Supporting Information

Enhancing emission of hexa-*peri*-hexabenzocoronene-containing polynorbornene *via* electron donating, unsymmetric constitution and solvent effects[†]

Chou-Yi Tsai, ^a Qiang Zhang, ^a Yi-Ze Wang, ^a Jocelyn Shyong, ^b Hsin-Lung Chen^c and Der-Jang Liaw^{*a}

^{a.} Department of Chemical Engineering, National Taiwan University of Science and Technology, 10607, Taipei, Taiwan.

^{b.} Thayer School of Engineering, Dartmouth College, Hanover NH 03755, USA.

^{c.} Department of Chemical Engineering, National Tsing Hua University, 30013, Hsin-Chu, Taiwan.

Synthetic procedure and identification data of prepared polymers were described below

1. Materials

Copper iodide (CuI), dicyclopentadiene, diphenyl ether, 4-Iodoanisole, iron(III) chloride (FeCl₃), phenylacetylene, piperidine, sodium hydride, *p*-toluenesulfonhydrazide, and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from Acros Organics. Anhydrous potassium carbonate (K₂CO₃) was purchased from Fisher Chemical. Allyl alcohol, boron tribromide, Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Hoveyda-Grubbs Catalyst 1st Generation), tetraphenylcyclopentadienone and ethyl vinyl ether were purchased from Sigma-Aldrich Chemical. The solvents (analytical grade) were purchased from Merck. Tetrahydrofuran and toluene were distilled from sodium/benzophenone (deep purple) under nitrogen before use. All other reagents were used as received.

2. Methods

IR spectra were recorded in the range 400-4200 cm⁻¹ for synthesized monomers and polymers in a KBr disk (Bio-Rad Digilab FTS-3500). NMR spectra were recorded using a Bruker Avance III HD-600 (¹H at 600 MHz and ¹³C at 150 MHz). Differential scanning calorimetric analysis was performed on a differential scanning calorimeter (TA instrument TA 910) under nitrogen at a flow rate of 50 cm³/min and a heating rate of 10 K/min. Thermogravimetric analysis was performed on a TA instrument Dynamic TGA 2950 under nitrogen at a flow rate of 30 cm³/min and a heating rate of 10 K/min. X-ray diffraction experiments were performed using a

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Bruker D8 X- ray Powder Diffractometer (Cu-Kα: 0.15406 nm) at a scanning rate of 0.1°/20 s. Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns (300 × 7.5 mm, guard, 105, 104, 103, and 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF; 1 mL/min) as the eluent. The eluents were monitored with a UV detector (JMST Systems, VUV-24, USA) at 254 nm, and polystyrene was used as the standard. Film thicknesses were measured using coating thickness measurement (Mode: PERMASCOPE MPO, Fischer). UV/vis absorption spectra of the specimens were recorded on a JASCO V-670 spectrophotometer at room temperature in air. Photoluminescence (PL) spectra and photoluminescence-excitation (PLE) maps were measured using a HORIBA JOBIN FluoroMax-3 with a 1 cm × 1 cm quartz cuvette. For the preparation of PHNB-HBC dispersion solution, one milligram PHNB-HBC powder and ten milliliter solvent were added in 30 ml sample cell. The mixture was ultrasonicated with total energy of 8000 J during 15 min. The ultrasonication was performed using Q700 sonicator (QSONICA, Newtown). No precipitation was observed during the optical spectra measurement (for absorption, photoluminescence, and PLE, the total time is about 2 h) when PHNB-HBC was dispersed in CHP. The precipitation could be observed after CHP solution was put on for 48 h, and the amount of dispersed PHNB-HBC is 88% (calculated from the maximum absorption peak)

3. Synthesis of NBOHPB

The **HPB-OH** (1 g, 1.8 mmol) and sodium hydride (65 mg, 2.7 mmol) were dissolved in anhydrous DMSO. The **NB-Br** (0.68 g, 3.6 mmol) was added to the mixture. The resulting solution was stirred at 120 °C for 12 h under the flow of nitrogen. After cooling, the solution was poured into excess DI water to afford pale yellow powder. The crude products were purified *via* silica gel column chromatography (CH_2Cl_2/n -hexane = 1/2) to obtain a colorless powder (0.8 g, Yield = 67 %).

¹H NMR (600 MHz, CDCl₃, Me₄Si): δ (ppm) = 0.51-0.57 (1H, H_{n6}), 1.13-1.20 (1H, H_{x6}), 1.23-1.35 (3H, H_{x4}, H_{x6}), 1.40 (2H, H_{n4}), 1.72 (1H, H_{x7}), 1.80-1.85 (1H, H_{n6}), 2.50 (1H, H_{n7}), 2.72 (1H, H_{x3}), 2.79-2.82 (1H, H_{n5}, H_{x5}), 2.89 (1H, H_{n3}), 3.36 (2H, H_{n8}), 3.46 (2H, H_{n8}), 3.63 (2H, H_{x8}), 3.81 (2H, H_{x8}), 5.86 (1H, H_{n1}), 6.07-6.13 (2H, H_{x1}, H_{x2}, H_{n2}), 6.38 (2H, H₉), 6.77 (2H, H₁₀), 6.81-6.89 (25H, phenyl-H of HPB aromatics); ¹³C NMR (150 MHz, CDCl₃, Me₄Si): δ (ppm) = 29.55 (C_{n6}), 30.08 (C_{x6}), 39.02 (C_{n7}), 39.16 (C_{x7}), 42.19 (C_{x5}), 42.86 (C_{n5}), 43.30 (C_{x3}), 44.51 (C_{n3}), 44.54 (C_{x4}), 49.93 (C_{n4}), 71.89 (C_{n8}), 72.49 (C_{x8}), 113.21 (C₉), 125.70, 127.05, 131.95, 132.13, 132.83, 132.90, 133.43 (C₁₀), 133.51 (C_{n1}), 136.97 (C_{x2}), 137.31 (C_{x1}), 137.95 (C_{n2}), 140.54, 140.67, 140.84, 141.18, 141.39, 141.43, 141.53, 157.24 (C_{11}). MS (ESI-TOF): m/z [M]⁺ $C_{50}H_{40}$ O: calc: 656.3079, found: 656.3059



4. Synthesis of PNB-HPB

The monomer, HPB-containing norbornene derivative NBOHPB (0.8 g, 1.23 mmol), was dissolved in 4 mL of anhydrous CH_2Cl_2 and then degassed via freeze pump-thaw cycles. A catalyst solution was prepared by dissolving Ru (G1) (1 mg, 1.23 × 10⁻³ mmol) in 0.5 mL of anhydrous CH_2Cl_2 in an argon-filled drybox. After degassing the monomer solution completely, the catalyst solution was injected into the monomer solution by a syringe. The polymerization was performed at 25 °C for 1 h. The reaction was terminated by the addition of a small amount of ethyl vinyl ether (0.2 mL). **PNB-HPB** was obtained by precipitation in excess methanol and was further purified by dissolving in benzene and reprecipitating in methanol. **PNB-HPB** dissolved in benzene was filtered, frozen, and dried to afford colorless powder (0.65 g, Yield = 80%).

¹H NMR (600 MHz, CDCl₃, Me₄Si): δ (ppm) =0.70-3.10 (7H, H₃-H₇), 3.25-3.72 (2H, H₈), 5.07-5.41 (2H, H₁ and H₂), 6.13-6.42 (2H, H₉), 6.68 (2H, H₁₀), 6.72-6.90 (25H, phenyl-H of HPB aromatics); ¹³C NMR (150 MHz, CDCl₃, Me₄Si): δ (ppm) = 14.11, 19.73, 22.68, 27.11, 27.52, 29.71, 30.05, 31.92, 37.25, 39.97, 42.49, 44.49, 69.45, 70.58 (C₈), 112.87 (C₉), 125.07, 125.13, 126.56, 131.41, 132.30 (C₁₀), 132.70, 134.95 (C₁ and C₂), 140.00, 140.13, 140.32, 140.57, 140.71, 140.80, 156.59.



5. Synthesis of PHNB-HPB using hydrogenating agents

The polymer **PNB-HPB** (0.6 g, 0.92 mmol) was dissolved in 8 mL of xylene in a Schlenk tube. To the above solution hydrogenating agent, *p*-toluenesulfonhydrazide (1.25 g, 6.7 mmol), and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) were added. The polymer solution with hydrogenating agent was then degassed three times via a freeze-pump-thaw cycle and sealed. The solution was stirred at 120 °C for 12 h until the evolution of nitrogen stopped. The hydrogenated polymer **PHNB-HPB** was obtained by precipitation in excess methanol and was further purified by dissolving in benzene and reprecipitating in methanol. **PHNB-HPB** dissolved in benzene was filtered, frozen, and dried to obtain white powder (0.5 g, Yield = 83%).

¹H NMR (600 MHz, CDCl₃, Me₄Si): δ (ppm) =0.57-2.32 (11H, H₁-H₇), 3.43-3.85 (2H, H₈), 6.37 (2H, H₉), 6.71 (2H, H₁₀), 6.75-6.88 (25H, phenyl-H of HPB aromatics); ¹³C NMR (150 MHz, CDCl₃, Me₄Si): δ (ppm) = 25.60, 29.87, 35.35, 35.88, 36.27, 39.12, 39.32, 40.37, 41.44, 44.05, 67.96, 69.36 (C₈), 112.88 (C₉), 125.04, 125.12, 126.61, 131.21, 132.31 (C₁₀), 132.68, 139.94, 140.00, 140.13, 140.32, 140.56, 140.66, 140.71, 140.80, 156.71.



6. Synthesis of PHNB-HBC through cyclodehydrogenation

A total of 36 equivalents of iron (III) chloride in nitromethane (300 mg/mL) per hexaphenylbenzene unit were added dropwise to a solution of **PHNB-HPB** (100 mg, 0.15 mmol) in dichloromethane (100 mL). The resulting suspension was stirred for 2 days at room temperature and nitrogen stream was bubbled through the mixture throughout the entire reaction. The reaction was quenched with methanol (50 mL). The precipitate was filtered, washed with methanol followed by CH_2CI_2 and dried under vacuum (90 mg, Yield = 90%)



Fig. S1 (a) ¹H NMR and (b) ¹³C NMR spectra of NBOHPB in CD_2CI_2 .



Fig. S2 (a) ¹H NMR and (b) ¹³C NMR spectra of PNB-HPB in CDCl₃.



Fig. S3 (a) ¹H NMR and (b) ¹³C NMR spectra of PHNB-HPB in $CDCI_3$.



Scheme S1. The synthesis of model compound hexa-peri-hexabenzocoronene (HBC).



Fig. S4 3D structure of single unit of PNB-HPB

HRTEM, PLE map and optical properties data of polymers were described below



Fig. S5. HRTEM of PHNB-HBC.



Fig. S6. Schematic diagram of PHNB-HBC (solid state) according to the HRTEM image.



Fig. S7. PLE image of PHNB-HPB in THF (10⁻⁶ M).



Fig. S8. PLE spectra of PHNB-HBC dispersion (0.1 mg ml⁻¹) in (a) CHP, (b) NMP, (c) THF and (d) toluene.

Table 1. Optical properties of PHNB-HBC, P1 and P2 dispersed in different solvents

	Dispersion λ (nm)			
Polymer	Solvent	Abs. max	PL ^b	(A _{max} /A ₄₂₁) _{Ind} ^c
PHNB-HBC	СНР	360 (1.77) ^a	465, 496	4.44
PHNB-HBC	NMP	360 (1.91) ^a	465, 496	2.01
PHNB-HBC	THF	358 (0.79) ^a	463, 494	1.60
PHNB-HBC	Toluene	360 (0.59) ^a	464, 495	1.31
P1	THF	372 (0.39) ^a	416, 659	1.34
P2	THF	364 (1.54) ^a	470, 483, 493, 517, 616, 651	1.56
^a Absorbance value of dispersions (0.1 mg/mL) from UV-Vis spectra.				
^b Excitation wavelength was at Abs. max of the dispersions.				

^c Ratio of absorbance at Abs. max to absorbance at 421 nm for the exfoliation of **PHNB-HBC, P1** and **P2**.