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An electroactive porous network from covalent metal–dithiolene links†

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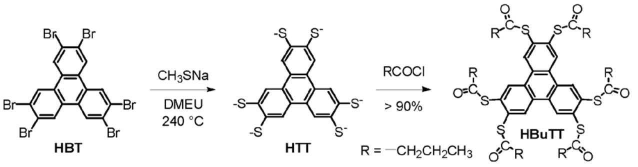
Simple synthesis and versatile functions: by directly reacting a triphenylene hexathiol molecule (HTT) with $PtCl_2$, a covalent metal–organic framework (CMOF) has been prepared that features substantial porosity, redox activity and ion exchange capability.

The porous solid reported here is conveniently prepared from $PtCl_2$ and the rigid, chelating thiol molecule HTT (Scheme 1), and it is one with notable functions and synthetic design. The function resides in an integration of highly electroactive and porous properties that closely bear on the broad energy and environmental technologies of supercapacitors, batteries, catalysts and sensors. The synthesis, on the other hand, builds on the electroactive metal–dithiolene complexes as a classical system in molecular coordination chemistry, but simultaneously embraces the latest advances in the design of porous materials of metal–organic[1] and polymer frameworks.[2] Such advances are best captured in the phrase "rigidity begets porosity", meaning that, to access a porous product, the best bet is to use molecular building blocks with open and rigid geometries.

The principle is best seen in the syntheses of porous polymer frameworks (PPFs),[2] in which rigid and open-shaped molecules directly polymerize, *via* covalent bonding links, to give strong structures with surprisingly large porous features (*e.g.*, with surface areas of over 5000 m^2 g^{-1},[3] about 10 times that of activated charcoal). Of interest is a comparison with the parallel field of metal–organic frameworks (MOFs),[1] wherein metal ions and organic linkers are networked *via* reversible interactions (*e.g.*, metal–carboxylate bonds) to give highly ordered and crystalline products. PPFs, on the other hand, are often less ordered or even amorphous, because of the irreversible polymerization steps involved. The corollary implied is that porosity need not entail crystallinity. Indeed, by relenting on crystallinity, one gains strength and functionality, for one is now free to explore metal–thiolate and other covalent metal-based links, so as to better energize the study of porous frameworks. In other words, a thiol molecule with a well-chosen rigid and open geometry might, upon reacting with metal ions, serve to obviate the tendency to close-pack in the solid state, a tendency that is seen in the growing number of extended metal thiolate structures.[4]



Scheme 1 Synthesis of the HBuTT molecule.

In line with the rigidity principle, a molecule like HTT offers obvious advantages. Besides the rigid and symmetrical shape imposed by the triphenylene core, the chelating dithiolene unit of HTT tends to lock in metal ions in well-defined bonding motifs.[5] Also, the sulfur atoms are fully conjugated with the aromatic core to promote charge transport in the prospective framework solid. On a practical plane, the synthesis of HTT (or its thioesters as the protected form, see HBuTT in Scheme 1) is highly feasible—it has already been well described in the literature.[6]

Reaction of the hexaanion of HTT (generated *in situ* from the thioester derivative HBuTT by NaOH/methanol) and $Pt(CH_3CN)_2Cl_2$ (dissolved in DMA, *N*,*N*-dimethylacetamide) produced a solid product, which exhibited a dark-red color when initially precipitated from the N_2-protected reaction mixture, but turned black upon exposure to air in the work-up steps.‡ The darkening of color points to air sensitivity associated with the highly reduced thiolate product initially formed. The black solid obtained as such (denoted as HTT-Pt-*a*) was then purified by Soxhlet extraction in refluxing MeOH, and then evacuated at 90 °C to provide the activated solid product (HTT-Pt-*b*). The activated sample (HTT-Pt-*b*) features the composition $HTT{\cdot}(Pt)_{1.5}{\cdot}(Na)_{0.9}$ as jointly determined by ICP (this indicates a Pt/Na molar ratio of 1.5 : 0.9) and the regular CHN elemental analyses (H_2O and residual DMF were also present in

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† Electronic supplementary information (ESI) available: General procedures, details on sample preparations and the structural modeling on the HTT-Pt framework using the Materials Studio software, and the result exported in CIF format. See DOI: 10.1039/c4cc00408f

the sample, see ESI† for details). The composition points to an anionic HTT-Pt framework counter-balanced by the sodium ions. The sodium content, as well as the formal charge of the HTT moiety, is dependent on the degree to which the sample is oxidized. In the present case, the average formal charge on each HTT is balanced to be about −4 (*cf.* −6 in the as-formed hexaanion shown in Scheme 1).

The significantly porous character of the activated sample of HTT-Pt-*b* was revealed in N_2 sorption experiments (at 77 K). A typical type-I gas adsorption isotherm (Fig. 1) was observed, with a Brunauer–Emmett–Teller (BET) surface area of 329 m^2 g^{-1}. Monte-Carlo analysis of the pore size distribution and pore volume indicated an average pore width of 0.57 nm and a pore volume of 0.124 cm^3 g^{-1}. The surface area data are comparable to a catecholate system that also builds upon the triphenylene core.[7]

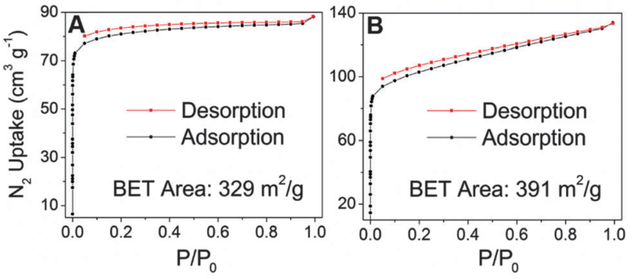

Fig. 1 N_2 sorption isotherms at 77 K for the activated solid samples of HTT-Pt-*b* (panel A) and HTT-Pt-*c* (I_2-treated; panel B).

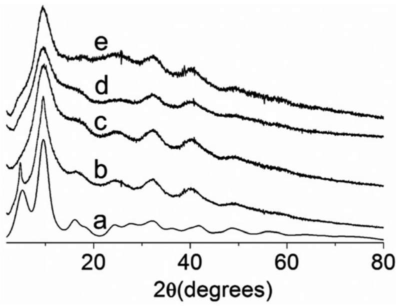

Fig. 2 Powder X-ray patterns for HTT-Pt: (a) calculated from a crystal structure model based on standard bonding geometries; (b) an as-made sample; (c) an activated sample; (d) an I_2-treated sample; (e) a Cs^+-exchanged sample.

X-ray powder diffraction of the HTT-Pt-*b* sample shows a series of broad, but distinct peaks indicative of some ordering of the structure (Fig. 2, pattern b). Both the positions and intensity profile are consistent with a hexagonal grid modeled on standard bonding interactions between the tritopic HTT molecule and the square planar Pt(II) centers (*e.g.*, Pt–S distance: 2.36 Å; see Fig. 3 for the model), with a staggered stacking among the neighboring sheets (Fig. 3c; interlayer distance: 3.46 Å; see also ESI†). The 2D honeycomb model is also consistent with the distinct laminae revealed by scanning electron microscopy (SEM, Fig. S1–S4, ESI†). Additional data from XPS (*e.g.*, binding energies of the Pt^{2+} in HTT-Pt-*a*: $4f_{7/2}$, 71.6; $4f_{5/2}$, 75.0 eV;[8] Fig. S5, ESI†) and IR (*e.g.*, the strong band around 1100 cm^{-1} corresponding to the C–S stretch;[9] Fig. S6, ESI†) are in line with the Pt(II)–dithiolene-based motif.

The anionic framework HTT-Pt-*b* can be further oxidized by I_2 to give a near-neutral system of $(HTT)_2{\cdot}(Pt)_{3.0}$ (*e.g.*, the Na/Pt molar ratio was shown by ICP to be lower than 1 : 20; see ESI†). The I_2-treated sample (denoted as HTT-Pt-*c*) retains the hexagonal structure as indicated by X-ray diffraction (Fig. 2, pattern d). The structural integrity was also reflected in the results of N_2 sorption experiments (at 77 K), in which a typical type-I gas adsorption isotherm (Fig. 1b) was observed. Compared with the parent sample HTT-Pt-*b*, the BET surface area of HTT-Pt-*c* exhibits a nearly 20% increase, reaching 391 m^2 g^{-1}. The additional surface area can be attributed to the removal of the Na^+ ion and its associated water molecules from the voids as a result of the I_2 treatment (*i.e.*, the network becomes nearly neutral). The slight slope observed in the higher relative pressure of the isotherm is normally attributed to the sorption by the mesopores in the system, which might have been made accessible by the removal of the sodium ions.

Electrical conductivity measurements help to reveal the semiconductive nature of the HTT-Pt samples. In a two-probe configuration, the as-made, activated and I_2-treated samples all exhibit linear current–voltage characteristics (see Fig. S8 in the ESI†) yielding conductivity values on the order of 10^{-4} S m^{-1} (3.86×10^{-4}, 2.47×10^{-4} and 1.09×10^{-4} S m^{-1}, respectively). The inherent conductivity, however, can be expected to be higher, as the

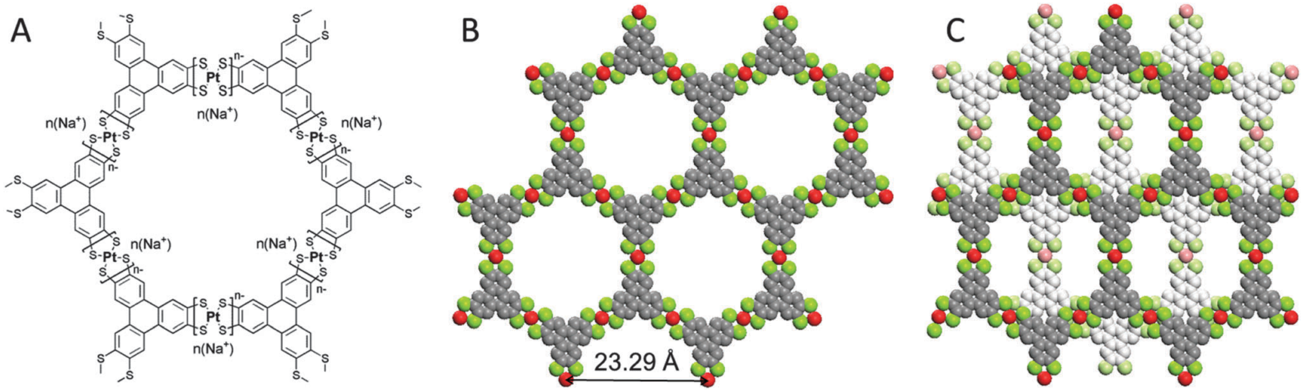

Fig. 3 A schematic drawing of the honeycomb net of HTT-Pt (panel A), a single net from a crystal structure model based on standard bonding geometries (B), and two neighboring sheets showing the staggered alignment thereof (C). The Na^+ ions are not included in the model.

2-probe setting does not eliminate contact resistance (while the 4-probe one does). In any case, the values thus obtained are on par with the porous pyrazine-thiolate–metal crystals recently reported.[10] Further study of the electronic properties (*e.g.*, magnetic susceptibility, ESR, Hall mobility) would be especially relevant.

The robustness of the HTT-Pt network is also demonstrated by ion exchange experiments. For example, after the 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 hours, the resultant solid was analyzed by ICP to feature a 1 : 9.45 Na/Cs molar ratio, indicating that over 90% of the Na^+ was replaced by Cs^+. In a similar experiment using LiF, effective ion exchange was also observed, *e.g.*, over 95% of Na^+ in HTT-Pt-*a* can be replaced by Li^+. The ion exchanged solid samples continue to exhibit similar crystalline order as shown by PXRD (*e.g.*, Fig. 2, pattern e), and sodium ions can be readily inserted back into the system by simply soaking in an aqueous solution of NaCl (see ESI†). Along this line, the current system is reminiscent of the polysulfide chalcogels and other inorganic chalcogenide open frameworks developed by the Kanatzidis group, in which a wide range of versatile ion exchange properties have been demonstrated.[11] We are probing further ion exchange behaviors (*e.g.*, selectivity with regards heavy and transition metals) as well as the resultant impacts upon the electronic properties of HTT-Pt as a covalent metal–organic framework (CMOF).

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Notes and references

‡ Synthesis of HTT-Pt. HBuTT (100 mg, 0.12 mmol) and a methanol (10 ml) solution of NaOH (67 mg, 1.67 mmol) were refluxed under N_2 for 6 hours, after which a deaerated *N*,*N*′-dimethylacetamide (DMA, 5.0 ml) of $Pt(CH_3CN)_2Cl_2$ (63 mg, 0.18 mmol) was added to the refluxing system *via* cannula under N_2 protection. A dark-red precipitate starts to form one or two minutes afterwards. The reaction mixture was kept at a steady reflux for another 4 hours, cooled to rt, and mixed with additional DMA (about 20 ml). The solid product therein was collected on a Buchner funnel, washed by DMA (about 40 ml), deionized water (about 60 ml), MeOH (about 30 ml), and air-dried in a fume hood 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). The crude product was purified by Soxhlet extraction in refluxing MeOH for 24 hours, and then evacuated by an oil pump at 90 °C for one hour to provide an activated solid product (HTT-Pt-*b*). CHN elemental analyses on the activated sample (HTT-Pt-*b*) found [C (23.74%), H (3.50%), 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%)].

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