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Spiroconjugated Intramolecular Charge-Transfer Emission in Non-Typical Spiroconjugated Molecules: The Effect of Molecular Structure upon the Excited-State Configuration

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A set of terfluorenes and terfluorene-like molecules with different pendant substitutions or side groups were designed and synthesized, their photophysical properties and the excited-state geometries were studied. Dual fluorescence emissions were observed in compounds with rigid pendant groups bearing electron-donating N atoms. According to our earlier studies, in this set of terfluorenes, the blue emission is from the local π–π* transition, while the long-wavelength emission is attributed to a spiroconjugation-like through-space charge-transfer process. Herein, we probe further into how the molecular structures (referring to the side groups, the type of linkage between central fluorene and the 2,2′-azanediyldiethanol units, and—most importantly—the amount of pendant groups), as well as the excited-state geometries, affect the charge-transfer process of these terfluorenes or terfluorene-like compounds. 9-(9,9,9′′,9′′-tetrahexyl-9H,9′H,9′′H-[2,2′:7′,2′′-terfluoren]-9′-yl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolone (TFPJH), with only one julolidine pendant group, was particularly synthesized, which exhibits complete "perpendicular" conformation between julolidine and the central fluorene unit in the excited state, thus typical spiroconjugation could be achieved. Notably, its photophysical behaviors resemble those of TFPJ with two pendant julolidines. This study proves that spiroconjugation does happen in these terfluorene derivatives, although their structures are not in line with the typical orthogonal π fragments. The spiroconjugation charge-transfer emission closely relates to the electron-donating N atoms on the pendant groups, and to the rigid connection between the central fluorene and the N atoms, whereas the amount of pendant groups and the nature of the side chromophores have little effect. These findings may shed light on the understanding of the through-space charge-transfer properties and the emission color tuning of fluorene derivatives.

1. Introduction

Dual fluorescence emissions originating from two different emitting states in one molecule, for example, one locally excited state and one formed in an intramolecular charge-transfer state, have been intensively studied in the past several years.[1–3] The mostly studied dual-emission systems usually include an ICT (intramolecular charge transfer),[4–8] a TICT (twisted intramolecular charge transfer), and the formation of an excimer/exciplex system.[9–12] In the above-mentioned courses, ICT and TICT are the most common CT emission characters, and could be considered as through-bond charge-transfer processes, whereas the formation of the exciplex is a through-space charge transfer, in which the donor and the acceptor moiety are generally linked by a flexible non-conjugated chain.[13–15]

Apart from these systems, there is also a special through-space charge transfer, that is, the spiroconjugation, depicting two mutually perpendicular π-systems (donor and acceptor) linked by a spirojunction. An interaction that allows for electronic coupling between the two parts will occur, provided that the molecular orbitals of the mutually perpendicular fragments are antisymmetric with respect to the two perpendicular bisecting planes.[16–20] The interactions between these orbitals thus lead to charge delocalization spanning the entire molecule, and to the formation of two new spiroconjugated orbitals, a new HOMO (corresponding to the bonding combination of the subsystem orbitals) with lower energy, and a new LUMO (corresponding to the higher-energy antibonding combination) with higher energy (Scheme 1). This kind of through-space interaction is controlled by the energy and symmetry of these frontier orbitals. However, spiroconjugation caused fluorescence emission is rarely reported to date.

Earlier in 2008, we first reported a novel terfluorene, TFOH, with 4-(bis(2-hydroxyethyl)amino)phenyl as side chains, exhibiting dual fluorescence emissions in polar solvents.[21] Though its photophysical behavior is similar to the TICT character, the emission cannot be assigned to a TICT mechanism because the conjugation between fluorene and the pendent 4-(bis(2-hydroxyethyl)amino)phenyl group is interrupted by the sp^3 hybridization of the C9 atom in the central fluorene unit. To further investigate the emission mechanism, then we specially synthesized an analogue of TFOH, namely, TFPJ, with the amino nitrogen immobilized in the planar position of the juloli-

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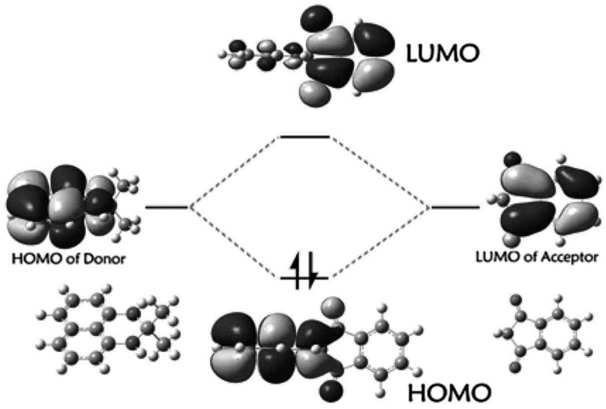
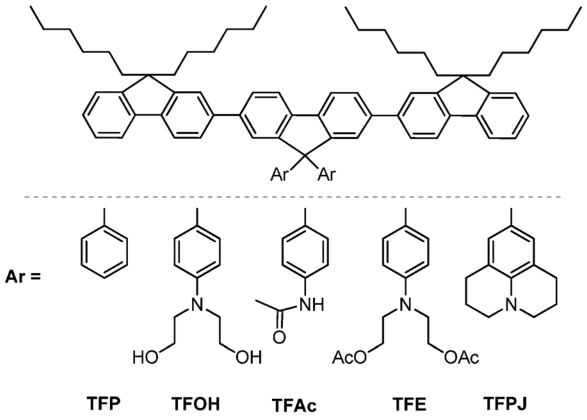


Scheme 1. Molecular orbitals responsible for the spiroconjugation effect.



Scheme 2. Molecular structures of TFP, TFOH, TFAc, TFE, and TFPJ.

dine groups (Scheme 2). In this case, the charge-transfer emission should be totally inhibited if the terfluorenes went through a TICT mechanism. Unexpectedly, the photophysical properties of TFPJ still resembled those of TFOH, though the rotation of the C–N single bond is fully restricted in TFPJ, which thereby rules out the TICT mechanism. At the same time, we synthesized two analogues of TFOH, that is, TFAc (with 4-(acetamido)phenyl as pendent groups) and TFE [with 4-(bis(2-acetoxyethyl)amino)phenyl as pendent groups], that are distinguished from the electron-donating abilities of the pendant groups (Scheme 2).[22] From their fluorescence spectra, no charge-transfer emission can be observed in TFP or TFAc (with no N atoms on the pendants, or quite weak electron-donating pendant groups), whereas dual fluorescence emission and a bathochromic shift of the long-wavelength emission can be observed in TFE, with relatively weak electron-donating aminophenyl groups. It turned out that the stronger the electron-donating ability, the larger the bathochromic shift. Common ICT behaviors were gradually excluded, and finally a process related to the spiroconjugation-like mechanism was put forward. Obviously, the terfluorenes are not structurally in accordance with the typical spiroconjugated molecules bearing orthogonal donor and acceptor fragments; however, the interaction between the HOMO in the pendant aminophenyl moieties and the LUMO in the fluorene moieties is demonstrated to be of spiroconjugation-like nature, from both experimental results and theoretical studies.

The purpose of this work is to probe deeper into the photophysical processes occurring in these molecules to study the structure–property relationship by structure modification and exploitation, and thereby to investigate the scope and generality of the emission mechanism. In this article, we design and synthesize a set of terfluorenes and terfluorene-like molecules with systematically varied side groups (using phenyl rings and its derivatives), or with different spacer groups between fluorene and the 2,2′-azanediyldiethanol pendant groups (hexyl chains are introduced instead of rigid phenyl rings, Scheme 3). The influences of the structure modifications on the emission behaviors are discussed, including the effect of the side groups, and of the bridge ligand between the central fluorene and the 2,2′-azanediyldiethanol units, as well as the amount of the pendant groups. Notably, for comparison with TFPJ, TFPJH (with only one julolidine substitution) was particularly synthesized, taking into account that the small steric effect on the C9 position of the central fluorene should bring enough space for structure adjustment in the excited state, which might lead to a “real” perpendicular configuration of the pendant julolidine and the central fluorene group, and as a result, a typical spiroconjugated conformation could be achieved in TFPJH. Correspondingly, the photophysical properties, together with the excited-state geometries of these compounds, were investigated. By comparison with the previously reported results on terfluorenes, showing spiroconjugation-like charge-transfer emission, the intrinsic interaction between pendant substitutions and fluorene moieties in the excited states could be well understood. More importantly, this special charge-transfer emission mechanism could be finally determined by both experimental results and theoretical calculations.

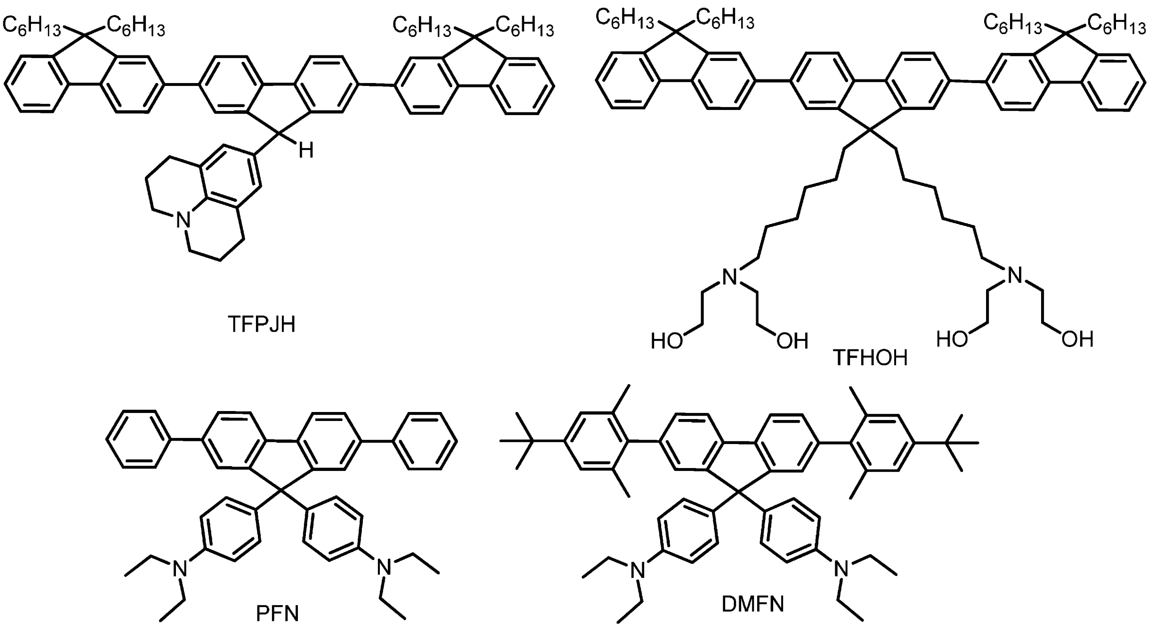
2. Computational Methodology

The geometries of the ground states were optimized at the PBE0[23] def2-SVP[24] and PBE0 6-31G(d) levels for comparison. Excited-state geometry optimizations were performed at the TD/PBE0 def2-SVP level. Then, the vertical excitation energies were calculated by TD/PBE0 def2-SVP and TD/PBE0 6-311+G(d) for comparison. Calculations using the def2-SVP and 6-31G(d), 6-311+G(d) basis sets were performed with the Turbomole 6.0 Package[25] and the Gaussian 03 program,[26] respectively.

3. General Information

3.1. Methods

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a MERCURYVX 300 spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. MALDI-TOF was measured on a Voyager-DE STR MALDI TOF instrument, using α-cyano-4-hydroxyclinnamic acid



Scheme 3. Chemical structures of the compounds studied in this article.

(CHCA) as a matrix. EI Mass was recorded on a Finnigan TRACE mass spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from the dilute solution of the terfluorenes (ca. 10^{-6} mol L^{-1}) by an absolute method using an Edinburgh Instruments system (FLS920) integrating sphere excited with a Xe lamp. Fluorescence decays were measured at room temperature by a single-photon-counting spectrometer from Edinburgh Instruments (FLS920) with a hydrogen-filled pulse lamp as the excitation source. The data were analyzed by iterative convolution of the luminescence-decay profile with the instrument response function using the software package provided by Edinburgh Instruments. The goodness of the nonlinear least-squares fit was judged by the reduced χ^2 value (<1.3 in all cases). The concentration of all the compounds in the UV/Vis absorption, fluorescence emission, and lifetime experiments was 5×10^{-6} M.

3.2. Materials

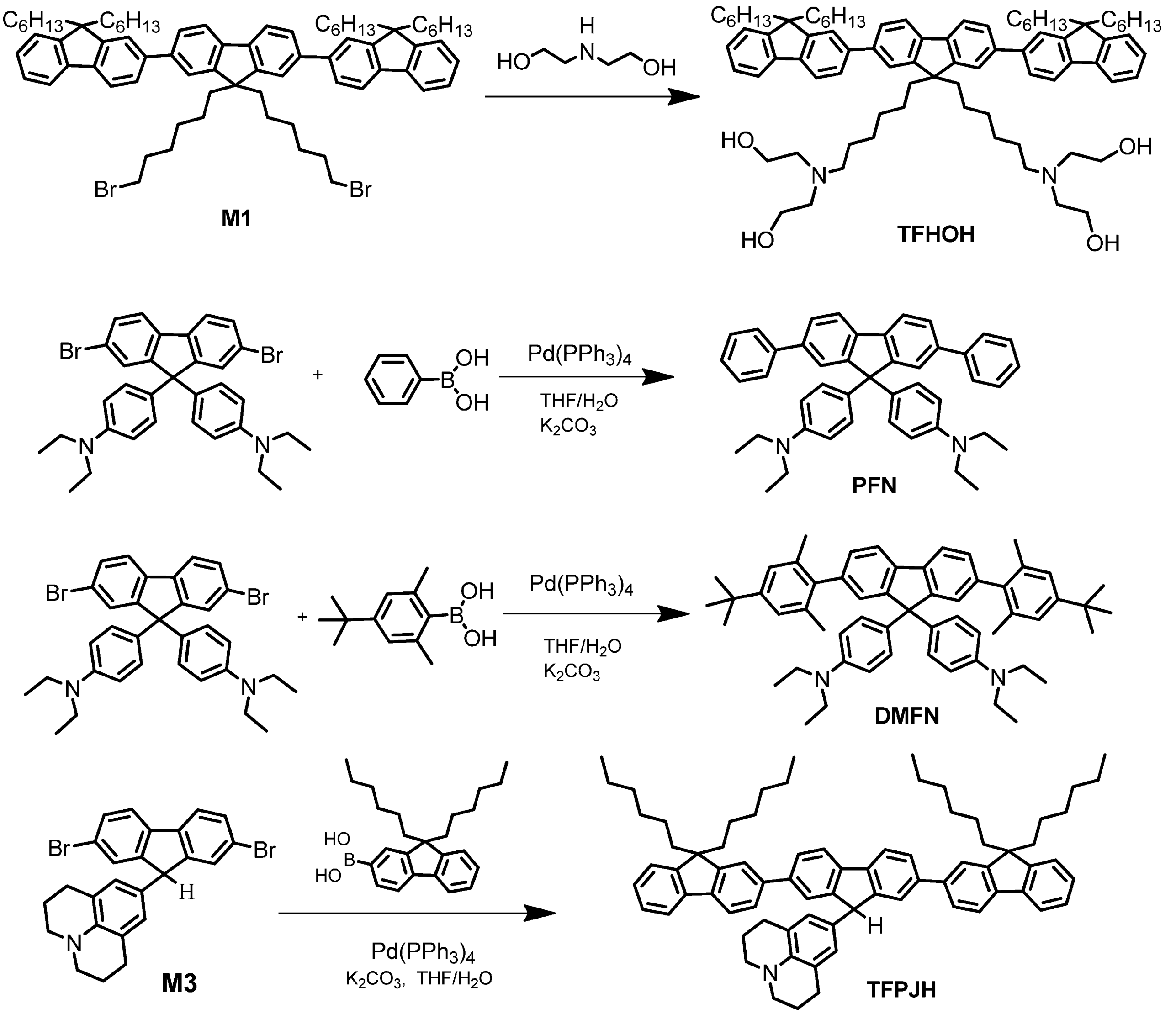
Phenylboronic acid and tetrakis-(triphenylphosphine)palladium were purchased from Acros. Other materials were used directly without further purification unless otherwise stated. The compounds 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diethylaniline) and 4-tert-butyl-2,6-dimethylphenylboronic acid were synthesized according to literature procedures.[27–29] The synthesis of 2,7-dibromo-9-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-9*H*-fluoren-9-ol (**M2**) has been reported elsewhere.[22] The synthetic procedures for the intermediates **M1** and **M3** are described in the Supporting Information (SI).Synthetic routes for the final compounds are shown in Scheme 4.

3.3. Synthesis of TFHOH

An amount of **M1** (150 mg, 0.13 mmol) was added to a stirred mixture of diethanolamine (0.5 mL) and Na_2CO_3 (42.4 mg, 0.4 mmol) in acetonitrile (10 mL). The mixture was then refluxed for 48 h with stirring under argon atmosphere. After reaction, the mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ and washed with brine. The organic phase was dried over anhydrous Na_2SO_4. The compound **TFHOH** was gained as a clear oil after column chromatography using CH_3OH/EA (1:5, VV^{-1}) as eluent. Yield: 60 mg, 38%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.84$–7.66 (m, 16H, phenyl *H*), 7.37–7.34 (m, 4H, phenyl *H*), 3.53 (t, $J=6.0$ Hz, 8H, CH_2OH), 2.56 (t, $J=6.0$ Hz, 8H, NCH_2CH_2), 2.40 (br, 4H, CH_2CH_2N), 2.08–2.02 (m, 12H), 1.13–1.09 (m, 40H), 0.88–0.75 ppm (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=153.53$, 152.87, 142.65, 142.41, 142.25, 141.91, 128.98, 128.75, 127.95, 124.86,123.24, 121.96, 121.85, 121.67, 61.43, 57.90, 57.11, 56.55, 42.30, 33.40, 31.85, 31.61, 28.90, 28.68, 25.71, 24.49, 15.96 ppm. Anal. Calcd. for $C_{83}H_{116}N_2O_4$ (%): C, 82.67; H, 9.70; N, 2.32; Found: C 82.73, H 9.44, N 2.21. MALDI-TOF-MS: *m/z* 1204.1 (M^+).

3.4. Synthesis of PFN

A mixture of 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*′-diethylaniline) (200 mg, 0.33 mmol), phenylboronic acid (119 mg, 0.98 mmol), $Pd(PPh_3)_4$ (22.5 mg, 0.02 mmol), and 2 M K_2CO_3 aqueous solution (2 mL) in THF (6 mL) was stirred at 75 °C for 24 h. After reaction, the organic layer was extracted by CH_2Cl_2, and was washed with saturated brine, then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the compound **PFN** was gained as a white solid after column chromatography using EA/PE (1:10, *V*/*V*) as eluent. Yield: 0.13 g, 63%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=$



Scheme 4. Synthetic routes for the compounds studied in this article.

8.1 Hz, 2 H, fluorene *H*), 7.65 (s, 2 H, fluorene *H*), 7.60-7.56 (m, 6 H), 7.43-7.38 (m, 6 H), 7.30-7.26 (m, 6 H), 7.14 (d, $J=8.0$ Hz, 4 H, pendant Phenyl *H*), 6.53 (d, $J=8.0$ Hz, 4 H, pendant Phenyl *H*), 3.27 (q, $J=12.0$ Hz, 8 H, CH_2), 1.10 ppm (t, $J=6$ Hz, 12 H, CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=152.67$, 145.29, 140.56, 139.28, 137.82, 131.44, 128.15, 127.58, 126.16, 125.93, 125.09, 123.90, 119.19, 110.21, 62.99, 43.12, 11.65, 11.62 ppm. Anal. Calcd. for $C_{45}H_{44}N_2$ (%): C, 88.19; H, 7.24; N, 4.57; Found: C 88.73, H 7.44, N 4.21. EI-MS: *m/z* 613.5 ($M^+ + 1$).

3.5. Synthesis of DMFN

A mixture of 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(*N*,*N*-diethylaniline) (308 mg, 0.5 mmol), 4-tert-butyl-2,6-dimethylphenylboronic acid (309 mg, 1.5 mmol), Pd(PPh$_3$)$_4$ (35 mg, 0.03 mmol), and 2 M K$_2$CO$_3$ aqueous solution (2.5 mL) in THF (7.5 mL) was stirred at 75 °C for 24 h. After reaction, the organic layer was extracted by CH$_2$Cl$_2$, and was washed with saturated brine, then dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the compound **DMFN** was gained as a white solid after column chromatography using EA/PE (1:20, V V^{-1}) as eluent. Yield: 0.33 g, 85 %. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=7.77$ (d, $J=8.0$ Hz, 2 H, fluorene *H*), 7.14-7.10 (m, 8 H, fluorene *H*), 7.05 (d, $J=8.0$ Hz, 4 H, phenyl *H*), 6.46 (d, $J=8.0$ Hz, 4 H, phenyl *H*), 3.25 (q, $J=6.0$ Hz, 8 H, CH_2CH$_3$), 2.06 (s, 12 H, CH_3), 1.34 (s, 18 H, C(CH_3)$_3$), 1.08 ppm (t, $J=6$ Hz, 12 H, CH$_2$CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=152.91$, 149.49, 146.17, 139.75, 139.41, 138.21, 135.69, 133.04, 129.04, 127.99, 127.58, 124.24, 119.59, 111.68, 63.87, 44.28, 34.26, 31.40, 21.33, 12.47 ppm. Anal. Calcd. for $C_{57}H_{68}N_2$ (%): C, 87.64; H, 8.77; N, 3.59; Found: C, 87.71, H 8.66, N 3.32. ESI-MS: *m/z* 782 ($M^+ + 1$).

3.6. Synthesis of TFPJH

A mixture of **M3** (300 mg, 0.61 mmol), 9,9′-dihexyl-9*H*-fluoren-2-ylboronic acid (693 mg, 1.83 mmol), Pd(PPh$_3$)$_4$ (46 mg, 0.04 mmol) in THF (12 mL) and 2 M K_2CO_3 aqueous solution (4 mL) was stirred at 75 °C for 24 h. After reaction, the organic layer was extracted with $CHCl_3$, and washed with saturated brine, then dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel using EtOAc/PE (1:15, *v*/*v*) as eluent to give a light-yellow powder. Yield: 0.24 g, 40 %. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.90$ (d, $J =$ 6.0 Hz, 2 H, fluorene *H*), 7.73-7.58 (m, 12 H, fluorene *H*), 7.36-7.30 (m, 6 H, fluorene *H*), 6.68 (s, 2 H, julolidine *H*), 5.07 (s, 1 H, fluorene *H*), 3.15 (br, 4 H, julolidine CH_2), 2.75 (br, 4 H, julolidine CH_2), 2.00-1.98 (m, 12 H), 1.12-1.05 (m, 32 H), 0.76-0.72 ppm (br, 12 H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 151.67$, 151.15, 140.91, 140.69, 140.11, 139.95, 127.25, 126.99, 126.29, 124.24, 123.11, 121.54, 120.46, 120.14, 119.96, 55.39, 54.11, 40.66, 40.61, 31.70, 29.93, 23.98, 22.81, 14.25 ppm. Anal. Calcd. for $C_{75}H_{87}N$ (%): C, 89.86; H, 8.75; N, 1.40; Found: C 90.00, H 9.15, N 1.31. MALDI-TOF-MS: *m*/*z* 1002.4 (M^+).

4. Results and Discussion

4.1. Photophysical Properties

Figure 1 shows the UV/Vis absorption and fluorescence spectra of the compounds in THF. Both TFHOH and TFPJH show absorption peaks at approximately 350 nm, ascribed to the π–π^* transition from the terfluorene moiety. For PFN and DMFN, with side phenyl substitutions, the absorptions locate at shorter wavelengths (namely, 313 and 277 nm) due to the shorter conjugation length in the two molecules. In addition, the maximum absorption of these compounds has almost no shifts when the solvent polarity increases (see SI for details), suggesting a small intramolecular charge-transfer character in the ground state, as had been observed for the other terfluorenes previously studied.

The photoluminescence behaviors of the studied compounds in THF show remarkable differences. TFHOH, with a hexyl spacer, exhibits a strong blue emission around 410 nm, and no prominent solvatochromic effect appears (Figure 2 a), representing a typical fluorene emission which is similar to that of TFP and TFAc, with no electron-donating pendant phenyl groups (see supporting information). TFPJH, bearing only one julolidine group, exhibits a quite similar photoluminescence behavior to that of TFPJ, with two julolidine groups, namely, a dual fluorescence emission, and the long-wavelength emission shows a significant bathochromic shift when the solvent polarity increases (Figure 2 b). Yet, for PFN and DMFN, with shorter conjugation lengths, the maximum emission bands gradually shift to longer wavelengths when the solvent polarity increases, indicating the existence of intramolecular charge-transfer process. Overall, both PFN and DMFN exhibit similar emission behaviors, although in PFN, two side phenyl rings can freely rotate around the single bond with respect to the central fluorene ring. Meanwhile, the rotation is mostly restricted in DMFN owing to the steric effect of the methyl substitutions on the side phenyl rings. The phenomena described above indicate that charge transfer apparently occurs in TFPJH, PFN and DMFN, but not in TFHOH. A common structural feature in TFPJH, PFN and DMFN is the electron-donating aminophenyl group directly connected to the C9 position of the central fluorene unit, whereas for TFHOH, the presence of hexyl chains between fluorene and the pendant N atoms totally excludes the possibility of charge-transfer emission,in spite of the two electron-donating bis(2-hydroxyethyl)amino groups. Therefore, the phenomena above imply that the rigid phenyl pendant groups, as well as the electron-donating units, are quite essential for the charge-transfer emission.

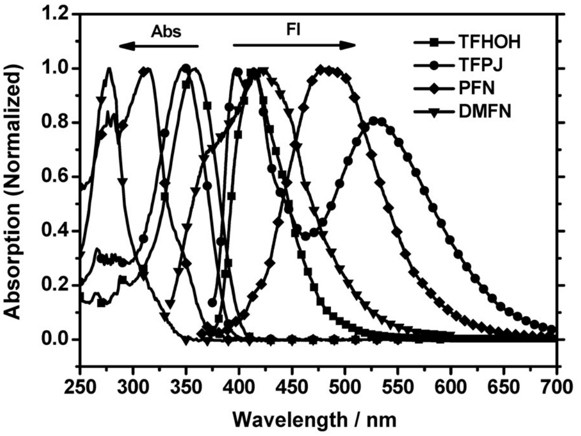


Figure 1. UV/Vis absorption and normalized fluorescence emission spectra of the compounds in THF solution, with a concentration of 5 μM. The excitation wavelength for PFN and DMFN is 320 nm, and that for TFHOH and TFPJH is 350 nm.

Table 1 summarizes the photophysical data of these compounds in solvents with different polarities. Obviously, TFHOH is strongly emissive, despite the solvent polarity—and with very high quantum efficiency (> 90 %), yet quite short excited-state lifetime, which represents the typical strong blue emission of terfluorene. This behavior is almost the same as that observed for TFP and TFAc. In contrast, the emission efficiency of the other compounds studied herein gradually decreases with increasing solvent polarity, which is consistent with their emission behavior in solution. In addition, their emission decays are in accordance with those of the previously reported terfluorenes TFOH and TFPJ, that is, apart from a short lifetime, there is also a longer lifetime corresponding to the charge-transfer emission band. This indicates that relaxation of the excited state may lead to a lower energy emission.

Concerning the nature of the charge-transfer emission, when we first found this phenomenon in TFOH, we tentatively attributed it to an analogue of the TICT mechanism, that is, the rotation of a pendant C–N bond was supposed to cause the TICT state. But this speculation was overthrown upon the synthesis and investigation of TFPJ, in which the rotation of the C–N bond in the pendant groups is completely restricted. After that, we also excluded the through-space D–A dyad mechanism by measuring the fluorescence spectra of the terfluorene-bearing hexyl chains (5 μM) in the presence of julolidine in THF solution. As a result, the blue emission of the fluorene fluorophore is greatly quenched upon addition of julolidine, and meanwhile, a new weak emission band around

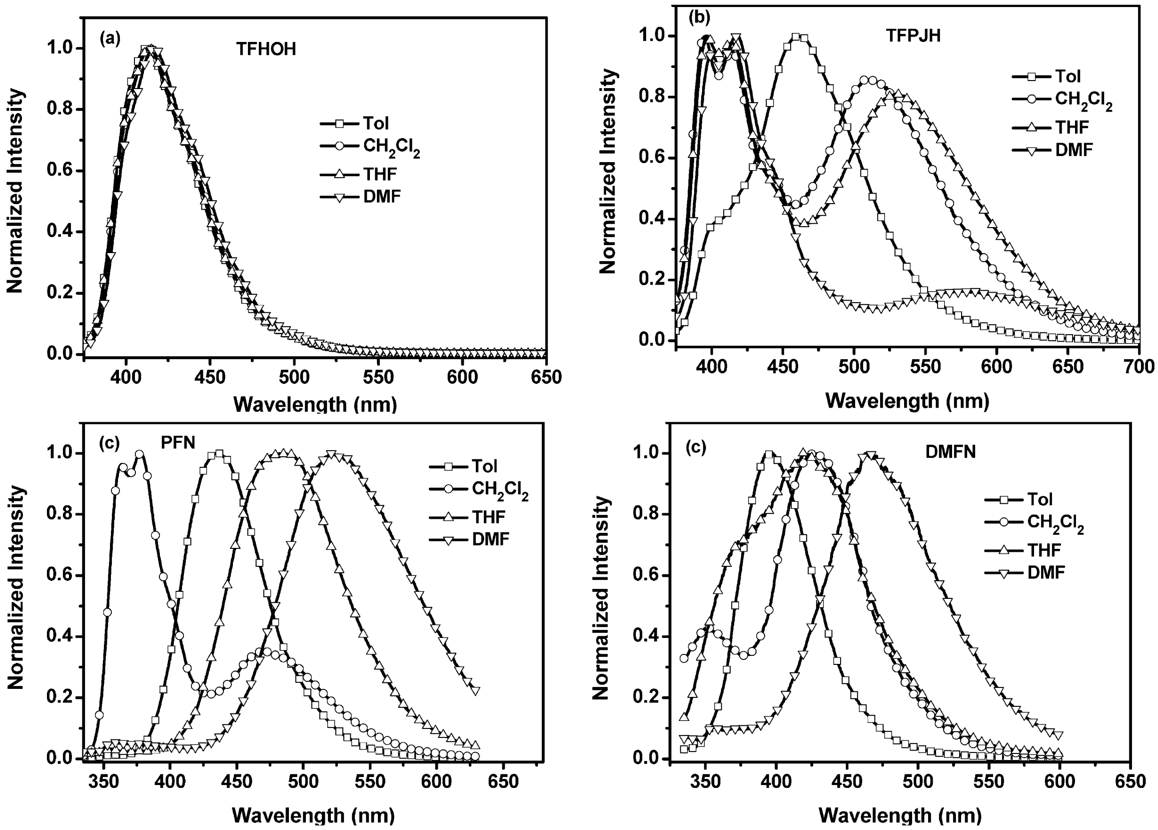


Figure 2. Normalized fluorescence emission spectra of a) TFHOH, b) TFPJH, c) PFN, and d) DMFN in different solvents. The concentrations of the compounds are 5 μm. The excitation wavelength for PFN and DMFN is 320 nm, and that for TFHOH and TFPJH is 350 nm.

Table 1. Fluorescence data for TFHOH, TFPJH, PFN, and DMFN in different solvents.

	Tol				CH_2Cl_2				THF				DMF			
	λ_{em} [nm]	Φ[a] [%]	τ[b] [ns]	[%][c]	λ_{em} [nm]	Φ [%]	τ [ns]	[%][c]	λ_{em} [nm]	Φ [%]	τ [ns]	[%][c]	λ_{em} [nm]	Φ [%]	τ [ns]	[%][c]
TFHOH	412	97	0.5	99.2	414	94	0.5	99	415	98	0.5	97	417	98	0.5	99
			5.0	0.8			4.3	1			3.5	3			4.2	1
TFPJH	398	92	0.6	91.4	398	56	0.8	94.5	398	34	0.7	95.6	398	25	0.7	89.0
	460		8.0	8.6	512		9.3	5.5	530		5.6	4.4	570		7.6	11.0
			0.7	13.5			1.5	11.6			2.4	14.3			3.0	46.4
			12.0	86.5			23.8	88.4			12.7	85.7			10.9	53.6
PFN	350	21	1.3	70.5	363	24	1.1	75	355	21	1.3	47	356	13	1.3	99.6
	434		8.1	29.5	470		12.8	25	485		10.4	53	520		3.6	0.4
			0.7	5.7			0.7	2.7			0.8	5.2			2.3	4.3
			8.5	94.3			18.3	97.3			12.8	94.8			23.7	95.7
DMFN	396	21	0.2	11	351	12	1.9	43.4	370	17	1.1	52	355	18	1.2	84.3
			4.7	89	426		12.6	56.6	421		8.7	48	465		11.9	15.7
							0.4	6.7			0.5	12			0.8	5.2
							7.6	96.3			7.7	88			19	94.8

[a] Φ denotes the fluorescence quantum efficiency. [b] The fluorescence decays were recorded at a concentration of 5 μm in different solvents. τ represents the fluorescence lifetime (there are two lifetimes at each emission wavelength). [c] % denotes the contribution of each component.

570 nm becomes evident, attributed to the exciplex emission. These findings indicated that the strong green emission of TFPJ in THF solution (536 nm) was not from the exciplex. Common ICT processes are gradually excluded from our experimental results.

According to our previous studies on terfluorene derivatives with spiroconjugated emission,[22] the existence of spiroconjugated charge transfer in this series of compounds could simply be determined by their photophysical behaviors. TFPJH, PFN and DMFN all exhibit a distinct charge-transfer character, with the common structure of pendant electron-donating amino-

Table 2. Calculated values of the excited states of TFPJH, PFN and DMFN. The absorption and fluorescence properties in CH_2Cl_2 solution (experimental results) are also included.[a]

	Geometry	Transition	Orbitals involved	f	(Calcd.)	(Exptl.) [nm]	Dipole [debye]
PFN	Ground state	S0-S1	H→L	0.0025	375.39	–	2.89
		S0-S2	H-1→L	0.0645	365.75	–	
		S0-S3	H-2→L	1.0911	316.08	314	
	Relaxed S3	S0-S3	H-2→L	1.229	371.51	377	4.81
	Relaxed S1	S0-S1	H→L	0.0268	454.53	475	17.24
DMFN	Ground state	S0-S1	H→L	0.0028	337.36	–	2.84
		S0-S2	H-1→L	0.0347	329.86	–	
		S0-S7	H-2→L	0.5756	275.02	276	
	Relaxed S7	S0-S7	H-2→L	1.291	401.73	402	8.09
	Relaxed S1	S0-S1	H→L	0.0254	411.02	425	16.86
TFPJH	Ground state	S0-S1	H→L	0.0674	389.82	–	2.2366
		S0-S2	H-1→L	2.1368	351.59	348	
	Relaxed S2	S0-S2	L→H-1	2.2093	418.85	398	4.6728
	Relaxed S1	S0-S1	L→H	0.0453	487.85	512	19.5379

[a] In this table, the dipole moment is given in debye, and the vertical excitation energy in nm. The oscillator strength is that in the ground state (absorption). H and L represent the HOMO and LUMO orbitals, respectively.

phenyl groups that could be assigned to a spiroconjugation-like charge transfer. The charge-transfer emission is regardless of the side chromophores, which only act by changing the whole conjugation length of the compound (the emission wavelengths of PFN and DMFN are shorter than those of the other terfluorenes). Regarding the hexyl linkage, the strong blue emission of TFHOH, irrespective of the solvent polarity, provides further evidence that the phenyl pendants are necessary to offer proper orbitals that may interact with the orbitals of the central fluorene moiety, thus leading to charge transfer. The above phenomena bring us to the following conclusions: 1) the existence of electron-donating N atoms in company with the pendant phenyl rings guarantees the orbitals needed for the charge-transfer process; 2) the side chromophores mainly affect the conjugation length, and the rotation of side chromophores will not lead to charge transfer; 3) one or two pendant amino-phenyl groups can both result in charge-transfer emission.

Calculation Details

DFT calculations were performed to investigate the electronic structures of these compounds, to identify the charge-transfer character in the excited state. Taking the terfluorene TFPJH as an example, its absorptions could be clearly assigned as follows: Firstly, the HOMO orbital is located on the julolidine moiety, the LUMO orbital is distributed on the terfluorene moiety. There is little overlap between the two orbitals in the ground state, and the electron transition from HOMO to LUMO is quite weak, which is in accordance with the little absorption changes. On the other hand, the HOMO-1 is mainly contributed from HOMO in terfluorene, and the transition from HOMO-1 to LUMO ($f=2.1368$, $\lambda_{max}=351.59$ nm) matches well with the absorption maximum of TFPJH ($\lambda_{max}=348$ nm) measured in dichloromethane.

When this molecule is excited to the S2 state, the vibrational relaxation firstly makes the excited-state molecule back to the 0 vibrational level of the S2 singlet state. In the relaxed S2 excited state, the dihedral angle between the side fluorenes and the central fluorene is reduced to get better planarity of the whole terfluorene fragment. The relaxed S2 state thus has two subsequent pathways. One is the vertical transition from S2 to S0 ($f=2.2093$, $\lambda_{max}=418.85$ nm), correlating well with the experimentally observed blue emission ($\lambda_{max}=398$ nm); the other one is the internal conversion from S2 to S1 (see Table 2 for detail). In the relaxed S1 state of TFPJH, the calculated vertical transition from LUMO to HOMO ($f=0.0453$, $\lambda_{max}=487.85$ nm) is in good agreement with the experimentally observed green emission ($\lambda_{max}=512$ nm) in CH_2Cl_2 solution. Additionally, the calculated S1 excited-state dipole moment (19.5379 D) is much larger than the ground state (2.2366 D), accounting for the large solvatochromic effect of the lower energy emission. The evidence that the HOMO orbitals are delocalized over the central fluorene unit in the S1 relaxed geometry suggests enhanced spiroconjugation between julolidine and terfluorene in the S1 state. This is because that this HOMO orbital can be considerd as anti-bonding combination between HOMO of julolidine and the HOMO of terfluorene. So in the ground state the spiroconjugation is disfavored. When an electron is excited from this orbital to LUMO in the S1 state, the weakened anti-bonding interaction leads to energy in favor of spiroconjugation. This kind of CT excited-state-enhanced-spiroconjugation character is the same as we have observed from the other terfluorene derivatives (TFOH, TFPJ and TFE). Similar phenomena are also observed in PFN and DMFN, their Kohn–Sham frontier orbitals are presented in the supporting information, and their electronic properties are summarized in Table 2.

We specially note that in TFPJH, there is a small steric effect on the C9 position of the central fluorene ring, due to the single julolidine pendant group. In the excited state, the julolidine group could be in an orthogonal relationship with the central fluorene plane, implying that a typical spiroconjugated conformation is achieved in the excited state of TFPJH (Figure 3). It turns out that the photophysical properties of TFPJH are consistent with those of TFPJ bearing two julolidines, which directly reveals that spiroconjugation does exist in this set of terfluorene derivatives, whether their structures are in line with the typical orthogonal π fragments or not.[30,31] Moreover, the spiroconjugated charge-transfer emission has little to do with the amount and conformation of pendant groups.

We had reported that the electron-donating ability of the pendant groups directly affects the charge-transfer energy. The stronger the electron-donating ability of the pendant nitrogen atom, the lower

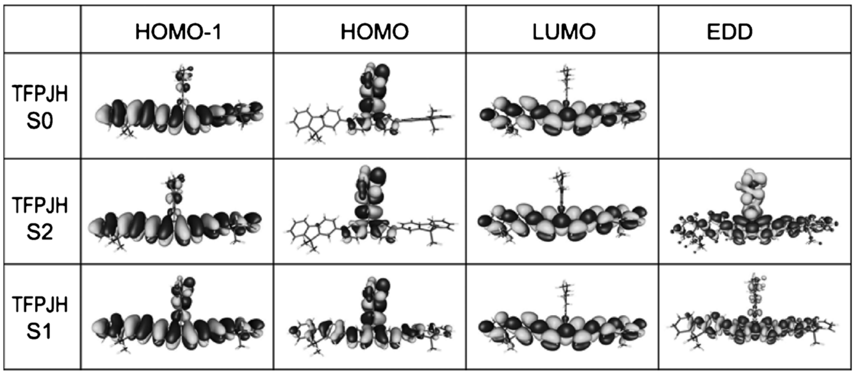


Figure 3. Kohn–Sham frontier orbitals of **TFPJH**. S0, S1 and S2 mean ground state, first singlet excited state, and second excited state, respectively. **EDD** indicates the differential density for the corresponding excited state, in which the blue part represents a negative value (electron-density decrease) and orange represents a positive value (electron-density increase).

the energy of the charge-transfer emission. Hereby we further disclose the influence of the molecular structures and the excited-state conformations on the emission behaviors. It turns out that the rigid pendant groups, as well as the electron-donating N atoms, are necessary for the charge-transfer emission, whereas the side substitutions have no effect on the charge-transfer emission. We especially investigated a complete "spiroconjugation" configuration in TFPJH with a small steric effect on the pendant groups, and a similar charge-transfer emission was observed compared to other terfluorenes we had studied earlier. The calculations confirm that spiroconjugation does exist in those compounds with electron-donating aminophenyl pendants directly connected to the C9 position of the central fluorene unit, although their chemical structures are not in line with the typical orthogonal conformations.

5. Conclusions

In summary, a series of compounds containing aminophenyl as pendant groups and fluorene derivatives as main chains were synthesized through the Suzuki coupling reaction. Their photophysical properties were studied. By combining experiments with DFT studies of the excited-state properties, we are able to conclude that terfluorenes with pendant phenyl rings linked to the C9 position of the central fluorene, together with electron-donating N atoms, provide sufficient orbital and energy for an unusual intramolecular charge transfer, substantiated as the spiroconjugation interaction. This study has expanded the theory that spiroconjugation only existed in systems with orthogonal π-fragments, and has made a contribution to the application of the through-space electronic effect. From another point of view, fluorescence emission could be facilely tuned by structure modification of the system, and might find use in other electrical and optical fields, for example, as chemical or biological sensors. We are now working on the development of their application as fluorescent sensors.[32]

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