Supporting Information for

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

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NMR Spectroscopy

$^1$H 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 $\mu$s ($^1$H) and 14.5 $\mu$s ($^{13}$C) using Bruker standard parameter sets and pulse programs. $^1$H 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.

$\delta(^1$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)
$\delta^{(13)}$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
/144.5/144.4/144.0/143.76/143.75/143.1/143.03/142.99/142.93/142.90/142.3/142.2/142.1
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)

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

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

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

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

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

$\delta(^1H)$, 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**: $^1$H NMR spectrum of C23 PCB-diyne in CDCl$_3$, 400.1 MHz, 0.5-8.0 ppm.
Figure S4: $^1$H 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/Δm = 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 g·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.
Figure S11: thermogravimetric analysis (TGA) of C23 PCB-diyne.

1) Heat from 30.00°C to 900.00°C at 20.00°C/min
**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-diyn 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.