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Protonation behaviour of 2-phenyl-1,3-diazaazulene derivatives

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Three 2-phenyl-1,3-diazaazulene derivatives were synthesized and their protonation behaviours were investigated systematically *via* UV–vis absorption titration and ^{1}H NMR titration, as well as theoretical calculations. One of them exhibited a monoprotonation process while the others displayed prominent halochromic diprotonation responses. Interestingly, upon protonation of 2-phenyl-1,3-diazaazulene derivatives, the coplanarity and conjugation of the 16-π-conjugated backbones were well kept, while the electronic structures were controllably adjusted. The response mechanism of 1,3-diazaazulene derivatives towards acid is through the attachment of acid proton to the nitrogen atom in the diazaazulene ring, resulting in the change of the hybridization of protonated-N from sp^2 to sp^3, which differed from that of the well-known azulene (analogue of 1,3-diazaazulene, protonation at carbon atom). This work would provide a new insight into the protonation research of the organic functional molecules.

1. Introduction

Functional organic chromophores are drawing more and more attention due to their potential applications in optoelectronic fields,[1] including light-emitting diodes,[2] solar cells,[3,4] nonlinear optical materials,[5] and sensors.[6] The protonation of organic chromophores, which is considered as a facile and effective way to tune the transition gaps, alter the molecular interactions and control the aggregation morphology of the organic chromophores, has been one of the hottest research topics due to its potential utilities in drug delivery,[7] chemical sensors[8] and fluorescence switching devices.[9] For example, perylene bisimides were reported to exhibit near-infrared absorptions beyond 1100 nm due to the great bathochromic shift of their charge transfer bands resulted from the acid-base stimuli.[10] Dihydro-teraazaacene diimides containing 6 or 7 laterally fused six-membered rings show obvious colour changes upon protonation-deprotonation process.[11]

Generally, the response mechanism is based on the acid-base reactions between the organic chromophores and extra acid stimulus, which results in the chromophore-based cation with proton attached to a special site. Upon the transformation of the chromophore from neutral state to a positively charged cation, some properties including molecular geometry[12] and orbital energy gaps[13] could exhibit certain alterations, and some compounds even demonstrate dramatic halochromic behaviours. Usually, the molecular geometry would be greatly influenced upon protonation.

Among various organic chromophores, azulene derivatives were reported to display fine-tuned photophysical and optical behaviours owing to their unique polarized charge distribution on the fused seven- and five-membered rings,[14] thus showing great advantages as optical material candidates.[15] Researches towards azulene derivatives have also involved the halochromic responses owing to their specific structures.[16–22] It was reported that, upon protonation, the dipole moments of azulene derivatives with special substituents could be largely enhanced,[16] resulting in the adjustment of the electronic structures and the changes of corresponding physical properties, such as the typical halochromic response.[13,23,24] Studies have indicated that the protonation of azulene-based derivatives always occurs on the C1 (or C3) atom in the five-membered ring,[13,21,25,26] with the formation of tropylium cation.[27] Based on the protonation response mechanism, the protonation of azulene derivatives would undoubtedly convert the hybridization of the protonated carbon atom from sp^2 to sp^3, leading to the decrease of the molecular conjugation, which might break the planarity of azulenes and induce dramatic geometric variations.

1,3-diazaazulene (DAA) is a unique derivative of azulene in which two carbon atoms are replaced by nitrogen atoms, with a rather large dipole moment locating within the heteroaromatic

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core.[28,29] Our group and collaborators have previously reported a series of donor-π-acceptor typed DAA derivatives which show relatively small ground dipole moment (μ_g) and large first-order hyperpolarizability (β).[30–32] The above mentioned DAA derivatives all contain a basic conjugated skeleton of 2-phenyl-1,3-diazaazulene (**1**, as shown in Scheme 1), which should be responsible for their superior performances in nonlinear optics. As is proved, the simple molecule **1** is coplanar, indicating that the introduction of phenyl group to 2 C atom of DAA would enlarge the conjugation system to form a 16-π-conjugated construction.[30] Meanwhile, considering the two nitrogen atoms in the five-membered ring, which would probably facilitate the protonation behaviour, it is supposed that structures based on **1** would exhibit rather novel performances compared with azulene derivatives as promising acid-stimuli responsive materials.

Thus in this paper, based on the three typical DAA derivatives 2-phenyl-1,3-diazaazulene (**1**), 2-(p-*N*,*N*-dimethylaminophenyl)-1,3-diazaazulene (**2**), and 6-nitro-2-(p-*N*,*N*-dimethylaminophenyl)-1,3-diazaazulene (**3**) (Scheme 1), the protonation behaviours were detailedly investigated through UV–vis absorption titration and ^{1}H NMR titration experiments. Moreover, the protonation mechanisms of the chromophores were proposed combined with the theoretical calculations. It was found that **1**, **2**, and **3** well kept their 16-π-conjugated and coplanar structures during protonation while the molecular HOMO-LUMO energy gaps were greatly changed, indicating that the electronic structures of the **1**-based derivatives could be well tuned *via* protonation without damaging the conjugation and planarity.

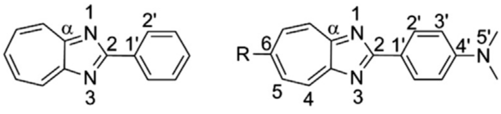
2. Results and discussion

2.1. Synthetic route

Synthetic procedures for **1**, **2** and **3** were shown in Scheme 2. They were generally obtained through the condensation reactions between 2-methoxy tropone (or 2-methoxy-5-nitro tropone) and corresponding benzamidinium hydrochlorides under reflux condition, with potassium *tert*-butoxide as base and ethanol as solvent. Detailed procedures and characterizations were presented in the experimental section. 3 was synthesized according to our previous report.[30,32,33] **1** was obtained as white powder, **2** as red powder and **3** as light violet powder. They were all soluble in many organic solvents, such as dichloromethane, chloroform, ethanol, ethylacetate and so on.

2.2. UV–vis absorption studies

The typical UV–vis absorption spectra of **1**, **2**, and **3** measured in dichloromethane are shown in Fig. 1. **1** exhibited a major absorption band at 356 nm, similar to that of DAA.[34] Compared with **1**, a pronounced red-shift of the peak to 455 nm was observed for **2**. As for **3**, a peak with rather larger red-shift to 580 nm was obtained, with a Δλ value of 224 nm compared with that of **1**. These red shifts should be caused by the introduction of electron-donating group (*N*,*N*-dimethylamino) and/or electron-withdrawing group (nitro) to **1**, which induces marked intramolecular charge transfer and tunes the electron transitions of **2** and **3**.

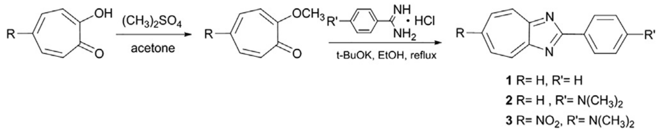


1

2 R=H

3 $R=NO_2$

Scheme 1. Chemical structures for **1**, **2**, and **3**.



Scheme 2. Synthetic route for **1**, **2** and **3**.

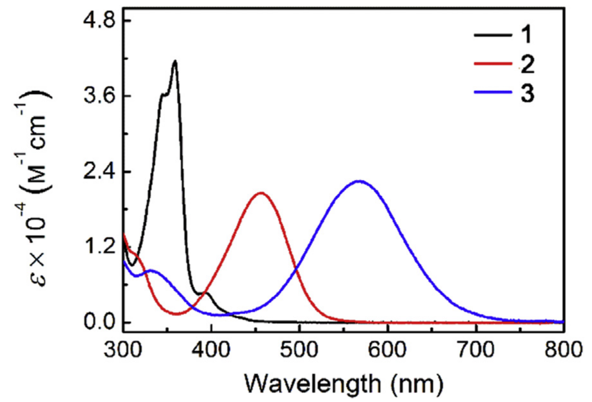


Fig. 1. UV–vis absorption spectra of **1** (20 μM), **2** (15 μM), and **3** (15 μM) in dichloromethane.

2.3. UV–vis absorption titration studies

UV–vis absorption titration, a common method for investigation of the halochromic behaviours of organic chromophores,[35,36] was used to monitor the protonation processes of **1**, **2**, and **3** in dichloromethane upon the addition of trifluoroacetic acid (TFA) as the proton donor.

With the increasing addition of TFA, the intensity of original peak of **1** at 356 nm was slowly decreased with the emerging of a new peak around 392 nm (Fig. 2a). The isobestic point at 367 nm further proved the protonation process of **1**. The absorption value at 392 nm was plotted *versus* the equivalents of TFA (inset of Fig. 2a), which exhibited a linear relationship up to 1.4 equivalent of TFA, implying that about 1.4 equivalent of TFA was needed for the one protonation of **1**. The excess addition of TFA afterwards did not induce any other new absorption peak (Fig. 2b). Subsequent addition of triethylamine (TEA) could neutralize the system back to the pristine state (the gray line in Fig. 2b). In this case, the protonation of **1** probably only need one proton, with slight solution colour change.

Fig. 3a shows the absorption spectra evolution for **2** when TFA was increased from 0 to 6 equivalents. Upon the gradual addition of TFA, a new absorption was formed at around 515 nm. The increasing of this absorption was accompanied with the. bleaching of the primary absorptions at 455 nm and 290 nm, respectively. The isobestic point at 477 nm indicated the spectral changes of two different species. As the equivalent of TFA was increased from 2 to 6, the peak at 515 nm was slightly red-shifted towards 520 nm, with the shape unchanged. The absorption value at 515 nm was plotted *versus* the equivalents of TFA (inset of Fig. 3a), which exhibited a linear relationship up to 1.1 equivalent of TFA, implying that about 1.1 equivalent of TFA was needed for one protonation of **2**. In addition, the solution colour gradually changed from light yellow to dark pink (Fig. 3c). However, when TFA was dramatically increased