Supporting Information

Rigid Organic Nanotubes From Phenylene-Butadiynylene Macrocycles

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1. General

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co., TCI America Co. or Oakwood Products Inc. and were used as received. Solvents used for organic synthesis were obtained from Fisher Scientific (except THF from Sigma- Aldrich Co. Canada) and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). Other solvents were obtained from Fisher Scientific and were used as received. Tetrahydrofuran (THF) and triethylamine (Et_3N) used for Castro-Stephen-Sonogashira reactions were degassed 30 minutes prior to use. All anhydrous and air sensitive reactions were performed in oven-dried glassware under positive argon pressure. Analytical thin-layer chromatographies were performed with silica gel 60 F254, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Compounds were visualized using 254 nm and/or 365 nm UV wavelength and/or aqueous sulfuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL H_2SO_4 + 900 mL H_2O). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada).

Apparatus

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz (^1H) and 100 MHz (^{13}C). High-resolution mass spectra (HRMS) were recorded with an Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with an ESI or APPI ion source (Agilent Technologies, Toronto, Canada). MALDI-TOF measurements were performed on a Bruker Biflex IV equipped with nitrogen laser. UV-visible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500) using 3-mm path length quartz cells. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6360 LV. Transmission electron microscopy (TEM) images were taken using a JEOL-1230. High resolution transmission microscopy (HRTEM) images were taken using a JEOL 2100 equipped with a field emission gun. X-ray diffraction was recorded on Siemens X-rays Diffractometer (Model S3 D5000). Raman spectra were recorded at 22.0 ± 0.5° C using a LABRAM 800HR Raman spectrometer (Horiba Jobin Yvon, Villeneuve d'Ascq, France) coupled to an Olympus BX 30 fixed stage microscope. The excitation light source was the 632.8 nm line of an He-Ne laser (Melles Griot, Carlsbad, CA). The laser beam was focused 100× long working distance objectives, generating an intensity at the sample of approximately 5-10mW. The confocal hole and the entrance slit of the monochromator were generally fixed at 200 and 100 μm, respectively. Data were collected by a one-inch open electrode Peltier-cooled CCD detector (1024 × 256 pixels).

Gelation test

To test the gelation properties of PAMs in a given solvent, we proceeded as follow: in a vial, a PAMs was dissolved in a solvent. After dissolution by sonication, the vial was sealed and heated until a clear solution was obtained. The clear solution was allowed to slowly cool down at room temperature. The stability of the gel was confirmed by tube inversion.

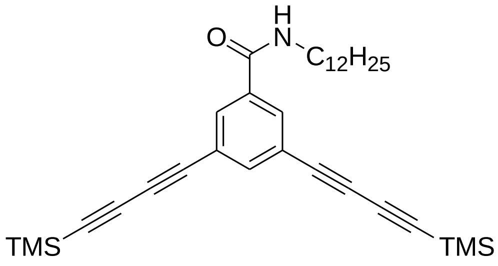
SEM imaging

Organogel obtained in cyclohexane was deposited on a stainless steel substrate and allowed to dry for 3-4 days. Then, gold particles were sputtered on dried gel prior to imaging.

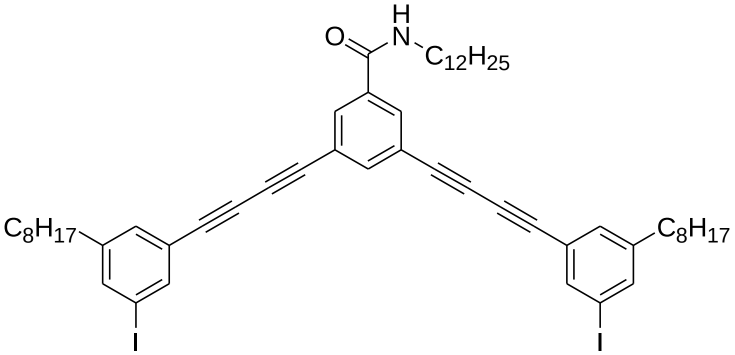
TEM imaging

The SEC-purified cross-linked material (PDA-walled nanotubes) was dissolved in $CHCl_3$ and was sonicated for two hours. The resulting solution was directly deposited on a copper grid pre-coated with amorphous carbon prior to imaging.

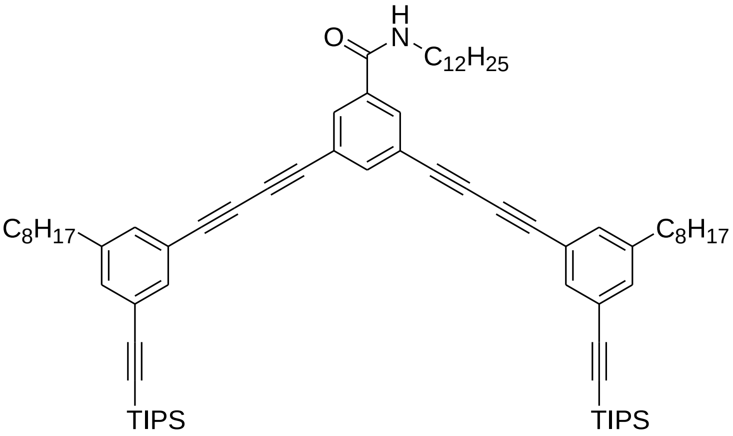
2. Synthetic procedure



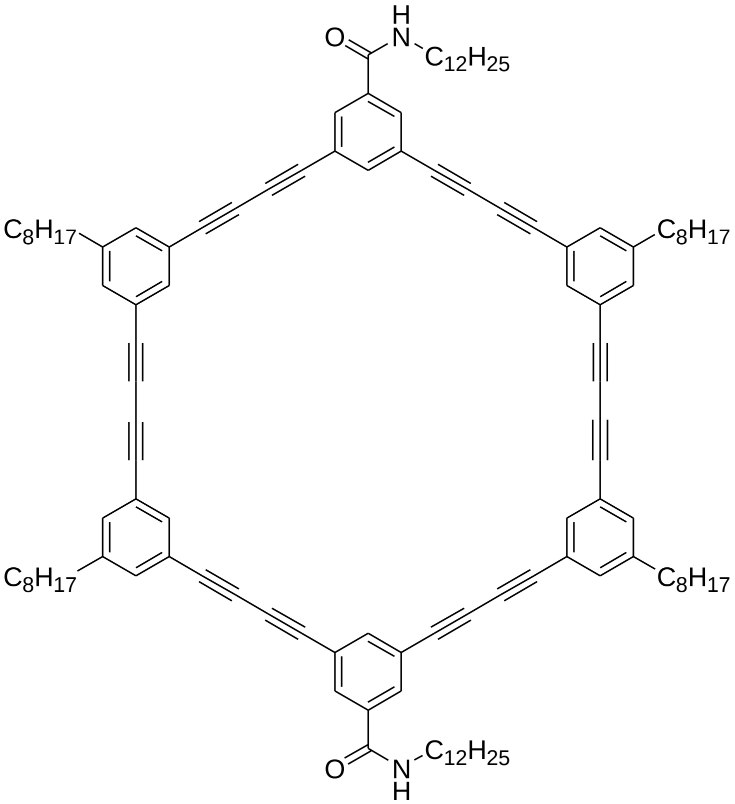
Compound **1**. An oven dried 500 mL round bottom flask equipped with a magnetic stir bar was charged with (trimethylsilyl)buta-1,3-diyne (3.0 g, 15.4 mmol), THF (170 mL) and methyllithium lithium bromide complex in THF (10.3 mL, 15.4 mmol, 1.5 M solution). The reaction mixture was stirred under nitrogen atmosphere for 3 hours and diluted with *n*-pentane. The organic layer was extracted with NH_4Cl (3x), dried with Na_2SO_4 and concentrated under vacuo to 10% of the initial volume. The organic layer was then added to a 250 mL round bottom flask equipped with a magnetic stir bar charged 3,5-diiodododecylamide (2.76 g, 5.09 mmol), $PdCl_2(PPh_3)_2$ (143 mg, 0.20 mmol), CuI (39 mg, 0.20 mmol) and triethylamine (51 mL). The reaction mixture was stirred overnight and diluted with CH_2Cl_2. The organic layer was extracted with NH_4Cl (3x), dried with Na_2SO_4 and the solvents were removed under reduce pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 5% EtOAc/hexanes as eluents to afford compound **1** (2.22 g, 82% yield) as an orange oil. ^1H NMR ($CDCl_3$, 400 MHz): 7.81 (s, 2H), 7.63 (s, 1H), 6.20 (m, 1H), 3.41 (q, *J* = 6.4 Hz, 2H), 1.59 (m, 2H), 1.32 (m, 18H), 0.88 (m, 3H), 0.24 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.7, 138.7, 136.1, 131.9, 123.1, 92.6, 87.6, 76.3, 74.7, 40.7, 32.3, 30.0 (3C), 29.9 (2C), 29.8, 29.7, 27.4, 23.1, 14.5, 0.08. HRMS (APPI-TOF) *m/z* calcd for $C_{33}H_{47}NOSi_2[M+H]^+$: 530.3269, found 530.3293.



Compound **2**. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **1** (1.50 g, 2.56 mmol), K_2CO_3 (1.06 g, 7.68 mmol), THF (6 mL) and MeOH (6 mL). The reaction mixture was stirred until complete disappearance of the starting product by TLC. The reaction mixture was then diluted with benzene, washed with 10% aqueous HCl (2x), dried with sodium sulfate and the solvent was concentrated under vacuo to 10% of the initial volume. The organic layer was added without further purification to a 50 mL round bottom flask equipped with a magnetic stir bar charged with 3,5-diiodooctylbenzene (3.78 g, 8.56 mmol), degassed Et_3N (14 mL), $PdCl_2(PPh_3)_2$ (80 mg, 0.11 mmol) and CuI (22 mg, 0.11 mmol). The reaction mixture was stirred overnight and diluted with CH_2Cl_2. The organic layer was washed with saturated aqueous NH_4Cl (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 10% acetone/hexanes as eluents to afford compound **2** (1.04 g, 28% yield) as a dark orange oil. ^{1}H NMR (CDCl$_3$, 400 MHz): 7.86 (s, 2H), 7.71 (s, 1H), 7.68 (s, 2H), 7.55 (s, 2H), 7.30 (s, 2H), 6.28 (s, 1H), 3.44 (q, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 4H), 1.58 (m, 8H), 1.29 (m, 36H), 0.88 (m, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz): 165.7, 145.3, 138.8, 138.2 (2C), 135.8, 131.8, 131.3, 122.9 (2C), 93.7, 81.1, 79.7, 75.5, 74.2, 40.3, 35.3, 31.9, 31.8, 31.0, 29.6 (4C), 29.5, 29.4, 29.3 (2C), 29.2, 29.1, 26.9, 22.7, 22.6, 14.1 (2C); HRMS (APPI-TOF) *m/z* calcd for $C_{55}H_{69}I_2NO[M+H]^+$: 1014.3541, found 1014.3583.

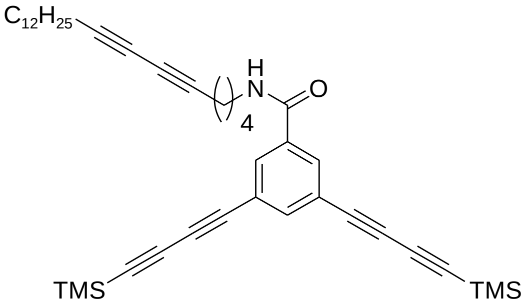


Compound **3**. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **2** (500 mg, 0.49 mmol), degassed THF (5 mL), degassed Et$_3$N (0.54 mL, 3.95 mmol), PdCl$_2$(PPh$_3$)$_2$ (14 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol) and triisopropylsilylacetylene (0.44 mL, 1.98 mmol). The reaction mixture was stirred overnight, diluted with CH$_2$Cl$_2$, washed with NH$_4$Cl and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to 5% acetone/hexanes as eluents to afford compound **3** (510 mg, 92% yield) as an orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.85 (s, 2H), 7.72 (s, 1H), 7.47 (s, 2H), 7.29 (s, 4H), 6.17 (m, 1H), 3.44 (q, *J* = 6.2 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 4H), 1.61 (m, 8H), 1.29 (m, 36H), 1.12 (s, 42H), 0.88 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.7, 143.7, 138.4, 136.0, 133.7, 133.3, 132.6, 131.4, 124.1, 123.1, 121.6, 106.2, 91.7, 82.4, 79.5, 75.9, 73.7, 40.6, 35.7 (2C), 32.2, 32.1, 31.4, 29.8 (4C), 29.6 (3C), 29.5, 27.2, 22.9 (2C), 18.9, 18.8, 14.4 (2C), 11.5 (2C). HRMS (APPI-TOF) *m/z* calcd for $C_{77}H_{111}NOSi_2[M+H]^+$: 1122.8277, found 1122.8324.

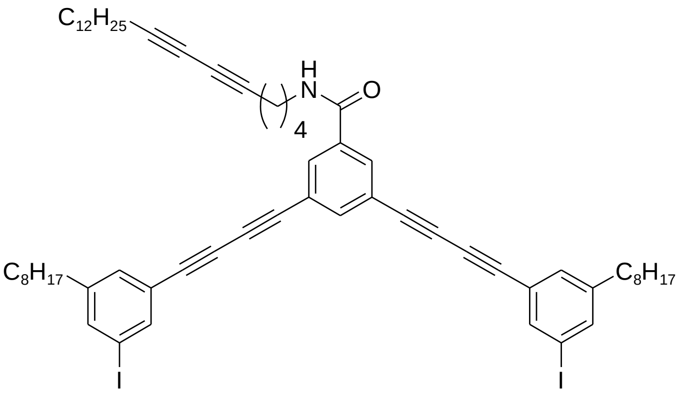


PBM 1. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **3** (500 mg, 0.45 mmol), THF (9 mL) and TBAF (1.34 mL, 1.34 mmol, 1.0M

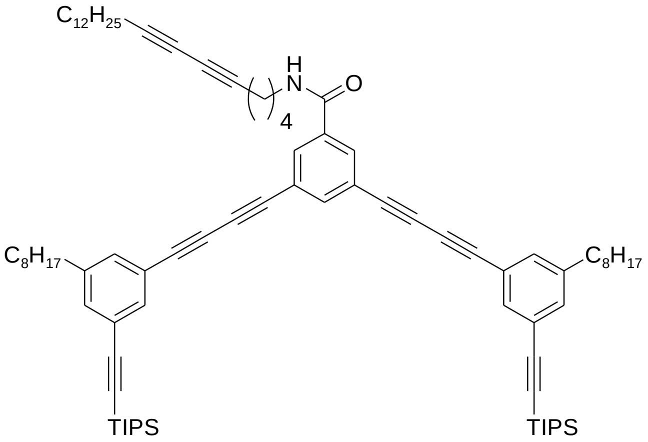
solution in THF). The reaction mixture was stirred until complete disappearance of the starting product by TLC, diluted with CH_2Cl_2, washed with water (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The resulting product was charged without further purification in a 50 mL round bottom flask equipped with a magnetic stir bar with degassed pyridine (16 mL). Another round bottom flask equipped with a magnetic stir bar was charged with CuCl (3.47 g, 35.1 mmol), $CuCl_2$ (730 mg, 5.43 mmol) and degassed pyridine (70 mL) under N_2 atmosphere. The first solution was added dropwise to the catalyst solution over 4 days using a syringe pump and the reaction mixture was stirred for an additional 7 days. The reaction mixture was diluted with $CHCl_3$ and poured in water. The organic layer was extracted successively with water, 25% aqueous NH_4OH, water, 10% aqueous acetic acid, water, 10% aqueous NaOH and brine. The organic layer was dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using 20% hexanes/$CHCl_3$ to $CHCl_3$ as eluents to afford **PBM 1** (37 mg, 9 % yield) as a light yellow amorphous powder. ^{1}H NMR (C_6D_6, 400 MHz): 7.73 (s, 2H), 7.71 (s, 4H), 7.58 (s, 4H), 7.28 (s, 4H), 6.96 (s, 4H), 5.03 (m, 2H), 3.17 (q, J = 6.7 Hz, 4H), 2.18 (t, J = 7.2 Hz, 8H), 1.57 (s, 10H), 1.33 (s, 58H), 1.20 (m, 20H), 0.88 (m, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.5; 143.8; 143.5; 135.8; 133.8; 133.6; 133.2; 131.1; 121.9; 121.8; 121.7; 81.7; 80.8; 79.5; 75.6; 74.3; 73.9; 40.4; 35.9; 31.9; 31.8; 30.9; 29.7 (2C); 29.6 (2C); 29.5; 29.4 (2C); 29.2; 29.1; 27.0; 22.7; 22.6; 17.7; 14.1 (2C). HRMS (APPI-TOF) m/z calcd for $C_{118}H_{138}N_2O_2[M+H]^+$: 1616.0758, found 1616.0751.



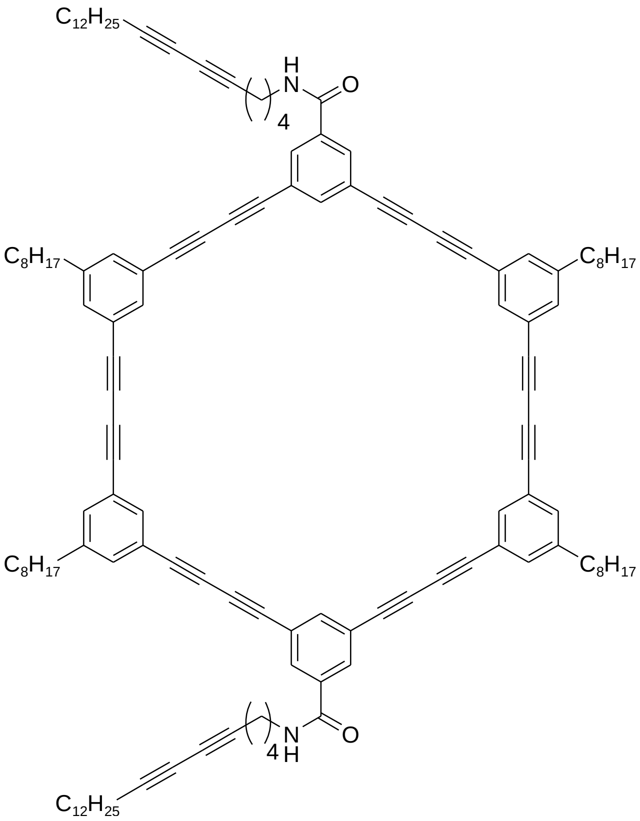
Compound **4**. An oven dried 500 mL round bottom flask equipped with a magnetic stir bar was charged with (trimethylsilyl)buta-1,3-diyne (2.5 g, 12.9 mmol), THF (143 mL) and methyllithium lithium bromide complex (8.6 mL, 12.9 mmol, 1.5 M solution in THF). The reaction mixture was stirred under nitrogen atmosphere for 3 hours and was diluted with *n*-pentane. The organic layer was extracted with NH_4Cl (3x), dried with Na_2SO_4 and concentrated under vacuo to 10% of the initial volume. The organic layer was then added to a 250 mL round bottom flask equipped with a magnetic stir bar charged with *N*-icosa-5,7-diynyl-3,5-diiodo-benzamide (2.74 g, 4.24 mmol), $PdCl_2(PPh_3)_2$ (119 mg, 0.17 mmol), CuI (32 mg, 0.17 mmol) and triethylamine (53 mL). The reaction mixture was stirred overnight and diluted with CH_2Cl_2. The organic layer was extracted with NH_4Cl (3x), dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 7% acetone/hexanes as eluents to afford compound **4** (1.87 g, 69% yield) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.82 (s, 2H), 7.64 (s, 1H), 6.24 (m, 1H), 3.6 (q, *J* = 6.6 Hz, 2H), 2.33 (t, *J* = 6.6 Hz, 2H), 2.25 (t, *J* = 6.6 Hz, 2H), 1.73 (m, 2H), 1.61 (m, 2H), 1.51 (m, 2H), 1.36 (m, 2H), 1.26 (m, 16H), 0.88 (m, 3H), 0.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8; 138.9; 135.9; 131.9; 123.1; 92.7; 87.6; 78.6; 76.9; 76.3; 74.6; 66.5; 65.4; 40.0; 32.3; 32.0; 30.0 (3C); 29.9; 29.8; 29.5; 29.3; 28.9; 28.7; 25.9; 23.1; 19.6; 19.3; 14.6; 0.59. HRMS (APPI-TOF) *m*/*z* calcd for $C_{41}H_{55}NOSi_2[M+H]^+$: 634.3895, found 634.3903.



Compound **5**. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **4** (1.80 g, 2.84 mmol), KOH (478 mg, 8.51 mmol), THF (7 mL) and MeOH (7 mL). The reaction mixture was stirred until complete disappearance of the starting product by TLC. The reaction mixture was then diluted with benzene, washed with 10% aqueous HCl (2x), dried with sodium sulfate and the solvent was concentrated under vacuo to 10% of the initial volume. The organic layer was added without further purification to a 50 mL round bottom flask equipped with a magnetic stir bar charged with 3,5-diiodooctylbenzene (5.87 g, 13.3 mmol), degassed THF (13 mL), degassed DIPEA (3.70 mL, 21.2 mmol), $PdCl_2(PPh_3)_2$ (75 mg, 0.11 mmol) and CuI (20 mg, 0.11 mmol). The reaction mixture was stirred overnight and diluted with CH_2Cl_2. The organic layer was washed with saturated aqueous NH_4Cl (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 10% acetone/hexanes as eluents to afford compound **5** (1.4 g, 47% yield) as a dark orange oil.^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (s, 2H), 7.75 (s, 1H), 7.57 (s, 2H), 7.49 (s, 2H), 7.32 (s, 2H), 6.19 (m, 1H), 3.50 (q, *J* = 6.6 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 4H), 2.36 (t, *J* = 6.6 Hz, 2H), 2.26 (t, *J* = 6.6 Hz, 2H), 1.77 (m, 2H), 1.61 (m, 10H), 1.53 (m, 2H), 1.27 (m, 34 H), 0.89 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.4; 145.2; 138.7; 138.3; 135.6; 131.7; 131.3; 129.5; 127.0; 123.2; 122.9; 93.3 (2C); 80.9; 79.6; 77.8; 76.3; 75.5; 74.3; 65.1; 41.9; 39.6; 36.1; 35.3; 34.5; 31.9; 31.1; 29.7; 29.5; 29.4; 29.3; 29.2; 29.1; 29.0; 28.9; 28.6; 28.4; 26.9; 25.6; 25.2; 19.2; 18.8; 11.3. HRMS (APPI-TOF) *m/z* calcd for $C_{63}H_{77}I_2NO[M+H]^+$: 1118.4167, found 1118.4188.



Compound **6**. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with compound **5** (1.35 g, 1.21 mmol), degassed THF (12 mL), degassed Et_3N (1.32 mL, 9.66 mmol), $PdCl_2(PPh_3)_2$ (34 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) and triisopropylsilylacetylene (1.08 mL, 4.83 mmol). The reaction mixture was stirred overnight, diluted with CH_2Cl_2, washed with NH_4Cl and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to 5% acetone/hexanes as eluents to afford compound **6** (860 mg, 58% yield) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (s, 2H), 7.75 (s, 1H), 7.49 (s, 2H), 7.31 (s, 2H), 6.15 (m, 1H), 3.50 (q, *J* = 6.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 4H), 2.36 (t, *J* = 6.6 Hz, 2H), 2.26 (t, *J* = 6.6 Hz, 2H), 1.78 (m, 2H), 1.61 (m, 10H), 1.53 (m, 2H), 1.27 (m, 34 H), 1.14 (m, 42H), 0.88 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.5; 143.5; 135.6; 133.4; 132.3; 129.6; 127.0; 123.9; 122.9; 121.4; 105.9; 91.4; 90.2; 82.1; 81.5; 79.3; 78.0; 76.5; 75.7; 73.6; 66.1; 65.1; 41.9; 39.7; 35.5; 31.9 (2C); 31.1; 29.7 (2C); 29.6; 29.5; 29.4; 29.3; 29.2; 29.1; 28.9; 28.6; 28.4; 25.6; 22.7 (2C); 19.2; 18.9; 18.6; 18.5; 14.1; 11.3. HRMS (APPI-TOF) *m/z* calcd for $C_{85}H_{119}NOSi_2$-$[M+H]^+$: 1226.8903, found 1226.8918.4



PBM 2. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **6** (850 mg, 0.69 mmol), THF (14 mL) and TBAF (2.08 mL, 2.08 mmol, 1.0M solution in THF). The reaction mixture was stirred until complete disappearance of the starting product by TLC, diluted with CH_2Cl_2, washed with water (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The resulting product was charged without further purification in a 50 mL round bottom flask equipped with a magnetic stir bar with degassed pyridine (19 mL). Another round bottom flask equipped with a magnetic stir bar was charged with CuCl (4.61 g, 46.6 mmol), $CuCl_2$ (970 mg, 7.22 mmol) and degassed pyridine (94 mL) under N_2 atmosphere. The first solution was added dropwise to the catalyst solution over 4 days using a syringe pump and the reaction

mixture was stirred for an additional 7 days. The reaction mixture was diluted with $CHCl_3$ and poured in water. The organic phase was extracted successively with water, 25% aqueous NH_4OH, water, 10% aqueous acetic acid, water, 10% aqueous NaOH and brine. The organic layer was dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using 20% hexanes/$CHCl_3$ to $CHCl_3$ as eluents to afford **PBM 2** (146 mg, 24 % yield) as a white amorphous powder.^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (s, 2H), 7.65 (s, 4H), 7.44 (s, 4H), 7.19 (s, 4H), 7.17 (s, 4H), 6.77 (m, 2H), 3.51 (q, J = 6.4 Hz, 4H), 2.49 (t, J = 7.3 Hz, 8H), 2.38 (t, J = 6.4 Hz, 4H), 2.26 (t, J = 6.4 Hz, 4H), 1.81 (m, 4H), 1.65 (m, 8H), 1.54 (m, 8H), 1.31 (m, 76H), 0.91 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 143.3, 137.3, 135.4, 134.1, 132.8, 130.7, 129.4, 126.9, 122.8, 121.9, 81.4, 80.6, 79.3, 78.0, 76.4, 75.5, 74.2, 73.8, 65.9, 64.9, 41.8, 35.3, 31.8, 31.7, 30.8, 29.5 (2C), 29.4, 29.3, 29.2, 29.1, 28.9, 28.7, 28.4, 28.2, 25.5, 22.5, 21.3, 19.1, 18.8, 17.9, 17.6, 13.9, 12.1. HRMS (APPI-TOF) *m/z* calcd for $C_{134}H_{154}N_2O_2[M+H]^+$: 1824.2083, found 1824.2019.

3. NMR spectra (^{1}H and ^{13}C)

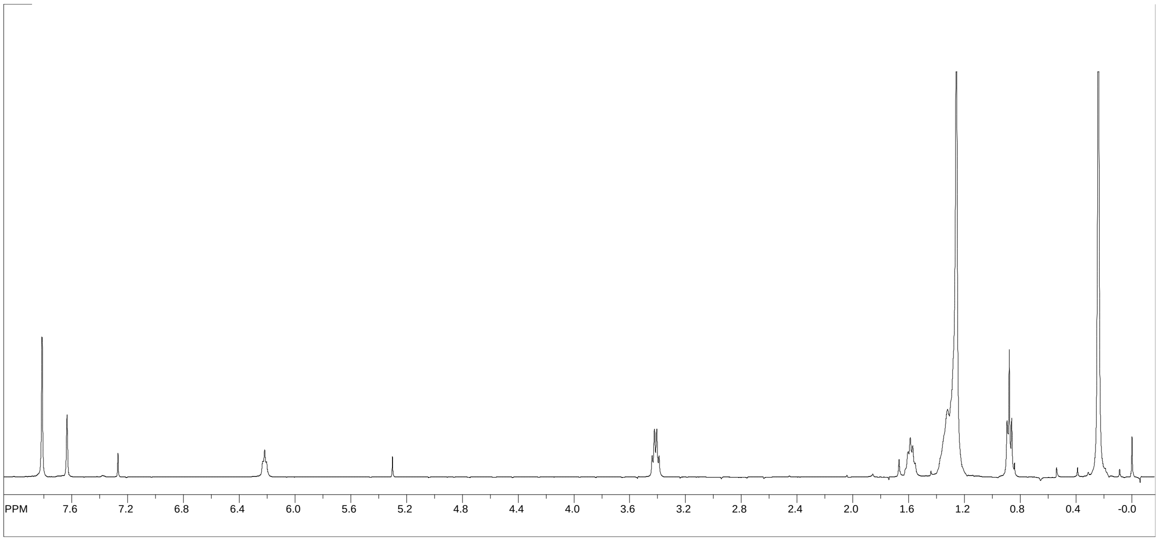


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$

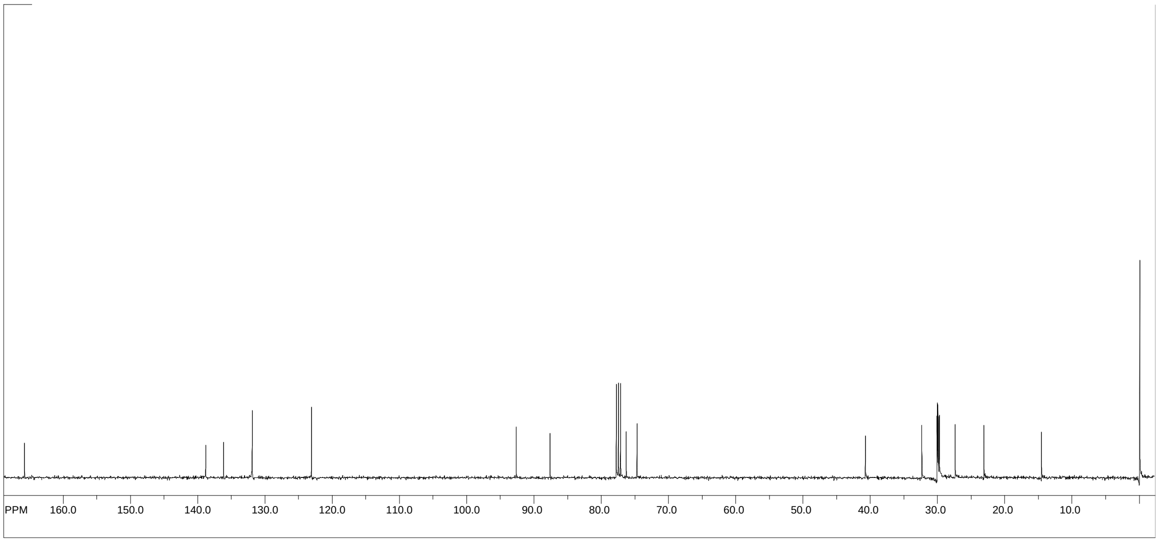


Figure S2. ^{13}C NMR spectrum of compound **1** in $CDCl_3$

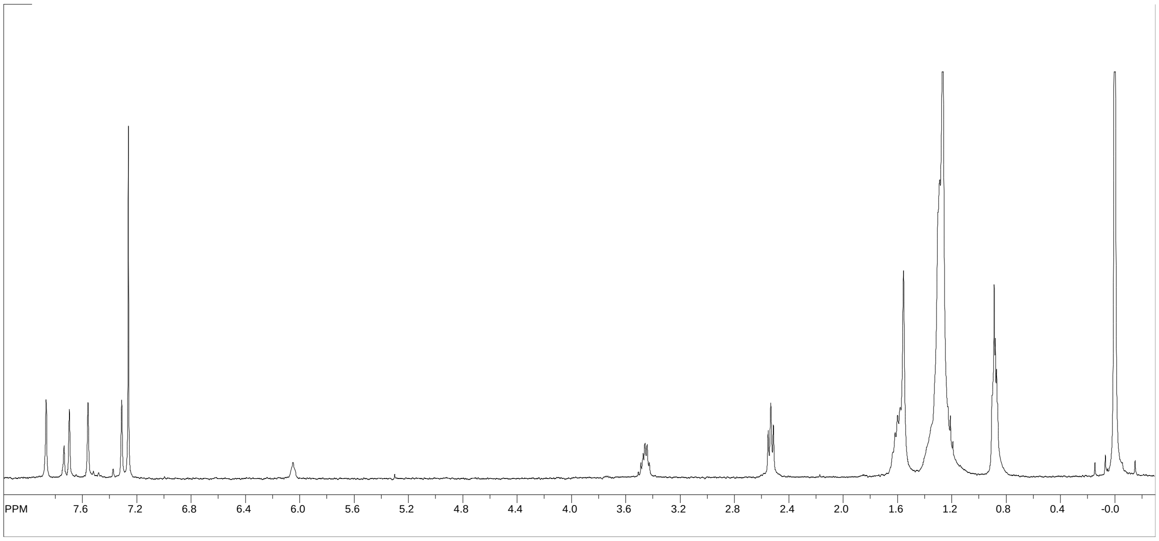


Figure S3. ^{1}H NMR spectra of compound **2** in $CDCl_3$

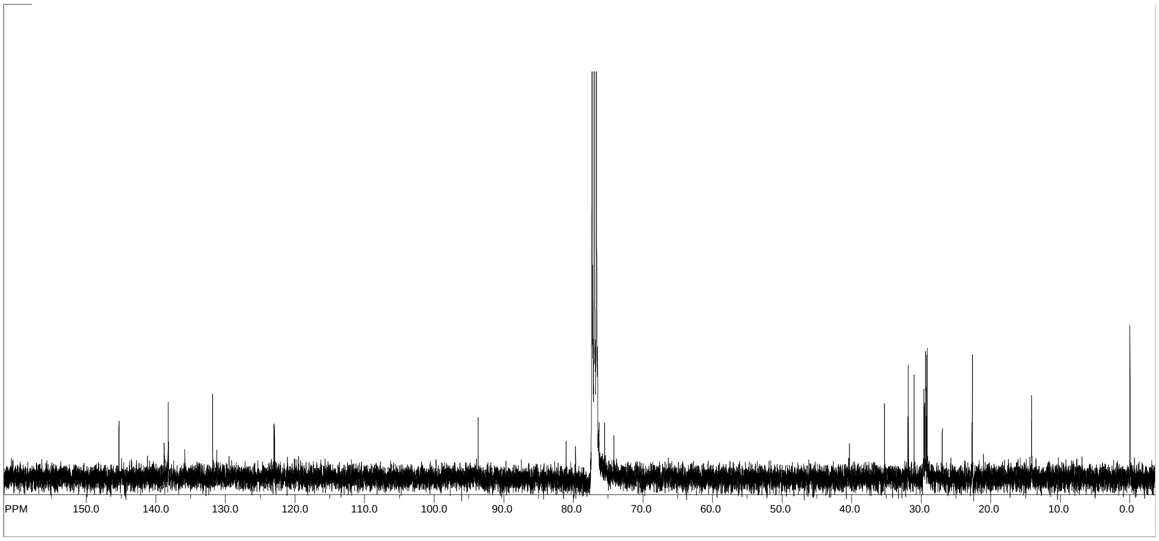


Figure S4. ^{13}C NMR spectra of compound **2** in $CDCl_3$

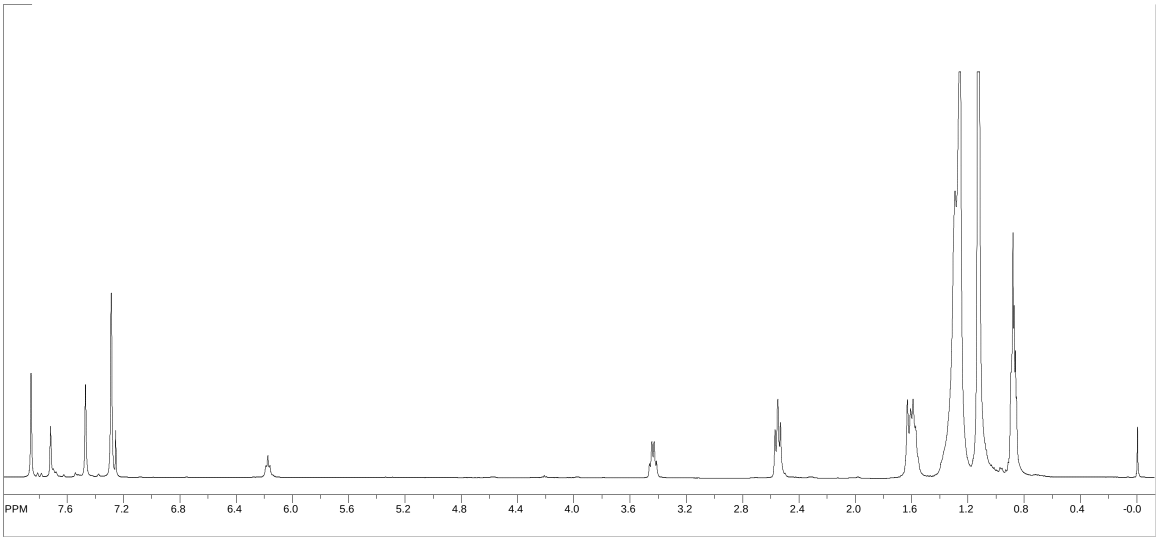


Figure S5. ^{1}H NMR spectra of compound **3** in $CDCl_3$

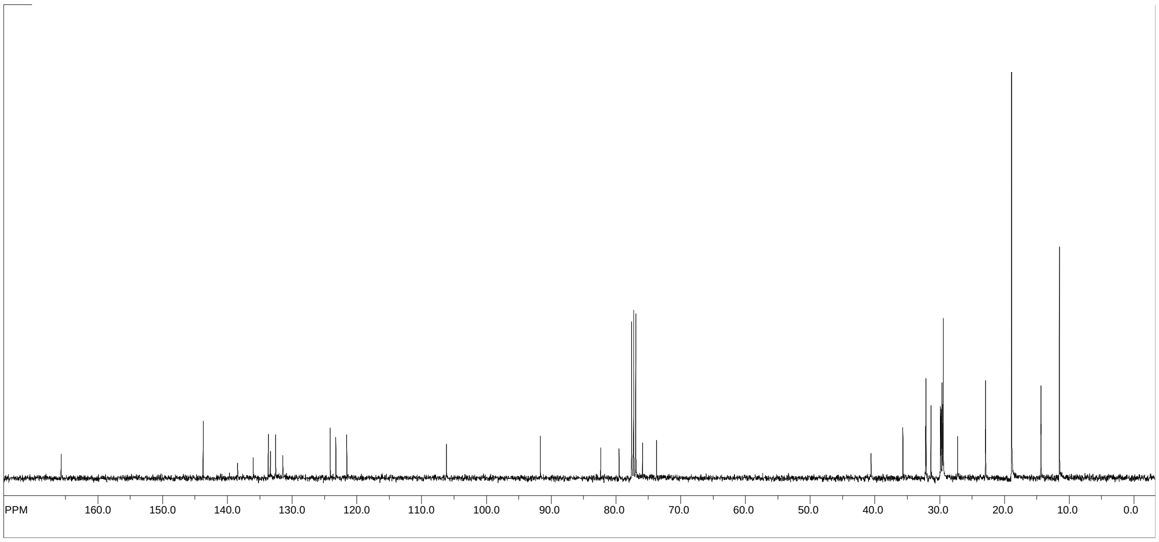


Figure S6. ^{13}C NMR spectra of compound **3** in $CDCl_3$

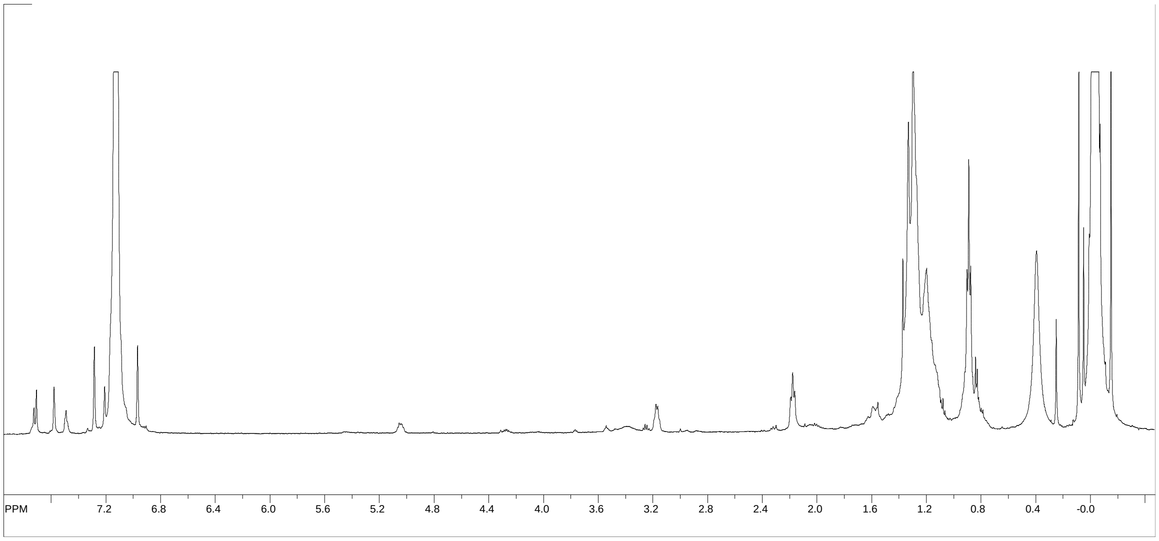


Figure S7. ^{1}H NMR spectra of **PBM 1** in C_6D_6

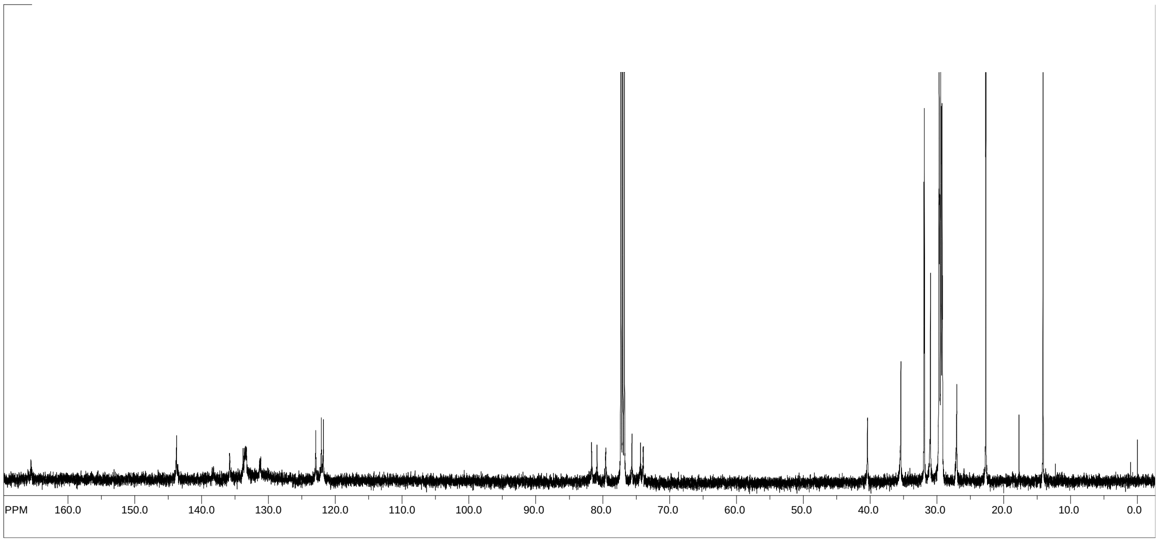


Figure S8. ^{13}C NMR spectra of **PBM 1** in $CDCl_3$

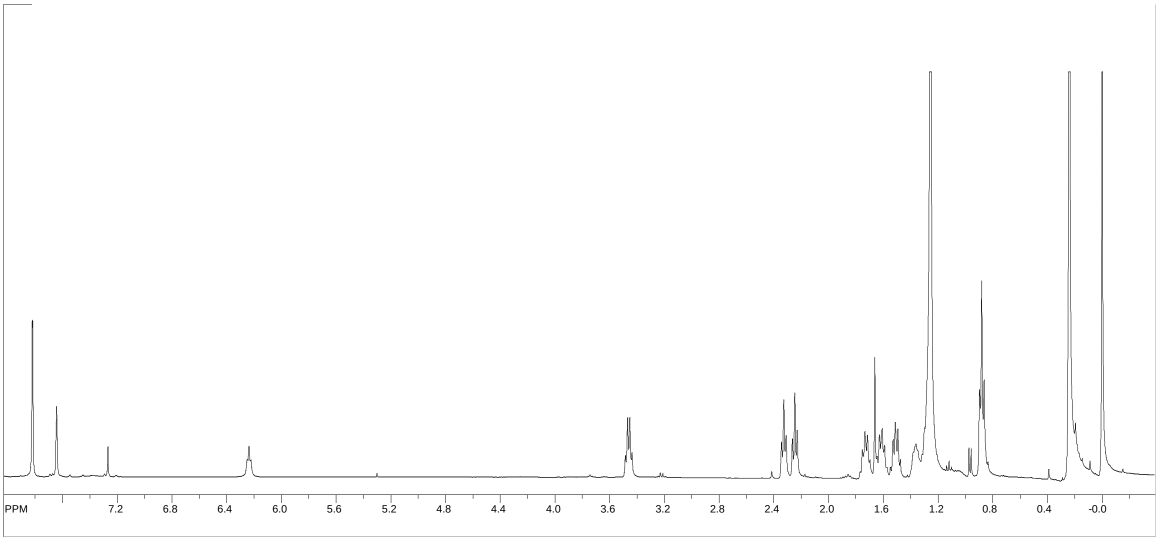


Figure S9. ^{1}H NMR spectra of compound **4** in $CDCl_3$

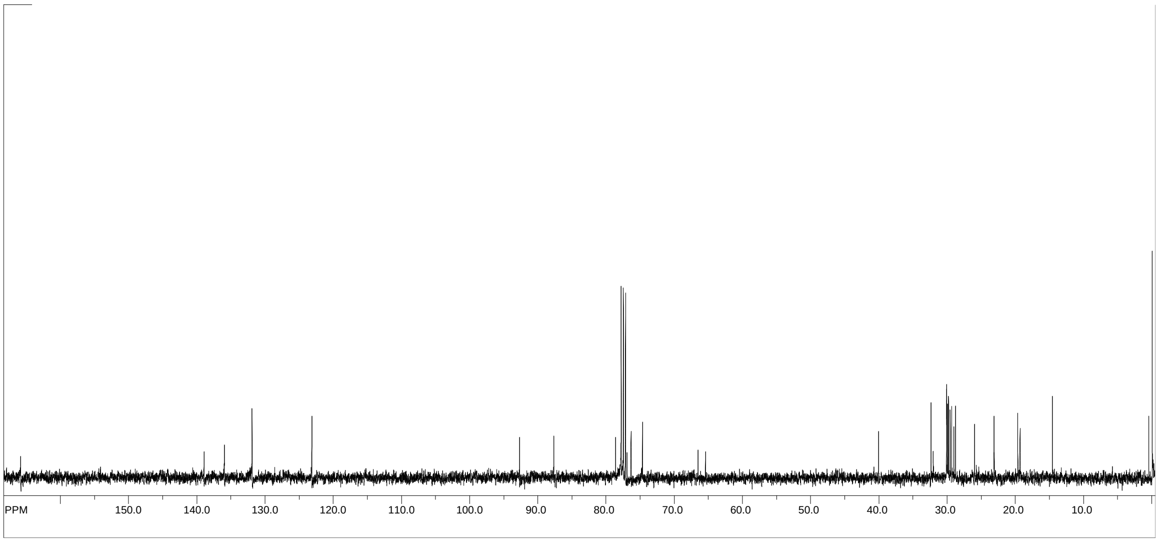


Figure S10. ^{13}C NMR spectra of compound **4** in $CDCl_3$

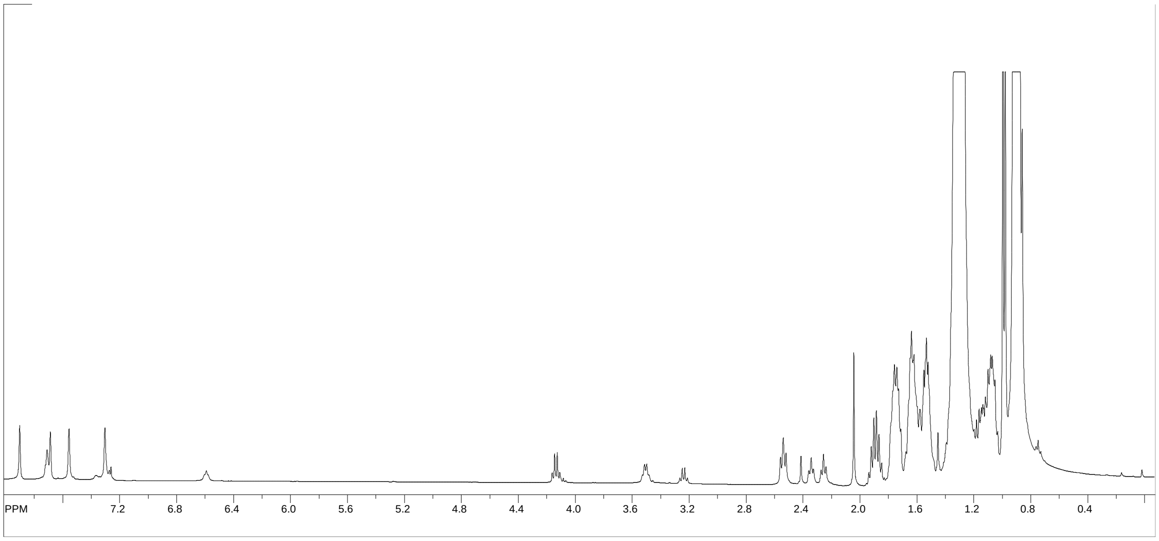


Figure S11. ^{1}H NMR spectra of compound **5** in $CDCl_3$

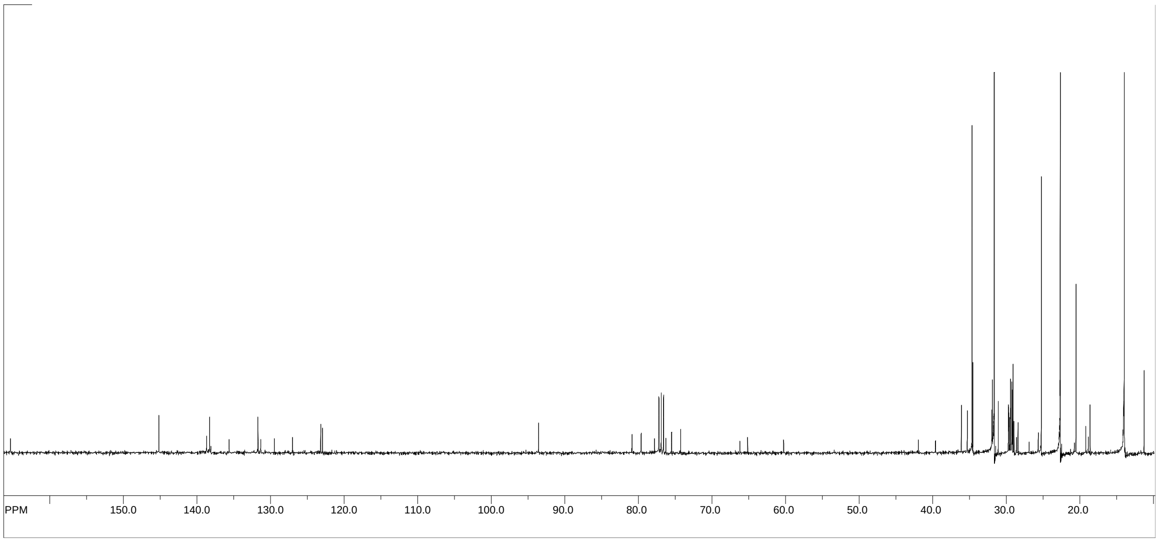


Figure S12. ^{13}C NMR spectra of compound **5** in $CDCl_3$

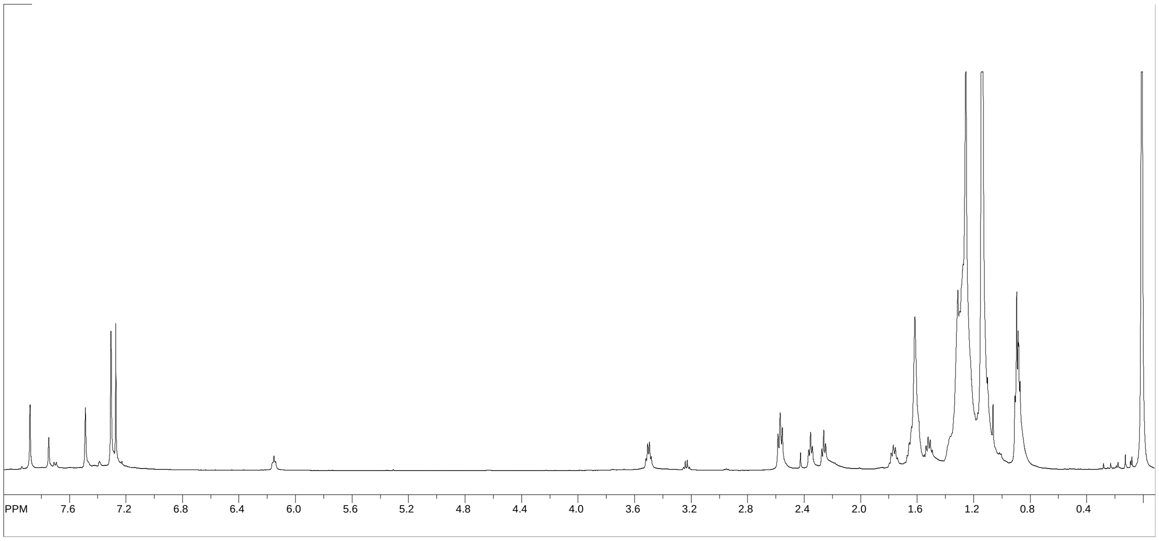


Figure S13. ^{1}H NMR spectra of compound **6** in $CDCl_3$

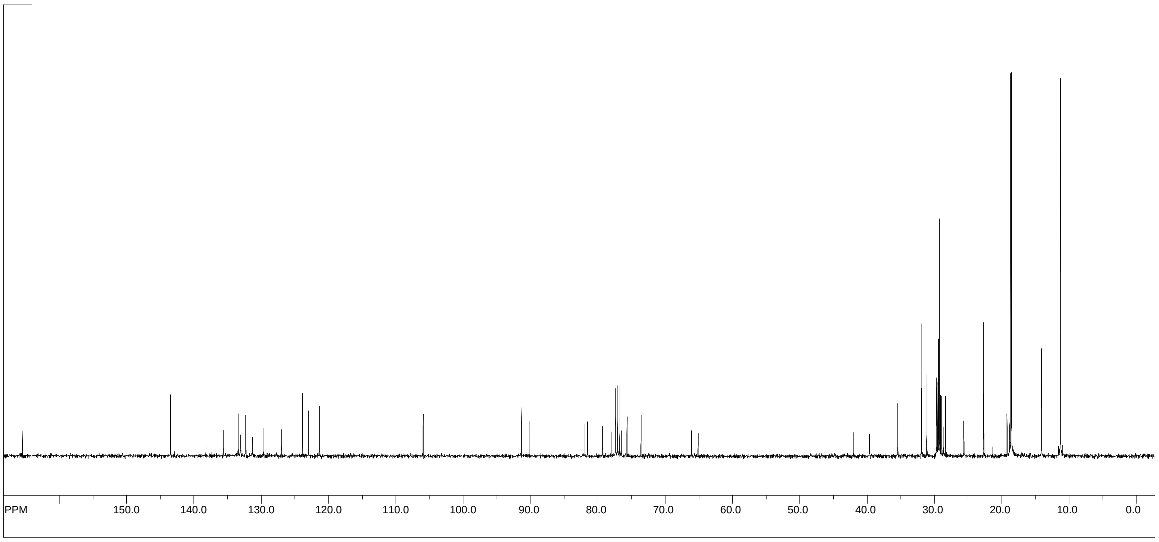


Figure S14. ^{13}C NMR spectra of compound **6** in $CDCl_3$

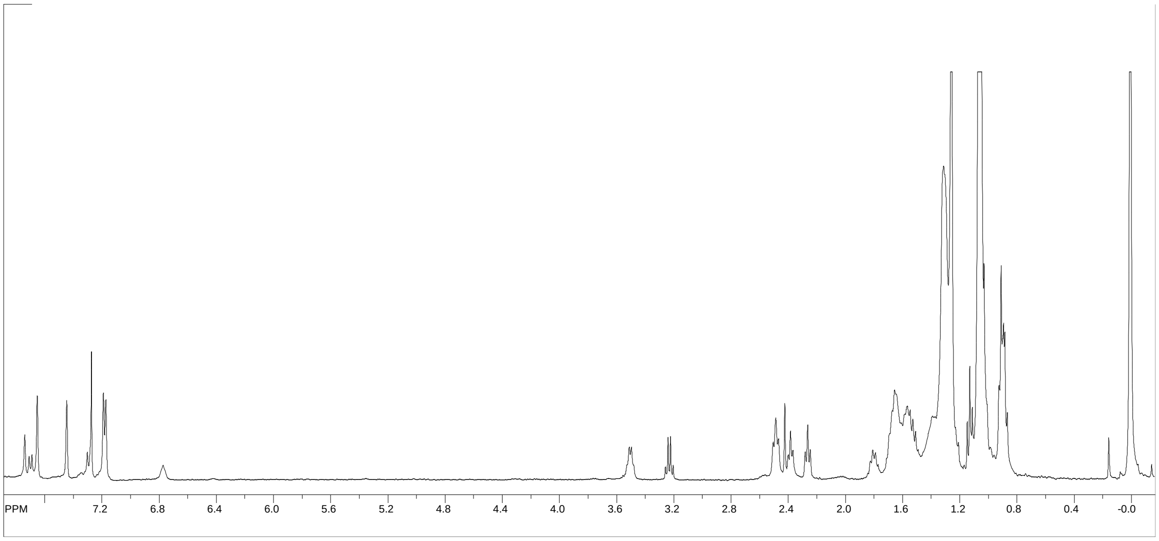


Figure S15. ^{1}H NMR spectra of **PBM 2** in $CDCl_3$.

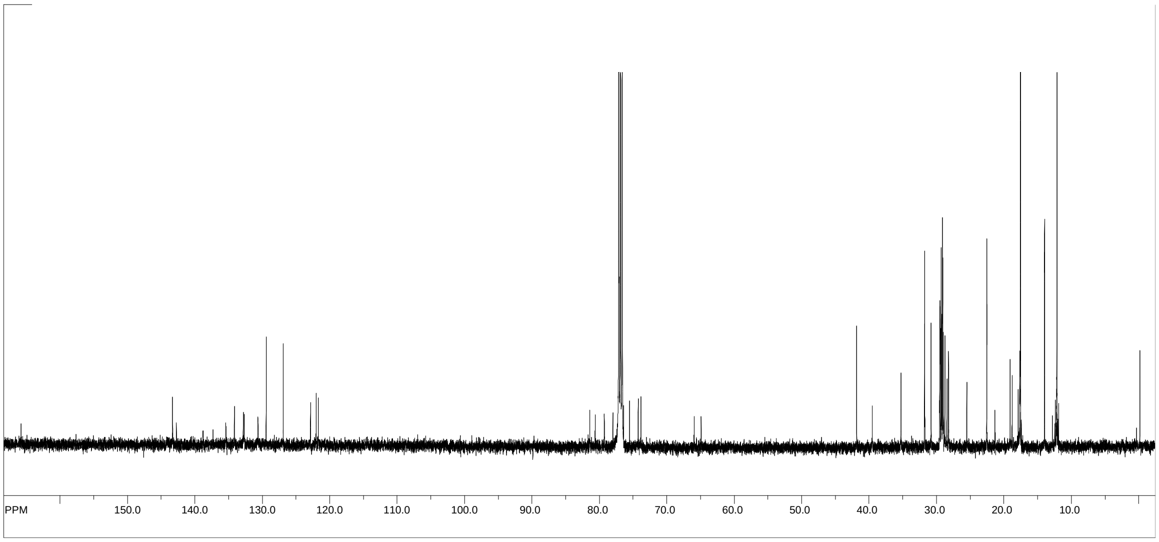


Figure S16. ^{13}C NMR spectra of **PBM 2** in $CDCl_3$.

4. Scanning-electron microscopy (SEM) imaging

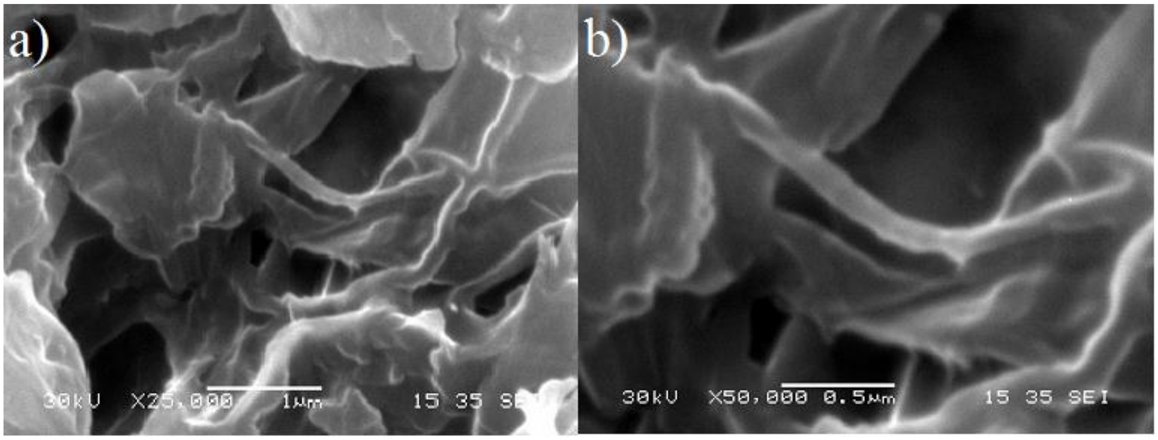


Figure S17. SEM images of dried gel of **PBM1** in cyclohexane (10 mg/mL)

5. Powder X-rays diffraction analysis

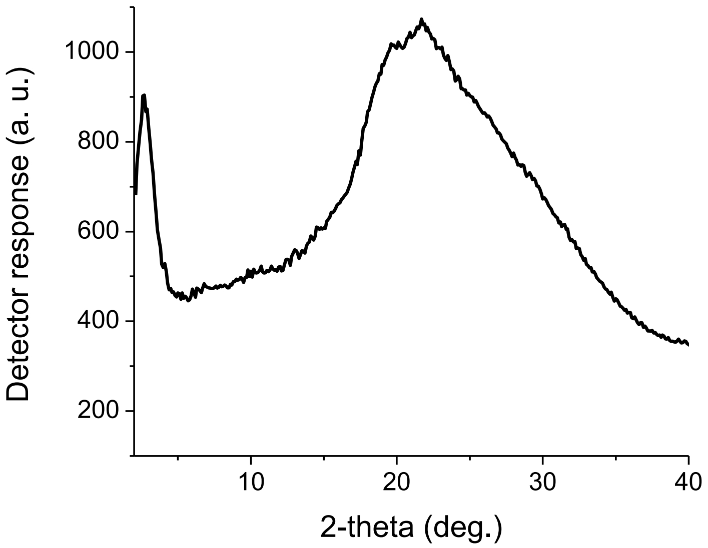


Figure S18. X-rays diffractogram for **PBM1** gel in cyclohexane (10 mg/mL).

6. UV Visible spectroscopy

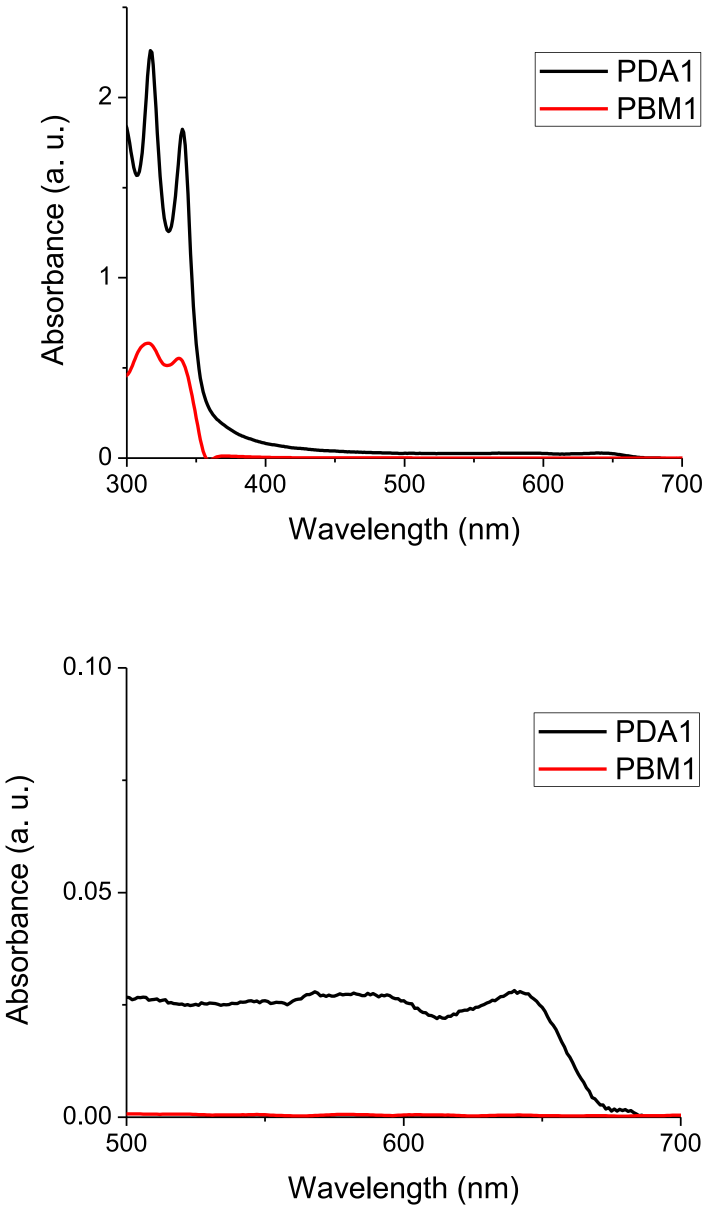


Figure S19. UV visible spectra of **PBM1** and **PDA1** in $CHCl_3$

7. Raman spectroscopy

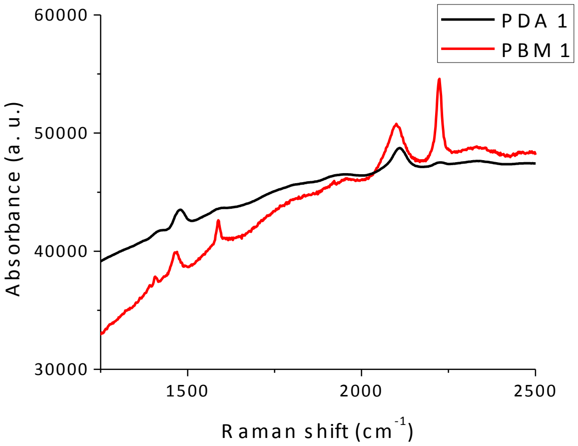


Figure S20. Raman spectra of **PBM1** (red) and **PDA1** (black).

8. TEM image of the nanotubes

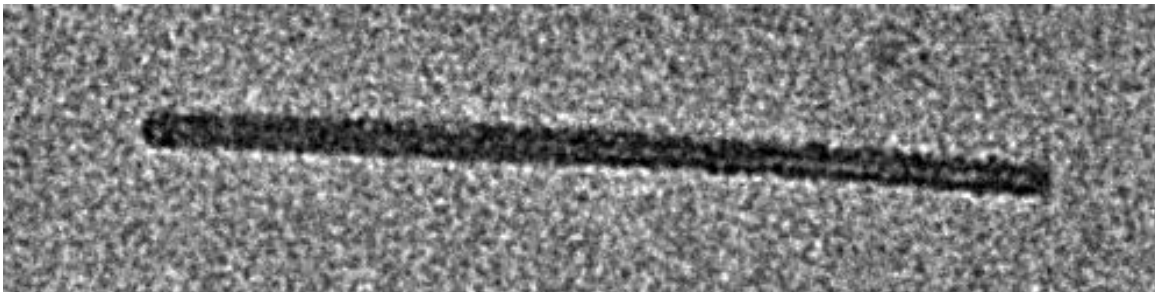


Figure S21. TEM image of a single nanotube. The channel inside the nanotube can be clearly differentiate, especially on the right side of the nanotube.