Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Synthesis and photovoltaic properties of carbazole-substituted fullerene derivatives

Yuling Zhao^a, Xin Wang^b, Tianzhi Yu^{b,*}, Hui Zhang^b, Chengjin Wei^b, Xiaoxiao Liu^c

^aSchool of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

^bKey Laboratory of Opto-Electronic Technology and Intelligent Control (Ministry of Education), Lanzhou Jiaotong University, Lanzhou 730070, China

^cSchool of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

E-mail: yutzh@mail.lzjtu.cn

Contents

I. General Information	S2
II. Experimental Details and Characterization Data	S4
III. Copies of the ¹ H, ¹³ C NMR & mass spectra for the synthesized compounds	S 8
IV. References	S14

I. General Information

Materials and methods

Carbazole and 1-bromobutane were purchased from Shanghai Zhongqin Chemical Reagent Co. Ltd (China). Methyl 5-chloro-5-oxopentanoate and *p*-toluene-sulfonyl hydrazide were obtained from Energy Chemical (China). Anhydrous aluminum trichloride was bought from Tianjing Chemical Reagent Co. Ltd (China). Sodium methoxide was purchased from Alfa Aesar. Fullerene (C_{60}) (99.9%) was bought from Puyang Yongxin Fullerene Technology Co. Ltd (China). Dichloromethane, pyridine and 1,2-dichlorobenzene were purified and freshly distilled prior in the related reaction. All the other chemicals were analytical grade reagent.

9-Butyl-9H-carbazole was synthesized as previously described.¹

¹H and ¹³C NMR spectra were recorded on Varian Mercury Plus 400 MHz and Agilent Technologies DDZ 600 MHz. IR spectra (400–4000 cm⁻¹) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. Mass spectra were recorded using a Thermo Scientific Orbitrap Elite mass spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris system. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Cyclic voltammetry (CHI Instruments 760 B) was performed with a 0.10 mol/L solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in *o*-DCB/Chloroform (4:1), with the analyte present in a concentration of 10⁻³ mol/L and employing a scan rate of 50 mV/s at room temperature. A glassy carbon electrode was used as the working electrode, while a Pt wire and a Ag/Ag⁺ electrode were used as the counter electrode and reference electrode, respectively.

Fabrication and characterization of photovoltaic devices

The organic photovoltaic devices with a device architecture of ITO/PEDOT:PSS (40 nm)/P3HT:acceptor (1:x, w/w) (100 nm)/Ca (10 nm)/Al (100 nm) were fabricated. Poly(3,4ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) was spin-coated onto precleaned and O₂-plasma-treated indium tin oxide (ITO) substrates with a sheet resistance of 10–15 Ω /square, yielding layers ca. 40 nm thick, and then dried by baking in a vacuum oven at 160 °C for 30 min. The active layer was then deposited on top of the PEDOT:PSS layer by spin-casting from o-dichlorobenzene solution containing P3HT/acceptor (1:x, w/w), and drying at 150 °C for 20 min. At a base pressure of 6×10^5 Pa, a 10 nm Ca layer was thermally evaporated at an evaporation rate of 0.1 Å/s. Finally, a 100 nm Al layer was evaporated with a shadow mask. The active area of the devices defined a pixel size of 0.1 cm². The power conversion efficiency (PCE) of the resulting OPVs was measured using an AM 1.5 G solar simulator (Oriel model 91160). The current density versus voltage (J-V) characteristics were recorded with a Keithley 2400 source measurement unit under simulated 100 mW cm⁻² irradiation from a Newport solar simulator. The external quantum efficiencies (EQEs) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM, MFP-3D-SA). The R_s and R_{sh} of the solar cells were calculated from the inverse of the slope of the J-V curve at the open circuit voltage and short circuit condition, respectively.

II. Experimental Details and Characterization Data

Synthesis and characterization of Cz-C₆₀ and Cz-2C₆₀

Methyl 5-(9-butyl-9H-carbazol-3-yl)-5-oxopentanoate (1). 9-Butyl-9H-carbazole (4.00 g, 17.91 mmol) and anhydrous aluminum trichloride (4.80 g, 36.00 mmol) were dissolved in dichloromethane (100 mL), and 5-chloro-5-oxopentanoate (2.50 mL, 17.91 mmol) was slowly added to the reaction mixture under N₂ atmosphere. The mixture was first stirred at 0 °C for 2.5 h and then warmed to room temperature. After stirring overnight, the reaction was quenched by the dropwise addition of an aqueous solution of 2 mol/L HCl. The mixture was poured into water (100 mL) and extracted with dichloromethane (100 mL \times 3). The combined organic phase was dried over anhydrous MgSO₄ and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of ethvl acetate/petroleum ether (1:8, v/v) as the eluent to obtain compound 1 as pale vellow oil (5.04 g, 80%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.76 (s, 1H), 8.19–8.09 (m, 2H), 7.55–7.47 (m, 1H), 7.42 (dd, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 4.32 (t, *J* = 8.0 Hz, 2H), 3.70 (s, 3H), 3.19 (t, *J* = 8.0 Hz, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 2.15 (m, 2H), 1.92–1.80 (m, 2H), 1.46–1.32 (m, 2H), 0.95 (t, J = 8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 198.75, 173.87, 143.15, 141.07, 128.25, 126.35, 126.08, 123.13, 122.55, 121.51, 120.59, 119.89, 109.19, 108.30, 51.55, 43.06, 37.31, 33.30, 31.02, 20.48, 19.82, 13.82.

Dimethyl 5,5'-(9-butyl-9*H***-carbazole-3,6-diyl)bis(5-oxopentanoate) (2).** The compound **2** was prepared by the same procedure for the compound **1**, which was synthesized from 9-Butyl-9*H*-carbazole (4.00 g, 17.91 mmol), anhydrous aluminum trichloride (9.60 g, 72.00 mmol) and 5-chloro-5-oxopentanoate (5.00 mL, 35.82 mmol). The residue was purified by

column chromatography on silica gel using ethyl acetate/petroleum ether (1:4, v/v) as the eluent to yield compound **2** as pale yellow solid (4.72 g, 54.95%). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 8.81 (d, *J* = 6.0 Hz, 2H), 8.18 (d, *J* = 6.0 Hz, 2H), 7.45 (d, *J* = 6.0 Hz, 2H), 4.35 (t, *J* = 6.0 Hz, 2H), 3.71 (s, 6H), 3.21 (t, *J* = 12.0 Hz, 4H), 2.52 (t, *J* = 6.0 Hz, 4H), 2.19–2.12 (m, 4H), 1.90–1.83 (m, 2H), 1.44–1.37 (m, 2H), 0.96 (t, *J* = 6 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃, δ , ppm): 198.61, 173.83, 143.87, 129.30, 126.74, 122.89, 121.67, 109.03, 51.59, 43.37, 37.43, 33.27, 31.01, 20.44, 19.74, 13.77.

(*E*) Methyl 5-(9-butyl-9*H*-carbazol-3-yl)-5-(2-tosylhydrazono)pentanoate (3). Compound 1 (5.00 g, 14.23 mmol) and *p*-toluene-sulfonyl hydrazide (4.00 g, 21.48 mmol) were dissolved in methanol (150 mL). A catalytic amount of concentrated HCl was added to the mixture, then the mixture was refluxed for 18 h. After cooling, there were a lot of pale yellow solids in the reaction mixture, which were filtered out and washed several times with methanol, and finally we got pale yellow solid compound 3 (5.31 g, 71.9%). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 9.04 (s, 1H), 8.30 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.51–7.23 (m, 7H), 4.30 (t, *J* = 8 Hz, 2H), 3.83 (s, 3H), 2.82–2.71 (m, 2H), 2.45–2.30 (m, 5H), 1.90–1.72 (m, 4H), 1.45–1.32 (m, 2H), 0.94 (t, *J* = 8 Hz, 3H).

Dimethyl 5,5'-(9-butyl-9*H*-carbazole-3,6-diyl)(5*E*,5'*E*)-bis(5-(2-tosylhydrazono)pentanoate)

(4). The compound 4 was synthesized from compound 2 by the same procedure used to make the compound 3. We got pale yellow solid compound 4 (4.6 g, 68%). ¹H NMR (600 MHz, CDCl₃, δ, ppm): 9.15 (s, 2H), 8.36 (s, 2H), 7.98 (d, *J* = 6.0 Hz, 4H), 7.85 (d, *J* = 12.0 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 6H), 4.25 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 6H), 2.83–2.74 (m, 4H), 2.44–2.33 (m, 10H), 1.80 (dd, *J* = 6.0, 6.0 Hz, 6H), 1.40–1.29 (m, 2H), 0.92 (t, *J* = 6 Hz, 3H).

(9-Butyl-9H-carbazole-3-yl)-C₆₁-butyric acid methyl ester (Cz-C₆₀). Compound 3 (1.00 g, 1.93 mmol) and sodium methoxide (0.21 g, 3.89 mmol) were dissolved in dry pyridine (20 mL) under nitrogen. The mixture was stirred at room temperature for 2 h. To the mixture, a solution of C₆₀ (1.11 g, 1.54 mmol) in dry 1,2-dichlorobenzene (200 mL) was added, and the mixture was stirred at 80 °C under nitrogen for 32 h. The mixture was refluxed at 180 °C for 24 h. After cooling, the solvent was removed by distillation, and the residue was purified by column chromatography on silica gel using toluene/petroleum ether (1:3, v/v) and chloroform/petroleum ether (1:2, v/v) as the eluents, then the crude product was purified by several reprecipitations in methanol followed by extraction with hexane and methanol in a Soxhlet extractor to give a brown-black solid Cz-C₆₀ (0.72 g, 44.2%). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 8.57 (s, 1H), 8.20 (d, J = 6.0 Hz, 1H), 7.99 (d, J = 6.0 Hz, 1H), 7.60–7.39 (m, 3H), 7.25 (s, 1H), 4.36 (t, J = 6.0 Hz, 2H), 3.64 (s, 3H), 2.98 (d, J = 6.0 Hz, 2H), 2.52 (t, J Hz, 2H), 2.31–2.14 (m, 2H), 2.01–1.84 (m, 2H), 1.60–1.51 (m, 2H), 1.01 (t, J = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃, δ, ppm): 173.54, 149.14, 148.23, 146.00, 145.15, 144.77, 144.41, 143.94, 143.76, 143.03, 142.90, 142.26, 142.12, 140.94, 140.70, 140.04, 138.04, 137.82, 129.56, 126.80, 126.02, 124.05, 122.61, 120.70, 119.07, 108.94, 108.61, 80.69, 51.63, 43.16, 33.99, 31.26, 29.70, 22.59, 20.70, 13.95. FT-IR (KBr, cm⁻¹): 2956, 2925 (CH₃ stretch), 2857 (-CH₂- stretch), 1732 (ester C=O), 1598, 1490 (aromatic C=C stretch), 1464 (-CH₂- bend), 526 (coming from C₆₀). MS: calcd for C₈₂H₂₅NO₂, 1056.08; found, 1056.19.

(9-Butyl-9*H*-carbazole-3,6-diyl)-bis(C₆₁-butyric acid methyl ester) (Cz-2C₆₀). Cz-2C₆₀ was synthesized from compound 4 by the same procedure for Cz-C₆₀. The residue was purified by column chromatography on silica gel using toluene/petroleum ether (1:3, v/v) and

chloroform/petroleum ether (1:1, v/v) as the eluents. Then the crude product was purified by several reprecipitations in methanol followed by extraction with hexane and methanol in a Soxhlet extractor to give brown-black solid **Cz-2C₆₀** (0.52 g, 25%). ¹H NMR (600 MHz, CDCl₃, δ , ppm): 8.69 (s, 2H), 8.04 (d, *J* = 6.0 Hz, 2H), 7.59 (d, *J* = 6.0 Hz, 2H), 4.42 (t, *J* = 6.0 Hz, 2H), 3.64 (s, 6H), 3.03 (d, *J* = 6.0 Hz, 4H), 2.53 (s, 4H), 2.27 (s, 4H), 2.06–1.96 (m, 2H), 1.58 (dd, *J* = 12.0, 6.0 Hz, 2H), 1.06 (t, *J* = 12.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm): 173.51, 168.95, 167.71, 148.13, 145.99, 145.13, 145.01, 144.76, 144.65, 144.61, 144.44, 144.40, 143.75, 143.68, 143.00, 142.96, 142.89, 142.26, 142.11, 142.09, 140.92, 140.68, 140.57, 138.03, 132.43, 130.84, 129.45, 128.77, 68.13, 52.35, 51.63, 38.71, 33.97, 30.34, 29.68, 28.91, 23.73 22.96, 14.03, 10.94. FT-IR (KBr, cm⁻¹): 2952, 2922 (CH₃ stretch), 2854 (-CH₂- stretch), 1732 (ester C=O), 1598, 1491 (aromatic C=C stretch), 1464 (-CH₂- bend), 526 (coming from C₆₀). MS: calcd for C₁₄₈H₃₃NO₄, 1888.85; found, 1889.25.

III. Copies of the ¹H, ¹³C NMR & mass spectra for the synthesized compounds



Compound 1 for ¹³C NMR



 $Cz-C_{60}$ for ¹H NMR



Cz-C₆₀ for HRMS

S10





 $Cz-2C_{60}$ for ¹H NMR



Cz-2C₆₀ for HRMS

IV. References

1 T. Z. Yu, Y. Cao, W. M. Su, C. C. Zhang, Y. L. Zhao, D. W. Fan, M. J. Huang, K. Yue and

Stephen Z. D. Cheng, RSC Adv., 2014, 4, 554–562.