This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
An Electroactive Porous Network from Covalent Metal-Dithiolene Links

Jieshun Cui and Zhengtao Xu*

Simple synthesis and versatile functions: by directly reacting a triphenylene hexathiol molecule (HTT) with PtCl₂, a covalent metal-organic framework (CMOF) has been made that features substantial porosity, redox activity and ion exchange capability.

The porous solid reported here is conveniently made from PtCl₂ and the rigid, chelating thiol molecule HTT (Scheme 1), and it is one of notable function 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 and polymer frameworks. Such advances are best captured in the phrase “rigidity begets porosity”, meaning that, to access a porous product, the best bet is with molecular building blocks with open and rigid geometries.

The principle is best seen in the syntheses of porous polymer frameworks (PPFs), 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 over 5000 m²/g, about 10 times that of activated charcoal). Of interest is a comparison with the parallel field of metal-organic frameworks (MOFs), 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. Corollary implied: 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 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.

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. 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.

Reaction of the hexaanion of HTT (generated in situ from the thioester derivative HBuTT by NaOH/methanol) and Pt(CH₃CN)₂Cl₂

Scheme 1. Synthesis of the HBuTT molecule.

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.

Reaction of the hexaanion of HTT (generated in situ from the thioester derivative HBuTT by NaOH/methanol) and Pt(CH₃CN)₂Cl₂

Fig. 1 N₂ sorption isotherms at 77 K for the activated solid samples of HTT-Pt-b (panel a) and HTT-Pt-c (I₂-treated; panel b).
(dissolved in DMA, N,N-dimethylacetamide) produces a solid product, which exhibited a dark-red color when initially precipitated from the N$_2$-protected reaction mixture, but turned black upon exposed 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.

**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.

(HTT-Pt-b). The activated sample (HTT-Pt-b) features the composition HTT$_3$Pt$_{1.5}$(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$_2$O and residual DMF were also present in 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 balances to about -4 (cf. -6 in the as-formed hexaanion shown in Scheme 1).

Significant porous character of the activated sample of HTT-Pt-b was revealed in N$_2$ sorption experiments (at 77K). A typical type-I gas adsorption isotherm (Fig. 1) was observed, with a Brunauer–Emmett–Teller (BET) surface area of 329 m$^2$/g. Monte-Carlo analysis on 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. 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.

**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.

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 ESI) yielding conductivity values on the order of $10^{-4}$ S/m ($3.86\times10^{-4}$, 2.47$\times10^{-4}$ and 1.09$\times10^{-4}$ S/m, respectively). The inherent conductivity, however, can be expected to be higher, as the 2-probe setting does not eliminate contact resistance (while 4-probe one does). In any case, the values thus obtained are on par with the porous pyrazine-thiolate-metal crystals recently reported. Further study on 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 hrs, the resultant solid analyzed by ICP to feature a 1.9:45 Na/Cs molar ratio, indicating 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 exhibits the lamellar order as shown by PXRD (e.g., Fig. 2, pattern e), and sodium ions can be

The anionic framework HTT-Pt-b can be further oxidized by I$_2$ to give a near-neutral system of (HTT)$_2$(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-ct) 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 77K), in which a typical type-I gas adsorption isotherm (Fig. 1b) was observed. Compared with the parent sample HTT-Pt-a, the BET surface area of HTT-Pt-ct exhibits a nearly 20% increase, reaching 391 m$^2$/g. The additional surface area can be attributed to 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.
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. We are probing further ion exchange behaviors (e.g., selectivity with regards heavy and transition metals) as well as the resultant impacts on the electronic properties on HTT-Pt as a covalent metal-organic framework (CMOF).

This work is supported by the Research Grants Council of HKSAR (GRF Project 103212). ZX acknowledges the Alexander von Humboldt Foundation for a Humboldt Research Fellowship for Experienced Researchers (host: Prof. Markus Antonietti). We also thank Dr. Jens Weber in Prof. Antonietti’s group for initial PXRD measurement, and Ms. Danqing Liu in Prof. Qian Miao’s group for conductivity measurements.

Notes and references

Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China.

E-mail: zhengtao@cityu.edu.hk; Fax: +852-27844679.

† Synthesis of HTT-Pt·HbU(TT (100 mg, 0.12 mmol) and a methanol (10 ml) solution of NaOH (67 mg, 1.67 mmol) were refluxed under N2 for 6 hrs, after which a deaerated NaCl solution (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. We are probing further ion exchange behaviors (e.g., selectivity with regards heavy and transition metals) as well as the resultant impacts on the electronic properties on HTT-Pt as a covalent metal-organic framework (CMOF).

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/c000000x/


