Supporting Information

Controllable growth of organic nanostructures from 0D to 1D with different optical properties

Yusen Luo, Zheng Xue, Yongjun Li, HuibiaoLiu, Wensheng Yang and Yuliang Li



Scheme S1. Synthetic route of the target compounds TBC and TCP.

Materials

All chemical reagents were purchased from Alfa Aesar or Aldrich Chemicals and used without further purification. Column chromatography was performed on silica gel (size 200–300 mesh). 2,5,8,11-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene $(1)^1$ and 9-(4-iodophenyl)-9H-carbazole $(2)^2$ were prepared according to the literature methods.

2,5,8,11-tetrakis(**4-(9H-carbazol-9-yl)phenyl)perylene (TCP).** To a solution of **1** (100 mg, 0.13 mmol) in toluene/ethanol (54 mL/ 18 mL) was added **2** (280 mg, 0.76 mmol), the resulting solution was stirred under N₂ at room temperature for 30 min. Subsequently, $Pd(PPh_3)_4$ (36 mg, 0.03 mmol) and K_2CO_3 (200mg, 1.45 mmol, dissolved in distilled water) were added and the

reaction vessel was placed in an oil bath at 70 °C for 48 h. After that, the solvent was evaporated in vacuo and the crude product was purified by column chromatography silica gel with CH₂Cl₂ / petroleum ether (1:2) to afford **TCP** as yellow solids (87 mg, 54%). IR (v, cm⁻¹) 1601.1, 1516.5, 1478.9, 1448.6, 1355.2, 1334.2, 1313.8, 1226.0, 1169.3, 831.7, 746.1, 720.6. ¹H NMR (500 MHz, CDCl₂CDCl₂) δ 8.78 (s, 1H), 8.74 (s, 2H), 8.66 (s, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.31 (s, 1H), 8.24 - 8.14 (m, 8H), 8.14 - 7.98 (m, 8H), 7.93 (s, 1H), 7.91 (s, 1H), 7.84 - 7.69 (m, 8H), 7.57 (ddd, *J* = 28.3, 20.1, 8.1 Hz, 8H), 7.45 (ddd, *J* = 20.2, 13.5, 7.4 Hz, 8H), 7.37 - 7.24 (m, 8H). Due to its poor solubility, the ¹³C NMR is not available. Hires-MS (MALDI-TOF): calcd for C₉₂H₅₆N₄: 1216.4505; found: 1216.4524. Anal. Calcd for C₉₂H₅₆N₄, C, 90.76; H, 4.64; N, 4.60; Found C, 90.79; H, 4.60; N,4.58.

9,9',9''-(perylene-2,5,8-triyltris(benzene-4,1-diyl))tris(9H-carbazole) (**TBC).** Compound **1** could easily loss one boric acid ester during the synthesis of compound **TCP**. Thus **TBC** was obtained as a by-product with 30 mg (yellow). IR (v, cm⁻¹) 1602.2, 1518.2, 1479.2, 1449.8, 1336.6, 1315.3, 1228.4, 1170.8, 833.3, 747.7, 722.8. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, J = 6.1 Hz, 2H), 8.61 (s, 1H), 8.45 (d, J = 7.6 Hz, 1H), 8.19 (t, J = 7.1 Hz, 6H), 8.13 (s, 2H), 8.12 - 8.04 (m, 7H), 7.90 (d, J = 8.2 Hz, 1H), 7.78 (m, J = 8.2, 5.2 Hz, 6H), 7.65 (t, J = 7.8 Hz, 1H), 7.58 - 7.51 (m, 6H), 7.47 (m, J = 8.1 Hz, 6H), 7.34 (m, J = 7.4 Hz, 6H). Due to its poor solubility, the ¹³C NMR is not available. MS (MALDI-TOF): calcd for C₇₄H₄₅N₃: 975.3613; found: 975.36180. Anal. Calcd for C₇₄H₄₅N₃, C, 91.05; H, 4.65; N, 4.30; Found C, 91.11; H, 4.61 N, 4.27.

Characterization

¹H NMR spectra were obtained at Bruker ARX400 spectrometer using tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometric measurements were obtained on the Bruker Biflex III MALDI-TOF. SEM images were taken from Hitachi S-4800 microscopes at an accelerating voltage of 15 kV. TEM images were taken from a JEOL JEM-1011 microscope at an accelerating voltage of 100 kV. UV-Vis spectra were measured on a Hitachi U-3010 spectrometer. The fluorescence spectra were measured on a Hitachi F-4500 spectrometer. Fluorescence images of the microstructures were taken by using a laser-based fluorescence microscope (Olympus IX81) and an intensified charge-coupled device (CCD, Olympus DP71) detection system. Cyclic voltammograms (CVs) and differential pulse voltammetric curves (DPVs) were recorded on a CHI660D electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode and calomel electrode as the reference. 0.1 M Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in chromatographically pure CH_2Cl_2 was employed as the supporting electrolyte.

References:

- 1. Y. Chen, G. Huang, C. Hsiao and S. Chen, J. Am. Chem. Soc., 2006, 128, 8549-8558.
- 2. D. Coventry, A. Batsanov, A. Goeta, J. Howard, T. Marder and R. Perutz, *Chem. Commun.*, 2005, 16, 2172-2174.



Figure S1. Cyclic voltammetry curves of **TBC** (a) and **TCP** (c) and differential pulse voltammetry curves of **TBC** (b) and **TCP** (d).



Figure S2. Normalized UV-Vis absorption and excitation spectra of the spin-casting film, nanosphere, nanotube/nanorod of **TBC** and **TCP**.



Figure S3. SEM images of TBC prepared in CH_2Cl_2 / acetone with different volume ratio (v/v) by solvent vapor technique. (a) v/v = 40:0, (b) v/v = 40:3, (c) v/v = 40:10 and (d) v/v = 40:40.



- . . .

