

Syntheses and Tunable Emission
Properties of 2-Alkynyl Azulenes

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ABSTRACT



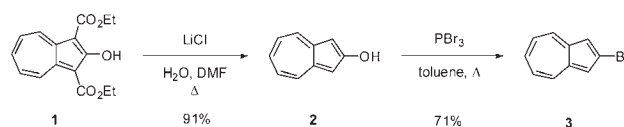
Various substituted 2-azulenes have been synthesized via Sonogashira coupling. Doping with superacids allows tunable emission from 443 to 750 nm depending on the substitution. The proton doped compounds are the first azulene alkyne based systems that show emission originating only from the S₁ excited state.

In recent years push–pull chromophores have been extensively studied owing to their promising optoelectronic properties,¹ especially second- and third-order optical nonlinearities (NLO).^{2,3} A typical organic push–pull chromophore consists of an electron acceptor and a donor bridged by a π -conjugated spacer.⁴ This arrangement facilitates efficient intramolecular charge transfer and enables further tuning of the polarizability of the chromophore. Additionally, a planar structure ensures the π -conjugation is retained over the entire donor–spacer–acceptor system.⁵

Azulene is known for its intense blue color which is a result of its interesting electronic properties. Despite the fact that azulene possesses donor–acceptor character, its optoelectronic properties have been rarely explored.^{6,7}

This is due to azulene's low emission quantum yields owing to the domination of fluorescence from the excited

Scheme 1. Synthesis of 2-Bromoazulene 3



S₂ state to the S₀ state, due to the violation of Kasha's rule.⁸ The emission from S₁ to S₀ can only be observed with very little intensity.⁹ Since the S₂ to S₀ emission is bathochromically shifted with respect to the S₁ to S₀ emission, it is desirable to alter the azulene structure in such a way that the S₁ to S₀ transition becomes the dominant emission pathway and which is expected to allow the preparation of NIR emitters based on azulene. 1- and 1,3-disubstituted alkynyl azulenes are widely known, and their properties have been extensively investigated in contrast to the 2-alkynyl azulenes that have been explored only rarely.^{10,11}

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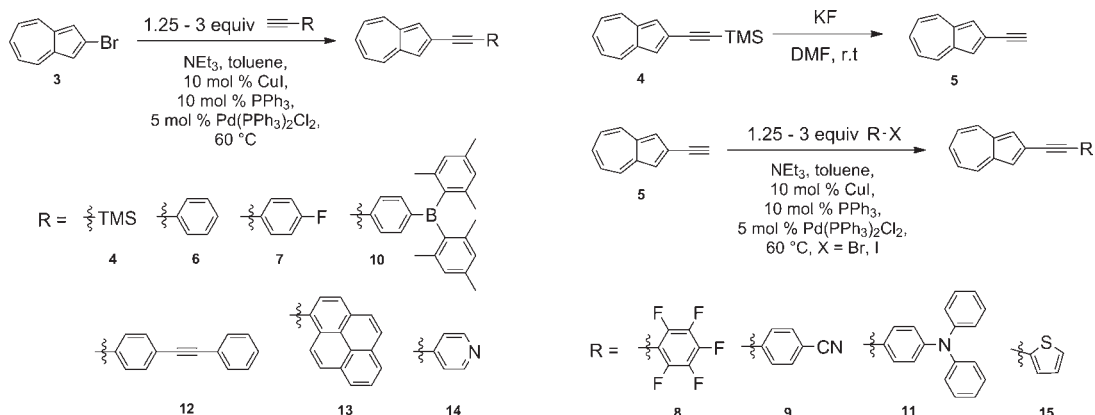
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Scheme 2. Sonogashira Coupling and Deprotection of **4**



It has been previously shown that proton doping of azulene leads to an azulonium cation with the proton at the 1-position.¹² It was expected that substitution with alkyne at the 2-position of the azulene would not alter the conjugation after doping and enhance the luminescence properties by switching the emission from the S_1 to S_0 state. Also the 2-substitution should retain the linearity of the molecule, which should favor charge delocalization over the entire molecule, since the dipole moment is expected to be maximum in this configuration. One of the main reasons for the rare exploration of the 2-alkynyl azulene moiety is due to the daunting synthetic access associated with this class of molecules. In this work, we report a stepwise protocol for the good to high yielding synthesis of 2-alkynyl azulenes starting from the easily accessible diethyl 2-hydroxyazulene-1,3-dicarboxylate. Further, detailed photophysics in conjunction with TD-DFT calculations of the various 2-alkynyl azulenes have been examined in both the doped and undoped state.

Diethyl 2-hydroxyazulene-1,3-dicarboxylate **1** was thermally dealkoxycarboxylated in a DMF/water mixture in the presence of an excess of LiCl to give 2-hydroxyazulene **2** in 91% yield (Scheme 1). **2** was further reacted with PBr_3 in toluene at 95 °C to give 2-bromoazulene **3** in 71% yield as a violet powder.¹³ This was utilized as the key starting material to prepare the corresponding 2-alkynyl azulene by reacting in Sonogashira coupling conditions that include an alkyne with catalytic amounts of CuI and $Pd(PPh_3)_2Cl_2$ in the presence of an excess amount of Et_3N (general coupling procedure I). Various substituted 2-ethynylazulenes have been synthesized starting from 2-bromoazulene (Scheme 2). The coupling product **4** was deprotected almost quantitatively to give **5**, which then was further used as a starting material for the reactions using Sonogashira coupling conditions (general coupling procedure II)

with aryl halides. Although the reaction times were longer and the yields of this second approach were generally lower than those for the coupling of the 2-bromoazulene, this was a convenient procedure for substituents whose corresponding alkynes are not commercially available or the synthesis comprises tedious steps. Single crystal X-ray diffraction studies carried out on **6**, **7**, **8**, **10**, and **15** revealed a linear planar configuration.¹⁴ In all cases the aromatic ring directly attached to the 2-ethynylazulene shows alternating bond distances¹⁵ which is suggestive of the π electrons from azulene being pushed into the π^* orbital of the attached ring. This is strongly indicative of the electronic nature of the azulene alkynes behaving as a push–pull system.

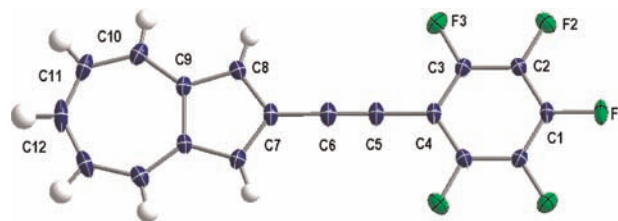


Figure 1. Thermal ellipsoid plot of **8** (30% probability level of thermal ellipsoids) with selective atomic numbering scheme. Selected bond distances (Å) and angles (deg): C4–C5 1.427(2), C5–C6 1.191(2), C6–C7 1.423(2), C4–C5–C6 180.0, C5–C6–C7 180.0.

TD-DFT calculations performed at the PBE1PBE/6-31+G(d) level¹⁵ indicate that the absorption bands of **8** (Figure 1) at 394 and 310 nm correspond to the singlet–singlet excitations from its electronic ground state S_0 to the higher electronic states S_2 (386 nm, $f = 0.911$) and

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(14) CCDC 858052–858056 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk.

(15) See Supporting Information.

S_4 (301 nm, $f = 1.400$), respectively. The major contribution to $S_0 \rightarrow S_2$ is from the HOMO-1 \rightarrow LUMO transition with the orbitals delocalized all over the molecule ($\pi_{\text{all}} \rightarrow \pi_{\text{all}}^*$), while $S_0 \rightarrow S_4$ is mainly from the HOMO \rightarrow LUMO+1 transition with molecular orbitals exclusively located on the azulene moiety ($\pi_{\text{azulene}} \rightarrow \pi_{\text{azulene}}^*$). The lowest excitation $S_0 \rightarrow S_1$ calculated at 537 nm from HOMO \rightarrow LUMO ($\pi_{\text{azulene}} \rightarrow \pi_{\text{all}}^*$) exhibits a quite small oscillator strength f of 0.017 and is not experimentally observed. The wavelength of the absorption maximum can be tuned from 372 nm (**5**) to 442 nm (**13**) using different substituents at the 2-position of the azulene resulting in emission wavelengths between 400 nm (**5**) and 474 nm (**13**) (Table 1). In the emission spectra only a weak fluorescence

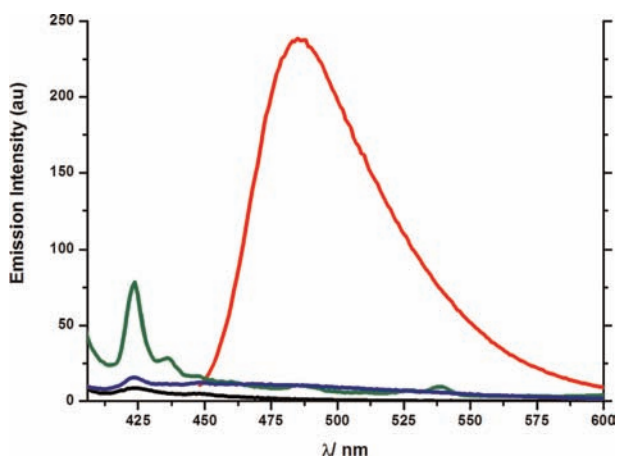


Figure 2. Emission spectra of **8** in CH_2Cl_2 (black line). After treatment: with TBAF (blue line), with nPr_4NBF_4 (green line), and with TFA (red line).

was observed when excited at the wavelength of the HOMO–LUMO transition. Doping with an anion resulted in an increase in the fluorescence intensity without altering the emission wavelength (Figure 2). In the case of **8** the presence of fluorine functional groups even roughly doubled the intensity, while the presence of BF_4^- ions increased the intensity by a factor of ~ 12 .

Recently it has been shown that doping with superacids leads to a bathochromic shift of the emission band in oligomers of azulene.¹⁶ After MeSO_3H doping, the absorption spectrum of the cationic species **8-H⁺** shows a single red-shifted band (in comparison with **8**) at 440 nm.¹⁷ This band corresponds to the lowest singlet–singlet excitation $S_0 \rightarrow S_1$ (437 nm, $f = 1.238$) and consists of an intramolecular charge transfer from the HOMO to the LUMO with the two orbitals delocalized all over the molecule ($\pi_{\text{all}} \rightarrow \pi_{\text{all}}^*$). It is important to note that the $\pi_{\text{azulene}} \rightarrow \pi_{\text{azulene}}^*$ transition (HOMO \rightarrow LUMO+1 for **8**)

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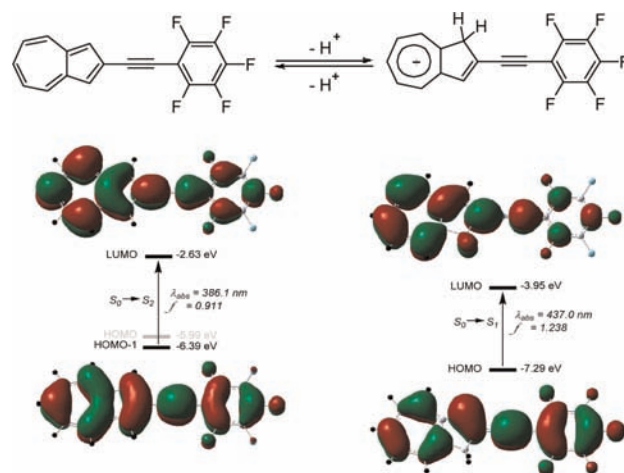


Figure 3. Doping of **8** with superacids; DFT calculations of **8** and **8-H⁺**.

is no longer observed in **8-H⁺** (Figure 3). According to Kasha's rule, which states that the fluorescence emission is expected in appreciable yield only from the lowest excited state S_1 , the proton doping of **8** resulted in an increase in the fluorescence intensity by a direct S_1 to S_0 emission. To the best of our knowledge the obtained azulene alkynes in the proton doped state are the first examples of azulene alkyne based small molecules that strongly emit only from the S_1 to S_0 state. Proton doping showed a huge effect on the absorption properties of the alkyne azulenes.

The intensity of the HOMO–LUMO band increased significantly while the HOMO-1-LUMO band disappeared (Figure 4). This is indicative of the absence of the S_2 state in the protonated molecule. This results in an emission solely from the S_1 state and the increase in intensity depending strongly on the substitution, which results in a

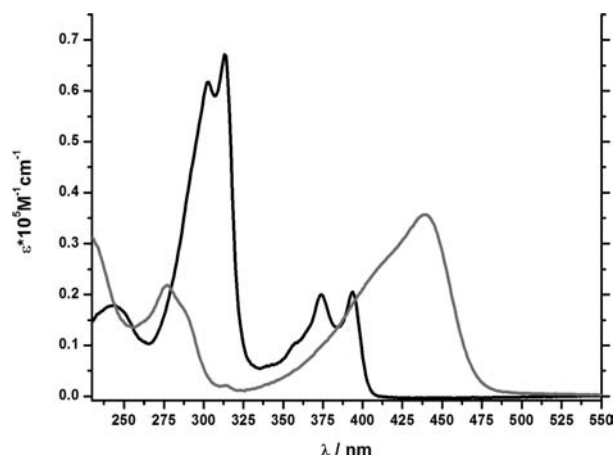


Figure 4. UV–vis absorption spectra of **8** in CH_2Cl_2 . Black line undoped; gray line treated with MeSO_3H .

Table 1. Absorption and Emission Data of Undoped and Doped Species in CH₂Cl₂ at rt

compd	undoped		doped ^a	
	$\lambda_{\max}(\text{abs})$ [nm]	$\lambda_{\max}(\text{emm})$ [nm]	$\lambda_{\max}(\text{abs})$ [nm]	$\lambda_{\max}(\text{emm})$ [nm]
azulene	340	376	355	422
4	381	410	417	467
5	372	400	394	463
6	401	424	471	533
7	400	424	473	539
8	394	424	440	487
9	402	430	452	497
10	412	425	488	535
11	413	424	450	490
12	414	426	506	649
13	442 ^b	474	608	750 ^c
14	394	424	412	443
15	414	422	509	592

^a Doping with MeSO₃H. ^b Shoulder. ^c Very weak intensity and very broad band.

factor of roughly up to 100 (Supporting Information). Tuning of the emission properties over a wide range of wavelengths from 443 to 750 nm was achieved with the electron-donating or extended conjugation leading to emission with longer wavelengths, while the electron-withdrawing substituents result in shorter emission wavelengths (Figure 5). It is worth noting that the doping process is reversible and upon neutralization with Et₃N the absorption and emission properties of the undoped species completely recovered. According to expectations the doped **8** shows the most relative emission intensity. The huge change in the emission wavelength upon doping as well as the significant increase in its intensity makes this system amenable to use in various scaffold in sensors.

In conclusion, we have described a facile route to a series of alkyne substituted azulenes synthesized via Sonogashira coupling by utilizing two different approaches. The obtained azulene alkynes possess high molar absorption coefficients and exhibit weak luminescence. The wavelength of the emission maximum does not change upon anion doping, but its intensity increases significantly. However,

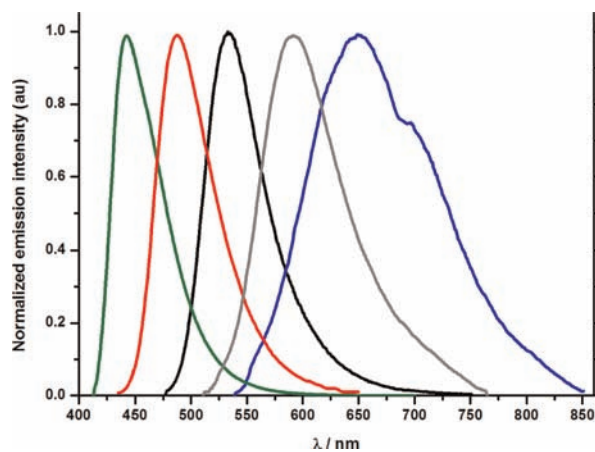


Figure 5. Emission spectra in CH₂Cl₂ after treatment with MeSO₃H of **6** (black), **8** (red), **12** (blue), **14** (green), and **15** (gray).

upon doping with superacids, these compounds showed a strong shift from blue to red emission in the electromagnetic spectrum originating from the S₁ state. Strong emission from this state has been unprecedented for azulene alkyne based compounds to date. Based on their facile synthesis and interesting emission properties, azulenes are interesting candidates for organic optoelectronic materials.

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Supporting Information Available. Experimental procedures, spectral characterization data, computational details, crystallographic data and CIF files for compounds **6**, **7**, **8**, **10**, and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.