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Facile Synthesis of Complicated

BF₃·Et₂O-Mediated Friedel–Crafts

9,9-Diarylfluorenes Based on

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ABSTRACT



BF₃·OEt₂-mediated Friedel–Crafts reaction of 9-phenyl-fluoren-9-ol with electron-rich aromatic substrates to prepare a new family of complicated 9,9-diarylfluorenes is described. The 9,9-diarylfluorenes tethered with various functional substituents, e.g., bulky spiro units, hole-transporting moieties, and fluorescent dyes, will be promising building blocks for the construction of optoelectronic materials.

Recently, oligofluorenes and polyfluorenes have been recognized as very promising classes of organic semiconductors in the field of organic electronics, especially in OLEDs and PLEDs.¹ 9,9-Diarylfluorenes are of great importance because aryl moieties at the C9 position of fluorene can afford various functionalities, e.g., improvement of solubility,² increase of charge carrier mobility,³ tunable electronic structures,⁴ and aggregate suppression to improve morphological stability.⁵

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Two synthetic routes have been utilized to introduce aryl substituents into the C9 position of fluorene starting from fluorenone in the literature, as shown in Scheme 1 (route I



and route II). Route I provides an effective method to introduce the two same substituents into the C9 position of fluorene. Müllen has employed synthetic route I to introduce two bulky triphenylamine groups into the C9 position of

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fluorene.⁶ Chou has also exploited synthetic route I to achieve coupling of "Fréchet-type" dendrons and POSS to fluorene.⁷ Route II mainly involves an addition reaction of the Grignard reagent to fluorenone and a Friedel–Crafts reaction of tertiary alcohol. Wong has achieved a series of efficient large-gap blue-light emitters and hole-transporting materials with highly morphological stability via route II.⁸ However, Friedel–Crafts reaction has not been fully exploited for the preparation of 9,9-diarylfluorenes. For example, an alternative pathway could be utilized for the carbazole derivative in the literature,⁹ as shown in Scheme 2.



In this contribution, we focus on the BF₃•OEt₂-mediated Friedel–Crafts reaction for the preparation of various optoelectronic building blocks based on 9,9-diarylfluorenes via route II. Using our strategy, we have designed and synthesized a series of wonderful functional building blocks by incorporating bulky spiro structures, hole-transporting carbazole, and fluorescent dye pyrene into the C9 position of fluorene. In addition, multibrominated diarylfluorenes with nonplanar conformations will be useful monomers for the hyperbranched architectures and potential interrupting monomers for semiconjugated polymers.

Our expectation that the $BF_3 \cdot OEt_2$ complex¹⁰ as a Lewis acid may be an effective catalyst for the Friedel–Crafts reaction of 9-phenyl-fluoren-9-ol (tertiary alcohol **1**) with aromatic substrates was experimentally confirmed. A 1:2 mixture of thiophene and tertiary alcohol **1** in CH_2Cl_2 did

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 Table 1. Reaction of Tertiary Alcohol with Different

 Substrates^a



entry	alcohol	arene	product ^b	yield
1		SJ	GES GO	97%
2	OH Br 2	SJ	Br S S P2 Br	96%
3	Он	s <u>∽</u> √s		69%
4	Br OH Br 3		P4 Br Br	70%
5		S	AS P5	85%
6	Он	SSS	S S S P6	73%
7	Он	H N N	PT PT	74%
8	Он		P8	70%
9	Он		A C P3	30%
10	Он	$\bigcirc +$	$\overset{\times}{\underset{P10}{\overset{P10}}{\overset{P10}}{\overset{P10}}{\overset{P10}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	0% (70%)

^{*a*} Reaction conditions: 0.6, 1.2, or 4.8 mmol of tertiary alcohol, 0.5 mmol of aryl derivatives, and 0.6, 1.2, or 4.8 mmol of the BF₃•Et₂O complex in 100 mL of CH₂Cl₂ at room temperature for 30 min to 10 h. ^{*b*} The main products for entries 1, 2, 6, 7, and 8 are 2:1 adducts, and the main products for entries 4, 5, 9, and 10 are 1:1 adducts.

react smoothly at room temperature, as shown in Table 1 (entry 1). To our delight, the efficiency of BF_3 ·OEt₂ could

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be further confirmed by the following reaction of thiophene derivatives with tertiary alcohol 1. The reaction of 3,3bithiophene with 4 equiv of 1 gave the congested tetrasubstituted products P3 with a high yield of 69% (entry 3). The electrophilic substitution reaction illustrated that steric hindrance showed little impact on the reactivity of tertiary alcohol 1, which was useful information for the complicated optoelectronic system, e.g., dendrimers. The fact was also demonstrated by entry 4, a reaction of a highly sterically hindered substrate with tertiary alcohol 3 in a good yield of 70%. In addition, this reaction reveals that the dibromo substituents hardly have an impact on the reactivity of tertiary alcohol 3. We also prepared the spiro-containing 9,9diarylfluorenes P5 and P6 in good yields (entries 5 and 6), which are potential building blocks for the construction of stable amorphous molecular glasses.

We then examined Friedel–Crafts reaction of tertiary alcohol **1** with other electron-rich substrates, e.g., carbazole and phenyl ether, which indeed exhibits the excellent reactivity with yields of 74% and 70% (entries 7 and 8), respectively. We have also attempted the reaction with weakly electron-rich substrates, such as pyrene and *tert*-butylbenzene (entries 9 and 10). As a result, a low yield of 30% was observed for the monosubstituted product **P9**, and no **P10** was obtained. The main byproduct, 9-phenylfluorene, in entry 10 was obtained in a yield of 70%, in which the mechanism is still unknown. Therefore, the BF₃•OEt₂-mediated Friedel–Crafts reactions are more favorable for strongly electron-rich substrates.

Finally, a stable blue-light emitter 2,5-bis(2,7,-bis([1,1'biphenyl]-4-yl)-9- phenyl-fluoren-9-yl) thiophene (TBPFTF) with nonplanar conformation was constructed by a Suzuki coupling reaction of 4 equiv of biphenyl boronic acid with the tetrabrominated **P11**, which was obtained from the reaction of thiophene with tertiary alcohol **3** (Scheme 3).



The structures of all the above products were confirmed by ¹H and ¹³C NMR, MALDI-TOF-MS, and elemental analysis. The monosubstituted pyrene (**P9**) was characterized by X-ray crystallographic analysis (Figure 1).¹¹ The sterically congested **P3** shows special splitting signals in the ¹H NMR spectrum, as shown in Figure 2. It was found that, unexpectedly, two double peaks with an integrated ratio of 2:2 instead of a double peak with four protons are assigned to one of



Figure 1. ORTEP drawing (30% probability) showing the X-ray structure of **P9** and the crystal packing.

the two pairs of protons in the fluorene ring. The splitting phenomenon is probably attributed to nonequivalent magnetic environments due to steric hindrance among the 9-phenylfluorene groups.

TBPFTF has poor solubility in common organic solvents except for CHCl₃ and THF but has much higher solubility than the dispiro analogue.¹² The optical spectra of TBPFTF in chloroform are shown in Figure 3. TBPFTF exhibits a strong $\pi - \pi^*$ absorption with λ_{max} at 341 nm and two wellresolved emission peaks at 386 and 405 nm with an optical band gap (3.19 eV). The thermal properties of TBPFTF were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TBPFTF showed a high



Figure 2. ¹H NMR spectra of P1 and P3 in CDCl₃.



Figure 3. UV and PL spectra of TBPFTF in CHCl₃ solution.

decomposition temperature up to 470 °C (5% loss weight temperature) and a high T_g up to 247 °C. Cyclic voltammetry was performed on the film of TBPFTF deposited on a glassy carbon electrode measured in Bu₄⁺PF₆⁻ (0.1 M)/acetonitrile with a platinum counter electrode and a Ag⁺/Ag reference electrode (Figure 4). On the basis of the onset potentials of the oxidation and reduction, the HOMO and LUMO energy levels of TBPFTF were estimated to be -5.82 and -2.28 eV, respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level). Therefore, the electrochemical band gap (3.54 eV) does not closely match the optical band gap (3.19 eV). In addition, the HOMO energy level of the TBPFTF is lower than that reported for POF (-5.8 eV). The results indicate that the conjugation length of TBPFTF is shorter than that of POF.

In conclusion, we have utilized the BF₃•OEt₂ complex as a Lewis acid catalyst to examine the reactivity of 9-phen-



Figure 4. CV curve of TBPFTF.

yl-fluoren-9-ol and its derivatives with several aromatic substrates. The results show that the BF₃•OEt₂ complex is an effective catalyst for the Friedel–Crafts reaction of strong electron-rich substrates. We also prepared a series of complicated 9,9-diarylfluorenes with nonplanar conformations bearing various functional substituents, and they are promising candidates for construction of organic semiconductors. Further attempts to synthesize special dendrimers on the basis of Friedel–Crafts reaction could be achieved via a rational design, which is currently being pursued.

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Supporting Information Available: The experimental procedures for the new compounds and ¹H and ¹³C NMR, MS spectra, TGA, DSC thermograms, and an X-ray crystallographic file (CIF) for **P9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽¹¹⁾ Crystal data for **P9**: Crystals were grown from CDCl₃. The structure was solved on a Bruker SMART CCD diffractometer using Mo Ka radiation. C₃₅H₂₂, (M_r = 442.5): monoclinic, space group $P2_1/c$, D_c = 1.296 g cm⁻³, a = 14.922(4), b = 8.735(2), c = 17.450(5) Å, α = 90°, β = 94.143(4)°, γ = 90°, V = 2268.5(11) Å³, Z = 4, λ = 0.71073 Å, μ = 0.073 mm⁻¹, T = 297(2) K, R = 0.0402 for 12 903 observed reflections [I > 2 σI] and R_w = 0.1017 for all 4460 unique reflections.

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