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Complex from Ionic β-Cyclodextrin Polyrotaxane and Sodium Tetraphenylthiophenesulfonate: Restricted Molecular Rotation and Aggregation-Enhanced Emission

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As restricted intramolecular rotation (RIR) is the main mechanism responsible for the aggregation-induced or -enhanced emission (AIE or AEE), we thereby use rigid polyrotaxane to impose effective RIR for an ionic water-soluble, AEE-active luminogen of sodium 4,4',4",4"'-(thiophene-2,3,4,5-tetrayl)tetrabenzenesulfonate (TPS). Jeffamine-included β-cyclodextrin (JA-included β-CD) with cationic ammonium terminals was used as rigid component to complex with sulfonate anions of TPS, resulting in iTP-CD-JA complex for characterization. Comparison is also made on complex of iTP-JA prepared from the complexation of TPS with the flexible JA chains. Without the incorporation of rigid β-CD rings, the iTP-JA complex is inferior to the iTP-CD-JA complex in the emission efficiency. The role of rigid template in imposing effective RIR on AEE-active luminogen is thus demonstrated in this study.

Introduction

As the first-discovered molecule with aggregation-induced emission (AIE) properties, 2,3,4,5,6-pentaphenyl-1-methylsilole[1,2] (PMS) exhibits the interesting emission behaviour that the non-luminescent dilute solution of PMS can be tuned to emit intensely in the solution aggregated state. With the beneficial emission properties in the aggregated state, lots of AIE-active luminogens containing tetraphenylethylene,[3,4] phenothiazine,[5,6] anthracene,[7,8] triphenylethylene,[9.10] distyrylanthracene,[11,12] carbazolyl[13,14] groups and AIE-active metal complexes[15,16] had been prepared and characterized and for the practical aspects, AIE-active materials in biomedical applications[17-19] were also explored extensively. Theoretically, study[20-22] on AIE-active luminogens of different molecular shapes has concluded that the restriction of intramolecular rotations and vibrations (RIR and RIV) are the main causes for the AIE phenomena observed in the propeller-shaped and shell-like luminogens, respectively. Most of AIE-active luminogens are propeller-shaped molecules and therefore, efficient RIR is considered to be the most important mechanism for the AIE-related emission behaviour. By efficient RIR in the aggregated state, the non-radiative decay pathways of the exciton via vibrational/torsional energy relaxation can be largely reduced to result in the desired enhanced luminescence. With the beneficial strong emission in the solid application state, several organic and polymeric materials[23-28] with AIE or aggregation-enhanced emission (AEE) properties have been developed and well characterized.

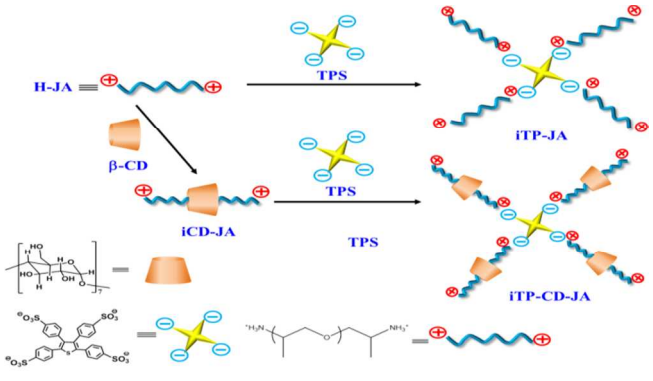
Conceptually, molecular rotation of organic lumingens can be hampered internally or externally. Internally, bulky substituents with high rotation energy barrier can be introduced via chemical bonds[23,25,29-31]. Externally, molecular motion of luminogens can be effectively frozen in a rigid media; hence, viscous polymer matrix can be used as rigid matrix to impose effective rotational restriction on the AIE-active lumingens, causing the desired emission enhancement of the luminogen/polymer blend. To ensure full miscibility between luminogens and polymer matrix, hydrogen bond (H bond)[32-39] and electrostatic interactions forces[40,41] had been

previously used to generate AIE-active blend systems with intense luminescence. Bound by the viscous polymer chains through preferable H bond or ionic interaction forces, the AIE-active luminogens are considerably restricted in rotational motion and therefore emit intensely.

Unlike the pair-like H bond interactions, the electrostatic interactions involved in ionic species are non-site specific. To accomplish complexation reaction, AIE-active luminogens must be functioned with cationic (or anionic) groups to complex with polyelectrolytes (PELs) of opposite charges. After complexation, the hydrophobic aromatic luminogens tend to form aggregates phase-separated from the hydrophilic PELs. The resulting complexes thus contain two phases, in between stabilized by the intermediate ionic layer. An ammonium-functionalized tetraphenylthiophene (TP) derivative[41] of TP-NH_3^+ was therefore synthesized and reacted with different amounts of anionic PEL of poly(sodium vinylsulfonate) (PSV). The non-site specific long-range electrostatic interaction forces and the self-aggregation of TP-NH_3^+ species increase with increasing PSV content; therefore, emission of the PEL-stabilized TP-NH_3^+ aggregates can be successfully raised by increasing PSV content in the solution and solid states. Conversely, adding NaCl will dissociate the long-range electrostatic interactions, resulting in emission quenching of the complex blends.

Cyclodextrin molecules (CDs) are cyclic oligosaccharides made up of six (α), seven (β), eight (γ) or more glucopyranoside units[42] and the three-dimensional structure of the CDs can be considered as a hollow truncated cone (host) for including small molecules[43-45] or linear polymers[46-52] to generate different polypseudorotaxane or polyrotaxane for potential applications in controlled release of drugs in living organisms and drug delivery.[53-55] The hydrophobic cavity of CDs is also an ideal loci to impose efficient RIR for the AIE-active luminogens. A diboric acid-functionalized tetraphenylethene (TPE) derivative[56] can cooperatively bind to two pairs of alternative diols on a β-CD, resulting in highly-emissive solution due to the effective RIR of the CD-incorporated TPE derivative. More recently, TPE was also linked to the α-, β- and γ-CDs[57] through ester bonds and the resulting complexes show varied emission responses dependent on the cavity size of CDs. Solution emission of the β-CD-linked complex is weaker than α-CD-incorporated complex but is stronger than the one linked by γ-CD. The highest emission efficiency of the α-CD-linked complex is owing to that the smaller cavity of α-CD restricts the motions of luminogen more efficiently than the larger-sized β- and γ-CD cavities. Recently, AIE-active amphiphilic tetraphenylethylene derivatives[58] were prepared and reacted with γ-CD to show new insight for AIE behaviour. When included in the cavity of γ-CD, the amphiphilic luminognes showed an enhanced monomer emission and a decreased aggregate emission. All the examples illustrate the use of CD in constructing new AIE-active systems.

This study tests the concept that a rigid Jeffamine-included β-CD can serve as efficient template in imposing rotational restriction to an AEE-active complex stabilized by long-range electrostatic interactions. To demonstrate the important role of chain rigidity, Jeffamine (H-JA), as the representative flexible chain, and the β-CD-included Jeffamine (iCD-JA), as the representative rigid chain, with ammonium terminals (Scheme 1) were employed as cationic components to complex with sulfonate anions in an AEE-active luminogen of sodium 4,4',4",4'"-(thiophene-2,3,4,5-tetrayl)tetrabenzenesulfonate (TPS), generating the respective flexible iTP-JA and rigid iTP-CD-JA complexes for comparison. Stabilized by long range electrostatic interaction forces, the hydrophobic TPSs will associate to form aggregates separated from the hydrophilic Jeffamine (H-JA) or β-CD-included Jeffamine (iCD-JA). For iCD-JA, the outer β-CD rings will stiffen the flexible Jeffamine chain to result in rigid template efficient in imposing rotational restriction to the neighbouring TPSs. Without the rigid β-CD as outer jacket, the flexible chains of H-JA are less effective in restricting molecular motion of TPS; hence, flexible iTP-JA complex is expected to be inferior to rigid iTP-CD-JA complex in emission efficiency. Study on emission behaviour of TPS, iTP-JA and iTP-CD-JA therefore help elucidating the important role of RIR on the AEE-active luminogens.



Scheme 1 Chemical structures of Jeffamine and TPS and the preparation of iTP-JA and iTP-CD-JA complex.

Experimentals

Materials

Dichloromethane, methanol, hydrochloric acid and sodium hydroxide were purchased from Aldrich Chemical Co. Chlorosulfonic acid was purchased from Lancaster Synthesis. Jeffamine D-400 (diamino-terminated poly(propylene glycol) was purchased from Alfa Assar. β-Cyclodextrin was purchased from Tokyo Chemical Industry Co. TP was prepared according to the reported procedures[59].

Instrumentations

The ^{1}H and ^{13}C NMR spectra were recorded by a Varian VXR-500 MHz instrument. UV-vis absorption spectra were recorded with an Ocean Optics DT 1000 CE 376 spectrophotometer. Emission spectra were obtained from a LabGuide X350 fluorescence spectrophotometer using a 450 W Xe lamp as the continuous light source. Ultraviolet-visible (UV-vis) absorption spectra were recorded with an Ocean Optics DT 1000 CE 376 spectrophotometer. A quartz cell with dimensions of 0.2 x 1.0 x 4.5 cm^3 was used for the UV-vis absorption and the emission spectra measurements. Solution quantum yield (Φ_F) was determined by comparison with a quinine sulfate standard solution (10^{-4} M in 1 N H_2SO_4). Quantum yield of the solid samples was measured from an integration sphere made by Ocean Optics. Fourier-transform infrared **(**FTIR) spectra were obtained on a Bruker Tensor 27. Elemental analyses were performed on an Elementary Vario EL-III C, H, N, O and S analyzer. The decomposition temperature and char yield of the complexes were obtained from a TA Q-50 thermogravimetry analyzer (TGA) with a scan rate of 10°C/min.

Synthesis of sodium tetraphenylthiophenesulfonate (TPS).

Into the nitrogen-blanketed stirred solution of TP (2.0 g, 5.15 mmol) in dichloromethane (30 mL), chlorosulfonic acid (1.54 mL, 23.18 mmol) was added dropwise. The reaction mixture was then stirred at room temperature for 24 h before poured into crushed ice. Into the ice-cooled mixture, aq. NaOH (0.5 N) was added slowly until pH > 9. The precipitate was filtered off and was recrystallized from distilled methanol before vacuum dried at 80°C for 24 h to give the white solid product (2.3 g, 56.1 %). ^{1}H NMR (500 MHz, D_2O) (ppm): 7.72, 7.71 (d, 4H, aromatic H), 7.63, 7.61 (d, 4H, aromatic H) , 7.47, 7.45 (d, 4H, aromatic H), 7.22, 7.20 (d, 4H, aromatic H) (Figure S1A), ^{13}C NMR (500 MHz, D_2O) (ppm): 141.53, 141.22,139.128, 138.80, 138.72, 136.27, 131.32, 129.64, 125.74, 125.35 (Figure S1B). MS m/e: calcd for $C_{28}H_{16}Na_4O_{12}S_5$: 795.9; found, 796.6 (M+); Anal. Calcd for $C_{28}H_{16}Na_4O_{12}S_5$: C, 42.21; H, 2.02; O, 24.10; S, 20.12. Found: C, 42.32; H, 2.08; O, 24.07; S, 20.1.

Preparation of H-JA.

Hydrochloric acid (1.18 M, 2 mL) was dropped slowly into solution of Jeffamine (2.92 g) in deionized water (4 mL). The whole mixture solution was then under vigorous stirring for overnight. The resulting stocked solution (1.13 M) of H-JA was stored in refrigerator before use.

Preparation of iCD-JA complex from H-JA and β-CD.

Into the solution of β-CD (0.38 g, 0.335 mmol) in deionized water (15 mL), stocked solution of H-JA (0.2 ml, 0.067 mmol) was slowly added dropwise. The resulting mixture was subjected to ultrasonic agitation for 24 h before precipitation from methanol. The white precipitant was collected by filtration and dried in the vacuum oven at 50 °C for 24 h. The stoichiometry of the resulting complex was determined by the solution ^{1}H NMR spectrum of iCD-JA (Figure 3), The number of the included β-CD per Jeffamine chain is 1.1 calculated from the integrated ratio between propylene methyl protons (peaks **a** and **b** in Figure 3) of Jeffamine and aromatic protons of TPS.

Preparation of iTP-JA complex

Solution of TPS (0.025 M) in deionized water was added into solution of H-JA and the resulting mixtures were ultrasonically shaken for 24 h. The solvent was then removed from the product solution by rotary evaporator and the final product was obtained after drying in vacuum oven at 50 °C for 24 h.

Preparation of iTP-CD-JA complex

The inclusion complex of iCD-JA was primarily prepared by ultrasonically shaking the solution of β-CD (0.38 g, 0.335 mmol) and H-JA (0.2 ml, 0.067 mmol) in deionized water (10 mL). To the resulting mixtures, solution of TPS (0.025 M) in deionized water (5 mL) was subsequently added slowly. After shaking for another 24 h, methanol was then added to precipitate white powder from the solution. The final product was obtained by drying the filtered solid at 50 °C under vacuum for 24 h.

Results and discussion

The key material (Scheme 1) used for the formulations of iTP-JA and iTP-CD-JA complexes is the water-soluble luminogen of TPS. This new AIE-active luminogen of TPS was prepared from sulfonation reaction of TP. Similar to the TP precursor, the ionic TPS is AEE-active material; however, since an AEE-active TPS is the premise for an AEE-active complex system, we need to identify the AEE property of TPS before further characterization on the complex system.

AEE emission behaviour of TPS

AEE property of the water-soluble TPS can be verified by its emission responses towards concentration and aggregation. The concentration effect was confirmed by the emission spectra of the solution and the solid TPS (Figure 1 A). The emission spectra in Figure 1A basically contain two overlapped bands with the short- (at ~415 nm) and the long-wavelength (at ~480 nm) ones from the monomer and the aggregate emissions, respectively. For the solution samples, increasing solution concentration from 10^{-5} to 10^{-3} M results in the intensity gains of both emissions and for the most condensed solid sample, the resolved monomer and aggregate emissions are both stronger than the solution emissions. With extensive aggregation and frozen molecular motion, solid sample should be higher in emission intensity in respect to more efficient rotational restriction compared to the mobile solution state. Aggregation is beneficial for the aggregation emission and that is why fraction of aggregation emission continuously increases as concentration of TPS is increased from 10^{-5} to 10^{-3} M. For sure, the most condensed solid sample possesses the highest fraction of aggregation emission among all spectra in Fig. 1A. The concentration-enhanced emission is therefore correlated with the AEE property.

Aggregates formed upon non-solvent inclusion also change the emission behaviour of the AEE-active material. Here, DMF is the poor solvent used to generate suspended aggregates from the aqueous TPS solution. As illustrated in Figure 1B, raising content of DMF from 0 to 80 vol% changes little on the emission spectra but careful inspection indicates a consistent trend that the fraction of aggregate emission gradually increases, at the sacrifice of monomer emission, with increasing DMF content in the solution. Although small in magnitude, the systematic variations of the monomer and aggregate emissions still illustrate the important role of aggregation on the emission of TPS; therefore, the water-soluble TPS is an AEE-active luminogen.

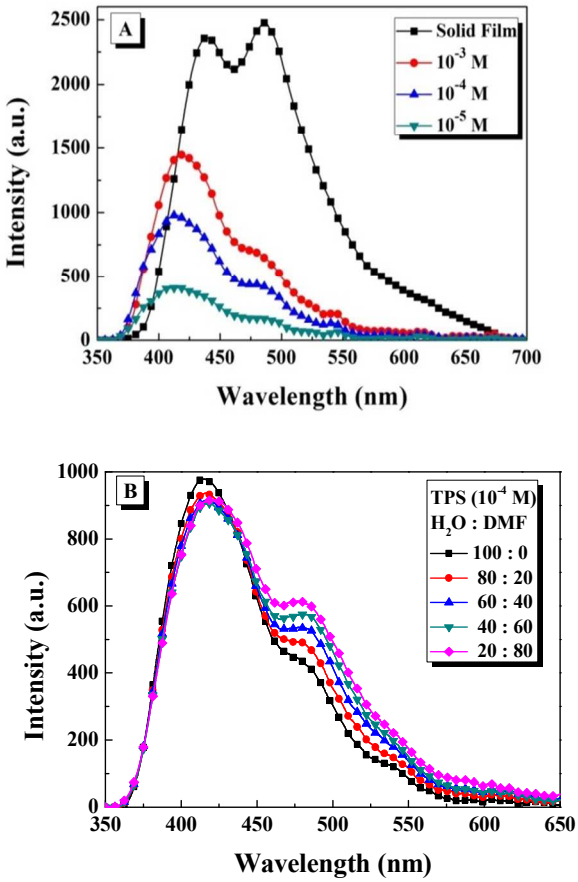


Figure 1 The emission spectra of (A) the aqueous TPS solutions of different concentrations and (B) the TPS (10^{-4} M) in H_2O/DMF mixtures of different volumetric ratios (λ_{ex} = 350 nm).

Solution properties of the complexes

Mixtures of TPS and H-JA (or iCD-JA) with equivalent molar ratio of ammonium cation and sulfate anion were primarily mixed in deionized water to generate stable aqueous solutions, from which solid complex of iTP-JA (or iTP-CD-JA) can be obtained after water removal. Before discussion on the solid system, primary study on the solution precursors was conducted first with the purpose to clarify the relationship between RIR and AEE-related emission behaviour.

The solution emission spectra in Figure 2A were measured under the condition that the concentration of the fluorescent TPS is kept at a constant value of 10^{-2} M. Since the content of the luminogen is the same, the resulting emission spectra should be the same if no other environmental factor was involved. The spectra in Figure 2A are nevertheless different, with the emission intensity varied in the order of iTP-JA > iTP-CD-JA > TPS. The emission difference is

nevertheless due to the absorption difference of the solutions since the corresponding UV-vis spectra in Figure 2B show a relative absorbance order of TPS > iTP-JA > iTP-CD-JA. To have more accurate assessment on the emission behaviour, we hence measured the solution quantum efficiency (Φ_F), using quinine sulfate standard.

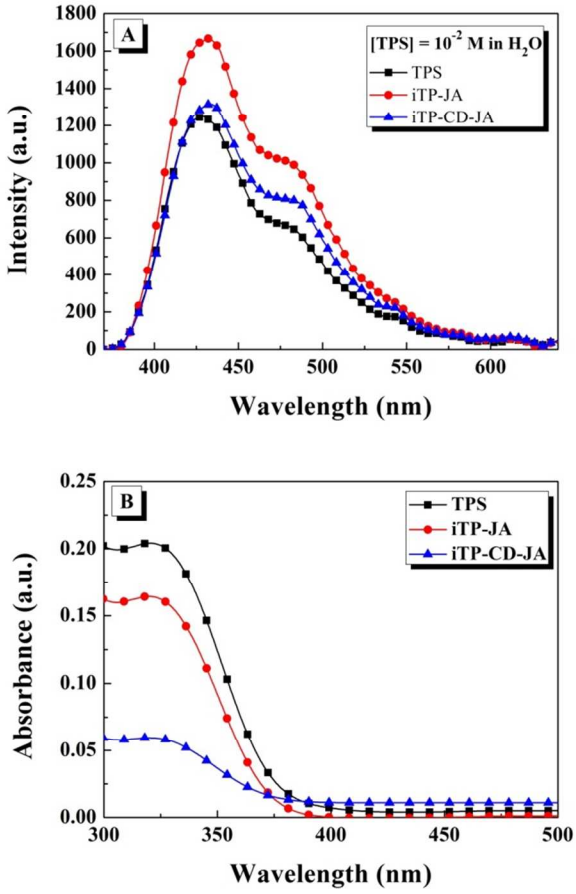


Figure 2 Solution (A) emission and (B) absorption spectra of pure TPS, iTP-JA and iTP-CD-JA complex in H_2O ([TPS] = 10^{-2} M, λ_{ex} = 350 nm).

By taking into accounts the data from the absorption and the emission spectra, the resulting Φ_Fs (Table 1) actually follow an order of iTP-CD-JA > iTP-JA > TPS, essentially different from the emission intensity order shown in Figure 2A. Upon photo irradiation, the excited iTP-CD-JA species actually emit more efficiently than the excited iTP-JA and the excited TPS. The resolved Φ_Fs reflect the relative rotational restriction imposed by the surrounding environment. Compared to flexible H-JA, the rigid iCD-JA is more efficient in imposing rotational restriction on the neighbouring TPS luminogens. We may also indirectly conclude that β-CDs in iCD-JA are indeed threaded by Jeffamine chain because without the incorporated rigid β-CDs, iCD-JA in the complex should not exert different extent of rotational restriction to result in an emission essentially distinguished from the flexible iTP-JA. Without polymer ingredient, the small-mass TPSs are free to move in the mobile water media, rendering an emission with the least efficiency among three solution samples. Effective rotational restriction is the key factor controlling the solution emission and we can also evaluate the relative extent of rotational restriction by the solution ^{1}H NMR spectra conducted below.

Table 1 Quantum yield (Φ_F) of TPS, iTP-JA, and i-TPS-CD-J in the solution and solid states.

Sample	Φ_F[a] (solution)	Φ_F[b] (solid)
TPS	0.031	0.18
iTP-JA	0.059	0.21
iTP-CD-JA	0.117	0.36

[a] measured by using an quinine sulfate standard (in 1 N H_2SO_4). [b] measured from integration sphere.

The ^{1}H NMR band shape analysis had been previously utilized in the studies of rotation-induced conformational changes around the axes of the single bonds linked to the central rings of AIE-active silole derivative[60] The fast conformational exchanges caused by the fast molecular ratations give sharp resonance peaks, whereas the slower exchanges due to restricted molecular rotation broaden the resonance peaks. Accordingly, the ^{1}H NMR band shape analysis can be used to evaluate the relative extent of rotational restriction in the solutions of TPS, iTP-JA and iTP-CD-JA. Except the spectrum of pure β-CD, the ^{1}H NMR specra of TPS, iTP-JA and iTP-CD-JA (Figure 3) were all conducted on a solution with the same TPS concentration (= 10^{-2} M), in order to eliminate potential complication from concentration difference. In the spectral range of 7 to 8 ppm, spectrum of pure TPS contains four large and sharp doublets, in correlation to the resonances of aromatic protons of TPS. The sharp aromatic resonance peaks became broaden and reduced in intensity in the solutions of iTP-JA and iTP-CD-JA. The viscous polymer chains of H-JA and iCD-JA therefore impose effective rotational restriction on the neighboring TPSs, resulting in sluggish response of the aromatic protons of TPS toward the stumuli of external magnetic field. Comparatively, the rigid iCD-JA is more effective in imposing rotational restriction than the flexible H-JA

since the aromatic resonance peaks in the spectrum of iCD-JA turn out to be more borader and lower in intensity than those in the spectrum of iTP-JA. The band shape analyis reveals that the relative rotational restriction in three systems are in the order of iTP-CD-JA > iTP-JA > TPS, which is in correlation to the emission intensity shown in Figure 2A.

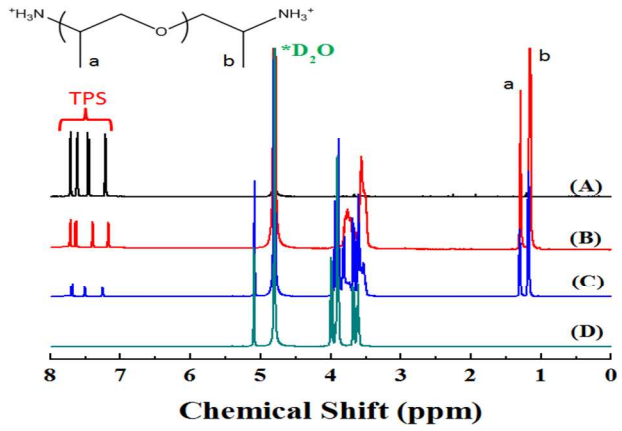


Figure 3 ^{1}H NMR spectra of (A) pure TPS, (B) iTP-JA, (C) iTP-CD-JA and (D) β-CD in D_2O ([TPS] = 10^{-2} M).

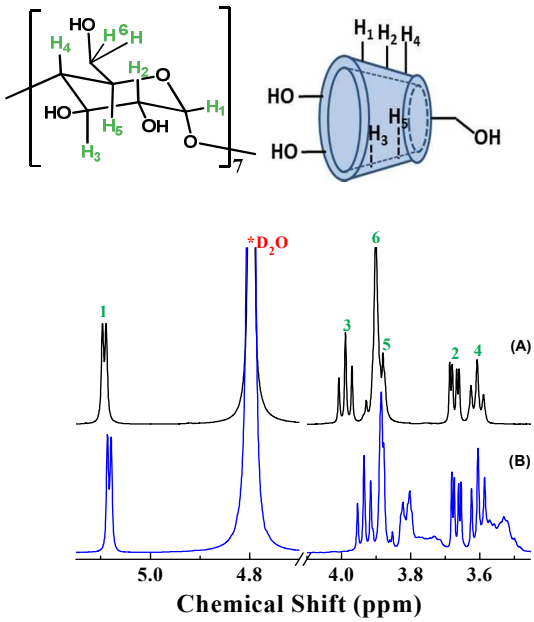


Figure 4 Solution ^{1}H NMR spectra of (A) pure β-CD (B) iTP-CD-JA in D_2O. [TPS] = 10^{-2} M.

Inclusion of Jeffamine also changed the proton resonances of β-CD. Previous study[61-63] indicates that inclusion of polymer causes upfield shifts of the resonance peaks of β-CD and the chemical shifts of the inside protons, named H_3 and H_5 (Figure 4), are slightly higher than other protons (H_1, H_2, H_4 and H_6) located at outside layer. Figure 4 is the solution ^{1}H NMR spectra of β-CD and iTP-CD-JA in the spectral range (3.4 to 5.2 ppm) covering the resonance peaks of β-CD. Values of chemical shifts from Figure 4 were summarized in Table 2 to illustrate the chemical shift difference caused by polymer inclusion. Due to the high electronic density, all of the resonance peaks of iTP-CD-JA appear at higher field than those for pure β-CD. However, the upfield shifts are especially significant for the interior protons of H_3 and H_5 and the upfield shifts are therefore attributed to the polymer inclusion. This result demonstrates the successful preparation of polymer-included complex system.

Table 2 Chemical shifts (ppm) of resonance peaks in pure β-CD and in iTP-CD-JA complex.

Sample	H_1	H_2	H_3	H_4	H_5	H_6
β-CD	5.0928	3.6733	3.9884	3.6074	3.8799	3.9005
iTP-CD-JA	5.0825	3.6679	3.9347	3.6049	3.8135	3.8848
$\Delta\delta^a$	0.0103	0.0054	0.0537	0.0025	0.0664	0.0157

[a] chemical shift difference between β-CD and iTP-CD-JA.

Solid properties of the complexes

By comparing TGA thermograms of β-CD, TPS, iTP-JA and iTP-CD-JA (Figure 5) solids, we are able to verify that β-CDs in the iTP-CD-JA are indeed threaded by Jeffamine. Pure TPS, β-CD and complexes of iTP-JA and iTP-CD-JA all show an early weight-loss at low temperatures (< 100 °C) due to the absorbed water; except that, the resolved decomposition traces should be true reflection of the thermal stability of all samples. The small-mass TPS turns out to be superior in thermal stability with the major decomposition initialized at high temperature (> 500 °C). The high thermal stability of TPS is due to the ionic sodium sulfonate bonds since the neutral analogue of tetraphenylthiophene (TP) decomposes at quite low a temperature (< 300 °C, Figure S2). In contrast to the stable TPS, pure β-CD is quite unstable and its decomposition starts at a low temperature of ~332 °C[64] and proceeds rapidly with little residues after 350 °C. Therefore, incorporation of β-CD is detrimental for the thermal stability of the complexes; in contrast, TPS component acts to reinforce thermal stability of the complexes as evidenced by the late decomposition of the iTP-JA complex. With both β-CD and TPS in the complex, iTP-CD-JA exhibits a dual-decomposition behaviour

with the early-stage decomposition, originated from the easily-degraded β-CD, at a low temperature of ~300 °C and the second-stage high-temperature decomposition, due to the degradation of the ionic TPS, beginning at a high temperature of 700 °C. The main decomposition at the early stage corresponds to a 49 % weight-loss, which approximates the theoretical weight percentage (53 %) of the β–CD rings in iTP-CD-JA. The result therefore indicates that most of the β-CDs added in the solution preparation step are still present in the solid iTP-CD-JA, acting to rigidify the flexible Jeffamine chains to result in iCD-JA template efficient in imposing the desired rotational restriction. The resulting iTP-CD-JA complex should be good emitter with the effective rotational restriction.

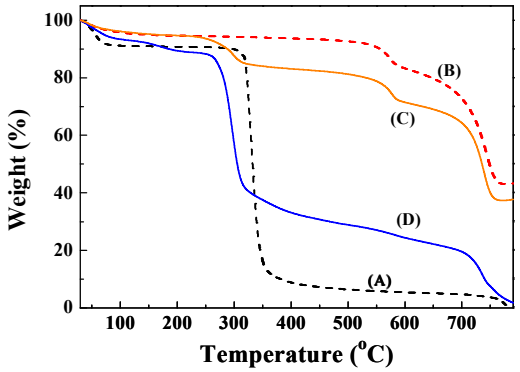


Figure 5 TGA thermograms of (A) β-CD, (B) TPS, (C) iTP-JA and (D) iTP-CD-JA (heating rate = 10 °C/min).

The advantage of Jeffamine-included β-CD (iCD-JA) in immobilizing the luminogenic TPSs can be evaluated from the solid emission spectra shown in Figure 6. Primarily, all three solids of TPS, iTP-JA and iTP-CD-JA emit with higher intensity compared to their solution analogues (cf. Figure 2A). Particularly, solid iTP-CD-JA shows much better emission intensity than its solution precursor. Quantum yields (Φ_F) determined from the solution and the solid samples (Table 1) also illustrate the same conclusion that Φ_Fs of the solid samples are all comparatively higher than their solution counterparts. The high solid state emission is reasonable in considering that molecular rotation of the fluorescent TPSs should be considerably blocked in the frozen solid state. The resulting Φ_F values measured from the integration sphere are in the order of iTP-CD-JA (= 0.36) > iTP-JA (= 0.21) > TPS (= 0.18). In corresponding to the effective rotational restriction imposed by the rigid iCD-JA, iTP-CD-JA complex exhibit the highest Φ_F of 0.36. With lower content (= wt%) of the fluorescent TPS, iTP-CD-JA is however higher in emission efficiency than pure TPS and iTP-JA. Effective rotational restriction, rather than the content of the luminogen, is therefore the key factor in determining the emission efficiency of the AEE-active system.

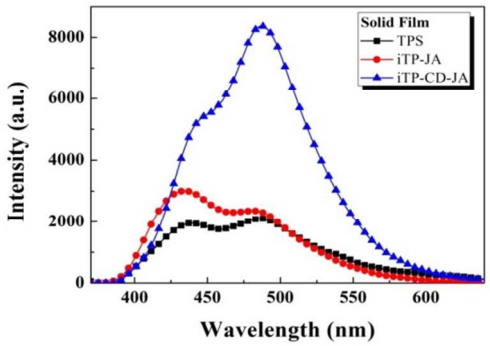
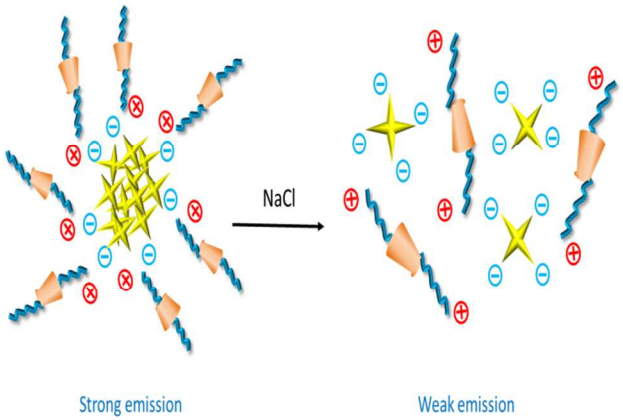


Figure 6 Solid FL spectra of pure TPS, iTP-JA and iTP-CD-JA complex (λ_{ex} = 350 nm).

Besides the intensity difference, the most noticeable feature in Figure 6 is the large aggregate emission, with intensity higher than the monomer emission, shown in the spectrum of iTP-CD-JA. The large aggregate emission for iTP-CD-JA refers to a high degree of aggregation of TPSs in the complex. In the highly-aggregated phase-separated domains, TPSs are supposed to be tightly packed and clumsy in rotation, resulting in the intense aggregated emission. The effective rotational restriction imposed by the rigid iCD-JA template is thus verified from the emission of iTP-CD-JA.

Long-range electrostatic interaction of the iTP-CD-JA complex

Emission behaviour of the iTP-CD-JA complex is closely related to the extent of aggregation of the luminescent TPS. As illustrated in Scheme 2, the molecular chain arrangements of complex iTP-CD-JA are determined by the long-range electrostatic interactions between the cationic iCD-JA and the sulfonate anions of TPS. With non-site specific, long-range interactions, the aromatic rings of TPSs tend to associate together to form interpolymer aggregates, which are phase separated from the hydrophilic iCD-JA chains, stabilized by the long-range electrostatic forces between the ammonium cations of iCD-JA and the sulfonate anions of TPS. The long-range electrostatic forces should be prevalent in the solution preparative state. After solvent removal, the solid blend remains to have the fundamental two-phase morphology, within which the TPS anions do not distribute randomly but rather form aggregates with high local concentration. With the high local concentration, TPSs are therefore tightly packed to contribute the large aggregate emission in the spectrum of iTP-CD-JA (Figure 6).



Scheme 2 Schematic illustration for the association and dissociation of long-range interactions between TPS anions and iCD-JA cations.

In the solution preparative state, relative strength between the hydrophobic dispersion forces of the aggregated luminogens and the long-range electrostatic interactions affect the stability of the aggregated particles. Formation of aggregated TPSs is beneficial for the AEE-related emission efficiency; conversely, dissociation of the aggregated TPS phase will lead to the lowering of the luminescence. To demonstrate, strong polyelectrolytes of NaCl were intentionally added to the complex solution of iTP-CD-JA. With small size and strong ionic strength, NaCl ions are capable to penetrate into the interior of the aggregated complexes of iTP-CD-JA, dissociating the ionic ammonium-sulfate bonds in between iCD-JA and TPSs.

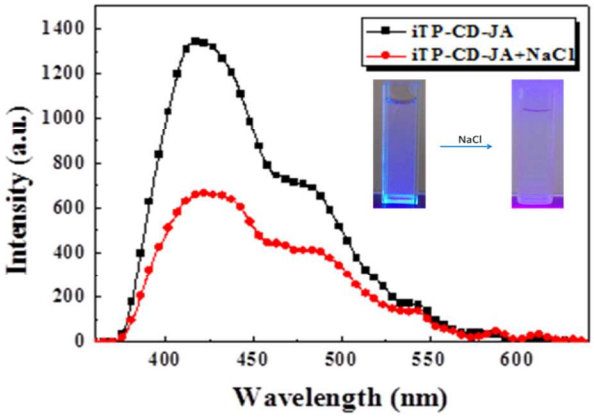


Figure 7 Emission spectra of the aqueous iTP-CD-JA solutions with and without NaCl additive ([TPS] = 10^{-4} M, [NaCl] = 10^{-2} M, λ_{ex} = 350 nm) and the luminescence difference upon adding NaCl (λ_{ex} = 365 nm).

Certain fractions of the ionic ammonium-sulfate bonds are thus ruptured by the strong NaCl electrolytes, leading to the collapse of the aggregated TPSs and the release of free TPSs (Scheme 2). The released TPSs in the aqueous media are no longer hampered in rotation as compared to when they are in the aggregated TPSs; therefore, adding NaCl to the aqueous iTP-CD-JA solution results in emission spectra (Figure 7) with comparatively lower intensity and broader feature compared to the pure iTP-CD-JA without NaCl additive. The important role of long-range electrostatic interaction on the AEE-related emission behaviour is therefore demonstrated.

Conclusion

In present work, water-soluble luminogen of TPS was synthesized and was identified to be AEE-active by its emission responses toward concentration and aggregation. The water-soluble TPS was then mixed with H-JA and iCD-JA to generate flexible and rigid complexes of iTP-JA and iTP-CD-JA, respectively, for evaluating the relationship between rotational restriction and AEE-related emission. Result from solution ^{1}H NMR spectra indicates a more effective rotational restriction is operative in the iTP-CD-JA complex as compared to the flexible iTP-JA. With more effective rotational restriction, solution of iTP-CD-JA emits with higher efficiency than the solution of iTP-JA.

Emission of solid iTP-JA is higher in intensity than the small-mass TPS but is inferior to the solid iTP-CD-JA. The results suggest that the rigid iCD-JA is more effective in imposing rotational restriction on the luminogenic TPSs, as compared to the flexible H-JA used in iTP-JA. Instead of the content of the luminogen in the complex, effective rotational restriction is the real operative factor controlling the emission efficiency of the complex blend.

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Notes and references

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