

Supporting Information for

Excellent Supercapacitor and Sensor Performance of Robust Cobalt Phosphinate Ferrocenyl Organic Framework Materials Achieved by Intrinsic Redox and Structure Properties

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Experimental section

1. Synthesis

Reagents 1,1'-ferrocenylenbis(*H*-phosphinic) acid (H_2fcdHp), was prepared according to a literature procedure.¹ All other chemicals and solvents were purchased reagent grade and used as received.

Synthesis of $[Co(H_2O)_2(Fc(PHO_2)_2) \cdot 2H_2O]_n$ (2**)** $Co(NO_3)_2 \cdot 6H_2O$ (46.6 mg; 0.16 mmol) and $Fc(P(O)(H)OH)_2$ (50.2 mg; 0.16 mmol) were dissolved in 4 ml of water/acetone mixture (1:3). After several hours at room temperature, orange crystals of **2** were obtained. Yield: 63.3 mg (89%) based on 1,1'-ferrocenediyl-bis(*H*-phosphinic acid).

Anal. Calcd. for **2** $C_{10}H_{18}FeCoO_8P_2$ (442.97 g/mol): C: 27.09; H: 4.63%. Found: C: 27.01; H: 4.62%. IR (nujol, cm^{-1}): 3386 s, 3135 w, 3116 w, 2454 m, 1642 s, 1563 m, 1425 m, 1325 m, 1193 s, 1185 s, 1133 vs, 1064 sh, 1044 vs, 1034 s, 1028 s, 991 s, 925 w, 910 m, 881 m, 838 s, 650 s, 531 s, 493 s, 474 s, 456 s.

Synthesis of $[Co(FcPHOO_2)]_n$ (2'**)**. The compound **2'** was obtained by drying **2** under vacuum for 24 h at 150 °C. Removal of all solvent molecules was proved by TGA. Anal. Calcd. for **2'** $C_{10}H_{10}FeCoO_4P_2$ (370.91 g/mol): C: 32.35; H: 2.70%. Found: C: 32.59; H: 2.91%. IR (nujol, cm^{-1}): 3386 w, 3097 w, 2340 m, 1574 w, 1425 m, 1313 w, 1189 vs, 1180 vs, 1163 vs, 1070 s, 1051 s, 1016 s, 986 s, 897 m, 837 m, 642 s, 472 s.

Elemental analyses were carried out using CHNS-O high-temperature element analyzer Eurovector EuroEA3028-HT-OM.

2. Structure Determination

Data sets for single crystal **2** were collected on a Bruker Kappa APEX II diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using APEX3 [2] for data collection, SAINT [3] for data reduction, SHELXS [4] for structure solution, SHELXL [4] for structure refinement by full-matrix least-squares against F^2 , and SADABS [5] for multi-scan absorption correction. Hydrogen atoms at carbon atoms were placed into calculated positions and refined as riding atoms. Hydrogen atoms of the hydroxyl groups were revealed from difference Fourier map and refined isotropically with geometry constraints. CCDC 1946867 contains the supplementary crystallographic data for this paper.

Crystal data: formula $C_{10}H_{14}CoFeO_6P_2 \cdot 2(H_2O)$, $M = 442.96 \text{ g/mol}$, monoclinic, space group $P 2_1/c$ (No. 14), $Z = 2$, $a = 10.0734(6) \text{ \AA}$, $b = 5.3953(3) \text{ \AA}$, $c = 13.2485(7) \text{ \AA}$, $\beta = 99.316(3)^\circ$, $V = 710.55(7) \text{ \AA}^3$, $\rho_{\text{calc}} = 2.070 \text{ g}$

cm^{-3} , $\mu = 2.451 \text{ mm}^{-1}$, multi-scan absorption correction was applied using SADABS⁴, 10412 reflections collected ($-13 \leq h \leq 13$, $-7 \leq k \leq 7$, $-17 \leq l \leq 17$), θ range = 2.049° to 27.994° , 1718 independent ($R_{\text{int}} = 0.0433$) and 1416 observed reflections [$I \geq 2 \sigma(I)$], 123 refined parameters, $R = 0.0277$, $wR^2 = 0.0718$, max. residual electron density 0.485 (-0.539) $\text{e} \text{ \AA}^{-3}$.

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 $10^\circ\text{C}/\text{min}$.

4. IR spectroscopy

IR spectra of samples were measured using Bruker Vector-27 FTIR spectrometer in the $400 - 4000 \text{ cm}^{-1}$ range (optical resolution 4 cm^{-1}). The samples were prepared as KBr pellets. have been registered using Bruker Vector-27 FTIR spectrometer in the $400 - 4000 \text{ cm}^{-1}$ range (optical resolution 4 cm^{-1}). The samples were prepared as KBr pellets. The spectra of 2' and 3' registered in KBr pellets contain bands at ca. 3400 and 1637 cm^{-1} due to adsorbed in KBr water.

5. UV/Vis 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.

6. Quantum-chemical computations

All quantum-chemical calculations were performed with the Gaussian 16 suite of programs.[51] The hybrid B3LYP functional [52,53] and the Ahlrichs' triple- ζ def-TZVP AO basis set [53] were used for optimization of all structures. In all geometry optimizations, the D3 approach [54] to describe the London dispersion interactions together with the Becke-Johnson (BJ) damping function [55-57] were employed as implemented in the Gaussian 16 program.

7. Electrochemistry

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 $\text{An Fc}^+/\text{Fc}$ system was served as reference electrode, and a Pt wire as the counter electrode. $0.1 \text{ M Et}_4\text{NBF}_4$ 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 cells were charged in the galvanostatic mode with an Autolab (ECO-Chemie, Utrecht, Netherlands). They were discharged by using a resistor, voltmeter, and multimeter by constant current discharge. The duration of each charge and discharge was 4 min and the cycling was performed without rest time. The change in cell voltage during charging and discharging was measured at intervals of 5 min.

8. Physisorption experiments of nitrogen were performed at 77 K up to 1 bar using Quadrasorb apparatus (Quantachrome Co.). Water and methanol vapor physisorption was investigated at 298 K using Hydrosorb 1000 apparatus (Quantachrome Co.).

9. X-ray powder diffraction (XRPD) experiments.

The X-ray diffraction analysis was performed on the equipment of Spectral-Analytical Center of FRC Kazan Scientific Center of RAS.

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using Cu radiation (40 kV, 40 mA) monochromated by the curved Johansson monochromator (λ Cu $K_{\alpha 1}$ 1.5406 Å). Room-temperature data were collected in the reflection mode. The samples were loaded on a standard zero diffraction silicon plate, which was kept spinning (15 rpm) throughout the data collection. The sample **1** of initial Co₂D-composite was preliminarily ground to a homogeneous state and then, without pressing, was applied onto a silicon plate, which reduces background scattering. Sample **2** was applied in liquid form on the surface of a standard zero diffraction silicon plate. After drying the layer, a few more layers were applied on top of it to increase the total amount of the sample. Patterns were recorded in the 2θ range between 3° and 70°, in 0.008° steps, with a step time of 0.1–1.0s. Several diffraction patterns in various experimental modes were collected for the samples. Processing of the obtained data performed using EVA [DIFFRAC Plus Evaluation package EVA, Version 11 (2005). User's Manual, Bruker AXS, Karlsruhe, Germany. - 258 p] software packages. The PDF-2 powder X-ray diffraction database (ICDD PDF-2, Release 2005-2009) was used to identify the crystalline phase.

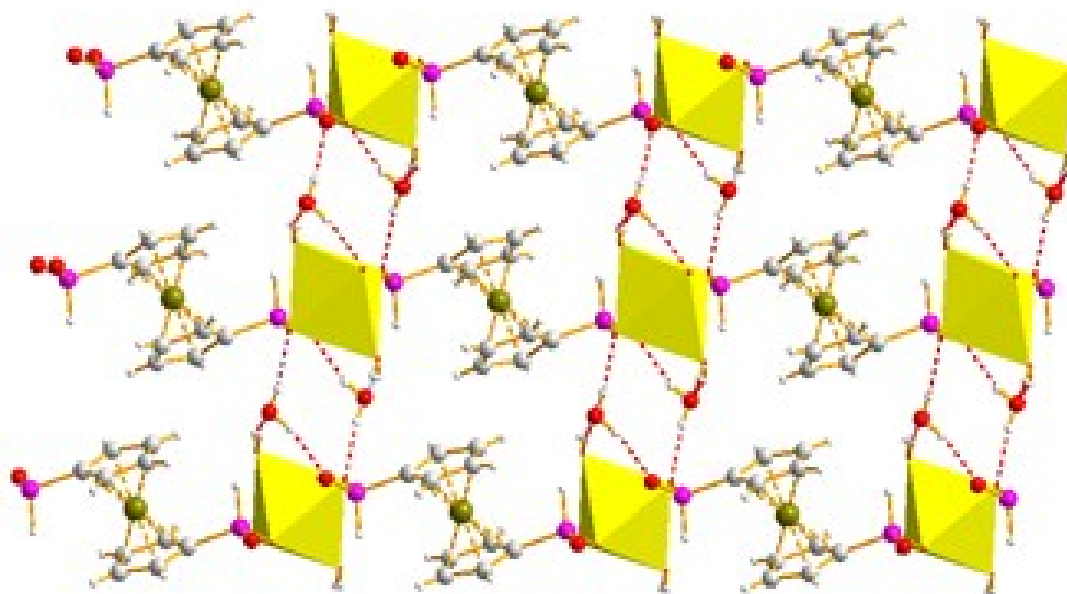


Figure S1. The hydrogen bonding (dashed lines) in cobalt (1,1'-ferrocenediyl-bis(*H*-phosphinate)) tetrahydrate.

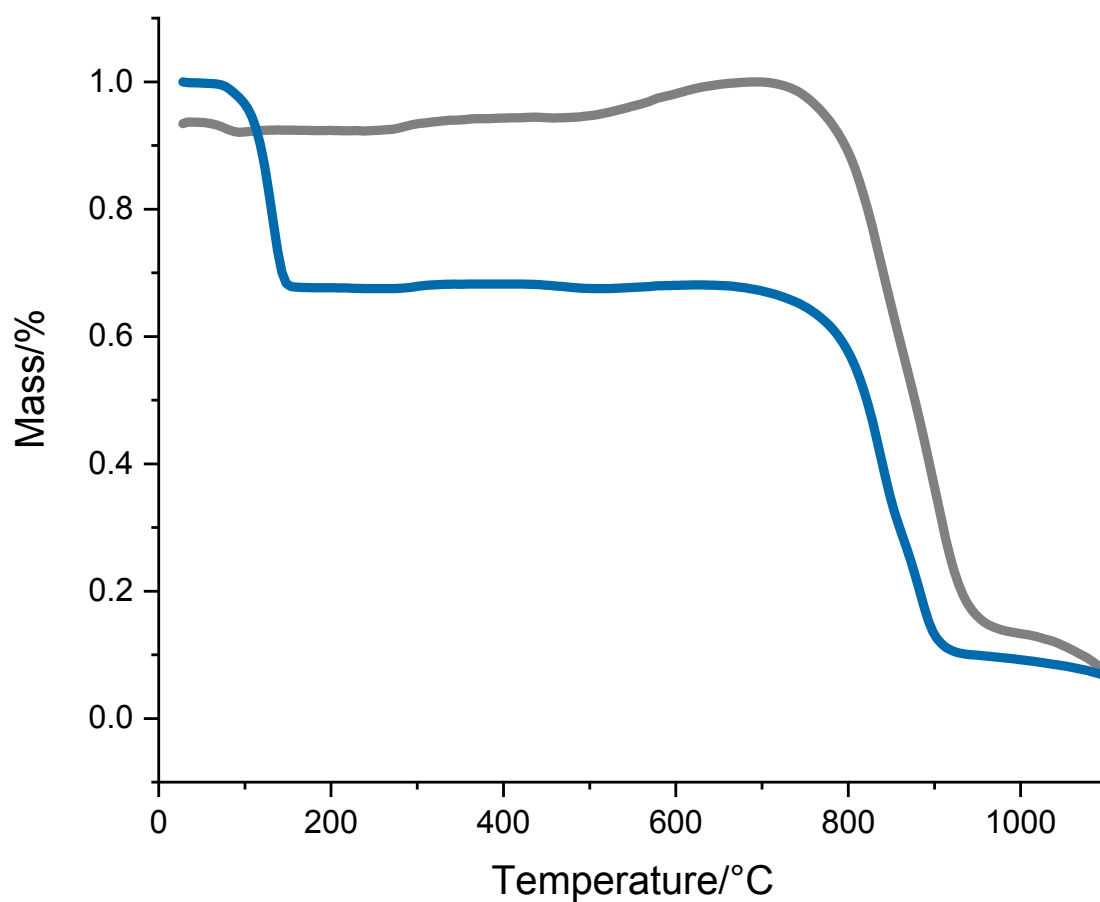


Figure S2. TG curves for the as-synthesized (blue) and dehydrated (grey) forms of 2 in Ar atmospheres at a heating rate of 5 K/min.

To estimate the binding energies of lattice and coordinated water the simplified models had been optimized: tetrahedral model **m1** for the dehydrated $\text{Co}(\text{Fc}(\text{PHOO})_2)_n$ complex; by octahedral model **m2** for “half-hydrated” complex $[\text{Co}(\text{H}_2\text{O})_2(\text{Fc}(\text{PHOO})_2)]_n$ and octahedral model **m3** with two additional water molecules for “fully” hydrated complex $[\text{Co}(\text{H}_2\text{O})_2(\text{Fc}(\text{PHOO})_2) \cdot 2\text{H}_2\text{O}]_n$ (Figure S). Quantum-chemical computations predict the energy difference between m2 and m1 with four water molecules to be 79 kcal/mole (19.8 kcal/mole per one H_2O molecule). The predicted difference between m3 and m2 with two water molecules is 34.2 kcal/mole (17.1 kcal/mole per one H_2O molecule). These results explain the simultaneous elimination of both types of water molecules.

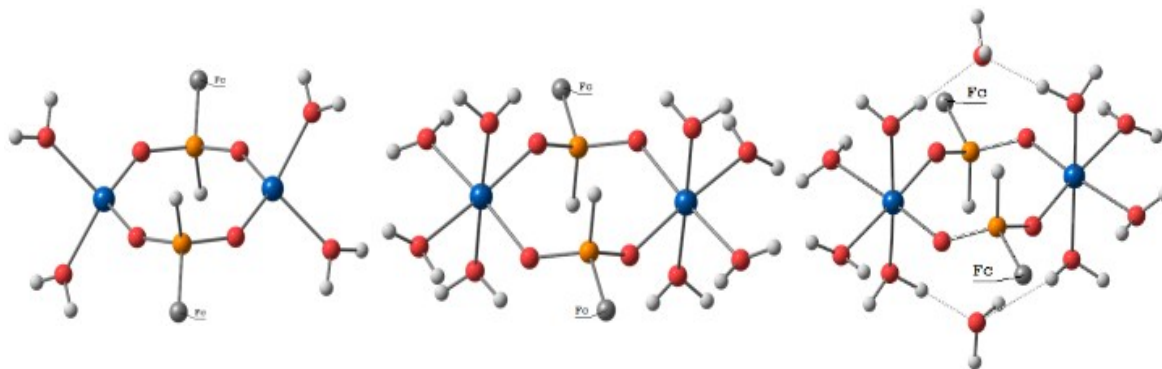


Figure S3. Optimized structures of models m1-m3.

The following equation is used to calculate the specific capacitance of the electrode (C, F g⁻¹)

$$C = \frac{It}{m\Delta V}$$

Where ***I*** is the constant current (A) of the charge-discharge processes; ***t*** is the discharge time (s); ***m*** is the mass of the electroactive material (Co-polymers) on the electrode (g); and **ΔV** (V) is the potential window.

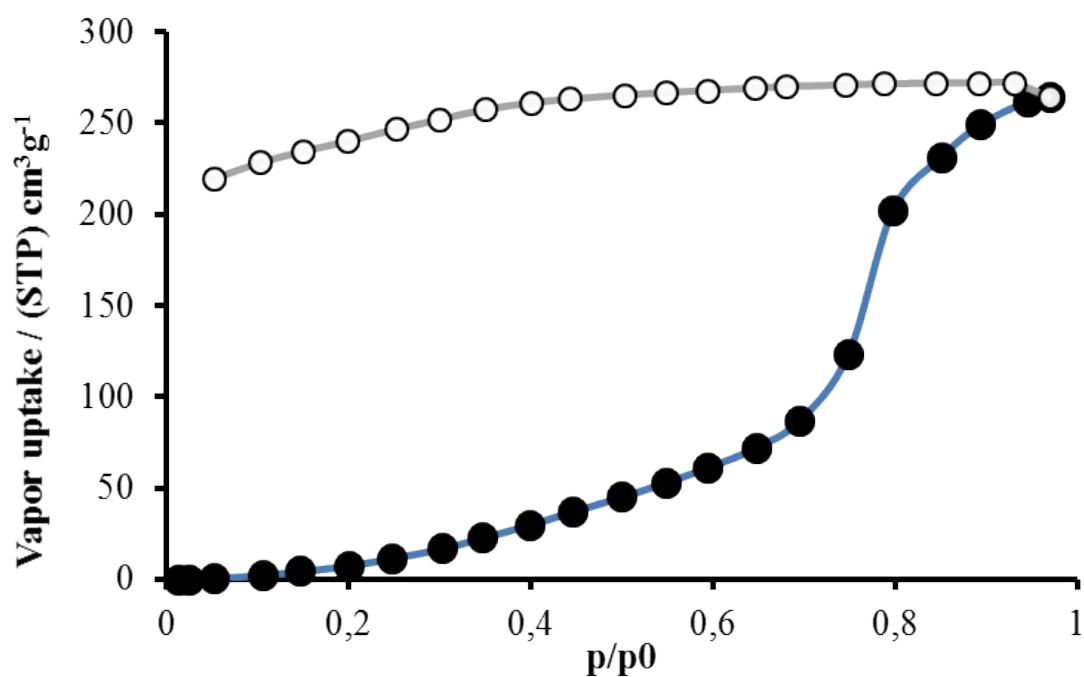


Figure 4. Adsorption (closed symbols) and desorption (open symbols) isotherms of H_2O vapor (298 K) for **2'**.

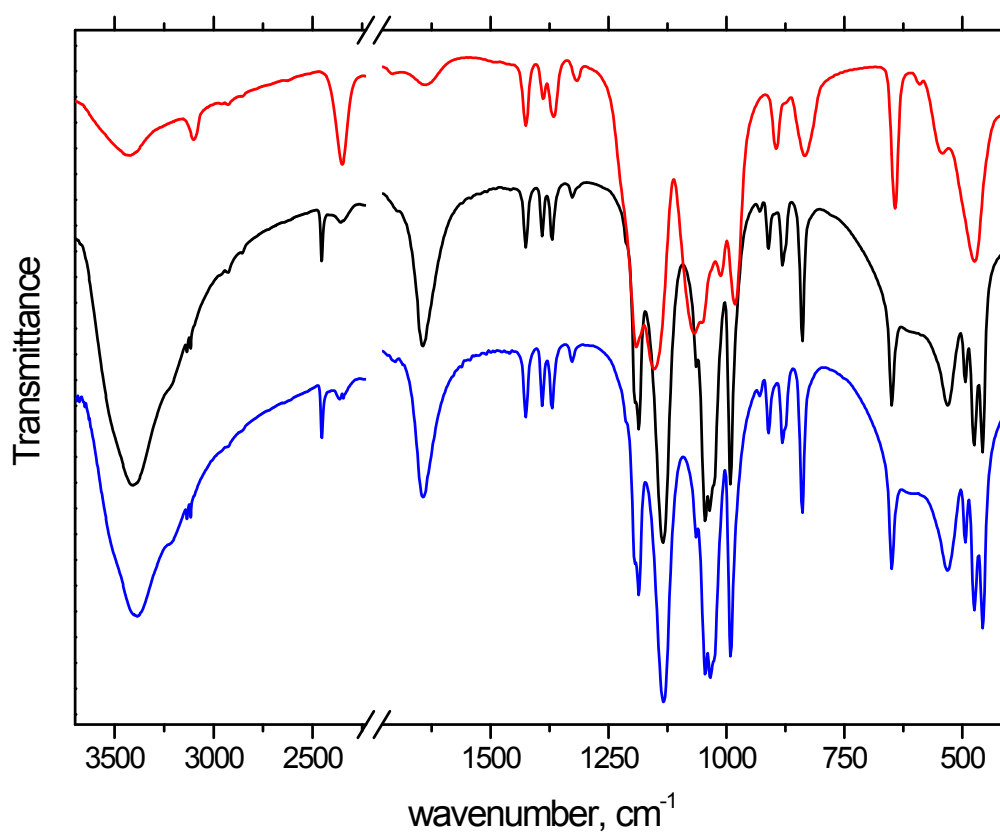


Figure S5. Comparison of IR spectra of **2** (black), **2'** (red), **2'** after water sorption (blue).

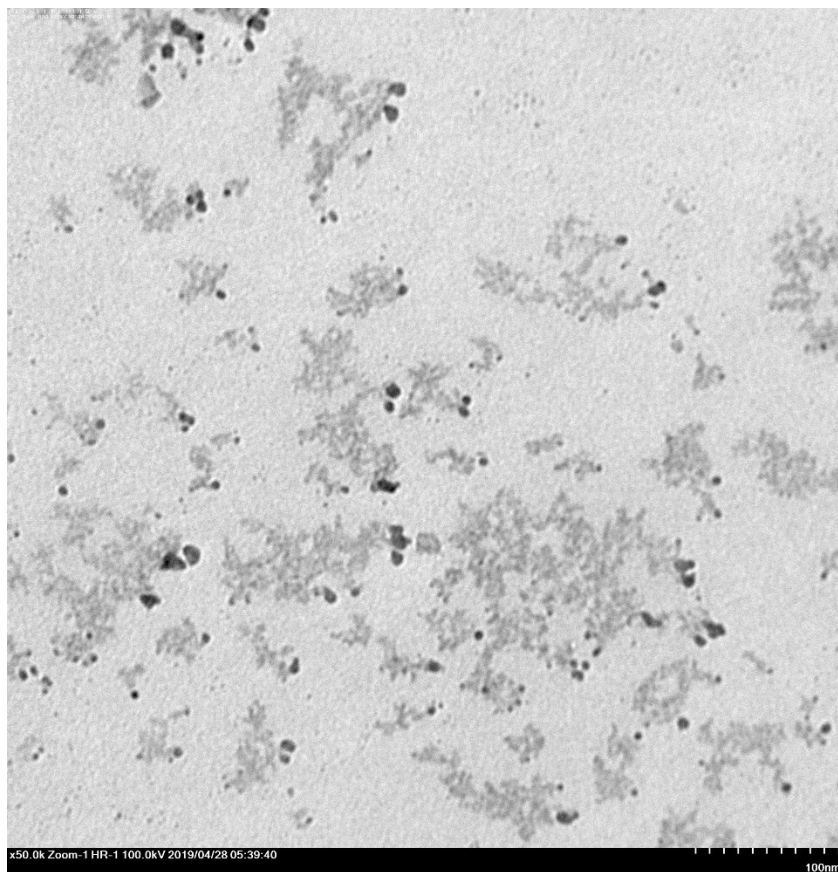


Figure S6. TEM image of $[\text{Co}(\text{Fc}(\text{PHOO})_2)]_n$ (dehydrated form)

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