Title
Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water.

Permalink
https://escholarship.org/uc/item/1p74w1gb

Journal
Science (New York, N.Y.), 349(6253)

ISSN
0036-8075

Authors
Lin, Song
Diercks, Christian S
Zhang, Yue-Biao
et al.

Publication Date
2015-09-01

DOI
10.1126/science.aac8343

Peer reviewed
ELECTROCHEMISTRY

Covalent organic frameworks comprising cobalt porphyrins for catalytic CO\(_2\) reduction in water

Song Lin,1,2* Christian S. Diercks,1,3* Yue-Biao Zhang,1,3,4* Nikolay Kornienko,1 Eva M. Nichols,1,2 Yinbo Zhao,1 Aubrey R. Paris,1 Dohyung Kim,5 Peidong Yang,1,3,5,6 Omar M. Yaghi,1,3,6,7* Christopher J. Chang1,3,5,8†

Conversion of carbon dioxide (CO\(_2\)) to carbon monoxide (CO) and other value-added carbon products is an important aspect for clean energy research. Here we report modular optimization of covalent organic frameworks (COFs), in which the building units are covalent porphyrin catalysts linked by organic struts through imine bonds, to prepare a catalytic material for aqueous electrochemical reduction of CO\(_2\) to CO. The catalysts exhibit high Faradaic efficiency (90%) and turnover numbers (up to 290,000, with initial turnover frequency of 9400 hour\(^{-1}\)) at pH 7 with an overpotential of ~0.55 volts, equivalent to a 26-fold improvement in activity compared with the molecular cobalt complex, with no degradation over 24 hours. X-ray absorption data reveal the influence of the COF environment on the electronic structure of the catalytic cobalt centers. The COF could be tuned electronically and sterically (26) while providing ready access for the substrate (27–32) (Fig. 1). Moreover, these crystal-line porous frameworks offer the possibility to perform multivariate synthesis, in which topologically identical and yet functionally modified building blocks can be introduced into the structure. This approach can potentially be applied to materials with emergent properties that are greater than the sum of the individual molecular parts, because one can predictably prepare a topologically ordered framework yet introduce heterogeneity in the number and ratio of functionalities by the choice of building blocks (30). Here we show that incorporation of covalent cobalt porphyrin (34) units into COFs along with multivariate synthesis of frameworks bearing catalytic cobalt and structural copper units, gives highly active, stable, and selective catalysts for electrochemical reduction of carbon dioxide to carbon monoxide in water. A member of the COF series that we studied exhibits a 26-fold increase in activity compared with the parent molecular precursor and, in many respects, outperforms state-of-the-art molecular and solid-state catalysts, with broad opportunities for further improvement through modular synthesis using appropriate combinations of building units. X-ray absorption measurements reveal that the COF framework can directly influence the electronic structure of the catalytic cobalt centers, in a manner akin to redox noninnocent ligand behavior observed in molecular systems (35), thereby contributing to the observed gains in reaction selectivity and activity beyond the steric effects of surface area and site isolation.

We focused our initial electrocatalysis studies on COFs, as we sought to exploit the charge-carrier mobility of these materials derived from n conjugation and π stacking (22, 36–38), as well as the stability from reticular assembly with strong covalent bonds. We synthesized a model framework (COF-S66-Co) by the imine condensation of 3,10,15,20-tetrakis(4-aminophenyl)porphyrinato(cobalt (Co(TAP)) with 1,4-benzenedicarboxaldehyde (BDA) (Fig. 1). The porous COF material was evacuated by activation with supercritical carbon dioxide and heating to 100°C for 18 hours. The retention of cobalt in the coordinating porphyrin units within the framework was confirmed by elemental analysis (supplementary materials section S11), thermogravimetric analysis (fig. S1), and...
solid-state ultraviolet-visible (UV-Vis) spectroscopy (fig. S9). The formation of the imine linkages in the COF was confirmed by attenuated total reflectance–Fourier transform infrared spectroscopy, which showed the characteristic imine stretching vibration band at 1621 cm\(^{-1}\), as well as the absence of the aldehyde stretching vibration band at 1684 cm\(^{-1}\) (fig. S10). The morphologies of the activated COF samples were examined by scanning electron microscopy (SEM), which showed aggregation of only one kind of crystallographic structure with a distance of 4.4 Å between the stacking 2D channels, 21 Å in width, running along the crystallographic direction. These refinements revealed one-dimensional (1D) channel patterns were carried out for full profile fitting against the proposed models, resulting in a good agreement factor (weighted-profile R factor \(R_p = 2.59\%\) and unweighted-profile R factor \(R_w = 1.38\%\) after convergence) and reasonable profile differences. These refinements revealed one-dimensional (1D) channels, 21 Å in width, running along the c axis, with a distance of 4.4 Å between the stacking 2D sheets. The porosity and specific surface area were determined using nitrogen adsorption isotherms at 77 K (Fig. 2C). The Brunauer-Emmett-Teller (BET) surface area was determined to be 1360 m\(^2\)/g. Density functional theory (DFT) fitting of the adsorption branches showed relatively narrow pore size distributions (10 to 18 Å), in agreement with that of the proposed model.

For electrochemical experiments, the activated microcrystalline COF powders were deposited by scanning electron microscopy (SEM), which showed aggregation of only one kind of crystallographic structure. The PXRD patterns (Fig. 2B) showed intense peaks in the expected low-angle range, with no residual peaks characteristic of the starting materials. To elucidate the constitution of the framework, we used Materials Studio 7.0 to build a structural model (Fig. 1) in an orthorhombic Cmmm space group to allow the lattice distortion from regular parallelepipeds. The space-filling structural models of COF-366-M and COF-367-M were obtained using Materials Studio 7.0 and refined with experimental PXRD data. Cyclic voltammetry (CV) measurements on COF-366-Co were conducted in pH 7 aqueous phosphate buffer (fig. S10). The morphologies of the activated COF samples were examined by scanning electron microscopy (SEM), which showed aggregation of only one kind of crystallographic structure with a distance of 4.4 Å between the stacking 2D channels, 21 Å in width, running along the crystallographic direction. These refinements revealed one-dimensional (1D) channel patterns were carried out for full profile fitting against the proposed models, resulting in a good agreement factor (weighted-profile R factor \(R_p = 2.59\%\) and unweighted-profile R factor \(R_w = 1.38\%\) after convergence) and reasonable profile differences. These refinements revealed one-dimensional (1D) channels, 21 Å in width, running along the c axis, with a distance of 4.4 Å between the stacking 2D sheets. The porosity and specific surface area were determined using nitrogen adsorption isotherms at 77 K (Fig. 2C). The Brunauer-Emmett-Teller (BET) surface area was determined to be 1360 m\(^2\)/g. Density functional theory (DFT) fitting of the adsorption branches showed relatively narrow pore size distributions (10 to 18 Å), in agreement with that of the proposed model.

For electrochemical experiments, the activated microcrystalline COF powders were deposited by scanning electron microscopy (SEM), which showed aggregation of only one kind of crystallographic structure. The PXRD patterns (Fig. 2B) showed intense peaks in the expected low-angle range, with no residual peaks characteristic of the starting materials. To elucidate the constitution of the framework, we used Materials Studio 7.0 to build a structural model (Fig. 1) in an orthorhombic Cmmm space group to allow the lattice distortion from regular parallelepipeds. The space-filling structural models of COF-366-M and COF-367-M were obtained using Materials Studio 7.0 and refined with experimental PXRD data.

Fig. 1. Design and synthesis of metalloporphyrin-derived 2D covalent organic frameworks. The space-filling structural models of COF-366-M and COF-367-M were obtained using Materials Studio 7.0 and refined with experimental PXRD data.
temperature and pressure (STP), equivalent to 1.6 mmol per milligram of COF. This corresponds to a turnover number (TON) of 1392 [TON per electroactive cobalt based on the measurements described above (TON\textsubscript{EA} = 34,000), with an initial turnover frequency (TOF) of 58 hour\textsuperscript{-1} [TOF per electroactive cobalt (TOF\textsubscript{EA}) = 2500]. This result represents a substantial improvement over the molecular Co(TAP), which showed an initial TOF of 58 hour\textsuperscript{-1} (TOF\textsubscript{EA} = 360) and a TON of 794 (TON\textsubscript{EA} = 8300) after 24 hours of reaction [surface coverage of electroactive sites on a Co(TAP)-modified electrode constitutes ~10% of the total cobalt]. PXRD (fig. S73) and SEM (fig. S74) measurements on the COF catalyst after electrolysis showed neither marked changes in crystallinity and microscopic morphology nor evidence of cobalt nanoparticle formation. By incorporating this molecular unit into a COF scaffold, the resulting hybrid catalyst could be recovered from the electrolysis mixture and reused at least five times without decrease in activity and selectivity (table S8). Control experiments with COFs containing COF-367-Co was obtained as a dark purple powder comprising rectangular rod-shaped crystallite aggregates (~100 nm in length) (Fig. 2D). The structural model based on PXRD data and DFT fitting indicated that the constitution and topology of COF-367-Co is analogous to that of COF-366-Co, with the former showing an increased channel width (24 Å) and interlayer distance (4.6 Å) (Fig. 2E). The BET surface area was determined by nitrogen adsorption isotherm (Fig. 2F) as 1470 m\textsuperscript{2}/g, and pore size distribution was consistent with the model (12 to 23 Å). Cyclic voltammetry studies with COF-367-Co on a carbon fabric electrode in bicarbonate buffer indicated that this extended organic framework exhibits an improved surface concentration (2 × 10\textsuperscript{10} mol/cm\textsuperscript{2}) of electroactive cobalt porphyrin sites over COF-366-Co, which corresponds to accessibility of 8% of the cobalt sites in the bulk material. When the solution was saturated with CO\textsubscript{2}, a catalytic current was evident with an onset potential at ~0.40 V and a 2.2-fold enhancement at ~0.67 V, indicating a prominent effect of COF-367-Co on the catalysis of CO\textsubscript{2} reduction at these potentials (Fig. 3A). As predicted, electrolysis under the same conditions described above revealed that this expanded COF displays improved catalytic efficiency as compared with COF-366-Co. At an applied potential of ~0.67 V, COF-367-Co produced more than 100 ml of carbon monoxide (STP, equivalent to 4.5 mmol) per milligram of COF during a 24-hour period (TON = 3901, TON\textsubscript{EA} = 48,000), with high Faradaic efficiency (91%). The increased TON\textsubscript{EA} over COF-366-Co indicated that lattice expansion allowed for more efficient exposure of the electroactive sites to the reactants.

In addition to framework expansion, we also sought to optimize catalyst performance by introducing building-block heterogeneity through a multivariate strategy (33), as we hypothesized that not all electroactive cobalt porphyrin sites in the material fully participated in electrocatalysis, owing to the low aqueous solubility of carbon dioxide. Specifically, we reasoned that using isostructural metalloporphyrin units that are catalytically inactive for carbon dioxide reduction (fig. S76) to dilute electroactive cobalt porphyrin active sites within the extended lattice could increase the proportion of the active sites exposed to the reactant and thereby improve the turnover frequency on a per-cobalt basis. Copper porphyrin was chosen for this study, as the corresponding COF-367-Cu had the highest surface area among all analogous COF-367-M (M = Ni, Zn, H\textsubscript{2}) synthesized. The resulting bimetallic COF-367 derivatives, termed COF-367-Co(10%) and COF-367-Cu(1%), were prepared; the numbers in the parentheses indicate the proportion of cobalt in all metal sites (Fig. 1). Inductively coupled plasma
ICP analyses confirmed that the final chemical composition of the COFs obtained reflected the initial ratio of the two metalloporphyrin starting materials that we used (supplementary materials section S1.1). The TOF per electroactive cobalt site for carbon monoxide production in these multivariate Co/Cu COF-367 catalysts showed a substantial improvement with each 10-fold dilution of cobalt loading. The average TOF per active cobalt for the first 4 hours of reaction was measured as follows: COF-367-Co, 165 hour$^{-1}$ (TOF$_{EA}$ = 1900); COF-367-Co(10%), 360 hour$^{-1}$ (TOF$_{EA}$ = 4400); and COF-367-Co(1%), 76 hour$^{-1}$ (TOF$_{EA}$ = 9400) (Fig. 3C). The TOF$_{EA}$ values were roughly estimated, assuming that all three frameworks had comparable percentages of electroactive sites (6%). Although the low cobalt concentration in COF-367-Co(10%) and COF-367-Co(1%) hampered the accurate determination of the surface concentration of electrochemically accessible cobalt sites by CV, the bimetallic frameworks had nearly identical pore sizes, interlayer distances, and surface areas to the parent COF-367-Co on the basis of PXRD and nitrogen adsorption measurements (figs. S25 and S32 to S43), which suggests that such an assumption may be valid. Owing to the moderate

![Diagram](https://example.com/diagram.png)

**Fig. 3.** Electrochemical and spectroelectrochemical characterizations and carbon dioxide reduction performance of the COFs. (A) Cyclic voltammograms of COF-366-Co and COF-367-Co in carbon dioxide-saturated medium (blue and red solid lines, respectively) or nitrogen-saturated medium (blue and red dotted lines, respectively). The black solid line shows background (bare carbon electrode) CV responses in carbon dioxide-saturated medium. The medium was pH 7.2 aqueous potassium phosphate buffer (0.2 M) with additives: 0.5 M K$_2$CO$_3$ under carbon dioxide atmosphere to maintain a neutral pH, or 0.5 M NaClO$_2$ under nitrogen atmosphere to match the ionic strength. (B) Long-term bulk electrolyses at $-0.67$ V (versus RHE), showing the volume of carbon monoxide produced by COF-367-Co (red solid triangles), COF-366-Co (blue solid circles), or Co(TAP) (black solid squares) and the volume of hydrogen produced by COF-367-Co (red open triangles), COF-366-Co (blue open circles), or Co(TAP) (black open squares). (C) Bulk electrolyses of bimetallic COFs at $-0.67$ V (versus RHE), showing TON per electroactive cobalt for the first 4 hours of reaction was measured as follows: COF-367-Co, 165 hour$^{-1}$ (TOF$_{EA}$ = 1900); COF-367-Co(10%), 360 hour$^{-1}$ (TOF$_{EA}$ = 4400); and COF-367-Co(1%), 76 hour$^{-1}$ (TOF$_{EA}$ = 9400) (Fig. 3C). The TOF$_{EA}$ values were roughly estimated, assuming that all three frameworks had comparable percentages of electroactive sites (6%). Although the low cobalt concentration in COF-367-Co(10%) and COF-367-Co(1%) hampered the accurate determination of the surface concentration of electrochemically accessible cobalt sites by CV, the bimetallic frameworks had nearly identical pore sizes, interlayer distances, and surface areas to the parent COF-367-Co on the basis of PXRD and nitrogen adsorption measurements (figs. S25 and S32 to S43), which suggests that such an assumption may be valid. Owing to the moderate

![Diagram](https://example.com/diagram.png)

**Fig. 3.** Electrochemical and spectroelectrochemical characterizations and carbon dioxide reduction performance of the COFs. (A) Cyclic voltammograms of COF-366-Co and COF-367-Co in carbon dioxide-saturated medium (blue and red solid lines, respectively) or nitrogen-saturated medium (blue and red dotted lines, respectively). The black solid line shows background (bare carbon electrode) CV responses in carbon dioxide-saturated medium. The medium was pH 7.2 aqueous potassium phosphate buffer (0.2 M) with additives: 0.5 M K$_2$CO$_3$ under carbon dioxide atmosphere to maintain a neutral pH, or 0.5 M NaClO$_2$ under nitrogen atmosphere to match the ionic strength. (B) Long-term bulk electrolyses at $-0.67$ V (versus RHE), showing the volume of carbon monoxide produced by COF-367-Co (red solid triangles), COF-366-Co (blue solid circles), or Co(TAP) (black solid squares) and the volume of hydrogen produced by COF-367-Co (red open triangles), COF-366-Co (blue open circles), or Co(TAP) (black open squares). (C) Bulk electrolyses of bimetallic COFs at $-0.67$ V (versus RHE), showing TON per electroactive cobalt for the first 4 hours of reaction was measured as follows: COF-367-Co, 165 hour$^{-1}$ (TOF$_{EA}$ = 1900); COF-367-Co(10%), 360 hour$^{-1}$ (TOF$_{EA}$ = 4400); and COF-367-Co(1%), 76 hour$^{-1}$ (TOF$_{EA}$ = 9400) (Fig. 3C). The TOF$_{EA}$ values were roughly estimated, assuming that all three frameworks had comparable percentages of electroactive sites (6%). Although the low cobalt concentration in COF-367-Co(10%) and COF-367-Co(1%) hampered the accurate determination of the surface concentration of electrochemically accessible cobalt sites by CV, the bimetallic frameworks had nearly identical pore sizes, interlayer distances, and surface areas to the parent COF-367-Co on the basis of PXRD and nitrogen adsorption measurements (figs. S25 and S32 to S43), which suggests that such an assumption may be valid. Owing to the moderate
proton reduction ability of the copper porphyrin sites in the hybrid organic framework, the TOF increased as the Co/Cu ratio decreased, at the expense of Faradaic efficiency for carbon monoxide production (\(FE_{\text{CO}} = 70\%\) for COF-367-Co(10%) and 40% for COF-367-Co(1%)). In a long-term electrolysis experiment (Fig. 3D), COF-367-Co (1%) displayed a TOF of \(29,000 \text{ TOF}_{\text{CO}} = 296,000\), which indicates that it is one of the most efficient electrochemical carbon dioxide reduction catalysts reported to date (3, 4).

The observed activity enhancements for the bimetallic COFs are due to their multivariate nature; indeed, the analogous physical mixture of COF-367-Co and COF-367-Cu in a 1:9 ratio produced far less catalytic activity than the CoF-367-Co (Fig. S1) compared with COF-367-Co(10%) (Table S1).

In addition to challenges posed by the low aqueous solubility and limited diffusion of CO\(_2\) within the COF, only a small portion (4 to 8%) of the cobalt centers in the COF material deposited in this manner proved to be electroactive, presumably because of the limited electrochemical contact between the COF powder and the electrode (44). As such, we explored the possibility of growing COF directly onto the surface of an electrode substrate in the form of oriented thin films (42–44). Layers of COF sheets could be successfully synthesized directly on glassy carbon, fluoride-doped tin oxide (FTO), and silicon oxide. Grazing incidence wide-angle x-ray scattering (GIWAXS) patterns showed the formation of highly crystalline COF thin films (figs. S48 to S51) (45). With the use of ICP, the concentration of COF on the substrate surface was determined to be \(1.3 \times 10^{-7} \text{ mmol Co per square centimeter, corresponding to a thickness of ~350 nm, which is consistent with images obtained using cryo-electron microscopy (figs. S54 and S55).}\)

The charge transport through the COF-366-Co thin films was characterized using spectro-electrochemistry. Under an applied potential more negative than ~0.37 V in nitrogen- or carbon dioxide-saturated pH 7 aqueous buffer, the UV-Vis spectrum of the FTO-supported COF underwent a light-onset spectral change associated with the CO\(_2\) reduction (Fig. 3G and figs. S78 to S82). Using the steady-state spectroscopic response to the reduction potentials in combination with the Nernst equation, the redox potential (\(E_{\text{RCO}}\)) could be estimated to be more negative than ~0.52 V (fig. S63), in agreement with the CV measurements (\(E_{\text{RCO}} = -0.67 \text{ V}\) (46)). The temperature dependence of the UV-Vis response of a COF-coated FTO electrode to an applied potential of ~0.57 V was studied in a CO\(_2\)-saturated KHCO\(_3\) solution (Fig. 3G), and a fit of the data to a modified Cottrell equation afforded an apparent diffusion coefficient of \(2 \times 10^{-10} \text{ cm}^2/\text{s}\) (fig. S81), a value substantially higher than that obtained with analogous metal-organic frameworks (MOF) thin films bearing cobalt porphyrin units (47). Using the silicon oxide–hosted sample, we measured the direct current conductivity of COF-366-Co to be ~10\(^{-3}\) S/cm, which is also higher than that of the MOF (figs. S84 and S85). In addition to a presumably increased portion of electroactive cobalt sites, the favorable charge-transport properties led to a higher catalytic efficiency. Under the same electrolysis conditions, COF-366-Co thin films on glassy carbon exhibited a TOF of 665 hour\(^{-1}\), a value seven times as high as that of the same material deposited on a carbon fabric, with a high current density of 45 mA/m\(^2\) and a Faradaic efficiency of 86%.

Electrokinetics experiments indicated that covalently linking cobalt porphyrin active sites within a COF influences the mechanistic pathways for carbon dioxide reduction. For the systems employing COF-366-Co, COF-367-Co, and COF-367-Co(10%), Tafel plots of the logarithm of current density \((\log(I/I_0))\) versus the overpotential \((\eta)\) display comparable slopes between 470 and 550 mV/dec (where 1 dec is one order of magnitude) in the linear, lower current density regime (fig. 3A). The time-dependence of the linear, lower current density regime \((\log(I/I_0))\) versus the overpotential \((\eta)\) displayed a TON of >24,000 (TON~296,000), which indicates that it is one of the most efficient electrochemical carbon dioxide reduction catalysts reported to date (3, 4).

The electronic properties of molecular centers coupled to heterogeneous systems and promote carbon dioxide reduction to carbon monoxide with exceptionally high activity and selectivity compared with existing systems (table S2). We anticipate that these hybrid molecular-material platforms will be applicable to a broad range of catalytic applications, particularly those that require sustainable electrical and/or solar input and aqueous compatibility.
GEOPHYSICS

Stress orientations in subduction zones and the strength of subduction megathrust faults

Jeanne L. Hardebeck

Subduction zones pose a considerable hazard as the main source of great earthquakes (magnitude ≥ 8). Relative to other fault types, subduction zone megathrust faults may also have unique physical properties, due to the deeply buried fluids that are entrained by the subducting oceanic plate (1). The presence of fluids, particularly at high fluid pressures, can weaken faults substantially (2). Direct evidence suggests that subduction zone megathrust faults slip with low frictional resistance near Earth’s surface (3). The strength of these faults at seismicity depths is less clear, as they can only be studied indirectly. The orientation of a fault with respect to the stress field can be an indicator of the fault’s strength. Faults optimally oriented for frictional failure make an angle of ~30° to the maximum compressive stress axis, \( \sigma_1 \). Nonoptimally oriented faults can also be active, but faults with typical frictional strength should not slip at a high angle to \( \sigma_1 \) (≥ 60°) (4). Faults operating at a high angle to \( \sigma_1 \) must be very weak compared to the surrounding material to slip at relatively low applied shear stress. Similarly, faults oriented at a very low angle to \( \sigma_1 \) (< 10°) must also be weak. The traction at Earth’s surface is zero, requiring an Andersonian stress state in which one principal stress axis is vertical (5). Most crustal faulting is consistent with an Andersonian stress state (6). The very shallow dip (~10°) of the upper portion of many subduction zone megathrusts (7) suggests that, if these faults exist within an Andersonian stress state, they operate at a high angle to one principal stress axis (and at a low angle to the other two) and are therefore frictionally weak. However, observations from some subduction zone locations indicate that the stress in these locations is not Andersonian (8–12).

I systematically investigate the stress orientations in subduction zones worldwide, to determine whether the stress state is generally non-Andersonian and whether megathrust faults are well-oriented for failure. I compile the moment tensors (12, 13) of earthquakes located within 20 km of the subduction zone interface (7) to represent the megathrust region, and more shallow events to represent the upper plate. I stack the events for each subduction zone to invert for stress orientation (14) as a one-dimensional function of subduction interface depth. For the several subduction zones near Japan, there are enough moment tensors to invert for the two-dimensional spatially varying stress field as well. The stress state in the subduction zones near Japan is generally not Andersonian. The \( \sigma_1 \) axis in most megathrust regions plunges systematically trenchward (opposite the direction of subduction zone dip), generally plunging between 10° and 50° (Fig. 1A). A similar plunge of the \( \sigma_1 \) axis is observed within the upper plate above the Japan Trench, Kuril Trench, and Nankai Trough (Fig. 1G), whereas back-arc extension (near-vertical \( \sigma_1 \)) dominates above the Ryukyu and Izu-Bonin trenches.

Comparing the plunge of the \( \sigma_1 \) axis in the megathrust region to the dip of the subduction interface (7) gives the angle of \( \sigma_1 \) to the megathrust fault (Fig. 1B). For the Kuril, Japan, and Izu-Bonin trenches, the \( \sigma_1 \) axis is typically at an angle of 20° to 50° to the fault. For the Ryukyu Trench, the \( \sigma_1 \) axis makes somewhat larger angles of 30° to 80° to the fault. In the Nankai Trough, \( \sigma_1 \) is oriented at 10° to 30° to the fault in the upper 20 km, while at deeper depths, the \( \sigma_1 \) axis is near-vertical. The plunge of the \( \sigma_1 \) axis is stable with depth (Fig. 1C), except in the Nankai Trough (Fig. 1D), and the subduction megathrust is generally well oriented for failure from the near-surface to at least 60 km depth (Fig. 1E). The stacked Kuril, Japan, and Izu-Bonin trenches (the subducting Pacific plate) above a megathrust fault that is optimally oriented for failure, at ~30° to \( \sigma_1 \), over the full depth range. The megathrust at the Ryukyu Trench is generally well oriented for failure at <60° down to 30 km depth, and is marginally oriented at ~80° from 30 km to 60 km depth. The exception is the Nankai Trough (Fig. 1F), which is well oriented at ~20° to \( \sigma_1 \), only in the upper 20 km. Below 30 km, the megathrust is not oriented for reverse faulting within the error bounds. This suggests that 30 km is the downward limit of coupling between the subducting and overriding plates.

For all global subduction zones studied, for almost all depths, the \( \sigma_1 \) axis plunges systematically trenchward, with plunge generally between 10° and 50° (Fig. 2A). The plunge tends to decrease with depth, while the subduction zone dip increases (7), so that the angle of \( \sigma_1 \) to the subduction interface is remarkably stable with depth (Fig. 2B). This angle is also remarkably similar across subduction zones, most falling within the range 45° to 60°.

The Japan and South American subduction zones are anomalous in being more optimally

References

U.S. Geological Survey, Menlo Park, CA, USA.
E-mail: jhardebeck@usgs.gov

SCIENCE scienmag.org

11 SEPTEMBER 2015 • VOL. 349 ISSUE 6233 1213

RESEARCH | REPORTS

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/349/6253/1208/suppl/DC1

Materials and Methods

Fig. S1 to S5

Tables S1 to S2

References (S2–72)

19 June 2015; accepted 5 August 2015

Published online 20 August 2015
10.1126/science.abc9343


ACKNOWLEDGMENTS

Financial support for energy catalysis in the C.J.C. laboratory was provided by U.S. Department of Energy (DOE)/Lawrence Berkeley National Laboratory (LBNL) grant 501258-002. Financial support for COF research in the G.M.V. laboratory was provided by BASF SE (Ludwigshafen, Germany) for synthesis and by DOE, Office of Science, Office of Basic Energy Sciences, Energy Frontier Research Center grant DE-SC0001015 for adsorption and multivariate metallation. Financial support for energy catalysis in the P.Y. laboratory was supported by the support for energy catalysis in the P.Y. laboratory was supported by the

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/349/6253/1208/suppl/DC1

Materials and Methods

Fig. S1 to S5

Tables S1 to S2

References (S2–72)

19 June 2015; accepted 5 August 2015

Published online 20 August 2015
10.1126/science.abc9343
Covalent organic frameworks comprising cobalt porphyrins for catalytic CO$_2$ reduction in water

Song Lin, Christian S. Diercks, Yue-Biao Zhang, Nikolay Kornienko, Eva M. Nichols, Yingbo Zhao, Aubrey R. Paris, Dohyung Kim, Peidong Yang, Omar M. Yaghi and Christopher J. Chang

Science 349 (6253), 1208-1213.
DOI: 10.1126/science.aac8343 originally published online August 20, 2015

Improving cobalt catalysts

Tethering molecular catalysts together is a tried and trusted method for making them easier to purify and reuse. Lin et al. now show that the assembly of a covalent organic framework (COF) structure can also improve fundamental catalytic performance. They used cobalt porphyrin complexes as building blocks for a COF. The resulting material showed greatly enhanced activity for the aqueous electrochemical reduction of CO$_2$ to CO.

Science, this issue p. 1208