Electronic supplementary information (ESI)

Cationic metal-organic frameworks constructed from a trigonal imidazole-containing ligand for the removal of $Cr_2O_7^{2-}$ in water

Zi-Peng Chen,[a] Ding Li,[a] Lei Xu,[b] Yu-Fei Jiang,[a] Kai Lin,*[c] Yue Zhao,*[a] and Jing Zhao*[a]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.*

[b] *Jiangsu Key Lab of Data Engineering and Knowledge Service, School of Information Management, Nanjing University, Nanjing 210023, China.*

[c] *Jiangsu Environmental Resources Co., LTD, Nanjing 210019, China.*

Email address: jingzhao@nju.edu.cn (J. Zhao), zhaoyue@nju.edu.cn (Y. Zhao).

Table S1. Crystal data and structure refinements for **1** and **2**.

	1	**2**
Formula	$Ag_{13}C_{247}H_{234}N_{76}O_{53}$	$C_{338}F_{66}H_{427}N_{91}O_{78}Si_{11}Zn_{12}$
Formula weight	6517.40	9360.11
T (K)	193(2)	193(2)
λ (Å)	1.34139	0.71073
Crystal system	Orthorhombic	Trigonal
Space group	*Pnnn*	*R*-3
a (Å)	15.2129(7)	36.301(4)
b (Å)	27.1725(12)	36.301(4)
c (Å)	34.1250(15)	29.712(3)
V (Å^3)	14106.3(11)	33909(8)
Z	2	3
D_{calc} (g cm^{-3})	1.534	1.375
μ /mm^{-1}	5.274	0.757
F(000)	6566	14472
Reflections collected	153223	70371
Unique reflections	12455	13766
Goodness-of-fit on F^2	1.031	1.030
R_1[a] [$I > 2\sigma(I)$]	0.0702	0.0607
wR_2[b] [$I > 2\sigma(I)$]	0.2279	0.1638
R_1 [all data]	0.0907	0.1012
R_1 [all data]	0.2490	0.1891

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where w = m= $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. P = $(F_o^2 + 2F_c^2)/3$

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2.**

1			
Ag2-N55	2.091(5)	Ag2-N75#1	2.106(5)
Ag3-N15	2.101(5)	Ag3-N18	2.110(5)
Ag4-N78#2	2.086(6)	Ag4-N48	2.114(6)
Ag4A-N48	2.242(13)	Ag4A-N78#2	2.273(9)
Ag16-N16#3	2.053(15)		
N55-Ag2-N75#1	174.6(2)	N15-Ag3-N18	178.6(2)
N78#2-Ag4-N48	177.5(3)	N48-Ag4A-N78#2	136.9(10)
N16#4-Ag16-N16	180.0(7)		
Ag2-N55	2.091(5)	Ag2-N75#1	2.106(5)
2			
N8-Zn1	1.992(3)	N5-Zn1#2	1.993(3)
N7-Zn1	1.966(3)	O1-Zn1	2.033(3)
N14-Zn2	1.963(4)	N12-Zn2#3	1.970(4)
N3-Zn2#1	2.000(4)	O2-Zn2	2.072(5)
N5#4-Zn1-O1	99.48(14)	N7-Zn1-N5#4	129.45(15)
N7-Zn1-N8	121.86(15)	N7-Zn1-O1	97.43(13)
N8-Zn1-N5#4	101.61(14)	N8-Zn1-O1	99.67(15)
N3#5-Zn2-O2	100.45(18)	N12#6-Zn2-N3#5	107.62(17)
N12#6-Zn2-O2	98.75(17)	N14-Zn2-N3#5	113.67(17)
N14-Zn2-N12#6	131.33(18)	N14-Zn2-O2	98.01(17)

Symmetry codes: #1 x-1/2, y+1/2, -z; #2 x+1/2, y-1/2, -z+1; #3 -x+1/2, y-1/2, -z; #4 x-1, -y+1, -z for **1**. #1 y, -x+y+1, -z+1; #2 -x+y+1/3,-x+5/3,z-1/3; #3 x-y+2/3,x+1/3,-z+4/3; #4 -y+5/3,x-y+4/3,z+1/3; #5 x-y+1,x,-z+1; #6 y-1/3,-x+y+1/3,-z+4/3 for **2**.

Table S3. The Ring-Interactions data in **1** including the π…π, C-H…π and Ag(I)…π interactions.

CgI-CgJ	d_{Cg-Cg} (Å)	α (°)	β (°)	γ (°)	d_{CgI_Perp}	d_{CgJ_Perp}	Slippage
Cg1-Cg1	3.979(4)	26.0(4)	23.9	23.9	3.639(3)	3.639(3)	
Cg1-Cg3	5.881(4)	71.9(4)	53.7	55.4	3.338(3)	3.485(3)	
Cg1-Cg8	4.566(3)	21.9(3)	39.5	37.4	3.628(3)	3.525(2)	
Cg1-Cg11	5.187(4)	25.4(3)	43.7	54.7	2.997(3)	3.747(2)	
Cg1-Cg13	4.725(4)	38.0(3)	46.8	38.2	3.712(3)	3.233(2)	
Cg2-Cg6	4.548(4)	10.1(4)	40.9	37.8	3.592(3)	3.438(3)	2.978
Cg2-Cg8	5.103(3)	52.7(3)	44.6	31.6	4.346(3)	3.636(2)	
Cg2-Cg10	5.913(3)	25.5(3)	57.5	57.0	3.218(3)	3.175(2)	
Cg3-Cg3	4.849(4)	44.2(3)	46.9	46.9	3.314(2)	3.313(2)	
Cg3-Cg6	5.035(4)	28.4(4)	53.9	49.3	3.282(2)	2.968(3)	
Cg3-Cg10	3.898(3)	6.4(3)	22.9	23.5	3.575(2)	3.591(2)	1.514
Cg3-Cg12	4.063(3)	21.1(3)	4.5	18.3	3.856(3)	4.050(2)	
Cg6-Cg14	4.046(8)	13.7(8)	26.5	36.7	3.246(3)	3.621(7)	1.806
Cg7-Cg9	4.365(5)	28.5(5)	8.2	21.6	4.060(4)	4.321(2)	
Cg7-Cg16	5.260(6)	19.1(5)	39.9	39.7	4.048(4)	4.032(4)	3.378
Cg7-Cg16	4.477(6)	48.0(5)	30.7	44.2	3.207(4)	3.849(	
Cg9-Cg9	5.304(3)	0.0(3)	58.1	58.1	2.801(2)	2.801(2)	4.504
Cg12-Cg14	5.991(8)	24.2(7)	59.6	54.9	3.441(2)	3.033(7)	
Cg12-Cg14	4.394(7)	24.2(7)	46.2	26.8	3.923(2)	3.041(7)	
Cg13-Cg14	4.441(7)	44.6(7)	20.6	54.9	2.553(2)	4.157(7)	
Cg13-Cg15	5.657(11)	80	51.2	53.5	3.364(2)	3.541(11)	

Cg(I)-Met(J)	d_{Cg-Met} (Å)	Met(I)_Perp	β (°)
Cg6-Ag2	3.411	-3.302	14.48
Cg8-Ag3	3.651	3.233	27.70
Cg10-Ag2	3.866	-3.464	26.33
Cg11-Ag3	3.664	-3.320	25.04
Cg16-Ag4	3.926	3.895	7.18
Cg16-Ag4A	3.171	3.167	2.86

X-H(I)-Cg(J)	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg
C62-H62-Cg14	2.72	5.03	142	3.524(9)	57
C158-H158-Cg2	2.94	8.26	116	3.467(6)	35

Cg1: N18-->C18-->N28-->C38-->C28; **Cg2:** N48-->C168-->C178-->N58-->C188; **Cg3:**

N68-->C258-->N78-->C278-->C268; **Cg4:** N12-->C2A-->C3A-->N22-->C12; **Cg5:** N12-->C12-->N22-->C3B2-->C2B2; **Cg6:** N52-->C162-->N42-->C182-->C172; **Cg7:** N62-->C252-->N72-->C272-->C262; **Cg8:** C48-->C58-->C68-->C78-->C88-->C98; **Cg9:** C108-->C118-->C128-->C138-->C148-->C158; **Cg10:** C198-->C208-->C218-->C228-->C238-->C248; **Cg11:** C42-->C92-->C82-->C72-->C62-->C52; **Cg12:** C102-->C152-->C142-->C132-->C122-->C112; **Cg13:** C202-->C212-->C222-->C232-->C242-->C192; **Cg14:** N19-->C19-->N29-->C39-->C29; **Cg15:** N69-->C259-->N79-->C279-->C269; **Cg16:** C49-->C59-->C69-->C79-->C89-->C99; **Cg17:** C199-->C209-->C219-->C229-->C239-->C249.

CgI/J: Plane number I/J; Alpha: Dihedral angle between planes I and J; Beta: Angle Cg(I)-->Cg(J) or Cg(I)-->Met vector and normal to plane I; Gamma: Angle Cg(I)-->Cg(J) vector and normal to plane J or Angle between Cg-H vector and ring J normal; Cg-Cg: Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I; Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I; H-Perp: Perpendicular distance of H to ring plane J; Gamma: Angle between Cg-H vector and ring J normal; X-H..Cg: X-H-Cg angle; X..Cg: Distance of X to Cg; X-H, Pi: Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)

Table S4. The Ring-Interactions data in **1** including the π…π, C-H…π and Ag(I)…π interactions.

CgI-CgJ	d_{Cg-Cg} (Å)	α (°)	β (°)	γ (°)	d_{CgI_Perp}	d_{CgJ_Perp}	Slippage
Cg1-Cg4	5.016(4)	46.4(4)	30.8	50.2	3.209(2)	4.309(3)	
Cg2-Cg5	4.705(4)	41.1(4)	35.0	36.3	3.793(2)	3.856(4)	
Cg3-Cg18	5.237(6)	0.0(4)	9.4	0.0	4.366(4)	5.167(6)	0.856
Cg4-Cg10	4.872(5)	24.6(5)	25.1	25.1	4.414(3)	4.412(4)	
Cg4-Cg18	4.878(6)	0.0(4)	22.9	0.0	6.527(5)	4.493(5)	1.899
Cg5-Cg8	4.801(5)	18.1(5)	18.6	25.2	4.344(3)	4.551(4)	1.528
Cg5-Cg13	4.741(5)	0.0(5)	25.8	0.0	4.629(6)	4.270(5)	2.061
Cg5-Cg15	5.564(7)	0.0(6)	33.3	0.0	5.466(8)	4.653(6)	3.051
Cg6-Cg6	3.974(4)	0.0(4)	29.0	29.0	3.477(3)	3.477(3)	1.925
Cg6-Cg15	4.472(7)	35.9(5)	29.6	44.5	3.192(3)	3.890(6)	
Cg6-Cg16	4.398(7)	20.2(6)	30.0	45.8	3.065(3)	3.809(6)	
Cg8-Cg17	5.163(7)	11.0(6)	30.6	28.0	4.557(5)	4.446(6)	2.625
Cg8-Cg18	5.153(6)	57.5(5)	30.9	49.6	3.343(4)	4.420(5)	
Cg10-Cg13	5.236(6)	18.6(5)	21.8	35.6	4.256(5)	4.862(4)	1.942
Cg11-Cg18	4.843(6)	3.7(5)	12.4	8.9	4.785(4)	4.730(4)	1.037
Cg12-Cg14	4.842(5)	20.7(4)	13.1	12.8	4.723(4)	4.717(4)	
Cg12-Cg17	4.899(6)	66.8(5)	53.6	53.1	2.941(4)	2.911(5)	
Cg12-Cg18	4.818(5)	47.6(4)	52.9	8.5	4.765(4)	2.907(4)	
Cg13-Cg18	5.796(6)	0.0(5)	38.3	0.0	4.336(6)	4.550(6)	3.590

Y--X(I)-Met(J)	d_{X-Met} (Å)	γ (°)	Y-X..Cg	Y..Cg	Y-X,Pi
Si2-F5->Cg2	3.884(4)	0.00	130.69(10)	5.162(3)	43.04

X-H(I)-Cg(J)	H..Cg (Å)	H-Perp (Å)	Gamma (°)	X-H..Cg (Å)	X..Cg (Å)	X-H,Pi
C6-H6->Cg5	2.95	2.48	32.59	132	3.655(11)	64
C9-H9->Cg17	2.98	2.83	18.24	151	3.838(12)	48

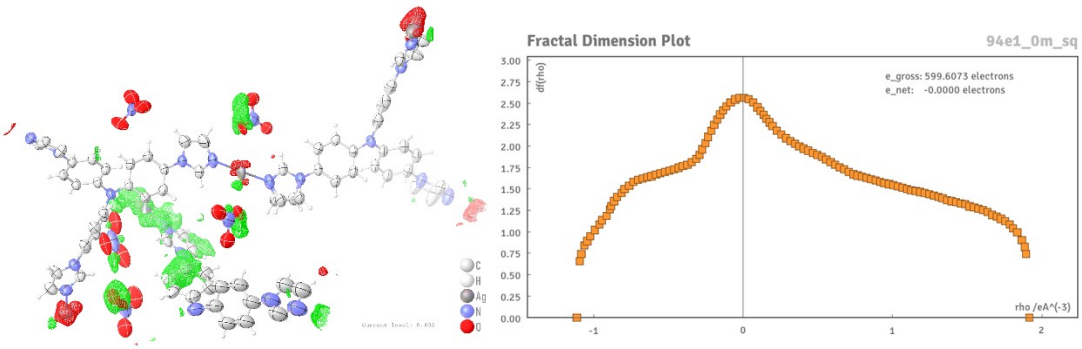
Cg1: N2-->C22-->C23-->N3-->C24; **Cg2**: N4-->C2-->C1-->N5-->C3; **Cg3**: N6-->C25-->C26-->N7-->C27; **Cg4**: N8-->C46-->N9-->C48-->C47; **Cg5**: N11-->C52-->C54-->N12-->C53; **Cg6**: N13-->C49-->C50-->N14-->C51; **Cg7**: C4-->C6-->C9-->C5-->C8-->C7; **Cg8**: C4-->C6'-->C9'-->C5-->C8'-->C7'; **Cg9**: C10-->C13-->C15-->C11-->C12-->C14; **Cg10**: C10-->C13'-->C15'-->C11-->C12'-->C14'; **Cg11**: C16-->C19-->C18-->C17-->C21-->C20; **Cg12**: C16-->C19'-->C18'-->C17-->C21'-->C20'; **Cg13**: C28-->C30-->C31-->C29-->C33-->C32; **Cg14**: C28-->C30'-->C31'-->C29-->C33'-->C32'; **Cg15**: C34-->C36'-->C37'-->C35-->C39-->C38; **Cg16**: C34-->C36-->C37-->C35-->C39'-->C38'; **Cg17**: C40-->C42-->C44-->C41-->C45-->C43; **Cg18**: C40-->C42'-->C44'-->C41-->C45'-->C43'.

CgI/J: Plane number I/J; Alpha: Dihedral angle between planes I and J; Beta: Angle Cg(I)-->Cg(J) or Cg(I)-->Met vector and normal to plane I; Gamma: Angle Cg(I)-->Cg(J) vector and normal to plane J or Angle between Cg-H vector and ring J normal; Cg-Cg: Distance between ring Centroids; CgI_Perp = Perpendicular distance of Cg(I) on ring J; CgJ_Perp = Perpendicular distance of Cg(J) on ring I; Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I; H-Perp: Perpendicular distance of H to ring plane J; Gamma: Angle between Cg-H vector and ring J normal; X-H..Cg: X-H-Cg angle; X..Cg: Distance of X to Cg; X-H, Pi: Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees).

Table S5. Hydrogen bonding data of **1** and **2**.

1				
D–H···A	d(*D*–H) (Å)	d(H···A) (Å)	d(*D*···A)(Å)	*D*–H···A (°)
C18-H18···O17	0.95	2.28	3.149(16)	152
C18-H18···O17	0.95	2.48	3.358(16)	153
C28-H28···O23	0.95	2.51	3.196(11)	129
C38-H38···O25	0.95	2.32	3.25(2)	166
C58-H58···O25	0.95	2.47	3.40(2)	166
C148-H148···O24	0.95	2.38	3.312(8)	167
C188-H188···O310	0.95	2.58	3.314(11)	134
C218-H218···O14	0.95	2.59	3.306(12)	132
C258-H258···O210	0.95	2.23	3.153(18)	165
C19-H19···O14	0.95	2.51	3.151(18)	125
C99-H99···O110	0.95	2.18	2.804(19)	122
C212-H212···O24	0.95	2.52	3.314(9)	141
C122-H122···O15	0.95	2.40	3.34(3)	169
C12-H12···O13	0.95	2.27	3.122(12)	150
C12-H12···O13	0.95	2.60	3.408(12)	143
C92-H92···O13	0.95	2.60	3.460(15)	151
C232-H232···O37	0.95	2.59	3.457(15)	152
C162-H162···O210	0.95	2.47	3.339(18)	152
C162-H162···O110	0.95	2.44	3.39(2)	176
C262-H262···O27	0.95	2.52	3.459(15)	171
2				
D–H···A	d(*D*–H) (Å)	d(H···A) (Å)	d(*D*···A)(Å)	*D*–H···A (°)
C2-H2···F2	0.95	2.36	3.204(7)	148
C3-H3···F3	0.95	2.36	3.306(5)	172
C3-H3···F5	0.95	2.28	2.940(5)	126

C12-H12···F8	0.95	2.44	3.243(11)	142
C19-H19···F4	0.95	2.42	3.361(11)	170
C20-H20···F8	0.95	2.48	3.398(10)	163
C22-H22···F1	0.95	2.44	3.064(11)	123
C22-H22···F2	0.95	2.26	3.211(8)	175
C24-H24···F8	0.95	2.29	3.207(7)	163
C24-H24···F9	0.95	2.31	2.966(6)	126
C25-H2···F6	0.95	2.46	3.202(5)	135
C27-H27···F5	0.95	2.24	2.870(4)	123
C27-H27···F4	0.95	2.39	3.332(5)	174
C36'-H36'···F10	0.95	2.40	3.323(13)	164
C42-H42···F7	0.95	2.32	3.247(19)	163
C46-H46···F4	0.95	2.37	3.297(6)	167
C46-H4··· F5	0.95	2.27	2.955(5)	129
C48-H48···F8	0.95	2.53	3.428(12)	159
C49-H49···F11	0.95	2.31	3.248(5)	169
C51--H51···F9	0.95	2.41	2.970(5)	117
C51-H51···F10	0.95	2.47	3.276(6)	142
C52-H52···F3	0.95	2.49	3.286(11)	141
C52-H52···F4	0.95	2.25	3.146(11)	157
C53-H53···F7	0.95	2.35	3.283(7)	166
C53-H53···F9	0.95	2.26	2.935(7)	127


Fractal Dimension Plot
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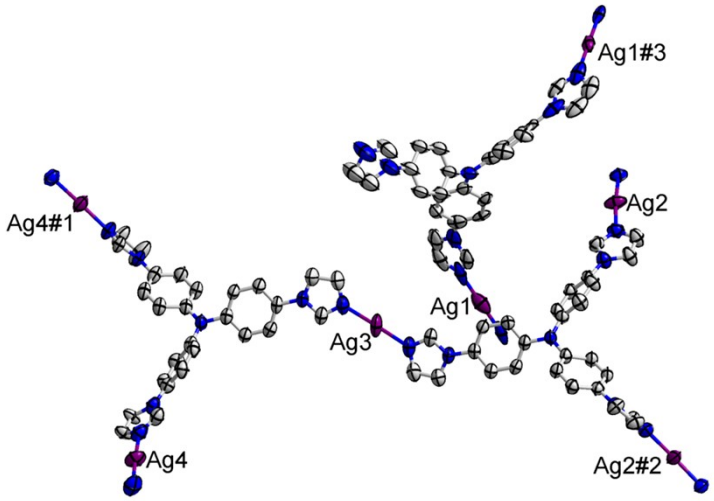
d(rho)
rho /eA^(-3)
C
H
Ag
N
O

(a)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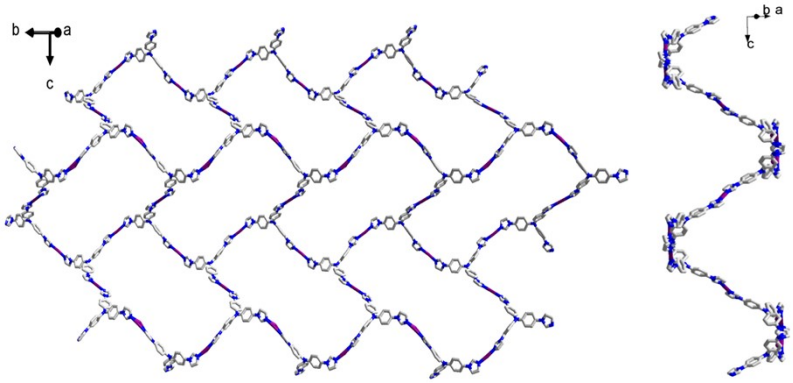
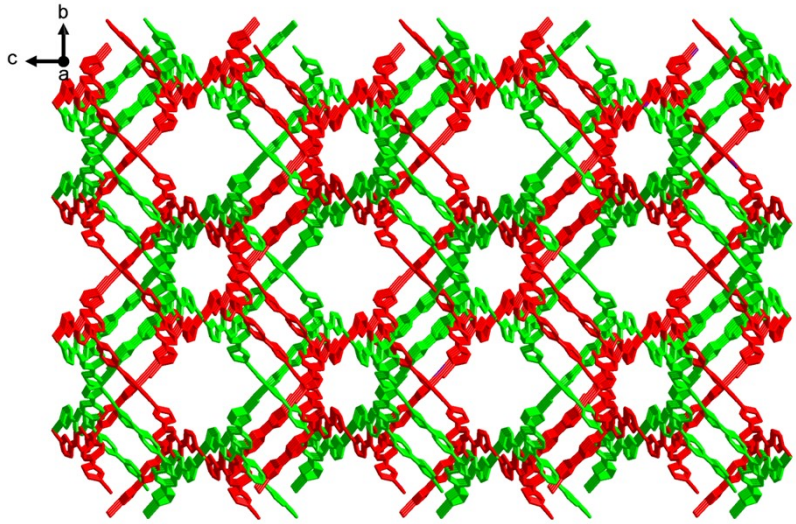
Ag4#1
Ag1
Ag3
Ag4
Ag2#2

(b)


b
a
c
b a
c

(c)



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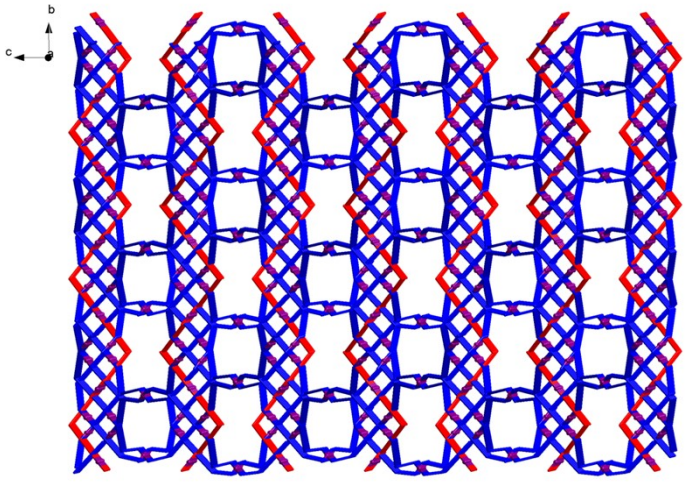

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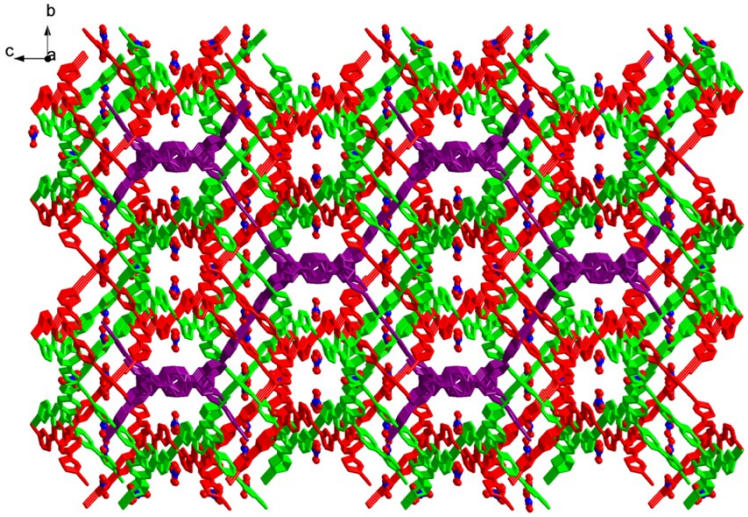
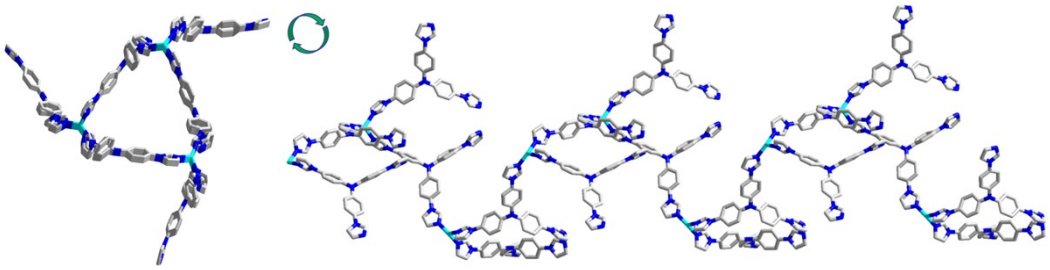


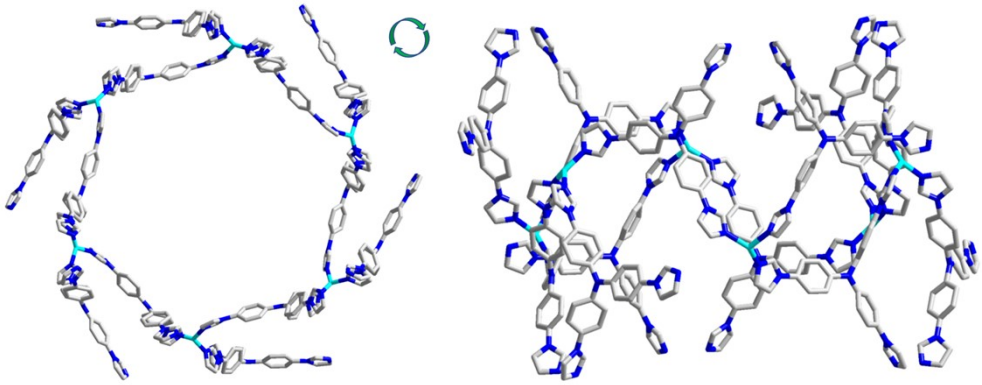
(f)

Fig. S1. (a) Residual density map and Fractal Dimension Plot. (b) The coordination

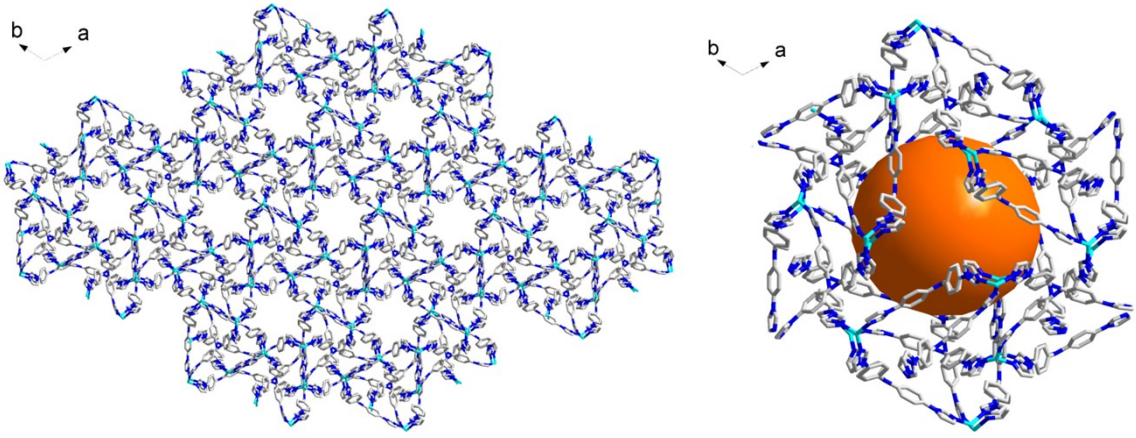
environments of Ag(I) atoms with the ellipsoids drawn at the 30% probability level. The hydrogen atoms and NO_3^- are omitted for clarity. Symmetric code: #1 #1 x-1/2, y+1/2, -z; #2 x+1/2, y-1/2, -z+1; #3 -x+1, -y+1, -z; #4 x-1/2, y+1/2, -z+1; #5 x+1/2, y-1/2, -z; #6 -x+3/2, -y+3/2, z; #7 x+1/2, y+1/2, -z. (c) The front and side view of the 2D wavelike coordination layers constructed from tipa and Ag(I) cations. (d) The $\{[Ag_3(tipa)_2]_4^{12+}\}_n$ coordination networks along a-axis. (e) Topological structure of **1**. (f) The final strcture of **1** with enormous NO_3^- entrapped in the channels.



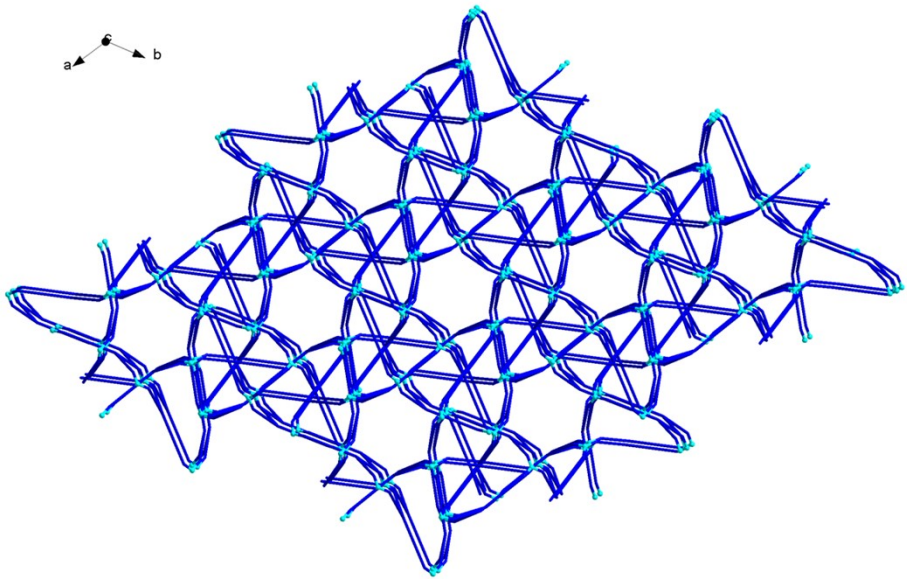
(a)



(b)



(c) (d)



(e)

Fig. S2. (a) The coordination chain constructed from tipa and Zn2 atoms in **2**. (b) The macrocyclic coordination rings constructed from tipa and Zn1 atoms in **2**. (c) The 3D cationic frameworks of **2**. (d) The pores in the frameworks of **2**. (e) Topological structure of **2**.

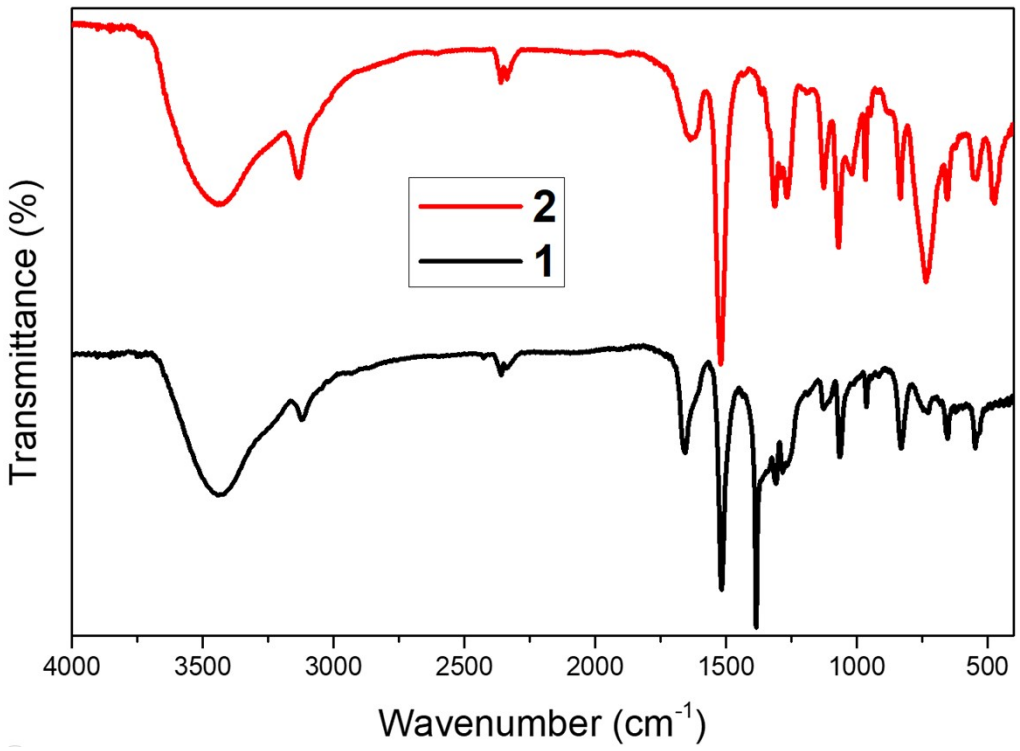


Fig. S3. IR spectra at room temperature of **1** and **2**.

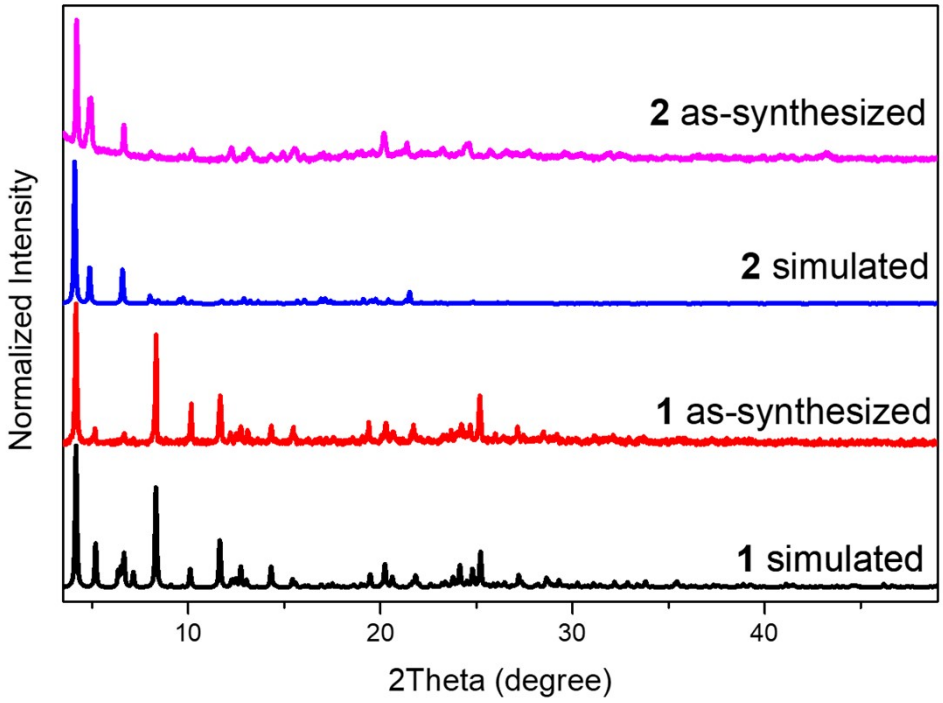


Fig. S4. PXRD patterns of **1** and **2**.

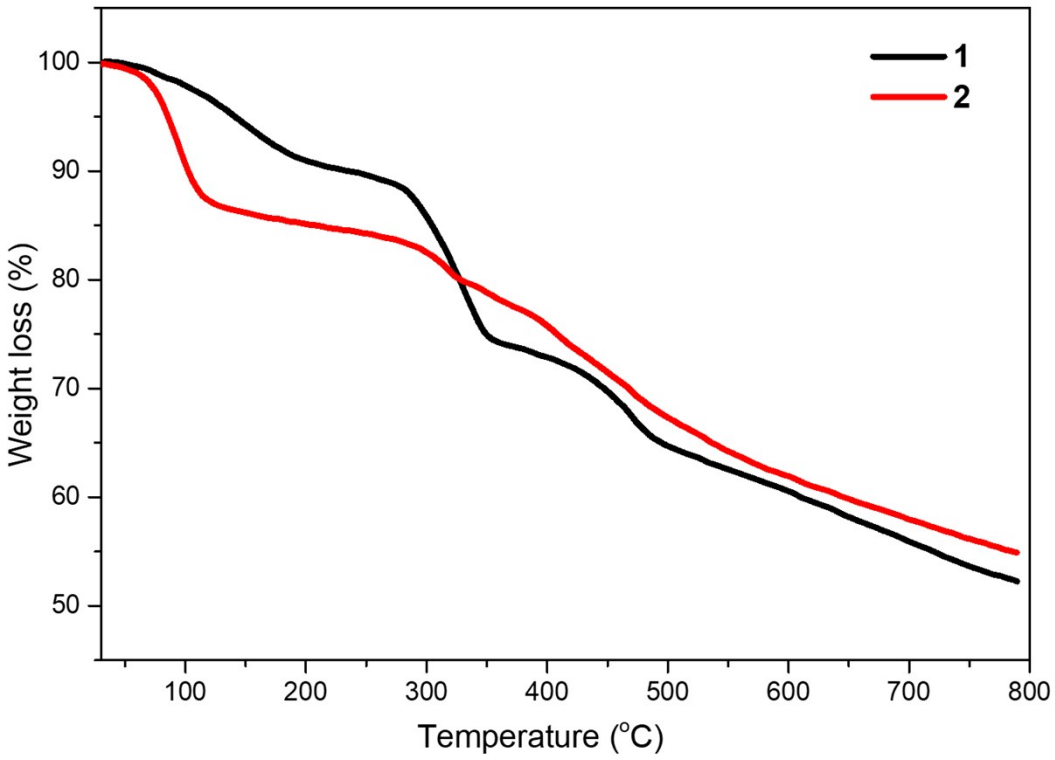


Fig. S5. TG curves of **1** and **2**.

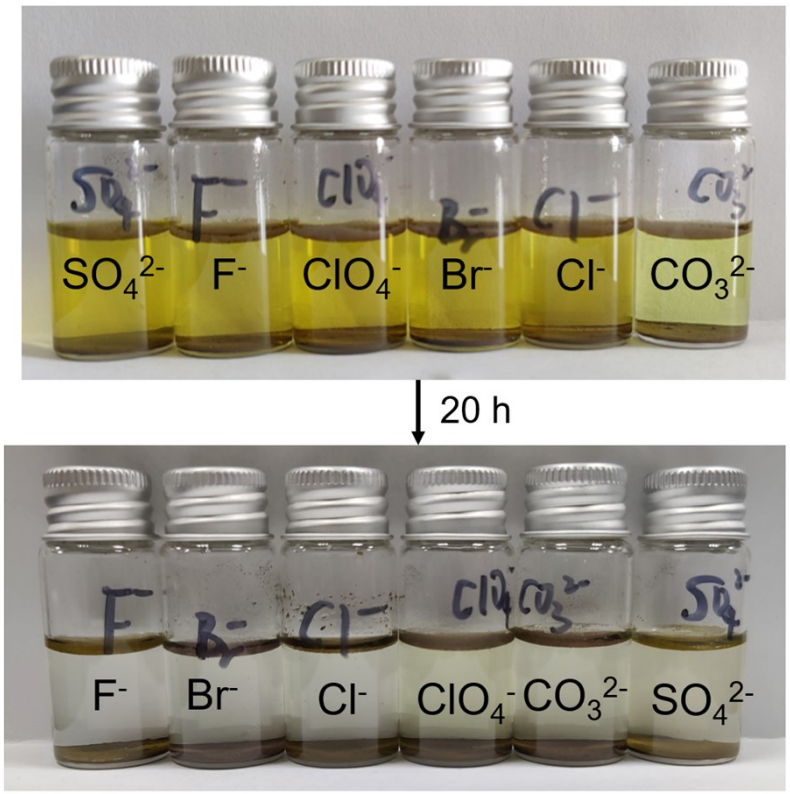


Fig. S6. The color change of the mixed solution containing $Cr_2O_7^{2-}$ and other common anions upon the addition of **1**.

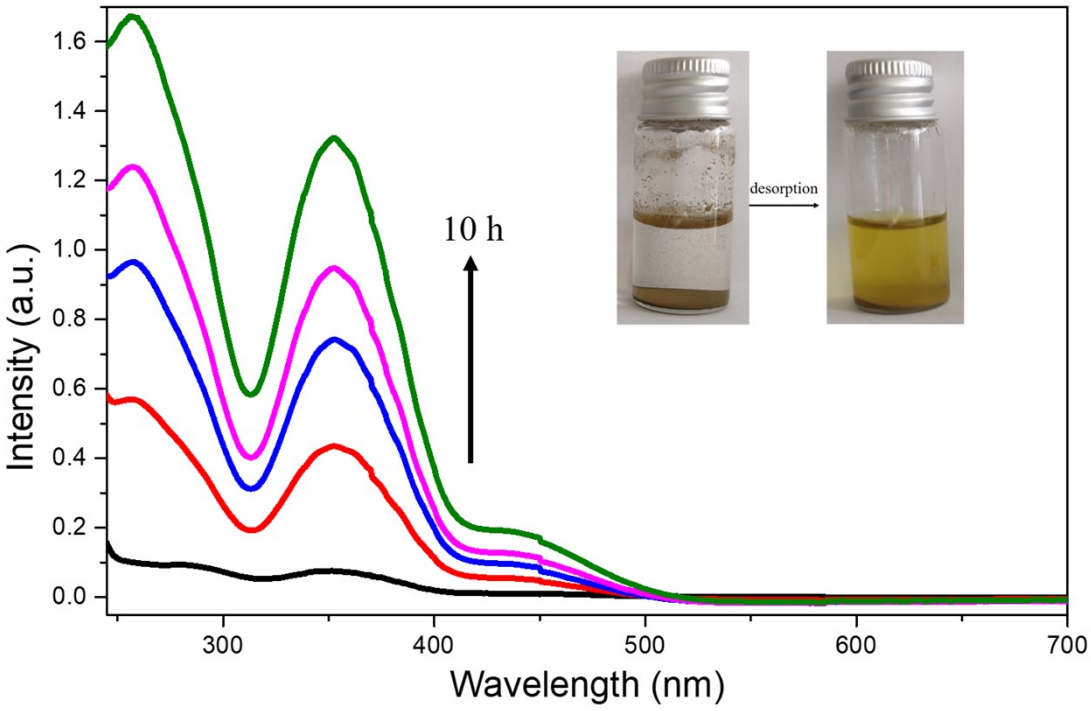


Fig. S7. Time-dependent UV-vis desorption spectra of the aqueous KNO_3 solution upon the addition of $Cr_2O_7^{2-}$-treated **1** (inset: The colour change of the aqueous KNO_3 solution after the addition of $Cr_2O_7^{2-}$-treated **1**.).

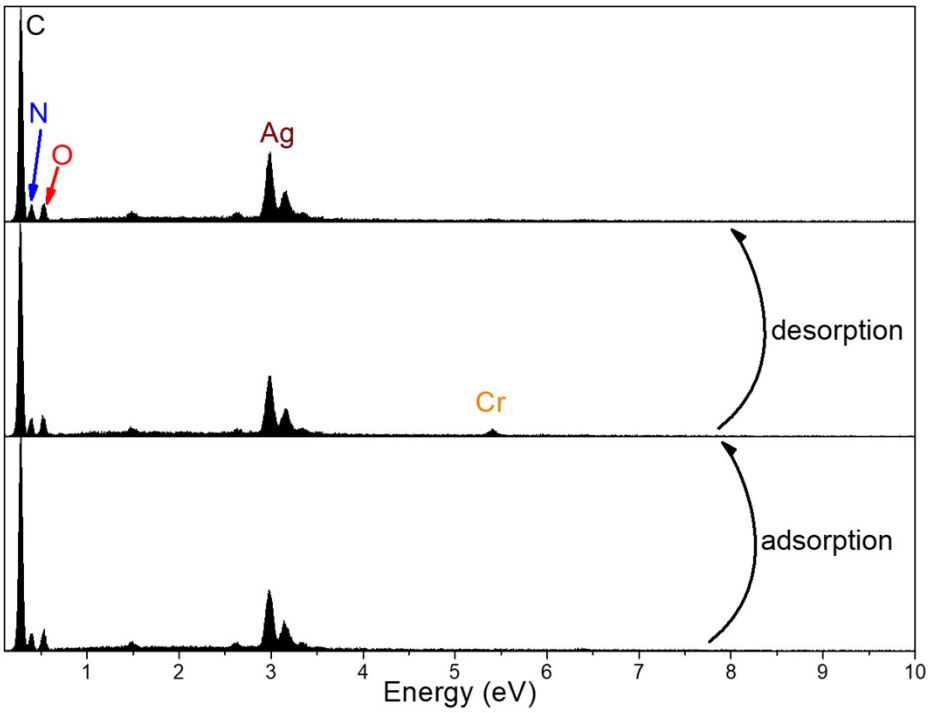


Fig. S8. EDS spectra of **1** upon the adsorption and desorption of $Cr_2O_7^{2-}$.

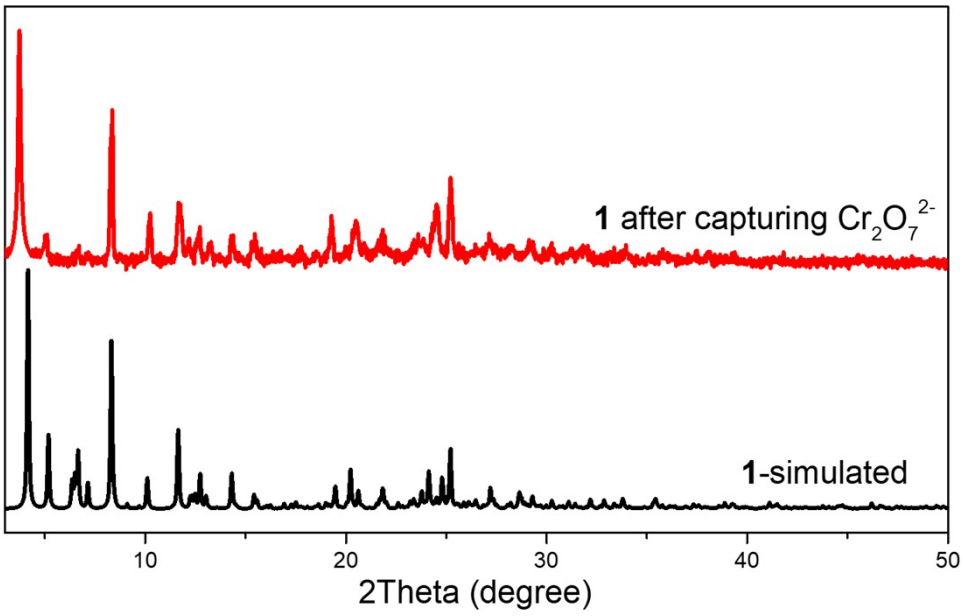


Fig. S9. PXRD patterns of the sample of **1** after the adsorption of $Cr_2O_7^{2-}$.

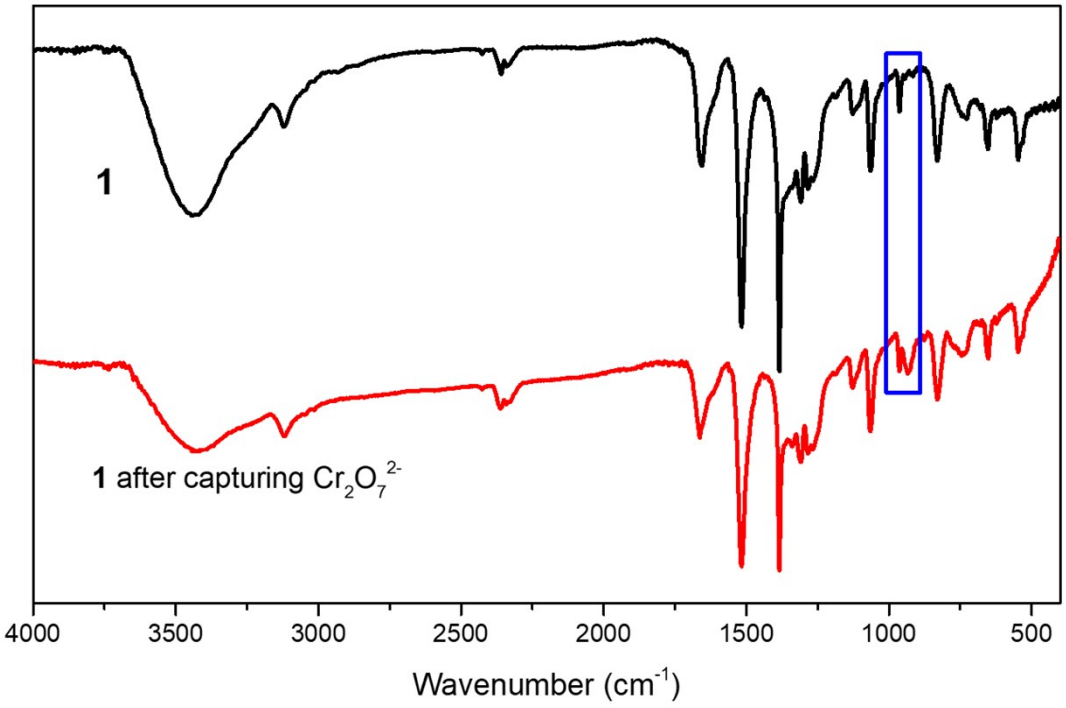
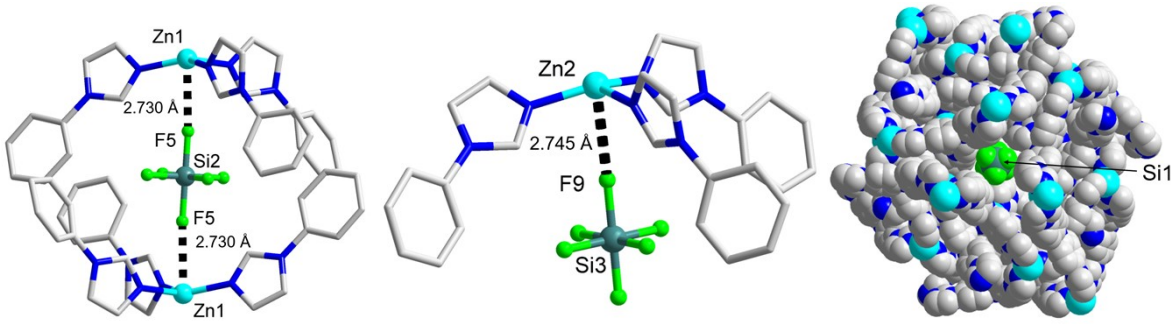


Fig. S10. IR spectra at room temperature of **1** before and after the adsorption of $Cr_2O_7^{2-}$.



(a) (b) (c)

Fig. S11. (a, b) The distances between Zn(II) cations and F atoms of SiF_6^{2-}. (c) Space-filling mode of SiF_6^{2-} anion in the pores.

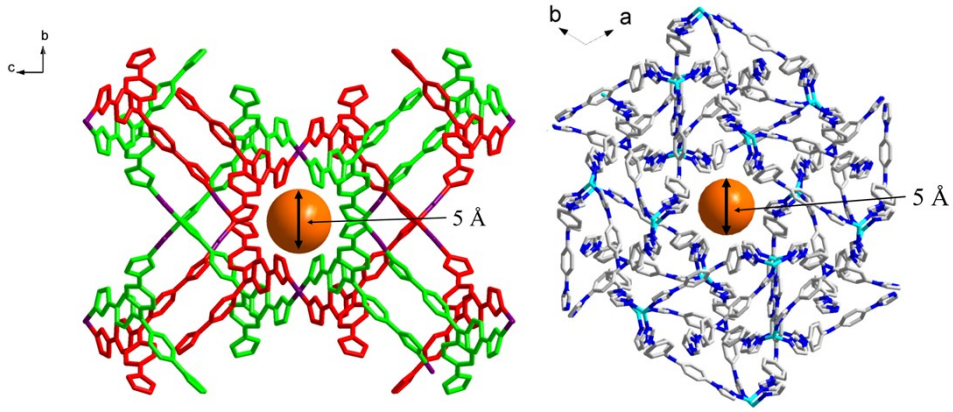


Fig. S12. The opensing size of the pores in complex **1** (left) and **2** (rignt).