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Electrochemically-Mediated Synthesis of Titanium(III)-Based Metal-Organic Frameworks

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Abstract

Although metal-organic frameworks featuring coordinatively-unsaturated transition metal sites are relatively common, examples with redox-active cations are rare. In this report, we describe the electrochemically-mediated synthesis of Ti^{III} -MIL-101 from the inexpensive Ti^{4+} precursor TiCl_4 . The framework obtained via electrosynthesis is identical to that prepared from the significantly more expensive and air-sensitive starting material TiCl_3 . The above electro-synthetic strategy was also extended to prepare Ti^{III} -MIL-100 for the first time. This material represents only the second example of a Ti^{3+} based MOF. Gas adsorption, powder X-ray diffraction, SEM, XPS, and TGA experiments demonstrate that this material is superior in quality to samples of the analogous MOF prepared via conventional routes from starting TiCl_3 . Given the ease with which the electrosyntheses may be carried out and their compatibility with a broad range of bridging ligands, we expect that this new methodology will find utility for the synthesis of a number of novel materials containing coordinatively-unsaturated, redox-active metal cations.

Graphical Abstract

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Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures (PDF)

Spectroscopic and PXRD data (PDF)

Metal-organic frameworks (MOFs) have garnered considerable attention, as they display high surface areas,^{1–3} tunable pore chemistry,^{4–6} and can be prepared from virtually any transition metal cation. These factors distinguish MOFs as highly tunable for numerous applications.⁷ Of the broad material space that is occupied by MOFs, those featuring accessible metal cations on their pore surface, are particularly interesting as such systems can facilitate selective gas binding,⁸ high-density gas storage,⁹ sensing,¹⁰ and serve as sites for small-molecule activation and catalysis.¹¹ However, particularly for the latter which require redox-active metal cation sites, the number of reported materials is limited.^{12–16} For example, although numerous Cr³⁺ MOFs exist, there are only two examples containing this metal in the 2+ oxidation state.¹⁷ Similarly, many examples of Ti⁴⁺ metal-organic frameworks have been reported,^{18–20} but to date there is a single Ti³⁺-based MOF.²¹ This material, Ti^{III}-MIL-101 (Figure 1), is based on trimeric clusters connected to terephthalic acid (H₂bdc) and features a high BET surface area, exposed Ti³⁺ sites, and strong Ti–O₂ interactions via the formation of peroxide adducts. Further, its exposed Ti³⁺ sites are substrate accessible and can strongly bind gas molecules such as CO₂ and H₂.

The preparation of redox-active MOFs generally relies on the use of air-sensitive starting materials, necessitating the use of rigorously air-free reaction conditions and limiting materials discovery throughput. Moreover, for many metal ions in reduced oxidation states, the number of available starting materials are limited, as the synthesis of a metal-organic framework often relies on screening a number of parameters, including counter anion identity, placing additional bottlenecks on discovery of new structures.²² In addressing these limitations, electrochemical methods present an intriguing alternative strategy for synthesis of reduced MOF materials.

Redox reactivity has been coupled to synthesis of MOFs. For example, redox chemistry has been used to drive ligand deprotonation reactions coupled to MOF syntheses.^{23–25} Additionally, electrochemical dissolution of metallic anodes to generate oxidized metal ions (*i.e.*, M⁰ → Mⁿ⁺), has been utilized to synthesize Cu²⁺ and Zn²⁺ based MOFs. Despite these examples, we are aware of no published examples, in which electrochemistry has been

leveraged to alter the oxidation state of a *dissolved metal ion in solution* prior to MOF synthesis. Such a strategy is attractive as it can allow for the oxidation state of dissolved ions to be rapidly tuned via controlled potential electrolysis (CPE) for the targeted synthesis of MOFs containing metal centers in non-traditional, reduced-oxidation states. Additionally, this strategy permits the large number of high-oxidation state metal starting materials that are inexpensive and readily accessible to be converted to higher value reduced forms and facilitate the discovery of new materials containing metal ions in reactive oxidation states. This method also has the advantage that a larger number of reaction conditions can be screened, as they can be set up in the presence of air, then deoxygenated prior to electrochemical reduction. To this end, we targeted the synthesis of novel Ti^{3+} frameworks given their scarcity and potential for small molecule storage and activation.

The Ti^{3+} based MOF Ti^{III} -MIL-101 can be prepared by reaction of exogenous TiCl_3 with terephthalic acid (H_2bdc) at 120 °C in 10:1 N,N'-dimethylformamide (DMF):ethanol for 18 hours under rigorously air-free conditions. In order to prepare this material from Ti^{3+} generated electrochemically from Ti^{4+} sources, we utilized cyclic voltammetry (CV) to determine potentials (Figures S1 – S3) at which Ti^{3+} can be generated from a series of Ti^{4+} based sources (e.g., TiCl_4 , $\text{Ti}(\text{O}^i\text{Pr})_4$, Cp_2TiCl_2). In particular, CVs recorded for solutions of TiCl_4 (Figure 2a) showed a cathodic wave corresponding to Ti^{4+} reduction at $E_{\text{cat}} = -1.20$ V (all potentials reported versus Ag/AgNO_3). Preparative scale reduction of TiCl_4 by CPE at $E_{\text{applied}} = -1.20$ V using a nickel electrode could be monitored by UV-vis spectroscopy (Figure 2b,c). The complete reduction of starting Ti^{4+} to Ti^{3+} was accomplished in as little as 60 minutes. A four-hour CPE ($E_{\text{applied}} = -1.20$ V) of TiCl_4 in the presence H_2bdc and 0.1 M TBAPF₆ as supporting electrolyte in a 10:1 DMF/EtOH mixture using a nickel foam working electrode, followed by heating at 120 °C for 18 hours afforded a crystalline dark purple powder in high yield.

Powder X-ray diffraction experiments indicated the resulting material is isostructural to the previously reported Ti^{III} -MIL-101 phase (Figure S6). The structure is comprised of trimeric Ti^{3+} clusters connected to form tetrahedral building units with bdc^{2-} anions on their vertices. The tetrahedral units are edge linked to afford a structure containing two large mesoporous cages, one with both pentagonal and hexagonal windows and the other comprised solely of pentagonal windows. Ti^{III} -MIL-101 obtained via the previously reported solvothermal method from starting Ti^{3+} displays a BET (Langmuir) surface area of 2970 (4440) m^2/g .²¹ The corresponding material synthesized via electrochemical generation of Ti^{3+} from TiCl_4 has a BET (Langmuir) surface area of 3285 (4360) m^2/g . Although PXRD, SEM, XPS, and TGA analyses indicate the solvothermally and electrochemically generated materials are indistinguishable, synthesis of the latter is accomplished using inexpensive TiCl_4 , as opposed to relying on exogenously prepared and highly air-sensitive TiCl_3 . Of further note is the fact that commercial TiCl_4 is routinely available in 99.9% (and higher purity), while TiCl_3 is typically prepared via aluminum reduction that result in Ti^{3+} starting materials containing appreciable levels of Al^{3+} .

A particular advantage of electrochemically-synthesized reduced metal frameworks, is the management of proton balance throughout the reaction. Significant concentrations of H^+ are generated during the course of solvothermal MOF syntheses as ligands are deprotonated to

form M–L bonds. As many MOF syntheses are dependent on pH, the continually increasing proton concentration can complicate synthesis of phase-pure materials. The electrochemical strategy described above proves a convenient means to manage H^+ build up associated with formation of the bdc^{2-} anions needed for Ti^{III} -MIL-101 synthesis. The nickel foam working electrodes used to generate the Ti^{3+} from $TiCl_4$ show excellent HER activity at significantly lower potentials than those used for the reduction of Ti^{4+} .²⁶ Accordingly, CPE of the $TiCl_4/H_2bdc$ solutions with the nickel cathode not only generates Ti^{3+} , but also reduces the carboxylic acid protons to generate the bdc^{2-} ligands and H_2 , which is evolved from the cathode compartment.

To follow the production of H_2 over the course of the CPE, we monitored the reaction headspace during Ti^{III} -MIL-101 electrosynthesis via gas chromatography.^{27,28} Initial formation of H_2 was detected within as little as 5 min and plateaued after ~3–5 hours. Initial Faradaic efficiencies for HER were <20% and slowly increased to ~70% as concentrations of Ti^{4+} were depleted to generate Ti^{3+} . In accounting for both the reduction of $TiCl_4$ to Ti^{3+} and H_2bdc (or H_3btc , vide infra) protons to H_2 , we consistently observed net current efficiencies in excess of 75 % over the course of the entire CPE.

Given the potentially broad applicability of MOF electro-synthesis from *soluble* metal precursors, we sought to employ this method to expand the library of Ti^{3+} MOFs by targeting other multitopic carboxylate-based ligands. Since the μ_3 -O centered trimeric cluster is ubiquitous to a large number of MIL-type MOFs, we targeted H_3btc -based MIL-100. This structure has previously been reported for trivalent Al,²⁹ Sc,³⁰ V,³¹ Cr,³² Fe,³³ and mixed-metal systems and features connectivity that is analogous to the MIL-101 structure type, but where ligands occupy sites on the faces rather than vertices of the tetrahedral building units. The electrochemical reduction of a $TiCl_4/H_3btc$ DMF:EtOH (10:1) solution containing 0.1 M TBAPF₆ followed by reaction at 120 °C for 18 hours afforded the target material, as confirmed by powder X-ray diffraction (Figure 3). Interestingly, identical solvothermal reaction conditions utilizing commercial $TiCl_3$ rather than electrochemically reduced $TiCl_4$ afforded MOF powders with significantly diminished crystallinity (Figure 3). After thorough solvent exchanges and activation at 100 °C the solvothermally and electrochemically prepared materials showed BET (Langmuir) surface areas of 1304 (1568) and 1736 (2708) m²/g, respectively (Figure 3a). The latter value is in good agreement with those reported for analogous MIL-100 materials.^{30,32}

Despite several attempts, solvothermal syntheses utilizing exogenous $TiCl_3$ as starting material consistently afforded frameworks with lower surface areas compared to those obtained using Ti^{3+} that had been electrochemically generated from $TiCl_4$. The lower surface areas obtained for the solvothermal materials may coincide with a Ti^{4+} -based framework with MIL-100 topology exhibiting a BET surface area of 1321 m²/g that was recently reported.³⁴ We note that XPS analysis of solvothermally-prepared samples of both Ti^{III} -MIL-101 and Ti^{III} -MIL-100 show that each retain chloride as a charge-balancing anion in the frameworks. Electrochemically-prepared samples of these two Ti^{3+} -based frameworks both contain fluoride anions (in place of chloride), which is presumed to originate from the TBAPF₆ supporting electrolyte.

To determine whether the presence of supporting electrolyte improved the surface area of the electrochemically prepared Ti^{III} -MIL-100, TBAPF_6 was added to the solvothermal reaction mixture (exogenous $\text{TiCl}_3/\text{H}_3\text{btc}$). The thusly obtained dark brown product was both amorphous and nonporous. Further, solvothermal syntheses with exogenous $\text{TiCl}_3/\text{H}_3\text{btc}$ consistently afforded materials of smaller particle size (Figure 3c) as compared to syntheses utilizing electrochemically reduced TiCl_4 (Figure 3d).

Given the near complete dearth of Ti^{3+} -based metal-organic frameworks, we sought to further expand the scope of this method to extended pore structures. Although materials of this type based on the M_3O building block have been reported, they typically feature surface areas that are significantly lower than calculated values. MIL-101(Fe)_BPDC, which is a biphenyldicarboxylate-based material that adopts the MIL-101 structure type, displays a BET surface area of just $210 \text{ m}^2/\text{g}$ as compared to the theoretical value of $4500 \text{ m}^2/\text{g}$. A MIL-100 structure based on an expanded tritopic linker displays a BET surface area of just $26 \text{ m}^2/\text{g}$ vs. the expected value of $3990 \text{ m}^2/\text{g}$.³⁵ Analogous to the synthesis of Ti^{III} -MIL-101 and Ti^{III} -MIL-100, the electrochemical reduction of a TiCl_4 solution containing either 4,4'-biphenyldicarboxylic acid (H_2bpdc) or 4,4',4''-[1,3,5]triazine-2,4,6-triyl-tris-benzoic acid (H_3tatb) followed by solvothermal reaction affords Ti^{III} -MIL-101-bpdc and Ti^{III} -MIL-100-tatb, respectively. Ti^{III} -MIL-101-bpdc displays a BET surface area of $3263 \text{ m}^2/\text{g}$ and a pore volume of $2.20 \text{ cm}^3/\text{g}$ which are greatly diminished for a solvothermally-prepared sample ($2139 \text{ m}^2/\text{g}$ and $1.32 \text{ cm}^3/\text{g}$). Similarly, electrochemically-synthesized Ti^{III} -MIL-100-tatb has a BET surface area and pore volume of $5842 \text{ m}^2/\text{g}$ and $4.04 \text{ cm}^3/\text{g}$ as compared to just $740 \text{ m}^2/\text{g}$ and $0.49 \text{ cm}^3/\text{g}$ for solvothermally-synthesized MOF. The pore volume of the electro-chemically-synthesized material is in excellent agreement with the value reported for the analogous Al-based MOF, PCN-333 ($3.81 \text{ cm}^3/\text{g}$).

In conclusion, we have leveraged electrochemical methods to synthesize reduced metal-organic frameworks. Electro-chemical synthesis of Ti^{III} -MIL-101, Ti^{III} -MIL-100, Ti^{III} -MIL-101-bpdc, and Ti^{III} -MIL-100-tatb using the inexpensive, accessible and highly pure Ti^{4+} -based starting material, TiCl_4 generated frameworks with crystallinities and adsorption properties that are as good or superior to those of materials synthesized using exogenous/commercial TiCl_3 . Furthermore, the electrochemically mediated synthesis of Ti^{III} -MIL-100 has provided to first reported route to this MOF.

The electrosynthetic methods disclosed in this report not only generate the high-purity Ti^{3+} ions from which Ti^{III} -MIL-101 and Ti^{III} -MIL-100 structure types are built, but also provides a means to manage solution pH, as the H^+ ions generated upon formation of the frameworks' $\text{Ti}^{3+}\text{-O}_2\text{C-Ar}$ bonds are readily reduced and evolved as H_2 gas. Accordingly, we believe the methods outlined herein provide a new general strategy for the electrochemically mediated synthesis of new redox-active metal-organic frameworks and for the isolation of reduced MOF materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Portions of the MIL-100 and MIL-101 structure types that depict the large pores in the materials. Use of H_2bdc generates MIL-101; use of H_3btc generates MIL-100.

Figure 2.

(a) Cyclic voltammogram recorded of TiCl_4 (1.0 mM) in 10:1 DMF:EtOH containing 0.1 M TBAPF_6 at a scan rate of 100 mV/s. (b) UV-Vis absorption spectra of a $\text{TiCl}_4/\text{H}_2\text{bdc}$ DMF:EtOH solution containing 0.1 M TBAPF_6 during CPE at $E_{\text{applied}} = -1.20$ V. (c) Change in absorbance at $\lambda = 650$ nm during CPE described in (b). (d) Total current density and overall Faradaic efficiency for TiCl_4 and H^+ reduction from $\text{TiCl}_4/\text{H}_2\text{bdc}$ DMF:EtOH solution ($E_{\text{applied}} = -1.20$ V).

Figure 3.

(a) N_2 adsorption in Ti^{III} -MIL-100 at 77 K. (b) PXRD patterns of electrochemically- (blue) and solvothermally-synthesized (red) Ti^{III} -MIL-100 as compared to the predicted powder pattern (black). SEM images for (c) solvothermally- and (d) electrochemically-synthesized Ti^{III} -MIL-100.

Figure 4.

SEM images for (a) electrochemically- and (b) solvothermally-synthesized Ti^{III}-MIL-101-bpdc (c) N₂ adsorption in MIL-101-bpdc at 77 K. SEM images for (d) electrochemically- and (e) solvothermally-synthesized Ti^{III}-MIL-100-tatb (f) N₂ adsorption in MIL-100 tatb at 77 K.