Synthesis and Properties of 9,9-Diarylfluorene-Based Triaryldiamines

Ken-Tsung Wong,* Zi-Jien Wang, Yuh-Yih Chien, and Chien-Lung Wang

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

kenwong@ccms.ntu.edu.tw

ABSTRACT

9,9-Diaryl-2,7-dibromofluorene was synthesized by a triflic acid promoted Friedel–Crafts reaction. Introduction of diarylamino groups at its C2 and C7 positions by a Pd-catalyzed amination results in the formation of a novel class of triaryldiamines. The 9,9-diaryl substituents at the central linkage play a less important role in the photophyscial properties but affect the oxidation potential and improve the morphological stability of these new triarylamines.

Amorphous triarylamines with high glassy state stability are suitable as hole-transporting materials in organic light-emitting devices (OLED). Many endeavors have been made to develop new amorphous triarylamines with high morphological stability. For example, dendritic molecules with a triarylamine core have shown to form thin films of good quality with high glass transition temperatures (T_g)[1]. Introduction of a spiro linkage has also generated triarylamines with higher T_g.[2] Another approach involves replacing the phenyl group of triarylamines by a bulkier aryl group. Asymmetric substituted triarylamines normally yield thin films of high thermal stability.[3] The primary structural feature for an amorphous triarylamine to exhibit high morphological stability is a stable non-coplanar conformation, which can inhibit the crystallization efficiently. However, a chromophore without a rigid planar skeleton usually emits fluorescence with a low quantum yield.[4] To have an efficient OLED device, it is important to improve the quantum yield of photoluminescence and also to retain the morphological stability of a triarylamine that is used as a hole transporter as well as a light emitter.

By introducing two bulky groups at the C9 position of polyfluorene, Müllen and Leising not only blocked the interchain interaction but also improved the thermal stability of polyfluorene.[5] Inspired by their results, we report here a new synthetic route for the preparation of 9,9-diarylfluorene-based triaryldiamines. The rigidity of the fluorene core could be beneficial for improving the quantum efficiency. Systematic tuning of the structure of the central linkage by introducing different aryl substituents at the C9 position of fluorene provides new possibilities for probing the properties of resulting triaryldiamines. According to Müllen's addition–cyclization strategy, only symmetric aryl groups can be introduced at C9 of fluorene as substituents. We developed another synthetic strategy for the synthesis of 2,7-dibromo-9,9-diarylfluorene, in which the two aryl groups can be different. The synthetic route to 9,9-diarylfluorene-based triaryldiamines is shown in Scheme 1.

Three different aryl Grignard reagents, i.e., C_6H_5MgBr, p-TolMgBr, and 1-NpMgBr (where Np is naphthyl) were selected for the reaction with 2,7-dibromofluorenone **1**[6] in diethyl ether at reflux temperature. The corresponding alcohol derivatives **2a**,[7] **2b**, and **2c** were isloated in 90%, 82%, and 97% yields, respectively. The Friedel–Crafts reaction[8] of **2a** with benzene was carried out in the presence of an excess

(1) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.

(2) Salbeck, J.; Yu, N.; Bauer, J.; Weissörtel, F.; Bestgen, H. *Synth. Met.* **1997**, *91*, 209.

(3) Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235.

(4) Nizhegorodov, N. I.; Downey, W. S. *J. Phys. Chem.* **1994**, *98*, 5639.

(5) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.

(6) Hauser, A.; Thurner, J.-U.; Hinzmann, B. *J. Prakt. Chem.* **1988**, *330*, 367.

(7) Weber, E.; Dorpinghaus, N.; Csoregh I. *J. Chem. Soc.; Perkin Trans. 2* **1990**. 2167.

(8) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1983**, *24*, 71.

Scheme 1

^{a} Et$_2$O, Ar^{1}MgBr (2 equiv), reflux, 2−6 h. ^{b} CF$_3$SO$_3$H (2 equiv), Ar^{2}H, 50 °C, 10−30 min; see text. ^{c} Pd(OAc)$_2$ (5 mmol %), P^{t}Bu$_3$ (20 mmol %), NaO^{t}Bu (2 equiv), toluene, 100 °C, 4−8 h.

amount of CF$_3$SO$_3$H for 6 h at 80 °C to give 2,7-dibromo-9,9-diphenylfluorene (**3a**) with a yield of 88% (entry 1, Table 1). Under the same condition, the reaction of **2c** with benzene

Table 1. Isolated Yields for the CF$_3$SO$_3$H-Promoted Friedel−Crafts Reaction of the Alcohol Derivatives **2** with Benzene or Toluene

entry	substrate	product	yield (%)
1	**2a**	**3a**	88
2	**2a**	**3b**	84
3	**2b**	**3c**	91
4	**2c**	**3d**	56
5	**2c**	**3e**	86

failed and led to the decomposition of the starting material. Only a low yield of **3b** (less than 10%) was obtained when the same reaction mixture was stirred at room temperature overnight. However, **3b** could be isolated in 56% yield after a reaction time of 30 min at 50 °C (entry 4, Table 1). As a result of its electron richness, toluene reacted very efficiently with **2a**, **2b**, and **2c** in a period of 10 min at 50 °C. This led to the 9,9-diarylfluorene derivatives **3c**, **3d**, and **3e** in good

yields (entries 2, 3, and 5, Table 1).[9] The reactions of the 9,9-diaryl-2,7-dibromofluorene derivatives **3a**−**3e** with different diarylamines were carried out in the presence of a catalytic amount of Pd(OAc)$_2$ and P^{t}Bu$_3$ in toluene at 100 °C with NaO^{t}Bu as the base.[9,10] After column chromatography purification, the isolated yields for the products **4a**−**4g** were good to excellent (Table 2). This synthetic strategy

Table 2. Isolated Yields for the Pd-Catalyzed Reactions of 9,9-Diaryl-2,7-dibromofluorene **3** with Diarylamines

entry	substrate	product^a	yield (%)
1	**3a**	**4a**	85
2	**3b**	**4b**	89
3	**3c**	**4c**	96
4	**3d**	**4d**	87
5	**3e**	**4e**	92
6	**3a**	**4f**	69
7	**3a**	**4g**	96

^{a} α-Np is 1-naphthyl.

allows us to tailor the desired properties of the products by the use of different combinations of aryl substituents at the C9 position and the diarylamino substituents at the C2 and the C7 positions of the central fluorene linkage.

The electronic absorption maxima (λ_{max}), the emission maxima (λ_{em}), and the quantum yields for the 9,9-diarylfluorene-based triaryldiamine derivatives **4** are summarized in Table 3. Triaryldiamines **4** with N-α-naphthyl-N-phenylamine as diarylamino substituents (**4a**−**4e**) have demon-

Table 3. Physical Properties of 9,9-Diarylfluorene Bearing Triaryldiamines **4**

compound	λ_{max} (nm, log ϵ)[a]	λ_{em} (nm)[a]	Φ_F (%)[b]	E^1_{pa}, E^1_{pc} [mV, (onset)]	E^2_{pa}, E^2_{pc} (mV)	ΔE (mV)[c]	T_g (°C)[d]
4a	352, 4.55 379, 4.55	457	15	740, 640 (625)	1080, 1000	340	129
4b	378, 4.55 356, 4.53	461	15	720, 620 (600)	1060, 980	340	125
4c	353, 4.46 379, 4.46	455	16	780, 700 (670)	1140, 1060	360	127
4d	274, 4.40 381, 4.54	450	18	740, 660 (600)	1100, 1000	350	109
4e	350, 4.53 379, 4.56	457	15	720, 640 (600)	1080, 980	360	134
4f	308, 4.17 380, 4.38	401, 420	58	700, 620 (600)	1040, 940	340	97
4g	337, 4.55 387, 4.62	410, 427	69	780, 700 (675)	1100, 1000	330	125
α-NPD	335	449	16	840, 740 (730)	1100, 1020	280	100[e]

[a] In EtOAc, photoluminesence maximum was recorded upon irradiation at the absorption maximum. [b] Quantum yield of PL, compared to coumarin I in EtOAc. [c] $\Delta E = E^2_{pa} - E^1_{pa}$. [d] Determined by differential scanning calorimetry (DSC) analysis of the liquid nitrogen quenched samples. [e] From ref 3.

strated a similar photophysical behavior, irrespective of the different aryl substituents at the C9 position of the fluorene linkage. The second absorption bands of **4a**−**4g** are significantly red-shifted with respect to that of α-NPD (*N,N′*-di-α-naphthyl-*N,N′*-diphenyl-4,4′-diphenyl). This indicates that the rigid and planar fluorenyl core plays an important role in reducing the HOMO−LUMO energy gap.

However, the triaryldiamine derivatives **4a**−**4e** with *N*-α-naphthyl-*N*-phenylamine substituents, as well as α-NPD, exhibited similar emission maxima and quantum yields. The introduction of different diarylamino substituents into the 9,9-diaryl-substituted fluorenyl core (e.g., **4f**, **4g**) results in a substantial blue shift of the first absorption band and the λ_{em} with respect to that of **4a** and α-NPD. A comparison of the UV−vis spectra and the photoluminescent spectra of **4a**, **4f**, and α-NPD is shown in Figure 1. The photopysical properties of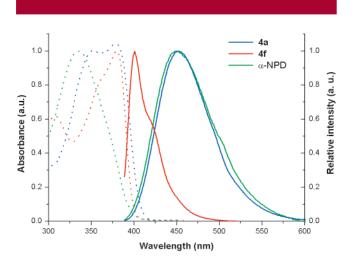 triaryldiamines **4** are dominated by the stuctural feature of diamino substituents at C2 and C7 of the central fluorene linkage.

Cyclic voltammetry was performed in CH_2Cl_2 (with 0.1 M tetra-*n*-butylammonium hexafluorophosphate,$TBAPF_6$, as supporting electolyte). Similarly to the conventional triaryldiamines, the 9,9-diarylfluorene-based triaryldiamines **4** have two quasireversible anodic redox couples, corresponding to the removal of an electron from each triarylamine group. The results are summarized in Table 3, and a comparison of cyclic voltammogrammes of **4c**, **4e**, **4f**, and α-NPD is shown in Figure 2. As a result of the rigidity and planarity of the
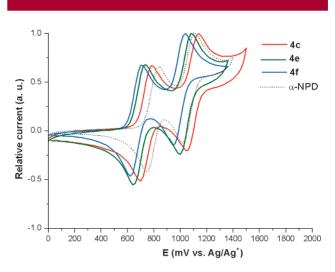

Figure 1. A comparison of normalized absorption and photoluminescence specta of **4a**, **4f**, and α-NPD.

Figure 2. A comparison of normalized cyclic voltammograms of **4c**, **4e**, **4f**, and α-NPD (0.1 M $TBAPF_6$ in CH_2Cl_2)

central fluorene linkage, the onset of the first oxidation step of triarydiamines **4** is evidently lower compared to that of

α-NPD. These observations could be attributed to the better π-conjugation along the molecular axis in **4** compared to that in α-NPD. Significant potential differences between the first oxidation step and the second oxidation step also reveal that the radical cation could efficiently delocalize in the molecule once it is formed. For the case that the central linkage carries electron-rich aryl substituents (e.g., **4c**), the first oxidation step is obviously more difficult. By introducing the electron-rich diarylamino substituents (e.g., **4f**) both oxidation potentials were reduced. However, for **4e** with the same diarylamino substituents as α-NPD, the second oxidation potential exhibited no significant changes.

The morphological stability of **4** was investigated by differential scanning calorimetry (DSC) analysis. The triaryldiamines derivatives **4** exhibited good glass forming properties with relative high glass transition temperatures (Table 3). The triaryldiamines **4** with the same diarylamino substituents as α-NPD exhibited a higher T_g compared to that of α-NPD. The increase of the morphological stability could be explained by an increase of the molecular weight of the triaryldiamines **4**, due to the introduction of the aryl substituents at the central linkage. However, the two aryl substituents at the C9 position of fluorene may hinder the further crystallization process, which could also be ascribed to the increase in T_g of triaryldiamines **4**.

(9) Please see Supporting Information for the experimental procedures.
(10) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367.

In summary, we have successfully established a new method for the synthesis of sterically hindered 9,9-diarylfluorene-based triaryldiamines. This new class of compounds has revealed that the planarity of the fluorenyl core has a significant effect on reducing the HOMO−LUMO energy gap, which is observed from the red shifts in the absorption spectra and the lower anodic oxidation onset. The diarylamino substituents at C2 and C7 of 9,9-diarylfluorene, introduced by Pd-catalyzed amination, play a predominant role in the photophysical properties. The introduction of diaryl substituents at the C9 position of fluorene significantly enhances the morphological stability of these fluorene-based triaryldiamines. Further modifications of the central fluorene linkage by introducing various aryl substituents with a higher molecular weight and the application of these triaryldiamines in OLED are currently under investigation.

Supporting Information Available: Experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL016051Y