Cr(III) supramolecular network composite membrane with high water stability and proton conductivity

Shu-Fang Zhou,[a] Hong-Jie Zhang,[a] Chen-Xi Zhang[ab] and Qing-Lun Wang*[cd]*

Table S1. The Crystallographic data for complex **1**

Compound	**1**
Formula	$C_{18}H_{14}Cr_2N_8O_{10}$
Mr	606.36
T/K	113(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/ Å	7.2581(15)
b / Å	19.176(4)
c/ Å	7.9267(16)
α /°	90
β /°	102.24(3)
γ/°	90
Z	2
Volume /Å^3	1078.2(4)
ρ /g cm^{-3}	1.868
μ /mm^{-1}	1.087
F(000)	612.0
Crystal size /mm^3	0.20×0.18×0.12
2θ /°	2.836 to 27.786
Index ranges	$-9 \le h \le 9$
	$-25 \le k \le 25$
	$-10 \le l \le 10$
Reflections collected	11829
$R_{(int)}$	0.0530
Data/ restraints / parameters	2550 / 0/ 172
GOF on F^2	1.230
Final *R* indices [$I>2\delta(I)$]	R_1=0.0847,wR_2=0.1656
R indices(all data)	R_1=0.0910,wR_2=0.1686

Table S2. Selected bond distances and angles for **1**

Cr(1)-O(9)	1.966(4)
Cr(1)-O(2)	1.989(4)
Cr(1)-N(1)	2.052(4)
Cr(1)-O(9)#1	1.950(3)
Cr(1)-O(3)#1	1.986(4)
Cr(1)-N(4)#1	2.058(4)
Cr(1)-Cr(1)#1	2.9754(18)
O(3)-Cr(1)#1	1.986(4)
O(9)-Cr(1)#1	115.71(9)
N(4)-Cr(1)#1	2.058(4)
O(9)-Cr(1)-O(3)#1	94.98(15)
O(2)-Cr(1)-N(4)#1	94.50(17)
N(1)-Cr(1)-N(4)#1	167.93(18)
O(9)-Cr(1)-N(4)#1	92.55(16)
O(9)#1-Cr(1)-O(9)	81.08(16)
O(9)#1-Cr(1)-O(2)	94.59(16)
O(3)#1-Cr(1)-O(2)	89.99(16)
O(9)#1-Cr(1)-N(1)	95.71(16)
O(3)#1-Cr(1)-N(1)	90.46(17)
O(3)#1-Cr(1)-N(4)#1	79.10(16)
O(9)#1-Cr(1)-O(3)#1	172.90(15)
O(9)#1-Cr(1)-N(4)#1	95.10(16)
O(9)#1-Cr(1)-Cr(1)#1	40.74(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1

Table S3. Comparison of the proton conductivity values of **1** with other proton conducting materials.

Materials	Conductivity ($S \cdot cm^{-1}$)	Conditions	References
1	1.03×10^{-3}	367K, 98% RH	This work
$Zn(o\text{-}H_2BrPhIDC)_2(H_2O)_2]\bullet CH_3CH_2OH\bullet 3H_2O$	1.14×10^{-4}	373K, 98% RH	1s
$Co(o\text{-}H_2BrPhIDC)_2(H_2O)_2]\bullet CH_3CH_2OH\bullet 3H_2O$	3.11×10^{-4}	373K, 98% RH	1s
$Mg(L)(H_2O)_5 \cdot H_2O]$	5.87×10^{-4}	343K, 75% RH	2s
MHOF1	$7.50 \times 10{-}4$	353K, 98%RH	3s
MHOF2	3.50×10^{-4}	353K, 98%RH	3s
$\{(H_3O)[Tb(BODSDC)\text{-}(H_2O)_2]\}_n$	6.57×10^{-4}	358K, 95% RH	4s
$[Cu_{12}(MES)_6(H_2O)_3]_n$	3.63×10^{-5}	333 K, 98% RH	5s
$\{[Cu_{12}(MPS)_6(H_2O)_4] \cdot 6H_2O\}_n$	2.75×10^{-5}	333 K, 98% RH	5s
ICR-11	4.26×10^{-4}	350 K, 100% RH	6s

Table S4. Comparison of the proton conductivity values of **1**@CS/PVP-10 with other membranes.

Materials	Conductivity ($S \cdot cm^{-1}$)	Conditions	References
1@CS/PVP-10	8.64×10^{-2}	363K, 98% RH	This work
MOF-801@PP-60	1.84×10^{-3}	325K, 98% RH	7s
H_3PO_4@Ni-BDC-PAN	1.05×10^{-2}	353K, 90% RH	8s
1@PVA-10	2.78×10^{-4}	353K, 98% RH	9s
JUC-200@PVA-10	1.25×10^{-3}	323K, 97% RH	10s
Zn-MOF-NH_3/Nafion-5	2.13×10^{-2}	353K, 98%RH	11s
Naf-1SZM	2.96×10^{-3}	353K, 35%RH	12s
N_U200-10	1.10×10^{-2}	355K, 50% RH	13s
UiO-66-NH_2 + UiO-66-SO_3H/ Nafion-0.6	2.56×10^{-1}	363K, 95%RH	14s
IL-COF-SO_3H@SNF-35	2.24×10^{-1}	363K, 100%RH	15s

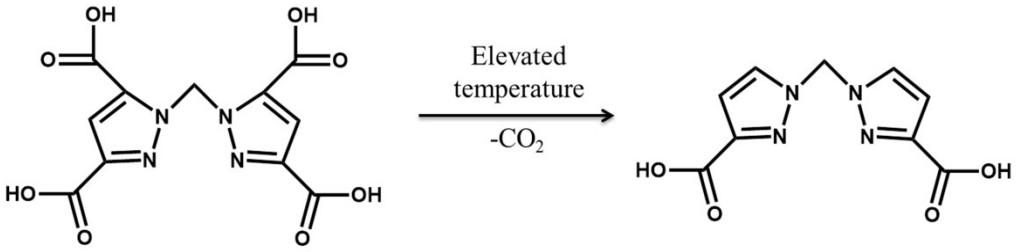

Figure S1. Decarboxylation of H_4DBPZ taking place and transformation to H_2DBPZ at elevated temperature.

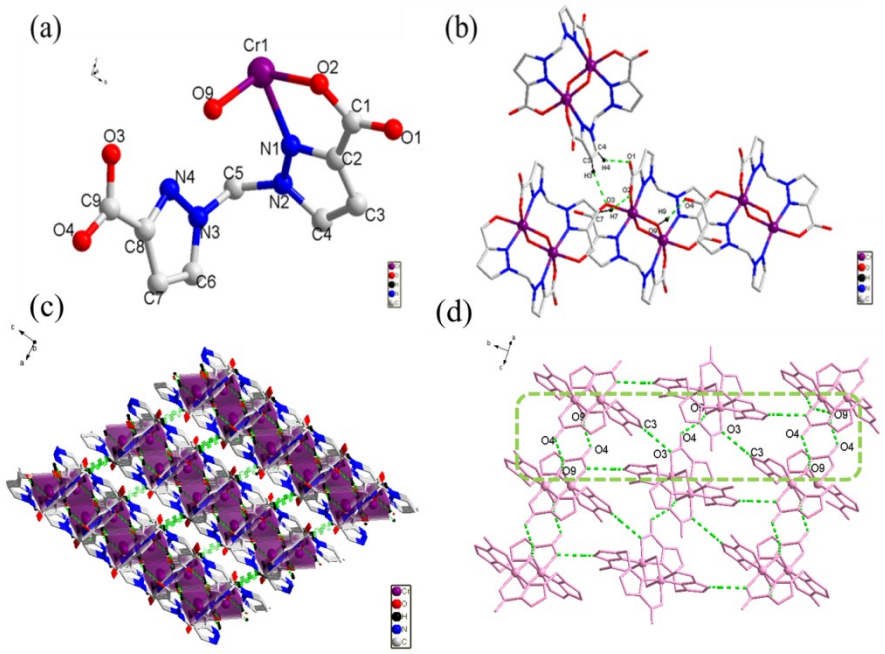

Figure S2. (a) The asymmetric unit of **1**; (b) Four kind of hydrogen-bonds of **1**; (c) The three-dimensional supramolecular network structure of **1**; (d) Hydrogen bonds in three-dimensional structure of **1.**

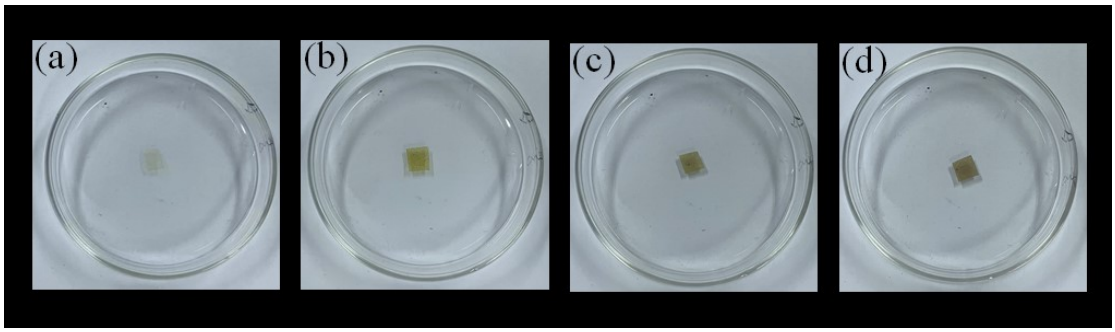

Figure S3. Photographic images of (a) pure CS/PVP, (b) **1**@CS/PVP-5%, (c) **1**@CS/PVP-10%, (c) **1**@CS/PVP-15%.

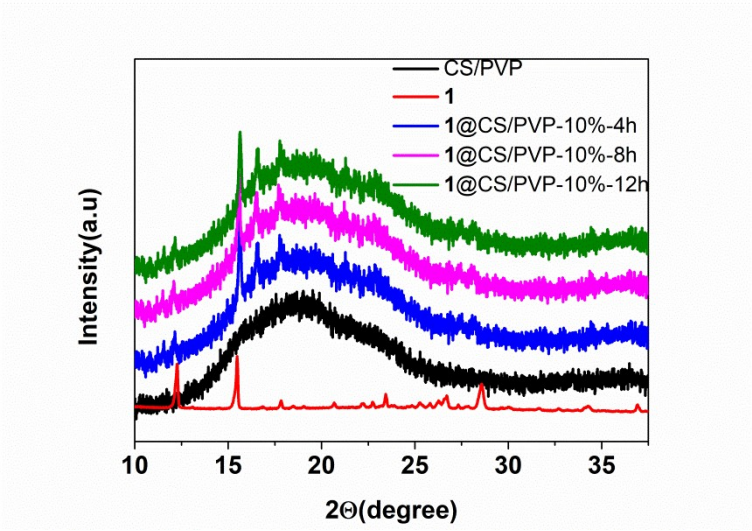

Figure S4. XRD patterns of **1**@CS/PVP-10% treated with water at different periods of time.

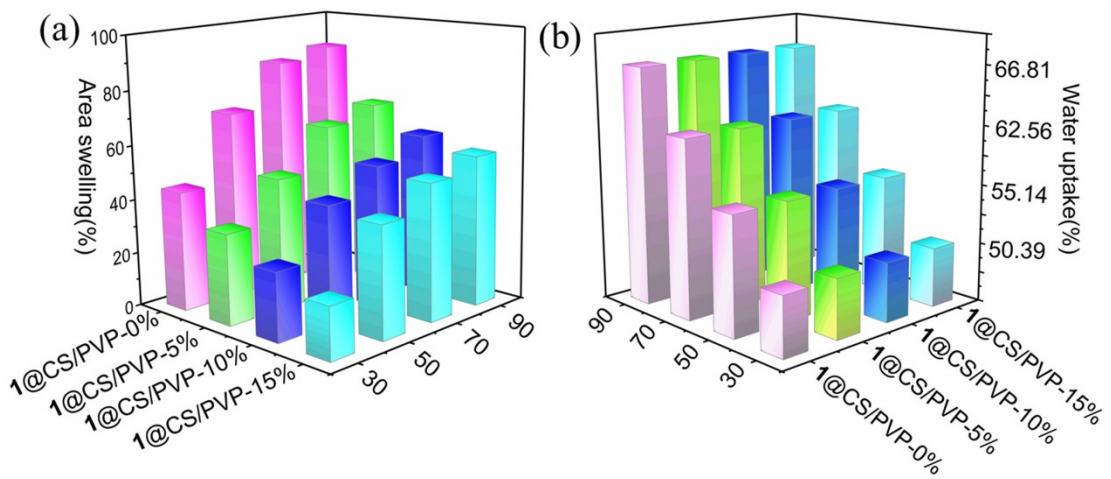

Figure S5. Area swelling and water uptake of **1**@CS/PVP-0%, **1**@CS/PVP-5%, **1**@CS/PVP-10%, and **1**@CS/PVP-15%.

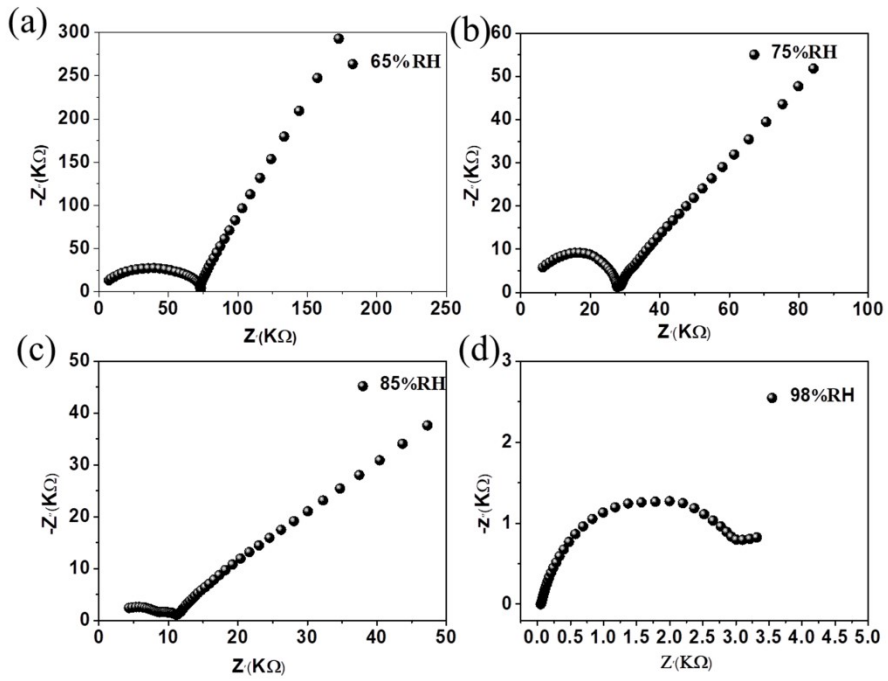

Figure S6. Nyquist plots of **1** at different relative humidity and 299 K

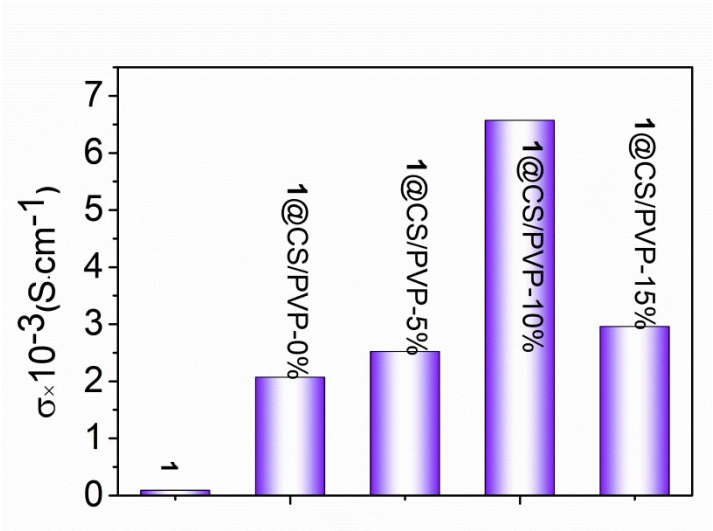

Figure S7. The proton conductivity of **1**@CS/PVP-X at 98% RH and 299 K

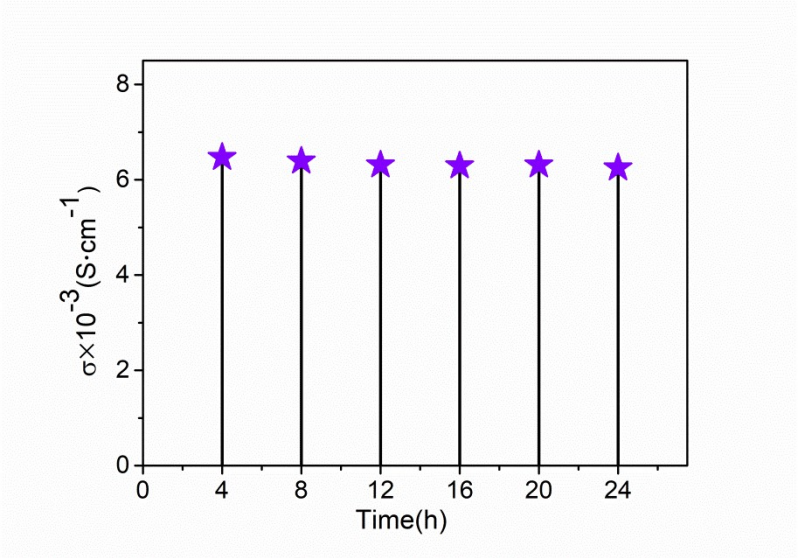

Figure S8. Proton conductivities of **1**@CS/PVP-10% measured at 299 K under 98% RH for 24 h;

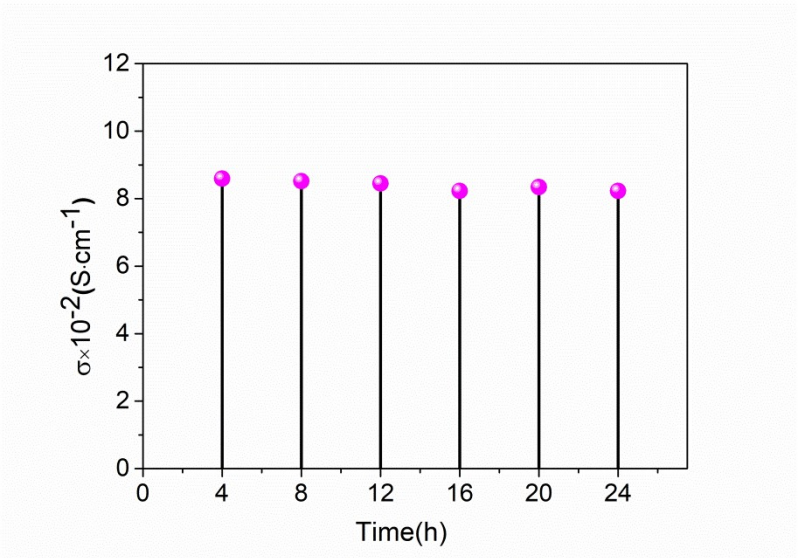

Figure S9. Proton conductivities of **1**@CS/PVP-10% measured at 363 K under 98% RH for 24 h;

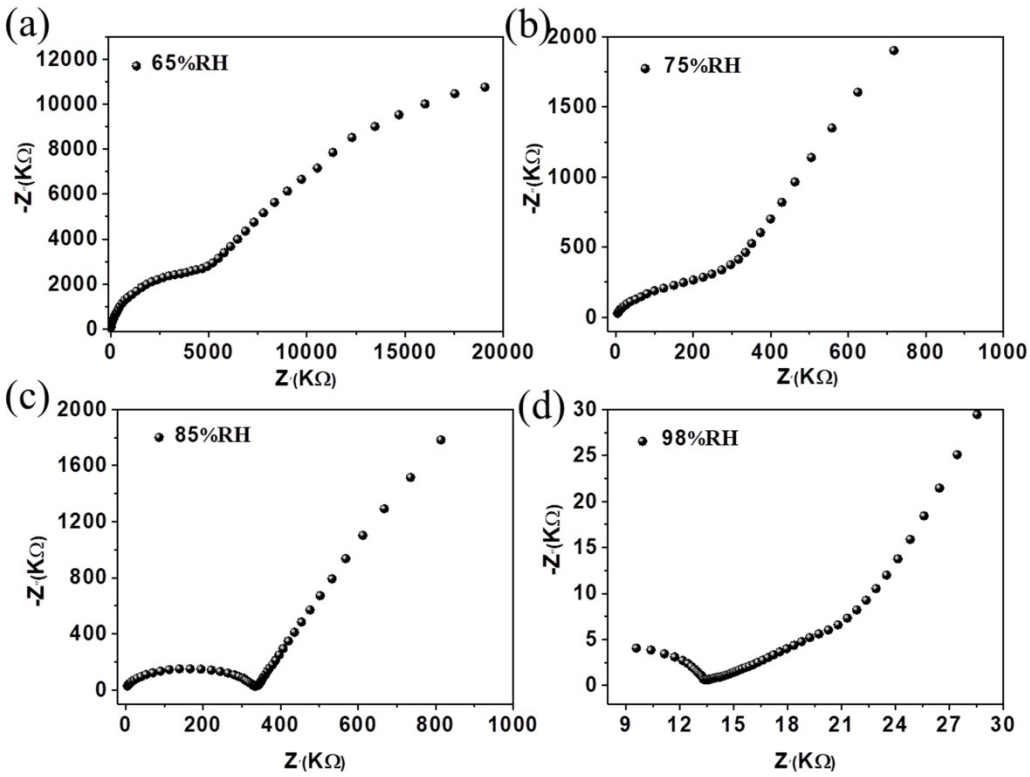

Figure S10. Nyquist plots of **1**@CS/PVP-10 at different relative humidity and 299 K

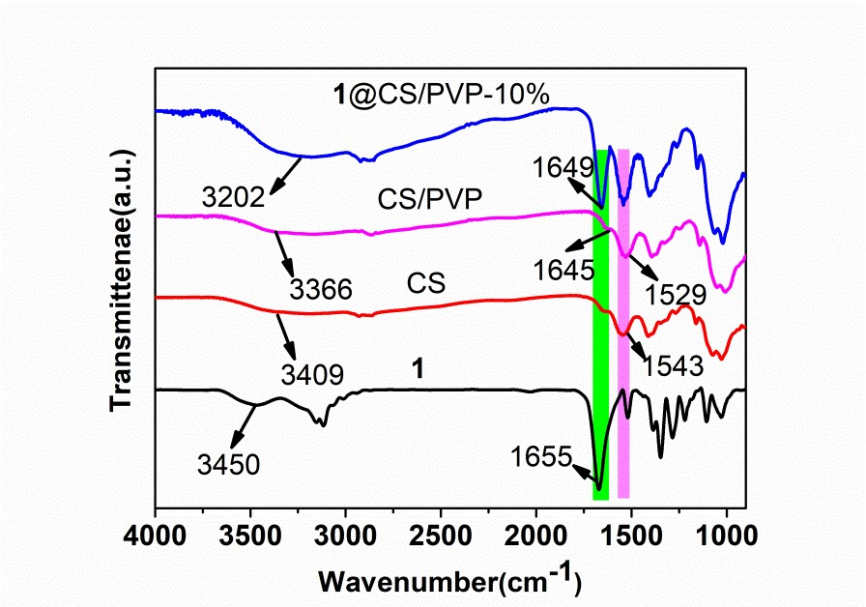

Figure S11. ATR-FT-IR spectra of **1**, CS, CS/PVP and **1**@CS/PVP-10%

NOTES AND REFERENCE

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