Supporting Information

Soft Matter Nanocomposites by Grafting a Versatile Organogelator to Carbon Nanostructures

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Contents:

General remarks and materials. NMR experiments were recorded on a Varian Gemini 200 MHz or 400 MHz spectrometer. Chemical shift are denoted in δ units (ppm) relative to TMS both for ^{1}H-NMR and ^{13}C{^{1}H}-NMR. All FT-IR spectra were recorded on a Perkin-Elmer FT-IR 881 spectrometer except for carbon nanotube derivatives which were recorded a Bruker FTIR Spectrometer (Mod. VERTEX-80 V) equipped with a broad band MCT detector cooled at the liquid N_2 temperature. All CNT samples were prepared by mixing spectroscopic grade KBr with MWCNTs or *f*-MWCNTs (2-3 wt%) and analyzed in the 400-4000 cm^{-1} range (800 scans) with a resolution of 1 cm^{-1}.The pristine MWCNTs IR spectrum was acquired and used as background then automatically subtracted from that recorded for *f*-MWCNTs. Absorption frequencies are expressed in wavenumbers ν (cm^{-1}) and s, m and w notations refer to signal intensity and meaning strong, medium and weak, respectively. Elemental analysis was performed with a Perkin-Elmer 240 Analyzer. MS spectra of all molecular compounds are recorded using the ESI technique. Polarimetric measurements were performed with a Jasco-J-715 polarimeter equipped with a Jasco Spectropolarimeter Power Supply PS-150J and a thermostatic bath; all measurements were performed using quartz cells (0.01 cm path). All commercially available compounds were purchased from either Sigma-Aldrich, Fluka or Alfa Aesar and were used (otherwise stated) as received. Toluene was distilled from sodium; triethylamine and *N*-ethyl-*N*,*N*-diisopropyl amine were distilled from KOH prior to use. R_f values refer to spots as observed on silica TLC films over aluminium (0.25 mm thick - Merck F254). ***Differential scanning calorimetry.*** DSC measurements were performed with a TA Instrument DSC Q2000 apparatus using sealed steel pans. All reported results refer to scans with heating/cooling gradient of 1°C/min. All measurements were performed on weighing small amounts of freshly prepared gels or gel-CNT composites (balance sensibility 1/100mg) transferred with a spatula in the steel pans. ***Atomic force microscopy.*** AFM measurements carried out on C_{60}-based nanostructure were performed using either a Solver P47pro Scanning probe Microscope (NT-MDT co., Zelenograd, Moscow, Russia) equipped with a

NCS36/B μ-masch silicon cantilever with force constrain of 1.75 N/m while a Park System XE-100E AFM instrument has been used in the characterization of SWCNT-based nanofibers. Samples for AFM characterizations were obtained by spin-coating (3000 rpm, 60 seconds) a gel (or a gel-CNT composite) deposition (50 μl) on a freshly cleaved mica surface. ***Transmission Electron Microscopy.*** TEM analysis on the CNT xerogel-composite sample was performed using a Philips CM12 microscope operating at 120 kV. Samples were prepared by spin-coating (4200 rpm, 20 s) a gel (or a gel-CNT composite) deposition (≈ 50 μl) over carbon coated grids. TEM images were recorded with a CCD camera (Gatan 791). ***Thermogravimetric analysis.*** TGA was performed under N_2 atmosphere (50 mL/min) on an EXSTAR Thermo Gravimetric Analyzer (TG/DTA) Seiko 6200 coupled with a ThermoStar™ GSD 301 T (TGA-MS) for MS gas analysis of volatiles. ***SAXS measurement.*** Small-Angle X-ray Scattering (SAXS) experiments were performed on the Hecus X-ray System GMBH Graz S3micro equipped with an ultra brilliant point microfocus source Gemix-Fox 3D (Xenoxs, Grenoble). The scattered X-rays were detected by a two-dimensional position sensitive detector with a sample-to-detector distance of 269 mm. This configuration allow values of the scattering vector q [$Å^{-1}$] in the range $0.0008<q<0.54$. Here q is defined as $q=(4\pi/\lambda)\sin(\Theta/2)$. Samples were prepared in glass capillaries of 2 mm diameter. Hot sample solutions were introduced in the capillary, which was immediately sealed with dual glue, and then allowed to cool and gel. All measurements were collected at room temperature and employing a X-Ray source power of 50W (50 kV, 1mA).

General procedure for the synthesis of compounds 5-7: A 100 mL round bottomed flask was charged with a H_2O/THF mixture (1:1, 15 mL), the alkyne derivative **1** (180 mg, 0.15 mmol),[1] the azido derivative (**2**,[2] **3**[3] or **4**,[4] 0.30 mmol), $CuSO_4$ (1.2 mg, 0.0075 mmol) and sodium ascorbate (6

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[1] G Ghini, L. Lascialfari, C. Vinattieri, S. Cicchi, A. Brandi, D. Berti, F. Betti, P. Baglioni, M. Mannini, *Soft Matter,* **2009**, *5*, 1863-1869.

[2] M. A. Fazio, O. P. Lee, D. Schuster, *Org. Lett.*, **2008**, *10*, 4979-4982.

mg, 0.03 mmol). The resulting suspension was stirred at 65 °C for 18 h. The reaction was diluted with water (10 mL) and extracted with $CHCl_3$ (3 x 10 mL). The organic phases were collected, dried over Na_2SO_4, and concentrated to afford the crude reaction products. Each crude material was purified by flash column chromatography to give the corresponding pure compound. **Organogelator 5**: 60% Yield. R_f = 0.56, ($CHCl_3$-AcOEt 2:1). Waxy solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 10.08 (s, 1H, CHO); 8.23 (s, 1H, CH triazole ring); 8.09 - 7.94 (m, 4H, AA'BB' system of the aromatic ring); 5.59 (2H, AB system, OCH_2), 5.17 (m, 4H, HCO); 4.65- 4.62 (m, 4H, NH); 3.80- 3.60 (m, 8H, HCN); 3.15- 3.09 (m, 8H, $NHCH_2$); 1.40- 1.60 (m, 80H, chain's CH_2); 0.87 (t, ^3J = 6.6 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm): 190.6 (d); 173.6 (s), 173.5 (s), 154.8 (s); 154.7 (s), 145.1 (s); 140.9 (d); 136.0 (d); 131.4 (d); 121.3(d); 120.5 (d); 75.0 (d, HCO); 74.9 (d, HCO); 60.4 (t, CH2O); 50.8 (t, NCH2); 50.6 (t, NCH2); 41.2 (t, NHCH2); 31.9 (t); 29.9 (t); 29.8 (t); 29.7 (t); 29.6 (t); 29.5 (t); 29.3 (t); 29.2 (t); 26.7 (t); 22.7 (t); 14.1 (q, CH3). IR (KBr) cm^{-1}: 3339 (m), 2922 (s), 2851 (m), 1696 (s), 1587 (m), 1523 (m), 1414 (w), 1370 (w), 1250 (w), 1142.(w). ESI- MS (m/z, %): 1329.82 ($M+H^+$, 100); 1330.82 ($M+1+H^+$, 80); 1352.00 ($M+Na^+$, 40). Elem. Anal. Calcd. for $C_{73}H_{124}N_{12}O_{10}$ (1329,84): C, 65.93; N, 12.64; H, 9.40. Found C, 65.78; N, 12.42; H, 9.10.

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[3] W. Zhu, D. Ma, *Chemm. Comm.*, **2004**, 888-889.

[4] K. Barral, A. D. Moorhouse, J. E. Moses, *Org. Lett.*, **2007**, *9* (9), 1809-1811

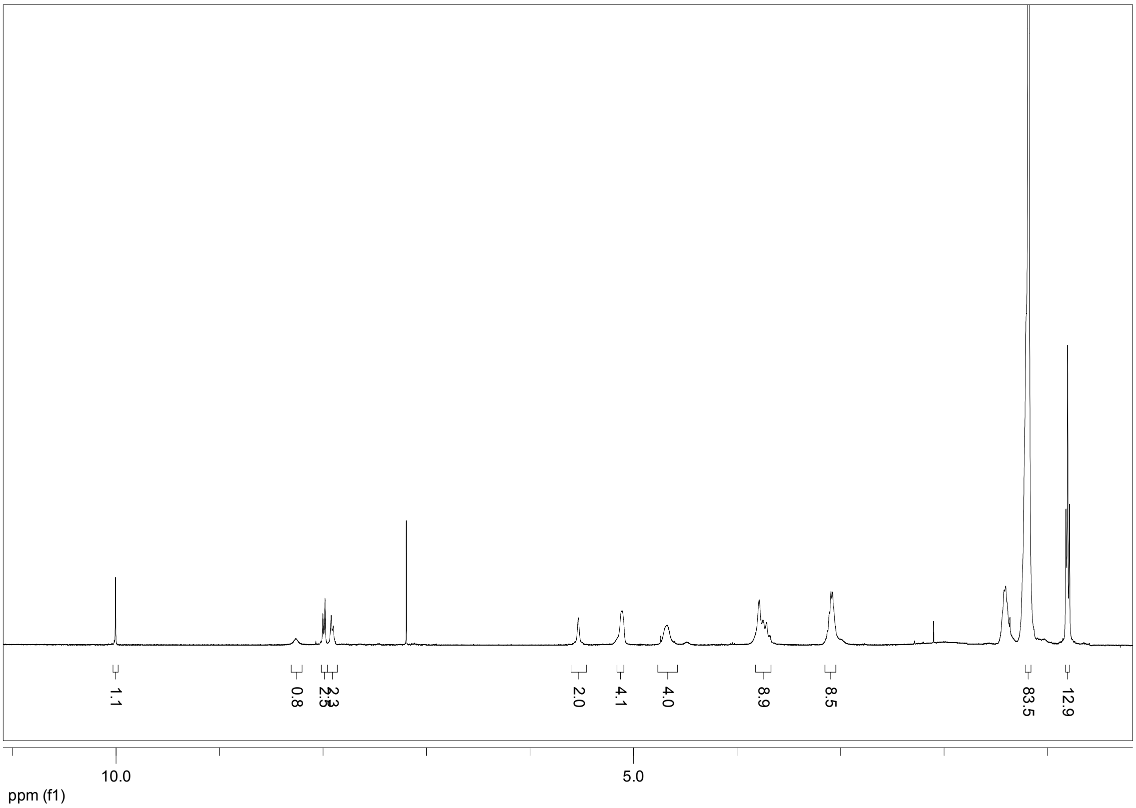


Figure S1. ^{1}H NMR (200 MHz, $CDCl_3$) of **5.**

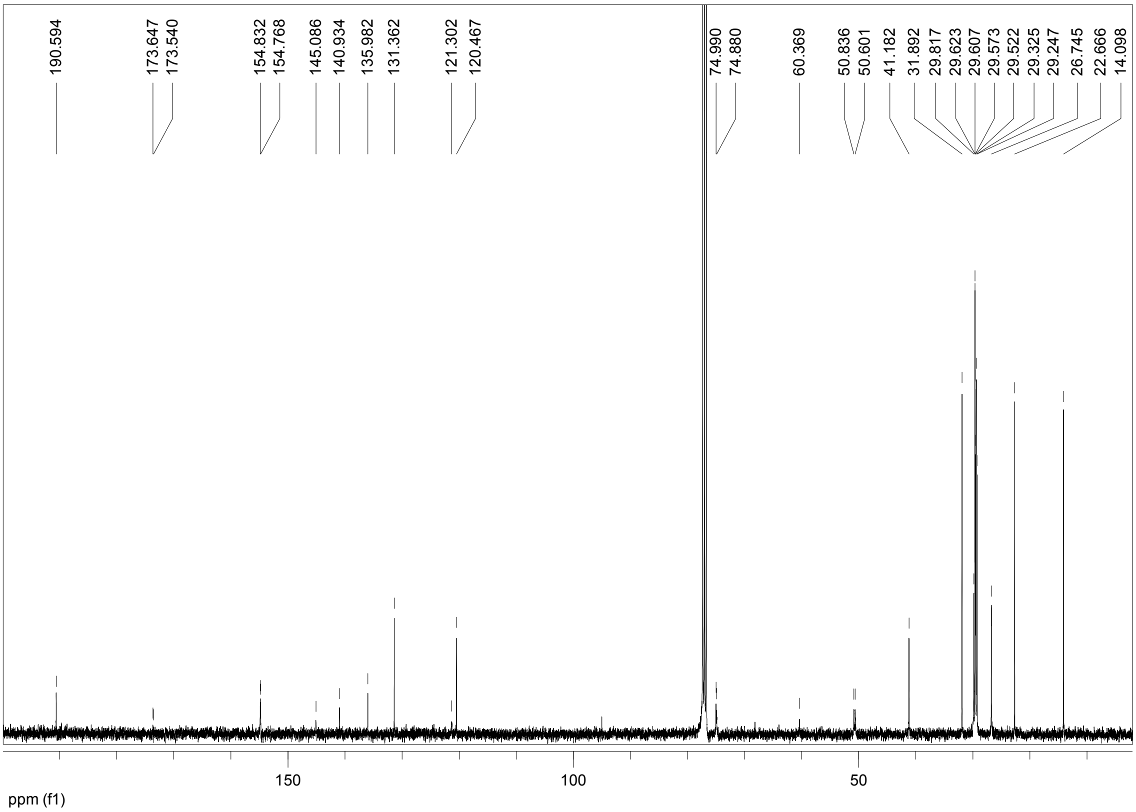


Figure S2. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of **5.**

Organogelator 6: 78% Yield. $R_f = 0.35$, ($CHCl_3$-AcOEt 2:1). Waxy solid. ^{1}H- NMR ($CDCl_3$, 200 MHz) δ(ppm): 7.97 (s, 1H, CH triazole ring); 7.45 (AA' component of an AA'MM' system, 2H, aromatic ring); 6.76 (MM' component of an AA'MM' system, 2H, aromatic ring); 5.55 (2H, AB system, OCH_2); 5.25- 5.15 (m, 4H, HCO); 4.80- 4.60 (m, 4H, NH); 3.80- 3.60 (m, 8H, HCN); 3.15- 3.09 (m, 8H, $NHCH_2$); 1.40- 1.60 (m, 80H, CH_2's chain); 0.86 (t, ^3J = 6.6 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ(ppm): 169.2 (s); 164.1(s); 154.5 (s); 154.4 (s), 146.7 (s) 143.7 (d), 128.3 (d); 122.0 (d); 121.2 (s); 114.9 (d); 74.7 (d, HCO); 59.9 (t, CH_2O), 50.4 (t, NCH_2); 50.1 (t, NCH_2); 40.9 (t); 31.7 (t); 29.6 ; 29.4; 29.1; 29.0; 26.5; 22.4 (t); 13.9 (q, CH_3). IR (KBr) cm^{-1}: 3340 (m), 2923 (s), 2852 (m), 1700 (s), 1584 (m), 1522 (m), 1265 (w). ESI- MS (m/z): 1316.82 ($M+H^+$), 100%). Elem. Anal. Calcd. For $C_{72}H_{125}N_{13}O_9$ (1316.84): C, 65.67, N,13.83, H, 9.57. Found C, 65.39, N, 13.52, H, 9.80.

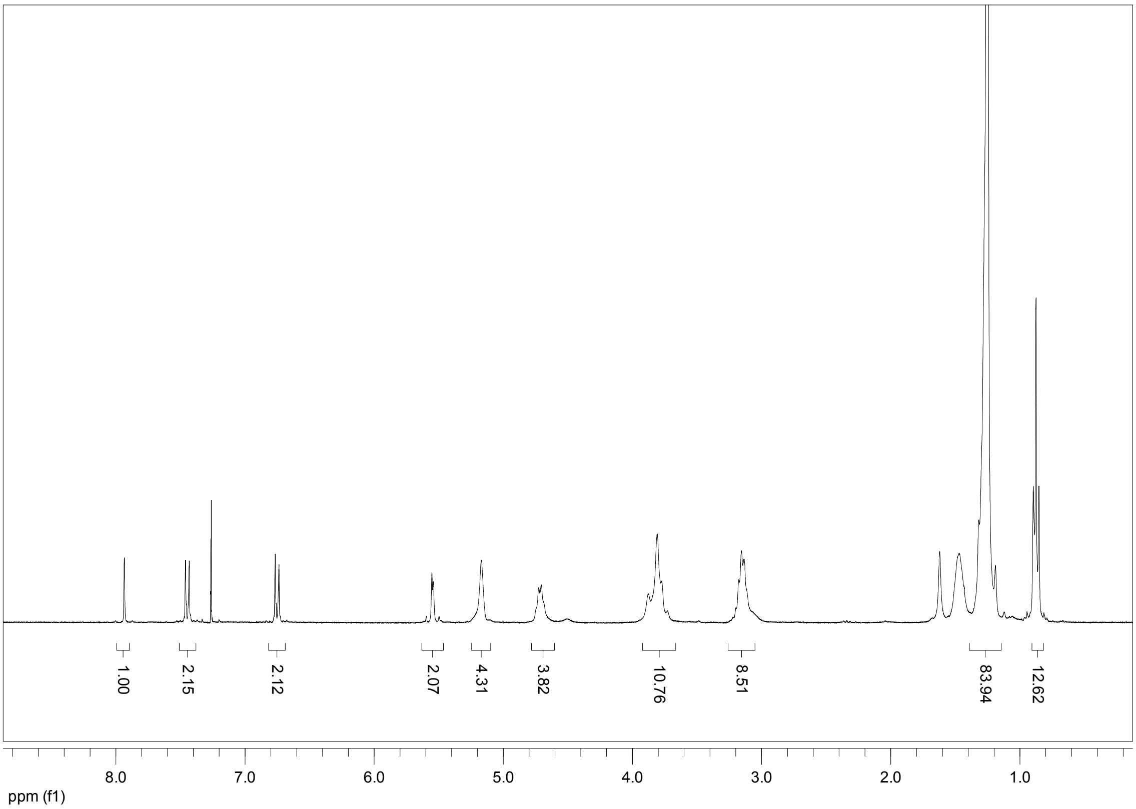


Figure S3. ^{1}H NMR (200 MHz, $CDCl_3$) of **6.**

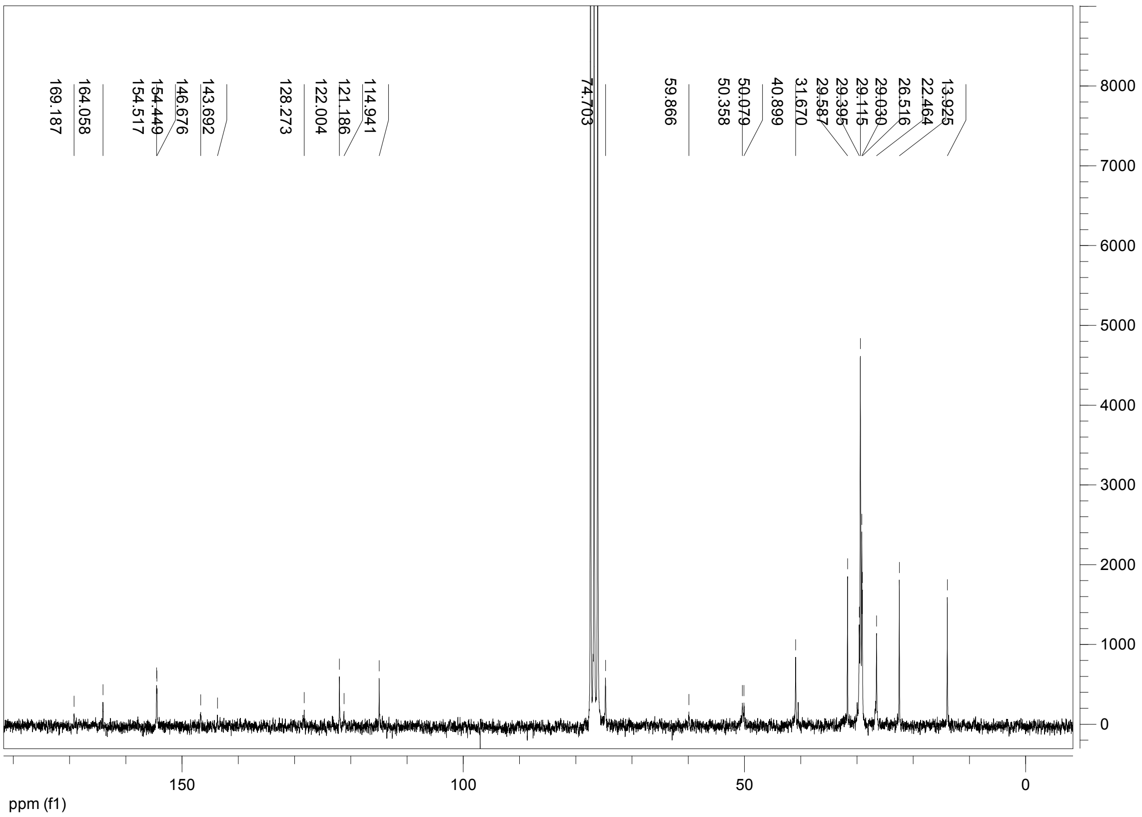


Figure S4. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) of **6.**

Organogelator 7: 73% Yield. R_f = 0.54, ($CHCl_3$-AcOEt 6:1). Waxy solid. ^1H- NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.09 (s, 1H, CH triazole ring), 7.73- 7.71 (m, 2H, AA’ system of the aromatic ring); 7.53- 7.49 (m, 2H, BB’ system of the aromatic ring); 7.45- 7.41 (m, 1H, C system of the aromatic ring); 5.56 (2H, AB system, OCH_2); 5.26- 5.09 (m, 4H, HCO); 4.65- 4.62 (m, 4H, NH); 3.89- 3.69 (m, 8H, HCN); 3.22- 2.96 (m, 8H, $NHCH_2$); 1.53- 1.39 (m, 8H, $CH_2CH_2NH_2$); 1.32- 1.20 (m, 72 H, chain’s CH_2); 0.86 (t, ^3J = 6.6 Hz, 12 H). $^{13}C\{^1H\}$ NMR (CDCl3, 100 MHz) δ (ppm): 169.4 (s); 164.3 (s); 154.9 (s); 144.6 (s); 137.0 (s); 129.7 (d); 128.7(d); 121.3 (d); 120.6 (d); 75.0 (d, HCO); 60.1 (t, CH_2O); 50.6 (t, NCH_2); 50.4 (t, NCH_2); 41.2 (t, $NHCH_2$); 31.9 (t); 29.8 (t); 29.5 (t); 29.4 (t); 29.6 (t); 29.3 (t); 29.2 (t); 26.7 (t); 22.7 (t); 14.1 (q). IR (KBr) cm^{-1}: 3340 (m), 2923 (m), 2845 (w), 1699 (s), 1576 (w), 1559 (m), 1541(m), 1508 (m), 1456 (w). ESI- MS (m/z, %): 1301.67 ($M+H^+$, 100); 1323.75 (M+Na$^+$, 12); Elem. Anal. Calcd for $C_{72}H_{124}N_{12}O_9$ (1301.83): C, 66.43; N, 12.91; H, 9.60. Found C, 66.27; N, 12.65; H, 9.37.

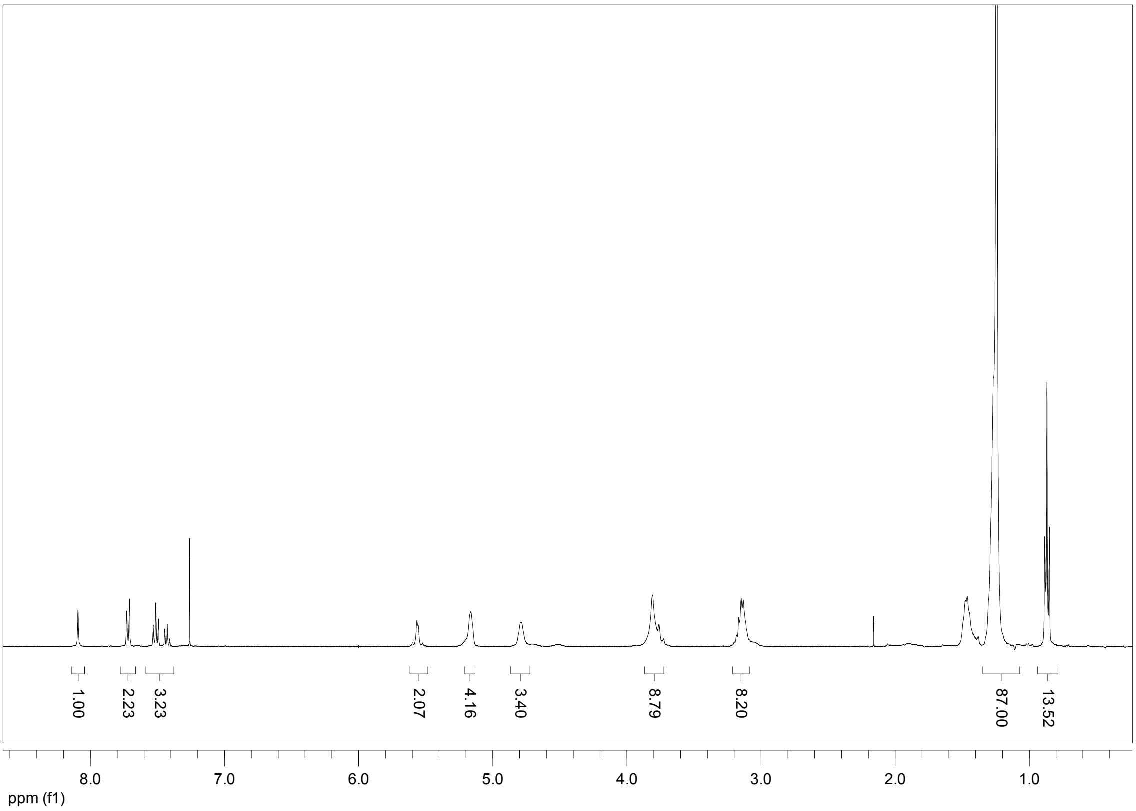


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of **7.**

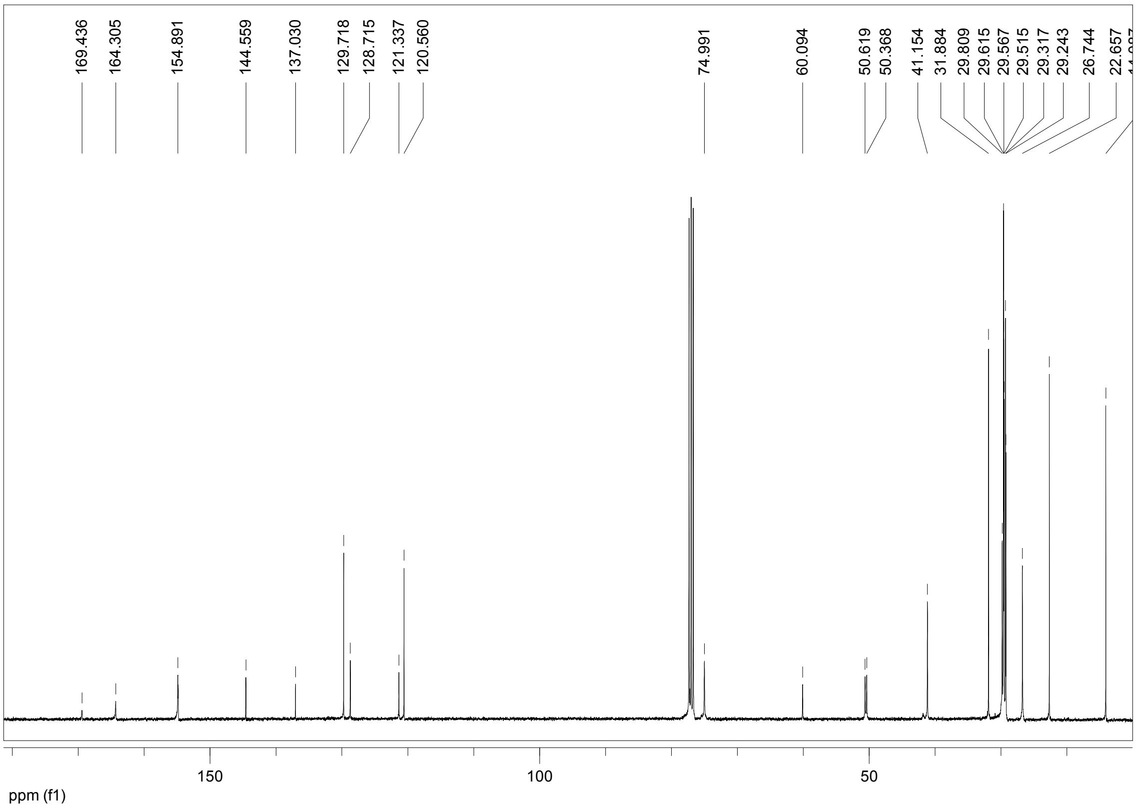
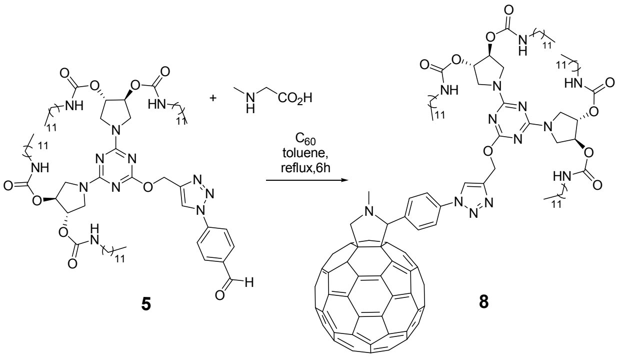


Figure S6. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$) of **7.**

Synthetic procedure for the fullerene cycloadduct 8: A 50 mL round bottomed flask was charged with **5** (55 mg, 0.038 mmol), *N*-methyl glycine (35.5 mg, 0.38 mmol), C_{60} (57.7 mg, 0.076 mmol) and dry toluene (5.4 mL). The mixture was refluxed, under N_2 atmosphere and maintained under stirring for 6h. Afterwards, the solution was concentrated under reduced pressure and the crude material was purified by flash column chromatography to give **8** as a brown waxy solid. **Compound 8**: 50% Yield. R_f = 0.82, ($CHCl_3$-AcOEt 2:1);^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.10 (s, 1H, CH of the triazole ring); 8.00 (bs, 2H, AA' part of a AA'BB' system), 7.80 (m, 2H, BB' part of a AA'BB'system); 5.50-5.40 (m, AB system, 2H, OCH_2); 5.25- 5.15 (m, 4H, HCO); 5.00 (d, ^2J = 11.0 Hz, 1H); 4.98 (s, 1H); 4.80- 4.60 (m, 4H, NH); 4.25 (d, ^2J = 11.0 Hz, 1H); 3.80- 3.60 (m, 8H, HCN); 3.15- 3.09 (m, 8H, $NHCH_2$);



2.80 (s, 3H, NCH_3); 1.46- 1.40 (m, 8H, CH_2CH_2NH); 1.25 (m, 72 H, chain's CH_2); 0.87 (t, ^3J = 6.6 Hz, 12 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ(ppm): 169.8 (s, C triazole ring); 164.3 (s, C triazole ring); 156.0 (s, CO); 154.5 (s, CO); 153.7; 152.8; 152.6; 147.3; 146.4;146.3; 146.3; 146.2; 146.2; 146.1; 146.1; 146.0; 145.8; 145.7; 145.6; 145.4; 145.3; 145.3; 145.3; 145.2; 145.2; 144.7; 144.5; 144.4; 144.3; 143.4; 143.1; 143.0; 142.7; 142.6; 142.5; 142.2; 142.2; 142.1; 142.0; 141.9; 141.9; 141.8; 141.7; 141. 6; 140.2; 140.0; 139.6; 138.3; 137.0; 136.7; 136.3; 136.0 ; 135.6; 130.7; 121.6; 120.7; 82.8; 77.2 ; 74.6 (d, CHO); 70.0 (d, CH pyrrolidine); 69.0 (t, CH_2); 61.2 (t, OCH_2); 51.2 (NCH_2); 51.2 (t, NCH_2); 41.2; (t, CH_2NH); 40.0 (q, NMe); 31.9 (t); 29.8 (t); 29.7 (t); 29.6 (t); 29.5 (t); 29.4 (t); 29.3 (t); 29.3 (t); 26.7 (t); 22.7 (t); 14.1 (q, CH_3). IR (KBr) cm^{-1}: 3440(s), 2924(s), 2845 (m), 1729 (m), 1712 (m), 1703 (s), 1699 (s), 1574 (m), 1557 (m), 1520 (s), 1505 (s), 1454 (m), 1256 (w), 1239 (w), 1140 (w), 1123 (w). ESI- MS (m/z, %): 2076.45 (M^+, 72); 2077.45 (($M+H^+$, 100%); 2078.55 (($M+1+H^+$, 72); 2099.64 ($M+Na^+$, 90), 2100.00 ($M+1+Na^+$, 72). Elem. Anal. Calculated for $C_{135}H_{129}N_{13}O_9$ (2077.55): C 78.05%; H 6.26%; N 8.76%; Found: C 77.65%; H 6.61%; N 9.03%.

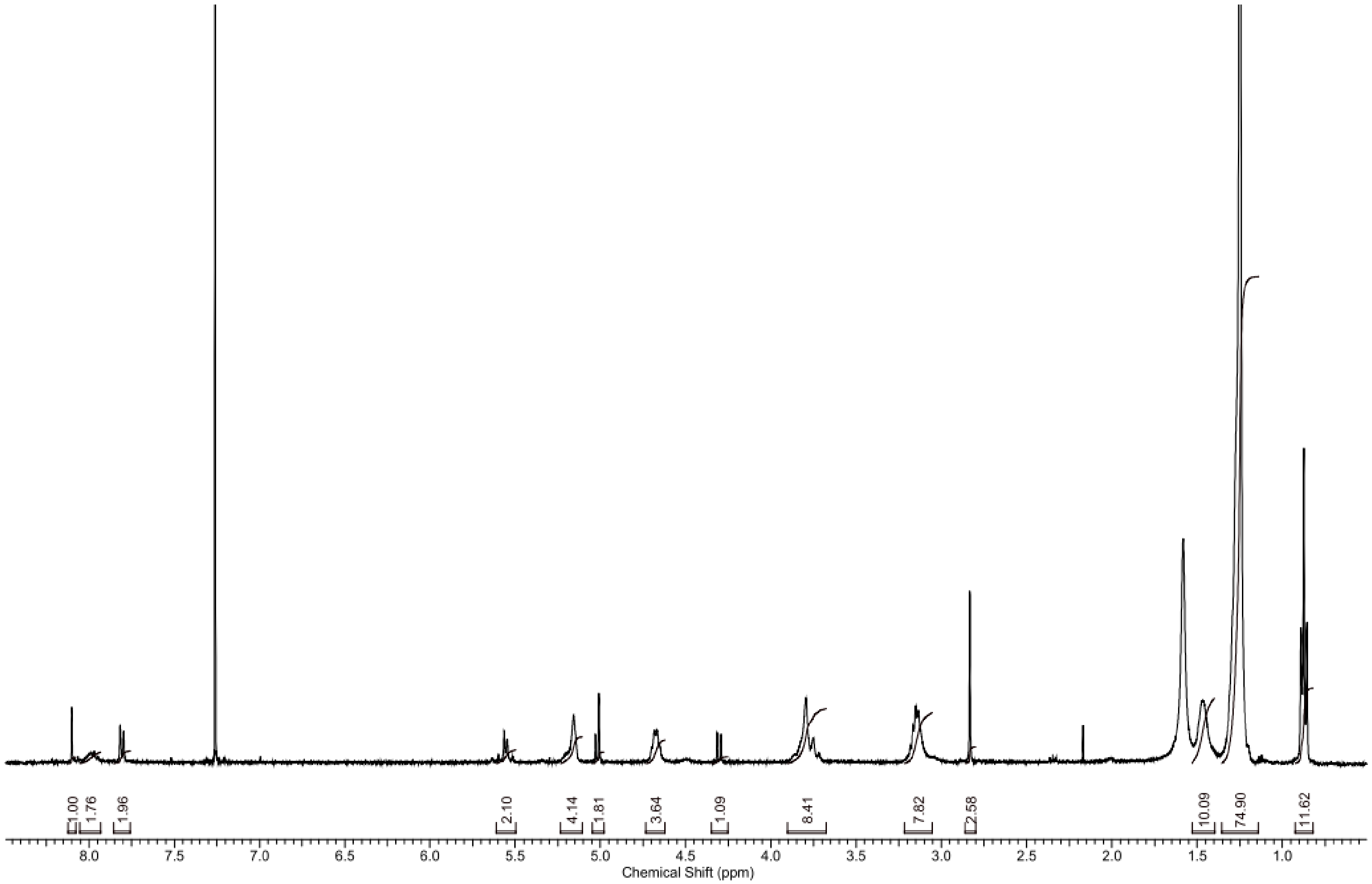


Figure S7a. ^{1}H NMR (400 MHz, $CDCl_3$) of **8**

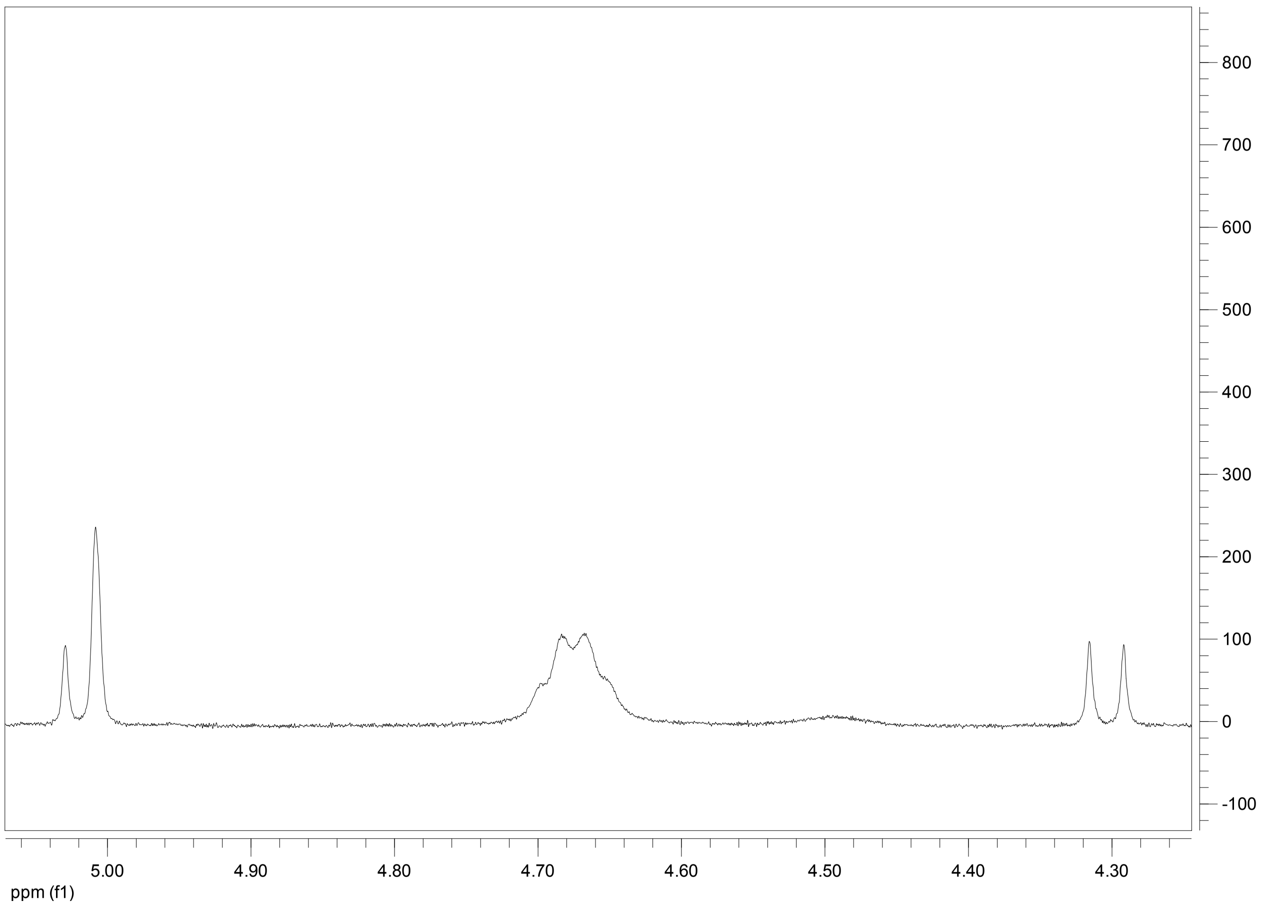


Figure S7b. ^{1}H NMR (400 MHz, $CDCl_3$) of **8.** Expansion 5.06-4.25 ppm**.**

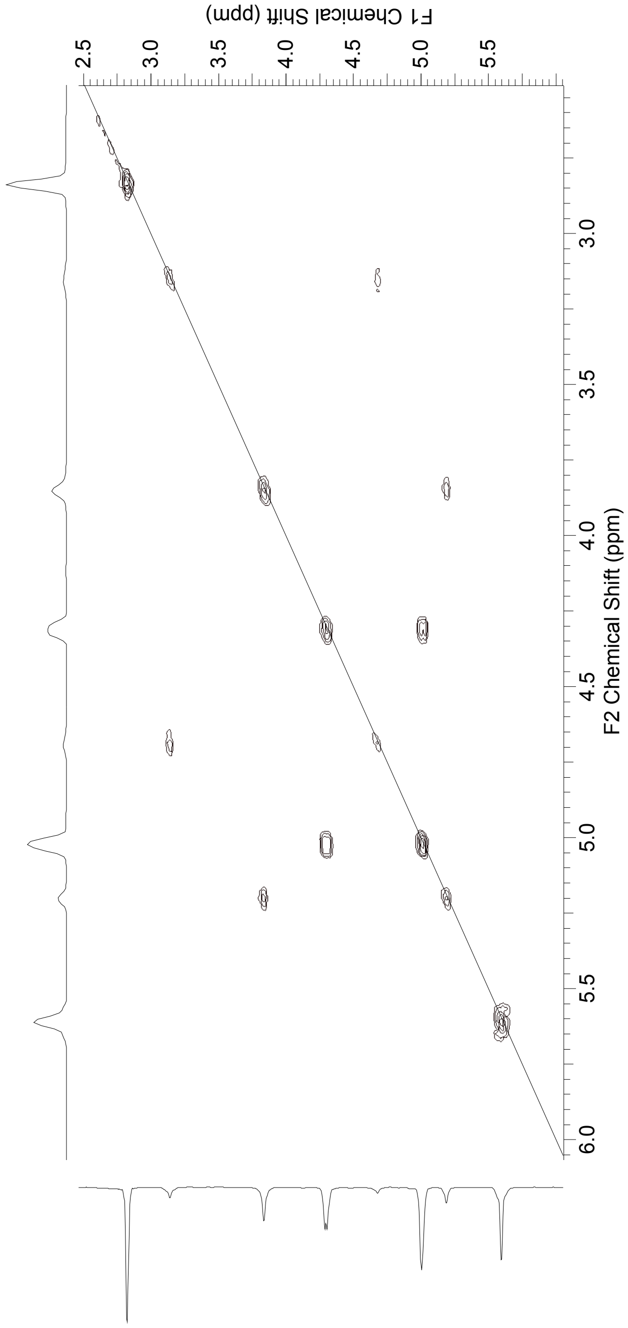


Figure S7c. g-Cosy spectrum expansion

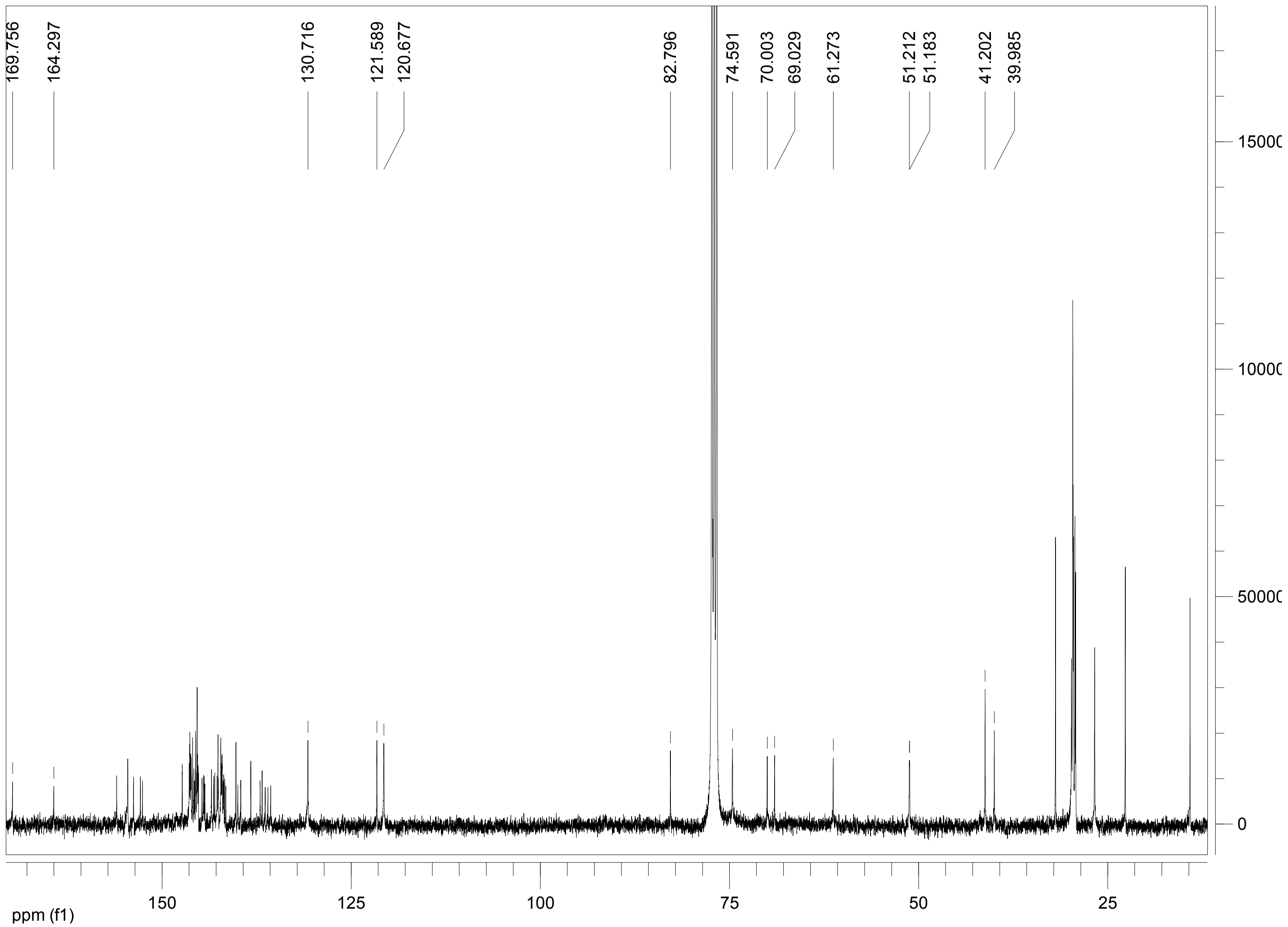


Figure S8a. $^{13}C\{^{1}H\}$ NMR (50 MHz, CDCl3) of **8.**

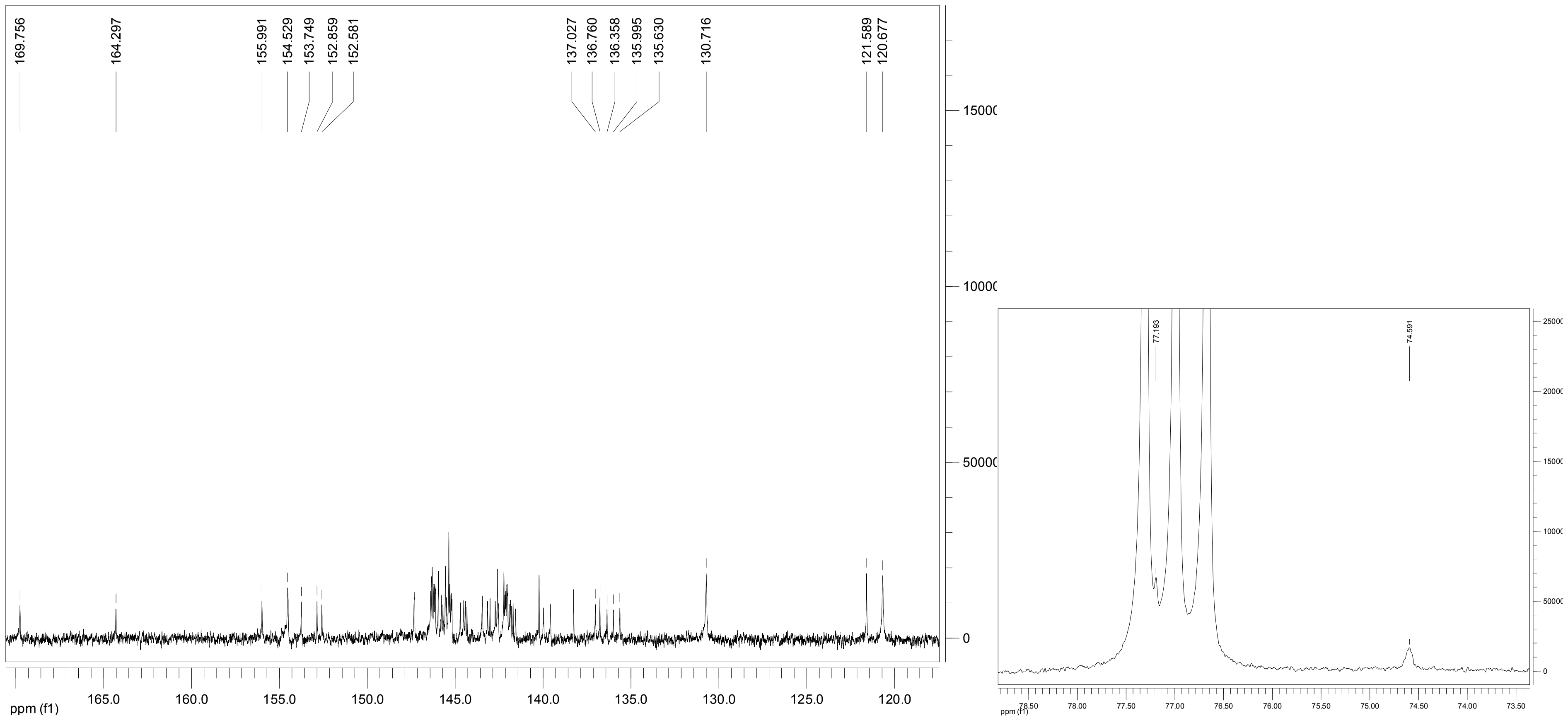
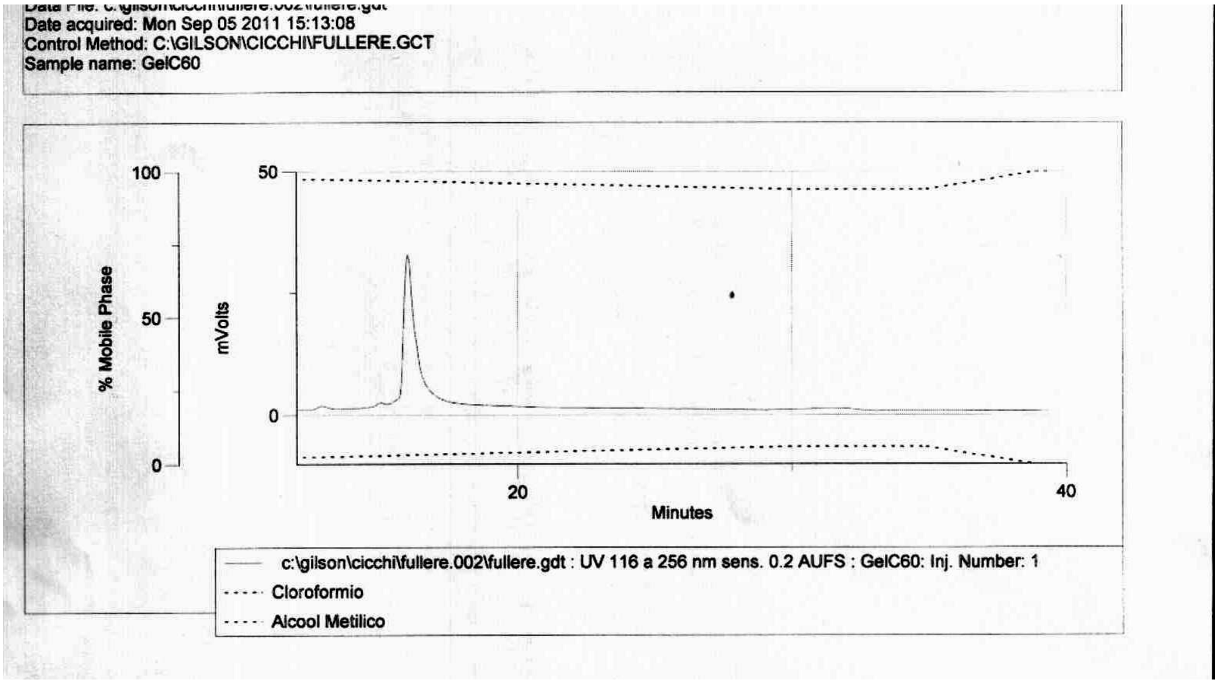


Figure S8b. $^{13}C\{^{1}H\}$ NMR (50 MHz, CDCl3) of **8,** expansions.



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Date acquired: Mon Sep 05 2011 15:13:08
Control Method: C:\GILSON\CICCHI\FULLERE.GCT
Sample name: GelC60

c:\gilson\cicchi\fullere.002\fullere.gdt : UV 116 a 256 nm sens. 0.2 AUFS : GelC60: Inj. Number: 1
Cloroformio
Alcool Metilico

Figure S9. HPLC analysis of compound **8.**

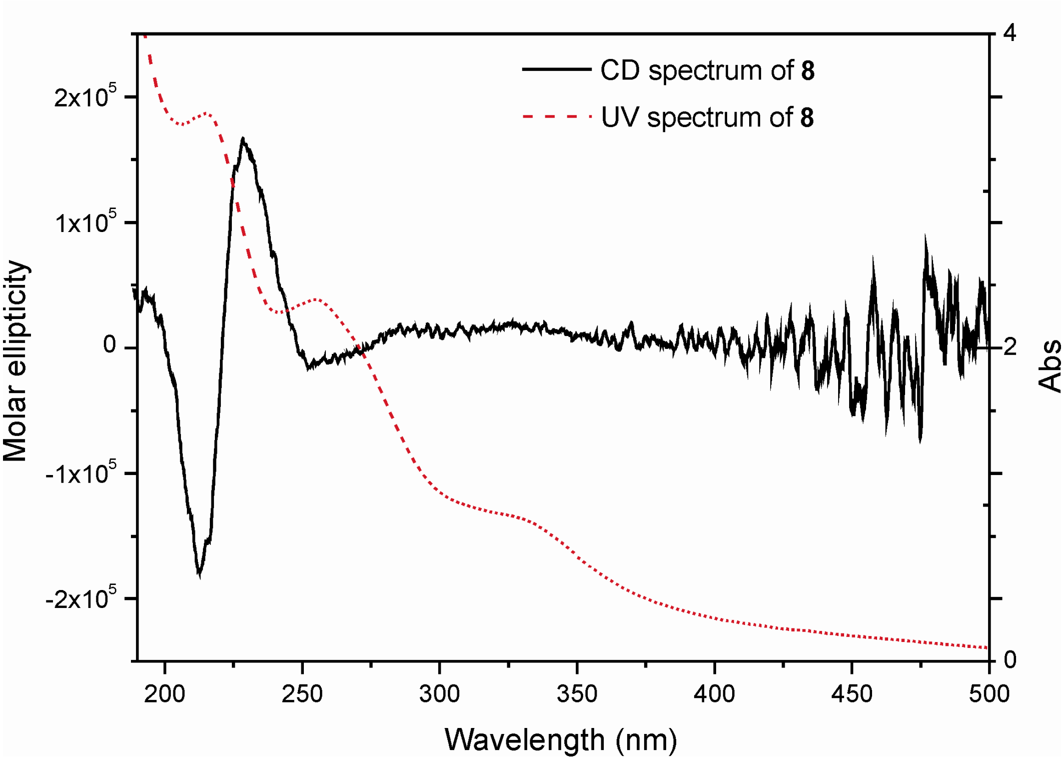


Figure S10. CD and UV spectra of compound **8** (cyclohexane, 0.67 mg/mL).

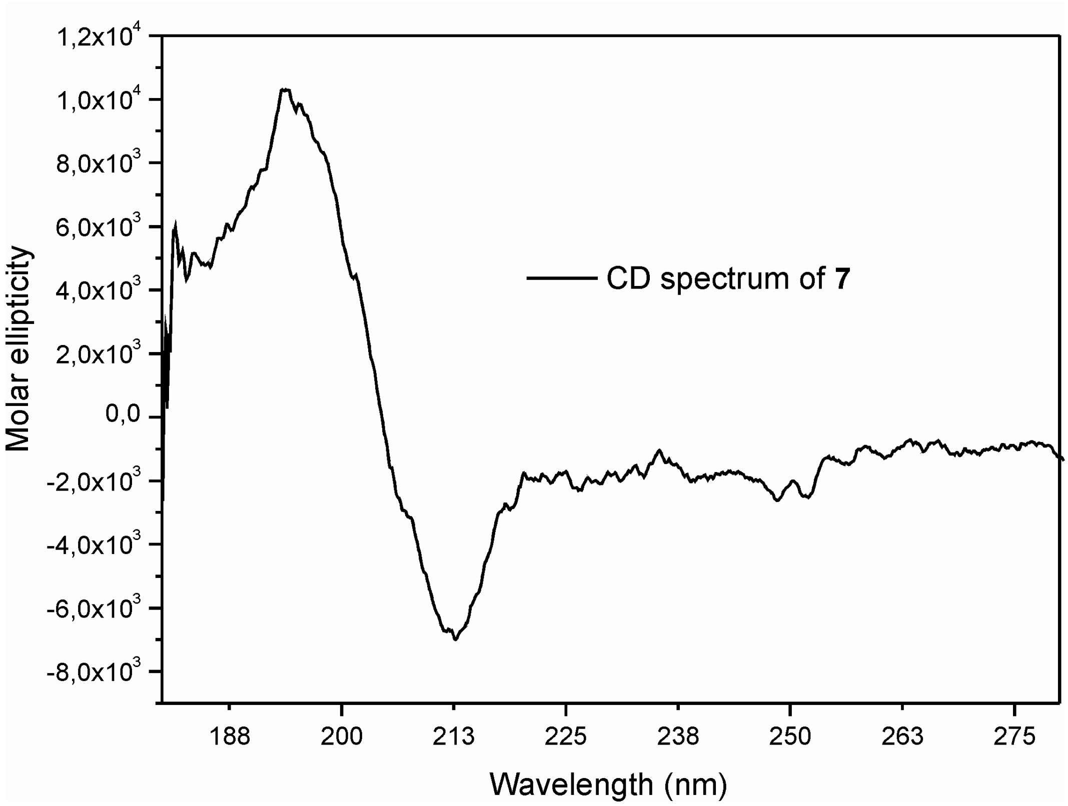


Figure S11: CD spectrum of gel of compound **7** in cyclohexane (6.7 mg/mL).

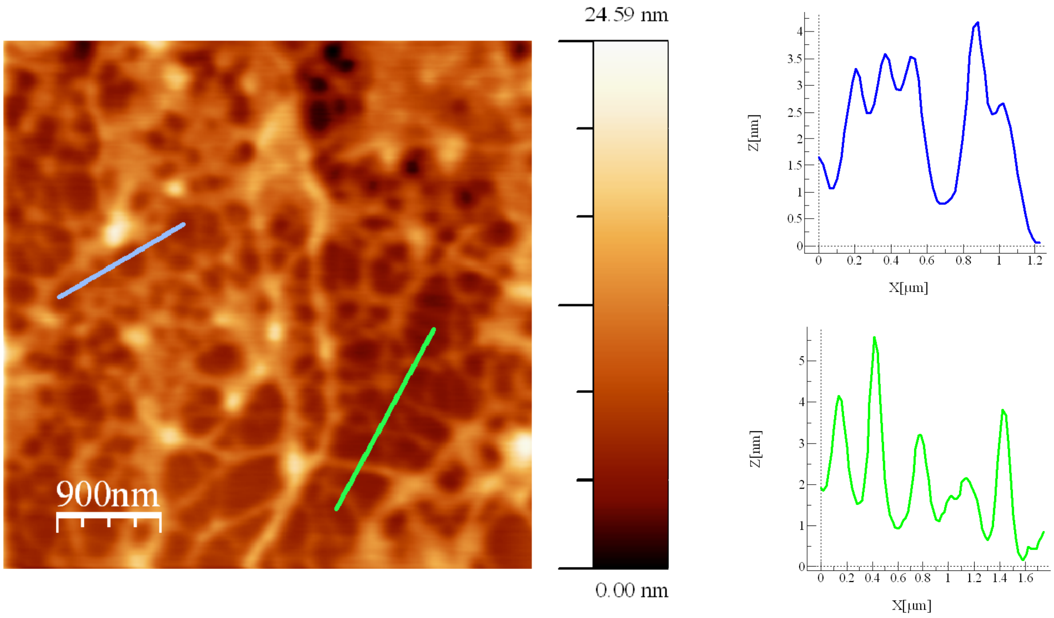


Figure S12. AFM analysis of a sample of gel obtained from compound **7** (6.7 mg/mL in cyclohexane).

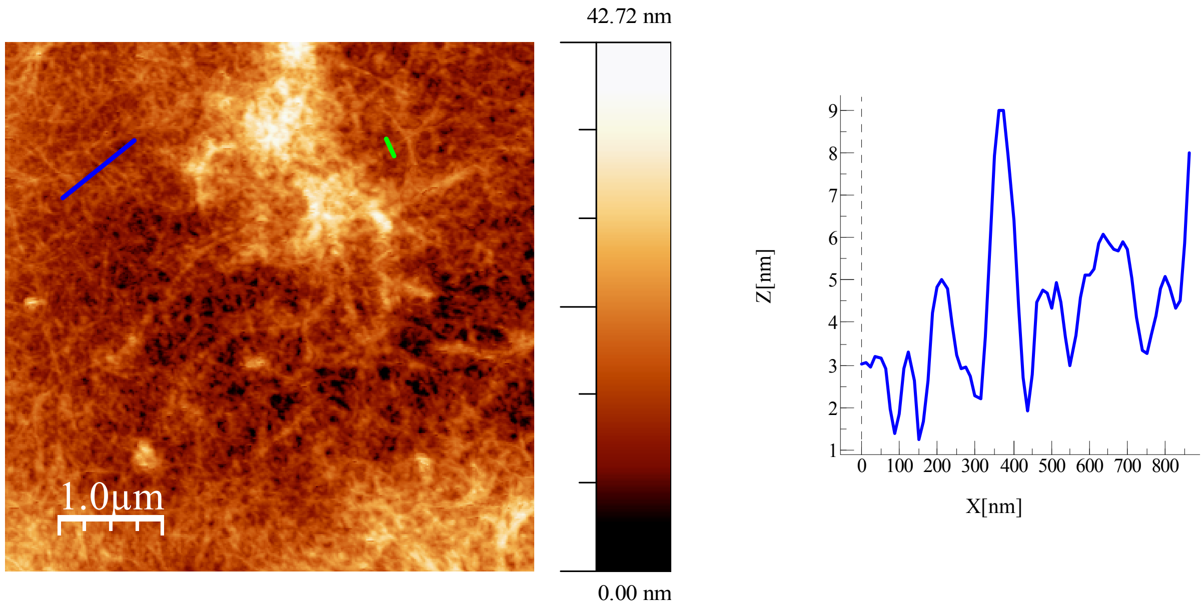


Figure S13. AFM analysis of a sample of gel obtained from a mixture of compound **7** (6.7 mg/mL in cyclohexane) and compound **8** (0.67 mg/mL).

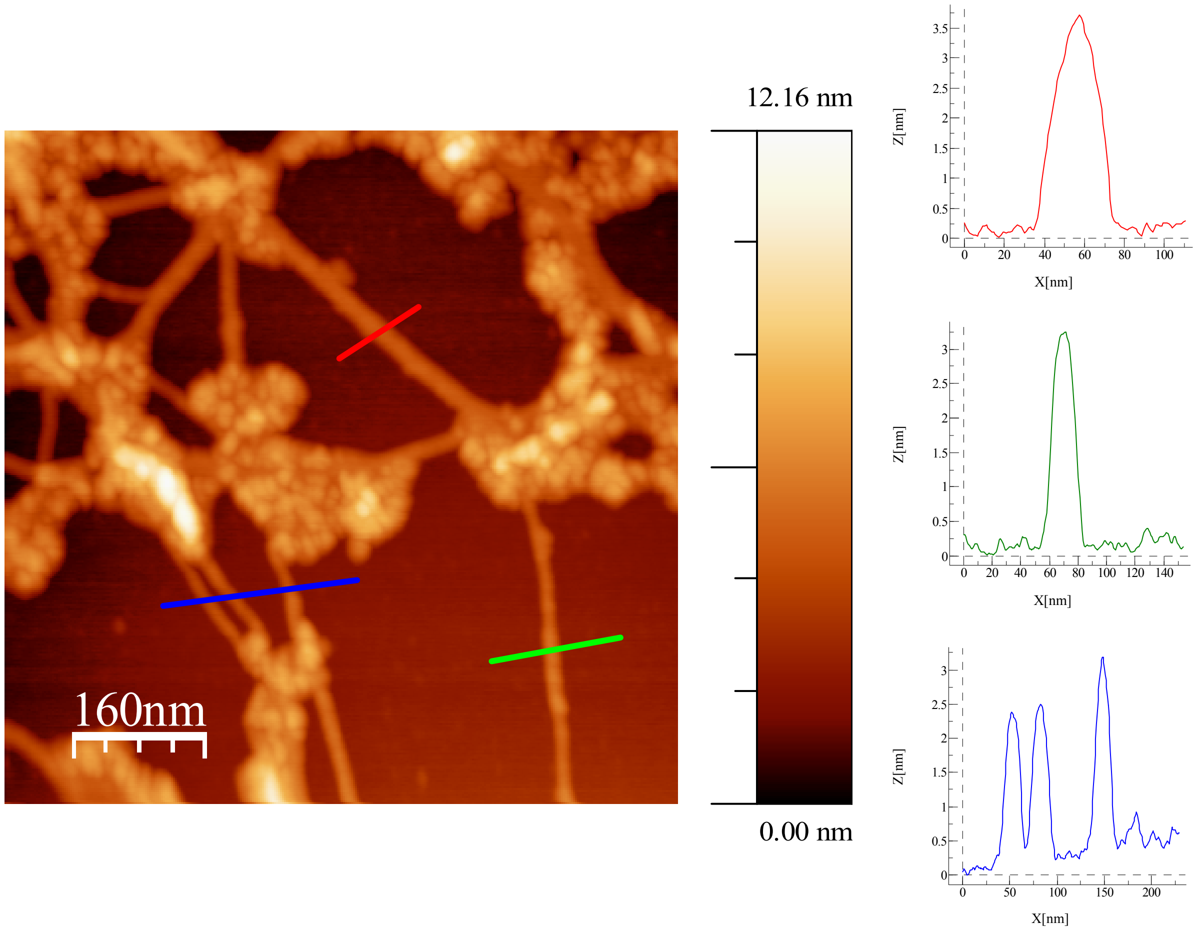


Figure S14. AFM analysis of a sample of gel obtained from **7** (6.7 mg/mL in cyclohexane) and **8** (0.67 mg/mL).

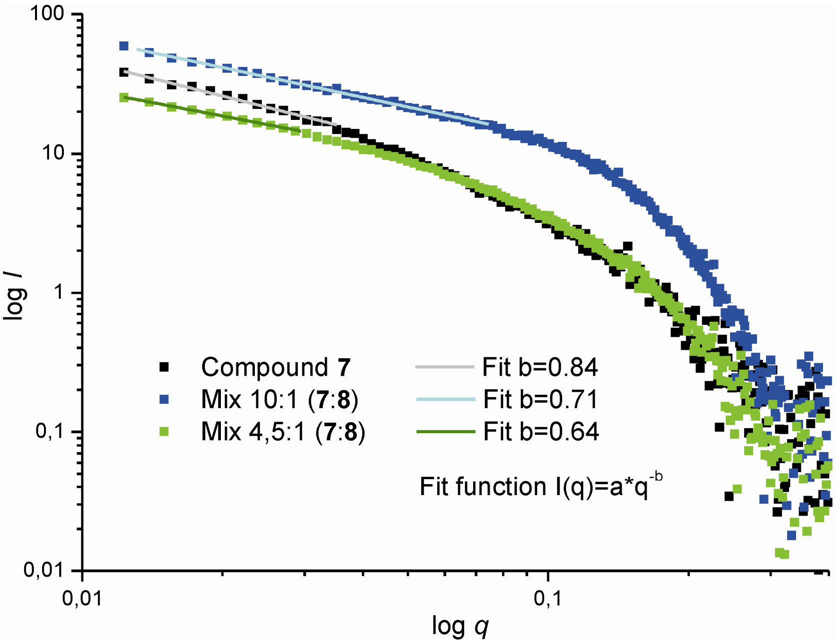
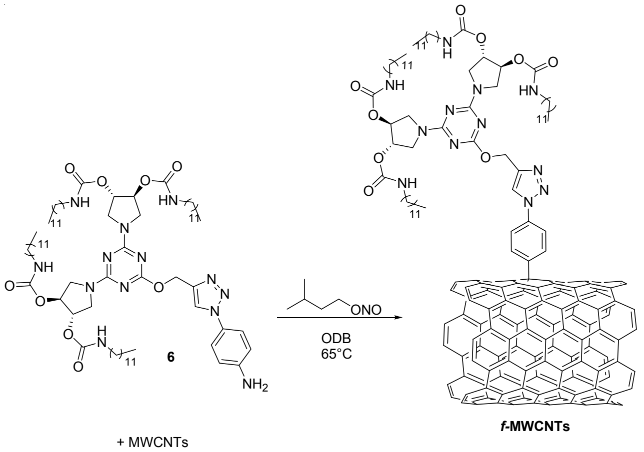


Figure S15. SAXS analyses of gel 7 (cyclohexane) and gels of mixtures **7**/**8**



Synthesis of *f*-MWCNTs using 6 as grafting organogelator. In a typical procedure, MWCNTs (20 mg) were weighed into a 100 mL schlenk equipped with a magnetic stirring bar and suspended in dry and degassed dichlorobenzene (19 mL). Afterwards, the dispersion was sonicated for 15 min under N_2 atmosphere and treated with a dichlorobenzene solution of **6** (90 mg, 0.068 mmol in 1 mL of $C_6H_4Cl_2$). The suspension was then sonicated for further 15 min prior of the addition of isopentyl nitrite (53 mg, 0.45 mmol, 6.6 eq). The mixture was then allowed to stir at 65 °C for 24 h. After that time, the cooled mixture was centrifugated for 1h to remove most of the suspended material (basically non-functionalized or scarcely derivatized MWCNTs) and the separated supernatant (a homogeneously dark solution) was filtered through an Anodisk filter (0.02 µm pores). The filtrate was washed several times with CH_2Cl_2 (5 x 10 mL) and the resulting buckypaper was transferred into a beaker, treated with CH_2Cl_2 (50 mL) under sonication for 20 min further. The black solution was filtered again on the Anodisc filter and the collected filtrate washed several times with fresh CH_2Cl_2 (5 x 10 mL). The buckypaper was again dispersed in CH_2Cl_2 by sonication and the resulting dispersion was concentrated and dessicated under vacuum to afford 16 mg of functionalized CNTs.

Elemental analysis performed on this sample afforded the following result:

Elem. Anal. Calcd for $C_{72+430}H_{124}N_{12}O_9$: H, 1.93; N, 2.60. Found H, 2.11; N, 2.56. This results roughly accounted for 1 molecule of organogelator every 430 carbon atoms

Blank reactions were performed on the pristine MWCNTs in the absence of either the organogelator **6** or the isopentyl nitrite. In both cases the centrifugation step led to a complete removal of the unreacted nanotubes (CNT separate from a colorless solution) which did not show any appreciable dispersion/dissolution once suspended in CH_2Cl_2 and sonicated.

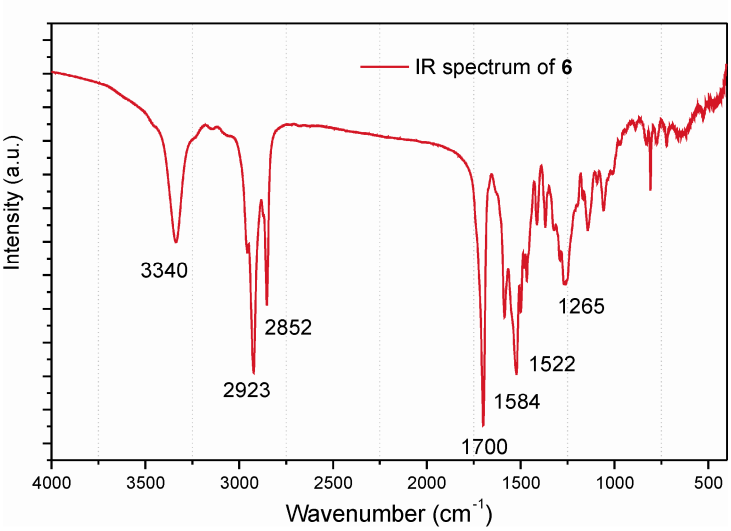


Figure S16. IR spectrum of **6** KBr.

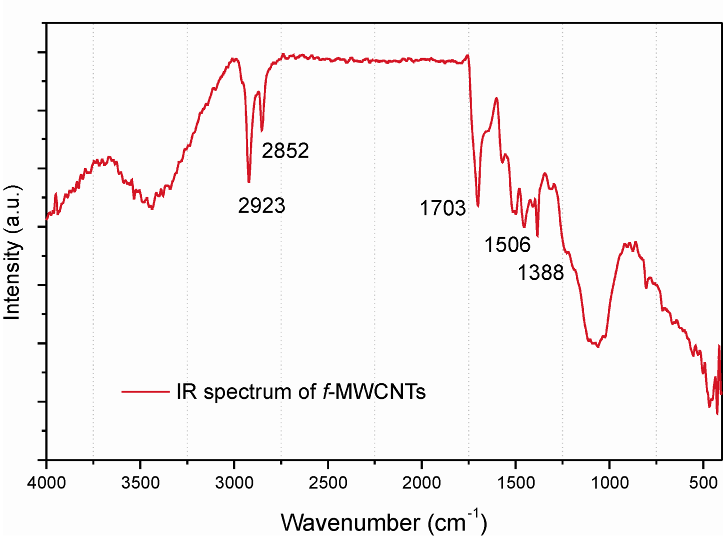


Figure S17. IR spectrum of *f*-MWCNTs (KBr).

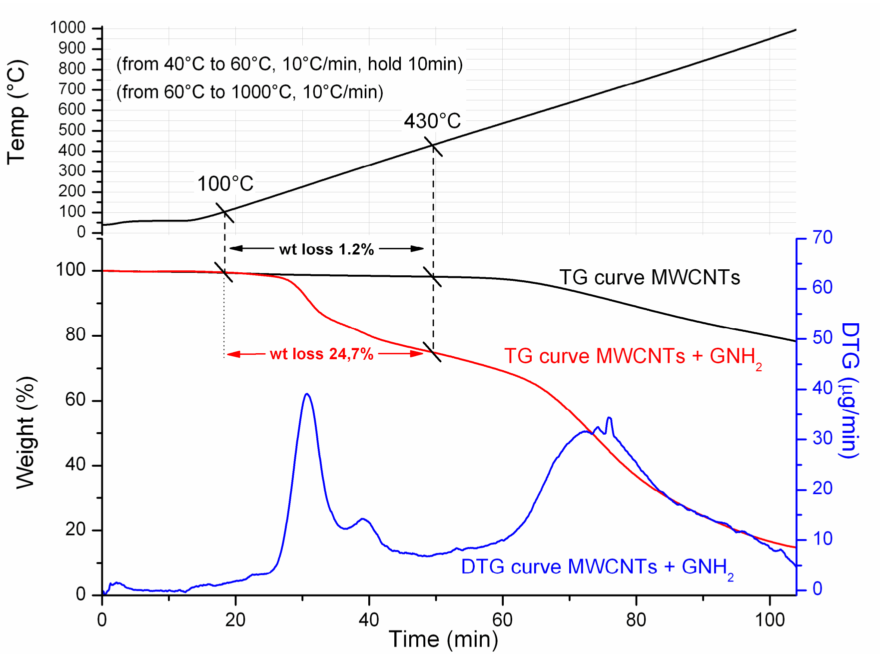


Figure S18. TGA analysis of *f*-MWCNTs.

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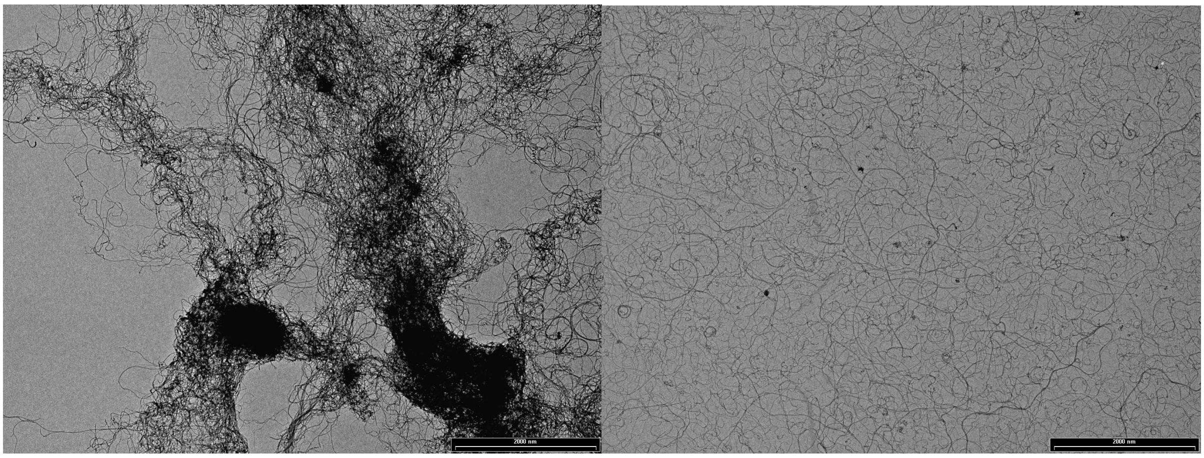


Figure S19. TEM images: a) pristine MWCNTs, b) *f*-MWCNTs

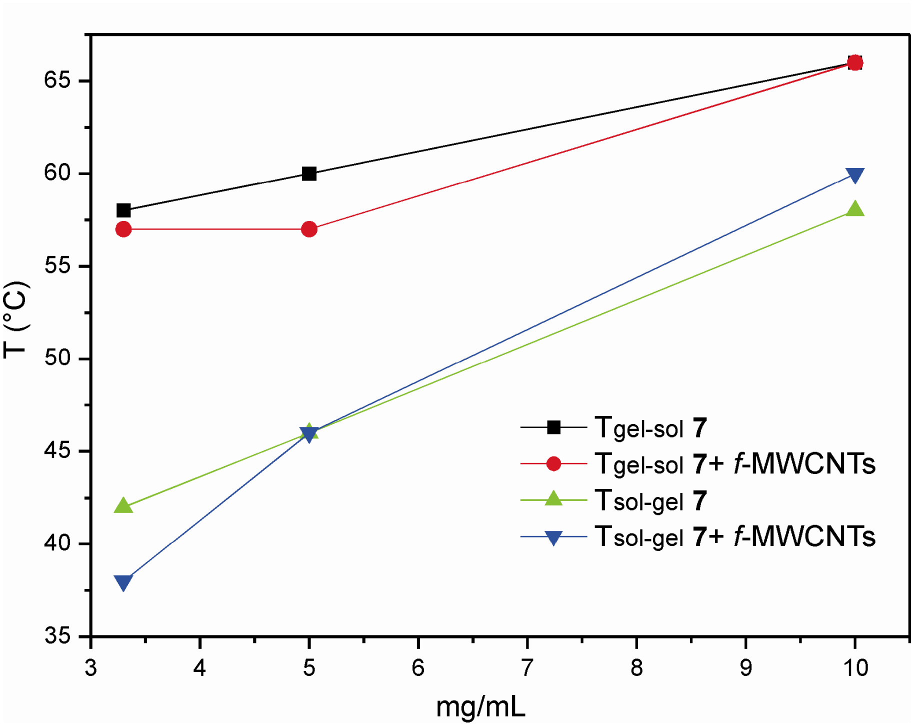
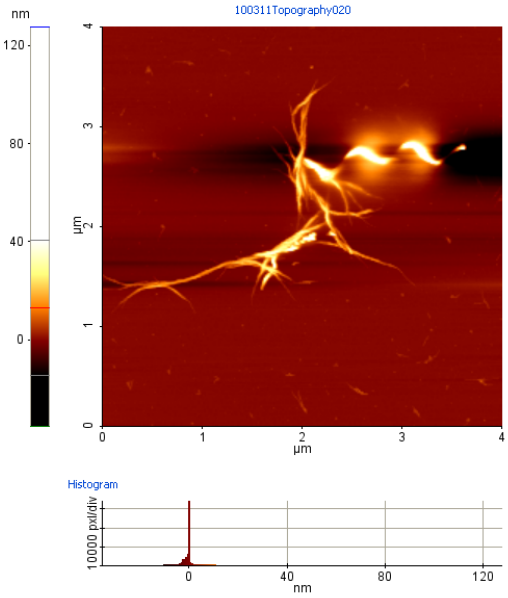
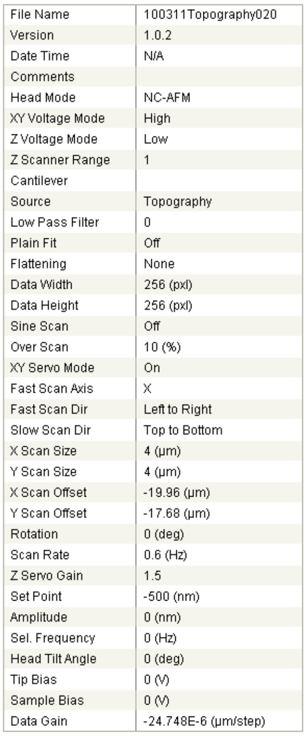


Figure S20. Variation of $T_{gel-sol}$ for **7** (■), **7**+ *f*-MWCNTS (●) and $_{Tsol-gel}$ of **7** (▲) and **7** + *f*-MWCNTs (▼)

a)





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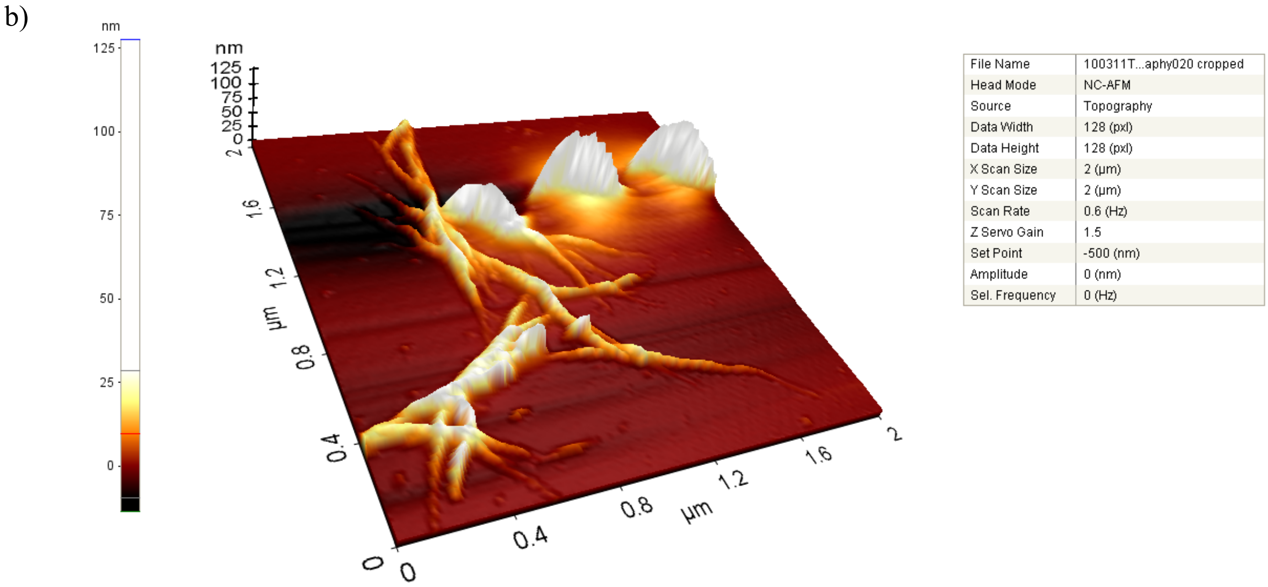

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Figure S21. a) AFM image of a gel made by *f*-MWCNTs + **7** dispersed on a mica support (topography). b) 3D topography representation.

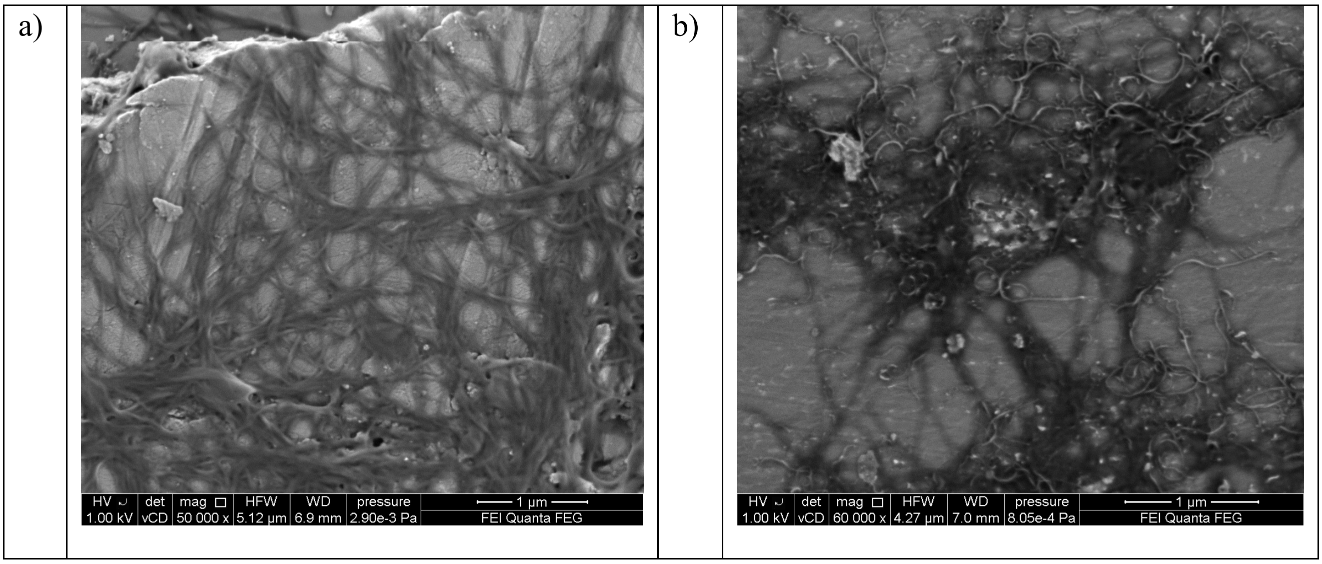

Figure S22. a) SEM image of fibers of gel of compound **7** dispersed on aluminum support. b) SEM image of fibers of gel of compound **7**+ ***f*-MWCNTs** dispersed on aluminum support (Quanta FEG apparatus, courtesy by FEI Company, Eindhoven, The Netherlands)