Photosensitizing Metal−Organic Framework Enabling Visible-Light-Driven Proton Reduction by a Wells−Dawson-Type Polyoxometalate

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ⓢ *Supporting Information*

ABSTRACT: A simple and effective charge-assisted self-assembly process was developed to encapsulate a noble-metal-free polyoxometalate (POM) inside a porous and phosphorescent metal−organic framework (MOF) built from $[Ru(bpy)_3]^{2+}$-derived dicarboxylate ligands and $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ secondary building units. Hierarchical organization of photosensitizing and catalytic proton reduction components in such a POM@MOF assembly enables fast multielectron injection from the photoactive framework to the encapsulated redox-active POMs upon photoexcitation, leading to efficient visible-light-driven hydrogen production. Such a modular and tunable synthetic strategy should be applicable to the design of other multifunctional MOF materials with potential in many applications.

As an emerging class of porous molecular solid materials, metal−organic frameworks (MOFs) provide a versatile platform for designing functional materials by judicious choices of bridging ligands and metal/metal cluster connecting points.[1,2] For example, by tuning ligand length, metal-connecting node, network topology, and framework catenation mode, a large number of extremely porous MOFs have been realized.[1−3] On the other hand, the incorporation of functional molecular building blocks into MOFs in the form of bridging ligands and metal cluster secondary building units (SBUs) has led to the rational design of single-site solid catalysts, chemical sensors, bioimaging agents, anticancer therapeutics, and other materials with great potential for many applications.[4−7] In rare examples, the bridging ligands and SBUs in MOFs work synergistically to provide functions that cannot be achieved with either building block alone.[8] To date, however, there are few examples of assembling multifunctional MOFs by incorporating disparate and unique functionalities into both the frameworks and cavities of MOFs.[9] Herein we report the hierarchical assembly of a robust polyoxometalate@MOF system for visible-light-driven proton reduction, a key step in total water splitting.

UiO MOFs have emerged as one of the most important classes of MOFs due to their high stability and porosity as well as the ability to incorporate a multitude of functional building blocks.[10,11] We and others have synthesized photoactive UiO MOFs by incorporating molecular chromophores into UiO frameworks and demonstrated their applications in light-harvesting and photocatalysis.[12] In particular, we have previously

reported effective photocatalysts for hydrogen evolution reactions (HERs) by encapsulating Pt nanoparticles in a photosensitizing UiO MOF.[9a]

Given the extraordinarily large scale of solar energy utilization, there is a strong need to develop earth-abundant element-based photocatalysts. Polyoxometalates (POMs), a class of discrete nanometric molecular clusters composed of earth-abundant elements,[13,14] are particularly attractive as potential catalysts for water-splitting half-reactions due to their ability to undergo fast, reversible, and stepwise multiple electron transfer reactions without changing their structures.[15] Considerable progress has recently been made on designing POM-based materials for light-driven water-splitting half-reactions by introducing a noble metal, transition metal, and other heteroatoms into laucunary POM units.[16,17] Among POMs, saturated Wells−Dawson POMs are the most widely recognized and thoroughly studied, whose reduced forms have been shown to act as catalysts for proton reduction.[18] However, all of the previous studies use either strong UV light or Pt(0) cocatalyst.[18] We demonstrate in this work the incorporation of a Wells−Dawson-type POM into the $[Ru(bpy)_3]^{2+}$-derived UiO MOF by a simple one-pot self-assembly process, which enables visible-light-driven proton reduction via synergistic visible-light excitation of the MOF framework and facile multielectron injection from the excited framework to POM guests (Figure 1).

The $[Ru(bpy)_3]^{2+}$-derived dicarboxylate ligand (H_2L) was prepared by heating $Ru(bpy)_2Cl_2$ with dimethyl (2,2′-bipyridine)-5,5′-dibenzoate (Me_2L) followed by base-catalyzed hydrolysis (Scheme S1). A mixture of H_2L and $ZrCl_4$ was heated at 100 °C for 96 h to afford the $[Ru(bpy)_3]^{2+}$-derived UiO MOF of the formula $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(L)_6](CO_2CF_3)_{12}$ (**1**) in 31.4% yield (Figures S3 and S4). Powder X-ray diffraction (PXRD) studies show that **1** adopts UiO topology, with the pattern matching that of a recently published UiO MOF built from a dicarboxylate ligand of an identical length (Figure 2a).[9a] **1** possesses tetrahedral and octahedral cavities with a triangular open channel with an edge length of 1.6 nm (Figure S4). Nitrogen adsorption measurements of **1** did not give any surface area, presumably due to severe framework distortion upon removal of solvent molecules. **1** is among the minority of MOFs with a highly cationic framework due to the dipositive charges of the H_2L ligand. We hypothesized that the large cavities in such a highly cationic MOF should provide an ideal environment for the
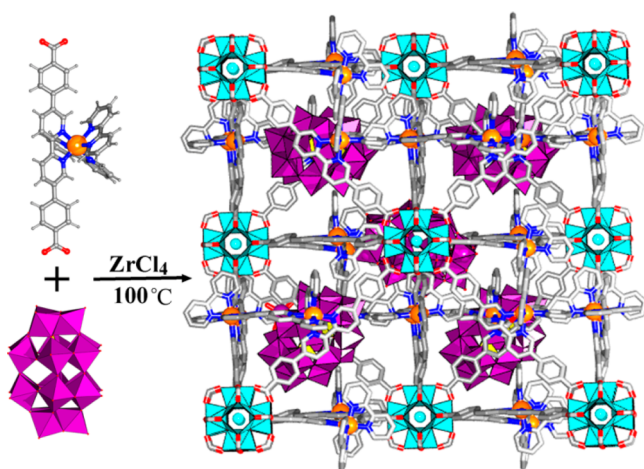
Figure 1. One-pot synthesis of the POM@UiO system via charge-assisted self-assembly. $[P_2W_{18}O_{62}]^{6-}$, purple polyhedra; Zr, cyan; Ru, gold; N, blue; O, red; C, light gray.
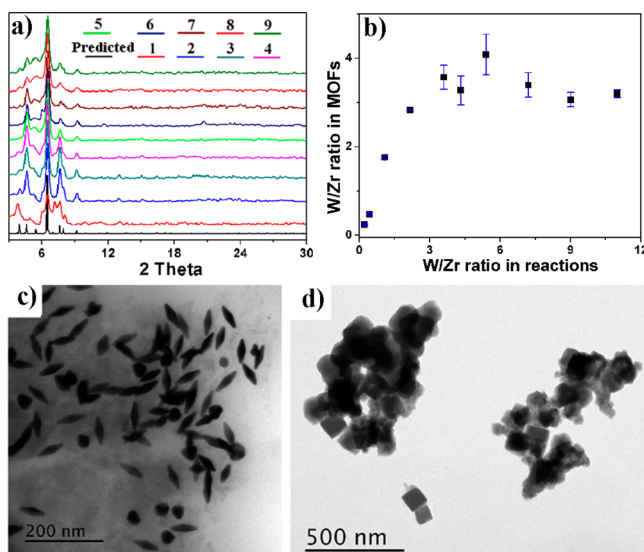

Figure 2. (a) Predicted and experimental PXRD patterns of **1**−**9**. (b) Dependence of the W/Zr ratios of POM@UiO MOFs on the W/Zr ratios in the reaction mixtures (by adjusting the amounts of $[P_2W_{18}O_{62}]^{6-}$ added in the reaction solutions). The W/Zr ratios were determined by ICP-MS. TEM micrographs of (c) POM-free UiO MOF **1** and (d) POM@UiO **3**.

encapsulation of functional anionic entities to lead to multifunctional materials.

The Wells−Dawson-type polyoxoanions $[P_2W_{18}O_{62}]^{6-}$ were loaded into the cavities of MOF **1** via in situ self-assembly by simply heating a mixture of $ZrCl_4$ and H_2L in the presence of the POM. By adjusting the POM feed amount in the reaction mixture, a series of POM@UiO materials, **2**−**9**, with varied POM loadings were obtained (Figures 1 and S5−S7). Inductively coupled plasma−mass spectrometry (ICP-MS) studies gave the W/Zr atomic ratio of 0.24 ± 0.02 to 3.40 ± 0.28 for **2**−**9** when the W/Zr atomic ratio in the feed ranged from 0.22 to 7.2 (Figure 2b). The W/Zr atomic ratio determined by ICP-MS remains essentially constant when the W/Zr atomic ratio in the feed was further increased to larger than 7.2, which was confirmed by the thermogravimetric analysis (Figure S5). Transmission electron microscope (TEM) images showed that the POM-free MOF (**1**) adopted distorted octahedral morphology with particle dimen-

sions of 70 × 25 nm, while the POM-loaded MOFs exhibited cubic morphology with the size of ∼85 nm. With the introduction of the POM, the strong diffraction peak at 2θ = 4.00° became weaker while the diffraction peak at 2θ = 4.58° grew stronger. This trend is consistent with that of the predicated PXRD patterns for POM@UiOs (Figure 2a).

The Ru−polypyridyl chromophores can be readily excited by visible light to the ^{1}MLCT excited state, which efficiently transfers to the ^{3}MLCT state through intersystem crossing.[19] The long-lived ^{3}MLCT state then returns to the ground state to lead to phosphorescence (Figure 3b). The POM-free framework
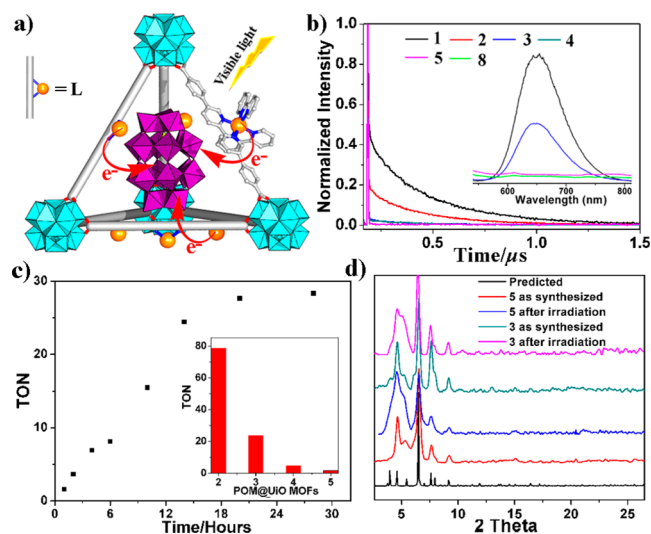

Figure 3. (a) Schematic showing synergistic visible-light excitation of the UiO framework and multielectron injection into the encapsulated POMs. (b) Decay transients measured at 650 nm (λ_{ex} = 450 nm) in acidic water (pH 2.0). Inset: Steady-state emission spectra of POM@UiO with λ_{ex} = 450 nm. (c) Time-dependent HER TONs of **3** with methanol as the sacrificial electron donor (inset: TONs of **2**−**5** after 14 h of HERs). (d) XRD of **5** (in aqueous solution) and **3** (in DMF/CH_3CN) before and after photocatalytic reaction.

1 exhibited a ^{3}MLCT lifetime of 261 ns upon excitation at 450 nm, which is similar to that of the corresponding Me_2L ligand (257 ns). Steady-state photoluminescence spectroscopy showed that ^{3}MLCT emissions were greatly reduced in the POM-loaded MOFs, as shown in Figure 3, and no ^{3}MLCT emission was observed when the W/Zr ratios increased above 2.83. When homogeneous solutions of POM and Me_2L were compared, the POM@UiO assemblies showed an enhanced quenching effect. Time-resolved photoluminescence spectroscopy revealed that the ^{3}MLCT lifetimes were 257, 239, 219, and 23 ns for **2**−**5**, respectively, and decreased to shorter than the instrument response time (<5 ns) when the W/Zr ratios were greater than 2.83 (for **6**−**9**) (Table S1). Lifetimes of the Ru−polypyridyl homogeneous controls exhibited similar behaviors (Table S1), consistent with an earlier report showing that the luminescence quenching is primarily static quenching through the formation of the POM/Ru(bpy)$_3$$^{2+}$ ion pairs.[19b] The efficient quenching of the Ru−polypyridyl ^{3}MLCT emission by encapsulated POMs indicates facile electron transfer from the **L** excited states ($[Ru^{III}(bpy)_2(bpy^{\bullet-})]$) to the POMs due to the ideal POM caging inside a photosensitizing framework, suggesting the possibility of using the POM@UiO assemblies for visible-light-driven proton reduction.

The POM@UiO assemblies were examined for HERs under visible light (>400 nm). In a typical experiment, the POM@UiO assembly was added to an acidic aqueous solution (pH 1.8) containing methanol as the sacrificial electron donor. The reaction mixture was irradiated by a solid-state white light source with a long-pass filter (λ > 400 nm). The headspace gas was analyzed by gas chromatography to quantify the amount of H_2 produced. The H_2 evolved under visible irradiation at rates of 699 and 193 μmol h^{-1} g^{-1} in 14 h with respect to $[P_2W_{18}O_{62}]^{6-}$ in **2** and **3**, respectively. Turnover numbers (TONs) for hydrogen production reached a maximum of 79 [defined as $n(1/2H_2)/n(POM)$]. The POM@UiO can be recovered from the photocatalytic reaction and used for at least three cycles with only slight loss of activity and crystallinity (Table S2 and Figure 3d). ICP-MS analysis of the supernatant after the first photocatalytic reaction showed 5.6% of the Ru leaching into the solution during the reaction, presumably due to photo-degradation of the Ru−polypyridyl chromophore in the MOF.[20] TEM micrographs of the POM@UiO assemblies recovered from the reactions showed the same morphology as the pristine POM@UiO (Figure S12c). These results collectively establish that the POM@UiO assemblies maintain the UiO structure during the photocatalytic HERs. Further, we performed the photocatalytic HER with triethanolamine as the sacrificial electron donor in the DMF/CH$_3$CN mixed solution. TONs reached 307 in 14 h and 540 in 36 h. This level of HER activity is 13 times higher than that of the homogeneous control. The hierarchically encapsulated POM in the photoactive MOF is much more active than the covalent system under visible-light irradiation[17b] and the homogeneous systems under UV-light irradiation.[18a]

We compared the photocatalytic activities of POM@UiO assemblies to those of two homogeneous $[P_2W_{18}O_{62}]^{6-}$/Me$_2$**L** and $[P_2W_{18}O_{62}]^{6-}$/[Ru(bpy)$_3$]Cl$_2$ pairs as controls in the aqueous solution with methanol as the sacrificial electron donor to demonstrate the unique advantage of the POM@MOF assembly. No H_2 production was detected in 14 h for the homogeneous controls at the same POM and chromophore concentrations. It is worth noting that the homogeneous $[P_2W_{18}O_{62}]^{6-}$/Me$_2$**L** pair forms a precipitate after aging in the dark for 24 h (for **4** and **5**) or irradiation by visible light for 14 h (for **2**−**5**) (Figures S9 and S10). The homogeneous $[P_2W_{18}O_{62}]^{6-}$/[Ru(bpy)$_3$]Cl$_2$ pair (for **4** and **5**) also formed a precipitate at higher concentrations by aging in the dark for 24 h or irradiation by visible light for 14 h. In all cases, a red shift was observed for the MLCT bands of the Ru−polypyridyl complexes in the homogeneous systems after irradiation, suggesting decomposition of the Ru chromophores to form [Ru-(bpy)$_2$(H$_2$O)$_2$]$^{2+}$ and related species. This decomposition explains the slight decrease of TONs for the reused POM@UiO catalyst in HERs. POM-free **1** did not produce any hydrogen after a 14 h irradiation (Table S2), excluding the involvement of $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]$ SBUs in catalytic HER under visible irradiation. Actinometric measurements showed that HER for **2** has an average quantum efficiency (QE) of 1 × 10^{-4} at λ = 460 nm in 4 h, while the charge transfer state generation was estimated to have a QE of 0.19 based on steady-state luminescence spectra. The difference in quantum efficiencies of the two steps is consistent with a multielectron injection mechanism.

Cyclic voltammetry (CV) of $[P_2W_{18}O_{62}]^{6-}$ in acidic aqueous solution (pH 1.8) provided important insight into the HER process. $[P_2W_{18}O_{62}]^{6-}$ showed four reversible reduction peaks at 0.22, 0.04, −0.29, and −0.53 V vs NHE and an irreversible catalytic peak with an onset potential of −0.63 V (Figure S14). The CV results indicated the need to inject six or more electrons into each $[P_2W_{18}O_{62}]^{6-}$ for the POM to reduce protons catalytically.[21] The drastically different behaviors of POM@UiOs vs the $[P_2W_{18}O_{62}]^{6-}$/[Ru(bpy)$_3$]Cl$_2$ or $[P_2W_{18}O_{62}]^{6-}$/Me$_2$L$_2$ pair can be attributed to the ability of POM@UiOs to undergo facile multielectron injection into each POM encapsulated by six **L** ligands in the tetrahedral cage (Figure 3a) or by 12 **L** ligands in the octahedral cage (Figure S6). Furthermore, the HER TONs decreased drastically with increasing POM loadings (Figure 3c, inset), indicating that a large **L**/POM ratio is essential for HER and corroborating the necessity of multielectron injection before the onset of catalytic HER. Encapsulation of POMs in the cages of the UiO framework thus provides a unique approach to hierarchically organize the POM/chromophore assemblies and enable the multielectron injection process. The porosity of the POM@UiO assemblies makes the encapsulated POMs accessible to solvents, hydronium ions, and sacrificial agents to enable photocatalytic HER.

In summary, we have developed a simple and effective strategy to prepare a multifunctional molecular material based on a highly stable MOF bearing the $[Ru(bpy)_3]^{2+}$ moiety and an earth-abundant element-based POM. The integration of the photo-active MOF and POM molecules in POM@UiO enables the first example of visible-light-driven proton reduction by a Wells−Dawson-type POM via synergistic photoexcitation of the MOF framework and multielectron injection from the excited states of the $[Ru(bpy)_3]^{2+}$-based bridging ligands to the encapsulated POMs. The modular and tunable nature of this synthetic strategy should allow the design of multifunctional MOF materials for other applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, supplementary structural figures, and supplementary physical characterization 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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