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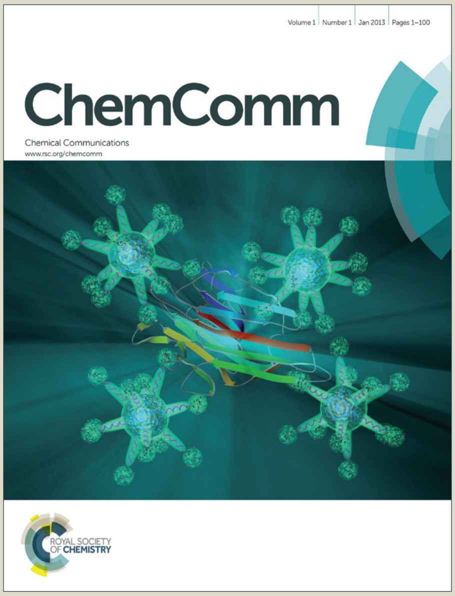

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N-type pyrazine and triazole-based luminogens with aggregation-enhanced emission characteristics

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N-type pyrazine-based 1,4- and 1,5-disubstituted 1,2,3-triazole derivatives, showing the unique aggregation-enhanced emission characteristics, were facilely prepared by the Cu- and Ru-catalysed azide-alkyne cycloadditions, respectively. Thanks to their electron-deficient property, 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 interests for their potential applications in optoelectronic devices, chemical sensors and biological probes.[1] However, most of conjugated organic molecules emit more efficiently in the solution but the 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, the aggregation-induced emission (AIE), conceptually termed in 2001 by Tang et al. is promising because it can enable the naturally occurred aggregation to play positive instead of negative roles in enhancing the emission efficiency in the aggregate or solid states.[3,4] The restriction intramolecular rotation (RIR) has been proved experimentally and theoretically to its mechanism, which has been widely adopted by researchers to explain their observed emission behaviors of AIE-active luminogens (AIEgens).[5]

The AIE phenomenon has been attracting increasing interests among the researchers worldwide. With their enthusiastic efforts paid, hundreds of AIEgens with full color emission have been developed and their potential high-tech applications in organic light-emitting diodes, high 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-diphenylpyrazine (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 electron property has not been revealed yet. Inspired by this prospect, in this work, we expanded and systematically investigated this pyrazine-based system in the hope to develop new N-type AIEgens.

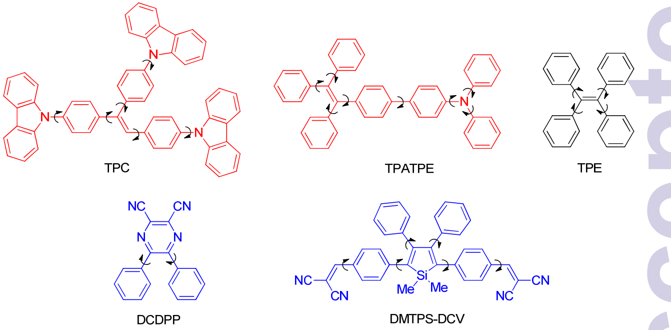


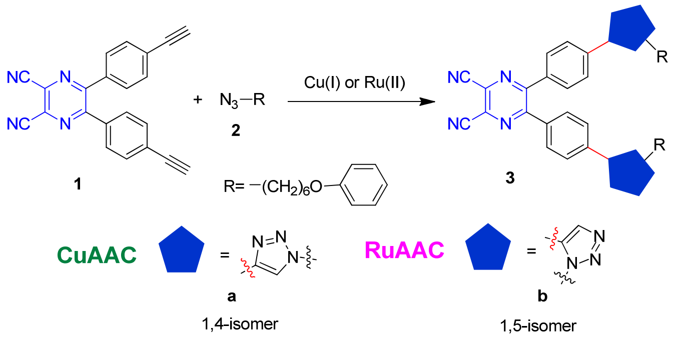
Chart 1. Chemical structures of representative P-type (red), neutral (black) and N-type (blue) AIEgens.

During the course of chemical decoration of AIEgens, click reaction was employed as it shares such fascinating merits as high efficiency, regioselectivity and atom economy.[9] For example, tetraphenylethene (TPE)-cored 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 formed 1,4-disubstituted 1,2,3-triazole rings, the *E*/*Z* isomers were facilely isolated via column 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 property as demonstrated in our previous work.[12] Nevertheless, few study has 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 reaction of 2,3-dicyano-5,6-bis(4-ethynylphenyl)pyrazine (**1**) and 1-(6-azidohexyloxy)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 Electronic Supplementary Information, (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 Figure S1 (ESI†), the temperatures for 5% weight losses are higher than 390 °C. However, they possess the glass transition temperatures of ca. 50 °C probably due to the containing alkyl chains.



Scheme 1. Synthetic routes to 1,4- and 1,5-regioregular triazole containing pyrazine-based N-type AIEgens.

Their structures were fully characterized by 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†), from which we found the resonance of ethynyl protons of **1** at δ 3.27 was disappeared in **3a** and **3b**. However, the peaks severely overlapped in the down-field, which makes the identification of regioisomers difficult. Delightfully, in our previous work, we have shown that the ^{1}H NMR spectra of triazole-containing molecules and polymers have 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 find the protons of 1,4- and 1,5-regioregular triazole resonated at δ 8.68 and 7.96, respectively. Furthermore, no resonance proton signal of 1,5-regioregular triazole was found in **3a** (*vice versa*), indicating that pure 1,4- and 1,5-regioisomers were obtained. [13]

After confirming their structures, we studied their photo-physical 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 16 nm red-shift compared to **3b** (Fig. 1A and Fig. S9, ESI†). The theoretical calculation using DFT/B3LYP/6-31G(d,p) basis set also showed that 1,4-isomer of **3a** is structurally more planar than that of 1,5-isomer of **3b**, and hence electronically more conjugated due to the less steric effect between triazole rings and adjacent phenyl rings (Table S2, ESI†).[12a] In addition, the emission of **3a** and **3b** 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. Whether its derivatives of **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 with addition of water into their THF solutions (Fig. S10, ESI†), the Φ_F nearly sustained to decrease until the f_w reached to 60 and 70%, accompanying with 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 beyond these values, obvious enhanced Φ_F values were observed, which became the largest at the f_w 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

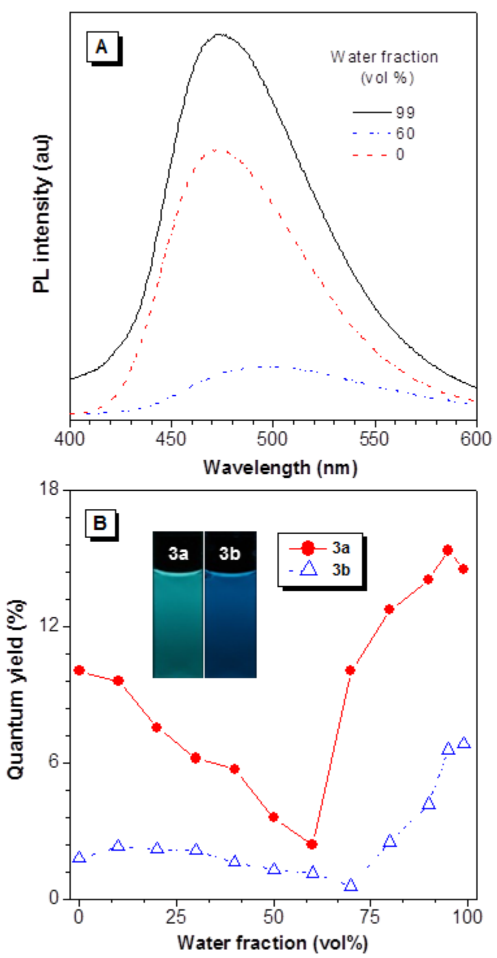


Figure 1. (A) PL spectra of **3a** in THF/water mixtures with different water fraction (f_w); λ_{ex} = 367 nm, [**3a**] = 10 μM. (B) Changes in the fluorescence quantum yield (Φ_F) of **3a** and **3b** in THF/water mixtures with f_w. Inset: photographs of **3a** and **3b** in THF/water mixtures with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

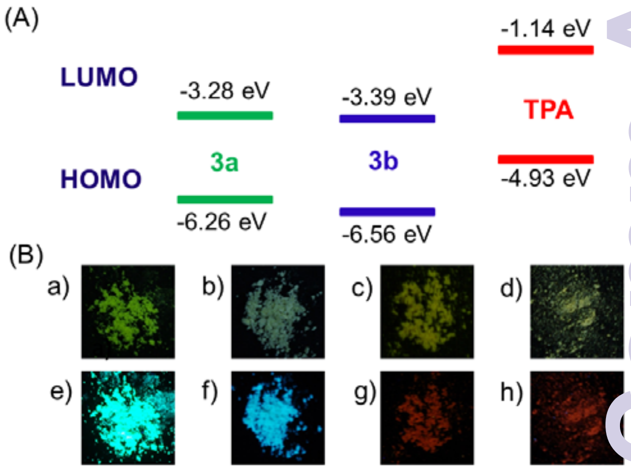


Figure 2. (A) Energy level diagram of **3a**, **3b** and TPA estimated by cycl voltammetry. (B) Photographs of **3a** (a, e), **3b** (b, f) and **3a**/TPA (c, g) ar **3b**/TPA (d, h) in solid states taken under room lighting (a-d) and U illumination (e-h). All isomer/TPA mixtures are prepared with the molar ratio of 1:1.

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 congest than that of **3a**, which offers it larger free volume for the phenyl rings to rotate even in the aggregate state and hence dissipate the energy of excited state non-radiatively.

As we 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 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 that 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 structure with excellent electron transporting property and also facilitates the electron injection from the LiF/Al cathode if they are used to fabricate light-emitting diodes (OLEDs).

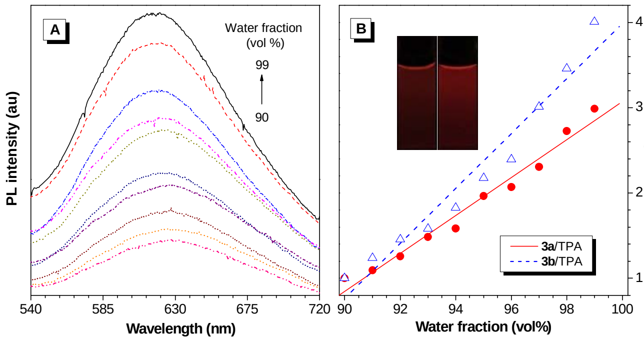


Figure 3. (A) PL spectra of **3a**/TPA in THF/water mixtures with f_w from 90 to 99%. λ_{ex} = 380 nm. (B) Changes of PL intensity (I/I_0) of **3a**/TPA and **3b**/TPA with f_w. [**3a**] = [**3b**] = [TPA] = 10 μM. Inset: photographs of **3a**/TPA (left) and **3b**/TPA (right) in THF/water mixture with f_w of 99%, which were taken under a UV lamp.

By taking advantage of their strong electron-withdrawing abilities, we fabricated their complexes with strong electron-donating molecule of triphenylamine (TPA). Mechanical trituration of **3a** or **3b** with TPA readily furnished homogeneous blends. Excitingly, the complexes gave conspicuous red fluorescence 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 (Fig. S12 and S13, ESI†) in the solid states. Moreover, no obvious variation of emission wavelength and intensity could be observed through modest alerting of the mixed molar ratio of **3a** or **3b** with TPA.

To have a detailed understanding of this phenomenon, the photo-physical property of the isomer/TPA complexes was investigated in their aggregates. As depicted in Figure 3A and Figures S14 and S15 (ESI†), the absorption profiles of **3a**/TPA and **3b**/TPA remained almost no changes in THF/water mixtures with f_w 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. With addition of water, the environment surround the complexes become 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 (molar ratio are both 1:1) in the thin film states also emit in the red light region with peaks at 610 nm (Fig. S16, ESI†), indicating that 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 by $Cu(PPh_3)_3Br$- and $Cp^*Ru(PPh_3)_2Cl$-catalyzed click reaction, respectively. Both isomers possess higher Φ_F in aggregate states than that 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 way to synthesize novel N-type AIEgens but also demonstrates a new strategy to generate AIE systems with red emission.

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† Electronic Supplementary Information (ESI) available: Synthetic details, ^1H and ^{13}C NMR spectra, absorption and photoluminescence spectra, and CV curves of **3a** and **3b**. See DOI: 10.1039/c000000x/

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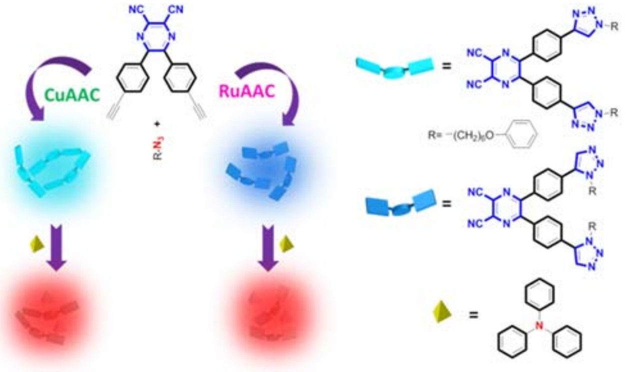

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