Electronic Supplementary Information

Water molecule-driven reversible single-crystal to single-crystal transformation of a multi-metallic coordination polymer with controllable metal ion movement

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Materials and measurement

All chemical reagents were obtained from commercial sources. Elemental analysis was performed on a Perkin–Elmer 240 CHN elemental analyzer. IR spectra were recorded in the range 400–4000 cm^{-1} on a Bruker TENOR 27 spectrophotometer by using KBr pellets. Powder X-ray diffraction measurements (PXRD) were recorded on Ultima IV X-ray diffractometer using Cu-Kα radiation. The simulated powder patterns were calculated by using Mercury 2.0. Thermogravimetric analysis was performed on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10°C min^{-1} under a nitrogen atmosphere. ICP measurement was performed on an ICP-9000(N+M), Thermo Jarrell-Ash Corp.

Synthesis of $[Gd(H_2CAM)_3]\cdot 5.25H_2O$:

The mixture of H_3CAM (H_3CAM = chelidamic acid monohydrate, 0.3mmol, 60.3mg), $Gd(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 45.2mg) and 2 mL DEF (N,N-diethylformamide) heated in 5mL glass vial at 90 °C for 3 days, and then cooled to room temperature at a rate of 2 °C h^{-1}.The block yellow crystals of **$[Gd(H_2CAM)_3] \cdot 14.25H_2O$** were obtained. The crystals was washed, filtered and dried to obtain the **$[Gd(H_2CAM)_3] \cdot 5.25H_2O$** in 41% yield based on Gd. Elemental analysis for **$[Gd(H_2CAM)_3] \cdot 5.25H_2O$**, Calc(%):C, 31.6; H, 2.8; N, 5.26. Found (%): 32.14; 2.75; 5.35. IR (KBr, cm^{-1}): 3230 m, 2849 m, 2500 m, 2277w, 1343 s, 1153 s, 981 w, 835 w, 741 w, 689 w, 655 w, 521 m, 445 m.

Synthesis of $\{[Co_{0.5}(H_2O)_3][Gd(CAM)(HCAM)_2Co_{1.5}(H_2O)_3]\}_n \cdot 3nH_2O$ (1) : The mixture of **$[Gd(HCAM)_3]\cdot 5.25H_2O$** (0.1mmol, 79.8mg), $Co(NO_3)_2\cdot 6H_2O$(0.3mmol, 87.3mg) and 5ml water heated in 20mL teflon cup at 140°C for 3 days, and then cooled to room temperature at a rate of 2 °C h^{-1}. The needle pink crystals were obtained in 73% yield based on Gd. Elemental analysis for 1, Calc (%): C, 25.75; H, 2.67; N, 4.29. Found (%):26.04; 3.25; 4.37. IR (KBr, cm^{-1}): 3230 m, 2849 m, 1343 s, 1153 s, 1085 m, 835 w, 741 w, 689 w, 521 m, 497 w, 445 m.

Synthesis of $\{[Co_{0.5}(H_2O)_2][Gd(CAM)(HCAM)_2Co_{1.5}(H_2O)_3]\}_n \cdot 2.5nH_2O$ (2) : 2 was obtained by heating **1** at 369K under nitrogen atmosphere. The transformation from single crystal **1** to single crystal **2** was confirmed by the X-ray crystallography. Elemental analysis for **2**, Calc (%): C, 26.47; H, 2.43; N, 4.41. Found (%):26.61; 2.72; 4.49.

Synthesis of $\{[Co_{0.5}][Gd(CAM)(HCAM)_2Co_{1.5}(H_2O)_3]\}_n$ (3) : 3 was obtained by heating **2** at 413K under nitrogen atmosphere. The transformation from single crystal **2** to single crystal **3** was confirmed by the X-ray crystallography. Elemental analysis for **3**, Calc (%): C, 28.94; H, 1.62; N, 4.82. Found (%):28.98; 1.73; 4.96. ICP (mg/L): Gd, 442.4; Co, 385.4; ratio of Gd: Co = 1:2.2.

Crystallographic studies and refinement of the crystal structures

Crystallographic data of **[Gd(H$_2$CAM)$_3$]·14.25H$_2$O**, **1**, **2** and **3** were collected with an SuperNova, Single source at offset, Eos diffractometer with a Mo Kα radiation (λ= 0.71073 Å). All the structures were solved by direct methods and refined anisotropically by full-matrix least-squares techniques based on F^2 using the SHELXS-97 and SHELXL-97 programs[1] contained on Olex 2. [2] The electron density of disordered guest water molecules in **[Gd(H$_2$CAM)$_3$]·14.25H$_2$O** and unassigned part of Co(II) ions in the cavity of **3** were treated as a diffuse contribution using the program SQUEEZE.[3] The electron density of disorder guest Co^{2+} ions in cavity region was presented in Fig. S1. The guest water molecule is disordered to two positions (O6, O6') in compounds **1** and **2**. The coordinated water molecule of the free Co^{2+} is disordered to two positions (O5, O5') in compounds **1** and **2**. All of the disordered atoms are restricted by ISOR command. Restraints (ISOR) are also placed on O3 in **1**, O3, C5, C8 in **2** and O1, O4, C5, C8 in **3**. Restraints (EADP) are placed on O3, C6, O2 in **3**. Restraints (EADP) are also placed on C8, O4 in **3**. The guest water molecules were crystallographically well defined in **1** and **2**, and the number of whole water molecules was determined on the basis of TGA and EA. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms of the ligand were generated geometrically; the hydrogen atoms of the water molecules were located in Fourier-difference electron density maps and refined with isotropic temperature factors. **1**, **2** and **3** crystalizes in hexagonal space group P6/mcc. **[Gd(H$_2$CAM)$_3$]·14.25H$_2$O** crystalizes in trigonal space group P31. In compound **1** and **2**, Gd1 atom is at a site with 32-symmetry, Co1 is at a site with 2/m-symmetry and Co2 is at a site with 6/m-symmetry. In compound **3**, Gd1 atom is at a site with 32-symmetry, Co1 is at a site with 62-symmetry and Co3 is at a site with 2/m-symmetry. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1, S2, S3 and S4. CCDC: 958890, 958891 and 958892 for **1**, **2** and **3**, respectively; 937632 for **[Gd(H$_2$CAM)$_3$]·14.25H$_2$O**.

Table S1. Crystal data and structure refinement for **[Gd(H$_2$CAM)$_3$]·14.25H$_2$O**

CCDC No	937632
Chemical formula	C_{21} $H_{40.5}$ Gd N_3 $O_{29.25}$
Formula weight	960.29
Radiation	Mo Kα
Wavelength (Å)	0.71073
Crystal system, space group	trigonal, P31
Unit cell parameter	a=13.9410(9) alpha=90
	b=13.9410(9) beta=90
	c=21.8405(15) gamma=120

Volume ($Å^3$)	3676
Z, Calculated density (g/cm^3)	3, 1.301
F(000)	1424
Crystal size (mm)	0.2×0.2×0.2
Completeness (to theta)	0.994 (25.01)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R = 0.0694, wR2 = 0.1734
Largest diff. Peak and hole	0.912, -1.118
Flack factor	0.06(2)

Table S2. Crystal data and structure refinement for **1**

CCDC No	958890
Chemical formula	$C_{42}\ H_{52}\ Co_4\ Gd_2\ N_6\ O_{48}$
Formula weight	1959.11
Radiation	Mo Kα
Wavelength (Å)	0.71073
Crystal system, space group	Hexagonal, P6/mcc
Unit cell parameter	a=15.7215(8) alpha=90
	b=15.7215(8) beta=90
	c=14.9689(6) gamma=120
Volume ($Å^3$)	3204
Z, Calculated density (g/cm^3)	2, 2.007
Adsorption coefficient	3.171

F(000)	1864
Crystal size (mm)	0.2×0.2×0.5
Completeness (to theta)	0.998 (26.32)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R = 0.0265, wR2 = 0.0656
Largest diff. Peak and hole	0.830, -0.540

Table S3. Crystal data and structure refinement for **2**

CCDC No	958891
Chemical formula	C_{42} H_{46} Co_4 Gd_2 N_6 O_{45}
Formula weight	1905.06
Radiation	Mo Kα
Wavelength (Å)	0.71073
Crystal system, space group	Hexagonal, P6/mcc
Unit cell parameter	a=15.7818(13) alpha=90
	b=15.7818(13) beta=90
	c=15.0060(8) gamma=120
Volume ($Å^3$)	3237
Z, Calculated density (g/cm^3)	2, 1.955
Adsorption coefficient	3.134
F(000)	1828

Crystal size (mm)	0.2×0.2×0.5
Completeness (to theta)	0.930 (24.995)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R = 0.0426, wR2 = 0.1169
Largest diff. Peak and hole	0.77, -1.92

Table S4. Crystal data and structure refinement for **3**

CCDC No	958892
Chemical formula	$C_{42}\ H_{28}\ Co_4\ Gd_2\ N_6\ O_{36}$
Formula weight	1742.92
Radiation	Mo Kα
Wavelength (Å)	0.71073
Crystal system, space group	Hexagonal, P6/mcc
Unit cell parameter	a=15.3945(12) alpha=90
	b=15.3945(12) beta=90
	c=14.6706(6) gamma=120
Volume ($Å^3$)	3011
Z, Calculated density (g/cm^3)	2, 1.922
Adsorption coefficient	3.350
F(000)	1673
Crystal size (mm)	0.2×0.2×0.5

Completeness (to theta)	0.993(25.01)
Refinement method	Full-matrix least-squares on F2
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R = 0.0916, wR2 = 0.2363
Largest diff. Peak and hole	0.773, -0.603

1 G. M. Sheldrick, *Acta Cryst,* 2008, **A64**, 112-122

2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

3. A.L.Spek, *Acta Cryst.* 2009, **D65**, 148-155.

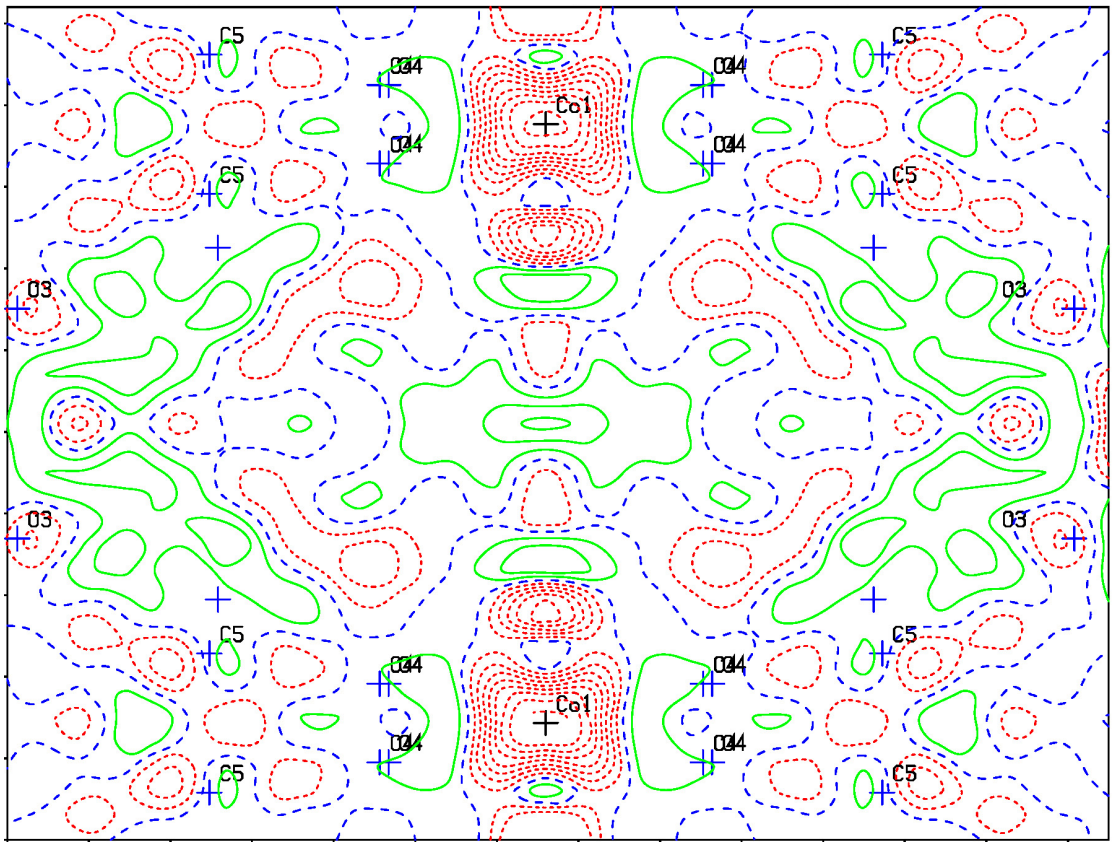

Fig. S1 Difference Fourier map of **3**. The electron density of disorder guest Co^{2+} ions in cavity region could be observed in centre region of the map.

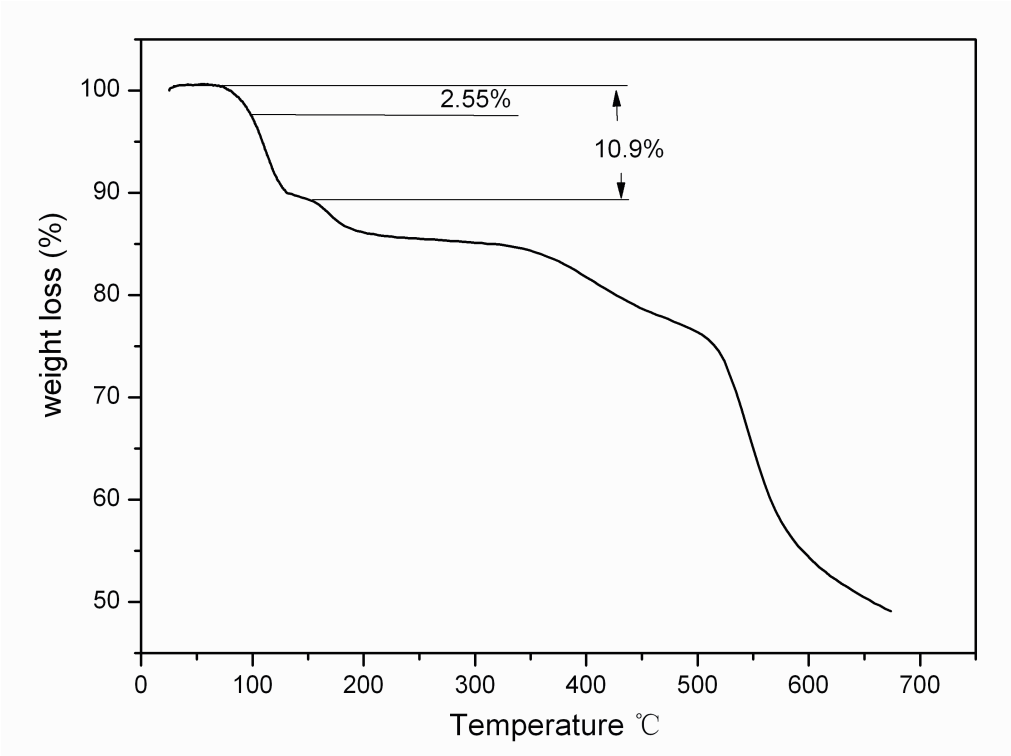

Fig. S2 Thermogravimetric analysis of **1**. The 2.55 % weight loss at 369K corresponds to the loss of one point five water molecules per asymmetric unit, which is also accord with the molecular formulation of **2**. The 10.9 % weight loss at 413K corresponds to the loss of six water molecules per asymmetric unit, which is also accord with the molecular formulation of **3**.

Table S5. Cell parameters of single crystal 1 at different temperature in the heating process.

Temperature (K)	**298**	**313**	**333**	**353**	**363**
a (Å)	15.721	15.782	15.805	15.792	15.831
b (Å)	15.721	15.782	15.805	15.792	15.831
c (Å)	14.969	15.006	15.005	15.006	15.012
γ (deg)	120	120	120	120	120
V (Å^3)	3204	3237	3246	3241	3258
Temperature (K)	**369**	**383**	**393**	**403**	**413**
a (Å)	15.812	15.858	15.781	15.784	15.478
b (Å)	15.812	15.858	15.781	15.784	15.478
c (Å)	15.006	15.016	15.021	15.011	14.734
γ (deg)	120	120	120	120	120
V (Å^3)	3249	3270	3239	3238	3057

Comparison of experimental and simulated powder XRD patterns of 1, 2 and 3.

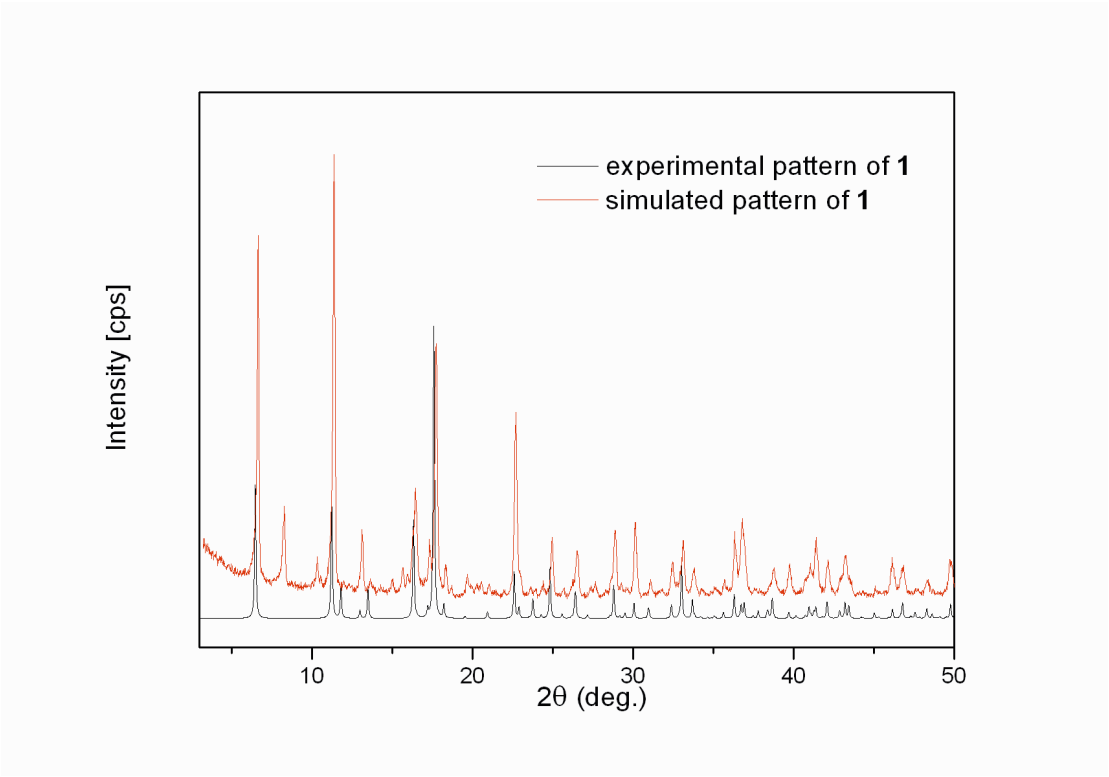

Fig. S3 Comparison of experimental and simulated powder XRD patterns of **1.**

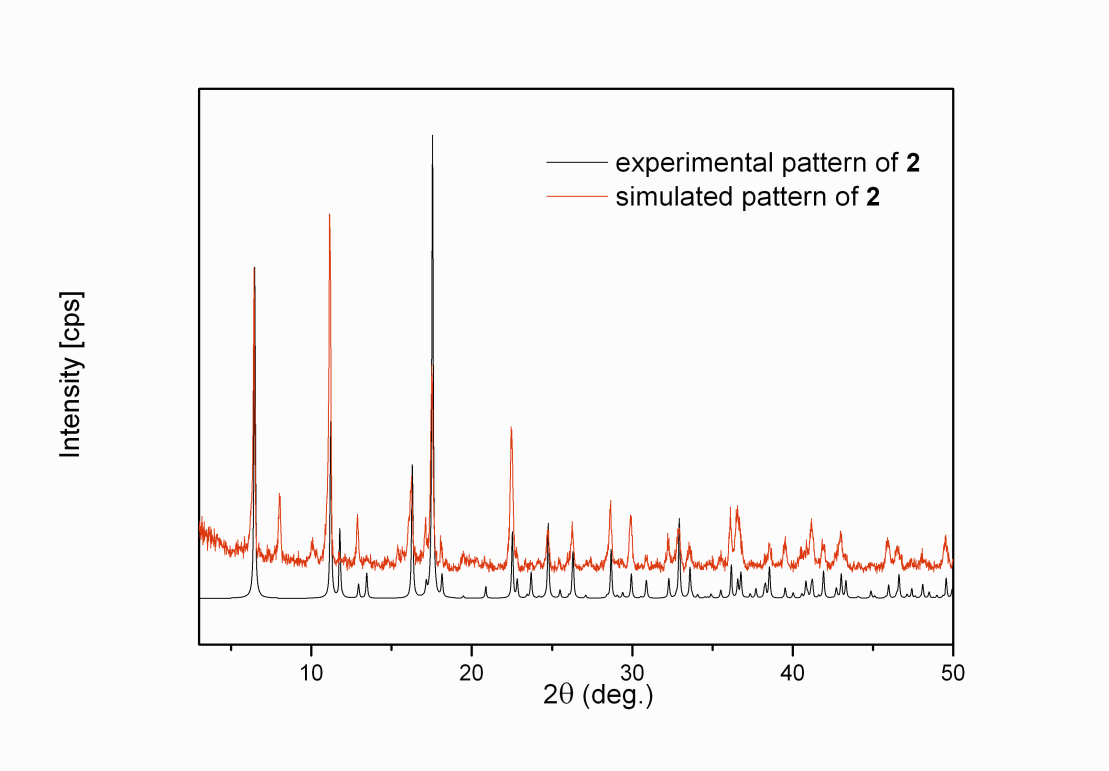

Fig. S4 Comparison of experimental and simulated powder XRD patterns of **2.**

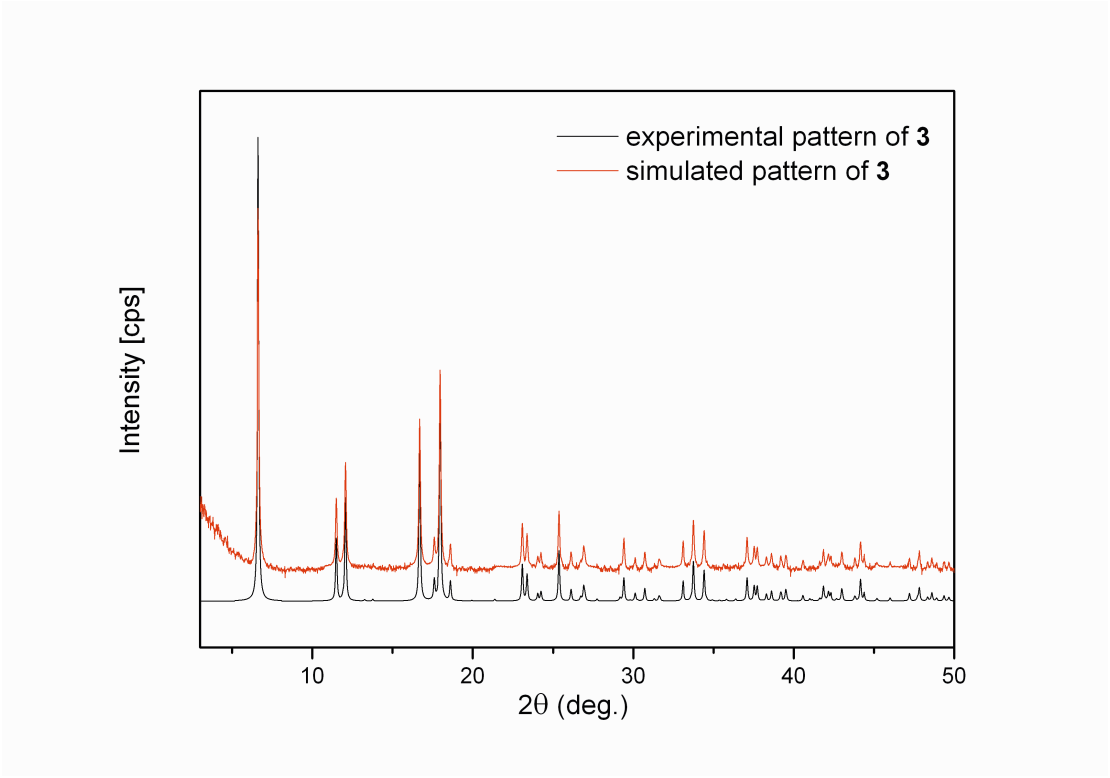

Fig. S5 Comparison of experimental and simulated powder XRD patterns of **3.**

The different states of the molecular device by powder XRD measurement.

Powder XRD patterns were measured after the 1st, 2nd, 4th, 6th, 8th and 10th cycle, respectively.

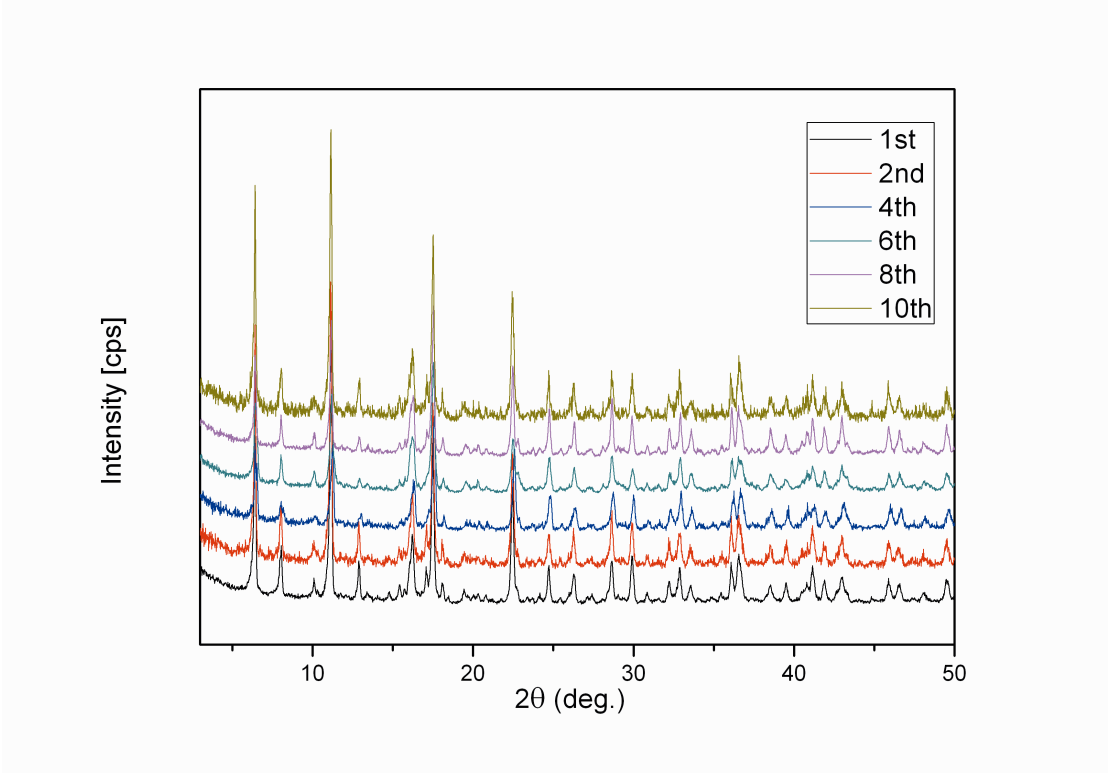

Fig. S6 Powder XRD patterns of "open" status at cycling operation experiment.

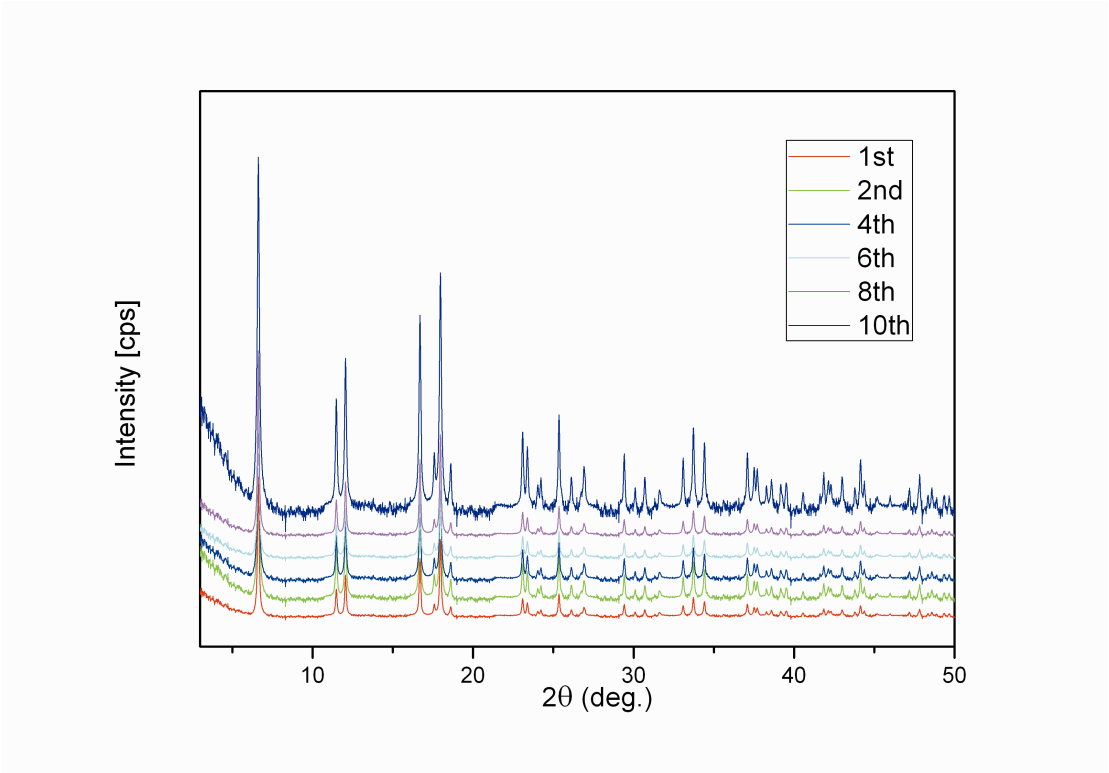

Fig. S7 Powder XRD patterns of "closed" status at cycling operation experiment.