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Azulene-containing organic chromophores with tunable near-IR absorption in the range of 0.6 to 1.7 μm†

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Near-infrared (NIR) absorption in the range of 0.75–2.5 μm is in great demand for a variety of applications but currently the majority of commercial NIR devices are based on inorganic materials due to the limited number of organic materials that are active in this range. Here we present the preparation and optical studies of a new series of stable azulene-containing NIR chromophores whose absorption can be tuned in the range of 0.6–1.7 μm. DFT calculation revealed that the protonation-induced low excitation gap was attributable to the substantial intramolecular charge transfer.

Near-infrared (NIR) absorption in the range of 0.75–2.5 μm is in great demand for a variety of applications such as optical communications, energy, optoelectronics, bio-imaging, biosensors, and thermal therapy.[1–5] Currently, the majority of commercial NIR devices are based on inorganic materials such as PbS, PbSe, and InGaAs nanoparticles as they show absorption that can be tuned in the range of 0.7–2.0 μm.[6] These devices are, however, only suitable for small-area applications due to the high cost of epitaxially grown inorganic devices. Organic materials that are optically and thermally active in the NIR region can in principle be used in NIR devices with advantages of low-cost fabrication, potential to produce large-area devices, light weight and flexibility. Currently, however, commercially available organic NIR optoelectronic devices operating in the range of 1–2 μm are extremely rare because of the limited number of organic materials that are active in this range.[5,7] Recently, various novel NIR chromophores like phthalocyanine derivatives,[8] porphyrins,[9] squaraines,[10] and polyaromatic dyes[11] have been developed but their structural complexity is generally associated with tedious multistep synthesis and their absorption is typically less than 1 μm. We here report the synthesis of azulene-containing organic chromophores, whose absorption can be tuned in the range of 0.6–1.7 μm simply by controlling the substitution of the molecule. Most importantly, the obtained azulene-containing NIR chromophores are very stable in air, making them promising for the fabrication of organic-based NIR photonic devices.

Azulene has recently been named as an “aromatic chameleon” because of its unique structural and electronic properties.[12] Azulene is a polar ($P_e = 1.08$ D),[13] resonance-stabilized nonalternant aromatic hydrocarbon. The large dipole moment arises from the electron drift from its seven-membered ring to its five-membered ring, which leads to its aromatic delocalization energy being 5 times lower than that of benzene.[14] Upon release or gain of a charge, totally different new resonance-stabilized species – azulenylium ions – are formed. Azulenylium ions are quite stable due to the formation of either the aromatic cyclopentadienyl anion or cycloheptatrienyl (tropylium) cation.[15] The confinement of charges on the azulene ring in azulene-containing conjugated compounds is expected to produce additional stability for the resultant ions. Four azulene-containing compounds and their corresponding ions with different substituents and conjugation length are thus designed and synthesized in this work.

The coupling of azulene with thiophene derivatives was achieved through the nickel-catalyzed Grignard reaction of 1,3-dibromoazulene with 2-bromo-3-methylthiophene and 2-bromo-3-phenylthiophene to obtain compounds **1** (yield: 78%) and **2** (yield: 62%), respectively (Fig. 1). To further extend the conjugation length, the

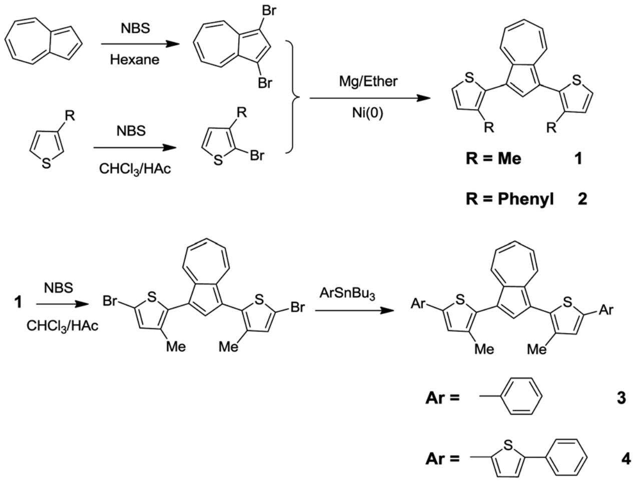

Fig. 1 Synthetic routes for neutral compounds **1–4**.

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obtained compound **1** was brominated with NBS to give the dibrominated intermediate (yield: 86%); this was then reacted with excess aromatic tins such as phenyl tri-*n*-butyltin and 5-phenylthienyl tri-*n*-butyltin. In the presence of a catalytic amount of tetrakis-(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) and the electron-donating ligand triphenylarsine (Ph_3As), we obtained target compounds **3** and **4** with yields of 61% and 56%, respectively.[16] All the obtained neutral compounds are soluble in organic solvents such as chloroform, THF, and dichloromethane. Their structures and purity were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy (see ESI†). The conversion of the neutral compounds to their corresponding ions was achieved easily by protonation with trifluoroacetic acid (TFA) (30%) in chloroform solution (Fig. 2). Addition of TFA to solutions of the neutral compounds induces an immediate color change. The conversion process can also be accelerated by water bath heating at 50 °C.

Due to the polarized and nonalternant π-electron system of azulene, modest perturbation is expected to induce bond alternations in azulene and significant changes of π-electron distribution on azulene rings and thus of optical properties.[17] The sensitivity of azulene π-electrons to different substituents can be clearly seen from the chemical shifts of its protons. A comparison of the proton chemical shifts of azulene protons in compounds **1–4** shows remarkable chemical shifts induced by the different substituents. The sensitivity of azulene π-electron distribution to substitution allows the optical properties of its derivatives to be easily tuned. As shown in Fig. 3, the absorption maxima (λ_{max}) of compounds **1**, **2**, **3**, and **4** in chloroform are observed at 299 ($\varepsilon = 5.9 \times 10^4$ M^{-1} cm^{-1}), 310 ($\varepsilon = 6.3 \times 10^4$ M^{-1} cm^{-1}), 326 ($\varepsilon = 7.1 \times 10^4$ M^{-1} cm^{-1}), and 375 ($\varepsilon = 5.7 \times 10^4$ M^{-1} cm^{-1}) nm, respectively (Fig. 3). This increasing red shift from compound **1** to **4** is attributed to the increase of effective conjugation length of these compounds induced by the substituents.[18]

The tuning of the absorption by substituents was more significant when the neutral compounds were protonated by TFA. Protonation of azulene-containing compounds leads to remarkable changes in the spectra and the appearance of new peaks in the visible and NIR regions (Fig. 4a). For example, upon protonation, the methyl-substituted compound **1A** shows a new peak at 548 nm, while the protonated phenyl-substituted compound **2A** shows absorption at 996 nm. The change from the methyl group to phenyl group induced a red shift of about 450 nm. The tuning can also be controlled by the substituent positions. The change of phenyl substituent position from C2 on thiophene ring (as in compound **2A**) to C5 (as in compound **3A**) leads to a change of the maximum absorption from 1.0 to 1.3 μm. The NIR region absorption can be further extended by increasing the conjugation length. We can adjust the maximum absorption to about 1.7 μm (compound **4A**) if one more thiophene ring is inserted into the conjugation backbone (Fig. 4a). In addition to the remarkable bathochromic shift of spectra, protonation also leads to significant enhancement of the molar extinction coefficient (ε) of these azulene-containing compounds. As shown in Fig. 4b, addition of TFA to the neutral compound solutions not only induces solution color change, but also remarkably increases solution optical density. The high optical densities of protonated compounds make their solutions darken and further dilution is required to see the real color of the solution by eye (Fig. 4b). The high optical densities of protonated compounds suggest that they exhibit light-harvesting ability as compared to neutral ones. The measured molar extinction coefficients for protonated compounds **1A**, **2A**, **3A**, and **4A** are 2.76×10^5 (λ_{max} = 548 nm), 3.14×10^5 (λ_{max} = 996 nm), 5.59×10^5 (λ_{max} = 1.3 μm), and 1.91×10^5 (λ_{max} = 1.7 μm) M^{-1} cm^{-1}, respectively. The enhanced molar extinction coefficient induced by protonation could be attributed to the higher polarity of the protonated compounds, which are expected to have a faster charge transfer from HOMO to LUMO. The thermal stability of the protonated compounds was investigated by incubation of the solutions in sealed vials for half a year at room temperature. UV-vis-NIR spectra of protonated

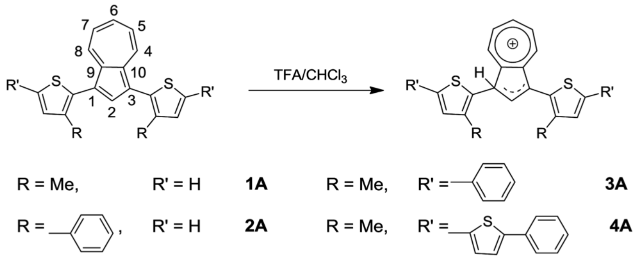

Fig. 2 The protonation of neutral compounds to give ions **1A–4A**.

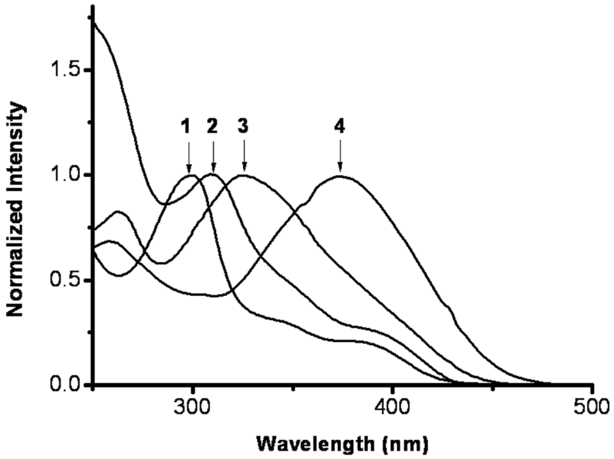

Fig. 3 UV-vis spectra of neutral compounds in chloroform.

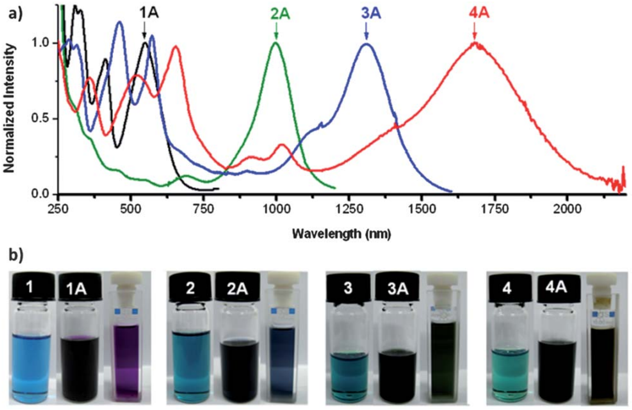

Fig. 4 Optical spectra and photos of protonated compounds **1A–4A** in 30% TFA–chloroform solution. (a) UV-vis-NIR spectra of protonated compounds **1A–4A**. (b) Photos of neutral and protonated compounds; solutions in spectrophotometer cuvettes are corresponding protonated compounds with further dilution.

compounds show no apparent spectral change as shown in the ESI†. This indicates that these azulene-containing organic chromophores are promising candidates for NIR device applications.

The newly appearing peaks in the vis–NIR region can be attributed to the intramolecular charge transfer (ICT) transition in the protonated azulene-containing compounds.[19] Protonation of azulene derivatives and azulene-containing polymers has been extensively studied by our group[20,21] and others,[22] and protonation has been employed to "switch on" the conductivity and luminescence of azulene-containing organic materials. Both quantum chemical calculation and experimental results have unambiguously demonstrated that protonation occurred predominately at the C-1 and C-3 atoms of azulene (Fig. 2), which are by far the most stable isomers.[23] Due to the large dipole moment of azulene, the protonation is expected to induce π-electron drift from the seven-membered ring of azulene to the five-membered ring, forming the stable cycloheptatrienyl (tropylium) cation. The delocalization of the charge on the azulene ring induces charge separation in the protonated compounds, forming a stronger electron-donating (D) and electron-accepting (A) structure.[24] Protonation thus has a profound impact on the geometry of azulene compounds and, as a consequence, significant effects on their optical properties.

The protonation was further studied by using nuclear magnetic resonance (NMR) spectral analysis, for which compounds were protonated by deuterated TFA (TFA-d). Typical ^{1}H NMR spectra of compound **1** before and after protonation in 30% TFA-d/CDCl$_3$ are shown in Fig. 5. Upon protonation, a remarkable downfield shift of proton signals of azulene can be observed, with the largest downfield shift up to 1.4 ppm. The large downfield shift of proton signals of azulene indicates strong deshielding effects of the localized positive charge, suggesting that the positive charge from protonation is mainly localized on the azulene ring. Furthermore, protonation changes the neutral compounds' symmetric structure to become asymmetric in protonated compounds. For instance, H-4 and H-8 (see the definition of proton numbers in Fig. 2 and 5) in neutral compound **1** show one double peak at 8.38 ppm due to the symmetric structure. They are, however, split into two double peaks at 9.78 ppm and 8.84 ppm in the protonated compound **1A**. Similarly, peaks of H-3 and H-5 change from one triple peak in neutral compound **1** to two triple peaks in the protonated compound **1A** with large downfield shift (Fig. 5). All these observations suggest that only monoprotonation of the azulene-containing compounds occurs, and the monoprotonation at position 1 or 3 induces an asymmetric structure of the protonated compounds (Fig. 2). This is consistent with previous reports, where it was established that only monoprotonation of the hydrocarbon derivatives of azulene can occur.[25]

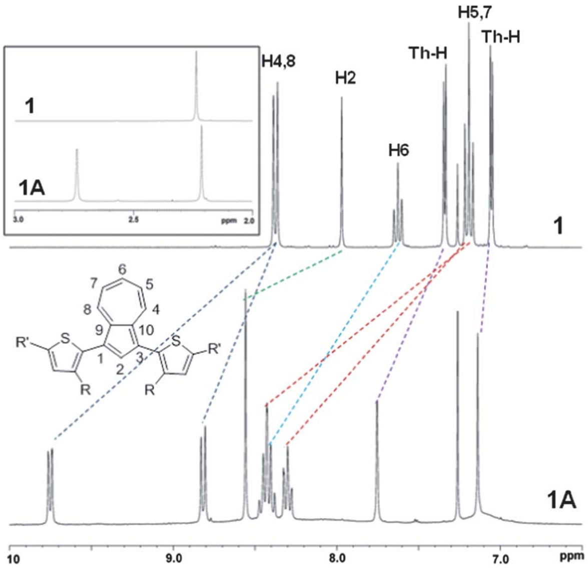

Fig. 5 ^{1}H NMR spectral change of compound **1** before and after protonation in 30% TFA-d/CDCl$_3$. Inset shows the splitting of methyl peaks after protonation.

To better understand the ICT transition of the protonated azulene-containing chromophores, the geometry of neutral and protonated azulene-containing chromophores was optimized by density functional theory (DFT) calculations using compounds **3** and **3A** (with trifluoroacetate as counter ion) as examples. Conformational properties and dipole moments of neutral compound **3** and protonated compound **3A** were theoretically calculated using B3LYP/6-31G* geometry and natural bond orbital (NBO) population analysis. As expected, protonation leads to a large increase in the dihedral angle between the azulene ring and thiophene ring. The calculated angle of protonated compound **3A** (87.1°) is much larger than that of the corresponding neutral compound **3** (44.5°), which is due to the change of the sp^2 carbon to sp^3 carbon by protonation. Most importantly, the calculated HOMOs and LUMOs show a remarkably different ICT interaction between the neutral and the protonated compounds (Fig. 6). The HOMOs in the neutral compound **3** are delocalized over the azulene ring and thiophene rings, while the LUMOs are located mainly on the azulene unit. However, the HOMOs of protonated compound **3A** are all located on the thiophene rings and benzene rings, and the LUMOs are all localized on the azulene ring. The distinct charge separation between HOMO and LUMO in the protonated compound **3A** indicates that substantial charge transfer from the donor moiety (thiophene and benzene units) to the accepting moiety (azulene unit) occurs when the molecules are irradiated by light. The HOMO–LUMO transition can be considered a charge-transfer transition. The significant intramolecular charge transfer in the protonated compound **3A** is also confirmed by the dipole moment change. The calculated dipole moment for neutral compound **3** is found to be 0.61 D, while the calculated dipole moment for the protonated compound **3A** is found to be 11.45 D.

In summary, we here presented a new series of azulene-containing NIR organic chromophores with a tunable absorption range of 0.6 to 1.7 μm. The tuning of the maximum absorption can be easily adjusted by the substituent groups, positions, and conjugated length. The NIR

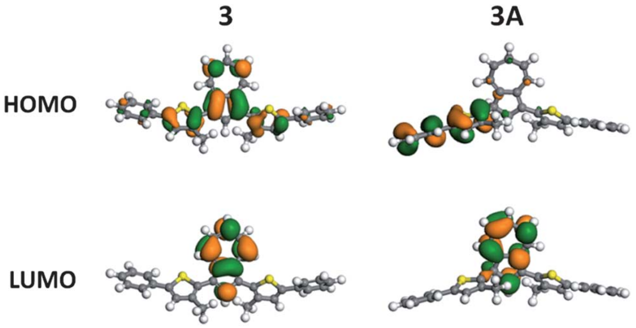

Fig. 6 Spatial distributions of the calculated HOMOs and LUMOs of compounds **3** and **3A**.

absorption bands can be attributed to the intramolecular charge transfer transition, which was illustrated clearly by theory calculations. Because of the ease of preparation and manipulation of the molecular structures of these azulene-containing chromophores, they show great potential as promising NIR dye materials, whose "color" can be varied over a wide range whilst maintaining their stability.

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