Sulfone Containing Covalent Organic Frameworks for Photocatalytic Hydrogen Evolution from Water

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ABSTRACT

Nature uses organic molecules for light harvesting and photosynthesis but most man-made water splitting catalysts are inorganic semiconductors. Organic photocatalysts, while attractive because of their synthetic tunability, tend to have low quantum efficiencies for water splitting. Here we present a crystalline covalent organic framework (COF) based on a benzo-bis(benzothiophene sulfone) moiety that shows a much higher activity for photochemical hydrogen evolution than its amorphous or semi-crystalline counterparts. The COF is stable under long-term visible irradiation and shows steady photochemical hydrogen evolution with a sacrificial electron donor for at least fifty hours. We attribute its high quantum efficiency of FS-COF to its crystallinity, its strong visible light absorption, and its wettable, hydrophilic 3.2 nm mesopores. These pores allow the framework to be dye sensitized, leading to a further 61% enhancement in the hydrogen evolution rate up to 16.3 mmol g^{-1} h^{-1}. The COF also retained its photocatalytic activity when cast as a thin film onto a support.

Photocatalytic solar hydrogen production—or water splitting—offers an abundant clean energy source for the future. The use of dispersed, powdered photocatalysts or thin catalyst films is attractively simple, but so far, no catalyst satisfies the combined requirements of cost, stability and solar-to-hydrogen efficiency. Since the first report of TiO_2 as a photocatalyst,[1] many inorganic semiconductors have been explored for water splitting, both in photoelectrochemical cells and as photocatalyst suspensions.[2–4] Recently, organic semiconductors have emerged as promising materials for photocatalytic hydrogen and oxygen evolution.[5–7] Poly(*p*-phenylene) was first reported as a photocatalyst for hydrogen evolution in 1985,[8,9] but its activity was poor and limited to the ultraviolet spectrum. Since then, more active organic materials have been reported as visible light photocatalysts for hydrogen production using sacrificial donors. This started with carbon nitrides[5,10] followed by poly(azomethine)s,[11] conjugated microporous polymers (CMPs),[6,12,13] linear conjugated polymers,[12,14–16] and covalent triazine-based frameworks (CTFs).[17–19] Carbon nitrides were further developed into hybrid systems that facilitate overall water splitting to produce both hydrogen and oxygen, for example by including metal co-catalysts.[20] CMPs were also claimed to exhibit overall photocatalytic water splitting.[21] However, while it is possible to tune semiconductor properties such as band gap by modular copolymerization strategies,[6] organic materials such as carbon nitrides, conjugated polymers and CTFs lack long-range order: they are amorphous or semi-crystalline.[17,22] This lack of order might limit the transport of photoactive charges to the catalyst surface.[23] More generally, it is challenging to construct atomistic structure-property relationships for materials where the three-dimensional architecture is poorly defined.

Covalent organic frameworks (COFs)[24–26] are a class of organic materials that combine crystallinity, modular synthetic versatility, high accessible surface areas, and, sometimes, good physicochemical stability.[27–30] With suitable building blocks and layered stacking sequences, COFs have been shown to have high charge-carrier mobilities.[31] So far, only a small number of COFs have been studied for their photocatalytic hydrogen evolution activity.[32,33] A hydrazone-based COF was reported by Lotsch and co-workers in 2014 to be active for sacrificial hydrogen production[34] and this team subsequently reported a series of 2D azine COFs with impressive photocatalytic hydrogen evolution rates of up to 1.7 mmol g^{-1} h^{-1} (**N₃-COF**; Fig. 1a) using

triethanolamine as a sacrificial donor and a platinum cocatalyst.[35,36] Recently, Thomas and co-workers described a diacetylene functionalized COF with good hydrogen evolution activity.[37] Kurongot and Banerjee reported a cadmium sulfide–COF composite material with a higher hydrogen evolution rate of 3.68 mmol g^{-1} h^{-1} using lactic acid as the sacrificial agent,[32] although the COF was the minor component in that composite (90 wt. % CdS). Porous COFs can also be modified after synthesis: for example, a molecular cobaloxime co-catalyst was introduced into an azine COF to give a hydrogen evolution rate of 0.78 mmol g^{-1} h^{-1}.[38] Hydrogen evolution rates for a given catalyst can vary substantially in different laboratories depending on the optical set up; with that caveat in mind, **N$_3$-COF** is the most active, unmodified COF for sacrificial hydrogen evolution reported so far.[35] COF films have also been used as carbon dioxide reduction catalysts[39] and, in film form, as photoelectrodes for light-driven water splitting.[40]

We showed before that a linear conjugated copolymer, **P7** (Fig. 1b), exhibits hydrogen evolution rates of up to 1.49 mmol g^{-1} h^{-1} with a sacrificial amine donor under visible irradiation ($\lambda > 420$ nm);[16] that is, close to the value reported for **N$_3$-COF**.[35] We ascribed this to the rigid, planar dibenzo[*b,d*]thiophene sulfone (DBTS) unit in the **P7** copolymer. Homopolymerization of this DBTS monomer gives a polymer, **P10** (Fig. 1b), with an even higher hydrogen evolution rate (3.26 mmol g^{-1} h^{-1}, Supplementary Fig. 95). Unlike COFs, these polymers are semi-crystalline: they are also non-porous and insoluble, which precludes post-synthetic modification strategies. Here, we set out to incorporate the DBTS unit into ordered COFs to investigate the influence of crystallinity and porosity on the photocatalytic activity. This led to a new crystalline organic material, **FS-COF**, which is a better photocatalyst than equivalent amorphous or semi-crystalline conjugated polymers. **FS-COF** also exhibits higher hydrogen evolution rates than other COFs studied so far; up to 16.3 mmol g^{-1} h^{-1} when dye-sensitized, which is almost ten times higher than **N$_3$-COF**.

RESULTS AND DISCUSSION

COF synthesis and characterization

Three COFs, **S-COF**, **FS-COF** and **TP-COF** (Fig. 1c), were synthesized via a Schiff-base condensation reaction of 1,3,5-triformylphloroglucinol with aromatic diamines (Supplementary Figs 1–3). The products undergo an irreversible keto-enol tautomerization, which enhances their chemical stability.[29] We used 3,7-diaminodibenzo[*b,d*]thiophene sulfone (**SA**) as the monomer for **S-COF**, which is a crystalline COF analogue of our semi-crystalline polymers **P7** and **P10** (Fig. 1b). We also used 3,9-diamino-benzo[1,2-*b*:4,5-*b'*]bis[1]benzothiophene sulfone (**FSA**) to produce **FS-COF**, which has fused, extended planar linkers. **TP-COF** was synthesized as before;[41] it was prepared from 4,4''-diamino-*p*-terphenyl (**TPA**) and it is, in essence, **FS-COF** minus the sulfone moieties (Fig. 1c).

All three linkers gave rise to crystalline COFs (Fig. 2, Supplementary Figs 24–28). Based on PXRD data, **FS-COF** (Fig. 2c) appeared to have more long-range order than either **S-COF** (Fig. 2d) or **TP-COF** (Supplementary Fig. 28). This might be because the C–N bond in the **FSA** monomer are parallel whereas the angle between the C–N bonds in the **SA** monomer is ~163° (Supplementary Fig. 14), and hence the regular hexagonal framework in **FS-COF** may be less sensitive than **S-COF** to the insertion of linkers in the 'wrong' geometry. More effective π–π stacking between the fused, planar **FSA** linkers might also help to stabilize **FS-COF**.

Powder X-ray diffraction (PXRD) was used to characterize the three COFs. **FS-COF** exhibited diffraction peaks at 2.71°, 4.73°, 5.52°, 7.35°, which were assigned to the (100), (110), (200) and (210) planes, respectively (Fig. 2c). The broad intensity at 25.19° was assigned to the (001) planes, corresponding to a layer spacing of 3.53 Å. Multiple reflections indicate that **FS-COF** has high periodicity in three dimensions. Le Bail refinements confirmed that the diffraction pattern was consistent with a primitive hexagonal lattice with unit cell parameters ($a = b = 36.205(6)$ Å, $c = 7.285(5)$ Å) similar to an idealized eclipsed model of the **FS-COF** (Fig. 2a, upper). **S-COF** exhibited lower crystallinity, indicated by the broadened diffraction profile. The

observable diffraction intensities can be accounted for by a primitive hexagonal structure with an in-plane lattice parameter of 27.44(2) Å and a π-stacking distance of approximately 3.7 Å. Based on both laboratory and synchrotron X-ray diffraction data (Supplementary Figs 24–27), we propose that FS-COF and S-COF have AA layer stackings (Fig. 1c), rather than AB stacking. However, there are a variety of possible AA stacking patterns (Supplementary Fig. 93) and the X-ray data do not allow us to distinguish between these (Supplementary Figs 25 and 26). For the purposes of structural comparisons with experimental data, we refer to the idealized, perfectly eclipsed AA stacking patterns (Fig, 2a,b) because properties such as porosity are not greatly affected by small shifts in the relative orientation of the layers. By contrast, calculations that are discussed later suggest that the electronic structure of **FS-COF** is quite strongly affected by small changes to the AA layer stacking.

The porosity of these COFs was assessed by nitrogen sorption measurements at 77.3 K. Brunauer–Emmett–Teller (BET) surface areas of **FS-COF**, **S-COF** and **TP-COF** were found to be 1288, 985, and 919 $m^2 g^{-1}$. The measured surface area for **FS-COF** equates to 78% of the calculated nitrogen-accessible surface area for the idealized, eclipsed structure shown in Fig. 2a (1652 $m^2 g^{-1}$). The experimental surface areas for the two less crystalline COFs were lower than the idealized, calculated values (1690 and 2172 $m^2 g^{-1}$ for **S-COF** and **TP-COF**), although both materials were still microporous. The pore diameters derived for **FS-COF**, **S-COF** and **TP-COF** by fitting nonlocal density functional theory models to the N_2 isotherms were 27.6 Å, 22.8 Å and 29.0 Å. All COFs gave rise to nitrogen isotherms with shapes consistent with mesoporosity and sequential, multilayer pore filling (Fig. 3a, Supplementary Figs 18–20).

HR-TEM images of **FS-COF** (Fig. 3b) confirm that it has an ordered, hexagonal pore structure oriented along the crystallographic *c*-axis with a periodicity of approximately 3.0 nm (highlighted area, Fig. 3b), which is consistent with the in-plane pore channels of 3.2 nm in the proposed AA-stacked COF structure. **S-COF** and **TP-COF** exhibited no such clear, ordered domains when analyzed by HR-TEM (Supplementary Fig. 31). Atomic force microscopy

(AFM) images of **FS-COF** deposited onto silicon wafers from water suspensions also show that this COF can be partially exfoliated into thin stacks, albeit not single layers, with thicknesses ranging from 5–25 nm (Supplementary Fig. 33).

UV–visible reflectance spectra of the COFs were measured in the solid-state and the absorption onset was found to be 670, 590 and 540 nm for **FS-COF**, **S-COF**, and **TP-COF** (Fig. 4a). The onsets for **FS-COF**, **S-COF** and **TP-COF** are red-shifted by 70, 45 and 90 nm compared to their diamine monomers. The UV-visible spectra of an amorphous analogue **FS-P**, discussed below, shows a blue shift compared with **FS-COF**, but it also exhibits a red-shifted absorption compared to the diamine monomer. **FS-COF** absorbs more light in the visible spectrum and shows a significant red-shift in its absorption onset compared to the corresponding linear dibenzo[*b*,*d*]thiophene sulfone-based polymers, **P7** and **P10**, by 210 and 184 nm.

Photocatalysis experiments

We next investigated the activity of these COFs for photocatalytic water reduction using ascorbic acid as a sacrificial hole-scavenger and platinum as a co-catalyst. All materials evolved hydrogen under visible light ($\lambda > 420$ nm, Fig. 4b) and the average hydrogen evolution rates were determined to be 1.6 mmol g^{-1} h^{-1} for **TP-COF**, 4.44 mmol g^{-1} h^{-1} for **S-COF**, and 10.1 mmol g^{-1} h^{-1} for **FS-COF**. As in previous reports for porous titania glasses[42], strontium titanate,[43] and carbon nitride,[5] we observed the production of smaller, though still significant, quantities of hydrogen without the addition of platinum for **S-COF** and **FS-COF** with rates of 0.6 mmol g^{-1} h^{-1} and 1.32 mmol g^{-1} h^{-1}, respectively. No hydrogen production was observed for **TP-COF** without platinum. The mass-normalized hydrogen evolution rate for **FS-COF** of 10.1 mmol g^{-1} h^{-1} is the highest reported for a photocatalytically active COF (Table 1). This rate is 22 times higher than for **N₃-COF** (0.47 mmol g^{-1} h^{-1}), as measured by us under identical conditions over 5 hours (with ascorbic acid), and around six times higher than the optimized rate reported for **N₃-COF** by Vyas *et al.* using triethanolamine as a sacrificial donor.[35]

An external quantum efficiency (EQE) of 3.2% was determined for **FS-COF** at 420 nm (violet light), whereas 1.3% was reported for the diacetylene COF[37] at 420 nm and 0.44% for **N₃-COF** at 450 nm both using TEOA as a scavenger.[35] At even longer-wavelengths (600 nm, orange light), **FS-COF** still displayed an EQE of 0.6% (Supplementary Fig. 40).

Longer-term photolysis experiments for **FS-COF** with up to 50 hours of visible light irradiation ($\lambda > 420$ nm, Fig. 4c) showed no significant decrease in the catalytic performance over time, suggesting good stability. No changes to the PXRD patterns were observed after long-term irradiation, showing that the crystallinity was retained (Supplementary Fig. 49). For comparison, we estimate that the 50 hour photolysis reported for **N₃-COF**,[35] also using ascorbic acid as a sacrificial donor, yielded an average hydrogen evolution rate of around 0.08 mmol g^{-1} h^{-1} (Supplementary Fig. 63 in ref. 35); about 125 times lower than we observe for **FS-COF**.

The marked difference in catalytic activity between **FS-COF** and the isostructural framework **TP-COF** can be explained at least in part by the red-shift in the absorption onset, which allows **FS-COF** to absorb more visible photons. The partial exfoliation of **FS-COF** may also contribute.[10,44] The higher BET surface area of 1288 m^2 g^{-1} for **FS-COF** versus 919 m^2 g^{-1} for **TP-COF** might also enhance the availabliity of photogenerated charges for water reduction. For context, diffusion lengths of up to around 10 nm have been reported for thin-films of conjugated polymers;[45–47] hence, photogenerated charges produced inside non-porous particles much larger than 10 nm may not reach the particle surface.

Introducing sulfone groups results in much lower contact angles with pure water for **FS-COF** (23.6°) and **S-COF** (43.7°) in comparison with **TP-COF** (59.7°) and **N₃-COF** (53.4°). These contact angles are low for organic materials: for reference, most organic polymers have contact angles in the range 60–110°, and poly(vinyl alcohol) has a contact angle of around 51°.[48] Water vapour uptake measurements (Fig. 3c) show type II isotherms for **FS-COF, S-COF** and **TP-COF**. Functionalized **FS-COF** and **S-COF** adsorb 67 wt. % and 42 wt. % water at 293 K and 22.9 mbar; by comparison, **TP-COF** adsorbs only 16 wt. % water under the same

conditions. This is due to water condensation[49] within the mesopores of **FS-COF**, which are decorated with a large number of polarized heteroatoms (Fig. 2a). Wetting matters in aqueous photocatalysis because particle dispersibility and favourable interactions with water and the sacrificial donor are required for good photocatalytic performance. The water isotherm for **FS-COF** shows that the internal pore structure of the material is accessible to water, as well as the external surface, thus increasing the number of potential sites for photocatalytic water reduction.

Besides light absorption, particle size, and wettability, crystallinity might be important in the catalytic the performance of **FS-COF**. In particular, the eclipsed AA layered structure of **FS-COF** (Fig. 2a) might facilitate charge-carrier transport in the material, although it is not possible at this stage to deconvolute this from other factors, such as surface area. Increased long-range order in carbon nitride was reported to improve photocatalytic activity by enhancing charge-transport to active sites.[22] In this study, both **S-COF** and **FS-COF** strongly outperformed the corresponding semi-crystalline conjugated co-polymers, **P7**[16] and **P10**, that were the inspiration for these frameworks (Fig. 1, Table 1): under comparable conditions, **FS-COF** is around twelve times more active than **P7**, and it is seven times more active than **P10** (Table 1).

To further investigate the effect of crystallinity on photocatalytic performance, we synthesized **FS-P**, an almost amorphous analogue of **FS-COF** (Supplementary Fig. 29). We did this by carrying out the synthesis using 1,2-dichlorobenzene as solvent, rather than mixture of 1,4-dioxane and mesitylene (Supplementary Section 2). Amorphous **FS-P** showed much lower photocatalytic activity ($\lambda > 420$ nm) and a hydrogen evolution rate of only 1.12 mmol g^{-1} h^{-1}; nine times lower than **FS-COF**. **FS-P** showed a slightly blue-shifted absorption on-set (Fig. 4a) relative to **FS-COF**, possibly because the delocalization that arises from π–π stacking in **FS-COF** is disrupted in this amorphous analogue, although its visible light absorption profile is still more favourable than **S-COF** or **TP-COF**. The low activity of **FS-P** may also be related to

its reduced surface area (209 m^2 g^{-1}) and a lower degree of condensation in the amorphous polymer. Weak absorption bands were observed in the FT-IR spectrum at 3371 and 3473 cm^{-1}, which are probably due to amine end-groups.[29] Another important factor could be the particle size of the *in situ* deposited platinum co-catalyst: **FS-COF** has well-defined 3 nm sized platinum nanoparticles on its surface (Supplementary Fig. 32), and it is possible that the size is controlled by the uniform mesopores in the COF. By contrast, undefined micrometer-sized platinum aggregates were formed on the surface of amorphous **FS-P**.

We used time-correlated single photon counting to estimate the excited state lifetimes for these materials in aqueous suspensions (Fig. 4d). The average weighted lifetime of **FS-COF** (τ_{avg} = 5.56 ns) was estimated to be significantly longer than that of **TP-COF** (τ_{avg} = 0.25 ns) or **FS-P** (τ_{avg} = 2.21 ns), which correlates with the higher photocatalytic performance observed for **FS-COF.**

Computational studies

For a COF to act as a hydrogen evolution photocatalyst, it must absorb light efficiently over a broad range in the visible spectrum as well transporting the electron–hole pairs, or excitons, that are formed upon light absorption. The COF must also thermodynamically drive the reduction of protons and the oxidation of water—or in this study, the sacrificial electron donor (SED), ascorbic acid. To achieve this, the electron affinity (EA) of the COF or its exciton ionization potential (IP*) and the ionization potential (IP) of the COF or its exciton electron affinity (EA*) should straddle the proton reduction and water/SED oxidation potentials.[50] Because the potentials of a polymer are difficult to measure experimentally,[51] we instead predicted them computationally using density functional theory (DFT). We did this using two different approaches; cluster calculations on representative fragments of the COFs embedded in a dielectric continuum to model the COF–water interface and periodic calculations on COF crystal structures. These two approaches complement each other. By necessity, the periodic calculations approximate IP and EA by the Kohn–Sham valence band maximum (VBM) and

conduction band minimum (CBM). Hence, these calculations cannot describe the effect of immersing the COF in water, but they do take into account the influence of layer stacking. Cluster calculations are limited to a fragment, but unlike the periodic calculations, they describe the effect of water and allow us to calculate the exciton potentials and the exciton binding energy (EBE). The latter is important for polymers, where the EBE is generally large relative to kT (26 meV at room temperature) such that spontaneous dissociation of excitons into free electrons and holes is unlikely.

The cluster DFT (B3LYP) calculations on fragments embedded in a continuum with the relative dielectric permittivity of water predict that **S-COF**, **FS-COF** and **TP-COF** should all have a substantial thermodynamic driving forces for proton reduction (Fig. 5a,b). Water oxidation is predicted to be endergonic or negligibly exergonic, providing a thermodynamic explanation for the inability of these materials to drive hydrogen evolution without a sacrificial agent. Ascorbic acid was used as a SED because its one-hole and two-hole oxidation potentials are more negative than the water oxidation potential, meaning it is more easily oxidized (Fig. 5a).

Cluster calculations for **N$_3$-COF** (Fig. 5a,b) suggest a different picture. While the IP and EA of N$_3$(L) straddle both water splitting half-reaction potentials, suggesting a driving force for overall water splitting, the EA* and IP* do not; this means that overall water splitting is still not thermodynamically favoured without bulk exciton dissociation—and the exciton binding energy is predicted to be as large as 0.92 eV. Calculations using range-separated density functionals also suggest that the exciton binding energy in **N$_3$-COF** is large (Supplementary Fig. 91). The IP* of N$_3$(L) is only marginally more negative than the potential of proton reduction and the EA* marginally more positive than the potential of the one-hole oxidation of ascorbic acid. The relatively low photocatalytic activity of **N$_3$-COF** with ascorbic acid might therefore be linked to the combined effects of difficult exciton dissociation in the bulk material and the small driving forces associated with exciton dissociation at the photocatalyst–solution interface.

Next, periodic DFT (HSE06) calculations were performed to investigate the electronic structures of the COF crystals. The position of the VBM and CBM for each COF crystal structure was referenced to a common vacuum level (Fig. 5c), determined by the value of the electrostatic potential at the centre of an internal pore. Both eclipsed (AA) and staggered (AB) stacking sequences were considered for **S-COF**, **FS-COF**, and **TP-COF** (Fig. 5d); the eclipsed AA layered structure of **N$_3$-COF** was also included for comparison. Our periodic results corroborate the molecular fragment picture; all of these COF materials are predicted, in certain AA packings, to be thermodynamically able to reduce protons and oxidize ascorbic acid, in line with experiments. The exact positions of VBM and CBM for **FS-COF** were found to be sensitive to the small changes to the crystal structure, and this is most likely true for the other COFs as well. The CBM of the idealized, eclipsed AA-stacked **FS-COF** structure lies, in fact, below the proton reduction potential: hence, in the absence of water at least, this structure is not predicted to drive proton reduction. However, calculations show that minor levels of disorder, such as small offsets between neighbouring layers or partial/full flipping of the FS linkers in alternating layers, can alter the band edge positions (black horizontal lines in Fig. 5c, also Supplementary Fig. 93). All of these possible AA-stacked structure models are close in computed total lattice energy (Supplementary Table 7) and we cannot distinguish between them using either laboratory or synchrotron PXRD data (Supplementary Fig. 26). These calculations, coupled with the photocatalytic proton reduction observed for **FS-COF**, suggest that the crystal packing might not be exclusively the idealized AA stacking, although we note that the effect of water, as discussed above, cannot be included in these periodic calculations.

As observed experimentally, calculations predict correctly that **FS-COF** has the smallest optical gap among the four COF materials studied here and thus, probably, the largest rates of visible photon absorption and exciton generation. This is combined with favourably positioned IP/EA*/VBM and EA/IP*/CBM levels, at least for certain AA packings, to sustain a driving force for both redox half reactions. Other factors may also contribute to the photocatalytic performance of **FS-COF**, such as its strong affinity for water (Fig. 3c), good wettability

(Supplementary Fig. 34), well-dispersed Pt cocatalyst particles (Supplementary Fig. 32), and the longer excited state lifetime in this material (Fig. 4d).

Dye sensitization

The ordered mesoporosity in these frameworks offers various opportunities for post-synthetic modification. For example, we explored the dye sensitization of **FS-COF** with the goal of further enhancing its photocatalytic performance.[52] Addition of 2′,7′-dichlorofluorescein (Supplementary Fig. 75) reduced the photocatalytic performance of **FS-COF**, while Rose Bengal (sodium salt of 4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein) slightly improved the performance. However, when Eosin Y (2′,4′,5′,7′-tetrabromofluorescein) was added, hydrogen evolution rates for **FS-COF** were enhanced by up to 60%; from 10.1 mmol g^{-1} h^{-1} to 13 mmol g^{-1} h^{-1} (10 mg dye, 5 mg of **FS-COF**) and to 16.1 mmol g^{-1} h^{-1} when 20 mg of the dye was added. Further increases in the dye loading reduced the catalytic rate (Supplementary Fig. 76). By contrast, the hydrogen evolution rate of 5 mg of amorphous **FS-P** was reduced from 1.1 mmol g^{-1} h^{-1} to 0.58 mmol g^{-1} h^{-1} in the presence of 20 mg of Eosin Y. The absorption spectrum of Eosin Y overlaps with the absorption spectrum of **FS-COF**, so the addition of dye enhances the total absorption cross section of the system. Likewise, when a larger amount of **FS-COF** was used with no dye, then a similar increase in the hydrogen evolution rate was observed (12.9 mmol g^{-1} h^{-1} for 10 mg **FS-COF** versus 10.1 mmol g^{-1} h^{-1} for 5 mg **FS-COF**).

Eosin Y has a similar absorption spectrum to **FS-COF**, so it does not harvest additional photons in the energy-rich near-infrared region of the solar spectrum where **FS-COF** does not absorb. A greater enhancement in the hydrogen evolution rate was observed when a near-infrared absorbing dye, WS5F, was used. Unlike the previous dyes, WS5F does not dissolve well in water so it was pre-loaded into the COF using acetone before the photocatalytic tests (loading conditions: 5 mg **FS-COF** + 5 mg WS5F). When 5 mg of this dye-sensitized material, **FS-COF+WS5F** was used, we observed a visible light hydrogen evolution rate of 16.3 mmol g^{-1} h^{-1}, again normalized to the mass of the COF. We ascribe this enhancement to the absorption

of more photons at higher wavelengths by the dye-loaded composite, as expressed in the EQE at 600 and 700 nm when using monochromatic light. At 600 nm, **FS-COF** has an EQE of 0.6%, which is increased to 2.2% for the **FS-COF+WS5F** composite. At 700 nm, the composite has an EQE of 0.7%, while **FS-COF** is completely inactive.

We attribute the dye-sensitization effect to host-guest interactions in the large, hydrophilic 1-D mesopore channels (Supplementary Fig. 94), which may help to explain why dye sensitization with Eosin Y and WS5F was unsuccessful for the less porous **FS-P** material. Control experiments using the neat dyes, Eosin Y and WS5F, in the absence of **FS-COF** showed negligible hydrogen production under visible light (0.1 M ascorbic acid solution plus platinum). Likewise, WS5F supported on mesoporous silica (SBA-15) showed no hydrogen evolution under the same conditions.

The photoluminescence (PL) spectra of **FS-COF+WS5F** were measured to investigate the interaction between **FS-COF** and WS5F. As shown in Supplementary Fig. 70, WS5F solution in acetone excited at 410 nm exhibits an intense emission peak at 630 nm, which can be quenched by increasing the concentration of colloidal **FS-COF**. Since there is no obvious overlap between the absorption spectrum of **FS-COF** and the PL emission of WS5F, the fluorescence quenching in **WS5F+FS-COF** is likely to be the result of interfacial electron transfer from the excited dye to **FS-COF**. This is supported by calculations that suggest a favorable energy alignment (Fig. 6d): for example, one possible scheme is that the photoexcited dye transfers electrons to **FS-COF** and is then regenerated by the sacrificial electron donor.[53]

Photocatalysis experiments with thin COF films

Sacrificial hydrogen production is a step on the path to overall water splitting, but the latter may require the construction of more sophisticated architectures, such as Z-schemes.[54-56] Z-schemes comprise two separate, coupled semiconductor phases, where each phase carries out one of the half-reactions in overall water splitting. To create such architectures, processability is important.[57] We found that FS-COF can be dispersed as a colloidal solution in various solvents

(Fig. 6f), and we used this to drop-cast platinized FS-COF onto glass supports. Photocatalytic hydrogen evolution rates (λ > 420 nm, 0.1 M ascorbic acid, 5 hours irradiation) were found to increase with the number of drop-casting cycles (Supplementary Fig. 84), presumably due to increased film thickness, up to 24.9 mmol h^{-1} m^{-2} after 20 successive depositions of the colloidal solution. Longer-term hydrogen evolution experiments for a COF film produced with just a single drop-cast cycle showed steady hydrogen production over 20 hours, indicating that the film was stable under the reaction condition (λ > 420 nm, 0.1 M ascorbic acid) (Figure 6e). We also tested hydrogen evolution of this film under solar simulator irradiation (AM1.5G, classification ABA, ASTM E927-10), which gave a hydrogen evolution rate of 15.8 mmol h^{-1} m^{-2} (~ 0.36 L h^{-1} m^{-2}). This can be compared with data obtained at the lab-scale for carbon nitride films (0.19 L h^{-1} m^{-2}).[58] Scanning electron micrographs (Supplementary Fig. 81) show that these COF films had smooth, uniform morphologies, and AFM analysis (Supplementary Fig. 82) indicates that the film after one drop-casting cycle is around 10 nm thick.

CONCLUSIONS

Although crystallinity is not required for all applications of porous materials,[59] here we see a dramatic enhancement in photocatalytic hydrogen evolution rates for ordered, crystalline COFs over structurally-related amorphous or semi-crystalline solids. Organic building blocks that function well in amorphous polymers, such as dibenzo[*b,d*]thiophene sulfone, lead to materials with better catalytic function when incorporated into COFs. A fused building block, benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene sulfone, forms a COF with a sacrificial hydrogen evolution rate that exceeds our best linear polymers, **P7** and **P10** under comparable conditions, and that is also higher than other reported COFs.[32–37] Because **FS-COF** is mesoporous, it can be dye sensitized to give even higher hydrogen evolution rates of up to 16.3 mmol g^{-1} h^{-1}. **FS-COF** is also stable for at least 50 hours of photolysis in water under visible light (λ > 420 nm), and can be cast as a colloid onto planar supports to form thin films while still retaining its photocatalytic activity and stability.

Computation suggests that the fine detail of the AA layer stacking in **FS-COF**, and by analogy other COF materials, may determine the prospects for thermodynamic proton reduction and

water oxidation. To improve our understanding of structure-property relationships, it would be helpful to produce COFs with greater degrees of long-range order. Recent synthetic developments, such as seeded growth strategies,[60] offer one way forward.

Proton reduction using a sacrificial electron donor is only the first step toward full water splitting,[61] but the mesoporous morphology of these COFs, their processability into films, and their high native photocatalytic activity makes them attractive platforms for developing hybrid photocatalysts. For example, the internal pore structure of COFs such as **FS-COF** could be decorated with quantum dots, photoactive organic molecules, fullerenes, or single-site molecular catalysts. COFs with even larger mesopores might be designed to accommodate a second organic or inorganic semiconductor in the pore channels to produce a Z-scheme photocatalyst for overall water splitting.[62]

METHODS

COF Synthesis. All COFs were prepared using a procedure based on the method described here for the synthesis of **FS-COF**. A Pyrex tube was charged with 2,4,6-triformylphloroglucinol (10.5 mg, 0.05 mmol), 3,9-diamino-benzo[1,2-b:4,5-b']bis[1]benzothiophene-5,5,11,11-tetraoxide (28.8 mg, 0.075 mmol), mesitylene (1.5 mL), 1,4-dioxane (1.5 mL), and aqueous acetic acid (0.3 mL, 6 M). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77.3 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles, before evacuating to a pressure of 100 mTorr. The tube was sealed and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with N,N-dimethylformamide (100 mL) and acetone (200 mL). After drying at 120 °C, the product was obtained a deep red powder (21 mg, 58%). Anal. Calcd for $(C_{30}H_{22}N_2O_8S_2)_n$: C, 61.42; H, 3.78; N, 4.78; S, 10.93. Found: C, 44.80; H, 3.21; N, 3.95; S, 9.93.

Dye sensitization. For water insoluble dyes such as WS5F, the dye was loaded into the COF using an organic solvent prior to hydrogen evolution experiments. To do this, 5 mg WS5F was dissolved in 10 mL acetone and then 5 mg FS-COF was added to the solution and stirred for 12 hours. The resulting mixture was filtered, and the filtrate was dried at 80 °C overnight. Amorphous FS-P was loaded with WS5F in the same way. For water-soluble dyes, the dye was added directly into the photocatalytic mixture. In a typical procedure, a flask was charged with

COF powder (or amorphous polymer) (5 mg), aqueous 0.1 M ascorbic acid solution (25 mL), and hexachloroplatinic acid (5 µL, 8 wt. % aqueous solution). In the case of dye sensitization experiments with water-soluble dyes (Eosin Y (2′,4′,5′,7′ -tetrabromofluorescein), 2′,7′ -dichlorofluorescein or Rose Bengal), the dye was added directly to the flask. Hydrogen evolution rates were normalized to the mass of the COF (or amorphous polymer) in all cases.

Hydrogen evolution experiments. A flask was charged with the photocatalyst powder (5 mg), 0.1 M ascorbic acid water solution (25 mL), hexachloroplatinic acid (5 µl, 8 wt. % aqueous solution) as a platinum precursor and water-soluble dye (if any). The resulting suspension was ultrasonicated for 20 minutes before degassing by N_2 bubbling for 30 minutes. The reaction mixture was illuminated with a 300 W Newport Xe light-source (Model: 6258, Ozone free) for the period specified using appropriate filters. The lamp was cooled by water circulating through a metal jacket. Gas samples were taken with a gas-tight syringe and analysed using a Bruker 450-GC gas chromatograph. Hydrogen was detected with a thermal conductivity S3 detector referencing against a standard gas of known concentration. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations. The rates were determined from a linear regression fit. After 5 hours of photocatalysis, no carbon monoxide associated with framework or scavenger decomposition could be detected on a GC system equipped with a pulsed discharge detector. After the photocatalysis experiment, the **FS-COF** was recovered by washing with water and acetone before drying at 120 °C.

Calculations. For the different molecular fragments representing the COFs, we calculated the standard reduction potentials of half-reactions for free electrons/holes and excitons, using density functional theory (DFT) and time-dependent DFT (TD-DFT). The B3LYP density functional was used for all the DFT and TD-DFT calculations (unless otherwise stated), together with the Def2-SVP basis set,[63] using the Gaussian 16 software.[64] S1 optimizations for the calculations of the exciton potentials (*i.e.*, IP* and EA*) used the Tamm–Dancoff approximation.[65] The effect of solvation by water was accounted for by using the PCM/SMD solvation model.[66,67] The potentials of the solution reactions for one-hole and two-hole oxidation of ascorbic acid were calculated as described in Supplementary section 22, while the experimental values were used for the proton reduction and water oxidation reactions.

Periodic DFT calculations on the COF crystal structures were carried out within the plane-wave pseudopotential formalism, using the Vienna *ab initio* Simulation Package (VASP) code.[69] Geometry optimizations were performed employing the Perdew−Burke−Ernzerhof exchange−correlation functional with the DFT-D3(BJ) dispersion correction.[70–72] A kinetic-

energy cutoff of 500 eV was used to define the plane-wave basis set. The electronic structure of each optimized COF structure was then computed using a screened hybrid exchange−correlation functional (HSE06),[73–75] giving key electronic properties, such as band gap and electrostatic potential. To achieve valence band alignment so that band energies can be compared for the different COF structures, we followed an approach devised for determining the vacuum level of porous structures.[76] Further computational details are provided in Supplementary section 22.

Data availability. All data generated or analysed during this study are included in this published article and the supplementary information files.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to A.I.C.

Author contributions

A.I.C. and X.W. conceived the project. X.W. synthesized the COFs and performed the characterization and photocatalysis experiments. L.C. and M.A.Z. conceived the modelling strategy and performed the calculations. S.Y.C. carried out powder X-ray diffraction analyses. M.A.L. carried out single-crystal X-ray structure analysis. R.S.S. performed the TSPC experiments and co-supervised, with A.I.C., the work on COF synthesis, characterization, and photocatalysis. Y. Y. collected the water sorption isotherms. R.C., X.W. and L.C. interpreted the gas sorption isotherms. Y. W. and W.-H. Z. synthesized and characterized the WS5F dye. All authors interpreted the data and contributed to the preparation of the manuscript.

Competing financial interests

The authors declare no competing financial interest.

Acknowledgements

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Figure 1. Chemical structures of the organic photocatalysts studied here. **a**,**b**, Chemical structures of previously reported photocatalysts (**a**) N_3-**COF**,[35] (**b**) **P7**,[16] and **P10**. **c**, Chemical structures of the COF photocatalysts reported in this work: **S-COF**, **FS-COF** and **TP-COF**.

Figure 2. Crystal structures of FS-COF and S-COF. a,**b**, Structural models for (**a**) **FS-COF** and (**b**) **S-COF** with perfectly eclipsed AA stacking patterns, shown parallel to the pore channel along the crystallographic *c*-axis (top) and parallel to the hexagonal layers (bottom). The pores of both COFs are lined with oxygen atoms. **c**,**d**, Experimental diffraction patterns (red), profiles calculated from Le Bail fitting (black) and residual (blue) and pattern simulated from structural model (green). Reflection positions are shown by tick marks. Grey, white, blue, red and yellow atoms represent carbon, hydrogen, nitrogen, oxygen and sulfur, respectively.

Figure 3. Evidence for ordered, wettable mesopores in FS-COF. a, Nitrogen adsorption isotherm (filled symbols) and desorption isotherm (open symbols) for **FS-COF** recorded at 77.3 K. Inset, profile of the calculated pore size distribution for **FS-COF**. **b**, TEM image of **FS-COF**. Hexagonal pore structure with a periodicity of approximately 3.0 nm outlined by the dashed red box. Scale bars: 50 nm (inset), and 100 nm (bottom). **c**, Water adsorption isotherms (filled symbols) and desorption isotherms (open symbols) for **FS-COF**, **S-COF** and **TP-COF**, measured at 293 K up to 22.9 mBar.

Figure 4. Optical properties, hydrogen evolution rates, and excited state lifetimes for the photocatalysts. a, UV–visible absorption spectra for **FS-COF**, **S-COF**, **TP-COF** and **FS-P** measured in the solid-state. **b**, Time-course for photocatalytic H_2 production using visible light for **FS-COF**, **S-COF**, **TP-COF**, and **FS-P** (5 mg catalyst in water, 5 μL (8 wt. % H_2PtCl_6), 0.1 M ascorbic acid, $\lambda > 420$ nm). **c**, H_2 production using visible light for **FS-COF** over 50 hours total photolysis (5 mg catalyst in water, 5 μL (8 wt. % H_2PtCl_6), 0.1 M ascorbic acid, $\lambda > 420$ nm). The sample was degassed after 5 and 10 hours to prevent saturation of the detector, then left under continuous illumination for 20 hours and again degassed after 40 and 45 hours. After 35 hours 1.25 mmol of ascorbic acid were added. **d**, Time-correlated single photon counting experiments for **TP-COF**, **FS-COF** and **FS-P** in water. The samples were excited with a $\lambda_{exc} = 370.5$ nm laser and emission was observed at $\lambda_{em} = 550$ nm.

Figure 5. Electronic structure calculations provide insights into the photocatalytic water splitting activities of the COFs. a,b, (TD-)B3LYP predicted IP, EA, IP* and EA* adiabatic potentials (**a**) of representative fragments of the different COFs (**b**) in water. **c,d,** Periodic DFT (HSE06) predicted valence band maximum (VBM; red) and conduction band minimum (CBM; blue) of the COFs with respect to a common vacuum level (**c**); both eclipsed (AA) and staggered (AB) stacking arrangements, illustrated in (**d**), were considered. For FS-COF, multiple AA stacked structures were generated, with calculated VBM and CBM for each individual stacking shown as black horizontal lines in (**c**), for which the assignment is shown in Supplementary Fig. 93. The dashed, coloured lines in **a** and **c** indicate the potentials for the different solution reactions: green, proton reduction; orange, two-hole (A/H_2A) and one-hole ($HA^{\cdot}/H_2A$) oxidation of ascorbic acid; magenta, overall water oxidation. All solution potentials shown are for pH 2.6, the experimentally measured pH of a 0.1 M ascorbic acid solution.

Figure 6. Dye sensitization of FS-COF and hydrogen evolution from an FS-COF film.
a, Time-course for photocatalytic H_2 production using visible light for **FS-COF**, a neat, near-infrared dye (WS5F), and a dye-sensitized COF (**FS-COF+WS5F**); 5 mg material in water, 5 µL (8 wt. % H_2PtCl_6), 0.1 M ascorbic acid, $\lambda > 420$ nm). **b**, External quantum efficiencies (EQE) at three different incident light wavelengths for **FS-COF** and **FS-COF+WS5F** (5 mg catalyst in water, 5 µL (8 wt. % H_2PtCl_6), 0.1 M ascorbic acid, $\lambda = 420 \pm 10$, $\lambda = 600 \pm 45$ and 700 ± 10 nm irradiation; Supplementary Fig. 43). **c**, Solid-state UV–vis spectra for **FS-COF**, WS5F and **FS-COF+WS5F**. **d**, Relative energy levels as calculated for ascorbic acid, **FS-COF**, and a near-infrared dye, WS5F; the dashed, green and orange lines indicate the potentials for proton reduction and the two-hole oxidation of ascorbic acid in solution, respectively. **e**,**f**, Photocatalytic H_2 production using **FS-COF** films: **e**, Longer-term hydrogen evolution experiments for a COF film produced with a single drop-cast cycle. **f**, Photograph showing, from left to right, solid FS-COF and colloidal dispersions in DMF, water, and acetone, respectively (*left*), see also Supplementary Figs. 33 & 87; **FS-COF** film on glass producing hydrogen (*right*) (20 drop-casting cycles, 0.1 M ascorbic acid, solar simulator AM1.5G, class ABA; see also video file, Supplementary Movie 1).

Table 1. Photophysical properties and hydrogen evolution rates (HERs) for the COF photocatalysts.

Photocatalyst	Degree of crystallinity	Optical gap[b] / eV	Hydrogen evolution rate[c] / mmol g^{-1} h^{-1}	Hydrogen evolution rate relative to FS-COF
TP-COF[a]	Crystalline	2.28	1.60 ± (0.08)	16%
S-COF[a]	Crystalline	2.10	4.44 ± (0.14)	43%
FS-COF[a]	Crystalline	1.85	10.1 ± (0.3)	–
FS-P[a]	Amorphous	1.88	1.12 ± (0.16)	11%
N$_3$-COF[35]	Crystalline	2.60	0.47 ± (0.06)	4.6%
P7[16]	Semi-crystalline	2.70	0.84 ± (0.06)[d]	8.3%
P10	Semi-crystalline	2.55	1.48 ± (0.1)[d]	15%
FS-COF + WS5F[a]	Crystalline	[e]	16.3 ± (0.29)	161%
FS-COF + Eosin Y[a]	Crystalline	[e]	16.1 ± (0.34)	159%
FS-P + WS5F[a]	Amorphous	[e]	0.23 ± (0.03)	2.3%
FS-P + Eosin Y[a]	Amorphous	[e]	0.58 ± (0.08)	5.8%

[a] This work; [b] Calculated from the on-set of the solid absorption spectrum; [c] All rates measured using the same instruments, optical set-up and reaction conditions: 5 mg COF catalyst, 5 µL (8 wt. % H_2PtCl_6), 25 mL ascorbic acid aqueous solution (0.1 M), 300 W Xe light source equipped with $\lambda > 420$ nm cut-off filter. Hydrogen evolution rates (HER) based on average over 5 hours irradiation and normalized to the COF mass; [d] As for [c], but with no additional platinum catalyst added (Supplementary Fig. 35); HER for P10 in the presence of Pt was 1.92 mmol g^{-1} h^{-1}. [e] Effective optical gap was not measurable due to the intense absorption of the organic dye.

a

N₃-COF

b

P7

P10

c

S-COF

FS-COF

TP-COF

a

b

c

$a = 36.205(6)$, $c = 7.285(5)$ Å
$R_{wp} = 4.35$ %, $\chi^2 = 1.99$

Intensity / a.u.

2θ / degrees

d

$a = 27.44(2)$, $c = 7.321(8)$ Å
$R_{wp} = 6.09$ %, $\chi^2 = 1.40$

Intensity / a.u.

2θ / degrees