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1 Introduction

Organic small molecules with visible fluorescence are very important species which have been widely used in an ever expanding multidisciplinary arena. A common phenomenon called the concentration-quenching effect in the aggregated state always leads to the reduced or quenched fluorescent intensity of a dye by forming sandwich-shaped excimers or exciplexes between dye molecules in the excited and ground states.¹ Due to such a deleterious effect, the conventional fluorescent technology has to work in dilute solutions with drawbacks such as poor sensitivity and rapid photo-bleaching.

However, some unique fluorophores, which are intensely emissive in the aggregated state but faintly or even not fluorescent in solution, bring about the aggregation-induced emission (AIE) effect.² These AIE-active dyes are revolutionary for luminescent materials, as they can be directly utilized in the solid state without a reduction in the emission intensity. In recent years, AIE-active molecules have found use in a wide range of applications, such as organic electroluminescence devices,³ fluorescent sensors⁴ and photodynamic therapy⁵ and so on.

In the literature, the most common types of AIE-active systems involve molecules with at least a rotatable σ -bond axis or a flexible alicyclic component. Either the rotation around an σ -bond axis or the flipping of an alicyclic moiety is mainly responsible for the

(Z)-3-(Quinolin-2-ylmethylene)-3,4dihydroquinoxalin-2(1H)-one derivatives: AIE-active compounds with pronounced effects of ESIPT and TICT⁺

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A new family of (*Z*)-3-(quinolin-2-ylmethylene)-3,4-dihydroquinoxalin-2(1*H*)-one derivatives, which exhibit aggregation-induced emission (AIE) activity, is synthesized and characterized. The qualitative structure property analysis reveals that the emission behaviors of these compounds are closely related to the locations of substituents on the molecules. The density functional theory (DFT) calculations elucidate that excited state intramolecular proton transfer (ESIPT) can smoothly occur in these compounds and a following twisted intramolecular charge transfer (TICT) in the lowest excited singlet state should account for their fluorescence quenching in solution. The restriction of such a TICT process in the aggregated state is assumed as the mechanism for their AIE behaviors.

dramatically diminished fluorescence quantum yields of these systems in solution. The considerable constraint of such movements in the aggregated molecules should account for their enhanced emission in the excited state. For example, tetraphenylethene^{6b,d,e} and polyphenylsilole^{6a,c,f} are two typical cores for AIE systems, since the multiple phenyls act as propellers to decay the excited energy in solution by their free rotation. However, the rigid and twisted molecular structure in the aggregated state makes the π - π stacking impossible so that the excited state has to be relaxed via the radiative channel. In the case of BF₂ complexes with N-phenyl-3-[(phenylimino)methyl]-2H-chromen/thiochromen/3,4dihydronaphthalen-4-amine ligands,⁷ the flipping of the aliphatic rings is considered as the main reason for their faint fluorescence in solution and the inhibition of such movement is responsible for their AIE activity. Although the twisted intramolecular charge transfer (TICT) process is also widely approved as an important pathway for the radiativeless deactivation of the excited states in solutions,8 the reports on molecules whose AIE activity is caused by prohibiting the occurrence of a TICT process in the aggregated state are quite scarce,⁹ especially those coupled with the excited state intramolecular proton transfer (ESIPT) reaction, just like in the 2-(2'-hydroxyphenyl)benzothiazole-based series, 10a-c salicylaldehyde azine family^{10d} and its analogue.^{10e}

ESIPT reactions have been of great scientific and technological interest in recent years, as one of the most intriguing phenomena that can be utilized in the design of novel fluorescent dyes.¹¹ When either the acidic or basic part of the same molecule becomes a stronger acid or base in the excited state, proton transfer takes place in the excited state to form a phototautomer. In general, ESIPT is extremely fast occurring, within picoseconds,



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and upon excitation the molecule passes to the potential well of the tautomeric species almost instantaneously and then relaxes vibrationally.13 Such molecules often show dual emissions, one corresponding to the normal emission from the locally excited species and the other from the phototautomer with an abnormally large Stokes shift which can effectively eliminate self-absorption and improve the resolution of the emitted light against the incident ray. This merit is particularly significant for the accurate fluorescence analysis in field of chemistry and biology. Herein, a novel family of (Z)-3-(quinolin-2-yl-methylene)-3,4-dihydroquinoxalin-2(1H)-one derivatives with a remarkable ESIPT character is synthesized and characterized. Detailed measurements and theoretical calculations are carried out to establish the fundamental structure-property relationship in this family. Several experimental and computational approaches are used to explore what is the decisive factor for the AIE activity in these compounds, and the restraint of an excited-state TICT process in the aggregated state is presumed to be responsible for their AIE behaviors. Compared with the other common AIEactive molecules caused by the suppression of σ -bond rotation or alicycle flipping, our unique AIE system involving a TICT coupled with an ESIPT process displays a strong long-wavelength emission and an extraordinarily large Stokes shift over 100 nm. Such advantages can be readily achieved without the necessity of building a molecule with a complicated structure.

2 Results and discussion

2.1 Synthesis

Theoretically, a product with two tautomers (the conjugated isomer **1** and the non-conjugated one **2**) can be generated when *o*-phenylenediamine reacts with 2-oxo-3-(quinolin-2-yl)-propanoate

in the presence of catalytic *p*-toluene-sulfonic acid (Scheme 1). The NMR analysis reveals that the distribution of the two tautomers in a given product is closely related to the location of the substituents on the molecule. When a hydrogen atom or dimethoxyls are imposed on the quinolinyl moiety, **1b** or **1c** are exclusively offered with a trace amount of **2b** or **2c** that cannot be detected by NMR. The case is identical for the product where the dimethoxylphenyl is grafted on the N atom of the amide, in which only **1d** is the detectable isomer. However, when the dimethoxyls are introduced on the 3,4-dihydroquinoxalinonyl moiety, a mixture of **1a** and **2a** in a ratio of about 3.3:1 is afforded. Unfortunately, it is hard to isolate **1a** from **2a**, so they have to be used as a mixture. Unexpectedly, the sole tautomer **2e** is gained in good yield when *o*-phenylenediamine is reacted with ethyl 2-oxo-3-(quinolin-2-yl)-butanoate under the same reaction conditions.

Calculations based on the density functional theory (DFT) at the B3LYP/6-31G (d,p) level with the polarizable continuum model (PCM) can predict the difference of the Gibbs free energy between **1** and **2** at 25 °C and 1 atm in DMSO (Table S1, ESI†). It is shown that **1b–d** and **2e** are the overwhelmingly major isomers but **1a** coexists with **2a** in a ratio of about 3 : 1, in the respective thermodynamic equilibrium, according to the estimations of the $\Delta G = -RT \ln K$ equation (where ΔG is the difference of the Gibbs free energy between **1** and **2**, *R* is the gas constant, *T* is the tautomerism temperature (298 K) and *K* is the equilibrium constant of the tautomerism). Clearly, the DFT-based prediction for the distribution of **1** and **2** in a given product is in very good agreement with the results of the experimental determination.

Actually, there are two other tautomers, 1N [(Z)-3-(quinolin-2-ylmethylene)-3,4-dihydro-quinoxalin-2(1H)-one] and <math>1T [(Z)-3-(quinolin-2(1H)-ylidenemethyl)quinoxalin-2(1H)-one], in compound 1 (Scheme 1). Although the DFT calculations indicate that 1N is



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more thermodynamically stable than **1T** in the ground state for **1a-d** (Table S1, ESI[†]), the equilibrium between them is so kinetically ultrafast that the common NMR technology at room temperature is unable to differentiate them for each other. Hence, only one set of NMR signals can be obtained for them.

2.2 Photophysical properties in solution state

In organic solutions, **1a–d** are not emissive to the naked eye but **2e** gives off a discernible blue fluorescence. In THF solution, the quantum yields are determined to be 0.28% for **1a**, 0.82% for **1b**, 0.34% for **1c**, 0.32% for **1d** and 18% for **2e** (Table 1). Obviously, the visually observable blue fluorescence of the **1a** and **2a** mixture dominantly comes from the emission of **2a**. The photos of **1a–d** and **2e** in THF solution under a hand-held ultraviolet lamp at 365 nm are presented in Fig. S1 (ESI†).

Usually, an ESIPT process is much faster than the radiative relaxation of an excited normal isomer $(N^*)^{18}$ so that an abnormally large Stokes shift can result from the absorption of a ground-state N isomer and the emission of an excited tautomeric isomer (T*). Certainly, if a rapidly nonradiative channel exists in the T* state, its emission will be drastically diminished in solution, just like the situation in our AIE-active system.

Although a ground-state **N** or **T** isomer cannot be discriminated by NMR technology, they can be resolved by the absorption spectra (Fig. 1 and Fig. S2–S4, ESI[†]). As the DFT calculations verify that the **N** isomer has the more thermodynamic stability and population than the **T** isomer in the ground state, the major band in the high energy region and the minor band in the low energy region are assigned to the absorption of the **N** and the **T** isomer, respectively. For **1b–d**, the two bands are separated and each of them has a double-peaked fine vibration. For **1a**, however, one of the double peaks in the low energy region is combined into the

Table 1	Photophysical properties of compound 1a-d and 2e						
Compd.	$\lambda_{\mathrm{abs}} (\mathrm{nm}) / \varepsilon_{\mathrm{max}}^{a}$ (×10 ⁴ M ⁻¹ cm ⁻¹)	$\lambda_{\mathrm{em}}{}^{b,j}$ (nm)	Stokes shift ^k (nm)	$\lambda_{\rm em}^{c,j}$ (nm)	$\lambda_{\mathrm{em}}^{d,j}$ (nm)	Φ^e	<i>I/</i> <i>I</i> _{ТН} ғ
1a	458, 481 (1.12)	566, 610	108	<i>561</i> , 599	620	0.0028	18
1b	426, 450 (3.42)	<i>553</i> , 596	127	<i>553</i> , 591	592	0.0082	50
1 c	427, 452 (2.17)	<i>541</i> , 581	114	<i>542</i> , 579	588, <i>611</i>	0.0034	40
1d	433, 455 (2.33)	<i>545</i> , 586	112	547	580, <i>607</i>	0.0032	36
2e	317 (0.93)	425	108	g	h	0.18^{i}	h

^{*a*} The absorption spectra are determined in 2.0 × 10⁻⁵ M THF solution and characterized for the major absorption peaks. ^{*b*} The emission spectra (excited at the absorption maxima) are measured in 2.0 × 10⁻⁴ M THF solution and characterized for the major emission peaks. ^{*c*} The emission spectra are detected by doping 0.5% (wt) of compound in thin film with 5% (wt) poly(methyl methacrylate) and excited at the absorption maxima. ^{*d*} The emission spectra are measured by solid powder and excited at the absorption maxima. ^{*e*} Measured by reference to fluorescein in 0.1 N NaOH aqueous solution ($\Phi_{\rm f} = 0.91$). ^{*f*} Ratio of emission intensity in 90% H₂O-THF mixture and in pure THF solution. ^{*g*} Not determined. ^{*h*} No emission. ^{*i*} Measured by reference to quinine sulfate in 0.05 N H₂SO₄ aqueous solution ($\Phi_{\rm f} = 0.55$). ^{*j*} In italics is the peak with the larger emission intensity. ^{*k*} The Stokes shift is referred to as the difference between the major absorption and emission peak.



Fig. 1 The normalized absorption, excitation (λ_{em} at 600 nm) and emission (λ_{ex} at 450 nm) spectra of **1c** in THF solution (1 × 10⁻⁴ M), PMMA film and solid state.

band in the high energy region. It is observed that the band intensity of the T isomer on the absorption spectra is the largest in 1a but the least in 1b. Such a qualitative intensity order is in good agreement with the order of the T isomer population in the corresponding tautomeric equilibrium calculated by the Gibbs free energy difference (Table S1, ESI⁺). Additionally, the excitation spectra of these compounds monitored at 600-615 nm in THF was investigated, and it was found that both the band shape and the maximum are very similar to those of their absorption spectra (Fig. 1 and Fig. S2-S4, ESI⁺). This indicates that all high-level excited states can only relax to the same lowest excited state. Due to an ultrafast ESIPT from an N* to a T* state, the N* emission is dramatically suppressed, hence, the major band in the low energy region and the minor band in the high energy region of the fluorescence spectrum can be assigned to the T* and N* emission, respectively. Similarly, the intensity of the N* emission is also in the order of $1a > 1c \sim 1d > 1b$. The Stokes shifts between the major absorption and emission bands are more than 100 nm for all these compounds. Moreover, the emission maximum makes a considerably bathochromical shift for the molecule with electron-donating groups on either the dihydroquinoxalinonyl or the quinolinyl moiety. Owning to the disconnected π -conjugation between the above two moieties, the maxima in the absorption and emission spectra undergo a dramatic blue shift in 2e (Fig. S5, ESI[†]).

Interestingly, a unique excitation wavelength dependence of the T^*/N^* emission intensity ratio is observed for 1a, 1c and 1d (Fig. S15–S17, ESI†). It is illustrated in Fig. S8 (ESI†) that the ratio is linearly increased as the excitation wavelength is bathochromically shifted. However, the intensity ratio does not respond to the change of the excitation wavelength for 1b. Such a phenomenon in 1a, 1c and 1d indicates that the ESIPT rates in these compounds are very sensitive to variations of the excitation energy. A similar excitation wavelength dependence of the T^*/N^* emission intensity ratio is also observed for 4'-*N*,*N*-diethylamino-3-hydroxyflavone in ionic liquids,¹² but the truth about the dependency in our system is still under investigation.



Fig. 2 Absorption spectra of the **1a/2a** mixture in 1.5 \times 10⁻⁴ M THF solution under irradiation at 254 nm and 25 °C in air; normalized absorption spectrum of isolated **3a** in THF (dash line).

The photostability of these novel compounds have also investigated and the absorption spectra of 1a/2a mixture in THF were recorded periodically under irradiation at 254 nm and 25 °C in air (Fig. 2). It is illustrated that the absorbance value of the mixture gradually decreases while that of a new band centered at 367 nm simultaneously increases as the irradiation goes on. It was found that no new peak appears if the mixture in the degassed THF solution is exposed to irradiation under a N2 atmosphere for a long enough time. The case is the same when the solution stands in air without any irradiation. Hence, the new absorption peak should originate from the photo-oxidation product 3a. However, the structure of 3a cannot be determined by NMR analysis, as its solubility in common deuterated solvents is so low that a satisfactory ¹³C NMR spectrum could be achieved, even by the prolonged measurement. Despite our best efforts, a single crystal of 3a could not be obtained either. Thus, it was treated with benzyl bromide (Scheme 2) and the corresponding product 3a-Bn was found to have a largely enhanced solubility. According to the 1D and 2D NMR spectra of 3a-Bn along with the ¹H NMR spectrum

of **3a**, the structure of **3a** was proved to be 6,7-dimethoxy-3-(quinoline-2-carbonyl)quinoxalin-2(1*H*)-one. It was observed that the absorption edge of **3a** perfectly passes through the isosbestic point at 400 nm. Although the photo -oxidation can occur on both **1a** and **2a**, the rate is much faster for **1a** than for **2a**. With reference to **1a**, the relative photo-oxidation rate is 34.73% for **1b**, 14.15% for **1c** and 13.88% for **1d**.

2.3 Photophysical features in aggregated state

In the solid state, compounds **1b–d** exhibit an intense orange to red fluorescence. As a cousin of **2e**, which is detected to be barely emissive, **2a** can be safely considered as dark in the solid state. Hence, the visible fluorescence of the **1a/2a** mixture should be solely contributed by the emission of **1a**. The photos of **1a–d** and **2e** coated on the inner wall of bottles under a hand-held ultraviolet lamp at 365 nm are presented in Fig. S1 (ESI[†]).

The emission spectra of **1a–d** obtained by doping 0.5% (wt) of the corresponding compound onto a film with 5% (wt) poly(methyl methacrylate) (PMMA) (Fig. 1 and Fig. S2–S4, ESI[†]) demonstrates that the peak shape and the maxima of the **T*** emission are almost identical to those in THF solution. This indicates that the molecules are still in the isolated state instead of in the aggregated state in the PMMA film. However, due to the strong intermolecular interactions among the aggregated molecules, a remarkably red-shifted maxima can be observed for both the solid-state excitation and emission spectra with respect to those in THF solution.

1c was selected as a model to check its AIE activity. A THF solution of **1c** was titrated with water and the change in the emission intensity was monitored (Fig. 3). In pure THF solution, **1c** had a negligible emission intensity, which was gently increased as the water fraction (f_w) was increased to less than 70% [Fig. S6(a), ESI†]. During this period, the aqueous solution is still transparent. Beyond this f_w point, however, the emission intensity starts to drastically increase as the water content rises [Fig. S6(c), ESI†]. At this stage, the aqueous solution becomes



Scheme 2 Photo-oxidation reaction of the 1a/2a mixture and the following benzylation.

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Fig. 3 Emission spectra (excited at 450 nm) of **1c** in 1×10^{-4} M THF solution (the insert is the fluorescence intensity of **1c** depending on the water fraction in the H₂O-THF mixture).

turbid and intensely emissive due to the formation of many visible aggregates by the addition of water [Fig. S6(d), ESI[†]]. The UV-vis spectrum of 1c in the THF-water mixture [Fig. S6(b), ESI[†]] also confirms that the f_w around 70% is the boundary for a transparent or turbid solution. Below this content, 1c is well dissolved in the THF-water mixture and the absorption curves are almost identical to that in pure THF solution, except for a slight reduction of the absorbance values. Above this content, remarkable level-off tails in the long wavelength region along with the disappearance of fine vibrations and a decrease of the absorbance values, caused by the Mie effect of nanoparticles,¹⁴ can be readily observed. It was observed that the emission intensities in the aqueous THF solution with a 90% water fraction is 18, 50, 40 and 36-fold higher than that in pure THF solution for 1a, 1b, 1c and 1d, respectively (Table 1). The average nanoparticle size was determined by DLS to be 222.3 nm for 1a, 402.8 nm for 1b, 310.3 nm for 1c and 392.1 nm for 1d in the THF-H₂O mixture with a 90% water content (Fig. S7, ESI⁺).

Notably, an intramolecular planarity or a J-aggregation effect in the solid state is not presumed to be related to our AIE-active compounds. Although the single crystals of these compounds could not be obtained even, despite our best efforts, the optimized geometries of 1a-d predicted by the DFT calculations show that they are completely planar in solution, owning to the considerable restraints of the intramolecular H-bonds. Hence, it seems that there is no driving force for them to adopt the intramolecular planarity strategy so as to become emissive in the solid state. Besides, it is well known that the formation of J-aggregates is an important pathway to improve the emission in the solid state, and this effect is characterized by a considerable red shift of the original absorption bands with largely reduced bandwidths or the appearance of a sharp new band in the long-wavelength region with respect to those of the isolated chromophores.¹⁵ However, the absorption spectra of 1c in the THF-H₂O mixtures with different water fractions [Fig. S6(b), ESI[†]] clearly illustrate that neither the bathochromic shift of the absorption band nor the appearance of a new one occurs in

the pure THF solution through to the high water content medium. The case is the same for the absorption spectra of **1c** in THF-H₂O (1:9, v/v) mixtures with different concentrations (Fig. S22, ESI^{\dagger}). Therefore, a specific mechanism should account for the AIE behaviors of our compounds.

2.4 Theoretical calculations

The simulated UV-vis and fluorescence spectra of these compounds by the DFT and TD-DFT calculations in THF reproduce the experimental results at the low-energy absorption and emission bands. The calculated λ_{ab} maxima are 432 (427, 452 nm) for **1c**, 433 (426, 450 nm) for **1b** and 443 (458, 481 nm) for **1a**, while the calculated λ_{em} maxima are 560 (541, 581 nm) for **1c**, 564 (553, 596 nm) for **1b** and 572 (566, 610 nm) for **1a**. The calculated values are in good agreement with the experimental ones (in brackets). For all the **N**-isomers in **1a–d**, the S₀ \rightarrow S₁ transition exclusively has the HOMO \rightarrow LUMO (π/π^*) character (Fig. S9, ESI†). It was shown that the electrons on 3,4-dimethoxylphenyl (in **1d**) participate the π -conjugation with the other part of the molecule in neither the HOMO nor the LUMO. Therefore, the photophysical property of **1d** is very close to that of **1c** due to the lack of the π -contribution by 3,4-dimethoxylphenyl.

To better understand the photophysical properties of these AIE-active compounds, construction of the potential energy curves (PECs) in the S₀ and the S₁ state was undertaken by using TD-DFT calculations. The distance of the transferable hydrogen from the N₁ atom (wherefrom it is dissociated during the IPT reaction) in an N-isomer is considered as the independent reaction coordinate following the "distinguished coordinate" approach.¹⁶ Fig. 4 depicts such PECs at the S₀ and the S₁ state in a vacuum and THF solution for **1c**, respectively. The inclusion of the solvent stabilization energy does not change the picture qualitatively, but it has a greater impact on the S₁ than on the S₀ state, which implies that the S₁ state has a larger dipole moment than the S₀ state.

For 1a-c, the simulated PECs generated double-well potentials in the two electronic states (Fig. 4 and Fig. S10-S11, ESI⁺): the global minimum rests on an N-isomer in the S₀ state while the same corresponds to a T*-isomer in the S1 state. Quantitatively, the N-isomer is more stable than the T-isomer by 0.85 kcal mol⁻¹ for **1a**, 1.81 kcal mol⁻¹ for **1b** and 1.30 kcal mol⁻¹ for **1c** in the S₀ state, while the T*-isomer is more stable than the N*-isomer by 3.96 kcal mol⁻¹ for **1a**, 4.30 kcal mol⁻¹ for **1b** and 4.10 kcal mol⁻¹ for 1c in the S₁ state. Thus, the IPT reactions of these compounds appear thermodynamically unfavorable in the S₀ state but plausible in the S_1 state. Kinetically, the PECs also explain the feasibility of the ESIPT reactions, as the activation energy in the S_0 state is 6.54 kcal mol⁻¹ for **1a**, 6.98 kcal mol⁻¹ for **1b** and 6.78 kcal mol^{-1} for **1c** while the same is reduced appreciably to 2.94 kcal mol⁻¹ for **1a**, 2.80 kcal mol⁻¹ for **1b** and 2.72 kcal mol⁻¹ for 1c in the S₁ state. Both the thermodynamic and the kinetic factors support the ESIPT reactions, which result in an abnormally large Stokes shift between the absorption of an N-isomer and the emission of a corresponding T*-isomer.

After an ESIPT process, either a radiative or nonradiative relaxation is the destination of a T^* state. The rotation *via* a

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Fig. 4 Relative molecule total energy with varied bond length of N_1 -H in **1cN** by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF and gas phase.

bond is one of its nonradiative pathways. The PECs of **1cT*** built by considering the torsion angle of N₁-C₃-C₄-C₅ or N₂-C₅-C₄-C₃ as the independent reaction coordinate respectively show that the rotation *via* the C₃-C₄ bond is unfavorable in the S₁ state (Fig. S12, ESI†), as the energy minimum rests on a completely planar conformation. Hence, the nonradiative decay by rotation *via* the C₃-C₄ bond should be irresponsible for the low quantum yields of the solution-state **T*** emission in this family.

By contrast, the PECs reveal that the rotation in a T*-isomer *via* the C_4 - C_5 bond is permitted in the S_1 state (Fig. S13, ESI[†]). In the 1cT* state, the PEC produces a remarkable energy well at the orthogonal conformation (90°) and double peaks at the two planar ones (0° and 180°). It should be noted that the initially formed 1cT* would be near the H-bonded position at 0° because the ESIPT occurs on the H-bonded planar 1cN*. The peak energy of the H-bonded planar conformation is significantly lowered over the other planar conformation without the H-bond, strongly supporting the role of the H-bond stabilization in the torsion via the C_4 - C_5 bond. Moreover, the orthogonal conformation exhibits the obvious TICT characters: (i) most of the π -electrons are concentrated on the quinoxalinone part (donator) in the HOMO while they are almost entirely distributed on the dihydroquinoline part (acceptor) in the LUMO (Fig. S14, ESI[†]); (ii) the calculated dipole moment is raised from 4.25 D for the planar conformation in the S_0 state to 13.57 D for the orthogonal one in the S₁ state. It is known that an obviously red-shifted maximum and considerably reduced quantum yield are generally observed for a TICT emission in a polar solvent.



Fig. 5 Relative molecule total energy with varied torsion angle of $N_2-C_5-C_4-C_3$ in **1aT***, **1bT*** and **1cT*** by TD-DFT calculations at B3LYP/ PCM/6-31G(d,p) level in THF.

However, the maxima and the quantum yield of the major emission band in **1c** are very slightly varied in THF ($\lambda_{em} = 541$, 585 nm and $\Phi = 0.0034$) and in MeCN ($\lambda_{em} = 543$, 590 nm and $\Phi = 0.0029$). Hence, the major emission band should be assigned to the radiative relaxation of the residual **1cT*** with H-bonded planar conformation which is not promptly converted into the nonfluorescent TICT state.

Although the perpendicular conformations via the C₄-C₅ bond torsion have the global energy minima for 1a-c, their kinetic processes are quite different (Fig. 5). The planar conformation (0° torsion angle) rests on the energy summits of the PECs in 1a and 1c, but there is a shallow energy well for the planar conformation in 1b. Accordingly, an ultrafast and barrierless torsion toward the TICT state can be easily accessed for **1a** and **1c** in the S₁ state so that the radiative channel of the planar conformations is effectively blocked. However, the TICT process is delayed by the energy well to some extent in 1b so that a few of the planar conformations have the chance to emit their fluorescence in time. Hence, the quantum yield of 1b is about 3-fold higher than that of 1a and 1c. Although there is a larger energy fall between the planar and orthogonal conformations occurring in 1c (4.35 kcal mol^{-1}) than in 1a (3.13 kcal mol^{-1}), the quantum yields of 1a and 1c are approximate to each other. This suggests that the rotation of double methoxyls in 1a may contribute to the nonradiative decay, because the energy fall on the PECs is generated by using the N_2 -C₅-C₄-C₃ torsion angle alone as the independent coordinate without considering the other modes of movement. In spite of this, it is still assumed that the deactivation of a T* state is dominantly controlled by torsion via the C4-C5 bond instead of the rotation of substituents, as in 1b, which also possesses the double methoxyls and has a higher quantum yield than 1a.

Apparently, a TICT process involving a largely volume-consuming perpendicular torsion is readily accessible in low-viscosity solutions as the friction induced by such movement is quite small. However, this torsion is substantially restricted and the emission is gradually increased as the viscosity of the medium goes up.¹⁷



Fig. 6 Emission spectra of $1c~(25~\mu\text{M})$ with varied glycerol fraction in THF-glycerol mixture.

Hence, it can be expected that a TICT process is extremely suppressed in the aggregated state owning to its great viscosity (estimated to be at least 10¹¹ cP¹⁹). The emission dependence of the viscosity experiments clearly show that the fluorescence of compound **1a-d** is continuously enhanced in the THF-glycerol mixture, as the glycerol fraction rises (Fig. 6 and Fig. S18-S20, ESI[†]). Notably, a slight red- shift of the emission wavelength occurs even in the medium with 95% glycerol with respect to that in pure THF solution. This may well be caused by the good dissolution of these compounds in glycerol so that the aggregates are not formed in the THF-glycerol mixture. Instead, these compounds are very poorly soluble in water. Thus, the redshifted emission caused by the intermolecular interaction appears in a high water content medium due to the aggregate formation in it. Therefore, the AIE mechanism of our compounds can be expected to result from the restraint of the TICT process in the aggregated molecules in the excited state. Actually, the shallow energy well on the PEC in 1b is presumed to be caused by the enlarged friction between the dihydroquinolinyl fragment with dimethoxyls and the surrounding environment, compared with the situation in 1a and 1c.

3 Conclusion

Although there is a great number of reports on various AIE compounds, few have been presented with the ESIPT aspect. Herein, we describe the synthesis, characterization and photophysical properties of a novel family with significant AIE activity. Each of them can readily go through an ESIPT reaction followed by TICT-caused fluorescence quenching in solvent. However, it was verified that only the ESIPT reaction, rather than the TICT process, can be smoothly carried out in the aggregated state. The restriction of the torsion between the quinoxalinone and the dihydroquinoline fragment *via* the C_4 - C_5 bond in the S_1 state should predominantly account for the AIE phenomenon in this system. Compared with other common AIE-active molecules with short-wavelength emissions, our compounds exhibit an

intensely red fluorescence, which is very helpful for the bioanalysis of living specimens. The simple preparation procedure and the ready availability of the starting substrates make our AIEactive molecules quite easily accessible. The application of them in bioanalysis by further modification is under investigation.

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