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Porphyrin Grafting on a Mercapto-Equipped Zr(IV)-Carboxylate Framework Enhances Photocatalytic Hydrogen Production

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between the mercapto (-SH) and arylfluoro (Ar–F) groups to achieve extensive and robust cross-linking of a coordination host by porphyrin guests that also serve the purpose of versatile postsynthetic functionalization. For this, a tritopic linker with three trident-like thiol-flanked carboxyl units are reacted with ZrOCl₂·8H₂O to afford a two-dimensional (3,6-connected) net. The wide aperture of the porous framework solid, together with its stability in both air and boiling water, facilitates the entry of bulky metalloporphyrin guests and the subsequent property studies. On the porphyrin side, four pentafluorophenyl (C₆F₅–) groups offer



multiple fluoro groups to facilitate their replacement by the thiol groups from the host net. The inserted metalloporphyrin bridges impart to the metal–organic framework (MOF) host stable and recyclable activities for photocatalytic hydrogen production. We also disclose an improvement in synthetic methodology, in which BBr_3 is used to simultaneously cleave the ester and benzyl thioether groups to more efficiently access thiol-equipped carboxylic acid building block.

■ INTRODUCTION

The versatile mercapto (-SH) function plays an increasingly important role in the development of advanced framework materials for heavy metal removal,¹⁻⁵ catalysis,⁶⁻¹⁰ and electronic/magnetic properties.¹¹⁻¹⁷ The recent synthetic breakthrough in widening the scope of thiol-equipped multitopic carboxylate linker molecules opens further possibilities for the construction and functionalization of metal-organic frameworks (MOFs). Specifically, the benzylthiol-based methodology^{2,9} allows for systematic variation of the thiol arrays/arrangements (e.g., in terms of number and geometric configuration) on the aromatic carboxylic backbone. The thiol-carboxyl building blocks become especially powerful in connection with the chemically hard, highly modular/ persistent Zr(IV)-based nodal units, e.g., in the form of the $Zr_6O_4(OH)_4$ cluster as first uncovered by Lillerud et al. in the original UiO series¹⁸ of coordination solids; the soft thiol groups refrain from bonding to the Zr(IV) centers and, thus, remain free-standing as accessible anchors for postsynthetic modification. Notably, even when it is flanked by the thiol groups (e.g., one on each side to give a symmetrical trident-like motif), the carboxyl donor continues to bind to Zr(IV) to form the prototypal MOF grid.

The versatile reactivity of the thiol-equipped MOF solids being generally underexplored, the newly accessed thiolflanked carboxyl trident motif merits even more attention. For example, the trident motifs serve to surround the $Zr_6O_4(OH)_4$ cluster with a dense array of thiol groups, which provide steric protection as well as disulfide S–S bridges (e.g., from air oxidation) across the linker molecules to promote framework stability.² The seemingly paradoxical pair of stability and reactivity is therefore organically united in the Zr(IV) framework built upon the thiol-flanked carboxyl units.

This study explores the trident motif in the new trigonal planar building block $H_3TTA-6SH$ (Figure 1), while aiming for



Figure 1. Structures of building block H_3 TTA-6SH featuring the trident motif of thiol-flanked carboxyl units, and the porphyrin guests MTFPP with C_6F_5 - units (for easy F-substitution by the thiol groups on the host net).

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a MOF host that proffers the highly nucleophilic thiol functions for conveniently anchoring and integrating the electronically and photochemically active metalloporphyrin guests (Figure 1). Together several design elements can be identified here. The long tris(biphenyl)triazine-based backbone of H₃TTA-6SH is intended to extend the pore aperture in the prospective MOF solid for entering the large porphyrin guests. The porphyrin guests (ZnTFPP, NiTFPP, and FeTFPP), on the other hand, are equipped with multiple fluoro groups, to facilitate their replacements by the thiol groups from the host net, and to help forge sulfide (-S-)crosslinks throughout the coordination host. The resulted thioether (-S-) links can also enhance stability as well as electronic interaction between the MOF scaffold and the porphyrin fragments. In the long run, it is our hope that the easily tunable amount and types of inserted porphyrin guests will help optimize the photochemical and catalytic efficacy in the solid state (e.g., to minimize concentration quenching of the chromophore¹⁹). We now describe the robust twodimensional ZrTTA-6SH network assembled from the H₃TTA-6SH molecule and ZrOCl₂·8H₂O, and the postsynthetic porphyrin anchoring that enhances its performance in photocatalytic hydrogen production from visible light.

EXPERIMENTAL SECTION

The general procedures for synthesis and characterization of ZrTTA-6SH samples (including details of structure simulation and refinement) are included in the Supporting Information (SI).

Synthesis of 2,4,6-Tris{4-[3,5-bis(benzylthio)-4-methoxycarbonylphenyl]phenyl]-1,3,5-triazine (M5). Molecule S1 (2.00 g, 4.36 mmol), bis(pinacolato)diboron (1.107 g, 4.36 mmol), PdCl₂(PPh₃)₂ (77 mg, 0.11 mmol), and anhydrous potassium acetate (941 mg, 9.59 mmol) were loaded in a 100 mL two-neck roundbottom flask and dried under vacuum for 10 min. The flask was then connected to a nitrogen atmosphere. Anhydrous 1,4-dioxane (30 mL, bubbled with nitrogen for 10 min beforehand) was added to the flask. The mixture was stirred at 90 °C for 12 h. After cooling to room temperature, K₃PO₄ aqueous solution (2.3 M, 5.0 mL bubbled with nitrogen for 10 min beforehand) was added, followed by the addition of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (tBPT, 693 mg, 1.27 mmol). The mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the mixture was poured into water (400 mL) and extracted with DCM (3×100 mL). The combined organic phases were washed by distilled water $(3 \times 200 \text{ mL})$. The organic phase was then dried over anhydrous MgSO4 and evaporated by a rotary evaporator. The solid residue obtained was purified by flash column chromatography to afford M5 as a white solid (1.190 g, 65% yield based on 2,4,6-tris(4-bromophenyl)-1,3,5-triazine). ¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.74 - 8.77$ (d, 6H, J = 8.4 Hz), 7.37-7.40 (d, 6H, J = 8.4 Hz, 7.22–7.31 (m, 36H), 4.12 (s, 12H), 4.01 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 171.38, 168.07, 143.22, 141.51, 141.40, 137.19, 135.82, 133.32, 131.89, 129.57, 129.37, 128.65, 127.51, 127.45, 52.74, 40.90 ppm.

Synthesis of 2,4,6-Tris{4-[3,5-bis(benzylthio)-4carboxyphenyl]phenyl}-1,3,5-triazine (MA5). Molecule M5 (578 mg, 0.40 mmol) was dissolved in tetrahydrofuran (7.0 mL) in a 100 mL two-neck round-bottom flask, followed by addition of a KOH solution (8.9 M, 7.0 mL in MeOH/H₂O, v/v = 1:1). The mixture was stirred at 70 °C for 24 h. After cooling to room temperature, 10% HCl (aq) was added to the resulting mixture to attain pH < 2. A yellow precipitate that formed was filtered, washed extensively by distilled water, and suction-dried on the filter paper to afford MA5 as a brown solid (550 mg, 98% yield based on M5). ¹H NMR (300 MHz, DMSO- d_6): δ = 8.80–8.82 (d, 6H, J = 8.4 Hz), 7.78–7.81 (d, 6H, J = 8.4 Hz), 7.53 (s, 6H), 7.24–7.38 (m, 30H), 4.34 (s, 12H) ppm. ¹³C NMR (75 MHz, DMSO- d_6): δ = 170.75, 168.03, 142.93, 140.09, 137.35, 137.07, 135.08, 134.00, 129.42, 129.17, 128.57, 127.60, 127.35, 126.56, 37.79 ppm.

Synthesis of 2,4,6-Tris{4-[3,5-bis(mercapto)-4-carboxyphenyl]phenyl}-1,3,5-triazine (H3TTA-6SH). Molecule MA5 (281 mg, 0.20 mmol), anhydrous AlCl₃ (640 mg, 4.80 mmol), anhydrous DCM (17.0 mL), and dry toluene (2.0 mL) were mixed in a reaction tube in a N2-filled glovebox. After the reaction tube was taken out, the tube was connected to a N2 manifold and stirred at room temperature for 2 h. Afterward, 10% HCl (ag, 10 mL, bubbled with N₂ for 5 min beforehand) was added to the mixture, followed by stirring at room temperature for 2 h. The yellow precipitate formed was collected by suction filtration and washed by 10% HCl (aq), distilled water, and then DCM and dried under vacuum to afford H₃TTA as a brown solid (147 mg, 85% yield based on MA5). ¹H NMR (400 MHz, DMF- d_7): $\delta = 8.91 - 8.94$ (d, 6H, J = 8.4 Hz), 8.02-8.05 (d, 6H, J = 8.4 Hz), 7.85 (s, 6H) ppm. ¹³C NMR (100 MHz, DMF- d_7): $\delta = 171.97, 169.02, 143.76, 142.07, 137.42, 136.52, 130.39,$ 129.82, 128.38, 126.70 ppm. ESI-MS m/z (%): calcd, 860.0 (100%) for [(M-H)⁻]; found, 860.1 (100%) (M – H)⁻; see also Figure S5.

Alternative Synthesis Route to $H_3TTA-6SH$ by Using BBr₃. Under nitrogen protection, molecule M5 (281 mg, 0.20 mmol) was dissolved in anhydrous DCM (3.0 mL) in a 50 mL Schlenk tube charged with a stirring bar and cooled by an ice bath. A BBr₃ solution (1.0 M, 9.0 mL in DCM) was then dropwise added over a period of 10 min. The resulted mixture was further stirred at room temperature for 12 h, after which distilled water was added to the reaction mixture. The resulted yellow precipitate was filtered, washed extensively by distilled water and DCM, and suction-dried on the filter paper to afford $H_3TTA-6SH$ as a yellow solid (164 mg, 95% yield based on M5). The FT-IR spectra of products from two synthesis routes were compared, as shown in Figure S2.

Preparation of Polycrystalline Framework Solid ZrTTA-65H. ZrOCl₂·8H₂O (90 mg, 0.28 mmol) and formic acid (720 mg, 88%, 13.77 mmol) were ultrasonically dissolved in DEF (*N*,*N*-diethylformamide, 5.0 mL). The solution was mixed with H₃TTA-6SH (38 mg, 0.044 mmol) and 1,2-ethanedithiol (170 mg, 1.81 mmol) in a 25 mL Pyrex glass ampule. The ampule was then flame-sealed and heated in an oven at 120 °C for 48 h, followed by programmed cooling to room temperature for 12 h. The pale yellow powder formed was collected by filtration (filter membrane, 0.22 μ m), then washed by DMF (*N*,*N*-dimethylformamide, 3 mL × 10) and acetone (3 mL × 10), and dried under nitrogen flow for weight measurement (63 mg, yield 85% based on H₃TTA-6SH). The above powder was denoted as as-made ZrTTA-6SH.

Activation of ZrTTA-6SH. In a nitrogen-filled glovebox, an asmade ZrTTA-6SH sample (~50 mg) and acetonitrile (6 mL) were added to an 8 mL glass vial with a screw cap (PTFE/Silicone Septa). After the mixture was kept still for 24 h at room temperature, the supernatant was replaced by fresh acetonitrile (6 mL). After three solvent changes, the precipitate was vacuum-dried and denoted as activated ZrTTA-6SH. Elemental analysis found [C (29.60%), H (3.711%), N (2.60%)], a fitting formula can be determined to be $Zr_6O_4(OH)_4(HCOO)_{2.2}(OH)_5(C_{42}H_{24}N_3O_6S_6)_{1.6}(H_2O)_{25}$ (mw 2688.3), which gives a calculated profile as [C (31.01%), H (3.73%), N (2.50%), S (11.45%), Zr (20.36%)]. The as-made ZrTTA-6SH sample was also characterized by TGA (Figure S6), which indicated a final residual weight fraction of 27.8% (ZrO₂), equivalent to a Zr content of 20.56%, matching the fitting formula. The linker/Zr₆ cluster ratio thus determined points to some linker deficiency (about 1.6 TTA-6SH instead of 2.0 for the full occupancy). The capping sites can be occupied by the formate (HCOO⁻) and HO⁻/H₂O species, but notice their ratios here cannot be pinpointed by the current data as their small weight fractions do not impact significantly the elemental and TGA results.

Modification of ZrTTA-6SH by MTFPP. MTFPP ($M = Zn^{2+}$, Ni²⁺, FeCl²⁺) (20 mg, ~0.02 mmol, the preparation of MTFPP molecules was included in SI), ZrTTA-6SH (30 mg, containing ~0.107 mmol S), DMF (1.0 mL), and triethylamine (50 μ L, 0.36 mmol) were loaded into a Pyrex glass tube. The tube was then sealed under vacuum, with the reagents being frozen in liquid nitrogen. After

returning to room temperature, the mixture was ultrasonicated for 30 min and heated at 100 °C in an oven for 24 h (Figure S14). The solid was collected by centrifugation and then washed by DMF (1.0 mL \times 3) and THF thoroughly until the supernatant became totally colorless. The above vacuum-dried sample was denoted as ZrTTA-6SH-MTFPP [ZrTTA-6SH-ZnTFPP (purplish red powder), ZrTTA-6SH-NiTFPP (red powder), ZrTTA-6SH-FeTFPP (green powder)].

Photocatalytic H₂ Production Measurement of ZrTTA-6SH Samples. The photocatalytic hydrogen evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum, i.e., a gas-closed system, at ambient temperature and pressure. Initially, the sample powder (1.0 mg) was stirred and suspended in aqueous triethanolamine (TEOA) solution (5.0 mL, water/TEOA, v/ v = 9:1). Then, a H₂PtCl₆ aqueous solution (10 μ L, 15.4 mM; equivalent to 0.03 mg of Pt, 3 wt % of the catalyst) was injected (for the subsequent in situ photoreduction deposition of Pt particles as cocatalyst). The resulted suspension was purged with argon gas for 20 min to ensure anaerobic conditions, and then it was placed 15 cm away from the lamp (CEL-HXF300). After 1.0 h of irradiation, the released gas (400 μ L) was syringed from the headspace of the reactor and analyzed by a gas chromatograph (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01 (5 Å molecular sieve column) and a thermal conductivity detector (TCD). The total content of photocatalytic H₂ evolution was calculated according to the standard curve. Continuous stirring was applied to the reactor for uniform dispersion and irradiation of the photocatalyst particles.

RESULTS AND DISCUSSION

Improved Linker Synthesis. The synthesis was based on the recently reported method using benzyl mercaptan as a masked thiol agent (e.g., in the form of the starting molecule S1, Figure S1).^{2,9} The difficulty in synthesizing thiol-equipped organic linkers had long been a hinderance in their deployment in MOF chemistry, while the synthesis of H₃TTA-6SH further showcases the wide scope of this method for accessing carboxyl-thiol linker building blocks. As shown in Figure S1, using a one-pot Suzuki-Miyaura protocol, S1 was borylated via bis(pinacolato)diboron and coupled with 2,4,6-tris(4bromophenyl)-1,3,5-triazine to establish the trigonal M5. M5 can be converted into ligand H₃TTA-6SH by the AlCl₃-based procedure, i.e., first hydrolyzing the ester groups in M5 and then removing the benzyl groups by AlCl₃ (Figure S1). Interestingly, the two transformations can be more efficiently accomplished by using BBr3 to simultaneously remove both the methyl and benzyl groups from M5 and to directly afford ligand H₃TTA-6SH in one pot. BBr₃ was previously used to cleave a benzylthio group *ortho* to a sulfonamino unit;²⁰ as the benzylthio groups of M5 are also ortho to the carboxyl unit, we suspect that the ease of benzyl removal in both cases may be assisted by the anchoring of the chemically hard center of BBr₃ onto the terminal oxygen atoms of the sulfonamino or the carboxyl unit, which consequently facilitates the attack on the adjacent benzylthio groups. In practice, the one-pot BBr₃ protocol simplifies the synthesis procedure, increases the yield (up to 95%), and therefore facilitates the exploitation of novel thiol-functionalized ligands.

Preparation and Characterization of MOF Solids. A solvothermal reaction of $H_3TTA-6SH$ and $ZrOCl_2 \cdot 8H_2O$ in DEF (*N*,*N*-diethylformamide), with formic acid as the modulator and 1,2-ethanedithiol to minimize linker oxidation, yielded a pale yellow, crystalline powder of the framework ZrTTA-6SH (nonemissive under UV light). Powder X-ray diffraction studies (Figure 2) indicate that ZrTTA-6SH crystallizes into a kgd net (Figure 3), being isoreticular to



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Figure 2. Powder X-ray diffraction patterns (Cu K α , λ = 1.5418 Å): (a) calculated from the structure model of ZrTTA-6SH (with modification of crystalline size (20 nm × 20 nm × 2 nm) and preferred orientation (March-Dollase, 100, 3); (b) measured from an as-made ZrTTA-6SH sample; (c) measured from an active ZrTTA-6SH sample; (d) measured from a boiling-water-treated ZrTTA-6SH sample.



Figure 3. Single layer (a) and packing structure (b) of ZrTTA-6SH. Zr coordination polyhedra are displayed in green. N, S, O, and C atoms are displayed as blue, yellow, red, and gray beads, respectively.

UMCM-309a, which is based upon the smaller tritopic linker 1,3,5-(4-carboxylphenyl)benzene.²¹ Specifically, the structure of ZrTTA-6SH can be modeled on a hexagonal cell, with the optimized parameters of a = b = 27.20 Å, c = 7.26 Å. The Pawley refinement produced a close match between the peak positions ($R_p = 4.63\%$, $R_{wp} = 3.13\%$) (Figure S13). The reliability of the structure model was also checked by comparing the calculated PXRD patterns with the experimental ones (as shown in Figure 2). The results confirmed the formation of eclipsed, hexagonal stacking of the MOF layers, which was built on planar tripod linkers to form the rhombustiled, binodal 3,6-connected kgd net. The particle size of ZrTTA-6SH was found by SEM imaging in a range of 200–400 nm (Figure S8), while transmission electron microscopy



Figure 4. (a) Kubelka–Munk plots of a series of ZrTTA-6SH. (b) Powder X-ray diffraction patterns (Cu K α , λ = 1.5418 Å) of modified ZrTTA-6SH samples. (c) Photocatalytic performance of a series of ZrTTA-6SH samples. The photocatalytic irradiation systems were purged by Ar every 3 h. (d) Schematic diagram illustrating the proposed mechanism of charge separation and hydrogen production upon irradiation with visible light.

(TEM) and selected area electron diffraction (SAED) images (Figure S9) confirmed the hexagonal geometry and layered morphology. The SEM and TEM also reveal very thin platelets (20–30 nm thick), corresponding to the thickness of 30–40 single layers. The elemental analysis results on an activated ZrTTA-6SH solid can be fitted with the formula $Zr_6O_4(OH)_{4^-}$ (HCOO)_{2.2}(OH)₅(TTA-6SH)_{1.6}(H₂O)₂₅ (mw 2688, TTA-6SH = $C_{42}H_{24}N_3O_6S_6$), indicating one-fifth of the 3-connected linkers are missing in the **kgd** net (see also Figures S6 and S7 for the TGA plot and FT-IR spectra).

 N_2 sorption (77 K) of activated ZrTTA-6SH features a typical type-I isotherm (Figure S10), revealing a BET surface area of 265 m²/g. QSDFT analysis on the sorption data showed an average pore size value of 1.26 nm and a micropore volume of 0.082 cm/g (Figure S11). Meanwhile, CO₂ sorption (195 K) and Langmuir linear fitting provided a type-I isotherm plot as well and a surface area of 360 m²/g (Figure S12). Powder X-ray diffraction (PXRD) of ZrTTA-6SH also indicated no degradation of crystallionity when the activated sample was exposed in air, or when it was boiled in water for 12 h (Figure 2, pattern d).

Postsynthetic Porphyrin Insertion. The facile substitution of aromatic fluorides by thiol nucleophiles has been well documented. In our earlier work,² the simple pentafluorobenzaldehyde (C_6F_5 CHO) guests were used to cross-link the mercapto side groups in the MOF solid of ZrOMTP (NU-1100-type net) to enhance the stability of the coordination host framework (e.g., against the corrosive NaF aqueous solutions). Further cross-linking studies using polyfluoro aromatics with more advanced functions, however, are still needed to impart more diverse properties to thiol-equipped porous solids. In this connection, we set our eyes on the porphyrin guests not only for the versatile chemical and photophysical properties of the porphyrin core but also for the multiple (i.e., 20 in total) fluoro groups on its four pentafluorophenyl arms. To incorporate the bulky π -conjugated planar metalloporphyrin guests of MTFPP (each molecule is about 1.30 nm wide), the large pore aperture (about 1.8 nm wide; see Figure S15 for an illustration) of the ZrTTA-6SH framework is helpful.

The reaction of the metalloporphyrin guests MTFPP ($M = Zn^{2+}$, Ni²⁺, and FeCl²⁺) with the MOF host ZrTTA-6SH was conducted using DMF as the solvent and triethylamine as base under anaerobic conditions. After the metalloporphyrin treatment (24 h at 100 °C), the colors of the MOF solids became darker (ZrTTA-6SH-ZnTFPP is purplish red, ZrTTA-6SH-NiTFPP is red, and ZrTTA-6SH-FeTFPP is green); accordingly, MTFPP modified solids exhibit strong absorption in the longer wavelength region, with relatively well-defined absorption edges identifiable for ZrTTA-6SH-ZnTFPP and ZrTTA-6SH-NiTFPP (corresponding band gaps: 1.75 eV; Figure 4a). The absorption edge for ZrTTA-6SH-FeTFPP, however, is less distinct, with a slowly decreasing absorption slope extending to as low as 1.2 eV. By comparison, the

pristine ZrTTA-6SH (light yellow in color) exhibits an optical band gap of about 2.74 eV (Figure 4a), being over 1.0 eV higher than the metalloporphyrin modified systems. The absorbance spectra of MTFPP-modified ZrTTA-6SH samples (Figure S16) reveal more clearly the characteristic Soret and Q bands (located around 400 and 550 nm, respectively) from the MTFPP moieties. The incorporation of the large MTFPP guest molecules into the MOF matrix is facilitated by the large pore width and the layered morphology (as revealed by the above SEM and TEM images): for example, the latter allows the exfoliation into many thin platelets to maximize contacts

the extoliation into many thin platelets to maximize contacts between the MTFPP guest molecules and the MOF phase. The expandable interlayer spacing of 2D MOF sheets has also been exploited by Choe for facile pillar replacement,²² and more recently by Wang, Yuan, and Zhou to anchor porphyrin ligands across the nanosheets of a 2D Zr-carboxylate solid as accessible photosensitizers for artemisinin production.²³

After the MTFPP modification, the crystalline lattice of the ZrTTA-6SH host remained unchanged, as indicated by the PXRD patterns (Figure 4b). The formation of thioether links between the MTFPP guests and the ZrTTA-6SH scaffold is consistent with the depletion of thiol groups (the weakening of the S–H stretch at 2570 cm⁻¹ in FT-IR, Figure S17), and with the emergence of higher binding energy peaks in the S 2p XPS spectra (see Figure S18). ICP-OES (Table S1) results also revealed the successful incorporation of the MTFPP guests: the ratios of the Zn/Ni/Fe ions over the Zr₆ cluster were determined by ICP-OES to be 0.460, 0.236, and 0.164, respectively. Semiquantitative EDX results (Figure S19) also confirm the decreasing order of ZnTFPP, NiTFPP, and FeTFPP for the amounts loaded. The loading possibly depends on the aggregation and solvation of the porphyrin guests in solution: e.g., the flat, square planar Ni²⁺ allows stronger porphyrin stacking (relative to the octahedral, axially coordinated Zn^{2+}), stacking that hinders the individual guest from entering the pores, while the polar, ionic Fe(III)-Cl unit in FeTFPP may induce even greater aggregation and solvation that further hamper diffusion. The quantitative difference between the ICP and EDX data can be partly due to surface enrichment; namely, EDX only detects elements near the sample surface—and it may be easier for the S atoms closer to the surface to anchor the MTFPP guests. The ICP-OES results, on the other hand, are more representative of the bulk sample. Incidentally, a longer time of treatment and higher guest concentrations did not increase the loading; perhaps, the inserted guest molecules into the narrow openings hamper the entry of additional guests (see Figure S15 for an illustration on the occupation of the channel by an MTFPP molecule).

Hydrogen Production Catalysis Studies. Metalloporphyrin compounds have been widely studied for their versatile photophysical properties, e.g., strong absorbance in the UV– visible region, photosensitizing capabilities, and flexible functionalization via peripheral substitution or inner metal complexations. Porphyrin-equipped MOF materials are much researched as heterogeneous catalysts (e.g., photocatalysts), because of the large accessible surface area, potentially easy separation, and good recyclability.^{22,24–35} In photocatalytic H₂ production,³⁶ for instance, a general mechanism for charge separation and catalysis proceeds as follows. Photonic excitation of the metalloporphyrin groups creates electrons and holes. The sacrificial electron donor (e.g., triethanolamine) quenches the hole subsequently, while the photoexcited electron migrates to cocatalyst Pt species, leading to reduction of the H^+ on Pt to produce hydrogen gas (as shown in Figure 4d).

The photocatalytic H₂ generation reaction was set up under visible light irradiation, in which different ZrTTA-6SH samples act as heterogeneous photocatalysts, TEOA acts as a sacrificial electron donor, and Pt acts as a cocatalyst to enhance the hydrogen-evolution capability. Initially, we tested the pristine ZrTTA-6SH as photocatalyst, which exhibited very little H₂ evolution, as shown in Figure 4c. Impressively, after the grafting of the ZnTFPP guests, the amount of H₂ evolution was found to be 110 μ mol/g/h and the generation rate was constant for 9 h (i.e., 3 cycles, driven by visible light), which is better than commercial Pt/Black TiO₂,³⁷ Pure TiO₂³⁸ and some reported MOF systems.^{39–42} Similarly, ZrTTA-6SH-NiTFPP and ZrTTA-6SH-FeTFPP samples also exhibit better catalytic activity (71 and 17 μ mol/g/h, respectively) than pristine ZrTTA-6SH (Figure 4c). The activities thus observed of the three systems formally correlate with the amount of the MTFPP guests anchored into the ZrTTA-6SH host: i.e., 175, 90, and 62 µmol/g for ZrTTA-6SH-ZnTFPP, ZrTTA-6SH-NiTFPP, and ZrTTA-6SH-FeTFPP, respectively. Heterogeneous photocatalytic processes are, however, complex, involving various intertwined steps of excitation and energy/ electron transfer; it therefore remains to be seen how the H₂ production activity relates to the concentration and electronic configuration of the metalloporphyrin moieties grafted. As for each individual site of MTFPP as an active center, the turnover frequency (TOF) was correspondingly determined to be 0.63, 0.79, and 0.28 h^{-1} , which is moderate compared with other heterogeneous photocatalytic MOFs.⁴³⁻⁴⁵ More than 95 wt % of the ZrTTA-6SH solids were collected by centrifugation after the photoirradiation and their crystalline structure of ZrTTA-6SH framework was maintained, as confirmed by PXRD (Figure S20).

The above preliminary tests therefore showcase the photocatalytic activity imparted by the anchoring of the metalloporphyrin guests. Also notable are the recyclability of the metalloporphyrin-modified MOF materials and their intact crystalline structures after multiple cycles of photocatalytic reactions. In this light, the strong C-S-C (thioether) covalent bonds between the framework and the metalloporphyrin (MTFPP) guests serve as a robust anchor that prevents guest leaching and ensures long-standing activity of catalysis. In future studies, it is of interest to probe how the triazine core, with its electron-withdrawing and polar features, impacts the optoelectronic properties, and whether it may facilitate the diffusion of the hydrophilic reagents (e.g., aqueous triethanolamine, TEOA) into the channels. It would also be instructive to investigate the roles of the multiple sulfur groups in the photocatalytic process, e.g., how they interact with and impact the catalytically active Pt species.

SUMMARY

Taken together, the accommodation and the covalent grafting of the metalloporphyrin guests onto the porous framework of ZrTTA-6SH have been demonstrated by the resultant enhancement of photocatalytic activity for H₂ production. The robust catalytic performance is reflected in the persistent activity as well as the intact crystallinity of the powder sample after multiple cycles of catalytic tests. The photoactive, large π conjugated metalloporphyrin bridges conveniently built into the MOF matrix represent another step forward in our longstanding efforts to both structurally and functionally integrate the two worlds of coordination and covalent frameworks. On the level of molecular design, the trigonal planar geometry of the H_3 TTA-6SH molecule, with its extended arms, helps to generate the two-dimensional ZrTTA-6SH coordination framework with large pore width to facilitate guest encapsulation. The 2D, lamellar ZrTTA-6SH net also facilitates exfoliation for future studies on solution dispersion, functionalization, and processing. Such future studies would clearly benefit from the framework stability and reactivity arising from the trident donor motif, in which the carboxyl unit is abutted by the mercapto groups in a symmetrical and appealing form.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01744.

TGA plot, IR and XPS spectra, solution ${}^{1}\text{H}/{}^{13}\text{C}$ NMR spectra, PXRD, and gas sorption data (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Yee, K.-K.; Reimer, N.; Liu, J.; Cheng, S.-Y.; Yiu, S.-M.; Weber, J.; Stock, N.; Xu, Z. Effective Mercury Sorption by Thiol-Laced Metal-Organic Frameworks: in Strong Acid and the Vapor Phase. *J. Am. Chem. Soc.* **2013**, *135*, 7795–7798.

pubs.acs.org/IC

(3) Ding, L.; Luo, X.; Shao, P.; Yang, J.; Sun, D. Thiol-Functionalized Zr-Based Metal–Organic Framework for Capture of Hg(II) through a Proton Exchange Reaction. *ACS Sustainable Chem. Eng.* **2018**, *6*, 8494–8502.

(4) Yang, P.; Shu, Y.; Zhuang, Q.; Li, Y.; Gu, J. A robust MOF-based trap with high-density active alkyl thiol for the super-efficient capture of mercury. *Chem. Commun.* **2019**, *55*, 12972–12975.

(5) Li, X.; Ma, W.; Li, H.; Zhang, Q.; Liu, H. Sulfur-functionalized metal-organic frameworks: Synthesis and applications as advanced adsorbents. *Coord. Chem. Rev.* **2020**, *408*, 213191.

(6) Pullen, S.; Fei, H.; Orthaber, A.; Cohen, S. M.; Ott, S. Enhanced photochemical hydrogen production by a molecular diiron catalyst incorporated into a metal-organic framework. *J. Am. Chem. Soc.* **2013**, *135*, 16997–17003.

(7) Fei, H.; Cohen, S. M. Metalation of a Thiocatechol-Functionalized Zr(IV)-Based Metal-Organic Framework for Selective C-H Functionalization. *J. Am. Chem. Soc.* **2015**, *137*, 2191–2194.

(8) Gui, B.; Yee, K.-K.; Wong, Y.-L.; Yiu, S.-M.; Zeller, M.; Wang, C.; Xu, Z. Tackling poison and leach: catalysis by dangling thiolpalladium functions within a porous metal-organic solid. *Chem. Commun.* **2015**, *51*, 6917–6920.

(9) Wong, Y.-L.; Diao, Y.; He, J.; Zeller, M.; Xu, Z. A Thiol-Functionalized UiO-67-Type Porous Single Crystal: Filling in the Synthetic Gap. *Inorg. Chem.* **2019**, *58*, 1462–1468.

(10) Liu, D.-C.; Ouyang, T.; Xiao, R.; Liu, W.-J.; Zhong, D.-C.; Xu, Z.; Lu, T.-B. Anchoring Co^{II} Ions into a Thiol-Laced Metal-Organic Framework for Efficient Visible-Light-Driven Conversion of CO₂ into CO. *ChemSusChem* **2019**, *12*, 2166–2170.

(11) Sun, L.; Miyakai, T.; Seki, S.; Dincǎ, M. $Mn_2(2,5-disulfhydrylbenzene-1,4-dicarboxylate): A Microporous Metal-Organic Framework with Infinite (-Mn-S-)_∞ Chains and High Intrinsic Charge Mobility.$ *J. Am. Chem. Soc.***2013**,*135*, 8185–8188.

(12) Cui, J.; Xu, Z. An electroactive porous network from covalent metal-dithiolene links. *Chem. Commun.* **2014**, *50*, 3986–3988.

(13) Sun, L.; Hendon, C. H.; Minier, M. A.; Walsh, A.; Dincǎ, M. Million-Fold Electrical Conductivity Enhancement in Fe₂(DEBDC) versus Mn_2 (DEBDC) (E = S, O). *J. Am. Chem. Soc.* **2015**, 137, 6164–6167.

(14) Huang, X.; Sheng, P.; Tu, Z.; Zhang, F.; Wang, J.; Geng, H.; Zou, Y.; Di, C.-a.; Yi, Y.; Sun, Y.; Xu, W.; Zhu, D. A two-dimensional π -d conjugated coordination polymer with extremely high electrical conductivity and ambipolar transport behaviour. *Nat. Commun.* 2015, *6*, 7408.

(15) Huang, J.; He, Y.; Yao, M.-S.; He, J.; Xu, G.; Zeller, M.; Xu, Z. A semiconducting gyroidal metal-sulfur framework for chemiresistive sensing. *J. Mater. Chem. A* **201**7, *5*, 16139–16143.

(16) Huang, X.; Li, H.; Tu, Z.; Liu, L.; Wu, X.; Chen, J.; Liang, Y.; Zou, Y.; Yi, Y.; Sun, J.; Xu, W.; Zhu, D. Highly Conducting Neutral Coordination Polymer with Infinite Two-Dimensional Silver–Sulfur Networks. J. Am. Chem. Soc. **2018**, 140, 15153–15156.

(17) Dong, R.; Zhang, Z.; Tranca, D. C.; Zhou, S.; Wang, M.; Adler, P.; Liao, Z.; Liu, F.; Sun, Y.; Shi, W.; Zhang, Z.; Zschech, E.; Mannsfeld, S. C. B.; Felser, C.; Feng, X. A coronene-based semiconducting two-dimensional metal-organic framework with ferromagnetic behavior. *Nat. Commun.* **2018**, *9*, 2637.

(18) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.

(19) Fateeva, A.; Chater, P. A.; Ireland, C. P.; Tahir, A. A.; Khimyak, Y. Z.; Wiper, P. V.; Darwent, J. R.; Rosseinsky, M. J. A Water-Stable Porphyrin-Based Metal–Organic Framework Active for Visible-Light Photocatalysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 7440–7444.

(20) Altamura, M.; Fedi, V.; Giannotti, D.; Paoli, P.; Rossi, P. Privileged structures: synthesis and structural investigations on tricyclic sulfonamides. *New J. Chem.* **2009**, *33*, 2219–2231.

(21) Ma, J.; Wong-Foy, A. G.; Matzger, A. J. The Role of Modulators in Controlling Layer Spacings in a Tritopic Linker Based Zirconium 2D Microporous Coordination Polymer. *Inorg. Chem.* **2015**, *54*, 4591–4593.

(22) Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W. Stepwise Synthesis of Metal-Organic Frameworks: Replacement of Structural Organic Linkers. J. Am. Chem. Soc. **2011**, 133, 9984–9987.

(23) Wang, Y.; Feng, L.; Pang, J.; Li, J.; Huang, N.; Day, G. S.; Cheng, L.; Drake, H. F.; Wang, Y.; Lollar, C.; Qin, J.; Gu, Z.; Lu, T.; Yuan, S.; Zhou, H.-C. Photosensitizer-Anchored 2D MOF Nanosheets as Highly Stable and Accessible Catalysts toward Artemisinin Production. *Adv. Sci.* **2019**, *6*, 1802059.

(24) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. Assembly of porphyrin building blocks into network structures with large channels. *Nature* **1994**, *369*, 727–729.

(25) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. Crystal engineering with tetraarylporphyrins, an exceptionally versatile building block for the design of multidimensional supramolecular structures. *Chem. Commun.* **1998**, 1435–1436.

(26) Kosal, M. E.; Chou, J. H.; Wilson, S. R.; Suslick, K. S. A functional zeolite analogue assembled from metalloporphyrins. *Nat. Mater.* **2002**, *1*, 118–121.

(27) Li, K.; Huang, G.; Xu, Z.; Zhang, M.; Zeller, M.; Hunter, A. D.; Chui, S. S.-Y.; Che, C.-M.; Wong, W.-Y. Multiple Bismuth(III)– Thioether Secondary Interactions Integrate Metalloporphyrin Ligands into Functional Networks. *Inorg. Chem.* **2007**, *46*, 4844–4849.

(28) Alkordi, M. H.; Liu, Y.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M. Zeolite-like Metal-Organic Frameworks as Platforms for Applications: on Metalloporphyrin-Based Catalysts. *J. Am. Chem. Soc.* **2008**, *130*, 12639–12641.

(29) Barron, P. M.; Wray, C. A.; Hu, C.; Guo, Z.; Choe, W. A Bioinspired Synthetic Approach for Building Metal-Organic Frameworks with Accessible Metal Centers. *Inorg. Chem.* **2010**, *49*, 10217–10219.

(30) DeVries, L. D.; Barron, P. M.; Hurley, E. P.; Hu, C.; Choe, W. Nanoscale Lattice Fence" in a Metal-Organic Framework: Interplay between Hinged Topology and Highly Anisotropic Thermal Response. J. Am. Chem. Soc. 2011, 133, 14848–14851.

(31) Gao, W.-Y.; Chrzanowski, M.; Ma, S. Metal-metalloporphyrin frameworks: a resurging class of functional materials. *Chem. Soc. Rev.* **2014**, *43*, 5841–5866.

(32) Johnson, J. A.; Zhang, X.; Reeson, T. C.; Chen, Y.-S.; Zhang, J. Facile Control of the Charge Density and Photocatalytic Activity of an Anionic Indium Porphyrin Framework via in Situ Metalation. *J. Am. Chem. Soc.* **2014**, *136*, 15881–15884.

(33) Johnson, J. A.; Luo, J.; Zhang, X.; Chen, Y.-S.; Morton, M. D.; Echeverria, E.; Torres, F. E.; Zhang, J. Porphyrin-metalation-mediated tuning of photoredox catalytic properties in metal-organic frameworks. *ACS Catal.* **2015**, *5*, 5283–5291.

(34) Liu, Y.; Howarth, A. J.; Hupp, J. T.; Farha, O. K. Selective Photooxidation of a Mustard-Gas Simulant Catalyzed by a Porphyrinic Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2015**, *54*, 9001–9005.

(35) Wang, K.; Lv, X.-L.; Feng, D.; Li, J.; Chen, S.; Sun, J.; Song, L.; Xie, Y.; Li, J.-R.; Zhou, H.-C. Pyrazolate-Based Porphyrinic Metal-Organic Framework with Extraordinary Base-Resistance. *J. Am. Chem. Soc.* **2016**, *138*, 914–919.

(36) Ladomenou, K.; Natali, M.; Iengo, E.; Charalampidis, G.; Scandola, F.; Coutsolelos, A. G. Photochemical hydrogen generation with porphyrin-based systems. *Coord. Chem. Rev.* **2015**, 304–305, 38–54.

(37) Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, *331*, 746–750.

(38) He, Z.; Fu, J.; Cheng, B.; Yu, J.; Cao, S. $Cu_2(OH)_2CO_3$ clusters: Novel noble-metal-free cocatalysts for efficient photocatalytic

hydrogen production from water splitting. Appl. Catal., B 2017, 205, 104–111.

(39) Guo, Y.; Zhang, J.; Dong, L.-Z.; Xu, Y.; Han, W.; Fang, M.; Liu, H.-K.; Wu, Y.; Lan, Y.-Q. Syntheses of Exceptionally Stable Aluminum(III) Metal–Organic Frameworks: How to Grow High-Quality, Large, Single Crystals. *Chem. - Eur. J.* **2017**, *23*, 15518–15528.

(40) Yu, Q.; Dong, H.; Zhang, X.; Zhu, Y. X.; Wang, J. H.; Zhang, F. M.; Sun, X. J. Novel stable metal-organic framework photocatalyst for light-driven hydrogen production. *CrystEngComm* **2018**, *20*, 3228–3233.

(41) Karthik, P.; Vinoth, R.; Zhang, P.; Choi, W.; Balaraman, E.; Neppolian, B. $\pi - \pi$ Interaction Between Metal–Organic Framework and Reduced Graphene Oxide for Visible-Light Photocatalytic H₂ Production. ACS Appl. Energy. Mater. **2018**, *1*, 1913–1923.

(42) Kamakura, Y.; Chinapang, P.; Masaoka, S.; Saeki, A.; Ogasawara, K.; Nishitani, S. R.; Yoshikawa, H.; Katayama, T.; Tamai, N.; Sugimoto, K.; Tanaka, D. Semiconductive Nature of Lead-Based Metal–Organic Frameworks with Three-Dimensionally Extended Sulfur Secondary Building Units. J. Am. Chem. Soc. 2020, 142, 27–32.

(43) Liao, W.-M.; Zhang, J.-H.; Wang, Z.; Yin, S.-Y.; Pan, M.; Wang, H.-P.; Su, C.-Y. Post-synthetic exchange (PSE) of UiO-67 frameworks with Ru/Rh half-sandwich units for visible-light-driven H₂ evolution and CO₂ reduction. *J. Mater. Chem. A* **2018**, *6*, 11337–11345.

(44) Song, Y.; Li, Z.; Zhu, Y.; Feng, X.; Chen, J. S.; Kaufmann, M.; Wang, C.; Lin, W. Titanium Hydroxide Secondary Building Units in Metal–Organic Frameworks Catalyze Hydrogen Evolution under Visible Light. J. Am. Chem. Soc. **2019**, *141*, 12219–12223.

(45) Feng, X.; Pi, Y.; Song, Y.; Brzezinski, C.; Xu, Z.; Li, Z.; Lin, W. Metal–Organic Frameworks Significantly Enhance Photocatalytic Hydrogen Evolution and CO_2 Reduction with Earth-Abundant Copper Photosensitizers. J. Am. Chem. Soc. **2020**, 142, 690–695.