Facile Synthesis of Novel Nonplanar Arylamine-centered Oligofluorenes Based on Complicated 9,9-Diarylfluorene Building Blocks by Friedel–Crafts Reaction

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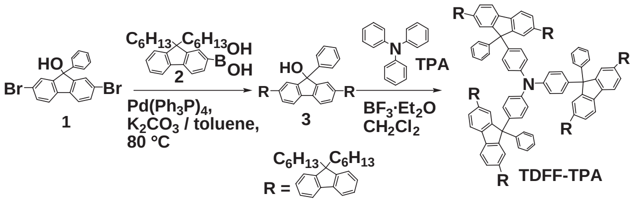
The syntheses of two well-defined organic nanomaterials, TDFF-TPA and TDFF-FBCz, with highly nonplanar structures, based on complicated 9,9-diarylfluorenes (DAF) by $BF_3 \cdot OEt_2$-mediated Friedel–Crafts reactions are presented.

Fluorene-based oligomers with a well-defined structure have attracted considerable attention because they may function as model compounds for poly[2,7-(9,9-dialkyl)fluorenes] (PFs), which are thought to be promising candidates for blue light emitting diodes (LEDs),[1,2] and potential active materials for applications in liquid crystals,[3,4] LEDs,[5,6] field-effect transistors,[7] and amplified spontaneous emitters.[8,9] Among the derivatives of fluorene, starburst and dendritic molecules have shown particularly impressive performance. However, most of them were synthesized via iterative reactions involving tedious purification steps and low yieldings,[10] which impaires the materials' scale-up and commercial applications.

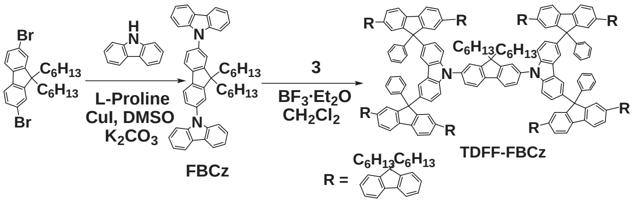
Previous investigations have demonstrated that the injection of electrons dominates in fluorene-based polymers and oligomers.[11] To increase the efficiency of the devices, the hole injection needs to be significantly boosted. The introduction of hole-transporting chromophores such as carbazole and triphenylamine (TPA) groups[12–14] into the fluorene-based derivatives may promote the injection and transport of holes. On the other hand, the film quality and the morphology of the surface also need to be optimized.[15] The deposition of high-quality films by solution-based spin-coating is most desirable for device fabrication.[1]

To increase hole injection and improve the quality of the films while still retaining the excellent optical and thermal properties of oligo-fluorenes, we have successfully synthesized novel fluorene-based compounds, TDFF-TPA and TDFF-FBCz, with TPA and/or carbazole derivative as core and peripheral dendrons of 9,9-diarylfluorene (DAF) through the $BF_3 \cdot OEt_2$-mediated Friedel–Crafts reaction.[16] Because the triphenylamine or carbazole core connected to the sp^3-hybridized carbon atom at the C-9 position of the fluorene moiety, which serves as a spacer to block extended π-conjugation,[17] the conjugation length and triplet energy of each individual building block in the resulting composite should remain essentially unperturbed. In addition, the 3D cardo structure of substituted fluorene derivative should improve the system's rigidity and hinder any unwanted aromatic π-stacking interactions, resulting in an amorphous material possessing enhanced morphological stability.[18] Such unique nonplanar conformation of these two compounds results in their amorphous state in nature and makes it difficult to pack them into detrimental aggregation in the film state.[19]

Both divergent and convergent routes were considered to synthesize TDFF-TPA and TDFF-FBCz, as shown in Schemes 1 and 2. Initially, we tried the divergent route to synthesize the target compound TDFF-TPA, as shown in Scheme 1. Tris[4-(2,7-dibromo-9-phenyl-9*H*-fluoren-9-yl)phenyl]amine (Br_6F-TPA) was synthesized with 87% yield through the $BF_3 \cdot OEt_2$-mediated Friedel–Crafts reaction of TPA with tertiary alcohol **1**.[16] However, Br_6F-TPA is difficult to be dissolved in general solvents due to its rigid aromatic rings without any flexible alkyl chains. Therefore, it is difficult to carry out the Suzuki reaction so as to have all bromo groups substituted by 2-(9,9-dihexyl)fluorene, even if much excess of boric acid **2** was added and the reaction was kept for quite a long time. The final product TDFF-TPA is difficult to be separated from various by-products.



Scheme 1.



Scheme 2.

The convergent route are preferred considering three important factors, such as the separation of by-procucts, the Friedel–Crafts reactivity in the dehydration cross-coupling reaction, and the convenience of scale-up. As shown in Scheme 1, TDFF-TPA with high yield (>90%) was synthesized by the reaction between TPA (1 equiv) and the intermediate **3** (3.3 equiv), which was obtained based on **1** and **2** by the Suzuki condensation reaction with the yield of 89%. In this process, the trace by-products were easily removed with silica gel column.

To tune the distance between the terfluorene dendrons, TDFF-FBCz was also designed. The carbazole is an important optoelectrical building block for organic semiconductors due to its remarkable hole-transporting ability, thermal stability, great solubility, and extended glassy state. As shown in Scheme 2, FBCz was synthesized as a core via the Ullmann reaction, catalyzed with CuI and K_2CO_3 in DMSO.[24] Compared to the diphenylamino analogue, the rigid structure of the carbazoyl

Table 1. Physical properties of TDFF-TPA and TDFF-FBCz

Compounds	UV $\lambda_{\max}$[a] /nm	PL $\lambda_{\max}$[a] /nm	Φ_f/%[b]	T_g/°C	T_d/°C[c]	Oxidation[d] E_{ox}/V	Reduction[d] E_{red}/V
TDFF-TPA	349	399/420	65	120	422	0.742	−2.26
TDFF-FBCz	349	400/425	79	143	428	0.785	−2.23

[a]Measured in THF solvent (10^{-6} M). [b]9,10-Diphenylanthracene in the cyclohexane solvent as standard. [c]The temperature was recorded corresponding to a 5% weight loss in air. [d]Onset oxidation and reduction potentials versus an Ag/Ag$^+$ reference.

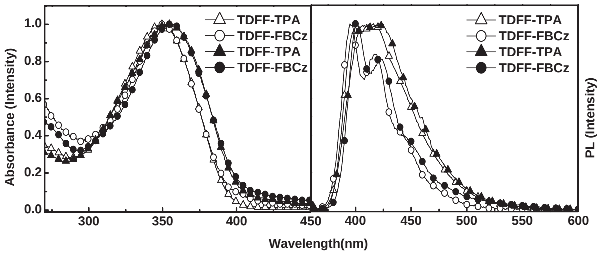


Figure 1. Absorption and fluorescence spectra of TDFF-TPA and TDFF-FBCz in THF solution (hole) and solid state (solid).

moiety is more liable to afford a glassy state.[20] In addition, under the same Ullmann reaction conditions, 9*H*-carbazole seemed to react more efficiently with 2,7-dibromo-9,9-dihexylfluorene than diphenylamine.[21,22] TDFF-FBCz was successfully synthesized with 83% yield using the same convergent procedure as TDFF-TPA. According to their GPC profiles, both of their polydistribution index were lower than 1.02. This one-step Friedel–Crafts type reaction is not only simple but, because of the use of inexpensive reactants at room temperature and using this synthetic strategy, TDFF-TPA and TDFF-FBCz can be produced readily on a 5 g scale.

The optical properties of TDFF-TPA and TDFF-FBCz were investigated by UV–vis absorption and photoluminescence (PL) spectroscopies in the THF solution as well as in the spin-casted film (shown in Figure 1). TDFF-TPA and TDFF-FBCz showed the nearly identical absorption profiles in THF and solid film (left of Figure 1), which suggests that the absorption band in the range of 300–400 nm is contributable to the dendrons of terfluorene units in TDFF-TPA and TDFF-FBCz.[23] And, there is slightly red-shifted for their absorption peaks in solid state.

As shown in Figure 1 (right), TDFF-FBCz shows the typical emission of terfluorene, which is somewhat different from that of TDFF-TPA. Considering their difference in structure, the spatial distance of the dendrons in TDFF-FBCz is larger than that in TDFF-TPA, so the interaction of dendrons in TDFF-FBCz is not as significant as that in TDFF-TPA. In addition, the PL spectra of TDFF-FBCz have small fwhm value (≈43 nm) compared to TDFF-TPA. The PL emission wavelength of TDFF-TPA and TDFF-FBCz in THF and solid film does not change significantly, which suggests that the unique conformation of TDFF-TPA and TDFF-FBCz significantly reduces aggregation in solid state as well as in solution. Furthermore, analysis of TDFF-TPA and TDFF-FBCz by PL quantum efficiencies reveals that both of them are highly fluorescent materials with very efficient blue emission in solution (the quantum yielding data are summarized in Table 1) (see Supporting Information),[24] which might be attributed to their unique 3D structure.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are carried out to investigate the thermal properties of TDFF-TPA and TDFF-FBCz, as shown in Table 1. Their decomposition temperatures (T_d) are up to 420 °C corresponding to a 5% weight loss in air with no weight loss at lower temperature. Thus, both TDFF-TPA and TDFF-FBCz show satisfying thermostabilities, which is the typical property of oligofluorenes or polyfluorenes with the 9 position of fluorene moiety substituted by aryl functional groups.[19] The glass-transition temperatures (T_g) of TDFF-FBCz is higher than that of TDFF-TPA. In addition, both the cathode and anode scans of TDFF-TPA and TDFF-FBCz are reversible according to the electrochemical investigation,[24] which indicate their stabilities towards the redox process and potential application for LEDs.[18]

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