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Triarylamines with branched multi-pyridine groups: modulation of emission properties by structural variation, solvents, and tris(pentafluorophenyl)borane

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Six triarylamine derivatives 1-6 with branched multi-pyridine substituents were prepared and characterized. These compounds are distinguished by the substituent on one of the phenyl group with NO₂ for 1, CN for 2, Cl for 3, *p*-C₆H₄OMe for 4, OMe for 5, and NMe₂ for 6, respectively. As revealed by single crystal X-ray analysis, these substituents play an important role in determining the configuration of the triarylamine framework and the crystal packing of 1–6. The emission properties of these compounds were examined in different solvents (toluene, CH₂Cl₂, acetone, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF)) and in solid states. Distinct dual emissions from the localized emissive state and the intramolecular charge transfer state were observed for compound 5 in CH₂Cl₂. Compounds 1 and 6 show apparent aggregated enhanced emissions in acetone/H₂O. The emission properties of these compounds were further modulated by the addition of tris(pentafluorophenyl)borane. In addition, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed on the ground and singlet excited states to complement the experimental findings.

triarylamines, luminescence, charge-transfer, pyridines, donor-acceptor

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1 Introduction

Luminescent molecular materials with controllable and tunable emissions are appealing for applications in organic light-emitting devices (OLEDs), sensing, and bioimaging [1–5]. Modification of chemical structures is a common synthetic approach to tune the photophysical properties of organic emitting materials [6–10]. When designing imaging probes [11–16] and emitting materials for other optoelectronic applications [17–23], molecular frameworks that would allow us to modify chemical structures and thus lar-

gely tune the emission properties are desirable. The frontier energy band gap and other related properties of conjugated organic emitting molecules can be considerably varied by attaching electron donor and/or electron acceptor moieties to the molecular framework [24–27]. This strategy is often used to modulate the emissions of organic molecular materials by balancing the π - π * localized emissive (LE) state and the intramolecular charge transfer (ICT) state [28–33].

In addition to the synthetic structural modifications, a complementary postsynthetic modulation strategy has received attention in the design of organic emitting molecules [34,35]. One example is molecules containing nitrogenbased functional heterocycles, such as pyridine [36–40],

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diazine [41–44], quinozoline [45,46], thiazole [47,48], among others [49,50]. By protonation or coordination with Lewis acids, the emissions of these materials can be quenched, increased, or distinctly shifted (often to the lower-energy region). These compounds show interesting multistimuli responsiveness and are potentially useful in bioimaging and emitting devices. In this contribution, the synthesis, single-crystal X-ray analysis, and emission studies of six triarylamine compounds 1-6 with branched multi-pyridine substituents are presented (Scheme 1). We considered in the outset that, in addition to the postsynthetic modulation on the pyridine groups, the presence of the branched multi-pyridine substituents around the periphery of triarylamine may restrict the rotation of pyridine rings when they are closely packed in solid states. This may lead to solid materials with aggregation-induced emission (AIE) or aggregation-enhanced emission (AEE) properties, which have received wide and intense interest recently [51-59]. We later found that the crystal packing and emission properties of these compounds are largely dependent on the substituents on the triarylamine. The modulation of their emission properties by structural variation, solvents, and postsynthetic modulation with tris-(pentafluorophenyl)borane (TPFB) [60-64] is presented herein. In particular, distinctive phenomena of dual emission [65-68] and AEE from some of these compounds are discussed. The experimental results were further rationalized with the aid of density functional theory (DFT) and timedependent DFT (TDDFT) calculations on the ground and singlet excited states.

2 Experimental

2.1 Synthesis and general experimental

All reactions were performed in N_2 atmosphere. Nuclear magnetic resonance (NMR) spectra were recorded in the deuterated solvent on a Bruker Avance 400 MHz spectrometer (Germany). Spectra are reported in ppm values from residual protons of deuterated solvent. Mass data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer (USA). The matrix for matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) measurements is α -cyano-4-hydroxycinnamic acid. Compounds 3,5-(pyrid-2-yl)bromobenzene [69] and 4-(*p*-methoxyphenyl)aniline [70] were prepared according to reported procedures.

2.1.1 N,N-bis(3,5-di(pyrid-4-yl)phenyl)-p-nitroaniline (1)

A suspension of 3,5-(pyrid-2-yl)bromobenzene (388 mg, 1.25 mmol), 4-nitroaniline (69.0 mg, 0.50 mmol), tris(dibenzylideneacetone)dipalladium $(Pd_2(dba)_3)$ 36.7 mg. 0.040 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 22.2 mg, 0.040 mmol), and NaO'Bu (120 mg, 1.25 mmol) in 20 mL of anhydrous toluene was stirred at 120 °C for 3 d under N₂ atmosphere. After cooling to room temperature, the mixture was filtered through a pad of celite to afford. The yellow filtrate was concentrated and purified through column chromatography on silica gel (eluent: CH₂Cl₂/MeOH, 10:1) to afford 118.3 mg of 1 as a yellow solid in 40% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (dd, J=4.5, 1.5 Hz, 8H), 8.19 (d, J=9.2 Hz, 2H), 7.72 (s, 2H), 7.54 (d, J=1.5 Hz, 4H), 7.47 (dd, J=4.5, 1.6 Hz, 8H), 7.21 (d, J=9.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 152.65, 150.63, 147.38, 146.64, 142.05, 141.61, 125.83, 124.75, 123.11, 121.56, 120.35. EI-HRMS calcd. for $[M]^+$ $C_{38}H_{26}N_6O_2$: 598.2117. Found: 598.2126.

2.1.2 N,N-bis(3,5-di(pyrid-4-yl)phenyl)-p-cyanoaniline (2)

A suspension of 3,5-(pyrid-2-yl)bromobenzene (373.4 mg, 1.2 mmol), 4-cyanoaniline (59.1 mg, 0.50 mmol), bis(dibenzylideneacetone)palladium $(Pd(dba)_2,$ 36.6 mg, 0.040 mmol), 'Bu₃P (8.1 mg, 0.040 mmol), and NaO'Bu (120 mg, 1.25 mmol) in 20 mL of anhydrous toluene was stirred at 120 °C for 3 d under N₂ atmosphere. After cooling to room temperature, the mixture was filtered through a pad of celite. The yellow filtrate was concentrated and purified through column chromatography on silica gel (eluent: CH₂Cl₂/MeOH, 12:1) to afford 207 mg of 2 as a white solid in 72% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.68 (d, J= 3.8 Hz, 8H), 7.68 (s, 2H), 7.58 (d, J=7.9 Hz, 2H), 7.51 (s, 4H), 7.46 (d, J=4.4 Hz, 8H), 7.22 (d, J=7.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 151.06, 150.83, 147.82, 146.97, 141.69, 134.04, 124.69, 122.90, 121.84, 121.79, 119.10, 105.63. MALDI-HRMS calcd. for $[M+H]^+$ C₃₉H₂₇N₆: 579.2292. Found: 579.2292.



2.1.3 N,N-bis(3,5-di(pyrid-4-yl)phenyl)-p-chloroaniline

(3)

Using the similar procedure for the synthesis of 2, compound **3** was prepared from 3,5-(pyrid-2-yl)bromobenzene (388 mg, 1.25 mmol), 4-chloroaniline (63.8 mg, 0.50 mmol). Pd(dba)₂ (23.0 mg. 0.040 mmol). ^tBu₃P (8.1 mg, 0.040 mmol), and NaO'Bu (120 mg, 1.25 mmol) as a yellow powder in 71% yield (209.2 mg of product was isolated). ¹H NMR (300 MHz, CDCl₃): δ 8.67 (d, J=5.7 Hz, 8H), 7.56 (s, 2H), 7.49–7.40 (m, 12H), 7.34 (d, J=8.7 Hz, 2H), 7.20 (d, J=8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 150.75, 149.00, 147.39, 145.68, 141.20, 130.33, 129.84, 126.18, 123.05, 121.80, 121.19. MALDI-HRMS calcd. for $[M+H]^+$ C₃₈H₂₇ClN₅: 588.1950. Found: 588.1950.

2.1.4 N,N-bis(3,5-di(pyrid-4-yl)phenyl)-p-methoxy(phen-4-yl)aniline (4)

Using the similar procedure for the synthesis of 2, compound 4 was prepared from 3.5-(pyrid-2-yl)bromobenzene (357.8 mg. 4-(p-methoxyphenyl)aniline 1.15 mmol). (99.6 mg, 0.50 mmol), Pd(dba)₂ (23.0 mg, 0.040 mmol), $^{t}Bu_{3}P$ (8.1 mg, 0.040 mmol), and NaO ^{t}Bu (120 mg, 1.25 mmol) as a yellow solid in 62% yield (204 mg of product was isolated). ¹H NMR (400 MHz, CDCl₃): δ 8.66 (d, J=5.5 Hz, 8H), 7.56 (dd, J=8.2, 4.9 Hz, 6H), 7.51 (d, J= 1.3 Hz, 4H), 7.46 (d, J=6.0 Hz, 8H), 7.30 (d, J=8.5 Hz, 2H), 6.98 (d, J=8.7 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): *δ* 159.35, 150.58, 149.15, 147.42, 145.46, 140.89, 137.01, 132.67, 128.08, 127.89, 125.21, 122.91, 121.72, 120.70, 114.46, 55.47. MALDI-HRMS calcd. for [M]⁺ C₄₅H₃₃N₅O: 659.2680. Found: 659.2675.

2.1.5 N,N-bis(3,5-di(pyrid-4-yl)phenyl)-p-methoxyaniline (5)

Using the similar procedure for the synthesis of 2, compound 5 was prepared from 3,5-(pyrid-2-yl)bromobenzene (388 mg, 1.25 mmol), *p*-anisidine (61.6 mg, 0.50 mmol), 0.040 mmol), ^tBu₃P $Pd(dba)_2$ (23.0 mg, (8.1 mg, 0.040 mmol), and NaO'Bu (120 mg, 1.25 mmol) as a yellow solid in 70% yield (203.6 mg of product was isolated). ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, J=4.7 Hz, 8H), 7.49 (s, 2H), 7.43 (dd, J=5.8, 3.5 Hz, 12H), 7.23 (d, J=7.8 Hz, 2H), 6.95 (d, J=7.9 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 157.50, 150.67, 149.60, 147.72, 140.85, 139.64, 127.96, 121.92, 121.82, 120.08, 115.67, 55.76. EI-HRMS calcd. for [M]⁺ C₃₉H₂₉N₅O: 583.2372. Found: 583.2369.

2.1.6 N,N-dimethyl-N',N'-bis(3,5-di(pyrid-4-yl)phenyl)-pphenylenediamine (6)

Using the similar procedure for the synthesis of 2, compound 6 was prepared from 3,5-(pyrid-2-yl)bromobenzene (388 mg, 1.25 mmol), N,N-dimethyl-p-phenylenediamine (68.1 mg, 0.50 mmol), Pd(dba)₂ (23.0 mg, 0.040 mmol), $^{t}Bu_{3}P$ (8.1 mg, 0.040 mmol), and NaO ^{t}Bu (120 mg, 1.25 mmol) as a light green solid in 35% yield (105 mg of product was isolated). ¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, J=6.1 Hz, 8H), 7.44 (d, J=6.3 Hz, 14H), 7.16 (d, J= 8.9 Hz, 2H), 6.75 (d, J=9.0 Hz, 2H), 3.00 (s, 6H). ¹³C NMR (100 MHz, CDCl₂): δ 150.63, 149.79, 148.71, 147.87, 140.68, 135.55, 128.03, 121.86, 121.57, 119.61, 113.88, 40.86. MALDI-HRMS calcd. for $[M]^+ C_{40}H_{32}N_6$: 596.2683. Found: 596.2683.

2.2 Spectroscopic measurements

Absorption spectra were recorded at room temperature on a TU-1810DSPC spectrometer from Beijing Purkinje General Instrument Co., Ltd. (China). Luminescence spectra were recorded on an F-380 spectrofluorimeter from Tianjin Gangdong Sci. & Tech. Development Co., Ltd. (China), with a red-sensitive photomultiplier tube R928F. All measurements were performed in a quartz cuvette with path length of 1 cm. The absolute quantum yields and emission lifetimes were measured by using the Edinburgh FLS980 spectrofluorometer system (England). Fluorescence microscopy characterization was carried out using Olympus IX83 Inverted fluorescence microscope (Japan) equipped with a spot-enhanced charge couple device (CCD, Diagnostic Instrument, Inc., USA)

2.3 X-ray crystallography

The X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer (Japan) on a rotating anode (Mo-K radiation, 0.71073 Å) at 293 K. The structure was solved by the direct method using SHELXS-97 and refined with Olex2 [71]. The detailed crystallographic data (CCDC 1577194– 1577199) are given in Tables S1 and S2 (Supporting Information online).

2.4 Computational methods

Density functional theory (DFT) calculations were carried out using the B3LYP exchange correlation functional and implemented in the Gaussian 09 package [72]. The electronic structures of complexes were determined using the 6-31G* basis set for all atoms. No symmetry constraints were used in the optimization (nosymm keyword was used). Frequency calculations have been performed with the same level of theory to ensure the optimized geometries to be local minima. All orbitals have been computed at an isovalue of 0.02 e/bohr³. TDDFT calculations were performed on the DFToptimized structures on the same level of theory. The emission wavelength was calculated based on the TDDFT-optimized S_1 excited state geometry [73,74].

3 Results and discussion

3.1 Synthesis and structural studies

As outlined in Scheme 1, triarylamine compounds 1–6 were prepared in moderate yields by the Pd-catalyzed C–N coupling of 3,5-(pyrid-4-yl)bromobenzene with substituted anilines. The intermediate 3,5-(pyrid-2-yl)bromobenzene was synthesized via the Suzuki coupling of 1,3,5-tribromobenzene with *p*-pyridyl boronic acid according to the known procedure [69]. One of the triarylamine phenyl ring of 1–6 contains the electron-withdrawing NO₂, CN, or Cl or the electron-donating *p*-C₆H₄OMe, OMe, and NMe₂ group, respectively. Each of the other two triarylamine phenyl rings contains two pyrid-4-yl groups on the *meta* position of the phenyl unit.

Single crystals of **1–6** suitable for X-ray analysis were obtained by slow diffusion of petroleum ether or *n*-hexane into the solution of these compounds in CH_2Cl_2 (Figures 1 and 2, Figures S1–S3, and Tables S1 and S2, Supporting Information online). The triarylamine core of these compounds has a three-wheel propeller configuration. Interestingly, the torsion angle between the central amine plane (the triangle plane shown in Figure 1) and the surrounding phenyl planes of these compounds differ significantly. As a result, the shapes and crystal packing of these compounds differ from each other significantly. Specifically, the torsion angle between the central amine plane is small as 9.522°, while those with the

other two phenyl rings are rather big (53.451° and 76.639°). This arrangement makes compound **1** take a three-dimensional configuration. In the crystal packing of **1**, a dimer-like structure is observed, where the two nitrobenzene rings are placed in an antiparallel fashion. The presence of hydrogen bond interaction between the NO₂ oxygen with the pyridine hydrogen of another molecule is evident (Figure 2(a, b)).

For compounds 5 and 6 with the electron-donating OMe or NMe₂ group, the situation is totally different. The torsion angle between the central amine plane with the OMe or NMe₂-containing phenyl ring is rather large (57.62° for 5 and 57.348° for 6, respectively) and those with other phenyl rings are relatively small (21.793°-29.454°). The configurations of 5 and 6 are relatively flat compared to other four compounds, and they display a columnar stacking along the central amine core (Figure 2(e, f) and Figure S3). Compound 6 has smaller torsion angles with respect to 5 and it has a relatively shorter distance between two neighboring amine planes along the column (4.41 Å for 5 and 4.17 Å for 6, respectively). There are considerable intermolecular CAr- $H \cdots \pi$ interactions (the C_{Ar}-H \cdots phenyl centroid distance is around 2.6 Å) present along the column stacking of 5 and 6. In contrast, the torsion angle between the central amine plane with surrounding phenyl rings are rather average for 2-4, in the range of 33.640°-48.36°. These compounds take a normal three-wheel propeller configuration as known triarvlamine compounds [75,76]. Compared to 1, 5, and 6, the crystal packing of 2-4 is relatively loose. It should be pointed



Figure 1 Thermal ellipsoid plots at 30% probability of the single-crystal X-ray structure of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6. Hydrogen atoms are omitted for clarity. Color code: carbon, grey; nitrogen, blue; oxygen, red; chlorine, green (color online).



Figure 2 Crystal packing in single crystals of (a, b) 1, (c, d) 2, and (e, f) 6 (color online).

out the influence of the electronic properties of substituents on the above-mentioned torsion angle is not unique to our compounds. For instance, we analyzed a recently reported triarylamine derivative [77] containing different substituents one each aryl groups and found a similar trend. The torsion angle between the central amine plane and an electron-deficient phenyl group (nitrophenyl, 27.994°) is much smaller with respect to that with an electron-rich phenyl group (ethyoxyphenyl, 73.16°) [77]. The small torsion angle between the central amine plane and the nitro-substituted benzene ring is caused by the strong electronic donoracceptor effect of the amine-benzene-nitro unit. The presence of an electron rich group tends to reduce the conjugation degree between the phenyl group and the central amine unit, leading to a big torsion angle. However, systematic studies on the influence of the substituent on the geometry and crystal packing of triarylamine derivatives have not been documented, to the best of our knowledge.

3.2 Photophysical properties

The variation of the electronic properties of the aniline moieties leads to distinctly different photophysical properties of these compounds. The NO₂-substituted compound **1** exhibits a broad and strong absorption band between 350 and 450 nm with an absorption maximum ($\lambda_{abs,max}$) at 395 nm in

 CH_2Cl_2 (Figure 3(a)). In contrast, the other five compounds (2-6) show rather weak absorptions in this region and an absorption maxima between 300 and 350 nm is observed. The shapes of the absorptions of these compounds are essentially independent on the polarity of solvents examined (Figure S4). Compounds 2-5 are moderately emissive with the emission maxima ($\lambda_{em,max}$) ranging from 419 to 488 nm and a quantum yield (Φ) between 5.8% and 9.8% in dilute CH₂Cl₂ (Figure 3(b), Table 1). In comparison, 1 and 6 are relatively weakly emissive (Φ <2.0%) with a $\lambda_{em,max}$ of 578 and 400 nm, respectively. In the solid state, all compounds are emissive. The $\lambda_{em,max}$ and emission color of the solid samples of 2-5 (from blue to cyan) are essentially in accordance with those of them in dilute CH_2Cl_2 (Figure 3(c, d)). The Φ of 2–5 decreased distinctly in the solid state compared to those of them in dilute CH₂Cl₂. The emission properties of 1 and 6 are rather peculiar compared to those of **2–5**. Compound **1** emits bright yellow color ($\lambda_{em,max}$ =553 nm) with an enhanced Φ of 12.5% in the solid state compared to the weak brown emission in dilute CH_2Cl_2 ($\lambda_{em,max}$ =578 nm). In contrast, the observed weak emission of **6** with a $\lambda_{em,max}$ of 400 nm shifted to 502 nm (green emissive) with an enhanced Φ of 5.4% in the solid state. This suggests that **1** and **6** may display AEE properties (see further discussions below). The emission lifetime (τ) of these compounds are normally shorter than 10 ns, suggesting characters of singlet excited



Figure 3 (a) Absorption and (b) normalized emission spectra (excited at the absorption maximum between 300 and 400 nm) of 1-6 in CH₂Cl₂ (10 μ M); (c) images of solutions in CH₂Cl₂ (upper) and solid samples (below) of 1-6 under a UV lamp (365 nm); (d) normalized emission spectra of solid samples of 1-6 (Excitation wavelength is 395 nm for 1, 380 nm for 2 and 3, and 400 nm for others. Optimal emission intensities were obtained under these excitation wavelengths. The emission wavelengths of all solid samples are independent on the excitation wavelength) (color online).

 Table 1
 Photophysical data of 1–6 in dilute solutions and solid state

	Solution in CH ₂ Cl ₂				Solution in toluene		Solution in THF ^{a)}		Solution in acetone		Solution in DMF ^{a)}		Solid		
	$\lambda_{abs,max}$ (nm)	λ _{em,max} (nm)	$arPhi^{ m b)}$ (%)	τ (ns)	$\lambda_{\rm em,max}$ (nm)	Φ ^{c)} (%)	$\lambda_{\rm em,max}$ (nm)	Φ ^{c)} (%)	$\lambda_{em,max}$ (nm)	Φ ^{c)} (%)	$\lambda_{ m em,max}$ (nm)	Φ ^{c)} (%)	$\lambda_{\rm em,max}$ (nm)	Φ ^{b)} (%)	τ (ns)
1	395	578	1.9	<1.0	482	3.8	525	27.3	580	0.5	576	0.3	553	12.5	2.7
2	328	419	5.6	2.6	412	10.5	423	10.3	433	7.0	442	10.2	423	3.2	1.8
3	318	442	6.3	4.4	423	6.8	440	6.4	447	6.3	456	6.2	442	3.2	2.4
4	328	469	8.9	7.1	448	5.5	467	6.3	482	3.0	500	3.2	449	3.5	3.2
5	330	398/488	10.4	5.2/10.1	451	13.9	475	8.9	493	1.7	504	1.6	463	4.4	10.2
6	328	400	1.0	5.2	532	1.7	455	0.2	411	0.4	410	0.1	502	5.4	6.8

a) THF is tetrahydrofuran, DMF is N,N-dimethylformamide; b) absolute photoluminescence quantum yields determined using a calibrated integrating sphere system; c) emission quantum yield relative to that of quinine sulfate in 1 N H₂SO₄ (Φ =55%).

states (Table 1, and Figures S5 and S6).

3.3 Solvatochromism

To further understand the luminescent properties of these compounds, their emissions in solvents of varying polarities (toluene, THF, CH₂Cl₂, acetone, and DMF) were examined and compared (Table 1 and Figure 4). With increasing solvent polarity, the emission maxima of **1–5** showed a distinct bathochromic shift, characteristics of the ICT excited states. The emission maxima shift of **1** is most significant. For instance, it has a $\lambda_{em,max}$ of 482 nm in toluene and it shifts to 576 nm in DMF. The emission quantum yield varies in different solvents. In particular, compound **1** was found to display bright yellowish emission in THF with a Φ of 27.3% (Figure S7). Interestingly, the emission maxima of **6** in dif-

ferent solvents display an inversed solvatochromic behavior. It has a lower-energy emission band ($\lambda_{em,max}$ =532 nm) in toluene and a higher-energy emission at 410 nm in DMF. However, the emission quantum yields of **6** in all solvents examined are rather low. These solvatochromic studies suggest that the emissions of **1**–**5** are clearly of ICT characters, while that of **6** is not. One possibility is that compound **6** has two different LE states. In polar solvent such as acetone, CH₂Cl₂, and DMF, the emission is of the higher-energy LE character. In nonpolar solvent (toluene) and solid state, the emission of **6** is of the lower-energy LE character.

3.4 Dual emissions of LE and ICT

We note that, in addition to the main emission band, compounds 3-5 exhibit another weaker emission band at the



Figure 4 Normalized emission spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6** in toluene, THF, CH₂Cl₂, acetone, and DMF (10 µM) at room temperature (color online).

higher-energy side in CH_2Cl_2 , suggesting dual emission properties of these compounds. The intensity ratio of the two emission maxima at 398 and 488 nm of **5** changed when the excitation wavelength was varied (Figure 5(a)). The excitation spectrum of the emission at 488 nm is distinctly redshifted with respect to that of the emission at 398 nm (Figure 5(b)). In addition, these dual emissions have distinctly different lifetime (5.2 ns for 398 nm and 10.1 ns for 488 nm, respectively, Figure 5(c)). The dual emissions of **5** are believed to originate from a balance between the LE and ICT excited states. In comparison, the dual emissions of **3** and **4** are less pronounced with respect to those of **5** (Figure S8).

3.5 AEE effect in acetone/H₂O

As pointed out in the above solid state emission studies, compounds **1** and **6** demonstrated a possible AEE effect. The absorption and emission spectra of them were thus further examined in a mixture of acetone (good solvent) and H₂O (poor solvent) of different volume ratios (Figure 6 and Figure S9). The absorption spectra of both compounds did not change distinctly by varying the H₂O/acetone ratio from 1:9 to 8:1 (Figure S9). However, when the H₂O content was further increased to 90%, their absorption spectra were significantly disrupted, indicating the formation of aggregates. Accordingly, the emissions of both compounds were significantly enhanced in mixed solvents containing 90% of H₂O. Compound **1** emits rather weakly at 574 nm in pure acetone and the emission band shifts to 552 nm with around 10 times enhancement of the emission intensity in the ag-

gregate state (similar to the yellow emission of the solid sample of 1). In comparison, the weak emission of 6 at 411 nm in pure acetone was red-shifted to 515 nm when the H₂O content was increased to 90%, exhibiting obvious green emission with around 4 times enhancement of the emission intensity. Similar green emission was observed for the solid sample of 6. Optical microscopic studies show that fibrous or diamond plate aggregates are formed for 1 and 6, respectively, in 9:1 H₂O/acetone mixed solvent (Figure 6 and Figure S9). We consider that the dimeric structure of 1, as revealed in Figure 2, greatly stiffens the twisted molecular conformation of the molecule and thus restricts the rotation of aryl groups. This restricted motion is believed responsible for the observed AEE phenomenon of 1 [55–59]. For the same reason, the presence of multiple intermolecular interactions confined in the compact column stacking of 6 in the solid state is believed responsible for its AEE properties. The AEE properties of 6 are somewhat peculiar with respect to those of 1 and most reported AIE or AEE examples showing blue-shifted emissions as result of reduced reorganization energy [51-59]. The red-shifted emission of 6 upon aggregate may be caused by the excitonic coupling along the column stacking direction.

3.6 Postsynthetic modulation by TPFB

As an example of postsynthetic modulation, the emission properties of 1-6 in CH₂Cl₂ in the presence of TPFB were examined. TPFB is an electron-deficient Lewis acid and has been used to modulate the emission properties of a number of



Figure 5 (a) Emission spectra of **5** as a function of excitation wavelength in CH_2Cl_2 (10 μ M). (b) Excitation spectra of the emission at 398 and 480 nm of **5**. The absorption spectrum (black curve) is included for comparison. (c) Decay profile of the emission of at 398 and 480 nm of **5** in CH_2Cl_2 (λ_{exci} is 310 nm) (color online).



Figure 6 (a, d) Emission spectra and (b, e) plot of the emission intensity at 552 and 515 nm, respectively, of (a, b) **1** and (d, e) **6** in acetone/ H_2O mixtures with different water fractions. Inset of (b, e) shows the images of **1** and **6** under a UV lamp (365 nm). (c, f) Fluorescence optical microscopic images of the aggregated samples of (c) **1** and (f) **6** under UV irradiation. The samples were prepared by drop casting of the suspension of **1** or **6** in mixed solvent of H_2O and acetone with a ratio of 9:1 (color online).

organic materials by boron-nitrogen coordination [60–64]. Two different kinds of absorption spectral changes were observed for these compounds in the presence of TPFB (Figure S10). These distinct absorption spectral changes suggest the strong interaction between these molecules and TPFB in the ground state. For the NO₂-containing compound 1, the absorption band between 350 and 450 nm slightly shifted to the higher-energy side. For the other five compounds, the main absorption band between 300 and 350 nm decreased, with the emergence of a broad and weak absorption band between 350 and 500 nm. The appearance of the latter absorption band is due to the decreased electron density on the pyridine moieties upon coordination with TPFB, leading to the stabilization of the lowest unoccupied

molecular orbital (LUMO) levels of these compounds and thus the decrease of the frontier energy band gap [61]. For compound **1**, the LUMO is believed to be dominated by the nitrobenzene segment (see DFT results below). The coordination of TPFB to the pyridine rings of **1** will slightly stabilize the HOMO level and thus increase the band gap. Accordingly, the emission of **1** at 578 nm was hypsochromically shifted to the slightly higher-energy region ($\lambda_{em,max}$ around 520 nm) in the presence of TPFB in CH₂Cl₂ solution (Figure 7(a)).

Interestingly, compounds 2-6 show completely different TPFB-induced emission spectral changes with respect to 1 (Figure 7). For compounds 2 and 3, with the addition of TPFB, the emission band at 417 or 442 nm gradually de-



Figure 7 Emission spectral changes of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6 in CH₂Cl₂ with different equiv. of TPFB added (color online).

creased and a new emission band around at 520 nm appeared in both cases. In other words, the emissions of 2 and 3 were red-shifted in the presence of TPFB, in accordance with their absorption spectral changes. In contrast, the ICT emission band at around 480 nm of the dual-emissive compounds 4 and 5 was completely quenched and the weak LE emission intensity at around 400 nm did not change distinctly in response to TPFB. No additional lower-energy emission band was observed. As for $\mathbf{6}$, the emission intensity at around 400 nm essentially remains unchanged upon coordination with TPFB, indicating a similar LE character. The reactions of these compounds with TPFB normally occur instantly and quantitatively. Electrospray ionization mass spectrometry (ESI-MS) of the adduct of 3 with TPFB suggests that it coordinates with four TPFB molecules (Figure S11). The emission spectra of 1-6 in the presence of aqueous HCl in THF solution were also examined, which indicated that the emission of these compounds was largely quenched upon protonation (Figure S12).

3.7 Computational studies

DFT calculations show that the highest occupied molecular orbital (HOMO) orbitals of 1-6 are all dominated by the triarylamine segment (Figure 8). The LUMO orbitals of 2-6 have major contributions from the two 3,5-dipyridylphenyl units, while that of 1 is dominated by the nitrobenzene moiety. Accordingly, the LUMO level of 1 is relatively stabilized with respect to those of 2-6. The HOMO-LUMO energy gap of 1 was calculated to 3.35 eV, which is smaller with respect to those of 2-5. This result is consistent with the

absorption and emission spectra of 1-5 (Figure 3). Compound **6** was calculated to have a similar small energy gap as **1** due to a destabilized HOMO level. However, the absorption and emission spectra of **6** in CH₂Cl₂ solution are located in the much higher-energy region than that of **1**, which seems inconsistent with the DFT results (see further discussions below). The difference in the HOMO or LUMO energy level among these compounds seems to strongly affect their photophysical properties. For instance, the distinctly stabilized LUMO level of **1** and destabilized HOMO level of **6** is believed to be an important cause for the peculiar emission properties of these two compounds.

In addition to the calculations on the ground state (S_0) , the geometrical optimizations on the singlet excited states (S_1 of 1-6) have been carried out. Table 2 shows the comparison of the torsion angle between the central amine plane (NC_3) and surrounding aryl groups $(C_6H_4R \text{ or } C_6H_3(Py)_2)$ based on the single-crystal X-ray data and the DFT-calculated ground S₀ and excited S1 states. The DFT-optimized ground state structures of 1-6 show some differences with their singlecrystal X-ray structures. In particular, the calculated torsion angle $\angle NC_3 - C_6H_4NO_2$ of 1 is much larger than that of the Xray data (27.06° vs. 9.52°). The observed dimeric structure in the single-crystal X-ray data of 1, which forces the nitrobenzene planes to take an antiparallel packing, is one possible reason to explain this difference. Such an intermolecular dimeric structure was not considered in DFT calculations. The basic trend of the DFT-optimized structures is however consistent with the X-ray data. For instance, both results show that the $\angle NC_3 - C_6H_4R$ torsion is the smallest for 1 and relatively large for 5 and 6 among six compounds. In



Figure 8 DFT-calculated energy diagram and LUMO and HOMO orbitals of 1-6 (color online).

Table 2 Comparison of the torsion angle between the central amine plane (NC₃) and surrounding aryl groups (C_6H_4R or $C_6H_3(Py)_2$) based on the singlecrystal X-ray data and DFT-calculated ground state and singlet excited state of **1–6**

Comp	X-ra	y data (°)	Calculated	ground state (°)	Calculated singlet excited state (°)			
Comp.	$\angle NC_3 - C_6H_4R$	$\angle NC_3 - C_6H_3(Py)_2$	$\angle NC_3 - C_6H_4R$	$\angle NC_3 - C_6H_3(Py)_2$	$\angle NC_3$ - C_6H_4R	$\angle NC_3$ - $C_6H_3(Py)_2$		
1	9.52	53.45, 76.64	27.06	49.41, 50.10	94.65	29.37, 31.26		
2	39.16	33.64, 42.92	31.63	46.87, 47.21	33.26	35.98, 49.31		
3	43.15	34.03, 42.82	42.69	41.22, 41.30	30.39	36.96, 52.90		
4	48.36	36.79, 37.73	45.95	39.30, 39.89	22.25	43.59, 60.78		
5	57.62	26.29, 29.45	53.25	36.42, 37.83	22.97	42.02, 61.54		
6	57.35	21.79, 23.13	56.35	35.46, 35.57	19.14	46.10, 65.95		

addition, both DFT and experimental data show that the difference between $\angle NC_3 - C_6H_4R$ and $\angle NC_3 - C_6H_3(Py)_2$ is relatively small for 2–4; however, the $\angle NC_3 - C_6H_4R$ torsion of 1 is much smaller than its $\angle NC_3 - C_6H_3(Py)_2$ torsion and the $\angle NC_3 - C_6H_4R$ torsions of 5 and 6 are much larger with respect to their $\angle NC_3 - C_6H_3(Py)_2$ torsions. Compared to the ground state structures, big changes occur to these torsions in the calculated geometries in the S₁ state. The torsion angle $\angle NC_3 - C_6H_4NO_2$ of 1 becomes 94.65°, compared to 27.06° in the ground state. This torsion is much bigger than its $\angle NC_3 - C_6H_4R$ torsions of 2–6 are all smaller with respect to their $\angle NC_3 - C_6H_4R$ torsions of 2–6 are all smaller with respect to their $\angle NC_3 - C_6H_4R$ torsions.

TDDFT calculations were performed on the optimized ground and excited state geometries (Table 3). The vertical $S_0 \rightarrow S_1$ excitations of **1–6** are dominated by the ICT transitions from HOMO to LUMO. The $S_0 \rightarrow S_1$ excitation of **1** has a big oscillator strength (*f*=0.5498), while those of **2–6**

are rather small (f < 0.04). These results are consistent with the observed absorption spectra of 1-6 (Figure 3(a)), with an intense ICT absorption band for 1 and only very weak absorptions for the others being observed between 350 and 450 nm. The calculated first transitions of the S₁ states (S₁ \rightarrow S_0) correspond to the theoretical emission wavelengths of 1– 6. The calculated emission energies decrease (wavelengths vary from short to long) in an order from 2, 3, 4, 5, to 1, which are in well agreement with the observed emission spectra of these compounds. These transitions are all dominated by the electron relaxation from the LUMO to the HOMO of the excited state (Figure S13). For compounds 2-5, these emissions are of the ICT character from the triarylamine unit to the dipyridylphenyl segments. For compound 1, the ICT transition from the triarylamine unit to the nitrobenzene segment plays the dominant role. These emissions are characteristic of the twisted charge-transfer emissions [24], where the donor and acceptor segments are

Comp.	Transition	E (eV)	λ (nm)	f	Dominant transition (percentage contribution)
GS-1	$S_0 \rightarrow S_1$	3.01	411.2	0.5498	HOMO \rightarrow LUMO (99%)
GS- 2	$S_0 \rightarrow S_1$	3.34	371.6	0.0357	HOMO \rightarrow LUMO (98%)
GS- 3	$S_0 \rightarrow S_1$	3.19	388.2	0.0312	HOMO \rightarrow LUMO (98%)
GS-4	$S_0 \rightarrow S_1$	3.04	407.9	0.0201	HOMO \rightarrow LUMO (97%)
GS- 5	$S_0 \rightarrow S_1$	3.06	404.8	0.0234	HOMO \rightarrow LUMO (98%)
GS- 6	$S_0 \rightarrow S_1$	2.83	437.7	0.0126	HOMO \rightarrow LUMO (98%)
ES-1	$S_1 \rightarrow S_0$	1.79	692.9	0.0431	LUMO \rightarrow HOMO (99%)
ES-2	$S_1 \to S_0$	2.88	429.9	0.0389	LUMO \rightarrow HOMO (99%)
ES- 3	$S_1 \rightarrow S_0$	2.68	462.2	0.0265	LUMO \rightarrow HOMO (99%)
ES-4	$S_1 \rightarrow S_0$	2.33	531.7	0.0160	LUMO \rightarrow HOMO (99%)
ES-5	$S_1 \to S_0$	2.22	557.5	0.0120	LUMO \rightarrow HOMO (99%)
ES-6	$S_1 \rightarrow S_0$	1.77	700.0	0.0086	LUMO \rightarrow HOMO (99%)

Table 3 TDDFT-calculated vertical electronic transitions based on the ground (GS) and singlet excited state (ES) of 1-6

twisted with a big torsion angle in the excited state as has been discussed in the above structural analysis.

Aside from the structural changes discussed above, the calculated dipole moments of **1–5** show big difference between the ground and excited states. The dipole moment of **1–5** in the S₀ state was calculated to be 5.24, 4.00, 0.87, 5.05, and 5.17 D, respectively, which increased to 23.71, 12.64, 16.07, 26.05, 21.37 D, respectively, in the S₁ state. This suggests the increased CT character in the excited state, in agreement with the positive solvatochromic effects of the emissions of these compounds (Figure 4).

The previous emission studies and DFT calculations show that compound **6** is a special example among all compounds studied. The ICT emission wavelength of **6** was calculated to be around 700 nm and the dipole moment of **6** was calculated to be 18.25 D in the S₁ state vs. 7.35 D in the ground state. However, only very weak emission at around 400 nm was observed for **6** in polar solvents such as CH₂Cl₂, acetone, and DMF and the emission shifts to the longer-wavelength region in THF and toluene. We consider that the ICT emission of **6** is forbidden as supported by the calculated low oscillator strength (*f*=0.0086). The observed emission of **6** is likely of the LE character as has been discussed previously. The above emission studies suggest that the emission of **6** at around 400 nm in CH₂Cl₂ essentially remains unchanged in response to TPFB, which is also consistent with the LE character.

4 Conclusions

In summary, we present the synthesis, crystal packing, and emission properties of a series of triarylamine derivatives containing multi-branched pyridine groups. The substituent on the aryl group was found to strongly influence the geometry of the triarylamine motif and the crystal packing of these compounds. The emission properties of these molecular materials could be largely modulated by substituents, solvents, and post-coordination with $B(C_6F_5)_3$. By varying the solvent and the electronic properties of the substituents on the aryl group, dual LE and ICT emissions and AEE properties were observed from some of these compounds. This work demonstrates the successful modulation of emission properties of molecular materials by structural variation and postfunctionalization, which provides useful information for the molecular design of emissive materials. Work is under way to further adjust the molecular structures of these compounds in order to improve their emission quantum yields for potential optoelectronic applications.

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