

Homochiral and Heterochiral Assembly Preferences at Different Length Scales –Conglomerates and Racemates in the Same Assemblies

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Materials and methods

General methods

¹H NMR and ¹³C NMR were recorded at room temperature on a Varian Mercury 400. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. Abbreviations used are s= singlet, d= doublet, dd= double doublet, t= triplet and m= multiplet.

Infrared (IR) spectra were run on a Perkin Elmer 1600 FT-IR spectrometer. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilizing α-cyano-4-hydroxycinnamic acid matrix.

CD and UV-visible absorption spectra were recorded on a JASCO 815 equipped with a Peltier temperature controller, PFD-425S.

The field emission scanning electron microscopy (FESEM) was performed on dried gel samples. The samples (5 mM in octane) were first coated with gold by the sputtering technique and then observed under a FEI Quanta 3D FEG microscope.

Atomic Force Microscopy (AFM): AFM images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the Tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 Nm⁻¹ were used. Samples for AFM study were prepared by drop casting a solution of OPV3I under a solvent atmosphere on freshly cleaved silicon wafer or highly oriented pyrolytic graphite (HOPG).

Scanning Tunneling Microscopy (STM): All STM experiments were carried out at 20–25 °C. Experiments were performed using a PicoSPM microscope (Agilent). Tips were mechanically cut from Pt–Ir wire (80:20 alloy, diameter 0.25 mm). Prior to imaging, the OPV3I were dissolved in phenyloctane (anhydrous, 99+%, Sigma-Aldrich), and a drop of the solution was applied onto a freshly cleaved surface of graphite (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, OH). The STM investigations were then performed at the liquid/solid interface at least 90 min after drop casting. Images are recorded in the constant current mode. V_{set} refers to the sample bias. The graphite lattice was recorded by lowering the sample bias

immediately after obtaining images of the monolayer. Drift effects were corrected via scanning probe image processor (SPIP) software (Image Metrology ApS).

Materials

All solvents, purchased from Acros Chimica or Sigma-Aldrich-Fluka, were of p.a. quality. Deuterated solvents were from Cambridge Isotope Laboratories. All other chemicals were commercially available and were used without purification.

Synthesis of OPV3I

To a solution of (*E,E*) - 4 - {4-(3,4,5-tridodecyloxystyryl) -2,5-bisbutoxystyryl} -2,5 - bisbutoxybenzaldehyde^{S1} (287 mg, 0.25 mmol) in toluene, was added 2-phenylglycinamide (37.5 mg, 0.25 mmol). The solution was refluxed overnight after which the solvent evaporated. After being recrystallized from methanol, OPV3I as a yellow solid was obtained. (*R*-OPV3I: 290 mg, 91%; *S*-OPV3I: 150 mg, 47%.) ¹H NMR (CDCl₃, 400MHz): δ 8.72 (s, 1H), 7.58 (s, 1H), 7.54 – 7.48 (m, 4H), 7.41 – 7.28 (m, 4H), 7.16 (s, 2H), 7.11 (s, 1H), 7.03 (d, *J* = 16.3 Hz, 2H), 6.74 (s, 2H), 5.55 (s, 1H), 5.02 (s, 1H), 4.10 – 3.96 (m, 14H), 1.87 – 1.72 (m, 14H), 1.64 – 1.60 (m, 14H), 1.45 (br, 48H), 1.05 – 1.01 (m, 12H), 0.99 -0.86 (m, 9H). ¹³C NMR (CDCl₃, 100MHz): δ 174.4, 159.2, 153.5, 153.3, 151.3, 150.9, 150.8, 139.5, 138.3, 133.1, 132.1, 129.1, 128.6, 127.8, 127.4, 127.3, 126.8, 125.3, 123.5, 122.8, 122.5, 110.8, 110.4, 110.3, 110.1, 105.2, 73.5, 69.2, 69.1, 68.9, 31.9, 31.6, 31.5, 31.4, 30.4, 29.78, 29.7(2), 29.4(3), 26.1, 22.7, 19.6, 19.5, 19.3, 14.1, 13.9, 13.8. MALDI-TOF MS (calc MW = 1282.98; C₈₃H₁₃₀N₂O₈): 1283.97 [M+H]⁺. IR (FT-IR) ν (cm⁻¹): 3454, 3189, 3060, 2953, 2918, 2851, 1505, 1423, 1203, 1119, 962, 696.

Figures

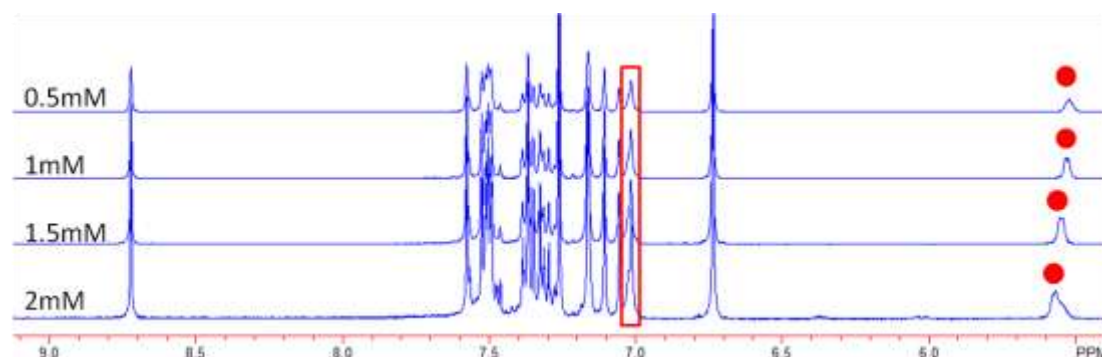


Fig. S1 Concentration-dependent ¹H NMR spectra of *R*-OPV3I in chloroform (CDCl₃). The red colours indicate the hydrogen resonances of the amide unit.

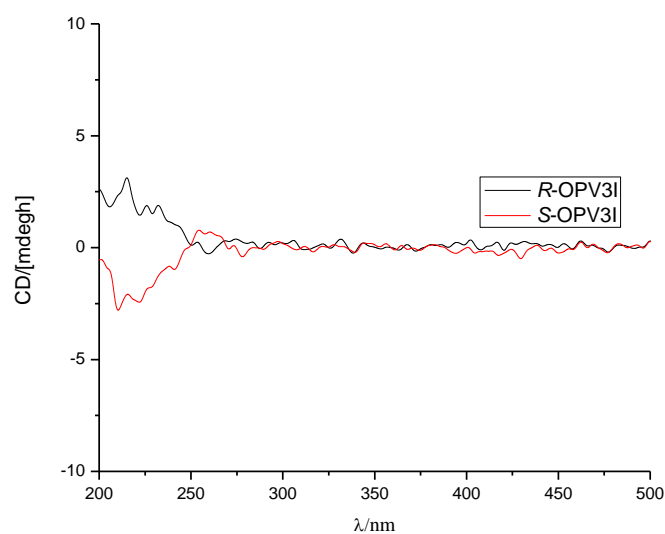


Fig. S2 CD spectra recorded at 25 °C of *R*, *S*-OPV3I (10^{-4} M in CHCl₃).

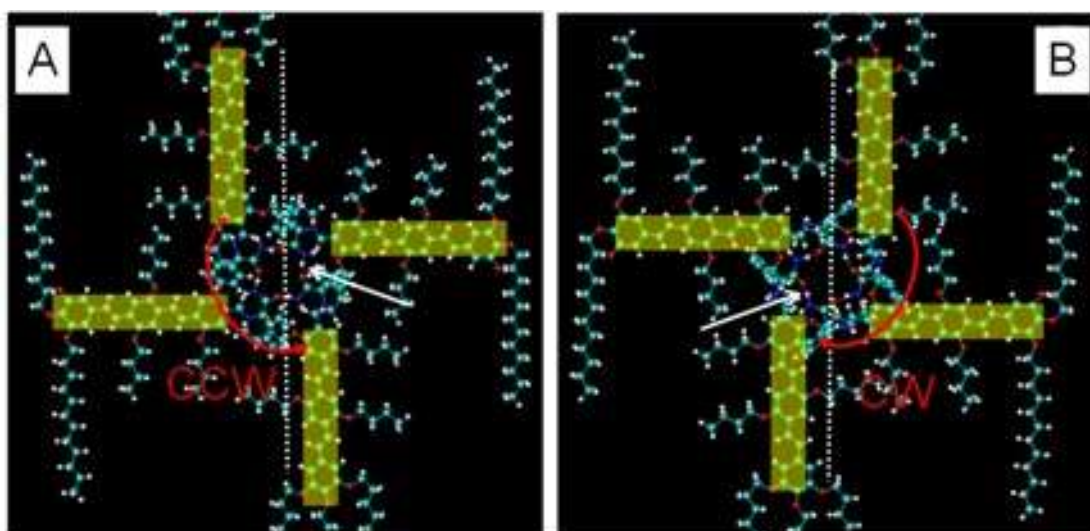


Fig. S3 Tetramer models of OPV3I based on the STM data (Fig. 1): (A) *R*-OPV3I and (B) *S*-OPV3I. White arrows indicate the H-bonds. Yellow rectangles are covering the four OPV3I units for showing the tetramer and the CCW and CW are indicated by red arrows.

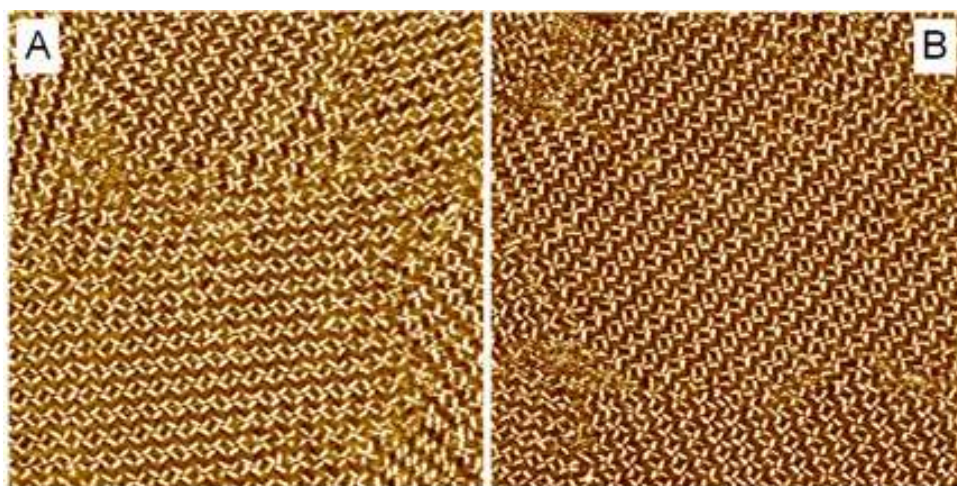


Fig. S4 Typical STM images of racemic OPV3I at 1-phenyloctane/HOPG interface. Scale is $80 \times 80 \text{ nm}^2$. $[R\text{-OPV3I}] = [S\text{-OPV3I}] = 0.5 \text{ mM}$. The surface coverage is $55 \pm 16\%$ for *R*-OPV3I and $45 \pm 15\%$ for *S*-OPV3I without concerning defects, for the interlaced *R*-OPV3I and *S*-OPV3I lamellas from 18 images with scale $80 \times 80 \text{ nm}^2$.

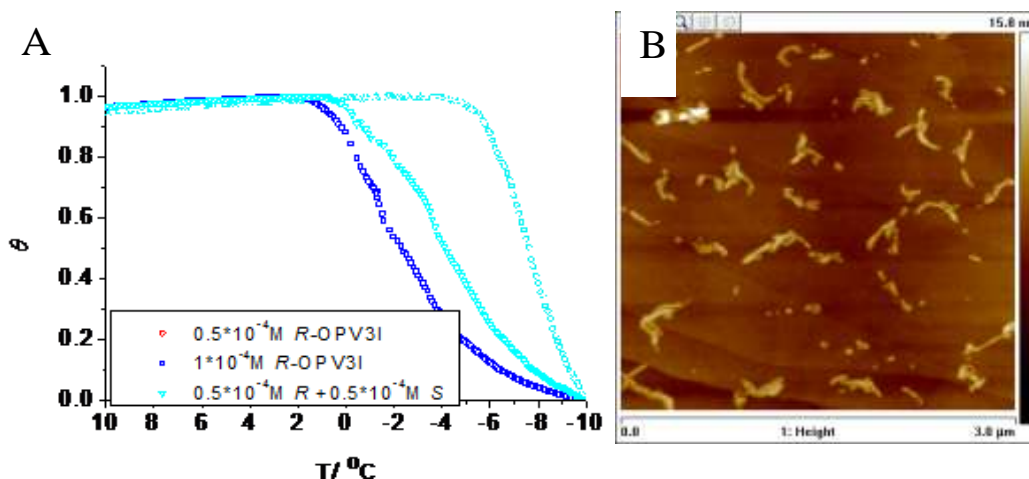


Fig. S5 (A) Cooling curves performed from the molecularly dissolved state at $60^\circ\text{C}/\text{h}$ in dodecane based on monitoring the absorption intensity at 425 nm . Operating temperature range -10 to 110°C . (B) AFM image of *S*-OPV3I in octane (10^{-4} M).

Reference

S1 S.J. George, Z. Tomovic, M.M.J. Smulders, T.F.A. de Greef, P.E.L.G. Leclere, E.W. Meijer and A.P.H.J. Schenning, *Angew. Chem. Int. Ed.*, 2007, **46**, 8206-8211.