Supporting information

Experimental Procedure

All the starting materials were used as received without further purification. The SmI_2 in THF was stored in a glove-box and dried before used.

Synthesis of 4,4',4''-*s*-triazine-2,4,6-tri-p-tolyl

In a glove-box, SmI_2 (1.0 g, 2.5 mol), p-tolunitrile (12 mL) and hexylamine (3.3 mL) were put into five Pyrex tubes and the tubes were removed from the glove-box. After frozen in liquid nitrogen, the tubes were sealed and heated at 120°C for 2 days. The product was scraped from the tube and washed with ether to give 11.3 g (Yield: 96%). IR(cm^{-1}): 1609 (w), 1583 (w), 1505 (vs), 1405 (m), 1361 (s), 1176 (m), 1016 (m), 852 (m), 796 (vs). ^1H NMR (200 MHz, CD_3Cl) δ 2.5 (s, 9 H), 7.34 (d, 6 H), 8.35 (d, 6 H), 7.95 (d, 8 H). (Ref. F. Xu, X.-H. Zhu, Q. Shen, J. Lu, J.-Q. Li, *Chinese Journal of Chemistry*, **2002**, 20(11), 1334-1339)

Synthesis of 4,4',4''-*s*-triazine-2,4,6-triyl-tribenzoic acid (H_3TATB)

Dilute HNO_3 (58 g of 65% HNO_3 in 131 mL water) was mixed with 35 g of 4,4',4''-*s*-triazine-2,4,6-tri-p-tolyl and heated to 220°C in a Teflon autoclave for 5 h to give H_3TATB in 56% of yield. IR (cm^{-1}): 2858 (w), 2546 (w), 1684 (s), 1583 (m), 1507 (vs), 1407 (m), 1360 (s), 1282 (vs), 1016 (m), 790 (s), 762 (vs). ^1H NMR (200 MHz, d_6-DMSO) δ 7.5 (d, 6 H), 8.7 (d, 6 H), 12.9 (br, 3H). (Ref. Deutsche Gold-und Silber-Scheideanstalt vorm. Roessler, GB 840209, CAN 55:8242)

Thermal Gravimetric Analysis (TGA) for complexes 1, 2 and 3

Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 instrument. The temperature was held for 1 minute at 50 °C and then heated from 50°C to 600 °C at the rate of 10 °C/min. The TGA plot is shown in Fig. S1-S3.

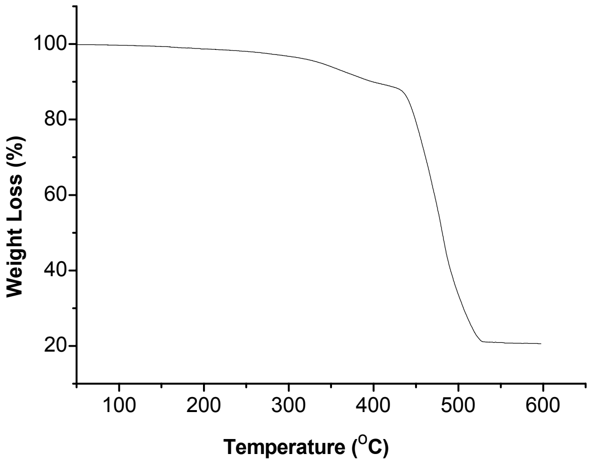

Fig. S1 TGA plot of **1**.

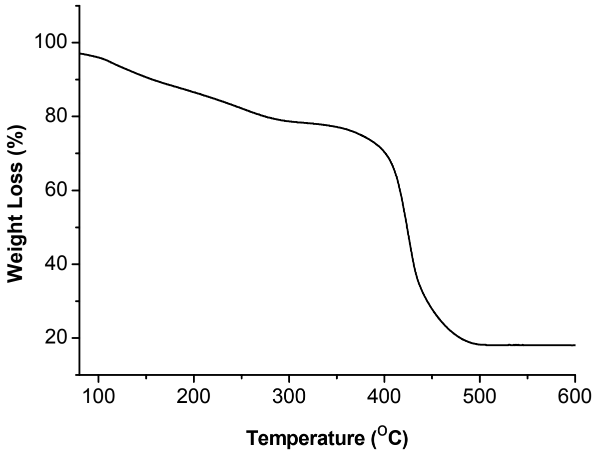

Fig. S2 TGA plot of **2**.

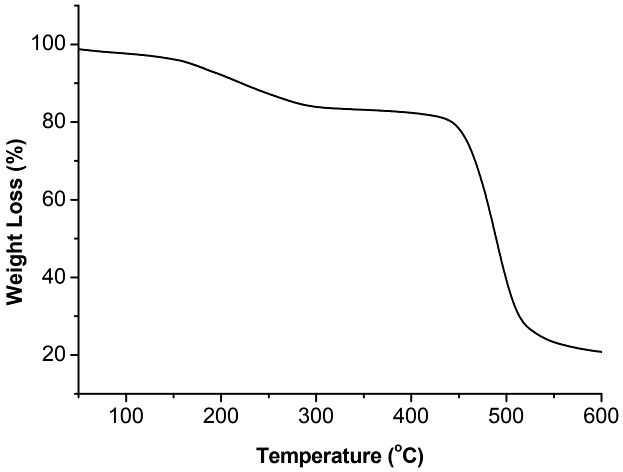

Fig. S3 TGA plot of **3**.

Photoluminescence studies for 3 and H_3TATB

Solid state photoluminescence for **3** and H_3TATB was measured with Perkin-Elmer LS 50 B Luminescence Spectrometer.

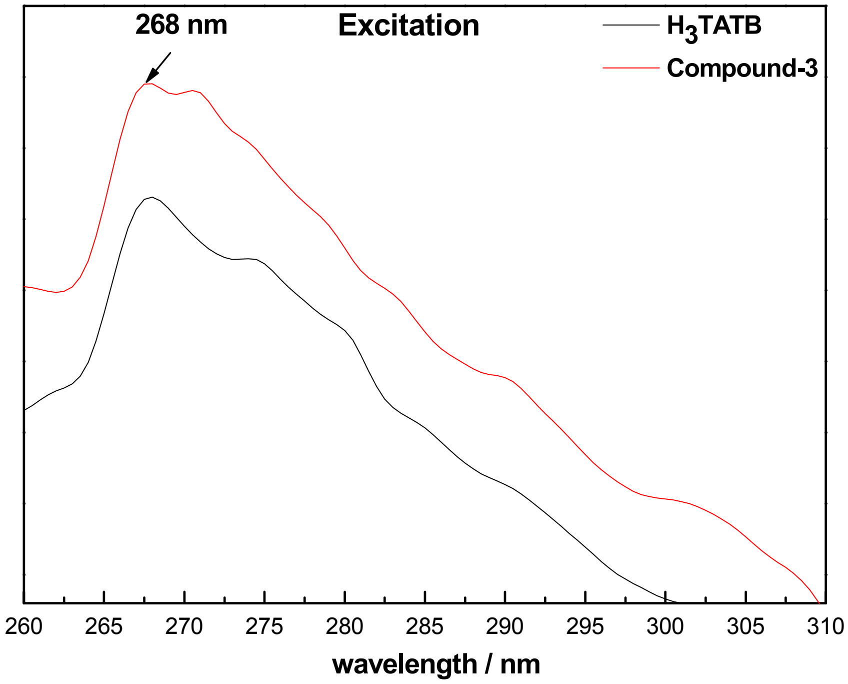

Fig. S4 Excitation spectrum of **3** and H_3TATB.

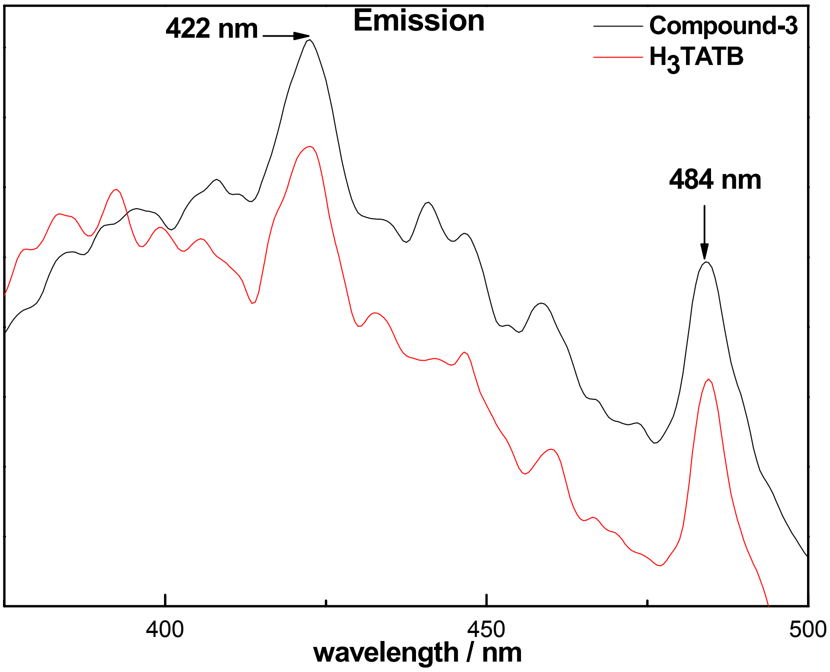

Fig. S5 Emission spectrum of **3** and H_3TATB.

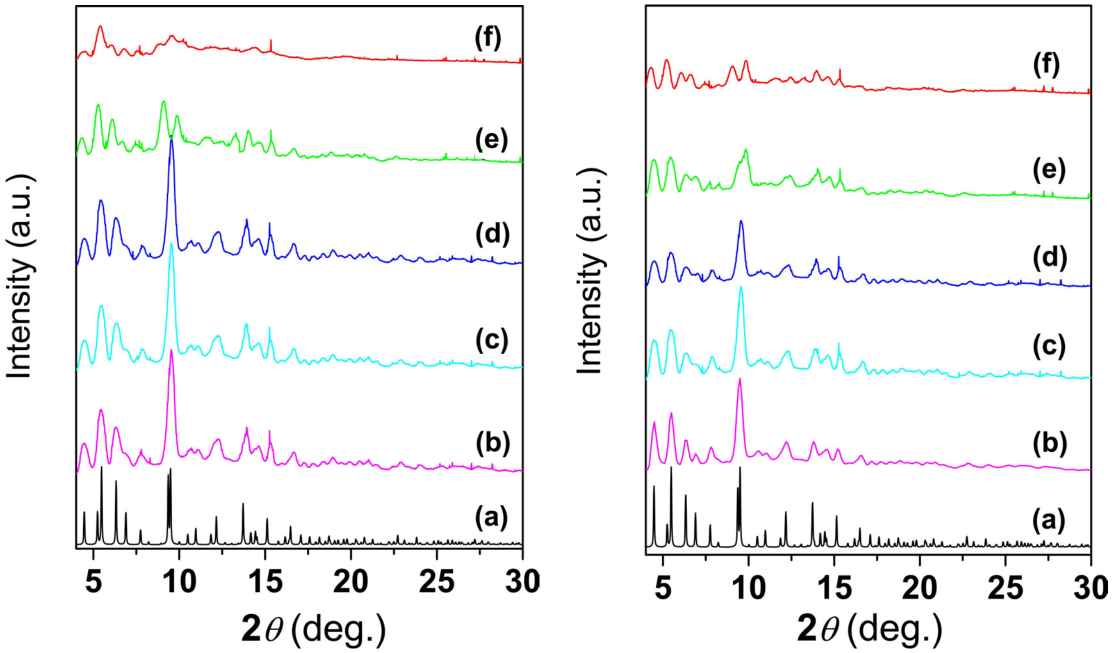

Fig. S6. Temperature dependent X-ray powder diffraction pattern of **1** (left) and **3** (right). (a) is the simulated powder X-ray diffraction pattern from single crystal structure data. (b), (c) , (d), (e) and (f) correspond to the sample heated at 100, 200, 300, and 405 °C.

X-ray powder diffraction (XRPD) was carried out on a Bruker Apex diffractometer with Mo-Kα radiation (0.71073 Å). The sample was filled in a 0.4 mm thin wall capillary. Diffraction frames with an exposure time of 300 s were taken and processed with the GADDS program to yield the diffraction pattern.

XRPD patterns of both samples fit well with simulated data below 200 °C. The deviations of the peaks at 9.5° are observed above 300 °C. The changes can be ascribed to the loss of guest molecules in the structure, which are confirmed by TGA analysis results. Diffraction patterns show that framework structures are preserved after the loss of guest molecules.

X-ray Structure determinations

Single crystal X-ray determinations were performed on a Bruker Smart Apex diffractometer equipped with an Oxford Cryostream low temperature device using Mo-Kα radiation ($\lambda = 0.71073$ Å). Frames were collected at -60°C using ω–scans with 0.3° steps. Raw data were processed using SAINT. Absorption corrections were applied using SADABS. Structures were solved by direct methods and refined via full-matrix least-squares on F^2 with anisotropic displacement using SHELX-97. Non-hydrogen atoms of metals and ligands were refined with anisotropic displacement parameters. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U\mathrm{eq}$ of the attached.

Compounds **1**, **2** and **3** are all isostructural. The potential solvent accessible area volume is 6.6%, but the solvent can not be well located due to disorder. In **2** and **3**, the highest residue peak is at the center of the cage structure. This peak is assigned to a partially occupied water molecule and refined with isotropic displacement. Two extra positive charges were needed to balance the negative framework charge, although they can not be determined in structure refinement. They may come from the protonated disorder solvent molecules in the cage or from the proton attached to the nitrogen or oxygen atoms in the TATB ligand.