Coordination-induced spontaneous resolution of a TPPE-based MOF and its use as crystalline sponge for guest determination

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1. Materials and General Procedures

All the chemicals are commercially available, and used without further purification. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an N_2 atmosphere with a heating rate of 10 ℃/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. CO_2 adsorption isotherms were measured using a Micrometritics ASAP 2020 surface area analyzer at 195 K. Before the adsorption measurement, the samples were exchanged with acetone for 4 times (6 h for each time) and then degassed on ASAP 2020 for 10 h at 60 °C.

X-ray Crystallography. All the single-crystal XRD data were collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 298 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Götingen, Götingen, Germany, 1996). The structures were solved using direct method, and refined by full-matrix least-squares on F^2 by the SHELXTL-2014 software package. Crystal data and details of the data collection are given in **Tables S1-S3**. CCDC 2071852-2071865 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis

The TPPE ligand was synthesized according to the reported procedures (*J. Am. Chem. Soc.* **2015**, *137*, 16209−16215)

2.1 Synthesis of 1: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (15.0 mg, 0.05 mmol), TPPE (31.4 mg, 0.05 mmol), DMF (3 mL), EtOH (0.75 mL) and 10 drops of HCl aqueous solution (v/v = 1/10) in a capped vial were heated at 100 ℃ for 6 hours. Saffron yellow crystals of **1** (89% yield) were filtered, washed with EeOH and Et_2O respectively, and dried at room temperature.

2.2 Synthesis of host-guest structures: Fresh prepared crystals of **1** were exchanged thoroughly with anhydrous acetone and then evacuated at 60 ℃ for 2 hours. The guest-free crystals of **1** were immersed into H_2O and anhydrous DMF, EtOH, Acetone, 2-butanol, and 2-butylamine respectively for at least 24 hours.

3. Table S1. Crystal data and structure refinement

Identification Code	1M	1P	Evacuated 1P
Empirical formula	$C_{58} H_{60} Cl_2 Co N_8 O_4$	$C_{58} H_{60} Cl_2 Co N_8 O_4$	$C_{46} H_{32} Cl_2 Co N_4$
Formula weight	1062.97	1062.97	770.58
Temperature (K)	298.0	298.0	298.0
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*I*222	*I*222	*I*222

Unit cell dimensions	$a = 11.903(5)$ Å $\alpha= 90º$ $b = 14.551(5)$ Å $\beta= 90º$ $c = 17.057(5)$ Å $\gamma = 90º$	$a = 11.710(5)$ Å $\alpha= 90º$ $b = 14.344(5)$ Å $\beta=90º$ $c = 17.216(5)$ Å $\gamma = 90º$	$a = 11.969(14)$ Å $\alpha= 90º$ $b = 14.578(16)$ Å $\beta=90º$ $c = 17.092(20)$ Å $\gamma = 90º$
Volume (Å^3), Z	2954.3(18), 2	2891.7(18), 2	2982(6), 2
Density (calculated) (mg/m^3)	1.195	1.221	0.858
Absorption coefficient (mm^{-1})	0.430	0.440	0.402
$F(000)$	1114	1114	794
Reflections collected / unique	7396 / 3397	7382 / 3263	5381 / 3288
Completeness to theta	25.240, 99.7%	25.240, 98.9%	25.242, 99.4%
R_{int}	0.0315	0.0351	0.0454
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3397 / 12 / 145	3263 / 16 / 145	3288 / 0 / 122
Goodness-of-fit on F^2	0.953	1.154	0.916
Final R indices [I>2sigma(I)]	$R_1 = 0.0628, wR_2 = 0.1807$	$R_1 = 0.0650, wR_2 = 0.1846$	$R_1 = 0.0450, wR_2 = 0.1200$
R indices (all data)	$R_1 = 0.0771, wR_2 = 0.1990$	$R_1 = 0.0779, wR_2 = 0.1960$	$R_1 = 0.0635, wR_2 = 0.1309$
Absolute structure parameter	0.048(15)	0.051(16)	0.08(2)
Largest diff. peak and hole (e.Å^{-3})	0.837 and -0.717	1.038 and -1.028	0.533 and -0.275

Table S2. Crystal data and structure refinement

Identification Code	**1M-DMF**	**1P-H$_2$O**	**1P-EtOH**
Empirical formula	$C_{58} H_{60} Cl_2 Co N_8 O_4$	$C_{46} H_{40} Cl_2 Co N_4 O_4$	$C_{54} H_{56} Cl_2 Co N_4 O_4$
Formula weight	1062.97	842.65	954.85
Temperature (K)	298.0	298.0	298.0
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$I222$	$I222$	$I222$
Unit cell dimensions	$a = 11.907(3)$ Å $\alpha= 90º$ $b = 14.568(3)$ Å $\beta= 90º$ $c = 16.881(4)$ Å $\gamma = 90º$	$a = 11.926(5)$ Å $\alpha= 90º$ $b = 14.364(5)$ Å $\beta=90º$ $c = 17.229(5)$ Å $\gamma = 90º$	$a = 12.234(5)$ Å $\alpha= 90º$ $b = 14.694(5)$ Å $\beta=90º$ $c = 16.978(5)$ Å $\gamma = 90º$
Volume (Å^3), Z	2928.1(11), 2	2951(2), 2	3052.1(19), 2

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Density (calculated) (mg/m^3)	1.206	0.948	1.039
Absorption coefficient (mm^{-1})	0.434	0.415	0.408
F(000)	1114	874	1002
Reflections collected / unique	7324 / 3350	11691 / 3444	7970 / 3533
Completeness to theta	25.242, 98.8%	25.242, 99.9%	25.240, 99.1%
R_{int}	0.0369	0.0978	0.0570
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3350 / 34 / 167	3444 / 4 / 131	3533 / 3 / 138
Goodness-of-fit on F^2	1.072	0.968	1.091
Final R indices [I>2sigma(I)]	$R_1 = 0.0596$, $wR_2 = 0.1683$	$R_1 = 0.0749$, $wR_2 = 0.1974$	$R_1 = 0.0845$, $wR_2 = 0.2357$
R indices (all data)	$R_1 = 0.0846$, $wR_2 = 0.2031$	$R_1 = 0.1293$, $wR_2 = 0.2261$	$R_1 = 0.1351$, $wR_2 = 0.2692$
Absolute structure parameter	0.116(17)	0.08(2)	0.07(2)
Largest diff. peak and hole (e.Å^{-3})	0.602 and -0.469	2.159 and -0.511	0.850 and -0.571

Table S3. Crystal data and structure refinement

Identification Code	**1P-Acetone**	**1P-(S)-2-butanol**	**1P-(S)-2-butylamine**
Empirical formula	$C_{58} H_{56} Cl_2 Co N_4 O_4$	$C_{62} H_{72} Cl_2 Co N_4 O_4$	$C_{62} H_{76} Cl_2 Co N_8$
Formula weight	1002.89	1067.06	1063.13
Temperature (K)	298.0	298.0	298.0
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	I222	I222	I222
Unit cell dimensions	a = 11.997(4) Å α= 90º b = 14.189(5) Å β= 90º c = 17.245(5) Å γ = 90º	a = 12.130(5) Å α= 90º b = 14.882(7) Å β=90º c = 16.881(7) Å γ = 90º	a = 11.8964(16) Å α= 90º b = 14.5101(19) Å β=90º c = 17.098(2) Å γ = 90º
Volume (Å^3), Z	2935.3(16), 2	3047(2), 2	2951.4(7), 2
Density (calculated) (mg/m^3)	1.135	1.163	1.196
Absorption coefficient (mm^{-1})	0.428	0.416	0.426
F(000)	1050	1130	1130

Reflections collected / unique	4618 / 2141	5210 / 2377	6820 / 3363
Completeness to theta	23.755, 98.3%	24.191, 98.1%	25.242, 99.8 %
R_{int}	0.0388	0.0519	0.0293
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2141 / 5 / 142	2377 / 9 / 138	3363 / 12 / 142
Goodness-of-fit on F^2	1.071	1.043	1.065
Final R indices [I>2sigma(I)]	$R_1 = 0.0516$, $wR_2 = 0.1405$	$R_1 = 0.0648$, $wR_2 = 0.1717$	$R_1 = 0.0590$, $wR_2 = 0.1737$
R indices (all data)	$R_1 = 0.0678$, $wR_2 = 0.1568$	$R_1 = 0.0944$, $wR_2 = 0.1924$	$R_1 = 0.0784$, $wR_2 = 0.1899$
Absolute structure parameter	0.05(2)	0.06(3)	0.015(14)
Largest diff. peak and hole (e.Å^{-3})	0.599 and -0.309	0.489 and -0.417	0.833 and -0.420

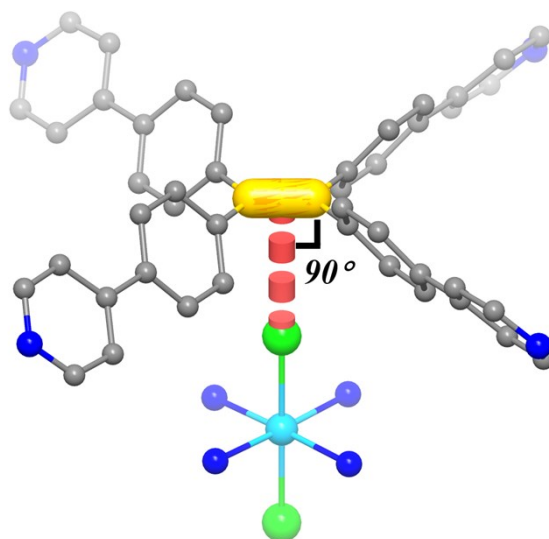## 4. Figures S1-S5. Additional X-ray crystallographic structures

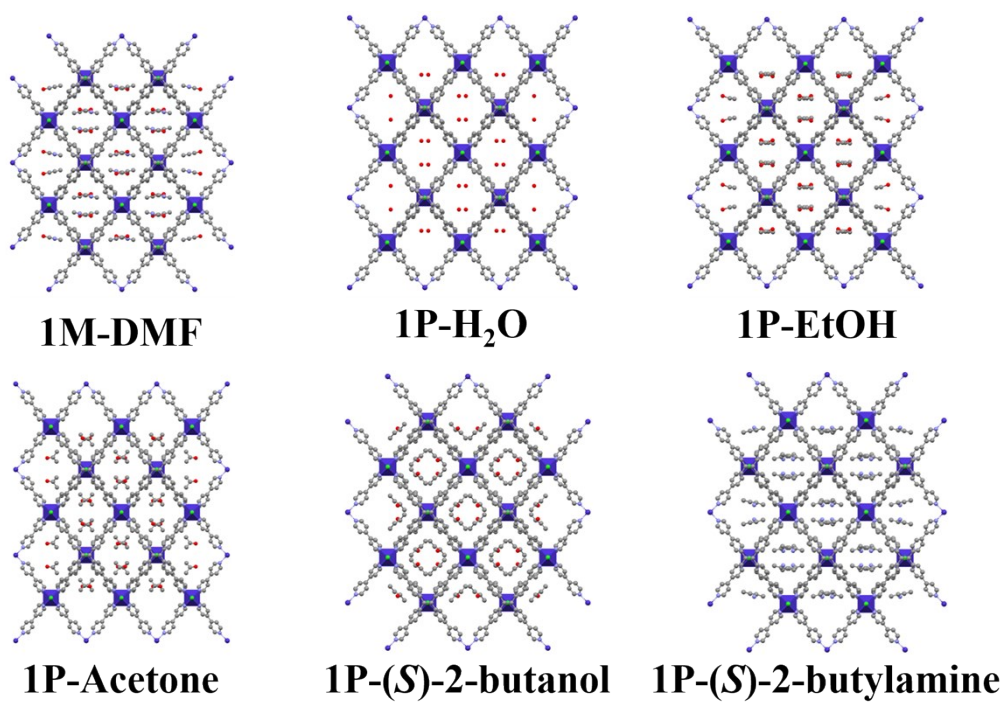### 4.1. Figure S1. The asymmetric unit of 1M (left) and 1P(right)
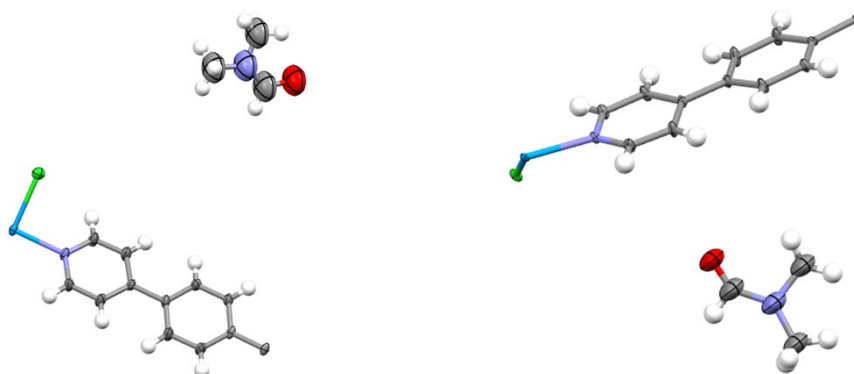
4.2. Figure S2. The 2D sql net (left) and its ABAB stacking to form a 3D supramolecular net (right)
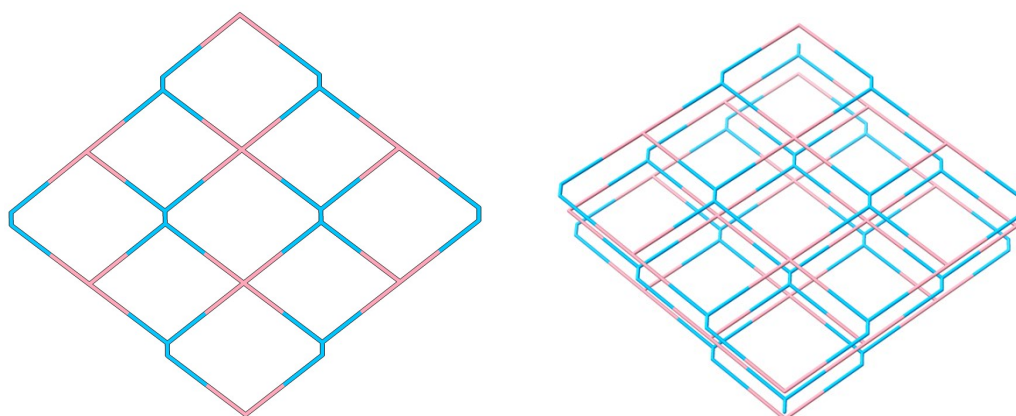
**4.3. Figure S3. The unconventional Cl…π interaction between the 2D layers**

4.4. Figure S4. The host-guest packing structures viewed from the a axis.

1M-DMF

1P-H₂O

1P-EtOH

1P-Acetone

1P-(S)-2-butanol

1P-(S)-2-butylamine

5. Table S4. The structure refinement parameters for 1 obtained from a statistical experiment to estimate the racemic character of 7 individual single crystals (3 Δ and 4 Λ forms).

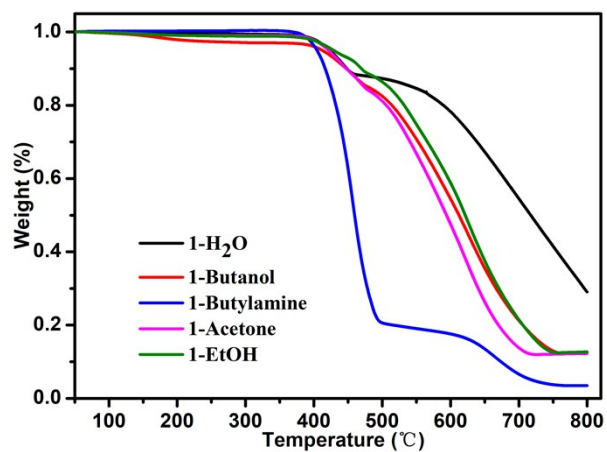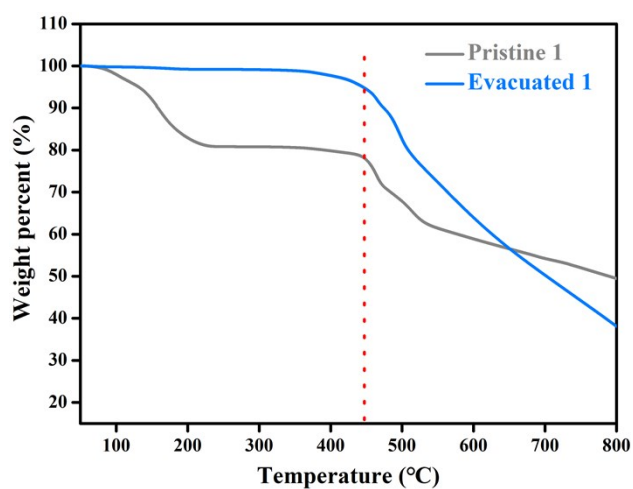| Form	R int	R [I>2σ(I)]	S	Flack parameter
Δ (delta)	0.0358	0.0550	1.039	0.066(17)
Δ (delta)	0.0314	0.0438	1.106	0.083(13)
Δ (delta)	0.0276	0.0430	1.024	0.048(16)
Λ (lambda)	0.0248	0.0416	1.117	0.048(14)
Λ (lambda)	0.0166	0.0393	1.157	0.069(18)
Λ (lambda)	0.0611	0.0575	1.032	0.08(3)
Λ (lambda)	0.0264	0.0361	1.018	0.047(12)

6. Figure S5. PXRD patterns
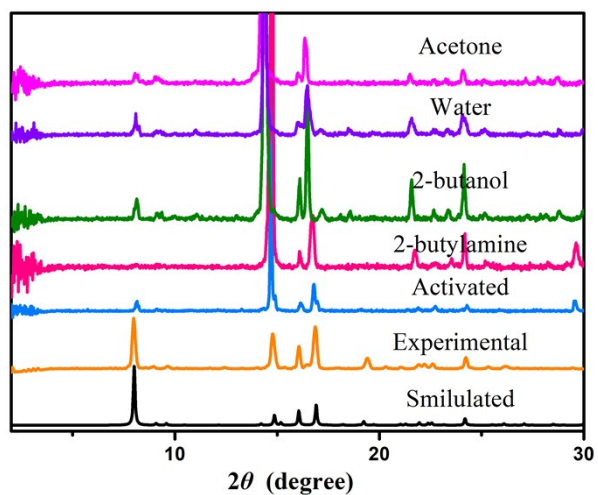
7. Figure S6. IR spectra of pristine 1 (up) and guest-loaded materials (bottom)
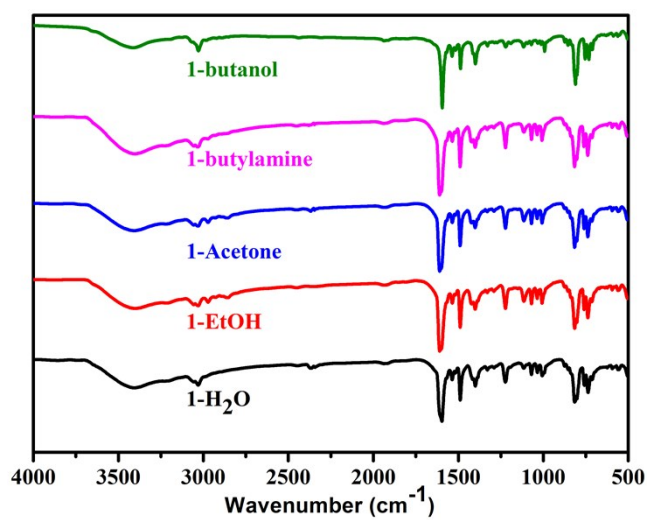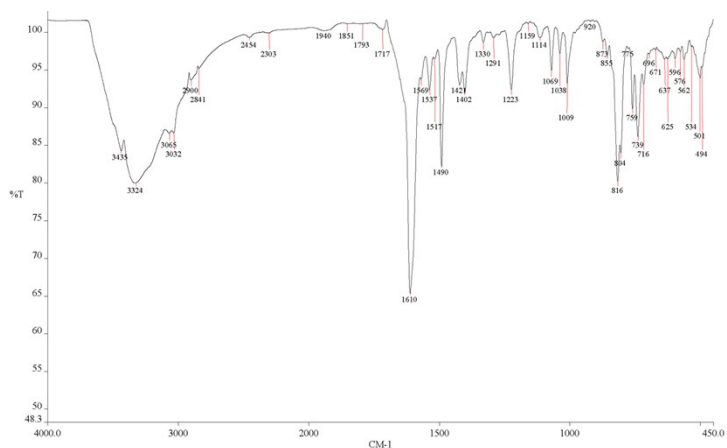
8. Figure S7. TGA curves

9. Figure S8. CD spectra