

Article

Subscriber access provided by UNIVERSITY OF ADELAIDE LIBRARIES

Efficient heterogeneous CO2 to CO conversion with a phosphonic acid fabricated cofacial iron porphyrin dimer.

Eman A. Mohamed, Zaki N. Zahran, and Yoshinori Naruta

Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.7b01115 • Publication Date (Web): 03 Aug 2017

Downloaded from http://pubs.acs.org on August 5, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Chemistry of Materials is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Efficient heterogeneous CO_2 to CO conversion with a phosphonic acid fabricated cofacial iron porphyrin dimer.

Eman A. Mohamed,⁺ Zaki N. Zahran,^{+¶*} Yoshinori Naruta.^{+§*}

⁺Institute for Chemical Energy Conversion Research and Institute of Science and Technology Research, Chubu University, Kasugai 487-8501, Japan, ^gFaculty of Science, Tanta University, Tanta, Egypt, ^gJST, Kawaguchi, Saitama, 332-0012, Japan. *znzahran@isc.chubu.ac.jp

ABSTRACT: For developing renewable fuels and controlling global warming, catalyst promoted CO_2 to CO is essential. Numerous CO_2 to CO conversion molecular catalysts have shown very high activity and stability. For large-scale conversion, immobilization of the molecular catalysts to conducting electrodes is essential. Several efficient molecular catalysts have been immobilized to conducting electrodes via physical bonds. We found that immobilization of a monolayer of the highly efficient Fe porphyrin dimer molecular catalyst via a phosphonic acid anchor to a fluorine-doped tin oxide electrode, FTO/**Fe₂DTPFPP-PO₃H**₂ showed high activity and stability for CO_2 to CO conversion at a very low catalyst loading in non-aqueous and aqueous solutions. A high current density was achieved for the CO_2 to CO conversion by loading more amount of the catalyst to a thin mesoporous layer of SnO₂ or TiO₂ nanoparticles on FTO. In neutral aqueous solutions, the non-innocent behavior of the FTO electrode was overcome by modifying its catalyst-free surface with hydrophobic *n*-butyl phosphonic acid groups.

Introduction

The CO₂ reduction to useful carbon resources is an essential reaction for developing renewable fuels and for controlling the global warming resulting from the CO₂ green house effect.^{1,2,3,4} The CO₂ reduction, however, is one of the biggest challenges in chemistry because of the high CO₂ thermodynamic stability and the versatile reduction products generated via single/multi-electron CO₂ reductions.⁵ Focusing on CO₂ to CO conversion, several efficient homogeneous or heterogeneous catalysts have been reported, mostly in non-aqueous solvents (CH₃CN, DMF, or mixture of the solvent and weak Brönsted acids). These include precious metal- (e.g. Re,^{67,8,9} Ru,^{10,11,12} Ir,¹³ Au,^{14,15} etc.) or non-precious metal- (e.g. Fe,^{16,17,18,19,20,21} Ni,^{22,23,24,25} Mn,^{26,27} Co,^{28,29,30,31,32} etc.) based catalysts. In terms of practical applications, the development of base metal is of great interest.³³

Inspired from the binuclear Ni, Fe-active center of carbon monoxide dehydrogenase (CODHs) that efficiently catalyzes the reduction of CO₂ to CO₁^{34,35,36,37,38} we recently reported several cofacial Fe porphyrin dimers, Fe2Dpor having binuclear Fe centers at a suitable Fe-Fe separation distance and bearing electron- donating/withdrawing substituents at the peripheral porphyrin rings as homogeneous molecular catalysts for CO2 to CO conversion in a DMF/10% H₂O solution without addition of any acids. The dimers efficiently and selectively catalyze the electrochemical CO₂ to CO conversion with high Faradic efficiency, more than 90 %, and benchmarking turnover frequencies, TOFs, up to $\log TOF = 5.8 \text{ s}^{-1}$. They showed superior activity and stability for the CO2 to CO conversion over the corresponding Fe porphyrin monomers. Control experiments with the mononuclear Fe porphyrin monomers and the 1,3-phenylene bridged binuclear Fe porphyrin dimer; indicated the importance of the binuclear Fe centers and the Fe-Fe

separation distance for the CO₂ to CO conversion. The substituents on the peripheral porphyrin rings greatly affect the activity and the overpotential, η of the catalysis process where the pentafluorophenyl Fe porphyrin dimer, Fe₂DTPFPP showed the lowest η (0.4 V) among the Fe porphyrin dimers for the CO₂ to CO conversion.^{39,40} Although the homogeneous catalysis is essential for developing and understanding the catalysis process and its mechanisms, the heterogeneous catalysis is necessary for both developing large scale electrolysis and for integrating the catalysts with suitable semiconductor for CO₂ to CO photo-assisted conversion.

Herein, we successfully fabricated the **Fe₂DTPFPP** molecular catalyst with a phosphonic acid anchor, **Fe₂DTPFPP-PO₃H**₂ to assemble on a surface of FTO, FTO/SnO₂, and FTO/TiO₂ electrodes through chemical bonds and use the assembly as a heterogeneous CO₂ to CO conversion catalyst. The low η of the **Fe₂DTPFPP-PO₃H**₂ dimer allowed us to safely use the assembly within the FTO potential window in non-aqueous DMF and CH₃CN solutions. The assembly was also tested in neutral aqueous solution after overcoming the non-innocent behavior of the FTO electrode using a suitable hydrophobic self-assembled hydrocarbon layer with alkyl phosphonic acid, *n*-BuPO₃H₂.

Experimental

Here we will present the details of the preparation of the cofacial Fe tetrapentafluorophenyl porphyrin dimer bearing a phosphonic acid anchor group, $Fe_2DTPFPP-PO_3H_2$ that was prepared by stepwise procedures developed in our group according to Figure 1. Other experiments are given in the supporting information, SI.

(a) Preparation of methyl 3-bromo-2-formylbenzoate. (compound 2, Figure 1). According to reported procedures,⁴¹ a mixture of 5-bromophthalide (1, 25 g, 0.117 mol) and *N*-bromosuccinimide (21 g, 0.118 mol) in CCl₄ (200 mL) was re-

fluxed for 1 day under irradiation of light from a 180-W sunlamp. After cooling the reaction mixture, the solid succinimide was removed by filtration, and the filtrate was evaporated in vacuo. The resulting pale yellow powder was mixed with water:acetone:THF (4:1:1, 600 mL). The mixture was refluxed for 1 day to give a clear colorless solution. On cooling, 23 g of a 5-bromo-2-formylbenzoic acid was produced that is isolated by filtration and washed with distilled water. The acid was then converted to the corresponding methyl ester by refluxing with MeOH (500 mL) in the presence of anhydrous InCl₃ (2.0 g) for about 18 h. The solvent was removed and after addition of water, white solid residue was extracted with CHCl₃ from water. The CHCl₃ layer containing the desired compound was dried over anhydrous Na2SO4 and the solvent was evaporated to give 24 g of 2 as a white powder in 84.4% yield. ¹H NMR $(CDCl_3): \delta 10.46$ (s, 1H, CHO), 7.87 (d, 1H, Ar-H), 7.75 (d, 1H, Ar-H), 7.65 (dd, 1H, Ar-H), and 3.88 (s, 3H, OCH₃). MALDI-TOF-MS m/z = 242.5 (found), 243.0 (calcd.).

(b) Preparation of 5-(5'-bromo-2'-methoxycarbonylphenyl)-10,15,20- trispentafluorophenylporphyrin (compound 3, Figure 1). A 2-L three-neck round-bottomed flask was charged with compound 2 (11 g, 0.045 mol), pentafluorobenz-aldehyde (26.6 g, 0.136 mol), freshly distilled pyrrole (12.1 g, 0.180 mol), and CHCl₃ (1300 mL). The colorless solution was purged with nitrogen for about 15 min. Then, boron trifluoride diethyl ether complex (BF3•Et2O, 15 mL) was added via s syringe. The color changed slowly to dark red. The mixture was stirred at room temperature under nitrogen and TLC monitored the progress of the reaction. After 10 h, excess DDQ (DDQ = 2,3-dichloro-5,6-dicyano-pbenzoquinone) solution (20 g/150 ml benzene, 0.088 mol) was added to the reaction mixture, where the color changed to dark green. The mixture was stirred at room temperature for further 4 h. The solvent was removed, the residue was dissolved in a small amount of CHCl₃, the solution was loaded into an activated Al₂O₃ column and the reaction mixture was eluted with CHCl₃. The first broad reddish violet band was collected. The TLC chromatography of this band showed the presence of light red band on the top followed by green band, strong reddish violet band then green and black bands on the bottom. The reddish violet band was collected, the solvent was removed, and the residue was further purified with silica-gel column eluted with *n*-hexane: CH_2Cl_2 (1:1) to give 5.0 g of the pure compound (3) in 10.8 % isolated yield based on the amount of compound **2**. ¹H NMR (CDCl₃): δ 8.85 (d, 8H, por- β pyrrole H), 8.33 (m, 2H, Ar-H), 8.09 (dd, 1H, Ar-H), 2.86 (s, 3H, OCH₃), and -2.78 (s, 2H, por-pyrrole H). MALDI-TOF-MS: m/z= 1023.0 (found), 1021.5 (calcd.).

(c) Preparation of 5-(5'-bromo-2'-hydroxymethylphenyl)-10,15,20-tris pentafluorophenylporphyrin (compound 4, Figure 1). A 500-mL flask was charged with 3 (2.0 g, 0.02 mol) and dry THF (50 mL). The solution was cooled to 0 °C, then LDBBA (30 mL, 0.33 M solution) was added dropwise. The reaction mixture was stirred for 4 h at 0 °C under N₂ atmosphere, while the progress of the reaction was monitored with TLC. After completed, the reaction was quenched by 2 N HCl and the product was extracted with CH₂Cl₂. The solvent was removed and the residue was purified with a silica-gel column using CH₂Cl₂ as an eluent to give 4 (1.94 g, 99 % yield) as a pure violet powder. ¹H NMR (CDCl₃): δ 8.85 (d, 8H, pyrrole β -H), 8.24 (t, 1H, Ar-H), 8.02 (dd, 1H, Ar-H), 7.87 (d, 1H, Ar-H), 4.27 (s, 2H, -CH₂OH), 2.17 (t, 1H, -OH), and -2.87 (s, 2H, por-pyrrole H). MALDI-TOF-MS: m/z = 994.1(found), 993.5 (calcd.). (d) Preparation of 5-(5'-bromo-2'-formylphenyl)-10,15,20trispentafluoro- phenylporphyrin (compound 5, Figure 1). Compound 4 (1.5 g, 0.02 mol) was dissolved into dry CH₂Cl₂ (200 mL) then an excess amount of activated MnO₂ (~5 g) was added. The solution was stirred under N₂ for 2 hours. The TLC showed complete conversion of the compound to 5. The MnO₂ was isolated by filtration. The solvent was removed *in vacuo* and the residue was purified with Silica-gel column using CH₂Cl₂ as eluent to give a pure violet powder (1.4 g, 93.5 % yield). ¹H NMR (CDCl₃, 400 MHz): δ 9.39 (s, 1H, -CHO), 8.92 (s, 4H, por- β -pyrrole H), 8.86 (d, 2H, por- β -pyrrole H), 8.80 (d, 2H, por- β -pyrrole H), 8.43 (d, 1H, Ar-H), 8.30 (d, 1H, Ar-H), 8.15 (dd, 1H, Ar-H), -2.82 (s, 2H, por-pyrrole H). MALDI-TOF-MS *m*/*z* = 990.0 (found), 991.5 (calcd.).

(e) Preparation of 5-bromo-1,2-bis[5,10,15-tris pentafluorophenyl porphyrinyl]benzene (compound 6, Figure 1). A 1-L three-necked flask was charged with compound 5 (1.8 g, 0.02 mol), pyrrole (1 g, 0.015 mol), pentafluoro-benzaldehyde (2.1 g, 0.01 mol), and dry CH₂Cl₂ (500 mL). The solution was stirred at room temperature for 20 min under N₂. Then, BF₃•Et₂O (4 mL) was added. After 4–h stirring, DDQ solution (5 g in 100 mL benzene) was added and the stirring was continued for additional 2–h. A pure violet powder of compound 6 was isolated (0.4 g, 12.4 % yield) after column chromatographic separation. ¹H NMR (CDCl₃): δ 9.31 (dd, 4H, pyrrole β -H), 9.01 (d, 1H, Ar-H), 8.70 (d, 1H, Ar-H), 8.49 (dd, 1H, Ar-H),) 8.38 (d, 12H, pyrrole β -H), -4.15 (s, 4H, pyrrole NH). MALDI-TOF-MS: m/z = 1770.4(found), 1769.9 (calcd.).

(f) Preparation of 5-bromo-1,2-bis[5,10,15-trispentafluorophenylporp-hyrinate zinc]benzene (compound 7, Figure 1). A solution of 6 (0.2 g, 0.001 mol) in CHCl₃/MeOH (50 mL, 1:1) was refluxed overnight with excess $Zn(OAc)_2 \cdot 4H_2O$ (0.3 g, 0.014 mol). The solvent was then removed, the desired compound was extracted with CHCl₃/water two times, and the organic layer was dried over anhydrous sodium sulfate. The compound was further purified with a silica-gel column using CH₂Cl₂ as an eluent. The reddish orange band was collected to give a reddish violet powder (0.2 g, 95.9 % yield). MALDI-TOF-MS: m/z = 1896.2 (found), 1896.7 (calcd.).

(g) Preparation of 5-diethylphosphonyl-1,2-bis(5,10,15-trispentafluoro-phenylporphyrinate zinc)benzene (compound 8, Figure 1). Following reported procedures,^{42,43} a 100-mL 2-necked flask was charged with 7 (200 mg, 0.11 mmol), Pd(OAc)₂, (23.7 mg, 0.11 mmol), triphenylphosphine (83.0 mg, 0.32 mmol), triethylamine (50 mg, 0.49 mmol), diethylphosphite, and dry THF/EtOH (50 mL, 1:1). The whole mixture was refluxed under N₂ for 5 days. A standard workup including chromatography (silica-gel, CH₂Cl₂/MeOH, 98:2 v/v) afforded reddish violet solid (195 mg, 90.7 % yield). MALDI-TOF-MS: m/z = 1953.9 (found), 1953.9 (calcd.).

(h) Preparation of 5-diethylphosphonato-1,2-bis[5,10,15-trispentafluoro-phenylporphyrin]benzene (compound 9, Figure 1). A CH₃Cl solution (50 mL) of 8 (195 mg, 0.10 mmol) was stirred with 6M HCl solution (50 mL) for 2–h. The organic layer was separated from the acidic aqueous layer, washed with aq. Na-HCO₃, then with water, and then dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified with a silicagel column using CH₂Cl₂:MeOH (98:2) as an eluent to afford 190 mg of 9 in 98% yield. ¹H NMR (CDCl₃): δ 9.29 (dd, 6H, pyrrole β -H), 9.02 (m, 1H, Ar-H), 8.88 (d, 1H, Ar-H), 8.82 (d, 1H, Ar-H)), 8.44 (d, 10H, pyrrole β -H), 4.60 (q, 4H, Et-CH₂), 1.63 (t, 6H, Et-

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 CH₃), -4.08 (s, 4H, pyrrole NH). MALDI-TOF-MS: m/z = 1827.6 (found), 1827.2 (calcd.). UV-vis spectrum shows a Soret band at 397 nm and two Q bands at 515 and 589 nm (Figure S1). Anal. Calcd for C₈₇H₃₇F₃₀N₈O₄P (H₂DTPFPP-PO₃Et₂•MeOH) C, 56.20; H, 2.01; F, 30.66; N, 6.03%. Found: C, 56.02; H, 2.54; F. 31.13; N, 6.04%.

(i) Preparation of $Fe_2(5$ -diethylphosphonato-1,2-bis[5,10,15trispentafluorophenylporphyrin]benzene)Cl₂ (compound 10, Figure 1). A 300-mL flask was charged with compound 9 (100 mg, 0.10 mmol), excess FeBr₂ (200 mg, 0.93 mmol), and dry DMF (30 mL). The mixture was refluxed overnight. The solvent was then removed and the desired compound was extracted with CHCl₃/HCl (1M in H₂O) three times then with CHCl₃/NaHCO₃ (saturated) three times and finally with the CHCl₃/H₂O three times. The organic layer containing the desired compound was dried over anhydrous sodium sulfate. The compound was further purified with silica gel column using CHCl₃ containing 5% MeOH as an eluent. The reddish brown band was collected to give a reddish brown powder (90.3 % yield) of the desired compound. MALDI-TOF-MS: m/z = 1934.6 (found), 1934.8 (calcd.).

(g) Preparation of $[Fe_2DTPFPP-PO_3H_2]Cl_2$ catalyst. A 50-ml flask was charged with 10 (195 mg, 0.10 mmol), TMSBr (TMSBr = trimethylsilylbromid) (310 mg, 2.0 mmol), TEA (246 mg, 2.4 mmol), and dry CH₂Cl₂ (30 ml). The mixture was refluxed overnight under N₂ atmosphere. After aqueous workup, the desired compound was extracted by CH₂Cl₂, several times from the mixture. The compound was further purified with silica-gel column using CHCl₃ containing 5% MeOH as an eluent. The reddish brown band was collected to give a reddish brown powder (90.3 % yield) of the desired compound. MALDI-TOF-MS of the Fe₂DTPFPP-PO₃H₂ dimer shows peaks at *m*/*z* values of 1878.9 corresponding to $[Fe_2DTPFPP-PO_3H_2]Cl$ (M⁺, calcd. 1913.7) (Fig. S2).

Results and discussion

Synthesis of Fe2DTPFPP-PO3H2 catalyst. Phosphonic acid groups have been previously reported to provide a strong chemical binding of several photo- and redox-active molecules to metal oxide surfaces in several applications such as anchoring of phosphonic acid fabricated bipyridine and terpyridine ruthenium dyes to TiO2 in dye sensitized solar cells^{44,45,46,47,48} and anchoring of a phosphonic acid fabricated terpyridine ruthenium water oxidation catalysts to ITO and FTO electrodes⁴⁹. Because of its previously successful results, we decided to fabricate the cofacial Fe porphyrin dimer that showed the lowest η in homogeneous solution with a phosphonic acid group to anchor it to the FTO, FTO/SnO₂, and FTO/TiO₂ electrodes surface and use the resultant assembly for the first time as a heterogeneous catalyst for CO₂ to CO conversion. Although the fabrication of the Fe porphyrin dimer, Fe₂DTPFPP-PO₃H₂ molecular catalyst with a phosphonic acid group is long procedures, it is straightforward and based on well-documented procedures. Figure 1 summarizes the stepwise procedures used to fabricate the Fe porphyrin dimer with a phosphonic acid anchoring group and its anchoring to the FTO electrode surface. Details of the preparation, purification, and characterization of the compound are presented in the experimental section and supporting information, SI (Figures S1 and S2).



Figure 1. Synthetic route of the CO₂ to CO Fe porphyrin dimer catalyst fabricated with a phosphonic acid anchor, Fe₂DTPFPP-PO₃H₂ and its anchoring to the FTO electrode surface. Reaction conditions, A: N-bromosuccinimide, CCl₄, H₂O, (CH₃)₂CO, THF, MeOH, InCl₃, B: pyrrole, pentafluorobenzaldehyde, BF₃.Et₂O, CHCl₃, DDQ, C: LDBBA, CH₂Cl₂ D: MnO₂, CH₂Cl₂, E: pyrrole, pentafluorobenzaldehyde, BF₃.Et₂O, CHCl₃, MeOH, G: Pd(OAc)₂, triphenyl phosphine, triethyl amine, diethylphosphite, and THF/EtOH, H: 6M HCl, CHCl₃ I: FeBr₂, DMF, HCl, H₂O, CHCl₃, J: Trimethylsilylbromide, triethylamine, CH₂Cl₂, K: 1mM Fe₂DTPFPP-PO₃H₂ (in EtOH), FTO, 120°C for 48 hrs.

Performance of Fe₂DTPFPP-PO₃H₂ for CO₂ to CO conversion as a molecular catalyst. As a homogeneous catalyst, Fe2DTPFPP-PO3H2 showed cyclic voltammetric behavior in a DMF/10% $H_2O/0.1M$ $TBAPF_6$ ($TBAPF_6$ = tetra-*n*butylammonium hexafluorophosphate) solution under Ar and CO₂ consistent with its high activity for the CO2 to CO conversion at a low η (Figure 2a). As the previously reported Fe porphyrin dimers,^{39,40} Fe₂DTPFPP-PO₃H₂, showed, under Ar, a simultaneous $2e^{-}$ redox couple (peaks 1/1') assigned for $2Fe^{III/II}$ at a reduction peak potential, $E_p = 0.05 \text{ V} vs.$ NHE (hereafter, all potentials are indicated against NHE except as noted). The irreversible reduction peak at $E_p = -0.47 \text{ V} \text{ (peak 1")}$ is, as previously reported,^{39,40} tentatively assigned to an Fe porphyrin dimer species having a strong axial ligand, Cl⁻, possibly between the two porphyrin Fe ions. The irreversibility of the peak indicates the loss of the axial ligand up on the reduction. Successive 2e⁻ redox couples, 2a and 2b, assigned to the $2Fe^{II/I}$ were observed at $E_p = -0.67$ V and -0.80 V, respectively. Finally a simultaneous quasi-reversible 2e⁻ redox couple, 3/3' for $2Fe^{1/0}$ at $E_p = -1.33$ V (Figures 2a and S3). The higher current of the reduction peak of the 3/3' couple compared to ones for 1/1'couple is possibly due to weak catalysis of residual protons. The peak currents increase linearly with the square root of the scan rates indicating its diffusion controlled processes (Figure S3 b).

Under CO₂, a strong catalytic current peak appeared at the top of the electro-generated Fe⁰ species indicative of the catalytic CO₂ reduction by the electro-generated Fe⁰ active species (Figure 2a).^{16,17,18,19,20,21,39,40} Indeed this behavior are similar to that shown by the previously reported Fe porphyrin dimers.^{39,40} Although, the catalysis looks like S-shaped, the catalyst TOF was estimated from the foot-of-the-wave analysis of the CVs based on equations 1-4 to avoid any side phenomena that might accompanying the catalysis process.^{17,18,40,50}

$$\frac{i}{i_p^o} = 2.24 \sqrt{\frac{RT}{Fv}} 2k[CO_2] \frac{1}{1 + \exp\left[\frac{F}{RT}(E - E_{cat}^o)\right]}$$
(1)

$$TOF = \frac{2k[CO_2]}{1 + \exp\left[\frac{F}{RT}(E - E_{cat}^o)\right]}$$
(2)

$$\log \text{TOF} = \log 2k[\text{CO}_2] - F/RT \ln 10 \left(E^o_{\text{CO}_2/\text{CO}} - E^o_{\text{cat}} \right) + F\eta/RT \ln 10$$
(3)

where; $\log 2k[CO_2] - F/RT \ln 10 \left(E^o_{CO_2/CO} - E^o_{cat}\right) = TOF^0$

$$\eta = E - E_{\rm CO_2/CO}^o \, , \, E_{\rm CO_2/CO}^o = \, -0.69 \, V \tag{4}$$

Plotting $i/i_{\rm p}^{0}$ vs. $1/\{1+\exp[F/RT(E-E_{\rm cat}^{0})]\}$ according to equation 1 gives rise to a straight line of slope $2.24(RT/Fv)^{1/2}(2k[CO_2])^{1/2}$ (v is the scan rate in 0.1 V/s) from which the catalysis pseudo-firstorder rate constant, $k[CO_2]$ is calculated. The $k[CO_2]$ is then used to calculate the TOF according to equation 2. The logTOF- η relationship was plotted according to equation 3, where i is the catalytic current in the presence of CO₂, i_{P}^{0} is the peak current in the absence of CO₂, F, R, T, E, and TOF⁰ are the Faraday constant, gas constant, absolute temperature (298 K), the electrode potential, and the intrinsic turnover frequency (turnover frequency at zero η), respectively.^{17,18,40} The value of η is calculated according to equation 4 based on the reported thermodynamic redox potential of the CO₂ to CO conversion in DMF/5% H₂O solution containing 0.1 M "But₄NPF₆ as a supporting electrolyte, standard redox potential, $E^0(CO_2/CO) = -0.69 \text{ V}^{.17}$ Recently, $E^0(CO_2/CO)$ was reported to be 0.51 V (–0.12 V vs. $Fc^{\scriptscriptstyle +/0}$, Fc stands for ferrocene) and $-0.1 \text{ V} (-0.73 \text{ V} \text{ vs. Fc}^{+/0})$ in dry CH₃CN and DMF, respectively.⁵¹ In wet CH₃CN ([H₂O] = 1M), E^0 (CO₂/CO was reported to be $-0.92 \text{ V} (-1.55 \text{ V} \text{ vs. Fc}^{+/0})^{52}$ which is more negative than the value reported previously, $-0.644 \text{ V} (-1.274 \text{ V} \text{ vs. Fc}^{+/0})^{17}$. In wet DMF, the reported $E^0(\text{CO}_2/\text{CO})$ is –0.69 V that we used to calculate η in this study.¹⁷ If this value has the similar error as found in wet CH₃CN, the η in this work as well as previously reported ones will become smaller than the one appeared here.

Figure 2b depicts the foot-of-the-wave analysis of Fe₂DTPFPP-**PO**₃**H**₂ catalyst that showed k_{cat} value of 2.2 x 10⁴ s⁻¹, where E_{cat}^{0} was determined to be -1.24 V from the CV recorded at 100 mV/s scan rate under Ar (Figure S3). The deviation of the results (black line) from the simulated one (red line) indicates that some side phenomena is accompanying the catalysis process even though the catalysis is very close to S-shape.¹⁷ Figure 2c shows the catalytic CVs responses of the Fe2DTPFPP-PO3H2 compared with the previously reported Fe porphyrin dimers (their chemical structures are presented in Figure S4). Figure 2d depicts the logTOF- η relationship for the current Fe2DTPFPP-PO3H2 catalyst and the previously reported Fe porphyrin dimers (Figure S4).40 Table S1 summarizes the catalysis parameters of the Fe2DTPFPP-PO3H2 catalyst and the reported most active CO₂ to CO conversion catalysts in homogenous solutions. Table S1 and Figure 2 clearly indicate that the current Fe2DTPFPP-PO3H2 catalyst shows high activity for CO₂ to CO conversion at low η . Its activity is quite similar to the phosphonic acid-free Fe porphyrin dimer, **Fe₂DTPFPP**, in homogeneous solutions. Unlike the prominent effects of the peripheral substituents of the porphyrin rings on the catalysis η ,⁴⁰ the phoshonic acid linker at the phenylene bridge induces less effect on the CO₂ to CO conversion η . Consistent with this observation, Fe porphyrin dimers bearing the bromophenylene and the diethylphosphonate-substituted phenylene, **Fe₂DTPFPP-Br** and **Fe₂DTPFPP-PO₃Et₂**, showed similar behaviors (Figures S5 and S6).



Figure 2. Performance of $Fe_2DTPFPP-PO_3H_2$ (0.5mM) catalyst for CO₂ to CO conversion in a homogeneous DMF/10% H₂O/ 0.1 M TBAPF₆ solution and comparison with other Fe porphyrin dimers. (a) CVs at 100 mV/s scan rate under Ar (blue lines) and CO₂ (red lines). (b) foot-of-the-wave analysis derived from (a). (c) Catalytic CVs responses (forward scan only shown for clarity) for $Fe_2DTPFPP$ -**PO**₃H₂ and other previously reported Fe porphyrin dimers. (d) Tafel plot [logTOF- η relationships] of the **Fe₂DTPFPP-PO₃H₂** and other previously reported Fe porphyrin dimers.

Anchoring of Fe₂DTPFPP-PO₃H₂ catalyst to FTO electrode surface. The Fe2DTPFPP-PO3H2 catalyst was fabricated to FTO surface by immersing a pre-cleaned FTO electrode into a 0.5 mM degased ethanolic solution of the catalyst in a gastight tube and heated it at 120 °C for 48 hrs. We found that heating at a 120 °C in a gastight tube reduces the modification time of the catalyst and increases its robustness on the electrode surface compared to soaking the electrode in the catalyst solution at room temperature.53 The FTO/catalyst assembly was then taken out, washed several times with EtOH, and allowed to dry at the room temperature for a couple of hours before further cyclic voltammetric, electrolysis, UV-vis, and X-ray photoelectron spectroscopy, XPS measurements. Although the use of phosphonic acid as a covalent bond linker to the metal oxide surfaces is well documented,44,45,46,47,48,49 we performed a control experiment by immersing FTO electrode in a phosphonic acid-free Fe porphyrin dimer, Fe2DTPFPP, solution under the same conditions used to prepare the FTO/ Fe₂DTPFPP-PO₃H₂ assembly. The Fe₂DTPFPP is completely detached from the FTO surface during washing in EtOH. The CV,

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 UV-vis, and XPS (Figure S7) measurements only showed the behavior of the bare FTO electrode. Indeed, the Fe porphyrin dimers are highly soluble in EtOH, DMF, and CH₃CN. This control experiment confirmed that the **Fe₂DTPFPP-PO₃H₂** catalyst is anchored to the FTO electrode surface via covalent chemical bonds not via physical adsorption to the electrode surface.

Performance of FTO/Fe₂DTPFPP-PO₃H₂ assembly for CO₂ to CO conversion in nonaqueous solutions. Figure 3a depicts the CVs of the FTO/ **Fe₂DTPFPP-PO₃H₂** assembly in a DMF/ 0.1M TBAPF₆ solution at different scan rates, *v* under Ar. Unlike its behavior in homogeneous solution, the FTO/ **Fe₂DTPFPP-PO₃H₂** assembly showed six consecutive 1e⁻ reduction peaks (peaks 1-6, Figure 3a) for the two Fe centers at 0.05, -0.15, -0.36, -0.55, -0.77, and -1.03 V suggesting fast electron transfer from the FTO electrode to the catalyst through the phosphonic acid anchor. Following a reported strategy,^{50,54} the amount of the surface loaded **Fe₂DTPFPP-PO₃H₂** catalyst on the FTO surface, *Γ*, was estimated to be 4.6 x 10⁻¹² mol/cm² from the *i*_p-*v* relationship based on the relation; *i*_p = n²*IF*²*v*/4*RT* (Figure 3a, insert).⁵⁴ The estimated *Γ* is similar to that recently reported for Mn₂DTPFPP-PO₃H₂ anchored to ITO electrode.⁵⁵

Figure S8 shows the UV-vis spectra of the FTO/Fe2DTPFPP-PO3H2 assembly and Fe2DTPFPP-PO3H2 in EtOH. The characteristic Soret band of the FTO/Fe2DTPFPP-PO3H2 assembly at 404 nm was red shifted by 4 nm relative to that of Fe2DTPFPP- PO_3H_2 catalyst in EtOH. This feature is in agreement with that previously reported for other porphyrin and metalloporphyrin modified with an undecanoic acid or phosphonic acid linkers on ITO surface and has been attributed to a side-by-side porphyrin π aggregation (J-aggregate).^{55,56} The saturation coverage, Γ , of the FTO/Fe2DTPFPP-PO3H2 assembly was evaluated from the absorption spectrum on the basis of the equation $\Gamma = 10^{-3} A / \varepsilon$ (A and ε (1.5 x 10⁵ mol⁻¹•cm⁻¹•L) are the absorbance of the monolayer and molar absorption coefficient, respectively).⁵⁷ Using this equation, Γ of Fe₂DTPFPP-PO₃H₂ on the FTO surface is estimated to be $4.7 \ge 10^{-12} \text{ mol/cm}^2$ consistent with that evaluated from the CV measurements.

XPS measurements of the FTO blank electrode and FTO/**Fe₂DTPFPP-PO₃H₂** assembly (before and after the electrolysis, see later) were recorded for N 1s (N in the porphyrin), P 1s (P in phosphonic acid linker) and Fe 2p as a third marker for the presence of the catalyst on the FTO electrode surface. We found that both N 1s and P 1s can be used as markers for the presence of the catalyst on the FTO electrode surface, however Fe 2p signal overlaps with that of the Sn 3p3 peak that comes from the FTO electrode. Figure 3b shows the XPS of the N 1s for the FTO blank and FTO/**Fe₂DTPFPP-PO₃H₂** assembly. The N 1s signal at 399.0 eV was observed only for the FTO/**Fe₂DTPFPP-PO₃H₂** assembly. Figure S9 depicts the XPS of the P 2p at 133.5 eV and Fe 2p spectral region for the FTO blank and FTO/**Fe₂DTPFPP-PO₃H₂** assembly. The XPS, UV-vis, and CV measurements clearly indicate the binding of the catalyst to the FTO electrode surface.

Figure 3c shows the CVs of the FTO/ $Fe_2DTPFPP-PO_3H_2$ assembly in a DMF/5% H₂O/0.1M TBAPF₆ under Ar (blue line) and CO₂ (red line) at 100 mV/s scan rate. Under CO₂, the assembly showed a strong catalytic current for the CO₂ reduction indicating the high activity of the assembly as a heterogeneous catalyst for the CO₂ to CO conversion. Similar behaviors were observed in a CO₂-saturated CH₃CN/5% H₂O/0.1M TBAPF₆ solution (Figure S10). Similar to the catalysis observed in homogeneous solution, the catalytic current is observed over the redox couple assigned for $\rm Fe^{I/0}$ reduction indicating the involvement of the $\rm Fe^0$ active species in the catalysis. 16,17,18,19,20,21,39,40

The activity, stability, and selectivity of the FTO/Fe2DTPFPP- PO_3H_2 assembly for the CO₂ to CO conversion were evaluated from single potential electrolysis experiments conducted for 6 h at -1.2 V and -1.1 V ($\eta = 0.51$ V and 0.41 V, E^0 (CO₂/CO) = -0.69V¹⁷) in an airtight one-compartment electrochemical cell filled with a DMF/5% H₂O/0.1M TBAPF₆ solution saturated with CO₂. A control experiment was performed using a blank FTO electrode. Figure 3c (inset, red line) shows the current density-time profile obtained from the assembly and that obtained from the blank FTO electrode (black line). The electrolysis of the assembly shows an average current density of 0.25 mA/cm² with consuming an amount of charge, Q = 5.4 C over a 6 h electrolysis at η = -0.51 V. The blank FTO electrode, on the other hand, generated an average current density of 15 μ A/cm² with consuming an amount of charge, Q = 0.32 C under the same electrolysis conditions. The gas chromatographic analysis of the headspace gas for the FTO/catalyst assembly resulted in the formation of 24.5 \pm 2 μ mole CO and 2.5 \pm 1 μ mole H₂. The headspace of electrolysis solution of the FTO blank, however, contained $2 \pm 1 \mu$ mole H₂ as the sole product. Subtracting the amount of H₂ produced during the control experiment and based on the theoretical amount of CO calculated from the consumed charge, the FTO/catalyst assembly selectively catalyzed the CO₂ to CO conversion with 93% Faradic efficiency. Based on the amount of the surface loading (Γ = 6 x 10⁻¹² mol/cm²) of Fe₂DTPFPP-PO₃H₂ on a FTO surface, the TOF of the catalysis was estimated to be 245 s⁻¹ based on the 6 h electrolysis at η = -0.51 V. The constancy of the current density (red line, Figure 3c, inset) generated from the FTO/Fe2DTPFPP-PO3H2 assembly during the 6 h electrolysis clearly indicates its stability for the CO2 to CO conversion as a heterogeneous catalyst. At η = -0.41 V (Figure S11), a 0.45 C charge was consumed and 2.2 μ mole CO was generated in 94% Faradaic efficiency and 22.9 s⁻¹ TOF from the assembly after 6 h electrolysis.



Figure 3. (a) CVs at different scan rates of FTO/ $Fe_2DTPFPP-PO_3H_2$ assembly (1 cm²) in a DMF/5% H₂O/0.1 M TBAPF₆ solution under Ar. Inset: i_p - ν relationship derived from the CVs (b) N 1s XPS spectra of the FTO blank and FTO/ $Fe_2DTPFPP-PO_3H_2$ assembly before and

after electrolysis (c) CVs at a 100 mV/s scan rate of the FTO/Fe₂DTPFPP-PO₃H₂ assembly under Ar (blue line) or CO₂ (red line). Inset: current density-time profile of controlled potential electrolysis conducted at -1.2 V vs. NHE for FTO blank electrode (black line) and FTO/Fe₂DTPFPP-PO₃H₂ assembly (red line) under CO₂ (d) Tafel plot [logTOF- η relationships] of FTO/Fe₂DTPFPP-PO₃H₂ assembly. Inset: foot-of-the-wave analysis of the catalytic CV response. * are the logTOF calculated from the 6-h electrolysis experiments at two different η values.

The XPS measurements of the N 1s of FTO/ $Fe_2DTPFPP$ -**PO**₃**H**₂ assembly after the electrolysis (Figure 3b, blue line) and the P 2p of the assembly (Figure S9a) showed the remaining of the catalyst on the FTO electrode surface. This clearly establishes the stability of the assembly for the CO₂ to CO conversion.

Foot-of-the wave analysis of the CVs for heterogeneous catalysis. Foot-of-the wave analysis of the CVs was previously reported as a quick estimation for the catalysis parameters in homogeneous and heterogeneous catalysis without the contribution of side phenomena such as substrate consumption, catalyst deactivation, and/or product inhibition.^{16,17,18,40} We report here the use of such analysis for heterogeneous catalysis to estimate their heterogeneous catalysis parameters. The analysis is based on the heterogeneous catalysis equations in a similar way reported for the homogeneous catalysis. The current, *i*, flowing through an electrode covered with [catalyst], Γ_{cat}^{e} in the presence of the substrate is given by equation 5;⁵⁴

$$\frac{i}{FS} = \frac{2k[CO_2]\Gamma_{cat}^o}{1 + \exp\left[\frac{F}{RT}(E - E_{cat}^o)\right]}$$
(5)

where *S* is the electrode surface area. In the absence of substrate, the peak current of the catalyst is linearly changed with scan rate, v, according to equation 6;⁵⁴

$$\frac{i_p^0}{FS} = \frac{F\nu\Gamma_{\rm cat}^0}{4RT} \tag{6}$$

To eliminate the dependence on [catalyst] and *S*, equation 5 is divided by equation 6 to give equation 7 for heterogeneous catalysis;

$$\frac{i}{i_p^o} = \frac{4RT}{Fv} 2k[\text{CO}_2] \frac{1}{1 + \exp\left[\frac{F}{RT}(E - E_{\text{cat}}^o)\right]}$$
(7)

The estimation of the catalysis rate constant, k_{cat} , was derived from the Foot-of-the-wave analysis of the CV. The analysis is based on plotting i/i_{p}^{0} vs. $1/\{1+\exp[F/RT(E-E^{\circ}_{cat})]\}$ according to equation 7 that gives rise to a straight line of slope $(4RT/Fv)2k[CO_{2}]$ (Figure 3d, inset), where the $k[CO_{2}]$ was estimated to be 231 s⁻¹. The $k[CO_{2}]$ is then used to calculate the TOF and the logTOF- η relationship (Figure 3d) according to equations 2 and 3, respectively, as discussed before for homogeneous catalysis. As shown in Figure 3d and Table 1, the assembly, as a heterogeneous catalysis system, shows a logTOF range of $1.2 \sim 2.3 \text{ s}^{-1}$ at a low η range, $0.4 \sim 0.6 \text{ V}$.

Comparing the TOF obtained from two single potential 6 h electrolysis at $\eta = 0.51$ V and 0.41 V (245 s⁻¹, 22.9 s⁻¹ blue * in Figure 3d) with the TOF obtained from the foot-of-the wave analysis of the CVs of the heterogeneous catalysis clearly indicate the validity

of the analysis as a quick investigation of the heterogeneous catalysis parameters.

Performance of Fe₂DTPFPP-PO₃H₂ catalyst for CO₂ to CO conversion in nonaqueous solutions with high current density. The successful assembly of Fe2DTPFPP-PO3H2 catalyst in a monolayer on the FTO surface allowed us to evaluate its CO2 to CO conversion efficiency without the effect of charge diffusion rate that controls the rate of the catalysis process in the case of the catalyst immobilized film on the conducting electrode surface.⁵⁸ However, the current modifications suffers from the limitation of the amount of the catalyst loaded to the electrode surface that leads to the low current density obtained for the CO2 to CO conversion (0.25 mA/cm², Figure 3c; Inset). To load more catalyst and test its performance for CO2 to CO conversion, we prepared a sintered mesoporous thin film of SnO2 nanoparticles on the FTO electrode (the details of the preparation is given in SI). Soaking of the FTO/SnO₂ electrode in the catalyst solution (0.1 mM, EtOH) for 1 h resulted in ~ 57 times more loading, 2.6×10^{-10} mole/cm² of the catalyst (by UV-vis) than one on an ordinary FTO electrode (Figure S12). The SEM images of the resultant FTO/SnO₂/Fe₂DTPFPP-PO₃H₂ assembly showed that the surface of the assembly consists of a mesoporous layer of SnO2 nanoparticles in 20-50 nm¢ and the particles are aggregated (Figures 4a, S13). The film thickness is ~1 µm (Figure 4b). The XPS measurements of the assembly before electrolysis showed the N 1s peak at 398.7 eV (Figure 4c, red line), P 2p, (Figure S14a) and F 1s (Figure S14b) in its XPS indicating the binding of the catalyst to the SnO2 surface. The CVs and the controlled-potential electrolysis at -1.2 V of the resultant FTO/SnO₂/ Fe₂DTPFPP-PO₃H₂ assembly in DMF/TBAPF₆ are shown in Figure 4d. The assembly consumed 59 C charge (corresponding to theoretical amount of CO = 305.7 µmol based on 2e⁻ reduction process) with generating an average current density of 3.0 mA/cm² in a 5.5 h constant potential electrolysis. CO (275 μ mol) and H₂ (30 μ mol) gases were detected corresponding to 90% CO and 10% H₂ faradic efficiencies and a TOF of 53.4 s^{-1} . The constant current density during the electrolysis and the XPS spectra of the N 1s, P 2p, and F 1s after electrolysis clearly indicate the stability of the assembly for the CO₂ to CO conversion. Although, the amount of the catalyst loading is about 56.5 times more than the catalyst loading to the bare FTO electrode, the current density increases only 12 times compared to the current density obtained from the $FTO/Fe_2DTPFPP-PO_3H_2$ assembly (0.25 mA/cm²) probably due to controlling the catalysis rate by the charge diffusion in the SnO₂ film. Although, the TOF decreased to 53.4 s^{-1} in the high current density operation heterogeneous catalysis it is still high remarkable value along with the other reported systems (Table 1).

Page 7 of 12



54

55

56

57

58

59

60



Figure 4. (a) and (b) top and side view SEM images of FTO/SnO_2 loaded with the $Fe_2DTPFPP-PO_3H_2$ catalyst. (c) N 1s XPS spectra of the FTO/SnO_2 blank and $FTO/SnO_2/Fe_2DTPFPP-PO_3H_2$ assembly before and after electrolysis. (d) CVs of $FTO/SnO_2/Fe_2DTPFPP$ - PO_3H_2 assembly (0.5 cm²) in DMF containing 0.1 M TBAPF₆ supporting electrolyte at a 50 mV/s scan rate under Ar (black line) and CO_2 (red line); Inset current density-time profile of controlled potential electrolysis conducted at -1.2 V vs. NHE of $FTO/SnO_2/Fe_2DTPFPP-PO_3H_2$ (red line) and $FTO/Fe_2DTPFPP-PO_3H_2$ (blue line).

Recently a phosphonic acid fabricated Mn complex, fac- $[MnBr(4,4)-bis(phosphonic acid)2,2)-bipyridinde)(CO)_3]$ was immobilized on a mesoporous TiO2 sintered on FTO electrode (7 μ m thickness, catalyst loading; 3.4 x 10⁻⁸ mol/cm²). The FTO/TiO₂/catalyst assembly generated an average current density of 0.15 mA/cm² with 67% CO faradic efficiency.⁵⁹ We also prepared a thin mesoporous film of TiO2 nanoparticles on a FTO electrode with film thickness ~ 5 μ m (Figure S15) that is ~ five times thicker than that of the FTO/SnO2 electrode. Soaking the FTO/TiO₂ electrode in the catalyst solution (0.1 mM, EtOH) for 1 h resulted in loading of more catalyst (in 16 times) than in the case of FTO/SnO₂ electrode 4.2 x 10⁻⁹ mole/cm² of the catalyst as measured using the UV-vis spectroscopy. The CVs and the controlled-potential electrolysis at -1.2 V of the resultant FTO/TiO₂/ Fe2DTPFPP-PO3H2 assembly in DMF/TBAPF6 are shown in Figure S15. The assembly consumed 18 C charge with generating an average current density of 2.5 mA/cm² in a 2 h constant potential electrolysis. A CO (74.0 μ mol) and a H₂ (19.3 μ mol) gases were detected corresponding to 80% CO and 20% H₂ faradic efficiencies and 2.4 s⁻¹ TOF. Although, the amount of the catalyst loading on the FTO/TiO2 is about 16 times more than the catalyst loading to the FTO/SnO₂ electrode, the current density and TOF are lower due to controlling the catalysis rate by the charge diffusion in the TiO₂ film that is less conductive than that of the SnO₂.

Performance of FTO/ $Fe_2DTPFPP-PO_3H_2$ assembly for CO₂ to CO conversion in aqueous solutions. For massive fuel production based on the CO₂ to CO conversion, the catalysis should be performed in aqueous media (H₂O is the ideal candidate for supplying the electrons and protons necessary for the CO₂ to CO conversion). Either using H₂O soluble molecular catalysts or im-

mobilizing the H₂O insoluble ones on conducting electrode surfaces and use the electrode/catalyst assembly in pure aqueous solutions is a plausible approach to achieve this goal. A few H₂O-soluble catalysts for CO₂ to CO conversion have been reported these include the well-known Ni cyclam^{22,23, 24} and the quaternary ammoniion-substituted FeTPP complex (TPP = mesoum tetraphenylporphyrin).⁶⁰ On the other hand, numerous efficient CO2 to CO conversion molecular catalysts have been immobilized on conducting electrodes through physical adsorption.^{61,62,63,64,65} Direct use of the current FTO/Fe2DTPFPP-PO3H2 assembly for CO₂ to CO conversion in a neutral aqueous 0.1 M borate solution (pH 7.0) is hampered by the non-innocent behavior of FTO electrode for both self-reductions and activity in the potential region of interest (-0.9 to -1.3 V). To overcome this problem, we hypothesized that covering the FTO surface with hydrophobic alkyl groups through phosphonic acid anchors will save the electrode from these self-reductions and activity. Indeed, n-hexylphosphonic acid has been reported to significantly protect the ZnO surface from the corrosion.⁶⁶ For our goal, the alkyl group should be with suitable length, not so long that might block the active site of the catalyst or too short that will allow the free penetration of water the FTO surface. So we decided to use n-butyl phosphonic acid, n-BuPO₃H₂ protective group. The FTO electrode surface was then modified with *n*-BuPO₃H₂ using the same procedures used for immobilization of the Fe coordination catalyst. The binding of the n-BuPO₃H₂ protective group to the FTO electrode surface was monitored by XPS measurements using the P 1s peak as a marker of its binding to the FTO surface. Figure S16 shows the P 1s XPS of the FTO blank and FTO/ n-BuPO₃H₂ assembly. The assembly showed a clear P 1s XPS peak at 133.5 eV indicating the successful modification of the FTO electrode surface with *n*-BuPO₃H₂. Figure S17 that compares the CVs of a bare FTO electrode and that modified with n-BuPO₃H₂ clearly showed the success of this hypothesis. The FTO/n-BuPO₃H₂ became completely innocent for electrochemical reactions in Ar or CO2 saturated neutral aqueous 0.1 M borate solution (pH 7.0).

In the next, the uncovered surface of FTO/Fe₂DTPFPP-PO₃H₂ assembly was similarly protected with *n*-BuPO₃H₂ and the assembly is used for the CO₂ to CO conversion in an aqueous solution. Figure 5a shows the CVs of FTO/ n-BuPO₃H₂ and FTO/Fe₂DTPFPP-PO₃H₂/n-BuPO₃H₂ assemblies (black and red lines, respectively) and the current density-time profiles at -0.95 V of them (inset) in CO₂ saturated neutral 0.1 M borate buffered solution (pH 7.0). A CO (2.7 μ mole) and H₂ (0.3 μ mole) were detected in the headspace and a net charge of 0.52 Coulombs was consumed in 6 h electrolysis corresponding to 90% CO production faradic efficiency and 24.4 s⁻¹ TOF (based on a surface coverage of the catalyst of 4.6 x 10 $^{-12}$ mole/cm², Figure S18 where a simultaneous 2e⁻ reduction was observed in the borate buffer solution, pH 7.0). The low TOF obtained in an aqueous solution compared to non-aqueous DMF solution is most likely due to the low solubility of CO2 in aqueous solution compared to its solubility in DMF solution.^{67,68}

The XPS measurements of the N 1s before and after the catalysis (Figure 5b) and the stability of the current density during the electrolysis clearly indicate the stability of the assembly for the CO₂ to CO conversion in neutral aqueous solutions. The FTO/SnO₂/ **Fe₂DTPFPP-PO₃H**₂/*n*-BuPO₃H₂ assembly with catalyst loading of 2.6 x 10⁻¹⁰ mole/cm² generated a stable current density of 1.47 mA/cm² (Figure S 18) at $\eta = 0.42$ V with 70% Faradaic efficiency and 20.6 s s⁻¹ TOF in a CO₂ saturated 0.1 M borate buffered solution (pH 7.0). We are currently optimizing this set up for an electrolyzer for CO_2 to CO conversion with coupling with suitable water oxidation catalysts.



Figure 5. (a) CVs of FTO/n-But-PO₃H₂ (black line) and $FTO/Fe_2DTPFPP$ -PO₃H₂/n-But-PO₃H₂ (red line) assemblies (1 cm²) at a 50 mV/s scan rate in a neutral borate buffered solution under CO₂. Inset: current density-time profile of controlled potential electrolysis conducted at -0.95 V vs. NHE for FTO/n-But-PO₃H₂ electrode (1 cm², black line) and $FTO/Fe_2DTPFPP$ -PO₃H₂/n-BuPO₃H₂ (1 cm²) in the same solution. (b) N 1s XPS spectra of $FTO/Fe_2DTPFPP$ -PO₃H₂/n-But-PO₃H₂ assembly before (red line) and after (blue line) electrolysis.

Comparison with other heterogenous catalysts. Table 1 summarizes the activity of the current FTO/Fe₂DTPFPP-PO₃H₂, FTO/SnO₂/Fe₂DTPFPP-PO₃H₂, and FTO/TiO₂/Fe₂DTPFPP-PO3H2 assemblies as heterogeneous catalysts in comparison with the reported highly active molecular catalysts supported on conducting electrode surfaces. The Table clearly showed that the current assembly is among the highly active catalysts for CO₂ to CO conversion. A recently reported cobalt phthalocyanine (CoPc) anchored to carbon nanotube (CN) and loaded on a porous carbon fibre paper electrode (CF) showed 4.1 s⁻¹TOF for CO production at $\eta = 0.52$ V in 0.2M phosphate buffer solution (pH = 7.2) with high Faradic efficiency (> 95%).69 A Co porphyrin catalyst linked by organic struts through imine bonds and deposited on a porous CF electrode showed an initial TOF value of 2.61 s⁻¹ for CO production at $\eta = 0.55$ V in NaHCO₃ solution (pH = 7.3) with high Faradic efficiency (90 %).⁷⁰ The highly active hydroxyl group substituted Fe porphyrin CO₂ to CO conversion catalyst is recently modified with a pyrene pendant, CAT_{pyr}, and immobilized onto a multi-walled carbon nanotubes (MWCNT) surface through a noncovalent van der Waals π - π interactions showed 144 h⁻¹ TOF (i.e. 0.04 s⁻¹) at η = 0.48 V in 0.5M NaHCO₃ aqueous solution (pH = 7.3) with high Faradic efficiency (97%).⁶¹ A reported Co protoporphyrin was immobilized onto a pyrolytic graphite (PG) electrode efficiently reduces CO₂ in an aqueous acidic solution (pH = 3) at η = 0.5 V. Several reduction products were detected with CO as the main product in only 40% Faradic efficiency at 1 atm. of CO2 at pH 3.0. The TOF for CO production are 0.2 s⁻¹ and 0.8 s⁻¹ at η = 0.5 and 0.7 V respectively.⁶² An optimized Co chlorin complex adsorbed physically on MWCNT and modified on glassy carbon electrode showed a TOF of a 0.039 s⁻¹ and 89% CO Faradic efficiency in acidic conditions (pH 4.6) at $\eta = 0.70$ V.²⁸ The carbon monoxide dehydrogenase (CODH) was successfully immobilized on a PG rotating desk electrode and showed intense electrocatalytic activity for CO₂ to CO conversion, however with low stability.⁶³ A $Mn(bpy)(CO)_3Br$ complex cast with MWCNT in a Nafion

membrane showed TON = 458 and product CO:H₂ = 2:1 at η = 0.77 V with 0.031 s⁻¹ TOF in a phosphate buffer (pH = 7.0).⁶⁴ Thin films of nano-sized metal organic frameworks incorporating a molecular Co porphyrin catalyst, Al₂(OH)₂TCPP-Co (TCPP = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) showed a CO Faradic efficiency of 76% and good stability (over 7 h) at η = 0.70 V with TOF = 0.055 s⁻¹.⁶⁵ Recently, a phosphonic acid modified bipyridine Mn CO2 to CO catalyst, fac-[MnBr(4,4/bis(phosphonic acid)-2,2[/]-bipyridine)(CO)₃] anchored to a mesoporoous TiO₂ electrode showed a benchmark TON of 112 ±17 in an CH₃CN/H₂O solution (19:1) indicating the advantage of using the chemical bond for immobilizing the molecular CO2 to CO conversion catalysts over the weak physical adsorption.⁵⁹ The current assemblies, however, showed very high activity and stability for the CO2 to CO conversion. This indicates the advantages of immobilization of the catalyst through strong chemical bonds that provided with the phosphonic acid anchor.

Table 1. Catalysis parameters of the phosphonic acid fabricated Fe porphyrin dimers, $Fe_2DTPFPP-PO_3H_2$ as heterogeneous catalyst (this work) and other reported heterogeneous CO_2/CO reduction catalysts.

Solvent	Catalyst	i,	<i>n</i> .V	TOF
$E^{0}(CO_{2}/CO), V$,	mA/cm ²	- I) -	s^{-1}
DMF/5% H ₂ O –0.69, this work	FTO/Fe ₂ DTPFPP -PO ₃ H ₂	0.25	0.51	245.0
DMF/5% H ₂ O –0.69, this wark	FTO/SnO ₂ /Fe ₂ D TPFPP-PO ₃ H ₂	3.0	0.51	53.4
DMF/5% H ₂ O –0.69, this work	FTO/TiO ₂ /Fe ₂ DT PFPP-PO ₃ H ₂	2.5	0.51	2.4
0.1M borate (pH 7.0) -0.53, this work	FTO/Fe2DTPFPP -PO3H2	0.04	0.42	24.5
0.1M borate (pH 7.0) –0.53, this work	FTO/SnO ₂ / Fe₂D TPFPP-PO₃H₂/ <i>n</i>- BuPO₃H₂	1.47	0.42	20.6
0.2 M phosphate buffer (pH 7.2) -0.55, ⁶⁹	CF/CN/Co-Pc	15.0	0.52	4.10
0.5 M NaHCO ₃ (pH 7.3) -0.55, ⁷⁰	CF/COF ^a	3.0	0.55	2.61
0.5 M NaHCO ₃ (pH 7.3) -0.55, ⁶¹	GC/MWCNT/ CAT _{Pyr} ^b	0.2	0.48	0.04
0.1 M NaClO ₄ (pH 3.0) –0.29, ⁶²	PG/MWCNT/Co (protoporphyrin)	0.33	0.50	0.20
0.005 M Na ₂ SO ₄ (pH 4.6) -0.39, ²⁸	PG ^c /MWCNT/Co (Chlorin)	0.075	0.70	0.04
Phosphate Buffer (pH 7.0) –0.53, ⁶⁴	GC/Nafion/MWC NT/Mn(bpy)(CO)3Br	0.064	0.77	0.03
NaHCO3 (pH 7.0) –0.53, ⁶⁵	Al ₂ (OH) ₂ TCP-Co	1.0	0.70	0.06

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60 ^aCOFs = covalent organic frameworks in which the building units are Co porphyrin catalysts linked by organic struts through imine bonds. ^bFe 5,10,15-tri((2,6-dihydroxyphenyl)-20-(pyrene)porphyrin. ^cPG = pyrolytic graphite electrode.

Conclusion. In conclusion, we successfully fabricated the Fe porphyrin dimer CO_2 to CO conversion molecular catalyst with a phosphonic acid anchor and assemble it on the FTO, FTO/SnO₂, and FTO/TiO₂ surface through chemical bonds that show unprecedented activity and stability as heterogeneous catalyst in different solutions. The foot-of-the-wave analysis of the CV was shown to be valid as a quick estimation of the catalysis parameters in a similar way used for homogeneous catalysis. By the co-modification of an alkane SAM layer on FTO with the Fe catalyst, we realized the selective CO_2 reduction in an aqueous solution by complete suppress of proton reduction. A high current density was achieved by loading more amount of the catalyst to thin mesoporous layers of SnO₂ or TiO₂ nanoparticles.

ASSOCIATED CONTENT

Supporting Information. Experimental details and additional Figures are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: znzahran@isc.chubu.ac.jp or naruta@isc.chubu.ac.jp

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by JST ACT-C (Grant No. JPMJCR12YV), JSPS KAKENHI (Grant No.15K13702), and Chubu University Research Grant.

REFERENCES

- Kang, P.; Chen, Z.; Brookhart, M.; Meyer, T. J. Electrocatalytic Reduction of Carbon Dioxide: Let the Molecules Do the Work. *Top. Catalysis.* 2015, 58, 30–45.
- (2) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: From CO₂ to Chemicals, Materials, and Fuels. Technological Use of CO₂. Chem. Rev. 2014, 114, 1709– 1742.
- (3) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels. *Chem. Soc. Rev.* 2014, 43, 631–675.
- (4) Costentin, C.; Robert, M.; Saveant, J.-M. Catalysis of the Electrochemical Reduction of Carbon Dioxide. *Chem. Soc. Rev.* 2013, 42, 2423–2436.
- (5) Tanaka, K.; Ooyama, D. Multi-Electron Reduction of CO₂ via Ru CO₂, C(O)OH, CO, CHO, and CH₂OH Species. *Coord. Chem. Rev.* 2002, 226, 211–218.
- (6) Hawecker, J.; Lehn, J.-M.; Ziessel, R. Electrocatalytic Reduction of Carbon Dioxide Mediated by Re(bipy)(CO)₃Cl (Bipy = 2,2'-

Bipyridine). J. Chem. Soc., Chem. Commun. 1984, 984, 328-330.

- (7) Machan, C. W.; Chabolla, S. A.; Yin, J.; Gilson, M. K.; Tezcan, F. A.; Kubiak, C. P. Supramolecular Assembly Promotes the Electrocatalytic Reduction of Carbon Dioxide by Re(I) Bipyridine Catalysts at a Lower Overpotential. J. Am. Chem. Soc. 2014, 136, 14598–14607.
- (8) Riplinger, C.; Sampson, M. D.; Ritzmann, A. M.; Kubiak, C. P.; Carter, E. A. Mechanistic Contrasts between Manganese and Rhenium Bipyridine Electrocatalysts for the Reduction of Carbon Dioxide. J. Am. Chem. Soc. 2014, 136, 16285–16298.
- (10) Chen, Z.; Chen, C.; Weinberg, D. R.; Kang, P.; Concepcion, J. J.; Harrison, D. P.; Brookhart, M. S.; Meyer, T. J. Electrocatalytic Reduction of CO₂ to CO by Polypyridyl Ruthenium Complexes. *Chem. Commun.* 2011, 47, 12607.
- (11) Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. Photocatalytic CO₂ Reduction with High Turnover Frequency and Selectivity of Formic Acid Formation Using Ru (II) Multinuclear Complexes. *Proc. Natl. Acad. Sci.* 2012, 109, 15673–15678.
- (12) Ohtsu, H.; Tanaka, K. An Organic Hydride Transfer Reaction of a Ruthenium NAD Model Complex Leading to Carbon Dioxide Reduction. Angew. Chem. Int. Ed. 2012, 51, 9792–9795.
- (13) Kang, P.; Cheng, C.; Chen, Z.; Schauer, C. K.; Meyer, T. J.; Brookhart, M. Selective Electrocatalytic Reduction of CO₂ to Formate by Water-Stable Iridium Dihydride Pincer Complexes. J. Am. Chem. Soc. 2012, 134, 5500–5503.
- (14) Chen, Y.; Li, C. W.; Kanan, M. W. Aqueous CO₂ Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles. J. Am. Chem. Soc. 2012, 134, 19969–19972.
- (15) Zhu, W.; Michalsky, R.; Metin, Ö.; Lv, H.; Guo, S.; Wright, C. J.; Sun, X.; Peterson, A. A.; Sun, S. Monodisperse Au Nanoparticles for Selective Electrocatalytic Reduction of CO₂ to CO. J Am. Chem. Soc. 2013, 135, 16833–16836.
- (16) Costentin, C.; Savéant, J. M. Cyclic Voltammetry of Electrocatalytic Films: Fast Catalysis Regimes. J. Phys. Chem. C 2015, 119, 12174– 12182.
- (17) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. A Local Proton Source Enhances CO₂ Electroreduction to CO by a Molecular Fe Catalyst. *Science*. 2012, 338, 90–94.
- (18) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J. M. Turnover Numbers, Turnover Frequencies, and Overpotential in Molecular Catalysis of Electrochemical Reactions. Cyclic Voltammetry and Preparative-Scale Electrolysis. J. Am. Chem. Soc. 2012, 134, 11235– 11242.
- (19) Costentin, C.; Drouet, S.; Passard, G.; Robert, M.; Savéant, J. M. Proton-Coupled Electron Transfer Cleavage of Heavy-Atom Bonds in Electrocatalytic Processes. Cleavage of a C-O Bond in the Catalyzed Electrochemical Reduction of CO₂. J. Am. Chem. Soc. 2013, 135, 9023–9031.
- (20) Costentin, C.; Passard, G.; Robert, M.; Savéant, J. M. Pendant Acid-Base Groups in Molecular Catalysts: H-Bond Promoters or Proton Relays? Mechanisms of the Conversion of CO₂ to CO by Electrogenerated iron(0)porphyrins Bearing Prepositioned Phenol

Functionalities. J. Am. Chem. Soc. 2014, 136, 11821-11829.

- (21) Costentin, C.; Passard, G.; Robert, M.; Savéant, J.-M. Ultraefficient Homogeneous Catalyst for the CO₂-to-CO Electrochemical Conversion. *Proc. Natl. Acad. Sci.* 2014, 111, 14990–14994.
- (22) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. Nickel(II)-Cyclam: An Extremely Selective Electrocatalyst for Reduction of CO₂ in Water. J. Chem. Soc. Chem. Commun. **1984**, 2, 1315–1316.
- (23) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. Electrocatalytic Reduction of Carbon Dioxide by Nickel cyclam²⁺ in Water: Study of the Factors Affecting the Efficiency and the Selectivity of the Process. J. Am. Chem. Soc. **1986**, 108, 7461–7467.
- (24) Froehlich, J. D.; Kubiak, C. P. Homogeneous CO₂ Reduction by Ni(cyclam) at a Glassy Carbon Electrode. *Inorg. Chem.* 2012, 51, 3932–3934.
- (25) Schneider, J.; Jia, H.; Kobiro, K.; Cabelli, D. E.; Muckerman, J. T.; Fujita, E. Nickel(ii) Macrocycles: Highly Efficient Electrocatalysts for the Selective Reduction of CO₂ to CO. *Energy Environ. Sci.* 2012, 5, 9502–9510.
- Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. [Mn(bipyridyl)(CO)₃Br]: An Abundant Metal Carbonyl Complex as Efficient Electrocatalyst for CO₂ Reduction. *Angew. Chem. Int. Ed.* 2011, 50, 9903–9906.
- (27) Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. Manganese Catalysts with Bulky Bipyridine Ligands for the Electrocatalytic Reduction of Carbon Dioxide: Eliminating Dimerization and Altering Catalysis. J. Am. Chem. Soc. 2014, 136, 5460–5471.
- (28) Aoi, S.; Mase, K.; Ohkubo, K.; Fukuzumi, S. Selective Electrochemical Reduction of CO₂ to CO with a Cobalt Chlorin Complex Adsorbed on Multi-Walled Carbon Nanotubes in Water. *Chem. Commun.* 2015, 51, 10226–10228.
- (29) Lacy, D. C.; Mccrory, C. C. L.; Peters, J. C. Studies of Cobalt-Mediated Electrocatalytic CO₂ Reduction Using a redox-active ligand. *Inorg. Chem.* 2014, 53, 4980–4988.
- (30) Shaffer, D. W.; Johnson, S. I.; Rheingold, A. L.; Ziller, J. W.; Goddard, W. A.; Nielsen, R. J.; Yang, J. Y. Reactivity of a Series of Isostructural Cobalt Pincer Complexes with CO₂, CO, and H⁺. *Inorg. Chem.* 2014, 53, 13031–13041.
- (31) Quezada, D.; Honores, J.; García, M.; Armijo, F.; Isaacs, M. Electrocatalytic Reduction of Carbon Dioxide on a Cobalt tetrakis(4-Aminophenyl)porphyrin Modified Electrode in BMImBF₄. New J. Chem. 2014, 38, 3606-3612.
- (32) Elgrishi, N.; Chambers, M. B.; Artero, V.; Fontecave, M. Terpyridine Complexes of First Row Transition Metals and Electrochemical Reduction of CO₂ to CO. *Phys. Chem. Chem. Phys.* 2014, *16*, 13635– 13644.
- (33) Thoi, V. S.; Chang, C. J. Nickel N-Heterocyclic Carbene-Pyridine Complexes That Exhibit Selectivity for Electrocatalytic Reduction of Carbon Dioxide over Water. *Chem. Commun.* 2011, 47, 6578–6580.
- (34) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Kenis, Paul J, A.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, Paul J, A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. *Chem. Rev.* 2013, 113, 6621–6658.

- (35) Can, M.; Armstrong, F. A.; Ragsdale, S. W. Structure, Function, and Mechanism of the Nickel Metalloenzymes, CO Dehydrogenase, and Acetyl-CoA Synthase. *Chem. Rev.* 2014, 114, 4149–4174.
- (36) Ensign, S. a. Reactivity of Carbon Monoxide Dehydrogenase from Rhodospirillum Rubrum with Carbon Dioxide, Carbonyl Sulfide, and Carbon Disulfide. *Biochemistry* 1995, 34, 5372–5378.
- (37) Heoung, J.-H.; Dobbek, H. Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase. *Science*. 2007, 318, 1461–1465.
- (38) Fesseler, J.; Jeoung, J. H.; Dobbek, H. How the [NiFe₄S₄] Cluster of CO Dehydrogenase Activates CO₂ and NCO⁻. Angew. Chem. Int. Ed. 2015, 54, 8560–8564.
- (39) Mohamed, E. A.; Zahran, Z. N.; Naruta, Y. Efficient Electrocatalytic CO₂ Reduction with a Molecular Cofacial Iron Porphyrin Dimer. *Chem. Commun.* 2015, *51*, 16875–17018.
- (40) Zahran, Z. N.; Mohamed, E. A.; Naruta, Y. Bio-Inspired Cofacial Fe Porphyrin Dimers for Efficient Electrocatalytic CO₂ to CO Conversion : Overpotential Tuning by Substituents at the Porphyrin Rings. Sci. Rep. 2016, 6, 24533.
- (41) Dhanasekaran, S.; Bisai, V.; Unhale, R. A.; Suneja, A.; Singh, V. K. A General Catalytic Route to Isoindolinones and Tetrahydroisoquinolines: Application in the Synthesis of (±)-Crispine A. Org. Lett. 2014, 16, 6068–6071.
- (42) Frlan, R.; Gobec, S.; Kikelj, D. Synthesis of Ethyl 3-(Hydroxyphenoxy)benzyl Butylphosphonates as Potential Antigen 85C Inhibitors. *Tetrahedron* 2007, 63, 10698–10708.
- (43) Gooßen, L. J.; Dezfuli, M. K. Practical Protocol for the Palladium-Catalyzed Synthesis of Arylphosphonates from Bromoarenes and Diethyl Phosphite. *Synlett.* 2005, 3, 445–448.
- (44) Pechy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-baker, R.; Gratzel, M. Preparation of Phosphonated Polypyridyl Ligands to Anchor Transition-Metal Complexes on Oxide Surfaces: Application for the Conversion of Light to Electricity with Nanocrystalline TiO₂ Films. J. Chem. Soc., Chem. Commun. 1995, 369, 65–66.
- (45) Yan, S. G.; Hupp, J. T. Semiconductor-Based Interfacial Electron-Transfer Reactivity: Decoupling Kinetics from pH-Dependent Band Energetics in a Dye-Sensitized Titanium Dioxide/Aqueous Solution System. J. Phys. Chem. 1996, 100, 6867–6870.
- (46) Saupe, G. B.; Mallouk, T. E.; Kim, W.; Schmehl, R. H. Visible Light Photolysis of Hydrogen Iodide Using Sensitized Layered Metal Oxide Semiconductors: The Role of Surface Chemical Modification in Controlling Back Electron Transfer Reactions. J. Phys. Chem. B 1997, 101, 2508–2513.
- (47) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Pechy, P.; Rotzinger, F. P.; Humphry-Baker, R.; Kalyanasundaram, K.; Grätzel, M.; Shklover, V.; Haibach, T. Molecular Engineering of Photosensitizers for Nanocrystalline Solar Cells: Synthesis and Characterization of Ru Dyes Based on Phosphonated Terpyridines. *Inorg. Chem.* 1997, 36, 5937–5946.
- (48) Trammell, S. A.; Wimbish, J. C.; Odobel, F.; Gallagher, L. A.; Narula, P. M.; Meyer, T. J. Mechanisms of Surface Electron Transfer. Proton-Coupled Electron Transfer. J. Am. Chem. Soc. 1998, 120, 13248– 13249.
- Liu, F.; Cardolaccia, T.; Hornstein, B. J.; Schoonover, J. R.; Meyer, T. J. Electrochemical Oxidation of Water by an Adsorbed M-Oxo-Bridged Ru Complex. J. Am. Chem. Soc. 2007, 129, 2446–2447.

Page 11 of 12

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29 30

31

32

33 34

35

36

37 38

39

40

Chemistry of Materials

- (50) Costentin, C.; Savøant, J. Multielectron, Multistep Molecular Catalysis of Electrochemical Reactions: Benchmarking of Homogeneous Catalysts. *ChemElectroChem* 2014, 1, 1226–1236.
 - (51) Pegis, M. L.; Roberts, J. A. S.; Wasylenko, D. J.; Mader, E. A.; Appel, A. M.; Mayer, J. M. Standard Reduction Potentials for Oxygen and Carbon Dioxide Couples in Acetonitrile and N,N-Dimethylformamide. *Inorg. Chem.* **2015**, *54*, 11883–11888.
 - (52) Matsubara, Y.; Grills, D. C.; Kuwahara, Y. Thermodynamic Aspects of Electrocatalytic CO₂ Reduction in Acetonitrile and with an Ionic Liquid as Solvent or Electrolyte. ACS Catal. 2015, 5, 6440–6452.
 - (53) Yamaguchi, S.; Khanna, R.; Matsushita, T.; Wang, A.; Ohta, T.; Naruta, Y.; Takadama, H. Preparation of a Titanium Metal Electrode with a Nitrogen-Doped One-Dimensional Titanium Oxide Surface Layer for the Support of Catalysts. RSC Adv. 2015, 5, 47876–47883.
 - (54) Bard, A. J.; Faulkner, L. R. Electrochemical Methods Fundamentals and Applications, 2nd ed., Wiley New York, 2000 (chapter 14).
 - (55) Mohamed, E. A.; Zahran, Z. N.; Naruta, Y. Covalent Bonds Immobilization of Cofacial Mn Porphyrin Dimers on an ITO Electrode for Efficient Water Oxidation in Aqueous Solutions. J. Catal. 2017, 352, 293–299.
 - (56) Araki, N.; Obata, M.; Ichimura, A.; Amao, Y.; Mitsuo, K.; Asai, K.; Yano, S. Redox and Photochemical Behaviour of a Porphyrin Monolayer on an Indium-Tin Oxide Electrode. *Electrochim. Acta* 2005, 51, 677–683.
 - (57) Taniguchi, T.; Fukasawa, Y.; Miyashita, T. Photoelectrochemical Response of Polymer Langmuir-Blodgett Films Containing Tris (2, 2'-Bipyridine) Ruthenium (II) Complex. J. Phys. Chem. B 1999, 103, 1920–1924.
 - (58) Hod, I.; Sampson, M. D.; Deria, P.; Kubiak, C. P.; Farha, O. K.; Hupp, J. T. Fe-Porphyrin-Based Metal-Organic Framework Films as High-Surface Concentration, Heterogeneous Catalysts for Electrochemical Reduction of CO₂. ACS Catal. **2015**, *5*, 6302–6309.
 - (59) Rosser, T. E.; Windle, C. D.; Reisner, E. Electrocatalytic and Solar-Driven CO₂ Reduction to CO with a Molecular Manganese Catalyst Immobilized on Mesoporous TiO₂. Angew. Chem. Int. Ed. 2016, 55, 7388–7392.
 - (60) Costentin, C.; Robert, M.; Savéant, J.; Tatin, A. Efficient and Selective Molecular Catalyst for the CO₂-to-CO Electrochemical Conversion in Water. *Proc. Natl. Acad. Sci.* 2015, 112, 6882–6886.

- (61) Maurin, A.; Robert, M. Noncovalent Immobilization of a Molecular Iron-Based Electrocatalyst on Carbon Electrodes for Selective, Efficient CO₂-to-CO Conversion in Water. J. Am. Chem. Soc. 2016, 138, 2492–2495.
- (62) Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J. P.; Mul, G.; Koper, M. T. M. Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. *Nat. Commun.* 2015, *6*, 8177.
- (63) Parkin, A.; Seravalli, J.; Vincent, K. A.; Ragsdale, S. W.; Armstrong, F. A. Rapid and Efficient Electrocatalytic CO₂/CO Interconversions by Carboxydothermus Hydrogenoformans CO Dehydrogenase I on an Electrode. J. Am. Chem. Soc. 2007, 129, 10328–10329.
- (64) Walsh, J. J.; Neri, G.; Smith, C. L.; Cowan, A. J. Electrocatalytic CO₂ Reduction with a Membrane Supported Manganese Catalyst in Aqueous Solution. *Chem. Commun.* **2014**, *50*, 12698–12701.
- (65) Kornienko, N.; Zhao, Y.; Kley, C. S.; Zhu, C.; Kim, D.; Lin, S.; Chang, C. J.; Yaghi, O. M.; Yang, P. Metal-Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. J. Am. Chem. Soc. 2015, 137, 14129–14135.
- (66) Perkins, C. L. Molecular Anchors for Self-Assembled Monolayers on ZnO: A Direct Comparison of the Thiol and Phosphonic Acid Moieties. J. Phys. Chem. C 2009, 113, 18276–18286.
- (67) Chang, C. C. J. The Solubility of Carbon Dioxide in Organic Solvents at Elevated Pressures. *Fluid Phase Equilib.* **1992**, 74, 235–242.
- (68) Gennaro, A.; Isse, A. A.; Vianeuo, E. Solubility and Electrochemical Determination of CO₂ in Some Dipolar Aprotic Solvents. J. Electroanal. Chem. 1990, 289, 203–215.
- (69) Zhang, X.; Wu, Z.; Zhang, X.; Li, L.; Li, Y.; Xu, H.; Li, X.; Yu, X.; Zhang, Z.; Liang, Y.; Wang, H. Highly Selective and Active CO₂ Reduction Electrocatalysts Based on Cobalt Phthalocyanine/carbon Nanotube Hybrid Structures. *Nat. Commun.* **2017**, *8*, 14675.
- (70) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO₂ Reduction in Water. *Science.* **2015**, *349*, 1208–1213.

