Supporting Information

Layered Graphitic Materials From a Molecular Precursor

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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 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). TEM copper grids pre-coated with amorphous carbon were purchased from Ted Pella, Inc. (Redding, USA).

Apparatus

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz (^{1}H) and 100 MHz (^{13}C). Highresolution 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. FT-IR was recorded in ATR mode on Infrared spectrometer (Thermo-Nicolet Magne 850) equipped with Golden Gate. UV-visible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500) using 3-mm path length quartz cells. DSC and TGA measurements were done on a Mettler Toledo (DSC 823e and TGA/SDTA851e). 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).

Gelation test

To test the gelation properties of **BD3** in a given solvent, we proceeded as follow: in a vial, a defined amount of **BD3** 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. Tube inversion method was used to confirm the gel stability.

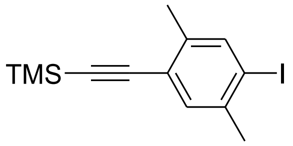
SEM imaging

Organogels obtained in ethyl acetate were 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.

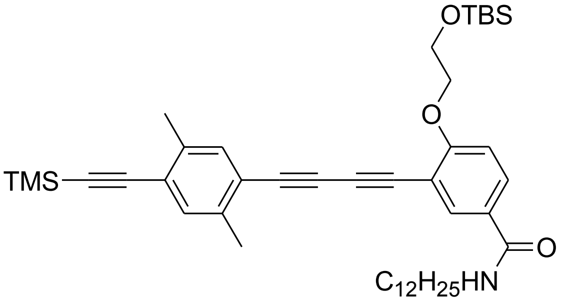
TEM and HRTEM imaging

The soxhlet-purified **PDA-BD3** was dissolved in THF and sonicated until clear solution was obtained. The resulting solution was directly deposited on a copper grid pre-coated with amorphous carbon and the solvent slowly evaporated prior to imaging.

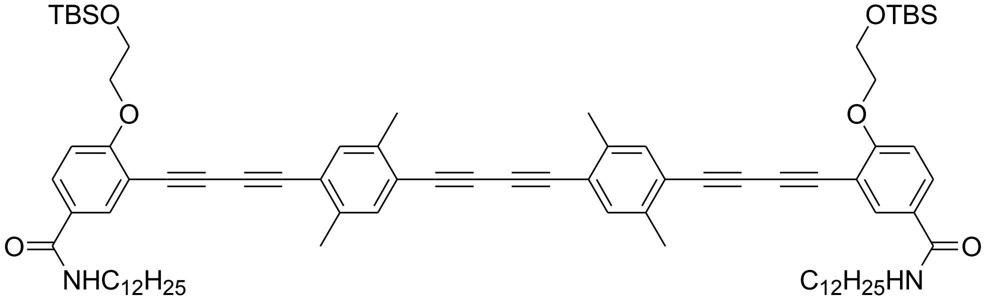
2- Synthetic procedure



Compound 2. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 1,4-diiodo-2,5-dimethylbenzene (4.00 g, 11.17 mmol), degassed THF (55 mL), degassed Et_3N (1.56 mL, 10.7 mmol), $PdCl_2(PPh_3)_2$ (314 mg, 0.44 mmol), CuI (85 mg, 0.044 mmol) and trimethylsilylacetylene (1.55 mL, 11.17 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then diluted with CH_2Cl_2, washed with NH_4Cl (3x) and dried over sodium sulfate. The solvent was removed under reduced pressure using a rotary evaporator and the crude product was purified by flash chromatography on silica gel using hexanes as eluent to afford compound **2** a yellowish liquid (1.44 g, 40% yield). ^1H NMR ($CDCl_3$, 500 MHz): 7.66 (s, 1H), 7.28 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 139.5, 139.4, 138.4, 132.6, 123.0, 103.3, 101.5, 99.2, 27.3, 19.6, 0.10; HRMS (APPI-TOF) *m/z* calcd for $C_3H_{17}ISi$ (M^{*+}): 328.0144, found 328.0139.

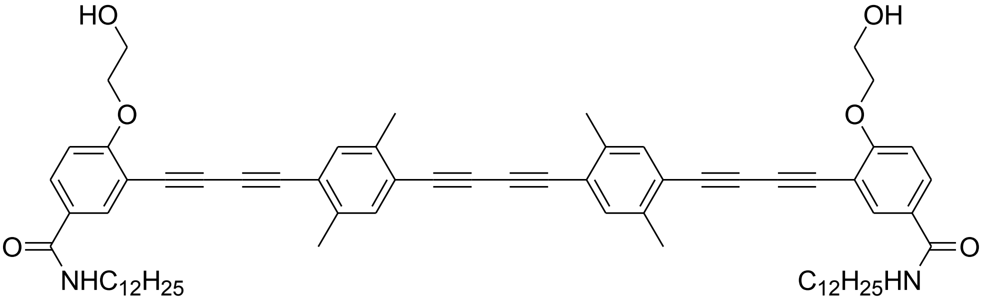


Compound **3**: In a 25 mL round bottom flask equipped with a stir bar, compound **1** (0.40 g, 0.69 mmol) was dissolved in a mixture 1:1 of THF/MeOH (3.5 mL) and K_2CO_3 (22 mg, 0.16 mmol) was added. After 15 minutes of stirring, the mixture was quenched with aqueous NH_4Cl and extracted with benzene. The organic layer was dried over Na_2SO_4 and filtered under vacuum. The mixture was evaporated under reduced pressure until 10% of the original volume. In the meantime, in a 25 mL oven-dried round bottom flask equipped with a stir bar, compound **2** (0.168 g, 0.559 mmol) was dissolved in Et_3N (7 mL). The previous solution was added and argon stream was continuously bulled through the mixture for 30 min. After that, $PdCl_2(PPh_3)_2$ (15 mg, 0.021 mmol) and CuI (4 mg, 0,021 mmol) were added. The flask was purged 4 times with argon. The mixture was stirred overnight at room temperature. Upon completion of the reaction as determined by TLC analysis, aqueous NH_4Cl was added and the mixture was extracted 3 times with ethyl acetate. The organic layers were combined and dried over Na_2SO_4. The mixture was filtered under vacuum and the solvent was removed under reduce pressure. The crude material was purified by column chromatography (silica gel, hexanes/ acetone 85:15 as eluant) to provide compound **3** as a brown oil in 55% yield. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) : 7.84 (d, J = 1.9 Hz, 1H) ; 7.80 (d, J_1 = 1.9, J = 8.7 Hz, 1H) ; 7.32 (s, 1H) ; 7.29 (s, 1H); 6.95 (d, J = 8.7 Hz, 1H) ; 6.01 (t, J = 5.6 Hz, 1H) ; 4.17 (t, J = 4.2 Hz, 2H), 4.05 (t, J = 4.8 Hz, 2H) ; 3.43 (m, 2H); 2,40 (s, 3H); 2.37 (s, 3H); 1.61 (m, 2H) ; 1.27 (m, 18H) ; 0.92 (s, 9H) ; 0.89 (t, J = 6.9 Hz, 3H; 0.26 (s, 9H); 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) :166.0, 162.9, 138.9, 138.0, 133.6, 133.5, 133.4, 133.0, 132.7, 132.7, 132.2, 131.9, 130.1, 127.2, 122.8, 122.1, 111,7, 111.3, 82.7, 82.1, 80.9, 78.9, 78.7, 78.3, 70.4, 61.8, 0.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 27.0, 25.9, 22.7, 20.0, 19.9, 18.4, 14.1, 0.0, -0.1, -5.3. HRMS: Calculated for $C_{44}H_{65}NO_3Si_2$: 711.4503 $[M+H]^+$; Found: 712.4576.



Compound 4. In a 10 mL round-bottom flask equipped with a magnetic stir bar, compound **3** (0.37 g, 0.52 mmol) was dissolved in a 1:1 mixture of THF/MeOH (22 mL) and K_2CO_3 (17 mg, 0.12 mmol) was added. The mixture was continuously stirred for 15 min. Then, aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered under vacuum and the solvent was removed under reduced pressure until 10% of the original volume with a water bath maintained at 30°C. In the meantime, a 25 mL round-bottom flask equipped with magnetic stir bar, CuCl (7 mg, 0.069 mmol) and tetramethylethylenediamine (TMEDA) (30 µL, 0.019 mmol) were dissolved in *o*-dichlorobenzene (6 mL). The mixture was heated at 50 °C with a continuous stream of air bubbling through the solution. Then, the previous solution containing the deprotected diyne was added dropwise. The mixture was stirred two hours. Then, aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered in vacuum and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (silica gel, hexanes/ethyl acetate 75:25 as eluent) to provide 272 mg of compound **4** as brownish solid (82%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.84 (d, J = 2.0 Hz, 2H) ; 7.81 (dd, J_1 = 2.0 Hz, J_2 = 8.7 Hz, 2H) ; 7.36 (s, 2H) ; 7.35 (s, 2H); 6.96 (d, J = 8.7 Hz, 2H) ; 5.99 (t, J = 5.4, 2H) ; 4.18 (t, J = 4.8 Hz, 4H), 4.06 (t, J = 4.8 Hz, 4H) ; 3.44 (m, 4H); 2,44 (s, 6H); 2.43 (s, 6H); 1.61 (m, 4H) ; 1.27 (m, 36H) ; 0.92 (s, 18H) ; 0.89 (t, J = 6.7 Hz, 6H); 0.15 (s, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) : 166.0, 163.0, 155.2, 138.3, 138.8, 133.7, 132.6, 130.1,127.2, 122.3, 122.4, 111.7, 111.3, 81.9, 79.6, 79.2, 79.1, 78.3, 77.3, 77.0, 76.8, 70.4, 61.8, 40.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3,

27.0, 25.9, 22.7, 20.1, 20.0, 18.4, 0.0, -5.3. HRMS: Calculated for $C_{82}H_{112}N_2O_6Si_2$: 1276.8059 $[M+H]^+$; Found: 1277.8177



BD3. In a 25 mL round-bottom flask equipped with magnetic stir bar, compound **4** (240 mg, 0.19 mmol), THF (2 mL) and TBAF (1*M* in THF, 0.77 mL) were added successively. After 1 hour, silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The crude was purified by column chromatography using silica gel (CH_2Cl_2/Acetone/MeOH 85:14:1 as eluent) to provide 137 mg (68%) of a yellowish compound. ^1H NMR ($CDCl_3$, 500 MHz): 8.38 (s, 2H), 8.06 (s,2H), 7.91 (d, *J*=7.5 Hz, 2H), 7.56 (s, 2H), 7.21 (d, *J*=8.0 Hz, 2H), 4.94 (s, 2H), 4.17 (s, 4H), 3.76 (s, 4H), 3.22 (s, 4H), 2.38 (s, 12H), 1.49 (s, 4H), 1.23 (m, 38 H), 0.84 (m, 6H); *^{13}C NMR spectrum was not recorded because of its lack of solubility*. HRMS: Calculated for $C_{70}H_{84}N_2O_6$: 148.6329 $[M+H]^+$; Found: 1049.6451

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

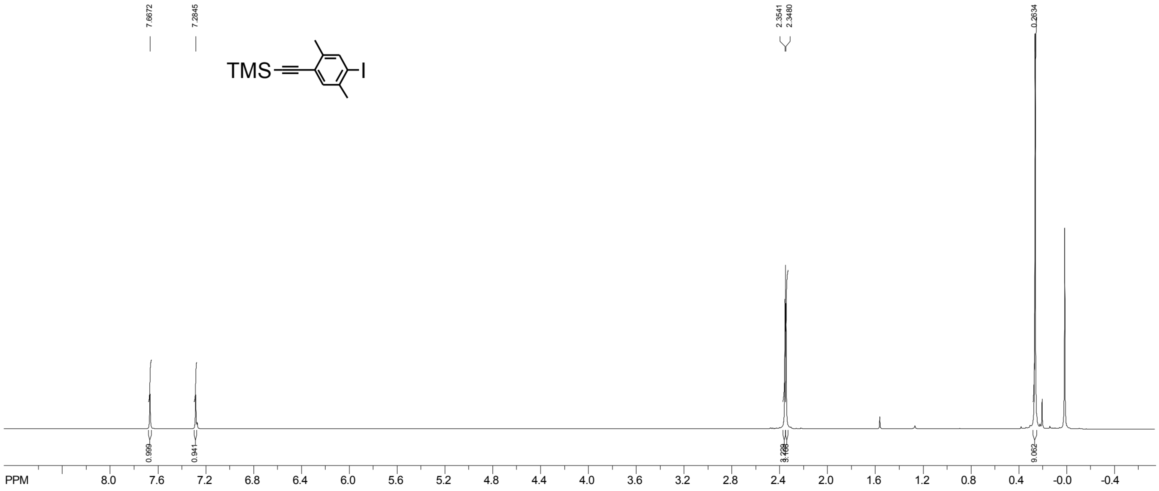


Figure S1. ^{1}H NMR of compound **2** in $CDCl_3$

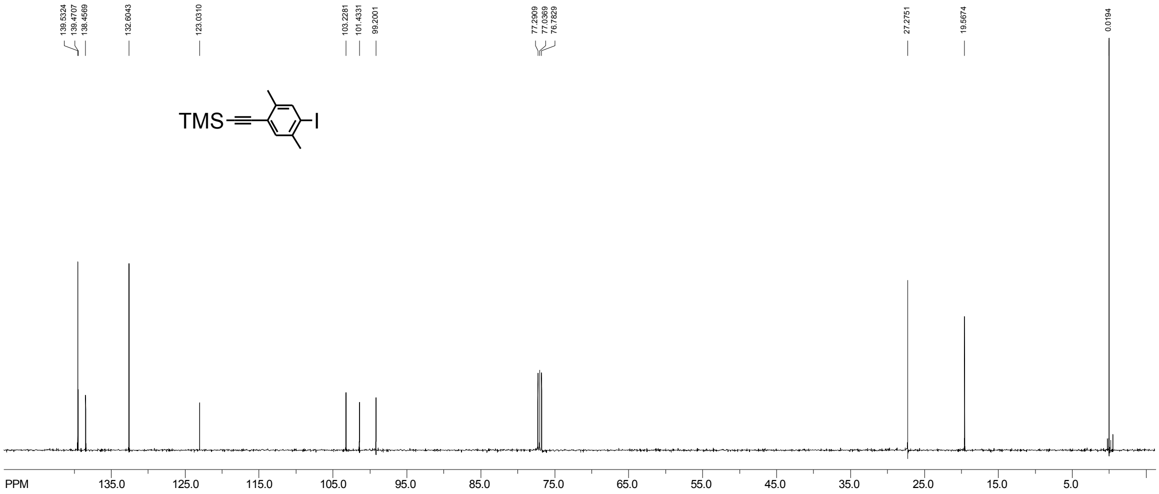


Figure S2. ^{13}C NMR of compound **2** in $CDCl_3$

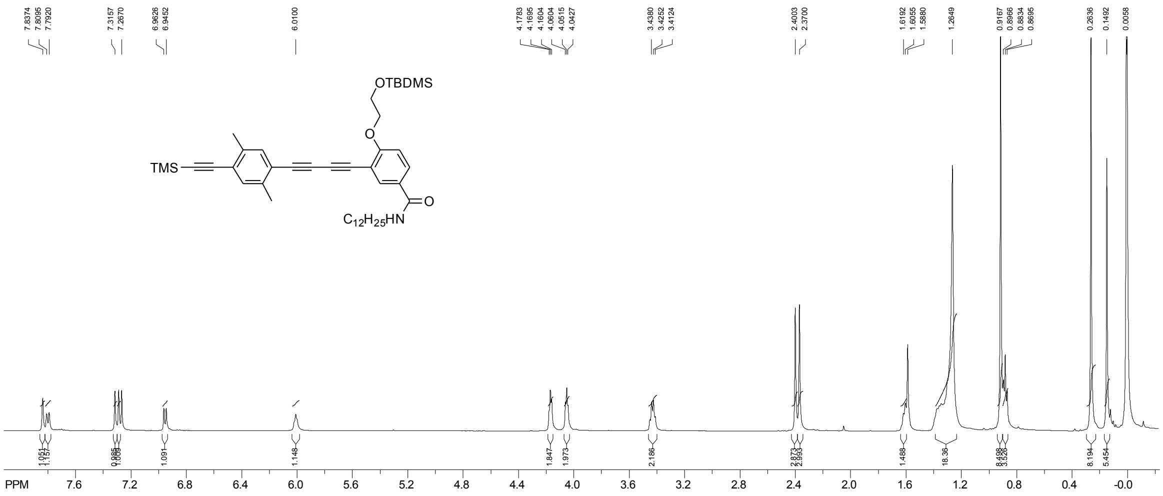


Figure S3. ^{1}H NMR of compound **3** in $CDCl_3$

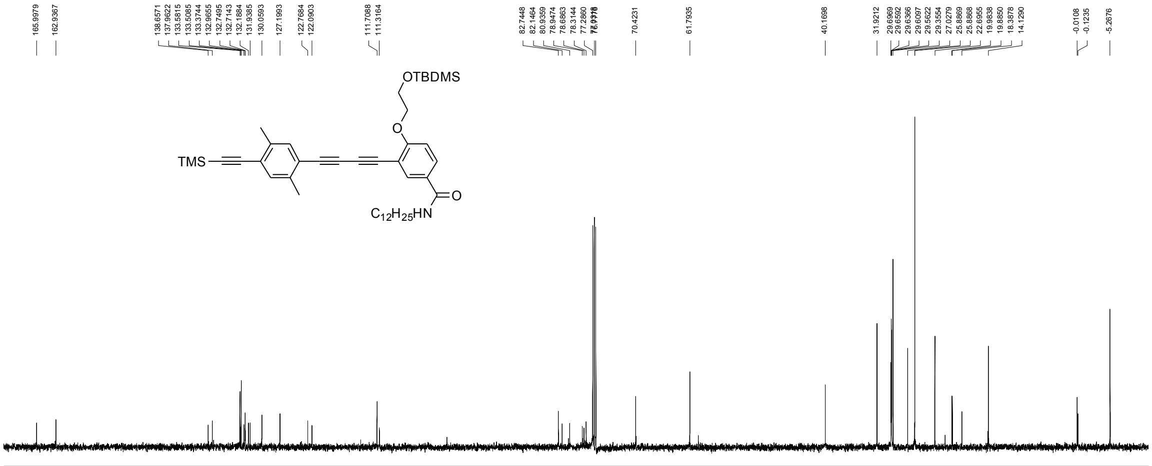


Figure S4. ^{13}C NMR of compound **3** in $CDCl_3$

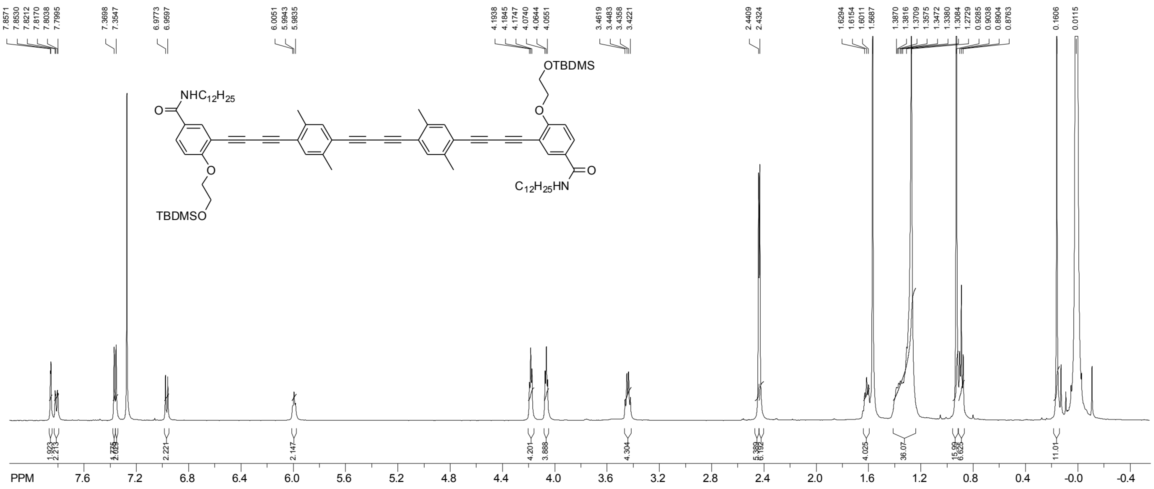


Figure S5. ^{1}H NMR of compound **4** in $CDCl_3$

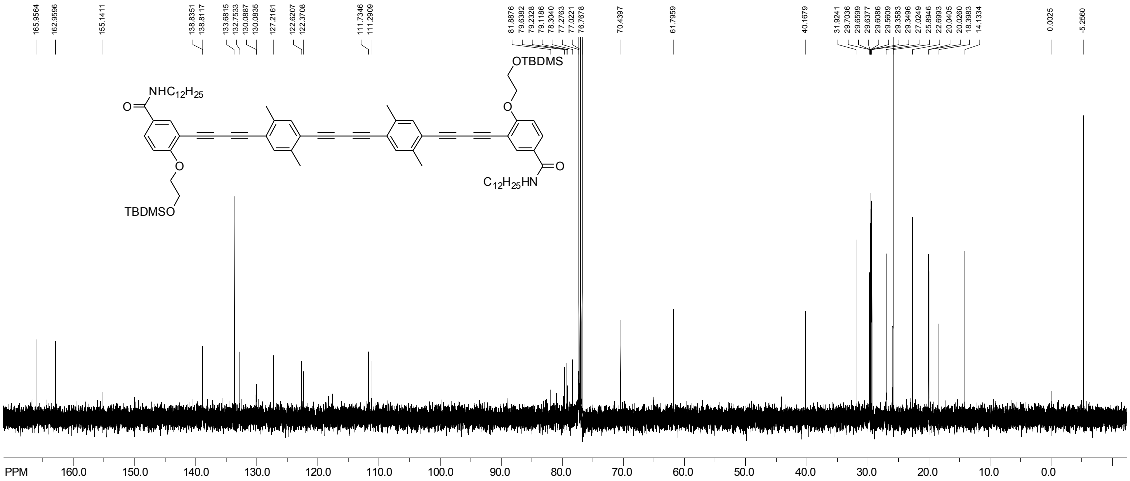


Figure S6. ^{13}C NMR of compound **4** in $CDCl_3$

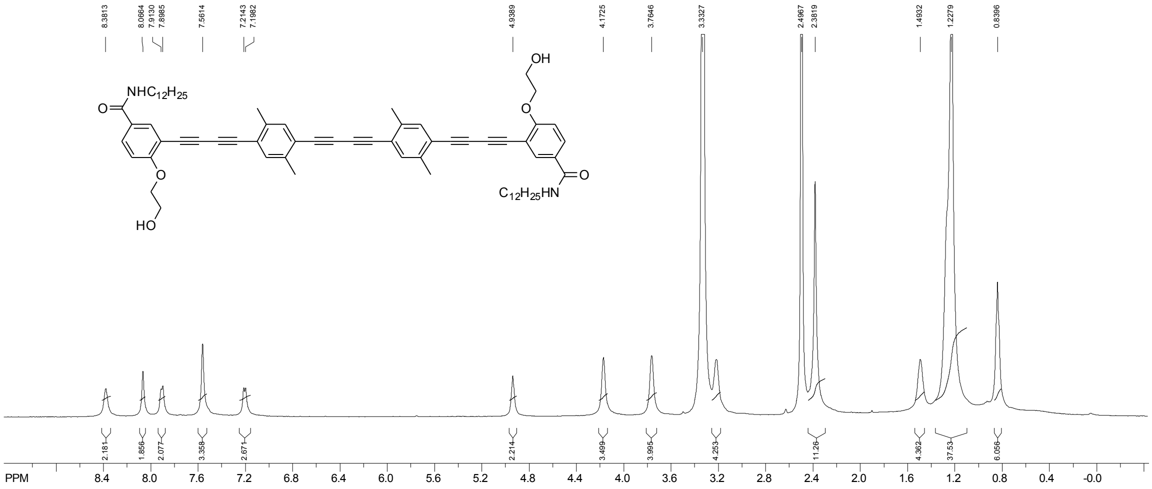


Figure S7. ^{1}H NMR of **BD3** in DMSO-d_6

4- Characterization of BD3, PDA-BD3 and G-BD3

Table S1: Gelation properties of **BD3** at 10 mg/mL

Solvent	Observations
Toluene	G
$CHCl_3$	P
CH_2Cl_2	G
Acetone	G
Benzene	G
o-DCB	G
Cyclohexane	I
Hexanes	I
MeCN	I
MeOH	I
AcOEt	G

G = Gelation
I = Insoluble

Figure S8. Ethyl acetate-based gel (10 mg/mL).

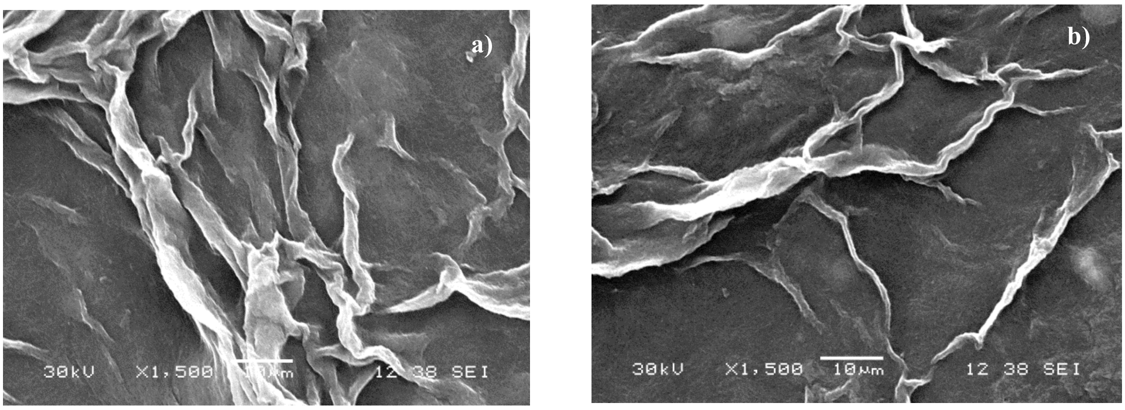


Figure S9. SEM images of ethyl-acetate-based xerogel of **BD3** (10 mg/mL). Scale bars are 10 µm (a), 10 µm (b) and 1 µm (c).

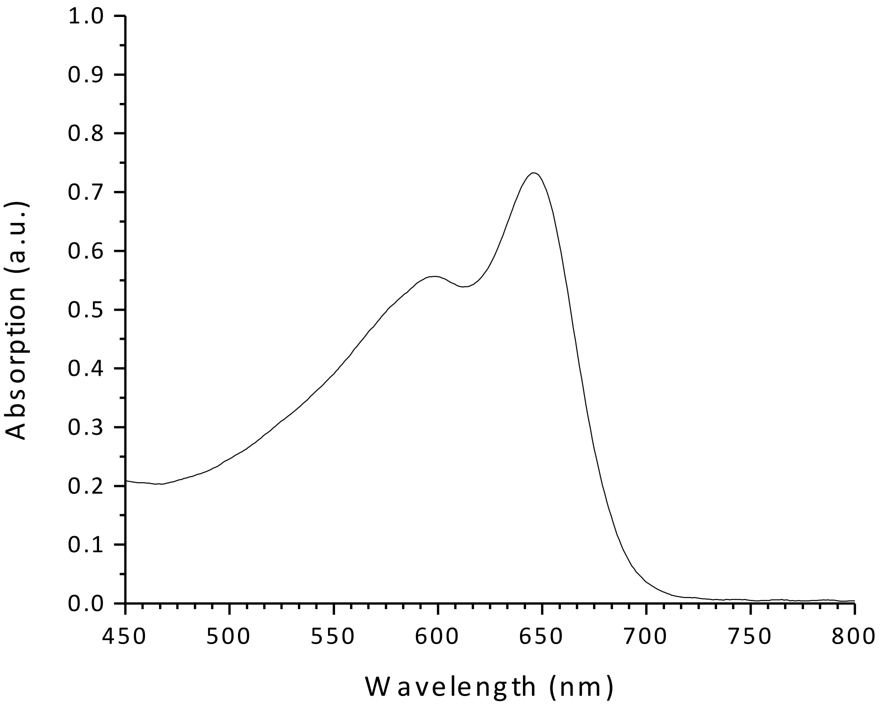


Figure S10. UV-visible spectrum of **PDA-BD3**

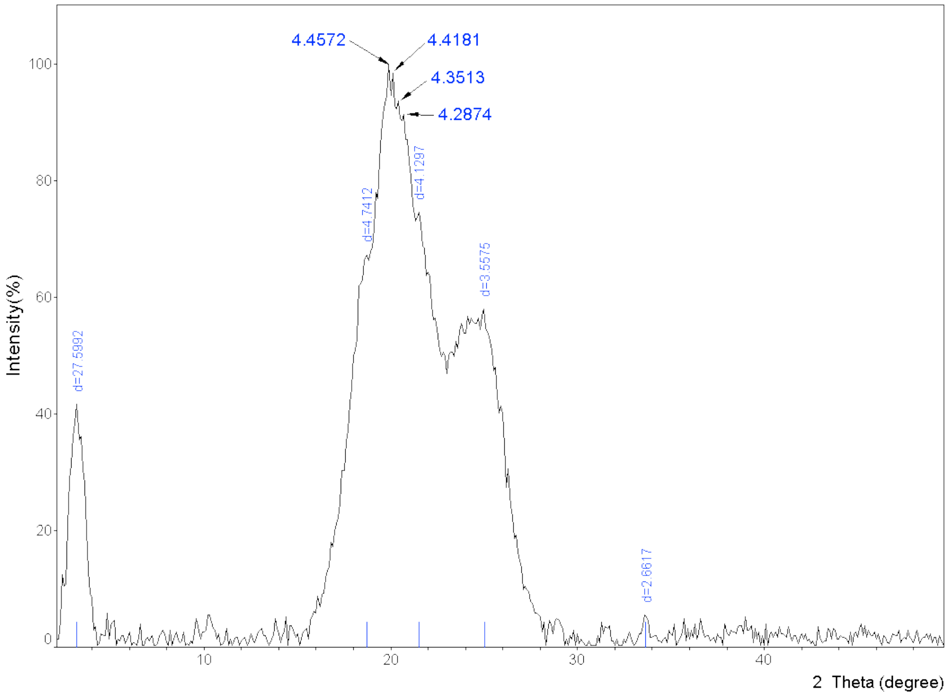


Figure S11. PXRD of ethyl acetate-based xerogel (10 mg/mL) of **BD3.**

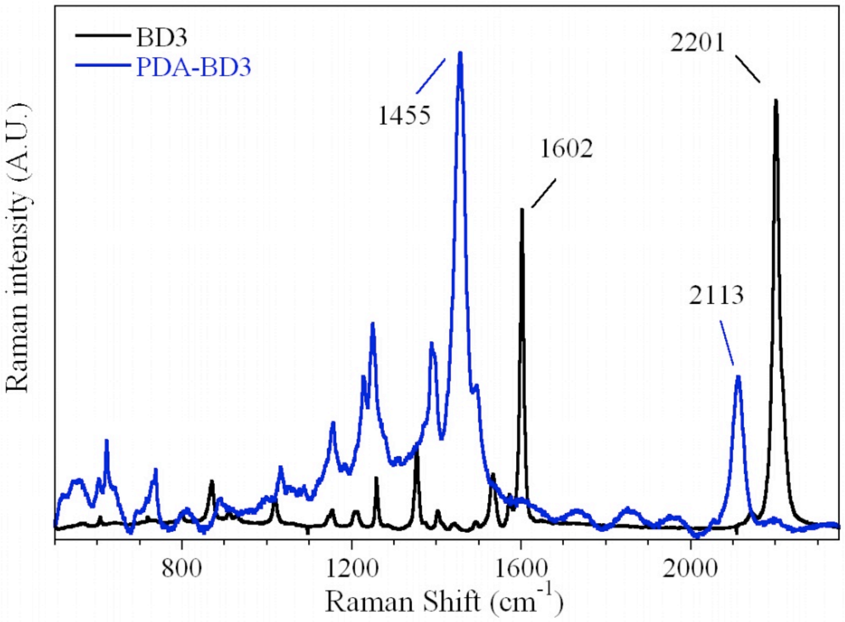


Figure S12. Comparative Raman spectra of **BD3** and **PDA-BD3**.

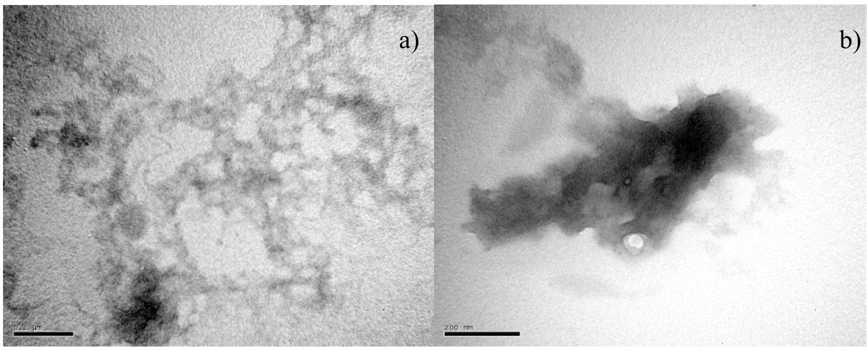


Figure S13. TEM images of purified **PDA-BD3**. Scale bars are 200 nm.

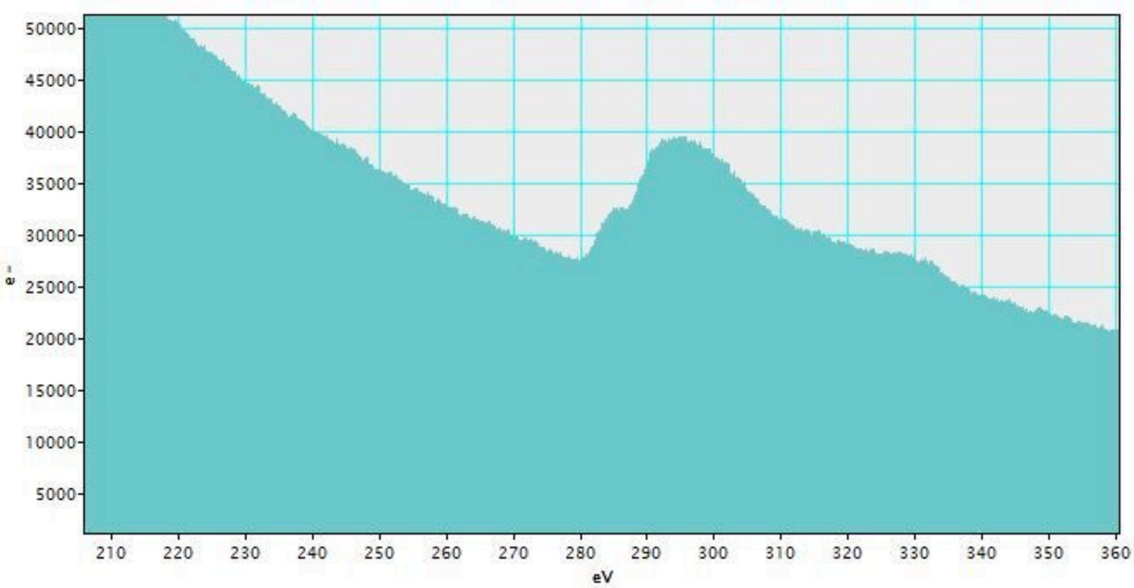


Figure S14. Electron energy lost spectrum of **G-BD3**

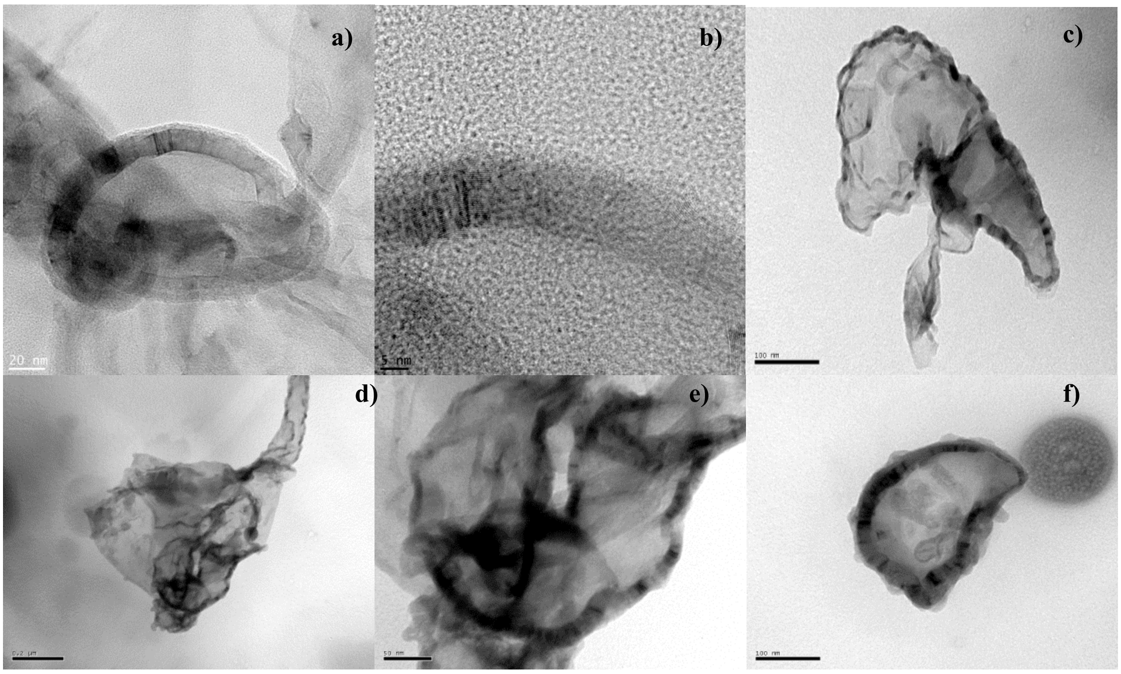
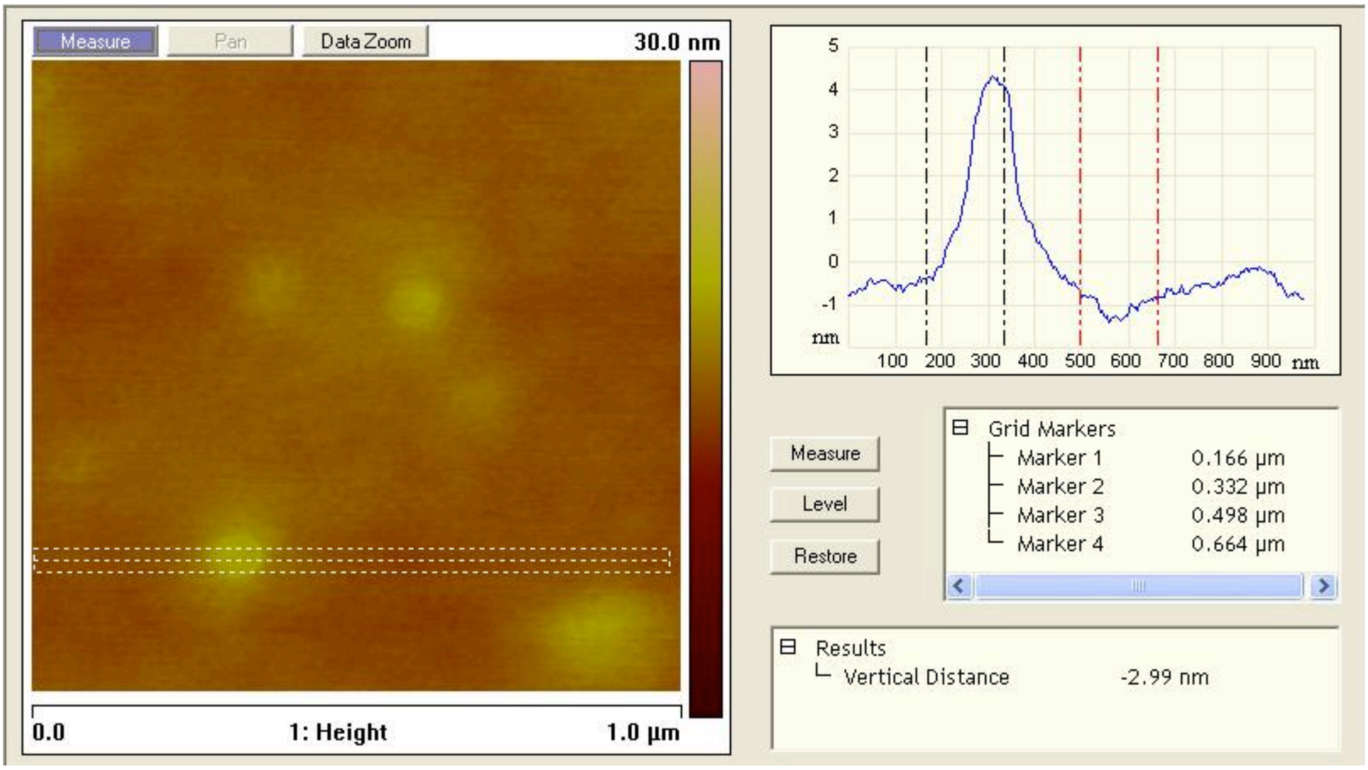


Figure S15. HRTEM images of **G-BD3**. Scale bars are 20 nm (a), 5 nm (b), 100 nm (c), 200 nm (d), 50 nm (e) and 100 nm (f).



⊟ Grid Markers
Marker 1 0.166 µm
Marker 2 0.332 µm
Marker 3 0.498 µm
Marker 4 0.664 µm

⊟ Results
Vertical Distance -2.99 nm

Figure S16. AFM (Tapping mode, left) and height profile of **G-BD3** deposited on a glass substrate.

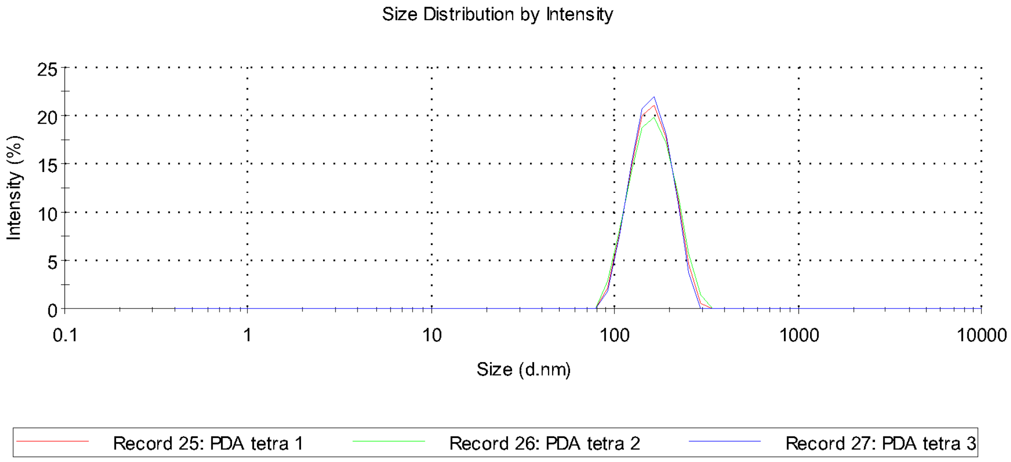


Figure S17. Dynamic light scattering (DLS) data for **PDA-BD3**

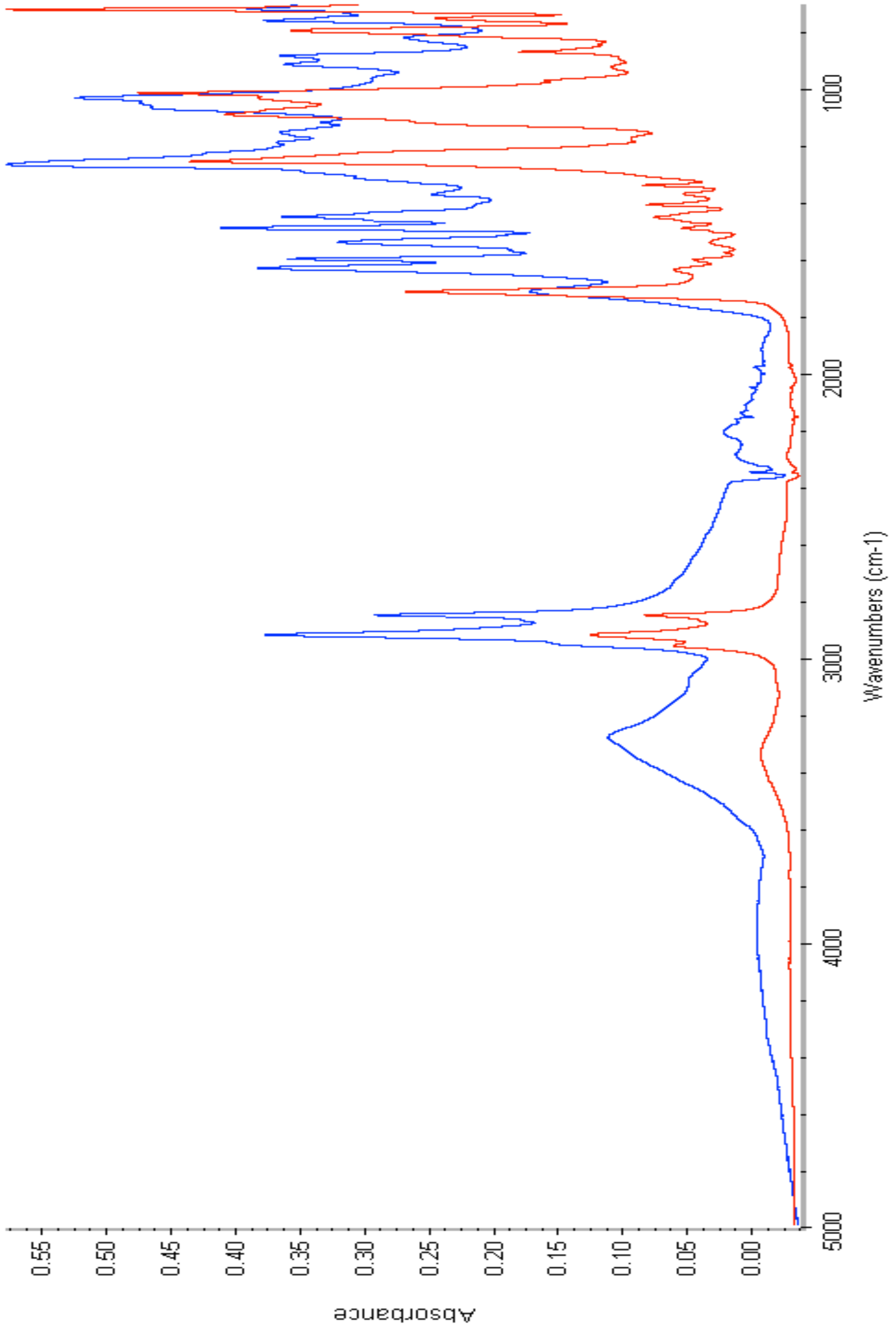


Figure S18. Comparative IR spectra of **PDA-BD3** (blue) and **G-BD3** (red).

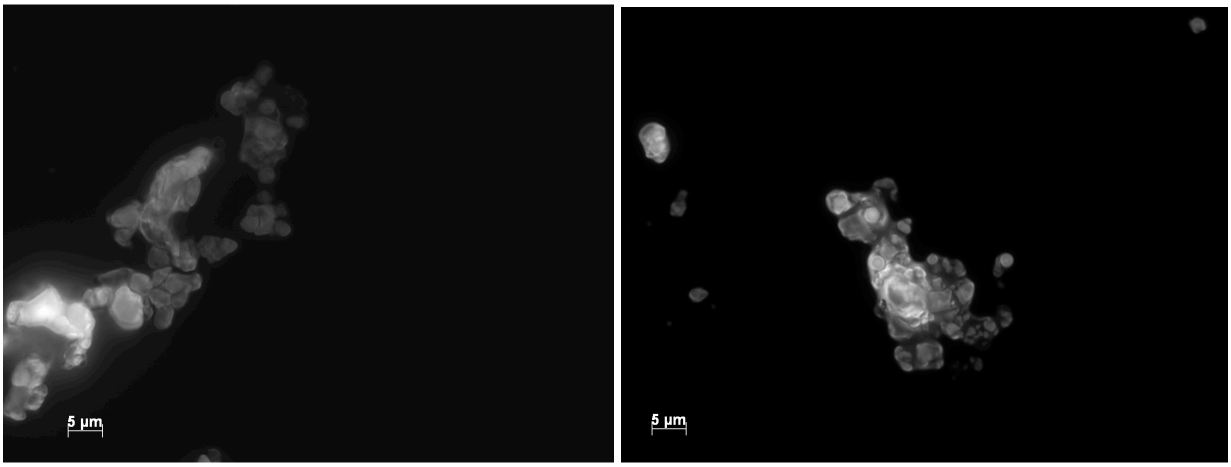


Figure S19. Fluorescence confocal microscopy of **G-BD3** suspended in methanol. Bright spot are aggregates of **G-BD3**. Excitation at 560 nm ± 20 nm and emission at 630 nm ± 35 nm.