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Stimuli-Responsive Cyclopenta[*ef*]heptalenes: Synthesis and Optical Properties

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Keywords: Cyclopenta[*ef*]heptalene / Stimuli response / Azulene / Electron transfer / Photoacid generator / Sensitizers / Photochromism / Natural products / Dyes/pigments

We report the one-pot synthesis, 1D and 2D NMR characterization, and UV/Vis study of a series of cyclopenta[*ef*]heptalenes **4a–c** that exhibit strong stimuli-responsive behavior, with a tunable energy gap as a result of perturbation of HOMO, LUMO, and LUMO+1 energies upon doping/dedoping with TFA/Et_3N. The approach employed allows for the extension of conjugation at C-4 of the cyclopenta[*ef*]heptalene skeleton from X = H (**4a**) to X = CN (**4b**) and X = 2-thiophenyl (**4c**), resulting in longer absorption maxima and smaller optical energy gaps of the cyclopenta[*ef*]heptalenium cations **4a–c**$^+$. Additionally, in the presence of a UV-activated (< 300 nm) photoacid generator (PAG), protonation of **4c** can be indirectly achieved by intermolecular photoinduced electron transfer (PeT) from the excited state of **4c** to the PAG, upon which the latter undergoes photodecomposition resulting in the generation of acid. This phenomenon facilitates the use of cyclopenta[*ef*]heptalenes **4a–c** as visible sensitizers of commercial PAGs.

Introduction

There is extensive growth in the research and development of organic materials whose optical, electronic, and conductive properties can be modulated upon application of external stimuli. The design of such chromophores has been based on various π-conjugated building blocks that are functionalized with electron-donor or -acceptor moieties, leading to extended push-pull chromophores.[1] Expanded π-conjugated organic materials are often known for poor physical and chemical stability, limiting their scope of application.[1,2] To address these drawbacks, efforts have been reported to exploit the azulene framework as a modular building block for the synthesis of chromophores having stimuli-responsive behavior.[3]

Similar to the various azure-blue derivatives of the bicyclic sesquiterpene azulene, guaiazulene exhibits unique electronic and optical properties that allow for its use in charge-transport,[4,5] nonlinear-optics,[6,7] and sensor applications.[8] Unlike other small aromatic hydrocarbons, guaiazulene exhibits a relatively large permanent dipole moment, owing to its fused electron-rich cyclopentadiene and electron-poor heptatriene skeleton (Figure 1).[9,10] Electronic properties of the azulene core result in the domination of fluorescence from the S_2 excited state to the S_0 state, in violation of Kasha's rule,[4] and very low emission intensity from the S_1 to S_0 state.

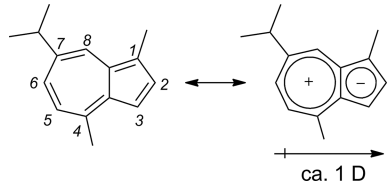

Figure 1. Resonance structures of guaiazulene with numbering scheme and permanent dipole moment.

Treatment of guaiazulene with strong acids leads to the protonation of the cyclopentadiene ring at the unsubstituted 3-position and yields the tropylium cation, which is accompanied by a change in the radiative decay pathway from the $S_2 \rightarrow S_0$ to the $S_1 \rightarrow S_0$ transition in the protonated species.[11]

Various substitution patterns on the azulene core have been tailored in order to alter the azulene structure and understand the effect of acid doping on the optical and electronic properties of azulene-containing systems.[12–15] The selective synthesis of azulene derivatives having a single isomeric arrangement of functional groups at the 4- and 7-positions of the seven-membered ring was reported.[12] Such a connectivity pattern allowed for the incorporation of two thiophenyl groups at these positions by Stille coupling. The corresponding azulenium cation showed a significantly smaller energy gap with a concomitant redshift of the ab-

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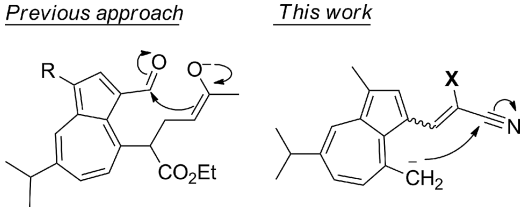
sorption maximum and a relatively strong $S_1 \rightarrow S_0$ fluorescence. Recently, a similar reversible color change and a strong redshift of the absorption maximum along with a smaller optical band gap was reported that can be tuned by the nature of the donor connected to the seven-membered ring (C4–C7 substitution).[13–15]

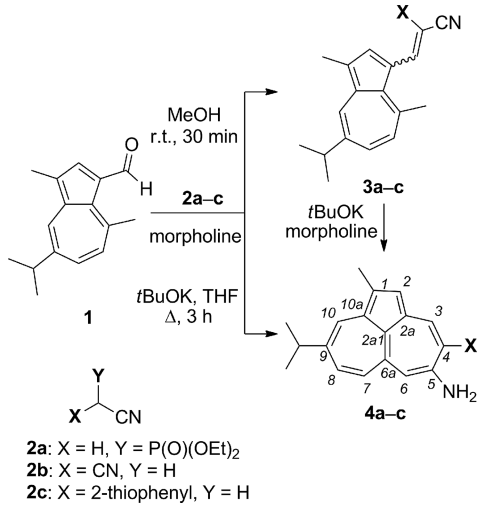
There have been limited reports on the extension of the azulene framework by annulation. As early as 1959, Hafner et al. used the immonium salts of 4,6,8-trimethylazulene-1-formaldehyde and 4,6,8-trimethylazulene-1-propenal to form by intramolecular cyclization the corresponding cyclopenta[*cd*]azulene and cyclopenta[*ef*]heptalene, respectively.[16] Recently, Wu and co-workers demonstrated a relatively lengthy method for the synthesis of two functionalized cyclopenta[*ef*]heptalenes,[17] and none of the prepared derivatives were fully conjugated throughout the skeleton. In addition, the doping of these tricyclic systems with acids has not yet been reported. We envisioned that a stimuli-responsive cyclopenta[*ef*]heptalene framework can be achieved by adopting a synthetic approach similar to the one reported by Wu.[16] As depicted in Scheme 1, the intermediate aldehyde is attacked by the enolate, leading to 7,8-dihydrocyclopenta[*ef*]heptalene. In this work, we employed the acidic protons of the Me group at C-4 of prepared guaiazulene-based acrylonitriles for the annulation of the fused seven-membered ring. This concomitantly introduces a basic amine on C-5 that is thought to be feasibly protonated by acids to generate a halochromic system. We concluded that, although protonation takes place at C-6 rather than at the amine, the system exhibits strong reversible stimuli-responsive behavior. Furthermore, when compared to previous literature procedures, the approach employed in this work is rather versatile in that it allows for various alkyl or (hetero)aryl groups to be installed on the C-4 position of the cyclopenta[*ef*]heptalene skeleton, hence yielding an array of cyclopenta[*ef*]heptalenes that may enable the study of photophysical structure-property trends.



Scheme 1. Ring formation through enol attack on the aldehyde group vs. methylene anion attack on the cyano group.

Results and Discussion

The syntheses of cyclopenta[*ef*]heptalenes **4a**–**c** are shown in Scheme 2. Initially, guaiazulene-3-carblaldehyde (**1**) was condensed with acetonitriles **2a**–**c** in the presence of morpholine as a base to afford the corresponding guaiazulene-based acrylonitriles **3a**–**c**. Treatment of **3a**–**c** with 2 equiv. of *t*BuOK led to the formation of the fused seven-membered ring compounds **4a**–**c**. The two-step synthetic route was reexamined in order to afford **4a**–**c** in a one-pot synthesis. Accordingly, condensation and ring formation were achieved when excess acetonitriles **2a**–**c** and *t*BuOK were used, leading to yields higher than those obtained by the step-wise approach (see Experimental Section).



Scheme 2. Syntheses of **4a**–**c**.

We predicted that protonation with trifluoroacetic acid (TFA) would occur on the amine, as observed with various other aromatic compounds having exocyclic amines. However, a thorough NMR study, including COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{15}N HSQC, HMBC, and INADEQUATE experiments, shows that protonation occurs at C-6, as evidenced by the presence of a CH_2 signal in the HSQC spectra of the protonated forms (Figure 2, inset). Further analysis of spectra corresponding to the neutral and protonated forms of **4** shows that all aromatic ^{1}H resonances appear at lower frequency than expected for aromatic systems, but shift significantly to higher frequency when protonated (Figure 2). This suggests that the NH_2 group does not behave as an aromatic amine, but rather as an enamine. This phenomenon can be interpreted by comparing the relative hardness of cyclopenta[*ef*]heptalene (0.285), azulene (0.439), and benzene (1.000). Coined by Parr and Zhou, relative hardness is an index used to identify aromatic, non-aromatic, and antiaromatic character of cyclic conjugated molecules, and incorporates high stability, low reactivity, and sustained induced ring current as defining measures of aromaticity.[18] Accordingly, the values of relative hardness suggest that **4** exhibits low aromatic character, which is consistent with the unusual low frequencies of aromatic ^{1}H resonances. Additionally, the higher frequencies of the ^{1}H resonances of **4a**–**c**$^+$ are comparable to those seen in azulene derivatives, suggesting that a larger sustained induced ring current exists, and hence a larger aromatic character for the protonated species. The resonances of cyclopenta[*ef*]heptalenes are assigned by analyzing the 1D and 2D NMR spectra, which became important to resolve any ambiguities, especially at C-2a, C-2a^1, and C-10a in the cyclopenta[*ef*]heptalene skeleton (see Scheme 2 for numbering). The assignment was validated by directly observing the ^{13}C-^{13}C con-

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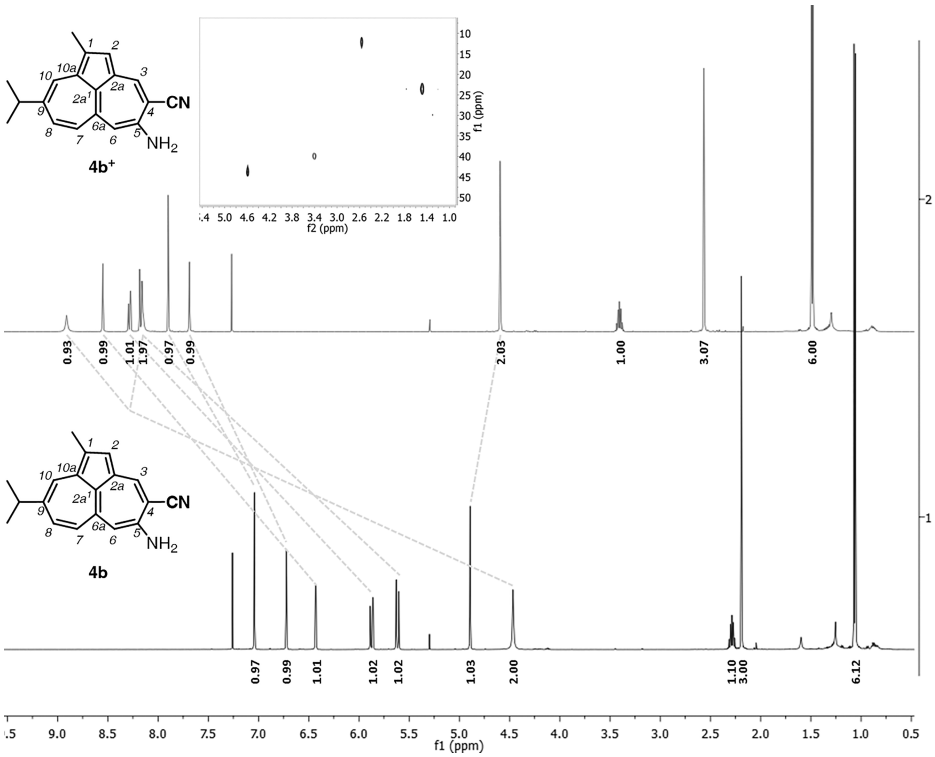

Figure 2. ^{1}H NMR spectra for **4b** (bottom, $CDCl_3$) and **4b$^+$** (top, $CDCl_3$ + 1% TFA) with aliphatic ^{1}H-^{13}C HSQC spectrum for **4b$^+$** (inset).

nectivity with an INADEQUATE experiment on **4b** (see Supporting Information). In the case of **4a**, protonation could potentially occur at either C-4 or C-6, which are at the β-position of the amino group. However, HMBC correlation between the ^{13}C resonance of C-7 and the CH_2 ^{1}H resonance indicate that protonation with TFA occurs at C-6.

Examination of the UV/Vis spectra of **4a**–**c** (Figure 3) in their neutral states (DCM + 1% Et_3N) shows that all derivatives exhibit an absorption maximum at ca. 400 nm that corresponds to the S_0–S_2 transition, consistent with other reported azulenes (Figure 3a, Table 1).[18] It is notable, however, that there is little to no indication of the long-wavelength absorption that corresponds to the $S_0 \rightarrow S_1$ transition seen in azulene derivatives.[13] Upon protonation of **4a**–**c**, there is a distinct bathochromic shift relative to the original π–π* transitions (Figure 3b). The absorption maxima of the new broad peaks are correlated with the extent of conjugation of the protonated heptalenes **4a**–**c$^+$**, where λ_{max} = 574, 587, and 609 nm for **4a**–**c$^+$**, respectively.

Table 1. Spectral data for compounds **4a**–**c** in DCM and DCM/TFA (9:1, v/v).

4	Neutral			Protonated		
	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	E_g[a] [eV]	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	E_g [eV]
a	390	498	2.49	574	647	1.92
b	406	510	2.43	586	692	1.79
c	400	521	2.38	609	752	1.65

[a] E_g = optical energy gap.

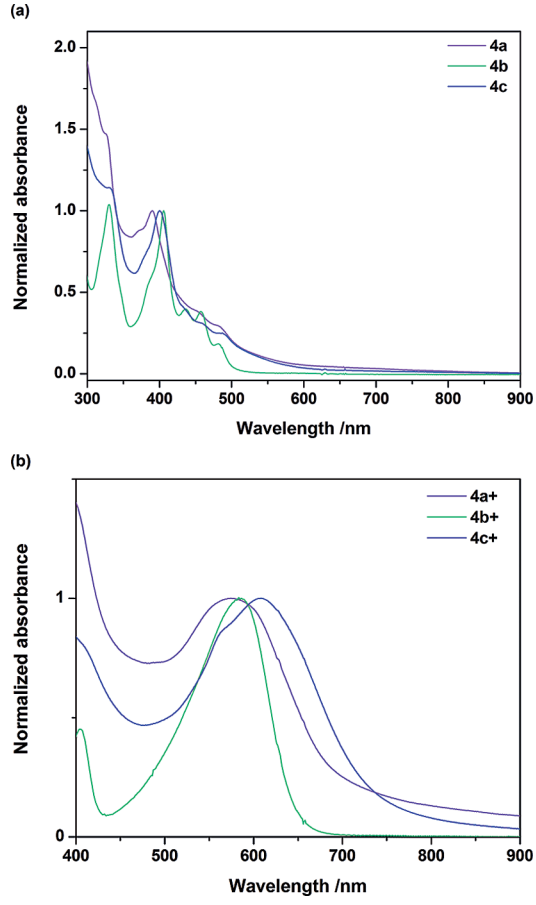

Figure 3. (a) Absorption spectra of **4a**–**c** in DCM and 1% Et_3N. (b) Absorption spectra of **4a**–**c$^+$** in DCM/TFA (9:1, v/v).

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By extrapolating the onset wavelength of the absorption spectra of cyclopenta[*ef*]heptalenes in their neutral **4a**–**c** and protonated forms **4a**–**c**$^+$, it is possible to estimate their corresponding optical energy gap, E_g (Table 1).[19] It can be seen that the energy gap decreases through the series of derivatives. These values are consistent with the difference between the HOMO and LUMO energies determined through quantum chemical calculations, and similar to other azulene derivatives previously reported.[12]

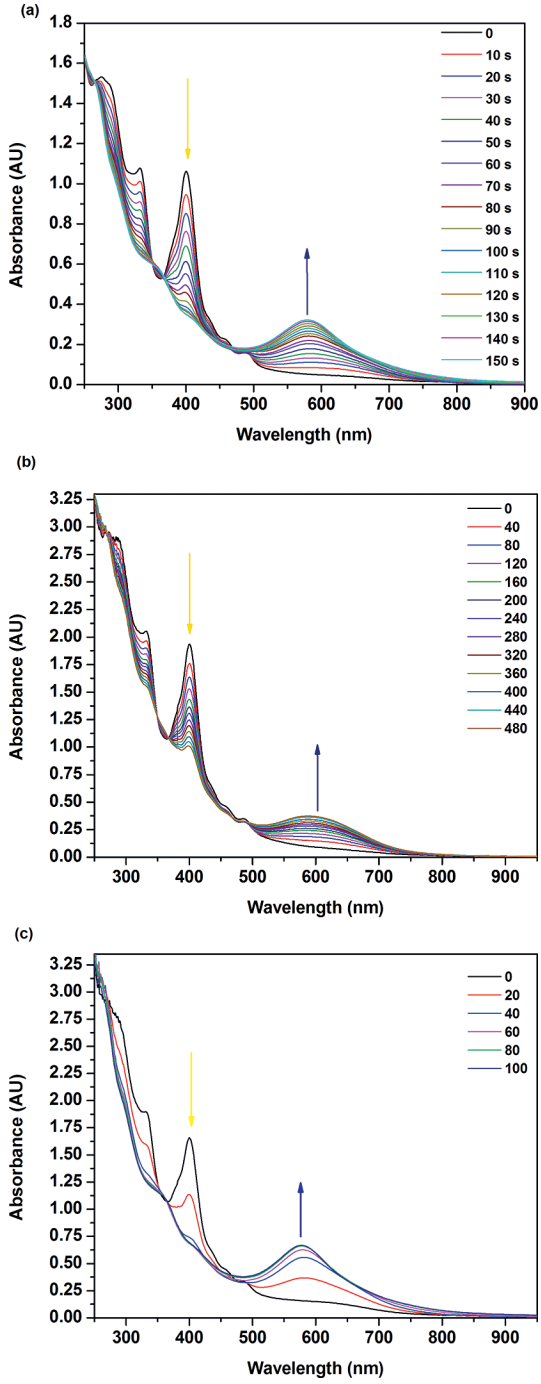

Figure 4. Absorption spectra recorded at (a) 10 s intervals of **4c**/DPIHFP (3.7×10^{-4} M, 12.5 mW cm^{-2}, 405 nm), (b) at 40 s intervals of **4c**/DPIHFP (1.25×10^{-3} M, 12.5 mW cm^{-2}, 532 nm) and (c) at 20 s intervals of **4c**/DPIHFP (1.1×10^{-3} M, 12.5 mW cm^{-2}, 254 nm).

Inspired by reports that discuss the intramolecular photoinduced electron transfer (PeT) from the S_2 state of azulene to the excited state of various electron acceptors,[20] the possible intermolecular PeT of **4** to the excited state of a commercial PAG, diphenyliodonium hexafluorophosphate (DPIHFP), was investigated. Such a PAG is photoactivated at wavelengths ranging from vacuum ultraviolet (VUV, $<$200 nm) to UV.[22] This presents a serious drawback, especially in certain applications as it limits their use to a spectral region that may overlap with functional groups that undergo, e.g., free radical photoinitiated polymerization.[21] As a proof of concept, sensitization of DPIHFP with **4** was investigated when **4c** was initially excited in the range of the S_0–S_2 transition (365–410 nm). Photoexcitation of **4c**/DPIHFP was recorded at 10 s intervals (Figure 4a). Acid generation was evident as the band at 580 nm, commonly observed in the UV/Vis profile of **4c**$^+$, gradually emerges with a concomitant decrease in intensity at 400 nm. An isosbestic point observed at 465 nm is indicative of the presence of two inter-converting optically different phases in the solution.

Interestingly, excitation of a **4c**/DPIHEP solution at 532 nm is similar in manner to that observed in Figure 4a, yet provides better controlled sensitization of DPIHFP as a result of lower absorptivity at longer wavelength (Figure 4b). On the other hand, the use of a 254 nm excitation source allows for a direct excitation of DPIHFP. This was observed when **4c**$^+$ was obtained by phototitration of an equimolar mixture of **4c**/DPIHFP in DCM by using a 254 nm hand-held UV lamp (average irradiance ca. 12.5 mW cm^{-2}) at 20 s intervals. Complete protonation was achieved in 80 s by using direct excitation at 254 nm, while requiring ca. 3 min when excited at 405 nm, and ca. 8 min for 532 nm excitation. This suggests that **4a**–**c** can be used as sensitizers for commercial UV-activated PAGs.

Conclusions

We report a new approach towards the efficient synthesis of stimuli-responsive cyclopenta[*ef*]heptalenes **4** from naturally occurring guaiazulene. Upon protonation with TFA, perturbation of the electronic states resulted in a switch from the dominant $S_0 \rightarrow S_2$ transition in the neutral state to the $S_0 \rightarrow S_1$ transition as seen in other reported azulene derivatives, where E_g of **4a**–**c**$^+$ is finely tunable by substituents at C-4. In addition, UV/Vis spectroscopy demonstrated that **4** can act as a sensitizer of DPIHFP. This suggests that such cyclopenta[*ef*]heptalenes may be employed as visible sensitizers in a variety of applications of PAGs.

Experimental Section

3-Formylguaiazulene (1): Phosphorus oxychloride (5.00 mL, 53.0 mmol) was added to a solution of guaiazulene (5.00 g,

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25.0 mmol) in DMF at 0 °C under an inert gas. After stirring in an ice bath for 1.5 h, the solution was carefully neutralized with concd. aqueous KOH solution. The purple solution was extracted with CH_2Cl_2 (3× 50 mL), and the organic fractions were dried with Na_2SO_4 and concentrated under reduced pressure. The resulting crude oil was purified by column chromatography (hexanes/EtOAc, 3:1) to afford the title product **2** as purple solid (4.55 g, 20.1 mmol, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.64 (s, 1 H), 8.29 (d, J = 2.1 Hz, 1 H), 8.23 (s, 1 H), 7.59 (dd, J = 10.8, 2.1 Hz, 1 H), 7.43 (d, J = 10.8 Hz, 1 H), 3.16 (p, J = 7.0 Hz, 1 H), 3.15 (s, 1 H), 2.59 (s, 1 H), 1.39 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 186.9, 147.5, 147.1, 144.1, 140.0, 139.7, 136.6, 136.0, 133.0, 128.0, 127.7, 38.7, 30.7, 25.1, 13.6 ppm.

2-[(5-Isopropyl-3,8-dimethylazulen-1-yl)methylene]malononitrile (3a): *t*BuOK (0.56 g, 5.0 mmol, 1.25 equiv.) was added in small portions to a solution of 3-formylguaiazulene (**1**) (0.90 g, 4.0 mmol) and diethyl (cyanomethyl)phosphonate (0.80 mL, 5.0 mmol) in anhydrous THF at 0 °C. The reaction mixture was warmed to room temperature and then heated at 50 °C for 1 h. The resulting green solution was dried under reduced pressure and subsequently purified by column chromatography (hexanes/EtOAc, 4:1) to afford the title product **3a** as a green-blue solid (1.00 g, 3.6 mmol, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, *trans*/*cis* = 2:1): δ = 8.46 (s, 0.34 H), 8.22 (d, J = 16.0 Hz, 0.63 H), 8.12 (dd, J = 14.4 Hz, 1 H), 7.94 (d, J = 11.6 Hz, 0.38 H), 7.72 (s, 0.62 H), 7.39 (dd, J = 10.8, 2.0 Hz, 1 H), 7.07 (d, J = 10.8 Hz, 1 H), 5.53 (d, J = 15.6 Hz, 0.62 H), 5.12 (d, J = 11.6 Hz, 0.36 H), 3.09–3.02 (m, 1 H), 2.93 (s, 3 H), 2.59 (s, 1 H), 2.56 (s, 2 H), 1.34 (d, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151, 146.7, 146.6, 146.4, 145.0, 145.0, 144.6, 143.1, 141.5, 137.8, 137.0, 136.5, 136.4, 135.9, 135.3 135.0, 131.3, 131.9, 128.1, 127.4, 122.6, 122.3, 121.3, 120.5, 89.9, 88.4, 38.4, 29.2, 25.0, 24.9, 13.5, 13.5 ppm. MS: calcd. for $C_{18}H_{19}N$ [M + H]$^+$ 250.1591; found 250.1564.[23]

2-[(5-Isopropyl-3,8-dimethylazulen-1-yl)methylene]malononitrile (3b): Compound **1** (0.90 g, 4.0 mmol) was added to a solution of malononitrile **2b** (0.33 g, 5.0 mmol, 1.2 equiv.) and *N*-methylmorpholine (1 mL, 2.5 equiv.) in methanol. After heating the resulting solution at 50 °C for 1 h, the volatile materials were evaporated under reduced pressure. The crude solid was purified by column chromatography (hexanes/EtOAc, 4:1) to afford the title product **3b** as dark yellow solid (1.00 g, 3.6 mmol, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.63 (s, 1 H), 8.46 (s, 1 H), 8.28 (d, J = 2.2 Hz, 1 H), 7.66 (dd, J = 10.8; 2.2 Hz, 1 H), 7.48 (d, J = 10.8 Hz, 1 H), 3.18 (sept, J = 6.9 Hz, 1 H), 3.10 (s, 3 H), 2.59 (s, 3 H), 1.41 (d, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.2, 150.4, 147.9, 145.7, 141.7, 138.0, 137.6, 136.0, 135.8, 130.8, 121.3, 117.8, 116.8, 38.5, 29.6, 24.7 ppm.[24]

3-(5-Isopropyl-3,8-dimethylazulen-1-yl)-2-(thiophen-2-yl)acrylonitrile (3c): The synthetic procedure for **3c** is similar to that described for **3a**. Purification of the crude reaction mixture by column chromatography (hexanes/EtOAc, 5:1) afforded the title product as dark yellow solid (1.12 g, 3.4 mmol, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.42 (s, 1 H), 8.22 (s, 1 H), 8.13 (s, 1 H), 7.75 (dd, J = 16.0, 2.0 Hz, 1 H), 7.61–7.60 (m, 1 H), 7.21 (dd, J = 16.0, 2.0 Hz, 1 H), 6.98–6.96 (m, 1 H), 6.90 (dd, J = 4.4, 1.2 Hz, 1 H), 3.14 (sept, J = 7.2 Hz, 1 H), 2.56 (s, 3 H), 1.38 (d, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 185.5, 147.4, 144.1, 144.0, 143.5, 140.3, 137.6, 136.0, 135.3, 132.6, 130.8, 128.0, 127.9, 127.2, 126.7, 126.5, 113.5, 38.3, 24.4, 12.9 ppm. MS: calcd. for $C_{22}H_{21}NS$ [M + H]$^+$ 332.1468; found 332.1440.

One-Pot Synthesis of 9-Isopropyl-1-methylcyclopenta[*ef*]heptalen-5-amine (4a): *t*BuOK (2.24 g, 20.0 mmol) was added to a hot solution of **1** (1.00 g, 4.4 mmol), **2a** (1.5 mL, 8.9 mmol) and morpholine (0.78 mL, 8.9 mmol) in dry THF (25 mL) and the mixture heated to reflux for 3 h. The formation of **4a** was monitored by TLC; interestingly, exposure of the developed TLC to TFA vapor resulted in a rapid change in the color of the spot corresponding to **4a** from pale yellow to purple-blue. The solution was cooled to room temperature and then diluted with DCM (50 mL) and washed with dilute HCl (2 N, 3× 50 mL). The organic layer was dried with Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by silica column chromatography using hexanes/EtOAc (5:1, v/v) to afford the title product as a dark yellow oil (15% for step-wise; 59% for one-pot). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.74 (d, J = 10.8 Hz, 1 H), 6.64 (s, 1 H), 6.39 (d, J = 2.0 Hz, 1 H), 5.70 (dd, J = 12.4, 2.0 Hz, 1 H), 5.43 (d, J = 12.4 Hz, 1 H), 4.94 (dd, J = 10.8, 2.4 Hz, 1 H), 4.84 (d, J = 2.4 Hz, 1 H), 3.72 (br. s, 2 H), 2.24–2.17 (m, 4 H), 1.04 (d, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.8, 144.2, 141.3, 138.7, 133.7, 133.1, 129.9, 129.3, 129.2, 123.8, 111.4, 109.9, 36.5, 22.8, 13.8 ppm. MS: calcd. for $C_{18}H_{19}N$ [M + H]$^+$ 250.1591; found 250.1579.

Synthesis of 8-Amino-4-isopropyl-2-methylcyclopenta[*ef*]heptalene-9-carbonitrile (4b) from 3b: *t*BuOK (0.22 g, 2.0 mmol) was added to a solution of **3b** (0.55 g, 2.0 mmol) in anhydrous THF (10 mL). The solution was heated to reflux for 12 h, and then cooled to room temperature. The solvent was evaporated, and the resulting crude product was dissolved with DCM (20 mL) and washed with dilute HCl (2 N, 3× 50 mL). The organic layer was dried with Na_2SO_4 and concentrated to dryness. Column chromatography (hexanes/DCM, 3:1) was used to isolate the title product as a dark yellow solid (23% for stepwise vs. 71% for one-pot). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.74 (s, 1 H), 6.44 (d, J = 2.0 Hz, 1 H), 5.88 (dd, J = 12.4, 2.0 Hz, 1 H), 5.62 (d, J = 12.4 Hz, 1 H), 4.90 (s, 1 H), 4.45 (br. s, 2 H), 2.29 (quint, J = 6.8 Hz, 1 H), 2.20 (s, 3 H), 1.07 (d, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.7, 154.4, 144.2, 142.6, 142.5, 138.2, 137.8, 134.2, 132.3, 130.1, 129.9, 128.2, 127.2, 127.7, 125.1, 124.3, 114.0, 109.5, 36.2, 22.5, 13.5 ppm. MS: calcd. for $C_{19}H_{18}N_2$ [M + H]$^+$ 275.1543; found 275.1503.

Isopropyl-2-methyl-9-(thiophen-2-yl)cyclopenta[*ef*]heptalen-8-amine (4c): Golden yellow solid (21% for stepwise vs. 92% for one-pot). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (dd, J = 5.2, 1.2 Hz, 1 H), 7.00 (dd, J = 5.2, 3.6 Hz, 1 H), 6.95 (s, 1 H), 6.93 (dd, J = 3.6, 1.2 Hz, 1 H), 6.62 (s, 1 H), 6.36 (d, J = 2.0 Hz, 1 H), 5.71 (dd, J = 12.4 Hz, 1 H), 5.46 (d, J = 12.4 Hz, 1 H), 4.92 (s, 1 H), 4.14 (br. s, 2 H), 2.26–2.17 (m, 4 H), 1.05 (d, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.8, 154.2, 144.3, 142.8, 142.6, 138.4, 137.9, 133.9, 132.5, 130.1, 130.1, 128.3, 127.1, 126.7, 125.1, 124.3, 114.0, 109.3, 36.2, 22.4, 13.5 ppm. MS: calcd. for $C_{22}H_{21}NS$ [M + H]$^+$ 332.1468; found 332.1440.

Spectroscopic Measurements: Absorption spectra were recorded in spectral-grade solvents and 10 mm quartz cuvettes with an Agilent 8453 spectrophotometer. Phototitrations of **4c** were performed in the presence of DPIHFP, and excited by using a LOCTITE 97034 UV lamp, a 532 nm diode laser, and a 254 nm hand-held UV lamp.

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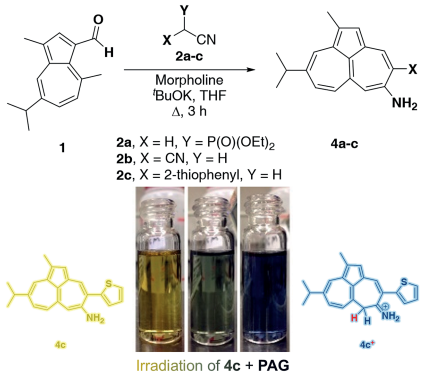
Chromophores

Cyclopenta[*ef*]heptalenes **4a**–**c**, prepared by annulation of 3-formylguaiazulene (**1**), revealed a stimuli-responsive behavior upon treatment with strong acids. 1D and 2D NMR spectroscopy indicated that protonation occurred on C-6, while photoacid titrations demonstrated that the reported tricyclic systems can serve as efficient visible sensitizers of UV-activated photoacid generators (PAGs).



Keywords: Cyclopenta[*ef*]heptalene / Stimuli response / Azulene / Electron transfer / Photoacid generator / Sensitizers / Photochromism / Natural products / Dyes/pigments

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