

## Supporting Information

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## Experimental Section

Preparation of  $C_{10}H_9N_5O_2Zn$  (**1**): *In a heavy walled Pyrex tube (~18cm long, 1 cm diameter and 0.25 cm thickness),* hydrothermal treatment of  $ZnCl_2$  (1.0 mmol), (S)-3-cyanophenylalanine (1.0 mmol),  $NaN_3$  (3.0 mmol) and water (3.0 ml) over 3 days at 105 °C yielded a colorless block crystalline product. The yield (0.193 g) of **1** was about 65% based on (S)-3-cyanophenylalanine. Anal. calcd for  $C_{12}H_{12}N_{10}O_2Zn$  (**1**); C 40.46; H 3.03; N 23.60; Found: C 40.57; H 2.91; N 23.91. IR spectrum (KBr,  $cm^{-1}$ ) of 3418(w), 3323(m), 3266(m), 2921(w), 1629(vs), 1597(vs) 1517(w), 1472(w), 1429(m), 1414(m), 1385(m), 1322(w), 1255(w), 1220(w), 1146(w), 1102(w), 1062(m), 1019(w), 936(w), 927(w), 914(w), 879(w), 854(w), 809(m), 780(w), 768(w), 704(w), 681(w), 599(w), 568(w), 549(w);  $C_{10}H_{11}N_5O_3Cd$  (**2**): *The procedure is identical to that of 1 except that  $CdCl_2$  was used to replace  $ZnCl_2$ . The yield (0.163g) of 2 was about 45% based on (S)-3-cyanophenylalanine.* Anal. calcd for  $C_{10}H_{11}N_5O_3Cd$  (**2**); C 33.18; H 3.04; N 19.36; Found: C 33.25; H 3.13; N 20.11. IR spectrum (KBr,  $cm^{-1}$ ) of **2**: 3421(w), 3328(w), 3267(m), 2916(w), 1611(vs), 1592(vs) 1519(w), 1473(w), 1431(m), 1411(m), 1382(m), 1324(w), 1260(w), 1219(w), 1152(w), 1092(w), 1066(m), 1020(w), 933(w), 922(w), 912(w), 878(w), 856(w), 809(m), 779(w), 764(w), 703(w), 679(w),

582(w), 563(w), 547(w), 456(w).

*Removal and Reintroduction of Guest Molecules.*

*A freshly ground sample of **2** (0.723g, 0.20 mmol) was subjected to vacuum at 120 °C. After 24 h, the sample exhibited a weight loss of 38mg, equivalent to the loss of one water molecule per formula unit ( calc. 36 mg).*

*Guest water molecules can be reintroduced into the evacuated sample of **2** via exposure to moisture. When 0.344g of an evacuated sample of **2** was exposed to water vapor at room temperature for 1 day, the sample experienced a weight gain of 18.5mg (calc. 18.0 mg). The same procedure is for compound **1**. There is no change on weight.*

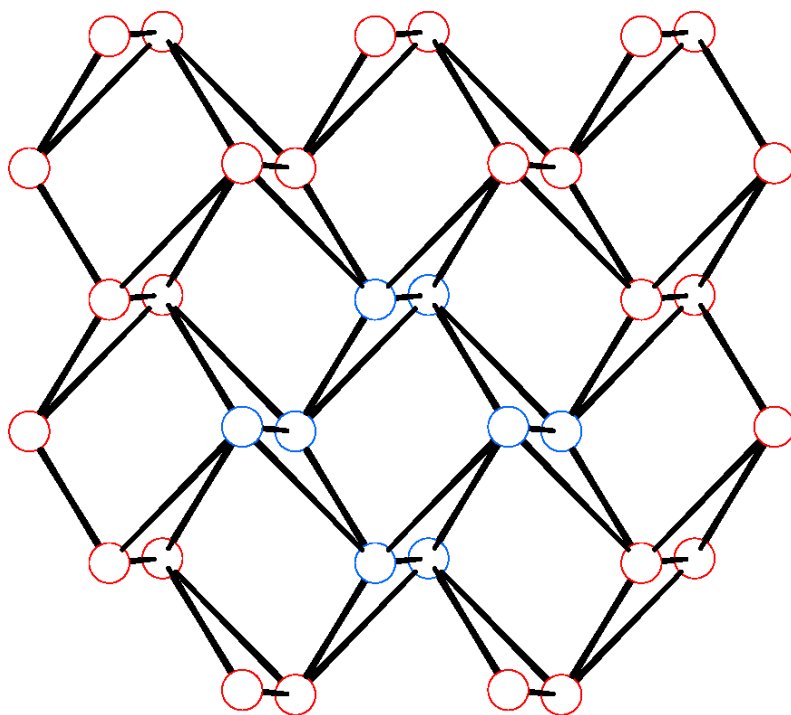


Figure S1 A simple network representation of compound **1**.

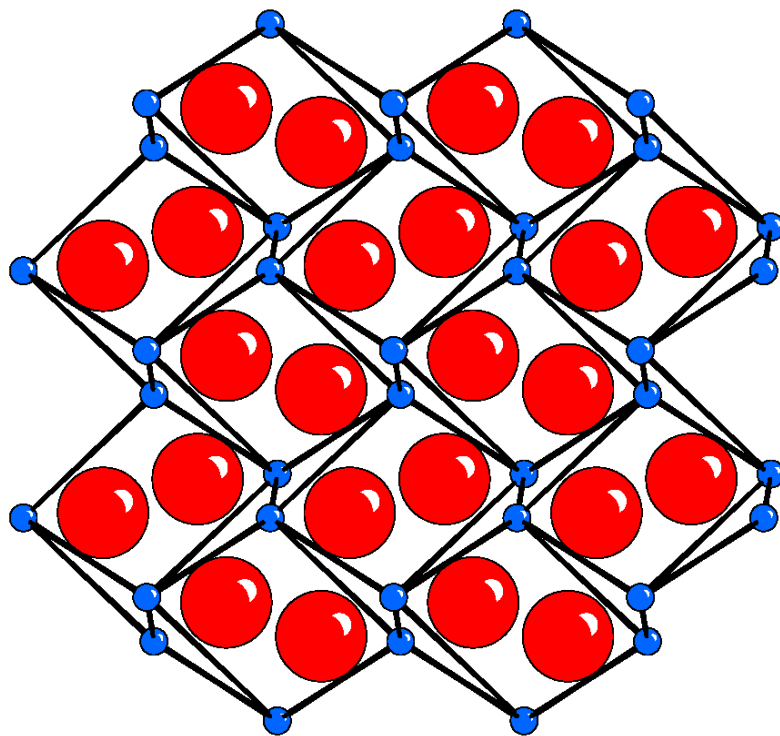
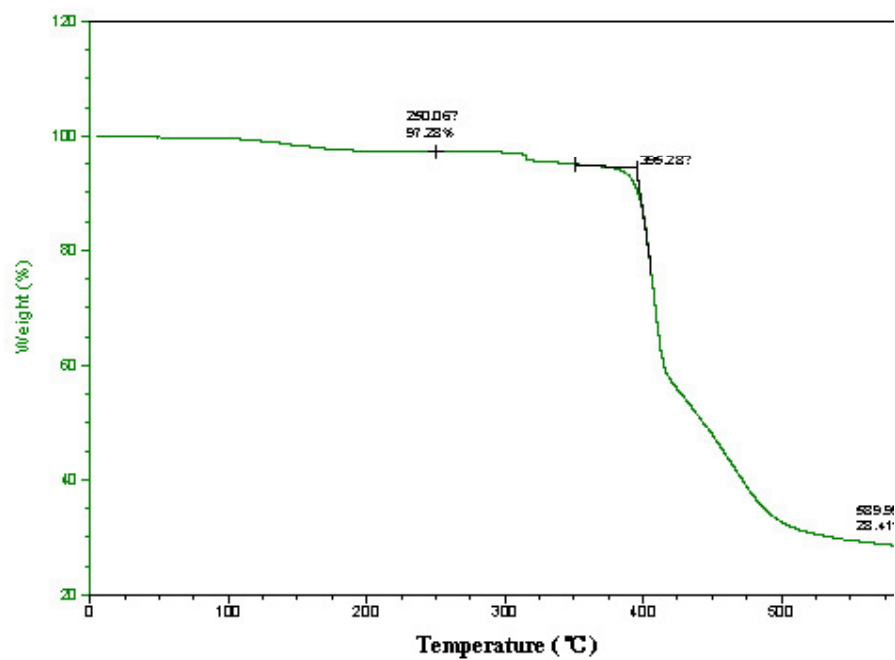


Figure S2 A simple network representation of compound **2** in which water (red ball) is included in cavity.

## TGA-DTA



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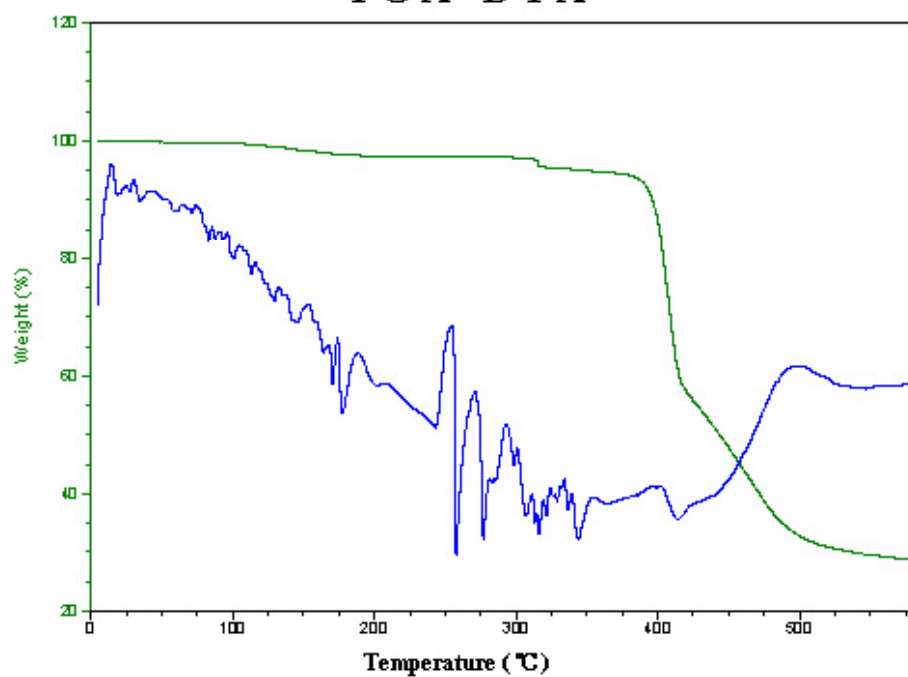


Figure S3 TGA of 2

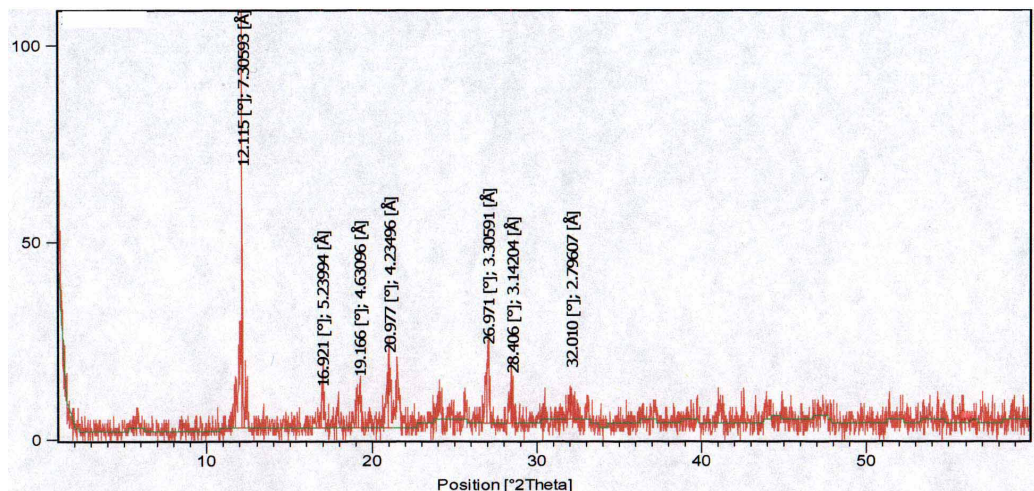


Figure S4 XRGD pattern of [Cd((S)-TPA)].

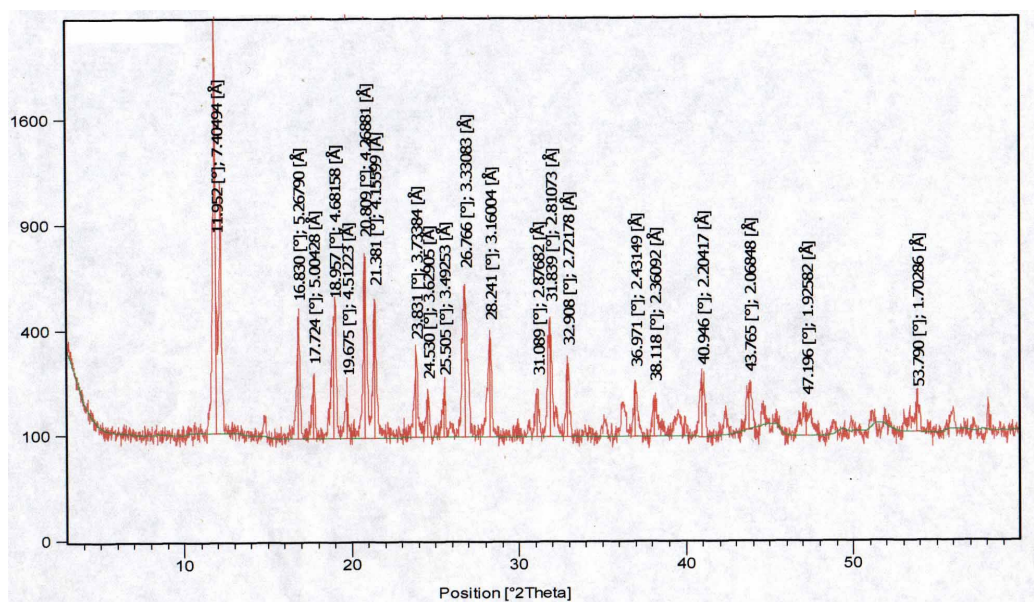


Figure S5 XRD pattern of 1.