## **Supporting information**

## **Dual-functional coordination polymers with high proton**

## conduction behavior and good luminescence properties

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Figure S1 (a) The ligand environment of complex 2(Symmetry codes: (i) 0.5+x, -0.5+y, 1-z; (ii) -0.5+x, 0.5+y, 1-z), (b) 1D chain structure of complex 2; (c) 2D planar structure of complex 2; (b) 3D stacking diagram of complex 2 connected by hydrogen bonds.



Figure S2 (a) PXRD patterns of complex 2 for the simulated, as-synthesized and after water treated samples; (b) TG analysis profile of complex 2.



**Figure S3** (a) Impedance spectra of complex **2** at 298 K under different humidity; (b) The variation trend of proton conductivity of complex **2** with humidity at 298 K; (c) Impedance spectra of complex **2** at different temperature under 98% RH; (d) Arrhenius plot for activation energy of complex **2** at 98% RH.



Figure S4 (a) PXRD after proton conduction test of complex 1; (b) PXRD after proton conduction test of complex 2.



**Figure S5** (a) Arrhenius plots for activation energy of pure SPEEK membrane and 1@SPEEK-X under 98%RH; (b) Arrhenius plots for activation energy of pure SPEEK membrane and 2@SPEEK-X under 98% RH.



Figure S6 Surface SEM images of (a) pure SPEEK membrane and (b) 2@SPEEK-5



Figure S7 The excitation and emission spectra of solid state fluorescence of (a) complex 1, and (b) complex 2.



**Figure S8** Emission spectra of (a) complex **2** in different anion solutions; (b) complex **2** with different concentrations of  $Cr_2O_7^{2-}$  ions; (c) The Stern–Volmer plot of  $I_0/I$  versus the concentration of  $Cr_2O_7^{2-}$  ions for complex **2** at low concentration (from 0 to

 $3 \times 10^{-5}$  M), (d) Complex 2 detected  $Cr_2O_7^{2-}$  ions in the presence of other anion solutions.



**Figure S9** Emission spectra of (a) complex **1** with different concentrations of  $\text{CrO}_4^{2-}$  ions; (b) The Stern–Volmer plot of  $I_0/I$  versus the concentration of  $\text{CrO}_4^{2-}$  ions for complex **1** at low concentration (from 0 to  $1 \times 10^{-4}$  M), (c) complex **2** with different concentrations of  $\text{CrO}_4^{2-}$  ions; (b) The Stern–Volmer plot of  $I_0/I$  versus the concentration of  $\text{CrO}_4^{2-}$  ions for complex **2** at low concentration (from 0 to  $5 \times 10^{-4}$  M)



**Figure S10** (a) The fluorescence reversibility study of complex 1 within 5 cycles; (b) Time-dependent response of complex 1 for  $Cr_2O_7^{2-}$  (C=1×10<sup>-3</sup>M)



**Figure S11** (a) The fluorescence reversibility study of complex **2** within 5 cycles; (b) Time-dependent response of complex **2** for  $Cr_2O_7^{2-}(C=1\times10^{-3}M)$ 



Figure S12 (a) The PXRD patterns of complex 1 after soaking in  $Cr_2O_7^{2-}$  aqueous solution. (b) The PXRD patterns of complex 2 after soaking in  $Cr_2O_7^{2-}$  aqueous solution.



Figure S13 The excitation spectra of complex 1, complex 2 and UV-vis absorption spectrum of  $Cr_2O_7^{2-}$  ions.

DonorH···Acceptor	D-H	Н…А	D····A	D-H····A
O(5)-H(5A)····O(2)	0.86	1.79	2.645	178
O(6)-H(6A)····O(5)	0.86	1.89	2.748	178
O(6)-H(6B)····O(3)	0.86	1.94	2.781	168
O(7)-H(7A)····O(8)	0.86	2.18	2.947	149
O(7)-H(7B)····O(3)	0.86	1.98	2.790	157
O(7)-H(7B)····O(4)	0.86	2.46	3.103	132
O(8)-H(8A)····O(1)	0.86	1.89	2.791	161
O(8)-H(8B)····O(4)	0.85	2.08	2.870	154

 Table S1 The hydrogen bonds in complex 1

Table S2 The hydrogen bonds in complex 2

DonorH···Acceptor	D-H	Н…А	D····A	D-H···A
O(5)-H(5A)····O(2)	0.82	1.83	2.646	176
O(6)-H(6A)····O(1)	0.85	1.84	2.642	158
O(6)-H(6B)····O(3)	0.85	1.83	2.655	162
O(7)-H(7A)····O(6)	0.85	1.95	2.794	174
O(7)-H(7B)····O(8)	0.85	2.28	2.966	138
O(7)-H(7B)····O(4)	0.85	2.49	3.227	145
O(8)-H(8A)····O(3)	0.85	1.83	2.677	172
O(8)-H(8B)····O(5)	0.85	1.86	2.710	177

 Table S3 The proton conduction of reported complexes in the literature

Complexes	condition	<b>Proton conductivity</b>	Ref.
		(S·cm <sup>-1</sup> )	
[Cd(5-hip)(H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub>	98% RH, 343K	1.53 × 10 <sup>-3</sup>	This work
[Zn(5-hip)(H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub>	98% RH, 353K	$5.27 \times 10^{-4}$	This work
HNU-38	98% RH, 353K	$1.45 \times 10^{-3}$	1
<b>MOF-808</b>	99% RH, 315K	$7.58 \times 10^{-3}$	2
<b>VNU-23</b>	90% RH, 343K	$1.54 \times 10^{-4}$	3
Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ( <i>p</i> -BDC) <sub>5.2</sub>	95% RH, 338K	$2.63 \times 10^{-4}$	4
Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>6</sub> ( <i>p</i> -BDC) <sub>5</sub>	95% RH, 338K	6.93 × 10 <sup>-3</sup>	4
<b>MOF-801</b>	98% RH, 298K	$1.88 \times 10^{-3}$	5
[Zn(L)Cl] <sub>n</sub>	98% RH, 398K	$4.72 \times 10^{-3}$	6
FJU-80	98% RH, 353K	$1.05 \times 10^{-3}$	7
FJU-81	98% RH, 353K	$4.53 \times 10^{-3}$	7

Membrane	<b>Proton conductivity</b>	$E_a$	Water uptake	Area swelling
	(S·cm <sup>-1</sup> )	(eV)	(%)	(%)
SPEEK	2.00×10 <sup>-3</sup>	0.24	37.71	30.21
1@SPEEK-1	$2.56 \times 10^{-3}$	0.21	31.72	25.88
1@SPEEK-3	3.14×10 <sup>-3</sup>	0.22	27.45	23.44
1@SPEEK-5	3.95×10 <sup>-3</sup>	0.22	24.87	16.3
1@SPEEK-7	$2.34 \times 10^{-3}$	0.23	20.63	14.23
<b>2</b> @SPEEK-1	2.23×10 <sup>-3</sup>	0.19	30.75	24.51
<b>2</b> @SPEEK-3	2.58×10 <sup>-3</sup>	0.21	26.57	18.21
2@SPEEK-5	3.17×10 <sup>-3</sup>	0.22	20.02	13.25
2@SPEEK-7	2.11×10 <sup>-3</sup>	0.23	17.2	11.89

**Table S4** The proton conductivity,  $E_a$ , water uptake and area swelling of compositemembrane

**Table S5** The performance of reported complexes for detecting  $Cr_2O_7^{2-}$  in  $H_2O$ 

Complexes	$K_{sv}$ (M <sup>-1</sup> )	LOD (µM)	Ref.
[Cd(5-hip)(H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub>	$1.15 \times 10^4$	0.8	This work
[Zn(5-hip)(H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub>	$1.80 \times 10^4$	1	This work
<b>BUT-28</b>	$1.02 \times 10^{5}$	0.12	8
BUT-39	$1.57 \times 10^4$	1.5	9
NU-1000	$1.34 \times 10^4$	1.8	10
[Ag(btx) <sub>0.5</sub> (DCTP) <sub>0.5</sub> ] <sub>n</sub>	$1.92 \times 10^4$	2.04	11
[Cd <sub>3</sub> (cpota) <sub>2</sub> (phen) <sub>3</sub> ] <sub>n</sub> ·5nH <sub>2</sub> O	$1.21 \times 10^{3}$	0.37	12
[Eu <sub>2</sub> (tpbpc) <sub>4</sub> ·CO <sub>3</sub> ·H <sub>2</sub> O]·DMF·solven	$1.04 \times 10^4$	0.33	13
$[Cd(IPA)(3-PN)]_n$	$2.91 \times 10^{3}$	12.02	14
[Zn(ttz)H <sub>2</sub> O] <sub>n</sub>	$2.19 \times 10^{3}$	2	15
[Zn(btz)] <sub>n</sub>	$4.23 \times 10^{3}$	2	15
[Y(BTC)(DMF) <sub>6</sub> ] <sub>n</sub> :0.1Eu	$4.52 \times 10^{3}$	0.04	16

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