*Electronic Supplementary Information*

# Highly efficient $Cr_2O_7^{2-}$ removal of a 3D metal–organic framework fabricated by tandem single-crystal to single-crystal transformations from a 1D coordination array

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## Experimental details

**Materials and general methods.** All chemicals and solvents were commercially available and used as received, with the exception of the ligand $L^{243}$ that was prepared according to the literature method.[1] Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer. Elemental analyses of C, H, and N were carried out on a CE-440 (Leeman labs) analyzer. Powder X-ray diffraction (PXRD) patterns were taken on a D/Max-2500 diffractometer (Rigaku) at 40 kV and 100 mA for a Cu-target tube ($\lambda$ = 1.5406 Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software package.[2] Thermogravimetric (TG) analysis was measured on a TG209 thermal analyzer (NETZSCH) in 25–600 °C region at a heating rate of 10 °C/min under nitrogen atmosphere. Solid state fluorescence spectra were taken on a Cary Eclipse spectrofluorimeter (Varian). UV-vis spectra of the solution were collected on a Lambda 35 spectrophotometer (PerkinElmer) to monitor the exchange progress. Inductively coupled plasma mass spectrometry (ICP-MS) measurement analysis was conducted on an Ultima2 spectrometer (HORIBA JY) after degradation of the sample in $HNO_3$.

**Single-crystal X-ray diffraction.** Single-crystal X-ray diffraction data for **1–4** were collected on a Bruker Apex II CCD diffractometer at 296(2) K for **1**, **3** and **4**, or 173(2) K for **2** with Mo Kα radiation ($\lambda$ = 0.71073 Å). Semi-empirical absorption corrections were used with SADABS and the program SAINT was applied for integration of the diffraction profiles.[3] All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.[4] The final refinements were performed by full-matrix least-squares methods on $F^2$ with anisotropic thermal parameters for all non-H atoms. The hydrogen atoms of the ligands were generated geometrically and isotropic displacement parameters of hydrogen were derived from their parents. For **2**, the nitrite anion and water molecules (O4 and O5) are disordered over two sites with the occupancy factors of 0.86/0.14, 0.47/0.28, and 0.41/0.09, respectively. The affiliated H atoms of lattice water molecules in **2** were not determined. For **3**, three fluorine atoms (F1–F3) of a trifluoroacetate are disordered over two sites, with the occupancy factor of 0.61/0.39. The lattice water molecules (O3 and O4) in **3** were assigned to the half occupancy to achieve the appropriate thermal parameters. Crystallographic parameters and selected bond lengths and angles are listed in Table S1 and Table S2.

**Syntheses.**

**$[Ag(L^{243})(NO_2)](CHCl_3)$ (1).** A $CH_3OH$ solution (5 mL) of $AgNO_2$ (15.4 mg, 0.10 mmol) was layered upon a $CHCl_3$ solution (5 mL) of $L^{243}$ (30.0 mg, 0.1 mmol), which was left to stand under ambient condition. Colorless block-shaped crystals of **1** suitable for X-ray diffraction were obtained upon slow evaporation of the solvents after ca. 1 week in 58% yield. Anal. Calcd for $C_{18}H_{13}AgCl_3N_7O_2$ (**1**): C, 37.69; H, 2.28; N, 17.09%. Found: C, 37.57; H, 2.39; N, 16.81%. IR ($cm^{-1}$): 3060m, 1592vs, 1573w, 1505m, 1450s, 1422m, 1270vs, 1169w, 1170w, 991w, 846w, 813w, 791w, 739w, 705m, 636w, 612w.

**$[Ag(L^{243})](NO_2)(H_2O)_{4.25}$ (2).** Well-shaped single crystals of **1** (30 mg) were immersed in a water solution (10 mL) in darkness, forming colorless block crystals of **2** after ca. 5 days. Anal. Calcd for $C_{17}H_{16.5}AgN_7O_{4.25}$ (**2**): C, 41.27; H, 3.36; N, 19.82%. Found: C, 41.08; H, 3.51; N, 19.57%. IR ($cm^{-1}$): 3434b, 1629s, 1591s, 1506w, 1446m, 1418w, 1385m, 1270vs, 1163w, 1083w, 988w, 843w, 787w, 703w, 633w, 608w.

**$[Ag(L^{243})](CF_3CO_2)(H_2O)_2$ (3).** Well-shaped single crystals of **1** or **2** were immersed into a water solution (10 mL) of $CF_3COONa$ (0.1 mol $L^{-1}$) in darkness for ca. 1 week (for **1**) or eight hours (for **2**), forming colorless block crystals of **3**. Anal. Calcd for $C_{19}H_{14}AgF_3N_6O_3$ (**3**): C, 41.27; H, 3.36; N, 19.82%. Found: C, 41.12; H, 3.50; N, 19.65%. IR ($cm^{-1}$): 3421b, 3057m, 1681vs, 1592s, 1569m, 1507m, 1444m, 1423m, 1208s, 1127s, 1026w, 990w, 841m, 794m, 721m, 705m, 631w, 611w, 516w.

**Anion exchange studies.** Dried single crystals of **3** (0.2 mmol) were immersed in a water solution (10 mL) of $K_2Cr_2O_7$ (0.1 mmol), which was left to stand at room temperature. The solution was monitored at various time intervals to follow the exchange progress by liquid UV-vis spectroscopy based on the typical sorption of $Cr_2O_7^{2-}$ anion at 352 nm. The water solution (0.1 mL) of $K_2Cr_2O_7$ was pipetted at different time intervals which was diluted by deionized water (2 mL) to measure the UV-vis intensity. The anion-exchange capacity of **3** was evaluated by measuring the decolorization rate for the solution of $K_2Cr_2O_7$ according to the Beer's Law. The crystals turn yellow and obscure, which were kept in $CH_3CN–H_2O$ (1 : 1). The yellow crystals suitable for single-crystal X-ray diffraction were determined to be $[Ag(L^{243})](Cr_2O_7)_{0.5}(CH_3CN)$ (**4**).

**Table S1** Crystallography data and structural refinement summary for **1–4**.

| Compound reference | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Chemical formula | $C_{18}H_{13}AgCl_3N_7O_2$ | $C_{17}H_{16.5}AgN_7O_{4.25}$ | $C_{19}H_{14}AgF_3N_6O_3$ | $C_{19}H_{15}AgCrN_7O_{3.5}$ |
| Formula mass | 573.57 | 494.74 | 539.23 | 557.25 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| $a$/Å | 9.355(5) | 10.0544(6) | 10.2840(4) | 10.1531(2) |
| $b$/Å | 9.509(5) | 14.8631(9) | 14.6472(6) | 13.2623(4) |
| $c$/Å | 13.743(7) | 13.3957(8) | 15.6111(5) | 15.5979(3) |
| $\alpha$/° | 76.120(7) | 90 | 90 | 90 |
| $\beta$/° | 84.113(8) | 98.2720(10) | 118.983(2) | 95.662(2) |
| $\gamma$/° | 66.219(7) | 90 | 90 | 90 |
| Unit cell volume/Å$^3$ | 1086.1(9) | 1981.0(2) | 2057.03(14) | 2090.07(9) |
| Temperature/K | 296(2) | 173(2) | 296(2) | 296(2) |
| Space group | $P$-1 | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ |
| $Z$ | 2 | 4 | 4 | 4 |
| $\mu$/mm$^{-1}$ | 1.328 | 1.058 | 1.042 | 1.496 |
| No. of reflections measured | 5689 | 14413 | 10334 | 8644 |
| No. of independent reflections | 3934 | 4915 | 3634 | 3660 |
| $R_{\text{int}}$ | 0.0125 | 0.0196 | 0.0140 | 0.0206 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0430 | 0.0334 | 0.0442 | 0.0471 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1088 | 0.0951 | 0.1264 | 0.0985 |
| Final $R_1$ values (all data) | 0.0479 | 0.0377 | 0.0487 | 0.0394 |
| Final $wR(F^2)$ values (all data) | 0.1127 | 0.0985 | 0.1315 | 0.0929 |
| Goodness of fit on $F^2$ | 1.052 | 1.046 | 1.051 | 1.046 |

**Table S2** Selective bond lengths (Å) and angles (°) for **1–4**.

**1**

| | | | |
|---|---|---|---|
| Ag1–N3 | 2.327(3) | Ag1–N5A | 2.404(3) |
| Ag1–O2 | 2.460(4) | Ag1–N1B | 2.495(4) |
| Ag1–O1 | 2.558(4) | | |
| | | | |
| N3–Ag1–N5A | 116.51(12) | N3–Ag1–O2 | 105.53(15) |
| N5A–Ag1–O2 | 126.67(15) | N3–Ag1–N1B | 91.80(12) |
| N1B–Ag1–N5A | 93.34(12) | N1B–Ag1–O2 | 117.41(16) |
| N3–Ag1–O1 | 152.11(16) | N5A–Ag1–O1 | 90.25(15) |
| O2–Ag1–O1 | 47.96(17) | N1B–Ag1–O1 | 94.46(15) |

Symmetry codes: A = $-x + 1, -y + 2, -z + 1$; B = $-x + 2, -y + 1, -z + 1$.

**2**

| | | | |
|---|---|---|---|
| Ag1–N5A | 2.319(2) | Ag1–N6B | 2.354(2) |
| Ag1–N1 | 2.381(2) | Ag1–N4C | 2.433(2) |
| | | | |
| N5A–Ag1–N6B | 139.13(8) | N5A–Ag1–N1 | 104.62(8) |
| N1–Ag1–N6B | 113.89(8) | N5A–Ag1–N4C | 98.30(8) |
| N6B–Ag1–N4C | 89.66(8) | N1–Ag1–N4C | 98.02(8) |

Symmetry codes: A = $x + 1/2, -y + 3/2, z + 1/2$; B = $-x + 1, -y + 1, -z + 1$; C = $-x, -y + 1, -z + 1$.

**3**

| | | | |
|---|---|---|---|
| Ag1–N5B | 2.311(3) | Ag1–N6A | 2.332(3) |
| Ag1–N1 | 2.504(4) | Ag1–N3C | 2.388(3) |

| | | | |
|---|---|---|---|
| N5B–Ag1–N6A | 141.41(12) | N5B–Ag1–N3C | 105.63(12) |
| N3C–Ag1–N6A | 110.03(12) | N5B–Ag1–N1 | 95.93(14) |
| N6A–Ag1–N1 | 94.50(13) | N1–Ag1–N3C | 96.14(12) |

Symmetry codes: A = $x - 1, y, z$; B = $-x, y - 1/2, -z + 3/2$; C = $-x, -y + 1, -z + 1$.

**4**

| | | | |
|---|---|---|---|
| Ag1–N4A | 2.278(3) | Ag1–N6B | 2.281(3) |
| Ag1–N2C | 2.488(3) | Ag1–N5 | 2.519(3) |

| | | | |
|---|---|---|---|
| N4A–Ag1–N6B | 158.74(12) | N4A–Ag1–N2C | 98.08(11) |
| N6B–Ag1–N2C | 103.17(11) | N4A–Ag1–N5 | 85.40(12) |
| N6B–Ag1–N5 | 91.86(12) | N2C–Ag1–N5 | 97.39(12) |

Symmetry codes: A = $x - 1/2, -y + 1/2, z + 1/2$; B = $x - 1, y, z$; C = $-x, -y + 1, -z + 1$.

**Table S3** Hydrogen bonding geometries in the crystal structure of **4**.

| D–H···A | D···A (Å) | H···A (Å) | D–H···A (°) | Symmetry code |
|---|---|---|---|---|
| C5–H5A···O4 | 3.292(10) | 2.60 | 132 | 1/2 – *x*, 1/2 + *y*, 1/2 – *z* |
| O9–H9A···O2 | 3.403(6) | 2.50 | 164 | 1 – *x*, 1 – *y*, 1 – *z* |
| O16–H16A···O4 | 3.272(9) | 2.43 | 151 | 3/2 – *x*, –1/2 + *y*, 1/2 – *z* |

**Table S4** Comparison of structural features for **3** and **4**.

|  | **3** | **4** |
|---|---|---|
| Dihedral angle [a] | 44.5°, 58.5°, 48.1° | 39.0°, 51.3°, 60.8° |
| Pore size [b] | 10.135 × 10.812 Å$^2$ | 9.769 × 10.389 Å$^2$ |

[a] Dihedral angle between the central triazole ring and 2-, 3-, or 4-pyridyl ring.

[b] Calculated from the diagonal distances of the 1D channels.

**Table S5** Adsorption capacities of dichromate anion for the reported materials.

| MOF-Type Adsorbents | Maximum Capacity (mg $g^{-1}$) | Ref. | Other Type Adsorbents | Maximum Capacity (mg $g^{-1}$) | Ref. |
|---|---|---|---|---|---|
| **3** | 207 | this work | uncalcined LDHs | 6 | **9** |
| **ZJU-101** | 245 | **5** | Calcined LDHs | 17 | **9** |
| **ABT·2ClO$_4$** | 214 | **6** | Amino strach | 12.12 | **13** |
| **MOF-867** | 53.4 | **7** | *β*-CD and quaternary ammonium groups modified cellulose | 61.05 | **14** |
| **FIR-53** | 74.2 | **7** | Hexadecylpyridinium bromide modified natural zeolites | 14.31 | **15** |
| **FIR-54** | 103.1 | **8** | Modified magnetic chitosan chelating | 58.48 | **16** |
| **SLUG-21** | 60 | **9** | $NH_2$-TNTs | 153.85 | **17** |
| **1-ClO$_4$** | 62.9 | **10** | Chitosan-coated fly ash | 33.27 | **18** |
| **SLUG-35** | 68.5 | **11** | Eichhornia crassipes root biomass-derived activated carbon | 36.34 | **19** |
| **1-SO$_4$** | 166 | **12** | Wheat-residue derived black carbon | 21.34 | **20** |
| | | | Saw dust | 41.5 | **21** |
| | | | Ethylenediamine-functionalized $Fe_3O_4$ magnetic polymers | 61.35 | **22** |
| | | | Porous Organic Polymers | 172 | **23** |

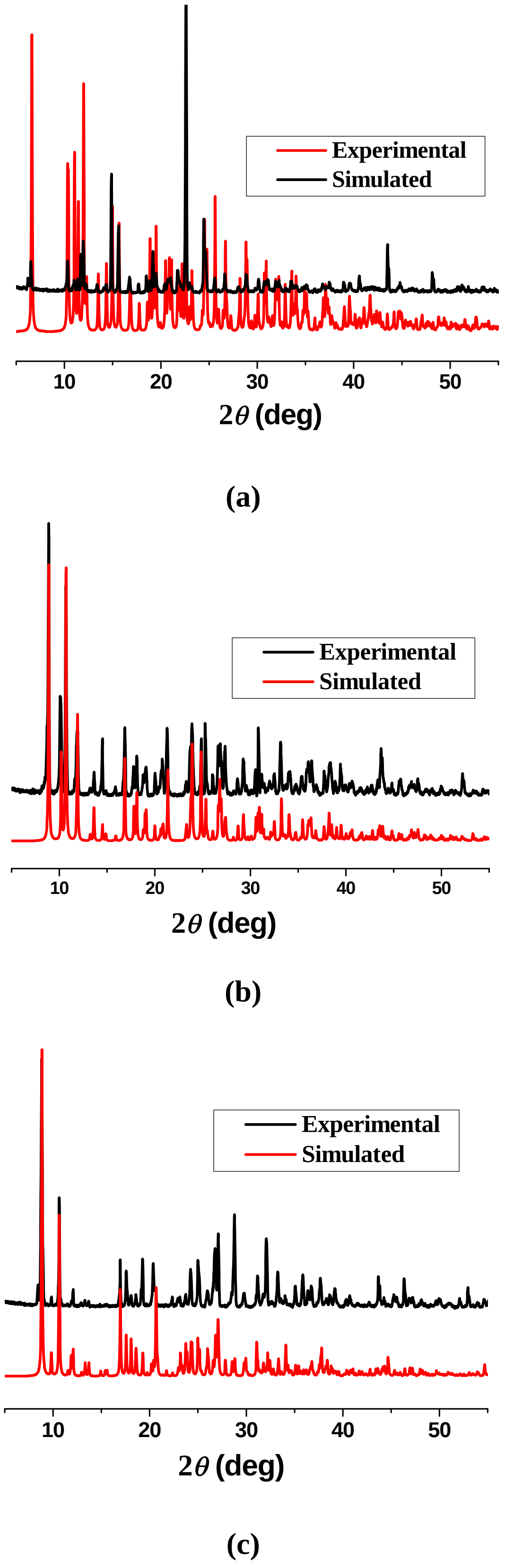
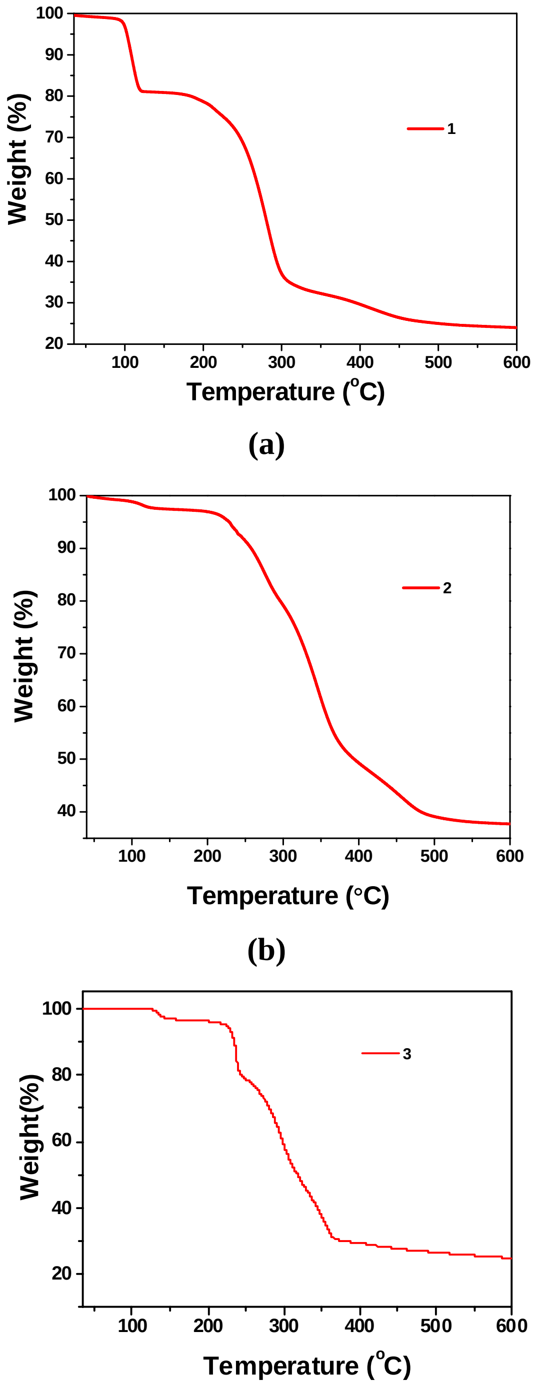


**Fig. S1** Powder X-ray diffraction (PXRD) patterns for **1–3**.



(a)

(b)

(c)

**Fig. S2** Thermogravimetric (TG) analysis curves for **1–3**.

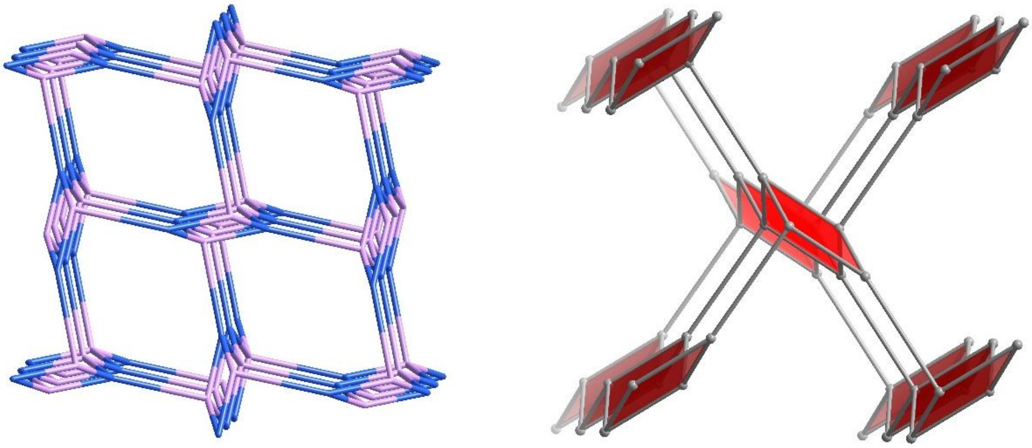


**Fig. S3** Topological view of the coordination network for **3**.

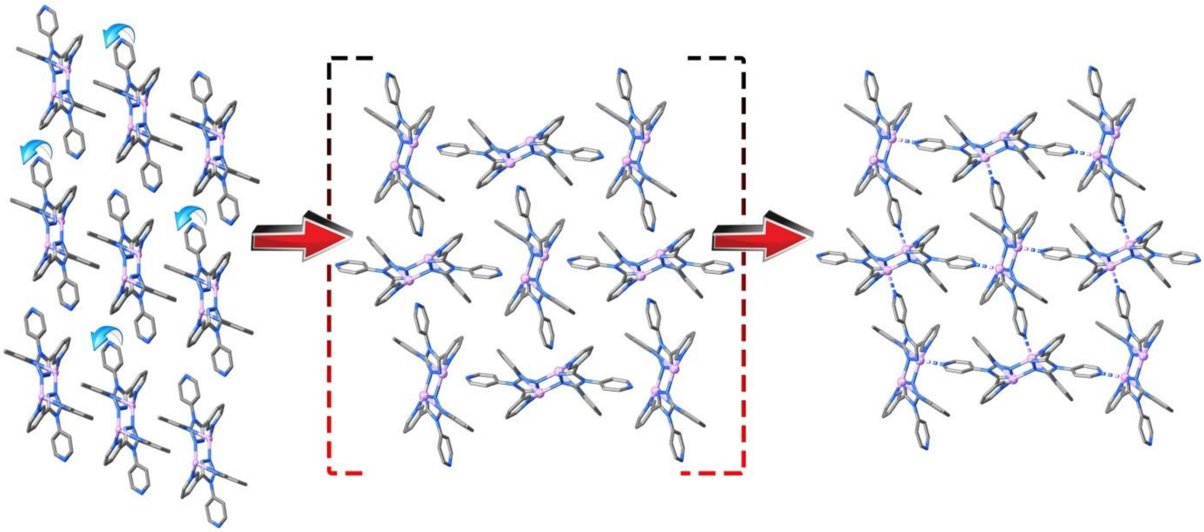


**Fig. S4** Rotation of the 1D chain SBUs during the structural transformation from **1** to **3**.

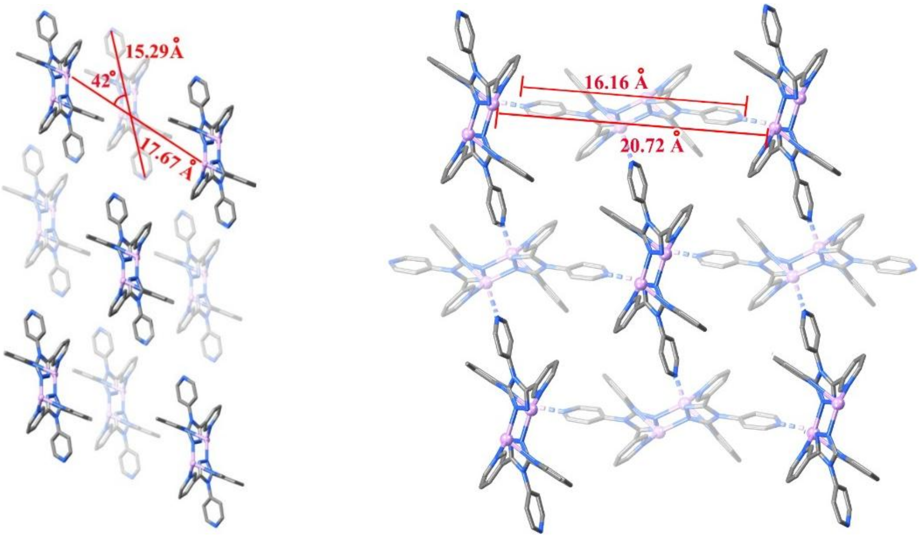


**Fig. S5** Comparison of the structural parameters between the 1D SBUs in **1** and **3**.

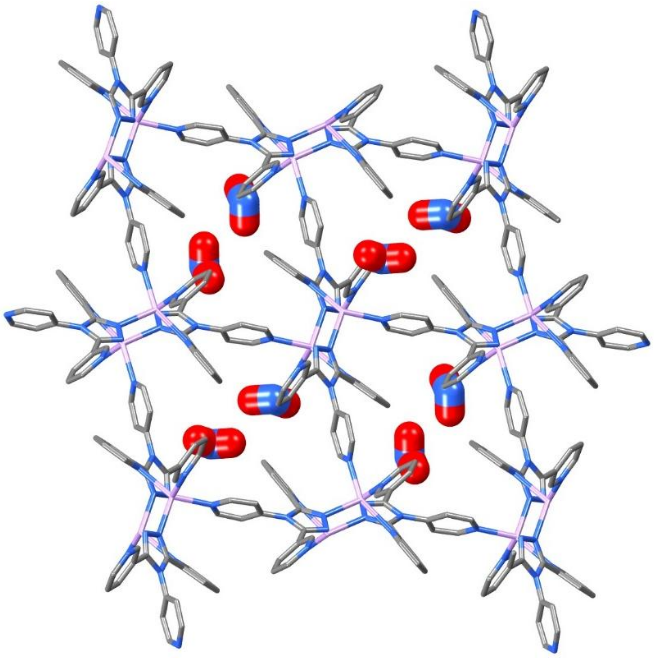


**Fig. S6** 3D cationic framework with the inclusion of lattice $NO_2^-$ anions in **2**.

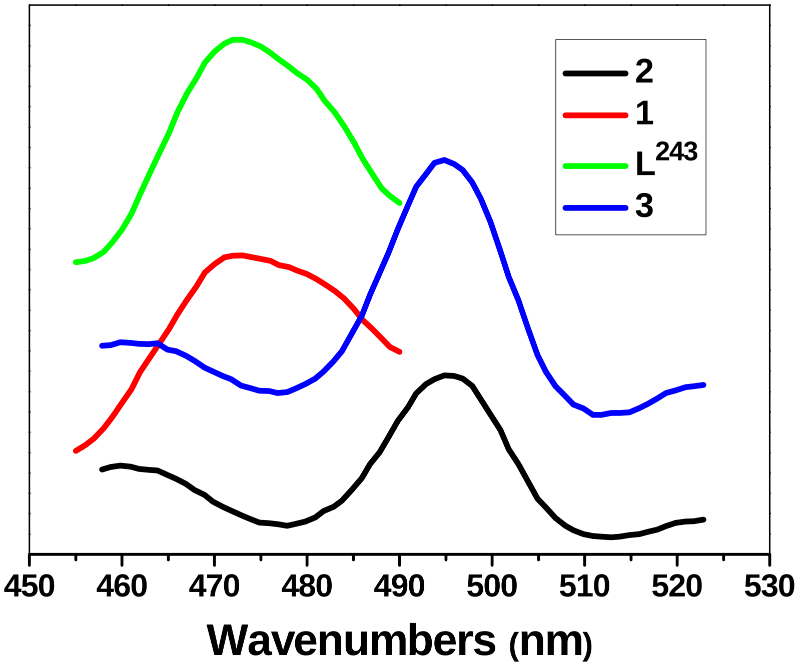


**Fig. S7** Solid state fluorescent emission spectra for **1–3** and $L^{243}$ ligand at room temperature.

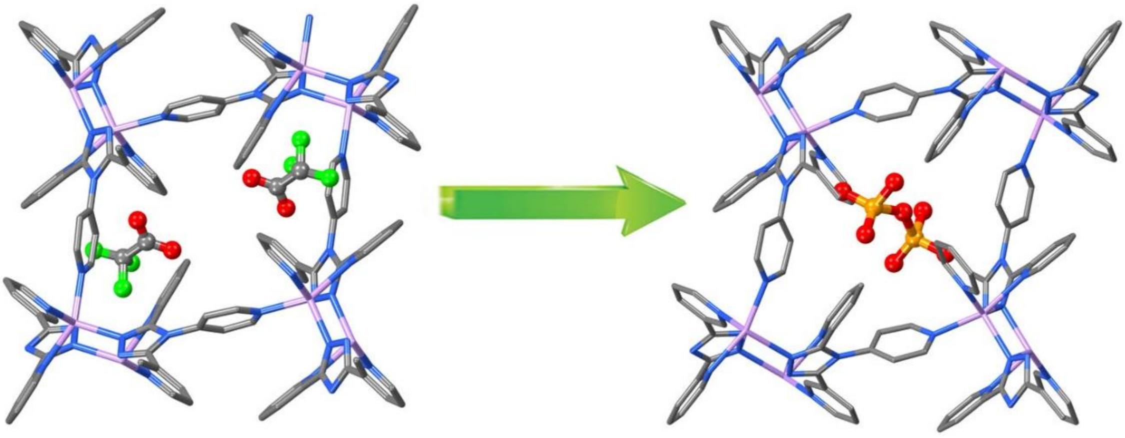


**Fig. S8** A portion view of the voids for anion inclusion in **3** and **4**.

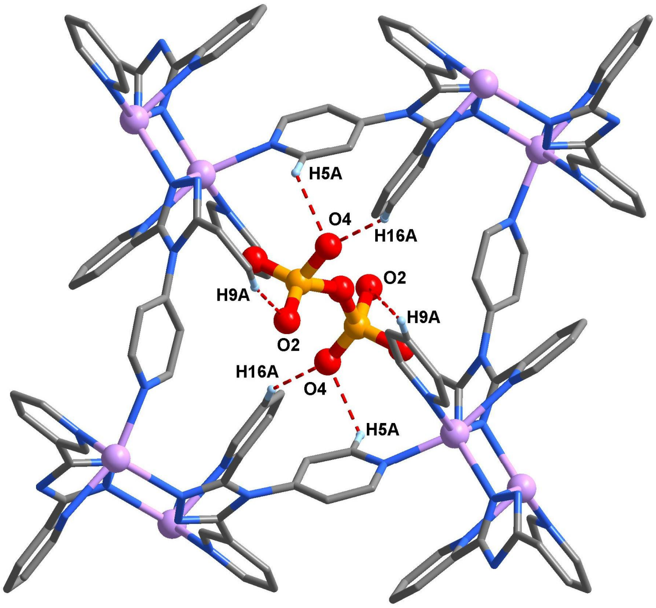


**Fig. S9** H-bonding interactions between $Cr_2O_7^{2-}$ and the cationic framework in **4**.

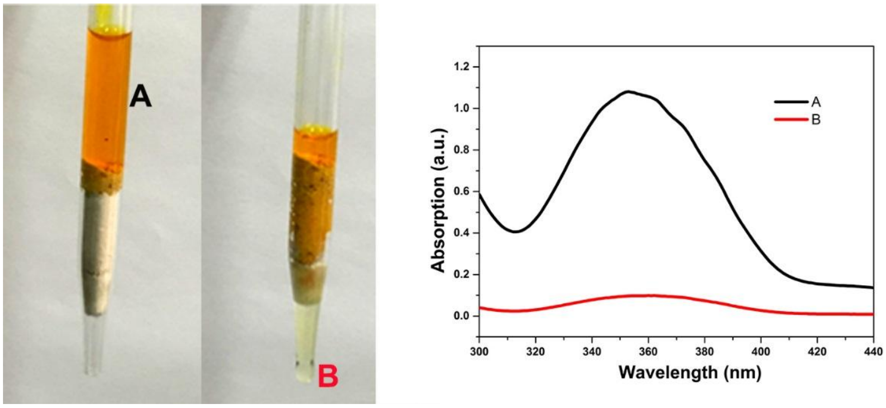


**Fig. S10** Column-chromatographic sorption for $K_2Cr_2O_7$ and the corresponding UV-vis spectra.

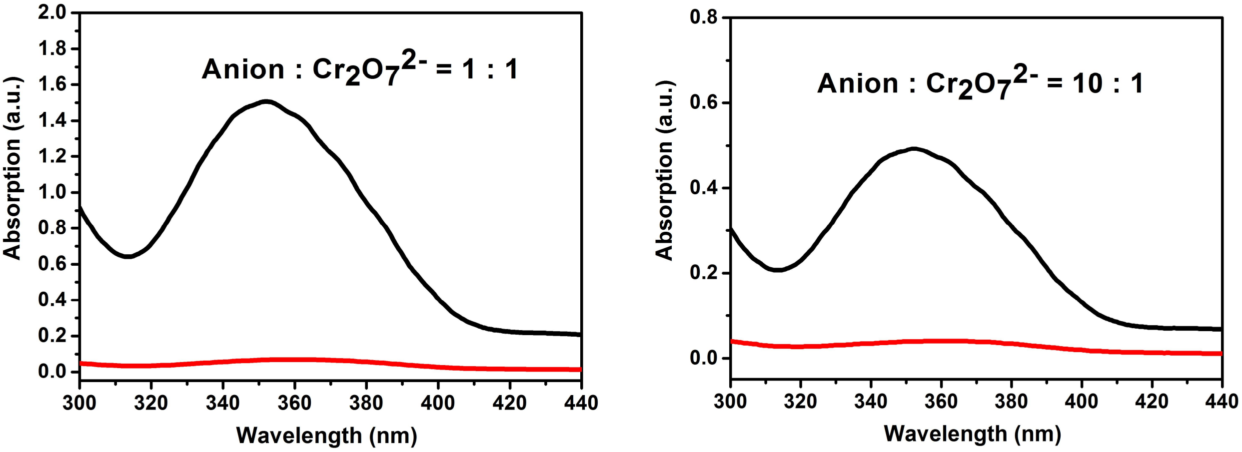


**Fig. S11** UV-vis absorbance spectra of $Cr_2O_7^{2-}$ in mixture solutions with disturbing anions ($F^-$, $Cl^-$, $Br^-$, $OAc^-$, $SO_4^{2-}$, $NO_3^-$, $BF_4^-$, $CH_3SO_3^-$, $CF_3SO_3^-$, and $ClO_4^-$) in different molar ratios.

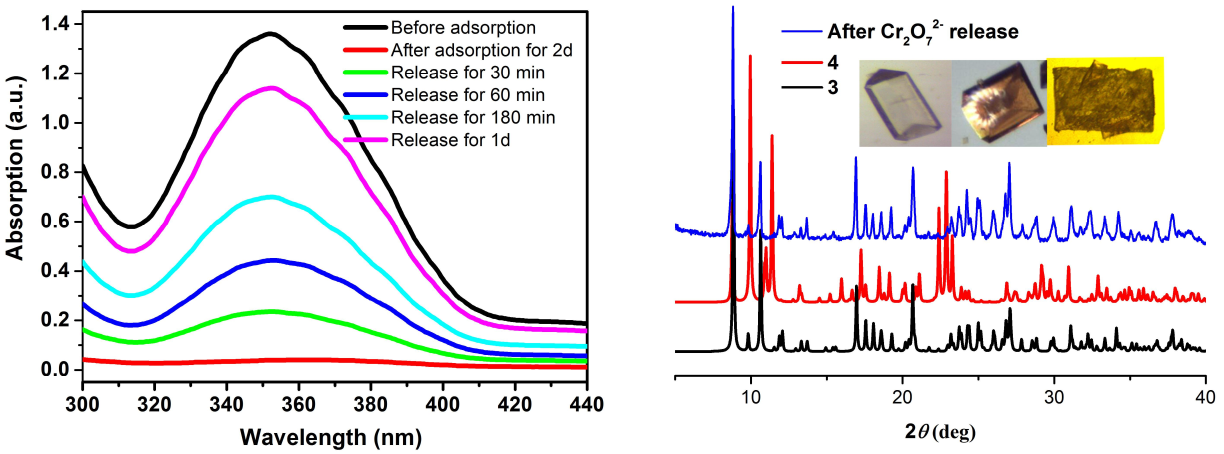


**Fig. S12** UV-vis spectra and powder X-ray diffraction (PXRD) patterns for $Cr_2O_7^{2-}$ release experiment. The inset photographs show the change of one single crystal in adsorption-desorption cycle.

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