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PAPER

# Aggregation induced emission in the rotatable molecules: the essential role of molecular interaction<sup>†</sup>

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Aggregation-induced emission (AIE) compounds, **dye2** and **dye3**, with a rotatable N–N single bond and aza-crown-ether, have been synthesized. The fluorescence intensities of both dyes are very weak in THF, while become extraordinarily strong in a mixture of H<sub>2</sub>O–THF (v/v 95%). They are increased by 88.9 and 70.7 times, respectively, indicating enhanced blue-green fluorescence emissions. The  $\lambda_{em}$  of these two compounds in different states has been well studied. Besides this, **dye1** and **dye2** were characterized by single crystal X-ray structural determination. The results show that molecular interactions are formed in the particles, which considerably restrict the intramolecular vibration and rotation.

# Introduction

Recently, multifunctional materials, especially the organic materials have been widely applied in electroluminescence devices,<sup>1</sup> optical sensors<sup>2</sup> and biological fields.<sup>3</sup> The advantages of the organic materials are multifarious compared to polymers, such as strong fluorescence, high purity and controllable design strategies. The traditional studies of organic luminescent materials are usually conducted in the dilute solutions.<sup>4</sup> The solution investigations have made great contributions to the understanding of the fundamental science under luminescence at molecular levels, while the insufficiency cannot be ignored. The conclusions drawn from dilute solution data are not applicable to concentrated ones. It's well known that luminescence is often quenched at high concentrations, referred to as "aggregationcaused quenching" (ACQ),<sup>5</sup> thus limited its applications in real world which requires materials to be solid and phragmoid films.

Since the AIE phenomenon was first noticed by Tang and coworkers in 2001,<sup>6</sup> aggregation-induced emission (AIE) has attracted broad scientific interest by offering a new mechanism for researchers to explore new kinds of luminogens in recent years.<sup>6a,7</sup> The main characteristic of luminescent materials with AIE attributes, exactly the opposite characteristic of the ACQ effect, is that the fluorescence intensities are low as isolated

species, while rapidly increase in poor solvents or when made into thin films by aggregating into nanoparticles. Research has been devoted to the AIE systems and the structure-properties relationships,8 trying to gain insight into their working mechanisms. For example, Tang reported a series of AIE-active TPE derivatives<sup>9</sup> and explored their applications as sensors,<sup>10</sup> blue organic light-emitting diodes<sup>11</sup> and in vivo imaging.<sup>12</sup> Tian reported a group of triaryl-amine derivatives, which exhibit aggregation-induced emission and large two-photon absorption cross sections<sup>13</sup> and are potential non-doped red emitters for organic light-emitting diodes and gas chemodosimeters.14 Aprahamian developed a new kind of AIE-molecule, BF<sub>2</sub>hydrazone, which can be easily transformed into a solid-state acid/base sensor.15 However, the working mechanisms of the AIE processes are so complicated that they still remain unclear, although various theories have been advanced to explain the AIE phenomenon, such as planarity and rotatability,<sup>16</sup> intramolecular restrictions,17 intermolecular interactions,18 ACQ-to-AIE transformation<sup>19</sup> etc. The intramolecular rotation, one of the most influential mechanisms, was researched in depth.9c,20 While most of the studies are based on steric hindrance, Tong and coworkers<sup>21</sup> reported a compound with AIE attributes which are due to the intramolecular hydrogen bonds.

In this paper, **dye2** and **dye3** were synthesized (Fig. 1) with aza-crown-ether as the substituent, in considering its good solubility, electron donating ability and crown structure. **Dye1** was fabricated without aza-crown-ether substituent for comparison in order to further discuss the role of the aza-crown-ether structure in the AIE systems. The advantages of this design strategy are as follows: (1) two conjugate groups are connected by rotatable N–N single bond rather than C–C bond; (2) the rotatable flexible aza-crown-ether is the substituent rather than a rigid structure.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available. CCDC reference numbers 856816 for **dye1**, 848148 for **dye2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm32405a

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Fig. 1 The target molecules.

# **Experimental section**

#### Materials

Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Dimethylformamide (DMF) was distilled and dried over molecular sieves type 4A. Quinine sulfate was purchased from Exciton Inc. Sodium hydride and 2,2'-(phenylimino)diethanol were purchased from Aldrich. Diethylamine, triethyene glycol, tetraethylene glycol, 4-fluoro-benzaldehyde, phosphorus oxychloride and aliquate 336 were available commercially.

#### Instruments

IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs) in the 4000–400 cm<sup>-1</sup> region. A Varian liquid-state NMR operated at 400 MHz for <sup>1</sup>H-NMR and 100 MHz for <sup>13</sup>C-NMR was used for NMR spectra measurements, using DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as solvent, respectively. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in Hz. Splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). The mass spectra were obtained on a Bruker Autoflex III smartbeam mass spectrometer.

The one-photon absorption (OPA) spectra were recorded on the UV-265 spectrophotometer. The one-photon excited fluorescence (OPEF) spectra measurements were performed using the Hitachi F-7000 fluorescence spectrophotometer. OPA and OPEF of **dye1-dye3** were measured in THF with the concentration of 10  $\mu$ M. The quartz cuvettes used were of 1 cm path length.

#### Synthesis

The three compounds, **dye1**, **dye2** and **dye3**, were prepared according to the synthetic routes shown in Scheme 1. Detailed procedures and characterization can be found in the ESI.<sup>†</sup>

# Preparation of aggregates

Stock THF solutions of the molecules with a concentration of 1.0 mM were prepared. An aliquot (50  $\mu$ L) of this stock solution was transferred to a 5 mL volumetric flask. After adding an



Scheme 1 Synthetic routes to dye1, dye2 and dye3.

appropriate amount of THF, water was added dropwise under vigorous stirring to furnish 5 mL THF–H<sub>2</sub>O mixtures with water fractions ( $f_w$ ) of 0–95 vol%. The absorption and emission spectra of the resultant mixtures were measured immediately.

# **Results and discussion**

#### Synthesis

Synthetic routes of **dye1**, **dye2**, **dye3** and their intermediates were depicted in Scheme 1. The intermediate **a1**, **a2** and **a3** were synthesized efficiently according to the literature.<sup>22–24</sup> The targeted compounds (**dye1**, **dye2** and **dye3**) were obtained by the condensation of aldehyde and 85% hydrazine.

#### **Photophysical properties**

The profiles of the absorption spectra of **dye1**, **dye2** and **dye3** resemble each other in both shapes and positions in the dilute THF solutions, with the molar extinction coefficients ( $\varepsilon_{max}$ ) in the range of  $3.9 \times 10^4$ ,  $4.9 \times 10^4$  and  $4.4 \times 10^4$ , respectively (Fig. S1, ESI†). The absorption peaks are assigned to  $\pi$ - $\pi$ \* electronic transitions between the ground state and the excited state of the chromophore moiety, which suggests that the substitution of the crown do not bring great changes to the conjugation of the molecular structure as isolated species (Table 1).

In the emission spectra, however, the three dyes show weak fluorescence when dissolved in organic solvents, for the fluorescence quantum yields ( $\Phi$ ) of the three dyes, using quinine sulfate (in 1 N H<sub>2</sub>SO<sub>4</sub>,  $\Phi = 0.54$ ) as standard, are only 0.08, 0.09 and 0.11% in the dilute THF solutions, respectively. The results can mainly be explained by the photoisomerization, *viz*, the molecular planarity is reduced due to the rotating of the flexible-center when the molecules accept energy in the dilute solutions.

#### Aggregation-induced emission

The influence of the water fractions. To investigate the AIE attributes of these three dyes, we added different amount of

	$\lambda_{ab}^{a/nm}$ ( $\varepsilon_{max}/M^{-1}$ cm <sup>-1</sup> )	$\lambda_{\rm em}{}^b/{\rm nm}$	$\Phi$	Stokes shift/cm <sup>-1</sup>
Dye1	388.5 (39 082)	451	0.0008	3567
Dye2	387.5 (49 577)	451	0.0009	3634
Dye3	387.0 (43 798)	451	0.0011	3667

Table 1 Substituent effect on the absorption and fluorescence spectra of dye1, dye2 and dye3 in the dilute THF solutions

water, a poor solvent for the luminogens, to the pure THF solutions by defining the water fractions ( $f_w$ ) of 0, 0.2, 0.4, 0.6, 0.8, 0.9 and 0.95, and then monitored the photo fluorescence (PL) change.

The PL intensity of **dye1** increase slowly in aqueous mixtures when  $f_w < 0.60$ , and it is weakened or quenched (ACQ) when  $f_w > 0.60$  (Fig. S2, ESI<sup>†</sup>). However, the behaviors of **dye2** and **dye3** are quite different from that of **dye1**. The PL intensities of **dye2** and **dye3** increase slowly in aqueous mixtures when  $f_w < 0.60$ , while increase dramatically when  $f_w > 0.60$  (Fig. 2 and 3). From the pure THF solution to THF–H<sub>2</sub>O mixture with the  $f_w = 0.95$ , the PL intensities increase by 88.9-fold for **dye2** and **dye3** are greatly enhanced by aggregation. In other words, these two compounds are AIE-active materials while **dye1** is not.

The different properties with the different states. To gain further insight into the AIE mechanism of dye2 and dye3, we conducted a series of PL measurements in pure solutions, the mixed solutions with  $f_w = 0.95$ , the film, the powder and the single crystal (Fig. 4). As shown in Table 2, both dye2 and dye3 exhibit the minimum values of  $\lambda_{em}$  as the film and pure THF solution, the middle values of  $\lambda_{em}$  as the powder. It is interesting that the maximum values of  $\lambda_{em}$  are in the form of crystal and in the mixed solution with  $f_w = 0.95$ .



**Fig. 2** (A) Photographs of **dye2** in THF–H<sub>2</sub>O mixtures with different water fractions ( $f_w$ ) taken under UV illumination. (B) Emission spectra of **dye2** in THF–H<sub>2</sub>O mixtures. (C) Plot of ( $I/I_0 - 1$ ) values *versus* the compositions of the aqueous mixtures.  $I_0$  = emission intensity in pure THF solution. Solution concentration: 10  $\mu$ M.

Several findings are evident from the results in Table 2. (1) In the pure THF solution, both dye2 and dye3 are molecularly isolated without any interactions between the adjacent molecules. (2) The molecules of dye2 and dye3 in the crystal state are arranged so regularly that the rotatable N-N single bonds are locked due to molecular interactions, thus strengthen the  $\pi$ conjugated systems. (3) The molecules of dye2 and dye3 in the thin film state indicate the isolated species referring to the similar values of  $\lambda_{max}$  in both solutions, which is quite different from other AIE-molecules. It is probably because the film was prepared from a dilute solution  $(1 \times 10^{-5} \text{ M})$  and the solvent evaporated quickly. Besides, the chaotic molecules caused by the quick evaporation of solvent have no contribution to the molecular interaction, which leads to the unlocked rotatable center. (4) The irregular arrangement of the powder state may cause the middle value of  $\lambda_{em}$ . In addition, the structure of the particles in the solution with  $f_w = 0.95$  are similar to that of crystals due to their very similar values of  $\lambda_{em}$ , which suggests that the AIE effect is caused by the crystallization-induced emission (CIE) effect.

The crystal structure. In order to better understand the mechanism, we obtained single crystals of dye1 and dye2.

*Planarity.* There are two different molecules in a unit cell of **dye1** taking the unique features of the ethyl into account. One is



Fig. 3 (A) Photographs of dye3 in THF–H<sub>2</sub>O mixtures with different water fractions ( $f_w$ ) taken under UV illumination. (B) Emission spectra of dye3 in THF–H<sub>2</sub>O mixtures. (C) Plot of ( $I/I_0 - 1$ ) values *versus* the compositions of the aqueous mixtures.  $I_0$  = emission intensity in pure THF solution. Solution concentration: 10  $\mu$ M.



Fig. 4 The fluorescence spectroscopy of (a) dye2 and (b) dye3 in the pure solvents, the mixed solution with  $f_w = 0.95$ , the film, the powder and the crystal.

**Table 2** The  $\lambda_{em}$  of **dye1**, **dye2** and **dye3** in the pure solvent, the mixed solution with  $f_w = 0.95$ , the film, the powder and the crystal

	λ <sub>em</sub> /nm						
	Pure solvent	Mixed solution	Film	Powder	Crystal		
Ove1	451	463 495	468	526	512		
ve2	451	490	457	469	503		
ye3	451	492	442	476	500		

order (molecule II), and the other is disorder (molecule I). The dihedral angles are  $0.04^{\circ}$  ( $P_{Ia}-P_{Ib}$ ),  $9.94^{\circ}$  ( $P_{IIa}-P_{IIb}$ ),  $2.62^{\circ}$  ( $P_{Ia}-P_x$ ),  $6.31^{\circ}$  ( $P_{Ib}-P_y$ ),  $2.96^{\circ}$  ( $P_{IIa}-P_z$ ), respectively (Fig. 5a,  $P_x$ ,  $P_y$ ,  $P_z$  are the planes which consist of the C12–N3–N2, N3–N2–C11, C23–N6–N6' in **dye1**, respectively.) In **dye2**, the dihedral angles are  $1.69^{\circ}$  ( $P_{2a}-P_{2b}$ ) and  $9.86^{\circ}$  ( $P_{2a}-P_i$ ), respectively (Fig. 5b,  $P_i$  is the plane which consists of C1–N1–N1' in **dye2**.). The data of the crystals show that the planarity of both two molecules is good. That is to say, **dye1** and **dye2** are similarly planar.

*Rotatability.* Fig. 6a shows the packing diagram of **dye1**. The distance from H22B in molecule I to N6 in molecule II is 2.75(0) Å, and the angle of C–H…N is  $150.16^{\circ}$ . The flexible N–N single



Fig. 5 The restricted twisting motions in crystals of (a) dye1 and (b) dye2.

(a) (a) (x) (x)(x)

**Fig. 6** (a) Molecular packing diagram of **dye1** (inset: packing diagram simplification of **dye1**) (b) no fixed of the rotatable N–N single bond (the aza-crown-ether in (a) and hydrogen atoms except H22B in (b) are omitted for clarity).

bond cannot be locked substantially by the interaction and it's free to twist. While in the molecule I, there is no interaction around the flexible center. Thus, the photoisomerization process can hardly be prevented (Fig. 6b).

However, the case is completely different in dve2 indicated from the packing diagram shown in Fig. 7a. The distance between molecule  $\mathbf{a}$  and  $\mathbf{d}$  is 3.06(6) A, and the dihedral angle between molecule **a** and **c** is  $60.56^{\circ}$ . This phenomenon can be explained by the fact that the molecular interactions (H17B-C15, H17B-O4, H17B-C16, H17B-H16A) caused by the crown between molecule **a** and **b**, **b** and **d** shorten the distance between molecule a and d. Likewise, molecule c also contributes to shortening the distance owing to the molecular interactions caused by the crown between molecule **a** and **c**, **c** and **d** (Fig. 7b). That is the main reason for the decreasing distance between molecule **a** and **d**. Most of all, the new molecular interactions, from H3 in molecule c to C1, N1 in molecule a, are formed because of the shortened distance between molecule **a** and **b** (Fig. 7c). The distances of the molecular interactions are 2.87(8) Å and 2.58(8) Å, and the angle of C-H···C and C-H···N are 128.45° and 168.58°, respectively, suggesting strong interactions.<sup>25</sup> The interactions inhibit free twisting motions around the N-N single bond by fixing rotatable N-N single bond. Therefore, the molecule becomes rigid. In other words, the photoisomerization process around the N-N bond is not important, which ensures light radiation from the torsional molecules. Besides, the face-to-face  $\pi$ - $\pi$  interactions are restrained due to the interactions by the aza-crown-ether substituents. Thus, the strong interactions lead to a special packing manner and rigid

I

I



**Fig. 7** (a) Molecular packing diagram of **dye2** (inset: packing diagram simplification of **dye2**) (b) the repeating unit in packing (c) the fixed of the rotatable N–N single bond (the aza-crown-ether in (a) and (b), and hydrogen atoms except H3, H6, H16A, H17A and H17B in (c) are omitted for clarity).

molecular structure, making the fluorescence intensities multiply when packing.

The X-ray analyses of **dye1** and **dye2** show that the aza-crownether has a significant effect on the molecular packing modes and the molecular interactions, which leads to AIE-active molecules.

### **Electronic structure**

For further investigation at the molecular level, density functional theory calculations of the luminogens are carried out using Gaussian 03 program. The nonlocal density functional of B3LYP with 6-31G basis sets was used for the calculations. Their



Fig. 8 Optimized molecular structures and molecular orbital amplitude plots of HOMO and LUMO levels of the dye1, dye2 and dye3 calculated using the B3LYP/6-31G basis set.

highest-occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots are shown in Fig. 8. The HOMO and LUMO of **dye1**, **dye2** and **dye3** are dominated by the orbitals from the rotatable core and the phenyl units, which reveals that their absorption and emission stem from the  $\pi$ - $\pi$ \* transitions. Besides, the calculated bandgaps of **dye1**, **dye2** and **dye3** are similar (3.20 eV, 3.19 eV and 3.17 eV, respectively), which indicates the weak influence of the substituent for the whole molecule. The theoretical study nicely explains the similar optical properties of the three dyes in the dilute solutions.

# Conclusions

In summary, a series of flexibly cored chromospheres, **dye1**, **dye2** and **dye3** with or without aza-crown-ether as the substituents, have been designed and synthesized. The three compounds show weak fluorescence in the pure THF solution. With the changing water fractions, **dye1** exhibits the ACQ effect, while **dye2** and **dye3** show the AIE attributes. The optical properties of three different states for the three dyes have been well studied. A new process with the influence of the molecular interactions, in combination with planarity and rotatability mechanisms, has been discussed, which is identified by the X-ray analysis.

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