

**Electronic Supplementary Information**

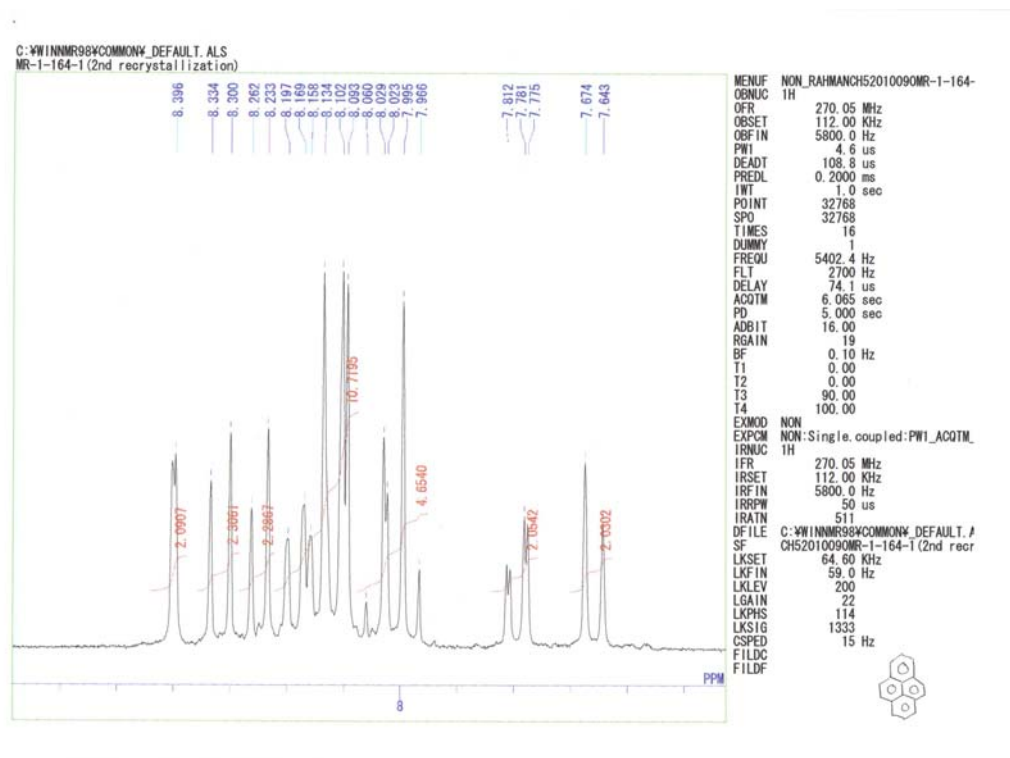
# Diameter-Based Separation of Single-Walled Carbon Nanotubes through Selective Extraction with Dipyrene Nanotweezers

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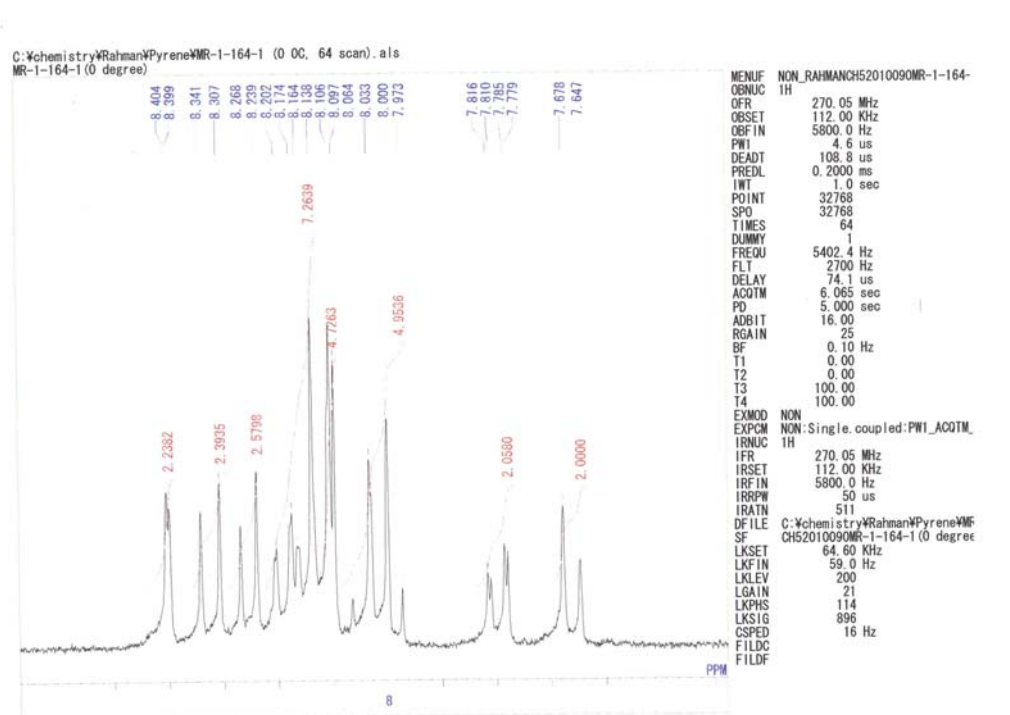
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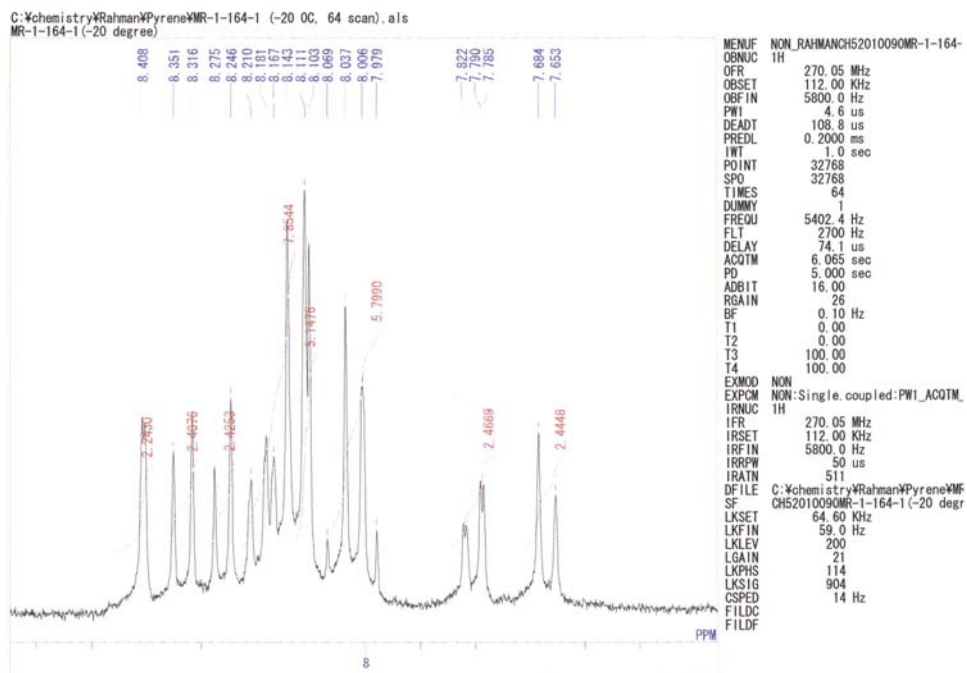
a) at room temperature



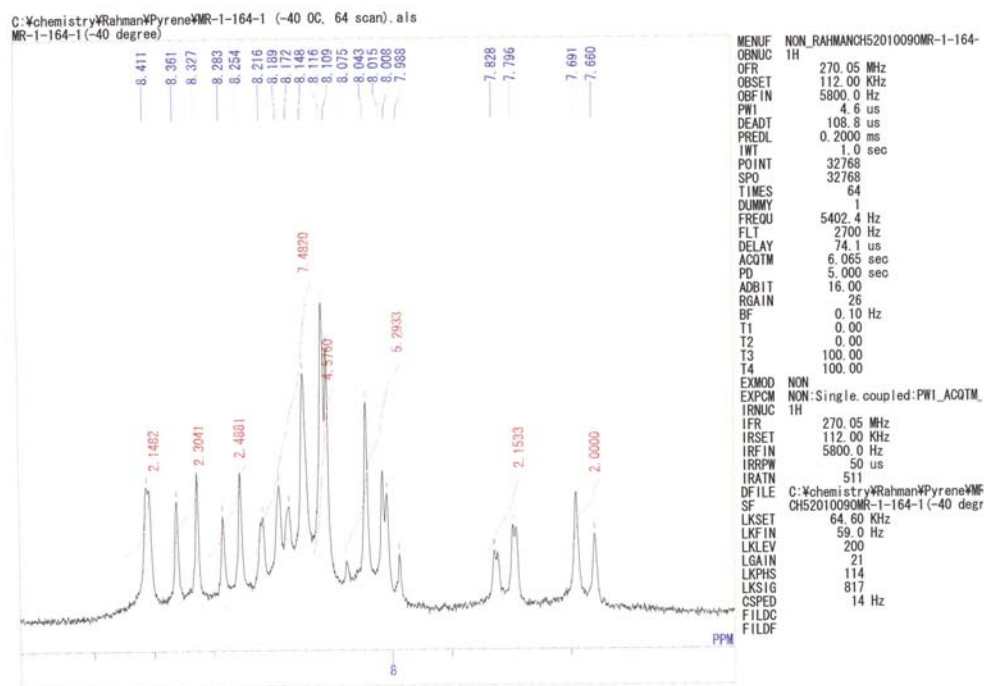
b) at 0 °C



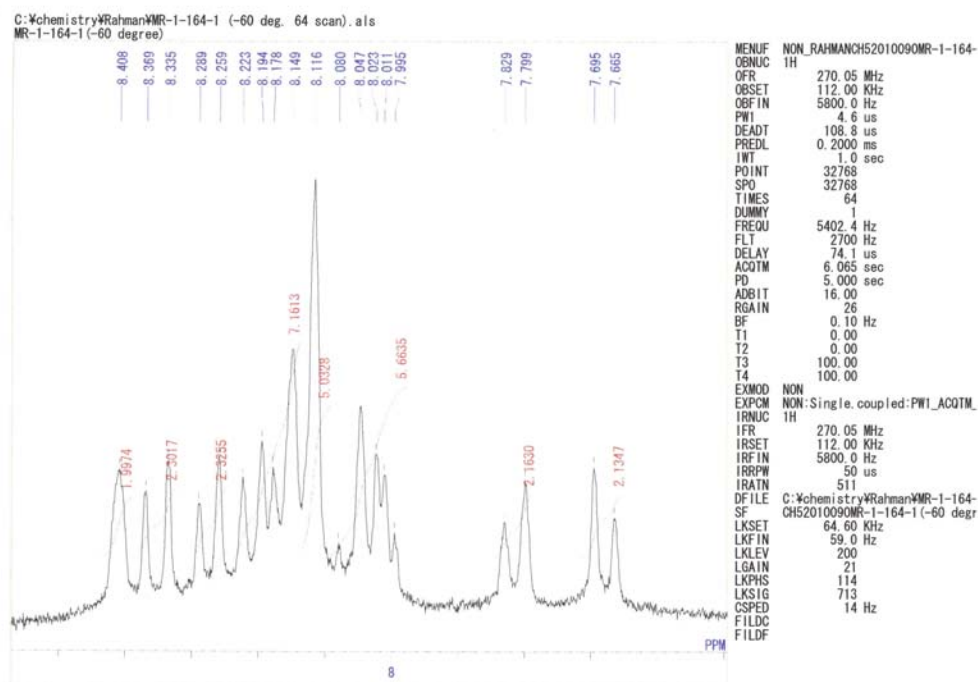
c) at  $-20\text{ }^{\circ}\text{C}$



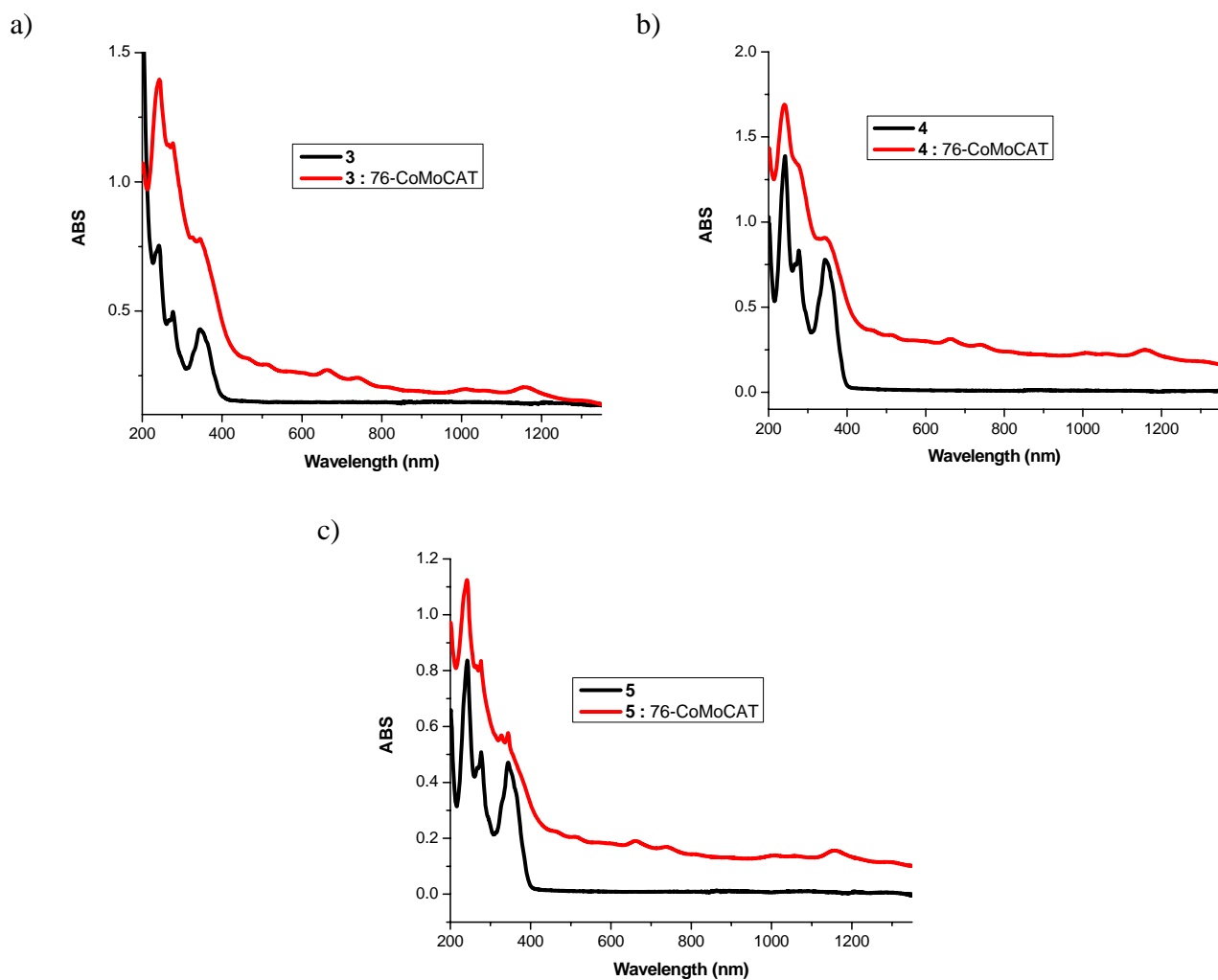
d) at  $-40\text{ }^{\circ}\text{C}$



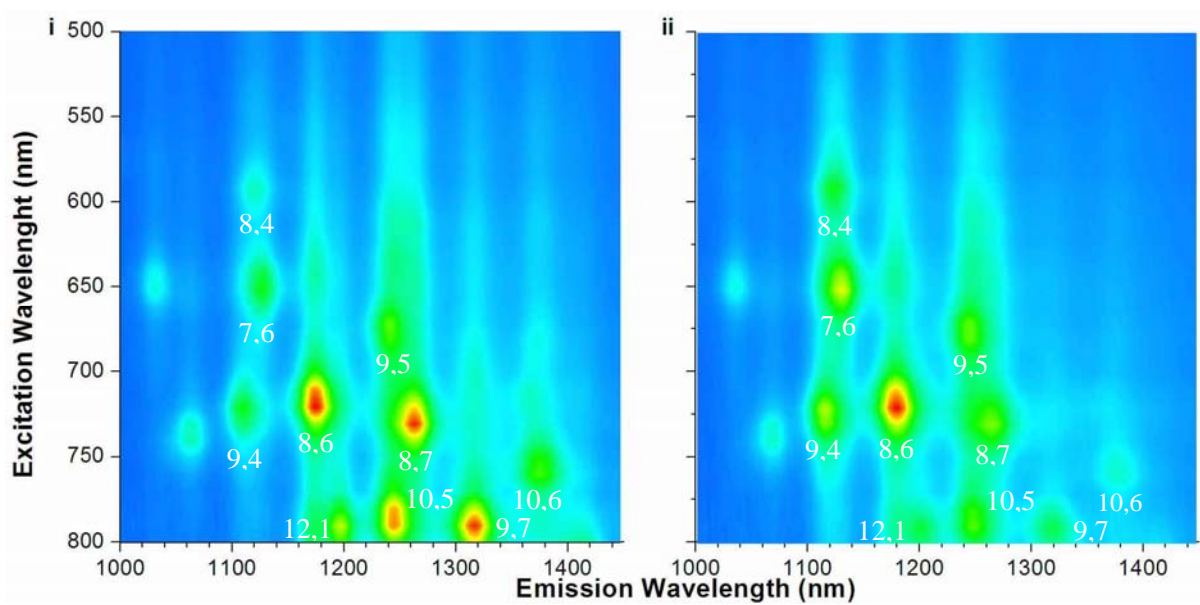
e) at  $-60\text{ }^{\circ}\text{C}$



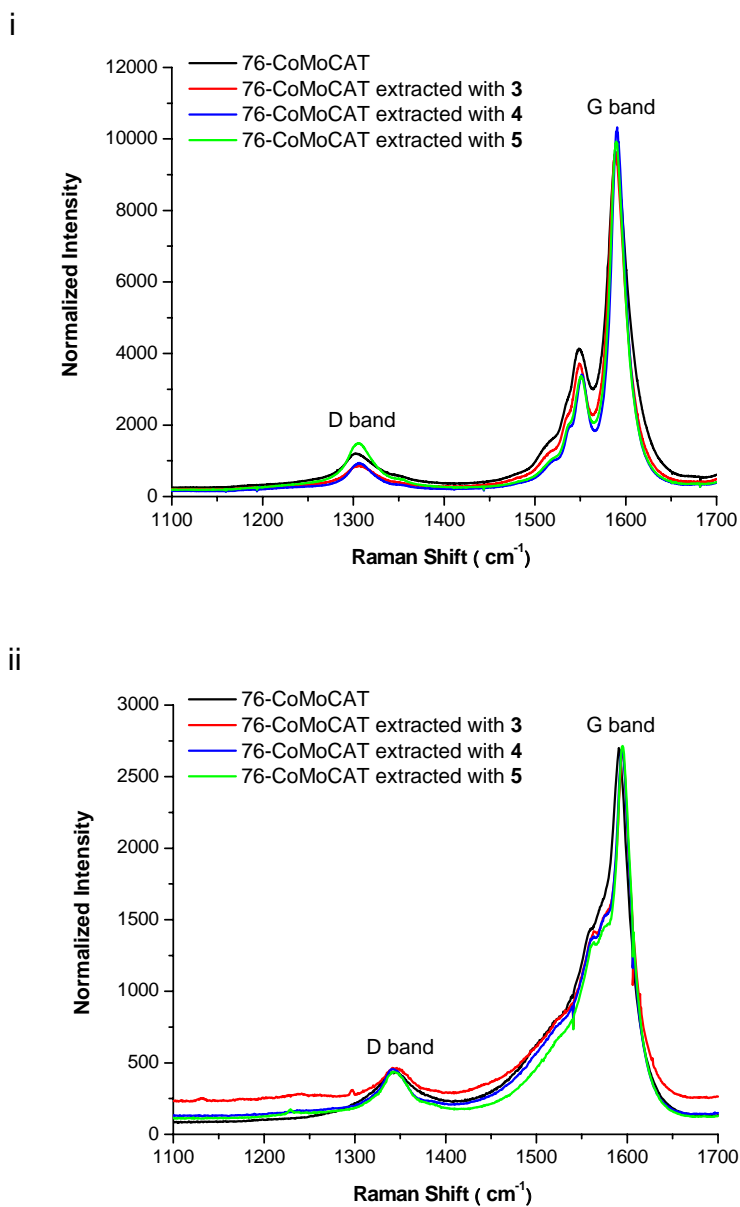
**Fig. S1.**  $^1\text{H}$ -NMR spectrum of **3** in  $\text{CDCl}_3$  at room temperature (a),  $0\text{ }^{\circ}\text{C}$  (b),  $-20\text{ }^{\circ}\text{C}$  (c),  $-40\text{ }^{\circ}\text{C}$  (d), and  $-60\text{ }^{\circ}\text{C}$  (e).



**Fig. S2.** UV-vis-NIR spectra of **3** (a), **4** (b), and **5** (c) in methanol and their methanol supernatants after extraction of 76-CoMoCAT.



**Fig. S3.** Photoluminescence (PL) spectra of HiPco-SWNTs (i) before and (ii) after extraction with **3**.



**Fig. S4.** Raman spectra of 76-CoMoCAT before and after extraction with **3**, **4** and **5** in the G- and D-band region at the excitation wavelength of 633 nm (i) and 488 nm (ii).

## Experimental section

### Materials

CoMoCAT SWeNTs SG65 and SG76, simply designated as 65-CoMoCAT and 76-CoMoCAT respectively in this paper, were purchased from SouthWest NanoTechnologies, Inc. All the reagents were obtained from Sigma-Aldrich Chemical Co., Wako Pure Chemical Industries, Ltd., and Tokyo Chemical Industry Co., Ltd. and were used as received, unless otherwise specified. For synthesis, DMF, toluene, and THF were distilled from MgSO<sub>4</sub>, Na/benzophenone, and Na/benzophenone, respectively, under nitrogen prior to use.

Equipment. UV–vis–NIR absorption and photoluminescence spectra were recorded on a UV-3100PC scanning spectrophotometer (Shimadzu Co.) and an NIR-PL system (Shimadzu Co.), respectively. Raman spectra of solid samples were measured on a LabRam HR800 (Horiba Ltd.) spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR (270 and 67.5 MHz, respectively) analysis, and MALDI-TOF MS measurement were performed on a JEOL JNM-EX270 spectrometer and Voyager RP (Applied Biosystems), respectively. Centrifugation was carried out with Beckman Avanti J-E, Optima-TL, and L-70. Tip-sonication was performed with MISONIX (550 W, 20 kHz).

### Synthesis of *N*-octyl-3,6-bis(2'-pyrenyl)carbazole **1**

To a suspension of Pd(PPh<sub>3</sub>)<sub>4</sub> (47 mg, 0.040 mmol), 2-(2-pyrenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>1</sup> (170 mg, 0.52 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (245 mg, 0.75 mmol) in DMF/toluene (1/1 v/v) (10 mL) was added *N*-octyl-3,6-dibromocarbazole<sup>2</sup> (109 mg, 0.25 mmol), and the mixture was stirred at 85 °C for 24 h under Ar. After cooling down to room temperature, water (10 mL) was added to the reaction mixture and it was extracted with chloroform (10 mL x 3). The combined extracts were dried over anhydrous sodium sulfate and concentrated. The residual solid was chromatographed on silica gel using hexane–AcOEt (10:1) to give **1**. Yield: 45%; white powder; mp: 282-285 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): 0.90 (3H, t, *J* 6.6), 1.30 (10H, s), 2.02 (2H, t, *J* 6.8), 4.45 (2H, t, *J* 7.0), 7.63 (2H, d, *J* 8.4,



CarH), 7.01 (2H, t, *J* 7.7, PyrH), 8.07 (2H, d, *J* 8.6, CarH), 8.17 (4H, d, *J* 8.9, PyrH), 8.19 (4H, d, *J* 9.1, PyrH), 8.20 (4H, d, *J* 7.6, PyrH), 8.57 (4H, s, PyrH), 8.75 (2H, s, CarH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): 14.08, 22.63, 27.41, 29.15, 29.22, 29.45, 31.84, 43.50, 109.41, 119.99, 123.92, 124.73, 125.04, 125.72, 126.26, 127.61, 127.71, 131.10, 131.68, 132.76, 139.86, 140.64; UV-vis (Dioxane): λ<sub>max</sub>: 246, sh 265.5, 277, 309, 324, and 340 nm; MALDI-TOF MS: *m/z* Calculated for C<sub>52</sub>H<sub>41</sub>N: 679.32; Found: 679.85.

### Synthesis of *N*-(2,5,8,11-tetraoxatridecan-13-yl)-3,6-bis(2'-pyrenyl)carbazole **2**

2-Pyrene nanotweezers **2** was prepared in the same procedure as that of **1** except for using *N*-(2,5,8,11-tetraoxatridecan-13-yl)-3,6-dibromocarbazole<sup>2, 3</sup> (102 mg, 0.20 mmol) as carbazole dibromide. Yield: 35%; brown solid; mp: 162-165 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): 3.32 (3H, s), 3.47–3.61 (12H, m), 4.01 (2H, t, *J* 5.8), 4.64 (2H, t, *J* 5.8), 7.68 (2H, d, *J* 8.4, CarH), 8.01 (2H, t, *J* 8.1, PyrH), 8.06 (2H, d, *J* 9.0, CarH), 8.11 (4H, d, *J* 8.9, PyrH), 8.19 (4H, d, *J* 9.1, PyrH), 8.20 (4H, d, *J* 7.6, PyrH), 8.57 (4H, s, PyrH), 8.73 (2H, s, CarH)); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): 43.53, 58.98, 69.45, 70.43, 70.55, 70.59, 70.64, 70.07, 71.84, 109.67, 119.84, 123.49, 123.85, 123.91, 124.65, 125.04, 125.71, 126.26, 127.57, 127.69, 131.03, 131.63, 132.92, 139.72, 140.75; UV-vis (MeOH): λ<sub>max</sub>: 224, sh 242.5, 261, 273, 304.5, 321.5, and 338 nm; MALDI-TOF MS: *m/z* Calculated for C<sub>53</sub>H<sub>41</sub>NO<sub>4</sub>: 757.32; Found: 757.76.

### Synthesis of *N*-octyl-3,6-bis(1'-pyrenyl)carbazole **3**

*N*-Octyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole<sup>2</sup> (106 mg, 0.2 mmol), 1-bromopyrene (126 mg, 0.45 mmol), Cs<sub>2</sub>CO<sub>3</sub> (196 mg, 0.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (34.5 mg, 0.030 mmol) were dissolved in a mixture of DMF/toluene (1/1 v/v) (10 mL) and distilled water (0.2 mL). The reaction mixture was allowed to react at 85 °C for 24 h under Ar. After cooling down to room temperature, water (10 mL) was added to the reaction mixture and it was extracted with chloroform (10 mL x 3). The combined extracts were dried over anhydrous sodium sulfate and concentrated. The residual solid was chromatographed on silica gel using hexane–AcOEt (10:1) to give **3**. Yield: 70%;

pale yellow solid; mp: 205-208 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz): 0.92 (3H, t,  $J$  6.8), 1.33 (10H, s), 2.08 (2H, t,  $J$  8.4), 4.51 (2H, t,  $J$  7.2), 7.66 (2H, d,  $J$  8.4, CarH), 7.79 (2H, d,  $J$  7.8, CarH), 8.00 (2H, t,  $J$  7.7, PyrH), 8.04 (2H, d,  $J$  8.4, PyrH), 8.09–8.16 (8H, m, PyrH), 8.19 (2H, d,  $J$  7.6, PyrH), 8.25 (2H, d,  $J$  7.7, PyrH), 8.32 (2H, d,  $J$  9.2, PyrH), 8.40 (2H, s, CarH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz): 14.12, 22.66, 27.48, 29.25, 29.26, 29.48, 31.86, 43.54, 108.69, 122.49, 123.06, 124.62, 124.62, 124.90, 124.99, 125.05, 125.69, 125.90, 127.13, 127.27, 127.47, 128.21, 128.71, 128.84, 130.24, 131.05, 131.53, 132.04, 138.63, 140.27; UV–vis (MeOH):  $\lambda_{\text{max}}$ : 243, 266, 277, 326, and 344.5 nm; MALDI-TOF MS:  $m/z$  Calculated for  $\text{C}_{52}\text{H}_{41}\text{N}$ : 679.32; Found: 679.61.

#### Synthesis of *N*-(2,5,8,11-tetraoxatridecan-13-yl)-3,6-bis(1'-pyrenyl)carbazole 4

1-Pyrene nanotweezers 4 was prepared in the same procedure as that of 3 except for using *N*-(2,5,8,11-tetraoxatridecan-13-yl)-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole<sup>2, 3</sup> (152 mg, 0.25 mmol) as carbazole diboronate. Yield: 32%; yellowish green powder; mp: 90-93 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz): 3.33 (3H, s), 3.49–3.69 (12H, m), 4.08 (2H, t,  $J$  5.7), 4.73 (2H, t,  $J$  5.9), 7.72 (2H, d,  $J$  8.4, CarH), 7.78 (2H, d,  $J$  8.4, CarH), 8.00 (2H, t,  $J$  7.7, PyrH), 8.05 (2H, d,  $J$  7.9, PyrH), 8.09–8.15 (8H, m, PyrH), 8.18 (2H, d,  $J$  7.6, PyrH), 8.25 (2H, d,  $J$  7.9, PyrH), 8.30 (2H, d,  $J$  9.2, PyrH), 8.39 (2H, s, CarH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz): 43.64, 58.97, 69.57, 70.53, 70.65, 70.74, 70.74, 71.14, 71.92, 108.97, 122.35, 123.20, 124.64, 124.64, 124.92, 125.01, 125.08, 125.65, 125.92, 127.17, 127.31, 127.47, 128.19, 128.77, 128.87, 130.31, 131.07, 131.57, 132.38, 138.59, 140.51; UV–vis (MeOH):  $\lambda_{\text{max}}$ : 242, sh 267.5, 277.5, and 343.5 nm; MALDI-TOF MS:  $m/z$  Calculated for  $\text{C}_{53}\text{H}_{43}\text{NO}_4$ : 757.32; Found: 757.69.

#### Synthesis of *N*-octadecyl-3,6-bis(1'-pyrenyl)carbazole 5

1-Pyrene nanotweezers 5 was prepared in the same procedure as that of 3 except for using *N*-octadecyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole<sup>2</sup> (235 mg, 0.35 mmol) as carbazole diboronate. Yield: 45%; light yellow solid; mp: 72-74 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz): 0.88 (3H, t,  $J$

6.7), 1.25 (30H, s), 2.08 (2H, t,  $J$  7.3), 4.51 (2H, t,  $J$  7.1), 7.66 (2H, d,  $J$  8.4, CarH), 7.79 (2H, d,  $J$  8.5, CarH), 8.00 (2H, t,  $J$  7.6, PyrH), 8.05 (2H, d,  $J$  8.4, PyrH), 8.09–8.15 (8H, m, PyrH), 8.18 (2H, d,  $J$  7.6, PyrH), 8.25 (2H, d,  $J$  7.9, PyrH), 8.32 (2H, d,  $J$  9.2, PyrH), 8.40 (2H, s, CarH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz): 14.22, 22.78, 27.58, 29.31, 29.44, 29.61, 29.78 (10 carbon), 32.00, 43.63, 108.64, 122.40, 123.02, 124.53, 124.53, 124.82, 124.94, 125.00, 125.62, 125.79, 127.05, 127.19, 127.39, 128.14, 128.64, 128.79, 130.18, 130.99, 131.48, 131.99, 138.56, 140.20; UV–vis (MeOH):  $\lambda_{\text{max}}$ : 242, 267, 277, sh 327, and 344 nm; MALDI-TOF MS:  $m/z$  Calculated for  $\text{C}_{62}\text{H}_{61}\text{N}$ : 819.48; Found: 819.71.

### Extraction of 76-CoMoCAT-SWNTs with 1-Pyrene Nanotweezers.

76-CoMoCAT (10 mg) and 1-pyrene nanotweezers (10 mg) in methanol (35 mL) were bath-sonicated (Branson, 5510, 42 kHz, 135 W) at 20 °C for about 65 h. After the resulting black suspension was centrifuged at 50400  $g$  at 20 °C for 1 h (Beckman Avanti J-E using JA-21 as a rotor), the supernatant was subjected to UV–vis–NIR measurements (Fig. S2). After concentration of the supernatant by evaporating the solvent with a rotavap and drying *in vacuo*, the resulting residue was washed with THF several times for thorough removal of the dipyrenes. The washed SWNTs were analyzed with Raman spectroscopy at excitation of 633 and 488 nm (Fig. 3). The solid sample was dispersed into  $\text{D}_2\text{O}$  (18.5 ml) in the presence of SDBS (10 mg/ml) by tip-type ultrasonication (Astrason XL2020, 550 W) at 0 °C for 2 h. After centrifugation at 136000  $g$  for 30 min, the upper layer (~75%) of the supernatant was subjected to vis-NIR (Fig. 2) and PL measurements (Fig. 1). For dissolution of as-obtained 76-CoMoCAT, tip-type ultrasonication was carried out for 40 min under the same conditions followed by centrifugation at 543000  $g$  for 60 min.

### Reference

1. D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder and R. N. Perutz, *Chem. Commun.*, 2005, 2172.
2. Y. Wang, L. Hou, K. Yang, J. Chen, F. Wang and Y. Cao, *Macromol. Chem. Phys.*, 2005, **21**,

2190.

3. S. J. Meunier, Q. Wu, S.-N. Wang and R. Roy, *Can. J. Chem.*, 1997, **75**, 1472.