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Synthesis and optoelectronic properties of a solution-processed red-emitting tetra(arylvinyl)anthracene cruciform

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ABSTRACT

In this paper, we report the synthesis and optoelectronic properties of a new anthracene-centered cruciform, 2,6-bis(9,9-di(2-ethylhexyl)fluorene-2-yl-vinyl-2)- 9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)anthracene (**FCA**). **FCA** was prepared by the Heck coupling 2,6-bis(diethoxylphosphorylmethyl)-9,10- dibromoanthracene and 9-(2-ethylhexyl)-3-vinylcabazole, followed by the Wittig–Horner reaction with 9,9-di(2-ethylhexyl)-2-formylfluorene. The existence of strongly twisted 9,10-branch made **FCA** exhibit moderate aggregation-enhanced emission and piezofluorochromism, and the introduction of numerous branched alkyl chains render **FCA** with good solubility and film-forming ability. **FCA** could be used as solution-processed light-emitting layer to afford red emission with peak wavelength of 612 nm and maximal luminous efficacy of 1.3 cd/A.

1. Introduction

Conjugated organic molecules have attracted much attention due to their potential applications in organic optical and optoelectronic fields, and much effort has devoted to the design and synthesis of new luminogens with unique structures and optoelectronic properties. While the linear π-conjugated organic molecules have been the mainstay of optical and optoelectronic materials, recently, higher orders, especially two dimensional arylene-centered oligomers, have started to draw serious research interest, and some benzene-, thiophene-, anthracene-, pyrazine-, benzobisoxazole-, and benzobisthiophene-centered cruciforms have been designed, synthesized and their optical and optoelectronic properties investigated [1–10]. These new configuration materials with unique geometric and electronic structures have greatly widened the scope of molecular candidates applicable in chemosensors, molecular switches, nonlinear optical materials, field effect transistors, and photovoltaic and electroluminescence devices [11–15].

We have been interested in 2,6,9,10-tetra(arylvinyl)anthracene derivatives due to their unique π-centered structure and distorted conformation. Compared to the extensively investigated benzene-centered and other aryl-centered, 2,6,9,10-tetra(arylvinyl)anthracene cruciforms have an asymmetric π-center and a strongly twisted 9,10-branch, which could render them with unique aggregation behaviors and optical properties [16–18]. For example, donor- and/or acceptor-capped cruciforms show large and enhanced two-photon absorption cross sections, and pyrindine- and/or dibutylaniline-capped cruciforms exhibit the selectively fluorescence sensing on metal ions and piezofluorochromism based on 9,10-bis- (arylvinyl)anthracene branch [19–22], etc. Since center-crossed cruciforms have multiple conjugation pathways for intramolecular charge transfer, donor- and/or acceptor-substituted anthracene-centered cruciforms usually exhibit more bathochromic shift emission than their linear building blocks 9,10- and 2,6-bis(aryl-vinyl)anthracenes [23–25]. Moreover, the existence of twisted branch 9,10-bis(aryl-vinyl)anthracene could alleviate from intermolecular tight stacking and strong interactions, which should improve the solid-state fluorescence efficiency and could be

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promising light-emitting materials with unique structure [26,27]. However, such tetra(arylvinyl)anthracene cruciforms usually have large and rigid conjugation skeleton, which is not beneficial to solubility and film fabrication by vacuum deposition. In the current work, we have introduced several branched alkyl chains into the molecular peripheries to improve the solubility and the film-forming capacity. We now report the synthesis and optoelectronic properties of a new and solution-processed 2,6,9,10-tetra(arylvinyl)anthracene cruciform, 2,6-bis(9,9-di(2- ethylhexyl) fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)- anthracene (**FCA**).

2. Experimental section

2.1. Materials

Acetonitrile (MeCN) and tetrahydrofuran (THF) (over metallic sodium) and triethylamine (over CaH_2) were distilled before use. Carbazole, 2-bromofluorene and other solvents and reagents (analytical grade) were commercial available and used as received, unless otherwise claimed. 2,6-Bis(diethylphosphorylmethyl)- 9,10-dibromo- anthracene was from the previous work [28].

2.2. Preparation of aqueous dispersion and ground sample

The stock solution of **FCA** in THF with a concentration of 1.0×10^{-4} M was prepared and reserved. THF/water mixtures with different water fractions (aqueous dispersion) were prepared by slowly adding distilled water into the THF solution of **FCA** under ultrasound at room temperature, and the final concentration was kept at 1.0×10^{-5} M. Ground sample was prepared by grinding **FCA** powder on a glass plate with a metal spatula at room temperature.

2.3. Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker-AC500 (500 MHz) spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed on a Perkin–Elmer 2400. UV–Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Emission spectra were measured with a Hitachi F-4600 spectrophotometer. The peak wavelength of the lowest energy absorption band was used as the excitation wavelength for the PL measurement. The fluorescence quantum yield (Φ) was determined at room temperature by the dilution method using rhodamine B in methanol as the reference. [29] Cyclic voltammetry (CV) was performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk (diameter = 3 mm) as the working electrode, a platinum wire as the auxiliary electrode with a porous ceramic wick, and Ag/Ag^+ as the reference electrode standardized by the redox couple ferrocenium/ferrocene. All solutions were purged with a nitrogen stream for 10 min before measurement. The procedure was performed at room temperature, and a nitrogen atmosphere was maintained over the solution during measurements [30–32]. Differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analysis were performed under nitrogen atmosphere on Netzsch DSC 204F1 and Netzsch 209F1 analyzers at heating rates of 10 °C/min and 20 °C/min, respectively.

2.4. Device fabrication

Indium-tin oxide (ITO) coated glass with a sheet resistance of 15–20 Ω/cm^2 was used as the cathode whose substrate was pre-patterned by photolithography to give an effective device size of 6.25 mm^2. Then, it was cleaned in an ultrasonic bath with acetone, detergent, deionized water, and isopropanol as the clean agent. After being dried in an oven, it is treated with oxygen plasma for 4 min, and then 40 nm of PEDOT:PSS layer was spin-coated and baked overnight in a vacuum oven at 80 °C. On the top of above active layer, a 60 nm of **FCA** bulk emitting layer was spin-casted from its chloroform solution (12 mg/mL). The **FCA** solution in chloroform has been filtered through a 0.45 μm PTFE filter before spin coating. Then 1,3,5-tri(phenyl-2- benzimidazol-yl)benzene (TPBi) as electron-transporting layer (50 nm) were vacuum deposited. Finally, 0.5 nm of LiF film and 100 nm of Al film was vacuum deposited to form the anode. The base pressure for vacuum deposition was at of 3×10^{-4} Pa. The thickness of each deposition layer was monitored using a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). Electroluminescence (EL) spectra were measured by a PR650 fluorescence spectrophotometer. Luminance-voltage and current density-voltage characteristics were recorded simultaneously by combining the spectrometer with a Keithley model 2400 programmable voltage–current source. All measurements were carried out at room temperature under ambient conditions.

2.5. Synthesis

2.5.1. 9,10-Bis(9-(2-ethylhexyl)carbazole-3-yl-vinyl-2)-2,6-bis(diethylphosphorylmethyl)- anthracene

A dried pressure tube was added 2,6-bis(diethyl phosphorylmethyl)-9,10-dibromo- anthracene (0.21 g, 0.33 mmol), 9-(2-ethylhexyl)-3-vinyl-carbazole (0.36 g, 1.18 mmol), $Pd(OAc)_2$ (7.4 mg, 0.033 mmol), tri(*o*-toyl)phosphine (68 mg, 0.23 mmol), *N*,*N*-dimethylformamide (DMF) (1.5 mL), and triethylamine (1.5 mL), and then purged by nitrogen and sealed with a Teflon screw top. The mixture was refluxed for 24 h and then extracted with dichloromethane. The solvent was removed and the crude product was separated by column chromatography on silica gel using petroleum ether/ethyl acetate (1/1) as the eluent. Yield: 0.21 g (58%). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.48 (d, 2H), 8.38 (s, 2H), 8.34 (s, 2H), 8.18 (d, 2H), 7.93 (d, 2H), 7.86 (d, 2H), 7.49 (m, 8H), 7.28 (d, 2H), 7.12 (d, 2H), 4.24 (m, 4H), 4.03 (m, 8H), 3.36 (d, 4H), 2.13 (m, 2H), 1.22 (m, 16H), 0.96 (t, 12H), 0.90 (t, 12H).

2.5.2. 2,6-Bis(9,9-di(2-ethylhexyl)fluorene-2-yl-vinyl-2)-9,10-bis(9-(2-ethylhexyl)carbazole- 3-yl-vinyl-2)anthracene (**FCA**)

Potassium *tert*-butoxide (0.16 g, 1.43 mmol) was added to a dried one-neck flask containing the solution of 9,10-bis(9-(2-ethylhexyl) carbazole-3-yl-vinyl-2)-2,6-bis- (diethylphosphorylmethyl) anthracene (0.17 g, 0.16 mmol) and 9,9-di(2-ethylhexyl)- 2-formylfluorene (0.19 g, 0.45 mmol) in anhydrous THF (10 mL) under nitrogen. The mixture was stirred overnight at room temperature and then 100 mL of methanol was added. The precipitate was collected and purified by a column chromatography on silica gel using petroleum ether/dichloromethane (2/1) as the eluent. Yield: 0.21 g (82%). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.52 (d, 2H), 8.48 (s, 2H), 8.42 (s, 2H), 8.22 (d, 2H), 8.01 (d, 2H), 7.94 (d, 2H), 7.86 (d, 2H), 7.64 (t, 4H), 7.58 (t, 2H), 7.50 (m, 8H), 7.30 (m, 10H), 7.23 (m, 4H), 4.27 (d, 4H), 2.16 (t, 2H), 1.98 (m, 8H), 1.05 (m, 4H), 0.80 (m, 12H), 0.75 (m, 12H), 0.70 (t, 6H), 0.65 (m, 24H), 0.56 (t, 6H), 0.48 (t, 24H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.98, 150.67, 141.42, 141.11, 141.00, 140.91, 138.29, 135.82, 135.77, 135.71, 134.20, 133.03, 130.28, 129.64, 129.58, 128.57, 128.12, 127.29, 126.69, 126.36, 126.10, 125.92, 124.47, 124.01, 123.29, 122.85, 122.19, 121.71, 120.51, 119.71, 119.55, 119.12, 118.78, 109.31, 109.22, 54.75, 47.56, 44.61, 39.49, 34.51, 33.56, 31.93, 29.71, 28.88, 27.00, 26.85, 24.42, 23.11, 22.68, 14.80, 14.00, 10.34.