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Aggregation-induced emission and intermolecular charge transfer effect in triphenylamine fluorophores containing diphenylhydrazone structures

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Three newly chromophores incorporating acceptor-π-donor-π-acceptor structural motifs and mono-, di- and tri-branched diphenylsulfone base linked to triphenylamine through a hydrazone  $\pi$ -bridge were synthesized, and the photoluminescence properties of three chromophores were studied in solutions as well as in aggregated states. All fluorophores emitted strong blue fluorecence in THF. Mono-, di-branched triphenylamine exhibited increasing blue fluorescence and displayed AIEE effect in aggregated state. And tri-branched triphenylamine emitted green fluorescence and presented AIE effect in aggregated state. These interesting phenomenons have been interpreted by molecular stacking mode with Molecular Dynamics (MD) and DFT calculations. The unique propeller shaped molecular configuration of triphenylamine prevented face to face  $\pi$ - $\pi$  stacking and induced the hindered rotation which resulted in AIEE or AIE effect in aggregated state. The enlarged coplanarity of diphenylhydrazone chains increased the conjugation of tribranched triphenylamine, which was beneficial to the formation of ICT and AIE and came into emitting green ICT fluorescence in aggregated state. Fluorescent microscope imaging and the fluorescent pictures of powder states certificated effect the strong AIEE effect AIE in solid.

## 1. Introduction

Generally, most of organic materials exhibited very strong fluorescence in dilute solution but showed weakly or nonemissive in the aggregated states, which was known as ACQ (aggregation-caused quenching) materials in the solid states, due to both strong intermolecular face to face  $\pi$ - $\pi$  interactions leading to energy transfer and other non-radiative pathways<sup>[1,2]</sup>, such as forming excimers or exciplexes. However, traditional organic molecular structural design strategy has been to increase the extent of  $\pi$ -conjugation by melding more and more aromatic rings together resulting bigger discotic plates. The discotic big molecules enjoyed stacking together in the manner of face to face  $\pi$ - $\pi$  interactions and caused ACQ. The ACQ effect has severely obstructed the application for the real-world [3-10]. For example, the ACQ materials can't be used as sensors to detect biological molecules in physiological buffers and as probes to monitor ionic species in river water [11<sup>13]</sup> on account of insolubility in water. Because the luminescent materials used as emitter layers in the light-emitting devices must be fabricated in a solid film form, it is limited to the fabrication of efficient organic light-emitting diodes (OLEDs)<sup>[14]</sup>. Development of luminescent materials which are strongly emissive in the solid and aggregated states is still a challenging issue due ACQ and other non-radiative pathways occurring in the excited state.

The appearance of AIE (aggregation-induced emission) or AIEE (aggregation induced emission enhancement) fluorescence materials termed by Prof. Tang in 2001<sup>[15]</sup> made it a possibility to apply the organic photoimaging materials in real-world applications. The AIE or AIEE fluorescence materials are a new family of luminescent materials, which show quenching or weakened emission in solution, but exhibit strong fluorescence upon aggregation. Various mechanistic pathways such as conformational planarization, J-aggregate formation, E/Z isomerization, twisted intramolecular charge transfer (TICT), excited state intramolecular proton transfer (ESIPT), restriction of intramolecular rotation (RIR), restriction of intramolecular vibration (RIV), and restriction of intramolecular motion (RIM) have been explored to achieve AIE by hampering the intermolecular  $\pi$ - $\pi$  stacking interaction<sup>[16-19]</sup>. The covalent bonds have also been used to fasten the aryl rotors to

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The triphenylamine (TPA) moiety has been employed generally as an activator to construction of AIE-active luminogens associated with its propeller-like structure and excellent electron-donating character <sup>[22-25]</sup>. Diphenylsulfone has been used as an electron-acceptor group to construct luminogens due to its V-shape structure character. The present contribution reports a distinctive approach for multi-branched triphenylamine containing diphenylhydrazone structure. Indeed, the multi-branched strategy constitutes a relevant tool to modulate the aggregated states of AIE-active fluorophores without drastic impacts on the energy position of the electronic transitions <sup>[26–30]</sup>. In this spectral range, the multibranched constructions were covalently linked to triphenylamine centers to induce hindered rotation and the desired emission enhancement. The molecular structure constructed by the control of intermolecular interactions and intramolecular charge transfer (ICT) effect considering the strong fluorescence, where the triphenylamine served as the central donor core, diphenylsulfone as the acceptor, two hydrazinyldiphenyl conjugated chains served as the  $\pi$ -bridge to extend the conjugation length at the molecular level have not yet been reported in the literature. The design strategy is purposed to have new AIE materials, which can be applied in both solution and solid state.

#### 2. Experimental section

#### 2.1 Materials and instruments

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Triphenylamine, 4-chlorodiphenylsulfone, hydrazine hydrate (85%), POCl<sub>3</sub>, DMF, NaOH, CH<sub>2</sub>Cl<sub>2</sub>, THF, MgSO<sub>4</sub>, CH<sub>3</sub>COOH, DMSO, acetone, CDCl<sub>3</sub> and MTT were used as HPLC grade purchased from J&K (CHINA). Melting points were determined on a Kofler melting point apparatus and uncorrected. IR spectra were obtained in KBr discs using a Nicolet 170SX FT-IR spectrometer. Elemental analyses were performed on a Yannaco CHNSO Corder MT-3 analyzer. <sup>1</sup>H NMR has been recorded on INOVA 400 at 400.13MHz, with TMS as internal standard using DMSO as deuterated solvents with chemical shifts reported as ppm. Thermogravimetric analysis (TGA) of the compounds was carried out simultaneously by employing a NETZSCH thermal analyzer. The sample was heated at a rate of  $10^{\circ}$ C/ min in a nitrogen atmosphere. The absorption and fluorescence spectra were recorded on a CARY50 UV-VIS spectrophotometer and an FLS920 fluorescence spectrophotometer. Fluorescence quantum yields ( $\Phi_f$ ) in pure THF and THF/water mixtures determined with anthracene as the fluorescence reference in ethanol ( $\phi$  = 0.27). Film samples for the measurements of UV-vis and fluorescence spectroscopy were prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from THF solutions

(100 mL) on quartz cell (12.5×12.5×45 mm). The fluorescence microscope imaging of the nano-aggregations were obtained by Leica DM2500M. All the experiments were carried out at room temperature. Film samples for the measurements of UVvis and fluorescence spectroscopy were prepared by drop casting and the subsequent spin-coating (2000 rpm, 30 s) from THF solutions (100 mL) on guartz cell (12.5 ×12.5×45 mm). Scanning electron microscope (SEM) images of the aggregations were obtained using a Hitachi S4800.

#### 2.2 Computational methods

The molecules were optimized with the Becke-3-Lee-Yang-Parr (B3LYP)<sup>[31-33]</sup> by density functional theory (DFT) calculations at the level of 6-311G (d) with Gaussian 09 program <sup>[34]</sup>. The vibrational frequencies calculations were also performed to ensure the stability of the calculation result and avoid virtual frequency. The MD (molecular dynamic) simulations were performed by Discover module within Materials Studio 7.0 with the COMPASS force field for the studied molecules with the amorphous cell [35]. It was carried out with constant temperature and constant volume ensemble (NVT). Temperature was set 300K and kept constant using a nose thermostat <sup>[36]</sup>. Pressure was set 1 atm. Electrostatic energies were calculated using the vdW & Coulomb method with a 9.5-Å non-bonded cutoff. The total simulation time of 10.0 ps was carried out with time step of 1.0 fs.

#### 3. Result and Discussion

#### 3.1 Synthesis

The synthetic route was shown in Scheme 1.

3.1.1 4-hydraziondiphenyl sulfone (1)

Two to three drops of triethylamine were added to a suspension of 4-chorophenyl phenyl sulfone (5.0g, 0.02mol) and 50mL hydrazine hydrate (85%) in the round flask (250mL). The mixture was reflux for 24 h until the solid was completely dissolved. The resulting solution was cooled and diluted with ice water; the precipitates was removed by filtration, wash to neutrality with water, and dried over KOH, The yield was 5.0g (90.0%). Found:  $M^+$ , 248; calculation, 248.

3.1.2 4-(diphenylamino) benzaldehyde (2) and Bis (4-benzoyl) aniline (3)

30mL dry DMF was ice-bathed and 29.5mL POCl<sub>3</sub> was added dropwise. After Stirred for 40 minutes under 0°C, the temperature was raised to room temperature. Then 2.5g triphenylamine was added and the reaction mixture was then heated at  $45^\circ\!\mathbb{C}$  and stirred for 14 h. After cooling down to room temperature, the reaction mixture was poured into ice-bath and neutralized with NaOH, then extracted with chloroform. The combined organic layer was dried with magnesium sulfate anhydrous, filtered. Concentrated the organic layer, the white purified compound was obtained by column chromatography from petroleum ether and ethyl acetate mixed solvent (10:1). The compound 3 was prepared according to the general procedure for compound 1 by using 15.5

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mL dry DMF, and 19 mL POCl<sub>3</sub>, and 2.0 g triphenylamine. Compound 2: Yield: 2.1g (85%).<sup>1</sup>H-NMR (DMSO, 400 MHz)  $\delta$  (ppm): 9.76(s, 1 H), 7.71(d, 2 H), 7.41(t, 4 H), 7.21(m, 6 H), 6.88(d, 2 H). Compound 3: Yield: 1.6g (76%). <sup>1</sup>H-NMR (DMSO, 400 MHz)  $\delta$  (ppm): 9.87(s, 2H), 7.84(d, 4H), 7.47(t, 2 H), 7.31(s, 1 H), 7.21(d, 2H), 7.16(d, 4H).

## 3.1.3 Tris (4-benzoyl-yl) amine (4)

5.8mL dry DMF was ice-bathed and 7.6mL POCl<sub>3</sub> was added dropwise. After they were stirred for 1h under 0  $^{\circ}$ C , the temperature was raised to room temperature. 0.98g Bis (4-benzoyl-yl) aniline was added and the reaction mixture was then heated at 95  $^{\circ}$ C and stirred for 4 h. After cooling down to room temperature, the reaction mixture was poured into ice-bath and eutralized with NaOH, and then extracted with chloroform. The combined organic layer was dried with magnesium sulfate anhydrous, filtered. Concentrated the organic layer, the white purified compound was obtained by column chromatography from petroleum ether and ethyl acetate mixed solvent (4:1). Yield: 0.55g (65%).<sup>1</sup>H-NMR (DMSO, 400MHz)  $\delta$  (ppm): 9.94(s, 3 H), 7.91(s, 6 H), 7.28(s, 6 H)

## 3.1.4 Compound 5, 6 and 7

20 mmol 2, 3, 4 and 40 mmol N, N- dimethyl-p-phenylenediamine were added to flask, then add 10 mL dioxane. The reaction mixtures were then heated at  $60^{\circ}$ C and stirred for 2 h. After cooling down to room temperature and concentrated the organic layer, the yellow purified solid powder 5, 6, 7 were obtained by recrystallized from ethanol. Yield: 81% (5), 82% (6) and 65% (7).

5: m.p.:166 °C. Anal. Calc. formula:  $C_{31}H_{25}N_3O_2S_{-}$  (%): C, 73.93; H, 5.00; N, 8.34, Found:  $C_{31}H_{25}N_3O_2S_{-}$ (%): C, 73.66; H, 4.98; N, 8.31. IR (Fig.S1): 3257, 3184 (N-H), 2895, 2822 (C-H), 1593 (C=N), 1273, 1145 (SO<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO-D<sub>6</sub>, Fig.S2)  $\delta$  10.92 (s, 1H), 7.93 (t, J=8.8Hz, 3H), 7.78 (d, J=9.2Hz, 2H), 7.68 (m, 1H), 7.62 (m, 4H), 7.38 (t, J=8.8 Hz, 4H), 7.18(d, J=8.8Hz, 2H), 7.14(t, J=9.2Hz, 2H), 7.11(m, 4H), 7.01 (d, J=8.8Hz, 2H). <sup>13</sup>C-NMR (100 MHz, DMSO, Fig.S3)  $\delta$ : 112.24, 122.50, 123.56, 124.94, 127.10, 127.51, 127.75, 129.06, 129.36, 129.70, 130.73, 132.49, 140.19, 142.87, 147.14, 148.45, 148.96. MS calc. for (M + H <sup>+</sup>) <sup>+</sup>: 503.6141, found: 504.1565 (Fig.S4).

6: m.p.:176°C. Anal. Calc. formula:  $C_{44}H_{35}N_5O_4S_2$ . (%): C, 69.36; H, 4.63; N, 9.19; Found:  $C_{44}H_{35}N_5O_4S_2$ . (%): C, 69.28; H, 4.64; N, 9.21. IR: (Fig.S1): 3336, 3276 (N-H), 3058, 2955(C-H), 1582(C=N), 1284, 1139(SO\_2). <sup>1</sup>H-NMR (400 MHz, DMSO-D\_6, Fig.S2):  $\delta$  10.14 (s, 2H), 7.15 (s, 2H), 7.10 (d, J=9.2Hz, 4H), 6.97 (d, J=9.2Hz, 4H), 6.83 (m, 10H), 6.59 (t, J=8.8Hz,2H), 6.38 (d, J=8.8Hz, 5H), 6.33 (d, J=8.8Hz, 2H), 6.26 (d, J=8.8Hz, 4H). <sup>13</sup>C-NMR (100 MHz, DMSO, Fig.S3)  $\delta$ : 112.11, 123.70, 125.40, 127.06, 127.94, 129.18, 129.92, 129.96, 130.21, 133.31, 140.40, 141.30, 143.20, 146.71, 146.78, 147.78, 147.75, 149.63. MS calc. for (M + H <sup>+</sup>) <sup>+</sup>: 761.2130, found: 762.2235 (Fig.S4).

7: m.p.:199°C. Anal. Calc. formula:  $C_{57}H_{45}N_7O_6S_3$ . (%): C, 67.11; H, 4.45; N, 9.61; Found:  $C_{57}H_{45}N_7O_6S_3$ . (%): C, 67.18; H, 4.42; N, 9.59. IR (Fig.S1): 3366, 3282, 3209 (N-H), 2988, 2822(C-H), 1666(C=N), 1267,

1151(SO<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO-D<sub>6</sub>, Fig.S2): δ 10.95 (s, 3H), 7.88 (m, 8H), 7.78 (m, 8H), 7.58 (m, 15H), 7.17 (t, J=8.8 Hz, 4H), 7.09 (d, J=8.8Hz, 4H), 6.83 (d, J=8.8Hz, 3H). <sup>13</sup>C-NMR (100 MHz, DMSO, Fig.S3) δ: 124.38, 126.83, 127.07, 128.02, 129.54, 129.82, 129.96, 132.97, 133.32, 140.30, 143.19, 143.80, 147.30. MS calc. for (M + H <sup>+</sup>) <sup>+</sup>: 1019.2593, found: 1020.2762 (Fig.S4).

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The TGA curves of synthesized compounds are depicted in Fig.S5. In the TGA curves of all compounds, the weight loss starts at around 200  $^{\circ}$ C. The high thermal stability of these compounds enables them to be used in AlEgens applications.



Scheme 1 the synthetic route of compound 5, 6 and 7

#### 3.2 Photo-physical properties

Optical properties of 5, 6 and 7 were investigated by UV-visible and fluorescence spectroscopy. Three compounds had good solubility in common organic solvents such as THF, chloroform, toluene, acetonitrile, and DMSO, partial solubility in protic solvents (methanol and ethanol) and insoluble in water and hexane. The absorption and emission spectra of them in THF were depicted in Fig. 1(a). All compounds presented two absorption bands in various solvents between 300 to 400 nm in their UV spectra. The absorption maxima shifted red with the increase of branch numbers. The maxima of high energy absorption located at 301, 309 to 315 nm and the second located at 378, 381 to 399 nm respectively for 5(single branch), 6 (double branch) and 7(triple branch) (Table 1). Similarly, the maxima emission wavelength ( $\lambda_{em}$ ) (446, 453 to 476 nm for 5, 6 and 7 respectively) shifted red with the addition of branch numbers. All of them are highly emissive in different polarity solvents, and the fluorescence quantum efficiencies are particular high ( $\Phi_f$ : 42.8, 46.1 and 58.8% for 5, 6 and 7 respectively) in pure THF.

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**Fig. 1** (a) UV- spectra and fluorescent emissions of 5, 6 and 7 in THF; (b) the absorption and fluorescence spectra of triple branched compound (7) in various solvents, (c) Lippert–Mataga plot of  $7(v_a = absorption wavenumber$ ,  $v_f = emission wavenumber$  and  $\Delta f = orientation polarizability = (\varepsilon - 1)/(2\varepsilon + 1) - (n2 - 1)/(2n2 + 1)$ , where  $\varepsilon =$  dielectric constant and n = refractive index).

 Table 1
 Maximum absorption wavelength, maximum emission wavelength and fluorescent quantum yield of 5, 6 and 7 in solutions, aggregated states and film states

THF					THF-water			Film	
	$\lambda_{a1}$ (nm)	$\lambda_{a2}(nm)$	$\lambda_{em}(nm)$	Ф <sub>f</sub> (%)	Water (%)	$\lambda_{em}(nm)$	Ф <sub>f</sub> (%)	$\lambda_{em}(nm)$	Ф <sub>f</sub> (%)
5	301	378	446	42.8	60	460	58.2	460	23.8
6	309	381	453	46.1	60	468	64.6	469	42.2
7	315	399	476	58.8	70	527	6.1	529	5.8

All compounds have the same donor and acceptor, the difference among them is only the number of branches. It is noteworthy that the effects of solvent polarity of 7 on the absorption and emission properties. UV-visible absorption spectra and emission spectra of 7 in different solvents were presented in Fig. 1(b). The absorption band located 315 nm could be assigned to  $\pi-\pi^*$  electronic transition of the respective TPA units <sup>[37]</sup>, and 399 nm was due to the transition of the conjugated TPA-diphenylsulfone backbone. Both peak positions of the absorption bands were almost unchanged in polar (acetonitrile and DMF), non-polar (toluene), and moderately polar (THF and dichloromethane) solvents with small contribution from tailing of the lower transition energies. This indicates that there was little influence of solvent polarity on the ground state and a negligible charge transfer process between the TPA donor and diphenylsulfone acceptor in ground state. Interestingly, the emission properties of 7 were dependent on solvent polarity (Fig.1 (b)), ( $\mathcal{D}_f$ : 72.0, 59.2, 58.8, 43.6, 40.8 % in n-Hexane, CH<sub>2</sub>Cl<sub>2</sub>, THF, CH<sub>3</sub>CN, and DMF) and show positive sol-vatochromism effect, which indicated the significant dipole moment change in excited state. For example, it was emitted at 454 nm in toluene, while in DMF it was at 485 nm, which indicated an intramolecular charge transfer emission of 7 in solution. A Lippert-Mataga plot of Stokes shift against the orientation polarizability of the solvent

(Fig. 1(c)) gives an upward straight line with a moderate slope, indicative of a moderate ICT feature <sup>[38]</sup>.

#### **3.3 AIE Properties**

A solvent-poor-solvent photoluminescence (PL) test, which was commonly used for studying the AIE phenomenon  $^{\left[ 39-41\right] },$  was performed to investigate the luminescent behavior of the purpose compounds. The dispersion system of nano-aggregated was obtained by gradual addition of water into THF with different ratios. AIE effect  $(I/I_0)$  of three derivatives was drawn in Fig.2 (a-c). The formation of aggregates can also be confirmed by the changes of UV-vis, PL spectra and fluorescence microscope imaging in THF/water mixtures with varying water volume fractions (fw). Single-branched chromophore 5 exhibited the strong absorption peaks at 378 nm and the weak absorption peaks at 301 nm in pure THF solution. With an increase in fw from 0% to 90%, the strong peaks decreased and the weak peaks increased (Fig.2 (a)). At the same time, in the solvent mixtures, both peaks shifted red and the maxima absorption located at 310 and 388 nm when the fw was increased to 80% and the leveled-off tails appeared in the visible region at fw equal to 60%. It indicated that the aggregates were probably at nanoscale sizes. Chromophore 5 also emitted strong blue fluorescence at 446 nm ( $\Phi_f$  =42.8%) in dilute THF solution (5×  $10^{-5}$  mol·L<sup>-1</sup>) (Table 1). The fluorescence intension increased when the fw was increased to 40% and the maximum emission shifted red

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when the fw was at 50%. The maximum emission reached the highest fluorescence quantum yield ( $\Phi_f$  =58.2%) and the maximum emission shifted red to 460 nm when the fw was at 60%. The inserted micro-imaging of Fig. 1 exhibiting bright blue fluorescence supported it. Subsequently, the fw increased continuously, the emission intensity decreased gradually and invariableness finally with the fw increased.

The influence of steric hindrance effects on the AIE properties was investigated by introduction of mutli-branch substituted into triphenylamine central. The fluorescence enhancement was exhibited with the increase the branch numbers. Fig.2 (b) depicted the aggregation effect of double-branched chromophore 6. As shown in Fig.2 (b), when the fw increased to 50%, both absorption and emission spectra presented an increase of fluorescence and accompanied an obvious bathochromic-shift. When the fw was increased to 60%, the maximum emission reached the highest  $\mathcal{O}_f$  (64.6%) and the maximum emission shifted red to 468 nm. The more bright blue fluorescence micro-imaging was showed in inserted picture of Fig.2 (b) due to the higher  $\mathcal{O}_f$  than that of monobranched chromophore 5. Subsequently, the *fw* increased continuously, the emission intensity decreased gradually and invariableness finally with the *fw* increased.



**Fig.2** (a-c) UV and emission spectra of 5, 6 and 7 respectively in THF–water mixtures ( $5 \times 10^{-5}$  M) (the fluorescence micro imaging were inserted ( $\lambda_e$ =365nm)); (d) AIE effect ( $I/I_0$ ) of 7 with the fw from 0 to 90% (left to right) under the UV lamp (365 nm).

Comparing with the absorption spectra in pure THF, the absorption spectra of triple-branched chromophore 7 in THF/water mixture. nothing seemed to have changed that much. The only difference was that the leveled-off tails was found appeared in the visible region at fw equal to 50% due to the aggregates at nanoscale sizes (SEM, Fig. S6). However, the PL spectra were different from those of 5 and 6, 7 in pure THF solution ( $5 \times 10^{-5}$  mol/L) emitted strong blue fluorescence at 476 nm and the  $\Phi_f$  reached to 58.8%. When the water was added to THF, the fluorescence intension decreased. The lowest fluorescence intensity appeared at the fw equal to 40%. When the fw was at 50%, double peak appeared in the fluorescence spectra. The maxima emissions were located at 469 and 513nm respectively. After that, the emissions at 469 nm decreased and the emissions at 513 nm increased gradually and shifted red with the water increased sequentially. When fw was equal to 70%, the fluorescence increased to a maximum value and the maximum emission was located at 527 nm. Connecting with the solvent effect of 7 (Fig. 1(b)), the emission at 527 nm had ICT characteristic of  $D-\pi$ -A- $\pi$ -D motifs. Fig. 2(d) showed the fluorescence under the UV lamp

(365 nm) with the *fw* from 0 to 90% (left to right). The blue fluorescence changed to green with the increase of the *fw*. The fluorescence micro-imaging in inserted picture of Fig.2(c) exhibited faint green fluorescence due to its low  $\Phi_f$  (6.1%). Subsequently, the *fw* increased continuously, the emission intensity is hardly changed with the *fw* increased.

#### 3.4 Emission characteristic in solid states

As shown in Fig.3 (a-c), both 5 and 6 emitted bright blue fluorescence in powder states. However, the fluorescence of 7 was faint green under the UV lamp (365nm). In order to determining the  $\mathcal{D}_f$  in solid states, the film samples were prepared by drop casting and the subsequent spin-coating from THF solutions (100 mL) on quartz cell. Fig.3 (d) showed the fluorescence emission in film and the  $\mathcal{D}_f$  was listed in Table 1. The level-off tail stretched into the longer wavelength region also proved the formation of aggregation state. Calculations of full-width half maximum (*fwhm*) revealed that the emission spectra in the film state are comparable or narrower as comparing with the emission spectra obtained in THF/water due to the formation of higher order aggregates in film.

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Fig.3 (a-c) the fluorescence image of 5, 6, 7 in powder state under the UV lamp (365nm) from left to right; (d) the fluorescence spectra of **5,6,7** in film states ( $\lambda_e$ =375nm) **3.5 Theoretical studies and AIE mechanism** branches. It led to the gradually bathochromis-shifts from single-,

To better understand the spectral behavior of these TPA derivatives, the fully optimized structures of 5, 6 and 7 calculated at DFT level (B3LYP/6-31G (d)) are carried out. Molecular structures of three derivatives exhibited quite similar structures as shown in Fig.4 (top). The triphenyl moiety globally presented  $D_3$ -like symmetry with twist angles around the bond connecting the central nitrogen atom to the phenylene rings for all molecules <sup>[42, 43]</sup>. The diphenylhydrazone branches adopted a quasi-planar conformation, which indicated the increase conjugation with the increase of

branches. It led to the gradually bathochromis-shifts from single-, double- and tri-branched triphenylamine in both absorption and emission bands. Time-dependent (TD) combining a SCRF method (CPCM, by THF as solvent) at the same level were applied to indicate the energies of HOMO and LUMO. The longest wavelength electronic transition corresponded to a pure HOMO-LUMO transition, which indicated an electronic delocalization all along the compound structure ( $\pi$ - $\pi$ \* type) with a slight charge transfer from the amino group to the diphenylsulfone moieties (Fig.4 middle and bottom).





Fig. 4 Molecular structures (top), HOMO (middle) and LUMO orbital (bottom) from left to right for 5, 6 and 7 calculated by B3LYP/6-31G (d) A fixed molecules can hindered the possibility of face to face  $\pi$ - $\pi$ stacking, and the rigid structure can also suppress the motion or vibration of the phenyl rings in aggregation states and can be related to the restricted intramolecular rotation (RIR), which provides an essential prerequisite of AIE phenomena [44-46]. Hydrogen bonds and strong molecular interactions are important intermolecular interactions in supramolecular structures of the solid state. The formation of intermolecular interactions can rigidify molecular structures and activate their RIR processes. AIEE effect in solid state of 5 should be attributed to intermolecular hydrogen

bonding (HB) interactions and strong molecular interactions. Fig.5 (a) showed the strong intermolecular hydrogen bonding and some strong interactions in packing cell of 5 calculated by MD method. A hydrogen bonding interactions of H-N-N-M-N-N existed between two hydrazone of the adjacent molecules. The distances between N and H were 1.943Å respectively. The strong interaction N···N with the distance 2.51 Å was also found. The interation O...O with the distance 2.65 Å forced two sulfone groups to approach each other. All of these interactions compelled a cross-shaped packing mode (Fig. 5(b)) and caused the AIEE effect of 5.



Fig.5 hydrogen bonding and strong interactions (a) and packing mode (b) in packing cell of 5, calculated by MD

The packing manner of 6 (Fig.6) was different from that of 5 on account of increasing diphenylhydrazone branches. There are four atom-atom interactions among three molecules in packing cell of 6 (Fig.6 (a)), which is constructed by an intermolecular hydrogen bond (HB) interaction and a strong intermolecular interaction. The HB of O…H-N is formed by oxygen atom of sulfone and H-N of the hydrazone of two hydrazone branch in one molecule with H-N of hydrazone and O of sulfone of one branch in other two molecules respectively The distances of O···H are 1.866 and 1.883 Å

respectively. The distance O···N are 2.577 and 2.687 Å respectively. The strong interaction is O···N interaction with the distance of 2.623 and 2.876 Å respectively. Another molecular packing mode is constructed by weak intermolecular HB interaction (O···H-C) and some weak interactions. These interactions gather sulfones of four molecules together (Fig.6 (b)). The hydrogen bonding interactions and strong intermolecular interactions resulted in a rigid structure, which induced the AIEE effect of 6.

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Fig.6 three molecular (a) and four molecular (b) packing modes in the cell of 6, calculated by MD

The packing mode of 7 was exhibited in Fig.7. Four atom-atom strong interactions (Fig.7 (b)) was constructed by a intermolecular HB, O…H-N (1.840 Å) interaction, and a strong intermolecular interaction, O...N (2.61 Å), which was similar to that of 6. Here, an oxygen atom of sulfone on one hydrazone branch in one molecule as acceptor and H-N of hydrazone of another molecule as donor with H-N of hydrazone and O of sulfone of a branch of the another

molecule formed O···H-N HB. The six atoms interaction, N-H···O=S=O···O (Fig.7(c)) constructed between another branch of the above-mentioned molecule and another molecule with the distance H…O, 1.713 Å and O…O, 2.879 Å. Three atom interactions, O…O…O (Fig.7 (d)) existed in the adjacent two molecules, the distances O···O were 2.667 and 2.597 Å respectively.



Fig. 7 (a) packing model, (b, c and d) the strong intermolecular interactions in the cell of 7, calculated by MD

Above all, all of molecules in cell are fixed effectively by the strong intermolecular interactions. The motion or vibration of the diphenylhydrazone in aggregation states can be suppressed by HBs, H-N···H-N(5) and S=O···H-N(6, 7) respectively. The strong intermolecular interactions, such as S=O···O=S (5, 7) restrict intramolecular rotation (RIR) and avoid the possibility of face to face  $\pi$ - $\pi$  stacking, which was considered as a basic requirement of AIE and AIEE phenomena.



Fig. 8 the dihedral angles (C-N-N-C) of hydrazone in molecule 5, 6 and 7(left to right), calculated by MD

From the results of fully optimized structures of 5, 6 and 7(Fig 4), it can be found that the charges of all three compounds are partial. And the charge transfer of all compounds from the amino group

(donating unit) to the diphenylsulfone moieties (accepting units). On the other hand, the moderate Stokes shift 68, 72 and 77 nm in THF and 82, 87 and 128 nm in THF-water for 5, 6 and 7 respectively

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were corresponding to this weak ICT characteristic. And the increase of Stokes shift with branch numbers increasing indicate the incremental emission of ICT characteristic, which can attributed to the enlarged conjunction with the enhancement of coplanarity for diphenylhydrazone chains.

The increase of ICT with branches increasing can be observed by the transmission from HOMOs to LUMOs (Fig 4 middle and bottom). The charge transfer from the amino group to the diphenylsulfone moieties was feeble for 5 and obvious for 7. The clear ICT characteristic could also be depicted by the solvent effect of PL spectrum. As shown in Fig. 1(b), the UV spectrum of 7 had two peaks at 315 nm and 399 nm in toluene, which changes little when the measurement is performed in other solvents with increasing polarity. But, the solvent polarity exerted moderate influence on the test of photoluminescence (PL) properties, with the emission maximum and intensity in toluene being 28 nm red-shifts from those in DMF, the most polar solvent used for the measurement (Fig. 1(b)). Fig.8 depicted the dihedral angles in cells of 5, 6 and 7. The dihedral angles in cells were  $133.57^{\circ}$ ,  $156.75^{\circ}$  and  $179.81^{\circ}$  for 5, 6 and 7. It indicated that both phenyl rings on two sides of hydrazone chains tend to a plane with the increase numbers of branch, which benefited to the formation of ICT. The phenomenon of the ICT enhancement resulted that 7 emitted double fluorescence: local (high energy) fluorescence and ICT fluorescence (low energy) in THF and only ICT fluorescence in aggregated state. The interactions in packing cell not only provided essential prerequisite of AIE effect but also caused the ICT fluorescence. Some strong intermolecular interaction, such as S=O···O=S and O···O···O were found in cell of 7. These interactions resulted in the more concentration of acceptors (sulfone) so that the stronger capacity of pull electron in cell induced the ICT fluorescence in aggregated state.

# Conclusions

Three new compounds linked to triphenylamine and mono-, di- and tri-branched diphenylhydrazone were synthesized and characterized by element analysis, <sup>1</sup>H NMR, FT-IR. All three triphenylamines emitted strong blue fluorescence in THF. Monoand di-branched triphenylamines showed the increasing blue fluorescence and presented the AIEE effect in aggregated states. However, the tri-branched triphenylamine emitted green fluorescence and presented AIE effect. The unusual performance has been well explained by MD and DFT calculations. The result indicates that the propeller shaped non-planar molecule of triphenylamine and the special packing manner by the strong intermolecular interactions prevented face to face  $\pi$ - $\pi$  stacking and induced the hindered rotation to cause AIEE effect of 5 and 6; otherwise, the increased conjugation owing to enlarged coplanarity of diphenylhydrazone chains and the stronger ICT effect caused by the more concentration of acceptors, lead to the emission of ICT fluorescence of 7 in aggregated state. Fluorescent microscope

imaging and the fluorescent pictures of powder states certificated the AIEE and ICT effect in solid.

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