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Boosting hydrogen evolution by using covalent frameworks of fluorinated cobalt porphyrins supported on carbon nanotubes[†]

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A cobalt(II) tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)porphyrin (FCoP-H) was designed and synthesized. With carbon-nanotubetemplated polymerization, covalent porphyrin frameworks using FCoP-H can be synthesized *via* the Hay-coupling. The resulting FCoP@CNT is efficient to catalyze the hydrogen evolution reaction (HER) in aqueous media, and its performance is superior, in terms of both lower overpotentials and larger catalytic currents, to covalent porphyrin frameworks using non-fluorinated cobalt porphyrin analogues and also monomeric fluorinated cobalt porphyrins simply adsorbed on CNTs. This work combines the merits of CNTtemplated covalent frameworks and fluorinated cobalt porphyrins to significantly improve the HER performance. This strategy is valuable to be explored in other electrocatalytic systems using molecule-engineered carbon materials.

Hydrogen is considered to be a clean and renewable energy carrier.^{1–3} The electrocatalytic HER provides an appealing strategy to generate H_2 and meanwhile to convert electrical energy to chemical energy.^{4,5} Tremendous efforts have been made in the past decade to develop cheap, efficient and robust HER electrocatalysts.^{6–12} This leads to the identification of a variety of molecular complexes of Fe,^{13–15} Co,^{16–21} Ni^{22–27} and Cu^{28,29} as active HER catalysts. Despite these achievements, however, immobilization of molecular catalysts on appropriate electrode materials is critical to make them practically useful.³⁰ It is demonstrated that immobilization of molecular catalysts.

Owing to large surface area, high chemical stability, and good electrical conductivity, carbon nanotubes (CNTs) have been used as supporting electrode materials.^{17,31–36} Typically, molecular catalysts can be simply loaded on CNTs *via* physical adsorption.

Although this method is easy and straightforward, the weak interactions between molecular catalysts and CNTs usually lead to poor electron transfer ability and stability, and thus poor catalytic performance. Two immobilization strategies have been used to improve the molecule–CNT interactions. The first one is to introduce large conjugated groups onto catalyst molecules, which will result in the increased π - π interactions with CNTs.^{37,38} The other one is to covalently graft catalyst molecules on CNTs.^{17,32} In both cases, improved catalytic performance is realized. In addition to these methods, CNT-templated polymerization is also a valuable method for the immobilization of catalyst molecules. For example, through the oxidative coupling of *meso*-ethynyl groups, covalent porphyrin frameworks can be synthesized on CNTs to show high catalytic performance for oxygen electrocatalysis.^{39,40}

Metal porphyrins have been shown to be highly active for the HER.⁴¹⁻⁴⁹ Strong electron withdrawing groups at the meso- and/or β-positions can cause large shifts of the reduction waves to the anodic direction and thus can boost catalytic HER performance by decreasing overpotentials.18 Herein we report the design and synthesis of Co^{II} tetrakis(2,3,5,6-tetrafluoro-4-ethynylphenyl)porphyrin (FCoP-H, Fig. 1a) and its CNT-templated covalent framework FCoP(a)CNT, which combines the merits of covalent porphyrin frameworks and the strong electron withdrawing feature of tetrafluorophenyl substituents. We show that FCoP@CNT is much more efficient for the HER in aqueous solutions than simply adsorbed monomeric Co porphyrins on CNTs and also the CNT-templated covalent framework using non-fluorinated Co^{II} tetrakis(4-ethynylphenyl)porphyrin (CoP-H, Fig. 1a). This work presents a CNT-templated polymerization strategy of fluorinated porphyrins, which will be valuable for other electrocatalytic systems using molecule-engineered carbon materials.

Monomeric **FCoP**-SiMe₃ was first synthesized (Fig. 1a and Scheme S1, ESI[†]). Details of synthesis and characterization are given in the ESI.[†] Crystals of **FCoP**-SiMe₃, suitable for single crystal X-ray diffraction studies, were obtained. Crystallographic studies revealed that **FCoP**-SiMe₃ crystallized in the monoclinic $P2_1/n$ space group (Fig. 1b). The Co ion is coordinated by the porphyrin ligand through four N atoms, giving a square-planar



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Fig. 1 (a) Molecular structures of Co porphyrins. (b) Thermal ellipsoid plot (50% probability) of the X-ray structure of FCoP-SiMe₃. Hydrogen atoms are omitted. (c) CVs of FCoP-SiMe₃ and CoP-SiMe₃ in DMF with 50 mV s⁻¹ scan rate at 20 °C. (d) Synthetic route to FCoP@CNT.

geometry. The average Co–N distance is 1.975(3) Å, which is consistent with a Co^{II} electronic structure. The four *ortho-* and *meta*-positions of the phenyl groups are all occupied by a fluoride atom, and the *para*-position bears a trimethylsilylethynyl group. This confirms the structure we designed. In addition, the identity and the purity of the bulk sample were confirmed by high-resolution mass spectrometry and elemental analysis, showing an ion at a mass-to-charge ratio of 1343.1683, which matches the calculated value of 1343.1720 with expected isotopic distribution (Fig. S8, ESI†). As a control, the nonfluorinated analogue **CoP**-SiMe₃ was also synthesized and characterized (Fig. 1a and Scheme S2, ESI†).

The cyclic voltammogram (CV) of FCoP-SiMe₃, measured in dimethylformamide (DMF) under N₂ (Fig. 1c), displays two reversible redox waves at -1.07 and -2.01 V vs. ferrocene, which correspond to the formal Co^{II}/Co^I and Co^I/Co⁰ redox couples, respectively.⁵⁰ For CoP-SiMe₃, it shows a reversible Co^{II}/Co^I wave and an irreversible Co^{II}/Co⁰ wave at -1.27 and -2.36 V vs. ferrocene, respectively. These waves are shifted to the cathodic direction by > 200 mV as compared to those of FCoP-SiMe₃, which is consistent with the strong electron withdrawing feature of the tetrafluorophenyl substituents of FCoP-SiMe₃.

An electrocatalytic HER was first studied in DMF with acetic acid as the proton source. As shown in Fig. 2a and b, for both



Fig. 2 CVs of 1 mM **FCoP**-SiMe₃ (a) and **CoP**-SiMe₃ (b) in DMF with increasing acetic acid. (c and d) Plots of i_{cat} measured at -2.25 V vs. ferrocene against the concentration of acetic acid with 1 mM **FCoP**-SiMe₃ and **CoP**-SiMe₃, respectively. (e and f) Plots of i_{cat} measured at -2.20 V vs. ferrocene against the concentration of **FCoP**-SiMe₃ and **CoP**-SiMe₃, respectively, with 40 mM acetic acid.

FCoP-SiMe₃ and **CoP**-SiMe₃, their first reduction waves do not show changes after the addition of acetic acid, but the second reduction waves change to catalytic ones. This is consistent with previous studies, showing that Co⁰ is the catalytically active species for the HER.⁵⁰ In both cases, the catalytic currents increased linearly with the concentrations of acid (Fig. 2c and d) and catalyst (Fig. 2e and f), implying the molecular nature of the catalysis. It is worth noting that the onset overpotential of **FCoP**-SiMe₃ is smaller than that of **CoP**-SiMe₃ by >250 mV. This result is consistent with the cathodic shifts of the redox waves of **CoP**-SiMe₃ as compared to **FCoP**-SiMe₃, further highlighting the positive role of tetrafluorophenyl groups in improving the HER performance.

After removing the protecting trimethylsilyl groups, the resulting **FCoP**-H and **CoP**-H were adopted for subsequent CNTtemplated polymerization. The products were carefully washed to remove unreacted monomeric porphyrins. Details of synthesis are given in the ESI.† The successful formation of **FCoP**@CNT and **CoP**@CNT was evidenced by UV-vis spectroscopy (Fig. 3a and b), transmission electron microscopy (TEM, Fig. 3c and d) and energy-dispersive X-ray spectroscopy (EDX, Fig. S17 and S18, ESI†). The loaded amount of catalysts was determined by inductively coupled plasma mass spectrometry (ICP-MS), giving 0.23 wt% and 0.18 wt% of Co in **FCoP**@CNT and **CoP**@CNT, respectively.

In UV-vis spectroscopy, the strong Soret band of FCoP-SiMe₃ at 410 nm is red-shifted to 426 nm in FCoP@CNT (Fig. 3a).



Fig. 3 UV-vis spectra of (a) FCoP@CNT, FCoP/CNT, FCoP-SiMe₃ and (b) CoP@CNT, CoP/CNT, CoP-SiMe₃. TEM images of (c) untreated CNTs and (d) FCoP@CNT. The thin layers of covalent Co porphyrin frameworks on CNTs are labelled.

In addition to this 16 nm shift, the Soret band of **FCoP**@CNT becomes much broader. In sharp contrast, simply adsorbed monomeric **FCoP**-SiMe₃ on CNTs, denoted as **FCoP**/CNT, does not show such a red shift for the Soret band. This result not only showed the loading of intact Co porphyrin molecules on CNTs, but also suggested the presence of strong π - π interactions between the catalyst molecules and CNTs.^{37,39} For **CoP**@CNT, a similar red shift of the Soret band by >20 nm is also observed as compared to monomeric **CoP**-SiMe₃ (Fig. 3b). In TEM, an untreated CNT has a very smooth surface with few flaws (Fig. 3c), while the **FCoP**@CNT shows the formation of thin layers coated on the surface of CNTs (Fig. 3d), further confirming the successful polymerization.

In order to examine electrocatalytic HER features, the linear sweep voltammogram (LSV) of FCoP@CNT on a glassy carbon (GC) electrode was recorded in 0.5 M H₂SO₄ aqueous solution under N2, displaying a catalytic current with an onset overpotential of 576 mV (measured at current density i = 1.0 mA cm⁻², Fig. 4a). This performance is comparable to immobilized molecular catalysts loaded on carbon materials operating under similar conditions (Table S1, ESI[†]). Note that only a few molecular complexes can stably catalyze the HER in such strongly acidic media. The rigid and stable coordination provided by porphyrin macrocycles is crucial to prevent demetallization under highly acidic conditions.^{32,37} The formation of gas bubbles on the surface of the GC electrode is indicative of the evolution of H₂. Significantly, the LSV of FCoP/CNT displays a much smaller catalytic current with a larger onset overpotential of 705 mV under the same conditions. Similarly, LSVs of CoP@CNT and CoP/CNT also show the catalytic HER with onset overpotentials of 648 and 743 mV, respectively (Fig. 4b). These results suggest that the covalent Co porphyrin frameworks grown on CNTs are much more efficient to catalyze the HER, in terms of both lower



Fig. 4 (a) LSVs of FCoP@CNT and FCoP/CNT. (b) LSVs of CoP@CNT and CoP/CNT. (c) LSV comparison of FCoP@CNT and CoP@CNT. (d) Tafel plots. Conditions: 0.5 M H_2SO_4 , N_2 atmosphere, 50 mV s⁻¹ scan rate, and 20 °C.

overpotentials and larger catalytic currents, than simply adsorbed monomeric Co porphyrins on CNTs. This improvement is likely due to the stronger π - π interactions between the molecules of covalent porphyrin frameworks and CNTs, which will facilitate the interfacial electron transfer.

It is interesting to compare the catalytic performance of FCoP@CNT and CoP@CNT. As shown in Fig. 4c, the onset overpotential of FCoP@CNT (576 mV) is smaller than that of CoP@CNT (648 mV). At 800 mV overpotential, the catalytic current of FCoP(a)CNT (25.1 mA cm^{-2}) is two times larger than that of CoP@CNT (11.5 mA cm⁻²). In addition, the Tafel plot of FCoP@CNT (126 mV dec⁻¹) is also smaller than that of **CoP**(a)CNT (167 mV dec $^{-1}$, Fig. 4d). These results demonstrate that FCoP@CNT outperforms CoP@CNT to catalyze the HER. This improvement is due to the strong electron withdrawing tetrafluorophenyl substituents in the structure of FCoP@CNT. The durability of FCoP@CNT and CoP@CNT for the HER was also studied. Controlled potential electrolysis at 750 mV overpotential showed stable currents for >7 h (Fig. S19 and S20, ESI \dagger). The produced H₂ gas was determined by gas chromatography, giving a faradaic efficiency of 94% (Fig. S21, ESI⁺).

In summary, we report the synthesis and electrocatalytic HER property of a covalent framework using fluorinated Co^{II} porphyrins. This **FCoP**@CNT is much more efficient to catalyze the HER in aqueous media than a covalent framework using non-fluorinated Co porphyrin analogue **CoP**@CNT and monomeric fluorinated Co porphyrins simply adsorbed on CNTs. The significantly improved efficiency, in terms of both low overpotentials and large catalytic currents, is a result of combining the merits of CNT-templated covalent frameworks and the strong electron withdrawing features of the tetrafluorophenyl substituents. This work highlights the role of molecular design in boosting the catalytic efficiency. The CNT-templated polymerization strategy using fluorinated porphyrins will be applicable for other electrocatalytic and electrochemical systems.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 J. R. McKone, S. C. Marinescu, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Chem. Sci.*, 2014, 5, 865–878.
- 2 J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, Acc. Chem. Res., 2009, 42, 1995–2004.
- 3 W. Zhang, W. Lai and R. Cao, Chem. Rev., 2017, 117, 3717-3797.
- 4 V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem., Int. Ed.*, 2011, **50**, 7238–7266.
- 5 H. Lei, X. Li, J. Meng, H. Zheng, W. Zhang and R. Cao, ACS Catal., 2019, 9, 4320–4344.
- 6 D. D. Zhang, J. Y. Shi, Y. Qi, X. M. Wang, H. Wang, M. R. Li, S. Z. Liu and C. Li, *Adv. Sci.*, 2018, 5, 1801216.
- 7 B. Wang, C. Tang, H.-F. Wang, B.-Q. Li, X. Cui and Q. Zhang, Small Methods, 2018, 2, 1800055.
- 8 B. Zhang, J. G. Hou, Y. Z. Wu, S. Y. Cao, Z. W. Li, X. W. Nie, Z. M. Gao and L. C. Sun, *Adv. Energy Mater.*, 2019, 9, 1803693.
- 9 J. Kibsgaard, T. F. Jaramillo and F. Besenbacher, *Nat. Chem.*, 2014, 6, 248–253.
- 10 Y. R. Xue, B. L. Huang, Y. P. Yi, Y. Guo, Z. C. Zuo, Y. J. Li, Z. Y. Jia, H. B. Liu and Y. L. Li, *Nat. Commun.*, 2018, 9, 1460.
- 11 L. Yang, H. Zhou, X. Qin, X. D. Guo, G. W. Cui, A. M. Asiri and X. P. Sun, *Chem. Commun.*, 2018, **54**, 2150–2153.
- 12 Z. C. Zhang, G. G. Liu, X. Y. Cui, B. Chen, Y. H. Zhu, Y. Gong, F. Saleem, S. B. Xi, Y. H. Du, A. Borgna, Z. C. Lai, Q. H. Zhang, B. Li, Y. Zong, Y. Han, L. Gu and H. Zhang, *Adv. Mater.*, 2018, **30**, 1801741.
- 13 X. Q. Li, M. Wang, D. H. Zheng, K. Han, J. F. Dong and L. C. Sun, Energy Environ. Sci., 2012, 5, 8220–8224.
- 14 M. J. Rose, H. B. Gray and J. R. Winkler, *J. Am. Chem. Soc.*, 2012, **134**, 8310–8313.
- 15 A. Rana, B. Mondal, P. Sen, S. Dey and A. Dey, *Inorg. Chem.*, 2017, 56, 1783–1793.
- 16 M. van der Meer, E. Glais, I. Siewert and B. Sarkar, Angew. Chem., Int. Ed., 2015, 54, 13792–13795.
- 17 H. Li, X. Li, H. Lei, G. Zhou, W. Zhang and R. Cao, *ChemSusChem*, 2019, 12, 801-806.
- 18 A. Mahammed, B. Mondal, A. Rana, A. Dey and Z. Gross, *Chem. Commun.*, 2014, **50**, 2725–2727.
- 19 H. Sun, Y. Han, H. Lei, M. Chen and R. Cao, *Chem. Commun.*, 2017, 53, 6195–6198.
- 20 P. L. Zhang, M. Wang, F. Gloaguen, L. Chen, F. Quentel and L. C. Sun, *Chem. Commun.*, 2013, **49**, 9455–9457.
- 21 A. G. Maher, G. Passard, D. K. Dogutan, R. L. Halbach, B. L. Anderson, C. J. Gagliardi, M. Taniguchi, J. S. Lindsey and D. G. Nocera, ACS Catal., 2017, 7, 3597–3606.

- 22 S. Gulati, O. Hietsoi, C. A. Calvary, J. M. Strain, S. Pishgar, H. C. Brun, C. A. Grapperhaus, R. M. Buchanan and J. M. Spurgeon, *Chem. Commun.*, 2019, 55, 9440–9443.
- 23 C. M. Klug, A. J. P. Cardenas, R. M. Bullock, M. O'Hagan and E. S. Wiedner, *ACS Catal.*, 2018, **8**, 3286–3296.
- 24 Z.-Y. Wu, T. Wang, Y.-S. Meng, Y. Rao, B.-W. Wang, J. Zheng, S. Gao and J.-L. Zhang, *Chem. Sci.*, 2017, **8**, 5953–5961.
- 25 M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois and D. L. DuBois, *Science*, 2011, 333, 863–866.
- 26 C. Tsay and J. Y. Yang, J. Am. Chem. Soc., 2016, 138, 14174-14177.
- 27 D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, K. Ohkubo, Y. Shiota, K. Yoshizawa, S. Fukuzumi and T. Kojima, *Inorg. Chem.*, 2018, 57, 7180–7190.
- 28 A. Z. Haddad, S. P. Cronin, M. S. Mashuta, R. M. Buchanan and C. A. Grapperhaus, *Inorg. Chem.*, 2017, 56, 11254–11265.
- 29 H. Lei, H. Fang, Y. Han, W. Lai, X. Fu and R. Cao, ACS Catal., 2015, 5, 5145–5153.
- 30 Y. M. Zhao, G. Q. Yu, F. F. Wang, P. J. Wei and J. G. Liu, Chem. Eur. J., 2019, 25, 3726–3739.
- 31 E. Antolini, Appl. Catal., B, 2009, 88, 1-24.
- 32 X. Li, H. Lei, J. Liu, X. Zhao, S. Ding, Z. Zhang, X. Tao, W. Zhang, W. Wang, X. Zheng and R. Cao, *Angew. Chem., Int. Ed.*, 2018, 57, 15070–15075.
- 33 P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem., Int. Ed.*, 2014, 53, 8709–8713.
- 34 J. Miao, Z. L. Lang, X. Y. Zhang, W. G. Kong, O. W. Peng, Y. Yang,
 S. P. Wang, J. J. Cheng, T. C. He, A. Amini, Q. Y. Wu, Z. P. Zheng,
 Z. K. Tang and C. Cheng, *Adv. Funct. Mater.*, 2019, 29, 1805893.
- 35 R. Gao, Q. B. Dai, F. Du, D. P. Yan and L. M. Dai, J. Am. Chem. Soc., 2019, 141, 11658–11666.
- 36 R. Cao, R. Thapa, H. Kim, X. Xu, M. G. Kim, Q. Li, N. Park, M. L. Liu and J. Cho, *Nat. Commun.*, 2013, 4, 2076.
- 37 X. Li, H. Lei, X. Guo, X. Zhao, S. Ding, X. Gao, W. Zhang and R. Cao, *ChemSusChem*, 2017, **10**, 4632–4641.
- 38 S. Gentil, D. Serre, C. Philouze, M. Holzinger, F. Thomas and A. Le Goff, Angew. Chem., Int. Ed., 2016, 55, 2517–2520.
- 39 I. Hijazi, T. Bourgeteau, R. Cornut, A. Morozan, A. Filoramo, J. Leroy, V. Derycke, B. Jousselme and S. Campidelli, *J. Am. Chem. Soc.*, 2014, **136**, 6348–6354.
- 40 H. Jia, Z. Sun, D. Jiang and P. Du, Chem. Mater., 2015, 27, 4586-4593.
- 41 Y. Han, H. Fang, H. Jing, H. Sun, H. Lei, W. Lai and R. Cao, Angew. Chem., Int. Ed., 2016, 55, 5457–5462.
- 42 S. Kasemthaveechok, B. Fabre, G. Loget and R. Gramage-Doria, Catal. Sci. Technol., 2019, 9, 1301–1308.
- 43 A. G. Maher, M. R. Liu and D. G. Nocera, *Inorg. Chem.*, 2019, 58, 7958–7968.
- 44 J. G. Kleingardner, B. Kandemir and K. L. Bren, J. Am. Chem. Soc., 2014, 136, 4–7.
- 45 N. Wang, H. T. Lei, Z. Y. Zhang, J. F. Li, W. Zhang and R. Cao, *Chem. Sci.*, 2019, **10**, 2308–2314.
- 46 G. B. Bodedla, L. L. Li, Y. Y. Che, Y. J. Jiang, J. Huang, J. Z. Zhao and X. J. Zhu, *Chem. Commun.*, 2018, 54, 11614–11617.
- 47 D. Khusnutdinova, B. L. Wadsworth, M. Flores, A. M. Beiler, E. A. R. Cruz, Y. Zenkov and G. F. Moore, ACS Catal., 2018, 8, 9888–9898.
- 48 H. X. Jia, Y. C. Yao, Y. Y. Gao, D. P. Lu and P. W. Du, Chem. Commun., 2016, 52, 13483–13486.
- 49 B. H. Solis, A. G. Maher, T. Honda, D. C. Powers, D. G. Nocera and S. Hammes-Schiffer, ACS Catal., 2014, 4, 4516–4526.
- 50 C. H. Lee, D. K. Dogutan and D. G. Nocera, J. Am. Chem. Soc., 2011, 133, 8775–8777.