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Supplementary Material

Structure and Facile Synthesis of a $[Fe(CN)_6]^{3-}$ Bridging Cd-Complex for Proton Conduction

Wei-Min Ding,[A] *Yao Zhao,*[A] *Hong-Yu Zhang,*[A] *and Feng-Ming Zhang*[A,B]

[A]Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, Harbin University of Science and Technology, No. 4, Linyuan Road, Harbin 150040, China.

[B]Corresponding author. Email: zhangfm80@163.com

Instrumentation

All the starting solvents and reagents, unless otherwise noted, were commercially available and used with no further purification. $K_3[Fe(CN)_6]$, $Cd(Ac)_2{\cdot}2H_2O$, 4,4′-bipyridine (bipy) were obtained from the Aldrich Chemical Co.

Scanning electron microscopy (SEM) micrographs was obtained with Hitachi S-4800 instrument. Infrared spectrum using the KBr pellet was measured on a Bruker Tensor 27 in the range of 4000-400 cm^{-1}. Thermogravimetric (TG) analysis was carried out on a Netzch STA449F3 analyser at a heating rate of 5 °C/min from ambient temperature to 800 °C. The room temperature powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max 2500/PC diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator.

X-ray crystallography. The single-crystal diffraction data for compound **1** was collected on a Bruker AXS smart Apex CCD diffractometer at 296 K. The X-ray generator was operated at 50 kV and 35 mA using Mo-Kα (λ = 0.71073 Å) radiation. The crystal structures were solved and refined by full matrix least-squares methods against F^2 by using the program SHELXL-2014[1] using the Olex-2 software.[2]All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen positions were fixed at calculated positions and refined isotropically. The topological analyses were performed with TOPOS.[3-4]

Impedance analysis. The samples were put into a homemade mould with a diameter of 0.2 cm radius to get circular pellets. The thickness was measured by a vernier caliper. And then the pellets were smeared by silver colloid on two sides which were fixed on the sample stage with gold wires. The proton conductivities were measured using an impedance/gain-phase analyzer (Solartron S1 1260) over a frequency range from 1 Hz to 1 MHz with an input voltage range from 100 mV to 3000 mV. The measurements were operated at temperatures (25 to 60 °C), with different relative humidities (40% to 98%RH). The proton conductivity was calculated using the following equation

$$\sigma = \frac{l}{SR}$$

whereσ is the conductivity (S cm^{-1}), l is the thickness (cm) of the pellet, S is the cross-sectional area (cm^2) of the pellet and R is the bulk resistance (Ω). The activation energy (E_a) was calculated from the following equation

$$\ln \sigma_T = \ln \sigma_0 - \frac{E_a}{KT} \qquad (K = 8.6\times10^{-5}\ \text{eV/K})$$

where$\sigma$is the conductivity (S cm^{-1}), K is the Boltzmann constant (eV/K) and T is the temperature (K).

ZView software was used to measure bulk resistance through an equivalent circuit simulation to get the Nyquist plots and resistance values by fitting the semicircles.

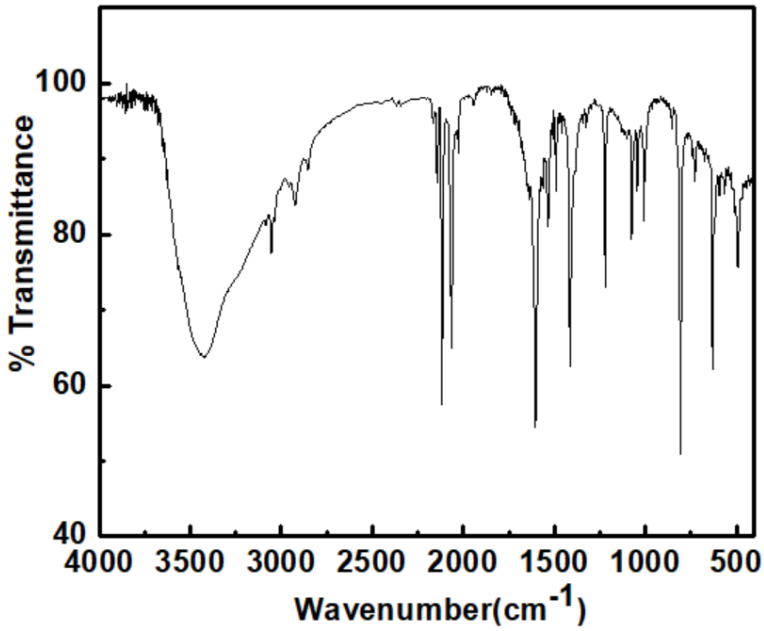

Figure S1. Infrared spectrum of compound **1**.

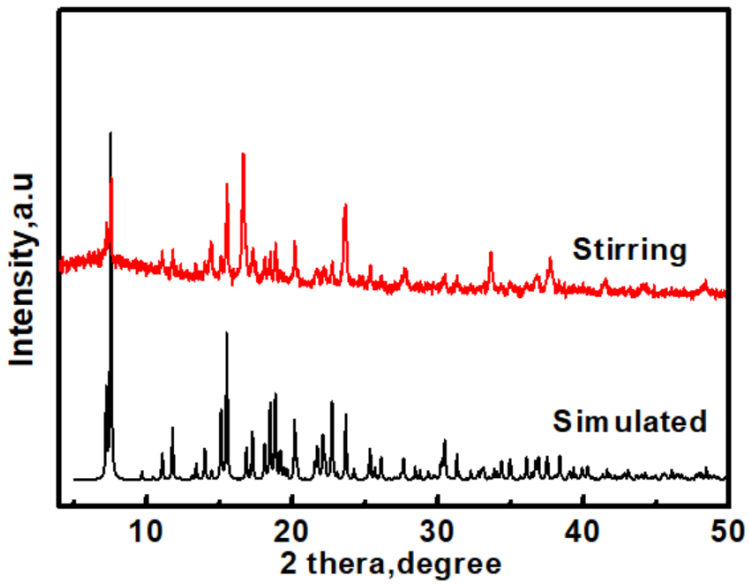

Figure S2. The PXRD patterns of compound **1** obtained by stirring method.

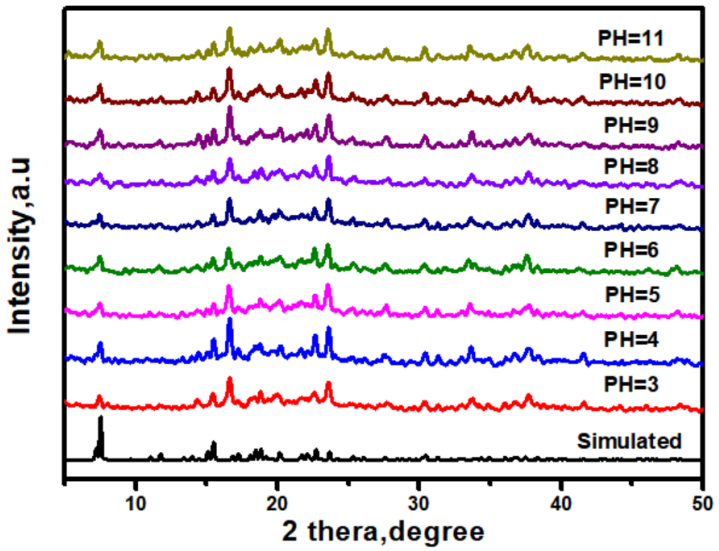

Figure S3. The PXRD patterns of compound **1** samples after immersed in different pH solutions.

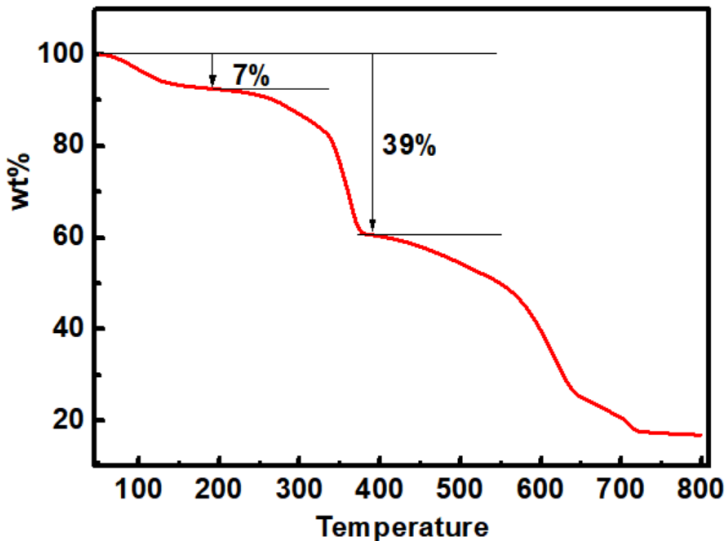

Figure S4. Thermogravimetric analyses of compound **1**.

Table S1. Comparison of proton conductivity of compound **1** with some other representative proton conductors measured under hydrous condition.

Compounds	**σ (S cm^{-1})**	***E*$_a$ (eV)**	**Reference**
compound **1**	8.36×10^{-4} (60°C, 95%RH)	0.602	This work
Nafion	5×10^{-2} (30°C, 98%RH)	0.22	5

$Fe(ox)\cdot 2H_2O$	3.23×10^{-3} (45°C, 98%RH)	0.37	6
PCMOF-3	3.5×10^{-5} (25°C, 98%RH)	0.17	7
$(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$	1.7×10^{-3} (40°C, 96%RH)	0.23	8
$Fe(OH)(bdc\text{-}(COOH)_2)$	7×10^{-6} (80°C, 95%RH)	0.21	9
$\{NMe_3(CH_2COOH)\}[FeCr(ox)_3]\cdot nH_2O$	0.8×10^{-4} (25°C, 65%RH)	/	10
$\{NEt_3(CH_2COOH)\}[MnCr(ox)_3]\cdot nH_2O$	2×10^{-4} (25°C, 80%RH)	/	10
$\{NBu_3(CH_2COOH)\}[MnCr(ox)_3]\cdot nH_2O$	5×10^{-6} (25°C, 90%RH)	/	10
$\{NBu_3(CH_2COOH)\}[FeCr(ox)_3]\cdot nH_2O$	0.9×10^{-7} (25°C, 90%RH)	/	10
Ca-SBBA	8.58×10^{-6} (25°C, 98%RH)	0.23	11
Sr-SBBA	4.4×10^{-5} (25°C, 98%RH)	0.56	11
In-IA-2D-1	3.4×10^{-3} (27°C, 98%RH)	0.61	12
In-IA-2D-2	4.2×10^{-4} (27°C, 98%RH)	0.48	12
PCMOF-5	2.51×10^{-3} (60°C, 98%RH)	0.16	13
$\{H[Cu(Hbpdc(H_2O)_2]_2[PMo_{12}O_{40}]\cdot nH_2O\}_n$	1.25×10^{-3} (100°C, 98%RH	1.02	14
$\{H[Cu(Hbpdc(H_2O)_2]_2[PW_{12}O_{40}]\cdot nH_2O\}_n$	156×10^{-3} (100°C, 98%RH)	1.02	14
$\{[Ca(D\text{-}Hpmpc)(H_2O)_2]\cdot 2HO_{0.5}\}_n$	8.9×10^{-4} (60°C, 97%RH)	0.21	15
$\{H[Ni(Hbpdc)(H_2O)_2]_2[PW_{12}O_{40}]\cdot 8H_2O$	1.35×10^{-3} (100°C, 98%RH)	1.01	16
$\{[H_3O][Cu_2(DSOA)(OH)(H_2O)]\cdot 9.5H_2O\}_n$	1.9×10^{-3} (85°C, 98%RH)	1.04	17
PCMOF2½	2.1×10^{-2} (85°C, 90%RH)	0.21	18
$\{[(Me_2NH_2)_3(SO_4)]_2[Zn(ox)_3]\}_n$	4.2×10^{-2} (25°C, 98%RH)	0.129	19
EuL	1.6×10^{-5} (75°C, 97%RH)	0.91	20
DyL	1.33×10^{-5} (75°C, 97%RH)	0.87	20
HKUST-1	1.08×10^{-8} (90°C, 70%RH)	0.69	21
NENU-3	4.76×10^{-5} (90°C, 70%RH)	0.41	21
NENU-3-Ina	1.81×10^{-3} (90°C, 70%RH)	0.36	21
$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 2H_2O$	7×10^{-5} (25°C, 100%RH)	/	22
$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$	8×10^{-3} (25°C, 100%RH)	/	22
$\{[Cu_3(L)_2(H_2O)_4][Cu(dmf)_4(SiW_{12}O_{40})]\cdot 9H_2O$	5.94×10^{-4}(100°C, 98%RH)	0.32	23
$[H_3O][CoLa(notp)(H_2O)_4]ClO_4\cdot 3H_2O$	4.24×10^{-5} (25°C, 98%RH）	0.28	24
$[Cu_3(u_3\text{-}OH)(H_2O)_3(atz)_3]_3[P_2W_{18}O_{62}]\cdot 14H$	4.4×10^{-6} (25°C, 97%RH)	/	25
$[Cu(H_2L)(DMF)_4]_n$	3.46×10^{-3} (95°C, 95%RH)	0.68	26
$[CaL_{0.5}(DMF)_{2.5}]_n$	1.27×10^{-5} (25°C, 95%RH)	0.17	26
$[CdL_{0.5}(DMF)_2]_n$	2.49×10^{-7} (25°C, 95%RH)	0.59	26
$[Cd_2(btc)_2(H_2O)_2]_n\cdot n(H_2bmib)\cdot 6n(H_2O)$	5.4×10^{-5} (60°C, 95%RH)	0.62	27

$[Cd_4(cpip)_2(Hcpip)_2]_n \cdot n(H_2bmib) \cdot n(H_2O)$	2.2×10^{-5} (60°C, 95%RH)	0.27	27
ZIF-8	4.6×10^{-4} (94°C, 98%RH)	/	28
PCMOF10	3.55×10^{-2} (70°C, 95%RH)	0.4	29
$\{[Zn(C_{10}H_2O_8)_{0.5}(C_{10}S_2N_2H_8)]\cdot 5H_2O]\}_n$	2.55×10^{-7} (80°C, 95%RH)	0.96	30
$\{[Zn(C_{10}H_2O_8)_{0.5}(C_{10}S_2N_2H_8)]\cdot 2H_2O]\}_n$	4.39×10^{-4} (80°C,95%RH)	0.84	30
$Cu_4(L)_2(OH)_2(DMF)_2$	7.4×10^{-4} (95°C, 95%RH)	1.32	31
$UiO\text{-}66(SO_3H)_2$	8.4×10^{-2} (80°C, 90%RH)	0.32	32
$UiO\text{-}66(Zr)\text{-}(CO_2H)_2$	2.3×10^{-3} (90°C, 95%RH)	0.17	33
$[Cu_3(BTC)_2(H_2O)_3]_4[SiW_{11}Mo^{V}O_{40}](C_4H_{12}N_5)$ $\cdot 30H_2O$	6.37×10^{-8} (25°C, 97%RH)	/	34
MFM-500(Ni)	4.5×10^{-4} (25°C, 98%RH)	0.43	35
Fe-CAT-5	5.0×10^{-2} (25°C, 98%RH)	0.24	36
Ti-CAT-5	8.2×10^{-4} (25°C, 98%RH)	0.43	36

Im = Imidazole, ox = oxalate, PCMOF-3 = $Zn_3(L)(H_2O)_2\cdot 2H_2O$ (L = 1,3,5-benzenetriphosphonate), H_2bdc = 1,4-benzenedicarboxylic acid, In-IA-2D-1 = $[In(IA)_2\{(CH_3)_2NH_2\}(H_2O)_2]$ In-IA-2D-2 = $[In(IA)_2\{(CH_3)_2NH_2\}(DMF)]$ (IA = isophthalic acid), PCMOF-5 = $LaH_5L(H_2O)_4$ (L = Benzene-1,2,4,5-tetramethylenephosphonic acid), H_2bpd = 2,2′-bipyridyl-3,3′-dicarboxylic acid, D-H_2pmpc = D-1-(phosphonomethyl)piperdine-3-carboxylic acid, Na_2H_2DSOA = disodium-2,2′-disulfonate-4,4′-oxydibenzoic acid, adp = adipic acid, $notpH_6 = C_9H_{18}N_3(PO_3H_2)_3$, Hatz = 3-amino-1,2,4,triazolate, H_3btc = 1,3,5-benzenetricarboxylic acid, H_3cpip = 5-(4-carboxyphenoxy)isophthalic acid, PCMOF10 = $Mg_2(H_2O)_4(H_2L)\cdot H_2O$ (H_6L = 2,5-dicarboxy-1,4-benzenediphosphonic acid), BTC = 1,3,5-benzenetricarboxylate, MFM-500(Ni) = $[M_3(H_3L)_2(H_2O)_9(C_2H_6SO)_3]$ (M = Ni, H_6L = benzene-1,3,5-p-phenylphosphonic acid), Fe-CAT-5 = $Fe(THO)\cdot Fe(SO_4)(DMA)_3$ (THO^{6-} = triphenylene-2,3,6,7,10,11-hexakis(olate)), Ti-CAT-5 = $Ti(THO)\cdot(DMA)_2$.

Table S2. Crystal data and structure refinement for compound **1**

Complexes	compound **1**
CCDC Number	2024549
formula	$C_{62}\ H_{52}\ Cd_3\ Fe_2\ N_{22}\ O_6$
fw	1650.15
crystal system	orthorhombic
space group	*P b a m*
a (Å)	16.4800(4)

b (Å)	18.2638(5)
c (Å)	11.7257(4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	3529.29(18)
Z	2
D_{calcd} (g cm^{-3})	1.553
R_1 [$I > 2\sigma(I)$]^a	0.0408
wR_2 [$I > 2\sigma(I)$]^b	0.1013
R_1 (all data)	0.0578
wR_2 (all date)	0.0408
GOF on F^2	1.145

$^a R_1 = \sum||F_o| - |F_c||/|F_o|$. $^b wR_2 = [\sum w (F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S3. Selected bond lengths (Å) and angles (deg) for compound **1**

Cd(2)−N(5)	2.281(5)
Cd(2)−N(6)	2.235(5)
Cd(2)−N(7)	2.342(4)
Cd(2)−N(4)	2.261(5)
Cd(2)−O(2)	2.375(6)
Cd(2)−O(1)	2.394(4)
Cd(1)−N(2)	2.335(5)
Cd(1)−N(1)	2.264(5)
Fe(2)−N(1)	2.044(8)
N(5)−Cd(2)−N(7)	89.99(10)
N(5)−Cd(2)−O(2)	81.3(2)
N(6)−Cd(2)−N(5)	104.5(2)
N(6)−Cd(2)−N(7)	94.50(11)

N(6)−Cd(2)−N(4)	93.4(2)
N(6)−Cd(2)−O(2)	174.3(2)
N(2)−Cd(1)−O(1)	90.000(1)
N(1)−Cd(1)−O(1)	94.67(19)

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