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Tetraphenylethylene-incorporated Squaraine Dyes: Structural and Theoretical Insight into the Diverse Emission Behaviors in Solution and Solid State

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Endowing organic dyes desired emissive behaviors in diverse state is of great importance for broad practical applications but remains a huge challenge. In this contribution, based on the incorporation of tetraphenylethylene (TPE) into squaraine dyes we successfully synthesized **2TPE-SQ** and **TPE-SQ**, both emitting in dual-state with emission efficiency (Φ_{PL}) up to 0.33 and 0.75, respectively. The intense emission in crystalline state can be ascribed to highly resisted π - π stacking, while their different degrees of intramolecular phenyl motions in **2TPE-SQ** and **TPE-SQ** resulted into weak and moderate emission in solution. Combining density functional theory (DFT) calculations, local excited (LE)/twisted intramolecular charge transfer (TICT) and excited-state intramolecular proton transfer (ESIPT) mechanism accounted well for their very different solution and crystalline emission wavelength. Besides, other emission behaviors such as aggregation-caused quenching (ACQ), crystalline-induced emission enhancement (CIEE) and thermo-/mechanochromism of these two derivatives were also verified in detail, and all these results would bring a new insight into the investigation of organic luminogens in solution and solid state.

Introduction

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It is known that traditional organic luminophores are generally in planar structures and highly emissive in solution but nonfluorescent in the aggregated state due to active non-radiative pathways.^{1,2} This phenomenon was referred to as (ACQ) by Förster and Kasper and often hampers many fluorescencerelative practical applications. In contrast to ACQ, the aggregation-induced emission (AIE) effect was proposed by Tang's group³ in 2001 in the study of a series of twisted silole derivatives, which was nonemissive in dilute solution but became highly luminescent in aggregated formation. Since then, a large number of AIE-active molecules were reported, and largely increased the possibility of exploring organic materials with high solid-state emission efficiency thereby promoted diverse applications.4-16 Still and all, these incompatible solution/aggregation fluorescence mean a large gap between ACQ and AIE compounds, thus urges researchers to take advantages of both two phenomena for developing the materials with efficient dual state emission (DSE).¹⁷ These DSEactive luminogens will definitely be beneficial for much broader applications and molecular-level understanding the

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relationship between the fluorescent properties and monomeric/aggregated states.

Squaraines (SQs), as an important organic dye, exhibit sharp and intense absorption associated with a strong fluorescent emission in solution from visible to near-infrared region, which renders them favorable in advanced fields such as optical sensors, solar cells and fluorescent histological probes.¹⁸⁻²¹ Nevertheless, SQs are generally non-fluorescent in solid state or aggregate assembly due to intermolecular π - π interactions.^{22,23} This typical ACQ phenomenon has greatly restricted their application in solid state and bioimaging. Based on previous researches, it is reasonable that preventing intermolecular close-packing could be a facile strategy to access and even tune fluorescent SQs in solid state by adjusting sterically hindered substituents on the conjugated backbone.²⁴⁻²⁷ Moreover, Yin and colleagues have constructed an intense emitting symmetric SQ with formation of J-type nanostructures by introducing H-bonding in side carboxylic acid groups.²⁸ Very recently our group has also been committed to the design and application of highly emissive SQs in solid state and achieved a record-setting case with $arPsi_{
m PL}$ up to 0.81.29-31 Although state-of-the-art, all those elaborate solid emissive SQs turned out to be weak or even nonfluorescent in the dilute solution. This reversed situation makes a challenge in the compatibility of their excellent emission performance in solution and solid state, which would greatly broaden the SQs practical applications.

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Herein, DSE-active symmetric 2TPE-SQ and asymmetric TPE-SQ (Scheme 1) were firstly designed and synthesized with intersection of TPE group. Based on spectral analysis, 2TPE-SQ turned out to be weak emissive in solution but bright green emissive at 531 nm ($\Phi_{\rm PL}$ = 0.75) in crystalline state, which can be mainly ascribed that substantial intramolecular phenyl rotated in solution but highly resisted in solid state. As for TPE-SQ, it emitted in both solution and crystalline state with the highest $\Phi_{\rm PL}$ up to 0.33 at 564/588 nm and 0.61 at 627 nm, respectively. Single crystal diffraction analysis revealed that the efficient emission of TPE-SQ in solution was due to the restricted intramolecular phenyl motions, and that in crystal responded by a special packing mode dominated by multiple C-H···O and C-H··· π interactions. Combining theoretical DFT calculations, the different emission mechanism as LE-TICT³²⁻³⁶ in solution and ESIPT³⁷ in crystal was proposed and responded to their different emission wavelength. Besides, other emission behaviors such as ACQ, CIEE³⁸ and thermo-/mechanochromism³⁹ of these derivatives were also verified in detail, and all these results would bring some new insight into the investigation of organic luminogens in solution and solid state.

Results and discussion

Molecular design and synthesis

Previously reported SQ derivatives were mainly based on the activated arenes and electron-rich anhydrobases, whose planar structures endow them excellent rigidity with impressive emission in solution but quenched via aggregation.⁴⁰ As reported, the propeller-like TPE unit has been widely used in the structural design and synthesis of novel AlEgens and even DSEgens.⁴¹⁻⁴⁵ So that under this consideration, we attempted to synthesize symmetric **2TPE-SQ** and asymmetric **TPE-SQ** by intersecting two or one TPE group on their conjugated skeletons. This design was expected to afford the product SQs with novel properties: (1) the twisted TPE was inserted to suppress closed intermolecular molecular packing in the solid state; (2) the intersected aniline

group with preset intramolecular H-bonds will enhance intramolecular planarity thereby promote their rigidity in solution; and (3) the potential ESIPT^{31,46,47} mechanism was incubated to facilitate the remarkable red-shift and efficient emission.

The overall synthetic route of desired 2TPE-SQ and TPE-SQ was shown in Scheme 1. Both of them were isolated in great crystalline state after reaction and exhibited bright-green and intense red emission under 365 nm UV lamp, respectively. It is worth mentioning that this condensation reaction can be easily implemented with satisfied yields in the refluxing EtOH solution, whereas a ester exchange reaction can be observed in the refluxing BuOH/toluene under long-time azeotropic conditions. The target intermediates and products were fully characterized by ¹H NMR, ¹³C NMR and mass spectra (Fig. S1-S8). Additionally, rational assignments of the proton resonances of 2TPE-SQ and TPE-SQ were carried out and closely compared, which obviously implied that 2TPE-SQ and TPE-SQ possessed similar steric configuration (see Supplementary Information for details).

The photophysical properties of 2TPE-SQ and TPE-SQ in solution

The absorption and emission spectra of **2TPE-SQ** and **TPE-SQ** were measured in dilute solution with different polarity, and the results were summarized in Fig. 1 and Table S1. Both of **2TPE-SQ** and **TPE-SQ** showed obvious dual absorption and emission spectra in various solvents (Fig. 1a, b, d, e), which was in a rather good mirror image relations and might be associated to two different excited state. As shown, **2TPE-SQ** showed the maximum absorption peak (λ_{ab}) at 448 nm and a shoulder peak at 430 nm in tetrahydrofuran (THF, Fig. 1a). The two peaks could undergo blue-shift upon increasing the solvent polarity and merge into one broad band with short wavelength centred at 425 nm in dimethylsulfoxide (DMSO). Meanwhile, **2TPE-SQ** presented the strongest cyan emission color in toluene with a maximum peak (λ_{em}) around 473 nm and a shoulder peak around 493 nm (Fig. 1b), but the emission

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Fig. 1 a, d) Absorption and b, e) emission spectra of **2TPE-SQ** ($10 \mu M$, $\lambda_{ex} = 420 \text{ nm}$) and **TPE-SQ** ($10 \mu M$, $\lambda_{ex} = 500 \text{ nm}$) in various solvents, respectively; and c, f) their emission changes in THF solution with different fractions of water (f_w), at room temperature. Insert, their corresponding fluorescent images in different solvents under a 365 nm UV lamp; from left to right: Toluene, n-hexane, THF, CH₂Cl₂, DMSO.

efficiency ($arPhi_{
m PL}$) was only 0.07, which can be mainly responded by the fact that too many free phenyl rotors were in the 2TPE-SQ molecule and consumed large excited energy⁴⁸. Upon increasing the solvent polarity, the emission intensity of 2TPE-SQ was gradually decreased except in toluene thus implying there existed a charge transformation (CT) effect (Table S1). The exception in toluene, however, may attribute to excellent solvation effect between aromatic molecules of 2TPE-SQ and toluene.17 As for TPE-SQ, it exhibited a red-shift dual absorption and emission peak around 515/545 nm and 565/590 nm in varying solvents (Fig. 1d-e), suggesting its much longer conjugation. Moreover, the emission intensity of TPE-SQ would undergo similar decreasement in polar solvents as compared to 2TPE-SQ, implying their extremely analogical exited-state electronic structures in solution. It should be notable that the $\Phi_{\rm PL}$ of **TPE-SQ** was up to 0.33 in toluene (Table S1), indicating its much higher intramolecular rigidity with decreased free phenyl rotors. As for these intramolecular phenyl motions, this can be furtherly monitored by their temperature-dependent luminescent characteristics in toluene solution. As show in Fig. S9, 12.98 and 1.48 folds increased of their emissive intensity can be observed in 77k as compared to that at room temperature, confirming substantial and less intramolecular phenyl motions in 2TPE-SQ and TPE-SQ molecule in solution, respectively. Additionally, moderate emission signals were always observed for those two molecules even the temperature reached 373K, implying their robust solution emission. Moreover, no ESIPT process

was involved evidenced by the small Stokes shift in various solvents. The fluorescence decay profiles of both **2TPE-SQ** and **TPE-SQ** in solution were effectively fitted by applying a single

exponential function, with fluorescence lifetimes in the nanosecond time scale (Table S1 and Fig. S10).

Since TPE is an archetype AIE luminogen, the emission behaviors of those compounds in THF solution with different fractions of water (f_w , by volume) were then conducted (Fig. 1c, f). When the f_w increased from 0 to 80%, no nanoparticles were observed and the emission intensity of 2TPE-SQ decreased evidently with λ_{em} blue-shifted from 472 to 465 nm. As for this unusual change, this can owe to that the protic H₂O was able to interact with 2TPE-SQ and TPE-SQ via multiple hydrogenbonding interactions, which may lead to a net stabilization of its ground state and activation of nonradiation pathway of its excited state for an abnormal blue-shift and the decrease of emission intensity in the spectra.⁴⁹ Upon $f_{\rm w}$ over 90%, the emission intensity continued to decrease accompanying with $\lambda_{\rm em}$ red-shifted into the long wavelength at 525 nm, in which tiny nanoparticles can be observed and the emission intensity still decreased with f_w reached 100%. Very similar emission behaviors can be detected for **TPE-SQ** with increasing the f_w values, indicating a typical ACQ effect in these TPEincorporated lumingens. The particle size distributions revealed that the average particle size was 356.2 nm and 82.09 nm for **2TPE-SQ** and **TPE-SQ** in mixture with f_w = 90%, respectively (details see Fig. S9). In viewing of intense green or red emission can be observed in their crystals, the rapid decrease of emission intensity can be mainly ascribed to the formation of amorphous aggregates in the THF-water mixtures with high $f_{\rm w}$, which quenched the fluorescence via rotations of the phenyl groups on TPE units. This typical CIEE^{50,51} behavior will be confirmed and discussed below in detail.

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Fig. 2 The molecular structures and packing mode in the **TPE-SQ** crystal. a) The molecular conformation and intramolecular hydrogen-bonding interactions. b) The dihedral angles between vinyl bond and phenyl rotors. c) Intermolecular hydrogen-bonding interactions between adjacent **TPE-SQ** molecules. d) Intermolecular hydrogen-bonding and Ar-H···π interactions along a-axis. e) Intermolecular hydrogen-bonding between **TPE-SQ** and n-hexane solvent viewing from crystallographic a-axis.

Structural analysis and solid-state emission of 2TPE-SQ and TPE-SQ

In order to further understanding emission behaviors in dilute solution, a detailed analysis of their molecular conformation was very necessary. Although it was difficult to obtain the crystal structure of 2TPE-SQ, the suitable single crystal of TPE-SQ was easy to obtain for X-ray crystallography, and all the data were well summarized in Table S2. As shown in Fig. 2, TPE-SQ crystal belonged to a monoclinic crystal system and crystallized in the space group of P21/c with four TPE-SQ molecules in one unit cell taking the parameters of a =12.232(13), b = 9.804(10) and c = 32.921(4) Å. In the whole TPE-SQ molecule, the SQ segment was nearly plane due to two kinds of strong intramolecular C=O····H hydrogen bonding (Fig. 2a). One was 2.16 Å between Ar-H and carbonyl in fourmember ring, and another one was 1.96 Å between N-H and adjacent methyl esters. This excellent conjugation was regarded to facilitate its rigidity thus benefit to the limitations of the intramolecular rotation. More importantly, another moderate intramolecular hydrogen bonding, between carbonyl in four-member ring and Ar-H at the zusammen side

of the viny bond, was also observed within 2.81 Å (Fig. 2a). This furtherly led to the locking of one phenyl rotor in the TPE-SQ molecule. As compared to TPE molecule, the dihedral angles between vinyl bond and phenyl rotors exhibited negligible change for θ_1 from 56.74° to 55.27° and θ_2 from 45.66° to 45.00° in **TPE-SQ** molecule, ⁵² while θ_3 and θ_4 increased from 46.18° to 63.92° and 48.43° to 54.12°, respectively (Fig. 2b). This remarkable changes of dihedral θ_3 and θ_4 also directly supported the enhanced rigidity of the whole TPE-SQ molecule. As such, these limitations of its intramolecular phenyl rotation would well respond to the fact that TPE-SQ exhibited efficient emission in solution. Considering the structural symmetry, it was reasonable that same intramolecular restriction also existed in 2TPE-SQ, but extra free phenyl rotors would consume large excited energy thus led to its extreme weak emission efficiency in solution.

Further analysis revealed that there exhibited no intermolecular π - π stacking but multiple hydrogen bonding interactions in the crystal of **TPE-SQ**. As shown in Fig. 2c, two types of moderate hydrogen bonding interactions were observed between adjacent **TPE-SQ** molecules. One was 2.50



Fig. 3 The emission spectra of a) 2TPE-SQ and d) TPE-SQ assemblies in different condition at room temperature, the XRD patterns of b) 2TPE-SQ assemblies and e) TPE-SQ assemblies and the simulated XRD patterns of corresponding crystals, PL microscopy and SEM images of c) 2TPE-SQ assemblies and f) TPE-SQ assemblies.

Å interaction in C=O…H between the oxygen atom of methyl ester and hydrogen atom of phenyl rotor, and another was 2.68 Å interaction in Ar-H…O between the oxygen atom of four-membered ring and hydrogen atom of phenyl rotor. Meanwhile, along the a-axis the 2.69 Å interaction in Ar-H…O between the oxygen atom of four-membered ring and hydrogen atom of phenyl rotor, accompanying a 3.08 Å interaction in Ar-H··· π between phenyl rotors, were observe in adjacent TPE-SQ molecules (Fig. 2d). It was noteworthy that the incorporated *n*-hexane solvent played a key role in the construction of the crystalline TPE-SQ. As shown in Fig. 2e, the continuous 2.61 Å interaction in C=O…H between the oxygen atom of four-membered ring and hydrogen atom of n-hexane was observed, which was in a "stair-like" type rising along the b and c-axis. As such, this special packing mode dominated by multiple intermolecular C-H…O and C-H… π interactions, instate of π - π stacking, would well support the fact that **TPE**-SQ exhibited efficient emission in crystalline state, so did that in 2TPE-SQ crystals.

With those hydrogen bonding interactions, both **2TPE-SQ** and **TPE-SQ** held strong crystallization tendency. As shown, well-defined 1D microrods and 3D microplates were easily obtained when assembly of **2TPE-SQ** and **TPE-SQ** molecules in CH_2Cl_2/n -hexane mixtures (detail see supplementary information). Photoluminescence (PL) microscopy and scanning electron microscopy (SEM) images revealed that the

microrods were more than ten micrometers in width and one hundred micrometers in length, whereas microplates were about 13 μ m in width and 20 μ m in length as well as a thickness around several micrometers (Fig. S11-12, Fig. 3c, f). Furthermore, power X-ray diffraction (PXRD) patterns of their pristine crystalline powders showed sharp and intense peaks, indicating good microcrystalline structures (Fig. S13). The simulated XRD patterns of TPE-SQ crystals turned out to be coincided with that of crystalline assemblies (Fig. S13b), suggesting the same molecular packing modes. Thermogravimetric analysis (TGA) experiments revealed that 2TPE-SQ microrods were able to be unchanged until 324 °C (Fig. S14a), suggesting no solvent molecules were incorporated in the crystals. While TPE-SQ microplates gradually lost \approx 5.94% of its weight before 74 °C (Fig. S14d), and then stable until \approx 260 °C. The proportions of weight loss coincided exactly with a molar ratio of 2:1 between TPE-SQ and *n*-hexane molecules as observed in the crystal structures.

With these well-ordered assemblies, we next tested their emission behaviors. As shown in Fig. 3, pristine **2TPE-SQ** and **TPE-SQ** assemblies emitted $\lambda_{\rm em}$ at 531 nm and 627 nm with the $\Phi_{\rm PL}$ up to 0.75 and 0.61, respectively. These higher $\Phi_{\rm PL}$ can be ascribed to their highly resisted intramolecular phenyl rotations accompanying with their dominated hydrogen bonding packing mode in crystals. It was worthy to noted that the $\lambda_{\rm max}$ both of **2TPE-SQ** and **TPE-SQ** underwent red-shift



Fig. 4 a) Calculated potential energy profiles (kcal mol⁻¹) and wavelengths (nm) of vertical excitation and emission of **TPE-SQ** at the B3LYP/6-311G (d, p) and TD-B3LYP/6-311G (d, p) levels. (red line: the proton transfer pathway; blue line: distortion of C1-N1 bond pathway) b) The image and energy level of HOMO and LUMO of all the transition of **TPE-SQ** (energy unit: ev).

about 60 nm from solution state to crystalline state, which was very different from most of the reported DSE-active luminogens generally possessed a very similar λ_{max} in blue to green region both in solution and solid state.^{17,53} Those results obviously suggested there would exist different emission mechanism for different state of **2TPE-SQ** and **TPE-SQ** molecules. Considering their large Stokes shift (\approx 80 nm) and configurational features, their intense emission in crystalline state can be mainly ascribed to the well-known ESIPT mechanism.

Considering that the *n*-hexane solvents were incorporated in TPE-SQ crystals, we then studied their photophysical properties under the external stimuli such as heating, grinding and solvent fuming. As for TPE-SQ, when its pristine assemblies were heated at 180 °C for 30 min, the TGA was recorded and indicated that the solvent molecules were mainly removed in the crystalline (Fig. S14f). Meanwhile, PXRD patterns of the annealed powders revealed broad and featured less reflection, suggesting the nearly amorphous feature (Fig. S17b). The same results were also obtained when thorough grinding the TPE-SQ assemblies over 30 min in the mortar, confirmed by its TGA and PXRD experiments (Fig. S14e, 18b). Both the annealed and ground assemblies showed quickly decreased intensity at λ_{em} = 631 nm and λ_{em} = 622 nm with \varPhi_{PL} of 0.08 and 0.02, respectively (Fig. 3d, S16a, S17a). Thus, we could conclude that removing *n*-hexane solvents from the crystalline lattice induced a disordered state in the molecular arrangements, which may facilitate the rotations of the phenyl groups on TPE unit in TPE-SQ assemblies thus quenching the emission, indicating a typical CIEE behavior. crystalline-amorphous transformation was also This responsible for the observed ACQ behavior of TPE-SQ in the pure water. Moreover, we then tested the reaccess of the solvent molecules in the annealed/ground assemblies. After exposure of these assemblies to the *n*-hexane vapor for 30 min

in a Petri dish at room temperature, the emission color and PXRD turned out to be unchanged, suggesting that the amorphous assemblies can not be recovered to the initial state by treating with n-hexane solvent vapor (Fig. S17b, 18b). As such, the thermo/mechanochromism of the TPE-SQ crystals permitted it a promising candidate for stimuli-responsive⁵⁴ emissive organic crystals. Incidentally. the thermo/mechanochromic behaviors of 2TPE-SQ were also examined and similar CIEE effect can be observed (Fig. S15, Fig. S16). It was worth pointing out that the annealed 2TPE-SQ assemblies exhibited slightly decreased intensity with $arPhi_{
m PL}$ changed from 0.75 to 0.58. This can be responded by the fact that the intermolecular interaction can not be collapsed with just annealling because no solvent was incorporated in crystalline 2TPE-SQ, which was very different from that in TPE-SQ crystals. As comparison with typical DSE-active molecules,^{17,53} TPE-SQ exhibited obvious different emission wavelength owing to distinct emission mechanism in solution and solid state, and more importantly, its crystalline assemblies manifested a intense red emission with λ_{max} =627 nm. This red-emission characteristic is urgently needed for enriching the design and tuning strategies of DSE-active molecules, thereby benefiting to promote their biological applications in the near future. All the photophysical data of 2TPE-SQ and TPE-SQ under different conditions were also summarized in Table S1 and Fig. S10.

Theoretical DFT calculations and LE-TICT/ESIPT mechanism

With the aim of gaining further insight into the optical behaviors, the absorption and emission spectra and emissive mechanisms for **TPE-SQ** in dual-state were calculated by timedependent density functional theory (TDDFT) method. All the optimized geometries of **TPE-SQ** in the ground state (S0) and in the excited state (S1) using B3LYP and TD-B3LYP calculations were plotted in Fig. S19 and the calculated potential energy Published on 12 February 2020. Downloaded on 2/13/2020 6:32:10 AM

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profiles of **TPE-SQ** photoreaction in S0 and S1 states were presented in Fig. 4. In the ground state, a one-step proton transfer mechanism was taken place via TS0 with an energy barrier of 32.32 kcal mol⁻¹ to produce PS0 that held an energy of 10.73 kcal mol⁻¹ above the reactant.

In the first excited state (S1), there were two possible photoreaction pathways. One occurred directly between RS1 and PS1a via TS1a accompanying the distortion of C1-N1 bond with an energy barrier of 5.27 kcal mol⁻¹ and an endothermic process of -2.22 kcal mol⁻¹ (the blue line), suggested a typical LE-TICT mechanism. The other that active H atom transferred to O atom of central ring, occurring between RS1 and PS1 via TS1 with only an energy barrier of 12.3 kcal mol⁻¹ and a heat release of 11.67 kcal mol⁻¹ (the red line), suggested a typical ESIPT mechanism. In fact, the distance between the active H atom and O atom of ester group was much shorter than that of O atom of central ring. For this, we initially believed that the active proton would transfer to the O atom of ester group in S1 state as well. However, when we optimized the structure that the H atom connected with the O atom of the ester group, the H atom spontaneously transferred to O atom of central ring. Moreover, the scan of potential energy surface (PES) of S1 state of TPE-SQ as a function of N-H bond length was done (Fig. S20), which showed that the transfer of H atom from N to O atom of ester group would increase the total energies both in SO and S1 states. This also indicated the ESPIT was difficult to take place from active H atom to the O atom of the ester group in S1 state. Therefore, we can conclude that the active proton of N atom transferring to O atom of central ring was more reasonable. Based on upon results, this dye molecule that exhibited ESIPT existed predominantly as keto (RS0) form in the ground state, however, by photoexcitation, they underwent tautomerization into enol (PS1) form (keto*→enol*) via an ultrafast and irreversible ESIPT process. The resulting proton-transfer tautomer was substantially different in structure and electronic configuration from its corresponding ground state, thereby led to a large Stokes shifted emission derived from $enol^* \rightarrow enol$.

Actually, because of low energy barrier, the distortion of C1-N1 bond was easier to carry out than the proton transfer in solution. While in the crystalline state, the distortion of C1-N1 bond was greatly prohibited because of the strong interaction between molecules, triggering the proton transfer pathway. Consequently, it was easy to draw the conclusion that the excited proton transfer mechanism was favorable in solid state, while the excited state C1-N1 bond distortion was easy to occur in solution. In addition, the calculated emission bands of PS1a and PS1 were centered at 576 and 610 nm, respectively, which was in agreement with the experiment data in dilute solution and crystalline state. At the same time, as shown in Fig. 4b, all the transition of **TPE-SQ** was obviously a predominant π to π^* -type transition from the HOMO to the LUMO.

Conclusions

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In summary, herein we demonstrated the videsign and successful synthesis of DSE-active 27PE-SQ03ah@TTPE-SQ() featuring emission in both solution and crystalline state. From spectra analysis, 2TPE-SQ turned out to be weak emissive (highest $\Phi_{\rm PL}$ = 0.07) in solution but bright green emission at 531 nm with $\Phi_{\rm PL}$ = 0.75 in crystalline state, while **TPE-SQ** emitted in solution and crystalline state with the highest $arPsi_{
m PL}$ up to 0.33 at 564 nm and 0.61 at 627 nm, respectively. Single crystal diffraction analysis revealed that their emission in solution can be ascribed to the restricted intramolecular motions with enhanced structural rigidity and intramolecular H-bonding interactions, while that in crystal was due to a special packing mode dominated by multiple C-H…O and C- $H \cdots \pi$ interactions. Based on theoretical DFT conclusions, the different emission mechanism as LE-TICT in solution and ESIPT in crystal was proposed and responded to their different emission wavelength. Meanwhile, the self-assembly and various emission behaviors such as ACQ, CIEE and thermo/mechanochromism of the these compounds were investigated in detail, and all these results would bring a novel vision on the investigation of organic lumingens in diverse state.

Conflicts of interest

There are no conflicts to declare.

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We report TPE-incorporated squaraines with dual-state emission and decode their LE/TICT mechanism in solution and ESIPT mechanism in crystalline state