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Syntheses and spectroscopic studies of spirobifluorene-bridged bipolar systems; photoinduced electron transfer reactions†

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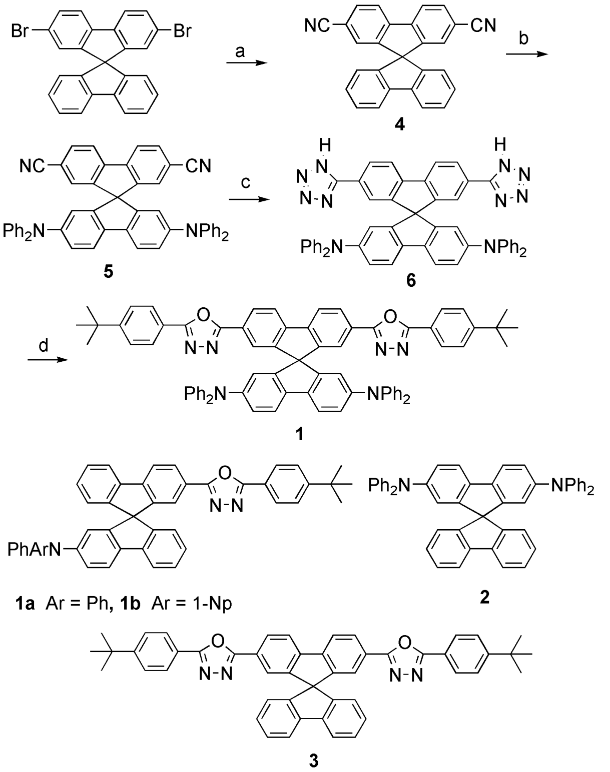
Some 9,9′-spirobifluorene-bridged bipolar systems 1–3 containing 1,3,4-oxadiazole-conjugated oligoaryl and triarylamine moieties have been synthesized, in which 1 exhibits remarkable solvent-polarity dependent fluorescence properties due to a highly efficient photoinduced electron transfer reaction.

Bipolar (*i.e.* dual chromophores) organic materials have received considerable attention due to their potential uses in molecular devices such as molecular rectifiers,[1] switches,[2] electrochemical sensors,[3] photovoltaic cells,[4] and nonlinear optical materials,[5a] *etc.* It has been a central interest to integrate such composite materials (or devices) *via* the modification of chromophores and linker structures so that the physical properties can be fine-tuned to a designated function. Recently, syntheses of materials aimed at increasing the dimensionality have been explored, among which the three-dimensional design based on spiro-bridged conjugated systems is of particular interest.[5] In this communication, we report the synthesis and photophysical studies of another new type of 9,9′-spirobifluorene-bridged bipolar system. In this bipolar molecule, the 1,3,4-oxadiazole-containing conjugated oligoaryl system, serves as the electron acceptor, while the triarylamine moiety acts as the donor counterpart. Such a configuration may conceptually lead to the development of new materials with an interfacial layer of bifunctional properties.

The synthetic pathways of 9,9′-spirobifluorene-bridged bipolar molecule **1** and model compounds **2** and **3** are shown in Scheme 1. Treatment of 2,7-dibromo-9,9′-spirobifluorene with CuCN in DMF at the reflux temperature gave the dicyano derivative **4** in a 90% yield. The unsubstituted branch of the 9,9′-spirobifluorene was then regioselectively brominated at C-2′ and C-7′ positions with Br$_2$ solution (in CH$_2$Cl$_2$) in the presence of Lewis acid, AlCl$_3$, which was used as a promoter. The dibrominated crude product was directly subjected to a Pd-catalysed amination with diphenylamine in the presence of a catalytic amount of P^{t}Bu$_3$ to give an 80% yield of **5**. The cyano groups in **5** were further converted to tetrazoles by treatment with NaN$_3$ and NH$_4$Cl in DMF at reflux temperature to form bis-tetrazole **6** in an 80% yield. Subsequently, treating **6** with 4-*tert*-butylbenzoyl chloride in pyridine leads to the formation of the final spiro-configured bipolar compound **1** in a 73% yield. In addition to the elemental analysis of **1**, which assigned the designated structural composition, the structure of **1** was further confirmed by single crystal X-ray diffraction analysis.[6] For comparison, two model compounds, **2** and **3** were synthesized from 2,7-dibromo-9,9′-spirobifluorene *via* a similar synthetic pathway. Compounds **1–3** sublime at a relatively low temperature, providing the feasibility in their integration into molecular devices.

As shown in Fig. 1 the absorption spectral features of **1** in THF exhibit a composite characteristic of **2**and **3**. Careful spectral analyses indicate that the absorption extinction coefficients, $\varepsilon(\lambda)$, within experimental error, are identical with those of **2** plus **3** (see Fig. 1). Thus, the merging of **2** and **3** into bipolar molecule **1** causes negligible interactions among chromophores in the electronic ground state. In contrast, the incorporation of chromophores provokes strong interactions in the excited state. Fluorescence maxima at 392 and 373 nm were observed for **2** and **3** in THF (see Fig. 1), of which the Stokes shift was calculated to be as small as ~ 670 and 365 cm^{-1}, respectively. Similar normal Stokes shifted fluorescence was observed for **2**



Scheme 1 *Reagents and condition*: a, CuCN, DMF, reflux; b, i, Br$_2$, AlCl$_3$, CH$_2$Cl$_2$, reflux; ii, Ph$_2$NH, Pd(OAc)$_2$, PtBu$_3$, NaOtBu, PhCH$_3$, reflux; c, NaN$_3$, NH$_4$Cl, DMF, reflux; d, 4-^{t}BuPhCOCl, pyridine, reflux.

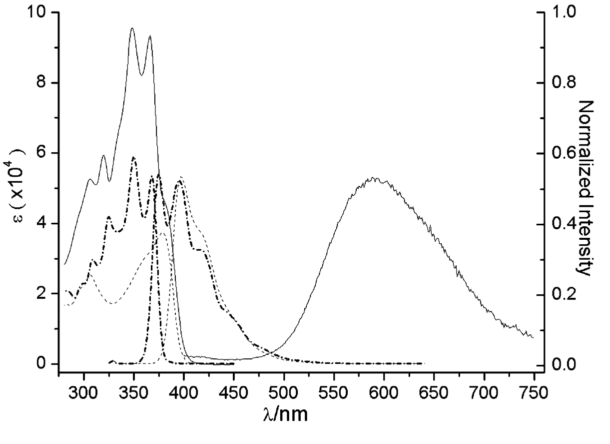


Fig. 1 Absorption and emission spectra of **1** (—), **2** (-----) and **3** (–·–·–) in THF. The emission intensities for **1–3** have been normalized for clarity.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b208269a/

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and **3** in other studied solvents. Conversely, **1** in THF exhibited exclusively a new emission band maximized at ~590 nm (a Stokes shift of ~9000 cm^{-1}), while the normal emission attributed to **2** or **3** individually was too weak to be resolved. The excitation spectrum is effectively identical to the absorption profile, excluding its origin from traces of impurity. Detailed analyses revealed that the intensity of the 590-nm emission was linearly proportional to the studied concentrations in the range of 10^{-5}–10^{-4} mol dm^{-3}. Thus, the possibility of the emission resulting from the aggregation effect can also be eliminated. Alternatively, the results can be more plausibly rationalized by a mechanism incorporating a photoinduced electron transfer (ET) process. This viewpoint can first of all be supported by the strong solvent-dependent spectral properties shown in Fig. 2. The spectral shift of the fluorescence upon increasing solvent polarity (Δf) depends on the difference in permanent dipole moments between ground and excited states, which can be quantitatively expressed as:

$$\tilde{\nu}_f = \tilde{\nu}_f^{vac} - (2|\vec{\mu}_e - \vec{\mu}_g|^2/hca_0^3)\Delta f \qquad (1)$$[7]

As shown in the inset of Fig. 2, the plot of $\tilde{\nu}_f$ *versus* Δf is sufficiently linear, in which the large slope of 14 200 cm^{-1} is obtained, supporting the proposed electron-transfer mechanism in the excited state. As a result, a charge transfer (CT) emission band was observed in **1**. Secondly, the free-energy change (ΔG) for photoinduced electron transfer between an excited donor molecule (D*) and a ground-state acceptor (A) at a distance (d) can be expressed as:

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E_{00}(\text{D}) - (e^2/\varepsilon d) - (e^2/2)(1/r_{\text{D}}{}^{+} + 1/r_{\text{A}}{}^{-})(1/\varepsilon_{\text{r}} - 1/\varepsilon) \qquad (2)$$

where $E_{\text{ox}}(\text{D})$ and $E_{\text{red}}(\text{A})$ are the oxidation and reduction potentials of triarylamine and 1,3,4-oxadiazole moieties, respectively, $E_{00}(\text{D})$ is the energy of zero–zero transition, $r_{\text{D}}{}^{+}$ and $r_{\text{A}}{}^{-}$ are effective ionic radii, ε is the dielectric constant of solvent, and d is the center-to-center distance between D and A. E_{ox} and E_{red} for **1**, measured by cyclic voltammetry experiments (see ESI†), were measured to be 0.88 and −1.69 V, respectively in THF. E_{00} of 3.25 eV (~382 nm) was obtained from the first vibronic peak of the UV spectrum. According to the X-ray structure, the center-to-center distance between D and A of **1** was estimated to be ~7.7 Å. A semi-empirical PM3 approximation was further made on $r_{\text{D}}{}^{+} \sim r_{\text{A}}{}^{-} = 5.3$ Å. With all values substituted into eqn. (2), the free energies of ET (ΔG) were calculated and shown in Table 1. As indicated by the ΔG values of < -0.63 eV, the excited state ET reaction is apparently an exergonic process in all solvents applied. This viewpoint can be further supported by the corresponding ET dynamics for **1** in various solvents. The fluorescence rise and decay dynamics were measured by a time-correlated photon counting system, rendering a temporal resolution of ~15 ps (see ESI†). The results listed in Table 1 clearly showed that except for the well-fitted single exponential decay, the rise dynamics of the emission for **1** was irresolvable (≪15 ps), indicating the occurrence of a fast ET process.

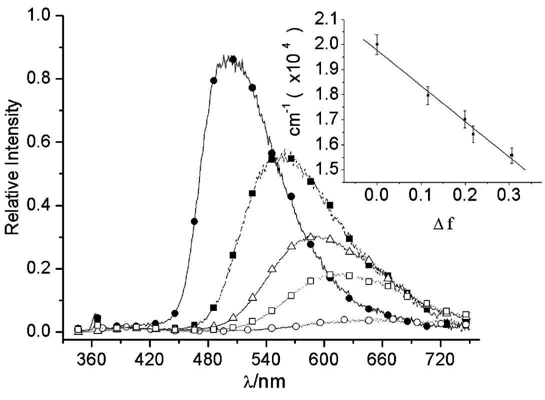

Fig. 2 The emission spectra of **1** in cyclohexane (●), benzene (■), tetrahydrofuran (Δ), dichloromethane (□) and acetonitrile (○). The optical density at the excitation wavelength (330 nm) was prepared to be 0.2 in all studied solvents. Inset: the plot of emission peak frequencies as a function of solvent polarities.

Table 1 Photophysical properties of **1**–**3** in various solvents

	Solvent	λ_{max}/nm^a	PL λ_{max}/nm	Φ	τ/ns^b	ΔG^c
1	CYC	382	500	4.49×10^{-2}	18.25	−0.63
	BEN	384	557	3.57×10^{-2}	42.09	−0.68
	THF	382	588	1.08×10^{-2}	37.77	−0.94
	DCM	383	609	5.20×10^{-3}	20.66	−0.96
	ACN	378	642	1.08×10^{-3}	6.45	−1.03
2	THF	382	392	0.58	1.05	
3	THF	368	373	~1.0	0.91	

^{a} Absorption, data was taken from the first vibronic peak. ^{b} Samples for the lifetime measurements were degassed *via* three freeze–pump–thaw cycles. ^{c} Free energies (ΔG) of the electron transfer for **1** in various solvents were calculated according to eqn. (2). See text for the detailed description.

Attempts have also been made by synthesizing two analogues **1a** and **1b** (Scheme 1, see ESI†), in which the molecular symmetry is lowered by bearing only a pair of D(triarylamine)/A(1,3,4-oxadizaole) chromophore rather than two D/A pairs in **1**. Our preliminary results revealed a similar highly efficient ET process, resulting in an anomalous CT band (not shown here). Thus, under a decent driving force (ΔG) the ET process can be generalized among the spirobifluorene-conjugated D/A systems.

Assuming an ET efficiency of approximately unity, the solvent-polarity dependent yields ranging from 10^{-3} to 0.05 for **1** (see Table 1) are relatively smaller than those of parent molecules **2** and **3** (Table 1). This can be rationalized by the facts that back electron transfer is considered a forbidden process and is normally dominated by the radiationless deactivation. In addition, as the local excitation (LE)-ET zero-order gap increases by increasing the solvent polarity, the radiative decay rate of the ET band decreases due to the reduction in LE/ET interaction.[8] The combination of these two factors rationalizes the decrease of the emission yield as the solvent polarity increases.

Theoretically, it is feasible to adjust the D/A strength as well as the number of spirobifluorene conjugation so that the flow of electrons can be precisely regulated. Such a conceptual design may be advantageously exploited in *e.g.* photovoltaic devices. To achieve this goal, focus on poly-spirobifluorene conjugated bipolar or triad systems is currently in progress.

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6 Crystal data for **1**: $C_{78.50}H_{70}Cl_5N_6O_2$, M = 1306.66, monoclinic, space group $P2_1/n$, a = 13.7737(1), b = 27.0557(3), c = 20.0245(2) Å, β = 105.0516(4)°, U = 7206.26(12) Å^3, Z = 4, Dc = 1.204 Mg m^{-3}, μ = 0.251 mm^{-1}, F(000) = 2736, T = 150 K, wavelength 0.71073 Å, crystal size 0.25 × 0.22 × 0.15 mm, θ_{max} 25.00°, 41176 reflections measured, final R [$I > 2\sigma(I)$] = 0.1091, CCDC 192594. See http://www.rsc.org/suppdata/cc/b2/b208269a/ for electronic files in CIF or other electronic format.

7 $\tilde{\nu}_f$ and $\tilde{\nu}_f^{vac}$ in eqn. (1) are the spectral position of the solvation equilibrated fluorescence maxima and the value extrapolated to the diluted gas-phase, respectively, $\mathbf{a}_0$ denotes the radius of solute, $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moment vectors of the ground and excited states, and Δf is the Lippert solvent polarity parameter expressed as $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$.

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