Electronic supplementary information

DOI: ((please add manuscript number))

Structural and Optical Analysis of a Carbazole-Containing Ethene as Highly Emissive Organic Solid

Yang Liu, Xin Ye, Guangfeng Liu, Yun Lv, Xiying Zhang, Shuming Chen, Jacky W. Y.

Lam, Hoi Sing Kwok, Xutang Tao and Ben Zhong Tang*

Contents

Experimental Section

Figure S1. (A) ¹H NMR and (B) ¹³C NMR spectra of BOC in chloroform-*d*.

Figure S2. High resolution mass spectrum of BOC.

Figure S3. High resolution mass spectrum of DCDPE.

Figure S4. (A) ¹H NMR and (B) ¹³C NMR spectra of DCDPE in chloroform-*d*.

Figure S5. UV spectra of DCDPE in THF/water mixtures with different water

fractions.

Figure S6. TEM image of nanoaggregates of DCDPE formed in THF/water mixtures

with 95% water fractions.

Figure S7. Comparison of the fluorescence of DCDPE in different morphologies.

(Left: crystalline; Right: amorphous)

Experimental Section

Materials and Instrumentations

THF was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. All the chemicals and other regents were purchased from Aldrich and used as received without further purification.

¹H and ¹³C NMR spectra were measured on a Bruker AV 400 spectrometer in CDCl₃ or CD₂Cl₂ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence spectra were recorded on а Perkin-Elmer LS 55 spectrofluorometer. High resolution mass spectra (HRMS) were recorded on a GCT CAB048 spectrometer operating MALDI-TOF premier mass in mode. Thermogravimetric Analysis (TGA) was carried on a TA TGA Q5500 under dry nitrogen at a heating and cooling rates are 10 °C/min. Thermal transitions were investigated by Differential Scanning Calorimetry (DSC) using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min. Cyclic voltammograms were recorded on a Princeton Applied Research (model 273A) at room temperature. The working and reference electrodes were glassy carbon and Ag/AgNO₃ (0.1 M in acetonitrile), respectively. All the solutions were deactivated by bubbling nitrogen gas for a few minutes prior to electrochemical measurements. TEM and electron diffraction patterns were obtained using JOEL 2010 transmission electron microscope at an accelerating voltage of 200 KV. Samples were prepared by casting a drop of suspensions onto copper 400-mesh carrier grids and dried in open air at room temperature.

Device fabrication and characterization

The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of $25\Omega/\Box$. Prior to load into the pretreatment chamber, the ITO coated glass were soaked in ultrasonic detergent for 30 mins, followed by spraying with de-ionized water for 10 mins, soaking in ultrasonic deionized water for 30 mins and ovenbake for 1 h. The cleaned samples were treated by CF_4 plasma with a power of 100 W, gas flow of 50 sccm and pressure of 0.2 Torr for 10 s in the pretreatment chamber. Then the samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr without breaking vacuum for depositing 60 a nm 4,4-bis(1-naphthylphenylamino)biphenyl (NPB), a 20 nm emitter, a 10 nm 2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi), and a 30 nm tris(8-hydroxyquinoline) aluminum (Alq₃), which serve as hole-transporting, light-emitting, hole-blocking, and electron-transporting layers, respectively. The samples were then transferred to the metal chamber for cathode deposition which composed of 1 nm LiF capped with 100 nm Al. The light-emitting area was 4 mm² defined by the overlap of cathode and anode. The current density-voltage characteristics of the devices were measured by the HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and

external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence (EL) spectra were obtained with the PR650 spectrophotometer. All measurements were carried out under air at room temperature without device encapsulation.

Synthesis

N-Ethyl-3-benzoylcarbazole (**BOC**): Into a stirred mixture of 1.953 g (10 mmol) of N-ethylcarbazole, 1.41 g (10 mmol) of benzoylchloride in 35 mL CS₂ solution was slowly added 1.33 g (10 mmol) of aluminum chloride under nitrogen. The mixture was heated under 35 °C for 3 h. After cooled to room temperature, the solvent was evaporated. Cold water was added to the residue and extract with dichloromethane. The organic layer was washed with water and diluted hydrochloric acid. The crude product was purified by silica-gel chromatography (DCM/hexane =2/3) to give a light yellow liquid in 70% yield (2.1 g). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.61 (d, 1H, J=1.6), 8.11 (d, 1H, J=7.6), 8.11 (dd, 1H, J₁=8.4, J₂=1.6), 7.86 (s, 1H), 7.84 (d, 1H, J=1.2), 7.63-7.44 (m, 6H), 7.31-7.27 (m, 2H), 4.42 (q, 2H, J=9.6), 1.49 (t, 3H, J=9.6); ¹³C NMR (100 MHz, CDCl₃, δ): 196.8 (C=O), 142.6, 140.8, 139.2, 131.8, 130.0, 128.6, 128.3, 126.6, 124.2, 123.3, 122.7, 120.9, 120.1, 109.1, 108.1, 38.0, 13.9; MS (MALDI-TOF): *m/z* 299.8072 [(M+1)⁺, calcd 299.1310].

1,2-bis(N-ethyl-3-carbazole)-1,2-diphenylethylene (DCDPE): In a two-necked flask equipped with a magnetic stirrer were added 0.52 g (8 mmol) of zinc powder, 0.60 g (2 mmol) of N-ethyl-3-benzoylcarbazole and 60 mL of THF. TiCl₄ (0.44 mL, 4 mmol) was slowly added by a syringe at 0 $^{\circ}$ C under nitrogen. The mixture was then

heated to reflux overnight. After cooled to room temperature, the reaction was quenched with 10% K₂CO₃ aqueous solution and extracted with CH₂Cl₂. The organic layer was collected and concentrated. The crude product was purified by silica-gel chromatography (DCM/hexane =2/5) to give a colorless solid in 85% yield (0.481 g). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.89-7.78 (m, 4H), 7.41-7.29 (m, 4H), 7.23-7.01 (m, 16H), 4.32-4.19 (m, 4H; -CH₂-), 1.44-1.32 (m, 6H; -CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 145.22, 140.82, 140.20, 138.64, 135.28, 131.82, 130.05, 129.90, 127.64, 126.12, 125.44, 123.56, 122.55, 120.55, 118.63, 108.41, 107.60, 37.60, 13.88; MS (MALDI-TOF): *m*/*z* 566.1929 [(M)⁺, calcd 566.2722]. Anal. Cal. For C42H34N2: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.83; H, 6.12; N, 4.94. Crystal data for DCDPE (C42 H34 N2): Mr = 566.71, Monoclinic, space group P2(1)/c, a = 12.6635(13) Å, α = 90°, b = 21.772(2) Å, β = 117.068(2)°, c = 12.6541(12) Å, γ = 90°, V =3106.7(5) Å³, Z = 4, ρ_{calcd} = 1.212 Mg/m³, T = 100(2) K, Crystal size 0.30 x 0.15 x 0.10 mm³, R1 = 0.0537, wR2 = 0.1110, [I>2sigma(I)].



Figure S1. (A) ¹H NMR and (B) ¹³C NMR spectra of BOC in chloroform-d. The solvent peaks are marked with asterisks.



Figure S2. High resolution mass spectrum of BOC.



Figure S3. High resolution mass spectrum of DCDPE.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C This journal is O The Royal Society of Chemistry 2013



Figure S4. (A) 1 H NMR and (B) 13 C NMR spectra of DCDPE in chloroform-*d*. The solvent peaks are marked with asterisks.



Figure S5. UV spectra of DCDPE in THF/water mixtures with different water fractions.



Figure S6. TEM image of nanoaggregates of DCDPE formed in THF/water mixtures with 95% water fractions.



Figure S7. Comparison of the fluorescence of DCDPE in different morphologies. (Left: crystalline; Right: amorphous)