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Tetrasubstituted adamantane derivatives with arylamine groups: Solution-processable hole-transporting and host materials with high triplet energy and good thermal stability for organic light-emitting devices

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ABSTRACT

Four new host/hole-transporting materials, namely 4,4′,4″,4‴-(adamantane-1,3,5,7-tetrayl)tetrakis(*N*,-*N*-diphenylaniline) (4TPA-Ad, **1**),4,4′,4″,4‴-(adamantane-1,3,5,7-tetrayl)tetrakis(*N*,*N*-di-p-tolylaniline) (4MTPA-Ad, **2**), 1,3,5,7-tetrakis(4-(9*H*-carbazol-9-yl)phenyl)adamantane (4Cz-Ad, **3**) and 1,3,5,7-tetraki s(4-(3,6-di-tert-butyl-9*H*-carbazol-9-yl)phenyl)adamantane (4tBuCz-Ad, **4**), were designed and synthesized by incorporating four electron-donating arylamine units into the rigid adamantane skeleton *via* a simple C–N coupling reaction. Their thermal, photophysical and electrochemical properties were investigated. The molecular design endows the materials with high triplet energies of ~3.0 eV, good solution processability, high thermal stability and appropriate HOMO levels. Two types of electroluminescent devices using **1**–**4** as hole-transporting or host materials were fabricated. The device based on **2** as solution-processed hole-transporting material and tris(quinolin-8-yloxy)aluminum as an emitter revealed a maximum current efficiency of 4.2 cd A^{-1}, which was comparable with the TAPC-based control device. The sky-blue device employing **2** as solution-processed host material and 4,6-(difluorophenyl)p yridine-N,$C^{2'}$)picolinate (FIrpic) as an emitter showed a maximum current efficiency of 16.6 cd A^{-1} with Commission Internationale de I'Eclairage (CIE) coordinates of (0.16, 0.32).

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable scientific and industrial interests due to their applications in display and illumination [1–4]. Multilayer device structures, including hole-transporting layer (HTL), emitting layer (EML) and electron-transporting layer (ETL), have been demonstrated to realize highly efficient OLEDs. Triarylamine and carbazole derivatives are usually used as hole-transporting materials, such as 1,4-bi s[(1-naphthylphenyl)amino]biphenyl (NPB) and 1,1-bis[4-[*N*,*N*-di (p-tolyl)-amino]phenyl]cyclohexane (TAPC) [5,6]. However, these hole-transporting materials usually show low glass-transition temperature (T_g), and their undesirable thermal stability may lead to easy degradation and short lifetime of devices.

The layer-by-layer thermal high-vacuum evaporation has been proven to be a successful technique in the fabrication of OLEDs; however, it is also restricted by high cost, time-consuming and low process yield. Solution processes, such as spin coating or ink-jet printing, offer an attractive alternative approach in terms of the potential to enable low-cost and large area manufacturability that is more amenable to commercial interests [7]. Recently, some solution-processed small molecules have been demonstrated as good hole-transporting materials [8–10]. For example, Usluer et al. reported a series of hole-transporting materials using dioctylfluorene, spirobi(fluorene) and spiro(cyclododecane-fluorene) as core with different peripheral groups, which possessed high decomposition temperature (T_d) and T_g values [11]; Promarak et al. developed two bifunctional materials based on anthracene with the combined characteristics of deep blue light-emitting

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and hole-transporting ability [12]; Our group also reported a series of star-shaped compounds with the core of planar triphenylamine or hexakis(9,9-dihexyl-9*H*-fluoren-2-yl)benzene as solution-processed hole-transporting materials [13,14].

In this article, we designed and synthesized a series of tetrasubstituted adamantane derivatives with arylamines as hole-transporting units. We anticipate that the incorporation of rigid and non-conjugated adamantane skeleton would impart these compounds with good thermal stability and high triplet energy, and the four arylamine units attached to the adamantane would endow them with good hole-transporting ability. The thermal, morphological, photophysical, electrochemical properties of these new compounds will be investigated. The characteristics of devices incorporating these materials as hole-transporting or host materials will be studied.

2. Experiment section

2.1. General information

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Unity 300 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal reference. Elemental analysis of carbon, hydrogen and nitrogen was performed on Vario EL-III microanalyzer. Matrix-assisted laser-desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on Bruker BIFLEX III TOF mass spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C/min from 20 to 300 °C under nitrogen. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument and the thermal stability of the samples under nitrogen atmosphere was determined by measuring their weight loss, heated at a rate of 10 °C/min from 25 to 600 °C. UV–vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. The PL lifetimes were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LED (EPLED330) as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function employing the software package provided by Edinburgh Instruments. Cyclic voltammetric measurements were carried out on a computer-controlled EG&G Potentiostat/Galvanostat model 283 using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in freshly distilled CH_2Cl_2 solution and conventional three-electrode cell with a Pt work electrode of 2 mm diameter, a platinum-wire counter electrode and a Ag/AgCl reference electrode with ferrocenium–ferrocene (Fc^+/Fc) as the internal standard were employed.

2.2. Device fabrication and measurement

The hole-injection material poly-(3,4-ethylenedioxythiophene): poly-(styrenesulfonate) (PEDOT:PSS), hole-transporting material 1,4-bis[(1-naphthylphenyl)amino]biphenyl (NPB) and 1,1-bis[4-[*N*,*N*-di(p-tolyl)-amino]phenyl]cyclohexane (TAPC), electron-transporting material 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), electron-transporting and emissive material aluminum tris(8-hydroxyquinoline) (Alq_3) and blue phosphor 4,6-(difluorophenyl)pyridine-N,$C^{2'}$)picolinate (FIrpic) were commercially available (Luminescence Technology Corp.). Commercial ITO (indium tin oxide, 170 nm) coated glass with sheet resistance of 10 Ω per square was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by oxygen plasma for 2 min. PEDOT:PSS (40 nm) was first spin-coated to smooth the ITO surface and dried at 120 °C for 30 min under vacuum. Then the emissive layer of host materials doped with 10 wt.% FIrpic or hole-transporting layer (60–70 nm) were spin-coated from chloroform solution onto the PEDOT:PSS layer and dried at 80 °C for 30 min to remove residual solvent. Then the samples were transferred to the deposition system. Finally, TmPyPB (35 nm) or Alq_3 (60 nm), and a cathode composed of lithium fluoride (LiF, 1 nm) and aluminum (Al, 100 nm) were sequentially deposited onto the substrate by thermal deposition in the vacuum of 10^{-6} Torr. Current density–voltage–luminance characteristics of the devices were measured using a Keithley 2400 source meter and a Keithley 2000 source multimeter equipped with a calibrated silicon photodiode. The EL spectra were recorded by JY SPEX CCD3000 spectrometer. The EQE values were calculated according to previously reported methods [15–17]. All measurements were carried out at room temperature under ambient conditions.

2.3. Materials

1,3,5,7-Tetrakis(4-iodophenyl)adamantane was prepared according to previously reported procedures [18]. The solvents were dried using standard procedures. All other reagents were used as received from commercial sources unless otherwise stated.

Synthesis of 4,4′,4″,4‴-(adamantane-1,3,5,7-tetrayl)tetrakis(*N*,*N*-diphenylaniline) (**1**). A mixture of 1,3,5,7-tetrakis(4-iodophenyl)adamantane (0.94 g, 1.0 mmol), diphenylamine (0.86 g, 5.1 mmol), CuI (0.1 g, 0.5 mmol), K_2CO_3 (2.1 g, 15 mmol), 18-crown-6 (132 mg, 0.5 mmol) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 3 mL) were heated at 190 °C under argon for 48 h. After cooling, the mixture was extracted with CH_2Cl_2, washed with $NH_3{\cdot}H_2O$ and water, and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using CH_2Cl_2/petroleum (1:5 by vol.) as the eluent to give a white powder. Yield: 56%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.35 (d, *J* = 9 Hz, 8H), 7.29–7.23 (m, 8H), 7.20–6.96 (m, 40H), 2.12 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 147.78, 145.58, 143.99, 129.07, 125.74, 124.03, 123.83, 122.39, 47.24, 38.81. MALDI-TOF, *m*/*z*: $[M]^+$ 1108.8. Anal. Calcd for $C_{82}H_{68}N_4$ (%): C, 88.77; H, 6.18; N, 5.05. Found: C, 88.54; H, 6.28; N, 4.98.

Synthesis of 4,4′,4″,4‴-(Adamantane-1,3,5,7-tetrayl)tetrakis(*N*,*N*-di-p-tolylaniline) (**2**). **2** was prepared according to the same procedure as **1** but using dimethyldiphenylamine to give a white power. Yield: 51%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.23 (d, *J* = 6 Hz, 8H), 7.05–6.95 (m, 40H), 2.30 (s, 24H), 2.08 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.92, 145.39, 143.16, 131.95, 129.70, 125.56, 124.09, 122.83, 47.38, 38.71, 20.74. MALDI-TOF, *m*/*z*: $[M+1]^+$ 1221.7. Anal. Calcd for $C_{90}H_{84}N_4$ (%): C, 88.48; H, 6.93; N, 4.59. Found: C, 88.39; H, 6.81; N, 4.47.

Synthesis of 1,3,5,7-tetrakis(4-(9*H*-carbazol-9-yl)phenyl) adamantane (**3**). **3** was prepared according to the same procedure as **1** but using carbazole to give a white power. Yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.17 (d, *J* = 9 Hz, 8H), 7.87 (d, *J* = 9 Hz, 8H), 7.64 (d, *J* = 9 Hz, 8H), 7.48–7.40 (m, 16H), 7.32–7.30 (m, 8H), 2.51 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 147.57, 141.09, 138.46, 127.28, 126.76, 126.08, 123.50, 120.06, 115.81, 109.15, 46.79, 31.11. MALDI-TOF, *m*/*z*: $[M]^+$ 1100.7. Anal. Calcd for $C_{82}H_{60}N_4$ (%): C, 89.42; H, 5.49; N, 5.09. Found: C, 89.53; H, 5.00; N, 5.27.

Synthesis of 1,3,5,7-tetrakis(4-(3,6-di-tert-butyl-9*H*-carbazol-9-yl)phenyl)adamantane (**4**). **4** was prepared according to the same procedure as **1** but using 3,6-di-tert-butyl-9*H*-carbazole to give a white power. Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.15 (s, 8H), 8.83 (d, *J* = 9 Hz, 8H), 7.62 (d, *J* = 9 Hz, 8H), 7.47 (d, *J* = 9 Hz, 8H), 7.40 (d, *J* = 9 Hz, 8H), 2.49 (s, 12H), 1.47 (s, 72H).