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Supplementary Information

An Electroactive Porous Network from Covalent Metal-Dithiolene Links

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Experimental details

General Procedure.

Starting materials (e.g., sodium thiomethoxide, CH_3SNa), reagents, and solvents were purchased from Aldrich and used without further purification. $Pt(CH_3CN)_2Cl_2$ was prepared by reacting $PtCl_2$ and refluxing acetonitrile at 90 °C for 5 hours under nitrogen protection (the solvent was subsequently removed in vacuo to give a light yellow solid in near quantitative yield). The molecule 2,3,6,7,10,11-hexabromotriphenylene (HBT) was prepared in high yields following a reported procedure.[1]

Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. The ratios of the metal ions were determined by using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer. Solution ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TG) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 5 °C/min. SEM pictures were taken by Environmental Scanning Electron Microscope (Philips XL30 ESEM). X-ray photoelectron spectroscopic (XPS) were measured by a VG ESCALAB 220I-XL XPS system.

The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Each sample was outgassed at 0.03 torr with a 2 °C/min ramp to 100 °C and held at 100 °C for 12 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995). High purity gases were used throughout the analysis.

Powder X-ray diffraction data was collected in the reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-Kα (λ = 1.5418 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA.

Structural modeling of the HTT-Pt framework was conducted using the Materials Studio (v6.1.0) suite of programs by Accelrys. A hexagonal cell (e.g., based on the similar case of RAYQAK) containing a Pt atom at (0.5, 0.5, 0.5) and the associated HTT fragment was first constructed. The *a* constant of 23.29 **Å** was calculated from standard/typical bonding geometries: Pd-S distance, 2.36 **Å**, being comparable to the ones observed in EFIXOH, EWAMUK, EWANIZ, LOKJEB, OYISEV of the CCDC database; the bonding geometries in the HTT fragment was based on known structures containing the HTT fragment, e.g., MAPYUY. The *c* constant was initially set at the typical aromatic-aromatic stacking distance of 3.4 **Å**. To develop a close match with the intensity profile of the observed PXRD pattern, the stacking features (e.g., the degree of offset and interlayer spacing) between neighboring layers were adjusted. For this, the symmetry was lowered to P1, and a parallel second layer was introduced with an interlayer spacing of 3.4 **Å** apart. The second layer was then shifted to create various staggered modes with regard to the first layer, and the corresponding calculated PXRD patterns were compared with the experimental pattern. To match the peak broadening observed, the crystallite size was chosen as L_a=L_b=30 **Å**, L_c=8 Å in the module of Reflex Powder Diffraction of the Materials Studio program. A decent match was found for the staggered mode shown in Figure 4, in which the two layers were offset by a/2 along the original *a* direction. The interlayer spacing was then adjusted to 3.46 **Å** to further match the overall peak positions. The proper symmetry was then found (via "Find Symmetry" from the program) to be *Fmmm* (No. 69, a=23.291, b=6.9214, c=40.3412 Å), and subsequently imposed on the structure, and the result was exported as a cif file (attached as part of the Supplementary Information). Such a treatment is largely empirical and qualitative in nature. A more rigorous refinement of the unit cell parameters and atom positions would likely entail better-quality diffraction data.

Conductivity measurement was conducted using a Keithley 4200-SCS Semiconductor Characterization System, equipped with 2-terminal probe station at room temperature. The samples were ground and pressed into 5-mm-diameter pellets using a Specac manual hydraulic press at the pressure of 2.0 tons. Silver paste was used to connect the pellet samples to the electrode probes (as shown in the schematic drawing below).

2,3,6,7,10,11-Hexakis(butyrylthio)triphenylene (HBuTT). In an N_2-filled glove-box, a magnetic stirrer, HBT (0.216 g, 0.3 mmol) and CH_3SNa (0.664 g, 9.0 mmol) were loaded into a 25-ml two-neck round-bottom flask. Then the flask was connected to a Schlenk line. DMEU (anhydrous, bubbled with N_2, 10 ml) was transferred into the flask via cannula. The reaction mixture was then stirred at 240 ºC for 48 h. After the mixture was cooled to 0 ºC (first naturally to rt, then by an ice bath), *n*-butyric chloride (1.24 ml, 12.6 mmol) was injected under N_2. After being stirred at 0 ºC for 2h, the mixture was poured into ice water (50 ml) and extracted by toluene (3x30 ml). The combined organic layer was then washed by water (4 x 30 ml), dried over $MgSO_4$, evaporated in vacuo. The crude product (black solid) was purified by chromatography (3:1 CH_2Cl_2/hexane) to afford an off-white solid (168 mg, yield 67%). ^1H NMR (400 MHz, $CDCl_3$): 8.50 (s, 6H), 2.71 (t, 12H), 1.82 (sextet, 12H), 1.06 (t, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 196.56; 132.55; 132.31; 129.82; 45.55; 19.10; 13.65. Chemical analysis of the product $C_{42}H_{48}O_6S_6$ yielded the following: Calcd [C (59.97%), H (5.75%)]; Found [C (59.45%), H (5.63%)].

2,3,6,7,10,11-Triphenylenehexathiolate-Pt (HTT-Pt). HBuTT (100 mg, 0.12 mmol) and a stir bar were loaded into a 50 ml two-neck round-bottom flask. The flask was fitted with a condenser and connected to a Schlenk line, evacuated and back-filled with N_2 (three times for purging). A methanol (10 ml) solution of NaOH (67 mg, 1.67 mmol), bubbled with N_2 for 5 min beforehand, was transferred into the flask via cannula. After the mixture was refluxed at 90 ºC for 6 hrs, $Pt(CH_3CN)_2Cl_2$ (63 mg, 0.18 mmol), dissolved in N,N'-dimethylacetamide (DMA, 5.0 ml) and then deaerated by N_2 for 5 min beforehand, was transferred into the refluxing reaction mixture via cannula under N_2 protection (note: a dark-red precipitate starts to form one or two minutes afterwards). The reaction mixture was kept at a steady reflux for another 4 hrs, cooled to rt, and mixed with DMA (about 20 ml, regular grade, no need to dry). The solid product therein was collect on Buchner funnel, washed by DMA (about 40 ml), deionized water (about 60 ml), MeOH (about 30 ml), and dried under air in a fume cupboard overnight to afford the as-made, crude product as a black solid (HTT-Pt-*a*; 113 mg; note: the color changed from dark red to black upon exposure to air). CHN analyses found [C (24.16%), H (3.526%), N (2.18%)]; ICP indicated Pt (27.79%); Na (2.32%) (molar ratio Pt/Na 1.41:1); A fitting formula can be determined to be $HTT\cdot(Pt)_{1.5}\cdot(Na)_{1.07}\cdot 10H_2O\cdot 1.7DMA$, which gives a calculated profile as [C (28.10%), H (3.93%), N (2.25%), Pt (27.60%); Na (2.32%)].

The crude product was purified by Soxhlet extraction in refluxing MeOH for 24 hrs, and then evacuated by an oil pump at 90 ^{o}C for one hour to provide an activated solid product (HTT-Pt-*b*; 104 mg, 88% as per the formula below). CHN elemental analyses on the activated sample (HTT-Pt-*b*) found [C (23.74%), H (3.496%), N (1.02%)]; ICP indicated Pt (28.68%); Na (1.94%) (molar ratio Pt/Na 1.74:1); and a fitting formula can be determined to be $HTT\cdot(Pt)_{1.5}\cdot(Na)_{0.86}\cdot 14H_2O\cdot 0.75DMA$, which gives a calculated profile as [C (24.15%), H (3.93%), N (1.01%), Pt (28.01%); Na (1.89%)].

HTT-Pt-*c*: from I_2 treatment of HTT-Pt-*b*. An activated sample of HTT-Pt-*b* (130 mg, containing 0.125 mmol of HTT), methanol (15 ml) and a stir bar were loaded into a 25-ml two-neck round-bottom flask. Iodine solid (I_2, 40 mg, 0.156 mmol) was then added and the mixture was heated to reflux for 0.5 hr (during which the color of the solution changed from dark red to light red), and cooled down to rt. The resultant solid (HTT-Pt-*c*) was collected by vacuum filtration through a Buchner funnel, washed with water (30 mL x 2) and methanol (about 30 ml), and then evacuated by an oil pump at 90 ^{o}C for one hour to provide the sample of HTT-Pt-*c*. CHN elemental analyses found [C (25.15%), H(3.392%), N (0.82%)]; ICP indicated Pt (28.95%); Na (0.17%) (molar ratio Pt/Na 20.14:1); A fitting formula can be determined to be HTT$\cdot$(Pt)$_{1.5}$$\cdot$(Na)$_{0.074}$$\cdot$11$H_2O$$\cdot$0.55DMA, which gives a calculated profile as [C (25.40%), H (3.48%), N (0.81%), Pt (30.64%); Na (0.18%)].

Ion exchange tests with CsF. An as-made sample of HTT-Pt-*a* (20 mg) was stirred with an aqueous solution (10 ml) of CsF (184 mg, 1.2 mmol, 1.8% w/w) at rt for 24 hrs. The resultant black solid was filtered by a Buchner funnel and then washed with water (30 ml x 3), EtOH (30 mL x 2) and diethyl ether (20 mL). The Cs-ion-exchanged sample (HTT-Pt-Cs) was analyzed by ICP (e.g., 6.20 mg of the sample was dissolved in 1:2 H_2SO_4/HNO_3 (3.0 ml), diluted to 50 ml with H_2O for ICP analyses) to reveal the molar ratio Pt/Na/Cs = 11.50:1:9.32; corresponding weight profile: Pt (29.35%), Na (0.30%), Cs (16.21%).

Reinsertion of Na$^+$ ions. The above Cs-ion-exchanged sample ((HTT-Pt-Cs, 10 mg, 0.011 mmol) was stirred with an aqueous solution (10 ml) of NaCl (80 mg, 1.38 mmol; 0.8% w/w) at rt for 24 hrs. The resultant black solid was filtered by a Buchner funnel and then washed with water (30 ml x 3), EtOH (30 mL x 2) and diethyl ether (20 mL). The resultant sample analyzed by ICP (e.g., 6.60 mg of the sample was dissolved in 1:2 H_2SO_4/HNO_3 (3.0 ml), diluted to 50 ml with H_2O for ICP analyses) to reveal the molar ratio Pt/Na/Cs = 1:1.26:0; corresponding weight profile: Pt (27.94%), Na (= 4.14%), Cs (not detected).

Ion exchange tests with LiF. An as-made sample of HTT-Pt-*a* (40 mg) was stirred with an aqueous solution (10 ml) of LiF (98 mg, 3.78 mmol, 0.97% w/w) at rt for 24 hrs. The resultant black solid was filtered by a Buchner funnel and then washed with water (30 ml x 3), EtOH (30 mL x 2) and diethyl ether (20 mL). The Li-ion-exchanged sample (HTT-Pt-Li) was analyzed by ICP (e.g., 5.60 mg of the sample was dissolved in 1:2 H_2SO_4/HNO_3 (3.0 ml), diluted to 25 ml with H_2O for ICP analyses) to reveal the molar ratio Pt/Na/Li = 19.2:1:24.7; corresponding weight profile: Pt (26.40%), Na (0.16%), Li (1.21%).

Reinsertion of Na^+ ions. The above Li-ion-exchanged sample (HTT-Pt-Li, 20 mg, 0.011 mmol) was stirred with an aqueous solution (10 ml) of NaCl (262 mg, 4.48 mmol, 2.55% w/w) at rt for 24 hrs. The resultant black solid was filtered by a Buchner funnel and then washed with water (50 ml x 3), EtOH (30 mL x 2) and diethyl ether (20 mL). The resultant sample analyzed by ICP (e.g., 5.20 mg of the sample was dissolved in 1:2 H_2SO_4/HNO_3 (3.0 ml), diluted to 25 ml with H_2O for ICP analyses) to reveal the molar ratio Pt/Na/Li = 1.15:1:0.004; corresponding weight profile: Pt (24.40%), Na (2.48%), Li (0.0044%).

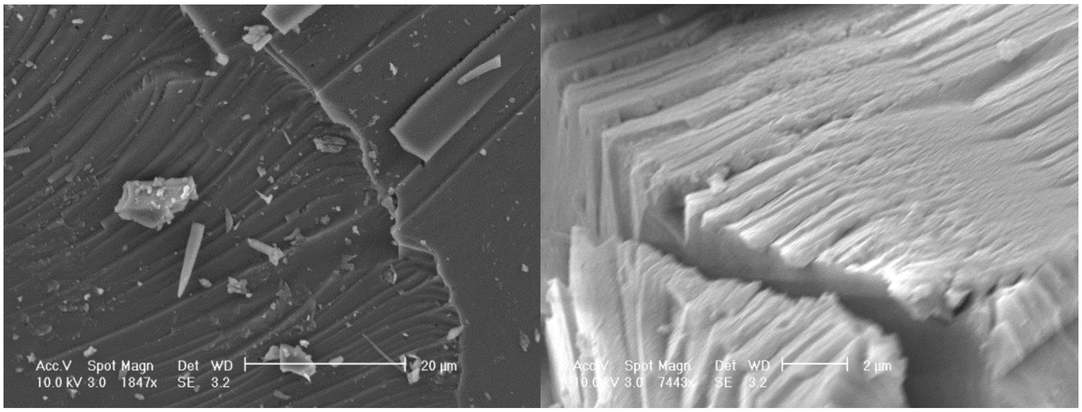

Fig. S1 Two scanning electron microscopy (SEM) images of an as-made sample of HTT-Pt (i.e., HTT-Pt-*a*). Magnifications: left, 1847x; right, 7443x.

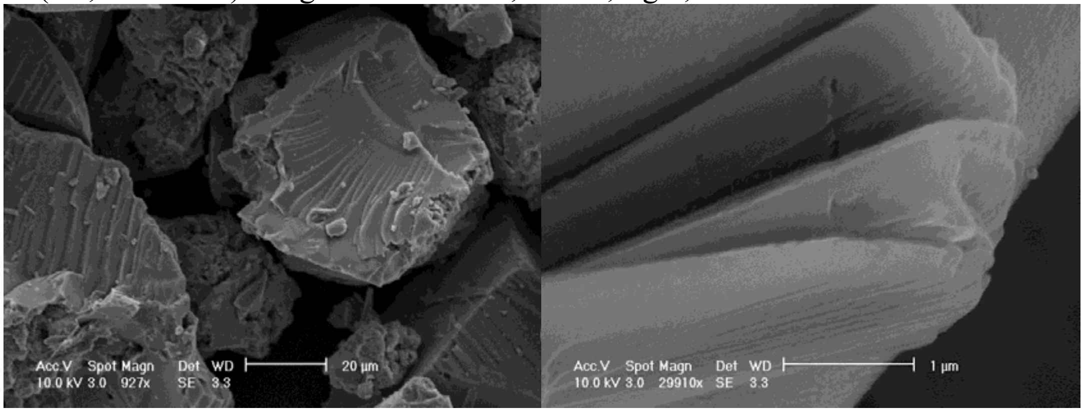

Fig. S2 Two scanning electron microscopy (SEM) images of an activated sample of HTT-Pt (i.e., HTT-Pt-*b*). Magnifications: left, 927x; right, 29910x.

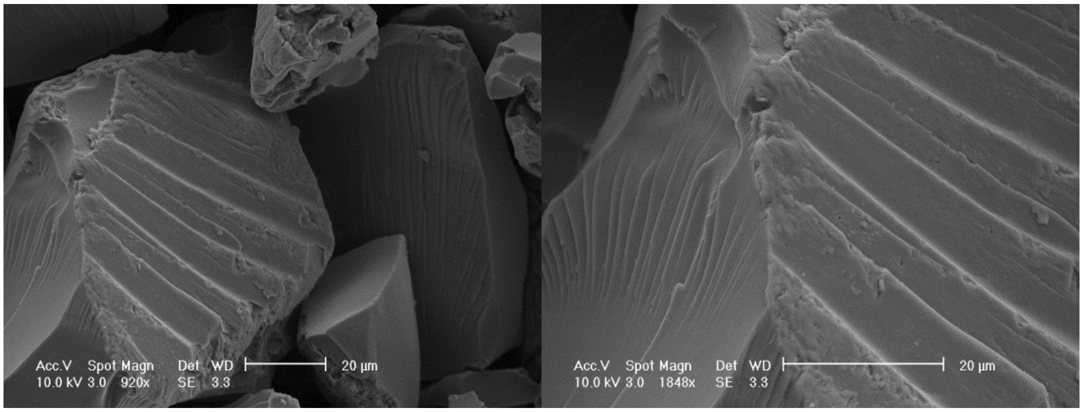

Fig. S3 Two scanning electron microscopy (SEM) images of an I_2-treated sample of HTT-Pt (i.e., HTT-Pt-*c*). Magnifications: left, 920x; right, 1848x.

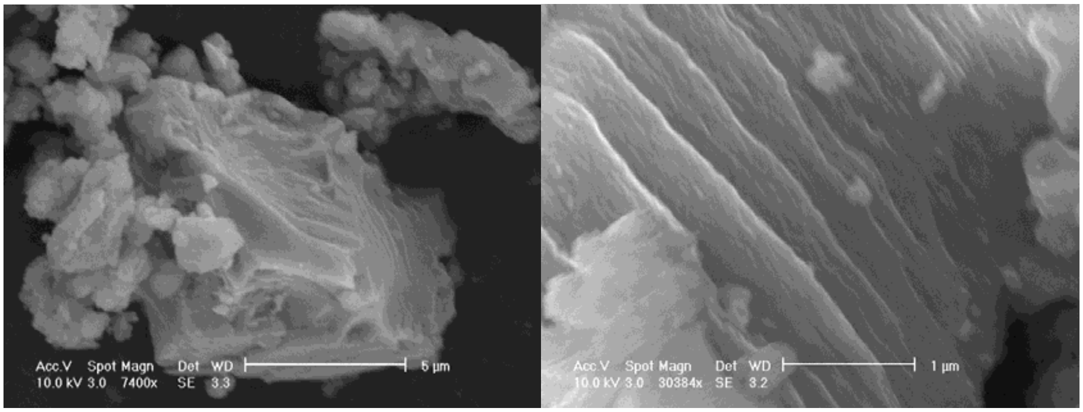

Fig. S4 Two scanning electron microscopy (SEM) images of an Cs$^+$-exchanged sample of HTT-Pt. Magnifications: left, 7400x; right, 30384x.

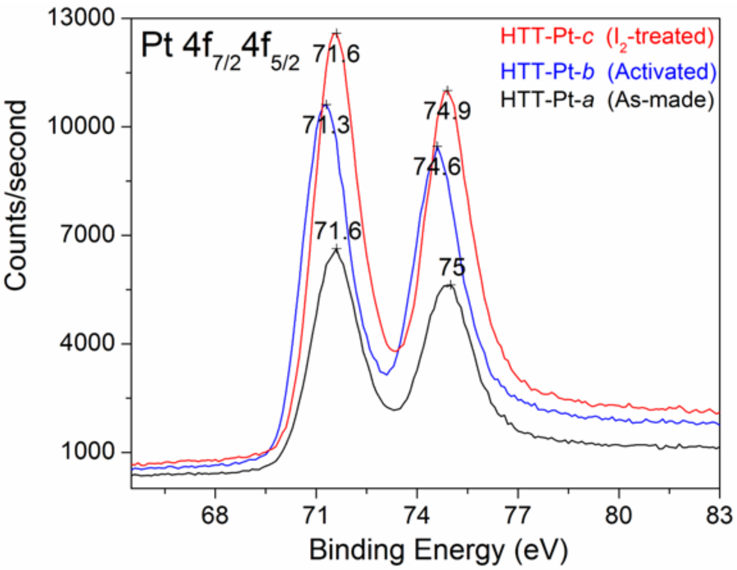

Fig. S5 XPS (X-ray photoelectron spectroscopy) peaks of the $4f_{7/2}$ and $4f_{5/2}$ states of the Pt(II) centers in HTT-Pt-*a* (black), HTT-Pt-*b* (blue) and HTT-Pt-*c* (red).

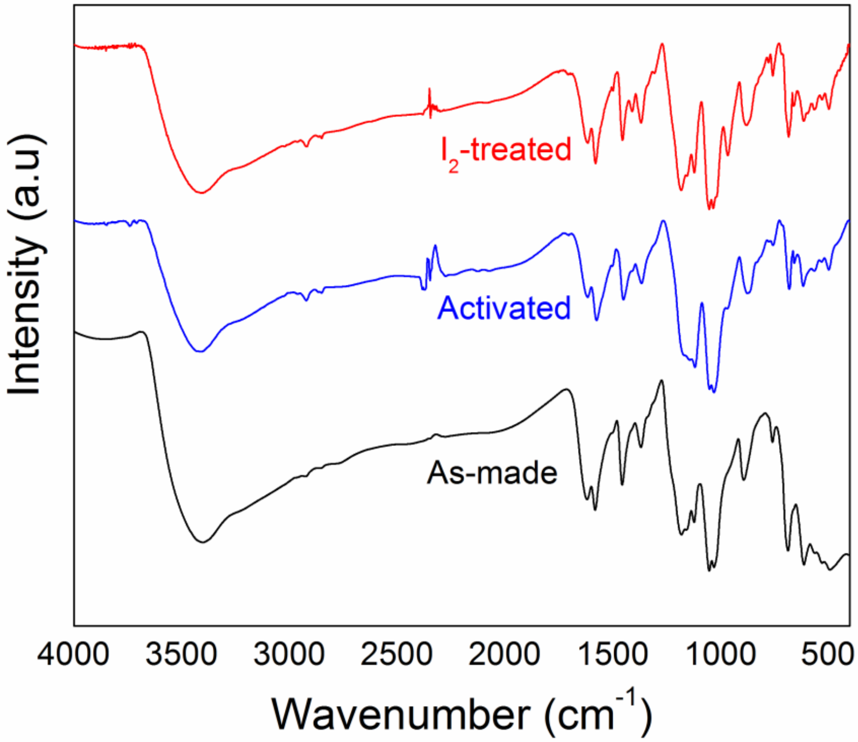

Fig. S6 IR spectra HTT-Pt-*a* (black), HTT-Pt-*b* (blue) and HTT-Pt-*c* (red).

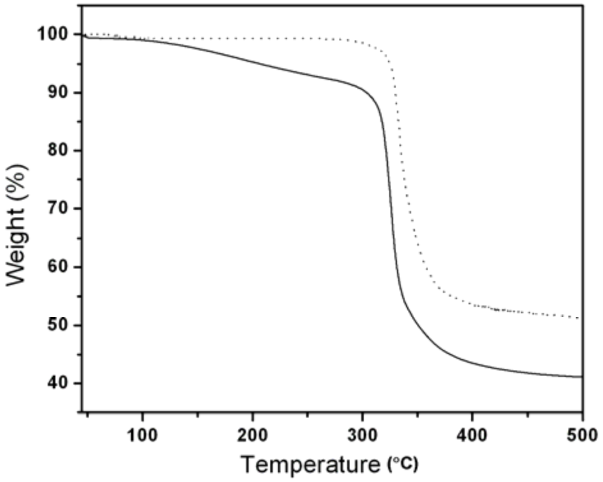

Fig. S7 Thermogravimetric analysis (TGA) plots for an as-made solid sample of **1** (solid line), and a guest-free sample of **1** (dotted line). The guest-free sample was generated by heating the as-made sample at 200 °C in vacuo.

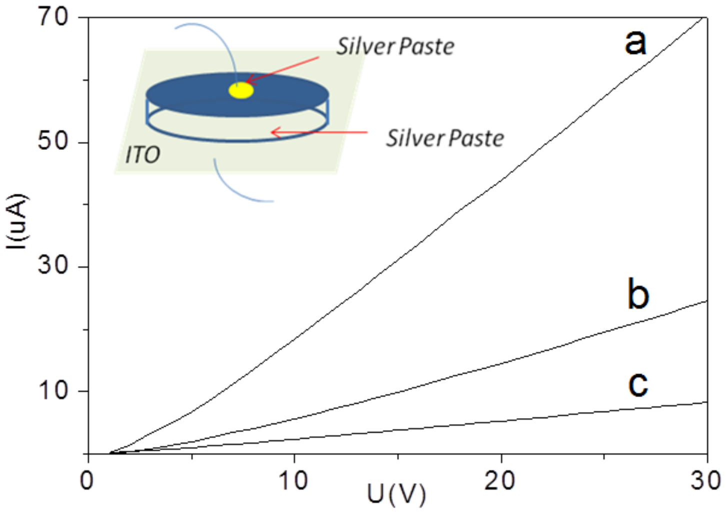

Fig. S8 The current–voltage characteristics of: a) an as-made sample (HTT-Pt-*a*, σ=3.86x10^{-4} S/m); b) an activated sample (HTT-Pt-*a*, σ=2.47x10^{-4} S/m); c) I_2-treated sample (HTT-Pt-*c*, σ=1.09x10^{-4} S/m). The inset is the schematic drawing for the two-probe configuration for the conductivity measurement.

(1) (a) Yatabe, T.; Harbison, M. A.; Brand, J. D.; Wagner, M.; Müllen, K.; Samori, P.; Rabe, J. P. *J. Mater. Chem.* **2000**, *10*, 1519; (b) Li, K.; Xu, Z.; Xu, H.; Ryan, J. M. *Chem. Mater.* **2005**, *17*, 4426.