Supplementary Material (ESI) for Chemical Communications

ESI (Electronic supporting information)

Self-organization of a new fluorous porphyrin and C60 films on indium-tin-oxide electrode

Alessandro Varotto, Louis Todaro, Mikki Vinodu, Jessica Koehne, Gang-yu Liu and Charles M. Drain

Fig. S1 High resolution mass spectrometry of **1**
Fig. S2 ^{1}H NMR of **1** in $CDCl_3$ 5% TFA.
Fig. S3 ^{19}F NMR of **1** in $CDCl_3$ 5% TFA
Fig. S4 ^{19}F NMR of **1** in $CDCl_3$ 5% TFA, expanded
Fig. S5 Electronic spectra of **1** in CCl_4
Fig. S6 Electronic spectrum of **1** on ITO
Fig. S7 AFM nanoshaving experiment of **1**/C_{60} film on ITO
Fig. S8 10x10 μm image of **1**/C60 film on ITO
Fig. S9 UV-Vis spectra of **1** and **1**/C60 film on ITO
Fig. S10 ^{1}H-NMR of compound **2** in CDCl3
Fig. S11 ^{1}H-NMR of compound **2** - expanded
Fig. S12 High resolution mass spectrometry of **2**
Fig. S13 UV-Vis spectra on **2**/C_{60} film on ITO
Fig. S14 AFM of **2**/C_{60} film on ITO

Experimental.

All reagents and solvents purchased from Sigma-Aldrich and used without further purification unless stated otherwise. UV-vis spectrophotometer was a Cary 1-Bio, fluorescence spectrophotometer was a Fluorolog tau-3 from Spex, Crystallographic data were collected using a Bruker-Nonius Kappa CCD with a sealed X-ray tube. Bruker-Nonius software was used for data collection. Structure solution and refinement: Bruker SHELXTL.[1] AFM experiments were conducted either with an Asylum AFM (MFP-3D, Asylum Research Corp.) or a Veeco Multimode SPM. A Bruker 500 MHz NMR instrument was used.. A High resolution MS was performed with a 6520 Accurate-Mass Spec Q-TOF LC-MS (Agilent Technologies).

1. G.M. Sheldrick, SADABS. University of Göttingen, Germany, 1997
2. A.L. Spek, PLATON. University of Utrecht, The Netherlands, 2006.

Preparation of compound 1. 1H,1H,2H,2H-perfluorododecane-1-thiol (65 mg, 112 μmol, FluoroFlash) was dissolved in 3 mL of ethyl acetate/DMF (2:1 v/v) with diethylamine (DEA) (20 μL, 194 μmol) under nitrogen. Pentafluoro-tetraphenylporphyrin TPPF$_{20}$ (11.5 mg, 11.8 μmol, TCI America), dissolved approximately 1 mL of dimethylformamide (DMF) was added to this solution. The product **1** precipitated after 5 minutes and was filtrated, re-dissolved in acetone and purified by silica gel chromatography using hexane/acetone (9:1 v/v). The yield was 36.8 mg (11.4 μmol, 97%). High resolution ms: $C_{92}H_{27}N_4F_{100}S_4$ 0.2688 ppm error. ^{1}H NMR (CDCl$_3$ 5% TFA) ppm: -0.81 (broad s, 2H, pyrrole NH); 2.78 to 2.73 (m, 8H, 2'H); 3.50 (t, 8H, 1'H); 8.98 (s, 8H, pyrrole βH). ^{19}F NMR (CDCl$_3$ 5% TFA) ppm: -137.88 to -137.78 (m, 8F, Ar-*o*-F); -132.20 to -132.12 (m, 8F, Ar-*m*-F); -126.61 to -126.10 (m, 8F, 3'F); -123.40 to -126.10 (m, 8F, 4'F); -123.00 to -122.70 (m, 8F, 5'F); -122.20 to -121.50 (m, 40 F, 6'-10'F); -114.20 to -114.12 (m, 8F, 11'F); -81.05, -81.07, -81.10 (t, 12F, 12'F).

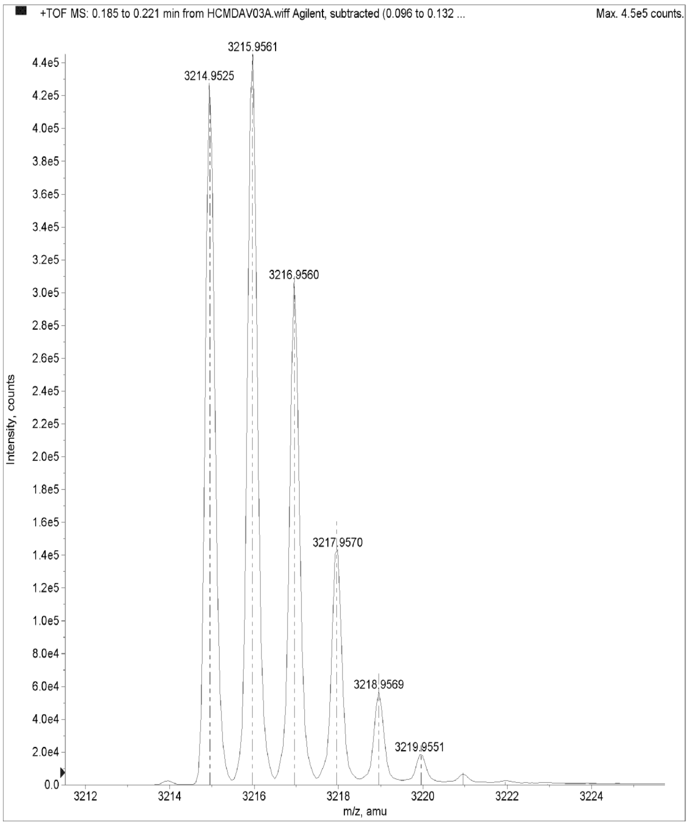

Fig. S1 High resolution ESI-MS of compound **1**.

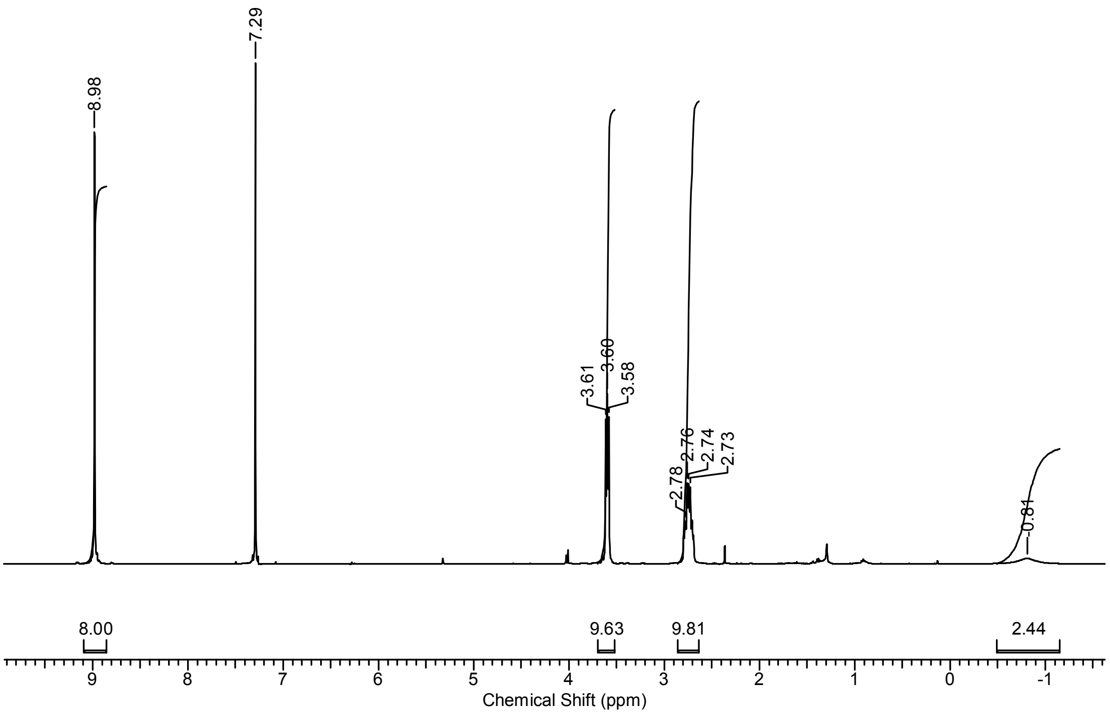

Fig. S2. ^{1}H NMR of **1** in $CDCl_3$ 5% TFA.

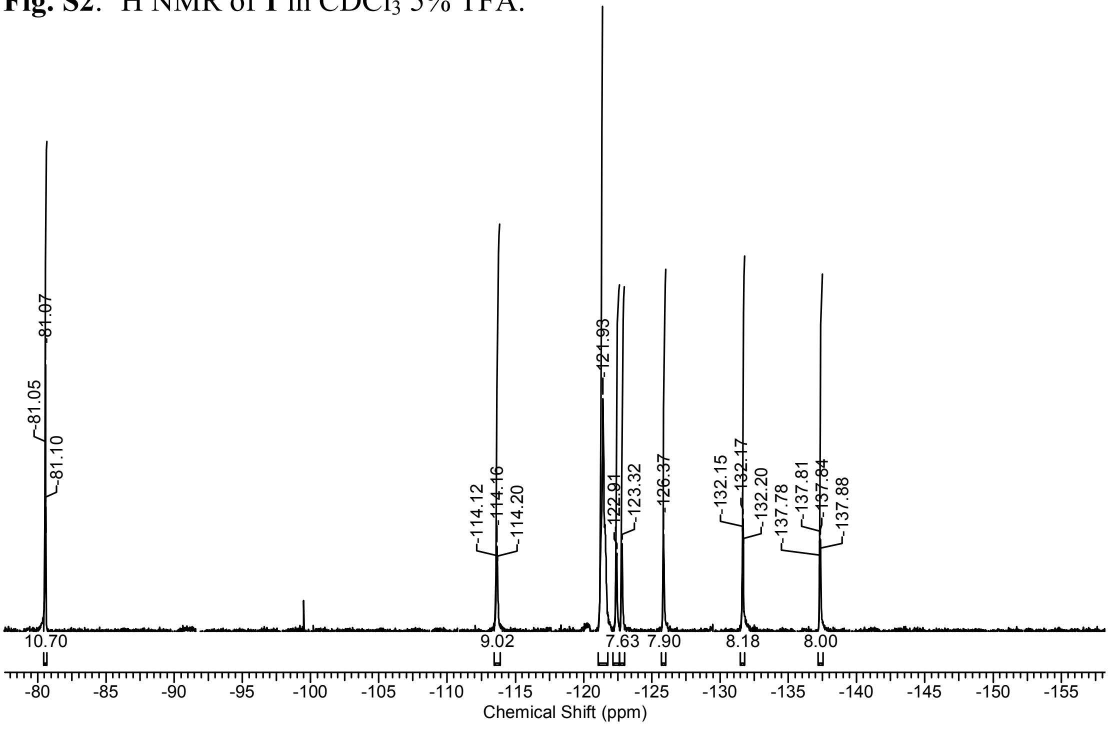

Fig. S3. ^{19}F NMR of **1** in $CDCl_3$ 5% TFA.

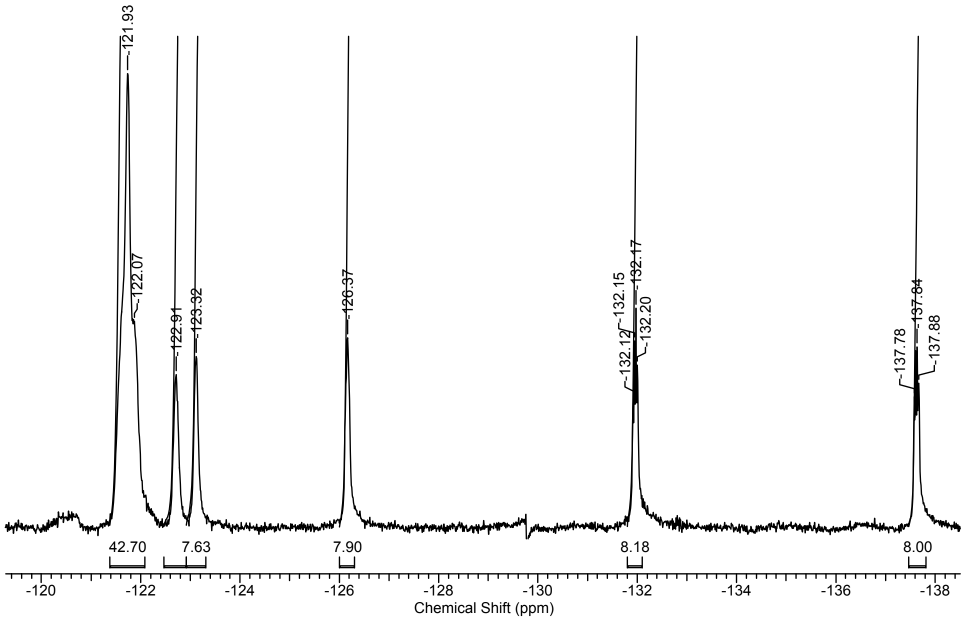

Fig. S4. ^{19}F NMR of **1** in $CDCl_3$ 5% TFA, expanded

Preparation of films on ITO.

The solution of **1** was prepared by dissolving approximately 5 mg in 10 mL of CCl_4 and heating the solution in a water bath at 50°C for the time necessary to dissolve the porphyrin, ca. 30 seconds. The concentration was calculated by UV-Vis spectroscopy using the extinction coefficient and then diluted to $6 \cdot 10^{-5}$ M. The solution of C_{60} was prepared by sonication of approximately 5 mg of fullerene (C_{60}, Aldrich, 99.5%) in 20 mL of CCl_4 for 3 hours obtaining a pale purple solution which was filtered through filter paper. Similarly the concentration was determined using the extinction coefecient.[18]

The 1:1 mole ratio solution of **1** and C_{60} was prepared by mixing the two solutions in the proper ratio and the final concentration of each was calculated using the extinction coefficients. The solutions were stored in the dark and used within one month. The thin films samples were prepared as follows: a slide of ITO coated glass (Aldrich, 70-100 Ω/sq surface resistivity) was ozone cleaned for 20 minutes, rinsed with ethyl alcohol (Pharmacia 200 proof, ACS/UPS grade) and thoroughly washed with nano-pure water. The slide was immersed vertically into the solution of **1** and C_{60} for 60 minutes, dried vertically in air, and then rinsed with nanopure water. The ITO coated slide was imaged by AFM before and after immersion using a Veeco Multimode, which was also used for nanoshaving experiments. An Asylum AFM (MFP-3D, Asylum Research Corp.) combined with a confocal laser scanning microscope (FluoView 1000, Olympus, USA) was used to correlate film morphology and photo activity. The back, glass side of the slides were cleaned of material before spectroscopic characterization.

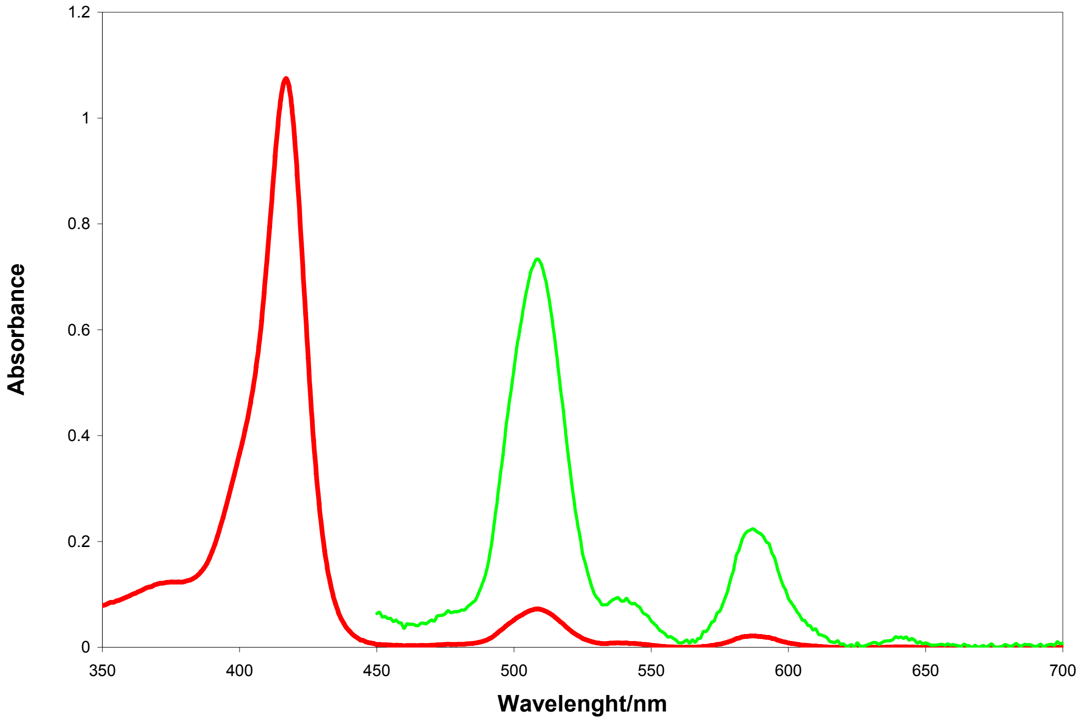

Fig. S5. Absorption spectrum of **1** in CCl_4 (red); expansion of the Q band region (10X; green)

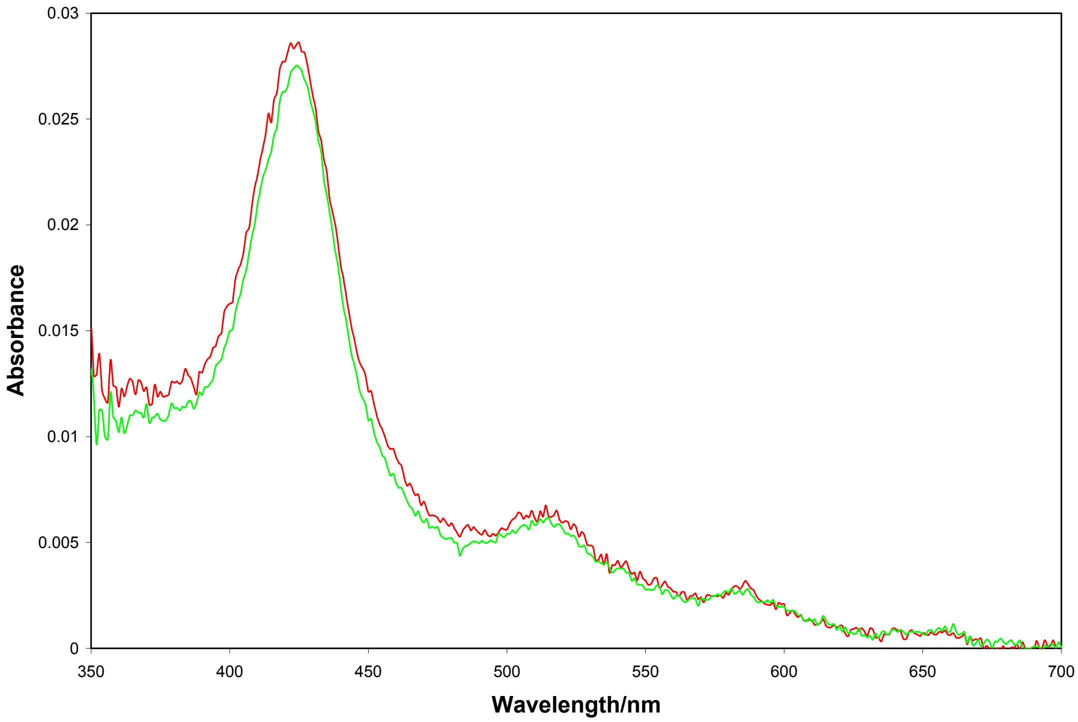

Fig. S6. Absorbance spectrum of **1** and C_{60} film on ITO co-deposited (red) and the same sample after 3 months of exposure to air in ambient light (green).

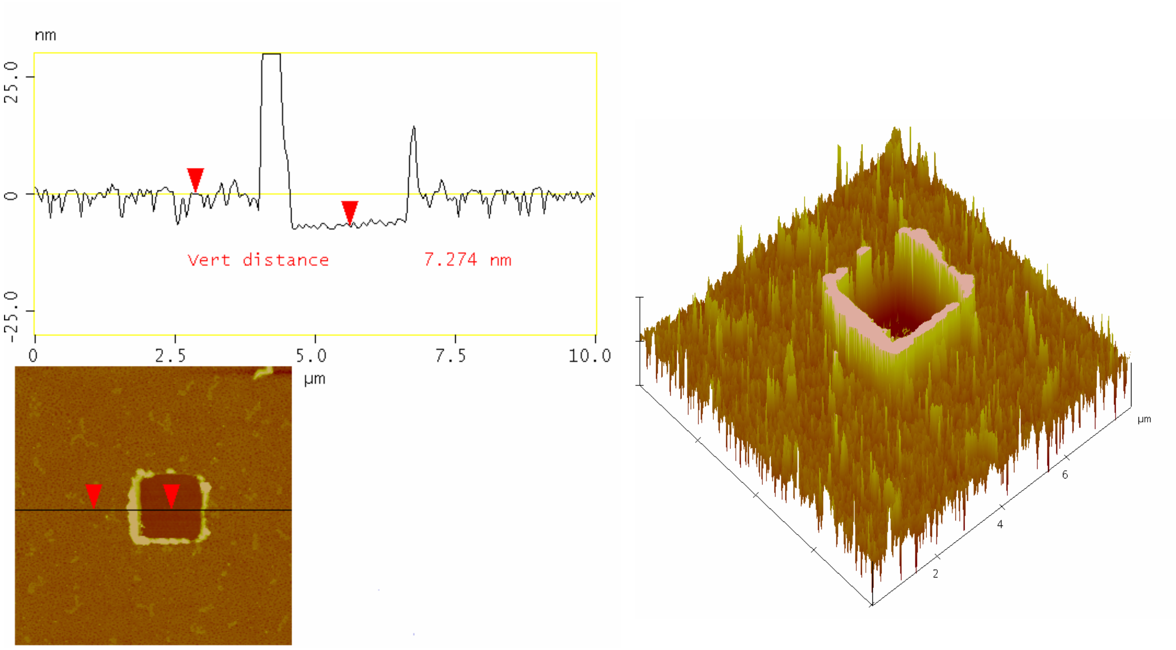

Fig. S7. Nanoshaving of a film of **1** and C_{60} ratio 1:1 on ITO electrode. The AFM image shows the granular morphology of film and the section analysis the thickness. A three dimensional version of the film on the right. Tapping/Height mode. Veeco Multimode AFM. Tip rectangular cantilever from Mikromasch NSC15 series Al BS (325 kHz, 40 N/m). Backside Al-coated. The well is shaved using a contact mode imaging tip with triangular cantilever from Mikromasch CSC21 series 100 kHz (2 N/m). Backside Al-coated. Spring constant calculated equal to 2.92 N/m. Force applied to shave off the film equal to 617.87 nN.

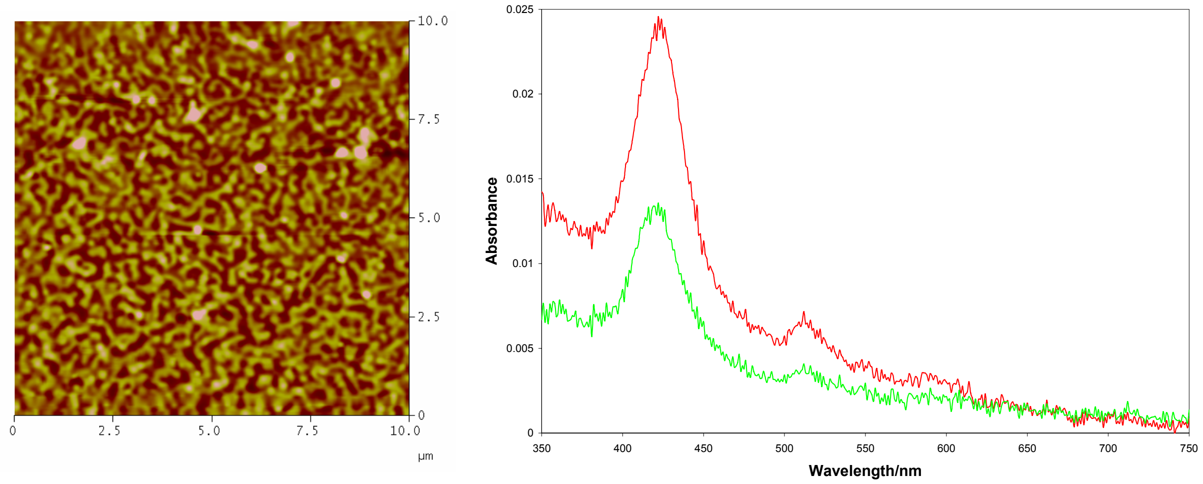

Fig. S8 Right: 10x10 µm AFM image of a film of 1 and C_{60} on ITO after two dipping in solution of 60 minutes each. Left: Corresponding absorbance after the first (green) and second (red) dipping.

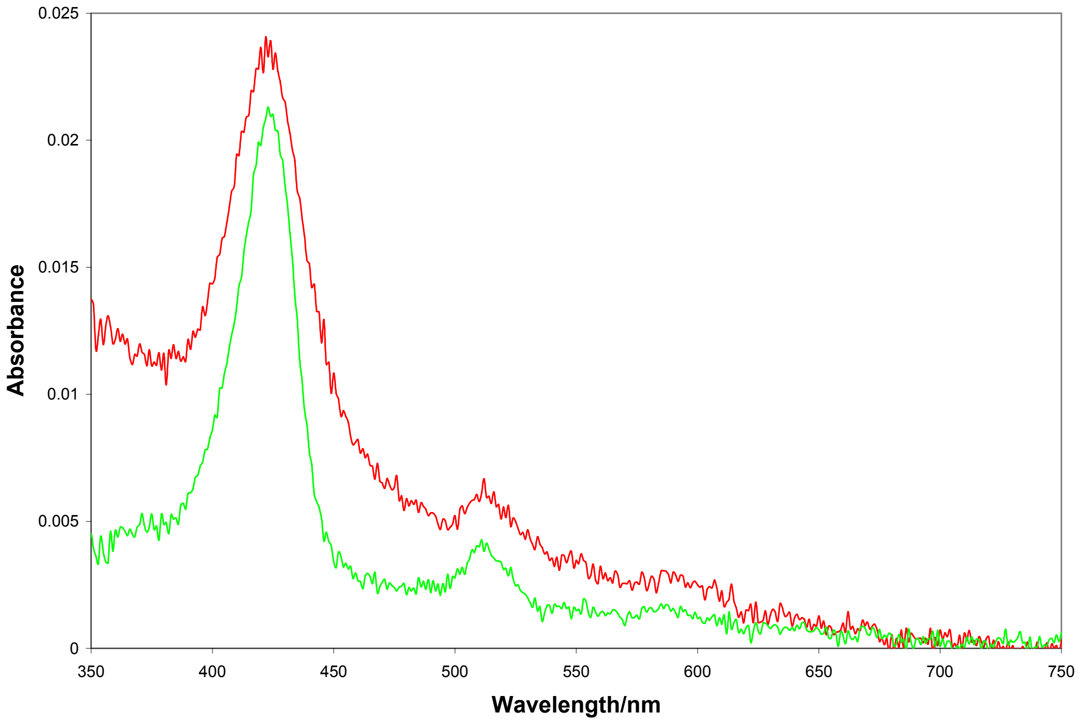

Fig. S9. Electronic spectra of **1** on ITO (green) and a film of **1** and C_{60} on ITO (red).

Synthesis of compound 2:

45 mg (220 µmol) of dodecanethiol were dissolved in 3 mL of DMF/Ethyl acetate 2:1 (v/v). 40 mg (40 µmol) of perfluoro-tetraphenylporphyrin TPPF$_{20}$ (TCI America) was added and the solution was stirred under nitrogen in presence of DEA (20 µL) for 8 hours. The reaction mixture was washed with water and the product was extracted with 3 portions of CH_2Cl_2, concentrated and purified by column chromatography on silica gel using hexane/ethyl acetate (9/1, v:v). The yield was 62 mg (36 µmol, 90%). High resolution FAB: $C_{92}H_{110}F_{16}N_4S_4$, Measured mass 1702.7364, 0.6 error (Service from University of Illinois, SCS Mass Spectrometry Laboratory). ^{1}H-NMR ($CDCl_3$) ppm: -2.86 (broad s, 2H, pyrrole); 0.85 to 0.87 (t, 12 H, 12'H); 1.28 to 1.44 (m, 64 H, 11-4 'H), 1.57 to 1.61 (m, 8H, 3'H), 1.83 to 1.89 (m, 8H, 2'H), 3.27 to 3.30 (t, 12H, 1'H); 8.93 (s, 8H, pyrrole βH).

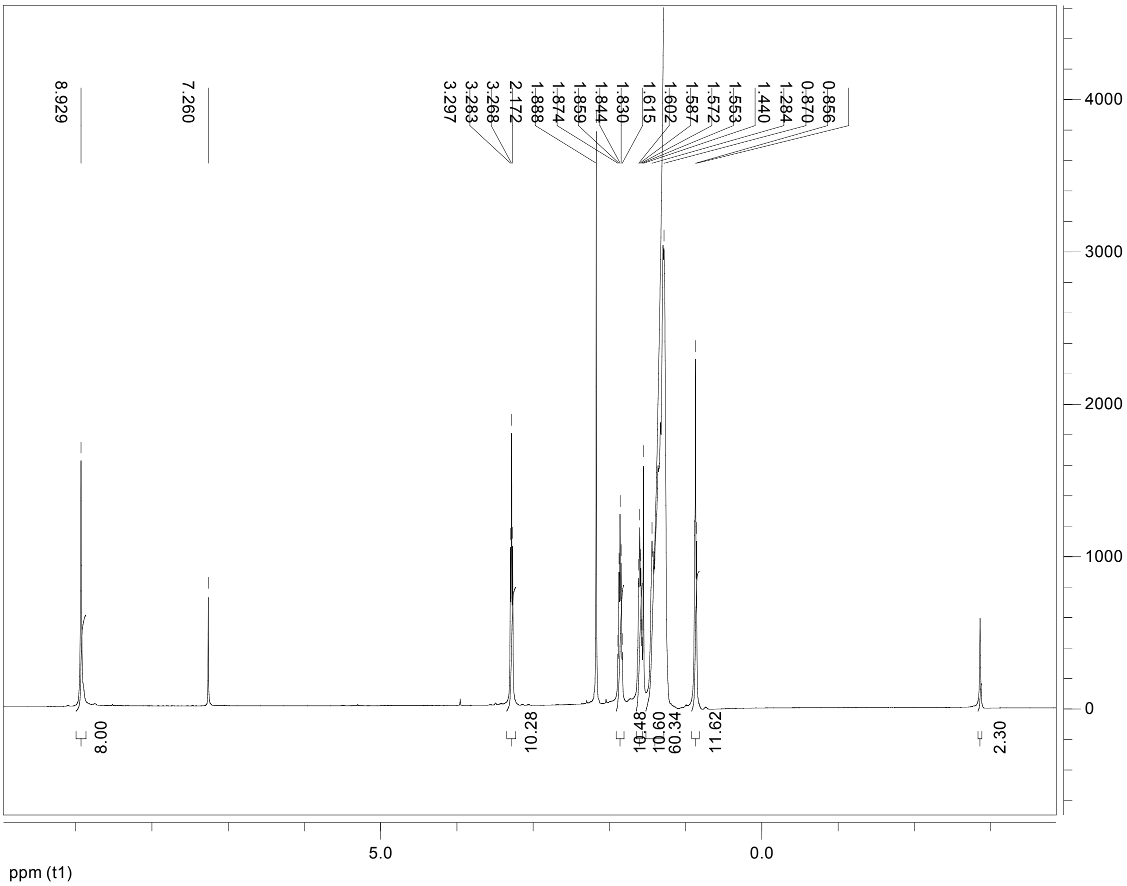

Fig. S10. ^{1}H-NMR of compound **2.**

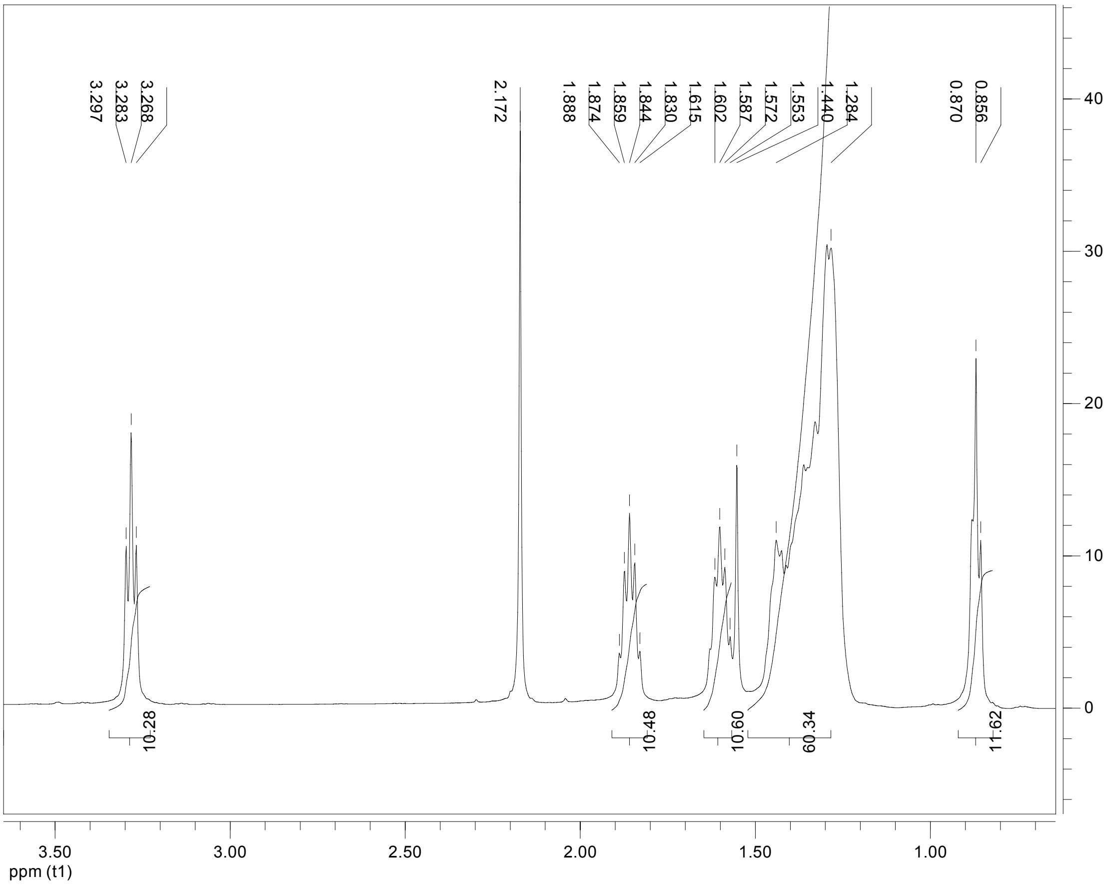

Fig. S11. ^{1}H-NMR of compound **2** expansion**.**

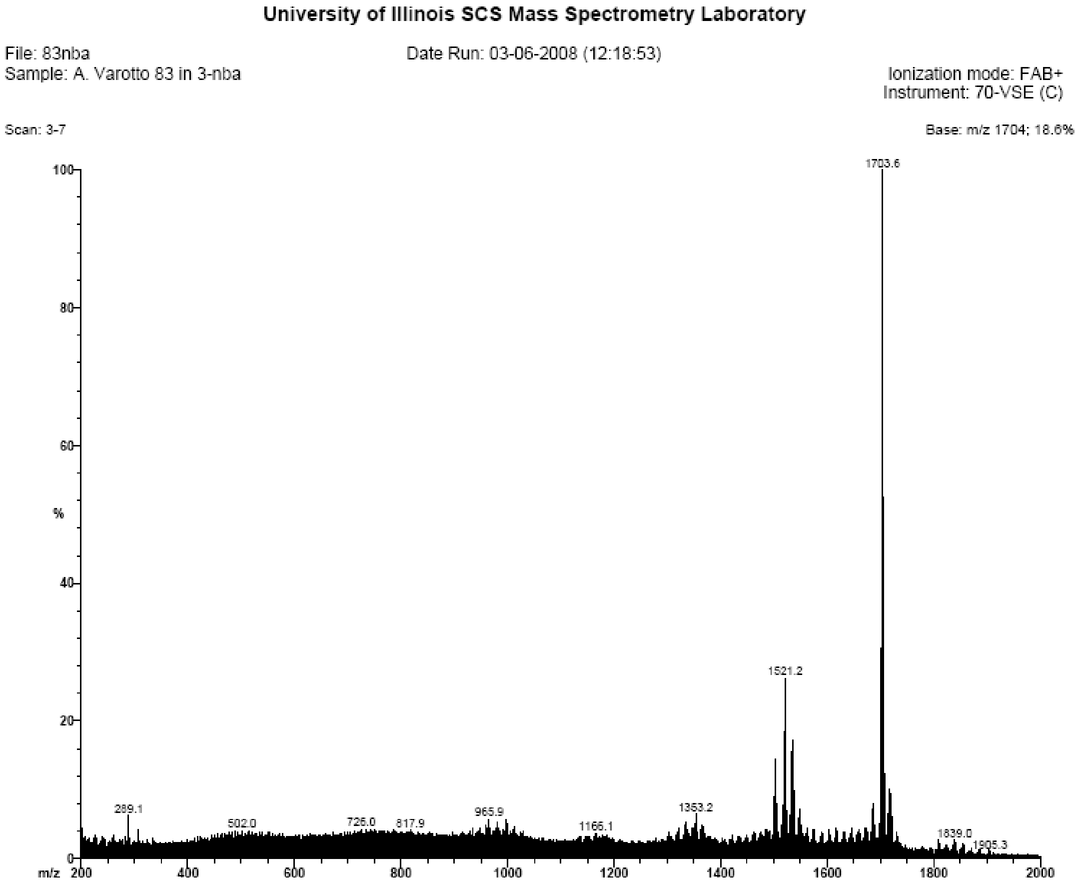

Fig. S12. FAB spectrum of compound **2**.

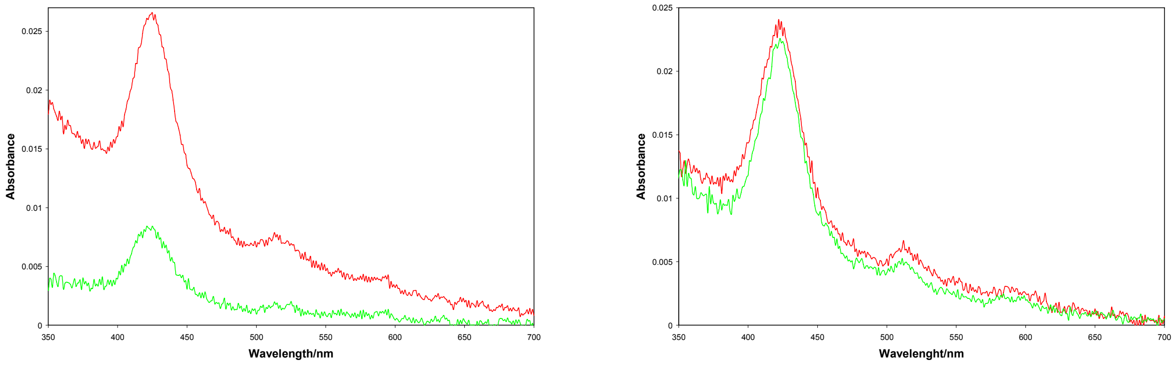

Fig. S13. Right: UV-Vis spectra of the co-deposition of compound **2** and C_{60} on ITO before (red) and after (green) sonication in a 50 mM NaCl aqueous solution. Left: the co-deposited material composed of **1** and C_{60} before (red) and after (green) sonication in an aqueous solution of 50 mM NaCl. The slides completed immersed in the solution were sonicated for 10 minutes (Fisher Scientific FS15 sonicator).

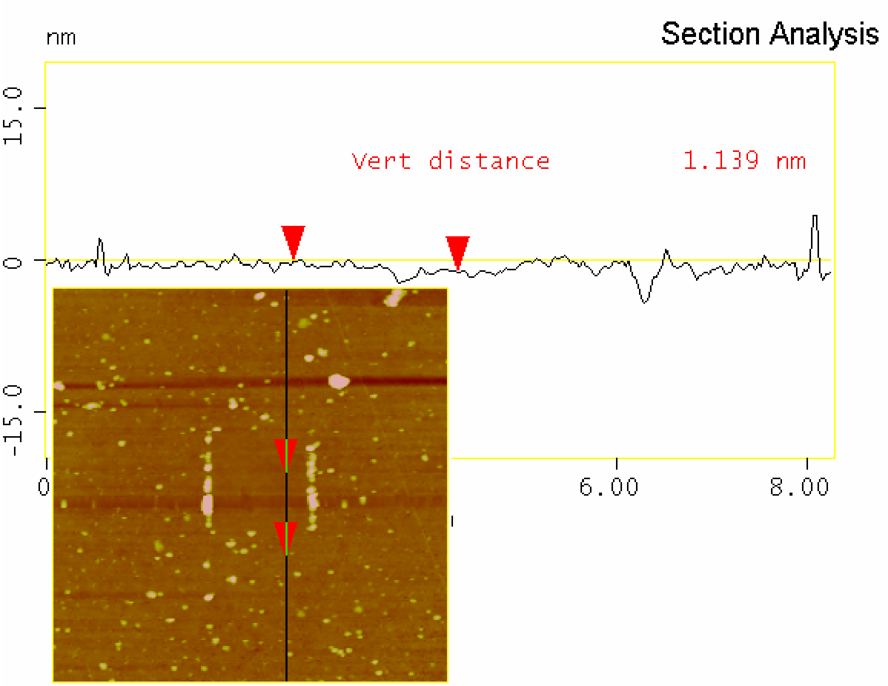

Fig. S14. AFM image with section analysis of co-deposition of **2** and C_{60} ratio 1:1 on ITO. Tapping/Height mode. Veeco Multimode AFM. Tip rectangular cantilever from Mikromasch NSC15 series Al BS (325 kHz, 40 N/m). Backside Al-coated. The well is shaved using a contact mode imaging tip with triangular cantilever from Mikromasch CSC21 series 100 kHz (2 N/m). Backside Al-coated. Spring constant calculated equal to 2.92 N/m. Force applied to shave off the film equal to 617.87 nN.