SUPPLEMENTARY INFORMATION

Charge transfer in mixed and segregated stacks of tetrathiafulvalene, tetrathianaphthalene and naphthalene diimide: a structural, spectroscopic and computational study

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Optical Microscopy and Crystallography

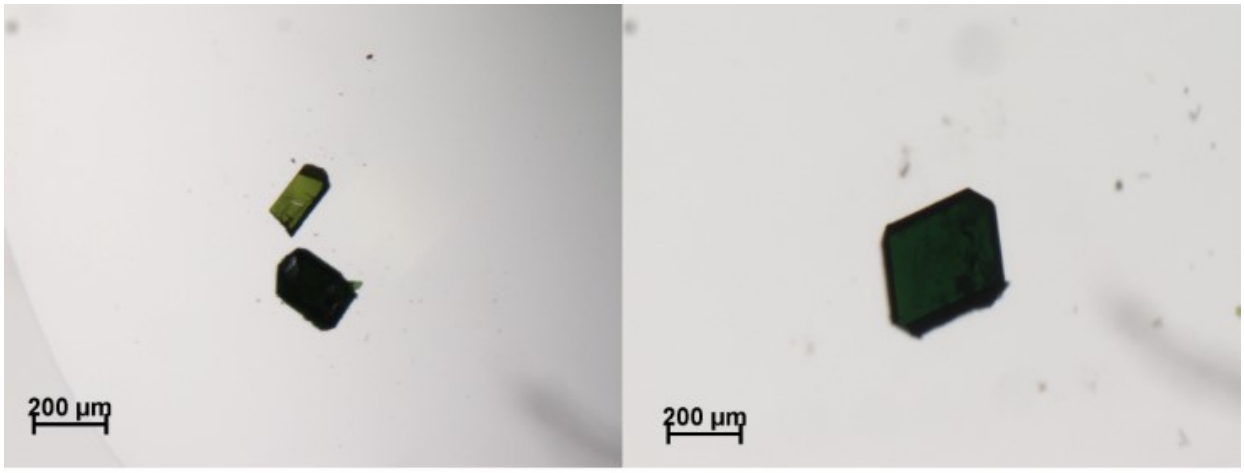

Figure S1. Microscope images of α-TTF-DPNI (left) and β-TTF-DPNI (right). The dichroism of α-TTF-DPNI due to polarisation of the light source is shown on the left.

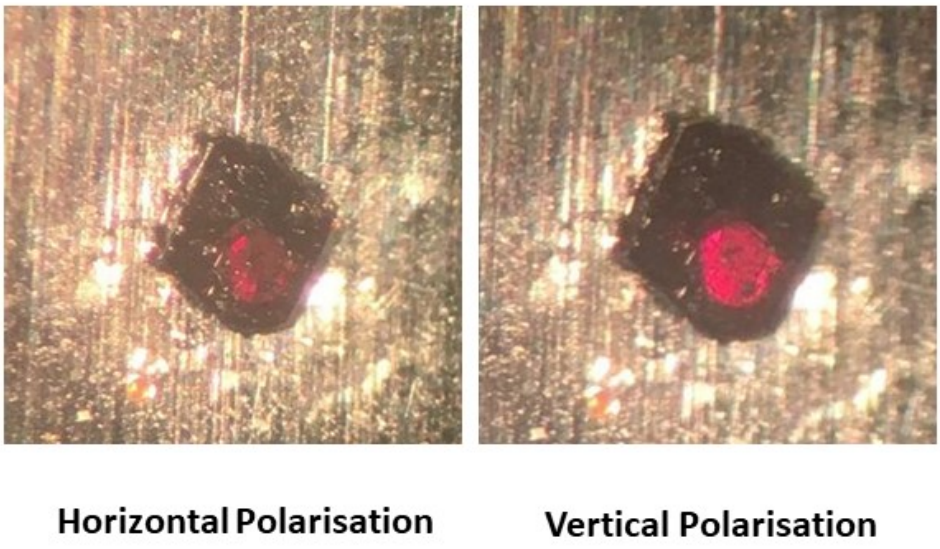

Figure S2. Microscope images α-TTN-DPNI prior to (left) and following plane polarisation. While not as dramatic as the α -TTF-DPNI CT complex, a lightening in crystal colour from black to red is still observable.

Crystallography

Table S1. Crystallographic data for α-TTF-DPNI, β-TTF-DPNI, and TTN-DPNI.

Parameter	**α-TTF-DPNI**	**β-TTF-DPNI**	**TTN-DPNI**
Empirical formula	$C_{60}H_{32}N_8O_8S_8$	$C_{15}H_8N_2O2S_2$	$C_{15}H_8N_2O_2S_2$
Formula weight	1249.42	312.36	312.36
Temperature (K)	150	150	299
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	11.094	13.3254	14.044
b (Å)	11.346	8.47110	8.232
c (Å)	22.454	11.82420	11.711
α (°)	102.51	90	90
β (°)	97.53	101.0860	103.51
γ (°)	100.71	90	90
Volume (Å³)	2667.6	1309.82	1316.4
Z	2	2	2
ρ_{calc} *(mg mm⁻³)*	1.555	1.264	1.586
μ *(mm⁻¹)*	3.673	3.602	3.722
F (000)	1280	508	648
Crystal size (mm)	0.03 × 0.01 × 0.01	0.10 × 0.08 × 0.06	0.06 × 0.03 × 0.02
2θ range for data collection	4.096 to 136.626°	6.76 to 151.79°	6.472 to 136.522°
Reflections collected	23781	24515	11251
Data/restraints/parameters	9250/0/757	2725/0/222	2375/0/190
Goodness-of-fit on F^2	0.882	0.855	1.052
Final R indices [I≥2σ(I)]	R_1 = 0.0848	R_1 = 0.0282	R_1 = 0.0292
Final R indices [all data]	R_1 = 0.0880, wR_2 = 0.882	R_1 = 0.0295, wR_2 = 0.0756	R_1 = 0.0296, wR2 = 1.052
Largest diff. peak/hole/e Å⁻³	0.579/-0.764	0.325/-0.322	0.195/-0.221

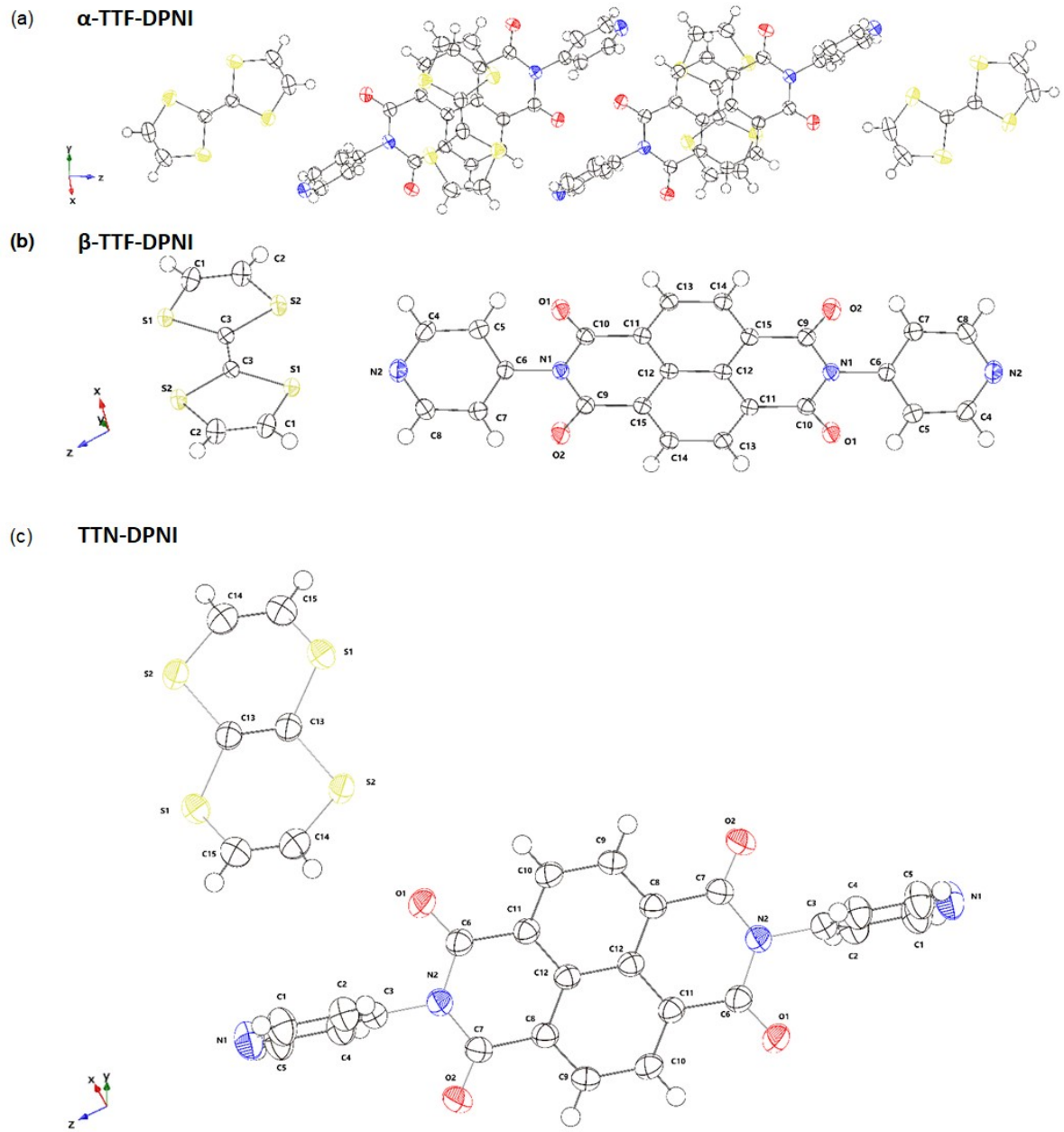

Figure S3. ORTEP depictions of (a) α-TTF-DPNI, (b) β-TTF-DPNI and (c) TTN-DPNI. Note that atom labels have been left off α-TTF-DPNI to improve clarity of the image. Colour scheme: N, blue; O, red; C, white; S, yellow; H, white circles.

Powder X-Ray Diffraction

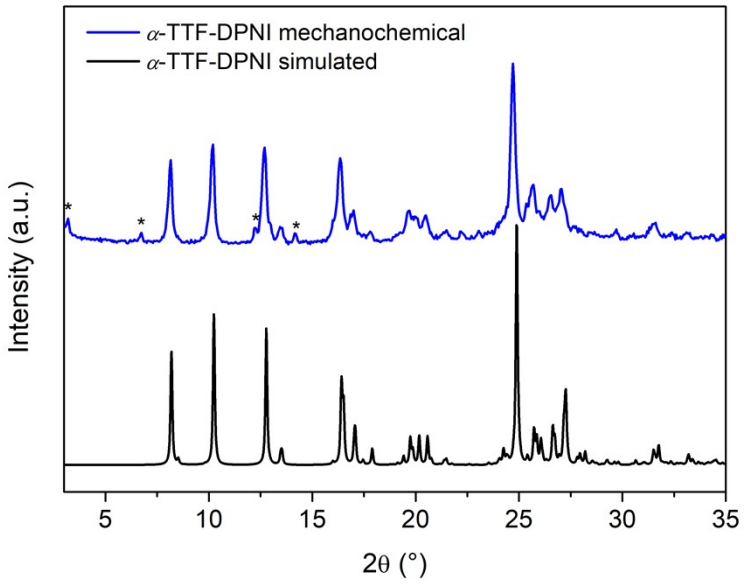

Figure S4. Simulated PXRD of α-TTF-DPNI and PXRD of α-TTF-DPNI prepared *via* mechanochemical synthesis. Asterisks indicate impurity/second phase.

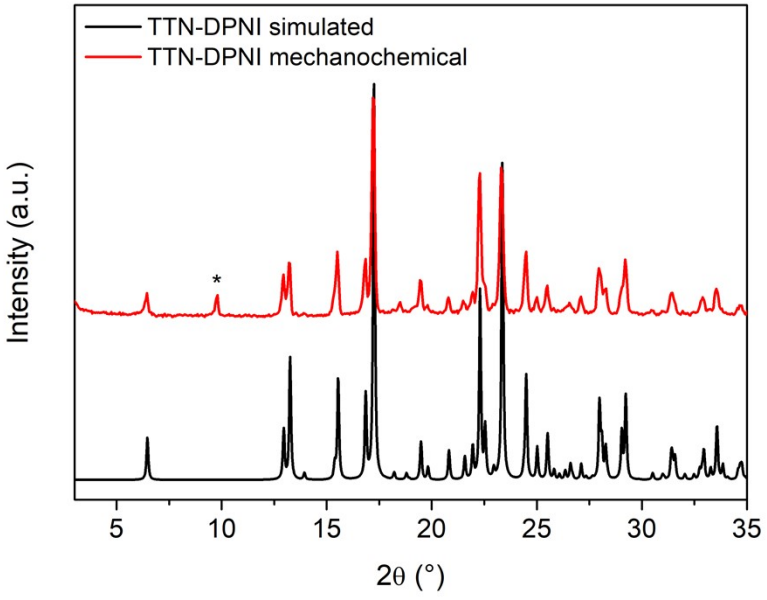

Figure S5. Simulated PXRD of TTN-DPNI and PXRD of TTN-DPNI prepared *via* mechanochemical synthesis. Asterisks indicate impurity.

Electrochemistry

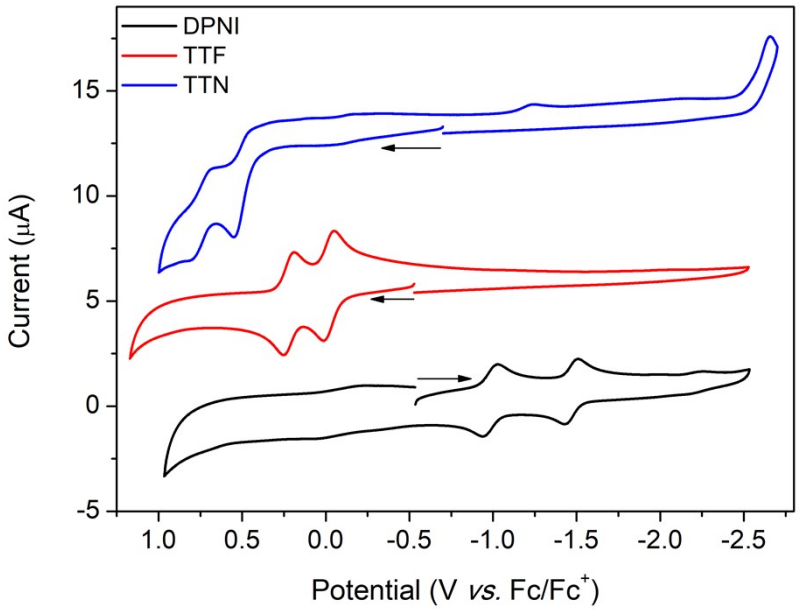

Figure S6. Solution state CV of DPNI, TTF and TTN collected at 100 mV/s in 0.1 M $TBAPF_6$/DMF electrolyte. Potentials references to the Fc/Fc^+ redox couple. Arrows indicate the direction of forward scan.

UV-Vis-NIR Spectroscopy

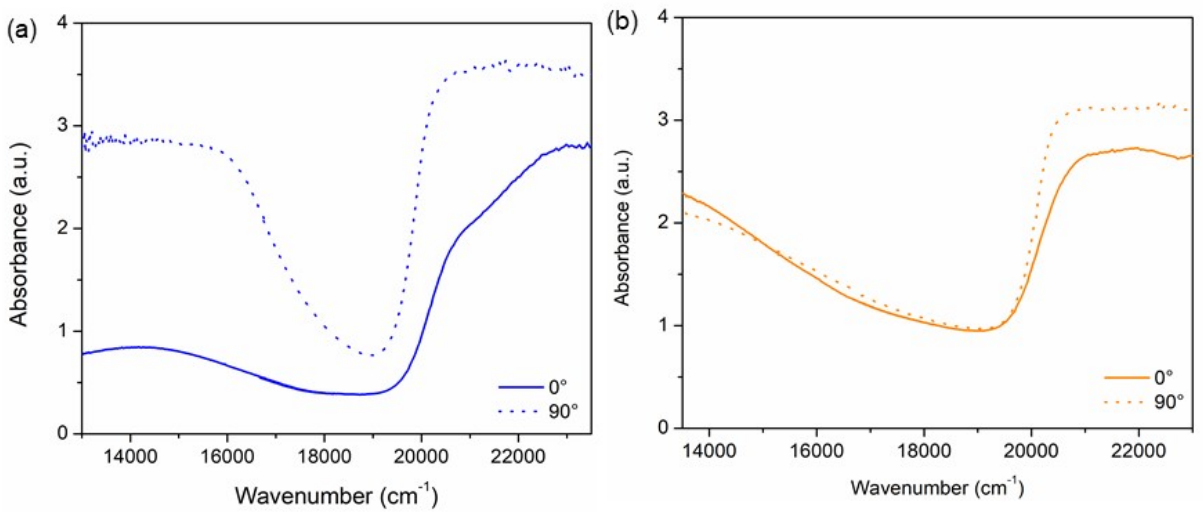

Figure S7. Single-crystal spectra of (a) α-TTF-DPNI in the NIR region (b) β-TTF-DPNI in the visible region

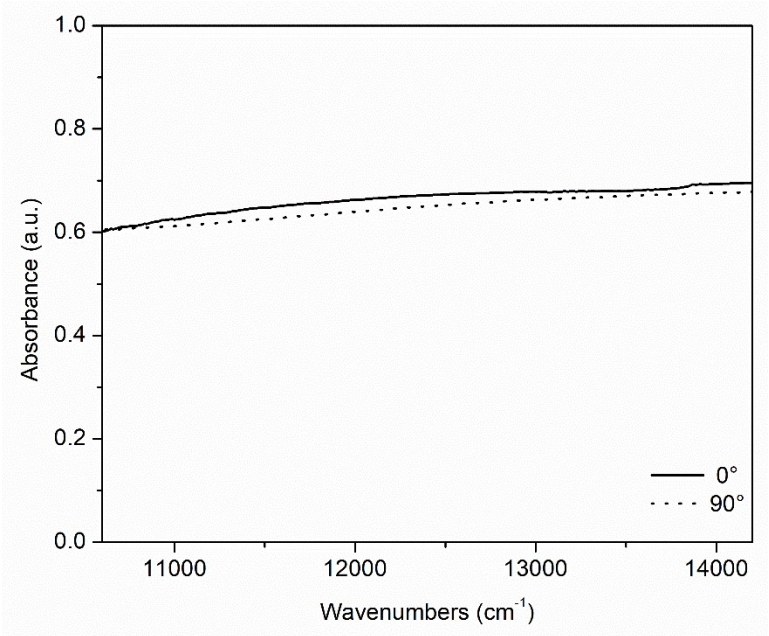

Figure S8. Single-crystal spectra of TTN-DPNI in the NIR region

Raman Spectroscopy

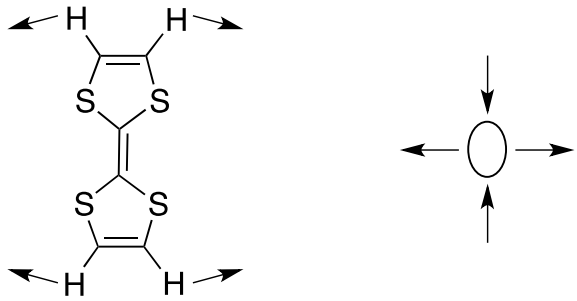

Figure S9. C-H bending mode in TTF that corresponds to its peak at ~ 1100 cm^{-1} in the calculated Raman spectrum, and the change in shape of its polarisability ellipsoid.

EPR Spectroscopy

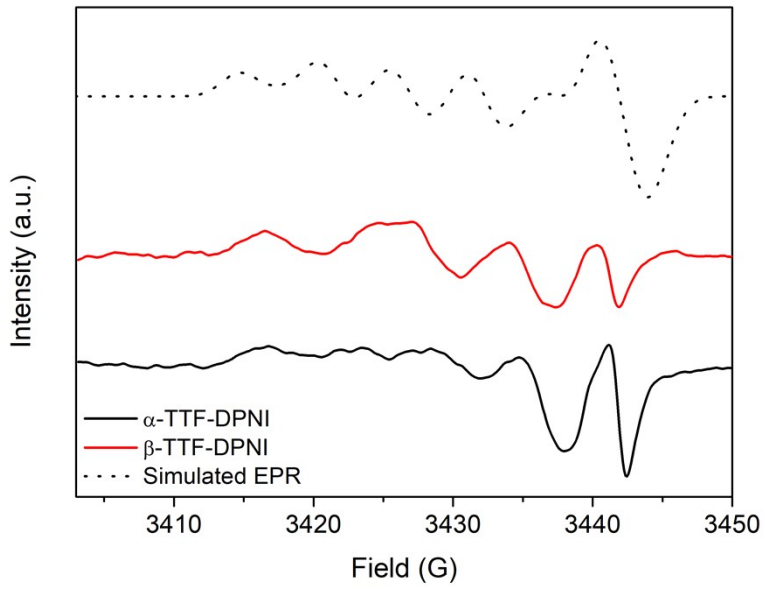

Figure S10. Experimental room temperature X-band EPR spectra of α-TTF-DPNI and β-TTF-DPNI and a model EPR spectrum simulated using the EasySpin package on MATLAB.

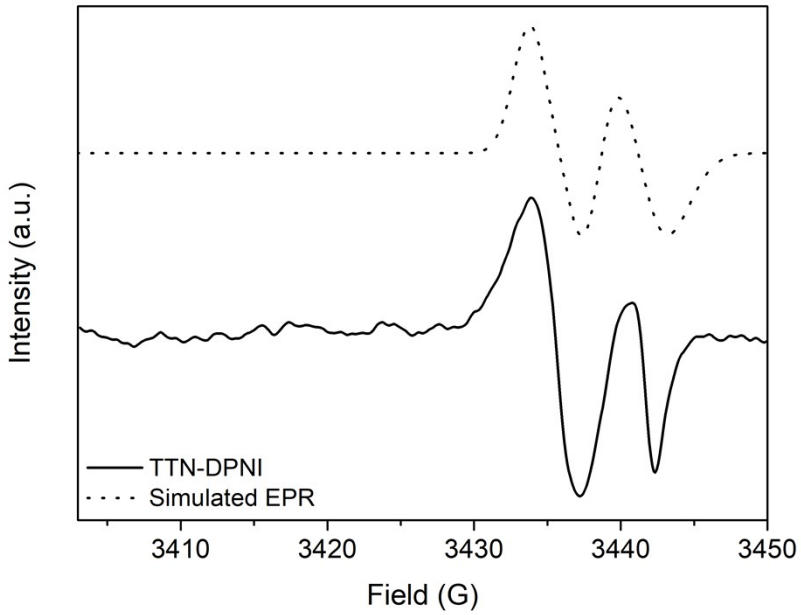

Figure S11. Experimental room temperature X-band EPR spectrum of TTN-DPNI and a model EPR spectrum simulated using the EasySpin package on MATLAB.

Conductivity

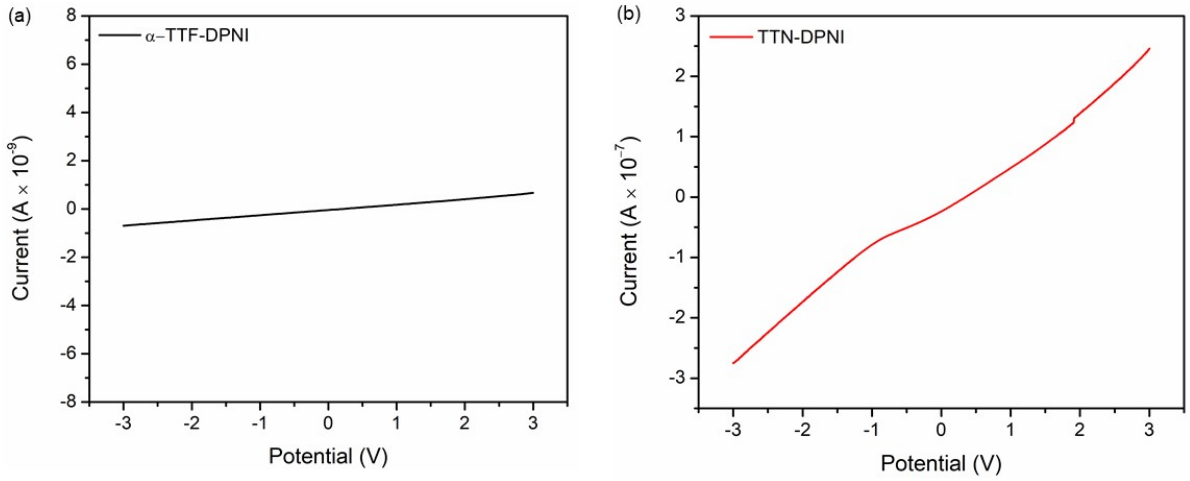

Figure S12. I–V curves of (a) α-TTF-DPNI and (b) TTN-DPNI obtained *via* the two-probe method at room temperature.