5″,7″-H), 7.44 (m, 4H, 1″,3″,5′,7′-H), 7.24–7.29 (m, 3H, 5,7-H), 1.43 (s, 18H, *t*Bu) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 149.37, 147.89, 146.42, 139.92, 138.70, 138.20, 138.09, 137.07, 136.62, 136.57, 135.75, 135.37, 135.05, 134.55, 134.45, 134.16, 131.05, 129.53, 125.86, 125.75, 125.62, 125.48, 125.42, 118.48, 34.69, 31.54 ppm; HRMS (MALDI-TOF, positive): Calcd for $C_{50}H_{44}$ [M]$^+$ 644.3438, found:644.3441.

Acknowledgments

This work was partially supported by the JSPS KAKENHI Grant Number 17K05780. We also thank Ms. Nanami Iida, Ms. Atsuyo Yamamoto, Ms. Erika Shimomura, and Mr. Yuta Inoue, Shinshu University, for their technical assistance. We appreciate late professor Klaus Hafner for his valuable comments on our research.

Conflict of Interest

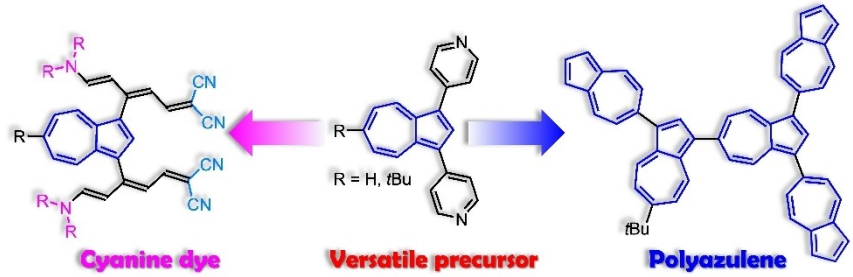
The authors declare no conflict of interest.

Keywords: cyanine dyes · donor-acceptor compounds · oligoazulenes · π-conjugated systems · Zinke salts

[1] a) T. Zincke, G. Heuser, W. Möller, *Justus Liebigs Ann. Chem.* **1904**, *333*, 296–345; b) T. Zincke, *Justus Liebigs Ann. Chem.* **1904**, *333*, 361–374.
[2] a) D. B. C. Martin, C. D. Vanderwal, *J. Am. Chem. Soc.* **2009**, *131*, 3472–3473; b) S. E. Steinhardt, C. D. Vanderwal, *J. Am. Chem. Soc.* **2009**, *131*, 7546–7547; c) A. Y. Hong, C. D. Vanderwal, *J. Am. Chem. Soc.* **2015**, *137*, 7306–7309.
[3] S. Asaftei, D. Huskens, D. Schols, *J. Med. Chem.* **2012**, *55*, 10405–10413.
[4] a) C. Reus, M. Stolar, J. Vanderkley, J. Nebauer, T. Baumgartner, *J. Am. Chem. Soc.* **2015**, *137*, 11710–11717; b) G. Das, T. Skorjanc, S. K. Sharma, F. Gándara, M. Lusi, D. S. S. Rao, S. Vimala, S. K. Prasad, J. Raya, D. S. Han, R. Jagannathan, J.-C. Olsen, A. Trabolsi, *J. Am. Chem. Soc.* **2017**, *139*, 9558–9565; c) C. Zhan, G. Zhang, D. Zhang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 12141–12149; d) A. Baheti, A. Vigalok, *J. Am. Chem. Soc.* **2019**, *141*, 12224–12228; e) T. Škorjanc, D. Shetty, M. A. Olson, A. Trabolsi, *ACS Appl. Mater. Interfaces* **2019**, *11*, 6705–6716.
[5] L. Štacková, P. Štacko, P. Klán, *J. Am. Chem. Soc.* **2019**, *141*, 7155–7162.
[6] a) H. Meier, *Angew. Chem. Int. Ed.* **2005**, *44*, 2482–2506; *Angew. Chem.* **2005**, *117*, 2536–2561; b) D. P. Harrison, G. W. Kosturko, V. M. Ramdeen, A. C. Nichols-Nielander, S. J. Payne, M. Sabat, W. H. Myers, W. D. Harman, *Organometallics* **2010**, *29*, 1909–1915; c) L. Štacková, E. Muchová, M. Russo, P. Slavíček, P. Štacko, P. Klán, *J. Org. Chem.* **2020**, *85*, 9776–9790; d) D.-H. Li, C. L. Schreiber, B. D. Smith, *Angew. Chem. Int. Ed.* **2020**, *59*, 12154–12161; *Angew. Chem.* **2020**, *132*, 12252–12259; e) R. M. Exner, F. Cortezon-Tamarit, S. I. Pascu, *Angew. Chem. Int. Ed.* **2021**, *60*, 6230–6241; *Angew. Chem.* **2021**, *133*, 6295–6306.
[7] a) A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *Chem. Rev.* **2000**, *100*, 1973–2012; b) K. Colas, S. Doloczki, M. P. Urrutia, C. Dyrager, *Eur. J. Org. Chem.* **2021** (doi.org/10.1002/ejoc.202001658).
[8] K. Ziegler, K. Hafner, *Angew. Chem.* **1955**, *67*, 301.
[9] K. Hafner, K.-P. Meinhardt, *Org. Syn. Coll.* Vol. 7, p.15.
[10] a) M. Oda, S. Kishi, N. C. Thanh, S. Kuroda, *Heterocycles* **2007**, *71*, 1413–1416; b) S. Wakabayashi, Y. Kato, K. Mochizuki, R. Suzuki, M. Matsumoto, Y. Sugihara, M. Shimizu, *J. Org. Chem.* **2007**, 72, 744–749; c) T. Shoji, K. Okada, S. Ito, K. Toyota, N. Morita, *Tetrahedron Lett.* **2010**, *51*, 5127–5130; d) S. Ito, T. Shoji, N. Morita, *Synlett* **2011**, *16*, 2279–2298.
[11] a) T. Shoji, R. Yokoyama, S. Ito, M. Watanabe, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett.* **2007**, *48*, 1099–1103; b) T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Tetrahedron Lett.* **2007**, *48*, 4999–5002; c) J. Higashi, T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2008**, 5823–5831; d) T. Shoji, S. Ito, T. Okujima, J. Higashi, R. Yokoyama, K. Toyota, M. Yasunami, N. Morita, *Eur. J. Org. Chem.* **2009**, 1554–1563; e) T. Shoji, S. Ito, J. Higashi, N. Morita, *Eur. J. Org. Chem.* **2011**, 5311–5322; f) T. Shoji, A. Maruyama, S. Ito, T. Okujima, M. Yasunami, J. Higashi, N. Morita, *Heterocycles* **2014**, *89*, 2588–2603.
[12] A part of this study was previously reported in its preliminary form: a) T. Shoji, A. Yamamoto, Y. Inoue, E. Shimomura, S. Ito, J. Higashi, N. Morita, *Chem. Lett.* **2012**, *41*, 1644–1646; b) T. Shoji, A. Yamamoto, E. Shimomura, M. Maruyama, S. Ito, T. Okujima, K. Toyota, N. Morita, *Chem. Lett.* **2013**, *42*, 638–640.
[13] T. Zincke, G. Heuser, W. Möller, *Justus Liebigs Ann. Chem.* **1904**, *333*, 296–345.
[14] F. Texier-Boullet, A. Foucaud, *Tetrahedron Lett.* **1982**, *23*, 4927–4928.
[15] a) F. Bureš, W. B. Schweizer, J. C. May, C. Boudon, J.-P. Gisselbrecht, M. Gross, I. Biaggio, F. Diederich, *Chem. Eur. J.* **2007**, *13*, 5378–5387; b) F. Bureš, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Eur. J. Org. Chem.* **2008**, 994–1004; c) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248; d) B. B. Frank, P. R. Laporta, B. Breiten, M. C. Kuzyk, P. D. Jarowski, W. B. Schweizer, P. Seiler, I. Biaggio, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Eur. J. Org. Chem.* **2011**, 4307–4317; e) P. Solanke, O. Pytela, F. Bureš, M. Klikar, *Dyes Pigm.* **2019**, *162*, 755–762.
[16] Deposition Numbers 1838801 (for **7aa**) and 1922390 (for **9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
[17] The time-dependence density functional calculations were performed with Spartan'10, Wave function, Irvine, CA.
[18] a) R. L. Parton, J. R. Lenhard, *J. Org. Chem.* **1990**, *55*, 49–57; b) H. John, C. Briehn, J. Schmidt, S. Hünig, J. Heinze, *Angew. Chem. Int. Ed.* **2007**, *46*, 449–453; *Angew. Chem.* **2007**, *119*, 453–457.
[19] a) Z.-i. Yoshida, M. Shibata, E. Ogino, T. Sugimoto, *Tetrahedron Lett.* **1984**, *25*, 3343–3346; b) S. E. Estdale, R. Brettle, D. A. Dunmur, C. M. Marson, *J. Mater. Chem.* **1997**, *7*, 391–401; c) K. Kurotobi, A. Osuka, *Org. Lett.* **2005**, *7*, 1055–1058; d) A. P. Gee, S. D. Cosham, A. L. Johnson, S. E. Lewis, *Synlett* **2017**, *28*, 973–975; e) Y. M. Poronik, L. M. Mazur, M. Samoć, D. Jacquemin, D. T. Gryko, *J. Mater. Chem. C* **2017**, *5*, 2620–2628.
[20] M. Hanke, C. Jutz, *Angew. Chem. Int. Ed.* **1979**, *18*, 214–215; *Angew. Chem.* **1979**, *91*, 227–227.
[21] M. Hanke, C. Jutz, *Synthesis* **1980**, 31–32.
[22] a) Y. Yamaguchi, K. Ogawa, K.-i. Nakayama, Y. Ohba, H. Katagiri, *J. Am. Chem. Soc.* **2013**, *135*, 19095–19098; b) Y. Yamaguchi, M. Takubo, K. Ogawa, K.-i. Nakayama, T. Koganezawa, H. Katagiri, *J. Am. Chem. Soc.* **2016**, *138*, 11335–11343.
[23] H. Langhals, M. Eberspächer, *Synthesis* **2018**, *50*, 1862–1866.
[24] a) P. A. Plattner, A. S. Pfau, *Helv. Chim. Acta* **1937**, *20*, 224–232; b) P. A. Plattner, H. Roniger, *Helv. Chim. Acta* **1943**, *26*, 905–912; c) P. A. Plattner, A. Fürst, *Helv. Chim. Acta* **1945**, *28*, 1636–1638; d) P. A. Plattner, A. Fürst, H. Schmid, *Helv. Chim. Acta* **1945**, *28*, 1647–1651; e) P. A. Plattner, E. Heilbronner, *Helv. Chim. Acta* **1947**, *30*, 910–920; f) P. A. Plattner, E. Heilbronner, A. Fürst, *Helv. Chim. Acta* **1947**, *30*, 1100–1105; g) P. A. Plattner, A. Fürst, K. Jirasek, *Helv. Chim. Acta* **1947**, *30*, 1320–1329; h) T. Shoji, M. Tanaka, S. Takagaki, K. Miura, A. Ohta, R. Sekiguchi, S. Ito, S. Mori, T. Okujima, *Org. Biomol. Chem.* **2018**, *16*, 480–489; i) T. Shoji, Y. Ariga, A. Yamazaki, M. Uda, T. Nagasawa, S. Ito, *Bull. Chem. Soc. Jpn.* **2021**, *94*, 1000–1009.
[25] a) L. H. Chopard-dit-Jean, E. Heilbronner, *Helv. Chim. Acta* **1952**, *35*, 2170–2193; b) D. H. Reid, W. H. Stafford, W. L. Stafford, G. McLennan, A. Voigt, *J. Chem. Soc.* **1958**, 1110–1117; c) E. C. Kirby, D. H. Reid, *J. Chem. Soc.* **1960**, 494–501; d) M. Murai, S. Iba, H. Ota, K. Takai, *Org. Lett.* **2017**, *19*, 5585–5588.
[26] a) T. Shoji, T. Araki, N. Iida, K. Miura, A. Ohta, R. Sekiguchi, S. Ito, T. Okujima, *Org. Chem. Front.* **2019**, *6*, 195–204; b) T. Shoji, K. Miura, A. Ohta, R. Sekiguchi, S. Ito, Y. Endo, T. Nagahata, S. Mori, T. Okujima, *Org. Chem. Front.* **2019**, *6*, 2801–2811; c) T. Shoji, N. Iida, A. Yamazaki, Y. Ariga, A. Ohta, R. Sekiguchi, T. Nagahata, T. Nagasawa, S. Ito, *Org. Biomol. Chem.* **2020**, *18*, 2274–2282; d) T. Shoji, S. Sugiyama, Y. Kobayashi, A. Yamazaki, Y. Ariga, R. Katoh, H. Wakui, M. Yasunami, and S. Ito, *Chem. Commun.* **2020**, *56*, 1485–1488.
[27] Voltammetry experiments of **12a,b**, and **13** were hampered by the low solubility toward the measurement solvent.
[28] a) S. Ito, T. Okujima, N. Morita, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1896–1905; b) S. Ito, H. Inabe, N. Morita, K. Ohta, T. Kitamura, K. Imafuku, *J. Am. Chem. Soc.* **2003**, *125*, 1669–1680; c) S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, A. Tajiri, *J. Org. Chem.* **2003**, *68*, 9753–9762; d) S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, J. Kawakami, A. Tajiri, *J. Org. Chem.* **2005**, *70*, 2285–2293; e) S. Ito, H. Inabe, N. Morita, A. Tajiri, *Eur. J. Org. Chem.* **2004**, 1774–1780; f) S. Ito, T. Iida, J. Kawakami, T. Okujima, N. Morita, *Eur. J. Org. Chem.* **2009**, 5355–5364; g) T. Shoji, M. Maruyama, E. Shimomura, A. Maruyama, S. Ito, T. Okujima, K. Toyota, N. Morita, *J. Org. Chem.* **2013**, *78*, 12513–12524; h) T. Shoji, S. Ito, T. Okujima, N. Morita, *Chem. Eur. J.* **2013**, *19*, 5721–5730; i) T. Shoji, M. Maruyama, A. Maruyama, S. Ito, T. Okujima, K. Toyota, *Chem. Eur. J.* **2014**, *20*, 11903–11912.

Manuscript received: April 15, 2021
Revised manuscript received: April 26, 2021
Accepted manuscript online: April 27, 2021

FULL PAPERS



Prof. Dr. T. Shoji, A. Yamazaki, Y. Ariga, M. Uda, D. Ando, N. Sasahara, N. Kai, Prof. Dr. S. Ito*

Azulene-substituted donor-acceptor polymethines, bi-, ter-, and quinqueazulenes composed of the 1,6′-biazulene unit have been successfully prepared from Zincke salts with an 1-azulenyl substituent. The structural, optical, and electrochemical properties of the azulene-substituted donor-acceptor polymethines, bi-, ter-, and quinqueazulenes were revealed by single-crystal X-ray structure analysis, UV/vis spectroscopy, voltammetry analysis, spectroelectrochemistry, and theoretical calculations.