

Covalent organic framework nanosheets embedding single cobalt sites for photocatalytic reduction of carbon dioxide

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ABSTRACT: Covalent organic framework nanosheets (CONs), fabricated from two dimensional covalent organic frameworks (COFs), present a promising strategy for incorporating atomically distributed catalytic metal centers into well-defined pore structures with desirable chemical environments. Here, a series of CONs was synthesized embedding single cobalt sites that were then evaluated for photocatalytic carbon dioxide reduction. A partially fluorinated, cobalt-loaded CON produced 10.1 μmol carbon monoxide with a selectivity of 76%, over 6 hours irradiation under visible light (turnover number = 28.1) and a high external quantum efficiency of 6.6% under 420 nm irradiation in the presence of an iridium dye. The CONs appear to act as a semiconducting support, facilitating charge-carrier transfer between the dye and the cobalt centers, and this results in a performance comparable with the state-of-the-art heterogeneous catalysts in the literature under similar conditions. The ultra-thin CONs outperformed their bulk counterparts in all cases, suggesting a general strategy to enhance the photocatalytic activities of COF materials.

INTRODUCTION

The conversion of carbon dioxide into chemical fuels is thought to be one potential avenue to address the rising levels of CO_2 in the atmosphere and the rising energy demand of our growing population.¹⁻³ Photocatalytic reduction of CO_2 has been extensively studied using homogeneous^{4,5} and heterogeneous catalysts.⁶⁻⁸ Homogeneous catalysts usually possess high initial photocatalytic activity and selectivity for the de-

sired products but they are often not stable during extended operation. The use of expensive precious metals, coupled with the difficulty in catalyst recovery and product separation, makes such homogeneous catalysis expensive.^{9,10} Heterogeneous catalysts can address some of these issues because they can be isolated by simple filtration and can show good stability, but are often hampered by their relatively low catalytic activity. One strategy to achieve the combined advantages of homo- and heterogeneous catalysis is to anchor individual

catalytic metal centers on supports, yielding the so-called single-atom or single-site catalysts. It is, however, a significant challenge to construct robust single-atom catalysts, which requires the mononuclear metal complexes or single metal atoms to be atomically distributed and strongly bound to the support, ideally also incorporating functional synergy between the catalytic sites and the support. Recently, metal-organic frameworks (MOFs)¹¹⁻¹³ and covalent organic frameworks (COFs)¹⁴⁻¹⁶ have been reported incorporating single-atom catalysts. Their well-defined pore structures can be tuned to provide optimal confinement of known, catalytically active coordination metal complexes.^{17,1}

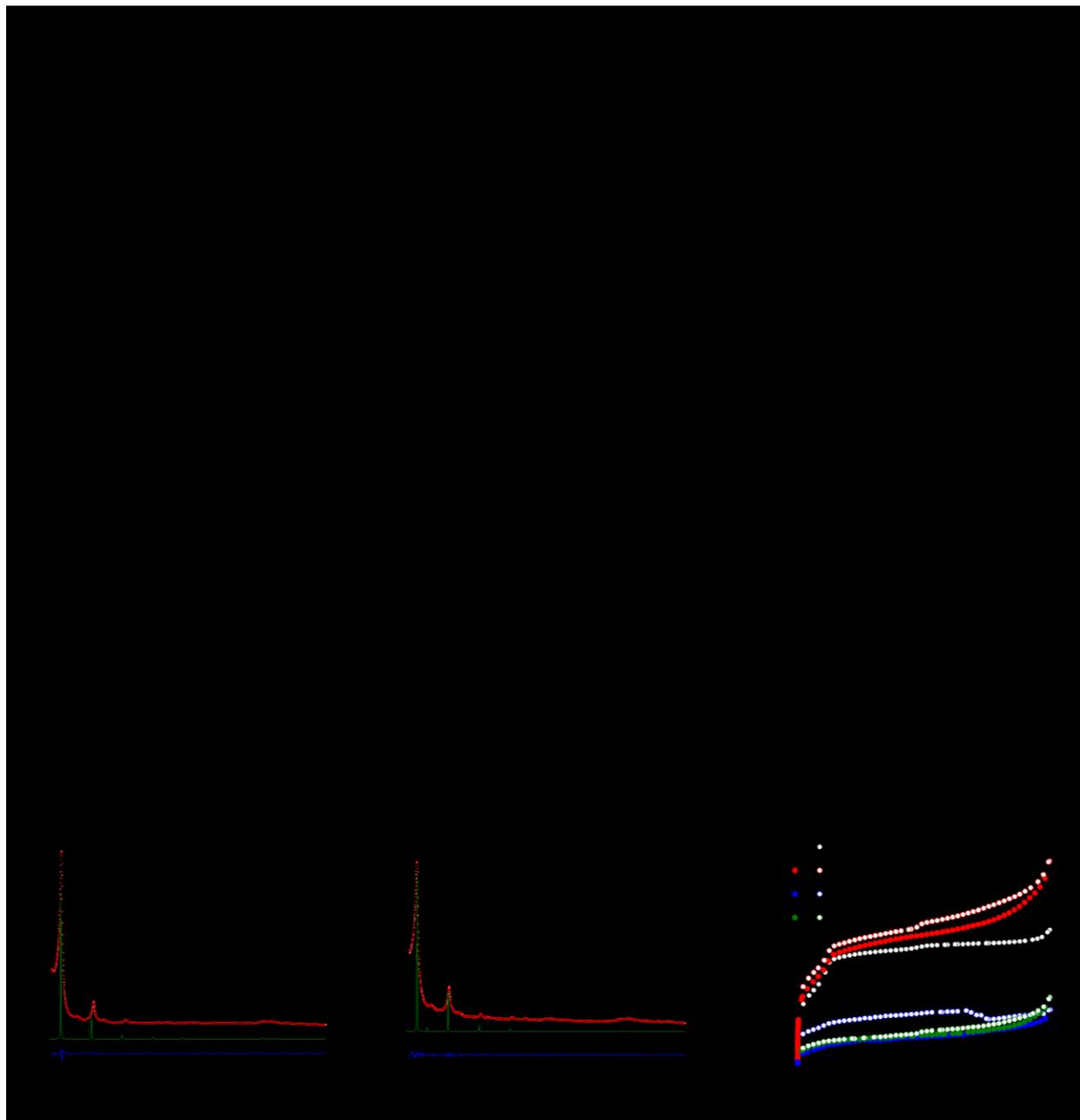


Figure 1. (a) Synthesis of Py-COF and FPy-COF, and fabrication of Co-Py-CON and Co-FPy-CON. (b, c) Experimental diffraction pattern (red), profile calculated from Le Bail fitting (black) and residual (blue), and pattern simulated from the structural model (green) for Py-COF (b) and FPy-COF (c); reflection positions are shown by tick marks. The observed peak shift can be accounted for

by a small difference in the experimental and simulated unit cells. (d) Nitrogen adsorption isotherms (filled symbols) and desorption isotherms (open symbols) for Py-COF, FPy-COF, Co-Py-CON and Co-FPy-CON, recorded at 77.3 K.

Alternatively, molecular catalysts can be chemically tethered together in the form of a COF or MOF to afford heterogeneous catalysts, possessing spatially arranged catalytic sites and a precise control of the chemical environment around them.^{14,19,20} MOFs have been shown to be active for photocatalytic for CO₂ reduction, producing CO or formate.²¹⁻²⁴ Similarly, two-dimensional (2D) COFs have been reported as highly active photocatalysts for hydrogen production²⁵⁻²⁷ and CO₂ reduction,^{14,28,29} and they have the potential to be ideal supports for anchoring atomically distributed metal centers. Comparing COFs to MOFs, the former are composed of covalent bonds rather than coordination bonds, often making (though not always) making them more stable. COFs can be conjugated in two dimensions, unlike MOFs which are usually not, offering a faster response to photoexcitation.¹⁴ Moreover COFs can be exfoliated, further increasing the surface area that can be in contact with the reaction medium. Also, COFs often have narrow band-gaps allowing efficient utilization of the solar spectrum.

Examples of COFs include materials that contain bipyridine-based units which have been previously used to stabilize metal atoms within the framework.^{14,15} Although these 2D COF

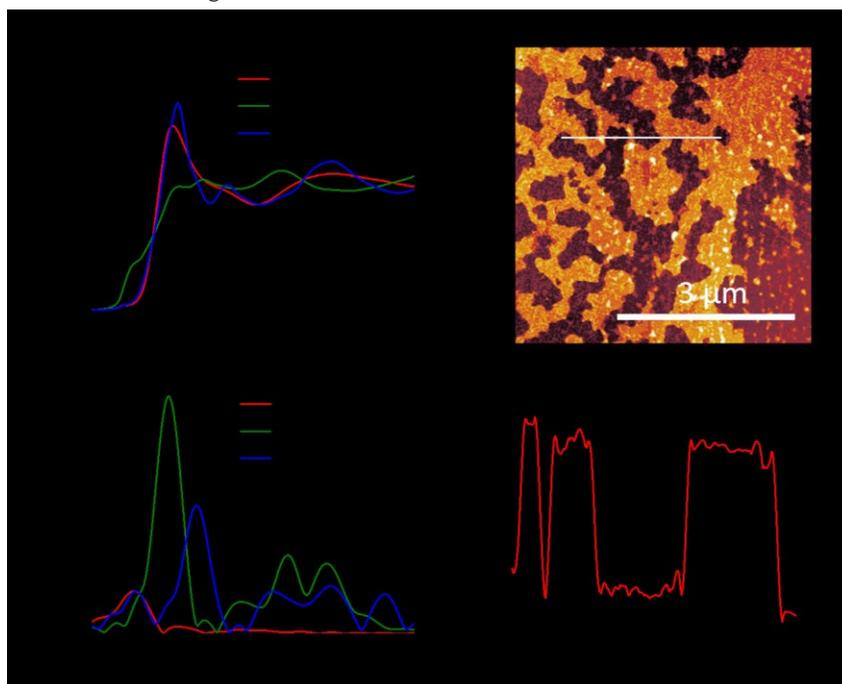


Figure 2. (a, b) XANES spectra at the Co K-edge (a), and k^3 -weighted Fourier-transformed Co K-edge EXAFS spectra (b) of Co-FPy-CON, CoO and Co foil. (c) AFM image of Co-FPy-CON, with measured thickness along the line shown in (d). materials show strong visible light absorption, utilization of the catalytic metal sites has often been shown to be poor, as expressed by their low turnover numbers (TONs).³⁰

Here, we report a new 2D COF, Py-COF, synthesized via a Schiff base condensation reaction, that bears metal coordination sites—iminopyridine moieties—that are formed by pyridine units and their adjacent imine groups. A partially fluorinated analogue of Py-COF, FPy-COF, was synthesized with the aim of improving the COF's binding affinity toward CO₂, thus enhancing its ability to enrich CO₂ around the catalytic sites. Exfoliation of bulk 2D COFs yielded covalent organic

nanosheets (CONs), which were then loaded with cobalt for photocatalytic CO₂ reduction. We also show that the iminopyridine moiety is a versatile metal coordination site for different transition metals, which has not yet been explored in the context of COF catalysts.

EXPERIMENTAL SECTION

COF synthesis. All COFs were prepared using a procedure based on the method described here for the synthesis of FPy-COF. A Schlenk tube was charged 5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl)tetrapicolinaldehyde (24.9 mg, 0.04 mmol), 4,4'-

diamino-2,2'-difluorobiphenyl (17.6 mg, 0.08 mmol), 1,2-dichlorobenzene (0.5 mL), *n*-butanol (0.5 mL), and aqueous acetic acid (0.1 mL, 6 M). This mixture was homogenized by ultrasonication for 10 minutes and the tube was then flash-frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was then sealed off and then heated at 120 °C for 7 days. The yellow precipitate was collected by centrifugation (3000 min⁻¹, 3 minutes) and washed with *N,N*-dimethylformamide (100 mL), THF (100 mL) and anhydrous acetone (200 mL). After drying at 120 °C, the product was obtained a yellow powder (35 mg, 88%). Anal. Calcd for (C₆₈H₅₀F₄N₈)_{*n*}: C, 77.40; H, 4.78; F, 7.2; N, 10.62. Found: C, 70.68; H, 3.48; N, 9.06.

Cobalt loading onto CONs. All cobalt loading procedures were based on the method described here for the synthesis of Co-FPy-COF. FPy-COF (20 mg) was mixed with CoCl₂·6H₂O (9 mg, 0.0378 mmol) in acetonitrile (20 mL) and the resulting suspension was ultrasonicated for 6 hours at room temperature. After this the solid was filtered off and washed with acetonitrile (200 mL). The resulting solid was dried under vacuum at 60 °C overnight to give Co-FPy-COF. The cobalt content of Co-FPy-COF was determined by inductively coupled plasma-optical emission spectrometry to be 2.1 wt. %.

Carbon dioxide reduction experiments. A quartz flask was charged with the COF nanosheets powder (1 mg), 2,2'-bipyridyl (1.5 mg), acetonitrile, water and triethanolamine (3:1:1 vol. mixture, 5 mL) and sealed with a septum. The resulting suspension was ultrasonicated for 5 minutes and then purged with CO₂ for 5 minutes. The reaction mixture was illuminated with a 300 W Newport Xe light source (Model: 6258, Ozone free) equipped with a λ > 420 nm cut-off filter. Gaseous products were taken with a gas-tight syringe and run on a Shimadzu GC-2014 gas chromatograph equipped with a ShinCarbon ST micropacked column (Restek 80-100 mesh, 2 m length, 0.53 mm inner diameter) and a thermal conductivity detector calibrated against standard gas mixtures of known concentration.

RESULTS AND DISCUSSION

Two COFs, Py-COF and FPy-COF, were synthesized via a Schiff base condensation of 5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl)tetracetaldehyde with aromatic diamines (Figure 1a). The COFs were then ultrasonicated in acetonitrile containing CoCl₂, resulting in exfoliated, Co-loaded COF nanosheets, Co-Py-COF and Co-FPy-COF (Figure 1a). Fourier-transform infrared spectroscopy (FT-IR) spectra of the materials were similar before and after ultrasonication in the presence of CoCl₂ (Figure S2), indicating that the COFs did not undergo decomposition during delamination and metal loading. Experimental powder X-ray diffraction (PXRD) patterns of Py-COF show diffraction peaks at 3.27, 4.77, 6.55, 7.56, and 9.83°, assigned to the (110), (210), (220), (130) and (330) planes, respectively (Figure 1b). The isostructural FPy-COF shows similar levels of crystallinity and the diffraction peaks at 3.20, 6.50, 7.30 and 9.62° were assigned to the (110), (220), (130) and (330) planes, respectively (Figure 1c). Unit cell parameters extracted by Le Bail refinements are similar to the parameters obtained by structure simulations. The simulated diffraction profile for the AA stacking model for both Py-COF (Figure 1b) and FPy-COF (Figure 1c) agree well with the experimental PXRD data. Both Co-Py-COF and Co-FPy-COF are less crystalline than their pristine COF counterparts (Figures

S7 and S8), as a result of the processes of exfoliation and metal loading.³¹

Nitrogen sorption experiments were performed at 77 K and the Brunauer–Emmett–Teller (BET) surface areas of Py-COF and FPy-COF were found to be 924 and 1136 m² g⁻¹, respectively. These experimental surface areas are lower than those derived from atomistic models of perfectly crystalline structures (2168 and 2044 m² g⁻¹, respectively).^{25,28} The pore diameters derived for Py-COF and FPy-COF by fitting nonlocal density functional theory models to the N₂ isotherms were 24.5 and 23.8 Å, respectively. Both COFs gave rise to nitrogen isotherms with shapes consistent with mesoporosity and sequential, multilayer pore filling (Figure 1d). Exfoliation and metalation resulted in a reduction of the BET surface area to 207 and 238 m² g⁻¹ for Co-Py-COF and Co-FPy-COF, respectively, though both materials were still microporous. Co-FPy-COF shows higher CO₂ adsorption amounts and larger isosteric heats than its non-fluorinated counterpart Co-Py-COF. Likewise, the bulk FPy-COF material shows a better CO₂ adsorption performance than its non-fluorinated counterpart (Figures S9–S12). This can be attributed to the enhanced binding between CO₂ and the fluorinated moieties of the COF, owing to the latter's ability to polarize CO₂.^{32,33}

The cobalt species in Co-FPy-COF were studied using X-ray absorption spectroscopy (XAS) at the Co K-edge, in reference to standard Co foil and cobalt (II) oxide (CoO). The Co K-edge absorption edge position for Co-FPy-COF is similar to CoO, meaning that the Co atoms on Co-FPy-COF are in the oxidation state of +2. These results are consistent with the X-ray photoelectron spectroscopy (XPS) data (Figure S19). The coordination environment of cobalt in Co-FPy-COF was further investigated by extended X-ray absorption fine structure spectroscopy (EXAFS). Fourier transformed R-space spectrum of Co foil shows a sharp peak at around 2.2 Å (Figure 2b), corresponding to the Co-Co bond, which is absent in the spectrum of Co-FPy-COF. Similarly, the peak centered at 2.6 Å that corresponds to the shortest Co···Co distance in CoO is also absent for Co-FPy-COF. For Co-FPy-COF, the only distinct peak is centered around 1.6 Å, which can be attributed to the Co-N bonds,³⁴ in line with the first peak (at 1.6 Å) of the CoO spectrum being assigned to the Co-O bond. By EXAFS curve fitting (Figure S20 and Table S3), the coordination number of the isolated Co atoms in Co-FPy-COF was determined to be 6.0, with a bond length of 2.13 Å. This shows that the Co atom is ligated onto the iminopyridine moiety of Co-FPy-COF, with the solvent acetonitrile molecules also participating the coordination with Co, as shown in the schematic diagram in Figure 1a. Although there are three different types of Co-N bonds in the Co-FPy-COF, only one peak in the EXAFS spectrum is assigned to the Co-N pair. This is because of the small differences in the Co-N bond lengths, approximately 0.1 Å,^{35,36} which are not distinguishable in EXAFS spectra. These EXAFS results show that short Co···Co distances are not present in Co-FPy-COF, hence Co centers can be considered atomically distributed in the material. In final catalytic system, the additional 2,2'-bipyridine was required to form catalytic Co centers (Figure 1a).¹⁴

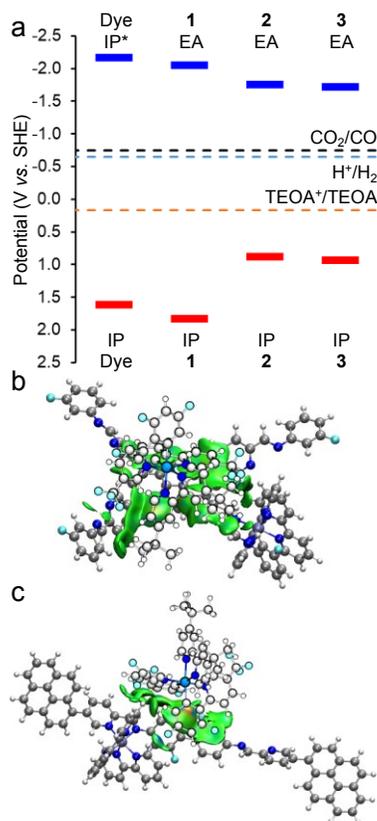


Figure 3. (a) (TD-)DFT predicted potentials of the free charge carriers (IP and EA) and excitons (IP*) of the dye, the molecular catalyst $[\text{Co}(\text{Bpy})_3]^{2+}$ (**1**), and representative fragments $[\text{Co-Py}(\text{L})]^{2+}$ (**2**) and $[\text{Co-FPy}(\text{L})]^{2+}$ (**3**) of Co-Py-COF and Co-FPy-COF, respectively. Dashed colored lines indicate the potentials for CO₂ reduction to CO, proton reduction, and triethanolamine (TEOA) oxidation, respectively. DFT-optimized adsorption configuration of the dye on the pyrene moiety (b) or the difluorobiphenyl moiety (c) of Co-FPy-COF. Colored isosurfaces are intermolecular interactions identified and quantified by non-covalent interaction analyses. COF fragments are shown in full atomic, ball-and-stick representation, with the dye shown as a lighter sketch.

Scanning electron microscopy images (SEM) for both Co-Py-COF and Co-FPy-COF show a microball-like agglomerate morphology (Figure S13). Elemental mapping images of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) for Co-Py-COF (Figure S14) show uniform distribution of C, N, Cl and Co in the material. HAADF-STEM for Co-FPy-COF show that C, N, F, Cl and Co are distributed uniformly over the sample (Figure S15). Co clusters or nanoparticles were not observed by HAADF-STEM (Figure S17a), indicating that the Co species were too small to be resolved. Aberration-corrected HAADF-STEM was therefore used to characterize the Co-FPy-COF. Figure S17b shows that

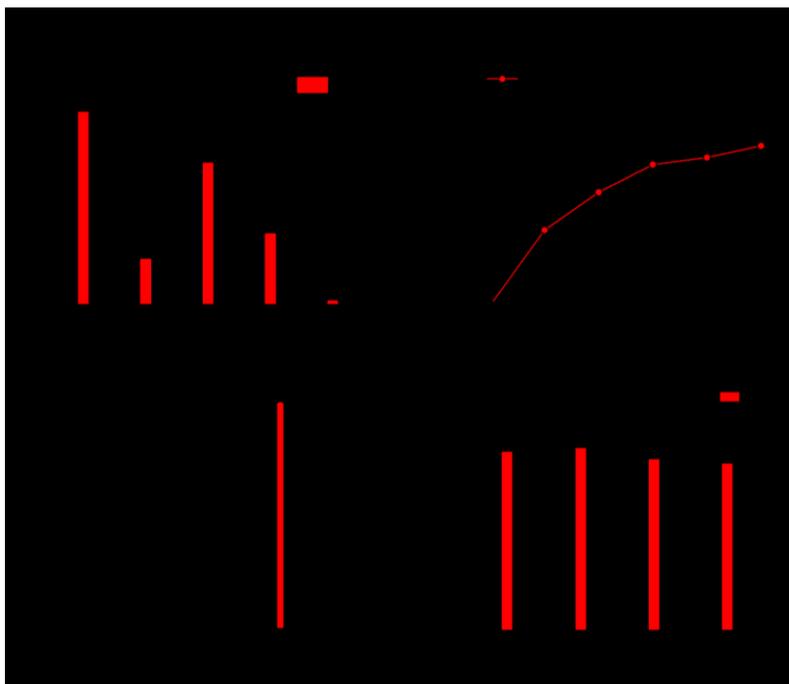


Figure 4. (a) CO and H₂ production by the nanosheet (denoted CON) and bulk (denoted COF) of Co-FPy-COF, Co-Py-COF and Co-Bp-COF, over 6 hours under visible-light irradiation ($\lambda > 420$ nm, 300 W Xe light source) with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as photosensitizer. (b) TONs of CO production by Co-FPy-CON and [Co(Bpy)_n]²⁺ under visible-light irradiation ($\lambda > 420$ nm, 300 W Xe light source) with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as photosensitizer. (c) Mass spectrum of ¹³CO produced using Co-FPy-CON as the catalyst in the photocatalytic reduction of ¹³CO₂; inset: the corresponding gas chromatogram. (d) CO and H₂ production by Co-FPy-CON over multiple 2-hour repeat runs. The sample was degassed and 1 μ mol of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ was added after each run.

isolated Co atoms are distributed on the COF matrix, identified by the bright dots with some highlighted by the red circles. Atomic force microscopy (AFM) images of Co-FPy-CON show that the nanosheets were thin stacks of the COF layers with thicknesses ranging from 1.9–4.4 nm (Figure 2c,d).

Next we used density functional theory (DFT) and time-dependent (TD-)DFT calculations—performed on representative molecular models [Co-Py(L)]²⁺ and [Co-FPy(L)]²⁺ of Co-Py-COF and Co-FPy-COF, respectively—to calculate the energy levels of the COFs. We find that the electron affinity (EA) and the ionization potential (IP) of both COFs straddle the reduction potential of CO₂ to CO, as well as the proton reduction potential, and the oxidation potential of triethanolamine (Figure 3a). This provides a thermodynamic explanation for the ability of both COFs to drive CO₂ reduction to CO in the presence of the sacrificial agent triethanolamine.

The photocatalytic CO₂ reduction activity of Co-FPy-CON was then tested in water, acetonitrile, and triethanolamine (1:3:1 vol. mixtures) under visible light irradiation ($\lambda > 420$ nm, 300 W Xe light source). Under these conditions the system was showed low activity and only trace amounts of carbon monoxide were produced (Figure S28).

We suspected that light harvesting and/or the following energy transfer might be responsible for the low activity of Co-FPy-CON. We therefore employed Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a photosensitizer in conjunction with Co-FPy-CON and found that the system worked efficiently producing carbon monoxide with a rate of 10.1 μ mol over 6 hours (TON = 28.1) with a selectivity of 76% over the competing H₂ generation reaction (Figures 4a,b and Table S7). The Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ dye on its own

was found to be inactive producing no measurable CO after 7 hours (Table S7).

The predicted relative energy levels of the dye and the molecular COF models confirm that it is thermodynamically allowed for excited electrons and excitons on the dye to be transferred to the COFs (Figure 3a), in line with the dye-sensitization effects that we observed experimentally. Monte Carlo simulations of the dye adsorption on a single Co-FPy-COF layer, followed by non-covalent interaction analyses using DFT calculations of cluster models (Figure 3b,c), show that the dye binds strongly to both the pyrene moiety and the difluorobiphenyl moiety of Co-FPy-COF. Both binding sites are in the immediate vicinity of the photocatalytic Co site, beneficial to charge transfer from the dye to the COF.

Analysis based on DFT results of excited-state, inter-fragment charge transfer between the building units of Co-FPy-COF and Co-Py-COF indicate that negligible amounts of electrons are transferred between the pyrene fragment and the Co-loaded iminopyridine fragment (Table S5), for the first three low-energy, excited electronic states with an appreciable oscillator strength. The corresponding intra-fragment electron redistributions within the individual fragments show that these low-energy states are local excitations, primarily located on the Co-loading iminopyridine moieties (Table S6). Further analyses of the natural transition orbitals for these electronic transitions indicate a metal-to-iminopyridine excitation mechanism, which is similar to the excitation of the molecular catalyst [Co(Bpy)₃]²⁺ in solution.

The fact that the COF does not act as a photocatalyst on its own requiring Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ as a photosensitizer to facilitate the catalytic reduction of CO₂ together with

the computational results indicate that the function of the COFs appears to be to allow for charge to be transferred and to provide metal coordination sites for the cobalt catalyst.

Isotope labeling study for $^{13}\text{CO}_2$ reduction using mass spectrometry confirmed that CO was produced from $^{13}\text{CO}_2$ (Figure 4c) ruling out degradation of the photosensitizer, photocatalyst or scavenger as the source of the produced CO. No hydrocarbon or alcohol products were observed. An external quantum efficiency (EQE) of 6.6% at 420 nm for the CO evolution of Co-FPy-CON was determined. This is higher than the previously reported EQE values of Ni-TpBpy-COF and Co-ZIF-9, both with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as photosensitizer and triethanolamine as scavenger at 420 nm.^{3,14} The bulk sample of Co-FPy-COF produced 2.36 μmol CO over 6 hours (TON = 15.5), 4.3-times lower than that of Co-FPy-CON, which may be partly attributed to the lower loading of Co in Co-FPy-COF (0.9 wt. % vs. 2.1 wt. %, as in the COF and CON, respectively). Co-Py-CON was less active than its fluorinated counterpart, producing 7.4 μmol of CO over 6 hours (TON = 10.9). This might be attributed to the fact that Co-FPy-CON has a stronger binding affinity for CO_2 (Figures S11 and 12) and to the dye (Figure S27), despite having a lower Co loading (2.1 wt. %) than Co-Py-CON (4.0 wt. %). The bulk sample of Co-Py-COF also showed a lower CO production than its CON counterpart.

Bp-COF was synthesized as a comparison, which incorporates pyrene units and bipyridine sites instead of the iminopyridine sites, as in Py-COF and FPy-COF, for ligation of the Co complex (section 2, Supporting Information). Under the same conditions, Co-Bp-CON showed a comparable photocatalytic performance to Co-Py-CON, though producing less CO with a lower CO/ H_2 selectivity. This suggests that it may be a promising, general strategy to incorporate iminopyridine based moieties into COFs as metal coordination sites for introducing catalytically-active metal centers into porous materials. Indeed, it was straightforward to prepare Zn-FPy-CON, which showed measurable CO_2 reduction activities (Table S7).

Over a total of 10 hours irradiation under visible light (Figure 4b), Co-FPy-CON showed a TON of 32.1; 2.8 times higher than its homogeneous counterpart $[\text{Co}(\text{bpy})_2]^{2+}$, which was deactivated after 3 hours, consistent with previous studies.³⁷⁻³⁹ Repeat experiments showed that the recycled Co-FPy-CON catalyst retained its photocatalytic activity over four two-hour runs (Figure 4d) when fresh $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbpy})]\text{PF}_6$ was added. It appears therefore that the decrease in activity observed for the extended 10-hour run (Figure 4b) is due to dye degradation and Co-FPy-CON appears to be stable under the photocatalysis conditions. This is further supported by post-illumination FT-IR spectra (Figure S21) of the sample after the repeat experiments. Furthermore, XPS measurements of the sample confirmed that the oxidation state of Co remained at +2 after the catalysis experiments (Figure S22). Only trace amounts of cobalt (6.6 ppm) were found in the filtered solution after photocatalysis, measured by inductively coupled plasma-optical emission spectrometry, suggesting that Co-FPy-CON was not demetallized during the catalysis. No iridium was detected indicating that no photodeposition of iridium onto the CONs occurs nor that dye was absorbed onto the surface.

CONCLUSIONS

COF nanosheets loaded with single Co sites for photocatalytic CO_2 reduction have been shown to be efficient in the presence of a dye and hole-scavenger. Co-FPy-CON achieved a high CO production of 10.1 μmol and a CO/ H_2 selectivity of 76%, over 6 hours irradiation under visible light (TON = 28.1). A high external quantum efficiency of 6.6% was determined under 420 nm irradiation. The performance of Co-FPy-CON is comparable to the state-of-the-art heterogeneous catalysts in the literature under comparable conditions (Table S8). The COF material in this case does not appear to act as a photocatalyst itself, but instead as a semiconductor support that transfers charge carriers that are generated in the dye to the cobalt centers, which are the active site. Nevertheless, COFs offer advantages, such as being tunable and can be exfoliated and we found across the systems studied here, the ultra-thin COF nanosheets were shown to consistently outperform their corresponding bulk materials in visible light driven CO_2 reduction to CO. Finally, the iminopyridine moiety seems to be a promising alternative to bipyridine as metal coordination sites for ligation of catalytic metal centers into the backbone of porous networks, such as COFs, metal-organic frameworks and conjugated microporous polymers.

ASSOCIATED CONTENT

Supporting Information.

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

Synthetic procedures, FT-IR spectra, NMR, TGA, UV-Vis spectra, PXRD patterns, CO_2 adsorption, SEM images, STEM images, AFM images, PL spectra and TCSPC experiments, PL quenching data, post-photocatalysis characterization data, and computational details.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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