Designing crystalline, flexible covalent metal–organic networks through controlled ligand deprotection

Journal:	*CrystEngComm*
Manuscript ID	CE-COM-06-2019-000875.R1
Article Type:	Communication
Date Submitted by the Author:	22-Jun-2019
Complete List of Authors:	Roy, Mrittika; University of Massachusetts Dartmouth, Chemistry & Biochemistry Lonardo, Alessandra ; University of Massachusetts Dartmouth, Chemistry & Biochemistry Pham, Duyen; University of Massachusetts Dartmouth, Chemistry & Biochemistry Kreider-Mueller, Ava; University of Massachusetts Dartmouth, Chemsitry & Biochemistry Golen, James; University of Massachusetts Dartmouth, Chemistry & Biochemistry Manke, David; University of Massachusetts Dartmouth, Chemistry & Biochemistry

Designing crystalline, flexible covalent metal-organic networks through controlled ligand deprotection

Mrittika Roy, Alessandra A. Lonardo, Duyen N. K. Pham, Ava Kreider-Mueller, James A. Golen, David R. Manke*

A strategy to generate crystalline coordination polymers with strong, covalent metal-linker bonds is presented. 1,6-pyrenedi(2-ethylhexylmercaptopropionate) (1) is converted to 1,6-pyrenedithiolate (PDT) via a base-mediated deprotection allowing for rate control of the metal-linker self assembly. This leads to the formation of a single-crystalline, flexible 2D coordination polymer, [Cd(PDT)$_2$][Cd(en)$_3$] (3).

The preparation of coordination polymers (CPs) and metal-organic frameworks (MOFs) with strong, covalent interactions give rise to various structural and functional advantages.[1] These materials were termed Covalent Metal-Organic Networks (CMONs) by Wolczanski in the late 1990s, when his lab focused on the synthesis of early transition metal phenoxide-based networks.[2-8] The hard-hard acid-base interactions provide significant covalency in the metal-linker bonds. Later work by Vaid and co-workers produced a number of late transition metal arylthiolate-based CPs focused on soft-soft acid-base interactions.[9-14] While such materials present a great deal of promise, the synthesis of these materials in crystalline form is difficult to achieve due to rapid rates of formation, with most syntheses yielding powdered or amorphous products. The majority of these materials were characterized through Reitveld refinement of data collected on microcrystalline materials at a synchrotron source.

Since CMONs were first presented in 1997, the MOF field has undergone an explosion, with the "MOF subset" of the Cambridge Structural Database now exceeding 75,000 entries.[15] The vast majority of MOFs are based upon carboxylate or amine linkages, which exhibit coordinate covalent bonding. The nature of this bonding generates crystalline materials in manners closer to ionic compounds. The benefits that MOFs present over other porous materials is the regularity exhibited in their porosity and functional group distribution, as well as their ability to incorporate functionality into both linker and secondary building units.[16] The ability to isolate these materials as single-crystals and characterize them as such has greatly helped the field to expand. It was against this backdrop that we sought to develop a synthetic strategy to generate CMON materials in single-crystalline form, and employed a strategy of controlled linker deprotection to generate such materials.

In our syntheses, we begin with 1,6-pyrenedi(2-ethylhexylmercaptopropionate) (1), which is prepared via a palladium-catalyzed C–S cross coupling reaction.[17] This is the protected version of our desired linker 1,6-pyrenedithiolate (PDT). Figure 1 illustrates the mechanism of deprotection for this linker, where ethylenediamine is used as the base, generating the bis(2-aminoethylammonium) pyrenedithiolate
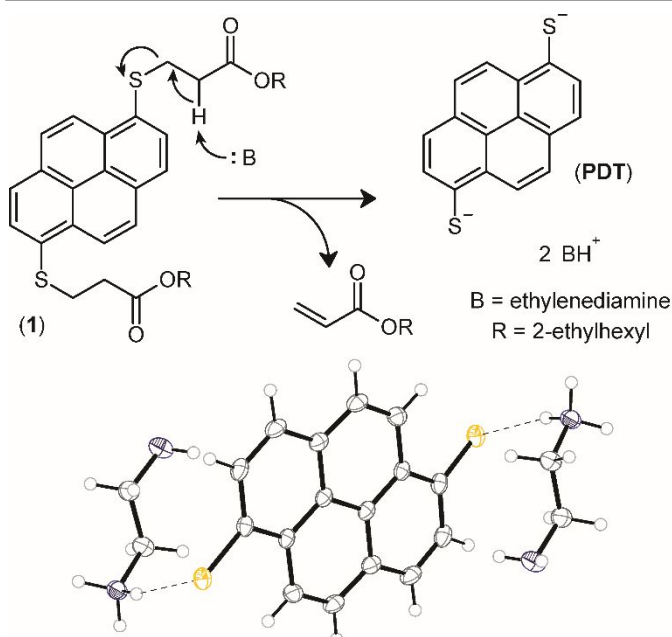
Department of Chemistry & Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, MA, 02747, USA
E-mail: dmanke@umassd.edu

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Fig. 1 The base mediated deprotection of the PDT linker (top). The crystal structure of the product from the deprotection with ethylenediamine (bottom).

salt (2). The crystal structure of the resulting salt is shown. This deprotection step is the basis for our synthetic strategy, as the concentration and strength of the base used can be varied to control the rate of deprotection, and the subsequent rate of network formation.

This strategy first showed success in generating a cadmium thiolate network. A solution of the protected PDT linker (1) was combined with a solution of cadmium acetate in ethylenediamine. The thiolate is readily oxidized to the sulfonate, so both solutions were degassed and combined under an atmosphere of dinitrogen. The selection of the acetate salt was also to avoid any oxidizing anions. The combined solution was heated to 90 °C in a sealed vial, resulting in the formation of large, single crystals. The crystals are bright orange and grow to sizes as large as two millimetres. The formation of the tris(ethylenediamine)cadmium counterions might help the crystal formation,[18] though attempts at generating the network with H_2PDT did not yield any crystalline product in these systems. The crystals decompose upon extended air exposure.

The single crystal X-ray structure shows the compound to be an anionic network with the formula $[Cd(PDT)_2][Cd(en)_3]$, (3). The structure exhibits a 2D network along the (1,2,1) plane. The sheets possess rings of six cadmium atoms bridged by PDT linkers forming honeycomb sheets (Figure 2c). Each cadmium atom in the network exhibits tetrahedral coordination to four thiolate linkers. The secondary building unit (SBU) around the cadmium has a trigonal planar configuration, with two pyrene linkers aligned in one direction and one pyrene linker directed along each of the other two trigonal angles (Figure 2a).

The empirical formula for the network is $Cd(PDT)_2$, giving a −2 charge per cadmium atom, which is charge balanced by a cadmium tris(ethylenediamine) dication that sits between network layers. There are also disordered ethylenediamine molecules throughout the open space in the lattice. The general composition is consistent with the network synthesized by Vaid and co-workers.[10]

When the network is grown in an aqueous solution of ethylene diamine, the same compound is formed, $[Cd(PDT)_2][Cd(en)_3]$, but as the structure is shifted because of the incorporated solvent, it crystallizes with a different unit cell (Figure 2b). The inclusion of hydrogen bonding between water molecules, the ethylenediamine molecules, and the cadmium complex cation leads to a two dimensional network along the (1,−1,−1) plane which exhibits the same connectivity as the one described above.

The major change in this structure is that it has been stretched compared to the one reported above (Figure 2d). This is most notable in the angles of the six-cadmium hexagons that are present in the two-dimensional sheets. The crystals from the ethylenediamine solution show Cd-Cd-Cd angles of 128.76(1)°, 121.53(1)° and 104.97(1)°, which are reasonably close to a trigonal arrangement. The Cd-Cd-Cd angles observed in the crystals grown from the aqueous solution all show significant stretching, with angles of 154.40(1)°, 130.36(1)° and 69.33(1)°. The stretching is also obvious in the coordination environment of cadmium in the network grown from an aqueous solution (Figure 2b).
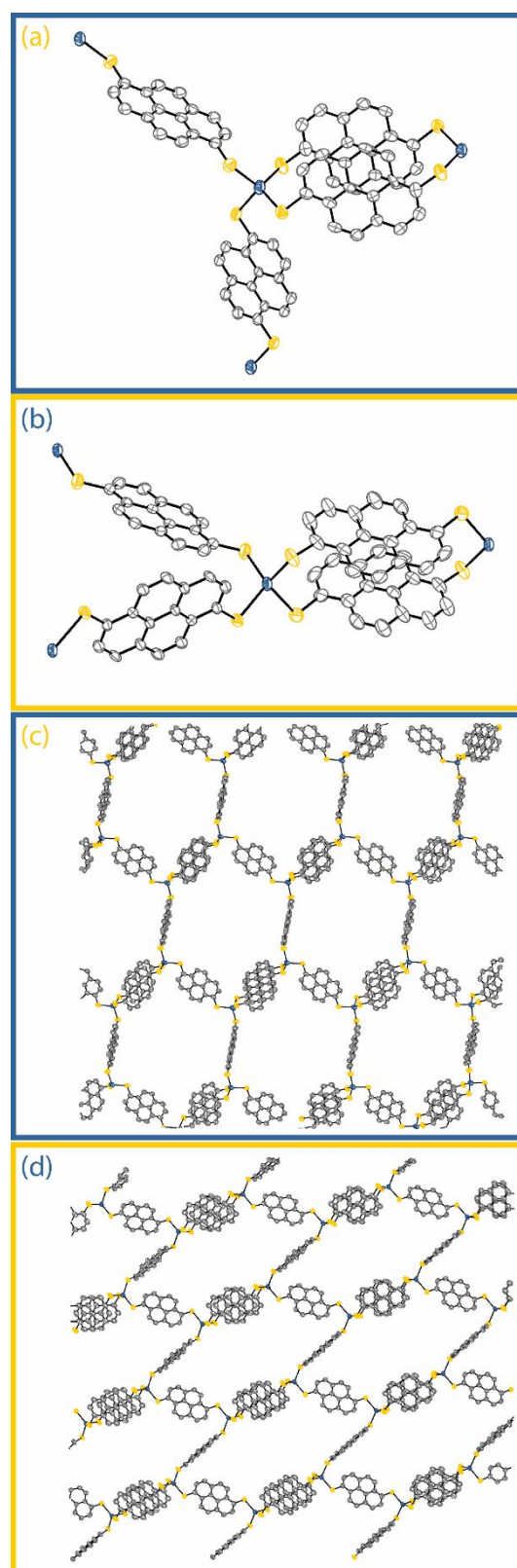

Fig. 2 The coordination environment of the cadmium atoms in the networks of compound 3 formed from pure ethylenediamine (a) and from an aqueous mixture of ethylenediamine (b). The 2D sheets formed from pure ethylenediamine (c) and from aqueous solutions of ehylenediamine (d). The cadmium tris(ethylenediamine) counterions have been removed for clarity.

The flexibility observed here would be considered a breathing mode, where changes in the incorporated solvent results in a displacement of atoms in the network, significantly altering the unit cell volume.[19] In these networks, the monodentate nature of the linkers allow free rotation about the Cd–S bonds, as well as the C–S bonds, which prevent rigidity from taking over. The disordered pyrene group in (3) further demonstrates the flexibility, as a 180° rotation is present in the solid state, with a 57:43 occupancy. Flexible CPs have the potential to possess reversible physical and chemical property changes, which could open up a broad range of applications.

Conclusions

This article reports a strategy to synthesize crystalline covalent metal-organic networks using a pH-dependent ligand deprotection step to control the rate of metal-linker reaction and thus, network formation. We believe that this approach has great promise for the further design of many crystalline coordination polymers. By altering the protecting group used for a given linker, the rate of crystal formation could be controlled by varying the pH, the temperature, the light flux, etc. We are continuing to explore this approach, generating more networks based upon the PDT linker, with other soft metals, and beginning to explore their optical, electronic and mechanical properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 L. Sun, M. G. Campbell and M. Dincă, *Angew. Chem. Int. Ed.*, 2016, **55**, 3566-3579.
2 T. P. Vaid, E. B. Lobkovsky and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1997, **119**, 8742-8743.
3 T. P. Vaid, J. M. Tanski, J. M. Pette, E. B. Lobkovsky and P. T. Wolczanski, *Inorg. Chem.*, 1999, **38**, 3394-3405.
4 J. M. Tanski, T. P. Vaid, E. B. Lobkovsky and P. T. Wolczanski, *Inorg. Chem.*, 2000, **39**, 4756-4765.
5 J. M. Tanski, E. B. Lobkovsky and P. T. Wolczanski, *J. Solid State Chem.*, 2000, **152**, 130-140.
6 T. P. Vaid, O. L. Sydora, R. E. Douthwaite, P. T. Wolczanski and E. B. Lobkovsky, *Chem. Commun.*, 2001, 1300-1301.
7 J. M. Tanski and P. T. Wolczanski, *Inorg. Chem.*, 2001, **40**, 2026-2033.
8 J. M. Tanski and P. T. Wolczanski, *Inorg. Chem.*, 2001, **40**, 346-353.
9 D. L. Turner, T. P. Vaid, P. W. Stephens, K. H. Stone, A. G. DiPasquale and A. L. Rheingold, *J. Am. Chem. Soc.*, 2008, **130**, 14-15.
10 D. L. Turner, K. H. Stone, P. W. Stephens and T. P. Vaid, *Dalton Trans.*, 2010, **39**, 5070-5073.
11 K. H. Stone, D. L. Turner, M. P. Singh and T. P. Vaid, *Acta Cryst.*, 2011, **B67**, 409-415.
12 D. L. Turner, K. H. Stone, P. W. Stephens, A. Walsh, M. P. Singh and T. P. Vaid, *Inorg. Chem.*, 2012, **51**, 370-376.
13 A. C. Stott, T. P. Vaid, E. J. Bylaska and D. A. Dixon, *J. Phys. Chem. C*, 2012, **116**, 8370-8378.
14 D. Tiana, C. H. Hendon, A. Walsh and T. P. Vaid, *Phys. Chem. Chem. Phys.*, 2014, **6**, 14463.
15 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst.*, 2016, *B***72**, 171-179.
16 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.* 2012, **112**, 673-674.
17 T. Itoh and T. Mase, *Org. Lett.*, 2007, **9**, 3687-3689.
18 N. Louvain, Y. Takashima, S. Kitagawa and S. Furukawa, *New J. Chem.*, 2011, **35**, 1265-1269.
19 A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062.

TABLE OF CONTENTS

Graphic
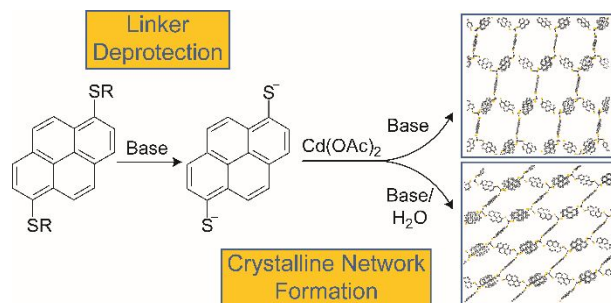
Caption

Our lab has developed a synthetic approach to control the growth of crystalline covalent metal-organic networks through a base-mediated deprotection of the organic linkers.