SUPPORTING INFORMATION

Phase segregation and affinity between a fluorinated perylene diimide dye and an alkyl-substituted hexa-*peri*-hexabenzocoronene

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Explanation of dense network formation during BPF-PDI drop casting

If the evaporation is carried out under observation through the microscope it is possible to notice that, at the beginning of the process, the network starts forming at the air/solution interface with a membrane-like consistency. This evidence can be linked to the scarce solubility of BPF-PDI in $CHCl_3$ at room temperature, and to the fact that this interface is the region of the drop cooling down more rapidly due to evaporation,[1] thus becoming the preferred site for the formation of the dense fibrillar network. The solvent then slowly evaporates through this network, and some folds form in the emptying membrane (white arrows in Fig. 10a), as a result of its dome-like shape collapsing onto a flat surface. The membrane-like texture of these deposits is also evidenced by a few microscopic tears in their structure that originate from the edges of the substrates (Fig. 10b,c), and that expose the fibers these samples consist of.

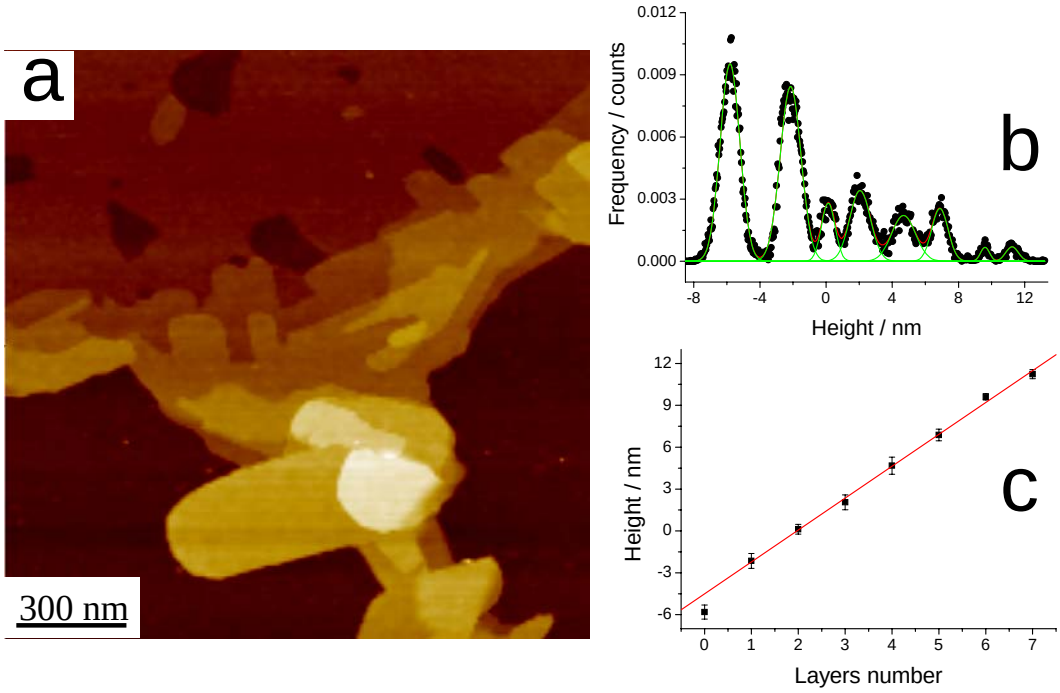


Fig. S1. (a) AFM topography image of a PDI7 sample spun on SiO_x from $CHCl_3$ solutions ([PDI7] = 500 μM), showing the formation of a well-defined multilayered structure. The height histogram is reported in (b), while (c) highlights the uniform thickness of (2.28 ± 0.05) nm of each layer. (a) Z-range: 21.9 nm. (c) $R^2 = 0.998$.

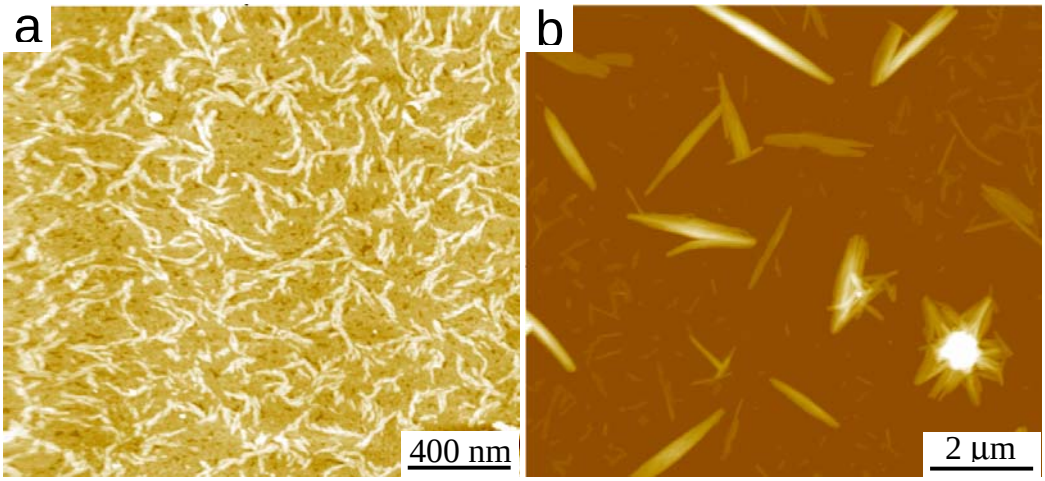


Fig. S2. (a) AFM topography image of a HBC-C_{12} samples spun on SiOx from $CHCl_3$ solutions ([HBC-C_{12}] = 500 µM), consisting in a continuous layer covered by a discontinuous network, both being ~ 2 nm thick. (b) AFM topography image of (a) after SVA in $CHCl_3$, showing the rearrangement of the layered material into micron-sized, tapered needles. Z-ranges: (a) 13.6 nm; (b) 148.5 nm.

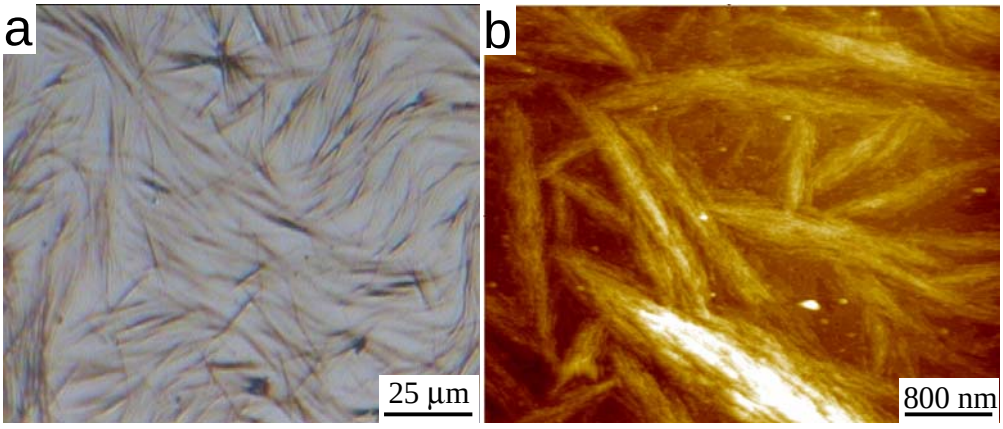


Fig. S3. (a) OM and (b) AFM topography image of a HBC-C_{12} samples drop cast on SiOx from $CHCl_3$ solutions ([HBC-C_{12}] = 500 µM), consisting in a network of long, entangled needles. (b) Z-range = 30.5 nm.

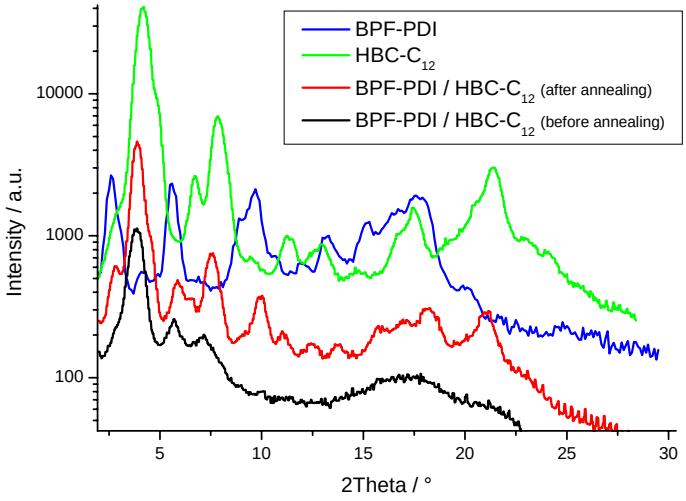


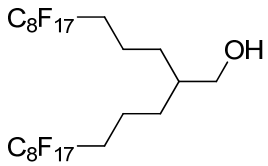
Fig. S4. Equatorial integrations of the 2D WAXS patterns in Fig. 17 of the main text.

Synthesis and characterization

General

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in deuterated solvents on a Bruker Avance 300 and Bruker Avance 500, using the residual proton resonance or the carbon signal of the solvent as the internal standard. Infrared spectra were recorded on a Nicolet 730 FT-IR SPECTROMETER with Endurance Diamant ATR unit. FD mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD. MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF spectrometer. All starting materials were purchased from Aldrich, Acros, ABCR, Fluorous Technologies Inc. or Lancaster, and used as received.

6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecane-1-ol (3)



6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecaneacid (**1**) [1] was dissolved in 10 mL anhydrous THF. Borane-THF complex (1 M solution in THF, 33.8 mL, 33.8 mmol) was added drop wise under argon atmosphere. The solution was refluxed over night. After cooling to room temperature, 20 mL of 2 M hydrochloric acid was carefully added to the reaction mixture. Water was added (150 mL) and the resulting precipitate was filtered and washed with water. The product was obtained as a white solid (6.15 g, 95%).

^{1}H-NMR (300 MHz,THF-d8, 293 K)
δ[ppm]: 3.47 (t, ^{3}J = 4.5 Hz, 2H), 2.48 (bs, 1H), 2.30-2.07 (m, 4H), 1.72-1.28 (m, 9H).

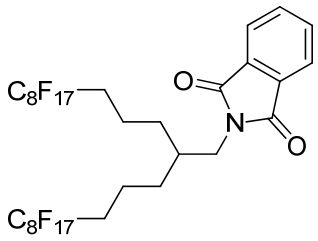
^{13}C-NMR (75 MHz,CD_2Cl_2, 293 K)
δ[ppm]: 64.46, 41.11, 31.79 (t, ^{2}J = 21.8 Hz, CF), 31.50, 18.63.

MALDI-TOF-MS
m/z (%): 966.8 (8) (calculated for $C_{24}H_{16}F_{36}O$: 966.3), 934.5 (100) (–CH_2OH).

IR-Spectra
ν [cm^{-1}] : 3289, 2951, 2877, 1197, 1145, 1134, 1116, 1041, 955, 703, 655, 559.

[1] For synthesis see: Julien Loiseau, Eric Fouquet, Richard H. Fish, Jean-Marc Vincent, Jean-Baptiste Verlhac, *Journal of Fluorine Chemistry*, 108, **2001**, 195-197

***N*-(2-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecyl))phthalimide (4)**



Alcohol **3** (3.5 g, 3.6 mmol), phthalimide (693 mg, 4.7 mmol) and triphenylphosphine (1.23 g, 4.7 mmol) were dissolved in 25 mL anhydrous THF. Diethylazodicarboxylate (0.74 mL, 820 mg, 4.7 mmol) was added drop wise. The reaction mixture was stirred for 72 h at room temperature. Water was added (150 mL) and the mixture was washed three times with ethyl acetate. The organic fractions were washed with water and dried with $MgSO_4$. Ethyl acetate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, toluene/ethyl acetate 1:1). The product was obtained as a yellowish solid (3.2 g, 82%).

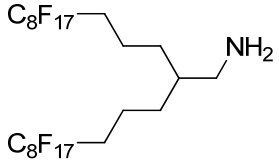
^{1}H-NMR (300 MHz, $CDCl_3$, 293 K)
δ[ppm]: 7.87-7.80 (m, 2H), 7.75-7.67 (m, 2H), 3.61 (d, ^{3}J = 6.8 Hz, 2H), 2.24-1.84 (m, 5H), 1.81-1.52(m, 4H), 1.44-1.32(m, 4H).

^{13}C-NMR (75 MHz,$CDCl_3$, 293 K)
δ[ppm]: 168.65, 134.07, 131.95, 123.34, 41.24, 64.6, 37.09, 31.05 (t, ^{2}J = 21.8 Hz, CF), 17.21.

FD-MS
m/z (%): 1096.3 (100), calculated for $C_{32}H_{19}F_{34}NO_2$: 1095.4.

IR-Spectra
ν [cm^{-1}]: 2925, 1711, 1371, 1330, 1198, 1146, 1115, 1074, 1035, 952, 721, 710, 655.

6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecane-1-amine (5)



1.5 g (1.4 mmol) phthalimide **4** and 0.5 mL hydrazine hydrate were dissolved in a mixture of 25 mL ethanol and 5 mL THF. The solution was refluxed for 16 h. After cooling down, water (150 mL) was added and the mixture was extracted with ethyl

acetate (3x150 mL). The organic fractions were washed with water and brine and dried over $MgSO_4$. Ethyl acetate was removed under reduced pressure and the crude product was recrystallised from toluene. The product was obtained as a white solid (1.2 g, 90%).

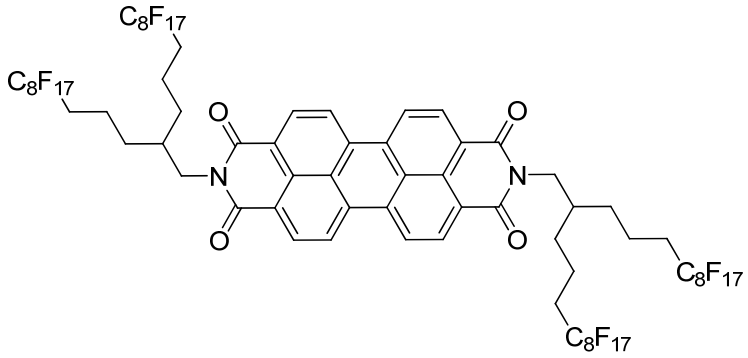
^{1}H-NMR (300 MHz, THF-d_8, 293K)
δ[ppm]: 3.47 (d, ^{3}J = 4.1, 2H), 2.16 (m, 4H), 1.71-1.31 (m, 9H).

^{13}C-NMR (75 MHz,$CDCl_3$, 293 K)
δ[ppm]: 63.45, 40.10, 30.78 (t, ^{2}J = 21.8 Hz, CF), 30.49, 17.62.

FD-MS
m/z (%): 966.8 (100), calculated for $C_{24}H_{17}F_{34}N$: 965.3.

IR-Spectra
ν [cm^{-1}]: 2951, 1700, 1661, 1331, 1197, 1144, 1134, 1116, 1041, 954, 703, 665.

***N,N'*-di-[1-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)tridecanyl)]perylene-3,4:9,10-bis(dicarboximide) (6)**



A suspension of 3,4:9,10-perylenetetracarboxylic dianhydride (39 mg, 0.1 mmol), amine **5** (309 mg, 0.32 mmol) and acetic acid (45 mg, 0.75 mmol) in 2.5 mL was stirred 16 h at 150°C under argon. After cooling down, the precipitate was filtered and washed thoroughly with THF. The crude product was recrystallised from chloroform. The product was obtained as orange-red solid (144 mg, 63%).

^{1}H-NMR (500MHz, $C_2D_2Cl_4$, 398 K)
δ[ppm]: 8.67 (d, ^{3}J=8.0Hz,4H), 8.57 (d, ^{3}J=8.0Hz, 4H), 4.19 (d, ^{3}J=7.0Hz, 4H), 2.24-2.01 (m, 10H), 1.88-1.64 (m, 8H), 1.61-1.45 (m, 8H).

^{13}C-NMR (126MHz, $C_2D_2Cl_4$, 398 K)
δ[ppm]: 159.75, 130.97, 127.63, 125.71, 122.81, 119.64, 119.20, 70.35, 70.13, 69.91, 40.28, 32.79, 27.79, 27.73 (t, ^{2}J = 22.68 Hz, CF), 27.55, 13.86.

^{19}F-NMR (471MHz, $C_2D_2Cl_4$, 333 K)
δ[ppm]: -80.85 (t, ^{3}J = 10.2 Hz, 3F), -112.98, -121.12, -121.34, -121.34, -122.18, -122.94, -125.52.

MALDI-TOF-MS
m/z (%): 2287.0 (100), calculated for $C_{72}H_{38}F_{68}N_2O_2$ 2287.0.

IR-Spectra
ν [cm^{-1}]: 2953, 1700, 1661, 1596, 1355, 1197, 1145, 1114, 1041, 954, 850, 809, 744, 703, 653.

Literature

1. C. Anandharamakrishnan, C. D. Rielly and A. G. F. Stapley, *Food Sci. Technol. - LWT*, 2008, **41**, 270-277.