

Supporting Information for

Diyne-functionalized fullerene self-assembly for thin
film solid-state polymerization

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NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded at 400.13 and 100.61 MHz on a Bruker Avance-400 NMR spectrometer (Bruker Biospin AG, Fällanden, Switzerland). The 1D and 2D NMR correlation experiments were performed at 298 K on a 5 mm broadband inverse probe with z-gradient (100% gradient strength of 53.5 G cm^{-1}) and 90° pulse lengths of $6.8 \mu\text{s}$ (^1H) and $14.5 \mu\text{s}$ (^{13}C) using Bruker standard parameter sets and pulse programs. ^1H and ^{13}C chemical shifts were referenced relative to the signals of chloroform at 7.26 ppm and 77.0 ppm, respectively.

PCB-Diyne

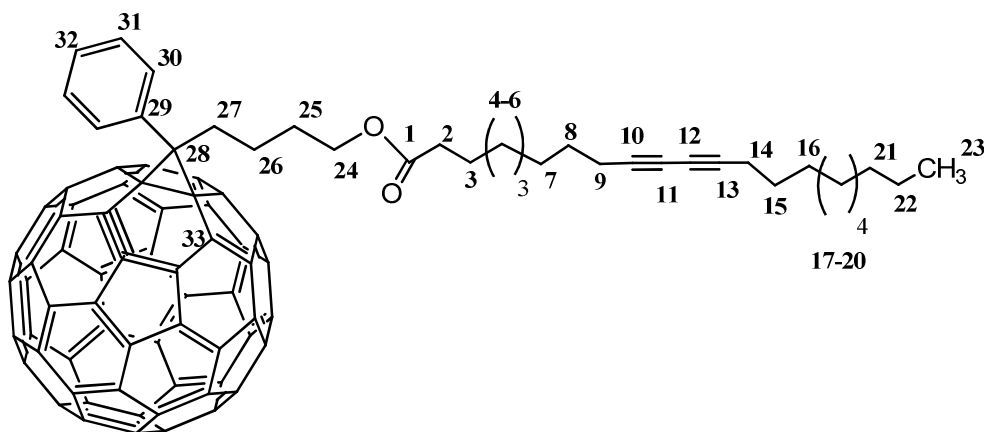


Figure S1: Assignment of C-H positions for **C23 PCB-diyne**.

$\delta(^1\text{H})$, CDCl_3 , 400.1 MHz:

7.91 (2H, m, H-30); 7.54 (2H, m, H-31); 7.47 (1H, m, H-32); 4.15 (2H, t, 6.4, H-24); 2.89 (2H, m, H-27); 2.25 (2H, t, 7.4, H-2); 2.23 (4H, t, 7.1, H-9/14); 1.92 (2H, m, H-26); 1.83 (2H, m, H-25); 1.58 (2H, m, H-3); 1.50 (4H, m, H-8/15); 1.36 (4H, m, H-7/16); 1.27 (2H, m, H-22); 1.25 (2H, m, H-21); 1.2-1.4 (14H, m, H-4-6; 17-20); 0.88 (3H, t, 6.9, H-23)

$\delta(^{13}\text{C})$, CDCl_3 , 100.6 MHz:

173.8 (C-1); 148.9/147.9/145.8/145.2/145.15/145.09/145.0/144.78/144.77/144.68/144.67
/144.5/144.4/144.0/143.76/143.75/143.1/143.03/142.99/142.93/142.90/142.3/142.2/142.12/142.1
0/141.0/140.7/138.0/137.5 (C-C60); 136.9 (C-29); 132.1 (C-30); 128.3 (C-31); 128.2 (C-32);
80.0 (C-33); 77.7/77.4 (C-10/13); 65.4/65.3 (C-11/12); 63.8 (C-24); 52.2 (C-28); 34.3 (C-2);
33.8 (C-27); 31.9 (C-21); 29.7/29.6/29.5/29.3/29.1/28.9/28.8 (C-4-6; 17-20); 29.1 (C-7/16); 28.5
(C-25); 28.3 (C-8/15); 25 (C-3); 23.4 (C-26); 22.7 (C-22); 19.2 (C-9/14); 14.1 (C-23)

^1H - ^{13}C HMBC correlations observed:

H-2 \rightarrow C-(1, 3, 4); H-7/16 \rightarrow C-(9, 14); H-8/15 \rightarrow C-(7, 9, 10, 13, 14, 16); H-9/14 \rightarrow C-(8, 10, 11,
12, 13, 15); H-21 \rightarrow C-(22, 23); H-22 \rightarrow C-(21, 23); H-23 \rightarrow C-(21, 22); H-24 \rightarrow C-(1, 25, 26); H-
25 \rightarrow C-(24, 26, 27); H-26 \rightarrow C-(24, 25, 27, 28); H-27 \rightarrow C-(25, 26, 28, 29, 33); H-3 \rightarrow C-(1, 2); H-
30 \rightarrow C-(28, 30, 32); H-31 \rightarrow C-(29, 30, 31); H-32 \rightarrow C-(30)

^1H - ^1H DQF-COSY correlations observed:

H-2 \rightarrow H-(3); H-3 \rightarrow H-(2, 4); H-7/16 \rightarrow H-(8, 15); H-8/15 \rightarrow H-(7, 9, 14, 16); H-9/14 \rightarrow H-(8, 15);
H-22 \rightarrow H-(23); H-23 \rightarrow H-(22); H-24 \rightarrow H-(25); H-25 \rightarrow H-(24, 26); H-26 \rightarrow H-(25, 27); H-27 \rightarrow H-
(26); H-30 \rightarrow H-(31); H-31 \rightarrow H-(30, 32); H-32 \rightarrow H-(31)

PCB-OH

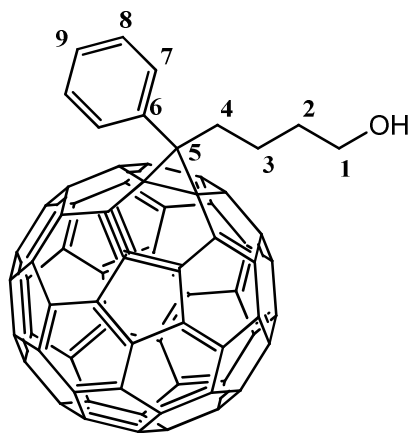


Figure S2: Assignment of C-H positions for **PCB-OH**.

$\delta(^1\text{H})$, CDCl_3 , 400.1 MHz:

7.91 (2H, m, H-7); 7.54 (2H, m, H-8); 7.47 (1H, m, H-9); 3.74 (2H, m, H-1); 2.91 (2H, m, H-4);
1.94 (2H, m, H-3); 1.78 (2H, m, H-2)

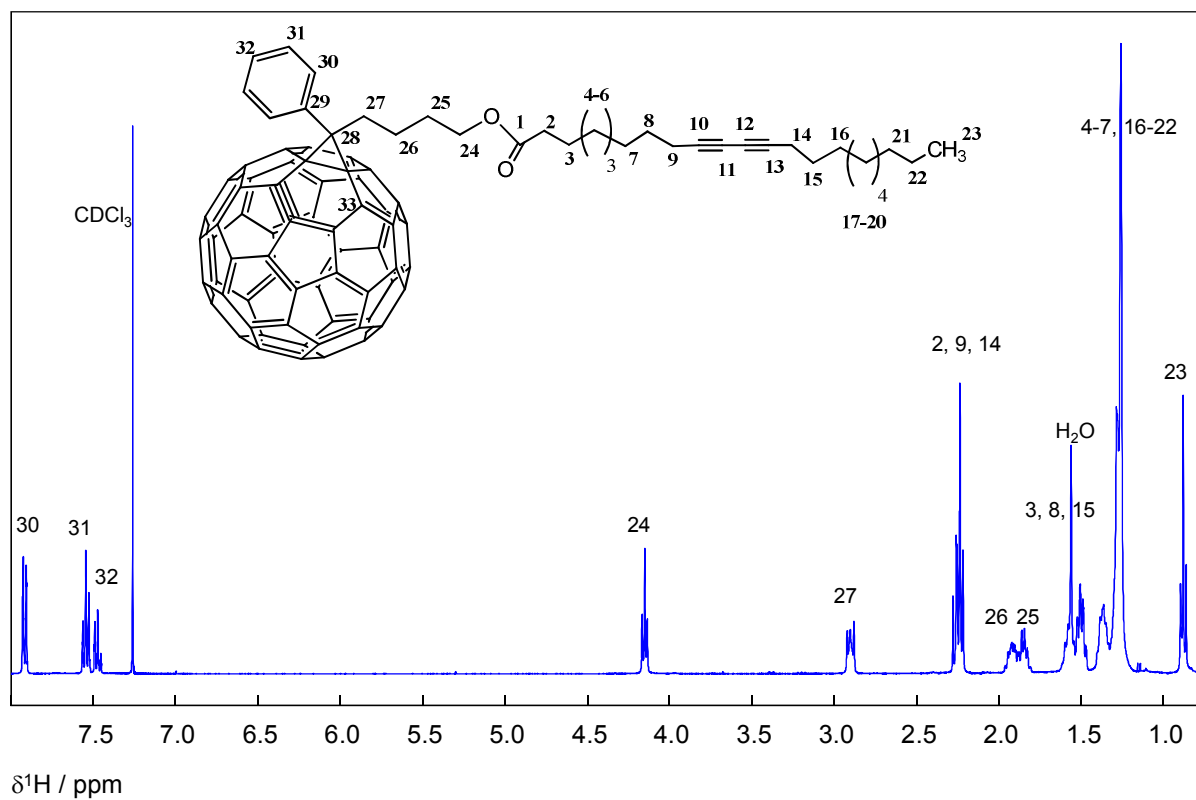


Figure S3: ^1H NMR spectrum of C23 PCB-diyne in CDCl_3 , 400.1 MHz, 0.5-8.0 ppm.

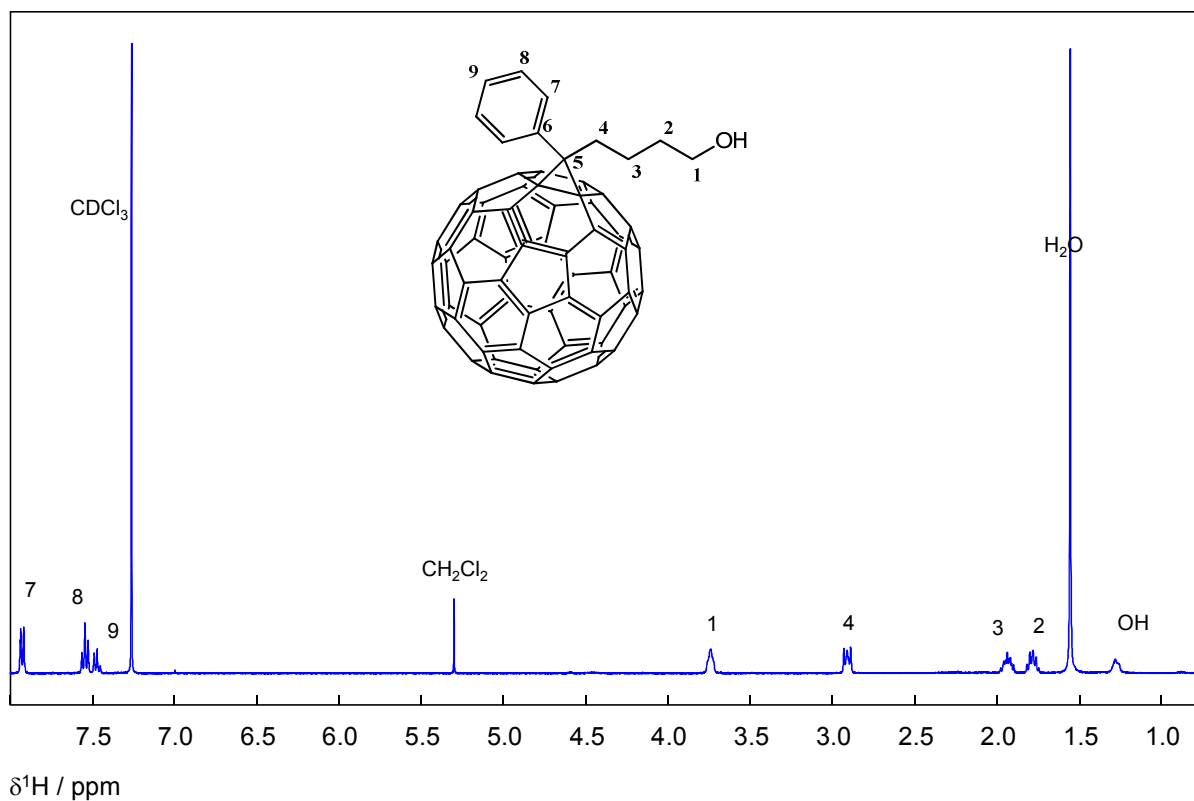
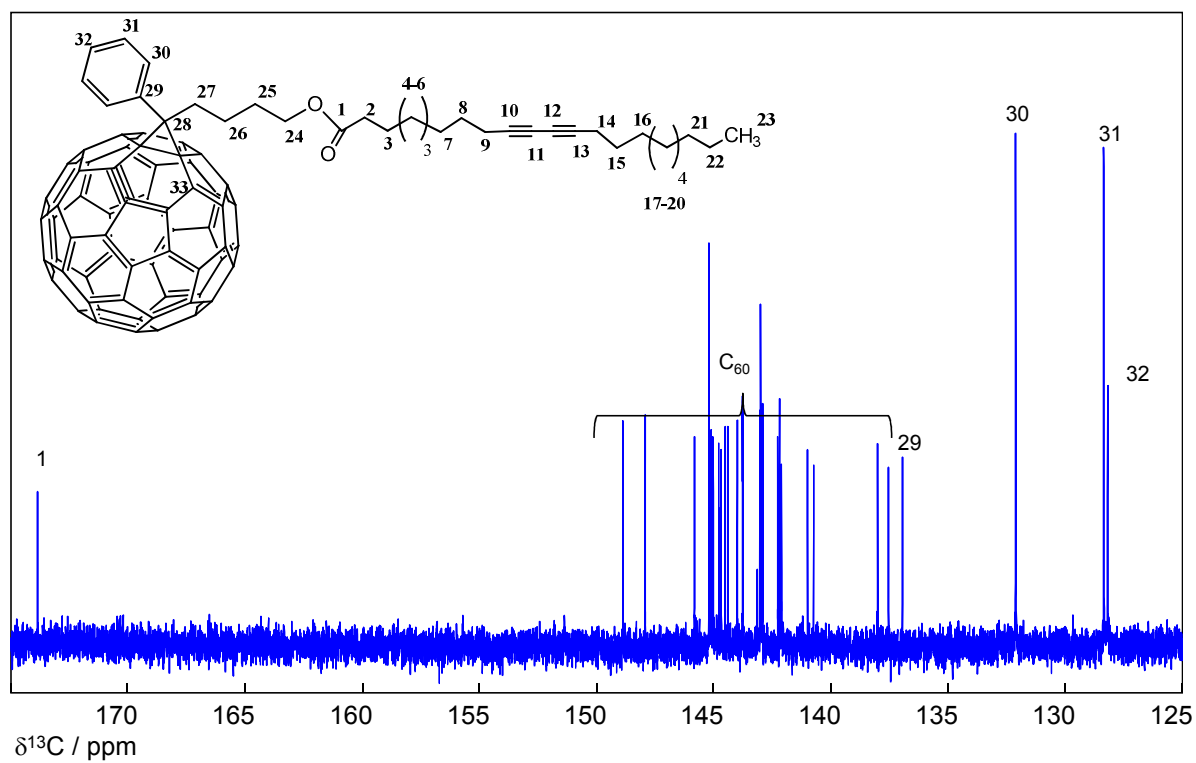


Figure S4: ^1H NMR spectrum of PCB-OH in CDCl_3 , 400.1 MHz, 0.5-8.0 ppm.



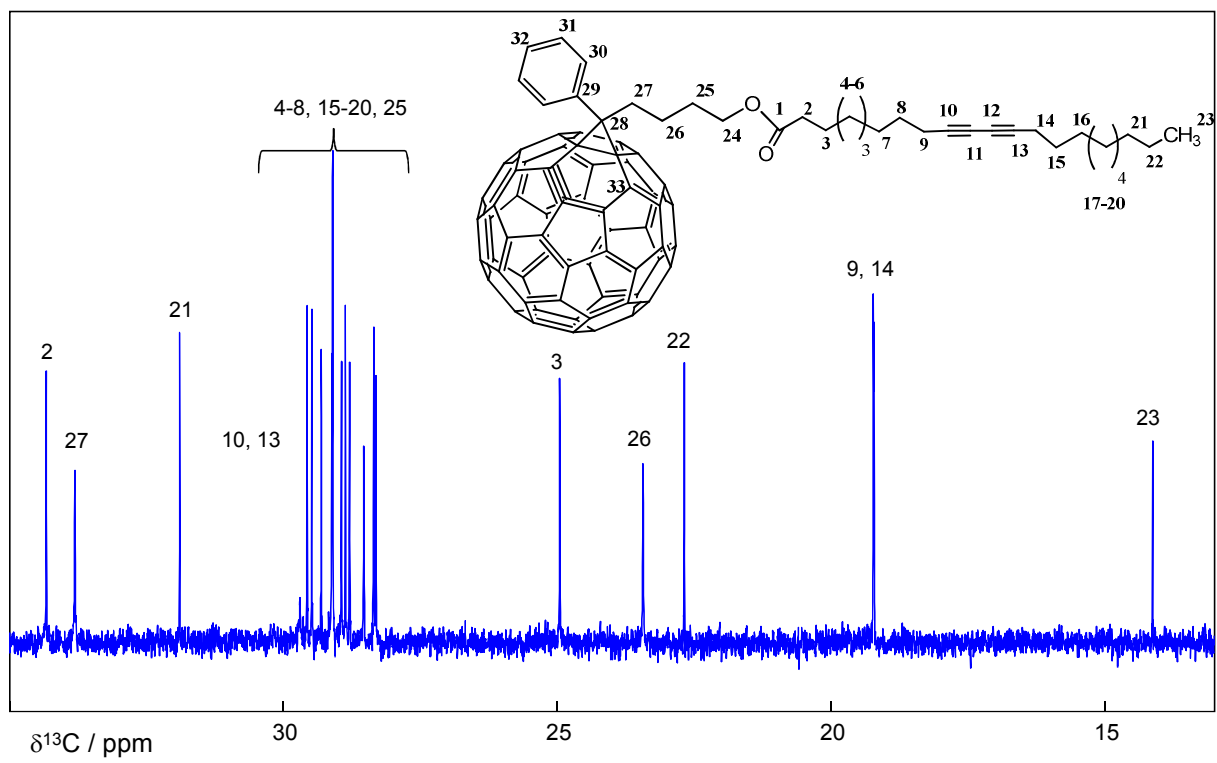
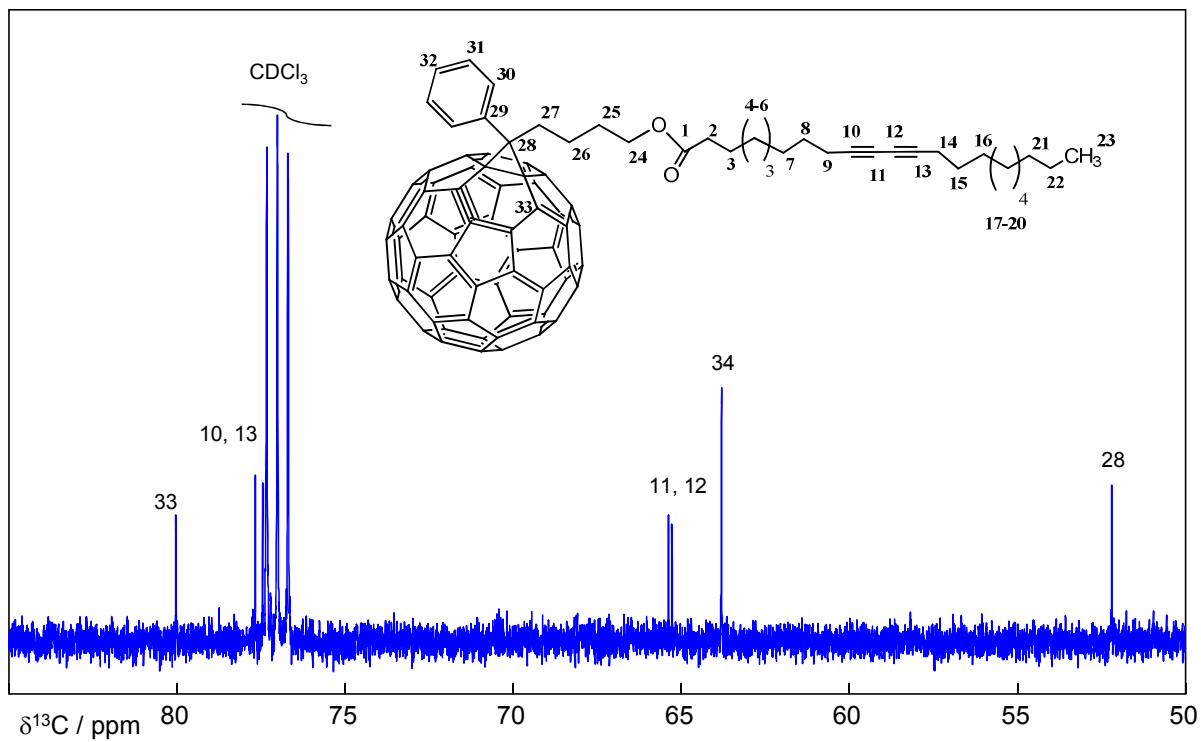


Figure S5: expanded ^{13}C NMR spectrum of C23 PCB-diyne in CDCl_3 , 400.1 MHz, 125-175 ppm (top), 50-85 ppm (middle), 10-35 ppm (bottom).

Mass spectrometry

C23 PCB-diyne mass determination was carried out on a MAT 95 mass spectrometer (Thermo Finnigan MAT, Bremen, Germany). The mass spectrometer was operated in high resolution mode (mass resolution $m/\Delta m = 7800$) using electron ionization (electron energy 70 eV) at an ion source temperature of 180 °C. Top: mass spectrum of C23 PCB-diyne with an exact mass of 1211.4 $\text{g}\cdot\text{mol}^{-1}$. Bottom: magnification of the main mass peak.

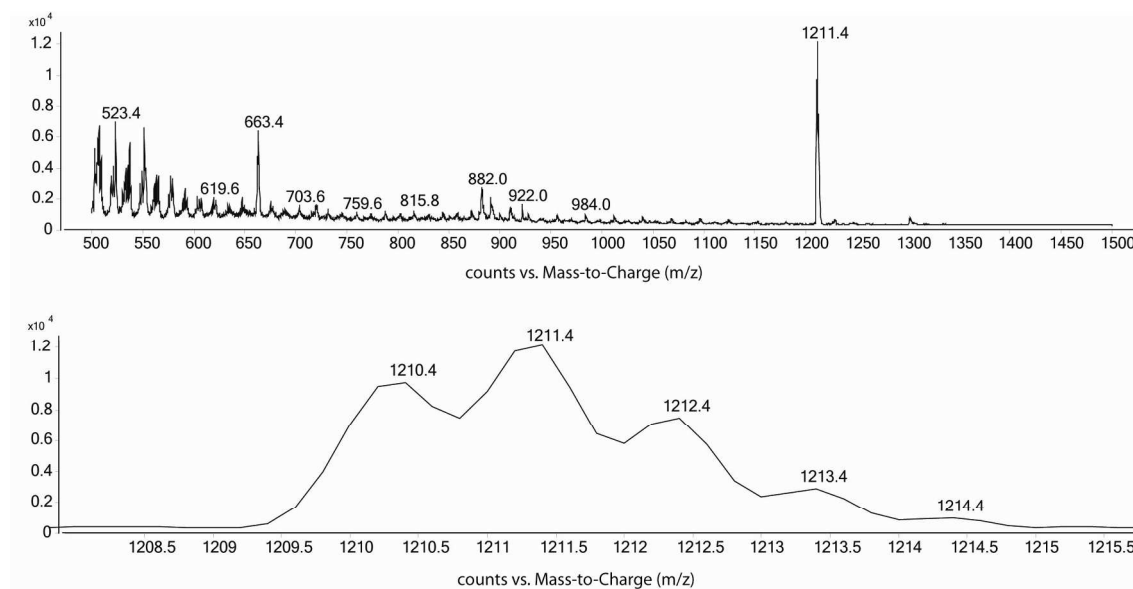


Figure S6: Mass spectra of C23 PCB-diyne

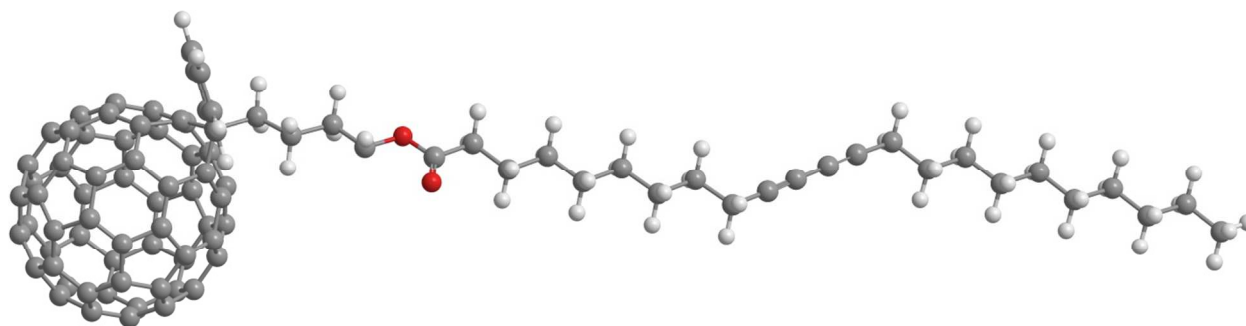


Figure S7: Conformation of C23 PCB-diyne.

The density functional theory (DFT) was chosen as modeling method to investigate the molecular structure of C23 PCB-diyne. The calculations were performed with the NWChem 5.1 software. The maximum length of the molecule is 3.6 nm.

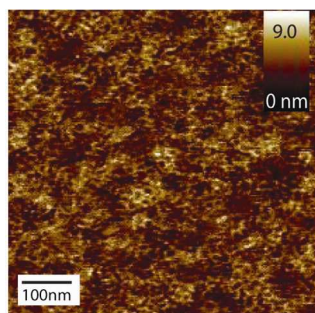


Figure S8: SFM image of a crystalline platelet drop-cast from 10 mg mL^{-1} C23 PCB-diyne in chlorobenzene

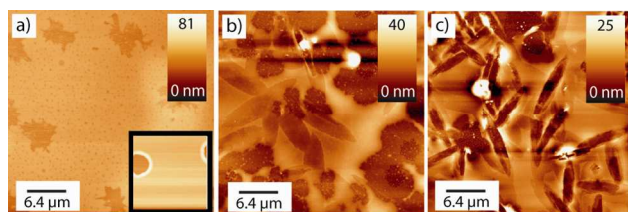


Figure S9: Coarsening of C23 PCB-diyne spin-coated films upon annealing.

(a) SFM image of a C23 PCB-diyne film coated from a 1 wt% solution in CB at 500 rpm, the inset shows a 500 nm wide zoom on a dewetted part of the film, (b) insoluble film after 2 h, and (c) after 4 h annealing at 120 °C.

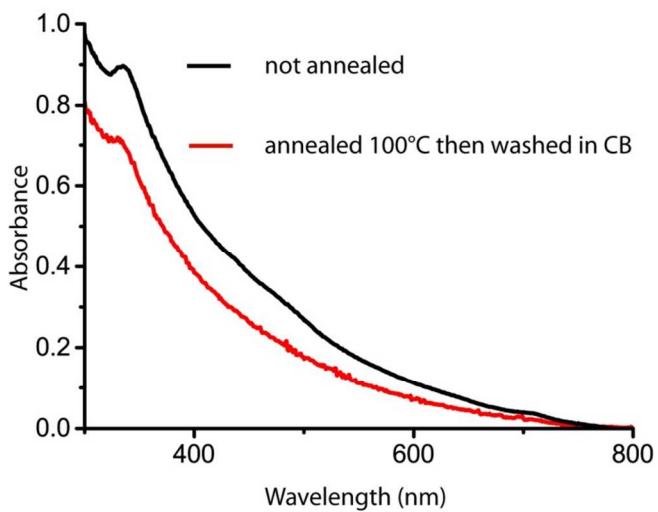
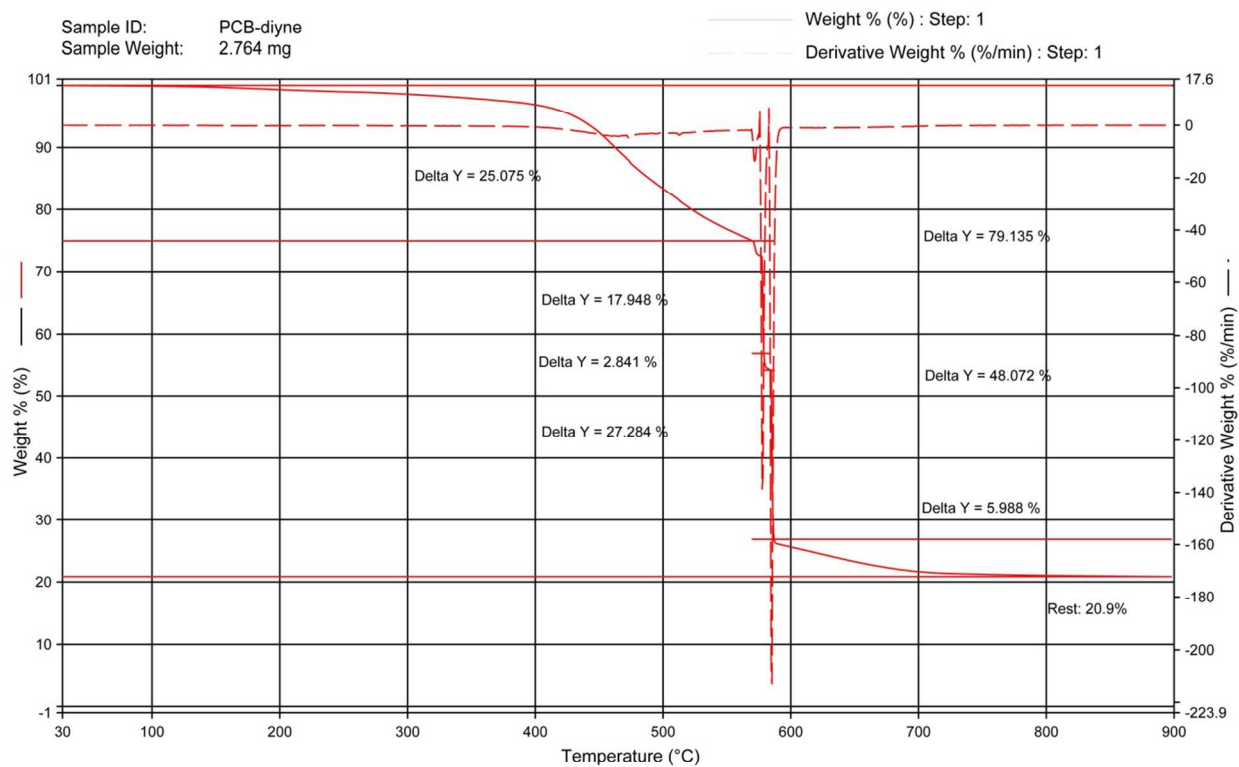


Figure S10: Insolubility of a C23 PCB-diyne film. Black: film spin-coated at 500 rpm from a 1 wt% solution in chlorobenzene before annealing and Red, after annealing at 100 °C for 24 h.



1) Heat from 30.00°C to 900.00°C at 20.00°C/min

Figure S11: thermogravimetric analysis (TGA) of C23 PCB-diyne.

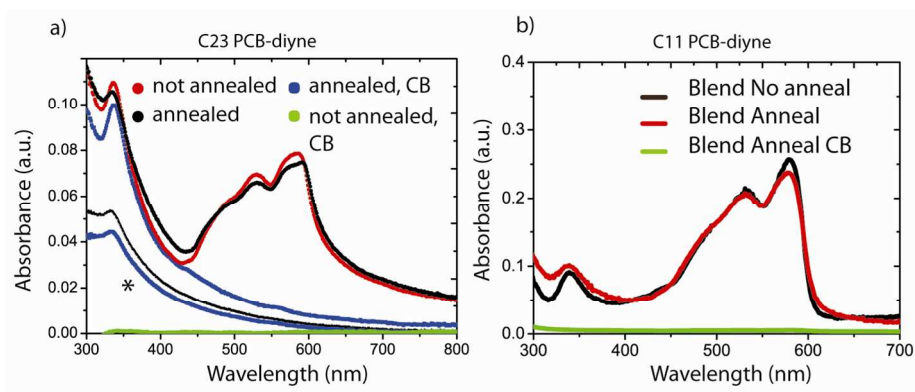


Figure S12: Changes in the UV-Vis spectra upon annealing and immersing the film in the coating solvent, (a) for C23 PCB-diyne: CyC films, 1:1 molar ratio 1 wt% in chlorobenzene, * represents blend films where CyC was removed prior to annealing; (b) for C11 PCB-diyne. The film remains soluble.

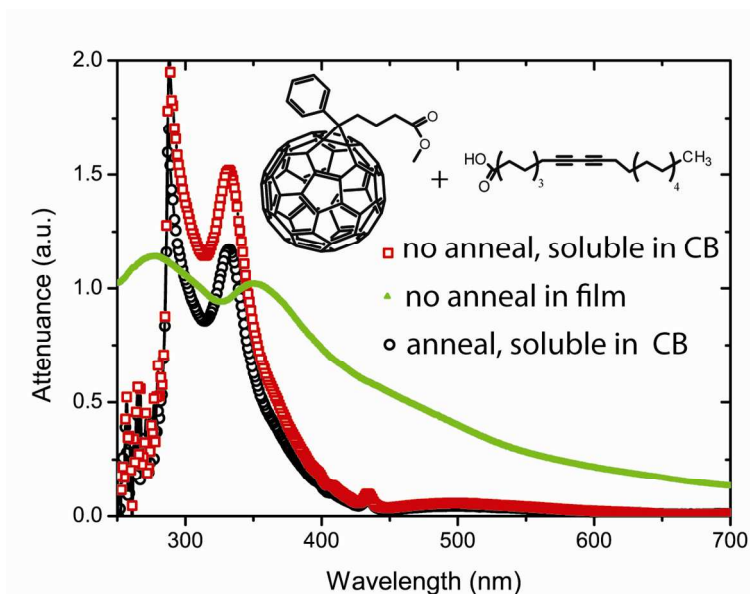


Figure S13: Blending of PCBM Diynoic acid, 1:1 molar blend, 2 wt% in CB. Blend films remained fully soluble in CB after annealing at 120 °C for 8 h and no difference in PCBM absorption was observed after annealing.

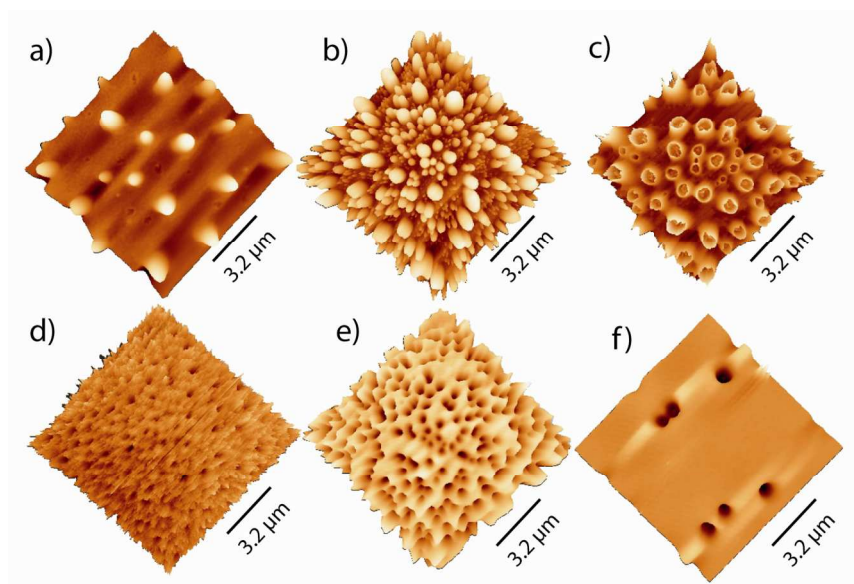


Figure S14: SFM scans of morphologies obtained by spin-coating blends of C23 PCB-diyne : CyC. (a) C23 PCB-diyne : CyC films, 1:1 molar ratio 1 wt% in chlorobenzene, spin-coated at 1000 rpm; (b) corresponding CyC phase; (c) corresponding insoluble PCB-diyne matrix and 2:1 molar ratio 1 wt% in chlorobenzene, spin-coated (d) at 4000 rpm; (e) 1000 rpm; (f) 400 rpm.

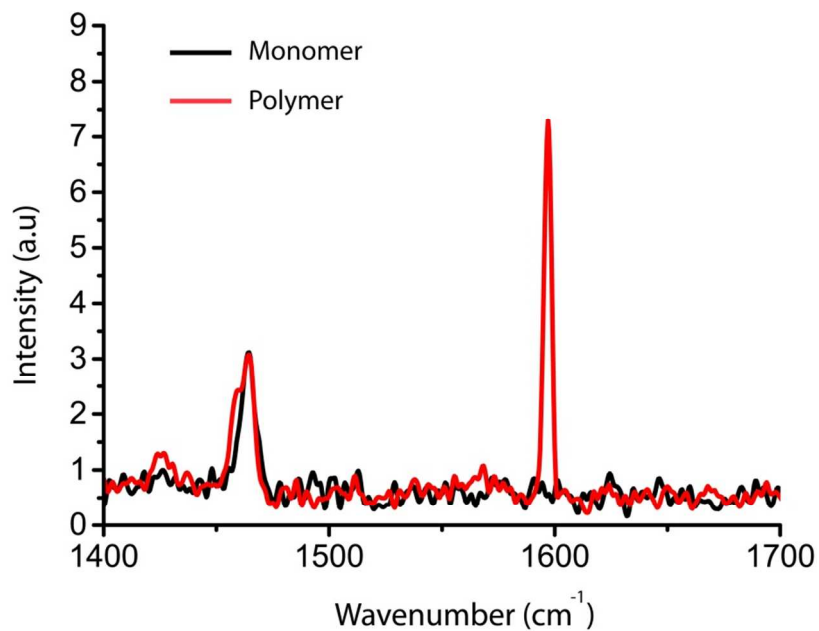


Figure S15: Raman spectroscopy of C23 PCB-diyne monomer (black) and polymer (red). We observe a peak at 1600 cm^{-1} which we attribute to the formation of C=C bonds in the polymer. The fullerene Raman band is at 1464 cm^{-1} . In the polymerized sample, a small (<10% intensity) peak shoulder at 1460 cm^{-1} might indicate a side reaction involving the PCBM core in a dimerization reaction with a nearby fullerene or an unsaturated carbon-carbon moiety.