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Highly solid-state emissive *para*-terphenyls laterally substituted with a diphenylamino group†

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Intense solid-state emissions with good to excellent quantum yields were achieved through the introduction of bulky electron-donating diphenylamino groups at the side positions of an electron-accepting *para*-terphenyl framework.

To design and synthesize highly emissive organic materials that can fluoresce, even in the solid-state, is a fundamental topic for realizing a wide range of new optoelectronic and photonic applications, such as organic light-emitting diodes (OLEDs),[1] organic light-emitting field-effect transistors (OLEFETs),[2] organic solid-state lasers[3] and organic fluorescent sensors.[4] In contrast to the great number of molecules that are known to be highly emissive in solution, the examples of highly emissive organic solids with a fluorescence quantum yield close to unity are still quite limited, due to the severe fluorescence quenching as a result of certain intermolecular interactions.[5] Therefore, the rational design of such emissive organic solids is still a challenging issue. To achieve an intense solid-state emission, several approaches have been adopted, such as dendritic or bulky substituent protection,[6] cross-dipole stacking,[7] aggregation-induced emission,[8] J-aggregate formation[9] and enhanced intramolecular charge transfer (CT) transition.[10,11] Among them, we and others have recently focused our attention on an interesting molecular design, in which the bulky electron-accepting dimesitylboryl groups were introduced at the side positions of an electron-donating π-conjugated framework.[10] This effective molecular design is attributed to two factors of the lateral dimesitylbroyl group. One is the steric bulkiness, which can prevent an intermolecular interaction. The other is the electron-accepting character, which induces an intramolecular CT transition with a large Stokes shift and thus effectively suppresses self-quenching in the condensed state. Based on this design principle, we envisioned that the bulky electron-donating groups, such as diarylamino groups, at the side positions of an electron-accepting π-conjugated framework would act in a similar manner, and thus we could provide another new molecule design for organic emissive solids through the introduction of lateral diarylamino groups into electron-accepting π-conjugated systems (Fig. 1a). Although triarylamines have been extensively utilized in various potential optoelectronic and photonic applications, those containing lateral diarylamino groups have been seldom investigated. So far as we know, only one poly(1,4-phenylenevinylene) (PPV) π-conjugated system bearing diphenylamino groups as side chains has been reported.[12] Herein, we designed a new kind of triarylamine, in which diphenylamino groups were introduced at the side positions of electron-accepting *para*-terphenyls **1–5** (Fig. 1b). We found that these diphenylamino-substituted terphenyls showed intriguing intense fluorescence, with good to excellent quantum yields mainly in the solid-state.

The diphenylamino-substituted terphenyls were readily synthesized in two steps, using 2,5-dibromoaniline as the starting material. Thus, the first copper-catalyzed Ullman coupling with iodobenzene afforded the key precursor 2,5-dibromo-*N*,*N*-diphenylaminobenzene in 48% yield. The following Pd(0)-catalyzed Suzuki coupling with a variety of *para*-substituted phenylboronic acids produced **1–5** in moderate to good yields.

Single crystals of **2** suitable for X-ray analysis were obtained by recrystallization from dichloromethane–hexane. The crystal structure of **2** together with its packing structure is shown in Fig. 2. Similar to other triarylamines, the benzene rings on the lateral diphenylamino moiety are almost orthogonal to the central benzene of the terphenyl framework. The dihedral angle between benzene rings A and B is 81.2°, which is similar to that between A and C (80.9°). Furthermore, the main chain terphenyl framework exhibits a significantly twisted structure. The terminal benzene ring D is twisted by a large dihedral

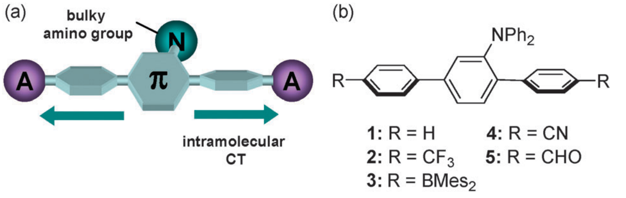

Fig. 1 (a) The schematic representation and (b) the structures of diphenylamino-substituted terphenyls **1–5**.

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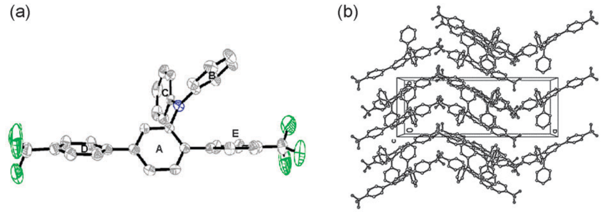

Fig. 2 The crystal structure of **2**: (a) an ORETP drawing (50% probability for the thermal ellipsoids) and (b) the packing structure. Hydrogen atoms are omitted for clarity.

angle (46.8°), relative to the central ring A, and the dihedral angle between benzene rings A and E is even larger (59.7°) due to the higher steric congestion between them. Apparently, the significantly twisted conformation of the main chain framework arises from the steric hindrance of the lateral diphenylamino group. Presumably owing to the nonplanar structure of diphenylamino moiety, as well as the main chain framework, the molecules are far apart from each other. The distance between the central A benzene planes of the two adjacent molecules is 7.33 Å, which is supposedly large enough to prevent intermolecular electronic interactions.

The UV/vis absorption and emission spectra of the diphenylamino-substituted terphenyl **2** are shown in Fig. 3. In cyclohexane, in addition to an intense absorption band below 300 nm, **2** shows a relatively weaker absorption at 362 nm (ε = 2480 M^{-1} cm^{-1}). In the fluorescence spectra, **2** exhibits an emission at 432 nm with a moderate quantum yield (Φ_F = 0.33). One noticeable feature is the large Stokes shift (4480 cm^{-1}) for this terphenyl unit with such a limited conjugation length, which may partially arises from significant structure differences between the twisted structure in the ground state and the presumably planar structure in the excited state.[10b,11] Single point calculations (B3LYP/6-31G(d) level) using the geometry derived from the crystal structure demonstrate that the HOMO is mainly localized over the central diphenylaminophenylene unit and the LUMO is delocalized over the entire terphenyl framework (Fig. 4). Moreover, the time-dependent DFT calculations indicate that the absorption at 362 nm is assignable to the intramolecular CT transition from the HOMO to the LUMO. These calculated results clearly suggest a polarized structure in the excited state, which was further evidenced by a large solvatochromism in fluorescence, from 432 nm in cyclohexane, to 453 nm in benzene, 471 nm in THF and 486 nm in MeCN. The significant intramolecular CT character in the excited state is probably another factor that contributes to the large Stokes shift of the present diphenylamino-substituted terphenyl **2**.[10b,11]

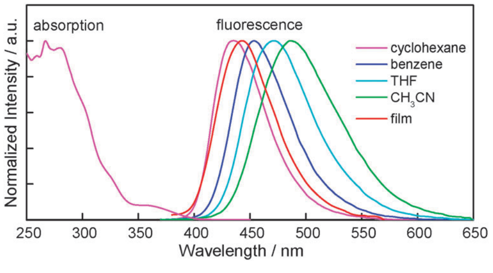

Fig. 3 UV/Vis absorption and fluorescence spectra of **2**.

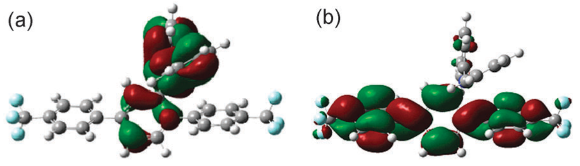

Fig. 4 Pictorial drawings of (a) the HOMO and (b) the LUMO of **2** calculated at the B3LYP/6-31G(d) level of theory by using its crystal structure.

It is most noteworthy that in spite of the moderately intense fluorescence in solution, the diphenylamnio-substituted terphenyl **2** exhibits a remarkably intense sky-blue fluorescence (λ_{em} = 443 nm) with extremely high quantum yield (Φ_F = 0.99) for its spin-coated film, as determined by the calibrated integrating sphere. A similar fluorescence property was also observed for the powder of **2**. In view of the absorption and emission spectra, almost the same spectra as those in benzene solution are maintained for the spin-coated film (see ESI†), suggesting the formation of neither aggregates in the ground state nor an excimer in the excited state.[10d] The present molecular design is very effective in suppressing the intermolecular interaction, which is presumably an important factor contributing to the high solid-state fluorescence efficiency. On the other hand, a large Stokes shift induced by the intramolecular CT transition from the electron-donating lateral diphenylamino group to the electron-accepting π-conjugated main chain framework may be another important factor in suppressing fluorescence quenching in the condensed state.[10,11]

The intense solid-state fluorescence is a general characteristic of the present molecular design. All of the other diphenylamino-substituted terphenyl derivatives show an intense solid-state emission with good to excellent quantum yields (Φ_F = 0.37–0.99) for the spin-coated films (Table 1). Since the emission comes from the singlet excited state generated by the intramolecular CT transition from the diphenylaminophenylene moiety to the terphenyl main chain framework, the emission maxima can be finely tuned by choosing different electron-withdrawing terminal groups. Thus, the introduction

Table 1 The photophysical properties of **1–5**

		λ_{abs}/nm^a (ε)^b	$\lambda_{em}{}^c$ [nm]	Φ_F
1	Benzene	353 (2860)	421	0.14^e
	Film^d	361	419	0.37^f
2	Benzene	357 (2580)	453	0.26^e
	Film^d	363	443	0.99^f
3	Benzene	391 (5250)	483	0.31^e
	Film^d	399	473	0.95^f
4	Benzene	377 (2600)	479	0.26^e
	Film^d	389	485	0.98^f
5	Benzene	390 (2800)	495	0.21^e
	Film^d	393	515	0.55^f

[a] Only the longest absorption maxima are shown. [b] M^{-1} cm^{-1}. [c] Excited at the longest absorption maxima. [d] Spin-coated film prepared from a chloroform solution. [e] Calculated using quinine sulfate as standard. [f] Absolute quantum yield determined by a calibrated integrating sphere system.

of dimesitylboryl groups (**3**) and cyano groups (**4**) at the terminal positions shift the emission to greenish-blue at 473 nm and bluish-green at 485 nm, respectively. The emission was further red-shifted to yellowish-green at 515 nm through the extension of the π-conjugation with formyl groups (**5**). It is worth noting that compound **1**, without the electron-withdrawing groups at the terminal positions, emits purple-blue fluorescence with a relatively low quantum yield ($\Phi_F = 0.37$) in the solid-state, confirming that the intramolecular CT is an important factor for the intense solid-state emission.[10,11] As for the fluorescence spectra, compounds **1–4** show very similar spectra in the spin-coated films to those in benzene solution, while the emission of **5** in the spin-coated film is more similar to that in THF solution, suggesting that the environment arising in the film is comparable to that in the dilute benzene solution for **1–4** and to that in the more polar THF solution for **5**. It is noteworthy that the intense emissions were also observed for the powder of these compounds, with quantum yields in the range 0.38–0.99. While the fluorescence spectra of the powder of **3** and **4** are very similar to those of the spin-coated films, the emission spectra of **1** and **5** are greatly blue-shifted when going from the spin-coated film to the powder (see ESI†). This probably arises from the significant difference in the molecular packing pattern between the film and the powder for **1** and **5**.[13] Another noticeable characteristic for the present diphenylamino terphenyls is that the quantum yields of **1–5** in solution are much lower than those in the solid-state. Such fluorescence behavior may be ascribed to the easily exchangeable multiple conformations of the nonplanar structure of the main chain, which facilitate the non-radiative decay of the excited state. In the solid-state, the exchanges between multiple conformations are greatly suppressed due to the spatial congestion of the molecular stacking in the solid-state.[8]

In summary, a series of lateral diphenylamino-substituted terphenyls have been designed and synthesized. Owing to the influence of steric bulkiness and the electron-donating property of the lateral diphenylamino group, these terphenyls exhibit a twisted main chain structure and efficient intramolecular charge transfer transition with a large Stokes shift, facilitating the suppression of fluorescence quenching in the solid-state. They display intense fluorescence with good to excellent quantum yields mainly in the solid-state. We here disclosed not only a new kind of emissive materials, but also a new molecular design concept to attain organic emissive solids with excellent quantum yields. Further studies on the applicability of the present molecular design to other π-conjugated systems, as well as the application of the obtained materials to organic optoelectronics, are under way.

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