Supporting Information for

Zn and Co Redox Active Coordination Polymers Based on Ferrocene-containing Diphosphinate Ligand as Efficient Electrocatalysts for Hydrogen Evolution Reaction

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EXPERIMENTAL SECTION

Reagents 1,1'-ferrocenylenbis(*H*-phosphinic) acid (H_2fcd*H*p), was prepared according to a literature procedure.[1] All other chemicals and solvents were purchased reagent grade and used as received.

Synthesis

Synthesis of **Znfcd*H*p (1)**. $Zn(NO_3)_2{\cdot}6H_2O$ (33 mg, 0.098 mmol) and H_2fcd*H*p (31 mg, 0.098 mmol) were placed into a 10 mL vial and dissolved in DMF/MeOH (1:3 v/v, 6 mL). The vial was placed into a preheated oven (80 °C) for 16 h. Orange crystals formed were washed with DMF/MeOH and dried in air. Yield: 77%. Anal. calcd. for $C_{10}H_{10}P_2O_4FeZn$: C, 31.82; H, 2.65. Found: C, 31.25; H, 2.60.

Synthesis of **Cofcd*H*p** (**2**). The identical reaction conditions except for the use of $Co(NO_3)_2·6H_2O$ (28 mg, 0.098 mmol) instead of $Zn(NO_3)_2·6H_2O$ were employed to produce dark green-bluish crystals of **2**. Yield: 57%. Anal. Calcd for $C_{10}H_{10}P_2O_4FeCo$: C, 32.35; H, 2.70. Found: C, 32.16; H, 2.61.

Structure Determination. The dataset from the single crystal of **2**, prepared in a glass capillary, was collected at beamline BL14.2, Joint Berlin-MX Laboratory of Helmholtz Zentrum Berlin, equipped with a MX-225 CCD detector (Rayonics, Illinois) and 1-circle goniometer.[2] The data collection was performed at room temperature using monochromatic radiation with $\lambda = 0.88561$ Å. XDSAPP software was used for processing of the diffraction images[3] []. Systematic absences were found for the screw axis 4_1 and therefore suggesting the chiral space group $P4_122$ (No 91) for the crystal structure solution and refinement. Data set for single crystal **1a** was collected on a Bruker AXS Kappa APEX Duo and for crystal **1b** was collected on a Bruker AXS Smart APEX II diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structures of both compounds **1a** and **1b** were solved by direct methods using following software: APEX3[4] for data collection, SAINT[5] for data reduction, SHELXS[6] for structure solution, SHELXL[34] for structure refinement by full-matrix least-squares against F^2, and SADABS[7] for multi-scan absorption correction. CCDC 1861598; 1861599; 1866808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1a: $C_{10}H_{10}FeO_4P_2Zn$, M = 377.34 g/mol, crystal size (mm) 0.180 x 0.120 x 0.120, temperature 150(2) K, tetragonal, space group $P4_122$ (No. 91), a = 8.254(2) Å, c = 18.660(4) Å, V = 1271.1(7) Å^3, Z = 4, ρ_{calc} = 1.972 g·cm^{-3}, μ = 3.279 mm^{-1}, θ range: from 2.70° to 25.62°, 3369 reflection collected ($-10 \le h \le 8, -10 \le k \le 7, -22 \le l \le 19$), 1194 independent reflections (R_{int} = 0.0527), 1051 observed reflections with $I \geq 2\sigma(I)$, 86 refined parameters, R = 0.0302, wR^2 = 0.0500, Flack parameter 0.03(2), max. residual electron density 0.271 (-0.266) eÅ^{-3}.

1b: $C_{10}H_{10}FeO_4P_2Zn$, M = 377.34 g/mol, crystal size (mm) 0.365 x 0.108 x 0.078, temperature 296(2) K, tetragonal, space group $P4_322$ (No. 95), a = 8.250(2) Å, c = 18.655(4) Å, V = 1296.7(7) Å^3, Z = 4, ρ_{calc} = 1.974 g·cm^{-3}, μ = 3.283 mm^{-1}, θ range: from 2.47° to 28.62°, 23622 reflection collected ($-11 \le h \le 11, -11 \le k \le 11, -24 \le l \le 24$), 1602 independent reflections (R_{int} = 0.0471), 1313 observed reflections with $I \geq 2\sigma(I)$, 86 refined parameters, R = 0.0320, wR^2 = 0.0724, Flack parameter -0.01(1), max. residual electron density 0.480 (-0.362) eÅ^{-3}.

2: $C_{10}H_{10}FeO_4P_2Co$, M = 370.90 g mol^{-1}, tetragonal, $P4_122$ *(No. 91)*, a = 8.2200(12) Å, c = 18.840(4) Å V = 1273.0(5) Å^3, Z = 4, ρ_{calc}= 1.935 g cm^{-3}, λ = 0.88561 Å, T= 293 K, $\theta_{\max}$ = 34.1°, reflections collected/unique 1374/1341, R_{int} = 0.023, R_1 = 0.0749, wR_2 = 0.2287, S = 1.15, Flack parameter 0.23(3), largest diff. peak 1.23 e Å^{-3} and hole -0.70 e Å^{-3}.

Thermogravimetry (TGA) and differential scanning calorimetry (DSC)

The thermal stabilities of solid samples were investigated by simultaneous thermogravimetry/differential scanning calorimetry (TG/DSC) analysis using NETZSCH (Selb, Germany) STA449 F3 instrument. Approximately 5 - 6 mg of samples were placed into an Al_2O_3 crucible with a pre-hole on the lid and heated from 30 to 1200 °C. The same empty crucible was used as the reference. High-purity argon was used with a gas flow rate of 50 mL/min. TG/DSC measurements were performed at the heating rates of 10 °C/min.

IR spectroscopy

IR spectra of samples were measured using Bruker Vector-27 FTIR spectrometer in the 400 – 4000 cm^{-1} range (optical resolution 4 cm^{-1}). The samples were prepared as KBr pellets.

Raman spectroscopy

Raman spectra were collected at room temperature using a BRUKER RAM II module attached to a BRUKER VERTEX 70 FTIR spectrometer (excitation 1064 nm, Ge detector at liquid nitrogen temperature, back-scattering configuration; range 10-4000 cm^{-1} , optical resolution 4 cm^{-1}, scan number 1024). The samples were inserted in a standard aluminum crucible.

UV-vis/DR ***spectroscopy***

Powder samples were characterized by **UV-vis/DR** technique using a Jasco V-650 spectrophotometer (Jasco International Co. Ltd., Hachioji, Tokyo, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition. $BaSO_4$ powder was used as the reference for baseline correction. The obtained reflectance spectra were transformed into the dependencies of KubelkaMunk function F(R) on the absorption energy hν using the equation

$$F(R) = \frac{(1 - R)^2}{2R}$$

where R is the measured diffuse reflectance from a semi-infinite layer [8].

Magnetic Measurements

Static magnetization measurements were performed with a commercial SQUID (superconducting quantum interference device) VSM (vibrating sample magnetometer) from Quantum Design in static magnetic fields up to 7 T in the temperature range 1.8 - 300 K.

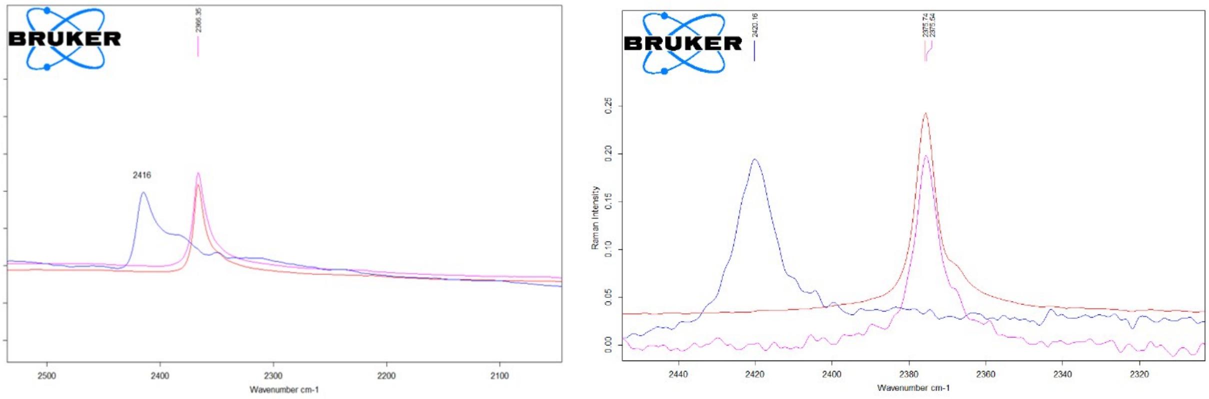

Fig. S1 IR (left) and Raman (right) spectra of ν(P-H): Ligand H_2fcd*H*p (blue), and **1** (purple), **2** (red) coordination polymers.

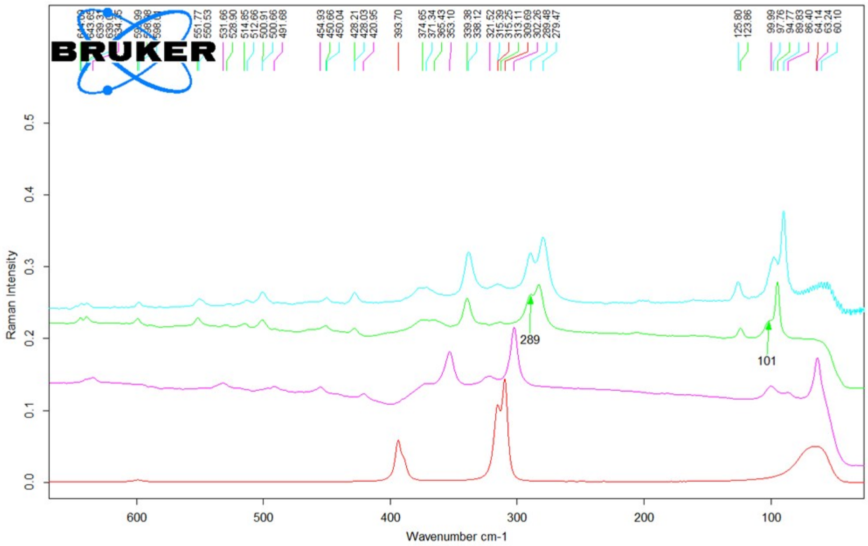

Fig.S2. Low-frequency range of Raman spectra of crystals: ferrocene (red), H_2fcd*H*p (purple), **1** (green), **2** (blue).

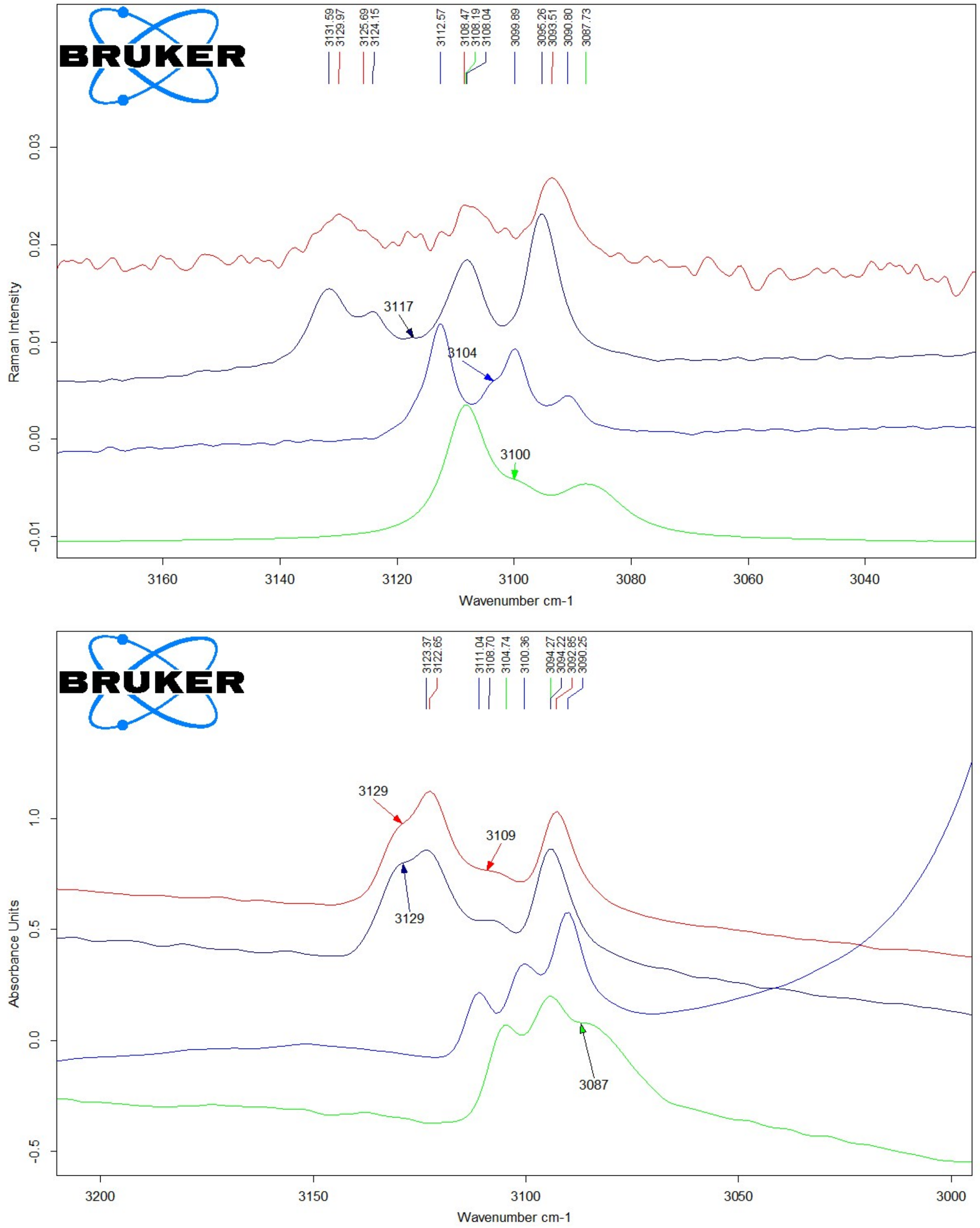

Fig. S3. Raman (up) and IR (bottom) spectra of crystalline ferrocene (green), ligand $H_2fcd\textit{H}p$ (blue), and coordination polymers **1** (dark blue), **2** (red).

Table S1. Positions and assignment of some bands in vibrational spectra of crystalline FeCp2, ligand H_2fcd*H*p, and coordination polymers: **1** and **2.**

Assignment	Ferrocene		H_2fcd*H*p		Co/Zn	
	IR	Raman	IR	Raman	IR	Raman*
C-H stretching	- - 3105 3095 - 3085 br	- - 3108 3100sh. - 3088 br	- - 3111 3104 - 3090 br	- - 3113 3103 sh 3100 3091	3129 sh. 3123/3125 3107 vw 3093/3095	3132 3124 3108 3095
P-H stretching	-	-	2414	2420	2366/2367	2376

*Only band frequencies of **1** are shown (see experimental part).

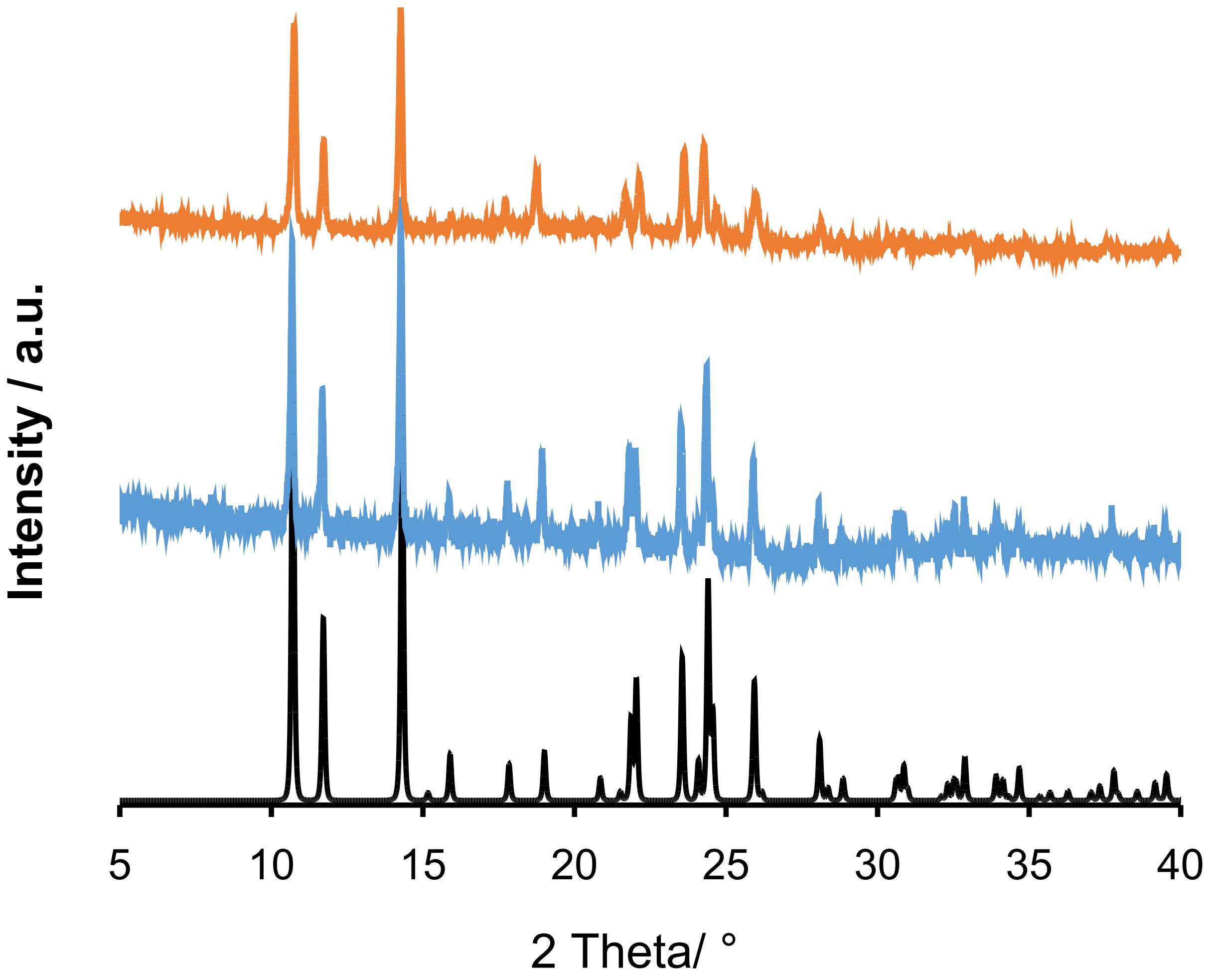

Fig. S4 Powder XRD CPs of Zn **1** (blue) and Co **2** (red) and Simulated for Zn (black)

Electrochemical data

Electrochemical measurements were taken on a BASiEpsilonE2P electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A conventional three-electrode system was used with glassy carbon for carbon paste electrode (CPE) solutions for powder samples as the working electrode, the An Fc^+/Fc system was served as reference electrode, and a Pt wire as the counter electrode. 0.1 M Et_4NBF_4 was used as the supporting electrolyte to determine the current–voltage characteristics. To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-*tert*-butyl)phosphonium tetrafluoroborate) composite electrode was prepared using a grinding a mixture of graphite powder and phosphonium salt with a 90/10 (w/w) ratio in mortar giving it a homogeneous mass. A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the CPs under study. As a result, a portion of the resulting paste was packed firmly into the (3 mm in diameter) a Teflon holder cavity. The performances of electrocatalysts can be evaluated by many parameters, such as the onset potential (E_{onset}), overpotential (η) at a specific current density ($j=10$ mA cm^{-2}), Tafel slope (TS), turnover frequency (TOF), stability/durability.

Supposing that all the current is used for the electrochemical reaction, the theoretical TOF value in 0.5 M H_2SO_4 can be simply calculated by $TOF_{theoretical} = j/(n \times F \times m/M)$ [9] where n is the number of electrons involved in reaction, m is the mass loading of the catalyst (mg cm–2), and M is the molecular weight of the catalyst unified with one active center per formula unit.

The turnover frequencies in CH_3CN using $[(DMF)H]^+$ as acid were determined using equation:

$$\mathrm{TOF} = \upsilon \cdot \left(\frac{i_{cat}/i_p}{0.72} \right)^2$$

from i_{cat}/i_p values [10]. i_{cat} is the catalytic current measured in the presence of acid, i_p is the peak current of the Co(II/I) couple in the absence of acid for **2,** v is scan rate in V/s.

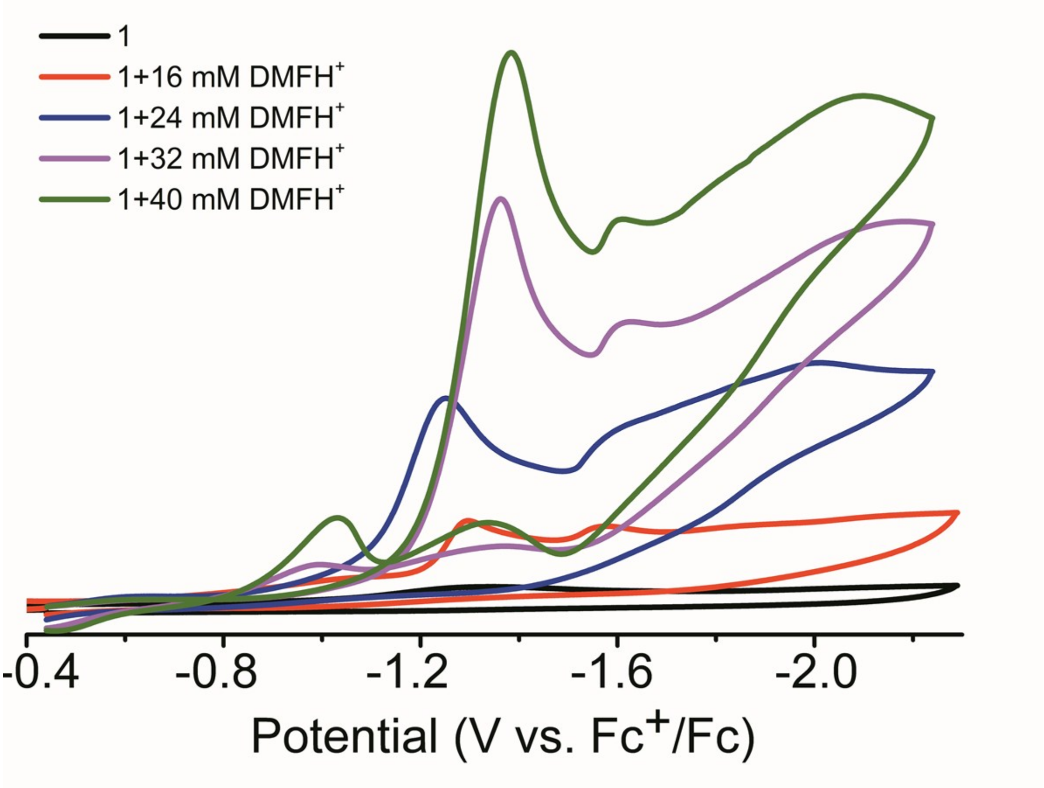

Fig. S5. Cyclic voltammograms obtained with a modified CPE for **1** in the presence of various amounts of [(DMF)H]OTf in acetonitrile. Conditions: 0.1 V/s scan rate, 0.1 M Bu_4NBF_4.

Dynamic study of the coordination polymers state in water and acids over time by CV and XRPD.

For illustration, the time intervals were chosen at which simultaneous changes were observed both on the voltammograms of polymers **1** and **2**, and on powder diffraction patterns, and color of **1** and **2** were changed.

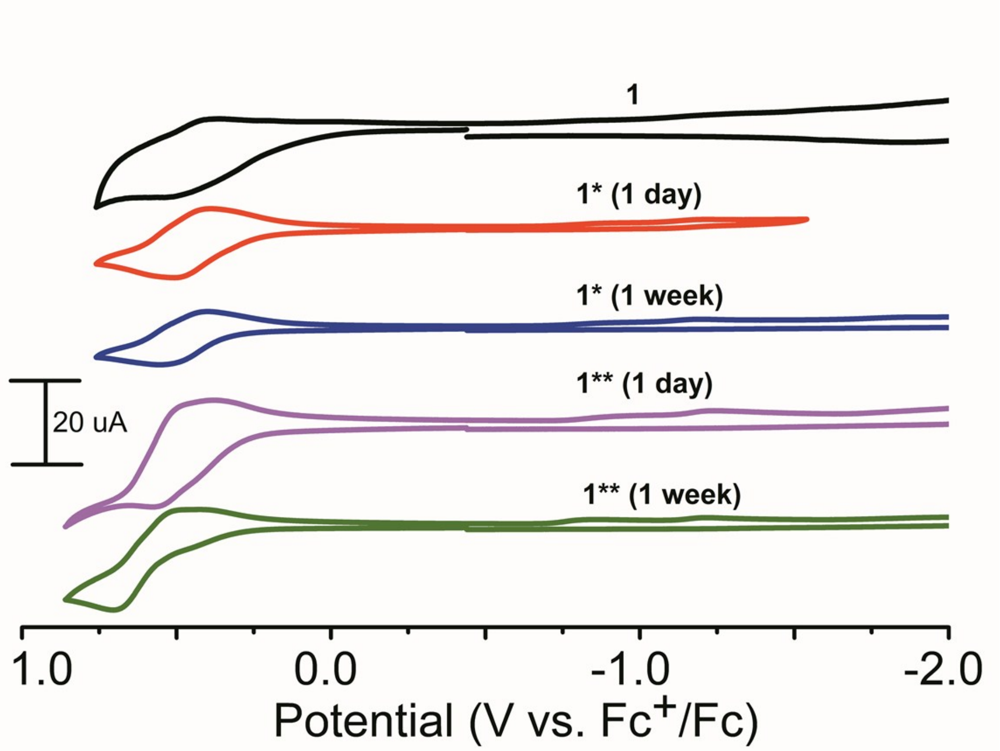

Fig.S6. CVs for **1** before and after 1 day or 1 week storing in water (**1***) or 0.5M H_2SO_4 (**1****) in CH_3CN.

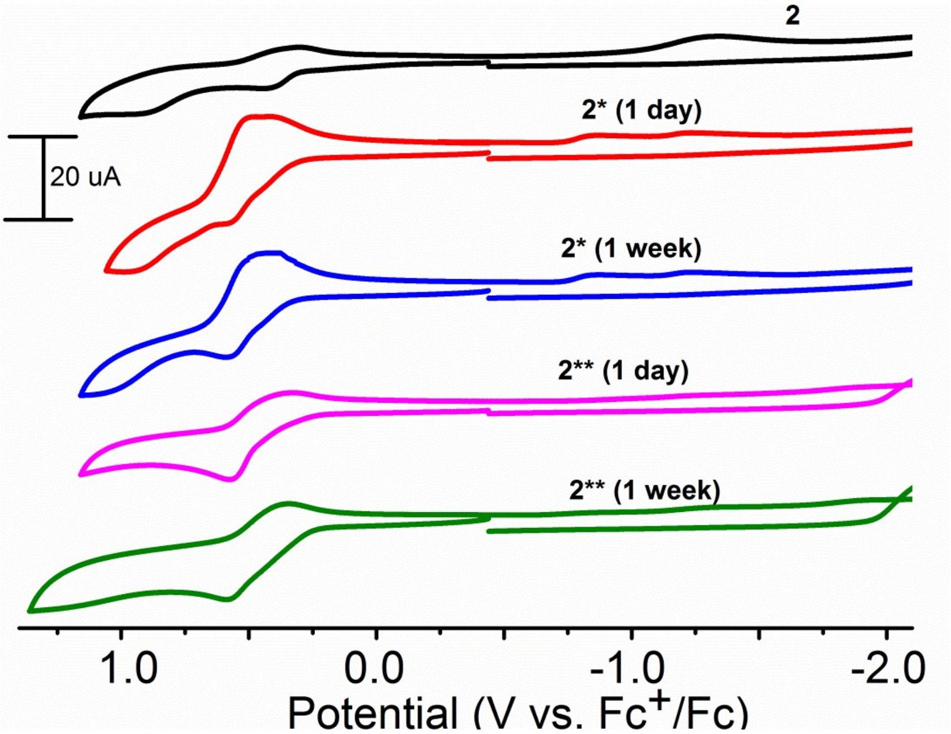

Fig.S7. CVs for **2** before and after 1 day or 1 week storing in water (**2***) or 0.5M H_2SO_4 (**2****) in CH_3CN.

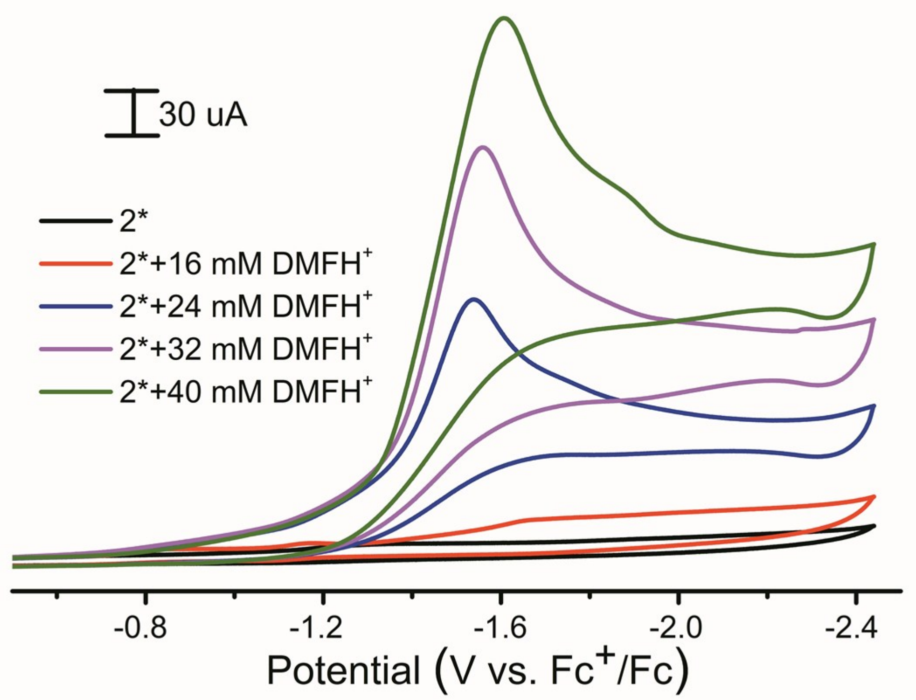

Fig.S8. CVs for **2** after 1 week storing in water (**2***) in the presence of DMFH$^+$ in CH_3CN

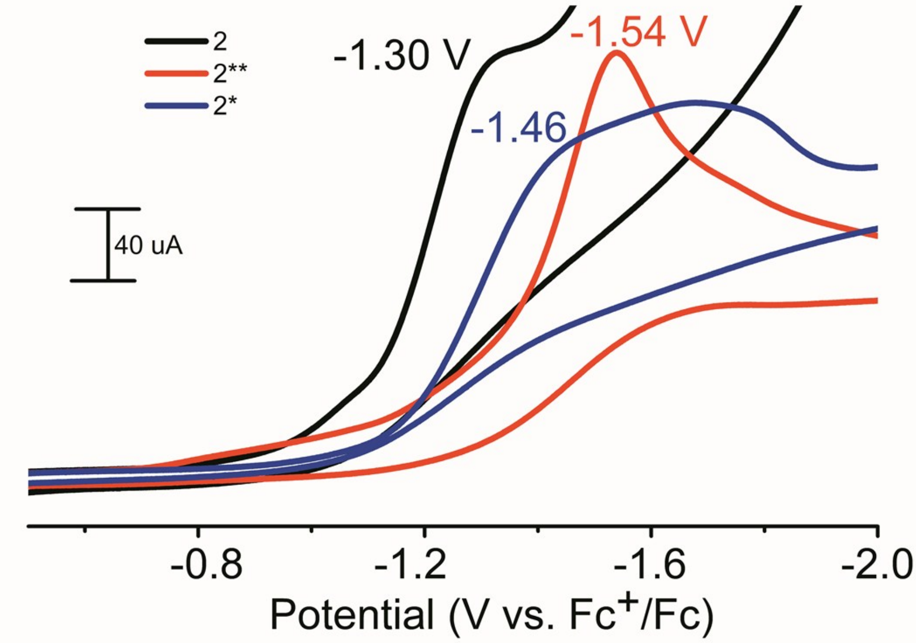

Fig.S9. CVs for **2** before and after 1 week storing in water (**2***) or 0.5M H_2SO_4 (**2****) in the presence of 24 mM DMFH$^+$ in CH_3CN

X-ray powder diffraction (XRPD) experiment

X-ray powder diffractograms were determined using Rigaku MiniFlex 600 diffractometer equipped with a D/teX Ultra detector. In this experiment, Cu*Kα* (λ = 1.54178 Å) radiation (30 kV, 10 mA) was used, Kβ radiation was eliminated with Ni filter. The diffractograms were determined at RT in the reflection mode, with step 0.02° and scanning speed 5°min^{-1}. Powder samples were loaded into a glass holder. Patterns were recorded without sample rotation. For each sample several experiments were performed, allowing to control stability of the samples and quality of the experiments. The experimental powder diffraction patterns show on Figure S4.

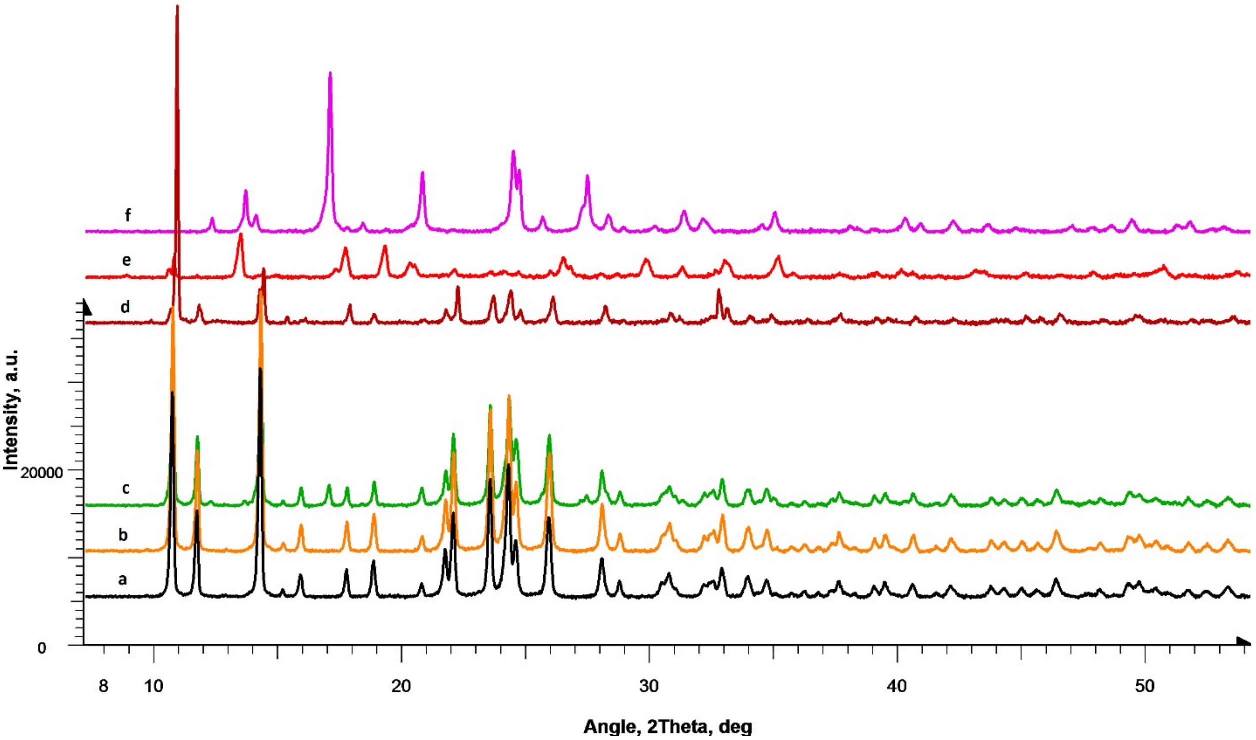

Figure S10. XRPD data for the samples (a) CPs of Zn (**1**), (b) CPs of Zn **1*** (1 week in H_2O), (c) CPs of Zn **1****(1 week in 0.5M H_2SO_4), (d) CPs of Co (**2**), (e) CPs of Co **2*** (1 week in H_2O), (f) CPs of Co **2****(1 week in 0.5M H_2SO_4).

According to XRPD data (Figure S10), the crystal form of **CPs-Zn** practically does not experience any changes after exposure to water, and the diffraction patterns for samples **a** and **b** are identical. Sulfuric acid treatment apparently leads to the appearance of an insignificant amount of a new crystalline phase, as evidenced by the appearance of several new interference peaks in the diffractogram of the sample **c** in the region of diffraction angles 2θ 12 °, 13-14 °, 17 °, 28-29 ° and 31-32 °.

The crystalline form of **CPs-Co** is characterized by a large lability of the crystal structure, which is expressed in a drastic change in the crystal structure of the compound (curve **d**) both after treatment with water (diffractogram **e**) and sulfuric acid (curve **f**). Moreover, a comparison of the diffractogram (**f**) with difference peaks in the diffractogram from a sample (**c**) of the form CPs-Zn after treatment with sulfuric acid, we can note the isostructural nature of the newly formed crystalline phase in CPs-Co with the similar minor crystalline phase in CPs-Zn.

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[1] Cao, C. Y.; Wei, K. J.; Ni, J.; Liu, Y., Solvent-induced two heterometallic coordination polymers based on a flexible ferrocenyl ligand. *Inorganic Chemistry Communications*. **2010**, *13*,

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19-21.

[2] Mueller, U.; Darowski, N.; Fuchs, M. R.; Förster, R.; Hellmig, M.; Paithankar, K. S.; Weiss, M. S., Facilities for macromolecular crystallography at the Helmholtz-Zentrum Berlin. *Journal of synchrotron radiation*. **2012**, *19*, 442-449.

[3] Krug, M.; Weiss, M. S.; Heinemann, U.; Mueller, U., XDSAPP: a graphical user interface for the convenient processing of diffraction data using XDS *J. Appl. Cryst.* **2012,** *45*, 568–572.

[4] Bruker, A. X. S. APEX2-Software Suite for Crystallographic Programs. *Bruker AXS, Inc., Madison, WI, USA*. **2009.**

[5] Bruker. Area detector control and integration software. Version 6.0. In: SMART and SAINT. *Madison, Wisconsin (USA): Bruker Analytical X-ray Instruments Inc.*; **2003.**

[6] Sheldrick, G. M. A short history of SHELX. *Acta Crystallographica Section A: Foundations of Crystallography*. **2008**, *64*, 112-122.

[7] Sheldrick, G. M., SADABS. Program for absorption correction. University of Göttingen, Institut für Anorganische Chemie, Tammanstrasse 4, D-3400 Göttingen, Germany, **1997**.

[8] Kubelka, P.; Munk, F. Z. *Thech. Phys*. **1931**, 12, 593.

[9] P.-Q. Liao, J.-Q. Shen, J.-P. Zhang, *Coord. Chem. Rev*., **2018**, 373, 22–48

[10] M.L. Helm, M.P. Stewart, R.M. Bullock, M.R. DuBois, D.L. DuBois, *Science*, **2011**, 333, 863-866.