

Supplementary Information

A tubular macrocycle from covalently linked anthracene and *meta*-phenylene spacers

K. Hagiwara, Y. Sei, M. Akita, and M. Yoshizawa*

Contents

- Materials and methods
- Synthesis of MOM-protected 1-bromo-3-(2-methoxyethoxy)phenol
- Synthesis of MOM-protected (2-methoxyethoxy)phenyl boronate
- Synthesis of half-tube **2**_{MOM} (¹H and ¹³C NMR, ¹H-¹H COSY, NOESY, HSQC, and MALDI-TOF MS spectra)
- Synthesis of half-tube **2**_{OTf} (¹H and ¹³C NMR, ¹H-¹H COSY, NOESY, HSQC, and MALDI-TOF MS spectra)
- Synthesis of half-tube **2**_{Bpin} (¹H and ¹³C NMR, ¹H-¹H COSY, NOESY, HSQC, and MALDI-TOF MS spectra)
- Synthesis of nanotube **1** (¹H and ¹³C NMR, ¹H-¹H COSY, NOESY, HSQC, and MALDI-TOF MS spectra)
- Synthesis of half-tube **2'**_{MOM}
- Synthesis of half-tube **2'**_{OTf}
- Synthesis of half-tube **2'**_{Bpin}
- Synthesis of tube **1'** (HRMS spectrum and X-ray crystal data)

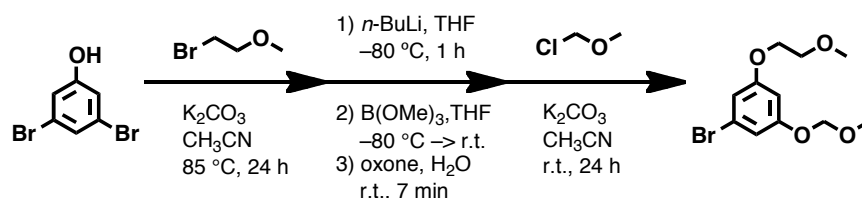
Materials and methods

NMR: Bruker AVANCE-400 (400 MHz), GC MS: Shimadzu Parvum2/ULBON HR-1, MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, FT IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Fluorescence: SHIMADZU RF-5300PC, X-ray single crystal structural analysis: Bruker APEXII ULTRA/CCD diffractometer, Elemental analysis: LECO CHNS-932 VTF-900, Absolute PL quantum yield: Hamamatsu C9920-02G with an integration sphere; recycled GPC: JAI

LC-9225NEXT.

Solvents and reagents: TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO CHEMICAL CO., INC., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc. 1,5-Di(10-bromoanthracen-9-yl)-2,4-di(2-methoxyethoxy)benzene (**3**) was synthesized according to previously reported procedures (M. Yoshizawa *et al.*, *J. Am. Chem. Soc.*, **2011**, *133*, 11438–11441).

Synthesis of MOM-protected 1-bromo-3-(2-methoxyethoxy)phenol KH-182



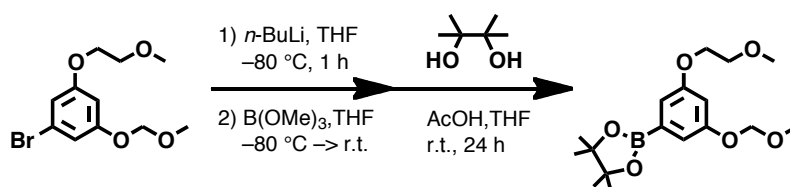
3,5-Dibromophenol (4.012 g, 15.92 mmol), K_2CO_3 (8.450 g, 61.14 mmol), and dry CH_3CN (40 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar and the solution was filled with N_2 . After stirring the mixture at $0\text{ }^\circ\text{C}$, 2-bromoethoxymethyl ether (4.80 mL, 51.1 mmol) was added to the solution. The resultant mixture was further stirred at $0\text{ }^\circ\text{C}$ for 10 min and then the solution was warmed to $85\text{ }^\circ\text{C}$ for 24 h. The crude product was extracted with CH_2Cl_2 and combined organic phase was dried over MgSO_4 , filtrated, and concentrated under reduce pressure to obtain a yellow solution. A 2-necked 100 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with N_2 after cooling to r.t. The yellow solution and dry THF (50 mL) were added to this flask. A hexane solution (2.69 M) of *n*-butyllithium (6.20 mL, 16.7 mmol) was then added dropwise to this flask at $-80\text{ }^\circ\text{C}$ under N_2 . After stirring the mixture at $-80\text{ }^\circ\text{C}$ for 1 h, a dry THF solution (20 mL) of $\text{B}(\text{OMe})_3$ (2.00 mL, 18.0 mmol) was added to the solution. The resultant mixture was further stirred at $-80\text{ }^\circ\text{C}$ for 1 h and then the solution was warmed to r.t. for 1 h. Oxone (10.620 g, 17.274 mmol) was added to the solution and stirred for 8 min at r.t. After stirring the mixture, a aqueous solution of NaHSO_3 was added to the solution and the crude product was extracted with CH_2Cl_2 and the combined organic phase was dried

over MgSO_4 , filtrated, and concentrated under reduce pressure to obtain a yellow solution. The obtained solution, K_2CO_3 (8.133 g, 58.84 mmol), and dry CH_3CN (40 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar and the solution was filled with N_2 . After stirring the mixture at 0°C , chloromethyl methyl ether (3.20 mL, 42.2 mmol) was added to the solution. The resultant mixture was further stirred at 0°C for 10 min and then the solution was warmed to r.t. for 24 h. The crude product was extracted with CH_2Cl_2 and combined organic phase was dried over MgSO_4 , filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to give MOM-protected 1-bromo-3-(2-methoxyethoxy)phenol as a yellow solution (3.063 g, 10.52 mmol, 66%).

^1H NMR (400 MHz, CDCl_3 , r.t.): δ 6.81 (dd, $J = 1.0, 0.8$ Hz, 1H), 6.73 (dd, $J = 1.0, 0.8$ Hz, 1H), 6.70 (dd, $J = 1.0, 1.0$ Hz, 1H), 5.12 (s, 2H), 4.07 (t, $J = 4.8$ Hz, 2H), 3.73 (t, $J = 4.8$ Hz, 2H), 3.46 (s, 3H), 3.44 (s, 3H).

GC-MS : m/z Calcd. for $\text{C}_{11}\text{H}_{15}\text{BrO}_4$ 290, Found 290 $[\text{M}]^+$.

Synthesis of MOM-protected (2-methoxyethoxy)phenylboronic acid pinacol ester KH-189



A 2-necked 100 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with N_2 after cooling to r.t. MOM-protected 1-bromo-3-(2-methoxyethoxy)phenol (1.549 g, 5.320 mmol) and dry THF (50 mL) were added to this flask. A hexane solution (2.69 M) of n -butyllithium (2.20 mL, 5.92 mmol) was then added dropwise to this flask at -80°C under N_2 . After stirring the mixture at -80°C for 1 h, a dry THF solution (20 mL) of $\text{B}(\text{OMe})_3$ (0.70 mL, 6.3 mmol) was added to the solution. The resultant mixture was further stirred at -80°C for 1 h and then the solution was warmed to r.t. for 1 h. Pinacol (0.729 g, 6.17 mmol) was

added to the solution and stirred at r.t. for 10 min. After stirring the mixture, AcOH was added to the solution and stirred at r.t. for 24h. The crude product was extracted with CH_2Cl_2 and combined organic phase was dried over MgSO_4 , filtrated, and purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford MOM-protected (2-methoxyethoxy)phenylboronic acid pinacol ester as a yellow solution (0.959 g, 2.83 mmol, 53%).

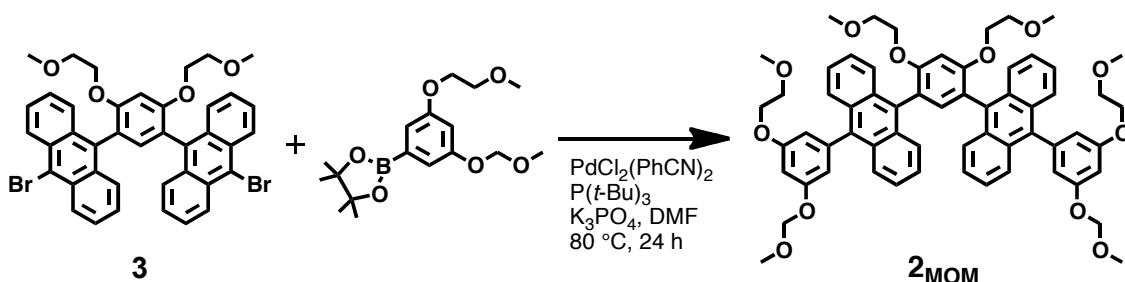
$^1\text{H NMR}$ (400 MHz, CDCl_3 , r.t.): δ 7.06 (d, $J = 2.4$ Hz, 1H), 7.00 (d, $J = 2.4$ Hz, 1H), 6.75 (dd, $J = 2.4, 2.4$ Hz, 1H), 5.17 (s, 2H), 4.14 (t, $J = 4.8$ Hz, 2H), 3.74 (t, $J = 4.8$ Hz, 2H), 3.46 (s, 3H), 3.44 (s, 3H), 1.33 (s, 12H).

GC-MS : m/z Calcd. for $\text{C}_{17}\text{H}_{27}\text{BO}_6$ 338, Found 338 $[\text{M}]^+$.

E.A.: Calcd. for $\text{C}_{17}\text{H}_{27}\text{BO}_6 \cdot 0.25\text{CH}_2\text{Cl}_2$: C, 56.29; H, 7.46. Found: C, 56.00; H, 7.66.

Synthesis of half tube 2_{MOM}

KH-167-2



Bromoanthracene dimer **3** (0.686 g, 0.932 mmol), MOM-protected (2-methoxyethoxy)phenylboronic acid pinacol ester (1.826 g, 5.399 mmol), K_3PO_4 (1.159 g, 5.459 mmol), and dry DMF (30 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar and the solution was stirred under N_2 . $\text{PdCl}_2(\text{PhCN})_2$ (0.041 g, 0.11 mmol) and dry DMF (10 mL) were added to a 2-necked 50 mL glass flask containing a magnetic stirring bar and the flask was filled with N_2 . A hexane solution (0.95 M) of tri-*tert*-butylphosphine (0.20 mL, 0.19 mmol) was added to this flask. After stirring the mixture for 30 min at r.t., the mixture was added to the 100 mL flask and then the resulted solution was further stirred at 80°C for 24 h. The mixture was concentrated under reduce pressure. The crude product was extracted with CHCl_3 . The resultant solid was purified by silica-gel column chromatography

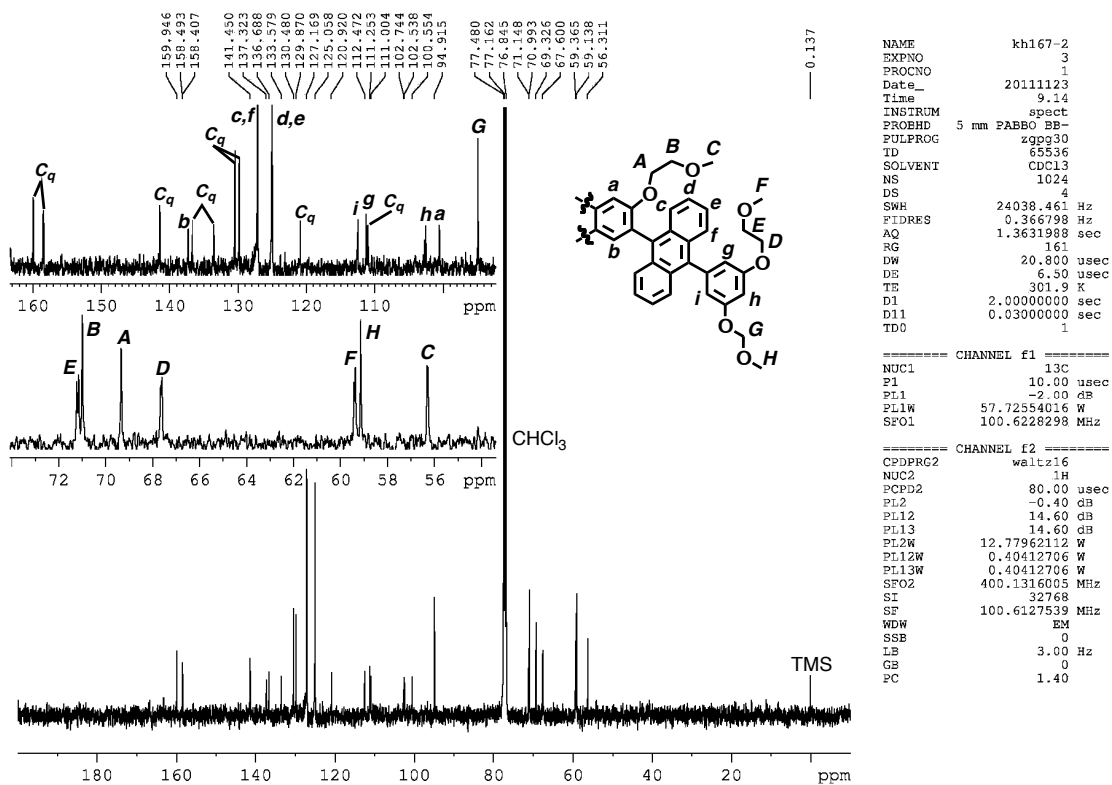


Fig. S2. ¹³C NMR (100 MHz, CDCl₃, r.t.) spectrum of 2_{MOM}.

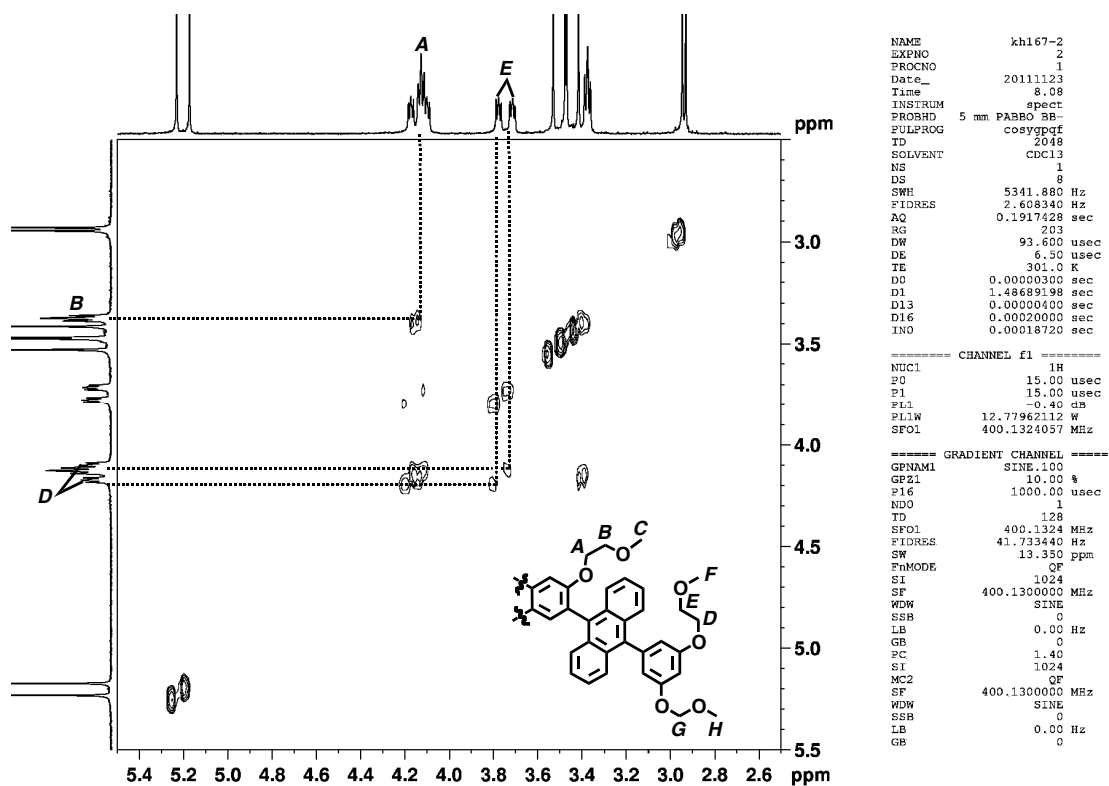


Fig. S3. HH COSY (400 MHz, CDCl₃, r.t.) spectrum of 2_{MOM} (aliphatic region).

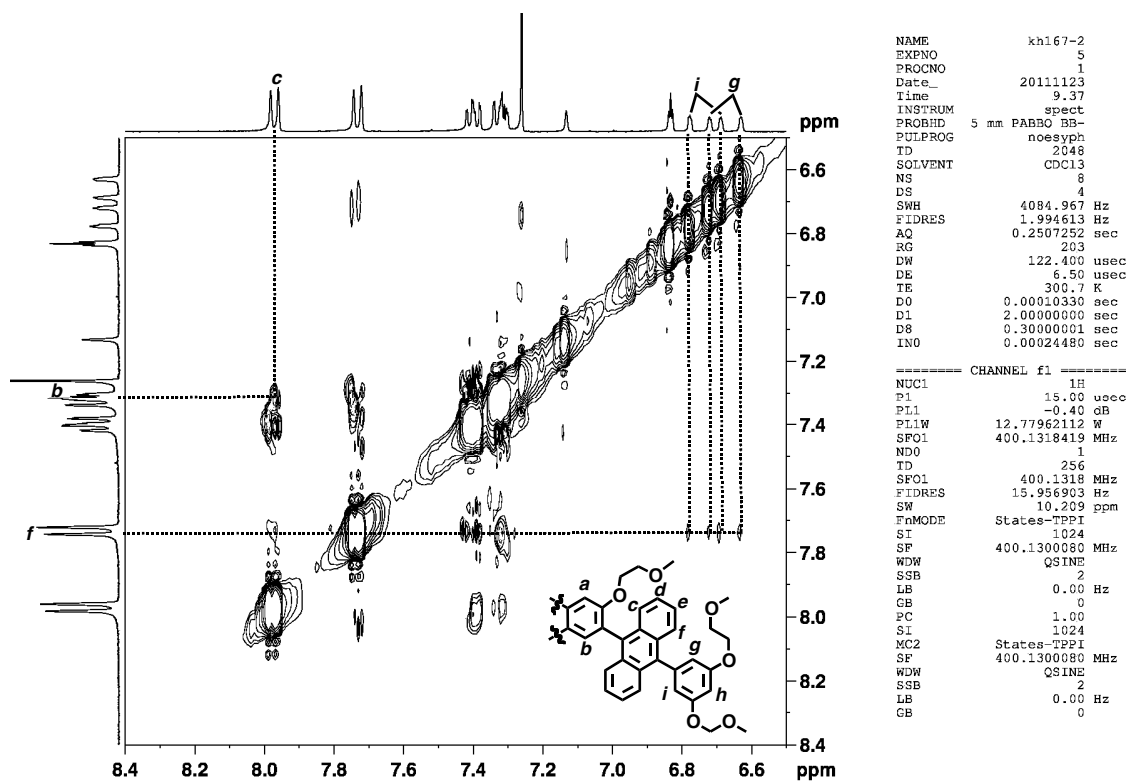


Fig. S6. NOESY (400 MHz, CDCl₃, r.t.) spectrum of **2**_{MOM} (aromatic region).

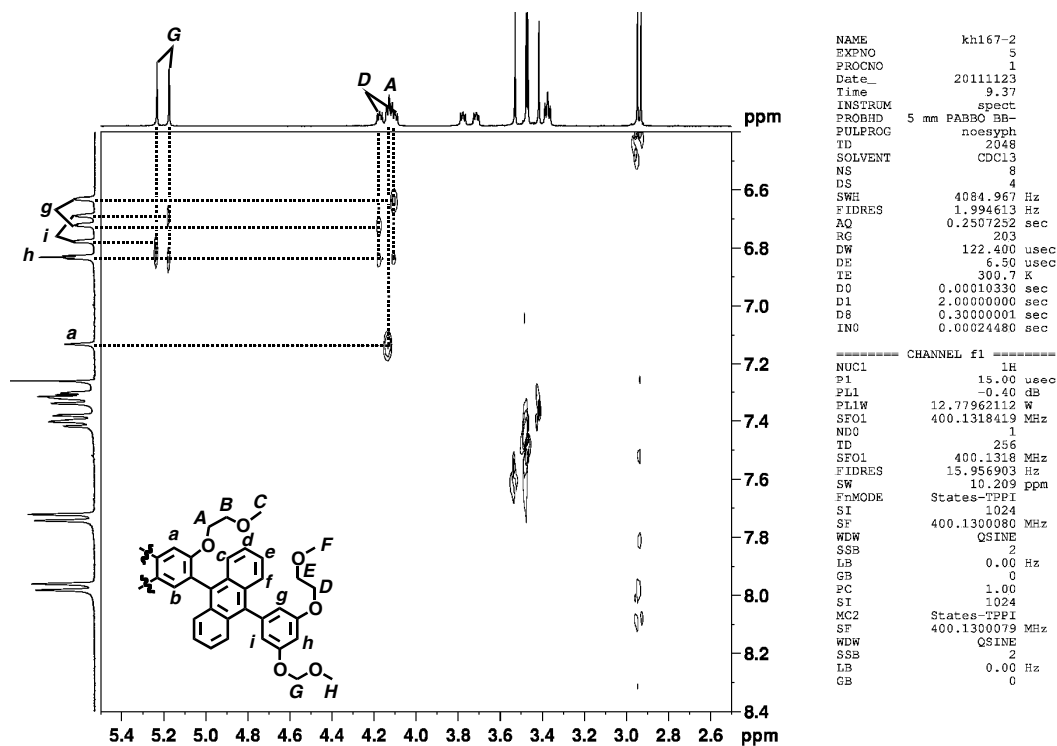


Fig. S7. NOESY (400 MHz, CDCl₃, r.t.) spectrum of **2**_{MOM}.

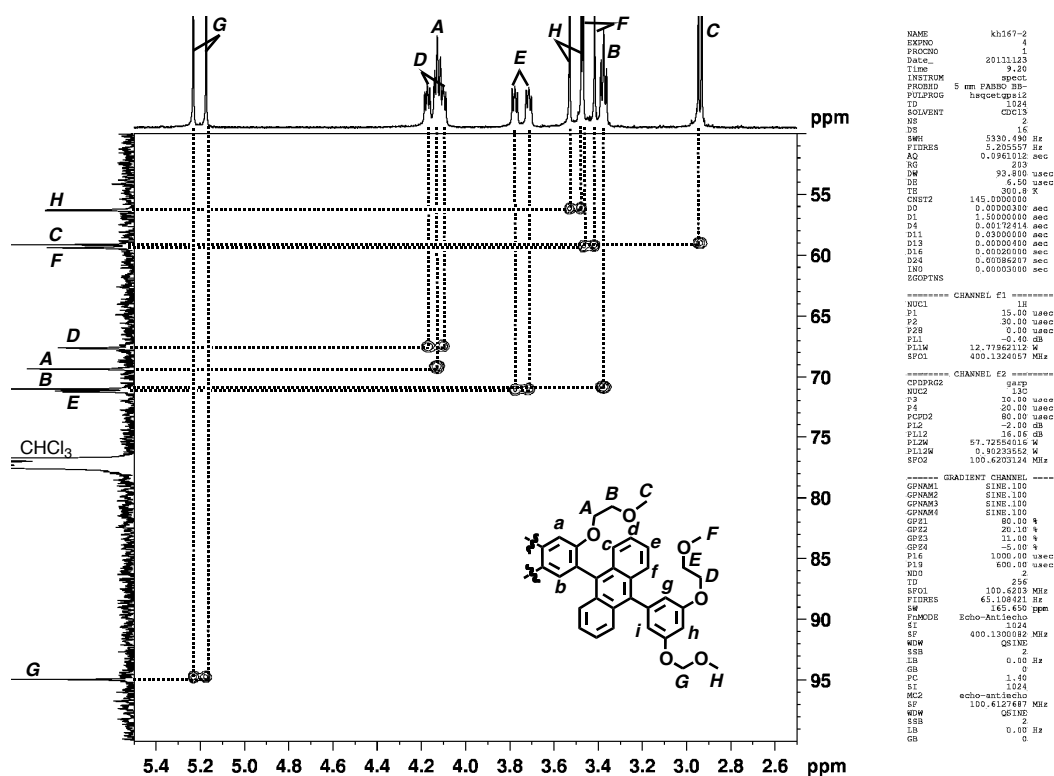


Fig. S8. HSQC (400 MHz, CDCl₃, r.t.) spectrum of **2**_{MOM} (aliphatic region).

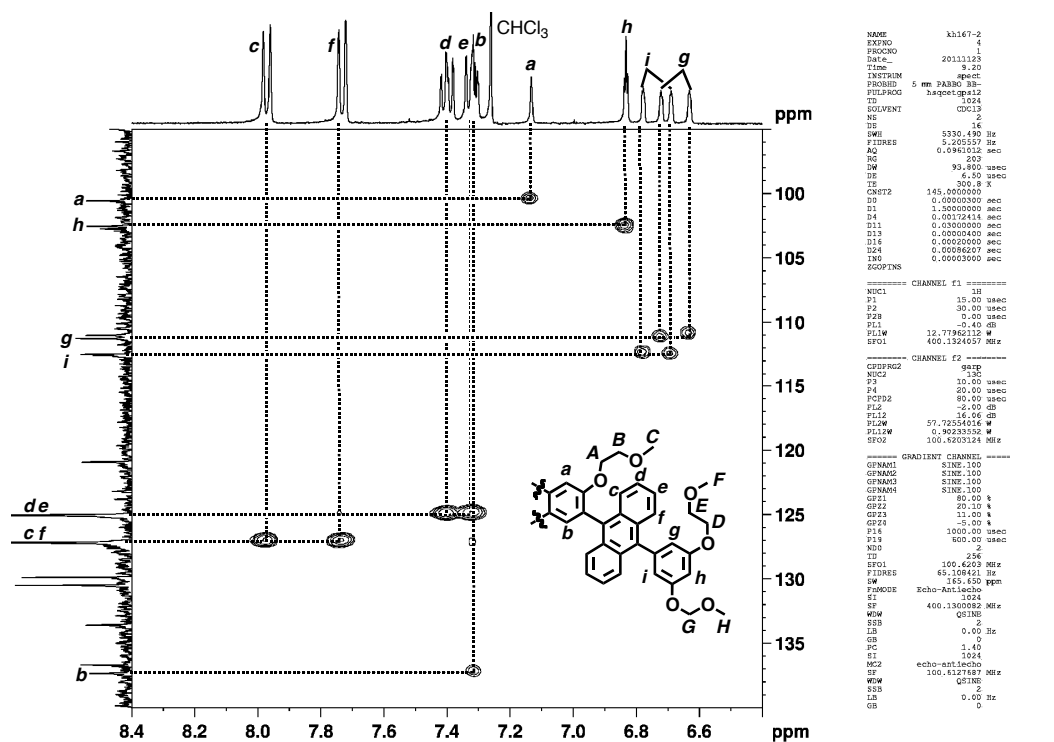


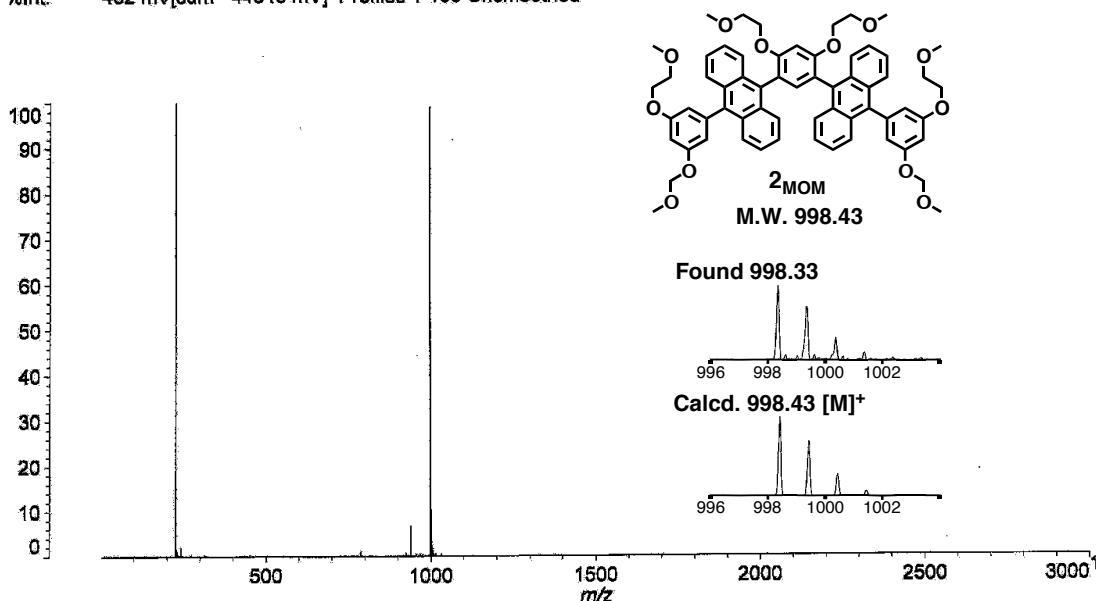
Fig. S9. HSQC (400 MHz, CDCl₃, r.t.) spectrum of **2**_{MOM} (aromatic region).

KH-167-1

Data: KH167-1-dith-1-10-0001.M1[c] 4 Jun 2011 14:37 Cal: akita-yoshizawa-ref 4 Jun 2011 14:36

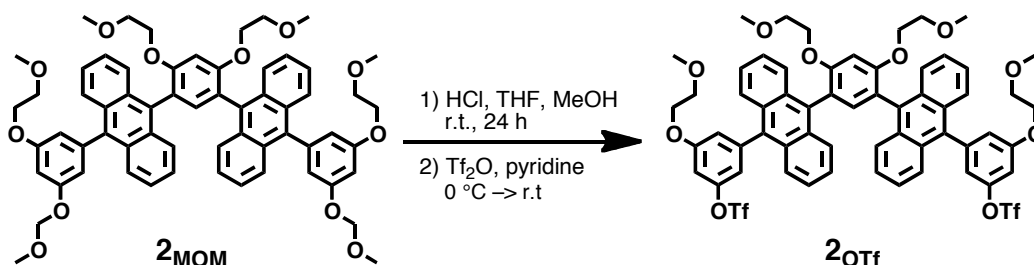
Shimadzu Biotech Axima CFRplus 2.8.4.20081127: Mode Reflectron, Power: 60, P.Ext. @ 999 (bin 87)

%Int. 432 mV[sum= 44546 mV] Profiles 1-103 Unsmoothed



Synthesis of half tube 2_{OTf}

KH-167-3



To a 100 mL glass flask containing a magnetic stirring bar, half tube 2_{MOM} (0.598 g, 0.599 mmol), THF (10 mL), and methanol (5 mL) were added. Concentrated hydrochloric acid (1.0 mL) was added dropwise to this flask and stirred at r.t. for 24 h. The crude product was extracted with ethyl acetate and combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduce pressure. The resultant solid and pyridine (10 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar. Triflic anhydride (0.40 mL, 0.40 mmol) was added dropwise to this flask at 0 °C. The solution was stirred at 0 °C for 30 min and at r.t. for 24 h. The crude product was extracted with ethyl acetate and combined organic phase was dried

over MgSO_4 , filtrated, and concentrated under reduce pressure. The resultant solid was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford half tube $\mathbf{2}_{\text{OTf}}$ as a yellow solid (0.674 g, 0.574 mmol, 96%).

^1H NMR (400 MHz, CDCl_3 , r.t.): δ 8.00 (d, $J = 8.4$ Hz, 4H), 7.60 (d, $J = 8.8$ Hz, 4H), 7.44 (dd, $J = 8.4, 7.6$ Hz, 4H), 7.37 (dd, $J = 8.8, 7.6$ Hz, 5H), 7.30-7.28 (m, 1H), 7.16 (m, 1H), 7.11 (br, 1H), 7.06 (br, 3H), 7.01 (br, 1H), 6.95 (br, 1H), 4.22 (t, $J = 4.4$, 2H), 4.16 (m, 6H), 3.80 (t, $J = 4.4$, 2H), 3.74 (t, $J = 4.4$, 2H), 3.48 (s, 3H), 3.43 (s, 3H), 3.40 (s, 4H), 2.98-2.96 (m, 5H).

^{13}C NMR (100 MHz, CDCl_3 , r.t.): δ 160.1 (C_q), 158.5 (C_q), 150.3 (C_q), 142.6 (C_q), 137.1 (CH), 134.6 (C_q), 134.2 (C_q), 130.5 (C_q), 129.8 (C_q), 127.4 (CH), 126.4 (CH), 125.7 (CH), 125.2 (C_q), 120.5 (C_q), 117.8 (CH), 117.6 (C_q), 116.8 (CH), 107.7, (CH), 100.3 (CH), 71.0 (CH_2), 70.9 (CH_2), 69.2 (CH_2), 68.2 (CH_2), 59.4 (CH_3), 59.1 (CH_3).

FT-IR (KBr, cm^{-1}): 3437, 3065, 2929, 2884, 2821, 1609, 1577, 1424, 1385, 1265, 1242, 1212, 1140, 1062, 983, 858, 835, 770, 607.

MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{60}\text{H}_{52}\text{F}_6\text{O}_{12}\text{S}_2$ $[\text{M}]^+$ 1174.27, Found 1174.22.

E.A.: Calcd. for $\text{C}_{60}\text{H}_{52}\text{F}_6\text{O}_{14}\text{S}_2$: C, 61.32; H, 4.46; F, 9.72; S, 5.46. Found: C, 61.19; H, 4.37; F, 9.72; S, 5.25.

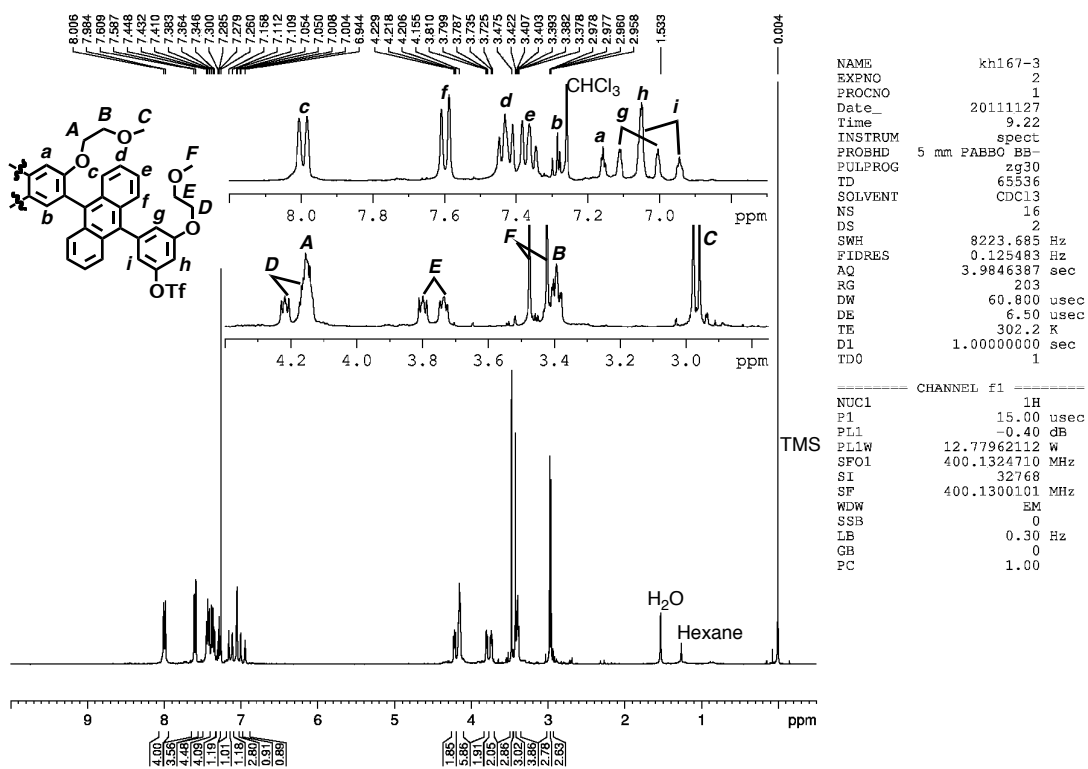


Fig. S11. ¹H NMR (400 MHz, CDCl₃, r.t.) spectrum of **2_{OTf}**.

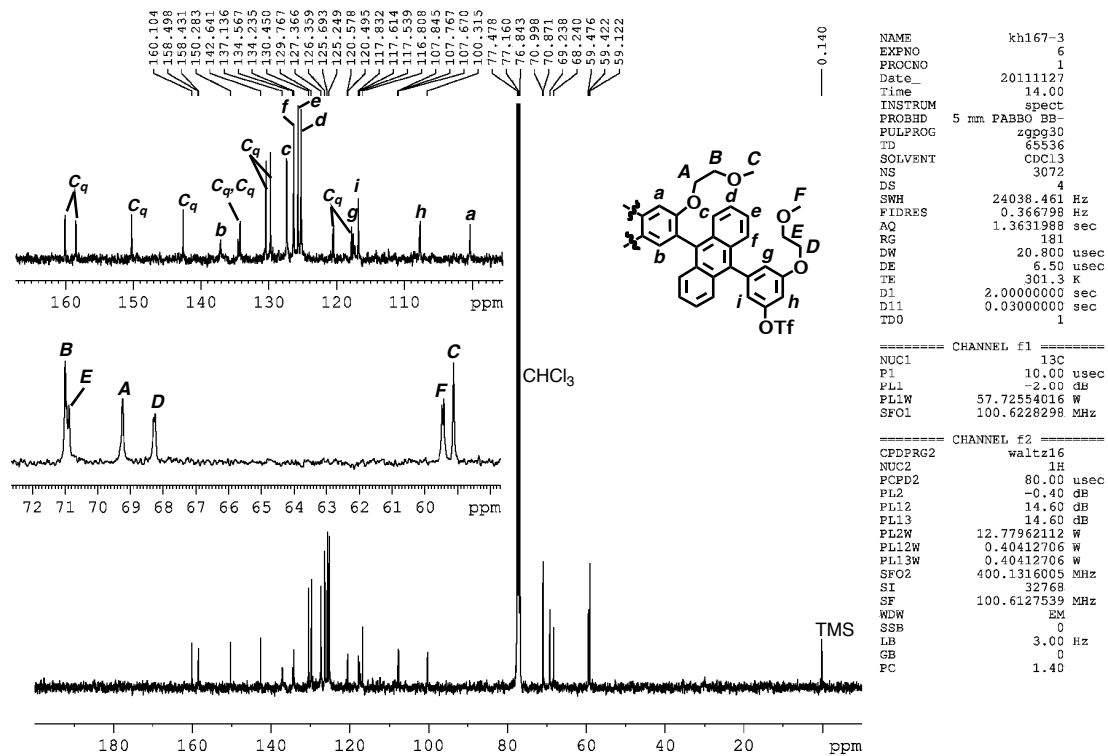


Fig. S12. ¹³C NMR (100 MHz, CDCl₃, r.t.) spectrum of **2_{OTf}**.

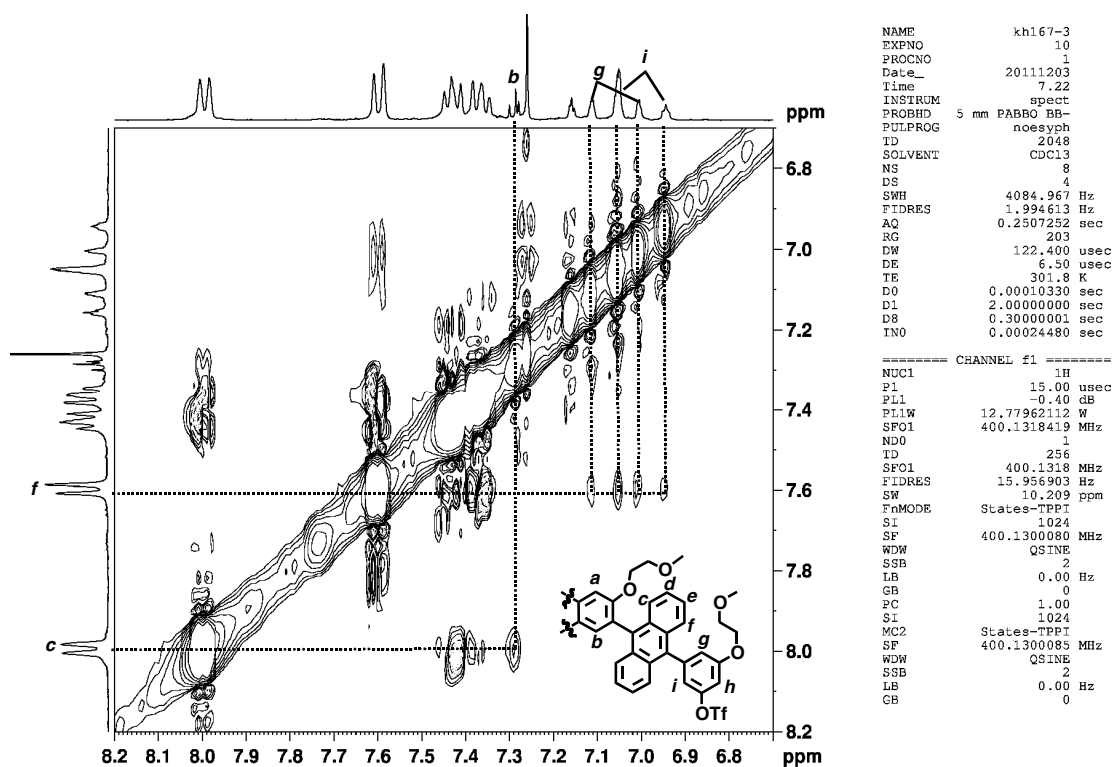


Fig. S15. NOESY (400 MHz, CDCl₃, r.t.) spectrum of **2**_{OTf} (aromatic region).

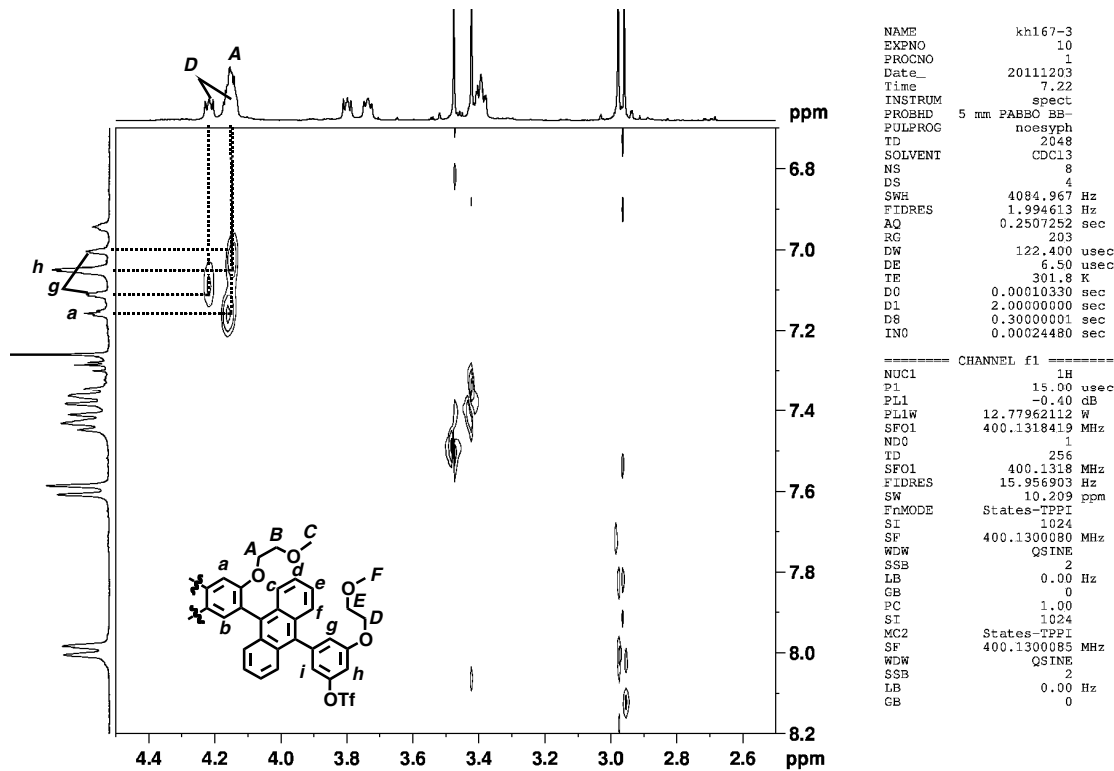


Fig. S16. NOESY (400 MHz, CDCl₃, r.t.) spectrum of **2**_{OTf}.

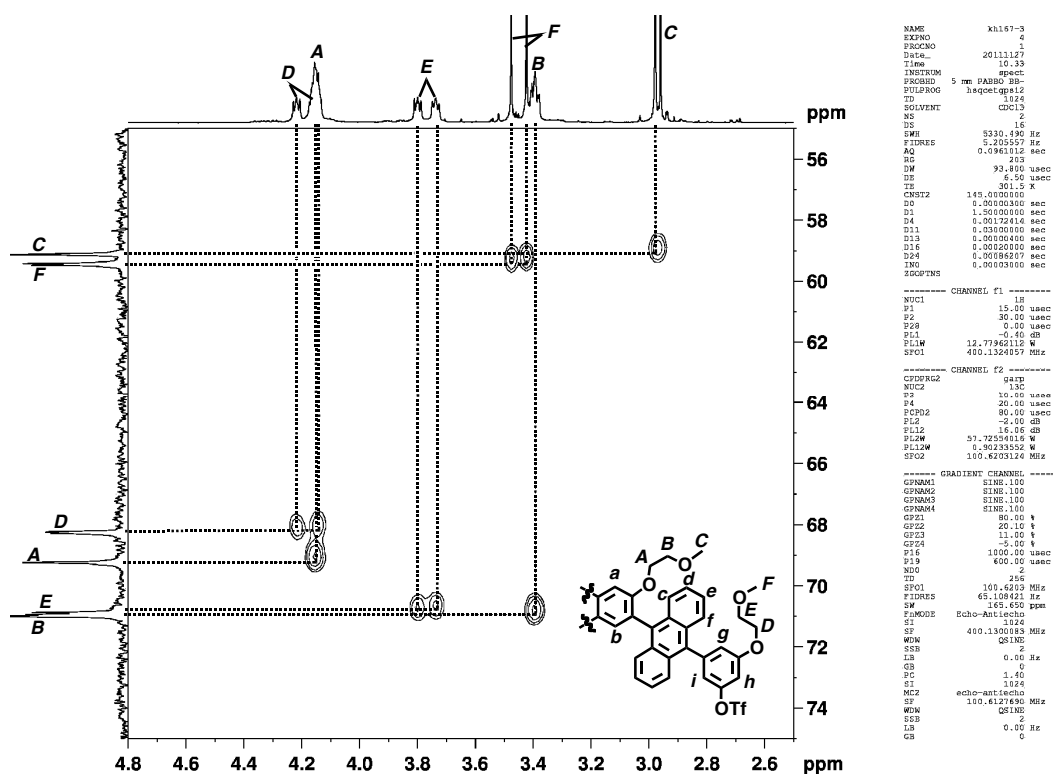


Fig. S17. HSQC (400 MHz, CDCl₃, r.t.) spectrum of 2_{ORT} (aliphatic region).

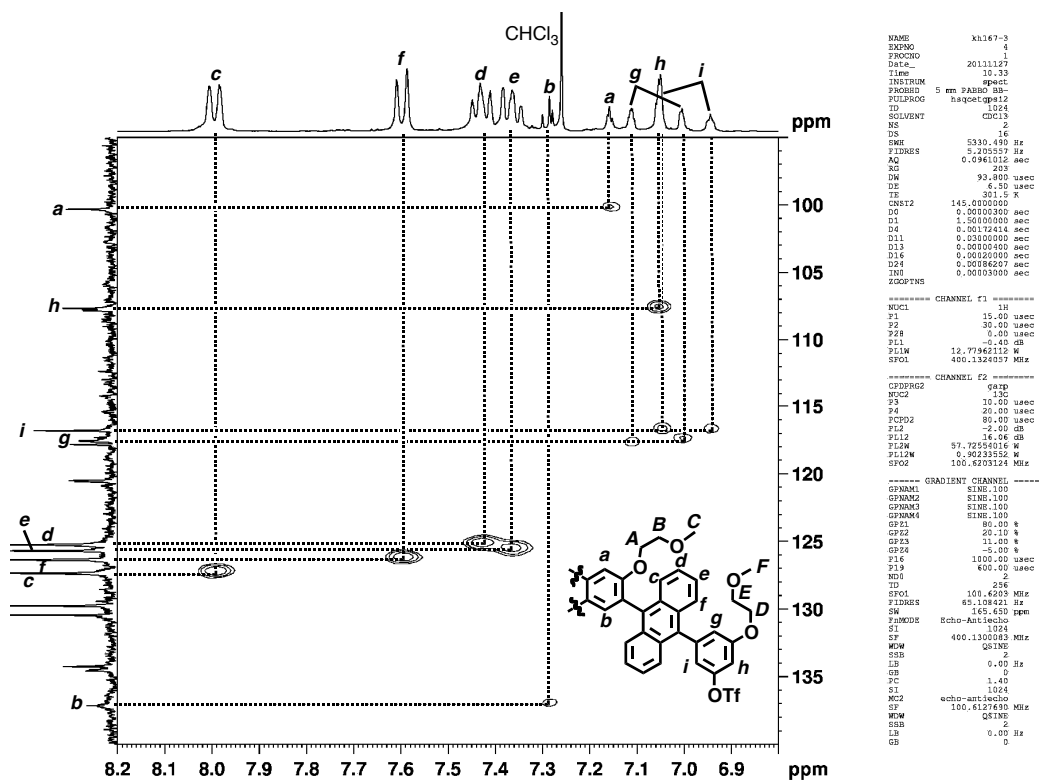


Fig. S18. HSQC (400 MHz, CDCl₃, r.t.) spectrum of half tube 2_{ORT} (aromatic region).

kh167-2
Data: KH167-2-4-dith-1-10-0001.F11[c] 1 Dec 2011 20:05 Cal: akita-yoshizawa-ref 1 Dec 2011 20:03
Shimadzu Biotech Axima CFRplus 2.8.4.20081127: Mode Reflectron, Power: 70, P.Ext. @ 1174 (bin 94)

%Int. 123 mV[sum= 12799 mV] Profiles 1-104 Smooth Av 1

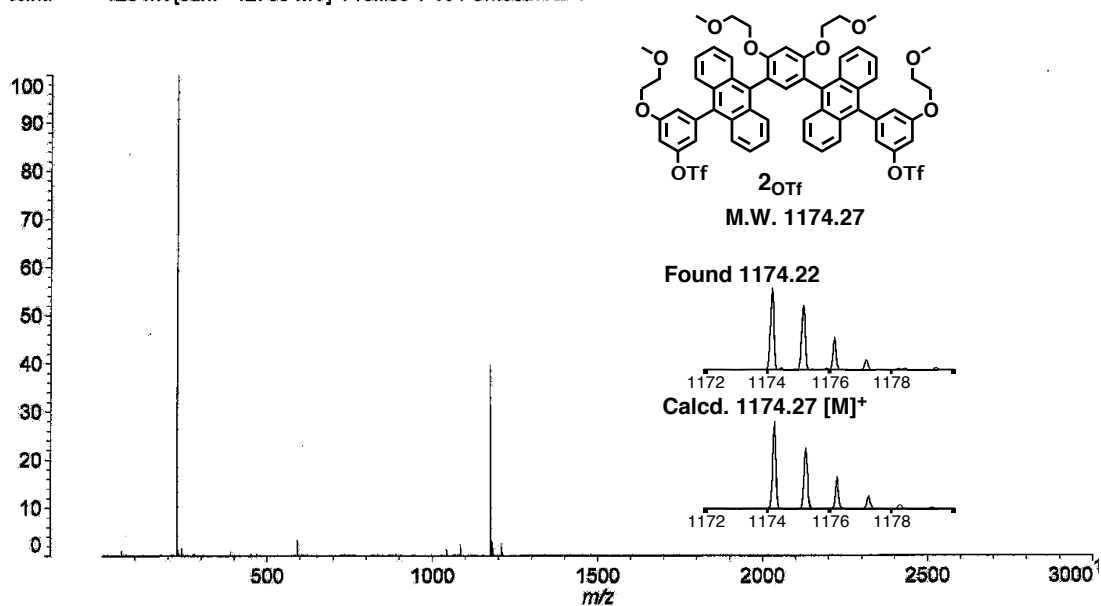
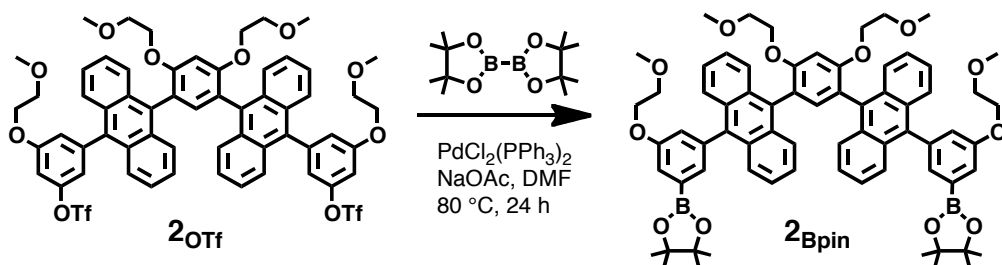


Fig. S19. MALDI-TOF MS (dithranol) spectrum of **2_{OTf}**.

Synthesis of half tube **2_{Bpin}**

KH-169



A 2-necked 200 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with N_2 after cooling to r.t. Half tube **2_{OTf}** (0.249 g, 0.212 mmol), bis(pinacolato)diboron (0.140 g, 0.551 mmol), NaOAc (0.094 g, 1.1 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.016 g, 0.023 mmol), and dry DMF (15 mL) were added to this flask, and the solution was stirred at 80 °C for 24 h. The mixture was concentrated under reduce pressure. The crude product was extracted with ethyl acetate and washed with methanol. The resultant solid was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford half tube **2_{Bpin}** as a yellow solid (0.092 g, 0.081 mmol, 38%).

^1H NMR (400 MHz, CDCl_3 , r.t.): δ 8.00 (m, 4H), 7.60 (d, $J = 8.4$ Hz, 4H), 7.53-7.51 (m, 3H), 7.46-7.45 (m, 1H), 7.41-7.40 (m, 4H), 7.34-7.28 (m, 6H), 7.18 (m, 1H), 7.13-7.10 (m, 2H), 4.26 (t, $J = 4.4$, 2H), 4.20 (t, $J = 4.4$, 2H), 4.12-4.11 (m, 4H), 3.80 (t, $J = 4.4$, 2H), 3.75 (t, $J = 4.4$, 2H), 3.47 (s, 3H), 3.43 (s, 3H), 3.38-3.36 (m, 4H), 3.00 (s, 3H), 2.90 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , r.t.): δ 158.5 (C_q), 158.4 (C_q), 140.3 (C_q), 137.2 (CH), 136.7 (CH), 133.4 (C_q), 130.7 (C_q), 130.5 (CH), 130.1 (C_q), 127.4 (CH), 127.1 (CH), 125.0 (CH), 124.9 (CH), 121.5 (CH), 121.2 (C_q), 121.0 (CH), 119.0 (CH), 118.6 (C_q), 100.6 (CH), 84.0 (C_q), 71.3 (CH_2), 71.0 (CH_2), 69.3 (CH_2), 67.6 (CH_2), 59.4 (CH_3), 59.2 (CH_3).

FT-IR (KBr, cm^{-1}): 3445, 3062, 2979, 2928, 2881, 2819, 1603, 1583, 1504, 1454, 1411, 1350, 1263, 1143, 1064, 852, 770.

MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{70}\text{H}_{76}\text{B}_2\text{O}_{12}$ $[\text{M}]^+$ 1130.55, Found 1130.54.

E.A.: Calcd for $\text{C}_{70}\text{H}_{76}\text{B}_2\text{O}_{12} \cdot 0.5\text{H}_2\text{O}$: C, 73.75; H, 6.81. Found: C, 73.62; H, 6.66.

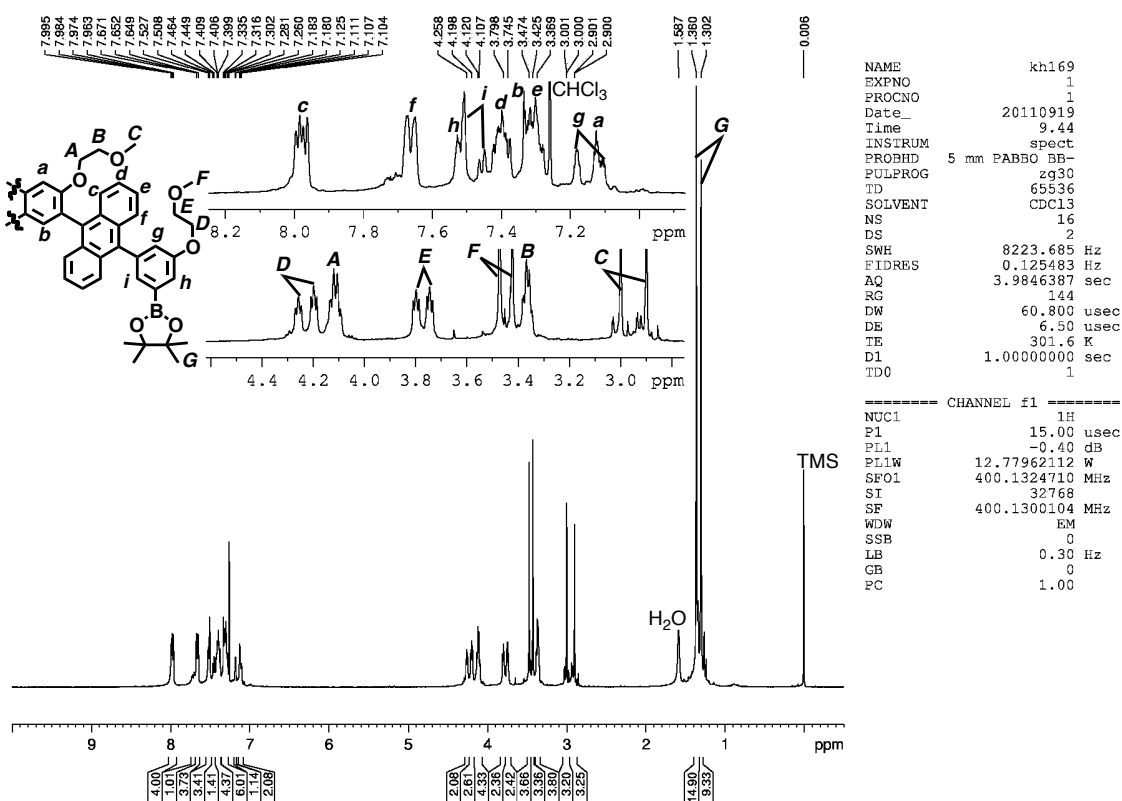


Fig. S20. ^1H NMR (400 MHz, CDCl_3 , r.t.) spectrum of half tube **2Bpin**.

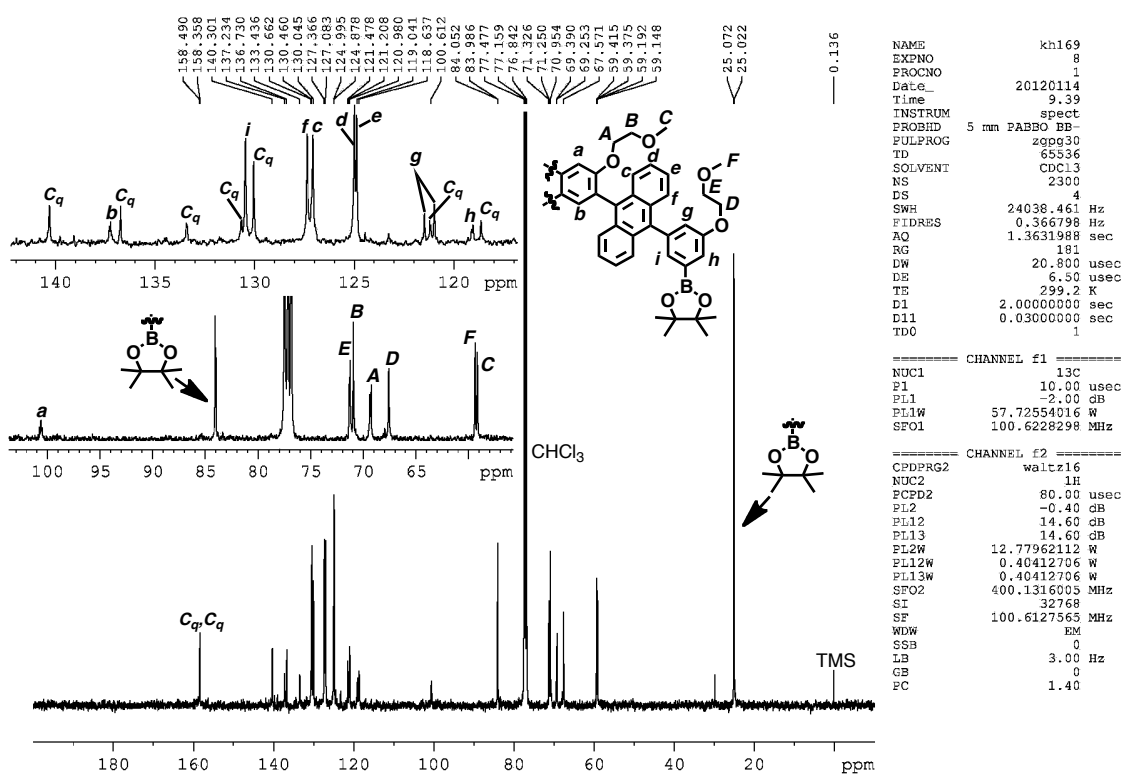


Fig. S21. ^{13}C NMR (100 MHz, CDCl_3 , rt) spectrum of half tube 2_{Bpin} .

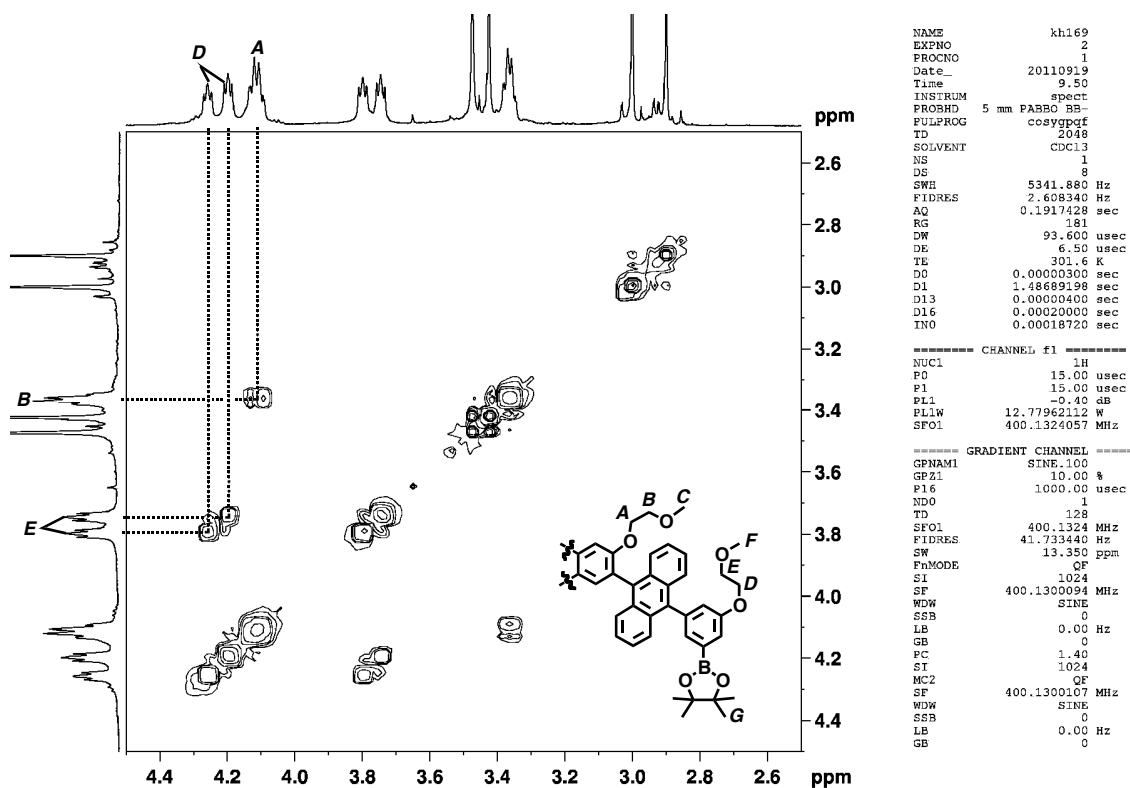


Fig. S22. HH COSY (400 MHz, CDCl_3 , rt) spectrum of half tube 2_{Bpin} (aliphatic region).

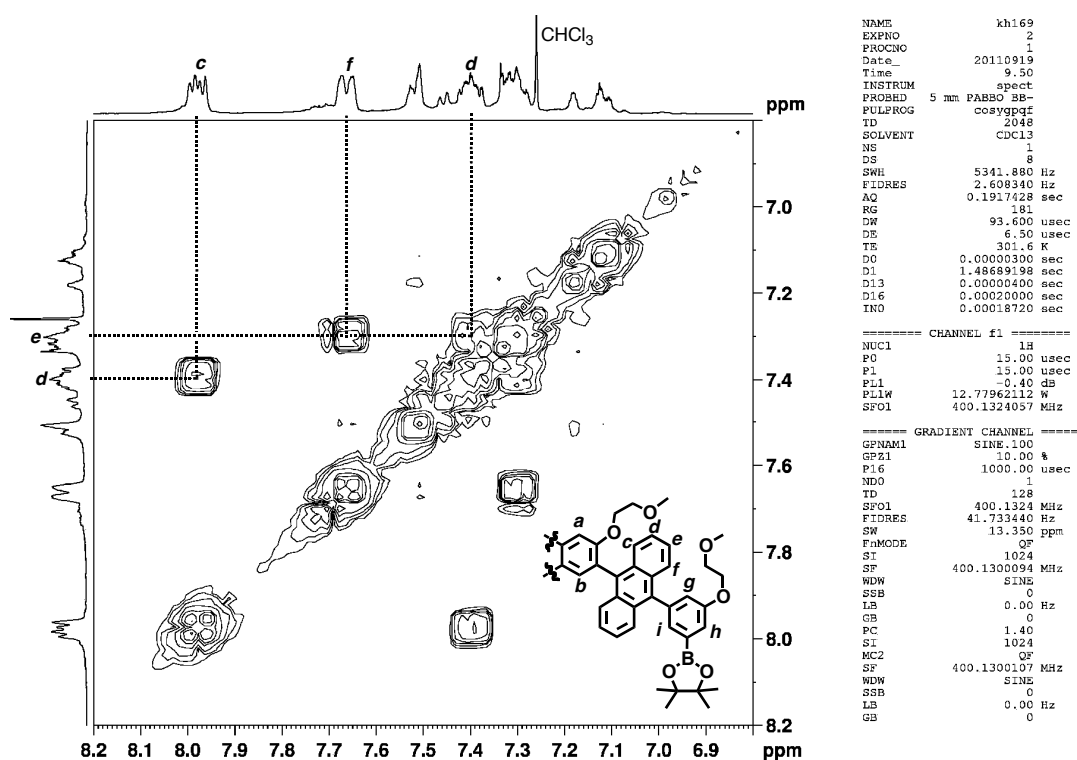


Fig. S23. HH COSY (400 MHz, CDCl₃, rt) spectrum of half tube **2_{Bpin}** (aromatic region).

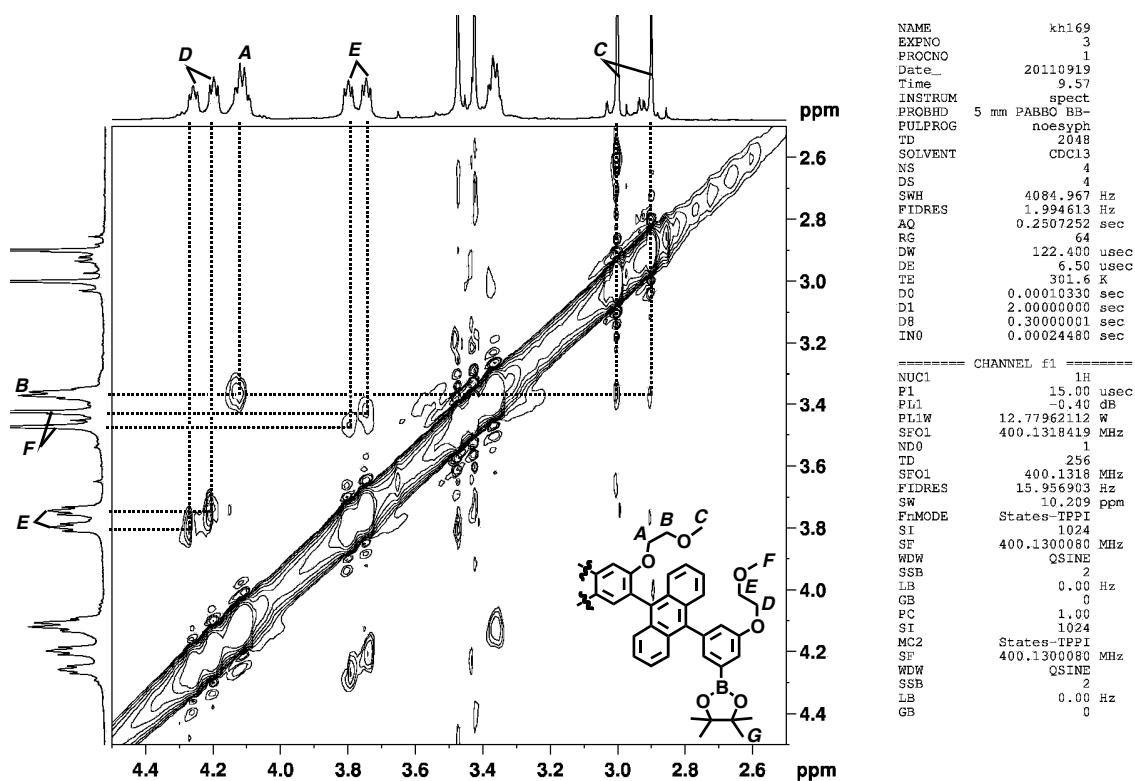


Fig. S24. NOESY (400 MHz, CDCl₃, r.t.) spectrum of half tube **2_{Bpin}** (aliphatic region).

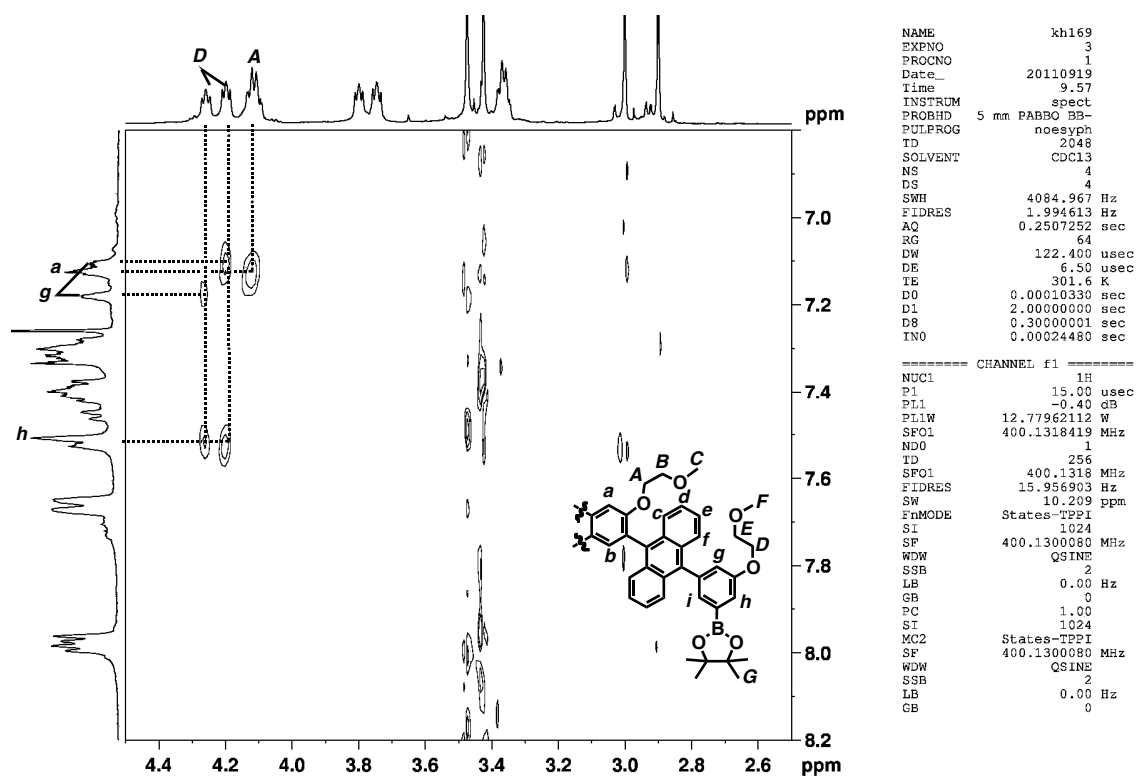


Fig. S25. NOESY (400 MHz, CDCl₃, r.t.) spectrum of half tube **2B_{pin}**.

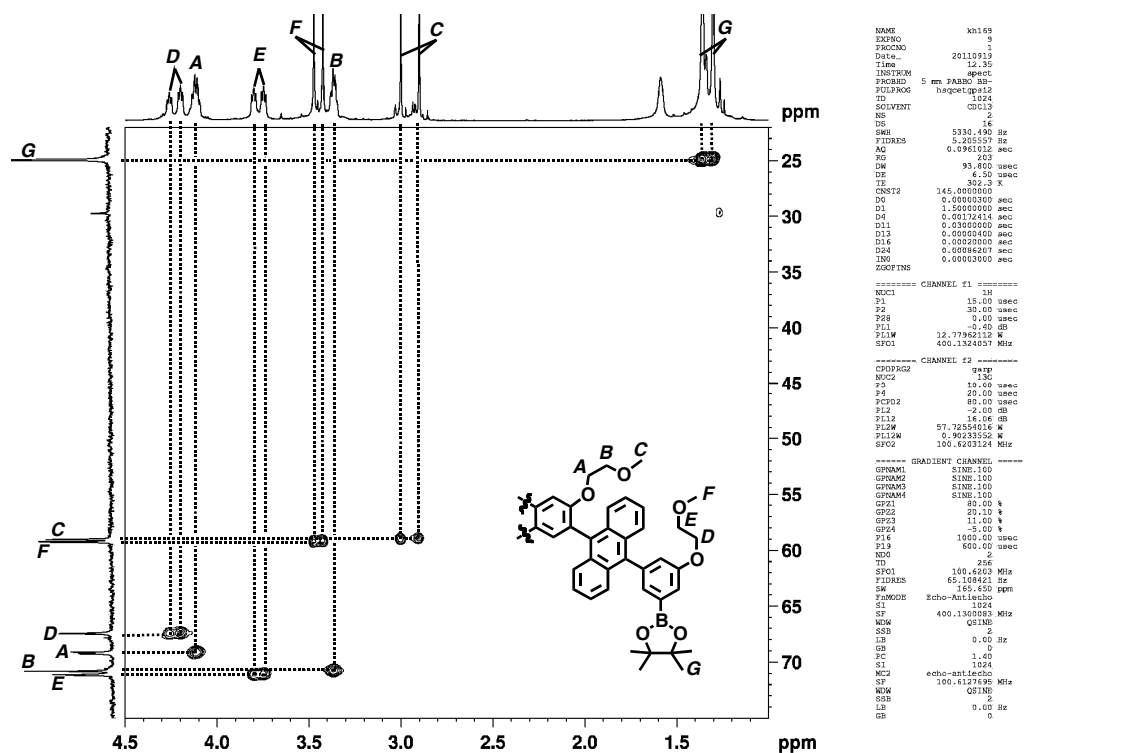


Fig. S26. HSQC (400 MHz, CDCl₃, r.t.) spectrum of half tube **2B_{pin}** (aliphatic region).

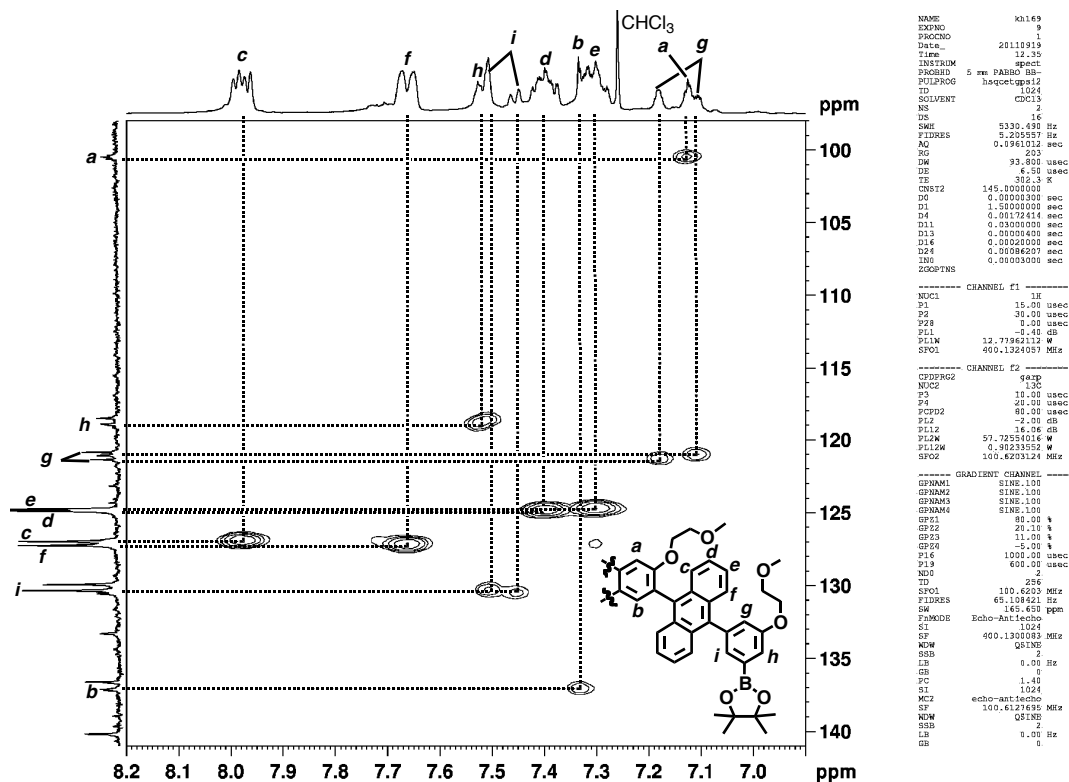


Fig. S27. HSQC (400 MHz, CDCl₃, r.t.) spectrum of half tube 2_{Bpin} (aromatic region).

kh167-3

Data: KH167-3-3-dith-1-10-0001.D11[c] 1 Dec 2011 20:04 Cal: akita-yoshizawa-ref 1 Dec 2011 20:03
 Shimadzu Biotech Axima CFRplus 2.8.4.20081127: Mode Reflectron, Power: 70, P.Ext. @ 1753 (bin 115)

%Int. 246 mV[sum= 24692 mV] Profiles 1-101 Smooth Av 1

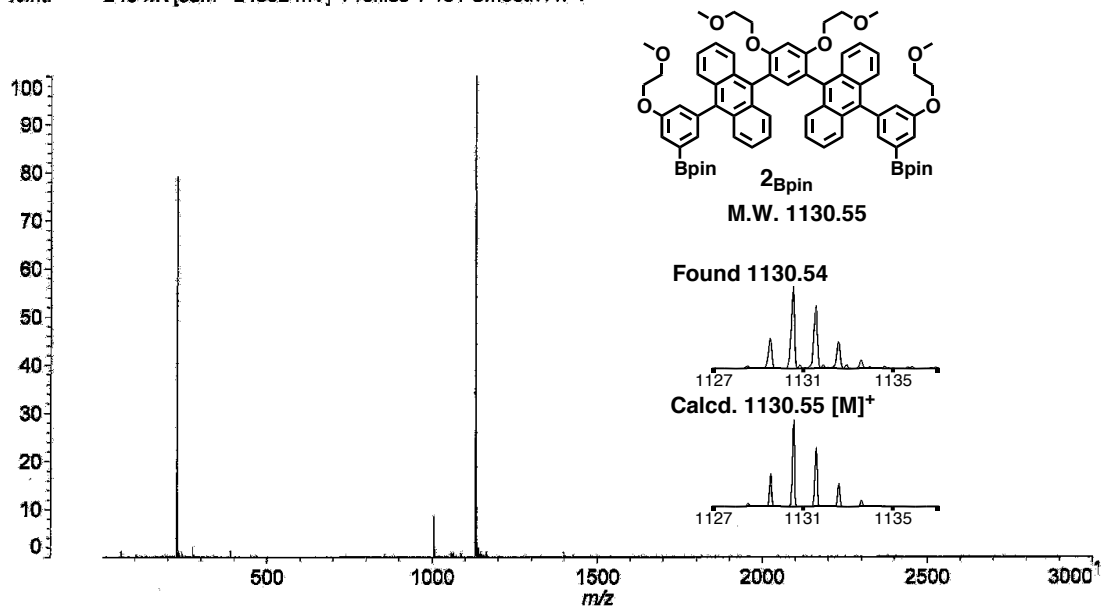
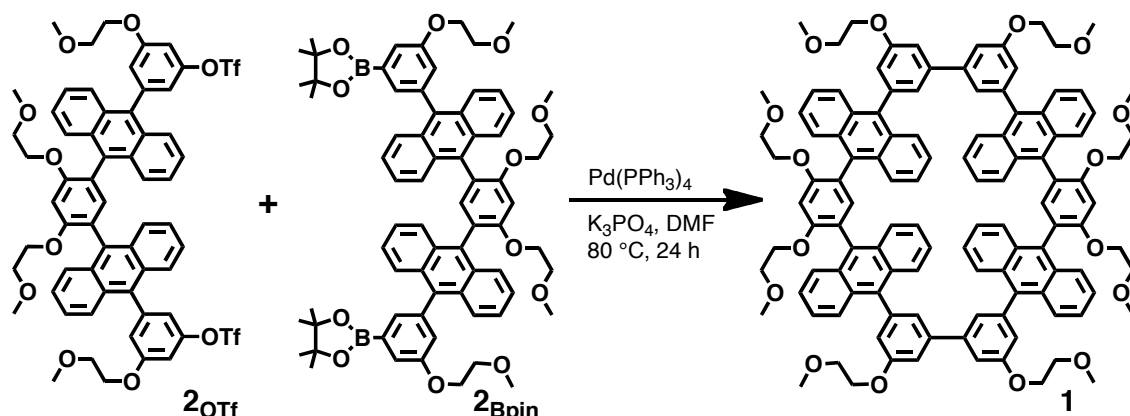


Fig. S28. MALDI-TOF MS (dithranol) spectrum of half tube 2_{Bpin}.

Synthesis of nanotube 1 KH-184



Half tubes **2_{OTf}** (0.053 g, 0.045 mmol) and **2_{Bpin}** (0.050 g, 0.045 mmol), K₃PO₄ (0.056 g, 0.26 mmol), Pd(PPh₃)₄ (0.014 g, 0.012 mmol), and dry DMF (60 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar and the solution was stirred at 90 °C for 24 h under N₂. The mixture was concentrated under reduce pressure. The crude product was extracted with CHCl₃. The resultant solid was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) and GPC to afford anthracene tube **1** as a white solid (3.3 mg, 1.9 μmol, 4%).

¹H NMR (400 MHz, CDCl₃, r.t.): δ 8.80 (d, *J* = 8.8 Hz, 8H), 8.58-8.56 (m, 12H), 7.24-7.16 (m, 20H), 7.07 (s, 2H), 7.03-7.02 (m, 6H), 4.30 (t, *J* = 4.4 Hz, 8H), 4.08 (t, *J* = 5.2 Hz, 8H), 3.85 (t, *J* = 4.4 Hz, 8H), 3.52 (s, 12H), 3.34 (t, *J* = 5.2 Hz, 8H), 2.93 (s, 12H).

¹³C NMR (100 MHz, CDCl₃, r.t.): δ 159.5 (C_q), 158.2 (C_q), 141.7 (C_q), 141.5 (C_q), 137.5 (CH), 136.4 (C_q), 133.4 (C_q), 130.2 (C_q), 129.9 (C_q), 127.1 (CH), 127.1 (CH), 125.0 (CH), 125.0 (CH), 122.9 (CH), 120.8 (C_q), 116.5 (CH), 112.6 (CH), 100.6 (CH), 71.3 (CH₂), 71.0 (CH₂), 69.2 (CH₂), 67.8 (CH₂), 59.5 (CH₃), 59.1 (CH₃).

FT-IR (KBr, cm⁻¹): 3446, 3062, 2979, 2926, 2877, 2817, 1585, 1504, 1442, 1429, 1389, 1366, 1312, 1263, 1239, 1192, 1151, 1127, 1104, 1064, 1029, 853, 798, 770.

MALDI-TOF MS (dithranol): *m/z* Calcd. for C₁₁₆H₁₀₄O₁₆ [M]⁺ 1753.74, Found 1753.45.

HRMS (ESI): *m/z* Calcd. for C₁₁₆H₁₀₄O₁₆ [M+Cs]⁺: 1886.6407, Found 1886.6444.

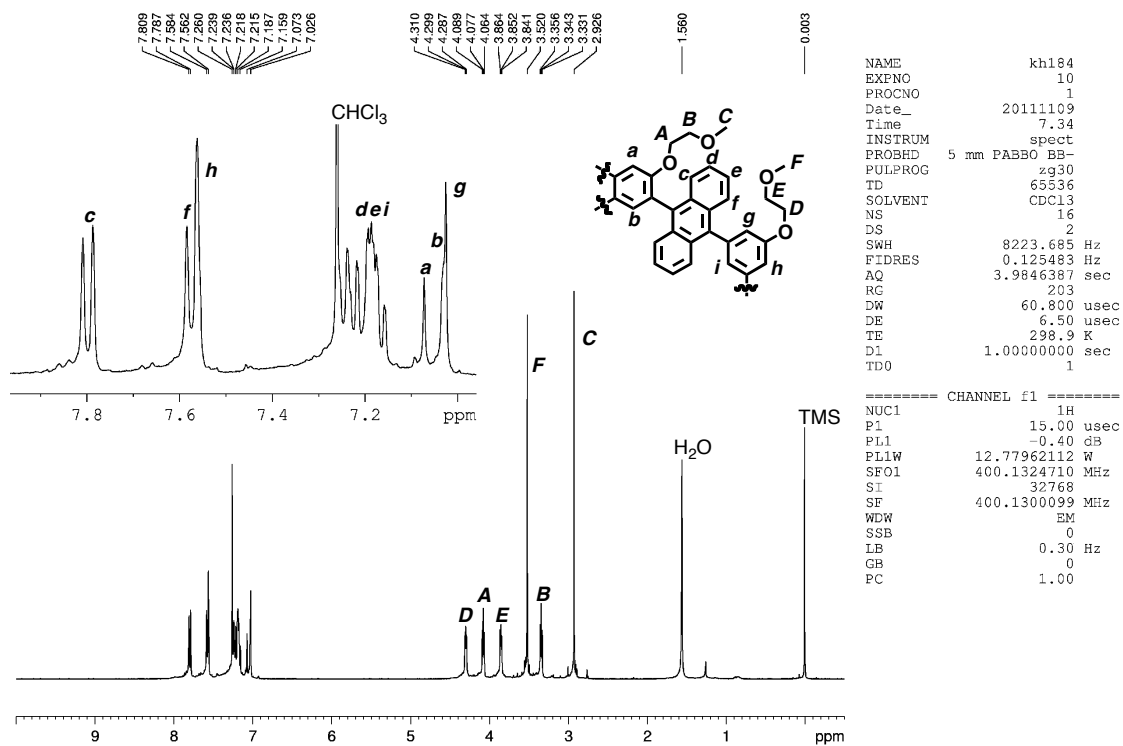


Fig. S29. ¹H NMR (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1.

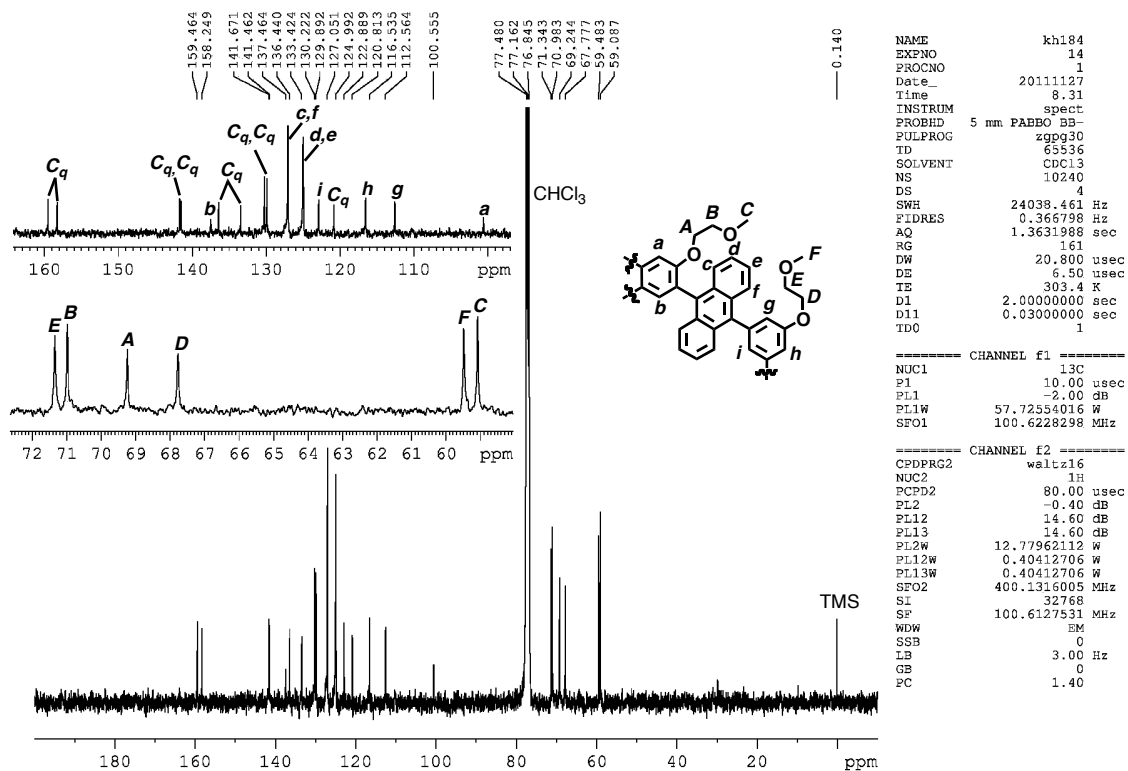


Fig. S30. ¹³C NMR (100 MHz, CDCl₃, rt) spectrum of nanotube 1.

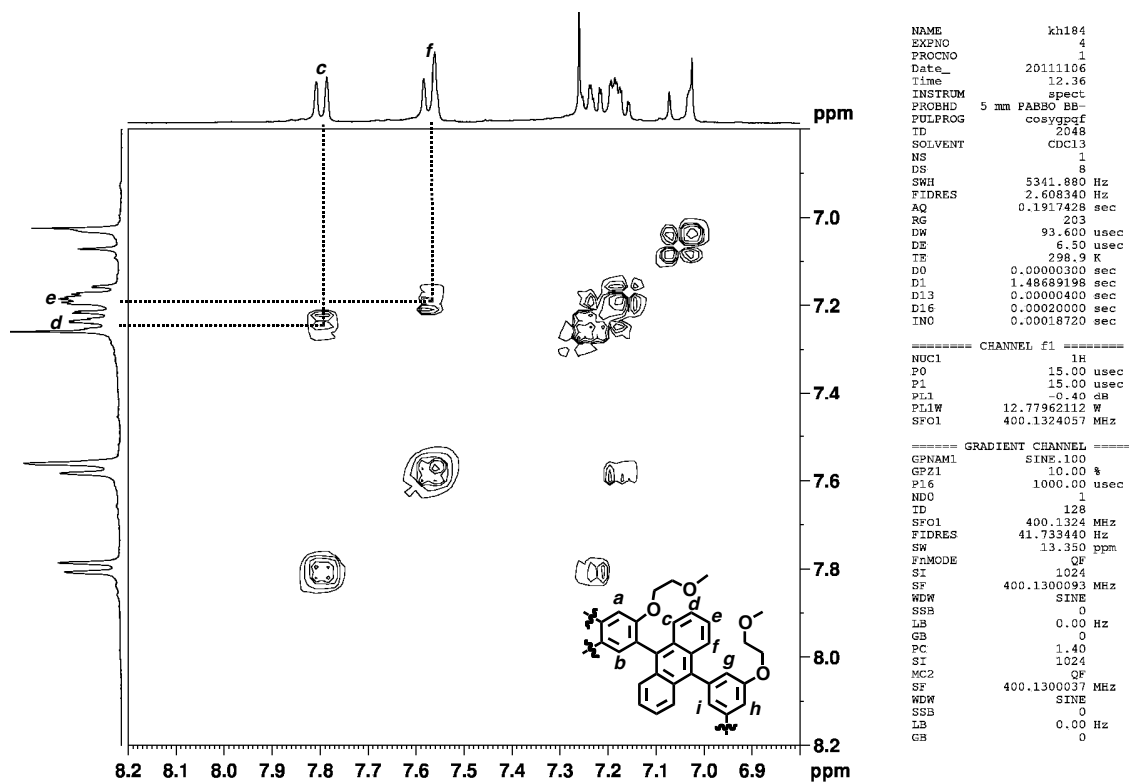


Fig. S31. HH COSY (400 MHz, CDCl₃, rt) spectrum of nanotube 1.

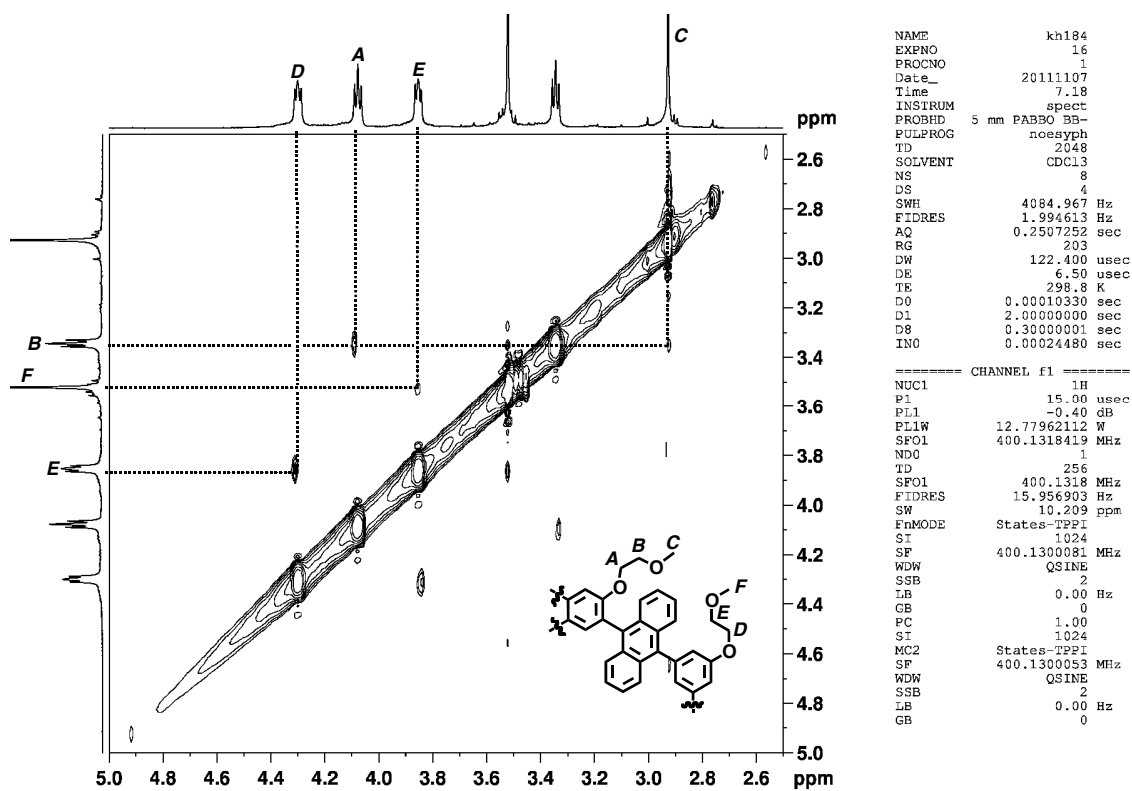


Fig. S32. NOESY (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1 (aliphatic region).

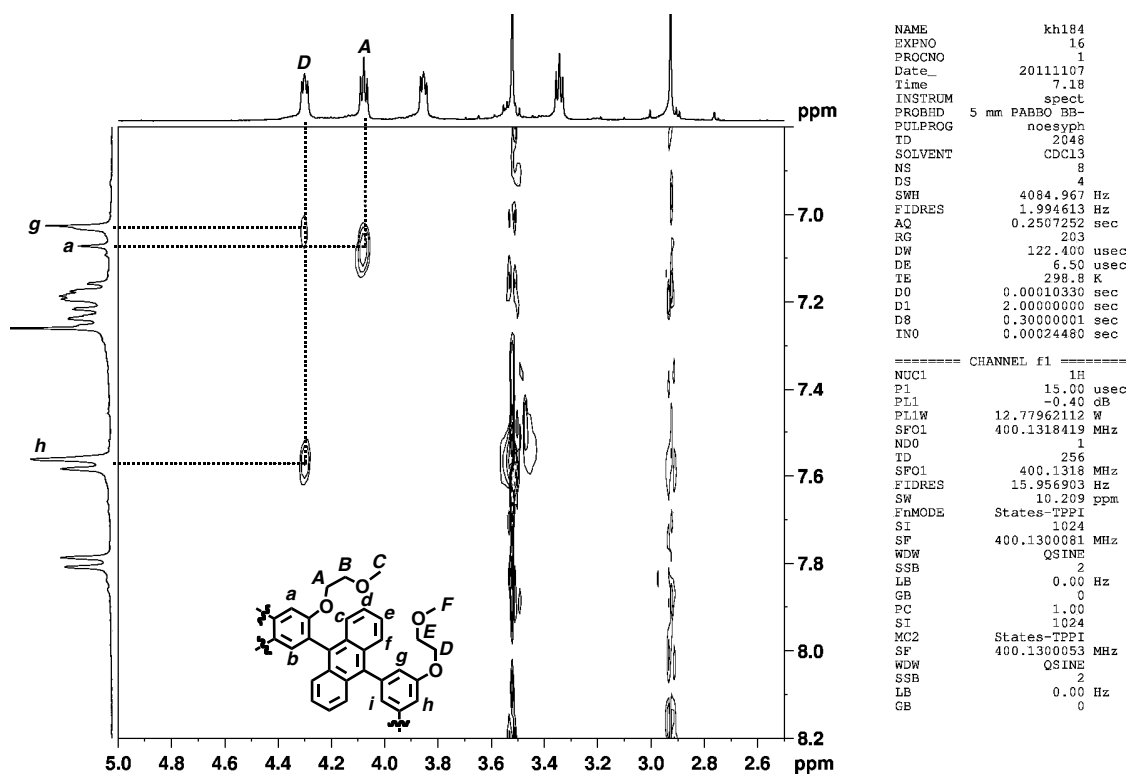


Fig. S33. NOESY (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1.

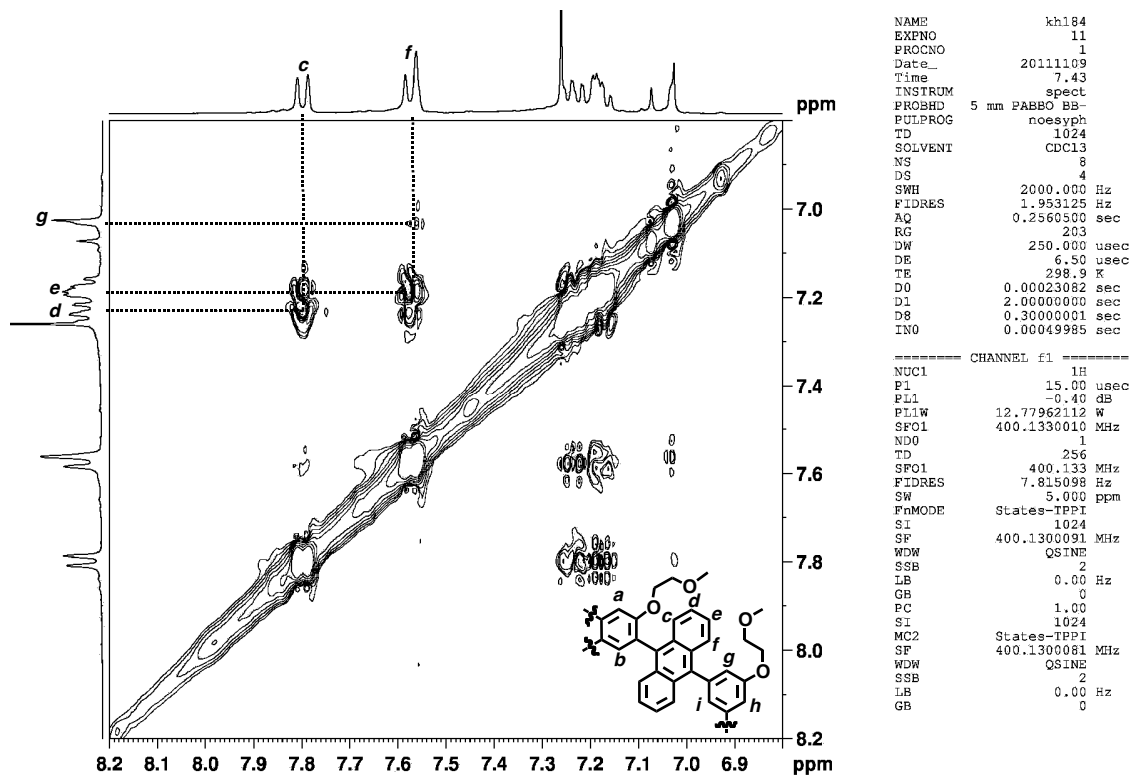


Fig. S34. NOESY (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1 (aromatic region).

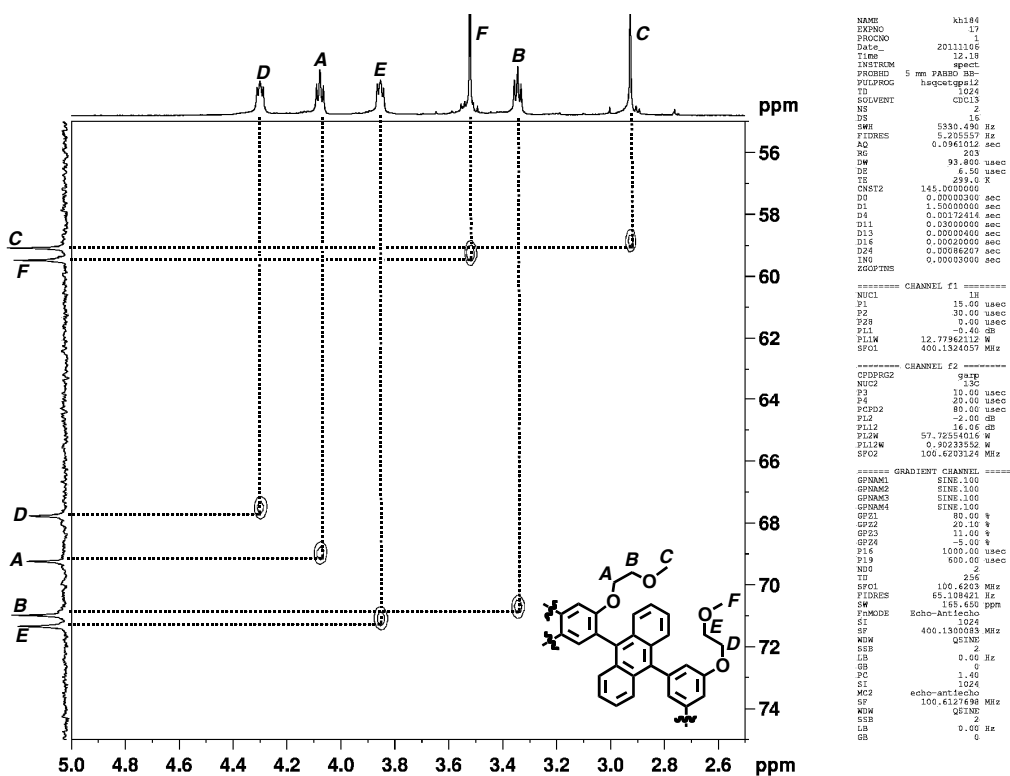


Fig. S35. HSQC (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1 (aliphatic region).

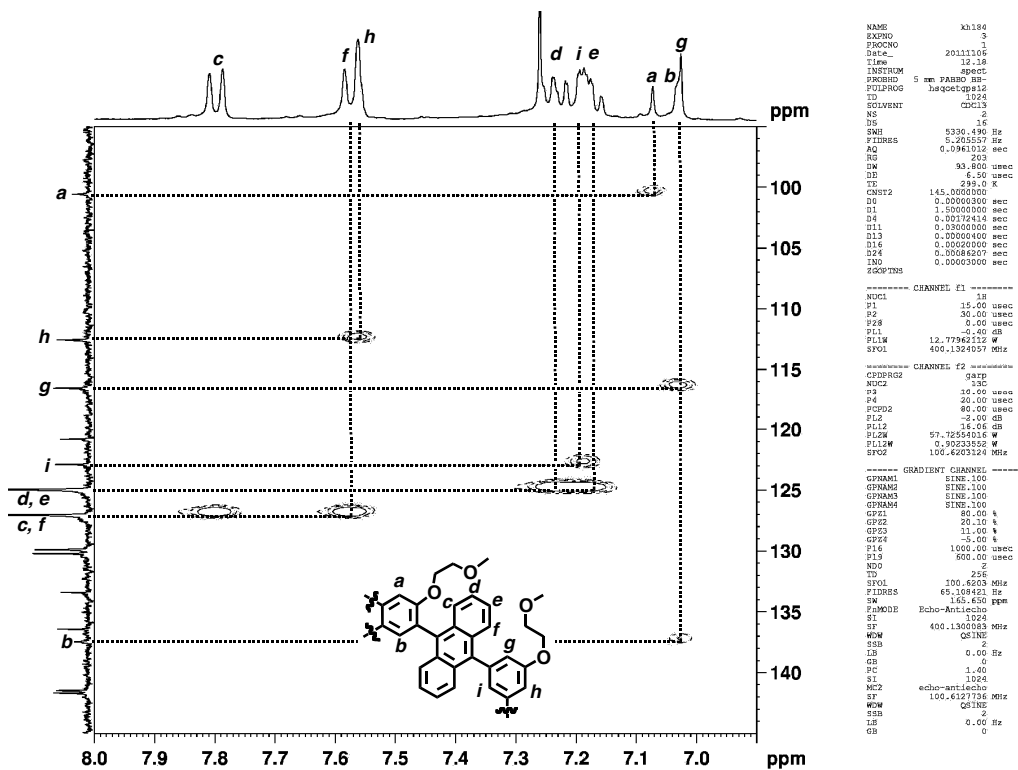


Fig. S36. HSQC (400 MHz, CDCl₃, r.t.) spectrum of nanotube 1 (aromatic region).

kh184-2
Data: KH184-4-dith-1-10-0001.F10[c] 1 Dec 2011 19:59 Cal: akita-yoshizawa-ref 1 Dec 2011 19:50
Shimadzu Biotech Axima CFRplus 2.8.4.20081127: Mode Reflectron, Power: 70, P.Ext. @ 1753 (bin 115)

%Int. 153 mV[sum= 17004 mV] Profiles 1-111 Smooth Av 1

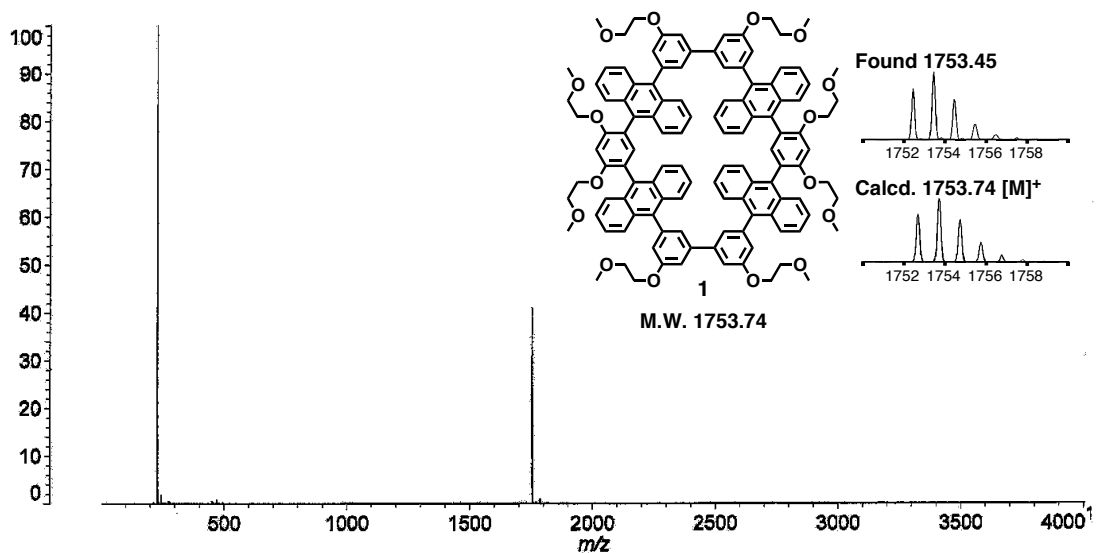
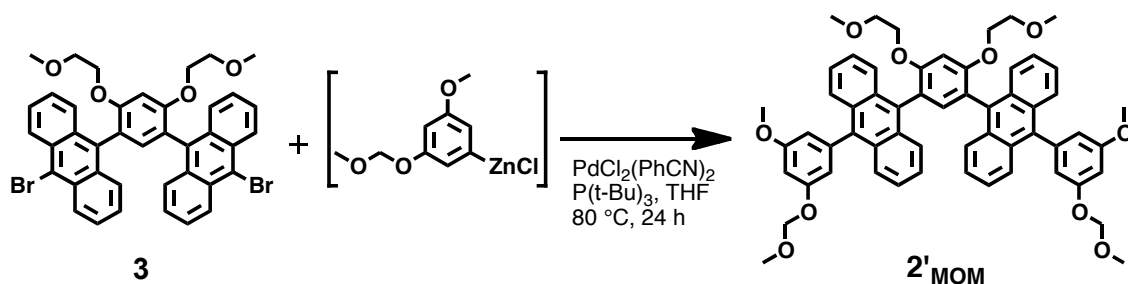


Fig. S37. MALDI-TOF MS (dithranol) spectrum of nanotube 1.

Synthesis of half tube 2'_{MOM}

KH146-1



A 2-necked 200 mL glass flask containing a magnetic stirring bar was flame-dried under vacuum and filled with N₂ after cooling to r.t. 1-Bromo-3-methoxy-5-(methoxymethoxy)benzene (1.138 g, 4.604 mmol) and dry THF (20 mL) were added to this flask. A hexane solution (2.66 M) of *n*-butyllithium (1.90 mL, 5.05 mmol) was then added dropwise to this flask at –80 °C under N₂. After stirring the mixture at –80 °C for 2 h, a dry THF solution (20 mL) of ZnCl₂ (0.772 g, 11.80 mmol) was added to the solution. The resultant mixture was further stirred at –80 °C for 1 h and then the solution was warmed to r.t. for 3 h to obtain (3-methoxy-5-(methoxymethoxy)phenyl)

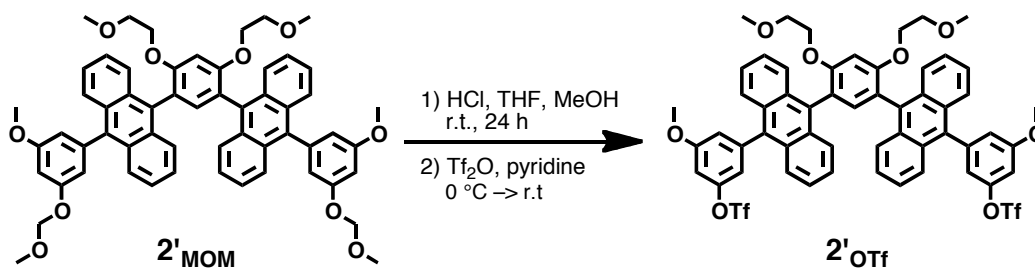
zinc chloride. Bromoanthracene dimer **3** (0.870 g, 1.18 mmol), PdCl₂(PhCN)₂ (0.050 g, 0.13 mmol), and dry THF (45 mL) were added to a 2-necked 50 mL glass flask containing a magnetic stirring bar and the flask was filled with N₂. A hexane solution (0.95 M) of tri-*tert*-butylphosphine (0.25 mL, 0.24 mmol) was added to this flask. After stirring the mixture for 30 min at r.t., the mixture was added to the 200 mL flask and then the resulted solution was further stirred at 80 °C for 4 h. The mixture was concentrated under reduce pressure. The crude product was extracted with ethyl acetate and combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduce pressure. The crude product was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford half tube **2'**_{MOM} as a yellow solid (0.458 g, 0.503 mmol, 43%).

¹H NMR (400 MHz, CDCl₃, r.t.): δ 7.98 (d, *J* = 8.8 Hz, 4H), 7.75 (d, *J* = 8.8 Hz, 4H), 7.42-7.39 (m, 4H), 7.35-7.31 (m, 5H), 7.14 (s, 1H), 6.79-6.78 (m, 3H), 6.71-6.70 (m, 2H), 6.62 (br, 1H), 5.24 (s, 2H), 5.18 (s, 2H), 4.13 (t, *J* = 5.2 Hz, 4H), 3.86 (s, 3H), 3.79 (s, 3H), 3.54 (s, 3H), 3.48 (s, 3H), 3.38 (t, *J* = 5.2 Hz, 4H), 2.95 (s, 3H).

MALDI-TOF MS (dithranol): *m/z*. Calcd. for C₅₈H₅₄O₁₀ 910.37, Found 910.40 [M]⁺.

E.A.: Calcd. for C₅₈H₅₄O₁₀•0.2H₂O: C, 76.21; H, 5.99. Found: C, 76.04; H, 6.02.

Synthesis of half tube **2'**_{OTf} KH146-2



Half tube **2'**_{MOM} (0.458 g, 0.503 mmol), THF (15 mL), and methanol (7.5 mL) were added to a 100 mL glass flask. Concentrated hydrochloric acid (1.0 mL) was added dropwise to this flask and the mixture was stirred at r.t. for 24 h. The crude product was extracted with ethyl acetate and combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduce pressure. Triflic anhydride (0.40 mL, 0.40 mmol) was added dropwise to this flask at 0 °C. The solution was stirred at 0 °C for

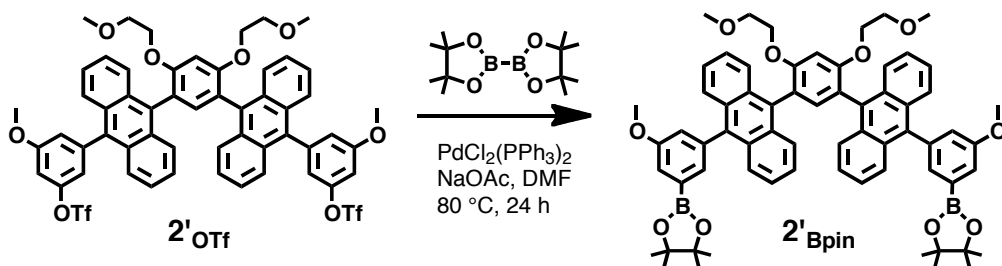
30 min and at r.t. for 24 h. The crude product was extracted with ethyl acetate and combined organic phase was dried over MgSO_4 , filtrated, and concentrated under reduce pressure. Purification by silica-gel column chromatography (hexane:ethyl acetate = 10:1) gave $2'_{\text{OTf}}$ (0.272 g, 0.250 mmol, 50%) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , r.t.): δ 8.00 (d, $J = 8.4$ Hz, 4H), 7.60 (d, $J = 8.8$ Hz, 4H), 7.45-7.41 (m, 4H), 7.39-7.35 (m, 4H), 7.30-7.28 (m, 1H), 7.16 (s, 1H), 7.08 (br, 1H), 7.04 (br, 1H), 7.00 (br, 3H), 6.98 (br, 1H), 6.94 (br, 1H), 4.16 (t, $J = 4.8$, 4H), 3.91 (s, 3H), 3.84 (s, 3H), 3.40 (t, $J = 4.8$, 4H), 2.98 (s, 4H).

MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{56}\text{H}_{44}\text{F}_6\text{O}_{12}\text{S}_2$ 1086.22, Found 1086.88 $[\text{M}]^+$.

Synthesis of half tube $2'_{\text{Bpin}}$

KH-147

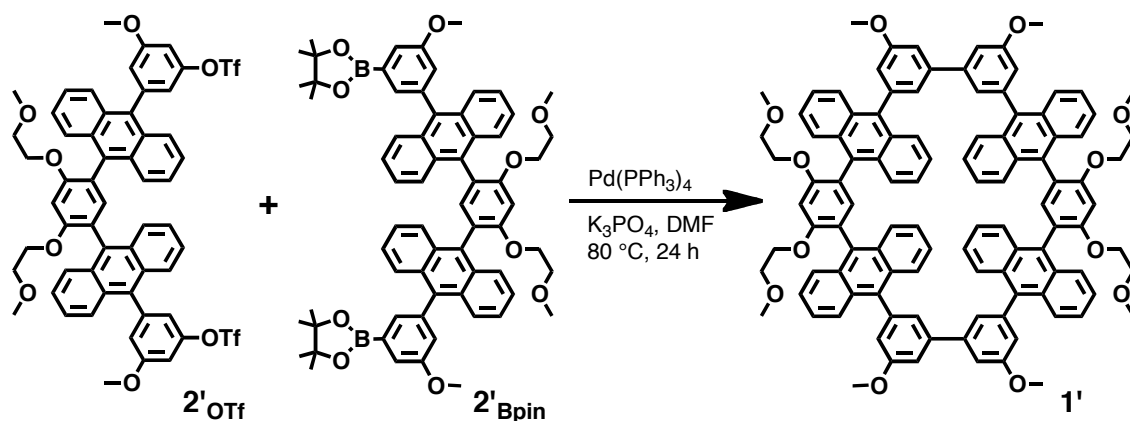


Half tube $2'_{\text{OTf}}$ (0.101 g, 0.0926 mmol), bis(pinacolato) diboron (0.063 g, 0.25 mmol), NaOAc (0.047 g, 0.58 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.010 g, 0.014 mmol), and dry DMF (10 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar. The mixture solution was stirred at 80 °C for 24 h and then concentrated under reduce pressure. The crude product was extracted with ethyl acetate and washed with methanol. The resultant solid was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford half tube $2'_{\text{Bpin}}$ (0.061 g, 0.058 mmol, 63%) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , r.t.): δ 7.99-7.96 (m, 4H), 7.68-7.66 (m, 4H), 7.52-7.46 (m, 4H), 7.44-7.39 (m, 4H), 7.34-7.28 (m, 5H), 7.14-7.13 (m, 2H), 7.08-7.07 (m, 2H), 4.12-4.10 (m, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 3.36 (t, $J = 5.2$, 4H), 3.00 (s, 3H), 2.92 (s, 3H), 1.36 (s, 12H), 1.30 (s, 12H).

MALDI-TOF MS (dithranol): m/z Calcd. for $\text{C}_{66}\text{H}_{68}\text{B}_2\text{O}_{10}$ 1042.50, Found 1042.23 $[\text{M}]^+$.

Synthesis of nanotube 1' KH-150



Half tubes **2'**_{OTf} (0.223 g, 0.213 mmol) and **2'**_{Bpin} (0.202 g, 0.186 mmol), K₃PO₄ (0.206 g, 0.972 mmol), Pd(PPh₃)₄ (0.029 g, 0.025 mmol), and dry DMF (70 mL) were added to a 2-necked 100 mL glass flask containing a magnetic stirring bar and the solution was stirred at 90 °C for 24 h under N₂. The mixture was concentrated under reduce pressure. The crude product was extracted with CHCl₃. The resultant solid was purified by silica-gel column chromatography (hexane:ethyl acetate = 10:1) to afford nanotube **1'** (0.035 g, 0.022 mmol, 12%) as a white solid.

¹H NMR (400 MHz, CDCl₃, r.t.): δ 7.80 (d, *J* = 8.8 Hz, 8H), 7.59 (d, *J* = 8.8 Hz, 8H), 7.52 (br, 4H), 7.24-7.17 (m, 20H), 7.08 (s, 2H), 7.02 (br, 6H), 4.08 (t, *J* = 5.2 Hz, 8H), 3.97 (s, 12H), 3.35 (t, *J* = 5.2 Hz, 8H), 2.95 (s, 12H).

MALDI-TOF MS (dithranol): *m/z* Calcd. for C₁₀₈H₈₈O₁₂ 1577.63, Found 1577.44 [M]⁺.

HRMS (ESI): *m/z* Calcd. for C₁₀₈H₈₈O₁₂ [M]⁺: 1577.6304, Found 1577.6300.

Display Report

Analysis Info

Analysis Name D:\Data\akita\09hagi\120215\hagi 1.d
Method esi_pos_wide.m
Sample Name
Comment 400v 250

Acquisition Date 2/14/2012 9:18:47 PM

Operator BDAL@DE
Instrument / Ser# micrOTOF 10321

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	200 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Diver Valve	Waste

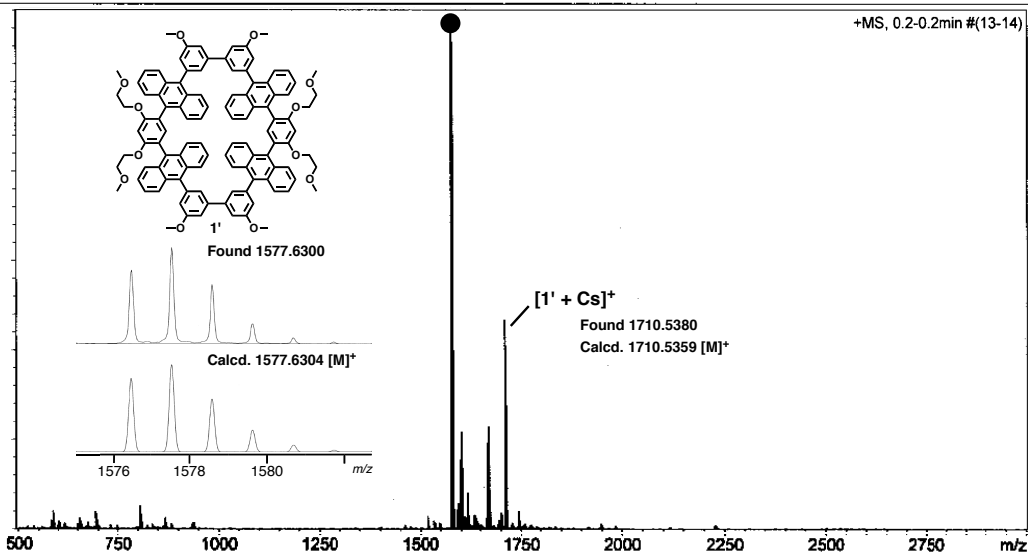


Fig. S38. HRMS (ESI) spectrum of nanotube 1'.

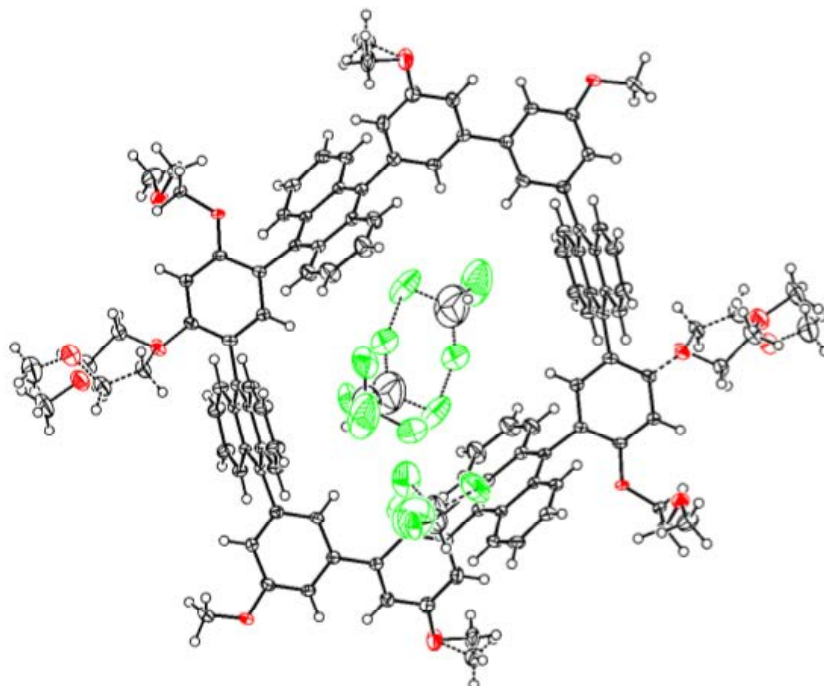


Fig. S39. ORTEP drawing of nanotube 1'.

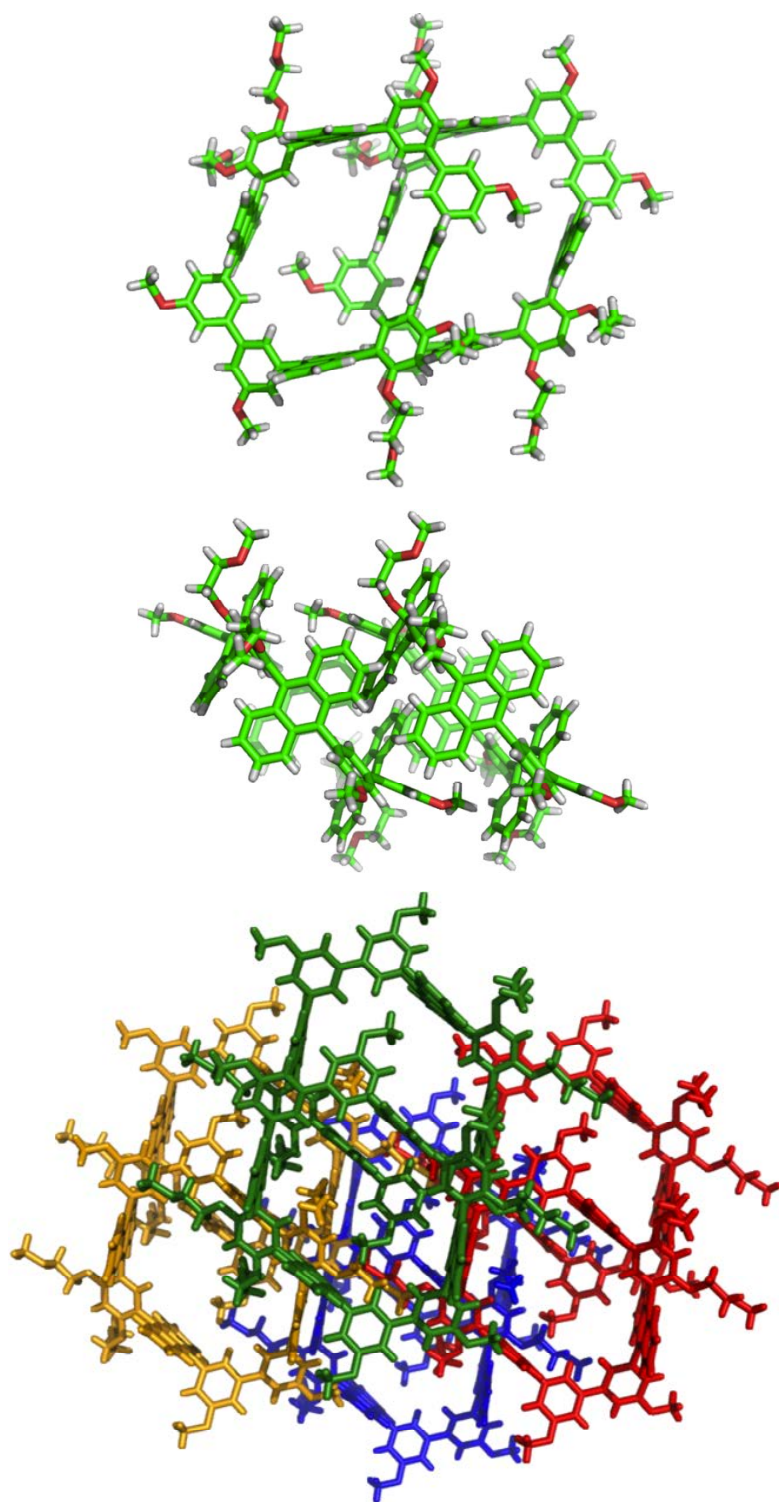


Fig. S40. Crystal packing of nanotube 1'.

Table S1. Crystal data and structure refinement for **1'**

Identification code	kh150_4_003	
Empirical formula	C112 H92 Cl12 O12	
Formula weight	2055.26	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	p-1	
Unit cell dimensions	$a = 9.2507(13)$ Å	$\alpha = 95.404(2)^\circ$
	$b = 15.609(2)$ Å	$\beta = 102.159(2)^\circ$
	$c = 17.265(2)$ Å	$\gamma = 90.147(2)^\circ$
Volume	2425.7(6) Å ³	
Z	1	
Density (calculated)	1.407 Mg/m ³	
Absorption coefficient	0.407 mm ⁻¹	
F(000)	1064	
Crystal size	0.20 x 0.07 x 0.04 mm ³	
Theta range for data collection	1.70 to 25.03°.	
Index ranges	-11 ≤ h ≤ 10, -15 ≤ k ≤ 18, -20 ≤ l ≤ 15	
Reflections collected	11489	
Independent reflections	8368 [R(int) = 0.0152]	
Completeness to theta = 25.03°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9839 and 0.9230	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8368 / 1142 / 738	
Goodness-of-fit on F ²	1.057	
Final R indices [I > 2σ(I)]	R ₁ = 0.0881, wR ₂ = 0.2378	
R indices (all data)	R ₁ = 0.1120, wR ₂ = 0.2598	
Largest diff. peak and hole	1.610 and -1.027 e.Å ⁻³	