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EDGE ARTICLE

Deciphering mechanism of aggregation-induced emission (AIE): Is *E*–*Z* isomerisation involved in an AIE process?[†]Nai-Wen Tseng,^{‡,ab} Jianzhao Liu,^{‡,ab} Jason C. Y. Ng,^{ab} Jacky W. Y. Lam,^{ab} Herman H. Y. Sung,^a Ian D. Williams^a and Ben Zhong Tang^{*abc}

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In this work, we address a mechanistic issue on AIE process and correct a long-held misconception on stilbene photoluminescence. *E*–*Z* isomerisation has been generally recognized as the cause of emission quenching in stilbene solutions. A natural question arisen from this common belief is whether suppression of *E*–*Z* isomerisation by aggregate formation in a stilbenic fluorogen system is responsible for its AIE phenomenon. Monitoring of the structural change of a stilbene derivative named 1,2-diphenyl-1,2-di(*p*-tolyl)ethene by NMR during UV irradiation reveals that the *E*–*Z* isomerisation is not involved in its AIE process under the normal photoluminescence spectral measurement conditions.

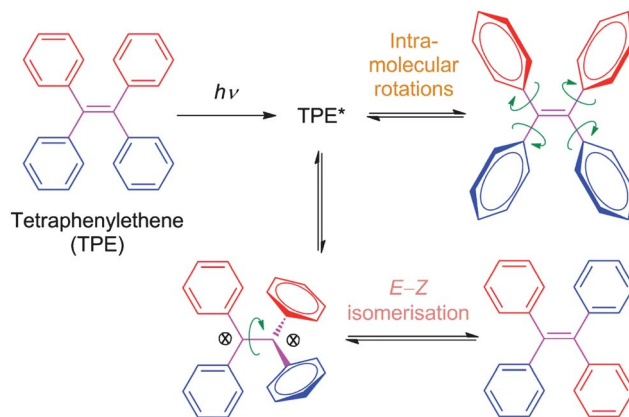
Introduction

Luminescence is usually quenched when luminophores are aggregated.¹ The aggregation-caused quenching (ACQ) effect is commonly observed in conventional luminophore systems and the ACQ phenomenon has thus been extensively studied. As a result, the ACQ process has been mechanistically well understood. The ACQ effect is undesired from the viewpoint of practical applications.^{1–3} For example, it poses a thorny obstacle to the development of efficient biosensors (working in aqueous media) and light-emitting diodes (serving in solid state), because organic luminophores are typically aromatic molecules, which have an intrinsic tendency to aggregate in the aqueous media and solid state.

We have discovered an exotic photophysical phenomenon of aggregation-induced emission (AIE): a series of propeller-shaped luminogens that are non-emissive in the solution state are induced to emit efficiently by aggregate formation in the solid state.^{4–6} The AIE effect is opposite to the ACQ effect discussed above and is technologically useful, as luminescent materials are utilized for real-world applications normally in the solid state. The AIE mechanism, however, is difficult to decipher, because the AIE effect is against what is taught in “classic” photophysics

textbooks.¹ Drawing a clear picture of the AIE mechanism is of fundamental significance and practical value, for it will help widen our photophysics knowledge and guide our research endeavors in developing new AIE systems and exploring their high-tech applications.

Tetraphenylethene (TPE) is an archetypal AIE fluorogen.⁷ Understanding its AIE mechanism is of importance, because many AIE fluorogens are its structural derivatives. We have proposed that its AIE effect is caused by a process termed restriction of intramolecular rotations (RIR).⁵ In the solution state, the multiple phenyl rotors in an isolated TPE molecule undergo dynamic intramolecular rotations on the axes of the σ -bonds linked to the central ethylene stator, which non-radiatively deactivates the excited state and renders TPE non-emissive (Scheme 1).^{5,6} In the aggregate state, however, the physical



Scheme 1 Potential pathways for deactivation of excited TPE species through intramolecular rotation and *E*–*Z* isomerisation processes. Symbol ⊗ denotes a radical, cation or anion.

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constraint obstructs the intramolecular rotations and activates the RIR process. This shuts down the non-radiative relaxation pathway and opens up the radiative decay channel, thereby making the TPE aggregates luminescent.

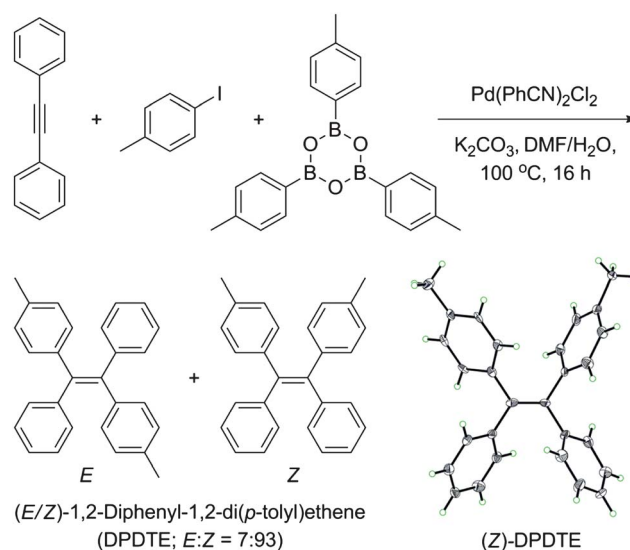
While the RIR mechanism has been well supported by a wealth of experimental data,^{5–7} one may wonder whether *E–Z* photoisomerisation is involved in the AIE process (Scheme 1). It is well-known that stilbene undergoes *E–Z* isomerisation upon UV irradiation, which has been generally recognized as the cause of emission quenching in the solutions of stilbene and its derivatives.^{8–11} Because TPE is structurally a stilbene derivative, extrapolation from this common knowledge leads to a conclusion that the *E–Z* photoisomerisation accounts for the non-emissive nature of its solution or that the suppression of the isomerisation by aggregate formation is responsible for the AIE effect of its aggregates.

Clarifying whether the *E–Z* isomerisation is involved in the fluorescence process of TPE is of great implications, as the photoinduced conformation change has often been blamed to be the funnel for quenching fluorescence of unrestrained or “free” fluorogens in biological systems, *e.g.*, blue-fluorescent antibodies¹⁰ and green fluorescence proteins (GFP).¹¹ It has been hypothesized that the capture of the stilbene hapten by the ligand-binding pockets of the antibodies and the trapping of the hydroxybenzylideneimidazolinone chromophore in the β -barrel of GFP have suppressed the *E–Z* isomerisation and revived the fluorescence processes.^{10,11} If it proves that the *E–Z* isomerisation is absent in the light-emission process of TPE, the biological fluorescence processes may need to be revisited mechanistically.

TPE has no *E/Z* isomers due to its symmetric structure and is thus unsuitable for studying the *E–Z* isomerisation process. In this work, we prepared a dimethylated TPE derivative called 1,2-diphenyl-1,2-di(*p*-tolyl)ethene (DPDTE) and investigated its photophysical behavior. The two methyl substituents in a DPDTE molecule serve as spectral reporters that enable the use of NMR for following conformational change, if any, in the photolysis process of the TPE derivative. Contrary to the general belief, our study shows that the *E–Z* isomerisation is not involved in the photoluminescence (PL) process of the stilbenic fluorogen under the normal PL spectral measurement conditions.

Results and discussion

Although many TPE derivatives can be readily prepared by Ti-catalyzed McMurry reaction, the products are typically 1 : 1 mixtures of *E/Z* conformers. To monitor the isomerisation process, it is a prerequisite to prepare a TPE derivative with a predominant or perfect *E* or *Z* conformation. We employed a Pd-catalyzed stereoselective coupling reaction,¹² with the aim of preparing a TPE derivative with a stereoregular structure. The reaction of toluene, *p*-iodotoluene and tri(*p*-tolyl)boroxin catalyzed by Pd(PhCN)₂Cl₂ produced DPDTE (Scheme 2), whose structure was duly verified by spectroscopic analyses [see Electronic Supplementary Information (ESI†) for details]. Careful inspection of its ¹H NMR spectrum (Fig. S1, ESI†) finds two small peaks at δ 6.89 and 2.24 besides the two main peaks at δ 6.91 and 2.26. Peak integration gives an *E/Z* ratio of 7 : 93, revealing that the product is *Z*-rich in conformation.



Scheme 2 Single-step synthesis of DPDTE and crystal structure of its (*Z*)-conformer.

Recrystallization of the *Z*-rich product afforded crystals of pure (*Z*)-DPDTE with quality suitable for X-ray diffraction crystallographic analysis. The crystal structure of (*Z*)-DPDTE is shown in Fig. S2, ESI† (CCDC 837495) and its crystal analysis data are summarized in Table S1 (ESI†). Like its parent form TPE (*cf.*, Fig. S3A, ESI†),^{7a} DPDTE takes a propeller-shaped conformation, with its phenyl rings twisted out of the central ethylene plane due to the involved steric effect. Its absorption spectrum in THF is similar to that of TPE (Fig. S4, ESI†). It shows an absorption peak at \sim 316 nm, which does not shift much when water is added into THF.

Same as TPE (Fig. S3B, ESI†), DPDTE is AIE active. Its solution in THF is non-emissive, whereas its aggregates in a THF/water mixture with a high fraction of water ($f_w > 80\%$) is emissive (Fig. 1A). The fluorescence quantum yields of its solution ($\Phi_{F,s}$) in THF and its aggregates ($\Phi_{F,a}$) in a THF/water mixture with $f_w = 95\%$ are 0.099% and 12.64%, respectively

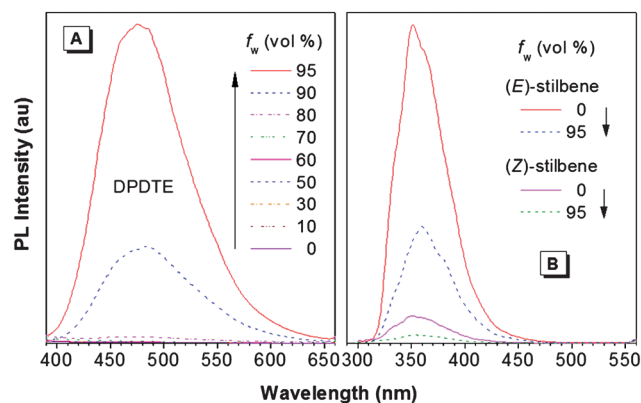


Fig. 1 Photoluminescence (PL) spectra of (A) DPDTE and (B) (*E*)- and (*Z*)-stilbenes in THF/water mixtures with different water fractions (f_w) and pure THF ($f_w = 0\%$). Fluorophore concentration: 10 μ M; excitation wavelength: (A) 340, (B) 290 nm.

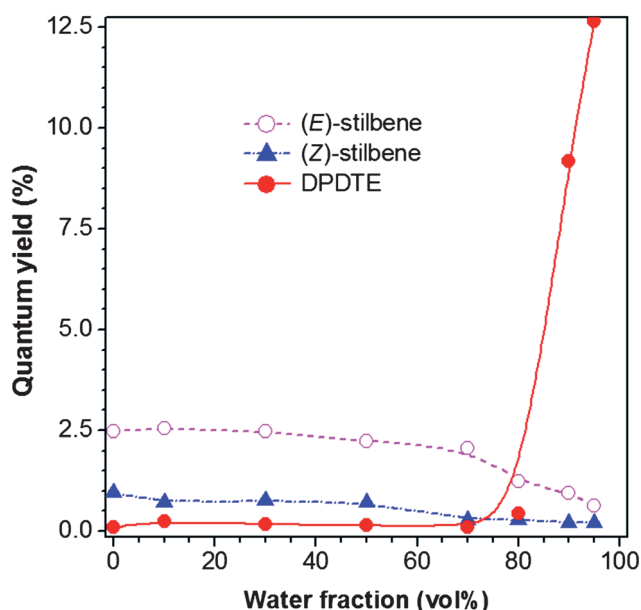


Fig. 2 Variations of fluorescence quantum yields of DPDTE and (*E*)- and (*Z*)-stilbenes with water fractions in THF/water mixtures. Dye concentration: 2.5 μ M; excitation wavelength: 320 (for DPDTE), 290 nm (for stilbenes).

(Fig. 2). This gives an α_{AIE} value as high as ~ 128 , when the AIE effect is defined as $\alpha_{\text{AIE}} = \Phi_{\text{F,a}}/\Phi_{\text{F,s}}$.¹³

After confirming the AIE nature of DPDTE, we checked whether *E*–*Z* isomerisation was involved in its fluorescence process. Luminescence spectra are commonly measured on a spectrofluorometer. We thus employed the light source in a standard spectrofluorometer to irradiate a solution of DPDTE for a prolonged period of time (29 min), although it usually takes just a short while (~ 1 min) to finish the measurement of a PL spectrum. The use of prolonged irradiation is to make sure that photoreactions, if any, will proceed to appreciable extents to induce enough changes that can be readily captured by an NMR spectrometer.

The serial ^1H NMR spectra taken at different time intervals during the course of photoirradiation (0–29 min) are shown in Fig. S5 (ESI †), while those taken at 0 and 14 min are given as examples in panels A and B of Fig. 3, respectively. The NMR spectrum remains intact throughout the whole course of UV irradiation. Integrations of the areas of the resonance peaks associated with the *E*- and *Z*-protons give the same *E*/*Z* ratio (7 : 93) for all the spectra. This indicates that the conformation of DPDTE is not altered by the UV irradiation, leading to a conclusion that the *E*–*Z* photoisomerisation is not involved in the PL process.

This conclusion is surprising, for it seems to contradict the above mentioned general belief.⁸ One possible reason for this contradiction is that the power of the UV light source in the spectrofluorometer ($\sim 52 \mu\text{W cm}^{-2}$) is too weak to give rise to a conformation change. To address this concern, we used a UV lamp with a much stronger power ($\sim 1.1 \text{ mW cm}^{-2}$) to irradiate the DPDTE solution. Change was instantly observed in the NMR spectrum (Fig. S6, ESI †). The resonance peaks for the protons in the *E*-conformer are intensified with lengthening

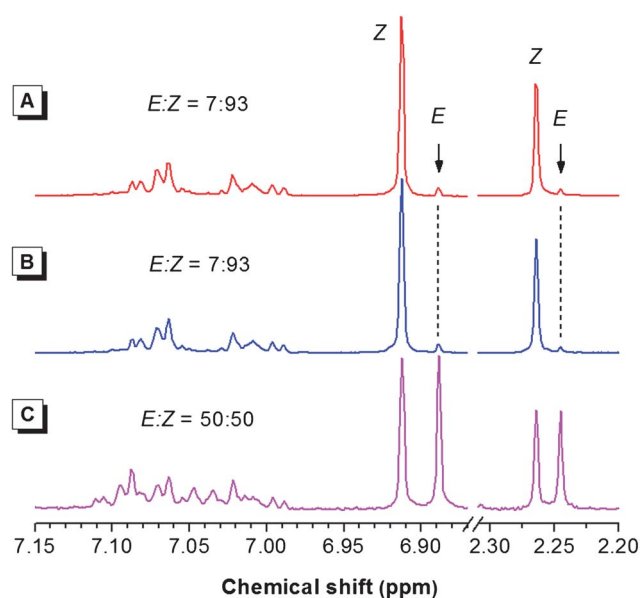


Fig. 3 ^1H NMR spectra of *Z*-rich DPDTE in CDCl_3 (A) before and (B, C) after exposure to the lights (B) in a fluorescence spectrometer and (C) from a UV lamp for 14 min. DPDTE concentration: 3.5 mM; excitation wavelength: 312 nm.

irradiation time. After irradiation for 14 min, the structure of DPDTE is totally randomized, as reflected by the *E*/*Z* ratio (50 : 50) of its photolysis product (Fig. 3C).

It has thus become clear that the DPDTE isomerisation is dependent on the power of the light source. Under the normal PL spectral measurement conditions, the *E*–*Z* isomerisation is not involved in the emission process, but when irradiated with a powerful UV light, the isomerisation readily occurs. In other words, the isomerisation is sufficient but not necessary for the PL quenching of DPDTE. To learn whether the photolysis of stilbene is also power dependant, we reinvestigated its photophysical behaviors. Similar to DPDTE, (*E*)-stilbene is a weak emitter. However, different from DPDTE, it becomes less emissive when its molecules are aggregated in the THF/water mixtures (Fig. S7, ESI †), showing an ACQ effect (Fig. 1B). (*Z*)-Stilbene shows similar behaviors, though its PL is always weaker than its (*E*)-isomer (Fig. 2).

No change in the NMR spectrum of (*E*)-stilbene is detected even after its solution has been irradiated by the light source in the spectrofluorometer for 30 min (panels A and B in Fig. S8, ESI †). Similarly, no change in its emission spectrum is observed. While the irradiation with the strong UV light does cause a conformational change, the extent of isomerisation is small, with the *Z* content increased by only 9%. Similar results are obtained for (*Z*)-stilbene. These data indicate that stilbene is more difficult to isomerize, in comparison to DPDTE.

The dissimilarity in the photophysical behavior of DPDTE and stilbene may stem from the difference in their molecular structures. As shown in Chart 1, most of the phenyl rings in (*Z*)-DPDTE are considerably twisted out of the ethene plane. The very large dihedral angles (up to -58.1°) indicate that the aromatic peripheries are little shackled by the alkene core. In an isolated DPDTE molecule, its conformational flexibility permits its phenyl rotors to undergo dynamic intramolecular rotations,

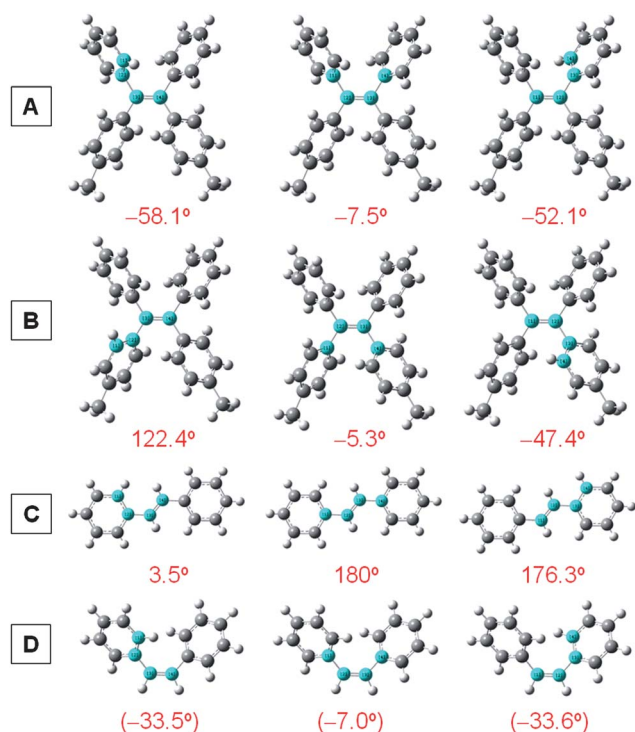


Chart 1 Molecular conformations and dihedral angles in (A, B) (Z)-DPDTE and (C) (E)- and (D) (Z)-stilbenes. Data for (E)-stilbene¹⁴ and (Z)-DPDTE are taken from single-crystal structures and data for (Z)-stilbene is obtained from DFT calculation.¹⁵

which annihilates its excited species and renders it non-emissive in the solution state. In the aggregate state, its non-planar propeller shape prevents molecular packing in a face-to-face fashion (CCDC 837495). ACQ effect is absent in this system due to the lack of π - π stacking interactions in the aggregates. The aggregate formation significantly stiffens the fluorogen conformation and activates the RIR process, thus endowing (Z)-DPDTE with the AIE activity.

(E)-Stilbene, on the other hand, has much smaller dihedral angles and is largely a planar luminophore (Chart 1C).¹⁴ The extended π -electron delocalization makes the conformation become more rigid, posing a barrier to the intramolecular rotations of its phenyl rings. The torsional motions of (E)-stilbene thus become less active and the twisting angles become smaller. As a result, its PL is attenuated to a less extent.⁵ This explains why its THF solution is somewhat fluorescent, with a $\Phi_{F,s}$ about 25-fold larger than that of (Z)-DPDTE (Fig. 2). When aggregated in the aqueous media, the PL process of (E)-stilbene is probably quenched by the π - π stacking interaction between the planar molecules, hence the observed ACQ effect.

Though crystal structure of (Z)-stilbene is unavailable as it is a liquid, theoretic modeling predicts that its dihedral angles (Chart 1D) are between those of (E)-stilbene and (Z)-DPDTE. Compared to the phenyl rotors in its (E)-isomer, those in (Z)-stilbene should be easier to undergo intramolecular rotations. This means that (Z)-stilbene is structurally more flexible and therefore its PL should be weaker.⁵ However, because it has only two phenyl rotors, their intramolecular rotations may not totally wipe out its radiative decay process, as in the case of

(Z)-DPDTE, where the active intramolecular rotations of its four phenyl rotors completely exterminate its PL process. The fact that the $\Phi_{F,s}$ value for the (Z)-stilbene solution is between those for the (E)-stilbene and (Z)-DPDTE solutions (Fig. 2) once again corroborates that the intramolecular rotations play a critical role in the fluorescence processes.

Conclusions

In this work, we have examined a mechanistic issue of the AIE process. Although it has been commonly accepted that *E*-*Z* isomerisation is the cause of weak PL in the solutions of stilbene derivatives, we prove it is not necessarily true. While DPDTE is a stilbene derivative, irradiating its solution with a UV light in a standard PL spectrometer for a prolonged time offers no sign of isomerisation. Similar data are obtained for the stilbene parent. Since emission processes are commonly studied by taking PL spectra on a spectrometer, it can thus be concluded that the isomerisation is not the cause for the PL quenching in the solutions of stilbene derivatives under the normal PL measurement conditions. While the RIR model has been supported by many experimental data,^{5,6} the exclusion of the involvement of the photoinduced *E*-*Z* isomerisation in the PL processes further validates the RIR mechanism for the AIE phenomenon.

The active chromophores in many advanced optoelectronic materials and fluorescent biosensors are stilbene derivatives. Our finding that the photoisomerisation is not a necessary, although sufficient, process to quench the stilbene emissions may stimulate research effort to revisit those well-established photophysical systems and to gain new mechanistic insights into the old problems. The further substantiation of the RIR mechanism for the AIE process in this work may facilitate the design of new AIE structures, synthesis of new AIE materials, and exploration of their technological applications, especially in the areas of development of solid-state emitters with high efficiency and nano-aggregate-based biosensors with excellent biocompatibility and strong photobleaching resistance.

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