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Friedel-Crafts arylmethylation: A simple approach to synthesize bipolar host materials for efficient electroluminescence

Chang-Jin Ou [a, b], Jin-Yi Lin [a, b], Jie Mao [b], Shuang-Quan Chu [b], Yu Zhao [b], Ling-Hai Xie [b, **], Hong-Tao Cao [b], Xin-Wen Zhang [b, ***], Ying Wei [b], Wei Huang [a, b, *]

[a] Key Laboratory of Flexible Electronics (KLOFE), Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 211816, China
[b] Institute of Optoelectronic Materials (IOM), Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, Nanjing 210046, China

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ABSTRACTS

In order to simplify the synthesis of bipolar host materials of OLEDs, a facile synthetic approach was developed and a series of sulfone-contained bipolar host materials were synthesized via mild one-step Friedel-Crafts arylmethylation. Due to π-conjugate-interrupted connection between donor moiety and sulfone moiety, those materials keep high triplet energy and separate the HOMO and LUMO levels. Furthermore, the introduction of sulfone group can significantly lower LUMO level. Based on newly synthesized sulfone-based bipolar host materials, efficient solution-processed sky-blue phosphorescent OLEDs were fabricated with high current efficiency of 16.5 cd/A. Our results demonstrate Friedel-Crafts arylmethylation is powerful synthetic strategy to construct bipolar host materials.

1. Introduction

The study enthusiasm on phosphorescence and thermally-activated delayed fluorescence (TADF)-based OLEDs is soaring since both can simultaneously harvest singlet and triplet excitons, which enables a 100% internal quantum efficiency [1–3]. While, due to long lifetime of triplet excitons, triplet-triplet annihilation and triplet-polaron annihilation become serious problems at high exciton density in both PhOLEDs and TADF OLEDs [4]. In order to solve the problems, the emitters should be dispersed into a host material with higher triplet energy level at low doped concentration to confine triplet excitons on emitters. Numerous studies demonstrate that bipolar host materials, incorporating electron-donating (D) and electron-accepting (A) components into molecule structures, can facilitate and balance the injection and transport of carriers, which determines the quantum efficiency of devices [5–10].

Phosphine oxide (PO) group is widely used to construct bipolar host materials, which have exhibited excellent device performance, while PO-based materials are synthesized via multiple steps [11–15]. Novel synthetic approaches should be developed to simplify synthesis and meet the need of commercialization of OLEDs. Lee and Kim groups respectively reported 4,5-diazofluorenone and thioxanthe-9-one-S,S-dioxide condensed with carbazole derivatives under acid catalysis and afforded bipolar host materials [16,17]. Huang group reported highly efficient blue PhOLEDs with maximum current efficiency of 42.1 cd/A based on carbazole-pyridine hybridized bipolar host materials, which were synthesized via one-step C–N coupling approach [18]. Generally, D components of bipolar host material, such as carbazole, triphenylamine, dibenzothiophene, are typically synthetic precursors for Friedel-Crafts (FC) reaction [19–21]. In addition, the D and A synthons are available individually, and can be freely combined via rational molecular design to construct a desired bipolar host material. So one-step FC arylmethylation may be an intriguing reaction to construct efficient bipolar host materials. Quan et al. reported 4,5-diazofluorene-9-ol (A synthon) facile attached to

* Corresponding author. Key Laboratory of Flexible Electronics (KLOFE), Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 211816, China.
** Corresponding author.
*** Corresponding author.
E-mail address: iamwhuang@njupt.edu.cn (W. Huang).

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triphenylamine (D synthon) via sulfuric acid-catalyzed FC arylmethylation, and they found the number of A component in host material affects device current efficiency dramatically [22]. Our group has utilized FC arylmethylation to construct several kinds of bipolar materials [23–25]. Huang et al. developed bulky 9-pyridinylfluorenyl moiety functionalized bipolar host materials via FC arylmethylation [24]. However, due to lack of A synthons of FC arylmethylation and harsh reaction condition, researchers have paid less attention to this synthetic strategy.

Nowadays, sulfone has become attractive building block in bipolar host materials and TADF emitters due to outstanding electron-accepting and transporting ability [17,26–34]. Kim [14], Poriel [28] and Su [29] groups respectively reported sp3-C connected thioxanthene 10,10-dioxide with carbazole or triphenylamine bipolar host materials, showing separated HOMO and LOMO energy levels, and high current efficiency of over 20 cd/A in Firpic-based sky-blue PhOLEDs. However, there is still a lacks of a general and convenient approach to construct sulfone-based bipolar host materials. Herein, two sulfone-contained A synthons, 9-hydroxy-9-phenylthioxanthene 10,10-dioxide and 9-hydroxy-9-(4-(octyloxy) phenyl)thioxanthene 10,10-dioxide, were synthesized via directed *ortho*-metalation of diphenyl sulfone. Those A synthons can effectively link to D synthons, and construct bipolar host materials under mild $BF_3 \cdot Et_2O$-mediated FC arylmethylation. Finally, efficient solution-processed sky-blue PhOLEDs were fabricated with high current efficiency of 16.5 cd/A based on synthesized bipolar host materials.

2. Experimental section

2.1. Materials and instruments

All of chemicals were purchased from J&K Scientific Co. Ltd., and were used without further purification unless otherwise state. Anhydrous THF was distilled from Na/benzophenone.

1H NMR and 13C NMR spectra were measured on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. Absorption and photoluminescence spectra were measured in dichloromethane solution using a SHIMADZU UV-3600 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. Low-temperature phosphorescence were measured in 2-methylTHF at 77 K using a HITACHI F4600 spectrophotometer. Thermogravimetric analysis (TGA) was undertaken with a Shimadzu thermogravimetry and differential thermal analysis DTG-60H at a heating rate of 10 °C/min under N_2. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at both heating and cooling rates of 10 °C/min, using Shimadzu DSC-60A. Elemental analyses were recorded at the Vario EL III (Elemeraor Co. Ltd, Germany). FT-IR spectra were recorded at Shimadzu IRPrestige-21. The single crystal data collection was performed at 100 or 298 K on a Bruker 2000 CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS-2014 and refined against F^2 using SHELXL-2014. Hydrogen atoms were fixed geometrically and refined isotropically. CCDC No. of PhSOH, OPhSOH, 1c, 1d and 1e are 1,473,561, 1,473,563, 1,479,132, 1,473,566 and 1,479,421, respectively.

2.2. Synthesis

9-hydroxy-9-phenylthioxanthene 10,10-dioxide (PhSOH). Diphenyl sulfone (7.2 g, 33 mmol) was dissolved in anhydrous THF solution (200 mL) and stirred at dry ice-alcohol bath, and then 2.5 M *n*-BuLi/n-hexane solution (27.7 mL, 69.3 mmol) was added slowly. Methyl 4′-bromobiphenyl-2-carboxylate (4.08 g, 30 mmol) was added into reaction after 3 h. Removing cool bath and stirring at room temperature about 24 h, then saturated NH4Cl solution was added to quench and hydrolyze, and extracted with dichloromethane. The combined organic abstract was dried over anhydrous MgSO4 and filtered. The solution was evaporated under vacuum condition and the crude product was purified by silica gel column chromatography to afford white solid (9.4 g) with 88.0% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.64 (dd, J = 7.6, 1.6 Hz, 2H), 7.56 (dd, J = 7.6, 1.2 Hz, 2H), 7.28–7.24 (m, 5H), 3.23 (s, 1H); 13C NMR (100 MHz, $CDCl_3$) δ 143.93, 143.63, 136.06, 132.92, 128.86, 128.44, 128.18, 127.89, 126.80, 123.69, 74.09. IR (KBr): υ = 3452 (O–H), 3057 (Aryl C–H), 1593 (Aryl C=C), 1581 (Aryl C=C), 1494 (Aryl C=C), 1469 (Aryl C=C), 1448 (Aryl C=C), 1437 (Aryl C=C), 1377 (O–H), 1280 (–SO_2–), 1213, 1157 (–SO_2–), 1142 (C–O), 1026, 906, 870, 760, 746, 594 cm^{-1}.

9-hydroxy-9-(4-(octyloxy)phenyl)thioxanthene 10,10-dioxide (OPhSOH). The synthetic procedure is similar to PhSOH, and afford light yellow solid product (8.5 g) with 72.1% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.6, 1.2 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.65 (td, J = 7.6, 1.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 9.2 Hz, 2H), 6.74 (d, J = 9.2 Hz, 2H), 3.86 (t, J = 6.8 Hz, 2H), 3.17 (s, 1H), 1.75–1.68 (m, 2H), 1.42–1.35 (m, 2H), 1.30–1.24 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 158.85, 144.03, 135.99, 135.92, 132.83, 128.69, 128.19, 127.54, 123.75, 114.19, 73.95, 67.96, 31.79, 29.30, 29.20, 29.17, 26.00, 22.63, 14.08. IR (KBr): υ = 3506 (OH), 3066 (Aryl CH), 2922 (CH_2, CH_3), 2854 (CH_2, CH_3), 1608 (Aryl C=C), 1579 (Aryl C=C), 1506 (Aryl C=C), 1465 (Aryl C=C), 1441 (Aryl C=C), 1392 (CH_3), 1288 (–SO_2–), 1248 (Ar-O-R), 1153 (–SO_2–), 1136 (C–O), 1043, 1024, 910, 825, 763, 756, 626, 592 cm^{-1}.

Synthesis of 1b. 9-phenylcarbazole (0.97 g, 4 mmol) and OPhSOH (0.45 g, 1 mmol) were dissolved in anhydrous dichloromethane solution (50 mL). Then, the $BF_3 \cdot Et_2O$ (0.14 g, 1 mmol) was added slowly into the reaction mixture. Large amount of water was added to quench reaction after 8 h, and extracted with dichloromethane. The combined organic abstract was dried over anhydrous MgSO4 and filtered. The solution was evaporated under vacuum condition and the crude product was purified by silica gel column chromatography to afford light yellow solid (0.61 g) with 91.0% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.6, 1.2 Hz, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.59–7.55 (m, 5H), 7.55–7.51 (m, 2H), 7.50–7.44 (m, 3H), 7.41–7.35 (m, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.24–7.19 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 8.8, 1.8 Hz, 1H), 6.81–6.74 (m, 4H), 3.93 (t, J = 6.4 Hz, 2H), 1.83–1.71 (m, 2H), 1.47–1.40 (m, 2H), 1.33–1.26 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 158.08, 146.37, 141.29, 139.75, 137.51, 137.32, 136.88, 136.18, 132.01, 131.68, 131.23, 129.87, 128.60, 127.82, 127.54, 126.96, 126.16, 124.02, 123.19, 122.77, 122.39, 120.36, 120.04, 113.92, 109.93, 109.35, 67.97, 58.64, 31.82, 29.37, 29.31, 29.24, 26.09, 22.65, 14.10. MALDI-TOF MS: calculated for $C_{45}H_{41}NO_3S$ 675.88; found: 675.14 (M+). Elemental analysis calculated for $C_{45}H_{41}NO_3S$: C, 79.97%; H, 6.11%; N, 2.07%; O, 7.10%; S, 4.74%. Found: C, 80.10%; H, 6.19%; N, 2.25%. IR (KBr): υ = 3061 (aryl CH), 2926 (CH_2, CH_3), 2854 (CH_2, CH_3), 1597 (Aryl C=C), 1502 (Aryl C=C), 1456 (Aryl C=C), 1440 (Aryl C=C), 1361, 1307 (–SO_2–), 1249 (Ar-O-R), 1234 (Ar-N-Ar), 1165 (–SO_2–), 1145, 1056, 827, 758, 731, 698, 584, 572 cm^{-1}. Molar extinction coefficient (ε, m^2/mol): 2150 (300 nm), 550 (346 nm). Melting point: 233 °C.

Synthesis of 2b. 9-phenylcarbazole (0.24 g, 1 mmol) and OPhSOH (0.95 g, 2.1 mmol) were dissolved in anhydrous dichloromethane solution (100 mL). Then, the $BF_3 \cdot Et_2O$ (0.42 g, 3 mmol) was added slowly into the reaction mixture. Large amount of water was added to quench reaction after 8 h, and extracted with dichloromethane. The combined organic abstract was dried over anhydrous MgSO4 and filtered. The solution was evaporated under vacuum condition and the crude product was purified by silica gel