Supporting Information

for

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Additional Results and Discussion

**Quantum-mechanical calculations.** In order to understand the spectroscopic and electrochemical properties of compound 5 we performed quantum mechanical DFT calculations. The geometry optimization and orbital energy calculations were performed on RB3LYP/6-31G* level of theory as implemented in Gaussian98. The accuracy of orbital energy calculations was confirmed by higher level single point calculations [RB3LYP/6-311+G(2df,p)], reproducing the HOMO and LUMO energy values to within 0.01 eV. To bring the computation time to an acceptable limit, we chose a model 5', which differs from the original molecule 5 by lacking three alkyl substituents in the TTF core. The calculations indicate that, due to flexibility of the σ-bridge between TTF and TCNQ, the molecule may exist in two possible conformations with very close energies: an “extended” one, where TTF and TCNQ fragments are separated in space (5'-e, $E = -1761805.8$ kcal mol$^{-1}$) and a head-to-tail folded conformation, where donor and acceptor moieties are situated close enough to form an intramolecular charge transfer complex (5'-c, $E = -1761807.2$ kcal mol$^{-1}$). The calculated RB3LYP wavefunction was found to be stable for both conformations according to the Gaussian98 stability test. According to our calculations, HOMO and LUMO orbital energies for 5'-c are $-4.90$ and $-4.61$ eV, respectively, which corresponds to a HOMO–LUMO gap ($E_g$) as low as $0.29$ eV; this is in good agreement with the electrochemically determined value of $0.17$ eV for 5 which bears three alkyl substituents. As expected from the D-σ–A structure of the molecule, the HOMO is completely localized on the TTF moiety, whereas the LUMO rests on the TCNQ fragment (Fig. S11). For the complexed conformation, 5'-c, the donor-acceptor interaction increases the orbital gap: HOMO and LUMO energies are $-5.07$ eV and $-4.37$ eV, respectively, i.e. the $E_g$ for this conformer is $0.70$ eV, perfectly fitting the energy of the ICT band ($0.75$ eV), and confirming its assignment as a HOMO–LUMO transition. Two other highest occupied and lowest unoccupied orbitals of 5'-c have energies of $-6.76$ eV (HOMO–1) and $-1.40$ eV (LUMO–1), which allow the assignment of a second long-wavelength absorption band of 5 at $550$ nm ($2.25$ eV, Fig. S2) as a HOMO–1/LUMO transition ($2.38$ eV).

**Spectroelectrochemistry.** Stepwise application of a potential up +0.5 V (vs. Pt wire) to a brown solution of neutral 5 in dichloromethane resulted in complete disappearance of the near-IR ICT band at $1630$ nm (Fig. 3 in the paper). Instead, bands characteristic of the TTF radical cation ($\lambda_{\text{max}}$ 405, 465 and 640 nm) arose, as the solution turned green. At more positive potentials (1.0 V) the two long-wavelength bands disappeared and the solution turned yellow indicating the formation of a dication species. Analogously, stepwise switching to $-0.5$ V gave rise to the radical anion ($\lambda_{\text{max}}$ 325, 425, 750 and 850 nm) turning the solution blue. A residue of the intense radical anion vibronic band ($\sim 1\%$) can be seen in the unelectrolysed 5 supporting the presence of the biradical state found in EPR experiments (0.7% according to the spin-counting experiments). The formation of the dianion species while scanning cathodically to $-1.4$ V is followed by complete loss of the radical anion bands, a further increase in the intensity of the 325 nm band, and the appearance of a new small band ($\lambda_{\text{max}}$ 480 nm, making the solution red. Both the two oxidation and two reduction processes are completely reversible, i.e. the initial spectra returned after re-setting the potential to $+0.2$ V.

**Solid state EPR behaviour.** On freezing the CH$_2$Cl$_2$ solution of 5 (<150 K) the spectrum (Fig. 3 in the paper) converts to an asymmetric broad resonance at $g = 2.0035$ ($\Delta B_{pp} = 6.0$ G) with a shoulder at $g = 2.0152$ (Fig. S5a). A broad rhombic pattern was observed for a powdered sample of 5 at $290$ K ($g_1 = 2.014$, $g_2 = 2.008$, $g_3 = 2.003$), which narrows slightly on cooling to $110$ K but with no significant change in the spectrum (Fig. S5b). A similar pattern was observed for the TTF-fluorene donor-acceptor diads.[1]

**Low angle X-ray reflection** experiments were performed for 40- and 180-layer LB films deposited onto HF-etched (hydrophobic) silicon at low pressure, Fig. S9. A Bragg peak at $20 = 10318\pm35$ seconds corresponds to a lattice d-spacing of $2.78\pm0.01$ nm. Assuming a head-to-head and tail-to-tail arrangement of the molecules in the transferred film, as suggested by the Y-type deposition, this repeat
distance will correspond to two LB layers. At smaller angles, well-defined Keissig fringes suggest a film with smooth upper and lower interfaces. The spacing of these fringes corresponds to a thickness of 1.39 nm per LB layer. Film thickness measurements using ellipsometry and surface profiling over the range 20 to 240 layers were in agreement with the X-ray data, i.e. the thickness of one LB layer of 5 was 1.39±0.08 nm (Fig. S10).

**AFM Characterization of LB films.** Topographical AFM data were acquired on a 20-layer LB film transferred at low pressure (Fig. S7). The organic film appears to be covered with small holes, typically around 5 nm in depth. Phase image measurements were undertaken to determine whether there were any compositional variations in the film and whether the holes were connected through to the silicon underlayer. Analysis of the mechanics of phase imaging has shown that the difference between the phase of a free oscillating and an interacting cantilever is defined by the energy dissipated in the tip sample contact. We would, therefore, expect any changes in the adhesive or mechanical properties of the sample to influence the phase contrast. These differences would also become more apparent the harder the tip was driven and the lower the set point. However, no obvious structural variations were observed in our experiments and the phase images showed the same material to be at the base of the holes, suggesting that these holes did not penetrate to the underlying silicon substrate.

**Experimental**

**General methods.** NMR and FTIR spectra were recorded on Varian Unity 300 and Perkin Elmer 1600 instruments, respectively. UV-Vis spectra in solutions and in the pressed pellets were taken on Varian Cary 5 spectrophotometer.

**EPR** spectra were recorded on Bruker EMX X-band spectrometers. Variable temperature EPR studies were performed at non-saturating conditions (1 mW microwave power, 100 kHz and 1 G modulation frequency and amplitude, respectively. Lower modulation amplitudes did not result in improved resolution). Spin counting experiments on 5 in CH$_2$Cl$_2$ solution were performed at room temperature by calibration against a range of concentrations of standard dpph solutions in benzene measured under identical, non-saturating conditions. The experimental protocol was tested for accuracy against solutions of known concentration of other radical species. Concentrations of 1–3 × 10$^{-5}$ M were used for all solution EPR measurements.

**Cyclic voltammetry** experiments were performed at ambient temperature with a BAS CV50 electrochemical analyzer, in a three-electrode cell (Ag/AgNO$_3$ in MeCN reference) using 1.6 mm diameter platinum disk as a working electrode. 0.2 M Bu$_4$NPF$_6$ or 0.1 M Bu$_4$NPF$_6$ in MeCN were used as the electrolyte. All the potentials (except in the spectroelectrochemical studies) are quoted vs. the ferrocene/ferrocenium (Fc/Fc$^+$) couple, which was used as the internal standard except when it overlapped with the oxidation peaks of the sample. The Fe/Fc$^+$ couple showed in MeCN: 0.08 V (vs. Ag/AgNO$_3$) and 0.46 V (vs. Ag/AgCl); in CH$_2$Cl$_2$: 0.21 V (vs. Ag/AgCl) and 0.50 V (vs. Ag/AgCl).

**Spectroelectrochemical** data were recorded for compound 5 (ca. 10$^{-4}$ M) in MeCN and CH$_2$Cl$_2$ with Bu$_4$NPF$_6$ (0.1 M) as supporting electrolyte on a Varian Cary 5 spectrophotometer between 250–2300 nm at ambient temperature. Spectra were corrected for background absorption arising from the cell, the electrolyte and the working electrode. The optically transparent thin-layer electrochemical cell used a Pt gauze working electrode, Pt wire counter and pseudo reference electrodes. The solutions were analyzed in situ: the working electrode was held at a potential at which no electrochemical work was being done in the cell and the spectrum of the neutral compound was recorded, which was identical to the spectrum recorded for open-circuit conditions. The potential was then increased in 50–200 mV increments and held until equilibrium had been obtained, as evidenced by a sharp drop in the cell current. The cell was based upon that described elsewhere,$^3$ and was driven by a home-built potentiostat.

**The electrical conductivity for powder** of 5 was measured on compressed pellets in a two probe apparatus.$^3$

**LB film formation and transfer.** Surface pressure versus area studies and LB deposition were carried out in a Class 10,000 microelectronics clean room using constant perimeter barrier troughs (Molecular Photonics LB700 series). Compound 5 was dissolved in chloroform (Merck, Aristar) to a concentration of 1.00 ± 0.01 g l$^{-1}$ before spreading a suitable volume (typically 50–200 µl) on the surface of a pure water subphase (prepared by reverse osmosis, two stages of deionisation and UV sterilisation) at a pH of 5.8 ± 0.2 and a temperature of 20 ±
2°C. 15 min were allowed for evaporation of the chloroform before pressure versus area isotherms were recorded at a compression speed of \((1.6 \pm 1) \times 10^{-2} \text{ nm}^2 \text{ molecule}^{-1} \text{ s}^{-1}\).

A variety of different substrate materials were used for deposition of LB films: glass microscope slides with hydrophilic and hydrophobic surfaces (a hydrophobic surface was obtained by immersing the slides in dimethylchlorosilane solution [2% in chloroform] for 10 min before washing with propan-2-ol and drying in a stream of nitrogen); Cr/Au coated glass slides; calcium fluoride slides; and hydrophilic and hydrophobic single crystal silicon wafers (silicon wafers were rendered hydrophobic either by using dimethylchlorosilane solution [see the above procedure for glass slides] or by etching with HF to remove the native oxide layer).

Multilayer LB deposition was performed at pressure 15 mN m\(^{-1}\) using the vertical dipping technique. Substrates were moved through the air/water interface at a speed of \(\sim 2 \text{ mm min}^{-1}\). Y-type deposition with a transfer ratio \(0.9\pm0.1\) was achieved (up to at least 240 layers) and very high quality films could be transferred onto calcium fluoride, hydrophobic glass, Cr/Au coated glass slides and HF etched silicon wafer substrates.

Low-angle X-ray scattering measurements were performed using a Bede Scientific GXR1 instrument with an operating wavelength of 1.3926 Å (Cu Kβ). Absorption spectra were recorded using a Perkin-Elmer Lambda 19 UV-VIS-NIR and Varian Cary 5 spectrophotometers with a resolution of 1 nm.

Ellipsometry was performed using a Rudolph Research AutoEL-IV instrument operating at 632.8 and 546.1 nm.

Surface profiling measurements were performed using a Tencor Instruments Alpha-step 200, stylus force 3.5

\(+/- 0.5 \text{ mg, scan length 1 mm, sample frequency 1 per micron.}\)

Direct current electrical conductivity studies of LB films were undertaken using a 2-probe technique in a screened metal chamber, which can be evacuated to a pressure of \(=10^{-7} \text{ mbar}\). Electrical bias was applied and currents monitored using a Keithley 2400 sourcemeter controlled by an IMB compatible PC via an IEEE 488 interface bus. For in-plane measurements, an LB film deposited on glass substrate was used, and electrical contacts (nominally 5.0 mm long and 1.0 mm apart) were formed from carbon cement (Neubauer Chemikalien). No differences were found in the value measured parallel or perpendicular to the LB dipping direction. Out-of-plane dc conductivity measurements were made by depositing LB layers onto a glass substrate that had previously been coated with Cr/Au by vacuum evaporation. Silver top contacts (0.5 mm diameter, thickness \(=160 \text{ nm}\)) were then evaporated at a pressure of \(=10^{-6} \text{ mbar}\) and a rate of \(=1.7 \text{ nm s}^{-1}\) on top of the LB film.

Electrical measurements in the frequency range 5 Hz to 13 MHz were performed using an HP 4192A impedance analyser.

Atomic force microscopy (AFM) investigations were undertaken using a Digital Instruments Nanoscope IIIA in tapping mode. Set point voltages were kept to a minimum, typically around 0.9× drive amplitude voltage to avoid damaging the film surface.

Computations. Quantum mechanical density functional theory calculations\(^{[4]}\) at the B3LYP/6-31G(d) level of theory\(^{[5]}\), were performed on a model homologue 5' lacking three alkyl substituents on TTF moiety (Fig. 2 in the paper), using Gaussian 98W program.\(^{[6]}\) The geometry optimization was carried out for two different conformations of this compound (extended and head-to-tail complexed). Due to the very flexible structure of the molecule, calculation of force constants had to be used during the geometry optimization to achieve the convergence. For the conformation 5'-c, however, the maximum displacement threshold (0.018), required by Gaussian98 algorithm was closely approached (0.025), but has not been achieved after over 200 optimization steps (but maximum force, RMS force and RMS displacement criteria were satisfied), in spite of force constants calculations. The frequency check for both conformations confirmed that they are true minima.

The molecular mechanics (MM+ method as implemented in Hyperchem 6.03 software) optimized conformation of 5 was used for the LB film structure simulation. The monolayer model was built by placing nine optimized molecules on the imaginary plane in a closest possible packing mode. This model was used for calculation of the molecular area and the monolayer thickness.
Supplementary Information to the paper


**Figure S1.** $^1$H NMR spectrum of compound 5 in acetone-$d_6$.

**Figure S2.** UV-vis-near-IR spectra of compound 5 in CH$_2$Cl$_2$ solution (blue) and in KBr pellets (red).
Figure S3. UV-vis-near-IR spectra of LB films of 5. The CT absorbance band at >800 nm for 180 and 240 layers is due to disorder in thicker films (not Y-type structure).

Figure S4. FT-IR spectra of compound 5 as LB films (on CaF$_2$, transferred at low pressure) and as a powder (in KBr pellets).
Figure S5. EPR spectra of 5 in (a) frozen CH₂Cl₂ solution at 115 K and (b) powder at 115 and 290 K.

Figure S6. Temperature dependence of the EPR signal of 5 in CH₂Cl₂ solution (red and blue marks present two independent experiments).

Figure S7. AFM image of a 19-layer LB film of 5.
Figure S8. The model structure (two views from different directions) of the LB films of 5 (simulated with molecular mechanics MM+ method) at low pressure, molecular area ~0.7 nm$^2$; layer thickness ~1.4 nm. The hydrogen atoms are omitted for clarity.

Figure S9. Low angle X-ray reflection data for LB films of compound 5.

Figure S10. Thickness of LB films of compound 5 measured by different methods.
Figure S11. Calculated (B3LYP/6-31G*) HOMO and LUMO orbitals for two conformations of 5'.