

Ligand Redox Non-innocence in the Stoichiometric Oxidation of $\text{Mn}_2(2,5\text{-dioxidoterephthalate})$ (Mn-MOF-74)

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S Supporting Information

ABSTRACT: Unsaturated metal sites within the nodes of metal–organic frameworks (MOFs) can be interrogated by redox reagents common to small molecule chemistry. We show, for the first time, that an analogue of the iconic $\text{M}_2(2,5\text{-dioxidoterephthalate})$ (M_2DOBDC , MOF-74) class of materials can be stoichiometrically oxidized by one electron per metal center. The reaction of Mn_2DOBDC with $\text{C}_6\text{H}_5\text{ICl}_2$ produces the oxidized material $\text{Cl}_2\text{Mn}_2\text{DOBDC}$, which retains crystallinity and porosity. Surprisingly, magnetic measurements, X-ray absorption, and infrared spectroscopic data indicate that the Mn ions maintain a formal oxidation state of +2, suggesting instead the oxidation of the DOBDC^{4-} ligand to the quinone DOBDC^{2-} . These results describe the first example of ligand redox non-innocence in a MOF and a rare instance of stoichiometric electron transfer involving the metal nodes. The methods described herein offer a synthetic toolkit that will be of general use for further explorations of the redox reactivity of MOF nodes.

Owing to their tunability and ordered structures, MOFs have been investigated as promising heterogeneous catalysts ever since their emergence as permanently porous materials.^{1–7} These materials typically mediate reactivity either through their pores, which can host catalytically active molecules or nanoparticles,^{8–10} or through their skeleton. Examples of the latter include the incorporation of known homogeneous catalysts within the bridging ligands^{11,12} and the use of the metal nodes, or secondary building units (SBUs), as active sites.¹³ When the SBUs are involved, they are most widely explored as Lewis-acid catalysts,^{5,14–17} while reports focusing on redox reactivity are rare. However, because SBUs are unique molecular entities,^{18,19} their redox reactivity should uncover new chemistry. So far, no report has demonstrated the ability of the constituent metal ions to stoichiometrically transform from one formal oxidation state to another, one of the fundamental requirements for establishing reactivity patterns at MOF SBUs. Despite notable examples of redox catalysis reportedly mediated by the SBUs,²⁰ only substoichiometric redox changes have been documented thus far at self-assembled MOF nodes.^{19–27}

To address the surprising paucity of examples of stoichiometric redox events at SBUs, we sought to answer the following critical questions: (1) Can all of the metal centers in any MOF

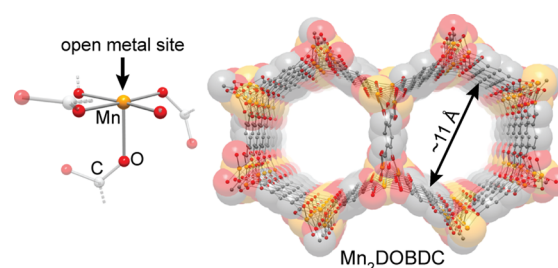


Figure 1. A portion of the X-ray crystal structure of Mn_2DOBDC viewed along the $[001]$ axis, and the coordination environment around the open Mn^{2+} site. H atoms are omitted for clarity.

support a change in oxidation state? (2) Can the porous lattice support the geometry changes that accompany the redox processes?

We chose as our study system the family of materials known as M_2DOBDC (MOF-74), which incorporates a variety of divalent ions.^{28,29} MOF-74 contains a high density of open metal sites lining one-dimensional cylindrical pores of ~ 1.1 nm diameter (Figure 1), which should shuttle reagents either in the gas phase or in solution. Each metal ion sits in a pentacoordinating all-oxygen pocket comprised of weak field carboxylates and phenoxides. Weak ligand fields are attractive for oxidative reactivity studies because they promote high spin electron configurations that afford more accessible redox couples, as is often seen in natural metalloenzymes such as methane monooxygenases and various hydroxylases.^{30,31} Lastly, the MOF-74 structure type exhibits good thermal stability, allowing solvent to be evacuated to furnish unsaturated metal sites with retention of crystallinity and porosity.

A previously unrecognized feature of the system was the possibility of ligand participation in redox events. We surmised that the *p*-hydroquinone unit could be oxidized to the quinone, thereby acting redox non-innocently and enhancing the reactivity at the metal center, similar to what has been documented in molecular catalytic systems.^{32–35} Herein, we show that these factors enable Mn_2DOBDC to withstand reactions with small molecule oxidants in a way that is unprecedented among MOFs. This reactivity showcases a rare example of a stoichiometric

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redox event and the first instance of ligand non-innocence mediated by SBUs in MOFs.^{36–39}

Through a modified procedure (see Supporting Information),^{40–42} we were able to obtain multigram quantities of high-quality Mn₂DOBDC in single batches to explore its gas/solid oxidation chemistry. Our first experiments revealed that kinetically inert oxidants such as O₂ and N₂O did not react with the activated framework at room temperature, while more aggressive oxidants such as O₃ and Cl₂ caused decomposition. The reaction with O₃, introduced as a ~4% (v:v) mixture in O₂, caused spontaneous combustion of the MOF with the concomitant formation of a black solid, even when the reaction was performed at -77 °C. IR spectroscopic analysis of the black material did not reveal any resonances in the 600–4000 cm⁻¹ region, suggesting that the organic portion of the framework had been completely consumed. PXRD analysis confirmed that this product was Mn₃O₄ (Figure S8), a material noted for catalyzing the combustion of organics,⁴³ whose formation may therefore contribute to a self-catalyzed decomposition. Although IR spectroscopy of a Cl₂-treated Mn₂DOBDC sample revealed features reminiscent of the starting material, it also evidenced a general increase in peak widths and a number of important differences (Figure S9). Extensive collapse of the structure was revealed by PXRD (Figure 2) and N₂ adsorption (Figure S10), which indicated poor crystallinity and porosity (S_{A,BET} = 64.2(3) m²/g), respectively.

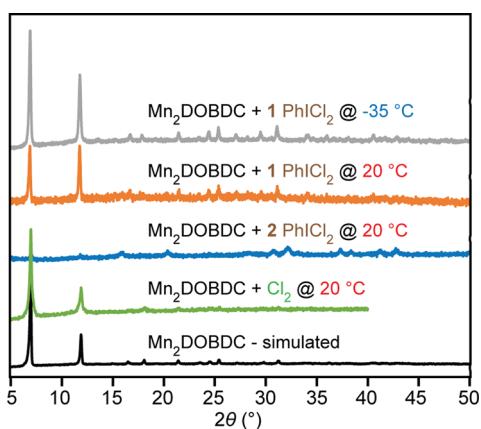


Figure 2. PXRD patterns for pristine, Cl₂- and PhICl₂-treated Mn₂DOBDC under various conditions.

We hypothesized that the aggressiveness of the oxidation reaction would be tempered through the use of solid reagents that could be used in non- or minimally coordinating solvents. For this purpose, we chose iodobenzene dichloride, PhICl₂, which serves as a convenient solid-state substitute for gaseous Cl₂.⁴⁴ Despite using this milder reagent, treatment of Mn₂DOBDC with excess PhICl₂ (PhICl₂:Mn₂DOBDC = 2:1) also produced a material that had lost almost all crystallinity (Figure 2) and porosity (S_{A,BET} = 85.9(3) m²/g) (Figure S10).

We achieved a more controlled process when the stoichiometry was limited to one Cl per Mn atom (i.e., PhICl₂:Mn₂DOBDC = 1:1), which gave a material with S_{A,BET} = 353.3(9) m²/g (Figure S10). A remarkable further improvement was made when the reaction was performed at -35 °C, when a much more gradual orange-to-brown color change of the starting material could be visibly followed. Analysis of the oxidized brown product revealed a highly crystalline material with distinguishable diffraction peaks well past 2θ = 30° (Figure

2). IR analysis of this product also revealed minimal changes in peak shape and position, with the exception of a notable new band at 1657 cm⁻¹, a vibrational frequency indicative of a C=O stretch (Figure 3).

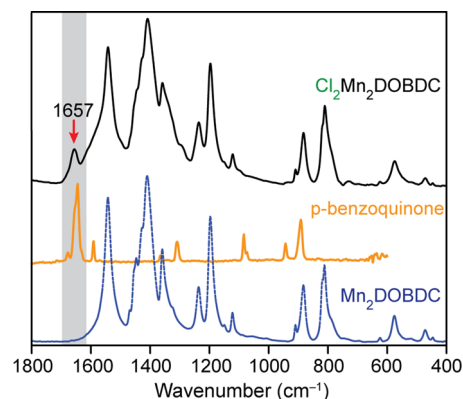


Figure 3. FTIR spectra of Mn₂DOBDC and Cl₂Mn₂DOBDC compared to that of *p*-benzoquinone.

Complete, stoichiometric oxidation of Mn₂DOBDC was confirmed by elemental analysis and a variety of spectroscopic techniques. X-ray photoelectron spectroscopy (XPS) confirmed the presence of chlorine and the absence of iodine (Figure S12), while combustion microanalysis revealed a precise 1:1 Cl:Mn stoichiometry, corresponding to a formula of Cl₂Mn₂(C₈H₂O₆) for PhICl₂-treated Mn₂DOBDC. To further confirm that PhICl₂ was completely consumed in the stoichiometric oxidation of Mn₂DOBDC, the reaction was repeated in CD₂Cl₂, and the formation of iodobenzene was followed by ¹H NMR. This experiment indicated that 36% of the PhICl₂ was consumed after 1 h (Figure S2) and that the reaction was complete after 12 h, when 97% of the initial PhICl₂ could be accounted for as PhI (Figure S3). Since PhICl₂ is known to decompose at elevated temperatures, we monitored the rate of PhICl₂ decomposition with and without Mn₂DOBDC by ¹H NMR to confirm that we were observing MOF-assisted PhI formation. Based on the relative ratios from integrating NMR signals, we observed that 100% of PhICl₂ converts to PhI after 6 h in the presence of Mn₂DOBDC, while only 28% decomposes by itself (Figure S4).

To prove that all chloride atoms were bound to Mn ions, we compared the far-IR spectra obtained for both the pristine and the oxidized materials and observed a new resonance at 237 cm⁻¹, shown in the difference spectrum in Figure S13. This value is within the expected range of M–Cl stretching frequencies.⁴⁵ Additionally, a N₂ adsorption measurement of Cl₂Mn₂DOBDC revealed a S_{A,BET} = 588(3) m²/g (Figure S10), compared to 1353(4) m²/g for the unoxidized sample. When comparing two MOFs with cylindrical pores, the ratio of surface areas is equal to the ratio of pore diameter. Taking into account the van der Waals radii for Mn in the pristine sample and the sum of the ionic radii for Mn and Cl plus the vdW radii for chloride in the oxidized sample and assuming an interatomic column diameter of 15.4 Å, the ratio of accessible surface areas would be 2.5, very consistent with the ratio of measured surface areas, 2.2. This implies a near perfect lining of the interior of the column with Cl bound to the pore-facing Mn ions.

Because all the data above pointed to a stoichiometric oxidation of Mn₂DOBDC and quantitative formation of Cl₂Mn₂DOBDC, we expected that the oxidation took place at the Mn²⁺ centers, with formation of Mn³⁺. However, a magnetic

susceptibility measurement of $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ revealed a room temperature magnetic moment, μ_{eff} of $5.55 \mu_{\text{B}}$, closer to the value of $5.92 \mu_{\text{B}}$ expected for Mn^{2+} with $S = 5/2$ than to $4.90 \mu_{\text{B}}$ expected for high-spin Mn^{3+} . More importantly, μ_{eff} for $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ was nearly identical to the room temperature value obtained for the unoxidized, all- Mn^{2+} sample Mn_2DOBDC ($\mu_{\text{eff}} = 5.47$). We surmised that μ_{eff} of both the oxidized and unoxidized samples were lower than expected for high-spin Mn^{2+} compounds due to antiferromagnetic coupling between neighboring Mn^{2+} sites and neighboring $\text{Mn}^{2+}-\text{O}_{\text{ph}}-\text{Mn}^{2+}$ chains. Indeed, fitting the variable temperature susceptibility data for $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ to the modified Fischer model used previously for Fe_2DOBDC ⁴⁶ gave an intrachain coupling value, J , of -2.3 cm^{-1} and an interchain value, J' , of -1.5 cm^{-1} (Figure S15 and Figure 4, inset). These data suggested that despite

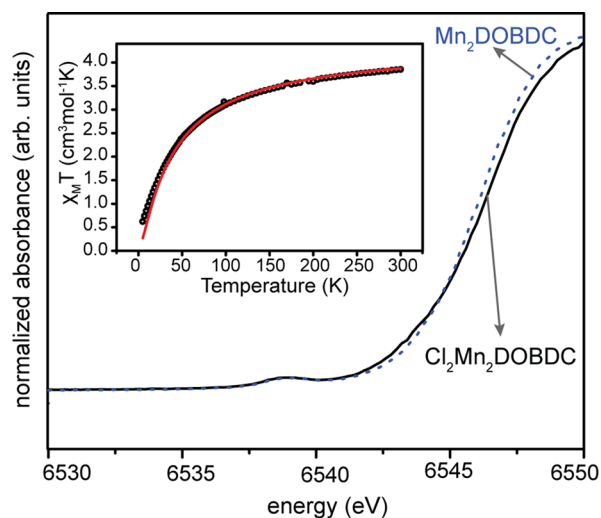


Figure 4. Normalized X-ray absorption near edge spectra of Mn_2DOBDC (blue dashes) and $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ (black solid line). Inset: Variable temperature magnetic susceptibility data in an applied field of 1 kOe. The red line represents a fit to the $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ data.

overall two-electron oxidation of Mn_2DOBDC , the formal oxidation state of Mn remains +2, while DOBDC^{4-} is oxidized to its quinoid form, DOBDC^{2-} . Oxidation of the ligand substantiates the observed antiferromagnetic coupling since bridging *p*-benzoquinone is known to mediate antiferromagnetic coupling in dinuclear complexes.⁴⁷ The formation of a quinone also explains the new IR absorption at 1657 cm^{-1} , which we ascribe to a $\text{C}=\text{O}$ bond, and which is indeed nearly identical to the $\text{C}=\text{O}$ stretch observed in neat *p*-benzoquinone itself (Figure 3).

We turned to X-ray techniques to unambiguously prove the Mn^{2+} oxidation state in $\text{Cl}_2\text{Mn}_2\text{DOBDC}$. Although XPS did not provide sufficient resolution for this purpose, Mn K-edge X-ray absorption spectroscopy revealed that the pre-edge features of both Mn_2DOBDC and $\text{Cl}_2\text{Mn}_2\text{DOBDC}$ occurred at identical energies of 6539 eV (Figure 4). Because the pre-edge feature is associated with a formally forbidden core-to-valence ($1s \rightarrow 3d$) transition band, it should shift to higher energy upon oxidation of 3d metals. Here it does not, and the XAS data thus corroborate our hypothesis of ligand-based oxidation in $\text{Cl}_2\text{Mn}_2\text{DOBDC}$.

To test the plausibility of the Mn ions mediating the ligand oxidation, we repeated the chlorination procedure with Mg_2DOBDC , a MOF-74 analogue with redox-inactive Mg^{2+} . Although PhICl_2 decomposition occurs in the presence of

Mg_2DOBDC to a greater extent than in its absence, the rate of PHI formation was still slower than in the presence of Mn_2DOBDC . More importantly, treatment of Mg_2DOBDC with PhICl_2 did not result in the appearance of a carbonyl peak, as observed for Mn_2DOBDC , and elemental analysis revealed that no Cl atoms were incorporated into the MOF. Together, these demonstrate that Mg_2DOBDC is not oxidized under these conditions and that the ligand remains in its reduced form.

We propose that the oxidation of Mn_2DOBDC occurs by transient formation of a $\text{Mn}^{\text{III}}-\text{Cl}$ intermediate, which mediates the oxidation of the ligand and the formation of the $\text{Cl}-\text{Mn}^{\text{II}}(\text{benzoquinone})$ thermodynamic product, presumably by sequential $1e^-$ steps, as schematically proposed in Figure 5.

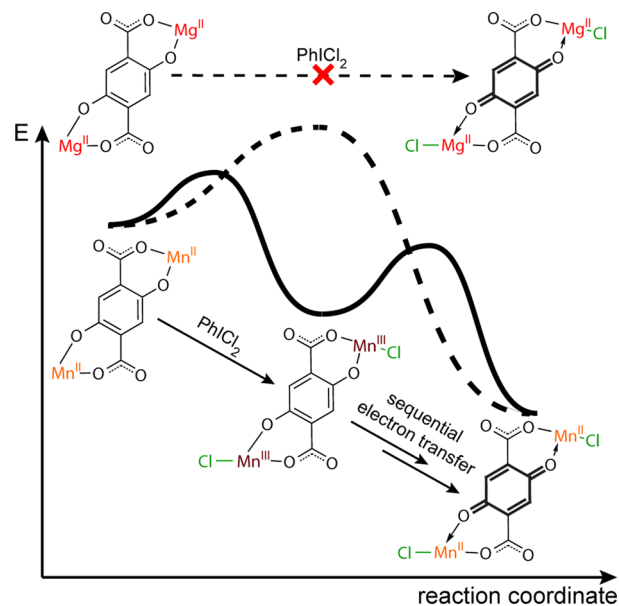


Figure 5. Proposed scheme for the oxidation of Mn_2DOBDC , including the transient formation of a kinetic Mn^{III} product. Presumed $1e^-$ oxidation intermediates are not shown. Because a “ $\text{Cl}-\text{Mg}^{3+}$ ” transient is not available in Mg_2DOBDC , it is not subject to oxidation by PhICl_2 .

These observations describe the first example of a MOF where the ligands engage the metal ions through redox non-innocence in a manner typically associated with small molecule complexes.^{33,48,49} Because catechol/*o*-benzoquinone ligands have been used to support redox catalysis,³⁵ these results may also speak to the utility of deliberately incorporating redox non-innocent ligands into MOFs for more complex reactivity. Because the phenoxide groups in DOBDC^{4-} also play an important structure-supporting role, their involvement in the redox process may be responsible for the observed material sensitivity and the irreversibility of the oxidation process.

Here we demonstrated that the metal nodes in microporous MOFs can be subject to clean stoichiometric oxidations. We also reported the first example of ligand redox non-innocence in MOFs, which may open a new area of exploration in these materials that parallels concepts of redox non-innocence in molecular complexes. During these studies, we established methods to interrogate the redox reactivity of MOF SBUs that maintain the integrity of the framework. These borrow from the synthetic toolkit of homogeneous (molecular) inorganic chemistry and may become general for future studies of SBU reactivity, a vastly underexplored subject in this otherwise popular area.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, NMR, IR, XPS, PXRD, and N₂ adsorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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