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Syntheses and properties of linear π-conjugated molecules composed of 1-azaazulene and azulene

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ABSTRACT

Two compounds, 6-(1-azaazulen-2-yl)ethynylazulene (**8**) and 6-(2-azulenyl)ethynylazulene (**10**), were synthesized using the Sonogashira-Hagihara cross-coupling reaction followed by decarboxylation with concentrated phosphoric acid. Compounds **8** and **10** were characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, ultraviolet−visible (UV−Vis) spectroscopy, cyclic voltammetry, and density functional theory (DFT) calculations. Based on the results, both compounds were confirmed to have π-conjugation throughout their molecular structures. The acidic responsivity of compounds **8** and **10** was evaluated using UV−Vis and ^{1}H NMR spectroscopy. Compound **8** was found to be highly sensitive to trifluoroacetic acid, with its 1-azaazulenyl moiety acting as a base. Compound **10** generated azulenium cations when mixed with excess amounts of trifluoroacetic acid.

1. Introduction

Azulene and 1-azaazulene are structural isomers of naphthalene and quinoline, respectively. Interestingly, their unique properties include: (i) controllable band gap energies [1,2], (ii) excellent chromogenic and electronic characteristics [3,4], and (iii) large dipole moments (azulene: 1.08 D [5]; 1-azaazulene: 3.05 D [6]). Recently, azulenyl derivatives have gained attention in the applications of conductive polymers [7,8], near-infrared-light-absorbing materials [9−12], and organic semiconductors [13−16]. These materials are composed of subunits which contain azulenyl group substituents. Specifically, combined azulenyl derivatives, having substituents in the 2- or 6-position have smaller band gap energies compared to those with substituents in the 1- or 3-position [17]. This is because they are strongly affected by dipole moments [18]. Linear azulenyl trimers, which are composed of combinations of azulenes in a head-to-tail manner, were reported by Yamaguchi and coworkers [14,15] to have unique properties. Comparatively, hetero-coupled compounds composed of azulenyl and azaazulenyl groups have been reported very little. Previously, our group reported the syntheses and properties of amino-bridged compounds composed of 1-azaazulenyl and azulenyl groups [19]. However, the planarity of the compounds was low because the two groups were twisted. Hence, the unique properties of azulene and 1-azaazulene were not utilized.

In this work, ethynylene-bridged linear dimers composed of azulenyl and 1-azaazulenyl moieties were synthesized. The ethynylene group was selected due to its high π-conjugation ability. To investigate the properties of linear dimers, 6-(1-azaazulen-2-yl) ethynylazulene (**8**) and 6-(2-azulenyl)ethynylazulene (**10**) were chosen because of their simple structures. These compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and mass spectrometry. Their properties were evaluated by ultraviolet−visible (UV−Vis) spectroscopy, cyclic voltammetry, and density functional theory (DFT) calculations (Scheme 1). Moreover, protonation of compounds **8** and **10** was studied based on changes in the UV−Vis spectra observed.

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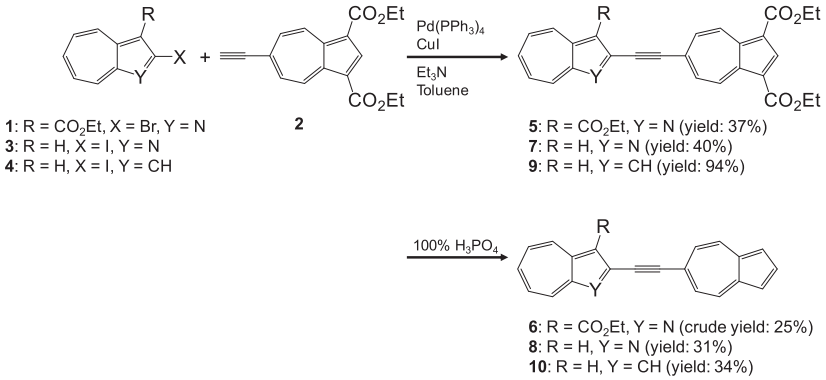

Scheme 1. Syntheses of compounds **6**, **8**, and **10**.

2. Results and discussion

2.1. Syntheses

In general, the 1- and 3-positions of azulenyl compounds and the 3-position of 1-azaazulenyl compounds are easily attacked by nucleophiles; therefore, 1,3-diethoxycarbonyl azulene (compound **2**) and 1-ethoxycarbonyl azaazulene (compound **1**) were selected to prevent side reactions. Decarboxylation was performed using concentrated phosphoric acid, using a method similar to that of other azulene derivatives [14,15,20]. Compound **5** was synthesized using the Sonogashira-Hagihara cross-coupling reaction of compounds **1** and **2** in the presence of $Pd(PPh_3)_4$, CuI, and triethylamine in toluene, with a 37% isolation yield. To synthesize compound **8**, compound **5** was decarboxylated using concentrated phosphoric acid. Based on the ^{1}H NMR spectrum of the product (Fig. 1), a doublet at 7.43 ppm was observed and assigned to the protons in the 1,3-positions of the azulene moiety (coupling constant = 3.6 Hz). Additionally, signals representative of an ethoxycarbonyl group in the azaazulene moiety appeared. Hence, the decarboxylation of compound **5** did not produce compound **8,** but instead produced compound **6**; furthermore, compound **6** was contaminated with byproducts. From these results, the decarboxylation of the azaazulenyl moiety was deemed to be very difficult.

In place of compound **1**, compound **3** was selected because side reactions of the Sonogashira-Hagihara cross-coupling reaction are prevented by the high reactivity of its iodo group. Compound **8** was synthesized through the reaction of compounds **3** and **2** in the presence of $Pd(PPh_3)_4$, CuI, and triethylamine in toluene, followed by decarboxylation using concentrated phosphoric acid. The ^{1}H NMR spectra of compounds **7** and **8** are shown in Fig. 2. In the 1–5 ppm region, no signals due to an ethoxycarbonyl group were present for compound **8**. Furthermore, in the aromatic region (7–10 ppm), a doublet at 7.41 and a triplet at 7.92 ppm were present (coupling constant = 3.5 Hz). This value was attributed to $^3J_{H-H}$ coupling interactions between protons of the 1-/3-position and 2-position. Compound **10** was synthesized using the same method as compound **8**, except compound **4** was used instead of compound **3**.

2.2. Properties of compounds *8* and *10*

The properties of compounds **8** and **10** were evaluated using UV–Vis spectroscopy, cyclic voltammetry, and DFT calculations. The UV–Vis spectra of compounds **8** and **10** are shown in Fig. 3. The absorption bands assigned to the transitions from the ground states to the second excited states ($S_0 \rightarrow S_2$) of 1-azaazulene and azulene occurred at 325 [21–23] and 341 nm [24,25], respectively. Furthermore, the transitions from the S_0 to the first excited states ($S_0 \rightarrow S_1$) of 1-azaazulene and azulene occurred at 440 [21–23] and 580 nm [24–26], respectively. As seen in Fig. 3, the strongest absorption bands in the visible region for compounds **8** and **10** occurred at 406 and 419 nm, respectively, which suggested $S_0 \rightarrow S_2$ transitions. Additionally, the longest absorption bands of compounds **8** and **10** occurred at wavelengths >600 nm and were assumed to be $S_0 \rightarrow S_1$ transitions. Based on these results, the conjugation of these compounds was obviously extended compared to that of azulene and 1-azaazulene.

The electrochemical properties of compounds **8** and **10** were evaluated using cyclic voltammetry (Fig. 4). The oxidation side (>0 V) was very complicated because compounds **8** and **10** decomposed to compounds such as azulene-1-carbonitriles [27],

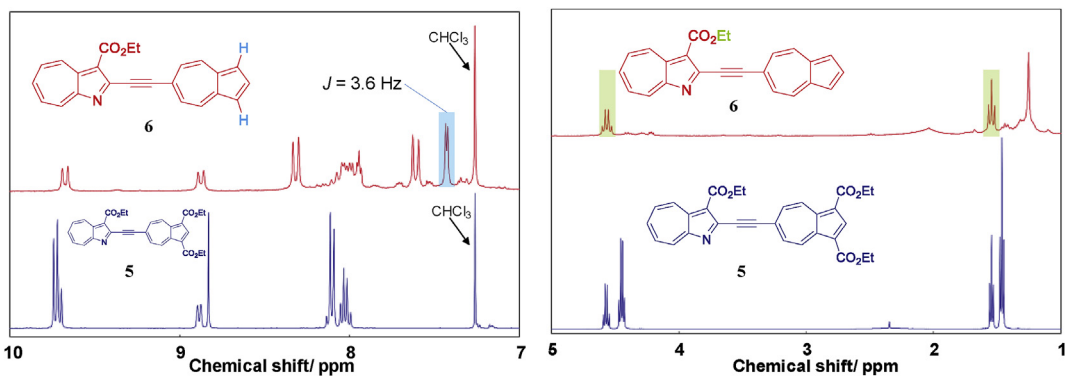

Fig. 1. ^{1}H NMR spectra of compounds **5** and **6** in the regions of 7–10 ppm (left) and 1–5 ppm (right).

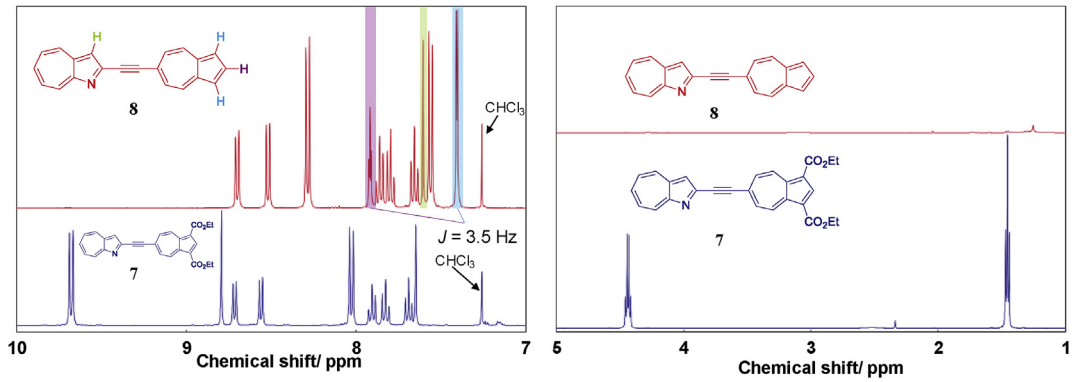

Fig. 2. ^{1}H NMR spectra of compounds **7** and **8** in the regions of 7–10 ppm (left) and 1–5 ppm (right).

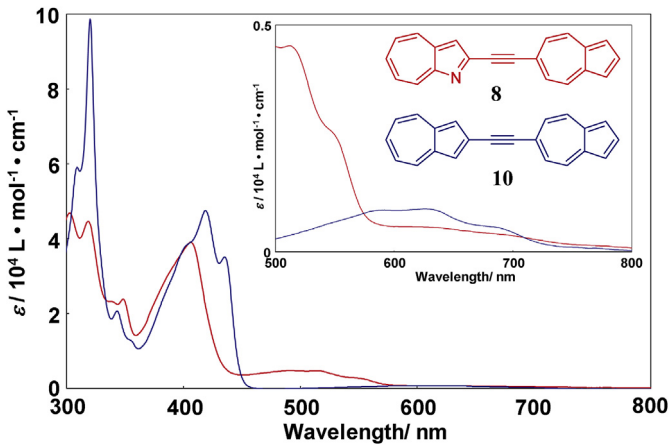

Fig. 3. UV–Vis spectra of compounds **8** and **10** in CH_2Cl_2.

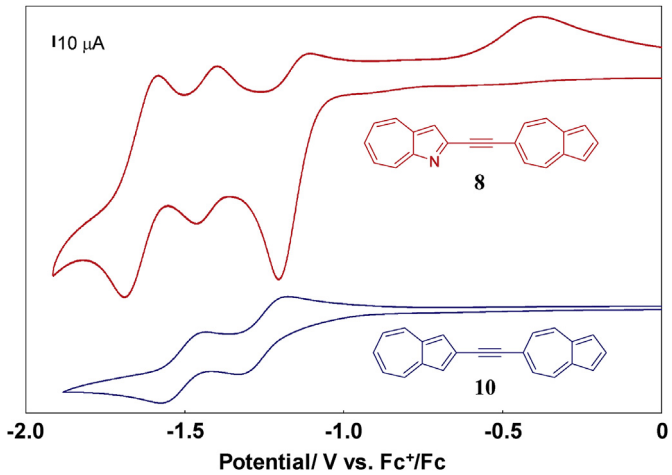

Fig. 4. Cyclic voltammograms of compounds **8** and **10** in CH_2Cl_2 (working electrode: glassy carbon; reference electrode: Ag^+/Ag; counter electrode: Pt; internal reference: Fc^+/Fc; and supporting electrolyte solution: 0.1 mol/L *n*-Bu_4NClO_4).

which were deposited onto the electrode. Hence, examination was limited to the reduction side. The voltammogram of compound **8** showed an irreversible reduction peak at −1.20 V, and two reversible redox peaks at −1.46 and −1.69 V. Due to the presence of the irreversible peak in the first stage, the anionic species formed by the reduction of compound **8** was found to be unstable. Comparatively, compound **10** had two reversible redox peaks at −1.30 and −1.56 V; suggesting the anionic species formed from this compound was stable.

DFT calculations of compounds **8** and **10** are shown in Figs. 5 and 6, respectively. The highest occupied molecular orbitals (HOMOs) of compounds **8** and **10** are distributed in their 6-ethynylazulenyl moieties, while the lowest unoccupied molecular orbitals (LUMOs) are distributed throughout the molecules. The orbital overlaps of the HOMO and the LUMO clearly differ; therefore, the transition probability from HOMO to LUMO is low (the calculated oscillator strength is shown in Figs. S1 and S2). This result corresponds to the low molar extinction coefficients of the absorption bands from 600 to 700 nm observed by UV–Vis spectroscopy. It was proposed that the strongest absorption bands in the visible regions of compounds **8** and **10** were due to $S_0 \rightarrow S_2$ transitions, that is, transitions from the HOMO to the LUMO+1. However, the orbital overlaps of the HOMO and the LUMO+1 are too different; thus the transition probability is low. From the DFT calculations, the strongest absorption bands in the visible regions of compounds **8** and **10** are possibly derived from transitions from the HOMO−1 to the LUMO and the HOMO−2 to the LUMO, respectively. These transitions would be possible because the calculated energy levels between the HOMO and the HOMO−1 for compound **8**, and the

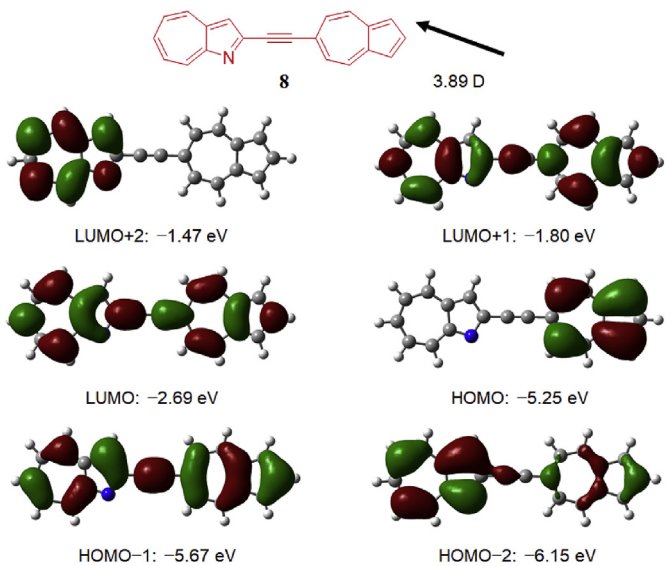

Fig. 5. Molecular orbitals, energy levels, and calculated dipole moment of compound **8**.

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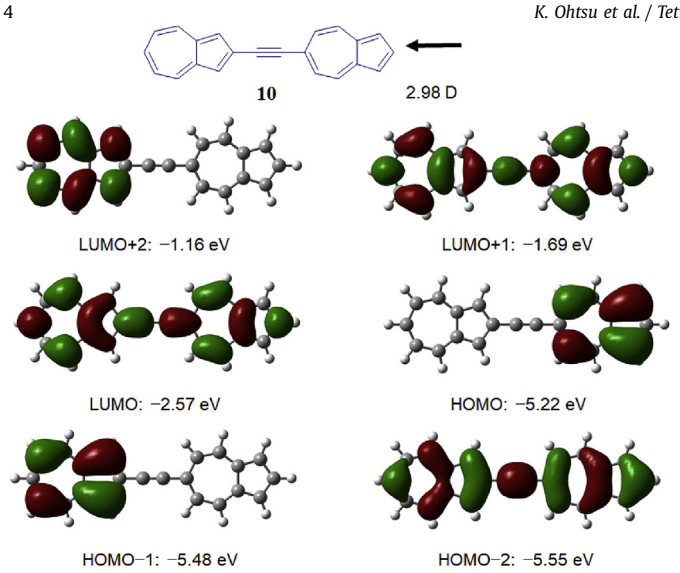

Fig. 6. Molecular orbitals, energy levels, and calculated dipole moment of compound **10**.

HOMO−2 and the HOMO for compound **10**, are relatively close.

The calculated dipole moment of compound **8** was 3.89 D, which is lower than the summation of the values of azulene (1.08 D [5]) and azaazulene (3.05 D [6]). Comparatively, the calculated dipole moment of compound **10** was 2.98 D, which is approximately three times that of azulene.

2.3. Acid protonation of compounds *8* and *10*

Azulenyl derivatives generally form azulenium cations (azulene−H^+) when a large excess of strong acid is added [18,28–30]. The colors of the azulenium cations differ from those of the original azulenyl derivatives because of changes in their molecular electronic structures. Using this knowledge, the acid responsivity of compound **10** was tested using trifluoroacetic acid (TFA). When a large amount of TFA was added, a change in the UV–Vis spectra of compound **10** was observed (Figs. S3–S6), suggesting the protonation of compound **10** proceeded in a similar manner to that of azulene [29]. When triethylamine was added to protonated compound **10**, the compound returned to its original de-protonated form, as supported by its UV–Vis and ^{1}H NMR spectra (Figs. S7 and S8, respectively). Therefore, the changes in the UV–Vis spectra observed were not due to decomposition of compound **10,** but due to its protonation.

To test the acid responsivity of compound **8**, protonation with TFA was performed. As shown in Fig. 7, compound **8** was found to be highly sensitive to TFA. Since a similar trend of acid responsivity was confirmed for a nitrogen-containing heterocycle [31], it can therefore be suggested that the azaazulenyl moiety acts as a base [19,32,33]. When a large excess of TFA was added, the UV–Vis spectra changed (Fig. 8). Therefore, similar to compound **10**, it was suggested that in the presence of excess TFA, protonation of compound **8** at the azulenyl moiety occurred [34]. Reversibility of the protonation of compound **8** was also observed (Figs. S9 and S10).

Protonation of compound **8** was also confirmed by ^{1}H NMR spectroscopy (Fig. 9). A large shift was observed even when only 0.1 equivalent of TFA was added. With increasing equivalents of TFA, the signals due to the azaazulenyl moiety (f, g, h, i, and j) were shifted to a lower magnetic field, and the signals due to the azulenyl moiety (a, b, c, and d) were slightly shifted to a lower magnetic field. Hence, it was suggested that the cationic species formed by

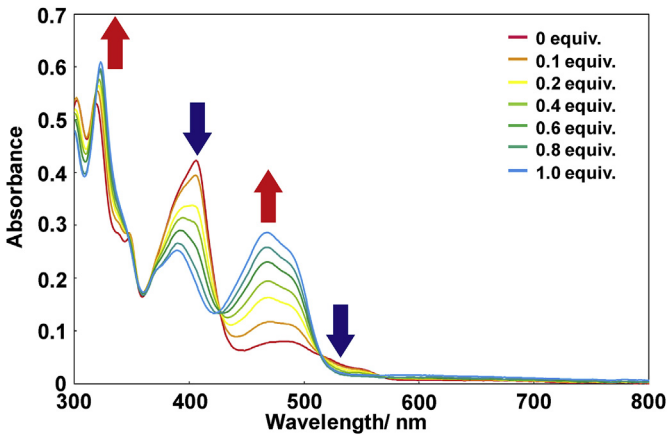

Fig. 7. UV–Vis spectra of compound **8** (10 μmol/L in CH_2Cl_2) upon increasing addition of TFA 0–1 equiv.

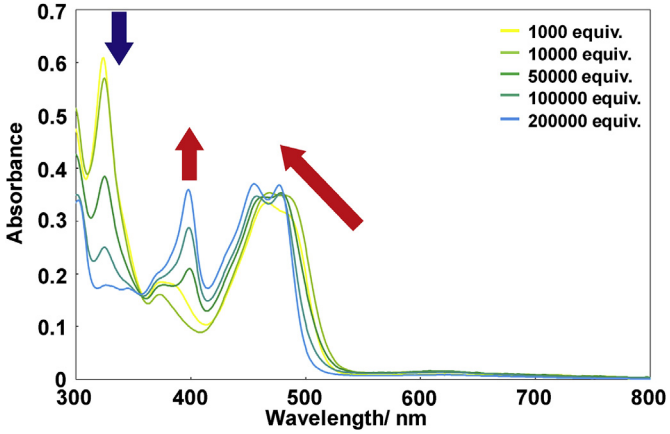

Fig. 8. UV–Vis spectra of compound **8** (10 μmol/L in CH_2Cl_2) upon increasing addition of TFA 1000–200000 equiv.

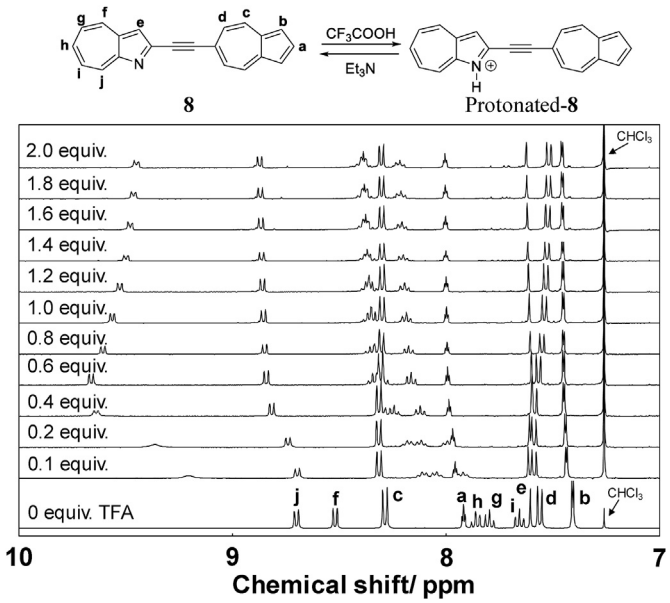

Fig. 9. ^{1}H NMR spectra of compound **8** upon increasing addition of TFA 0–2.0 equiv. in $CDCl_3$.

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protonation delocalized the cation across the entire molecule, and that the protonation of compound **8** must occur at the nitrogen atom.

Finally, acetic and hydrochloric acid were used instead of TFA. For acetic acid, no protonation of compound **8** or **10** was observed since acetic acid is a weak acid compared to TFA. When compound **10** was stored under HCl vapor, no protonation occurred. However, for compound **8** stored under HCl vapor, a solid was produced which was insoluble in organic solvents. When the solid was mixed with triethylamine, compound **8** was regenerated. For comparison, the protonation of compound **7** under HCl vapor was monitored using ^{1}H NMR spectroscopy (Fig. S11). Protonated compound **7** regenerated compound **7** when mixed with triethylamine. Based on these results, compounds **7** and **8** have potential application as proton sensors.

3. Conclusion

Compounds **5**, **7**, and **9** were synthesized using the Sonogashira-Hagihara cross-coupling reaction. Decarboxylation of these compounds was performed using concentrated phosphoric acid to produce compounds **6**, **8**, and **10**, respectively. The UV−Vis spectra of compounds **8** and **10** showed absorption bands from 700 to 800 nm. The electrochemical properties of compounds **8** and **10** were evaluated in terms of reduction. Compound **8** showed an irreversible reduction peak at −1.20 V and two reversible redox peaks at −1.46 and −1.69 V. Compound **10** presented two reversible redox peaks at −1.30 and −1.56 V. Based on the DFT calculations, the LUMOs of compounds **8** and **10** were distributed throughout the molecules. Moreover, the dipole moments of compounds **8** and **10** were calculated as 3.89 and 2.98 D, respectively. Protonation of compounds **8** and **10** was observed using TFA. Formation of singly protonated compound **10** increased with increasing concentrations of TFA (500−30000 equivalents). Comparatively, compound **8** was protonated stoichiometrically by TFA because its 1-azaazulenyl moiety was easily protonated. Protonated compound **8** was deprotonated by triethylamine to produce compound **8**. Moreover, a double-protonated compound **8** was formed when 200000 equivalents of TFA was added. Furthermore, protonation of compound **8** was confirmed through reaction with HCl vapor.

4. Experimental section

4.1. Measurements

NMR spectra were recorded using a JEOL Resonance JNM-ECP 300 spectrometer (JEOL, Akishima, Japan) [^{1}H at 300 MHz and ^{13}C{^{1}H} at 75 MHz] and a JNM-ECP 500 spectrometer [^{1}H at 500 MHz and ^{13}C{^{1}H} at 126 MHz]. The chemical shifts were reported in ppm relative to chloroform-*d* ($CDCl_3$) (^{1}H = 7.26 ppm by the residual chloroform and ^{13}C{^{1}H} = 77.16 ppm). High-resolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOF MS) was carried out on a JEOL JMS-T100CS "AccuTOF CS" spectrometer. UV−Vis absorption spectra were recorded on a JASCO V-670 UV-VIS-NIR spectrophotometer. FT-IR spectra were recorded on a JASCO FT/IR-6100 spectrometer (JASCO, Hachioji, Japan) using the KBr method. Elemental analysis was performed using a Perkin Elmer 2400II Elemental Analyzer. Melting points were recorded using a Bibbly Stuart Scientific SMP3 instrument; the reported melting points were uncorrected. Cyclic voltammetry was recorded with an ALS 650E electrochemical analyzer. Bu_4NClO_4 was used as a supporting electrolyte, which was recrystallized from EtOH and dried under vacuum for 24 h. A series of measurements were performed under an argon atmosphere in a three-electrode cell (BAS Inc.) using 3 mm-diameter glassy carbon as the working electrode (BAS Inc.), platinum wire as the counter electrode, and Ag/$AgClO_4$ as the reference electrode (0.01 M $AgClO_4$ in 0.1 M Bu_4NClO_4/dichloromethane, BAS Inc.). After each measurement, ferrocene was added as an internal standard. The three-parameter Becke−Lee−Yang−Parr (B3LYP) hybrid exchange-correlation functional was employed in our theoretical calculations. The 6-31G(d,p) basis set was used for H, C, O, and N [35−37]. All calculations were performed using the Gaussian 09W (Revision-A.02) software program [38].

4.2. Materials

All the solvents were purified using a standard process [39] and stored over activated molecular sieves. Ammonium chloride and phosphoric acid were purchased from Tokyo Chemical Industry (Tokyo, Japan). Copper(I) iodide was purchased from Kanto Chemical Industry (Tokyo, Japan). Tetrakis(triphenylphosphine) palladium(0), triethylamine, 85% phosphoric acid, phosphorus(V) oxide, and trifluoroacetic acid were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). Ethyl 2-bromo-1-azaazulene-3-carboxylate (**1**), diethyl 6-ethynylazulene-1,3-dicarboxylate (**2**), 2-iodo-1-azaazulene (**3**), and 2-iodoazulene (**4**) were prepared by according to the literature [17,40−51], as described in the supporting information. Silica-gel column chromatography was performed using Wakogel® C-200 (spherical, neutral, 75−150 μm) purchased from FUJIFILM Wako Pure Chemical Corp.

4.3. Synthesis of diethyl 6-(3-ethoxycarbonyl-1-azaazulen-2-yl) ethynylazulene-1,3-dicarboxylate (*5*)

Compound **1** (140 mg, 50 μmol), compound **2** (150 mg, 51 μmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), CuI (10 mg, 10 mol%), triethylamine (5 mL), and toluene (20 mL) were mixed and stirred at room temperature for overnight. Then, ammonium chloride aqueous solution was added, and the solution was extracted with CH_2Cl_2. The organic layer was washed with water followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was pre-purified by silica gel column chromatography (AcOEt: $CHCl_3$ = 1: 9 v/v). The solid was purified by recrystallization in toluene; the blackish brown solid was obtained (92 mg, 37%).

Compound 5: Decomp. 223.2−224.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (t, J = 7.0 Hz, 6H), 1,54 (t, J = 7.0 Hz, 3H), 4.44 (q, J = 7.0 Hz, 4H), 4.58 (q, J = 7.0 Hz, 2H), 8.01 (t, J = 10.0 Hz, 1H), 8.03 (t, J = 10.0 Hz, 1H), 8.09 (d, J = 10.0 Hz, 2H), 8.11 (t, J = 10.0 Hz, 1H), 8.83 (s, 1H), 8.88 (d, J = 10.0 Hz, 1H), 9.71 (d, J = 10.0 Hz, 1H), 9.73 (d, J = 10.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 14.7, 14.8, 60.3, 60.8, 91.6, 100.9, 117.3, 118.0, 133.0, 133.7, 135.3, 137.5, 138.8, 139.0, 140.8, 143.8, 144.4, 146.5, 150.0, 159.3, 163.7, 164.8 ppm. IR (KBr, cm^{-1}): 2194(νC≡C), 1690(νC═O). HRMS (APCI, *m/z*): Cacld. for $C_{30}H_{26}NO_6$ $[M+H]^+$ 496.17601; found: 496.17528. Anal. Calcd. for $C_{30}H_{25}NO_6$: C, 72.72; H, 5.09; N, 2.83; found: C, 72.74; H, 5.06; N, 2.80.

4.4. Decarboxylation of compound 5 using 100% phosphoric acid

This reaction was aimed to complete the decarboxylation of compound **5** (that is, the synthesis of compound **8**); however, compound **8** was not synthesized but compound **6** was obtained. This method was established as follows: 3 mL of 85% phosphoric acid and 2 g of P_2O_5 were mixed at room temperature for 10 min. The 100% phosphoric acid was added with compound **5** (38 mg, 7.6 μmol), followed by heating at 95 °C for 1 h. The solution was added with ice and neutralized with $NaHCO_3$. The mixture was extracted with CH_2Cl_2; the organic layer was washed with water

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followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was separated by silica gel column chromatography (AcOEt: $CHCl_3$ = 1: 9 v/v). The 6-(3-ethoxycarbonyl-1-azaazulen-2-yl)ethynylazulene (**6**) was obtained as blackish green solid, but contaminated with some by-products (6.6 mg, 25%).

Compound 6: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (t, J = 6.9 Hz, 3H), 4.56 (q, J = 6.9 Hz, 2H), 7.43 (d, J = 3.6 Hz, 2H), 7.61 (d, J = 10.2 Hz, 2H), 7.93–8.08 (m, 4H), 8.32 (d, J = 10.2 Hz, 2H), 8.88 (d, J = 9.6 Hz, 1H), 9.58 (d, J = 9.9 Hz, 1H) ppm. HRMS (APCI, *m/z*): Cacld. for $C_{24}H_{18}NO_2$ $[M+H]^+$ 352.13375; found: 352.13278.

4.5. Synthesis of diethyl 6-(1-azaazulen-2-yl)ethynylazulene-1,3-dicarboxylate (**7**)

Compound **3** (130 mg, 50 μmol), compound **2** (150 mg, 50 μmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), CuI (10 mg, 10 mol%), triethylamine (5 mL), and toluene (20 mL) were mixed and stirred at room temperature for overnight. After the reaction, ammonium chloride aqueous solution was added, and the solution was extracted with CH_2Cl_2. The organic layer was washed with water followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was purified by silica gel column chromatography (AcOEt: $CHCl_3$ = 1: 4 v/v), and dark red powder was obtained (85 mg, 40%).

Compound 7: Decomp. 190.5 °C.^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (t, J = 7.0 Hz, 6H), 4.44 (q, J = 7.0 Hz, 4H), 7.65 (s, 1H), 7.69 (t, J = 10.0 Hz, 1H), 7.83 (t, J = 10.0 Hz, 1H), 7.91 (t, J = 10.0 Hz, 1H), 8.03 (d, J = 10.5 Hz, 2H), 8.56 (d, J = 10.0 Hz, 1H), 8.72 (d, J = 10.0 Hz, 1H), 8.79 (s, 1H), 9.68 (d, J = 10.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 14.7, 60.3, 91.9, 98.3, 117.3, 119.0, 129.7, 130.6, 133.6, 135.4, 136.7, 137.3, 137.6, 139.2, 143.7, 144.2, 147.0, 148.2, 158.0, 164.9 ppm. IR (KBr, cm^{-1}): 2188(νC≡C), 1685(νC═O). HRMS (APCI, *m/z*): Calcd. for $C_{27}H_{22}NO_4$ $[M+H]^+$ 424.15488; found: 424.15484.

4.6. Synthesis of 6-(1-azaazulen-2-yl)ethynylazulene (**8**)

A 3 mL of 85% phosphoric acid and 2 g of P_2O_5 was mixed and stirred at room temperature for 10 min. The 100% phosphoric acid was added with compound **7** (99 mg, 24 μmol) and heated at 95 °C for 1 h. The solution was mixed with ice and neutralized with $NaHCO_3$. The mixture was extracted with CH_2Cl_2; the organic layer was washed with water followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was purified by silica gel column chromatography (AcOEt: $CHCl_3$ = 1: 9 v/v); the dark orange powder was obtained (21 mg, 31%).

Compound 8: Decomp. 150.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 3.5 Hz, 2H), 7.56 (d, J = 10.0 Hz, 2H), 7.61 (s, 1H), 7.66 (t, J = 10.0 Hz, 1H), 7.80 (t, J = 10.0 Hz, 1H), 7.86 (t, J = 10.0 Hz, 1H), 7.92 (t, J = 3.5 Hz, 1H), 8.29 (d, J = 10.0 Hz, 2H), 8.52 (d, J = 10.0 Hz, 1H), 8.71 (d, J = 10.0 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 88.8, 100.2, 118.5, 119.3, 126.4, 129.5, 130.4, 131.3, 135.1, 136.1, 136.7, 138.4, 138.5, 140.2, 147.0, 149.2, 158.1 ppm. IR (KBr, cm^{-1}): 2192(νC≡C). HRMS (APCI, *m/z*): Calcd. for $C_{21}H_{14}N$ $[M+H]^+$ 280.11262; found: 280.11174.

4.7. Synthesis of diethyl 6-(2-azulenyl)ethynylazulene-1,3-dicarboxylate (**9**)

Compound **4** (130 mg, 50 μmol), compound **2** (150 mg, 50 μmol), $Pd(PPh_3)_4$ (29 mg, 5 mol%), CuI (10 mg, 10 mol%), triethylamine (5 mL), and toluene (20 mL) were mixed and stirried at room temperature for overnight. After the reaction, ammonium chloride aqueous solution was added, and the solution was extracted with CH_2Cl_2. The organic layer was washed with water followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was pre-purified by silica gel column chromatography (CH_2Cl_2: hexane = 3: 1 v/v). The solid was purified by recrystallization with toluene; the dark green needle was obtained (200 mg, 94%).

Compound 9: M.p. 181.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (t, J = 7.0 Hz, 6H), 4.45 (q, J = 7.0 Hz, 4H), 7.22 (t, J = 10.0 Hz, 2H), 7.55 (s, 2H), 7.56 (t, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 2H), 8.31 (d, J = 10.0 Hz, 2H), 8.78 (s, 1H), 9.68 (d, J = 10.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 14.7, 60.3, 98.2, 98.8, 117.1, 121.3, 124.5, 128.7, 133.5, 136.8, 137.6, 137.8, 138.8, 140.5, 143.5, 143.7, 165.1 ppm. IR (KBr, cm^{-1}): 2185(νC≡C), 1693(νC═O). HRMS (APCI, *m/z*): Calcd. for $C_{28}H_{23}O_4$ $[M+H]^+$ 423.15963; found: 423.15975. Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25; found: C, 79.72; H, 5.16.

4.8. Synthesis of 6-(2-azulenyl)ethynylazulene (**10**)

A 3 mL of 85% phosphoric acid and 2 g of P_2O_5 was mixed and stirried at room temperature for 10 min. The 100% phosphoric acid was added with compound **9** (103 mg, 24 μmol), followed by heating at 95 °C for 1 h. The solution was added with ice and neutralized with $NaHCO_3$. The mixture was extracted with CH_2Cl_2; the organic layer was washed with water followed by drying over $MgSO_4$. After filtration, the solution was concentrated by rotary-evaporator. The residual solid was pre-purified by silica gel column chromatography (CCl_4). The solid was purified by recrystallization with CCl_4; the green film-like solid was obtained (23 mg, 34%).

Compound 10: Decomp. 272.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, 2H, J = 10.0 Hz), 7.40 (d, 2H, J = 4.0 Hz), 7.50 (d, 2H, J = 10.0 Hz), 7.53 (s, 2H), 7.58 (t, 1H, J = 10.0 Hz), 7.89 (t, 1H, J = 4.0 Hz), 8.29 (d, 2H, J = 10.0 Hz), 8.30 (d, 2H, J = 10.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 90.6, 100.3, 119.2, 121.0, 124.3, 126.3, 129.9, 132.6, 135.2, 137.2, 137.9, 138.2, 139.9, 140.5 ppm. IR (KBr, cm^{-1}): 2188(νC≡C). HRMS (APCI, *m/z*): Calcd. for $C_{22}H_{15}$ $[M+H]^+$ 279.11738; found: 279.11734. Anal. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07; found: C, 94.91; H, 4.78.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130658.

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