

## *Electronic Supplementary Information*

### **Boosting hydrogen evolution by using covalent frameworks of fluorinated cobalt porphyrin supported on carbon nanotubes**

Gelun Xu,<sup>‡</sup> Haitao Lei,<sup>‡</sup> Guojun Zhou, Chaochao Zhang, Lisi Xie, Wei Zhang, and

Rui Cao\*

Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education,  
School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an  
710119, China.

<sup>‡</sup>These authors contributed equally to this work.

\*Correspondence E-mail: [ruicao@ruc.edu.cn](mailto:ruicao@ruc.edu.cn)

## 1. General methods and materials.

Manipulations of air- and moisture-sensitive materials were performed under nitrogen using standard Schlenk line techniques. All reagents were purchased from commercial suppliers and were used as received unless otherwise noted. Dry solvents, including dimethylformamide, tetrahydrofuran, triethylamine, and dichloromethane, were purified by passage through activated alumina.  $^1\text{H}$  NMR measurements were made on Brüker spectrometer operating at 300 or 400 MHz. High-resolution mass spectrometry was made on Brüker high resolution liquid chromatography mass spectrometry. UV-vis absorption spectra were recorded using U-3900H spectrophotometer. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2100 with a 200 kV accelerating voltage. Energy-dispersive X-ray spectroscopy (EDX) analysis was measured on TEM. Elemental content analysis was made on Brüker M90 inductively coupled plasma mass spectrometry (ICP-MS).

## 2. Electrochemical Methods.

All electrochemical measurements were performed using a CH instruments (model CHI660E Electrochemical Analyzer). CVs recorded in dimethylformamide (0.1 M  $\text{Bu}_4\text{NPF}_6$ ) used a three compartment cell possessing a  $0.07\text{ cm}^2$  glassy carbon electrode as the working electrode, graphite electrode as the auxiliary electrode, and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode (BASi, 10 mM  $\text{AgNO}_3$ , 0.1 M  $\text{Bu}_4\text{NPF}_6$  in DMF). The solution was bubbled with nitrogen for at least 30 min before analysis, and the purity of the electrolyte medium was confirmed over the available

electrochemical window through background scans taken prior to the addition of analyte. Ferrocene was used as an internal standard. In aqueous solvents, Ag/AgCl (KCl-saturated) was used as the reference electrode. The aqueous and non-aqueous solutions were both bubbled with high-purity N<sub>2</sub> for at least 30 min before analysis. The H<sub>2</sub> gas produced during electrocatalysis was detected by SP-6890 Gas Chromatograph.

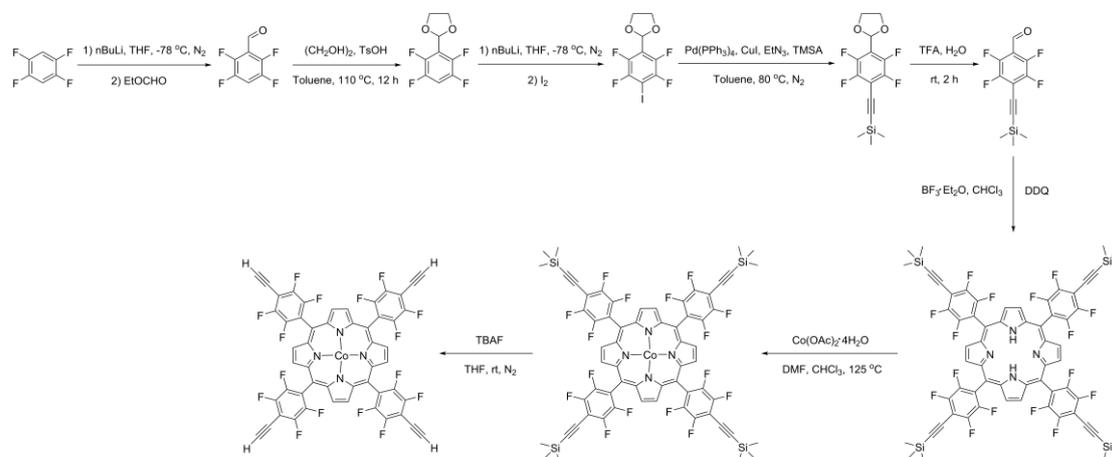
### 3. X-ray Diffraction Studies.

Complete X-ray data set for single crystal of **FCoP-SiMe<sub>3</sub>**, Co<sup>II</sup> complex of tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)porphyrin, was collected. Single crystals suitable for X-ray analysis were each coated with Parabar 10312, suspended in a small fiber loop, and placed in a N<sub>2</sub> gas stream on a Bruker APEX CCD X-ray diffractometer. Diffraction intensities were measured using graphite monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 153(2) K. Data collection, indexing, data reduction and final unit cell refinements were carried out using APEX3;<sup>1</sup> absorption corrections were applied using the program SADABS.<sup>2</sup> All structures were solved with direct methods using SHELXS<sup>3</sup> and refined against F<sup>2</sup> on all data by full-matrix least squares with SHELXL,<sup>4</sup> following established refinement strategies.

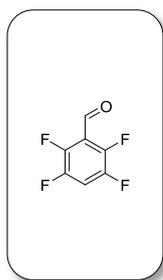
Crystallographic studies revealed that **FCoP-SiMe<sub>3</sub>** crystallized in the monoclinic space group *P*2<sub>1</sub>/*n* with *Z* = 2 (please see Table S2 for details). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms binding to

carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Automatic structure evaluation performed with PLATON as implemented in the CheckCIF routine results in one level A alert. This solvent accessible void is caused by severely disordered solvent molecules, which cannot be detected.

## Synthesis of $\text{Co}^{\text{II}}$ tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)porphyrin (FCoP-H).

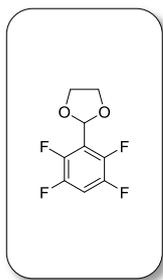


**Scheme S1.** Synthetic route of complex FCoP-H.



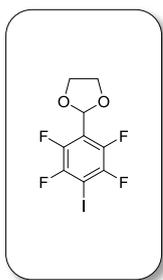
### Synthesis of 2,3,5,6-tetrafluorobenzaldehyde.

To a solution of 1,2,4,5-tetrafluorobenzene (4 g, 26.6 mmol) in 50 mL tetrahydrofuran (THF), *n*-BuLi (11.25 mL, 27 mmol) was added in a dropwise manner under  $\text{N}_2$  at  $-78\text{ }^\circ\text{C}$ , generating a large amount of precipitate. After stirring under  $\text{N}_2$  for 1 h at  $-78\text{ }^\circ\text{C}$ , ethyl formate (4 g, 54.0 mmol) was added. When the mixture turned to clear, the solution was rinsed with dichloromethane (DCM),  $\text{NaHCO}_3$  aqueous solution and then was dried with  $\text{MgSO}_4$ . The liquid product was dark yellow (3.32 g, 18.6 mmol, yield 70%).  $^1\text{H}$  NMR ( $\text{CHCl}_3$ , 300 MHz):  $\delta = 10.33$  (s, 1H), 7.34 (m, 1H) (Fig. S1).



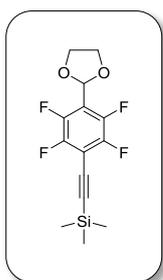
**Synthesis of 2-(2,3,5,6-tetrafluorophenyl)-1,3-dioxolane.** To a 50 mL dry toluene solution containing ethylene glycol (12.09 g, 195 mmol) and *p*-toluenesulfonic acid monohydrate (32 mg, 0.2 mmol), was added 2,3,5,6-tetrafluorobenzaldehyde (3.32 g, 18.6 mmol).

After stirring for 12 h at 110 °C with a water separator, the mixture was washed three times with NaHCO<sub>3</sub> aqueous solution and water, respectively and then was dried with MgSO<sub>4</sub>. The liquid product was dark yellow (4.12 g, 18.5 mmol, yield 99%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 7.07 (m, 1H), 6.24 (s, 1H), 4.13 (m, 4H) (Fig. S2).



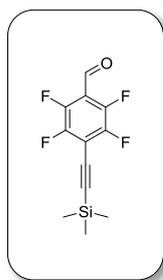
**Synthesis of 2-(2,3,5,6-tetrafluoro-4-iodophenyl)-1,3-dioxolane.**

To 2-(2,3,5,6-tetrafluorophenyl)-1,3-dioxolane (4.12 g, 18.5 mmol) in 50 mL dry THF was added dropwise *n*-BuLi (8.30 mL, 20.0 mmol) under N<sub>2</sub> at -78 °C. After stirring under N<sub>2</sub> for 1 h at -78 °C, iodine (5.08 g, 20.0 mmol) was added. The mixture was then rinsed with DCM, NaHCO<sub>3</sub> aqueous solution and was dried with MgSO<sub>4</sub>. The liquid product was light yellow (5.95 g, 17.1 mmol, yield 92%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 6.24 (s, 1H), 4.13 (m, 4H) (Fig. S3).



**Synthesis of 4-(1,3-dioxolan-2-yl)-2,3,5,6-tetrafluorophenyl-ethynyltrimethylsilane.** To a suspension of 2-(2,3,5,6-tetrafluoro-4-iodophenyl)-1,3-dioxolane (5.95 g, 17.1 mmol), tetrakis(triphenyl-phosphine)palladium (988.1 mg, 0.8 mmol) and

copper iodide (162.8 mg, 0.8 mmol) in 100 mL dry toluene, was added dry triethylamine (3 mL, 21.6 mmol) and trimethylsilylacetylene (3 mL, 21.2 mmol) under N<sub>2</sub>. During strong stirring for 20 h at 80 °C, the olive solution turned to brown. The mixture was purified on a silica column (20:1 petroleum ether (PE)-DCM → 10:1 PE-DCM) and was dried in vacuo to give a colorless oil (3.41 g, 10.7 mmol, yield 62%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 6.15 (s, 1H), 4.06 (m, 4H), 0.22 (s, 9H) (Fig. S4).



**Synthesis of 2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)-**

**benzaldehyde.** To a solution of 4-(1,3-dioxolan-2-yl)-2,3,5,6-tetrafluorophenylethynyl-trimethylsilane (2.08 g, 6.5 mmol) in 6 mL trifluoroacetic acid, was added dropwise 1 mL H<sub>2</sub>O at 60 °C with

stirring for 2 h. After that, the mixture was neutralized by the solution of NaOH and was dissolved in ethyl acetate. The solution was then washed with H<sub>2</sub>O and was dried with MgSO<sub>4</sub>. The oil product was light yellow (1.77 g, 6.5 mmol, yield 99%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 10.29 (s, 1H), 0.31 (s, 9H) (Fig. S5).

**Synthesis of tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)-**

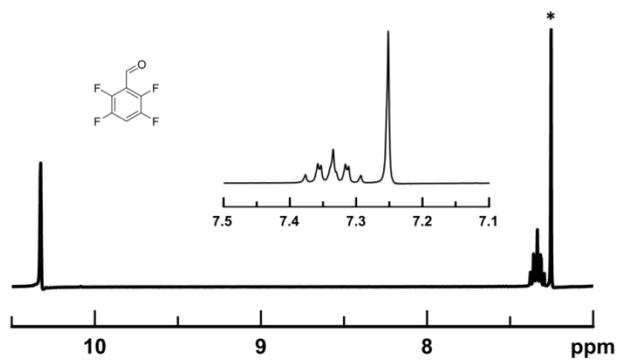
**porphyrin.** To a vigorously N<sub>2</sub> bubbled solution of 2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)benzaldehyde (1.23 g, 4.5 mmol) and pyrrole (301.9 mg, 4.5 mmol) in 600 mL CH<sub>2</sub>Cl<sub>2</sub> was added boron trifluoride - ethyl ether (BF<sub>3</sub> Et<sub>2</sub>O, 2 mL, 15.5 mmol). After stirring for 2 h under N<sub>2</sub> at room temperature, the mixture was

added 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ, 4.39 g, 3.37 mmol) and was stirred overnight in the air. The mixture was then filtered, purified on a silica column (2:1 PE-DCM) and was dried in vacuo to give a purple solid (141.7 mg, 0.1 mmol, yield 10%).  $^1\text{H}$  NMR ( $\text{CHCl}_3$ , 300 MHz):  $\delta = 8.94$  (s, 8H), 0.44 (s, 36H),  $-2.87$  (s, 2H) (Fig. S6). HRMS of  $[\text{M}+\text{H}]^+$ : calcd. for  $\text{C}_{64}\text{H}_{47}\text{F}_{16}\text{N}_4\text{Si}_4$ , 1287.2617; found, 1287.2601 (Fig. S7).

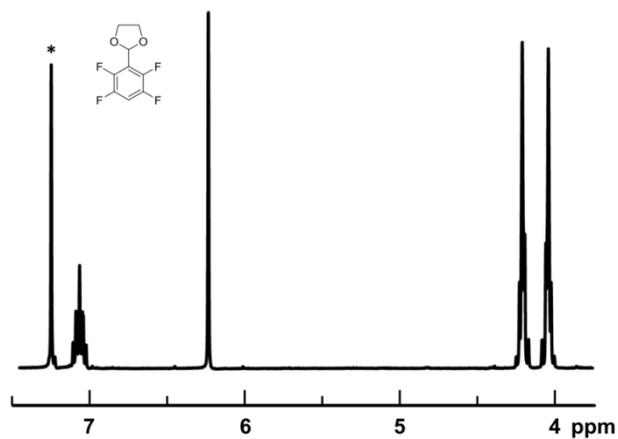
**Synthesis of  $\text{Co}^{\text{II}}$  tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)porphyrin.** To a solution of tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)porphyrin (141.7 mg, 0.1 mmol) in 15 mL DMF and 3 mL  $\text{CHCl}_3$ , was added cobalt acetate tetrahydrate (274.0 mg, 1.1 mmol). The mixture was stirred at 120  $^{\circ}\text{C}$  with reflux for 12 h. After that, the mixture was rinsed with 150 mL  $\text{H}_2\text{O}$  and then was dried with  $\text{MgSO}_4$ . The solid product was purple (65.1 mg, 0.05 mmol, yield 44%). HRMS of  $[\text{M}]^+$ : calcd. for  $\text{C}_{64}\text{H}_{44}\text{CoF}_{16}\text{N}_4\text{Si}_4$ , 1343.1720; found, 1343.1683 (Fig. S8).

**Synthesis of  $\text{Co}^{\text{II}}$  tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)porphyrin.** To a solution of  $\text{Co}^{\text{II}}$  tetrakis(2,3,5,6-tetrafluoro-4-((trimethylsilyl)ethynyl)phenyl)porphyrin (340 mg, 0.25 mmol) in 50 mL THF, tetra-*n*-butylammonium fluoride (1 mol/L, 1 mL) was added under  $\text{N}_2$  at room temperature. The mixture was purified on a silica column (5:1 PE-DCM) and was dried in vacuo to give a purple crystal (253 mg, 0.24 mmol, yield 96%). HRMS of  $[\text{M}]^+$ : calcd. for  $\text{C}_{52}\text{H}_{12}\text{CoF}_{16}\text{N}_4$ , 1055.0138; found, 1055.0107 (Fig. S9).

**Preparation of FCoP@CNT.**  $\text{Co}^{\text{II}}$  tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)-porphyrin (34 mg, 0.032 mmol) was added into a solution of CNTs (10 mg) in N-methyl pyrrolidone (NMP, 150 mL). The mixture was then sonicated at room temperature for 1 h. After that, a freshly prepared suspension of 100  $\mu\text{L}$  of N,N,N',N'-tetramethylethylenediamine (TMEDA) and 25 mg of copper(I) chloride ( $\text{CuCl}$ , 0.25 mmol) in 2 mL of NMP was added. The mixture was then stirred and bubbled with  $\text{O}_2$  overnight at room temperature. After the completion, the crude product was filtered and washed with NMP (20 mL  $\times$  3), deionized water (20 mL  $\times$  3), solution of  $\text{NH}_3$  (5%, 20 mL  $\times$  3), deionized water (20 mL), NMP (20 mL), deionized water (20 mL), THF (20 mL), and  $\text{CH}_2\text{Cl}_2$  (20 mL) sequentially to get the final product.



**Fig. S1**  $^1\text{H}$  NMR spectrum of 2,3,5,6-tetrafluorobenzaldehyde in  $\text{CDCl}_3$ . The solvent residue peak is labeled (\*).

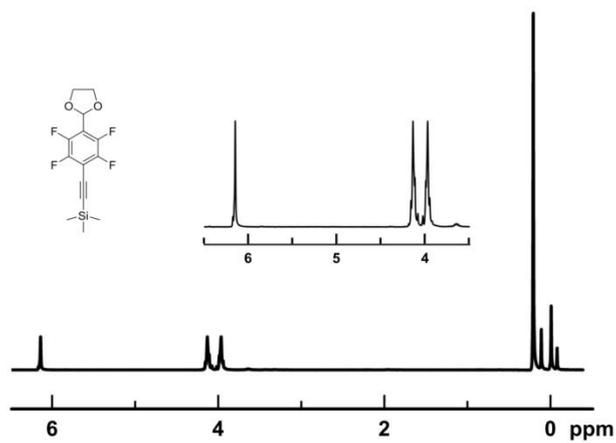


**Fig. S2** <sup>1</sup>H NMR spectrum of 2-(2,3,5,6-tetrafluorophenyl)-1,3-dioxolane in CDCl<sub>3</sub>.

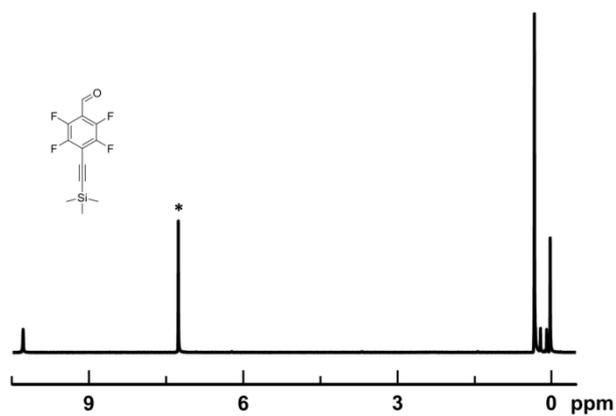
The solvent residue peak is labeled (\*).



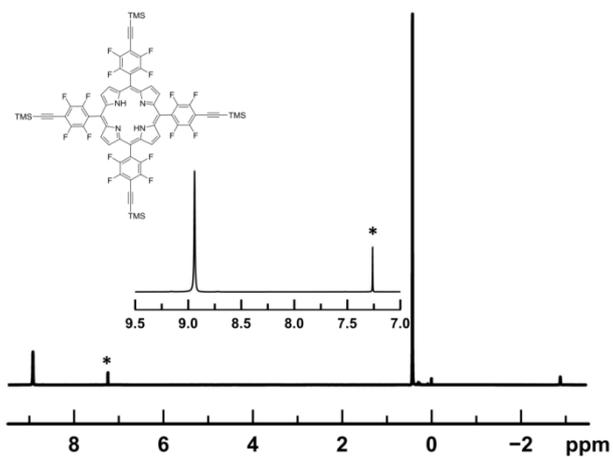
**Fig. S3** <sup>1</sup>H NMR spectrum of 2-(2,3,5,6-tetrafluoro-4-iodophenyl)-1,3-dioxolane in CDCl<sub>3</sub>.



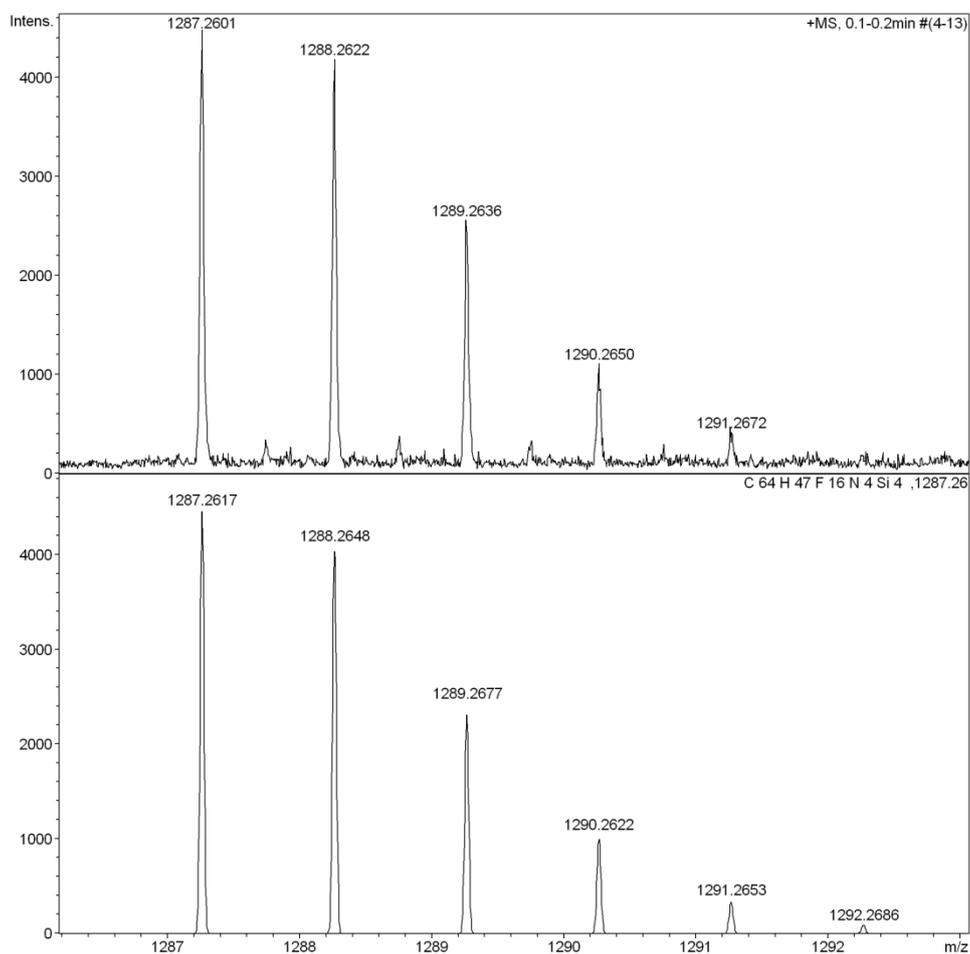
**Fig. S4** <sup>1</sup>H NMR spectrum of 4-(1,3-dioxolan-2-yl)-2,3,5,6-tetrafluorophenylethynyl-trimethylsilane in CDCl<sub>3</sub>.



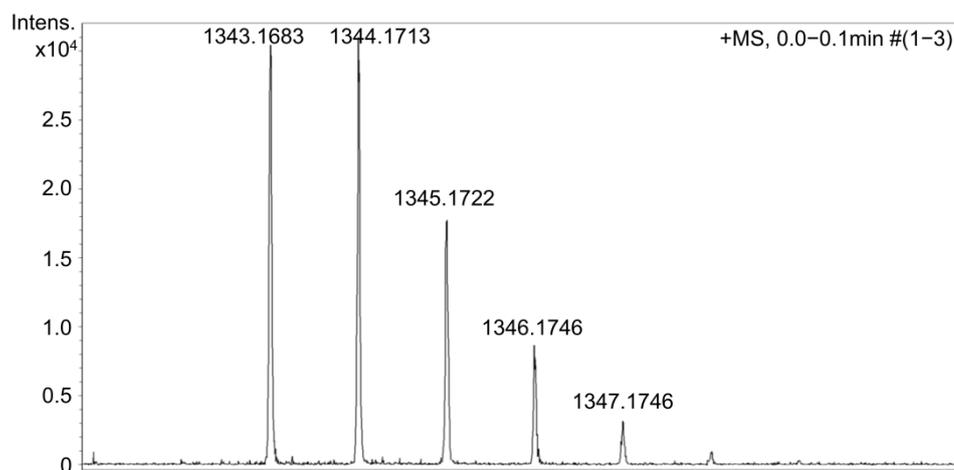
**Fig. S5** <sup>1</sup>H NMR spectrum of 2,3,5,6-tetrafluoro-4-(trimethylsilyl)ethynylbenzaldehyde in CDCl<sub>3</sub>. The solvent residue peak is labeled (\*).



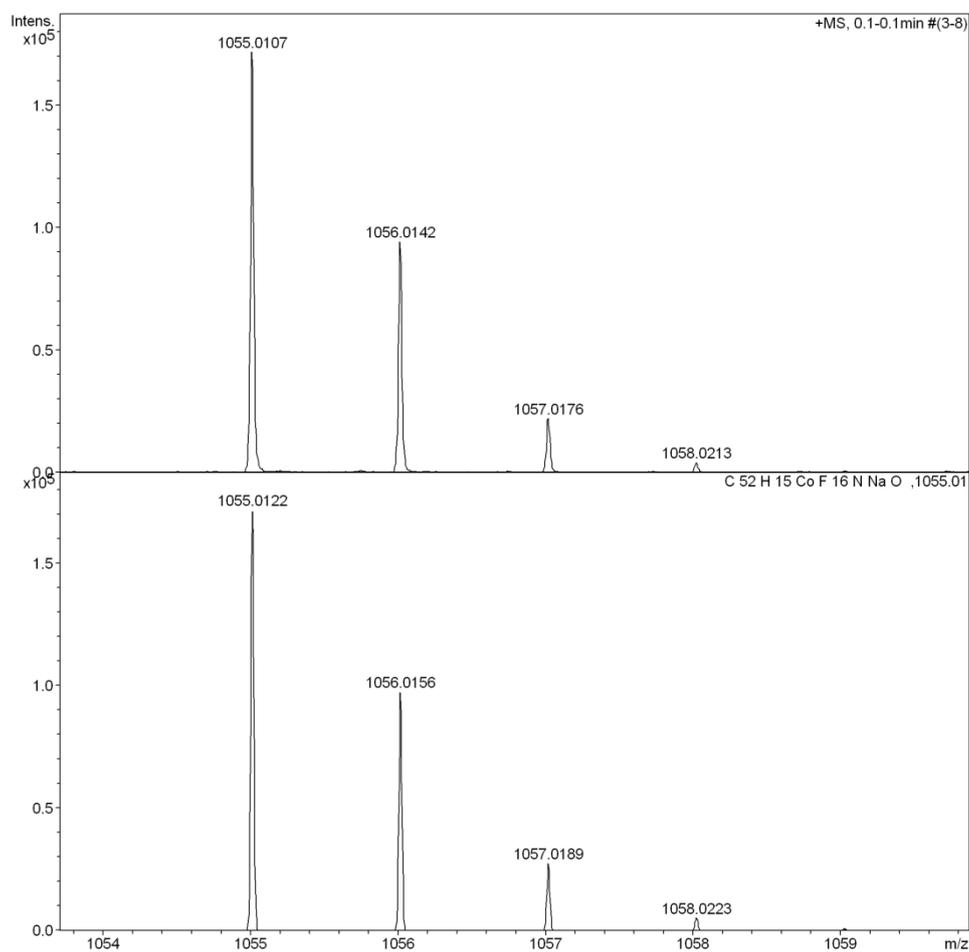
**Fig. S6** <sup>1</sup>H NMR spectrum of tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)-phenyl)porphyrin in CDCl<sub>3</sub>. The solvent residue peak is labeled (\*).



**Fig. S7** High-resolution mass spectrum of tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)porphyrin in methanol, showing an intense peak at 1287.2601. This signal corresponds to the formula of  $C_{64}H_{46}F_{16}N_4Si_4$ , which is consistent with a calculated number of 1287.2617 for  $[M + H]^+$ .

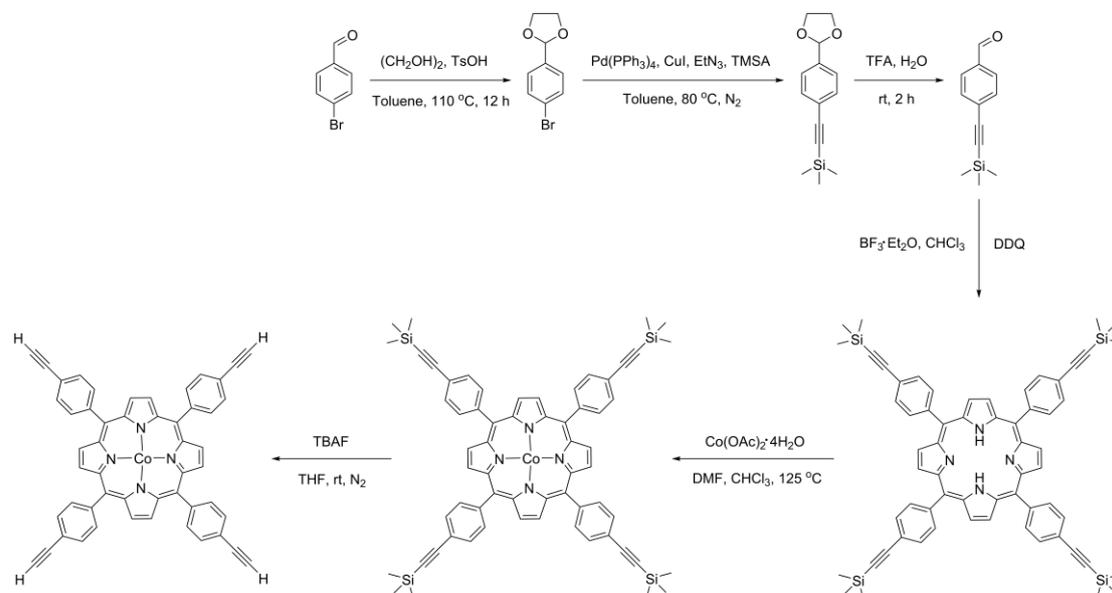


**Fig. S8** High-resolution mass spectrum of  $\text{Co}^{\text{II}}$  tetrakis(2,3,5,6-tetrafluoro-4-(trimethylsilylethynyl)phenyl)porphyrin in methanol, showing an intense peak at 1343.1683. This signal corresponds to the formula of  $\text{C}_{64}\text{H}_{44}\text{CoF}_{16}\text{N}_4\text{Si}_4$ , which is consistent with a calculated number of 1343.1720 for  $[\text{M}]^+$ .

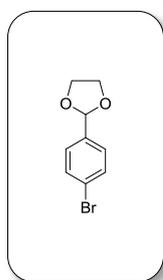


**Fig. S9.** High-resolution mass spectrum of Co<sup>II</sup> tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)porphyrin in methanol, showing an intense peak at 1055.0107. This signal corresponds to the formula of C<sub>52</sub>H<sub>12</sub>CoF<sub>16</sub>N<sub>4</sub>, which is consistent with a calculated number of 1055.0122 for [M]<sup>+</sup>.

## Synthesis of the Co<sup>II</sup> tetrakis(4-ethynylphenyl)porphyrin (CoP-H).

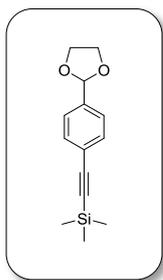


**Scheme S2.** Synthetic route of complex CoP-H.



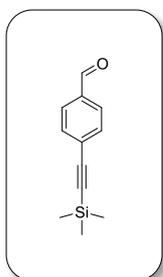
### Synthesis of 2-(4-bromophenyl)-1,3-dioxolane.

To a 50 mL dry toluene solution containing ethylene glycol (6.2 g, 100 mmol) and *p*-toluenesulfonic acid monohydrate (19 mg, 0.1 mmol) was added 4-bromobenzaldehyde (1.85 g, 10 mmol). After stirring for 12 h at  $110\text{ }^\circ\text{C}$  with a water separator, the mixture was washed three times with  $\text{NaHCO}_3$  aqueous solution and water, and then was dried with  $\text{MgSO}_4$ . The liquid product was colorless (2.29 g, 10 mmol, yield 100%).  $^1\text{H NMR}$  ( $\text{CHCl}_3$ , 300 MHz):  $\delta = 7.51$  (d, 2H), 7.35 (d, 2H), 5.77 (s, 1H), 4.07 (m, 4H) (Fig. S10).



**Synthesis of 4-(1,3-dioxolan-2-yl)phenylethynyltrimethylsilane.**

To a suspension of 2-(4-bromophenyl)-1,3-dioxolane (2.29 g, 10 mmol), tetrakis(triphenylphosphine)palladium (577.8 mg, 0.5 mmol) and copper iodide (95.2 mg, 0.5 mmol) in 100 mL dry toluene, was added dry triethylamine (1.5 mL, 10.8 mmol) and trimethylsilylacetylene (1.5 mL, 10.6 mmol) under N<sub>2</sub>. During strong stirring for 20 h at 80 °C, the olive solution turned to brown. The mixture was purified on a silica column (20:1 PE-DCM → 5:1 PE-DCM) and was dried in vacuo to give a colorless oil (2.29 g, 9.3 mmol, yield 93%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 7.47 (d, 2H), 7.40 (d, 2H), 5.79 (s, 1H), 4.07 (m, 4H), 0.25 (s, 9H) (Fig. S11).



**Synthesis of 4-(trimethylsilyl)ethynylbenzaldehyde.**

To a solution of 4-(1,3-dioxolan-2-yl)phenylethynyltrimethylsilane (566.7 mg, 2.3 mmol) in 2 mL trifluoroacetic acid was added dropwise 1 mL H<sub>2</sub>O at 25 °C with stirring for 10 h. After that, the mixture was neutralized by NaOH aqueous solution and was dissolved in ethyl acetate. The solution was then washed with H<sub>2</sub>O and was dried with MgSO<sub>4</sub>. The oil product was light yellow (461.3 mg, 2.3 mmol, yield 99%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 9.99 (s, 1H), 7.82 (d, 2H), 7.61 (d, 2H), 0.27 (s, 9H) (Fig. S12).

**Synthesis of tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin.**

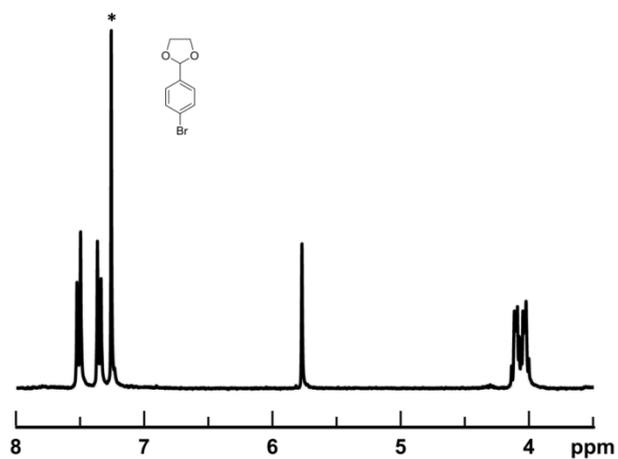
To a vigorously N<sub>2</sub> bubbled solution of 4-(trimethylsilyl)ethynylbenzaldehyde (461.3 mg, 2.3 mmol)

and pyrrole (153.0 mg, 2.3 mmol) in 600 mL CHCl<sub>3</sub> was added BF<sub>3</sub>·Et<sub>2</sub>O (1 mL, 7.9 mmol). After stirring for 2 h under N<sub>2</sub> at room temperature, the mixture was added DDQ (2.23 g, 1.71 mmol) and stirred overnight in the air. The mixture was then filtered, purified on a silica column (1:1 PE-DCM) and was dried in vacuo to give a purple solid (149.4 mg, 0.15 mmol, yield 26%). <sup>1</sup>H NMR (CHCl<sub>3</sub>, 300 MHz): δ = 8.74 (s, 8H), 8.06 (d, 8H), 7.79 (d, 8H), 0.30 (s, 36H), -2.92 (s, 2H) (Fig. S13). HRMS of [M+H]<sup>+</sup>: calcd. for C<sub>64</sub>H<sub>63</sub>N<sub>4</sub>Si<sub>4</sub>, 999.4130; found, 999.4108 (Fig. S14).

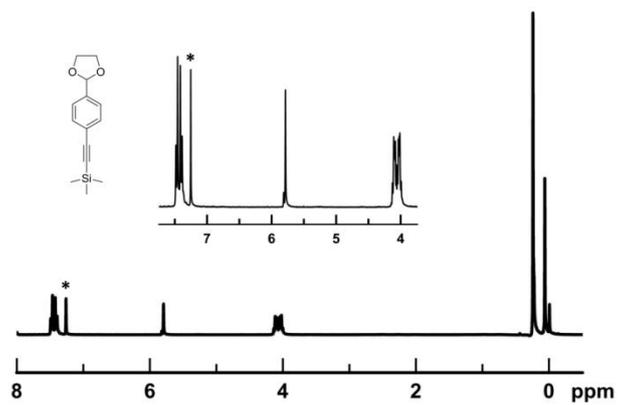
**Synthesis of Co<sup>II</sup> tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin.** To a solution of tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin (206.0 mg, 0.2 mmol) in 15 mL DMF and 3 mL CHCl<sub>3</sub>, was added cobalt acetate tetrahydrate (498.2 mg, 2.0 mmol). The mixture was stirred at 120 °C with reflux for 12 h. After that, the mixture was rinsed with 150 mL H<sub>2</sub>O and then was dried with MgSO<sub>4</sub>. The solid product was purple (188.4 mg, 0.18 mmol, yield 89%). HRMS of [M]<sup>+</sup>: calcd. for C<sub>64</sub>H<sub>60</sub>CoN<sub>4</sub>Si<sub>4</sub>, 1055.3227; found, 1055.3213 (Fig. S15).

**Synthesis of Co<sup>II</sup> tetrakis(4-ethynylphenyl)porphyrin.** To a solution of Co<sup>II</sup> tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin (260 mg, 0.25 mmol) in 50 mL THF, tetra-*n*-butylammonium fluoride (1 mol/L, 1 mL) was added under N<sub>2</sub> at room temperature. The mixture was purified on a silica column (5:1 PE-DCM) and was dried in vacuo to give a purple crystal (187 mg, 0.24 mmol, yield 99%). HRMS of [M]<sup>+</sup>: calcd. for C<sub>52</sub>H<sub>28</sub>CoN<sub>4</sub>, 767.1640; found, 767.1642 (Fig. S16).

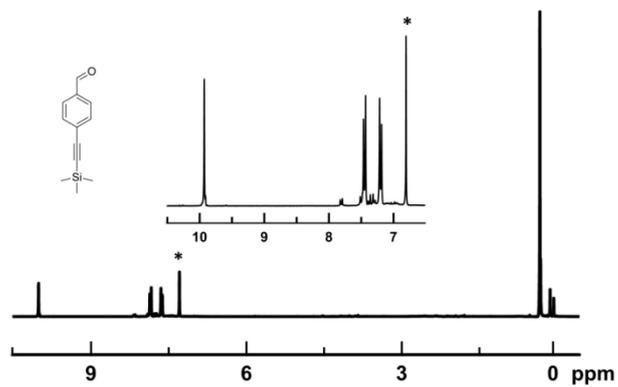
**Preparation of CoP@CNT.** Co<sup>II</sup> tetrakis(4-ethynylphenyl)porphyrin (25 mg, 0.032 mmol) was added into a solution of CNTs (10 mg) in NMP (150 mL). The mixture was then sonicated at room temperature for 1 h. After that, a freshly prepared suspension of 100  $\mu$ L of TMEDA and 25 mg of CuCl (0.25 mmol) in 2 mL of NMP was added. The mixture was then stirred and bubbled with O<sub>2</sub> overnight at room temperature. After the completion, the crude product was filtered and washed with NMP (20 mL  $\times$  3), deionized water (20 mL  $\times$  3), solution of NH<sub>3</sub> (5%, 20 mL  $\times$  3), deionized water (20 mL), NMP (20 mL), deionized water (20 mL), THF (20 mL), and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) sequentially to get the final product.



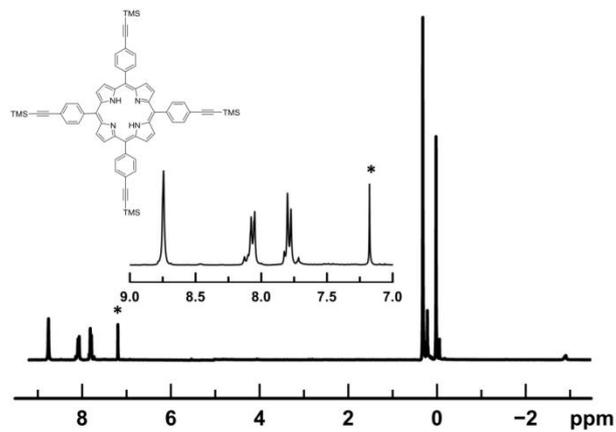
**Fig. S10**  $^1\text{H}$  NMR spectrum of 2-(4-bromophenyl)-1,3-dioxolane in  $\text{CDCl}_3$ . The solvent residue peak is labeled (\*).



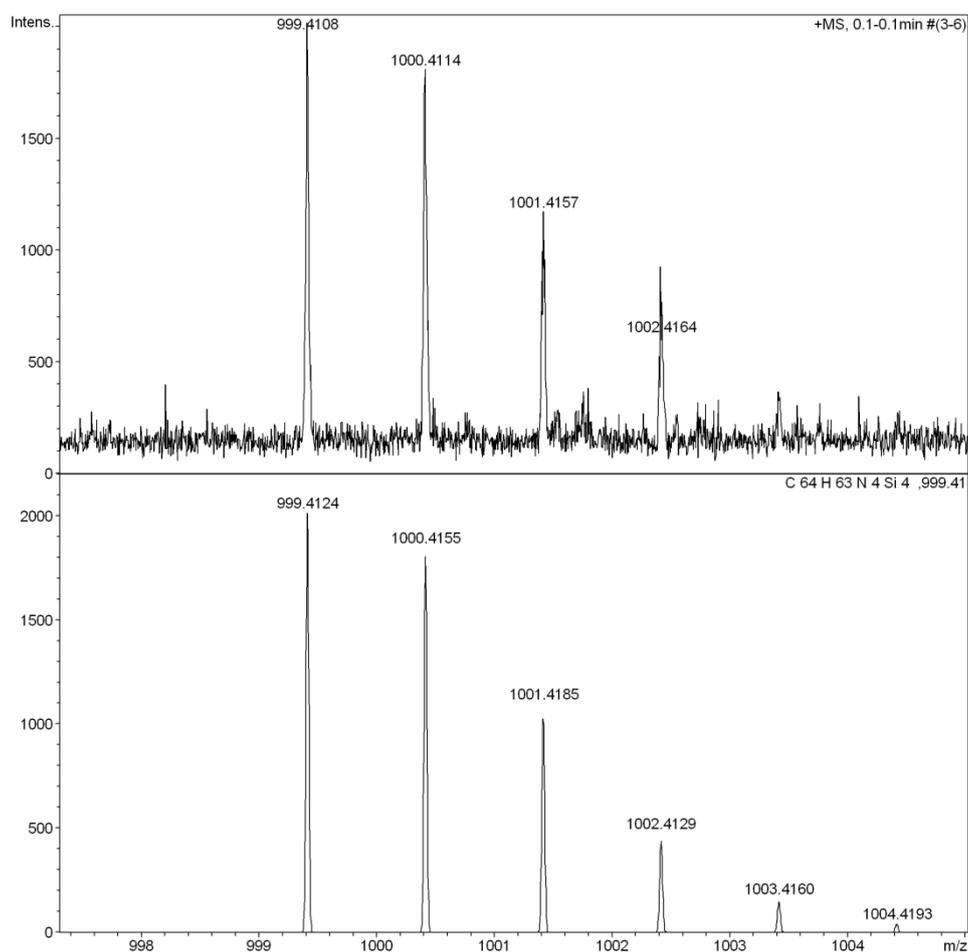
**Fig. S11** <sup>1</sup>H NMR spectrum of 4-(1,3-dioxolan-2-yl)phenylethyne-trimethylsilane in CDCl<sub>3</sub>. The solvent residue peak is labeled (\*).



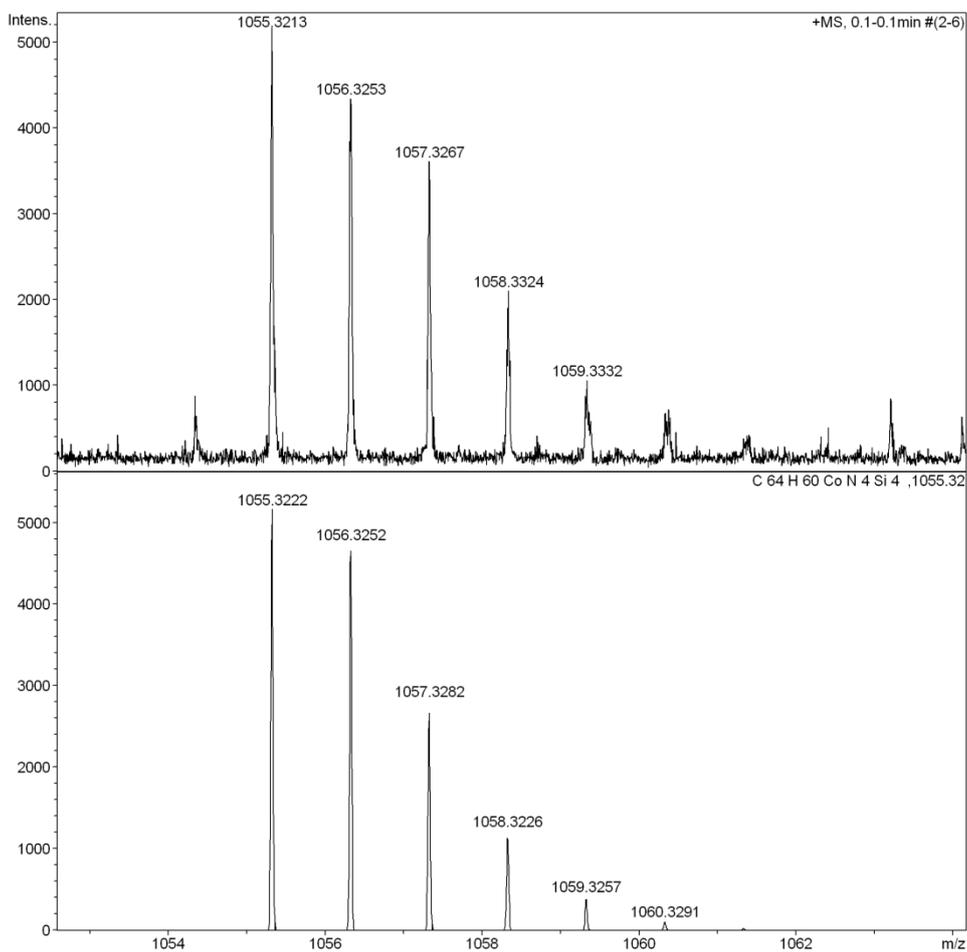
**Fig. S12** <sup>1</sup>H NMR spectrum of 4-(trimethylsilyl)ethynylbenzaldehyde in CDCl<sub>3</sub>. The solvent residue peak is labeled (\*).



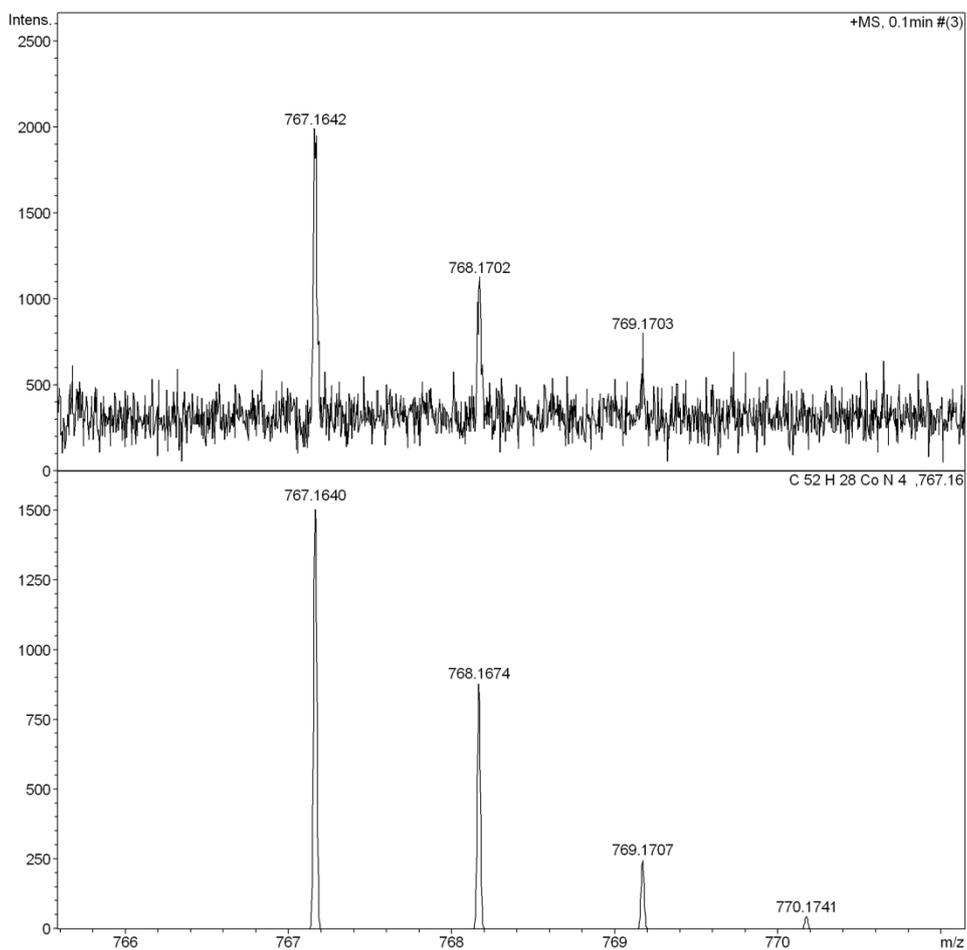
**Fig. S13** <sup>1</sup>H NMR spectrum of tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin in CDCl<sub>3</sub>. The solvent residue peak is labeled (\*).



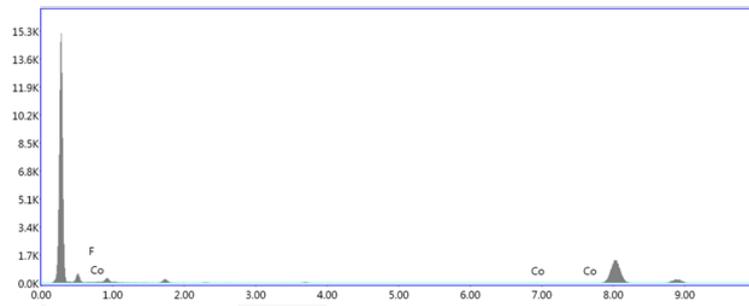
**Fig. S14** High-resolution mass spectrum of tetrakis(4-(trimethylsilylethynyl)phenyl)porphyrin in methanol, showing an intense peak at 999.4108. This signal corresponds to the formula of  $C_{64}H_{63}N_4Si_4$ , which is consistent with a calculated number of 999.4124 for  $[M + H]^+$ .



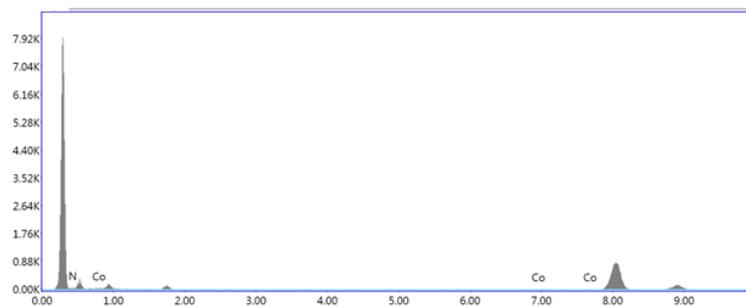
**Fig. S15** High-resolution mass spectrum of Co<sup>II</sup> tetrakis(4-(trimethylsilylethynyl)-phenyl)porphyrin in methanol, showing an intense peak at 1055.3213. This signal corresponds to the formula of C<sub>64</sub>H<sub>60</sub>CoN<sub>4</sub>Si<sub>4</sub>, which is consistent with a calculated number of 1055.3222 for [M]<sup>+</sup>.



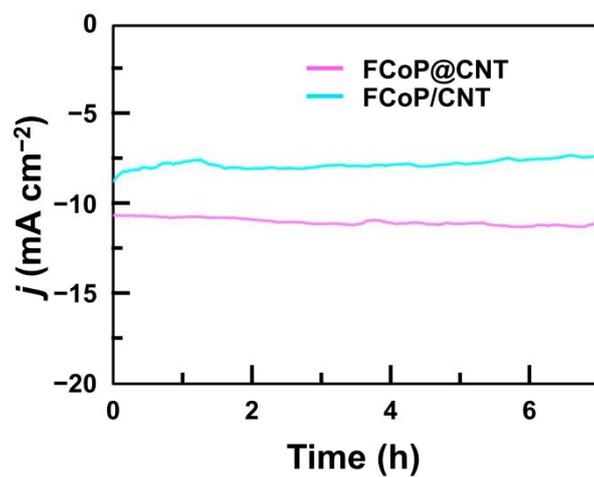
**Fig. S16** High-resolution mass spectrum of Co<sup>II</sup> tetrakis(4-ethynylphenyl)porphyrin in methanol, showing an intense peak at 767.1642. This signal corresponds to the formula of C<sub>52</sub>H<sub>28</sub>CoN<sub>4</sub>, which is consistent with a calculated number of 767.1640 for [M]<sup>+</sup>.



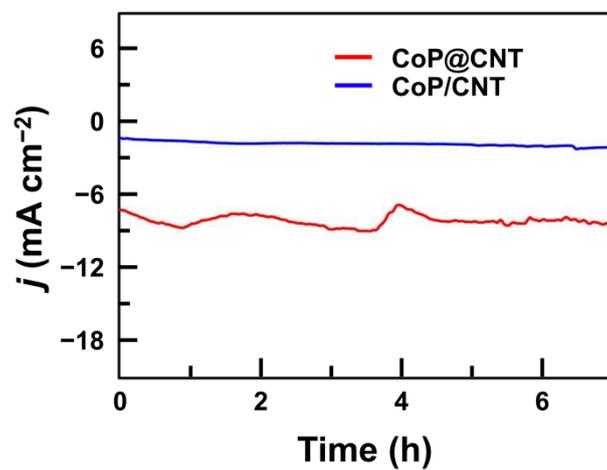
**Fig. S17** EDX analysis of **FCoP@CNT**.



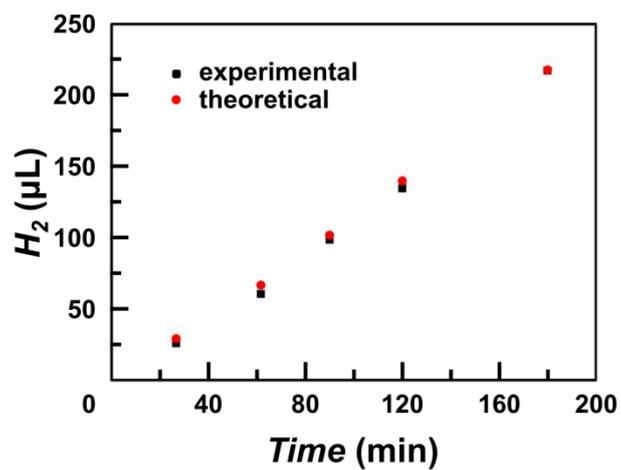
**Fig. S18** EDX analysis of **CoP@CNT**.



**Fig. S19** Controlled potential electrolysis at 750 V overpotential using GC electrode loaded with **FCoP@CNT** (pink) and **FCoP/CNT** (cyan) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution under N<sub>2</sub>.



**Fig. S20** Controlled potential electrolysis at 750 mV overpotential using GC electrode loaded with **CoP@CNT** (red) and **CoP/CNT** (blue) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution under N<sub>2</sub>.



**Fig. S21** Gas chromatography detection of evolved H<sub>2</sub> during 3 h electrolysis with **FCoP@CNT** (black) and the theoretical amount of H<sub>2</sub> produced (red) at 750 mV overpotential in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution under N<sub>2</sub>.

**Table S1.** Comparison of immobilized molecular catalysts on carbon materials for electrocatalytic HER.

Catalyst	Electrolyte	Electrode	Overpotential (at 1 mA cm <sup>-2</sup> )	Stability	Reference
<b>FCoP@CNT</b>	0.5 M H <sub>2</sub> SO <sub>4</sub>	GC	576 mV	7 h	This work
Co corrole- PPh <sub>3</sub> / Graphene	0.5 M H <sub>2</sub> SO <sub>4</sub>	GC	~560 mV	3 h	5
Co corrole /CNTs (hybrid)	0.5 M H <sub>2</sub> SO <sub>4</sub>	GC	~510 mV	10 h	6
CoCor-CNT-B	0.5 M H <sub>2</sub> SO <sub>4</sub>	GC	~500 mV	2 h	7
GC/MWCNT- amino-[Co]	0.1 M acetate buffer pH = 4.5	GC	~550 mV	not given	8
[Co(DO)(DO H)pnCl <sub>2</sub> ] / MWCNT	phosphate buffer pH = 2.2	GDL	~600 mV	20 h	9
GDL/ MWCNT/Co	0.1 M acetate buffer pH = 4.5	GDL	~580 mV	4 h	10

**Table S2.** Crystal data and structure refinement parameters for the X-ray structure of **FCoP-SiMe<sub>3</sub>**.

Complex	<b>FCoP-SiMe<sub>3</sub></b>
molecular formula	C <sub>64</sub> H <sub>44</sub> CoF <sub>16</sub> N <sub>4</sub> Si <sub>4</sub>
formula wt. (g mol <sup>-1</sup> )	1344.32
temperature (K)	153(2)
radiation (λ, Å)	0.71073
crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	12.176(2)
<i>b</i> (Å)	14.488(2)
<i>c</i> (Å)	23.065(4)
β (°)	92.255(5)
volume (Å <sup>3</sup> )	4065.7(11)
<i>Z</i>	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.098
μ (mm <sup>-1</sup> )	0.340
F(000)	1366
crystal size (mm <sup>3</sup> )	0.4 × 0.2 × 0.2
theta range	2.258 to 26.472°
reflections collected	42243
independent reflections	8305 [R(int) = 0.0642]
completeness	99.1%
goodness-of-fit on F <sup>2</sup>	1.048
final R indices	R1 <sup>a</sup> = 0.1211
[R > 2σ (I)]	wR2 <sup>b</sup> = 0.3037
R indices (all data)	R1 <sup>a</sup> = 0.1584
	wR2 <sup>b</sup> = 0.3251
largest diff. peak and hole (e Å <sup>-3</sup> )	1.426 and -0.725

$${}^aR_1 = \Sigma||F_o| - |F_c|| / |F_o|, {}^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]\}^{0.5}$$

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