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N-type pyrazine and triazole-based luminogens with aggregation-enhanced emission characteristics†

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N-type pyrazine-based 1,4- and 1,5-disubstituted 1,2,3-triazole derivatives, showing unique aggregation-enhanced emission characteristics, were facilely prepared *via* Cu- and Ru-catalysed azide–alkyne cycloadditions, respectively. Thanks to their electron-deficient properties, they could readily form red-emissive charge transfer complexes with electron-donating triphenylamine in the aggregate and solid states.

Over the past decades, exploitation of new luminogens with enhanced emission in the aggregate state has received considerable interest for their potential applications in optoelectronic devices, chemical sensors and biological probes.[1] However, most of the conjugated organic molecules emit more efficiently in solution but their luminescence is weakened or quenched when aggregated; that is, these molecules suffer from the notorious aggregation-caused quenching (ACQ) effect.[2]

Among the reported methods for tackling this difficulty, aggregation-induced emission (AIE), conceptually termed in 2001 by Tang *et al.*, is promising because it can enable naturally occurred aggregation to play positive instead of negative roles in enhancing the emission efficiency in the aggregate or solid state.[3,4] The restriction of intramolecular rotation (RIR) has been proved experimentally and theoretically to be a mechanism which has been widely adopted by researchers to explain the observed emission behaviors of AIE-active luminogens (AIEgens).[5]

The AIE phenomenon has been attracting increasing interest among the researchers worldwide. Due to their enthusiastic efforts, hundreds of AIEgens with full color emission have been developed and their potential for high-tech applications in organic light-emitting diodes, highly sensitive and selective chemo- and bio-sensors, *etc.* have been demonstrated.[6,7]

However, most of the developed AIEgens are electron-rich ones. The electron-deficient (N-type) AIEgens are rare though they could play indispensable roles in functions as electron transport and electron acceptor materials (Chart 1).[8] In 2009, we reported a new type of pyrazine-based AIEgen, named 2,3-dicyano-5,6-diphenyl-pyrazine (DCDPP), and unambiguously confirmed the RIR mechanism of AIE by covalently "locking" its two phenyl rings.[5c] Theoretically, the dicyanopyrazine moiety in DCDPP is electron-deficient, but its electronic property has not been revealed yet. Inspired by this prospect, in this work, we expanded and systematically investigated this pyrazine-based system with the aim to develop new N-type AIEgens.

During the course of chemical decoration of AIEgens, a click reaction was employed as it shares such fascinating merits as high efficiency, regioselectivity and atom economy.[9] For example, tetraphenylethene (TPE)-core AIEgens were readily and efficiently prepared by us using Cu(I)-catalyzed azide–alkyne cycloaddition, a typical click reaction. More importantly, thanks to the high polarity and electron-withdrawing ability of the formed 1,4-disubstituted 1,2,3-triazole rings, the *E/Z* isomers were facilely isolated *via* column
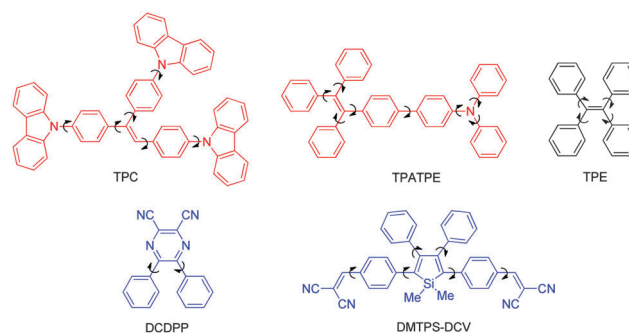
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Chart 1 Chemical structures of representative P-type (red), neutral (black) and N-type (blue) AIEgens.

chromatography for the first time. Using the pure isomers, the plausible E/Z isomerization for the AIE mechanism was excluded.[10]

Moreover, 1,5-regioisomers could also be prepared by the azide–alkyne click reaction in the presence of Cp*Ru(PPh$_3$)$_2$Cl.[11] The varying regioregularity of triazoles will endow them with distinctly different properties as demonstrated in our previous work.[12] Nevertheless, few studies have been carried out to investigate the effect of regioregularity of triazole-based AIEgens on their properties. In this work, we integrated pyrazine and triazole moieties together to generate new N-type AIEgens and to investigate their interesting properties.

The Cu(PPh$_3$)$_3$Br- and Cp*Ru(PPh$_3$)$_2$Cl-catalyzed click reactions of 2,3-dicyano-5,6-bis(4-ethynylphenyl)pyrazine (1) and 1-(6-azido-hexyloxy)benzene (2) under mild reactions readily furnish 1,4- and 1,5-regioregular 3a and 3b in yields higher than 80%, respectively [Scheme 1, see the ESI† for detailed synthetic procedures]. 3a and 3b are soluble in commonly used organic solvents, such as THF, dichloromethane, chloroform, and insoluble in water. They are thermally stable. As can be seen from Fig. S1 (ESI†), the temperatures for 5% weight losses are higher than 390 °C. However, they possess glass transition temperatures of ca. 50 °C probably due to the presence of alkyl chains.

Their structures were fully characterized using spectroscopic methods and satisfactory analysis data were obtained (Fig. S2–S8, ESI†). We first measured their ^{1}H NMR spectra in CDCl$_3$ (Fig. S6, ESI†), which showed that the resonance of the ethynyl protons of 1 at δ 3.27 had disappeared in 3a and 3b. However, the peaks are severely overlapped in down-field, which makes the identification of the regioisomers difficult. Delightfully, in our previous work, we have shown that the ^{1}H NMR spectra of triazole-containing molecules and polymers have a better resolution in DMSO-d_6 than that in CDCl$_3$.[12a] We thus re-measured the ^{1}H NMR spectra of 3a and 3b in DMSO-d_6 (Fig. S7, ESI†). From the spectra, we can observe that the protons of 1,4- and 1,5-regioregular triazole resonate at δ 8.68 and 7.96, respectively. Furthermore, no resonance proton signal of 1,5-regioregular triazole was seen in 3a (vice versa), indicating that pure 1,4- and 1,5-regioisomers were obtained.[13]

After confirming their structures, we studied their photophysical properties. The absorption spectra of 3a and 3b showed maximum absorptions at 367 and 346 nm in THF, respectively (Table S1, ESI†). Moreover, in solution, 3a emits at 474 nm, which has a 16 nm red-shift compared to 3b (Fig. 1A and Fig. S9, ESI†). Theoretical
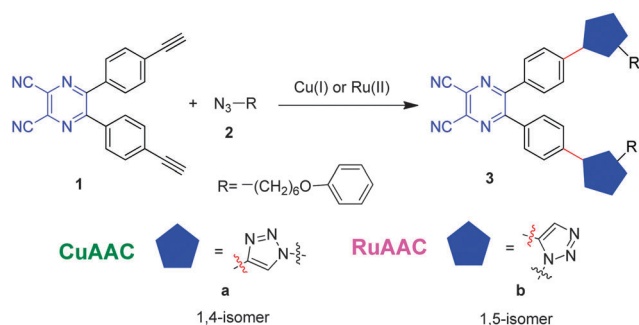
Scheme 1 Synthetic routes to 1,4- and 1,5-regioregular triazole containing pyrazine-based N-type AIEgens.
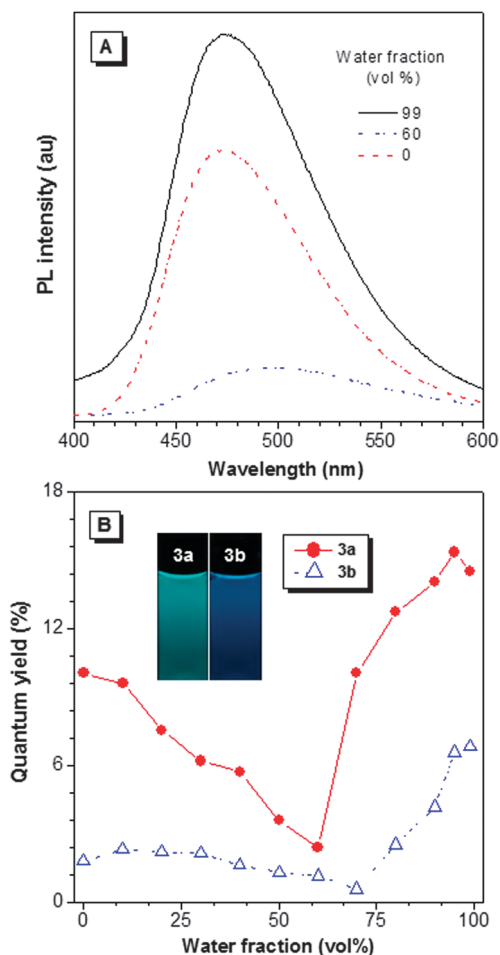

Fig. 1 (A) PL spectra of 3a in THF−water mixtures with different water fractions (f_w); λ_{ex} = 367 nm, [3a] = 10 μM. (B) Changes in the fluorescence quantum yield (Φ_F) of 3a and 3b in THF−water mixtures with f_w. Inset: photographs of 3a and 3b in THF−water mixtures with f_w of 99%, which were obtained under a UV lamp.

calculations using a DFT/B3LYP/6-31G(d,p) basis set also showed that 1,4-isomer of 3a is structurally more planar than the 1,5-isomer of 3b, and hence electronically more conjugated due to the less steric effect between the triazole rings and the adjacent phenyl rings (Table S2, ESI†).[12a] In addition, the emission of 3a and 3b is red-shifted compared to DCDPP (423 nm), manifesting that the triazole rings have extended the conjugation of the resultant molecules.[5c]

DCDPP is AIE-active. Do its derivatives 3a and 3b behave similarly? We measured their photoluminescence spectra and quantum yield (Φ_F) in THF−water mixtures with different water fractions (f_w). Although the absorption of 3a and 3b changed little upon addition of water into their THF solutions (Fig. S10, ESI†), the Φ_F showed nearly sustained decrease until the f_w reached 60 and 70%, accompanied by red-shifts of their emission peaks about 23 and 17 nm, respectively. This phenomenon could be reasonably explained by a twisted intramolecular charge-transfer (TICT) mechanism.[14] Once the f_w increased beyond these values, obviously enhanced Φ_F values were observed, which became the largest at the f_w values of 95 and 99%, respectively (Fig. 1B),

demonstrating an AIE activity. In this stage, **3a** and **3b** begin to aggregate because the solvating power of the aqueous mixture decrease, making the Φ_F enhanced due to the RIR effect. Meanwhile, the TICT effect is efficiently weakened. This mutual competition results in the enhancement of the emission and Φ_F.

It is interesting to note that the Φ_F of **3a** is much higher than that of **3b** both in the solution and aggregate states. The structure of **3b** is more congested than that of **3a**, which offers it a larger free volume for the phenyl rings to rotate even in the aggregate state and hence dissipates the energy of the excited state non-radiatively.

As discussed above, dicyanopyrazine and triazole moieties are electron-withdrawing groups, which make **3a** and **3b** electron-deficient, too. To prove this interesting property, we first characterized them using the cyclic voltammetry (CV) technique. The results (Fig. 2A and Fig. S11, ESI†) indicated that the LUMO energy levels of **3a** and **3b** are deduced to be −3.28 and −3.39 eV, respectively, which are much lower than those of conventional and commercial electron transport materials, such as tri(8-hydroxyquinoline) aluminum (Alq$_3$, −3.0 eV) and 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBi, −2.7 eV) (Table S1, ESI†), demonstrating a typical N-type property. This trait endows AIEgens containing such N-type structures with excellent electron transporting properties and also facilitates the electron injection from the LiF/Al cathode if they are used for the fabrication of organic light-emitting diodes (OLEDs).

By taking advantage of their strong electron-withdrawing abilities, we fabricated their complexes with a strong electron-donating molecule of triphenylamine (TPA). Mechanical trituration of **3a** or **3b** with TPA readily furnished homogeneous blends. Excitingly, the complexes showed conspicuous red emission under the illumination of a UV lamp (Fig. 2B). It is worth noting that new emission peaks of **3a**/TPA and **3b**/TPA complexes were recorded at ∼620 and 607 nm, respectively (Fig. S12 and S13, ESI†) in the solid states. Moreover, no obvious variation in emission wavelength and intensity could be observed through moderate change of the mixed molar ratio of **3a** or **3b** with TPA.
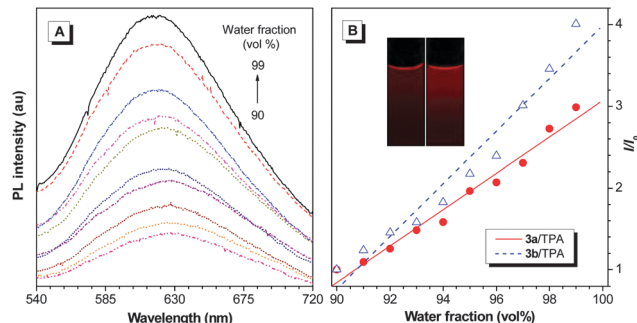
Fig. 3 (A) PL spectra of **3a**/TPA in THF−water mixtures with f_w from 90 to 99%. λ_{ex} = 380 nm. (B) Changes of PL intensity (I/I_0) of **3a**/TPA and **3b**/TPA with f_w. [**3a**] = [**3b**] = [TPA] = 10 μM. Inset: photographs of **3a**/TPA (left) and **3b**/TPA (right) in THF−water mixture with f_w of 99%, which were taken under a UV lamp.

To obtain a detailed understanding of this phenomenon, the photophysical properties of the isomer/TPA complexes were investigated in their aggregates. As depicted in Fig. 3A and Fig. S14 and S15 (ESI†), the absorption profiles of **3a**/TPA and **3b**/TPA showed almost no changes in THF−water mixtures with an f_w value of 90−99%. The peaked emission intensities of **3a**/TPA and **3b**/TPA at ∼617 and 633 nm in THF−water mixtures with f_w of 90−99%, however, increase linearly, respectively. Upon addition of water, the environment surrounding the complexes becomes hydrophilic, which forces the complexes to pack tightly and facilitates the charge-transfer and restricts the intramolecular rotation of **3a** and **3b** at the same time, thus leading to enhanced emissions. The 18 nm red-shift of emission of **3b**/TPA in THF−water mixture is likely due to the lower LUMO energy level and more twisted structural conformation of **3b** (Fig. 3B).[15] Moreover, **3a**/TPA and **3b**/TPA (both molar ratios are 1 : 1) in the thin film states also emit in the red light region with peaks at ∼610 nm (Fig. S16, ESI†), indicating that the charge-transfer process is a universal phenomenon in the condensed phases.

In summary, N-type pyrazine-based 1,4- and 1,5-disubstituted 1,2,3-triazole derivatives of **3a** and **3b** were facilely synthesized using Cu(PPh$_3$)$_3$Br- and Cp*Ru(PPh$_3$)$_2$Cl-catalyzed click reactions, respectively. Both isomers possess higher Φ_F values in aggregate states than in solution states, demonstrating an aggregation-enhanced emission. The addition of water into their THF solutions showed that the emission first decreased due to the TICT effect and then increased because of the RIR process. Thanks to their strong electron-withdrawing ability, their complexes with TPA readily red-shifted their emission from 474 and 458 nm in solution to 617 and 633 nm in the aggregate states, respectively. This work not only provides an efficient approach to synthesize novel N-type AIEgens but also demonstrates a new strategy to generate AIE systems with red emission.
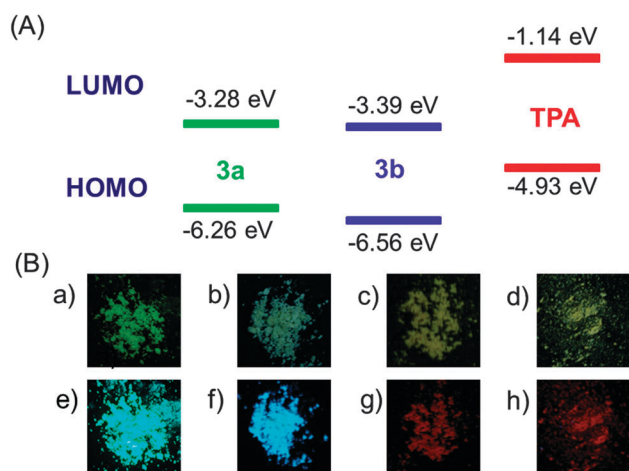
Fig. 2 (A) Energy level diagram of **3a**, **3b** and TPA estimated via cyclic voltammetry. (B) Photographs of **3a** (a, e), **3b** (b, f) and **3a**/TPA (c, g) and **3b**/TPA (d, h) in solid states obtained under room lighting (a−d) and UV illumination (e−h). All isomer/TPA mixtures are prepared with the molar ratio of 1 : 1.

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