Two resistance-switchable hybrid polyoxotantalates based on {Co$_2$Ta$_{12}$} cluster

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Experimental Procedures

Single–crystal X–ray Crystallograph: Single-crystal X-ray diffraction data for compounds **1** and **2** were collected on a Bruker APEX Due CCD area diffractometer equipped with a fine-focus, 2.0 kW sealed -tube X-ray source (MoKα radiation, λ= 0.71073 Å) operating at 170(2) K. The crystal structures were solved by the direct method and refined by full-matrix least-squares method on $F2$, according to Shelx-2014 and Olex2.2 The residual electron densities that could not be reasonably modelled as solvents or cations were removed by applying the SQUEEZE function in PLATON (the amount of solvent water dropped by squeezing in **1** and **2** is 6 and 5, respectively). The final formulae of **1** and **2** were determined by combining single-crystal X-ray diffraction with the elemental analysis, thermogravimetric analysis and charge balance, where elemental analysis verifies the number of metal atoms determined by single crystal diffraction, thermogravimetric analysis calculates the amount of crystal water (The weight loss before 150°C can be attributed to the removal of crystal water, with 22 H_2O for compound **1** and 33 H_2O for compound **2**), and the charge balance calculates the number of H atoms (4 H^+ for **1**, and 2 H^+ for **2**) that cannot be identified by single crystal diffraction data. All non-hydrogen atoms are refined with anisotropic thermal parameters. Crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Center with CCDC reference numbers 2327696 and 2327697 for compounds **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data request/cif. The selected crystal parameters, data collection, and refinements are summarized in Table S1.

Table S1 Crystal data and structure refinement for compounds 1 and 2

Identification code	1	2
Empirical formula	$H_4[Na(H_2O)_5]_2[Co(en)_3]_2[Co(en)]_2[Ta_6O_{19}]_2 \cdot 22H_2O$	$H_2K_2Na_6(H_2O)_{24}[Co(en)]_2[Ta_6O_{19}]_2 \cdot 33H_2O$
Formula weight	4121.92	4261.66
Temperature/K	170	170
Crystal system	monoclinic	triclinic
Space group	$I2/a$	P-1
a/Å	18.984(4)	10.3393(9)
b/Å	30.644(6)	12.4346(11)
c/Å	19.934(7)	15.4023(13)
α/°	90	75.6280(10)

β/°	92.149(2)	81.024(2)
γ/°	90	82.1310(10)
Volume/Å^3	11589(5)	1884.7(3)
Z	4	1
ρ$_{calc}$g/cm^3	2.342	3.422
μ/mm^{-1}	11.927	18.029
F(000)	7416.0	1768.0
Crystal size/mm^3	0.02 × 0.012 × 0.01	0.01 × 0.004 × 0.003
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.438 to 50.046	4 to 50.04
Index ranges	-22 ≤ h ≤ 16, -22 ≤ k ≤ 36, -23 ≤ l ≤ 23	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -9 ≤ l ≤ 18
Reflections collected	29336	10914
Independent reflections	10123 [R$_{int}$ = 0.0301, R$_{sigma}$ = 0.0373]	6440 [R$_{int}$ = 0.0271, R$_{sigma}$ = 0.0515]
Data/restraints/parameters	10123/488/715	6440/135/462
Goodness-of-fit on F^2	1.044	1.037
Final R indexes [I>=2σ(I)]	R$_1$ = 0.0416, wR$_2$ = 0.1166	R$_1$ = 0.0434, wR$_2$ = 0.1132
Final R indexes [all data]	R$_1$ = 0.0514, wR$_2$ = 0.1219	R$_1$ = 0.0606, wR$_2$ = 0.1243
Largest diff. peak/hole / e Å^{-3}	2.59/-1.47	3.97/-2.55

Table S2. Selected bond length (Å) and BVS calculations of the Co atoms in 1 and 2

Compound **1**

atom1	atom2	R	RO	Sij	SUM
Co2	N3	1.9566	1.62	0.323297582	2.46
	N3A	1.9734	1.62	0.103333427	
	N4	1.9779	1.62	0.286096834	
	N4A	1.9619	1.62	0.127616858	
	N5	1.9909	1.62	0.29673017	
	N5A	1.9794	1.62	0.101794993	
	N6	2.0074	1.62	0.265756463	
	N6A	1.9854	1.62	0.120335356	
	N7	1.9405	1.62	0.291698975	
	N7A	1.9597	1.62	0.149707465	

	N8	1.9716	1.62	0.269878636	
	N8A	2.0205	1.62	0.128596958	
Co1	O9	1.8783	1.65	0.586695109	2.98
	O4	1.931	1.65	0.514916772	
	O3	1.9329	1.62	0.467549525	
	O1	1.9477	1.62	0.451807082	
	N2	1.9559	1.65	0.484687949	
	N1	2.0236	1.65	0.474022732	

Compound **2**

atom1	atom2	R	RO	Sij	SUM
Co1	O9	1.8783	1.65	0.565101454	2.82
	O4	1.931	1.65	0.495345391	
	O3	1.9329	1.65	0.49299808	
	O1	1.9477	1.65	0.475090484	
	N2	1.9559	1.62	0.431818465	
	N1	2.0236	1.62	0.364583381	

Table S3 Hydrogen Bond Lengths (Å) and Bond Angles (o) in 1.

No	D-H	H⋯O	D⋯O	<(DHO)	Hydrogen bonds
1	0.91	1.94	2.78(4)	152.8	$N_4-H_{4A}\cdots O_{45}^1$
2	0.91	1.90	2.66(3)	139.4	$N_{4A}-H_{4AA}\cdots O_7^1$
3	0.91	2.17	3.02(4)	156.8	$N_5-H_{5A}\cdots O_{34}^1$
4	0.91	2.06	2.93(5)	157.3	$N_{5A}-H_{5AB}\cdots O_{18}^1$
5	0.91	1.97	2.86(2)	167.4	$N_7-H_{7B}\cdots O_{15}$
6	0.91	2.00	2.89(19)	164.4	$N_8-H_{8B}\cdots O_{18}^1$
7	0.91	1.87	2.74(4)	157.2	$N_{8A}-H_{8AA}\cdots O_{11}^1$
8	0.91	1.97	2.85(6)	160.2	$N_{8A}-H_{8AB}\cdots O_{45}^1$

[1]1/2+X,2-Y,+Z

Inductively coupled plasma spectroscopy (ICP) analysis:

ICP analysis was carried out on an Ultima2 spectrometer. Samples of **1** (8.95 mg) and **2** (10.5 mg) were dissolved separately in 10 mL of concentrated nitric acid, then, 2 mL of hydrofluoric acid was added, and the resulting solutions were diluted to 100 mL with 3% dilute nitric acid. These two solutions were suitable for testing unknown samples **1** and **2**. The following concentrations of standard solutions were prepared separately for calibration of the standard curve: Ta, 0 mg/L, 10 mg/L, 25 mg/L, 50 mg/L, 80 mg/L, and 100 mg/L; Co, 0 mg/L, 1 mg/L, 2 mg/L, 6 mg/L, 10 mg/L, and 15 mg/L. ICP was used to calculate each ion's concentrations down to the ppm level

Table S4 Inductively coupled plasma spectroscopy (ICP) analysis

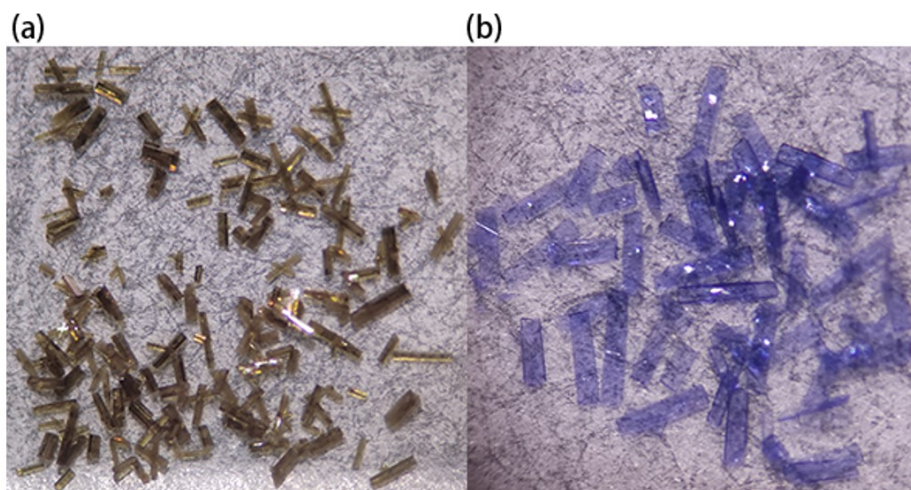| Sample name	Atom name	Ta	Co
1	Calculated (%)	52.69	5.72
	Found (%)	52.74	5.52
2	Calculated (%)	51.00	2.77
	Found (%)	51.60	2.76

Additional Figures

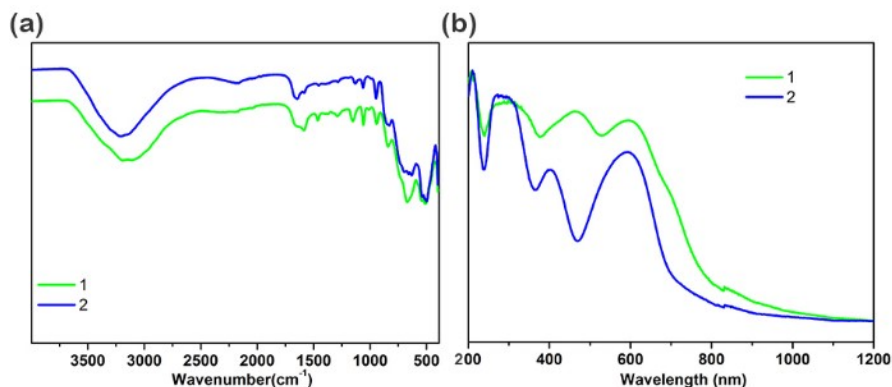**Fig. S1** The photographs of the crystal morphology of **1**(a) and **2**(b).

Fig. S2 (a) FT-IR spectra of **1** and **2**; (b) Solid-state UV-Vis absorption spectra of **1** and **2**.

IR Spectroscopic Analysis.

The IR spectra of compounds **1** and **2** show that the wide peak around 3500 - 2700 cm^{-1} can be attributed to the stretching vibration of the O-H groups, the peak at 1600 cm^{-1} corresponds to the H O H bending vibration of crystal water. The characteristic stretching vibration peak of ν (C–H) and ν (N–H) is still included in the broad peak at 3600–2700 cm^{-1} and the corresponding bending vibration peaks appear at 1700-1200 cm^{-1}. The peaks in the range of 1000–600 cm^{-1} may be attributed to ν (Ta O) stretching vibration peak. Co−O and Co−N stretching vibration are at about 500 cm^{-1}, 450 cm^{-1}, respectively.

UV−Vis−NIR Spectroscopic Analysis.

Compounds **1** and **2** exhibit different colors, and different UV/Vis absorption spectra in the range of 400 to 700 nm.

In the UV region, both **1** and **2** exhibit absorption peaks at 200 - 400 nm, which are attributed to the O→Ta charge transfer transition (LMCT). Additionally, the UV/Vis spectra of **1** and **2** shows a band at 480 - 586 nm, indicating the presence of an octahedral cobalt(III) ion undergoing a $1A_{1g} \rightarrow 1T_{1g}$ transition. Compound **1** shows absorption bands centered at about 420 nm, which corresponds to the d-d transition of Co(II).
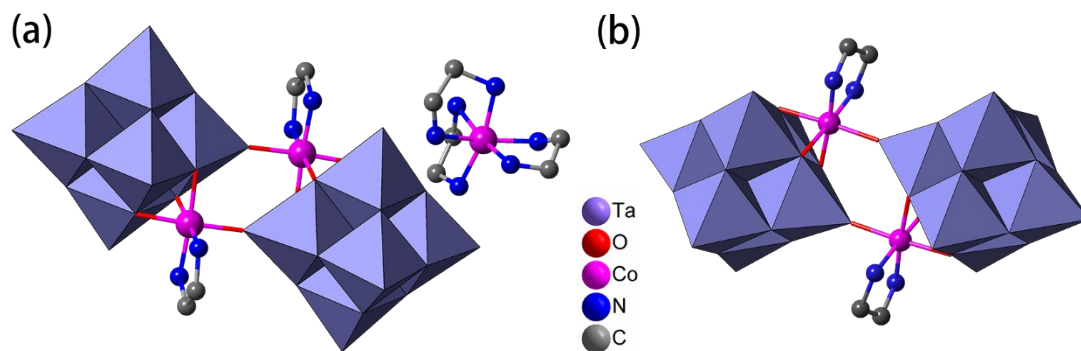
Fig. S3 The asymmetric units of **1**(a) and **2**(b)
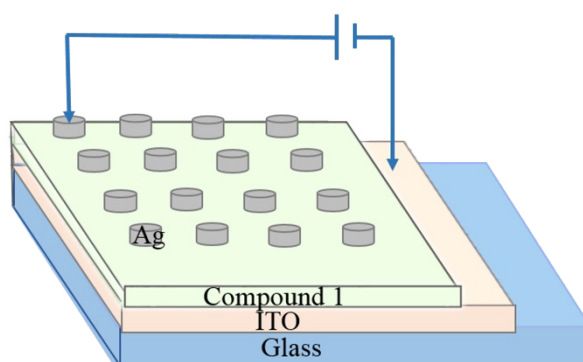
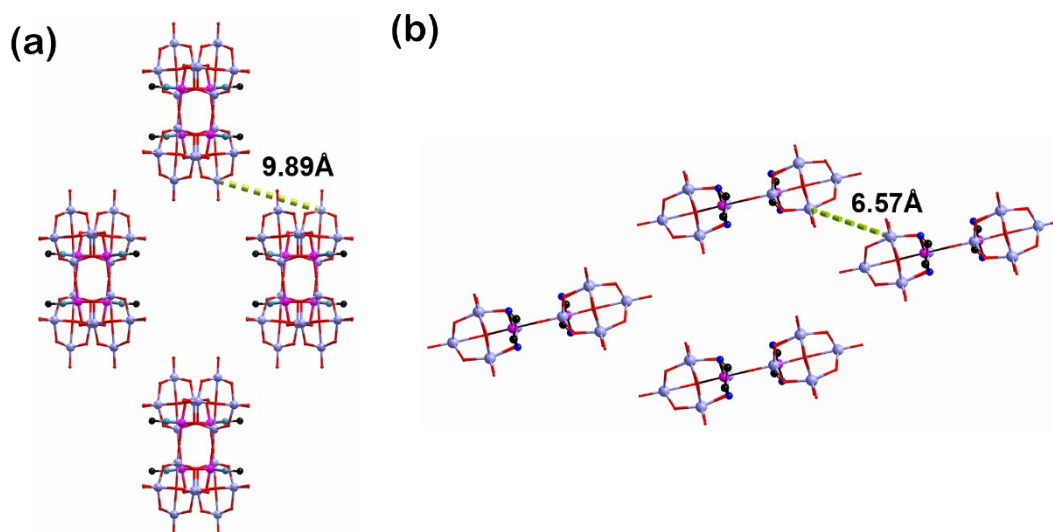**Fig. S4** 3D schematic illustration of the device

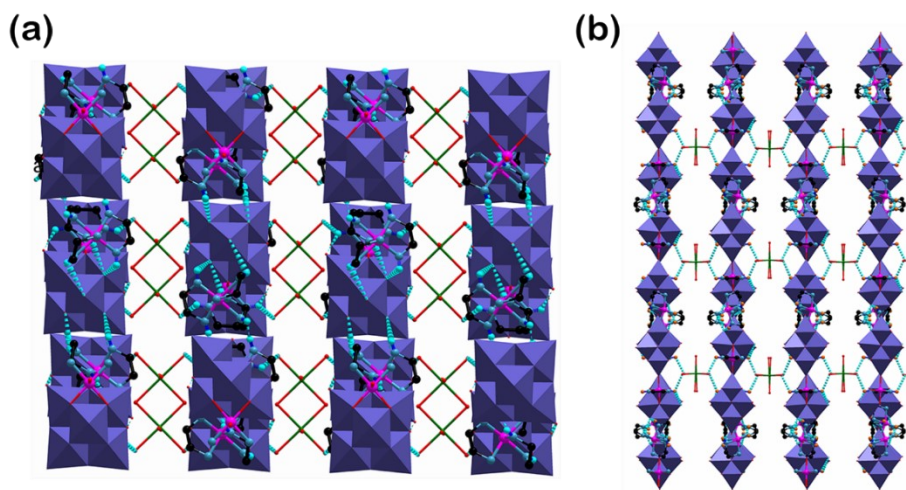**Fig. S5** Ball-and-stick diagram of adjacent clusters in compounds **1** and **2**.

Fig. S6 Three-dimensional (3D) supramolecular framework in compound **1** viewed along *b*-axis (a) and *c*-axis (b), all hydrogen atoms are omitted for clarity
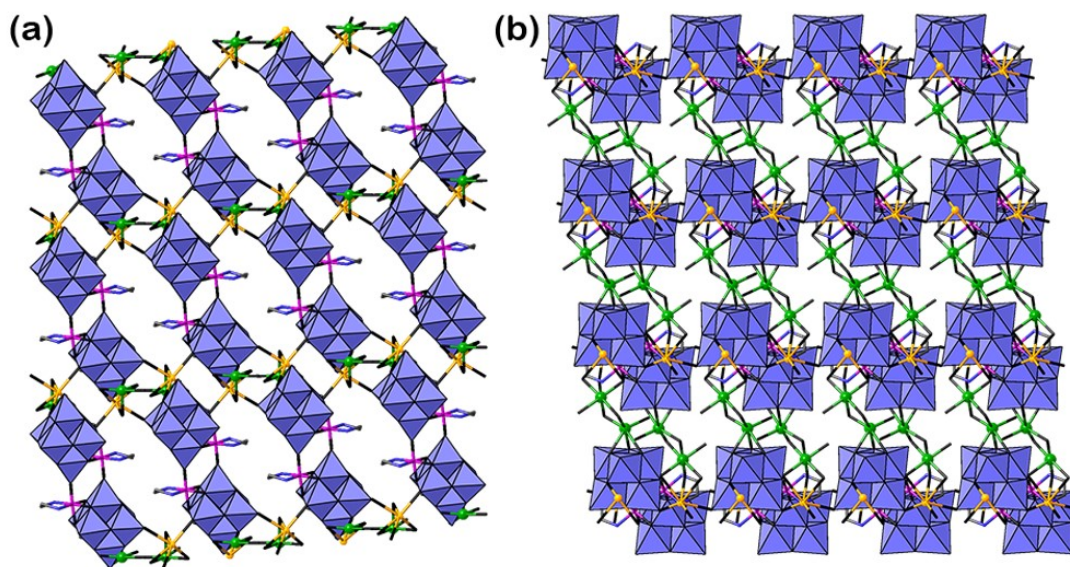

Fig. S7 Three-dimensional (3D) framework in compound **2** viewed along *b*-axis (a) and *c*-axis (b).
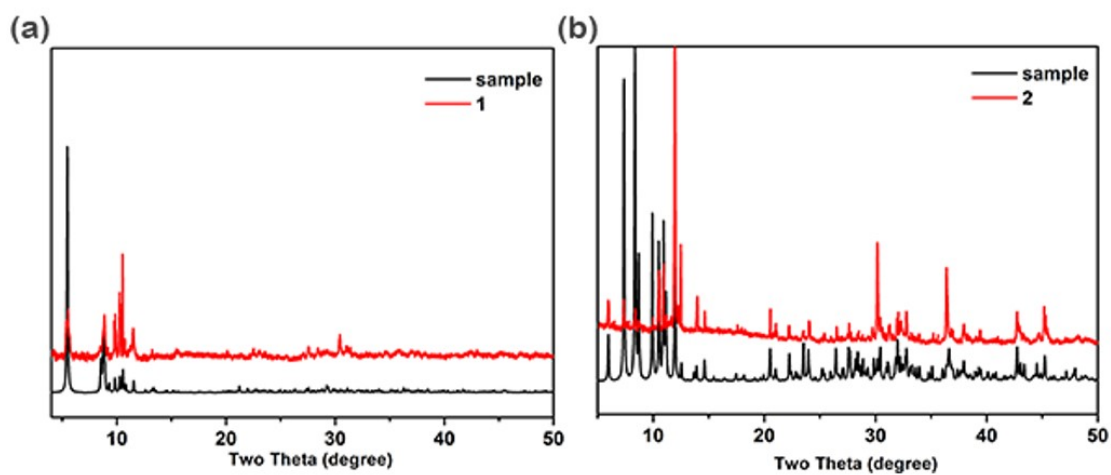

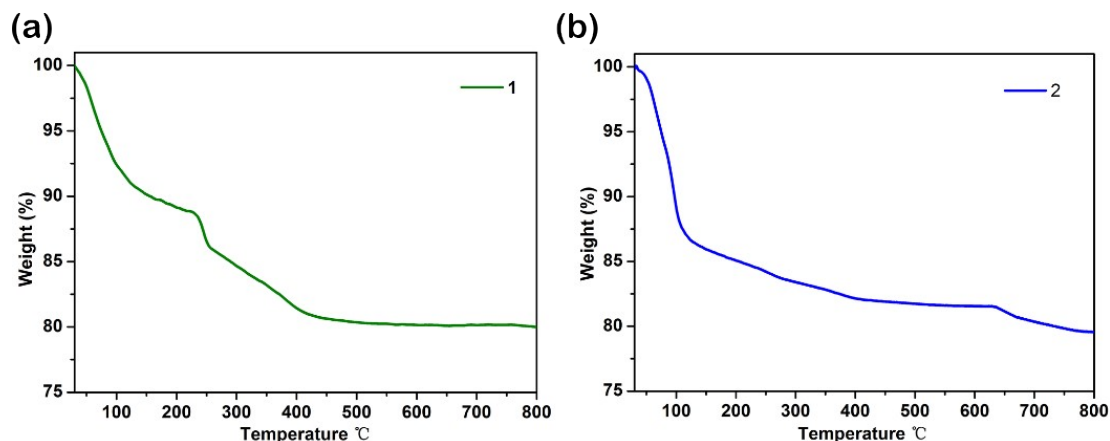**Fig. S8** PXRD patterns of compounds **1**(a) and **2**(b)

Fig. S9 TG curves of **1**(a) and **2**(b)

TG analyses of compounds **1** and **2** were performed under an argon atmosphere with the temperature ranging from 30°C to 800°C at a heating rate of 10 °C/min. As shown in Fig. S9, the TG curve of the compound **1** indicates that the first weight loss from 30°C to 137 °C is 9.46%, which is attributed to the loss of 22 free water molecules per formula unit (calcd 9.61%). The second loss of 4.44% is observed from 137 °C to 258 °C, which corresponds to the release of 10 coordinated water molecules per formula unit (calcd 4.36%). After 258 °C, compound **1** starts to decompose.

For **2**, the initial weight loss of 13.81% from 30°C to 139 °C corresponds   to the loss of 33 free water molecules per formula unit (calcd 13.94%). Between 139 °C and 400 °C, the second weight loss of 4.03% corresponds to the removal of about 10 coordinated water molecules per formula unit (calcd 4.22%). After 400 °C, compound **2** begins to decompose.
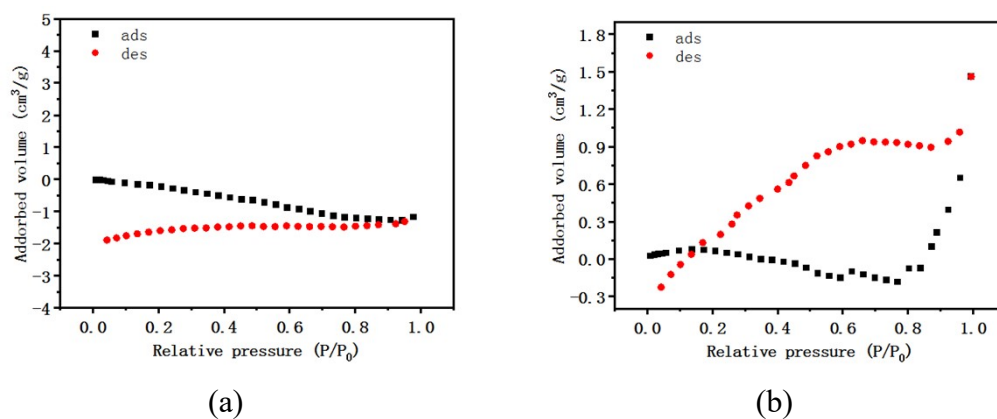

(a)   (b)

Fig S10 N_2 adsorption curves of **1** (a) and **2** (b)

The porosity of compound **1** and **2** was determined by the adsorption of N_2. No appreciable N_2 adsorption was observed in **1** and **2** (Fig S10).