

How to Manipulate Through-Space Conjugation and Clusteroluminescence of Simple AIEgens with Isolated Phenyl Rings?

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ABSTRACT: Apart from the traditional through-bond conjugation (TBC), through-space conjugation (TSC) is gradually proved as another important interaction in photophysical processes, especially for the recent observation of clusteroluminescence from nonconjugated molecules. However, unlike TBC in conjugated chromophores, it is still challenging to manipulate TSC and clusteroluminescence. Herein, simple and nonconjugated triphenylmethane (TPM) and its derivatives with electron-donating and electron-withdrawing groups were synthesized, and their photophysical properties were systematically studied. TPM was characterized with visible clusteroluminescence due to the intramolecular TSC. Experimental and theoretical results showed that the introduction of electron-donating groups into TPM could red-shift the wavelength and increase the efficiency of clusteroluminescence simultaneously, due to the increased electronic density and stabilization of TSC. However, TPM derivatives with electron-withdrawing groups showed inefficient or even quenched clusteroluminescence caused by the vigorous excited-state intramolecular motion and intermolecular photoinduced electron transfer process. This work provides a reliable strategy to manipulate TSC and clusteroluminescence.

INTRODUCTION

The use of light is the starting point for human civilization, which plays a vital role in the development of our society. Beginning from 5th B.C. when philosophers of ancient Greece raised the question about the essence of light, humanity started to investigate and utilize natural sources of light, such as sun and firelight.¹ In modern society, because of the deeper cognition on science and technology, people began to design artificial emitters, especially luminogens which can emit efficiently upon photoexcitation.²⁻⁵ Therefore, what are the laws behind the luminescent behaviors and how to design and manipulate artificial luminophores at different levels of hierarchical structures are important issues for scientists, as evidenced by the Nobel Prize in Chemistry in 2008 for the discovery of green fluorescent protein, and Physics in 2014 for the invention of efficient blue light-emitting diodes, respectively.

Compared with inorganic materials, organic fluorophores show better flexibility, biocompatibility,

processability, structural diversity, etc. Thus, they show great promise in practical application. Researchers have established many photophysical theories based on molecular science, which focus on the fluorescent mechanisms of organic fluorophores. For example, efficient fluorophores are closely correlated with large π conjugation through covalent bonds (e.g. double bond, triple bond or aromatic ring),⁶⁻⁷ and introduction of donor (D) and acceptor (A) groups into the molecular skeleton often leads to redder but weaker emission,⁸⁻⁹ especially for molecules showing twisted intramolecular charge transfer effect.¹⁰⁻¹¹ In most cases, these molecular theories are capable of revealing the photophysical mechanisms of organic luminescent materials. Based on these studies at molecular level, a paradigm of material research is gradually formed that molecular structures and properties always determine the performance of macroscopic materials. However, due to the continuous development of photophysical research, some abnormal phenomena were reported sporadically that aggregates performed entirely different properties

from single-molecule species. One example is the aggregation-caused quenching (ACQ) effect where most fluorophores are highly emissive in solution but become non-emissive in the aggregate state.¹² In contrast, some invisible phenomena of molecules in the isolated state could be observed in the aggregate state,¹³⁻¹⁵ such as the aggregation-induced emission (AIE) effect. Luminoogens with AIE effect (AIEgens) are non-emissive in dilute solution but luminesce strongly in the aggregate state. The flourishing development of ACQ and AIE-related studies brings a paradigm shift from molecular science to aggregate science.¹⁶⁻¹⁸

Recent research in aggregate science has reported that many nonconjugated structures, such as polystyrene,¹⁹ peptide,²⁰ and maleimide,²¹ are non-emissive in solution but can emit visible light in the solid state. This unconventional photophysical process is termed as clusterization-triggered emission and the corresponding emission is known as clusteroluminescence.²²⁻²⁵ The previous studies suggested that strong intermolecular interactions among the closely packed molecules generated new emissive species and stabilized excited excitons to produce clusteroluminescence.²⁶⁻²⁸ Apart from intermolecular interaction, intramolecular through-space conjugation (TSC) was also proved to play an important role in clusteroluminescence. For example, our recent study revealed that nonconjugated 1,1,2,2-tetraphenylethane with weak intermolecular interactions fluoresced efficiently in the aggregate state, and the intramolecular TSC among the four phenyl rings contributed greatly to the clusteroluminescence.²⁹ Based on the above results, two common questions are emerged: i) is TSC a general mechanism for clusteroluminescence, and ii) is it possible to manipulate TSC in clusteroluminogens?

In this work, nonconjugated triphenylmethane (TPM) and its derivatives with different electron-donating and withdrawing groups, namely 4,4',4''-trimethoxytriphenylmethane (TPM-MO), 4,4',4''-tris(*N,N*-dimethylaminophenyl)methane (TPM-DMA), 4,4',4''-tricyanotriphenylmethane (TPM-CN) and 4,4',4''-trinitrotriphenylmethane (TPM-NO₂), were synthesized and satisfactorily characterized (Figures S1-S11 in Supporting Information). All the molecules showed visible light in the solid state with different colors and efficiency. Experimental and theoretical results proved that TSC was also applicable to these clusteroluminogens. The electron-donating groups in TPM-MO and TPM-DMA could red-shift the wavelength and increase efficiency of clusteroluminescence simultaneously by enhancing the TSC. However, the electron-withdrawing groups in TPM-CN and TPM-NO₂ decentralized the electrons of phenyl rings and destabilized the intramolecular TSC, resulting in low

emission efficiency. On the other hand, the restriction of intramolecular motions (RIM),³⁰ which served as the mechanism of AIE phenomenon, helped to stabilize the preferential conformation for TSC in the aggregate state. The synergistic effect between TSC and RIM generated efficient clusteroluminescence of TPM and its derivatives. Thus, this study not only verified the general mechanism of TSC in clusteroluminogens but also provided a reliable strategy to manipulate clusteroluminescence at the molecular level.

Results and Discussion

2.1 Photophysical properties. TPM is a simple molecule with three isolated phenyl rings and was first prepared to study its photophysical properties. The absorption spectra of TPM both in THF solution and solid state exhibited an absorption maximum (λ_{ab}) corresponding to benzene ring at 264 nm, confirming the nonconjugated nature of the molecule (**Figure 1a**). In pure THF solution, TPM showed one emission peak at 285nm which was attributed to the intrinsic through-bond conjugation (TBC) of benzene. Addition of poor solvent such as water into the THF solution induced the formation of TPM aggregates (**Figure 1b**). During the aggregation process, the emission intensity at 285 nm first increased and then decreased, and the turning point was located at a water fraction (f_w) of 50% in volume. It was noteworthy that a new broad emission peak appeared at 350-380 nm at $f_w = 80-90\%$, and its intensity at 400 nm was 17 times higher than that in pure THF solution (**Figure 1c**). This long-wavelength emission demonstrated the AIE phenomenon and might be attributed to the formation of stable through-space interaction in the aggregate state that gave rise to clusteroluminescence.²⁹ At f_w of less than 50%, the enhancement of TBC emission was due to the increased polarity of the solvent mixture.³¹ However, aggregates merely formed at high water fraction whose internal polarity was less affected by the surrounding environment. Meanwhile, a portion of the TBC emission was reabsorbed by the TSC species via the Förster resonance energy transfer (FRET) process, which decreased the emission from TBC but increased the emission from TSC. The solid-state emission spectrum of TPM showed two maximums (λ_{em}) at 288 and 402 nm under 270 nm excitation (**Figure 1d**), which were assigned to the intrinsic emission from TBC of phenyl rings and clusteroluminescence with TSC, respectively. The excitation spectrum of TPM in the solid state exhibited a long-wavelength peak at 310 nm, suggesting the formation of new emissive species by TSC. Thus, only one peak with a fluorescence quantum yield (Φ_{TSC}) of 2.7% appeared at 403 nm with 310 nm excitation (**Figure S12**).

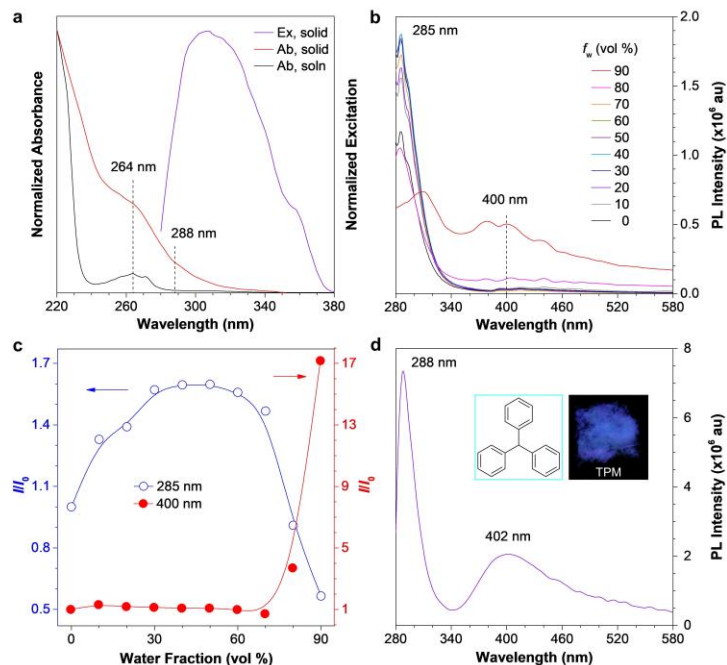


Figure 1. (a) Absorption (Ab) spectra of TPM in THF solution (soln) and solid state. Inset: excitation (Ex) spectrum in the solid state taken at $\lambda_{em} = 402$ nm. (b) Photoluminescence (PL) spectra of TPM in THF/water mixtures with different water fractions (f_w). (c) Plots of relative PL intensity (I/I_0) versus f_w at different emission wavelengths. Concentration = 10^{-4} M, $\lambda_{ex} = 270$ nm, $I_0 =$ intensity at $f_w = 0\%$. (d) PL spectra of TPM in the solid state taken at $\lambda_{ex} = 270$ nm. Inset: structure and fluorescent photo of TPM taken under illumination of a 365 nm UV lamp.

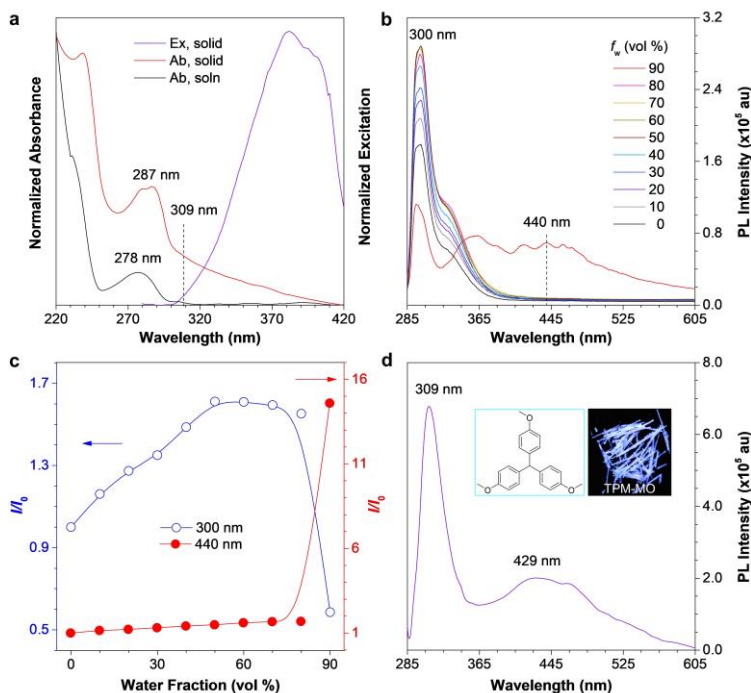


Figure 2. (a) Absorption (Ab) spectra of TPM-MO in THF solution (soln) and solid state. Inset: excitation (Ex) spectrum in the solid state taken at $\lambda_{em} = 429$ nm. (b) Photoluminescence (PL) spectra of TPM-MO in THF/water mixtures with different water fractions (f_w). (c) Plots of relative PL intensity (I/I_0) versus f_w at different emission wavelengths. Concentration = 10^{-4} M, $\lambda_{ex} = 280$ nm, $I_0 =$ intensity at $f_w = 0\%$. (d) PL spectra of TPM-MO in the solid state taken at $\lambda_{ex} = 280$ nm. Inset: structure and fluorescent photo of TPM-MO taken under illumination of a 365 nm UV lamp.

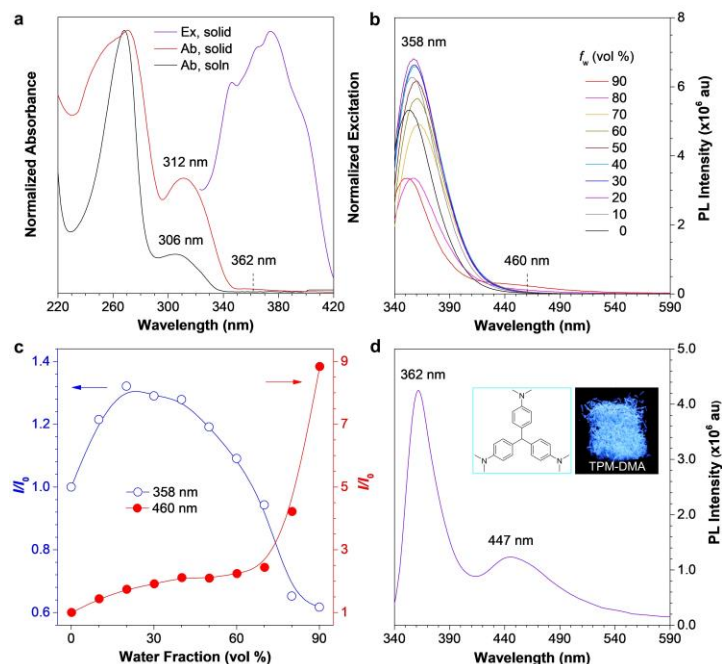


Figure 3. (a) Absorption (Ab) spectra of TPM-DMA in THF solution (soln) and solid state. Inset: excitation (Ex) spectrum in the solid state taken at $\lambda_{em} = 447$ nm. (b) Photoluminescence (PL) spectra of TPM-DMA in THF/water mixtures with different water fractions (f_w). (c) Plots of relative PL intensity (I/I_0) versus f_w at different emission wavelengths. Concentration = 10^{-4} M, $\lambda_{ex} = 320$ nm, I_0 = intensity at $f_w = 0\%$. (d) PL spectra of TPM-DMA in the solid state taken at $\lambda_{ex} = 320$ nm. Inset: structure and fluorescent photo of TPM-DMA taken under illumination of a 365 nm UV lamp.

The above results proved the existence of clusteroluminescence in TPM but with a low Φ . To adjust the through-space interaction among the three phenyl rings, electron-donating methoxy groups were introduced to increase the electron density of each phenyl ring. The obtained TPM-MO showed an λ_{ab} at 278 nm in THF solution (Figure 2a), which was similar to that of anisole (Figure S13). The λ_{ab} shifted bathochromically to 287 nm in the solid state. TPM-MO emitted short-wavelength emission at 300 nm in THF/water mixture, and its intensity also first increased but later decreased by increasing f_w (Figure 2b and 2c). At the same time, a new broad peak at ~ 440 nm was observed at $f_w = 90\%$, whose intensity was 15 times higher than that in pure THF solution. Also, the emission spectrum was well extended to 600 nm. The solid-state emission spectrum of TPM-MO exhibited two emission peaks at 309 and 429 nm at $\lambda_{ex} = 280$ nm, which originated from TBC and TSC, respectively (Figure 2d). The excitation spectrum of TPM-MO also showed a broad peak at around 370 nm in the solid state. Upon excitation at 370 nm, the clusteroluminescence of TPM-MO was red-shifted to 439 nm and the Φ_{TSC} was enhanced to 6.3% in comparison to TPM with $\lambda_{em} = 403$ nm and $\Phi_{TSC} = 2.7\%$, respectively (Figure S12).

A strong electron-donating group, *N,N*-dimethylamino (DMA) group, was also utilized to construct TPM-DMA. Its λ_{ab} was located at 306 nm and 312 nm in pure THF solution and solid state (Figure 3a), respectively, due to the better conjugation and donor (D)-acceptor (A) effect of DMA and phenyl ring. Figure 3b showed that only one emission peak was detected at 358 nm at low f_w , which was associated with the TBC of *N,N*-dimethylaniline (Figure S13). Similarly, TBC emission became weaker at f_w of more than 50% (Figure

3c). A long-wavelength emission at 460 nm was observed at $f_w \geq 80\%$, and its intensity at $f_w = 90\%$ was 9-fold higher than that in pure THF solution. In the solid state, TPM-DMA exhibited brightly sky-blue clusteroluminescence at $\lambda_{em} = 447$ nm and another invisible TBC emission at 362 nm with $\lambda_{ex} = 320$ nm (Figure 3d). When excited at the excitation maximum of 380 nm (Figure 3a), only the long-wavelength emission stemmed from TSC was observed at 453 nm (Figure S12). The corresponding Φ_{TSC} was 6.9%, which slightly higher than that of TPM-MO (6.3%).

Considering that electron-donating moieties could bathochromic-shift and enhance the Φ of clusteroluminescence, the effect of electron-withdrawing group on TSC was further explored. Thus, cyano and nitro groups were selected as substituents to synthesize TPM-CN and TPM-NO₂, respectively. The λ_{ab} of TPM-CN in THF solution and solid state was redder than TPM and was both located at 282 nm (Figure 4a), corresponding to the TBC emission of benzonitrile (Figure S13). As shown in Figure 4b, only the emission of TBC ($\lambda_{em} = 294$ nm) was observed at low f_w and another long-wavelength peak located at 457 nm was noticed at $f_w = 90\%$ (Figure 4c). In the solid state, two emission peaks appeared at 300 and 460 nm at 270 nm excitation (Figure 4d). The inset in Figure 4a showed that the λ_{ex} was much longer than the λ_{ab} in the solid state. Therefore, upon excitation at 380 nm, only one peak at 482 nm was detected, which was even redder than that of TPM-DMA ($\lambda_{em} = 453$ nm). The Φ_{TSC} of such TSC emission was low and was measured to be 2.2% at $\lambda_{ex} = 380$ nm, which was lower than that of TPM, TPM-MO and TPM-DMA. For TPM-NO₂, its absorption maximum was redder than TPM, but its emission was quenched in both solution and solid state at room temperature and could not be identified (Figure S14).

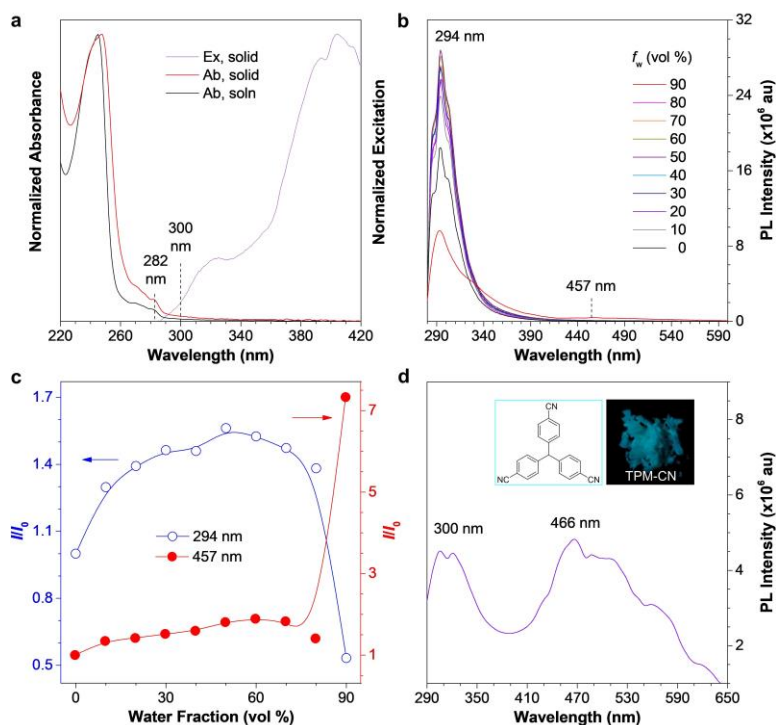


Figure 4. (a) Absorption (Ab) spectra of TPM-CN in THF solution (soln) and solid state. Inset: excitation (Ex) spectrum in the solid state taken at $\lambda_{em} = 466$ nm. (b) Photoluminescence (PL) spectra of TPM-CN in THF/water mixtures with different water fractions (f_w). (c) Plots of relative PL intensity (I/I_0) versus f_w at different emission wavelengths. Concentration = 10^{-4} M, $\lambda_{ex} = 270$ nm, I_0 = intensity at $f_w = 0\%$. (d) PL spectra of TPM-CN in the solid state taken at $\lambda_{ex} = 270$. Inset: structure and fluorescent photo of TPM-CN taken under illumination of a 365 nm UV lamp.

Table 1. Photophysical Properties of TPM and Its Derivatives (TPM-R)^a

TPM-R	λ_{ab} (nm)	$\lambda_{ex,solid}$ (nm)	TBC Emission		TSC Emission		Φ_{TSC} (%)
			λ_{TBC} (nm)	τ_{TBC} (ns)	λ_{TSC} (nm)	τ_{TSC} (ns)	
TPM-DMA	306	375	362	3.29	447	9.69	6.9
TPM-MO	278	382	309	2.61	429	3.57	6.3
TPM	264	307	288	< 1	402	3.64	2.7
TPM-CN	282	404	305	< 1	466	2.56	2.2
TPM-NO ₂	276						0.4

^a Abbreviation: λ_{ab} = absorption maximum in THF solution, $\lambda_{ex,solid}$ = excitation maximum in the solid state measured at emission maximum of 447 nm (TPM-DMA), 429 nm (TPM-MO), 402 nm (TPM) and 466 nm (TPM-CN). TBC = through-bond conjugation, λ_{TBC} = emission maximum through TBC in the solid state, τ_{TBC} = emission lifetime through TBC in the solid state, TSC = through-space conjugation, λ_{TSC} = emission maximum through TSC in the solid state, τ_{TSC} = emission lifetime through TSC in the solid state, Φ_{TSC} = absolute luminescence quantum yield at excitation wavelength of 380 nm (TPM-DMA), 370 nm (TPM-MO), 310 nm (TPM), or 380 nm (TPM-CN).

To exclude the interference from radical species which was reported to be responsible for some extrinsic emissions,³²⁻³³ electron spin resonance spectra of the present molecules were measured, but none of them showed obvious signals in the presence or absence of UV illumination (Figure S15). This result suggested the inherent emission of these stable structures. The photophysical properties of all molecules are summarized in Table 1. It was noteworthy that the emission lifetime caused by TSC (τ_{TSC}) was longer than that due to TBC (τ_{TBC}),

demonstrating the relatively stable excitons formed by through-space interaction (Figure S16). For example, the τ_{TSC} of TPM-DMA was measured to be 9.69 ns, which was three times longer than τ_{TBC} (3.29 ns). Besides, when the substituents were changed from electron-donating to electron-withdrawing groups, the τ_{TSC} became shorter and the Φ_{TSC} decreased from 6.9% in TPM-DMA to 0.4% in TPM-NO₂.

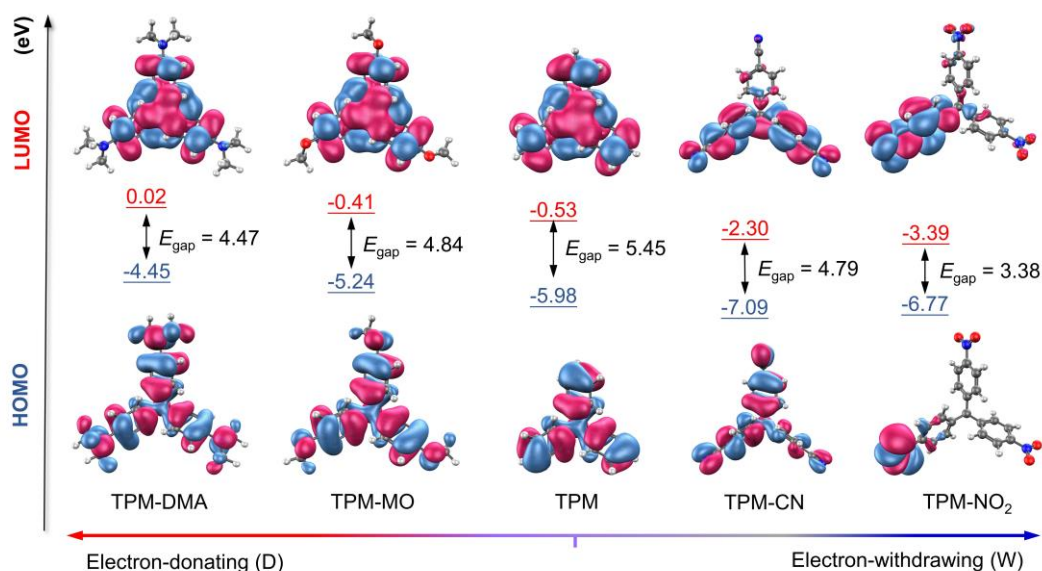


Figure 5. Frontier molecular orbitals of optimized excited-state geometries of TPM derivatives calculated by TD-DFT method at B3LYP-D3/6-31G(d,p) level, Gaussian 16 program.

2.2 Through-space Conjugation. To confirm TSC and investigate the electronic effect on clusteroluminescence, single-molecule calculation on present compounds were carried out. The density functional theory method at B3LYP-D3/6-31G(d,p) level was utilized to calculate the ground- and excited-state geometries. The reference plane was constructed to illustrate the structural information, which was set as atoms of 1-2-3 in **Table S1**. At ground state (S_0), all the optimized structures displayed a highly C_3 -symmetrical and propeller-like conformation, as evidenced by the dihedral angles between the reference plane and each of phenyl ring were around 55° . Frontier molecular orbitals at S_0 were shown in **Figure S17**, including electron cloud distribution and energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Electrons at HOMO were distributed on the phenyl rings and substituent groups.

However, the geometries and electronic effect became different at the excited state (S_1) (**Table S1**). The energy gap between HOMO and LUMO of TPM derivatives were narrower than TPM (**Figure 5**), which was consistent with their redder λ_{ab} and λ_{em} through TBC. Besides, the values were smaller than the corresponding substituted phenyl rings such as benzene, *N,N*-dimethylaniline, anisole,

benzonitrile and nitrobenzene, suggesting the existence of intramolecular through-space interaction (**Table S2**). As observed from the LUMO of TPM, a clear electronic overlapping among the three isolated phenyl rings was observed, which verified the effect of intramolecular TSC in TPM. For TPM-MO and TPM-DMA with electron-donating groups, apart from electronic overlapping, a noticeable D-A transition from the donor to phenyl ring was observed. Together with their symmetrical structures and the shortened atomic distances of 1-2, 2-3 and 3-1 at S_1 (**Table S1**), the dihedral angles between the reference plane and each phenyl ring decreased from 55° to around 46° . This indicated the closer distance between every two phenyl rings and more concentrated π electrons at the center of the molecular skeleton in comparison with S_0 . In TPM-CN, two phenyl rings displayed a nearly face-to-face conformation while the other one was perpendicular to them. Such a parallel arrangement was beneficial for efficient TSC, even though it was a binary rather than a ternary TSC, as proved in our previous report.²⁹ The parallel binary TSC caused red-shift in clusteroluminescence from 402 to 466 nm (**Figure 4d**). For nitro-substituted TPM-NO₂, a dark (n, π^*) transition showing no intramolecular TSC became dominant, deciphering its nonfluorescent behavior in the solution and aggregate state.³⁴

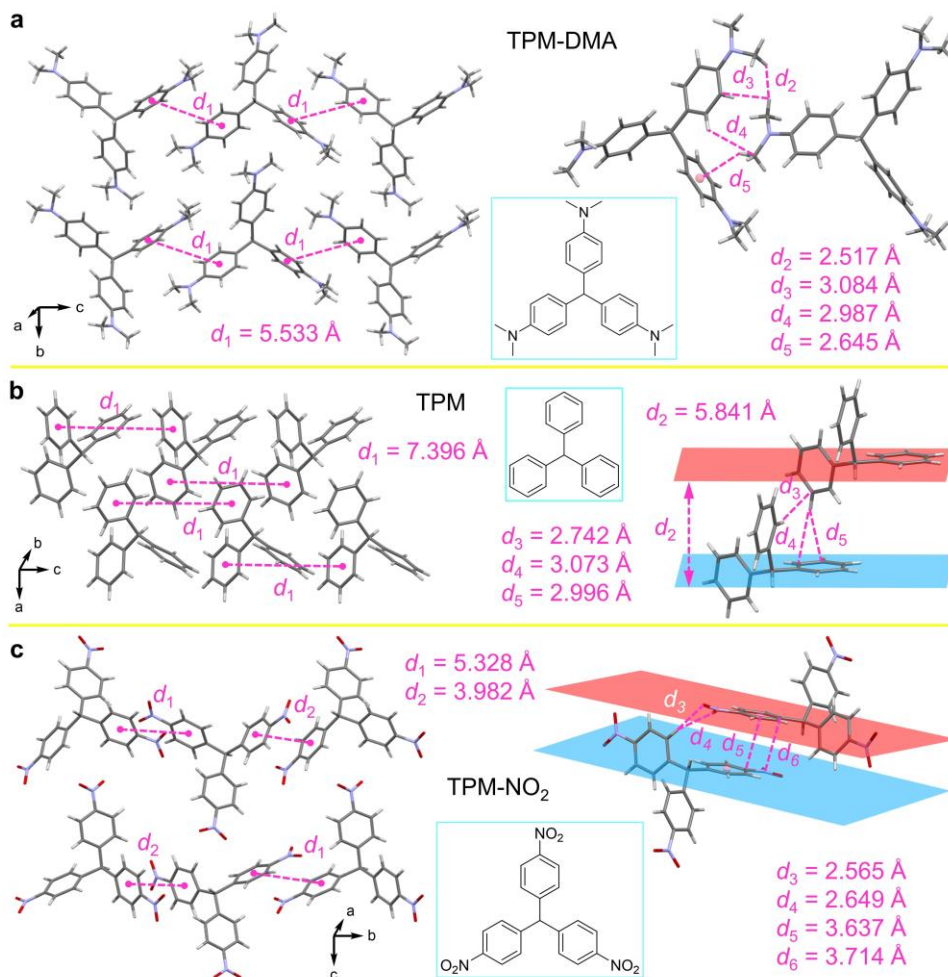


Figure 6. Crystal packing diagrams of (a) TPM-DMA, (b) TPM and (c) TPM-NO₂.

2.3 Crystal Structures. Single-molecule calculations had proved the important role of intramolecular TSC in clusteroluminescence of TPM derivatives, how about the intermolecular interaction? To explore the effect of intermolecular interaction on clusteroluminescence, crystal structures of all compounds were obtained and analyzed (**Table S3**). **Figure 6** showed the crystal packing structures of TPM-DMA, TPM and TPM-NO₂. In TPM-DMA, no parallel plane was observed and the centroid-centroid distance between two adjacent phenyl rings was 5.533 \AA (**Figure 6a**). Instead, some weak intermolecular interactions such as C...H, C-H... π and H...H were dominant. A quantitative analysis on intermolecular interactions based on Hirshfeld surface was utilized.³⁵ As showed in **Figure 7**, the full fingerprints appeared as grey shadows and the selected interaction was shown with blue. Thus, in TPM-DMA, the hydrogen-involved intermolecular interaction (P_{HII}) accounted for 99.7% of all intermolecular interactions. No intermolecular C...C interaction was detected, suggesting the absence of intermolecular TSC (**Figure 7a** and **S18**). The same situation was observed in TPM-MO, which showed almost no intermolecular TSC (**Figure S19** and **S20**). In TPM, although the two intermolecular phenyl rings were parallel to each other, the distance between the two planes was as far as 5.841 \AA (**Figure 6b**) and the P_{HII} of TPM was up to 100% without intermolecular C...C interaction

(**Figure 7b** and **S21**). Therefore, the above results suggested that the clusteroluminescence of TPM and its donor-based derivatives was a kind of intramolecular rather than intermolecular behavior. Whereas these weak intermolecular interactions could restrict intramolecular motions and stabilize excitons with intramolecular TSC.^{30,36}

For electron-withdrawing TPM-CN and TPM-NO₂, the closest intermolecular C...C distances determined from the crystal packing structures were 3.442 and 3.637 \AA , respectively, which suggested strong intermolecular π - π stacking (**Figure 6c** and **S22**). Meanwhile, intermolecular D-A interaction also existed, as proved by the presence of short intermolecular C...N distance. From the quantitative perspective, the proportion of intermolecular C...C interaction to total interactions ($P_{\text{C}\cdots\text{C}}$) in TPM-CN and TPM-NO₂ was 8.4% and 6.3 %, respectively (**Figure 7c**, **S23** and **S24**), which further confirmed the existence of intermolecular π - π stacking. Therefore, the redder clusteroluminescence of electron-withdrawing TPM derivatives than TPM resulted from both intramolecular and intermolecular through-space interactions. Meanwhile, the close packing of TPM-CN and TPM-NO₂ also brought the detrimental intermolecular photoinduced electron transfer from phenyl rings to cyano and nitro groups, which enhanced the nonradiative decay and decreased the efficiency of clusteroluminescence.

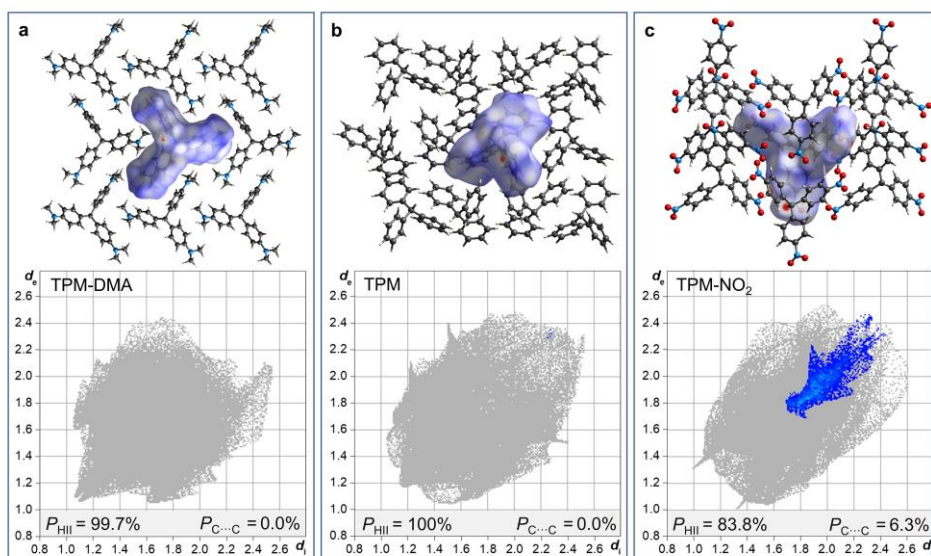


Figure 7. (Upper panel) Hirshfeld surfaces (mapped over d_{norm}) and (lower panel) decomposed fingerprint plots of (a) TPM-DMA, (b) TPM and (c) TPM-NO₂. The full fingerprints appeared as grey shadows underneath decomposed plots and intermolecular C...C interaction was shown as blue shadow. P_{HII} = proportion of hydrogen-involved intermolecular interaction to total intermolecular interaction, $P_{\text{C}\cdots\text{C}}$ = proportion of intermolecular C...C interaction to total intermolecular interaction.

2.4 Clusteroluminescence. Traditional clusteroluminogens based on macromolecular systems shows ambiguous spatial conformation and interaction, which makes it difficult to clarify the photophysical process of clusteroluminescence. In contrast, the identified single-molecule and packing structures in the current system enable deep studies on the working mechanisms of clusterization-triggered emission. Reorganization energy (λ) is a quantitative indicator of intrinsic geometry change upon photoexcitation, which also reflects the contribution of intramolecular motion to nonradiative decay.³⁷⁻³⁸ **Figure 8a** exhibited the λ of TPM-DMA at different wavenumbers in the isolated phase as an example. The total λ was 2142 cm⁻¹ and 66.17% of it was contributed by the twisting motion of dihedral angle located mainly at low-frequency region (< 500 cm⁻¹). The low-frequency vibration modes also tended to mix upon excitation to activate multiple nonradiative decay pathways. Hence, the potential energy surface (PES) of TPM-DMA in dilute solution was proposed and displayed in **Figure 8b**. Upon photoexcitation to S₁, some excitons decayed via radiative channel to produce TBC emission. At the same time, transient species with intramolecular TSC also formed but immediately evolved to the dark state near the conical intersection due to the vigorous low-frequency motions.³⁹ As a result, only the TBC emission was detected. Based on the crystal packing structure of TPM-DMA, its aggregate environment was also simulated using ONIOM model with combined quantum mechanics and molecular mechanics (QM/MM) approach (**Figure S25**). The central molecule acted as the high layer with QM at B3LYP-D3/6-31G(d,p) level, while the surrounding molecules played as the low layer using universal force field (UFF). The total λ in the aggregate state largely decreased to 1246 cm⁻¹ and the contribution of dihedral angle also declined to 40.38% (**Figure 8c**),

suggesting the restriction of intramolecular motion, especially twisting motion in the excited state. By combining experimental and theoretical results, **Figure 8d** drew the PES for TPM-DMA in the crystalline state. Similar to that in the solution state, some excited excitons released from the channel of TBC emission. However, according to Kasha's rule, more excitons went to the low-lying state of TSC which was further stabilized by restricted intramolecular motion. Thus, the nonradiative decay channel was blocked and clusteroluminescence was realized with comparatively high quantum yield.

Reorganization energy of other compounds in the isolated and crystalline phases was also calculated (**Figure S26-S29**). For TPM-MO and TPM, both total λ and contribution of dihedral angle became smaller in the crystalline phase than those in the isolated phase. Besides, the increased Φ_{TSC} from TPM (2.7%), then TPM-MO (6.3%) and to TPM-DMA (6.9%) was consistent with the enlarged $\Delta\lambda$ (the decline of λ from isolated to crystalline phase: 33 cm⁻¹ for TPM, 514 cm⁻¹ for TPM-MO and 896 cm⁻¹ for TPM-DMA), verifying that the restriction of intramolecular motion in the crystalline state had stabilized the TSC and boosted the emission efficiency of clusteroluminescence. However, the total λ of TPM-CN slightly increased from isolated (2857 cm⁻¹) to crystalline phase (3143 cm⁻¹) but the contribution of dihedral angle reduced from 57.34% to 26.95% (**Figure S28**), which resulted in the decreased emission efficiency but reddest clusteroluminescence among all molecules. So, within this molecule, intramolecular motion performs like a double-edged sword that produces the low-lying TSC state but cannot stabilize the excited-state through-space interaction. TPM-NO₂ is one of the extreme cases: its total λ was large and measured to be 7316 and 7370 cm⁻¹ in the isolated and crystalline phases, which quenched the emission in both phases (**Figure S29**).

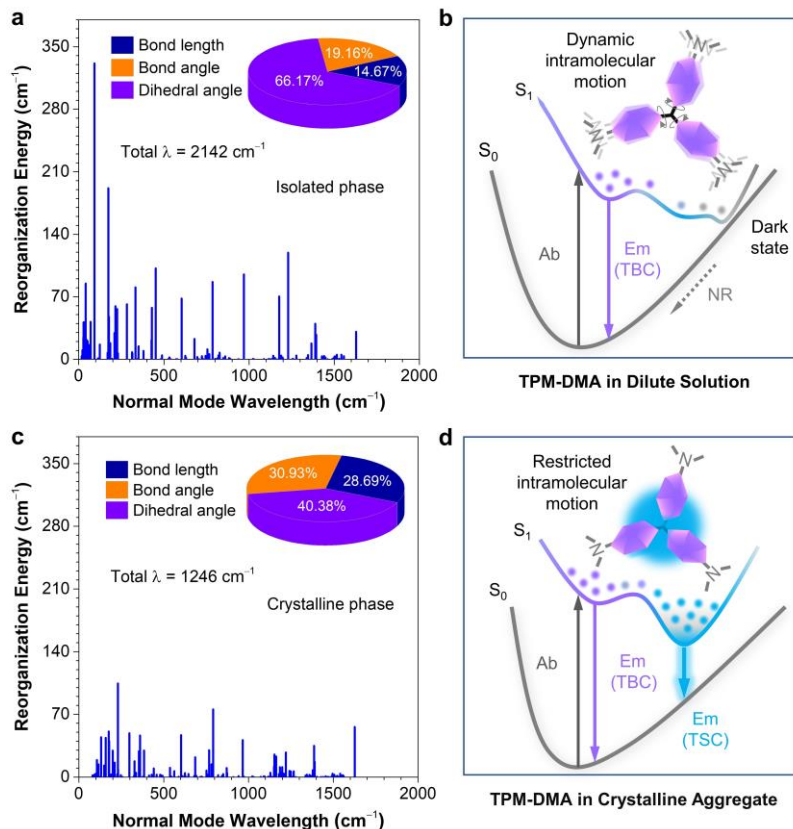


Figure 8. Plots of reorganization energy vs. normal mode wavenumber of TPM-DMA in (a) isolated and (c) crystalline phases calculated by TD-DFT, B3LYP-D3/6-31G(d,p), Gaussian 16 program. Inset: proportions of bond length, bond angle and dihedral angle contributed to total reorganization energy. Potential energy surfaces of TPM-DMA in (c) solution and (d) aggregate states. Ab = absorption, Em = emission, and NR = nonradiative decay.

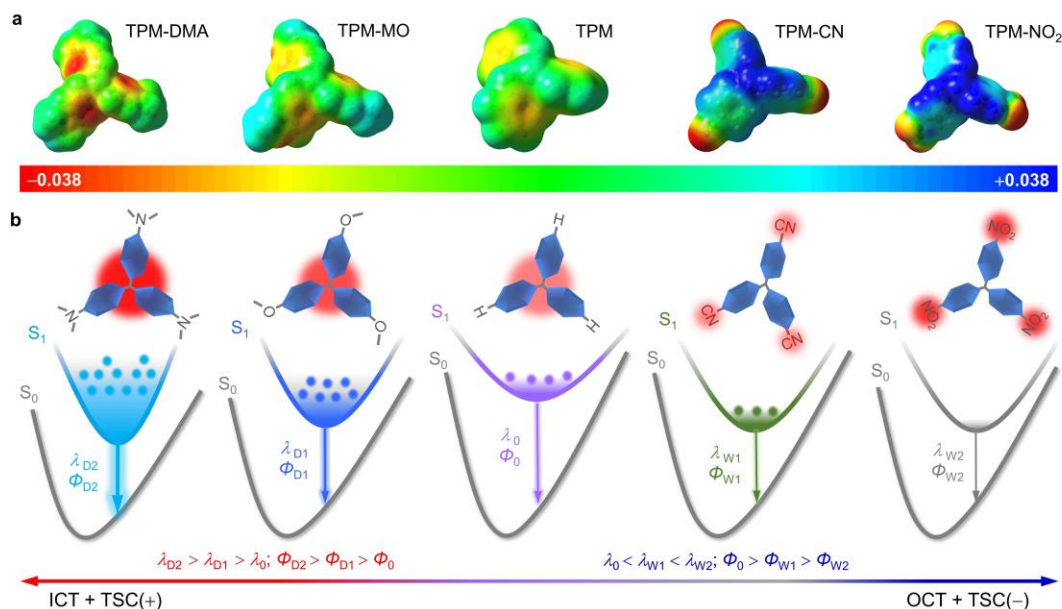


Figure 9. (a) Electronic static potential (ESP) mapped on the isosurface of electronic density, based on optimized excited-state geometries of TPM-R. Negative electrostatic potential (red) represented high electronic density, whereas positive one (blue) corresponded to low electronic density. The numbers of potential were given in au. (b) First line: effects of charge transfer (CT) and TSC; Second line: the proposed potential energy surfaces for the clusteroluminescence of TPM-R; ICT = inward charge transfer, OCT = outward charge transfer, + = stabilization/increment, - = destabilization/decrement.

To investigate how electron-donating or withdrawing groups affect TSC and clusteroluminescence, the excited-state electronic static potential based on electronic density was mapped. As shown in **Figure 9a**, the red parts represented high electronic density, while those showing blue corresponded to low density. Apparently, electron-donating groups provided more electrons to the central part of molecular skeleton as the red color was observed on the three phenyl rings of TPM-DMA and TPM-MO. TPM, as the basic compound, showed lower electronic density at the central phenyl rings than its electron-donating derivatives. In contrast, TPM-CN and TPM-NO₂ with strong electron-withdrawing groups exhibited low electronic density at the central phenyl rings, and the electrons were pulled to the exterior cyano and nitro groups. Accordingly, a complete picture of clusteroluminescence of these different systems was summarized from the perspective of intramolecular TSC (**Figure 9b**). In the excited state, electron-rich TPM derivatives pushed electrons from donors to the central phenyl rings, to trigger an inward charge transfer (ICT) process and stabilize the intramolecular TSC. Therefore, from TPM, then TPM-MO and finally to TPM-DMA, the wavelength and efficiency of clusteroluminescence became longer and higher. In contrast, TPM derivatives with electron-withdrawing groups attracted electrons from the central phenyl rings to the exterior acceptors, to produce an outward charge transfer (OCT) and destabilize the TSC. Finally, TPM-CN and TPM-NO₂ showed inefficient clusteroluminescence although the energy levels of their TSC states were lower than TPM and even their electron-rich cousins.

Conclusion

In this work, nonconjugated triphenylmethane (TPM) and its derivatives with electron-donating (TPM-DMA and TPM-MO) and electron-withdrawing (TPM-CN and TPM-NO₂) groups were synthesized and their photophysical properties were systematically investigated. Except TPM-NO₂, all the molecules exhibited dual emission in the aggregate state: a short-wavelength peak from TBC and a long-wavelength clusteroluminescence stemmed from TSC. Meanwhile, introduction of the electron-donating groups had been found to red-shift the wavelength and increase the efficiency of the clusteroluminescence at the same time. Crystal packing and theoretical calculation suggested that the addition of donors not only increased the electronic density for TSC but also stabilized the formed excitons by restricting the intramolecular motion. However, the introduction of acceptors decreased the emission efficiency, but still caused a bathochromic shift in clusteroluminescence. Different from TPM and the electron-donating counterparts, TPM-CN and TPM-NO₂ exhibited both intra- and intermolecular TSC to result in the reddest clusteroluminescence of TPM-CN. But the vigorous excited-state intramolecular motion and unfavorable intermolecular PET process destabilized the excited excitons to eventually quench the light emission. This work not only proves the general mechanism of through-space conjugation for clusteroluminescence in nonconjugated luminogens but also provides a reliable strategy to manipulate its emission efficiency and color simultaneously. It is anticipated that the development of TSC theories will

establish a significant linkage between molecular and aggregate photophysics.

ASSOCIATED CONTENT

Supporting Information. Materials and methods, synthetic procedures, characterization, crystallographic data (TPM-DMA, TPM-MO, TPM-CN and TPM-NO₂) and computational details, including Figures S1-S29 and Tables S1-S13. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was partially supported by the National Natural Science Foundation of China Grant (51773076, 21871060, 81271476 and 31870991), the Innovation and Technology Commission (ITC-CNERC14SC01), the Research Grants Council of Hong Kong (16305518, 16307020, C6014-20W, C6009-17G, and N-HKUST609/19), and the Material Science Foundation of Guangdong Province (2019B121205012 and 2019B030301003). H. Z thanks to the support from the Fundamental Research Funds for the Central Universities and the Open Fund of Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, and South China University of Technology (2019B030301003).

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