Electronic Supporting Information

On the transfer of cooperative self-assembled π-conjugated fibrils on a gold substrate: the role of an early formed monolayer

Martin Wolffsa, Mantas Malisauskasb, Željko Tomovića, Jeroen van Herrikhuyzena, Christianus M. A. Leenders,a Evan J. Spadafora, Benjamin Grévin,c Steven De Feyterb, E.W. Meijera, Albertus P.H.J. Schenning*a, and Philippe Leclèred*

*a Institute for Complex Molecular Systems and the Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands Fax: +31 (0)40 245 10 36; Tel: +31 (0)40 247 3101 ; E-mail: a.p.h.j.schenning@tue.nl.

b Department of Chemistry, Division of Molecular and Nanomaterials, and INPAC - Institute for Nanoscale Physics and Chemistry, University of Leuven (K.U.Leuven), Celestijnenlaan 200 F, b-3001 Heverlee, Leuven, Belgium. Fax: +3216327990; Tel: +3216327921; E-mail: Steven.DeFeyter@chem.kuleuven.be

c CEA-INAC-UMR 5819-SPrAM (CEA-CNRS-UJF), 17 Rue des Martyrs, F-38054 Grenoble Cedex 9, France. Fax: +33 (0) 04.38.78.50.97; Tel: +33 (0) 4 76 38 00 46; E-mail: benjamin.grevin@cea.fr.

d Laboratory for Chemistry of Novel Materials, Center for Innovation and Research in Materials and Polymers (CIRMAP), University of Mons (UMONS), Place du Parc 20, B 7000 Mons, Belgium. Fax: +32 (0)65 37 38 61; Tel: +32 (0)65 37 38 68; E-mail: philippe.leclere@umons.ac.be
Experimental section

General methods: $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Varian Gemini 300 or a Varian Mercury 400 MHz spectrometer. Chemical shifts are given in ppm ($\delta$) relative to tetramethylsilane. Abbreviations used are $s =$ singlet, $d =$ doublet, $t =$ triplet and $br =$ broad. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilizing a $\alpha$-cyano-4-hydroxycinnamic acid matrix. UV/Vis spectra were measured on a Perkin Elmer Lambda 40 spectrophotometer and a Perkin Elmer LS-50 B instrument, respectively. CD spectra were recorded on a JASCO J-600 spectropolarimeter.

AFM images were recorded with a Multimode Nanoscope V (Bruker, Santa Barbara, CA) and a MFD-3D (Asylum Research, Santa Barbara, CA) operating under ambient conditions in intermittent contact mode. Samples were prepared on freshly cleaved highly oriented pyrolytic graphite (HOPG) or on gold coated on cleaved muscovite mica. Microfabricated silicon cantilevers (FESP) were used with a spring constant of 1 - 5 Nm$^{-1}$.

FM-AFM images were recorded on a VT Omicron Ultra-vacuum microscope using ultrasharp tips (Nanosensors).

STM images were performed on a Molecular Imaging PicoSPM (Agilent). The tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.2 mm). The STM-images were obtained in the constant current mode. The molecules were dissolved in 1,2,4-trichlorobenzene (Sigma-Aldrich >99%) or tetradecane (Acros 99%) and were applied onto a freshly cleaved surface of HOPG (grade ZYB, Advanced Ceramics Inc., Cleveland, OH) or an annealed gold surface coated on cleaved muscovite mica. STM-images were recorded of stable self-assembled monolayers at the liquid/solid interface and the imaging parameters are indicated in the figure captions: tunneling current $I_{set}$ and sample bias $V_{set}$. For data analysis, scanning probe image processor (SPIP) software (Image Metrology ApS) was used.

Synthesis
Scheme S1. The molecular structure of OPV and OPV-s, where the dashed lines illustrate the dimerization capability of the ureidotriazine hydrogen bonding unit.

OPV-s. 150 mg (0.108 mmol) of 2,4-diamino-6-((E,E,E)-4-(4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(S)-2-methylbutoxy]-styryl)-2,5-bis[(S)-2-methylbutoxy]-styryl]-phenyl-s-triazine was dissolved in 8 mL dry pyridine at room temperature. Thiouctic-isocyanate (89 mg) was added and the reaction mixture was refluxed for 8 h. After evaporation of the solvent, the mixture was flushed with toluene to remove the pyridine. Using column chromatography (2% EtOH in CH₂Cl₂), pure OPV-s (110 mg, 64%) was obtained. 

$^1$H-NMR (400 MHz, CDCl₃): δ 0.88 (m, 9H, OCH₂CH₂(CH₂)₉C₃H₃), 1.01 (m, 12H, OCH₂CH(CH₃)CH₂CH₃), 1.12 (m, 12H, OCH₂CH(CH₃)CH₂CH₃), 1.3 (m, 54H, OCH₂CH₂(CH₂)₉CH₃), 1.5-1.9 (m, 8H, OCH₂CH(CH₃)CH₂CH₃), 2.00 (m, 6H, OCH₂CH(CH₃)C₂H₅), 2.43 (m, 1H, NCH₂(CH₂)₃C₂H₅), 3.11 (m, 2H, NCH₂(CH₂)₃CH₂C₂H₅), 3.47 (q, 2H, ArNHCONH₂), 3.56 (m, 1H, NCH₂(CH₂)₃CHCH₂C₂H₅), 3.67 (m, 1H NCH₂(CH₂)₃CHCH₂C₂H₅), 3.85-4.07 (m, 14H, OCH₂), 5.48 (br, 1H, ArNHCONHCH₂), 6.74 (s, 2H, ArH), 7.03 (d, J=16.4 Hz, 1H, ArCH=CHAr), 7.10 (s, 1H, ArH), 7.12 (d, J=16.4 Hz, 1H, ArCH=CHAr), 7.15 (d, J=16.4 Hz, 1H, ArCH=CHAr), 7.21 (s, 1H, ArH), 7.24 (d, J=16.4 Hz, 1H, ArCH=CHAr), 7.39 (d, J=16.4 Hz, 1H, ArCH=CHAr), 7.53 (s, 2H, ArHCH=CHArH), 7.63 (d, J=16.4 Hz, 1H, ArCH=CH), 7.65 (d, J=8.0 Hz, 2H, CH=CHArH(NC)₂), 8.21 (d, J=8.0 Hz, 2H, CH=CHArH(NC)₂), 9.27 (br, 1H, ArNHCONH), 9.95 (br, 1H, ArNHCONH), 10.26 (br, 1H, ArNH); $^{13}$C NMR (100 MHz, CDCl₃) δ 11.43, 11.48, 11.53, 14.1, 16.78, 16.87, 22.68, 26.12, 26.39, 26.86, 29.36, 29.39, 29.43, 29.66, 29.7, 29.75, 30.34, 31.92, 34.65, 34.97, 35.07, 35.14, 38.46, 40.16, 56.42, 69.09, 73.55, 74.06, 74.19, 74.4, 74.47, 77.53, 105.08, 109.61, 109.65, 109.92, 110.16, 114.83, 122.47, 123.08, 126.0, 126.52, 126.93, 127.27, 127.34, 127.61, 128.34, 128.4, 128.67, 133.2, 134.17, 138.15, 142.24, 150.96, 151.11, 151.14, 151.56, 153.23, 163.84; MALDI-TOF
MS (MW = 1594.5) $m/z = 1594.4$ [M$^+$]
Fig. S1 STM images of OPV monolayers on HOPG substrate formed upon dropcasting from 1,2,4-trichlorobenzene (TCB, a-c) or tetradecane (d-f). The STM images at the TCB/HOPG interface show the formation of ordered domains of counterclockwise (CCW) dimers. The unit cell parameters are: a=1.99±0.05nm, b=5.4±0.2nm and γ=85±3°. The STM images at the tetradecane/HOPG interface show the formation of ordered domains of clockwise (CW) and CCW dimers within disordered parts. The unit cell parameters are: a=1.96±0.06nm, b=5.44±0.08nm and γ=86±2°. a-b) I_{set}=39pA, V_{set}=-680mV; c-e) I_{set}=49pA, V_{set}=-860mV; f) I_{set}=79pA, V_{set}=-1040mV.
Fig. S2 STM images of OPV monolayers on a gold substrate formed upon dropcasting from TCB (a-b) or tetradecane (d-f). $I_{set}=161pA$, $V_{set}=-412mV$. The STM images at both the TCB/HOPG and the tetradecane/HOPG interface show a disordered pattern with some dimer formation. c) and g) show the 2D fast Fourier transform of the STM images in TCB and tetradecane, respectively. These indicate that the dimer rows follow approximately three main directions.
Fig. S3 STM images of OPV-s monolayers on HOPG substrate formed upon dropcasting from TCB (a-c) and tetradecane (d-f). The STM images at the TCB/HOPG interface show the formation of ordered domains of both clockwise (CW) and counterclockwise (CCW) dimers. The unit cell parameters are: $a=2.04\pm0.06\text{nm}$, $b=5.9\pm0.2\text{nm}$ and $\gamma=86\pm3^\circ$. The STM-images at the tetradecane/HOPG interface show the formation of ordered domains of CW and CCW dimers within disordered parts. a) and c) $I_{\text{set}}=33\text{pA}$, $V_{\text{set}}=-480\text{mV}$; b) $I_{\text{set}}=60\text{pA}$, $V_{\text{set}}=-1094\text{mV}$; d-f) $I_{\text{set}}=86\text{pA}$, $V_{\text{set}}=-925\text{mV}$. 
Fig. S4 STM images obtained after dropcasting OPV-s on a gold substrate from TCB (a-b) or from tetradecane (d-f). $I_{set}=161\text{pA}$, $V_{set}=-412\text{mV}$. The STM-images at both the TCB/HOPG and the tetradecane/HOPG interface are quite unclear but suggest that the surface is randomly covered with molecules.
**Fig. S5** TM-AFM images of dropcast MCH solutions \((c = 1 \times 10^{-5} \text{ M})\) (a) \textbf{OPV-s} (b) \textbf{OPV} and (c) \textbf{OPV-s} after rinsing with pure MCH on a gold substrate.
**Fig. S6** Temperature dependent CD and UV spectra illustrating the aggregation of OPV-s (1 x 10^{-5} M) in methylcyclohexane.
Fig. S7 Stability of OPV-s (left column) and OPV (right column) monolayers on gold surface illustrating the capabilities to transfer efficiently the self-assembled fibrils. In a first step, the monolayers were formed by drop casting a molecularly dissolved state (from chloroform solution) on the gold substrate. In a second step the fibrils are deposited from MCH on the substrate and then exposed to chloroform. The rinsing times were 0, 10, 20 and 30 seconds, respectively.
Fig. S8 TM-AFM images on a gold substrate after dropcasting a MCH solution of either OPV-s (a, c) or OPV (b, d) on a substrate having a monolayer of OPV-s (a,b) or of OPV (c,d).