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The Construction of H-shaped Fluorescent Materials Based on Building Blocks Consisting of Triphenylamine and Fluorene

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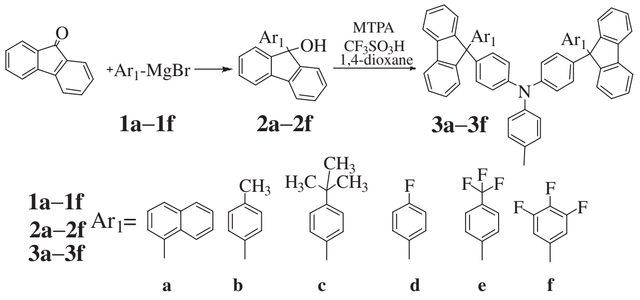
A class of complicated 9,9-diarylfluorenes as nonplanar building blocks were synthesized and utilized to prepare a novel H-shaped oligofluorene. High glass transition temperatures and excellent solubility of the obtained oligomers indicated the 9,9-diarylfluorenes would be promising building blocks for the construction of H-shaped optoelectronic materials.

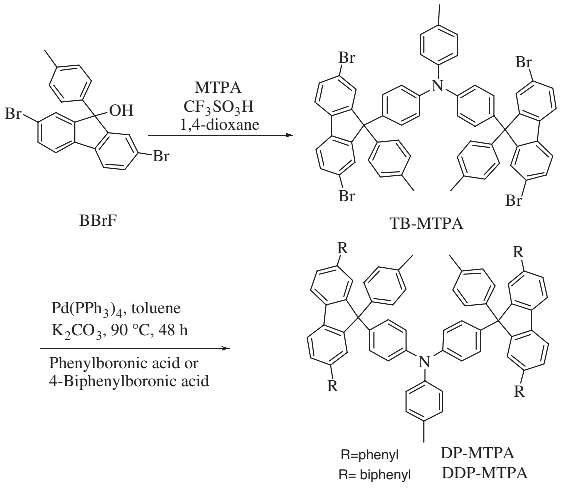
Fluorene-based materials, such as terfluorenes, oligofluorene, and polyfluorenes (PFs), have emerged as promising classes of organic semiconductors in the field of organic electronics, especially in OLEDs, because of their excellent thermal and chemical stability as well as high photoluminescence (PL) quantum efficiencies.[1] However, an obvious deficiency of fluorene derivatives concerns their tendency to form long-wavelength aggregates/excimers or keto defects in the solid state upon thermal annealing or device operation. Another intractable issue is the low HOMO energy level, which leads to inefficient hole injection.[2] Highly electron-rich triphenylamines known for their high hole mobility have been extensively used to increase the HOMO energy levels and reduce the energy barrier for hole injection from the indium tin oxide (ITO) to the emissive layer. Additionally, various strategies have also been developed to reduce the formation of aggregation, which include the introduction of sterically hindered side chains and spiro-links.[3]

9,9-Diarylfluorenes (DAF) have been proven to be an efficient building blocks to suppress the formation of aggregates or excimers of PFs main chains because of the three-dimensional cardo structure of substituted fluorene derivatives.[2b,4] Various 9,9-bis(triarylamines)-substituted fluorenes which help to improve hole-injection ability are reported recently.[5] Inspired by their results, in this study, a series of novel DAF building blocks consisting of triphenylamine core and fluorene/fluorinated arene peripheries is designed and prepared. Then, several novel H-shaped oligomers based on the above building blocks are synthesized. The desired oligomers consist of two parts: ter(biphenyls or phenyls) as the arms of the H-shape and 4-methyltriphenylamine (MTPA) as the rung. The fluorene and MTPA moieties are connected through the sp^3-hybridized C9 carbon atom, which may not only hinder close packing and crystallization but also lead to pronounced morphological stability of amorphous materials. Meanwhile, the hole injection ability of the resulting oligomers are effectively enhanced by the introduction of the MTPA group. More importantly, the introduction of MTPA groups to the 9-position of fluorine is confirmed to be easily achieved by the Friedel–Crafts reaction.

The different aryl Grignard reagents, **1a**–**1d** were synthesized for the reaction with fluorenone in tetrahydrofuran at room temperature (Scheme 1). The corresponding alcohols **2a**–**2d** were isolated in more than 80% yields. Under the same condition, only a low yield **2e** and **2f** (less than 35%) were obtained due to the coupling reaction of Grignard reagents. The Friedel–Crafts reaction of **2a**–**2f** with MTPA was carried out in the presence of an excess amount of CF_3SO_3H for 6 h at 80 °C, to obtain **3a**–**3f** with the yields of more than 83%. The results indicated that CF_3SO_3H as a Lewis acid is probably an effective catalyst for the Friedel–Crafts reaction of tertiary alcohol **2a**–**2f** with MTPA. Additionally, a novel approach for the synthesis of bipolar oligofluorenes containing triphenylamine and fluorinated arene using the Friedel–Crafts reaction and Grignard reagents is presented.



Scheme 1. Synthetic route of DAF building blocks.



Scheme 2. Synthesis of DP-MTPA and DDP-MTPA.

The efficiency of CF_3SO_3H could be further confirmed by the following reaction of tertiary alcohol BBrF with MTPA (Scheme 2), which indeed exhibited excellent reactivity with yield of 90%. In addition, this reaction revealed that the dibromo substituents had little influence on the reactivity of tertiary alcohol. Then, two stable blue-light emitters (DP-MTPA and DDP-MTPA) with nonplanar conformation were constructed with 4.4 equiv of corresponding boronic acid and the tetrabrominated TB-MTPA by the Suzuki coupling reaction. The yields were 72% and 65%, respectively.

The resulting oligofluorenes presented good solubility in common organic solvents and had much higher solubility than the

Table 1. Physical Properties of DP-MTPA and DPP-MTPA

Compounds	Abs λ_{max}/nm (sol/film)	PL λ_{max}/nm (sol/film)	T_g/°C	T_d/°C	E_{ox}/V	E_g/eV	HOMO[b]/eV	ε[c]/10^5	Φ_F[d]
DP-MTPA	316/322	421/431	178	450	0.77	3.23	−5.15	1.13	0.18
DDP-MTPA	337/342	445/450	201	—[a]	0.76	3.06	−5.14	1.08	0.24

[a]Up to 500 °C without obvious decomposition. [b]Estimated from the onset oxidation potentials by using $E_{HOMO} = -E_{ox} - 4.38$ eV.[7] [c]Molar extinction coefficient (ε, $M^{-1}\,cm^{-1}$). [d]Using quinine sulfate ($\Phi_F = 0.55$) in 0.05 M H_2SO_4 as a standard.

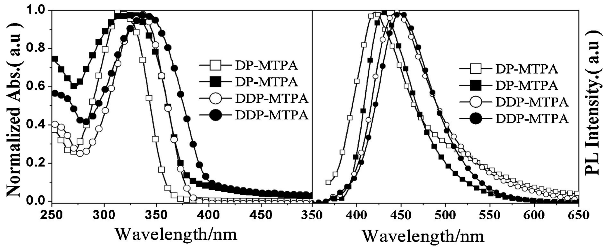


Figure 1. Absorption and fluorescence spectra of DP-MTPA and DDP-MTPA in $CHCl_3$ solution (hole) and solid state (solid).

dispiro analog.[6] The UV–vis absorption and emission spectra of DP-MTPA and DDP-MTPA were measured in dilute chloroform solutions, as shown in Figure 1. A strong π–π^* absorption band was observed in the solution spectrum with an absorption maximum at 316 nm for DP-MTPA and 337 nm for DDP-MTPA, showing a red-shift of the absorption band with the increase in the conjugation length of the oligofluorene arms. The PL emission wavelength of two H-shaped oligofluorenes from solution to solid film did not change remarkably, which suggested that the unique conformation significantly reduced aggregation. In addition, no obvious change in the emission film of DDP-MTPA was observed even after annealing at 120 °C for 12 h in air, which indicated that the luminescent stability of oligofluorenes was successfully improved.[9]

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to investigate the thermal properties of DP-MTPA and DDP-MTPA, as shown in Table 1. Compared with dispiro compounds[8] 2,2′,7,7′-tetraphenyl-9,9′-spirobifluorene and 2,2′,7,7′-tetra(biphenyl-4-yl)-9,9′-spirobifluorene, the two H-shaped oligofluorenes exhibited high decomposition temperature, more than 450 °C with 5% weight loss and a high T_g over 178 °C.[9] However, the fluorescence quantum yields (Φ_F) of the two dispiro compounds, with the better rigidity, are higher values than that of DP-MTPA (0.18) and DDP-MTPA (0.24).

Cyclic voltammetry (CV) was performed to probe eletrochemical proerties of obtained oligomers (Figure 2). The anode scans had similar values of onset oxidation potential (E_{OX}) for both oligofluorenes (0.77 V for DP-MTPA and 0.76 V for DDP-MTPA). The estimated E_{HOMO} were −5.15 eV for DP-MTPA and −5.14 eV for DDP-MTPA, respectively (Table 1). The results demonstrated that the energy barrier for hole-injection from the ITO anode (W_{ITO}) −4.8 eV) to the oligofluorenes were significantly lower than that of fluorene homopolymer (5.8 eV), which could be attributed to the existence of the MTPA-based rung in H-shaped oligofluorenes. Figure 2 also shown that p-doping processes of DP-MTPA and DDP-MTPA were reversible, indicating a high stability for hole injection. Under successive multiple potential scans, DDP-MTPA demonstrated extraordinarily high electrochemical stability, with the CV curves remaining unchanged in 10 scans.

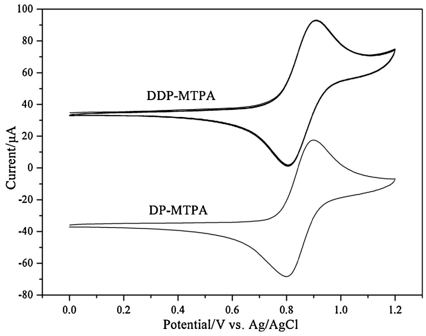


Figure 2. Cyclic voltammograms of DP-MTPA and DPP-MTPA (10 successive scans) in CH_2Cl_2 with 0.10 M of TBAP as a supporting electrolyte, scan rate 50 mV s^{-1}.

In conclusion, based on synthesis of the novel building block, H-shaped oligofluorenes with high thermal stability, solubility, and blue emission were prepared. The presence of the MTPA-based rung raised the HOMO energy levels of DP-MTPA and DDP-MTPA. Moreover, the conjugation length of the oligofluorene arms had less influence on the ability of hole-injection. The results shown that DAFs **3a**–**3f** are potential building blocks for constructing organic luminescent materials without the need for a hole-transporting layer.

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