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Stimuli-Responsive Azulene-Based Conjugated Oligomers with Polyaniline-like Properties

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Supporting Information

ABSTRACT: Novel azulene building blocks, prepared via the cycloaddition of thiophene-*S*,*S*-dioxides and fulvenes, allow for incorporation of the seven-membered ring of the azulene nucleus directly into the backbone of conjugated materials. This unique mode of incorporation gives remarkably stable, stimuli-responsive materials upon exposure to acid. This simple doping/dedoping strategy provides for effective optical band gap control and on/off fluorescence switching, reminiscent of polyaniline.

From medieval times, azure-blue-colored natural products based on the azulene ($C_{10}H_8$) skeleton have attracted particular attention, initially for their physical properties but more recently for their novel electronic structures. Significantly, the parent molecule, azulene, is a 10-π-electron isomer of naphthalene, yet it exhibits a dipole moment of 1.08 D and a deep-blue color. While unusual for small unsaturated aromatic hydrocarbons, these properties result from the fusion of an electron-rich five-membered ring and an electron-poor seven-membered ring.[1] This remarkable electronic structure of azulene allows for cation stabilization through aromatization of the seven-membered ring, which may be exploited in advanced materials for electronic, optoelectronic, and electrochromic devices.

The traditional synthetic approaches to these electronically unique building blocks are characterized by long and elaborate synthetic procedures that are low-yielding and in many cases do not afford the desired substitution patterns.[2] In fact, many azulene substitution patterns are difficult to access, if they can be accessed at all.[3] This limitation is particularly relevant for azulene-based polymeric materials, with all of the reported systems having the azulene unit incorporated into the polymeric backbone through the five-membered ring. Herein we report a versatile and modular strategy for the synthesis of azulene derivatives having a single isomeric arrangement of reactive functional groups on the seven-membered ring and the use of these functional azulenes as building blocks for the construction of stimuli-responsive oligomers.

It has been demonstrated that exposure of azulene-containing materials to an acidic environment leads to protonation of the electron-rich cyclopentadiene ring of azulene, forming a stable aromatic six-π-electron tropylium cation.[4] The ability to prepare novel azulene-containing materials where the seven-membered ring is directly incorporated into the backbone rather than being tangential, as in the case of connectivity via the five-membered ring,[5,6] represents a significant opportunity to introduce new properties into the field of conjugated polymers (Figure 1). This would directly affect the optical and electrical conductivity properties, opening up new areas of research on both azulene-based materials and conjugated polymers.[7,8] Significantly, among the family of conducting polymers and organic semiconductors, the closest analogy may be to polyaniline because of its unique environmental stability and simple doping/dedoping chemistry. This polyaniline-like behavior further increases the potential interest in, and application of, these novel materials.

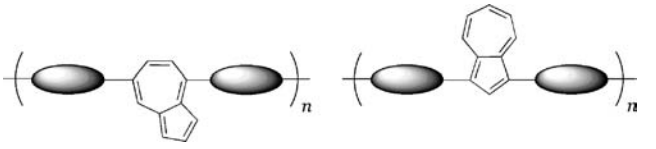
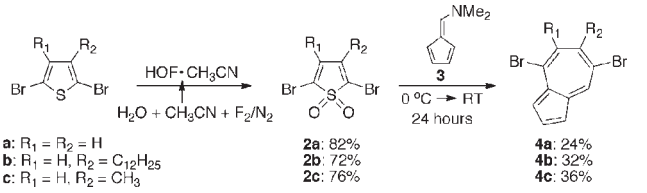


Figure 1. Schematic representation of incorporation of azulenes via (left) the seven-membered ring or (right) the five-membered ring.

Scheme 1. Synthesis of Substituted Azulenes 4a, 4b, and 4c



The requirement of regiospecific introduction of reactive functional groups on the seven-membered ring of azulene necessitated the development of a new synthetic strategy for these building blocks. To address this challenge, the $6\pi + 4\pi$ cycloaddition of thiophene-*S*,*S*-dioxides and fulvenes was examined (Scheme 1). This reaction allows the synthesis of the azulene nucleus in a single step[9,10] with the substitution pattern of the seven-membered ring being derived from that of the original thiophene ring. Another advantage of this strategy is the availability of a wide variety of substituted thiophene-*S*,*S*-dioxide derivatives through the use of the acetonitrile complex of hypofluorous acid ($HOF \cdot CH_3CN$),[11,12] which is a strong yet selective oxidizing agent. For this work, a freshly prepared solution of $HOF \cdot CH_3CN$ was used to oxygenate 2,5-dibromothiophene (**1a**), 2,5-dibromo-3-dodecylthiophene

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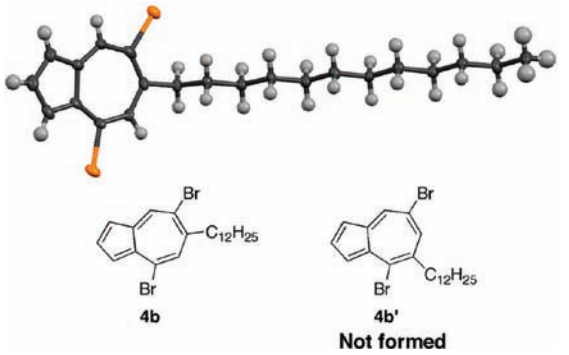


Figure 2. (top) Crystal structure of azulene product **4b**. (bottom) Molecular structures of the isomers **4b** and **4b′**.

(**1b**), and 2,5-dibromo-3-methylthiophene (**1c**), leading to the corresponding 2,5-dibromothiophene-*S*,*S*-dioxide **2a**[11] and the previously unknown alkyl-substituted thiophene-*S*,*S*-dioxides **2b** and **2c** in high yield (Scheme 1).

Examination of the cycloaddition reaction between thiophene-*S*,*S*-dioxide **2a** and dimethylaminofulvene (**3**) revealed that both the reaction conditions and the sequence in which the compounds are introduced are important for increasing the yield of 4,7-dibromoazulene (**4a**) [see the Supporting Information (SI)]. Similarly, the reaction between sulfone **2b** and **3** gave the previously unknown azulene derivative **4b** substituted with two bromines and a dodecyl group on the seven-membered ring (Scheme 1). The presence of the dodecyl chain is important to improve the solubility of oligomers and polymers containing azulene **4b**.

Traditionally, the reaction between fulvenes and unsymmetrical thiophene-*S*,*S*-dioxides substituted at C2 and C4 results in the formation of a mixture of two regioisomeric products.[13,14] Interestingly, in the case of azulene **4b**, a single regioisomer was exclusively produced. The structure of **4b** was confirmed by X-ray diffraction of the deep-blue needles formed from acetonitrile; the result revealed a configuration in which the dodecyl group of the seven-membered ring is located at C6, with no detectable formation of the isomeric product **4b′** wherein the dodecyl group is present at the 5-position (Figure 2).

In support of this observed selectivity, the same cycloaddition reaction was examined using a less sterically hindered thiophene-*S*,*S*-dioxide. Replacing the dodecyl chain with a methyl group allowed the evaluation of steric effects on the selectivity of the reaction, as the two substituents have very similar electronic character. Accordingly, 3-methyl-substituted sulfone **2c** was reacted with the same fulvene derivative **3**. The resulting azulene derivative, **4c**, was also isolated as a single regioisomer, with X-ray analysis confirming the same selectivity as obtained for azulene **4b** (see the SI).

To better understand the surprising selectivity of this reaction, density functional theory calculations at the B3LYP/6-31G* level were performed.[15] The $6\pi + 4\pi$ cycloaddition reaction between **2c** and **3** can yield two regioisomeric adducts, **5** and **5′**, that sequentially lead to the azulene regioisomers **4c** and **4c′** (Figure 3).[9,14] Adduct **5** is the precursor to product **4c**, which is analogous to **4b**. We investigated the eight possible modes of attack (of which only four are relevant to the formation of the final products) following the loss of SO_2 and dimethylamine. The two lowest-energy transition structures **5-TS** (12.2 kcal/mol) and **5′-TS** (14.6 kcal/mol) account for the adducts shown in Figure 3, where the SO_2 is pointing in the same direction as the

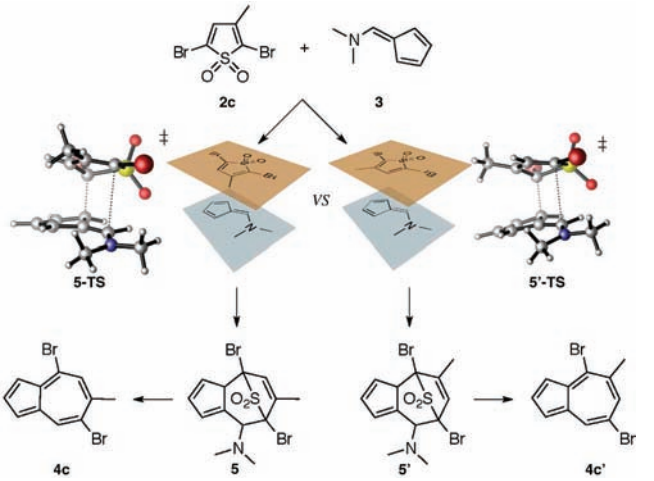
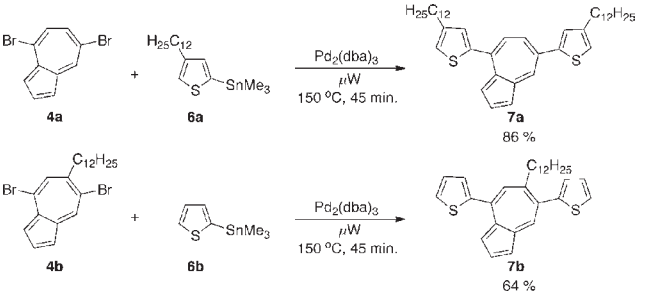


Figure 3. Two possible cycloaddition pathways forming lowest-energy transition intermediates **5** and **5′**, which subsequently lead to the corresponding azulenes **4c** and **4c′**.

Scheme 2. Synthesis of Azulene−Thiophene Oligomers 7a and 7b



dimethylamine group. The other two structures (not shown), in which the SO_2 points away from the dimethylamine were found to have barrier heights greater than 20 kcal/mol. With the assumption that the difference in the calculated barrier heights ($\Delta\Delta E^{\ddagger}$ = 2.4 kcal/mol) is consistent in rate theory, an estimated selectivity ratio of ~80:1 in favor of **5** is obtained, thus supporting the experimental observation that the reaction selectively yields the single azulene isomer **4c**.

Treatment of compounds **4a** and **4b** with trifluoroacetic acid (TFA) resulted in the formation of a complex mixture of products, most likely because of instability of the generated species (see the SI). In order to stabilize the azulenium cation, we designed conjugated oligomers based on the substitution of the seven-membered ring of the azulenes with thiophenes. Accordingly, 4,7-dibromoazulenes **4a** and **4b** were reacted with 2-(trimethylstannyl)thiophenes **6a**[16] and **6b**,[17] respectively, via a microwave-assisted Stille cross-coupling reaction.[18] Novel azulene−thiophene oligomers **7a** and **7b** were isolated in good yield as blue solids (Scheme 2).

The formation of azulenium cations from the conjugated azulene−thiophene oligomers **7a** and **7b** was then examined. Upon addition of TFA to a dichloromethane solution of **7a**, protonation of the five-membered ring of azulene occurred, generating a mixture of azulenium cations **8** (Figure 4). This was accompanied by an instant color change of the solution from deep-blue to orange-red. ^{1}H NMR spectroscopy showed shifts in

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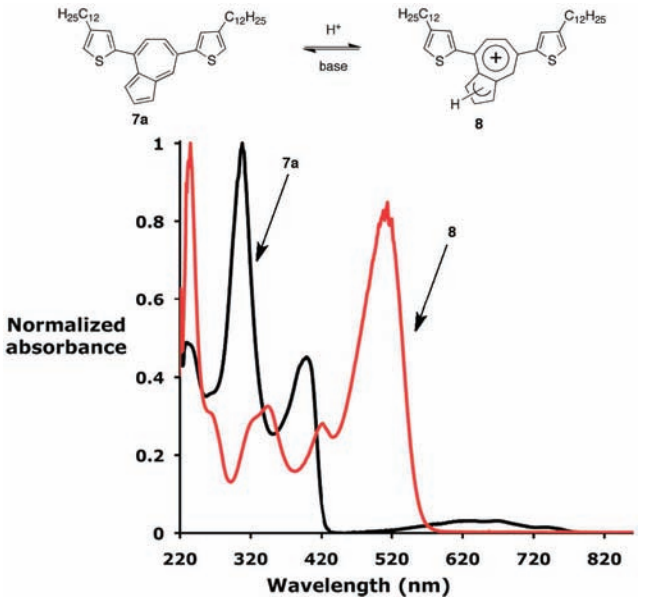

Figure 4. (top) Formation of azulenium cations, **8**, from thiophene–azulene oligomer **7a**. (bottom) UV–vis measurements in dichloromethane for neutral oligomer **7a** and after protonation to give **8**.

the proton signals in the aromatic area along with the appearance of a new peak at 4.2 ppm corresponding to the CH_2 protons of the protonated five-membered ring. Significantly, the formation of the azulenium cations proved to be a reversible process, with oligomer **7a** being regenerated upon addition of base (e.g., triethylamine) or by evaporation of the solvent and the acid. It is important to note that this process of protonation and deprotonation of the oligomer could be repeated multiple times (>10) with no observed degradation of the oligomer, demonstrating the stabilization of the azulene nucleus through conjugation with the thiophene rings. Furthermore, the protonation was not limited to TFA and could be achieved utilizing different acids (e.g., perchloric, hydrochloric, and sulfuric acids). Similar results were obtained for oligomer **7b** (see the SI).

Comparison of the neutral azulene derivative **7a** with the derived azulenium cations **8** showed a significantly smaller energy gap for **8**, as evidenced by the UV–vis spectra (Figure 4). The spectrum of **7a** exhibits two major maxima at 308 and 402 nm corresponding to $\pi-\pi^*$ transitions of the azulene and thiophene rings, respectively, with a weak, broad absorbance between 615 and 640 nm due to the S_0-S_1 transition of the azulene unit. Protonation resulted in the appearance of a new peak at 514 nm, which is attributed to the azulenium cation, and the efficient conjugation of the azulenium cation with the adjacent thiophene rings was evidenced by the significant red shift of this absorption maximum ($\Delta\lambda_{max}$ = 162 nm) relative to the value reported in the literature for the unsubstituted azulenium cation (352 nm).[19,20] Furthermore, λ_{max} for the protonated form of **7a** is higher than that for the protonated form of an extended 1,3-polyazulene chain (conjugated through the five-membered ring with M_n = 16 kDa) in TFA (λ_{max} = 508 nm).[21] Again, the original absorption spectrum of **7a** could be regenerated upon neutralization, and this cycle could be repeated multiple times. The optical band gaps, estimated by the onset point of the absorption bands, were found to be 2.91 eV for oligomer **7a** and 2.18 eV for the azulenium cations **8**, corresponding to a reduction of 0.73 eV due to generation of the stable tropylium cation along the backbone.

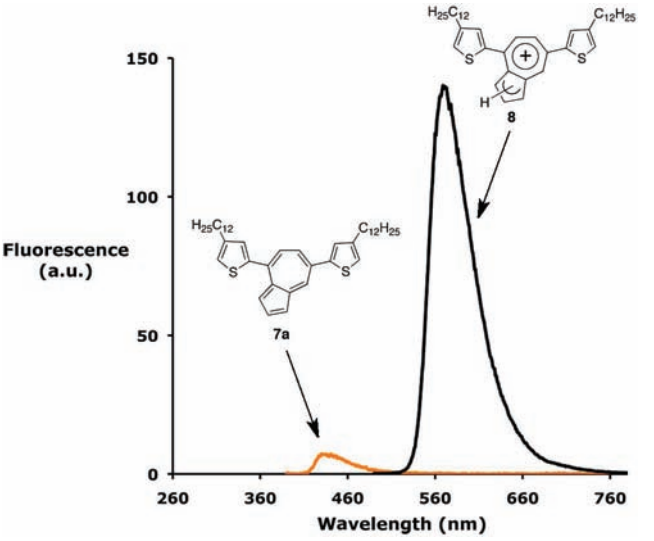

Figure 5. Fluorescence measurements in dichloromethane for neutral oligomer **7a** and after protonation to give **8**.

This modulation of physical properties upon protonation was even more evident during fluorescence studies. In this case, the fluorescence of substituted azulene **7a** could be "switched on" upon protonation (Figure 5). While the neutral compound **7a** is essentially nonfluorescent, similar to unsubstituted azulene, which has an extremely weak S_1-S_0 fluorescence,[22,23] the protonated system **8** revealed strong fluorescence (λ_{max} = 573 nm). In concert with the absorbance properties, the fluorescence could similarly be "switched off" by subsequent addition of base (Figure 5).

In conclusion, access to novel azulene derivatives has been obtained through the regiospecific cycloaddition of thiophene-*S*,*S*-dioxides and fulvenes and subsequent cross-coupling with trimethylstannylthiophenes. In a reversible process, the optical band gap of these azulene–thiophene oligomers could easily be modulated by simple protonation, with fluorescence being "switched on" upon generation of the corresponding azulenium cations. The presence of the thiophenes is essential for stabilizing the azulenium cations, and the modularity of our approach allows other substituents to be explored in order to tune the properties of these novel materials. We are currently developing strategies to incorporate these new azulene derivatives into polymeric materials and, in analogy with fullerene systems,[24] expand the study of novel aromatic systems for electronic and photovoltaic applications.

■ ASSOCIATED CONTENT

Supporting Information. General experimental and characterization procedures, complete ref 15, and CIF files for compounds **4b** and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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