



Communication

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*J. Am. Chem. Soc.*, Just Accepted Manuscript • DOI: 10.1021/ja4037516 • Publication Date (Web): 14 May 2013 Downloaded from http://pubs.acs.org on May 15, 2013

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## $Mn_2(2,5$ -disulfhydrylbenzene-1,4-dicarboxylate): a Microporous MOF with Infinite $(-M-S-)_{\infty}$ Chains and High Intrinsic Charge Mobility

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Supporting Information Placeholder

**ABSTRACT:** Replacement of phenol groups in 2,5dihydroxy-1,4-benzenedicarboxylate by thiophenol units and reaction of 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid ( $H_4DSBDC$ ) with  $MnCl_2$  led to the isolation of  $Mn_2(DSBDC)$ , a thiolated analogue of the  $M_2(DOBDC)$  series of metalorganic frameworks. The sulfur atoms participate in infinite one-dimensional Mn-S chains, and  $Mn_2(DSBDC)$  shows high surface area and high charge mobility similar to some of the most common organic semiconductors. The synthetic approach to  $Mn_2(DSBDC)$  and its excellent electronic properties provide a blueprint for a potentially rich area of exploration in microporous conductive MOFs with low-dimensional charge transport pathways.

Myriad applications have been found or proposed for microporous metal-organic frameworks (MOFs),<sup>1</sup> yet those that require electron transport or conductivity in combination with permanent porosity still lag behind because the vast majority of microporous MOFs are electrical insulators.<sup>2</sup> However, recent inroads in this area suggest that judicious choice of the metal and organic components can lead to crystalline porous materials with promising conductivity or charge mobility properties.<sup>3</sup> In fact, taking a cue from the more mature area of molecular conductors and conductive coordination polymers, one can envision that two main approaches can be employed to construct new MOFs with good charge transport properties.<sup>4,5</sup> One is "through-space" and relies on  $\pi$  stacking interactions between electroactive moleties. This approach has led to remarkable results with covalent-organic frameworks<sup>6</sup> and has also recently been used by us to make a tetrathiafulvalene (TTF)-based MOF with high charge mobility.<sup>3c</sup> The second approach relies on a "throughbond" formalism, where both symmetry and energy overlap must exist between the covalently-bonded components to promote good charge transport. This approach is synthetically more tractable because it allows control of the directionality of the metal-ligand bond. It has nevertheless seen limited success in MOFs, which are typically constructed from hard metal ions and oxygen- or nitrogen-based redoxinactive ligands<sup>7</sup> that rarely provide a good pathway for charge delocalization. Replacement of oxygen atoms by sul-



**Figure 1.** Conceptual design of MOFs consisting of  $(-M-S-)_{\infty}$  chains based on replacing phenol groups in  $M_2(DOBDC)$  with thiophenol groups. The purple bonds indicate the infinite  $(-M-O-)_{\infty}$  and expected  $(-M-S-)_{\infty}$  chains.

fur can alleviate the energy mismatch,<sup>8</sup> and has led to semiconducting non-porous coordination polymers9 and one of the only examples of a porous and conductive material, a Nidithiolene MOF.<sup>3a</sup> We sought to pursue a related approach, where oxygen atoms in metal-oxide chains of existing MOFs are replaced isomorphically by sulfur atoms, thereby giving rise to infinite metal-sulfur chains of potential interest towards charge transport. In essence, this approach would create dimensionally-reduced metal-organic chalcogenides, wherein organic spacers would create porosity while maintaining  $(-M-S-)_{\infty}$  units along one direction. Although theoretical and experimental studies indicated that dimensional reduction in bulk metal chalcogenides, which are usually intrinsic semiconductors or metals,<sup>10</sup> increases the band gap of these materials, the lower-dimensionality does not eliminate charge transport."

There are numerous MOFs that contain infinite onedimensional secondary building units (SBUs) where single oxygen atoms bridge pairs of two metal ions. One of the most iconic examples is the series of materials with the formula  $M_2(DOBDC)$  (M = Mg, Mn, Fe, Co, Ni, Zn,  $H_4DOBDC$ = 2,5-dihydroxybenzene-1,4-dicarboxylic acid).<sup>12</sup> The SBUs in these MOFs are  $(-M-O-)_{\infty}$  chains where each pair of metal atoms is bridged by one phenolate group. We surmised that replacing the phenol groups by thiophenol functionalities would give rise to isomorphous materials with linear  $(-M-S-)_{\infty}$  units and high charge mobility (Figure 1). Herein we show that the thiolated analogue of H<sub>4</sub>DOBDC, 2,5disulfhydrylbenzene-1,4-dicarboxylic acid (H<sub>4</sub>DSBDC) generates Mn<sub>2</sub>(DSBDC), a new material with permanent porosity and high charge mobility. To our knowledge, the new MOF has the highest surface area among MOFs that display electron delocalization, improving the previous record by almost 50% and reinforcing the idea that high surface area and charge delocalization can indeed coexist in crystalline hybrid materials.

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The ligand H<sub>4</sub>DSBDC was synthesized starting from hydroquinone in five steps and 19% overall yield, according to Scheme S1.<sup>13</sup> Heating a solution of H<sub>4</sub>DSBDC and anhydrous MnCl, in a dry and degassed mixture of N,Ndimethylformamide (DMF) and methanol (10:1 by volume) at 120 °C under an N<sub>2</sub> atmosphere for 1 day generated yellow crystals of [Mn<sub>2</sub>(DSBDC)(DMF)<sub>2</sub>]·0.2DMF (as-synthesized 1) and an unidentified orange powder. Single crystal X-ray diffraction analysis of 1 revealed a structure consisting of infinite Mn<sup>2+</sup> chains bridged by both carboxylate groups and thiophenoxide groups pertaining to anionic DSBDC<sup>4-</sup> ligands (Figure 2). Although related to the structure of  $M_2$ (DOBDC), the structure of 1 differs from the latter because two crystallographically independent Mn<sup>2+</sup> ions are found in the asymmetric unit, whereas only one is present in  $M_2(DOBDC)$ . In 1, one Mn<sup>2+</sup> ion is coordinated by four carboxylate oxygen atoms and two thiophenoxide groups, while another is coordinated by two carboxylate oxygen atoms, two thiophenoxide groups and two cis-oriented DMF molecules. Importantly, 1 contains infinite  $(-Mn-S-)_{\infty}$  chains defined by  $Mn^{2+}$ thiophenoxide linkages wherein the sulfur atoms at both crystallographic Mn sites are oriented trans with respect to each other, with Mn-S distances of 2.493(1) and 2.632(1) Å, respectively. This indicates that the S atoms interact with the same d-orbital on Mn, an important symmetry requirement for charge delocalization along the (-Mn-S-)<sub>∞</sub> chain. Bridging in each pair of neighboring Mn atoms is completed by one oxygen atom from carboxylate groups and  $\mu$ -carboxylate linkages. Neighboring chains are connected by DSBDC<sup>4-</sup> ligands, which together define a three-dimensional framework containing hexagonal one-dimensional pores with a van der Waals diameter of ~16 Å (for fully desolvated 1). As expected based on the longer Mn-S and C-S distances relative to M-O and C–O, respectively, this is approximately 2.4 Å larger than that found in M<sub>2</sub>(DOBDC) analogues<sup>12C</sup> and is much larger than those found in previous conductive MOFs,<sup>3</sup> suggesting potential applications in donor-acceptor studies.

Attempts to eliminate the unidentified secondary orange product led us to increase the methanol content of the solvent mixture. Although gradual increase of the methanol



**Figure 2.** Portions of the X-ray crystal structure of  $Mn_2(DSBDC)$ . Top: A view of a  $(-Mn-S-)_{\infty}$  chain SBU.  $Mn^4$  and  $Mn^6$  represent 4-coordinated and 6-coordinated Mn sites in activated  $Mn_2(DSBDC)$ . Bottom: A view of one-dimensional infinite pores along the c-axis. H atoms and DMF molecules were omitted for clarity.

content visibly decreased the amount of undesired orange product, it also decreased the crystal size of 1. Pure 1 was obtained as a microcrystalline yellow material when the DMF to methanol ratio reached 2:1. Its identity and purity was verified by powder X-ray diffraction, which revealed a pattern corresponding to that simulated from the single crystal X-ray structure (Figure 3).

Thermogravimetric analysis (TGA) of as-synthesized 1 exhibited a gradual weight loss of 31.8% between 50 °C and 365 °C (Figure S1), which matched well with the expected loss of 2.2 DMF molecules, including both guest and bound DMF molecules. A second weight loss was observed above 400 °C and likely corresponds to ligand and framework decomposition. A better defined TGA trace is obtained if the guest and bound DMF molecules are exchanged with lower-boiling methanol. To achieve this, as-synthesized 1 was subjected to a Soxhlet extraction with freshly dried and deaerated methanol for two days, during which the material acquired a green hue (methanol-exchanged 1). Replacement of DMF by methanol was tested by infrared (IR) spectroscopy, which confirmed the absence of the strong DMF C=O stretch at 1647 cm<sup>-1</sup> previously prominent in as-synthesized 1, and the appearance of a methanol C–O stretch at 1005 cm<sup>-1</sup> (Figure S<sub>3</sub>).  TGA of methanol-exchanged Mn<sub>2</sub>(DSBDC) showed a rapid weight loss below ~ 100 °C and a stable plateau between 150



**Figure 3.** PXRD patterns of as-synthesized 1, methanolexchanged 1, activated 1, and simulated 1. The inset shows an N<sub>2</sub> adsorption isotherm in activated 1 at 77 K.

°C and 400 °C (Figure S2). Accordingly, activation of  $Mn_2(DSBDC)$  was achieved by heating methanol-exchanged 1 at 150 °C and high vacuum (3 mTorr) for two days, to obtain activated 1. The structural integrity of activated 1 was verified by PXRD (Figure 3). The absence of guest and bound methanol was confirmed by IR spectroscopy, and the purity of the sample was confirmed by C, H, and S microanalysis. Upon activation,  $Mn_2(DSBDC)$  adsorbs approximately 240 cm<sup>3</sup>g<sup>-1</sup> of  $N_2$  at 77 K and exhibits a Type I isotherm, shown in Figure 3, inset. The corresponding BET surface area of 978 m<sup>2</sup>g<sup>-1</sup> (329 m<sup>2</sup>mmol<sup>-1</sup>) is comparable with those reported for  $M_2(DOBDC)$  (287 ~ 416 m<sup>2</sup>mmol<sup>-1</sup>).

The charge carrier mobilities of methanol-exchanged 1 and activated 1 were evaluated by flash-photolysis time-resolved microwave conductivity (FP-TRMC). FP-TRMC is a contactless technique which utilizes high frequency (GHz) microwaves to probe the laser-induced transient conductivity increase, giving information on charge transport on the multinanometer length scale. It is particularly informative when measuring anisotropic crystalline materials because it eliminates perturbations related to grain boundaries, defects, impurities, contact resistance, and high electric fields that affect the results obtained by the more common direct current time-of-flight and field-effect-transistor measurements, thereby revealing the intrinsic charge carrier mobility of a material.14 FP-TRMC experiments were performed on films made from PMMA and the above two Mn<sub>2</sub>(DSBDC) materials, which were mixed in 1:1 weight ratios. The films were inserted in a resonant microwave cavity, and were irradiated with 355 nm laser light. We obtained time-dependent values of the transient conductivity,  $\phi \Sigma \mu$ , where  $\phi$  is the quantum efficiency for the generation of charge carriers upon onephoton absorption, and  $\Sigma \mu$  is the sum of electron and hole mobilities. As shown in Figure 4a, the FP-TRMC profiles of methanol-exchanged and activated 1 are virtually identical, displaying maximum values of  $\phi \Sigma \mu = 2 \times 10^{-5} \text{ cm}^2 \text{V}^1 \text{s}^{-1}$ . The



**Figure 4.** (a) Conductivity transients observed by FP-TRMC upon excitation at 355 nm with  $1.4 \times 10^{16}$  cm<sup>-2</sup> photons per pulse for methanol-exchanged 1 and activated 1. (b) Photo-current transients observed by TOF upon excitation at 355 nm with  $1.9 \times 10^{14}$  cm<sup>-2</sup> photons per pulse for methanol-exchanged 1 and activated 1. The transients were observed with a terminate resistance of 10 k $\Omega$  under applied bias at  $3 \times 10^4$  Vcm<sup>-1</sup>.

values of  $\phi$  were estimated by a time-of-flight (TOF) transient current integration method, shown in Figure 4b. The TOF-derived  $\phi$  values for methanol-exchanged 1 and activated 1 were  $9.7 \times 10^{-4}$  and  $1.4 \times 10^{-3}$ , respectively.

The combination of FP-TRMC and TOF results revealed excellent charge carrier mobilities of 0.02 and 0.01 cm<sup>2</sup>V<sup>1</sup>s<sup>-1</sup> for methanol-exchanged and activated Mn<sub>2</sub>(DSBDC), respectively. The similarity between the two values suggests that the charge transport pathway, presumably the Mn-S chain, is not affected greatly by the presence of solvent. Based on the observed charge carrier mobility values and the frequency of the microwave field (9.1 GHz), the displacement lengths of charge carriers (defined as the distance that charge carriers can move in one period of microwave) in these two Mn<sub>2</sub>(DSBDC) materials are found to be approximately 2 ~ 3 nm, corresponding to charge delocalization over 8 ~ 12 Mn-S units.<sup>15</sup> This short displacement length of charge carriers confirms that the results indeed reveal the intrinsic charge

carrier mobility of the materials. As shown in figure 4b, the photo-current transients are principally dispersive ones; some inflection points are detectable to give mean flight time of charge carriers (figure S5). The estimated values of mobility are o.oo cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (E = 0 Vcm<sup>-1</sup>) according to TOF results, which are one order of magnitude lower than those in TRMC, and reflect long-range translational motion of charge carriers. An alternative charge transport pathway may involve transfer through the benzene ring, through the 1,4-benzenedithiol moiety.<sup>16</sup> Experiments that probe this possibility are currently underway.

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Importantly, the charge mobility values observed for  $Mn_2(DSBDC)$  are comparable with those found in organic conductors such as polythiophenes ( $\Sigma \mu = 0.003 \sim 0.1 \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$  $^{1})^{14a,17}$  and rubrene ( $\Sigma \mu = 0.05 \text{ cm}^{2} \text{V}^{-1} \text{s}^{-1}$ ),<sup>18</sup> as measured by the same technique, and highlight the potential utility of MOFs for the construction of various electronic devices that combine high surface area and high charge mobility. In fact, at 978 m<sup>2</sup>g<sup>-1</sup>, Mn<sub>2</sub>(DSBDC) has the highest surface area by almost 50% among MOFs that have demonstrated intrinsic charge delocalization thus far, such as Cu[Ni(pyrazine-2,3dithiolate)<sub>2</sub>] (385 m<sup>2</sup>g<sup>-1</sup>),<sup>3a</sup> Fe(1,2,3-triazolate) (450 m<sup>2</sup>g<sup>-1</sup>),<sup>3</sup> Cu- and Ni-catecholates (~425-490 m<sup>2</sup>g<sup>-1</sup>),<sup>3d</sup> and Zn<sub>2</sub>(TTFtetrabenzoate) (662 m<sup>2</sup>g<sup>-1</sup>).<sup>3c</sup> Notably, because the pore size of the M<sub>2</sub>(DOBDC) structure type can be extended into the mesoporous regime<sup>19</sup> and assuming that a similar isoreticular approach is applicable to Mn<sub>2</sub>(DSBDC), these results reinforce the idea that high surface area, porosity, and high charge mobility are not mutually exclusive.

In summary, a redox-matching strategy<sup>8</sup> aimed at isomorphous substitution of O atoms by S atoms to yield infinite one-dimensional metal-sulfur chains has led to the synthesis of a new MOF with high charge mobility. Because the isomorphous replacement strategy could be amenable to many other MOFs containing metal-oxygen chains, the study provides a potentially general mechanism for the formation of other porous crystalline materials with high charge mobility, not least of which are members of the M<sub>2</sub>(DEBDC) structure types with other transition metals.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Experimental details, table of X-ray refinement details, TGA traces, IR spectra, BET linear fit, and TOF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0006937. The NSF provided support to the DCIF at MIT (CHE-9808061, DBI-9729592). S.S. is supported by the Funding Program for the Next-Generation World-Leading Researchers (NEXT Programs) of the Japan Society for the Promotion of Science (JSPS).

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