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Sustained Solar H₂ Evolution from a Thiazolo[5,4-d]thiazole-Bridged **Covalent Organic Framework and Nickel-Thiolate Cluster in Water**

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ABSTRACT: Solar hydrogen (H₂) evolution from water utilizing covalent organic frameworks (COFs) as heterogeneous photosensitizers has gathered significant momentum by virtue of their predictive structural design, long range ordering, tunable porosity and excellent light harvesting ability. However, most photocatalytic systems involve rare and expensive platinum as the co-catalyst for water reduction, which appears to be the bottleneck towards economical and environmentally benign solar H₂ production systems. Herein, we report a simple, efficient and low cost all-in-one photocatalytic H₂ evolution system composed of a thiazolo[5,4-d]thiazole linked COF (**TpDTz**) as the photoabsorber and an earth-abundant, noble-metal-free nickelthiolate hexameric cluster co-catalyst assembled in situ in water, together with triethanolamine (TEoA) as the sacrificial electron donor. The high crystallinity, porosity, photochemical stability and light absorption ability of **TpDTz** COF enables excellent long-term H₂ production over 70 h with a maximum rate of 941 μ mol h⁻¹g⁻¹ and a turnover number, TON_{Ni} > 103 and a total projected $TON_{Ni} > 443$ until complete catalyst depletion. The high H₂ evolution rate and TON, coupled with long-term photocatalytic operation of this hybrid system in water, surpasses that of many previously known organic dyes, carbon nitride (CNx) and COF-sensitized photocatalytic H₂O reduction systems. Furthermore, we gather unique insights into the reaction mechanism, enabled by a specifically designed continuous flow system for non-invasive, direct H₂ production rate monitoring, providing higher accuracy in quantification compared to the existing batch measurement methods. Overall, the results presented here open the door towards the rational design of robust and efficient earth-abundant COF-molecular co-catalyst hybrid systems for sustainable solar H₂ production in water.

INTRODUCTION

Conversion and storage of solar energy in the form of chemical bonds in "solar fuels" like H2 through light-driven water reduction has evolved into a key technology over the last decade due to the fast depletion of fossil energy sources and rapid global climate change.¹ To drive the proton reduction half reaction in an efficient way, the major challenge is to find a robust and highly active, but at the same time low-cost and earth-abundant catalytic system in combination with a strongly absorbing, chemically stable photosensitizer (PS).² In this regard, covalent organic frameworks (COFs)³ have recently emerged as an exciting class of photoactive materials for light-driven H₂ production due to their tunable light harvesting⁴ and charge transport properties.⁵ In contrast to other porous materials, COFs are known for being mechanically robust and offering large accessible surface areas. By virtue of their modular geometric and electronic structure, COFs have attracted significant interest for a range of applications including adsorption, storage and separation,⁶ chemical sensing,7 electronics,8 and catalysis.9 In spite of their versatility, there are only few reports on COFs utilized as photoabsorbers for photocatalytic H₂ evolution so far.¹⁰ Although rare and expensive, all except one of these works has employed metallic platinum (Pt) as the co-catalyst to re-58 duce water efficiently, which appears to be the bottleneck

towards scalable, economical solar H₂ production. In addition, the use of nanoparticulate Pt co-catalysts precludes detailed insights into the nature of the catalytic sites and the intricacies of the photocatalytic cycle. Inspired by natural photosynthesis,¹¹ this shortcoming motivated researchers worldwide to search for single-site, earth-abundant, nonprecious metal-based co-catalysts with well-defined catalytic centers. So far, only one molecular co-catalyst-COF system for photocatalytic H₂ evolution has been demonstrated.12 This system is based on an azine-linked COF (N2-COF)^{10b} acting as the PS and a cobaloxime molecular proton reduction catalyst, which shows a H₂ evolution rate of 782 μ mol h⁻¹g⁻¹ and a TON_{Co} of 54.4. However, the limited photostability and especially the utilization of an organic solvent (acetonitrile/water mixture; 4:1) was a major concern.12

Notably, a majority of molecular catalysts decompose during prolonged catalysis, are inherently insoluble in water, and require the addition of organic solvents to accomplish water reduction.13 With cobaloxime-based systems for example, the catalyst often converts to an inactive form within a few hours (<6 h) of H₂ evolution, possibly due to ligand decomposition or hydrogenation.14

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Figure 1. Synthesis and structural characterization of TpDTz COF. a) Schematic representation of TpDTz COF synthesis; b) Space filling models of **TpDTz** COF pores with π - π stacking of successive 2D layers (grey: C; blue: N; red: O; yellow: S; and white: H); c) Indexed PXRD patterns of TpDTz COF with corresponding Pawley refinement (red) showing good fit to the experimental data (blue) with minimal differences (cyan), the inset shows close-up of the indexed experimental (blue) and simulated (black) PXRD patterns based on Pawley fits [Final Rwp = 2.59% and Rp = 1.89%].

To overcome these issues, the development of a scalable, earth-abundant and low-cost co-catalyst system which is soluble in water and can be coupled efficiently to a molecularly defined heterogeneous photoabsorber is in high demand. In this regard, Ni based synthetic photocatalytic H₂ evolution catalysts¹⁵ have attracted significant interest because of their robust and oxygen tolerant nature and importantly, their structural similarity to the active site in [Ni–Fe] hydrogenase¹⁶.

42 Likewise, small molecules and polymers containing fused 43 (bi)heterocyclic thiazolo[5,4-d]thiazole (TzTz) moieties 44 have received much attention as semiconductors in organic 45 electronics lately because of their n-type character featuring 46 high oxidative stability and their rigid planar structure.^{17a} The latter enables efficient intermolecular $\pi - \pi$ overlap that affords high electron and hole mobility.¹⁷ Such TzTz moieties further feature excellent photoabsorbing ability, which is likewise beneficial for photocatalysis.2a Nevertheless, TzTz-based COFs have not been explored so far. Notably, thus far, only a very limited number of COFs bearing photoactive functionalities such as triazine,^{10a,b} diacetylene,^{10c} or sulfone moieties^{10d} have been shown to produce H₂ from water, with the noble metal Pt acting as co-catalyst.

> Combining these aforementioned leverages, in this work, we present a light-driven hybrid proton reduction system employing a newly designed TzTz-linked COF (TpDTz) as a

photoabsorber and a molecular Ni-thiolate cluster (NiME)¹⁸ assembled in situ from a Ni(II) salt and 2-mecaptoethanol (ME). The combination of the NiME cluster co-catalyst and **TpDTz** COF enables sustained H₂ evolution with an excellent rate (941 μ mol h⁻¹g⁻¹) and a TON_{Ni} > 103 (70 h) in the presence of triethanolamine (TEoA) as the sacrificial electron donor (SED) in water under AM 1.5 light illumination. We thus report a single-site heterogeneous COF based photocatalyst system that operates with a noble-metal free cocatalyst in water as the solvent. We further carve out structure-property-activity relationships by comprehensively screening the parameter space of this heterogeneous-homogeneous hybrid photocatalytic system, including pH, SED, co-catalyst metal centres, different N/S containing chelating ligands for co-catalysts, and a variety of photosensitizers. Also, our study is built on a continuous flow photocatalytic reactor system which enables a non-invasive and direct monitoring of the H₂ evolution rate with high accuracy, in contrast to the routinely used standard photocatalytic batch reactors, and this allows gathering unique insights into the photocatalytic reaction modeling and kinetics. The results and understanding presented here thus contribute towards the rational development of robust and efficient single-site hybrid photocatalytic systems as a sustainable solution for solar H₂ production in water.

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Figure 2. Structural characterization of TpDTz COF. a) ¹³C and ¹⁵N CP–MAS solid-state NMR spectrum of **TpDTz** COF. Calculated NMR chemical shifts for the TpDTz-NMR model (Figure S49) obtained on B97-2/pcS-2//PBE0-D3/def2-TZVP level of theory (Table S4 & S5) are shown as grey dashes; b) Argon adsorption-desorption isotherm for **TpDTz** COF recorded at 87 K; inset: calculated pore size distribution of **TpDTz** COF according to the QSDFT method; c) TEM image of **TpDTz** COF showing the hexagonal pore structure with a periodicity of ~3.3 nm (scale bar 100 nm); d) UV-vis diffuse reflectance (DR) spectrum for **TpDTz** COF measured in the solid state, insets: plot showing the Kubelka-Munk function to extract the direct optical band gap, and photograph of **TpDTz** COF powder; e) Cyclic voltammogram (CV) of a **TpDTz** COF-modified FTO working electrode in 0.1M NBu₄PF₆ as the supporting electrolyte in anhydrous acetonitrile at a scan rate of 100 mV/s.

RESULTS AND DISCUSSION

 COF synthesis and characterization. The precursor 4,4'-(thiazolo[5,4-d]thiazole-2,5-diyl)dianiline (DTz) was synthesized as described in the supplementary information and characterized using single crystal X-ray diffraction, nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and mass spectrometry.
TpDTz COF was synthesized by solvothermally reacting Tp (1.0 eq.) and DTz (1.5 eq.) in the presence of 6M aqueous acetic acid using an *o*-dichlorobenzene and N,N-dimethylacetamide solvent combination in a high precision glass vial, which was sealed and heated to 120 °C for 3 days (Figure 1 and Section S2, Supporting Information). Following a similar protocol, TpDTP COF with a similar pore size was synthesized as a reference,¹⁹ with the DTz linker replaced with the linear terphenyl linker.

To verify crystallinity and phase purity, the as-synthesized **TpDTz** COF was analyzed *via* powder X-ray diffraction (PXRD). The PXRD pattern exhibits an intense first peak at 2.56° 2θ corresponding to the 100 reflection along with other diffraction peaks at 4.41, 5.23, 6.90 and 9.10° 2θ , attributed to the 110, 200, 210 and 220 reflections, respectively. In addition, at ~26° 2θ a broad set of reflections is visible, with 001 being the most intense, which corresponds to the π - π stacking of the 2D layers (Figure 1c). The experimental PXRD pattern is in good agreement with the simulated AA eclipsed stacking model (Figure S6.2). The lattice

parameters of **TpDTz** COF were extracted by Pawley refinement in the hexagonal space group *P6/m* (a = b = 39.27 Å, c = 3.46 Å, $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$) (Figure 1c). The relatively high level of order observed with PXRD may originate from effective π - π stacking interactions facilitated by the planarity of the **DTz** linker and thus, the 2D layers. The measured pore aperture is ~3.4 nm and the π - π stacking distance between individual layers is ~3.5 Å for **TpDTz** COF, as obtained from the structural model.

The FTIR spectrum of the as-synthesized **TpDTz** COF shows bands at ~1254 cm⁻¹ (–C–N), ~1571 cm⁻¹ (C=C) and ~1618 cm⁻¹ (C=O) (Figure S9), which confirms the formation of the proposed β -ketoenamine-linked framework. The TzTz moiety was identified by appearance of C=N vibrations (~1660 cm⁻¹) and C-S stretching bands between 650 and 700 cm⁻¹. The structural composition of TpDTz COF was further confirmed by ¹³C cross-polarization magic-angle spinning (CP-MAS) NMR spectroscopy (Figure 2a). The spectrum shows signals corresponding to the heterocyclic TzTz ring of the **DTz** building unit ($\delta = \sim 151$ ppm), together with a characteristic signal of the carbonyl carbon (C=O) at ~184 ppm, which further supports formation of the β -ketoenamine moiety. ¹⁵N NMR spectroscopy confirms the presence of two different kinds of nitrogen atoms with chemical shifts of - 93 ppm and - 243 ppm corresponding to the TzTz and enamine (=C-NH-) moieties, respectively (Figure 2a). All assignments are supported by quantumchemical calculations of NMR chemical shifts (Table S4, S5)

at the B97-2/pcS-2//PBE0-D3/def2-TZVP level using the FermiONs++ program package^{20a,b} based on a selected molecular model system (Figure S49). The corresponding structures were optimized at the RI-PBE-D3/def2-TZVP level using Turbomole (version 7.0.3)^{20c,d}. Scanning electron microscopy (SEM) images of **TpDTz** COF reveal a flower-like morphology composed of flakes with 1-3 µm lateral dimensions (Figure S11). Transmission electron microscopy (TEM) images confirm the layered morphology of the crystalline network with clearly visible 2D honeycomb-type pores oriented perpendicular to the crystallographic *c* axis with a periodicity of ~3.3 nm (Figure 2c). In order to evaluate the thermal stability of TpDTz COF, we further performed thermogravimetric analysis (TGA) in air. The TGA profile suggests that the COF pores are guest free and the material is thermally stable up to $\sim 400 \text{ }^{\circ}\text{C}$ (Figure S10).

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The permanent porosity of **TpDTz** COF was assessed by Ar adsorption analysis measured at 87 K (Figure 2b and Figure S13). A Brunauer-Emmett-Teller (BET) surface area of 1356 m²g⁻¹ was obtained for **TpDTz** COF, which is comparable to some of the most porous β -ketoenamine-based porous COFs previously synthesized via solvothermal methods.^{10c,d,21} The experimental pore size of 3.4 nm obtained from the adsorption isotherm using the quenched solid state density functional theory (QSDFT) cylindrical-slit adsorption kernel for carbon (inset of Figure 2b) is in excellent agreement with the pore size obtained from the structure model (\sim 3.4 nm) and TEM (~3.3 nm). Further, the measured water adsorption isotherm (total uptake - 309 cm³g⁻¹, 25 wt% at STP) of **TpDTz** COF suggests its relatively hydrophilic nature, induced by the polar N/S containing TzTz group and should thus lead to higher dispersibility of the COF in water during photocatalysis,^{10d,e} as opposed to the non-TzTz **TpDTP** COF (total uptake 75 cm³ g⁻¹, 6 wt% at STP) with similar pore sizes (Figure S15). This fact is also supported by the higher CO₂ uptake for **TpDTz** COF compared to **TpDTP** COF (Figure S16).

35 Since chemical stability is a crucial criterion for any mate-36 rial to be considered for practical applications, we investi-37 gated the chemical stability of **TpDTz** COF under strongly 38 acidic (12M HCl) conditions, and in boiling water up to 7 days. The retention of all characteristic peaks in the PXRD 39 pattern suggests a high chemical stability under the tested 40 conditions (Figure S7). It is important to note that TpDTz 41 COF is stable only under mild basic conditions (1M KOH) for 42 up to 3 days, while at harsher basic conditions (12M KOH 43 for 7 days) the framework decomposes. The high chemical 44 tolerance of **TpDTz** COF is ascribed to the combined effect 45 of the stabilizing enol-to-keto-tautomerism,²¹ and the pla-46 narity of the TzTz moiety,¹⁷ which allows for strong π - π in-47 teractions between the layers.

48 Opto-electronic properties and photocatalysis. The UV-49 vis diffuse reflectance (DR) spectrum of TpDTz COF reveals 50 efficient light absorption extending into the orange parts of 51 the visible spectrum with an absorption edge at ~598 nm 52 (Figure 2d). Kubelka-Munk analysis yields a direct optical 53 band gap of ~2.07 eV. In contrast, **TpDTP** COF shows a blue-54 shifted absorption band edge at ~531 nm, corresponding to a larger optical band gap of ~2.28 eV (Figure S18), due to 55 the absence of light harvesting TzTz units. The measured 56 photoluminescence (PL) spectra (Figure S19) reflect this 57 trend; TpDTz COF has a significantly red-shifted emission 58 $(\lambda_{max} = 690 \text{ nm})$ compared to **TpDTP** COF $(\lambda_{max} = 630 \text{ nm})$. 59

The fluorescence decays can be fitted with triexponential functions and the amplitude weighted average lifetimes for **TpDTz** and **TpDTP** COFs are 94 ps and 115 ps, respectively (Figure S20). Emission intensities were too low to measure accurate absolute emission quantum yields. The short excited state lifetimes together with low emission quantum yields suggest more pronounced non-radiative rates in the COF systems, relative to the radiative rates, similar to our previously reported N3-COF system.^{10b,f}

Cvclic voltammograms (CV) of TpDTz COF films were measured to estimate the band positions and the thermodynamic driving force for H₂ evolution. The voltammogram of a **TpDTz** COF-modified FTO working electrode²² shows an irreversible reduction wave with an onset potential of Ered, onset \approx -1.24 V vs. saturated calomel electrode (SCE) (Figure 2e and Figure S22). From the optical bandgap ($E_g = 2.07 \text{ eV}$) determined from the UV-vis DR spectrum, the valence band (VB) and conduction band (CB) edges of **TpDTz** COF can be estimated to be $E_{CB} = -3.46 \text{ eV}$ and $E_{VB} = -5.53 \text{ eV}$ vs. the vacuum level, following the equations $E_{CB} = -(E_{red,onset vs. SCE} + 4.7)$ eV and $E_{VB} = E_{CB} - E_{g,opt}$.²³ Quantum-chemical calculations of vertical ionization potentials and electron affinities on a TpDTz pore model (Figure S53), cut from a supercell built using the 2D periodic optimized unit cell of the TpDTz COF (Figure S52), support these findings (Table S8). By comparing these values with the oxidation potential of TEoA (0.57 V vs. SCE)^{23d} and the reduction onset potential of the NiME molecular catalyst system (-0.75 V vs. SCE) (Figure S21), it is likely that TpDTz COF can transfer electrons to the NiME co-catalyst system forming a reduced Ni(I) center and thereby enabling H₂ evolution in successive steps.^{18,23a} Also, TEoA can efficiently quench the photoexcited holes in the COF thereby replenishing its photoactivity.

Owing to the planar and conjugated structure, the electron deficient nature of the heterocyclic backbone, optimal band gap and hence light absorption ability, the TzTz-linked **TpDTz** COF was investigated as the heterogeneous photoabsorber for photocatalytic H₂ evolution in combination with the Ni-thiolate hexameric cluster (NiME) co-catalyst in water. The NiME cluster co-catalyst has a cyclic hexameric structure composed of six Ni(II) ions forming a planar ring and the Ni centers are bridged by twelve ME units, which has been confirmed by DFT calculation and single-crystal Xray diffraction analysis by others (Figure S35).^{18,24b} This NiME cluster co-catalyst has been shown to produce H₂ actively when sensitized by an organic xanthene dye (Erythrosin B).¹⁸ However, the generation of unstable PS radical species upon photochemical quenching of the excited-state dye (PS*) leads to a fast decomposition and hence poor photochemical stability of organic dye photosensitizers which hinders long-term performance of the photocatalytic system.^{15a,18} The strategy of combining a photochemically stable COF photoabsorber with the Ni-thiolate cluster co-catalyst in water could thus be a viable path to impart better long-term stability for H₂ production.

The beauty of the aforesaid NiME complex lies in its simple, quick *in situ* synthesis in water upon addition of a Ni(II) salt and ME at room temperature. This *in-situ* assembling strategy is different from most other Ni(II) and Co(II) co-catalyst complexes featuring arduous *ex situ* synthesis and purification of a water soluble analogue, thus adding to the cost-effectiveness of the NiME cluster co-catalyst approach.^{12,15}

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Figure 3. Continuous flow photocatalytic reactor design. Schematic diagram of the designed continuous flow photocatalytic reactor system (red streamlines are the continuous flow pathway of gas). In contrast, the batch configuration involves mass flow controllers as dead-ends after back purging the initial headspace, and replaces the autosampler by a septa-port or a manual sampling valve.

In addition, this cluster has been shown to be a potent H_2 evolution co-catalyst producing H_2 immediately after light illumination in the presence of a PS and SED, and hence does not require any photo-deposition nor does it show an activation time, contrary to Pt based photocatalytic systems.¹⁰

For better measurement accuracy and to gain insights into the photocatalytic mechanism, we developed a continuous flow system to monitor the H₂ evolution performance of the hybrid photocatalytic system (Figure 3 and Figure S23). In this measurement system, the molar flow entering the system, the pressure (0.5 bar) and temperature (25 °C) of the reactor are continuously controlled, while bypassing some of the out-flow to an open sampling loop gas chromatograph (GC) autosampler. In this way, the rate of H₂ production (R_{H_2}) can be monitored directly using only two experimental inputs: F_{in} from the mass flow controller, and $x_{H_2,ppm}$ from an on-line GC (BID) detection system (Eqn. 1), where F_{in} is the carrier gas (in this case He) flow in to the system and $x_{H_2,ppm}$ is the molar fraction of H₂ at the outlet.

$$R_{H_2} = \frac{F_{in} \times x_{H_2,ppm} \times 10^{-6}}{\left(1 - x_{H_2,ppm} \times 10^{-6}\right)} \qquad \text{Eqn.}(1)$$

Typically, the run-to-run error with this method is below 3%, compared to at least 15-20% error with a standard batch system. Also, this continuous flow system is independent of experimental conditions, and does not require human intervention when sampling or local derivative approximations as with regular batch system measurements (Figure S34). In addition to the better accuracy of this method in monitoring kinetic trends in the photocatalytic H₂ evolution process, the method also keeps the media unperturbed - since the presence of the GC sampling line does not affect the hydrogen balance - thus completely eliminating typical sampling losses and mathematical and experimental uncertainties associated with batch photocatalytic reactor systems.

In a typical photocatalytic experiment using our hybrid system, 5 mg of **TpDTz** COF was dispersed in 10 mL of H₂O containing TEoA (10 vol.%) as the SED and the pH was adjusted to 8.5 by adding HCl. Ni(OAc)₂.4H₂O (10 wt.%, 0.5 mg) and ME (10 eq., 1.4 µL) were then charged to instantaneously form the brown coloured NiME cluster co-catalyst. When irradiated with 100 mW/cm² AM 1.5 radiation, the resulting mixture produces H₂ actively over a period of at least 70 h - with \sim 40% of the highest production rate still preserved after this time - in a single run without adding additional TEoA or co-catalyst (Figure 4a). A maximum H₂ evolution rate of 941 μ mol g⁻¹h⁻¹ with a TON_{Ni} > 103 (70 h), and a TOF= 2.3 h⁻¹ when the system is fully active were obtained. A mathematically projected (Section S8, Supporting Information) TON_{Ni} > 443 (890 μ mol of total H₂ evolution) can be obtained for the photocatalytic H₂ evolution performance corresponding to a complete depletion of the co-catalyst. The relation between co-catalyst, SED and observed activity loss of the system in time was confirmed by in-situ addition of loss-equivalent amounts of ME or TEoA independently after 72 hours of illumination, which did not change the deactivation trends observed (Section S8, Supporting Information). It must be noted that the TON_{Ni} mentioned above is only a lower limit calculated based on the total amount of Ni(II) salt used for the photocatalysis experiment. Under identical conditions the Erythrosin B (EB) dye sensitized system¹⁸ produces H₂ with a maximum rate of 49297 µmol g⁻¹ h⁻¹ (attained in 1 h), however, the rate rapidly drops off and the whole system becomes completely inactive within 7 h. A TON_{Ni} >36.5 (73 μ mol of total H₂ evolution) was obtained after 7 h (TOF_{Ni} = 31.9 h^{-1}), which is 12 times lower than the value projected for the TpDTz COF sensitized system (Figure 4a). These results demonstrate the added value of using a heterogeneous photosensitizer to stabilize charge transfer in photocatalytic hybrid systems.



Figure 4. Photocatalytic H₂ evolution. a) A comparison of photocatalytic H₂ evolution rates in water (H₂O) and deuterium oxide (D₂O), using **TpDTz** COF over 72 h and **EB** dye under AM 1.5 light irradiation [COF photosensitizer: 5 mg of **TpDTz** COF in 10 ml of H₂O/D₂O with 10 vol.% TEoA, 0.5 mg of Ni(OAc)₂ and 1.4 µL of ME at a final pH of 8.5; dye photosensitizer: 1.33 mg of **EB** in 10 ml of H₂O with 10 vol.% TEoA, 0.5 mg of Ni(OAc)₂ and 1.4 µL of ME at a final pH of 8.5]; b) Light *on-off* cycles for photocatalytic H₂ evolution experiments with **TpDTz** COF in water over 26 h; c) photocatalytic H₂ evolution with **TpDTz** COF in water using different co-catalysts; d) photocatalytic H_2 evolution with **TpDTz** COF in water using different metal-ME co-catalysts; e) photocatalytic H_2 evolution from water using different photosensitizers; f) Overlay of the UV-vis DR spectra of TpDTz COF with apparent quantum efficiency (AQEs) for the photocatalytic H₂ evolution reaction with **TpDTz** COF at four different incident light wavelengths.

Also, the **TpDTz** COF-NiME photocatalytic system produces H₂ at a 17% higher maximum rate and has a TON nearly eightfold as high as our previously reported N2-COF-cobaloxime based system (782 μ mol h⁻¹ g⁻¹, TON_{Co} = 54.4), while operating in water.¹² The H₂ evolution rate and the sustained activity of this simple **TpDTz** COF-NiME system is competitive and even superior compared to many COFbased photocatalytic systems (Table S3) and other benchmark photocatalytic systems involving metallic Pt or molecular Ni co-catalysts. Examples include $g-C_3N_4/Pt$ (840 µmol ACS Paragon Plus Environment

g⁻¹ h⁻¹),^{25b} TP-BDDA/Pt (324 µmol g⁻¹ h⁻¹),^{10c} N2-COF/Pt (480 µmol g⁻¹ h⁻¹),^{10b} crystalline poly(triazine imide)/Pt (864 µmol g⁻¹ h⁻¹),^{25a} sg-CN-Ni (103 µmol g⁻¹ h⁻¹),^{25c} $Ni_{12}P_5/g-C_3N_4$ (536 µmol g⁻¹ h⁻¹),^{25d NCN}CN_x-NiP (763 µmol g⁻¹ h⁻¹),^{25e} and carbon quantum dots (CQDs)-Ni (398 µmol $g^{-1} h^{-1}$)^{25f}.

Control experiments were performed by sequentially removing one of the components, i.e. TpDTz COF, TEoA, Ni(OAc)₂.4H₂O and ME, at a time from our photocatalytic

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system to identify their importance and role for the H_2 evolution. Indeed, no H_2 evolution was observed for a period of 12 h unless all individual components act in concert, signifying that each is essential for the photocatalytic system to work and efficiently produce H_2 (Figure S27).

5 Furthermore, a 1:10 metal-to-ligand molar ratio and 10 6 wt.% of catalyst with respect to the PS were observed to 7 elicit the best photocatalytic performance (Figure S28 and 8 S28). To confirm water as the source of H₂, the photocatalytic reaction was performed in D₂O under identical condi-9 tions (Figure 4a). A similar production rate of D₂ was ob-10 served over 72 h as for H₂ in H₂O, taking batch-to-batch var-11 iations into account. This result suggests that water is the 12 hydrogen source responsible for the production of H₂, as-13 suming that no significant proton/deuterium exchange pro-14 cesses in the individual components are at play. This finding 15 was further confirmed by an almost complete disappear-16 ance of the m/z = 2 signal for H₂ in a mass spectrometric 17 measurement of the headspace gas of the photocatalytic re-18 action performed in D_2O (Figure S26). Note that D_2 is 19 evolved with a time lag compared to H₂, which is likely due to the kinetic isotope effect of deuterium as described be-20 low. Further, H₂ evolution experiments performed under 21 multiple light-on/off cycles over a period of 26 h (Figure 4b) 22 suggests a purely light driven H₂ evolution process in water. 23 Once the catalytic system is fully active, H₂ evolution activity 24 is seen to be restored even after a prolonged light-off period. 25

SED and the reaction pH are known to have a profound in-26 fluence on the activity of many H₂ production systems.^{10b,c,12} 27 In our case, we observed a similar effect; the rate of H₂ gen-28 erated from the photochemical reaction is the highest (941 29 umol g⁻¹h⁻¹) at pH 8.5 using TEoA as SED. However, at acidic 30 conditions (pH 6.5) there was negligible H_2 evolution (16 31 μ mol g⁻¹ h⁻¹). This could be attributed to the protonation of 32 TEoA or due to inhibition of proton loss from one-electron 33 oxidized TEoA⁺.^{13c} Notable H₂ evolution is observed over 24 34 h under alkaline conditions (pH 11), albeit at lower rates 35 $(308 \mu mol g^{-1} h^{-1})$ as compared to pH 8.5 (Figure S30). This is possibly due to the reduced driving force for protonation 36 37 of the Ni hydride intermediate co-catalyst species at higher pH to subsequently generate H₂. triethylamine (TEA) and 38 Na₂S were also explored as potential SEDs. Interestingly, 39 they produce H₂ but with significantly lower rates of 84 40 μ mol g⁻¹ h⁻¹ and 7 μ mol g⁻¹ h⁻¹, respectively (Figure S31). 41 Higher TEoA concentrations were found to decrease H₂ evo-42 lution rates; a TEoA concentration of 10 vol.% in water was 43 observed to result in the maximum H₂ production rate (Fig-44 ure S32). 45

H₂ evolution rates of the photocatalytic systems containing **TpDTz** COF PS and different Ni(II) co-catalysts were measured (Figure 4c). Different sulfur-containing compounds, such as thiourea (TU) and 2-mercaptophenol (MP), were explored as potential ligands for *in situ* formation of Ni(II) cocatalyst complexes. However, neither NiTU nor NiMP produced any H₂ with **TpDTz** COF, possibly due to unfavourable complexation of the ligands with Ni(II) in water: TU and MP are known to be poorer complexation agents as compared to ME.²⁶ Also, a reported *ex situ* synthesized Ni(*abt*)₂ complex^{15c} was studied as a potential H₂ evolution co-catalyst under our experimental conditions, but no H₂ evolution was seen most likely due to its poor solubility in water. It is also interesting to note that **TpDTz** COF produces H₂ with a significantly smaller rate of 23 µmol g⁻¹ h⁻¹ with metallic Pt co-

catalyst and TEoA at pH = 8.5 over a period of 24 h as compared to that with NiME. The significant difference between H₂ evolution of the molecular co-catalyst and photo-deposited Pt nanoparticles is difficult to explain by a single effect.^{12,25f} However, it may be argued that the higher activity of the NiME co-catalysed system in contrast to the surface bound Pt nanoparticles (Figure S48) is due to a more effective blocking of charge carrier recombination since the cocatalyst is physically separated from the framework (physisorbed), which may support better charge separation. We further screened the H₂ evolution activity of other transition metal-ME complexes, such as CoME and CuME, with TpDTz COF as the PS following a similar method as that of NiME. Although all systems produced H₂, they do so with a much lower rate following the order NiME (941 μ mol g⁻¹ h⁻¹) > CoME (85 μ mol g⁻¹h⁻¹) > CuME (52 μ mol g⁻¹h⁻¹). This could be due to the poor solubility of CoME and CuME clusters in water compared to the NiME, which is in accordance with the reported dye sensitized molecular system¹⁸ (Figure 4d).

We then evaluated the H₂ evolution ability of the NiME cluster co-catalyst with a variety of photoabsorbing materials; **TpDTP** COF,¹⁹ N3-COF,^{10b} an amorphous porous polymer containing TzTz groups (TzTz-POP-3),²⁷ and the diamine linker DTz were tested under identical conditions. Even though N3-COF is considered one of the most active COFs for photocatalytic H₂ generation (reported rate of 1700 $\mu mol~g^{\mbox{--}1}~h^{\mbox{--}1}$ when co-catalyzed by Pt),10b with NiME co-catalyst it produces H₂ only at a very low rate of 40 µmol g⁻¹ h⁻¹ (Figure 4e). Under similar conditions **TpDTP** COF produces H_2 at a rate of 160 μ mol g⁻¹ h⁻¹, which is nearly 6 times less compared to that of the TpDTz COF sensitized system. The marked difference in photocatalytic activity between TpDTz COF and TpDTP COF may in part be rationalized by the reaction conditions which were not optimized specifically for **TpDTP** COF, but also by their different photon absorption characteristics. A redshift of ~67 nm is observed for **TpDTz** COF with respect to **TpDTP** COF, which indicates that **TpDTz** COF absorbs photons more effectively in the visible range. This said, increased reactivity is only expected if the conduction band is not significantly lowered to maintain the thermodynamic driving force for the HER. In addition to that, the higher crystallinity, and the higher BET surface area of 1356 m² g⁻¹ for **TpDTz** COF versus 736 m² g⁻¹ for **TpDTP** COF, along with a better dispersibility of the more hydrophilic **TpDTz** COF in aqueous solution, are likely determining factors for the enhanced photocatalytic activity. Notably, the amorphous polymer TzTz-POP-3 and the diamine linker **DTz** are completely inactive at producing H_2 with the NiME co-catalyst (Figure 4e). Overall, the significantly lower reactivity of other photosensitizers in producing H₂ with the NiME co-catalyst is rationalized by a combined effect of unfavourable charge transfer processes, reduced light harvesting, low crystallinity and surface area, and poor dispersibility in water.

The apparent quantum efficiency (AQE) was calculated using four different bandpass filters with central wavelengths (± 20 nm) at 400, 500, 550, and 600 nm to quantify the spectral contribution towards H₂ evolution activity of the **TpDTz** COF photoabsorber. Figure 4f shows that **TpDTz** COF has a maximum AQE of 0.2% at 400 nm. Under AM 1.5 illumination, the AQE was estimated to be 0.044%, which is higher than that of our previously reported N2-COF-cobaloxime H₂ evolution system (0.027%).¹²

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Figure 5. Reaction limitations insights. a) A general schematic of the proposed pathway for H₂ evolution (color code: grey; C, red; O, yellow; S, blue; N and light pink/white; H); b) proposed key steps of the photocatalytic H₂ evolution reaction with **TpDTz** COF and NiME cluster co-catalyst. [Ni--L] denotes a ligand-coordinated co-catalyst state which is attained fast compared to the [R] state, [R] denotes the catalyst resting state, which is catalytically active nickel cluster species, [D] denotes the deactivated species and [I] denotes an intermediate reduced catalyst species able to run the HER step.

We further verified the photochemical stability of TpDTz COF after a 72 h long photocatalysis experiment. The isolated **TpDTz** COF sample was fully characterized using PXRD, ssNMR, SEM and TEM, and it was found that the framework structure, crystallinity, and morphology of **TpDTz** COF is retained (Section S9, Supporting Information) thus supporting the high chemical stability of this COF (vide supra). A small additional signal at 56.6 ppm in the ¹³C ssNMR spectrum possibly corresponds to trapped ME molecules inside the **TpDTz** COF pore. This, together with the observation of traces of Ni in the post-photocatalytic TpDTz COF using SEM-EDAX (Figure S46) may hint to chemisorption of small amounts of co-catalyst to the COF walls. However, ¹⁵N ssNMR of the TpDTz COF sample does not show any noteworthy difference in the chemical shifts of the N signals before and after photocatalysis (Figure S41), suggesting that there is no substantial direct interaction between the residual Ni and the nitrogen centers of the COF. Also, the as-recovered **TpDTz** COF sample does not produce any H₂ under identical photocatalytic conditions except for the absence of Ni(OAc)₂.4H₂O and 2-ME ligand. This suggests that the interaction between TpDTz COF and NiME is mostly physical and no lasting chemical interaction exists between the two components. Our finding thus suggests an outer sphere electron transfer to be at play, which nevertheless is efficient enough to allow facile charge transfer from the photoabsorber to the NiME co-catalyst (Figure 5a).

To obtain deeper insights into the photocatalytic mecha-48 nism, an overall coarse-grain mathematical model (Eqn. S6.2) of the photocatalytic reaction was developed (Section S8, Supporting Information for details) by taking advantage of the quantification of hydrogen evolution rates in our flow detection platform. Our model was based on three primary experimentally observed trends: the activation time required by the photocatalytic system to reach maximum rates in the first run (Figure 4a), the absence of this activation time during light on/off cycles or long dark periods before illumination (Figure 4b), and the kinetic isotope effect in D₂O, namely, smaller deuterium evolution rates and delayed response, together with the observation of a similar

initial activation time as with H₂O (Figure 4a). A possible reaction model is outlined in Figure 5b. The absence of an activation time during light on/off cycles (Figure 4b) suggests a light enhanced formation of a catalyst resting state [R] of the NiME complex upon illumination, as seen by the initial activation time required for the system to reach maximum efficiency. The reaction network can then be reduced to the following core steps using a microkinetics analysis. For the heterogeneous (COF) fast cycle: COF photoexcitation (hv), exciton recombination in the COF (k_{rec}), reductive quenching of the COF (k_q), and electron transfer from COF⁻ to [R] to form the active intermediate spcies [I] (k_a). Quantum-chemical calculations on the TpDTz pore model system (Figure S55) identify the lowest photoexcitation energy to be 2.30 eV (Table S9), the difference density of this excited state (Figure S57) visualizing the exciton. The spin density of the radical anion as a result of the reductive quenching of this state is shown in Figure S58. For the homogeneous (catalyst) cycle: formation of a rapidly coordinated complex [Ni--L] (*K*_{eq}), slow assembly of the catalytically active species (k_T, k_T^{-1}) , an apparent first order activation step from [R] to [I] (k_a) , an irreversible deactivation step [D] (k_d) , and the closing of the catalytic cycle via a dark step that produces H₂ (k_{HER}). If in such a system k_{T} and k_{T} -1 are significantly slower compared to the rest of the steps, the on/off behaviour can be explained, because in the absence of light the dark equilibrium is slow and the amount of [R] and [I] will not change significantly in time. Furthermore, the absence of HER in the dark during the light on/off cycles observed in Figure 4b suggests that a k_{HER} limited homogeneous cycle is unlikely. Then, once nickel enters the cycle as [R] more rapidly due to a light shifted equilibrium, [R] will build up until the rate of [D] leaving the system irreversibly is equal to the rate of formation of [R], [I] being stationary. This will lead to an expression for activation of the photocatalytic system such that the activation curve is an exponential asymptote with time constant t_{a} , which is dominated by electron transfer rate $k_{\rm a}$, a linear deactivation with an apparent time constant *t*_d, an HER apparent kinetic constant R_{H2,max}, and the apparent transient time t_0 only which corresponds to the initial

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time delay necessary for the the intermediate [I] to be pseudo-stationary (Eqn. S6.2). Our model further provides an accurate fit both to the data obtained in H₂O and D₂O, in line with an expected trend of a kinetic isotope effect (KIE). In this case, $R_{\rm H2,max}$, $t_{\rm d}$ and t_0 changed as expected, but the time constant for the activation step (t_a) being independent of the isotopic mass is almost unchanged (Table S2), further corroborating our proposed rate limiting steps (RLS). Our reaction model not only explains these qualitative trends but also provides an accurate fit with standard errors below 5% for different data sets. It is important to note that acquiring detailed insights into the H₂/D₂ evolution reaction mechanism for the **TpDTz** COF-NiME photocatalytic system became possible only with the use of a flow reactor system.

Our reaction modelling results suggest that as long as a slow catalyst activation time is observed, the RLS of the system is seemingly the electron transfer from the COF to the NiME complex. While this outcome is fully consistent with the assumed outer sphere electron transfer process, it reinforces the idea of studying the kinetics of such processes in more detail as this will be crucial to improve the HER rate by rational design of the COF – co-catalyst interface.

CONCLUSIONS

22 We report the first COF photosensitizer and noble-metal-23 free molecular co-catalyst photocatalytic system for sus-24 tained solar H₂ production from water. This single-site sys-25 tem comprises the newly designed N/S containing TpDTz 26 COF photosensitizer that absorbs strongly in the visible re-27 gion of the solar spectrum and is robust for long-term hy-28 drogen evolution. In combination with an earth-abundant 29 Ni-thiolate cluster co-catalyst which self-assembles in wa-30 ter, we obtain solar H₂ evolution rates as high as 941 µmol $h^{-1}g^{-1}$ and a TON_{Ni} > 103 (70 h) with persistent H₂ evolution 31 for more than 70 h in a single run, which surpasses many 32 benchmark photcatalytic H₂ evolution systems based on 33 COFs and carbon nitrides. To map out the parameter space 34 of this hybrid photocatalytic system, we comprehensively 35 screened the influence of various reaction components, in-36 cluding pH, SED, co-catalyst metal centres, different N/S 37 containing chelating ligands, and a variety of photosensitiz-38 ers on the photocatalytic activity. In addition, we have intro-39 duced a newly designed continuous flow system enabling 40 the non-invasive, direct detection of the H₂ production rate. 41 This platform does not only provide higher accuracy in 42 quantification; it also paves way for unprecedented insights 43 into the reaction mechanism which are difficult to obtain with the existing batch measurement methods. Microkinetic 44 modelling of the reaction system suggests that an outer 45 sphere electron transfer from the photoabsorber to the cat-46 alyst is the rate limiting step, thus spotlighting the im-47 portance of the rational design of the COF - co-catalyst in-48 terface. 49

ASSOCIATED CONTENT

Synthesis, crystallography, characterizations and photocatalysis experimental details are provided in the Supporting Information. 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 interests.

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REFERENCES

(1) a) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. Chemical Approaches to Artificial Photosynthesis. 2. Inorg. Chem. 2005, 44, 6802–6827; b) Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. Proc. Natl. Acad. Sci. U.S.A. 2006, 103, 15729-15735; c) Bard, A. J.; Fox, M. A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. Acc. Chem. Res. 1995, 28, 141-145; d) U.S. Department of Energy, Energy Information Administration, Annual Energy Outlook 2013 with Projections to 2040. U.S. Government Printing Office: Washington, DC, 2013; 55–90; e) Hoffert, M. I.; Caldeira, K.; Jain, A. K.; Haites, E. F.; Harvey, L. D. D.; Potter, S. D.; Schlesinger, M. E.; Schneider, S. H.; Watts, R. G.; Wigley, T. M. L.; Wuebbles, D. J. Energy Implications of Future Stabilization of Atmospheric CO₂ Content. Nature 1998, 395, 881-884; f) Vyas, V. S.; Lau, V. W.-h.; Lotsch, B. V. Soft Photocatalysis: Organic Polymers for Solar Fuel Production. Chem. Mater. 2016, 28 (15), 5191-5204.

(2) a) Banerjee, T.; Gottschling, K.; Savasci, G.; Ochsenfeld, C.; Lotsch, B. V. H₂ Evolution with Covalent Organic Framework Photocatalysts. *ACS Energy Lett.* **2018**, *3* (2), 400-409; b) Zouc, X.; and Zhang, Y. Noble Metal-free Hydrogen Evolution Catalysts for Water Splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148-5180.

(3) a) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, *310* (5751), 1166-70; b) Feng, X.; Ding, X.; Jiang, D. Covalent Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41* (18), 6010-6022; c) Xu, S.-Q.; Zhan, T.-G.; Wen, Q.; Pang, Z.-F.; Zhao, X. Diversity of Covalent Organic Frameworks (COFs): A 2D COF Containing Two Kinds of Triangular Micropores of Different Sizes. *ACS Macro Lett.* **2016**, *5* (1), 99-102; d) Kandambeth, S.; Dey, K.; Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. *J. Am. Chem. Soc.*, **2019**, *141* (5), 1807–1822.

(4) Keller, N.; Calik, M.; Sharapa, D.; Soni, H. R.; Zehetmaier, P. M.; Rager, S.; Auras, F.; Jakowetz, A. C.; Goerling, A.; Clark, T.; Bein, T. Enforcing Extended Porphyrin J-Aggregate Stacking in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140* (48), 16544–16552.

(5) Feng, X.; Liu, L.; Honsho, Y.; Saeki, A.; Seki, S.; Irle, S.; Dong, Y.; Nagai, A.; Jiang, D. High-rate Charge-carrier Transport in Porphyrin ACS Paragon Plus Environment Covalent Organic Frameworks: Switching from Hole to Electron to Ambipolar Conduction. Angew. Chem. Int. Ed. 2012, 51 (11), 2618-2622

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(6) a) Doonan, C. J.; Tranchemontagne, D. J.; Glover, T. G.; Hunt, J. R.; Yaghi, O. M. Exceptional Ammonia Uptake by a Covalent Organic Framework. Nat. Chem. 2010, 2 (3), 235-238; b) Oh, H.; Kalidindi, S. B.; Um, Y.; Bureekaew, S.; Schmid, R.; Fischer, R. A.; Hirscher, M. A Cryogenically Flexible Covalent Organic Framework for Efficient Hydrogen Isotope Separation by Quantum Sieving.. Angew. Chem. Int. Ed. 2013, 52 (50), 13219-13222; c) Biswal, B. P.; Chaudhari, H. D.; Banerjee, R.; Kharul, U. K. Chemically Stable Covalent Organic Framework (COF)-Polybenzimidazole Hybrid Membranes: Enhanced Gas Separation through Pore Modulation. Chem. Eur. J. 2016, 22 (14), 4695-4699; d) Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R. Removal of GenX and Perfluorinated Alkyl Substances from Water by Amine-Functionalized Covalent Organic Frameworks. J. Am. Chem. Soc. 2018, 140 (40), 12677-12681; e) Sun, Q.; Aguila, B.; Earl, L. D.; Abney, C. W.; Wojtas, L.; Thallapally, P. K.; Ma, S. Covalent Organic Frameworks as a Decorating Platform for Utilization and Affinity Enhancement of Chelating Sites for Radionuclide Sequestration. Adv. Mater. 2018, 30 (20), e1705479.

(7) a) Das, G.; Biswal, B. P.; Kandambeth, S.; Venkatesh, V.; Kaur, G.; Addicoat, M.; Heine, T.; Verma, S.; Banerjee, R. Chemical Sensing in Two Dimensional Porous Covalent Organic Nanosheets. Chem. Sci. 2015, 6 (7), 3931-3939; b) Gao, Q.; Li, X.; Ning, G. H.; Leng, K.; Tian, B.; Liu, C.; Tang, W.; Xu, H. S.; Loh, K. P. Highly Photoluminescent Two-Dimensional Imine-based Covalent Organic Frameworks for Chemical Sensing. Chem. Commun. 2018, 54 (19), 2349-2352.

(8) a) Keller, N.; Bessinger, D.; Reuter, S.; Calik, M.; Ascherl, L.; Hanusch, F. C.; Auras, F.; Bein, T. Oligothiophene-Bridged Conjugated Covalent Organic Frameworks. J. Am. Chem. Soc. 2017, 139 (24), 8194-8199; b) Dogru, M.; Bein, T. On the Road towards Electroactive Covalent Organic Frameworks. Chem. Commun. 2014, 50 (42), 5531-46.

(9) Ding, S. Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W. G.; Su, C. Y.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction. J. Am. Chem. Soc. 2011, 133 (49), 19816-19822.

(10) a) Stegbauer, L.; Schwinghammer, K.; Lotsch, B. V. A Hydrazone-based Covalent Organic Framework for Photocatalytic Hydrogen Production. Chem. Sci. 2014, 5 (7), 2789-2793; b) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-induced Hydrogen Generation. Nat. Commun. 2015, 6, 8508; c) Pachfule, P.; Acharjya, A.; Roeser, J.; Langenhahn, T.; Schwarze, M.; Schomaecker, R.; Thomas, A.; Schmidt, J. Diacetylene Functionalized Covalent Organic Framework (COF) for Photocatalytic Hydrogen Generation. J. Am. Chem. Soc., 2018, 140 (4), 1423-1427; d) Wang, X.; Chen, L.; Chong, S. Y.; Little, M. A.; Wu, Y.; Zhu, W. H.; Clowes, R.; Yan, Y.; Zwijnenburg, M. A.; Sprick, R. S.; Cooper, A. I. Sulfone-containing Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution from Water. Nat. Chem. 2018, 10, 1180–1189; e) Banerjee, T. and Lotsch, B. V. The Wetter the Better. Nat. Chem., 2018, 10, 1175-1177; f) Haase, F.; Banerjee, T.; Savasci, G.; Ochsenfeld, C.; Lotsch, B. V. Structure-property-activity Relationships in a Pyridine Containing Azine-linked Covalent Organic Framework for Photocatalytic Hydrogen Evolution. Faraday Discuss. 2017, 201, 247-264.

(11) Barber, J.; Tran, P. D. From Natural to Artificial Photosynthesis. J. R. Soc. Interface 2013, 10 (81), 20120984.

(12) Banerjee, T.; Haase, F.; Savasci, G.; Gottschling, K.; Ochsenfeld, C.; Lotsch, B. V. Single-Site Photocatalytic H₂ Evolution from Covalent Organic Frameworks with Molecular Cobaloxime Co-Catalysts. J. Am. Chem. Soc., 2017, 139 (45), 16228-16234.

(13) a) Zhang, P.; Wang, M.; Dong, J. F.; Li, X. Q.; Wang, F.; Wu, L. Z.; Sun, L. C. Photocatalytic Hydrogen Production from Water by Noble-Metal-Free Molecular Catalyst Systems Containing Rose Bengal and the Cobaloximes of BFx-Bridged Oxime Ligands. J. Phys. Chem. C 2010, 114, 15868-15874; b) Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. Cobaloxime-based Photocatalytic Devices for Hydrogen Production. Angew. Chem., Int. Ed. ACS Paragon Plus Environment

2008, 47, 564; c) Du, P. W.; Knowles, K.; Eisenberg, R. A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst. J. Am. Chem. Soc. 2008, 130, 12576-12577; d) Lazarides, T.; McCormick, T.; Du, P. W.; Luo, G. G.; Lindley, B.; Eisenberg, R. Making Hydrogen from Water Using a Homogeneous System Without Noble Metals. J. Am. Chem. Soc. 2009, 131, 9192-9194; e) Probst, B.; Rodenberg, A.; Guttentag, M.; Hamm, P.; Alberto, R. Highly Stable Rhenium-Cobalt System for Photocatalytic H2 Production: Unraveling the Performance-Limiting Steps. Inorg. Chem. 2010, 49, 6453-6460.

(14) a) Hawecker, I.: Lehn, I. M.: Ziessel, R. Efficient Homogenious Photochemical Hydrogen Generation and Water Reduction Mediated by Cobaloxime or Macrocyclic Cobalt Complexes. Nouv. J. Chim. 1983, 7, 271; b) McCormick, T. M.; Han, Z. J.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Impact of Ligand Exchange in Hydrogen Production from Cobaloxime-Containing Photocatalytic Systems. Inorg. Chem. 2011, 50, 10660-10666.

(15) a) Han, Z.; McNamara, W. R.; Eum, M. S.; Holland, P. L.; Eisenberg, R. A Nickel Thiolate Catalyst for the Long-lived Photocatalytic Production of Hydrogen in a Noble-metal-free System. Angew. Chem. Int. Ed. 2012, 51 (7), 1667-70; b) Rao, H.; Yu, W.-Q.; Zheng, H.-Q.; Bonin, J.; Fan, Y.-T.; Hou, H.-W. Highly Efficient Photocatalytic Hydrogen Evolution from Nickel Quinolinethiolate Complexes under Visible Light Irradiation. J. Power Sources 2016, 324, 253-260; c) Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Nickel Complexes for Robust Light-Driven and Electrocatalytic Hydrogen Production from Water. ACS Catal. 2015, 5 (3), 1397-1406.

(16) a) Bouwman, E.; Reedijk, J. Structural and Functional Models related to the Nickel Hydrogenases. Coord. Chem. Rev. 2005, 249, 1555 - 1581; b) Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. Structure/Function Relationships of [NiFe]- and [FeFe]-Hydrogenases. Chem. Rev. 2007, 107, 4273 - 4303; c) Tard, C.; Pickett, C. J. Structural and Functional Analogues of the Active Sites of the [Fe]-, [NiFe]-, and [FeFe]-Hydrogenases. Chem. Rev. 2009, 109, 2245 - 2274; d) Carroll, M. E.; Barton, B. E.; Gray, D. L.; Mack, A. E.; Rauchfuss, T. B. Active-Site Models for the Nickel-Iron Hydrogenases: Effects of Ligands on Reactivity and Catalytic Properties. Inorg. Chem. 2011, 50, 9554 - 9563.

(17) a) Bevk, D.; Marin, L.; Lutsen, L.; Vanderzande, D.; Maes, W. Thiazolo[5,4-d]thiazoles - Promising Building Blocks in the Synthesis of Semiconductors for Plastic Electronics. RSC Adv. 2013, 3 (29), 11418; b) Dessì, A.; Calamante, M.; Mordini, A.; Peruzzini, M.; Sinicropi, A.; Basosi, R.; Fabrizi de Biani, F.; Taddei, M.; Colonna, D.; di Carlo, A.; Reginato, G.; Zani, L. Thiazolo[5,4-d]thiazole-based Organic Sensitizers with Strong Visible Light Absorption for Transparent, Efficient and Stable Dye-sensitized Solar Cells. RSC Adv. 2015, 5 (41), 32657-32668; c) Olgun, U.; Gülfen, M. Effects of Different Dopants on the Band Gap and Electrical Conductivity of the Poly(phenylene-thiazolo[5,4-d]thiazole) Copolymer. RSC Adv. 2014, 4 (48), 25165-25171; d) Woodward, A. N.; Kolesar, J. M.; Hall, S. R.; Saleh, N. A.; Jones, D. S.; Walter, M. G. Thiazolothiazole Fluorophores Exhibiting Strong Fluorescence and Viologen-Like Reversible Electrochromism. J. Am. Chem. Soc. 2017, 139 (25), 8467-8473.

(18) Zhang, W.; Hong, J.; Zheng, J.; Huang, Z.; Zhou, J. S.; and Xu, R. Nickel-Thiolate Complex Catalyst Assembled in One Step in Water for Solar H₂ Production. J. Am. Chem. Soc., 2011, 133, 20680-20683.

(19) Zhu, Y.; Zhang, W. Reversible Tuning of Pore Size and CO2 Adsorption in Azobenzene Functionalized Porous Organic Polymers. Chem. Sci. 2014, 5, 4957-4961.

(20) a) Kussmann, J.; Ochsenfeld, C. Pre-selective screening for matrix elements in linear-scaling exact exchange calculations. J Chem Phys. 2013, 138, 134114; b) Kussmann, J.; Ochsenfeld, C. Preselective screening for linear-scaling exact exchange-gradient calculations for graphics processing units and general strong-scaling massively parallel calculations. J. Chem. Theory Comput. 2015, 11, 918-922; c) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic structure calculations on workstation computers: The program system turbomole. Chem. Phys. Lett. 1989, 162, 165-169.; d) TURBOMOLE V7.3 2018, a development of University of Karlsruhe

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and Forschungszentrum Karlsruhe *GmbH*, **1989-2007**, *TURBO-MOLE GmbH*, since **2007**; available from http://www.turbo-mole.com.

(21) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, *134* (48), 19524-19527.

(22) a) Peng, L.-Z.; Liu, P. Cheng, Q.-Q.; Hu, W.-J.; Liu, Y. A.; Li, J.-S.; Jiang, B.; Jia, X.-S.; Yang, H.; and Wen, K. Highly Effective Electrosynthesis of Hydrogen Peroxide from Oxygen on a Redox-active Cationic Covalent Triazine Network. *Chem. Commun.* **2018**, *54*, 4433-4436; b) Wei, P.-F.; Qi, M.-Z.; Wang, Z.-P.; Ding, S.-Y.; Yu, W.; Liu, Q.; Wang, L.-K.; Wang, H.-Z.; An, W.-K. and Wang, W. Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 4623–4631.

13 (23) a) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. 14 C. Electrochemical Considerations for Determining Absolute Fron-15 tier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. Adv. Mater. 2011, 23, 2367-2371; b) Calik, M.; Auras, F.; 16 Salonen, L. M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D. D.; 17 Dogru, M.; Löbermann, F.; Trauner, D.; Hartschuh, A.; and Bein, T. 18 Extraction of Photogenerated Electrons and Holes from a Covalent 19 Organic Framework Integrated Heterojunction. J. Am. Chem. Soc. 20 2014, 136, 17802-17807; c) Zhao, W.; Zhuang, X.; Wu, D.; Zhang, 21 F.; Gehrig, D.; Laquaib, F. and Feng, X. Boron-π-nitrogen-based Conjugated Porous Polymers with Multi-functions. J. Mater. Chem. A 22 2013, 1, 13878-13884; d) Pellegrin, Y.; Odobel, F., Sacrificial elec-23 tron donor reagents for solar fuel production. C. R. Chim. 2017, 20 24 (3), 283-295. 25

(24) a) Kagalwala, H. N.; Gottlieb, E.; Li, G.; Li, T.; Jin, R;. and Bernhard, S. Photocatalytic Hydrogen Generation System Using a Nickel-Thiolate Hexameric Cluster. *Inorg. Chem.*, **2013**, *52*, 9094–9101; b) Gould, R. O.; Harding, M. M. Nickel and Palladium Complexes of 1-Hydroxyethane-2-thiol and Analogues. Part 1. Crystal Structure of Cydohexakis[bis-(p-I -hydroxyethane-2-thiolato) -nickel (II)]. *J. Chem. Soc. A* **1970**, *6*, 875–881.

(25) a) Schwinghammer, K.; Tuffy, B.; Mesch, M. B.; Wirnhier, E.; 31 Martineau, C.; Taulelle, F.; Schnick, W.; Senker, J.; Lotsch, B. V. Tria-32 zine-based Carbon Nitrides for Visible-Light-Driven Hydrogen Evo-33 lution. Angew. Chem. Int. Ed. 2013, 52, 2435-2439; b) Zhang, J.; 34 Chen, X.; Takanabe, K.; Maeda, K.; Domen, K.; Epping, J. D.; Fu, X.; 35 Antonietti, M.; Wang, X. Synthesis of a Carbon Nitride Structure for Visible-light Catalysis by Copolymerization. Angew. Chem. Int. Ed. 36 2010, 49, 441-444; c) Indra, A.; Menezes, P. W.; Kailasam, K.; 37 Hollmann, D.; Schroder, M.; Thomas, A.; Bruckner A.; and Driess; M. 38 Nickel as a Co-catalyst for Photocatalytic Hydrogen Evolution on 39 Graphitic-carbon Nitride (sg-CN): What is the nature of the Active 40 Species? Chem. Commun., 2016, 52, 104-107; d) Kasap, H.; Caputo, C. A.; Martindale, B. C.; Godin, R.; Lau, V. W.; Lotsch, B. V.; Durrant, J. 41 R.; Reisner, E. Solar-Driven Reduction of Aqueous Protons Coupled 42 to Selective Alcohol Oxidation with a Carbon Nitride-Molecular Ni 43 Catalyst System. J. Am. Chem. Soc. 2016, 138 (29), 9183-9192; e) 44 Zeng, D.; Ong, W.-J.; Zheng, H.; Wu, Chen, M. Y.; Peng, D.-L.; and Han, 45 M.-Y. Ni₁₂P₅ Nanoparticles Embedded into Porous g-C₃N₄ Nanosheets as a Noble-metal-free Hetero-structure Photocatalyst 46 for Efficient H2 Production under Visible Light. J. Mater. Chem. A, 47 2017, 5, 16171-16178; f) Martindale, B. C. M.; Hutton, G. A. M.; Ca-48 puto, C. A.; and Reisner, E. Solar Hydrogen Production Using Carbon 49 Quantum Dots and a Molecular Nickel Catalyst. J. Am. Chem. Soc. 50 2015, 137, 6018-6025.

(26) Nanda, J.; Sapra, S.; Sarma, D. D.; Chandrasekharan, N.; Hodes, G. Size-Selected Zinc Sulfide Nanocrystallites: Synthesis, Structure, and Optical Studies. *Chem. Mater.* **2000**, *12*, 1018–1024.

(27) Biswal, B. P.; Becker, D.; Chandrasekhar, N.; Seenath, J. S.; Paasch, S.; Machill, S.; Hennersdorf, F.; Brunner, E.; Weigand, J. J.; Berger, R.; Feng, X. Exploration of Thiazolo[5,4-d]thiazole Linkages in Conjugated Porous Organic Polymers for Chemoselective Molecular Sieving. *Chem. Eur. J.* **2018**, *24* (42), 10868-10875.

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