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Two-Dimensional Covalent Organic Frameworks with Cobalt(II)-Phthalocyanine Sites for Efficient Electrocatalytic Carbon Dioxide Reduction

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ABSTRACT: The rapid development in synthesis methodology and applications for covalent organic frameworks (COFs) has been witnessed in recent years. However, the synthesis of highly stable functional COFs still remains a great challenge. Herein two-dimensional polyimide-linked phthalocyanine COFs (denoted as CoPc-PI-COF-1 and CoPc-PI-COF-2) have been devised and prepared through the solvothermal reaction of the tetraanhydrides of 2,3,9,10,16,17,23,24-octacarboxyphthalocyaninato cobalt(II) with 1,4-phenylenediamine and 4,4'-biphenyldiamine, respectively. The resultant CoPc-PI-COFs with a four-connected sql net exhibit AA stacking configurations according to powder X-ray diffraction studies, showing permanent porosity, thermal stability above 300 °C, and excellent resistance to a 12 M HCl aqueous solution for 20 days. Current–voltage curves reveal the conductivity of CoPc-PI-COF-1 and CoPc-PI-COF-2 with the value of 3.7×10^{-3} and 1.6×10^{-3} S m⁻¹, respectively. Due to the same Co(II) electroactive sites together with



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similar permanent porosity and CO₂ adsorption capacity for CoPc-PI-COFs, the cathodes made up of COFs and carbon black display a similar CO₂-to-CO Faradaic efficiency of 87–97% at applied potentials between -0.60 and -0.90 V (vs RHE) in 0.5 M KHCO₃ solution. However, in comparison with the CoPc-PI-COF-2&carbon black electrode, the CoPc-PI-COF-1 counterpart provides a larger current density (j_{CO}) of -21.2 mA cm⁻² at -0.90 V associated with its higher conductivity. This cathode also has a high turnover number and turnover frequency, amounting to 277 000 and 2.2 s⁻¹ at -0.70 V during 40 h of measurement. The present result clearly discloses the great potential of 2D porous crystalline solids in electrocatalysis.

INTRODUCTION

Covalent organic frameworks (COFs) with good crystallinity, as one kind of important porous organic polymers, have attracted intensive research interests due to their well-defined and long-range-order structures in addition to their various applications such as gas separation and storage, catalysis, and optoelectronics.¹⁻⁶ As can be easily expected, the definite architectures of COFs facilitate the deep understanding of structure-property correlation at the atomic level.⁷ In particular, the cofacial packing of two-dimensional (2D) COFs consisting of conjugated molecular building blocks linked via the in-plane covalent bonds and interlayer $\pi - \pi$ interactions enables the enhanced stability of this kind of artificial solids and efficient electron transfer in the optoelectronics.¹⁰⁻¹⁸ To date, great efforts in the field of COFs have been directed toward target synthesis, theoretical significance, and practical utilization through developing new synthetic methodologies and applications. In this regard, the successful predesign and synthesis strategy enabled by dynamic covalent chemistry reactions such as imine formation, boronic acid condensation, boronate ester formation, and so on has generated a vast range of functional COFs.¹⁹⁻³⁰ Furthermore, incorporation of metal-coordinating building blocks into COFs

provides more opportunities to improve their function diversity.³¹ However, the synthesis of highly stable functional COFs is still one of the most challenging subjects due to the contradictory thermodynamic and kinetic balance involved in the linkage strength and crystallization process, respectively.

Electrocatalytic carbon dioxide reduction reaction (CO_2RR) to obtain fuels/chemicals is one of the sustainable pathways to solve the energy crisis and global warming issues.^{32–38} Toward implementing electrocatalytic CO_2RR applicability, various homogeneous and heterogeneous catalysts with high conversion efficiency and selectivity have been developed.^{35–48} Electrochemical active metal-containing molecular (homogeneous) systems have been demonstrated to exhibit low overpotential through the low-valent active intermediate and excellent selectivity by the smart tailorability.³⁸ However, the

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facile deactivation, inefficient electron transfer, and organic media requirement in homogeneous systems for molecular catalysts restrict their further practical applications. Incorporation of molecular catalysts with conductive substrates into heterogeneous systems therefore opens an avenue for electrocatalytic CO_2RR , benefiting the catalytic efficiency, separation, reusability, and stability.^{39–42} In recent years, COFs, as one of the important reticular materials platforms, have been emerging as ideal heterogeneous candidates for electrocatalysis by integrating catalytically active molecular components in an accurate connection manner.^{33,36} As a consequence, electrocatalytic active metalloporphyrin molecules have been incorporated into 2D COFs since 2015, exhibiting excellent heterogeneous electrocatalytic CO2RR properties. 46-50 Toward further enhancing the electrocatalytic performance, other tetrapyrrole analogues, metallophthalocyanines, with excellent molecular electrocatalytic CO_2RR activity were assembled into 2D COFs in 2020, ^{15–17,51,52} affording two series of 2D COFs based on the only two building blocks of 2,3,9,10,16,17,23,24octa(hydroxyl)phthalocyanine and 2,3,9,10,16,17,23,24-octa-(amino)phthalocyanine (Scheme 1a). In this regard, more in-

Scheme 1. (a) Structures of Building Blocks (M = 2H and Metal): 2,3,9,10,16,17,23,24-Octa(hydroxyl/amino) Phthalocyanines (i and ii); Tetraanhydrides of 2,3,9,10,16,17,23,24-Octacarboxyphthalocyanine (iii); (b) Synthesis of CoPc-PI-COF-1 and CoPc-PI-COF-2



depth systematical studies toward the exploration of new molecular building blocks, connection mode, and structure–function correlation are certainly significant for the rational design and synthesis of COFs with desired properties.

Herein, a new kind of phthalocyanine building block, namely, tetraanhydrides of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine, were employed toward fabricating new reticular materials for the first time, Scheme 1a. Reaction of tetraanhydrides of 2,3,9,10,16,17,23,24-octacarboxyphthalocyaninato cobalt(II) (Co(TAPc)) with 1,4-phenylenediamine (PD) and 4,4'-biphenyldiamine (BD), respectively, generates two 2D polyimide (PI) COFs, denoted as CoPc-PI-COF-1 and CoPc-PI-COF-2 (Scheme 1b). The robustness of these COFs is associated with the in-plane rigid imide bonds in a four-connected square lattice (sql) net and strong $\pi-\pi$ interactions between the AA stacking layers. As a result, CoPc-PI-COFs display a moderate permanent porosity with a Brunauer– Emmett–Teller (BET) surface area of 181 and 291 m² g⁻¹, good thermal stability above 300 °C, and excellent chemical pubs.acs.org/JACS

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resistance to even a 12 M HCl aqueous solution for 20 days. In particular, the electron conductivity of CoPc-PI-COF-1 and CoPc-PI-COF-2 amounts to 3.7×10^{-3} and 1.6×10^{-3} S m⁻¹, respectively. The cathodes fabricated by CoPc-PI-COFs&carbon black show a similar high CO₂-to-CO Faradaic efficiency (FE_{CO}) of 87–97% at various applied potentials of -0.60 to -0.90 V (vs reversible hydrogen electrode (RHE)) with an overpotential (η) of -0.49 to -0.79 V in a 0.5 M KHCO₃ solution. The CoPc-PI-COF-1&carbon black electrode possesses a higher current density (j_{CO}) of -21.2 mA cm⁻² at -0.90 V than the CoPc-PI-COF-2-derived electrode associated with its higher electron conductivity. In addition, the turnover number (TON) of the CoPc-PI-COF-1 cathode is accumulated to 277 000 with a turnover frequency (TOF) of 2.2 s⁻¹ at -0.70 V after 40 h of continuous experiment. The present result clearly discloses the great potential of 2D porous crystalline solids in electrocatalysis.

EXPERIMENTAL SECTION

General Remarks. All regents were commercially available and directly employed. Co(TAPc) was synthesized referring to the published procedure. $^{\rm S3-S7}$

Synthesis of CoPc-PI-COF-1. A Pyrex tube $(9 \times 6 \text{ mm}, \text{ o.d.} \times$ i.d.) was filled with Co(TAPc) (17.0 mg, 0.02 mmol), PD (4.3 mg, 0.04 mmol), N-methylpyrrolidone (NMP) (0.5 mL), 1-butanol (0.5 mL), and isoquinoline (0.05 mL). After sonicating the tube for 10 min followed by flash freezing in a liquid N₂ bath, the frozen tube was degassed and slowly thawed to room temperature. After such a process was repeated three times, the tube was sealed by flame with a length of ca. 18 cm. The reaction was performed at 180 °C for 5 days, generating a black-green precipitate. The solid was isolated via centrifugation and successively washed with dimethylformamide (DMF), NMP, and acetone three times. The product was collected and dried at 100 °C under vacuum overnight to provide a black-green powder of CoPc-PI-COF-1 (17.1 mg) in a yield of 86% (calculated based on Co(TAPc)). IR (KBr): 1768, 1712, 1671, 1515, 1357, 1237, 1127, 736, 690 cm⁻¹. The Co content of 3.7 wt % in CoPc-PI-COF-1 was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Synthesis of CoPc-PI-COF-2. By employing the abovementioned procedure for preparing CoPc-PI-COF-1 using BD (7.4 mg, 0.04 mmol) instead of PD as starting material, a black-green powder of CoPc-PI-COF-2 (20.2 mg, a yield of 88% calculated based on Co(TAPc)) was obtained. IR (KBr): 1769, 1713, 1671, 1497, 1367, 1237, 1129, 736, 619 cm⁻¹. The Co content in CoPc-PI-COF-2 was determined by ICP-OES with a value of 3.3 wt %.

Carbon Dioxide Electrocatalytic Reduction Measurement. Before the fabrication of the electrode, a vial containing unsubstituted phthalocyaninato cobalt(II) compound (CoPc) or CoPc-PI-COFs (10.0 mg), Ketjen carbon black (10.0 mg), a Nafion perfluorinated resin solution (Sigma-Aldrich, 30 μ L, 10 wt %), and ethanol (1.0 mL) was sonicated for 60 min to prepare a homogeneous paste. It is worth noting that the mixture of catalyst and carbon black was ground prior to sonication. The electrode was fabricated by evenly transferring the paste (100.0 μ L) with a micropipet on a carbon fiber paper (1.0 × 1.0 cm², TGP-H-60), ensuring a CoPc-PI-COFs loading density of 1.0 mg cm⁻². The paper electrode was dried at room temperature overnight. The experiments for CO₂ electrochemical reduction were conducted in an H-type electrochemical cell consisting of two compartments separated by an anion exchange membrane (Nafion-117) on the electrochemical instrument (chi760E) at 25 °C in an airconditioned room. Two compartments contained 50.0 mL of electrolyte (0.5 M KHCO₃ aqueous solution) with Pt foil and a Ag/AgCl electrode in the saturated KCl solution as counter electrode and reference electrode, respectively. Prior to the electrochemical measurements, the electrolyte solution was saturated with Ar and CO₂ for 30 min. Linear sweep voltammetry (LSV) was operated with a scan rate of 10 mV s⁻¹ from 0 to -1.63 V vs Ag/AgCl in the CO₂-



Figure 1. PXRD characterizations of CoPc-PI-COF-1 (a) and CoPc-PI-COF-2 (b): experimental PXRD profile (black), refined profile (red), difference (orange), and simulation pattern based on the AA stacking manner (cyan). Simulated packing structures of CoPc-PI-COF-1 (c, d) and CoPc-PI-COF-2 (e, f) *via* $\pi - \pi$ interactions (C: gray; N: cyan; O: red; Co: pink; H: white). SEM, TEM, HRTEM, and EDS mapping photos for CoPc-PI-COF-1 (g, h, i, j) and CoPc-PI-COF-2 (k, l, m, n).

saturated 0.5 M KHCO₃ electrolyte (pH = 7.3). In this work, all mentioned potentials were converted to an RHE scale according to the equation of *E* (V vs RHE) = *E* (vs Ag/AgCl) + 0.059 × pH + 0.197. During the measurement, CO₂ gas at a flow rate of 20 mL min⁻¹ was transported into the tube, and the product was analyzed by gas chromatograph (GC) with the sampling loop (1.0 mL) each 15 min. Faradaic efficiency at different potentials was calculated on the basis of the stable electrocatalytic performance of the CoPc-PI-COFs electrode monitored by the *I*-*t* curve.

RESULTS AND DISCUSSION

Design and Fabrication of CoPc-PI-COFs. The imidization reaction enables the formation of PI polymers with excellent thermal stability, chemical resistance, and mechanical properties.^{58–60} In addition, the polyimide derivatives, especially the ones with long-range-order structure (i.e., metal–organic frameworks (MOFs) and COFs), have been widely investigated in the fields of electronics, semiconductors, and energy storage due to the strong π – π stacking of conjugated components and redox-active carbonyl sites.^{61–63} On the other hand, the excellent electrocatalytic CO₂RR properties of metallophthalocyanine compounds have been demonstrated in recent years.^{41,64,65} However, examples for fixation of catalytically active metallophthalocyanine units into reticular materials still remain rare, limited to MOF-1992,⁶⁶ CoPc-PDQ-COF,⁵¹ MPc-TFPN-COF,⁵² and MPc-M'-X series,^{67,68} to the best of our knowledge. As can be found, all the phthalocyanine-involved reticular materials reported thus far have been constructed from the 2,3,9,10,16,17,23,24-octa-(hydroxyl/amino)-substituted phthalocyanine building blocks (Scheme 1a). Herein, a new phthalocyanine compound, Co(TAPc), has been used to assemble reticular materials with the help of the linkers PD and BD, respectively, in NMP and 1-butanol catalyzed by isoquinoline at 180 °C for 5 days, Scheme 1b, affording two new 2D PI COFs, CoPc-PI-COF-1 and CoPc-PI-COF-2, with a high yield above 85%. The resultant COFs with desired porosity and $\pi - \pi$ stacking of metallophthalocyanine-tetraamide units should facilitate substrate diffusion and electron conduction during the electrocatalytic CO₂RR reduction.

Characterization of CoPc-PI-COFs. The structures of the two CoPc-PI-COFs with high crystallinity were analyzed by powder X-ray diffraction (PXRD), Figures 1a,b, S1, and S2. For CoPc-PI-COF-1, there are four obvious diffraction peaks in its PXRD pattern at $2\theta \approx 4.20^{\circ}$, 8.02° , 11.98° , and 27.01° . The peak indexing indicates that CoPc-PI-COF-1 is attributed to the tetragonal system with space group P4/mmm, showing



Figure 2. IR spectra, Co K-edge of EXAFS spectra, and N_2 adsorption (solid) and desorption (hollow) curves at 77 K of CoPc-PI-COF-1 (a, c, e) and CoPc-PI-COF-2 (b, d, f).

the cell parameters a = b = 21.02 Å and c = 3.34 Å. Similar to the phthalocyanine COFs reported previously, the planar metallophthalocyanine-tetraamide directs the extension of the four-connected polyamide sql layer along the a and b axis, Figure 1c, and an eclipsed AA-stacking of PI-bonded metallophthalocyanine layers perpendicular to the macrocycle plane has been built for CoPc-PI-COF-1, Figure 1d. The simulated PXRD profile deduced from the structural model is matchable with the experimental curve of CoPc-PI-COF-1, Figure 1a. The structural model is further verified by the Le Bail refinement result of CoPc-PI-COF-1 with agreement factors of $R_p = 0.96\%$ and $R_{wp} = 1.24\%$. As a result, the abovementioned four diffraction peaks for CoPc-PI-COF-1 are assigned to (100), (200), (300), and (001) reflections, respectively. Compared with CoPc-PI-COF-1, CoPc-PI-COF-2 constructed from the same phthalocyanine building block and BD with a longer length than PD possesses an isostructure but with a bigger cell parameter of a = b = 25.22 Å in addition to c = 3.30 Å ($R_p = 1.28\%$ and $R_{wp} = 1.63\%$ according to the Le Bail refinement). The corresponding (100), (200), (300), and (001) reflections shift to $2\theta \approx 3.53^\circ$, 7.00°, 10.05°, and 27.00°, respectively. According to the structural model of CoPc-PI-COFs, the distance of adjacent cobalt ions in the same layer amounts to 2.10 and 2.52 nm for CoPc-PI-COF-1 and CoPc-PI-COF-2, respectively, Figure 1c and e. PI-bonded phthalocyanine layers are further compiled together to form a three-dimensional supramolecular architecture via interlayered $\pi - \pi$ interactions with the neighboring layers at a distance of 0.33 nm for these two COFs, Figure 1d and f.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) photos manifest the nanoscale crystallite morphology of these two COFs with an irregular shape and size of *ca*. 100–300 nm, Figure 1g, k, h, and l. Highresolution transmission electron microscope (HRTEM) photos of CoPc-PI-COF-1 and CoPc-PI-COF-2 show the lattice fringes, further confirming their long-range order structures, Figure 1i and m. The *d*-spacing of 0.33 nm corresponds well to the simulated interlayer distance for these two materials. The element energy dispersive spectroscopy (EDS) mapping shows the homogeneous Co, C, O, and N atomic distribution, Figure 1j and n. ICP-OES analyses reveal a 3.7 and 3.3 wt % Co content in CoPc-PI-COF-1 and CoPc-PI-COF-2, respectively, indicating metallophthalocyanine contents of 62.7% and 64.3% among total phthalocyanine units for these two COFs. These values are slightly lower than that for Co(TAPc) (5.3 wt % Co content and 76% metallophthalocyanine content), indicating the occurrence of slight demetalation in the reaction process.

Comparison in the Fourier transform infrared (FT-IR) spectra of Co(TAPc), BD/PD, and CoPc-PI-COFs discloses the clean disappearance of the characteristic amino band of PD/BD at around 3300 cm⁻¹ and anhydride bands of Co(TAPc) at 1881 and 1767 cm⁻¹, Figure 2a and b. Instead, typical C=O bands of the imide moieties appear at ca. 1768and 1712 cm⁻¹ for both CoPc-PI-COF-1 and CoPc-PI-COF-2, and the other typical C-N-C stretching vibration for the imide rings of CoPc-PI-COF-1 and CoPc-PI-COF-2 is observed at 1357 and 1367 cm⁻¹, respectively.⁵⁸ These IR data indicate the complete conversion from molecular phthalocyanine building blocks to COFs. Thermal gravimetric analyses disclose that the decomposed temperature for both CoPc-PI-COFs is above 300 °C, Figures S3 and S4, indicating the prominent thermostability of these two new PI COFs. The robustness of these two COFs was also evaluated by immersing the samples into different solutions containing 0.5 M KHCO₃, concentrated HCl (12 M), NMP, tetrahydrofuran (THF), water, ethanol (EtOH), and DMF for 20 days. The treated CoPc-PI-COF-1 and CoPc-PI-COF-2 were revealed to retain the long-range-order structure by the consistent PXRD patterns with the as-synthesized samples, implying their excellent chemical stability, Figures S5 and S6. Composition of CoPc-PI-COF-1 and CoPc-PI-COF-2 was further detected by X-ray photoelectron spectroscopy (XPS), revealing the presence of C, N, O, and Co elements in these two samples,



Figure 3. LSV curves (a), Faradaic efficiency (b), partial CO current density (c), Tafel plots (d) of CoPc-PI-COF-1, CoPc-PI-COF-2, and CoPc. (f) Comparison of CO partial current densities between CoPc-PI-COF-1 with porphyrin/phthalocyanine electrocatalysts evaluated in an H-type electrochemical cell. (e) Stability test at -0.70 V for 40 h.

Figures S7 and S8. In the Co 2p XPS spectra, the peaks at 796.02 eV (Co 2p_{1/2}) and 780.54 eV (Co 2p_{3/2}) for CoPc-PI-COF-1 and 796.22 eV (Co 2p_{1/2}) and 780.71 eV (Co 2p_{3/2}) for CoPc-PI-COF-2 are comparable with those for divalent cobalt ions involved in the metallophthalocyanine derivatives.⁶⁹ Furthermore, the Co K-edge X-ray absorption nearedge structure spectroscopy (XANES) studies of CoPc-PI-COF-1 and CoPc-PI-COF-2 disclose a peak at 7713.96 and 7713.99 eV, respectively, Figures S9a and S10a, which is nearly identical to that for CoPc, indicating the similar coordination environment around cobalt ions in these three compounds. The Co K-edge extended X-ray absorption fine structure (EXAFS) curves for CoPc-PI-COF-1 and CoPc-PI-COF-2 possess similar profiles to that of the CoPc reference rather than Co foil, Figure 2c and d. These results suggest that the Co atoms in CoPc-PI-COF-1 and CoPc-PI-COF-2 are located in a N₄ square-planar coordination geometry. In order to acquire the detailed coordination information around cobalt(II) atoms, a square-planar Co-N₄ coordination model was applied into the quantitative EXAFS fitting for both CoPc-PI-COFs, Figures S9b and S10b. As can be found, the theoretical curve is comparable with the experimental result, giving the Co-N distance of 1.89 Å for both COFs and the CoPc benchmark, Table S1. These results disclose the square-planar Co-N₄ local coordination structure around the Co centers in COFs as the same as that of CoPc.

Gas Sorption Behaviors of CoPc-PI-COFs. The porous 2D layered structures of CoPc-PI-COF-1 and CoPc-PI-COF-2 might be beneficial to the mass transfer of substrates and enrichment of CO₂. The permanent porosity of CoPc-PI-COFs was checked by a N₂ sorption experiment at 77 K. CoPc-PI-COF-1 displays permanent porosity with a BET surface area of 181 m² g⁻¹. CoPc-PI-COF-2 has a slightly bigger BET surface area of 291 m² g⁻¹ attributed to its larger structural pore size, Figure 2e and f. Furthermore, the pore size distribution identifies the channel widths around 1.6 and 1.8 nm for CoPc-PI-COF-1 and CoPc-PI-COF-2 (Figures S11 and

S12), respectively. On the basis of CO₂ adsorption data at 196 K, the deduced BET surface area of CoPc-PI-COF-1 and CoPc-PI-COF-2 is calculated to amount to 230 and 339 m² g⁻¹, respectively, bigger than the corresponding value fitted from N₂ adsorption at 77 K. Both CoPc-PI-COFs have moderate CO₂ uptake capacities with values of 19.4 and 19.1 cm³ g⁻¹ at 298 K and 1.0 bar for CoPc-PI-COF-1 and CoPc-PI-COF-2 (Figures S13 and S14), respectively, indicating the favorable CO₂ affinity of these COFs. Thermal programmed desorption of CO₂ was also performed to check the interaction basic sites with carbon dioxide molecules from room temperature to 300 °C, Figure S15. The presence of only one peak at 110 °C for both CoPc-PI-COF-1 and CoPc-PI-COF-2 indicates the presence of a weak interaction of these two COFs with carbon dioxide molecules.

Electrocatalytic CO₂RR of CoPc-PI-COFs. Given the fact that CoPc-PI-COF-1 and CoPc-PI-COF-2 possess excellent chemical and thermal stability as well as permanent porous structures, both CoPc-PI-COFs can serve as promising candidates for promoting electrocatalytic CO₂RR. The electrocatalytic performance of CoPc-PI-COF-derived electrodes was investigated using a H-cell separated by a Nafion-117 membrane with a standard three-electrode configuration. In order to enhance the electron transfer, a doping mixture of carbon black and CoPc-PI-COFs was deposited on a piece of carbon fiber paper as a working electrode. For comparison, the electrocatalytic activity of CoPc was also evaluated under the same experimental conditions. LSV measurements were carried out in Ar and CO2-saturated 0.5 M KHCO3 electrolytes. As can be seen in Figures 3a and \$16, both CoPc-PI-COF-derived electrodes show much larger current densities at the applied potential range from -0.50 to -0.90 V (vs RHE) in CO2saturated 0.5 M KHCO₃ solution than in an Ar-saturated one, indicating the electrocatalytic CO2RR activity of CoPc-PI-COFs. The potentiostatic electrolysis was further performed to investigate the electrocatalytic CO2RR performance of CoPc-PI-COF-derived electrodes. The constant time-dependent total

geometric current density of CoPc-PI-COFs was determined at the potential range between -0.50 and -0.90 V with each potential for 20 min (Figures S17 and S18), indicating the good stability of COFs under the present electrode potential range.

GC and ¹H NMR spectroscopic analyses confirm the evolution of only CO and H₂ after the continuous electrocatalysis at potentials from -0.50 to -0.90 V of CoPc-PI-COFs in the CO₂-saturated 0.5 M KHCO₃ electrolyte without any liquid product, Figure S19. In good contrast, no CO product was detected in the control electrocatalysis performed under the Ar-saturated electrolyte and carbon cloth covered with acetylene black and Nafion in CO2-saturated 0.5 M KHCO₃ electrolyte, in Figures S20–S22, confirming the origin of a CO product from a CO₂ source. The CoPc-PI-COFs cathodes exhibit a high FE_{CO} of 87-97% at an applied potential range of -0.60 to -0.90 V (vs RHE), similar to the CoPc electrode, Figure 3b. In particular, at the applied potential of -0.80 V (vs RHE), FE_{CO} is able to reach up to 97% and 96% for CoPc-PI-COF-1 and CoPc-PI-COF-2, respectively, further demonstrating their excellent electrocatalytic CO_2RR activity. Besides FE_{CO} , j_{CO} for CoPc-PI-COF-1, CoPc-PI-COF-2, and CoPc was comparatively studied, Figure 3c. As can be found, the j_{CO} values of CoPc-PI-COF-2 at -0.40 to -0.90 V (vs RHE) are almost the same as that for CoPc. Nevertheless, CoPc-PI-COF-1 shows a significantly higher j_{CO} at the potential range of -0.60 to -0.90 V (vs RHE) than CoPc-PI-COF-2 and CoPc, implying the enhanced CO₂RR activity of CoPc-PI-COF-1. For example, at -0.90 V (vs RHE) CoPc-PI-COF-1 enables a high j_{CO} of -21.2 mA cm⁻² and shows a larger mass activity of 573 mA mg⁻¹ (calculation based on the CO partial current density divided by total Co(II) amount) than CoPc-PI-COF-2 (482 mA mg⁻¹) and CoPc (161 mA mg⁻¹). Tafel plots with the logarithm of current density $[\log(j_{CO})]$ and the overpotential (η) as the x and y axis, respectively, have been recorded to probe the possible mechanistic pathway of CO₂RR, Figure 3d. The Tafel slope of the linear part in the low overpotentials between -0.29 and -0.44 V is 95 and 105 mV dec⁻¹ for CoPc-PI-COF-1 and CoPc-PI-COF-2, respectively, suggesting the existence of single electron transfer to CO_2 and the generation of a $CO_2^{\bullet-}$ intermediate as a possible rate-determining step. In addition, Tafel slopes for COFs are smaller than that (146 mV dec⁻¹) for CoPc, hinting at their faster CO₂RR kinetics due possibly to the effective electron transfer and large active surface. The upward deviation of Tafel slope curvature at overpotentials above -0.50 V for these three electrodes might be caused by the mass transport restraint.

Moreover, the control CoPc@black electrode, containing the same cobalt content as the CoPc-PI-COF-1 electrode, exhibits an inferior electrochemical performance including FE_{CO} , j_{CO} , and the Tafel slope (167 mV dec⁻¹) to the abovementioned CoPc species under the same conditions, Figures S23-S25. Nevertheless, the TON, which was calculated on the basis of total cobalt content and the *I*-*t* curve at -0.70 V (vs RHE) for 20 min, is 22, 49, 81, and 71 for CoPc, control CoPc, CoPc-PI-COF-1, and CoPc-PI-COF-2, respectively, confirming the excellent electrocatalytic performance of COF electrodes.

The surface concentration of electrochemically active metallophthalocyanine sites on the CoPc-PI-COFs electrodes was determined through the integration of the anodic wave at the CV curve, Figures S26 and S27.^{47,51} The average value at

different scan rates for CoPc-PI-COF-1 is 2.2×10^{-8} mol cm⁻² (corresponding to 3.5% cobalt(II)-phthalocyanine moieties as active sites in CoPc-PI-COF-1), one-sixth higher than those of CoPc-PI-COF-2 (1.7×10^{-8} mol cm⁻² and 3.0%). These results confirm the enhanced CO2RR activity of CoPc-PI-COF-1 over CoPc-PI-COF-2, demonstrating the structural superiority of CoPc-PI-COF-1 in catalyzing CO2RR. As mentioned above in the structural analysis part, 2D CoPc-PI-COF-1 and CoPc-PI-COF-2 are isostructural, resulting in their similar Co(II) electroactive sites, surface area, and CO₂ adsorption capability. The only structural difference between CoPc-PI-COF-1 and CoPc-PI-COF-2 is the longer linker of CoPc-PI-COF-2 than CoPc-PI-COF-1, which may diminish the conductivity of CoPc-PI-COF-2. This might be responsible for the inferior CO₂RR activity of CoPc-PI-COF-2 to CoPc-PI-COF-1. To verify this assumption, electrochemical impedance spectroscopy (EIS) measurements were performed. As shown in Figure S28, the CoPc-PI-COF-1 electrode exhibits a much smaller charge transfer resistance than CoPc-PI-COF-2. This is beneficial to the charge transfer ability of CoPc-PI-COF-1 during the electrocatalytic CO₂RR process, indicating its advantage in the catalytic dynamics. Furthermore, conductivity measurement was employed to evaluate the intrinsic electrical conductivity of CoPc-PI-COFs, Figure S29. Current–voltage curves unveil the conductivity of 3.7×10^{-3} and 1.6×10^{-3} S m⁻¹ for CoPc-PI-COF-1 and CoPc-PI-COF-2, respectively, indicating their excellent conductive materials nature through space pathway.⁷⁰ The higher conductivity of CoPc-PI-COF-1 then promotes a higher electroactive coverage than CoPc-PI-COF-2, accounting for its outstanding electro-catalytic CO_2RR performance.⁴⁹ At-0.70 V (vs RHE), the TOF (calculated based on the electroactive Co sites in the electrochemical CO₂RR) of CoPc-PI-COF-1 and CoPc-PI-COF-2 is 2.2 and 1.9 s^{-1} , respectively. It is worth noting that, by combining the high conductivity, permanent porous structures, and the excellent CoPc active sites, FE_{CO} (93%), j_{CO} (-9.4 mA cm⁻²), and TOF (2.2 s⁻¹) of CoPc-PI-COF-1 at -0.70 V (vs RHE) are superior to most tetrapyrrole-containing porous counterparts reported thus far under similar experimental conditions, such as COF-367-Co (91%, -3.3 mA cm⁻², and 0.5 s⁻¹ at -0.67 V),⁴⁷ Co-TTCOF (91%, -1.8 mA cm⁻², and 1.3 s⁻¹ at -0.70 V),⁴⁶ Fe-PB (85%, -0.2 mA cm⁻², and 0.6 s⁻¹ at -0.63 V),⁴² and CoPc-Cu-NH (72%, -8.4 mA cm⁻², and 1.2 s⁻¹ at -0.74 V).⁶⁷ After a 2 h durability test at -0.80 V, the XPS peaks observed at 795.80 and 780.60 eV for divalent cobalt ions in the electrode, corresponding to Co $2p_{1/2}$ and Co $2p_{3/2}$ are in good agreement with those found for fresh CoPc-PI-COF-1, Figure S30. Furthermore, IR spectroscopic data disclose the lack of any significant band change between fresh CoPc-PI-COF-1 and used catalyst, Figure S31. These results indicate their prominent durability associated with the good chemical stability of these PI-linked COFs in electrochemical catalysis. This is also true for CoPc-PI-COF-1 and CoPc electrodes, Figures S32-S35. Fortunately, a similar PXRD pattern of CoPc-PI-COF-1@carbon black under the overpotential of -0.80 V to that of the as-synthesized sample was observed (Figure S36), indicating the maintenance of the periodic structure.

Toward practical applications, the long-term durability is crucial in electrocatalytic CO₂RR. For the present CoPc-PI-COFs electrodes, corresponding electrocatalytic stability measurement was performed at -0.70 V (vs RHE, η , -0.59 V). After 40 h, the Faradaic efficiency of CO for the CoPc-PI-

COF-1 electrode can be kept above 91%, with almost no decay in comparison with the fresh catalyst (93%), indicating its excellent durability, Figure 3f. During the 40 h electrocatalytic test at -0.70 V (vs RHE), the TON of CoPc-PI-COF-1 is accumulated to as large as 277 000. Obviously, according to the above-mentioned CO₂RR studies, the comprehensive electrocatalytic performance of CoPc-PI-COF-1, in terms of TOF, TON, FE_{CO} , j_{CO} , and durability, is superior to most of the reticular materials reported thus far under similar experimental conditions, Figure 3e and Table S2. Moreover, a flow cell with a gas diffusion electrode composed of CoPc-PI-COF-1 has been assembled, Figures S37-S40. This flow cell displays a high FE_{CO} of 95% and large j_{CO} of -44 mA cm⁻² at a low potential of -0.50 V (vs RHE), further revealing the possibility of CoPc-PI-COF-1 in practical electrocatalytic CO₂RR.

Electrocatalytic CO₂**RR Mechanism.** Theoretical simulation has been conducted on the periodic structure of CoPc, CoPc-PI-COF-1, and CoPc-PI-COF-2, giving an energy gap value of 1.53, 0.88, and 0.70 eV (Figure 4a and Table S3),



Figure 4. (a) Calculated energy gap of CoPc, CoPc-PI-COF-1, and CoPc-PI-COF-2. (b) Co–N bond orders of CoPc, A, and B without and with adsorbed CO. (c) Calculated free energy diagram of CoPc, A, and B catalyzing CO_2RR . Inset represents the optimized configurations of intermediates with A. H: white; C: gray; N: blue; O: red; Co: pink.

respectively. In comparison with CoPc, the narrower energy gap of CoPc-PI-COF-1 and CoPc-PI-COF-2 is helpful for the electrocatalytic CO₂RR. For the purpose of further elucidating the CO₂RR mechanism, finite cluster models of the respective COF structures (A and B) were built by extracting a structural segment from respective CoPc-PI-COF-1 and CoPc-PI-COF-2 and neglecting the long-range interaction among cobalt sites. For details, please see the Supporting Information. The similar Co–N bond orders calculated for CoPc, A, and B units indicate the similar coordination environment of Co in these materials, Figure 4b, in line with EXAFS data.

The calculated Gibbs free energy diagram of three CO_2RR processes for A, B, and CoPc is shown in Figure 4c and Table S4, including the generation of *COOH, the formation of *CO, and the CO desorption course. According to the calculation data, despite that the Gibbs energy barrier to afford *COOH increases from CoPc to A and B, the onset potential to initiate the CO₂RR decreases from CoPc-PI-COF-1 (-0.36)

V vs RHE) to CoPc (-0.44 V vs RHE) and CoPc-PI-COF-2 (-0.46 V vs RHE) because of the dependence of the determinant factor on the reduction of catalytic sites rather than the free energy barrier.⁴¹ Additional support for this point comes from the quite close free energy barrier for A and B but much smaller onset potential of CoPc-PI-COF-1 than CoPc-PI-COF-2. The Gibbs free energy of *CO shows the order of A > B > CoPc, indicating the decreased barrier for the CO desorption process in the same order. This result reveals that CoPc-PI-COF-1 is much more favorable for CO desorption. Investigation of Co-N bond orders reveals that CoPc-PI-COF-1, CoPc-PI-COF-2, and CoPc have a similar bond order for Co-N bonds before and after CO desorption, indicating the similar electrochemical stability of these three materials. In particular, the density functional theory (DFT)-calculated Gibbs free energy diagram also well explains the different CO₂RR efficiencies at different potentials. Nevertheless, despite the similar energy barrier calculated for *COOH formation between A and B, a much lower energy barrier revealed for CO desorption for the former species may contribute to the higher electrocatalytic CO₂RR activity of CoPc-PI-COF-1 than CoPc-PI-COF-2. The theoretical calculations for hydrogen evolution reaction (HER) and possible paths of CO2RR with CoPc-PI-COF-1 and CoPc-PI-COF-2 electrocatalysts were also performed, Table S4. On the basis of simulation results, the high free-energy gap in HER hinders its competing capability with electrochemical CO₂RR. With regard to other possible paths of CO₂RR (for example, generation of CH₄ and CH₃OH) with CoPc-PI-COF-1 and CoPc-PI-COF-2, following the *CO intermediate, the free energies of *COH and *CHO intermediates were calculated. It is worth noting that both *COH and *CHO are the intermediates of CO₂RR to generate CH₄ and CH₃OH. In comparison with the free energy of CO desorption, the much higher free energy of *COH is adverse to corresponding formation. Although *CHO has a similar free energy to that of CO desorption, carbon substrate and poor dispersion of COFs in making the present electrodes seem to preclude the generation of other chemicals such as CH₄ and CH₃OH.³⁹

At the end of this section, it is noteworthy that the present theoretical calculations overall rationalize the association of the electrocatalytic CO₂RR activity of phthalocyanine COFs with their intrinsic structural characteristics. The higher electron conductivity of CoPc-PI-COF-1 should further facilitate the charge transportation, therefore promoting its electrocatalytic CO₂RR performance from a kinetic perspective. This is further rationalized by the calculated electronic coupling result. Based on the calculation results, the electronic couplings for both hole and electron transfer between metallophthalocyanine segments in monolayered A' and B' (with a Zn ion to replace Co for the purpose of calculation) are negligibly small (less than 1 meV). This corresponds well with the findings derived from orbital distribution that the conjugation system is terminated by the imide nitrogen atom. However, the electronic coupling constants for hole/electron transfer between double-layered A' (668/462 meV) are revealed to be much larger than those between double-layered B' (294/ 156 meV) shown in Table S5, in line with the experimental fact that CoPc-PI-COF-1 exhibits much larger electron conductivity than CoPc-PI-COF-2.

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CONCLUSIONS

In summary, a new tetraanhydride-containing phthalocyaninato cobalt(II) building block has been used to construct 2D polyimide-linked functional COFs, which also provides a new perspective for constructing diverse phthalocyanine reticular structures. The porous structure, excellent thermal and chemical stability, and high electron conductivity for the newly developed phthalocyanine COFs have been well disclosed by various crystallographic, spectroscopic, and electronic measurements. These unique structural characteristics enable the highly efficient electrocatalysis of CO_2RR in terms of the mass active sites and thus the TOF, TON, and CO partial current density. These results not only present new metallophthalocyanine COFs with excellent chemical and thermal stability but also provide a clear example in engineering reticular materials electrocatalysts toward CO_2RR .

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c02145.

Experimental and theoretical calculation details, PXRD patterns, TGA curves, XPS spectra, XANES spectra, CO_2 sorption curves, and electrocatalytic performance of CoPc-PI-COF-1 and CoPc-PI-COF-2 (PDF)

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Notes

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