Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Two cage-based zinc-tetracarboxylate frameworks with white-light emission

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Experimental

Materials and Methods

Reactions were carried out in 20 ml glass vials under autogenous pressure. All the reactants are of reagent-grade quality and used as purchased commercially without further purification. The power X-ray diffraction patterns (PXRD) were collected by a Rigaku D using Cu Kα radiation (λ=0.154 nm). Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. Thermogravimetric analyses (TGA) were recorded on a NETZSCH STA 449C unit at a heating rate of 10 $^{o}C\cdot min^{-1}$ under flowing nitrogen atmosphere. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920.

Synthesis of $[Me_2NH]_2[Zn_4(abtc)_2(H_2O)_4]\bullet 3DMF\bullet 2H_2O$ (FJI-8).

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.40 mmol, 120 mg) and H_4abtc (0.1 mmol, 36 mg, in N,N'-diethylformamide (3.0 ml) and CH_3CN (3.0 ml) with an additional HNO_3 (0.1 ml, 65 wt %) was sealed in a 20 ml glass vial, which was heated at 85 °C for 10 days, and cooled down to room temperature. After washing with fresh DMF, orange crystals were obtained in ca. 50% yield based on the $Zn(NO_3)_3\cdot 6H_2O$. Elemental analysis was calculated for **FJI-8**: C, 26.17%; H, 5.18%; N_2, 10.99%. Found: C, 26.43%; H, 5.36%; N, 10.58%.

Synthesis of $[Zn_3(abtc)_{1.5}(H_2O)_3]\bullet 2DMA\bullet 5H_2O$ (FJI-9)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.10 mmol, 30 mg) and H_4abtc (0.1 mmol, 36 mg, H_4abtc = 5,5'-(diazene-1,2-diyl)diisophthalic acid) in N,N-Dimethylacetamide (DMA) (6 ml) with an additional HBF_4 (0.1 ml, Tetrafluoroboric acid, 40% in water) was sealed in a 20 ml glass vial, which was heated at 85 ^{o}C for 7 days, and cooled down to room-temperature. After washed by DMA, the orange crystals of **FJI-9** were obtained in *ca*. 66% yield based on the $Zn(NO_3)_3\cdot 6H_2O$. Elemental analysis was calculated for **FJI-9**: C, 36.75%; H, 4.14 %; N, 6.70%. Found: C, 36.43 %; H, 4.36%; N, 6.83%.

Single-Crystal X-ray Crystallography

The structures data of **FJI-8** and **FJI-9** were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ=0.71073Å) at room temperature and the structure was resolved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97[S1]. Crystallographic data and structure refinement parameters for **FJI-8** and **FJI-9** are listed in Table S1. We employed PLATON/SQUEEZE[S2] to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formula of **FJI-8** and **FJI-9** were calculated from the SQUEEZE results combined with elemental analysis data and TGA data. The crystal data of **FJI-8**, there are four remaining Q peaks with high value near 2 Zn(II) centers in the asymmetric unit (Q1, 2.36; Q2, 2.25; Q3,2.24 and Q4, 2.02). It is the high valued Q peaks that dramatically reduce the quality of the crystal structure and lead to series termination errors. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. Crystallographic data for the structures reported in this paper have been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC: 1021732 for **FJI-8** and 1021731 for **FJI-9**.

Table 1 Crystal Data and Structure Refinement for **FJI-8** and **FJI-9**

Compounds	**FJI-8**	**FJI-9**
CCDC	1021732	1021731
Formula	$C_{25}H_{59}N_9O_{25}Zn_4$	$C_{32}H_{43}N_5O_{22}Zn_3$
M*r*	1147.31	1045.85
Space group	*R*-3	*P*-3
a (Å)	38.569(9)	23.0687(1)
b (Å)	38.569(9)	23.0687(1)
c (Å)	28.647(9)	20.7587(2)
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	120
V (Å^3)	36905(2)	9567.0(2)
Z	18	6
D_c (g cm^{-3})	0.844	0.814
M (mm^{-1})	1.197	1.155
F(000)	9360.0	2340.0
GOF	1.053	1.007
$R_1{}^a$	0.1307	0.1126
$wR_2{}^a$	0.4265	0.3127

$^aR = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; [$F_o > 4\ (F_o)$].

PXRD patterns and thermal properties

The phase purity of **FJI-8** and **FJI-9** was confirmed by powder X-ray diffraction (XRD) analysis (Fig. S1). Thermogravimetric analysis (TGA) measurements are conducted in the temperature range of 30-800°C under a flow of nitrogen with the heating rate of 10°Cmin^{-1}. Compound **FJI-8** shows a

weight loss of ca. 24.76% from 25-200 °C, which is attributed to the loss of two dimethylamine, three guest DMF molecules and two lattice water molecules (calcd 24.72%), and then the framework begins to collapses upon further heating. The TGA curve of **FJI-9** has a weight loss of 25.60% from 40 to 200°C due to the loss of two guest DMA molecules and five lattice water molecules (calcd 24.91%), and then the framework begins to decompose upon further heating (Fig. S2).Their final formula with guest solvent molecules were calculated from the SQUEEZE results and combined with the TGA and elemental analysis data.

Reference

S1 (a) SHELXS, G.M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112; (b) SHELXL, G.M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112.

S2 (a) A. L. Spek, *J. Appl. Crystallogr.***2003**, *36*, 7; (b) P. v. d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, **1990**, *46*, 194.

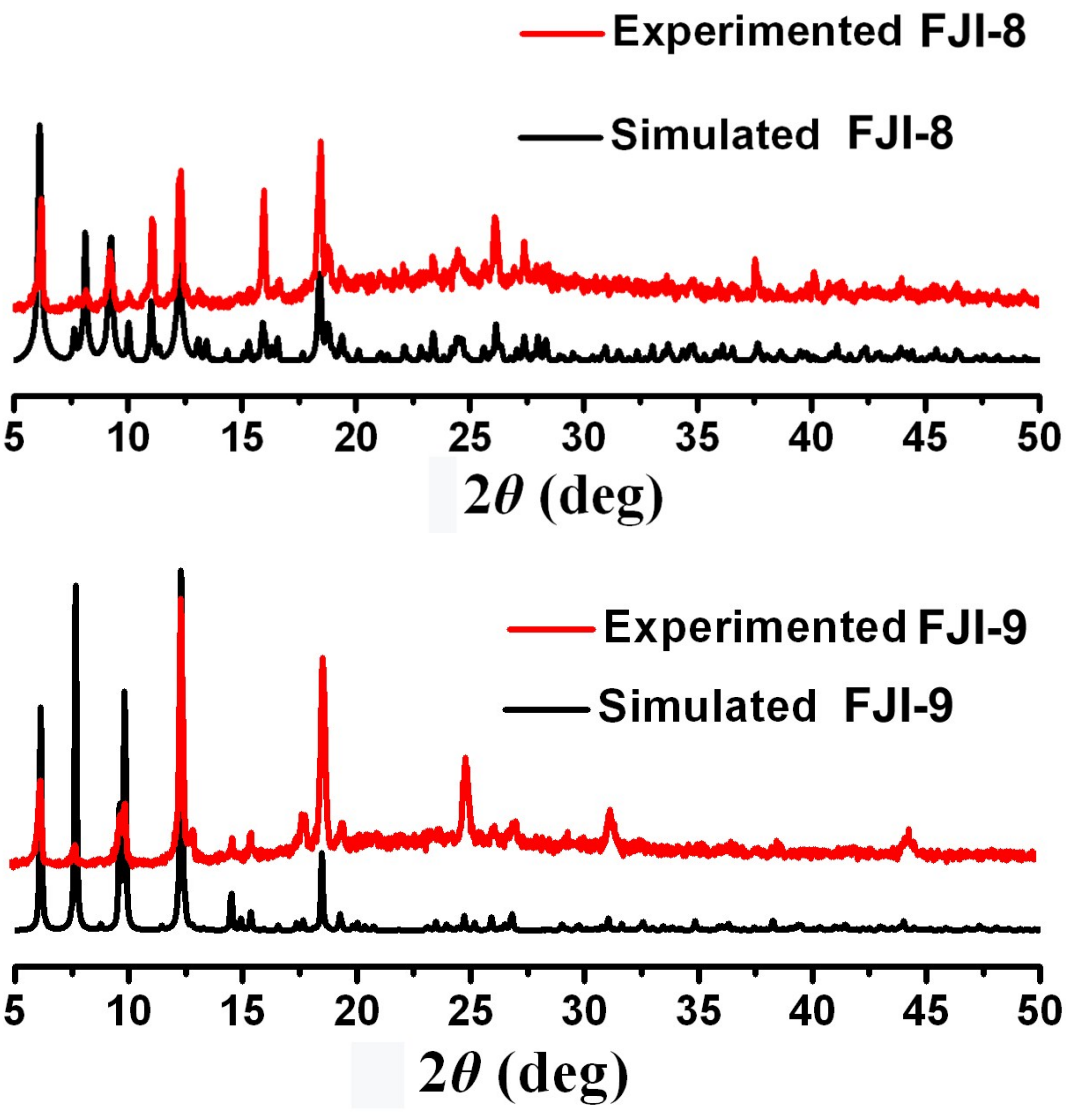
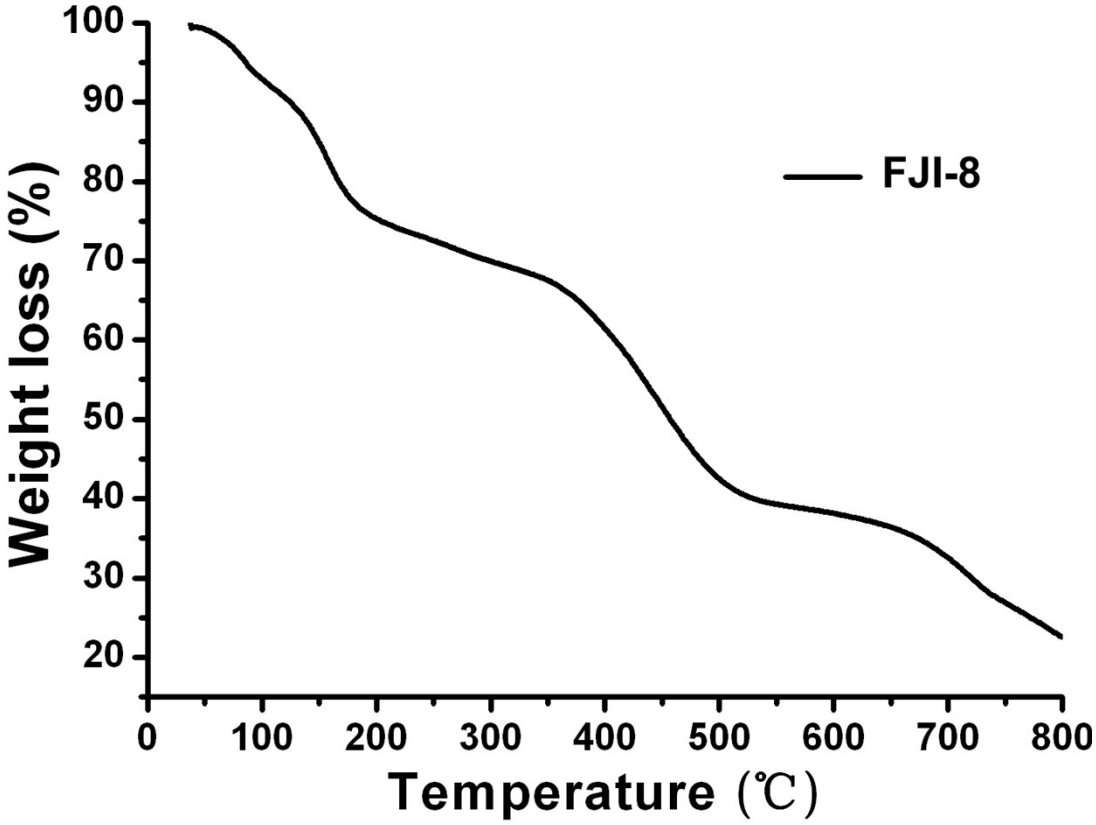


Fig S1 PXRD patterns of **FJI-8** (up) and **FJI-9** (down)



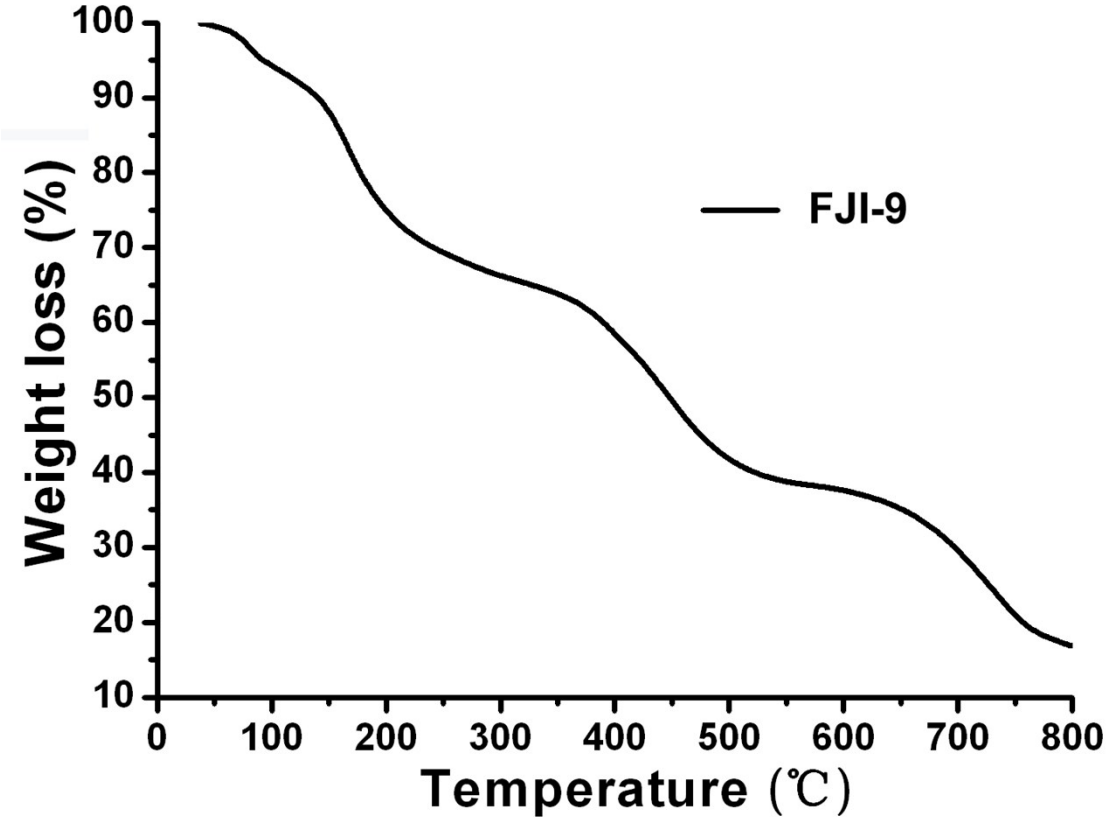


Fig S2 TGA curve for **FJI-8** (up) and **FJI-9** (down)

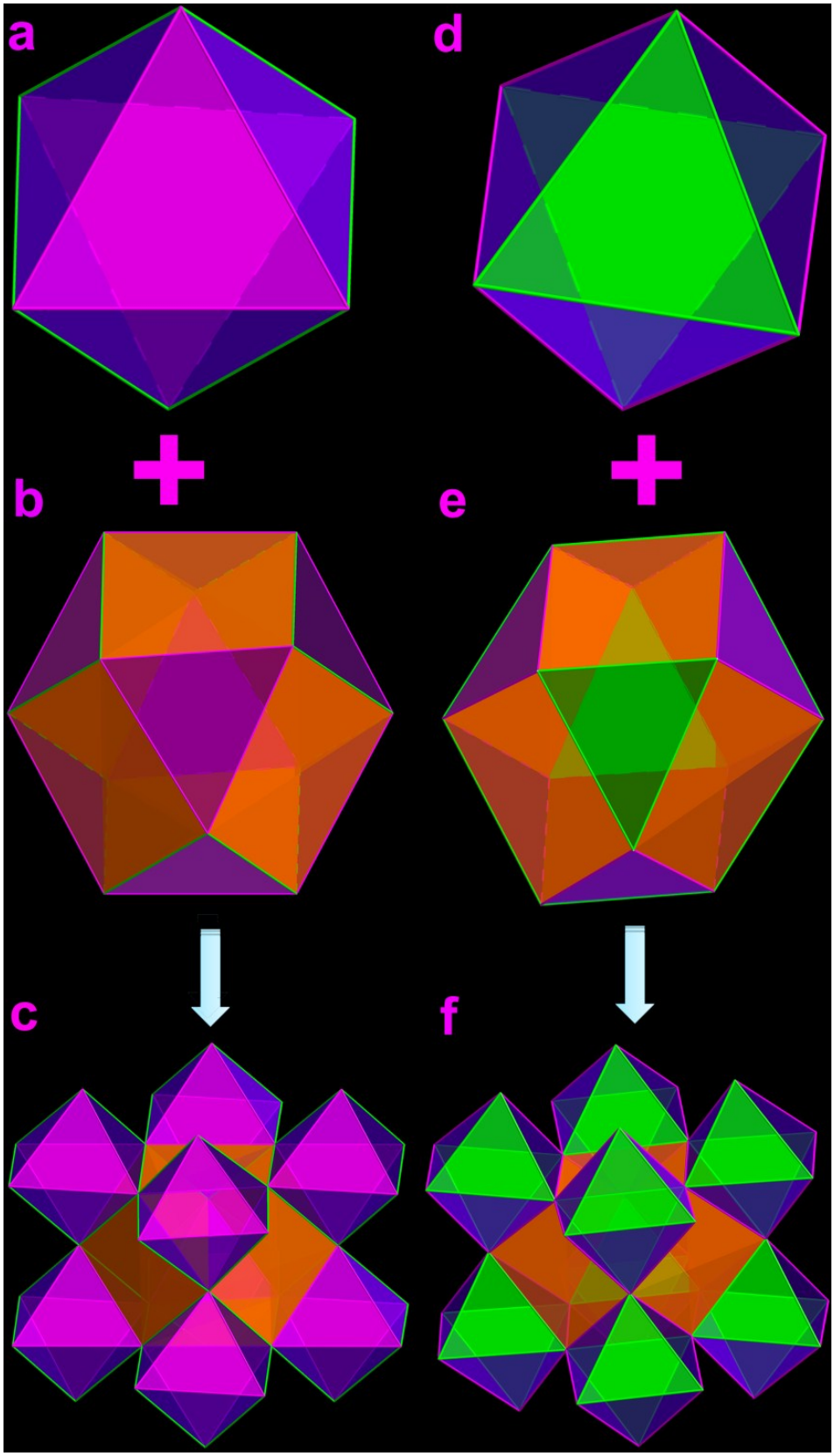


Fig S3 The octahedral cage composed of $Zn_2(CO_2)_4$ paddlewheels and ligands for **FJI-8 (a)** and for **FJI-9 (d)**. The cuboctahedral cage constructed by eight octahedral cages for **FJI-8 (b)** and for **FJI-9 (e)**. The 3D cage-stacking framework in **FJI-8 (c)** and **FJI-9 (f)**

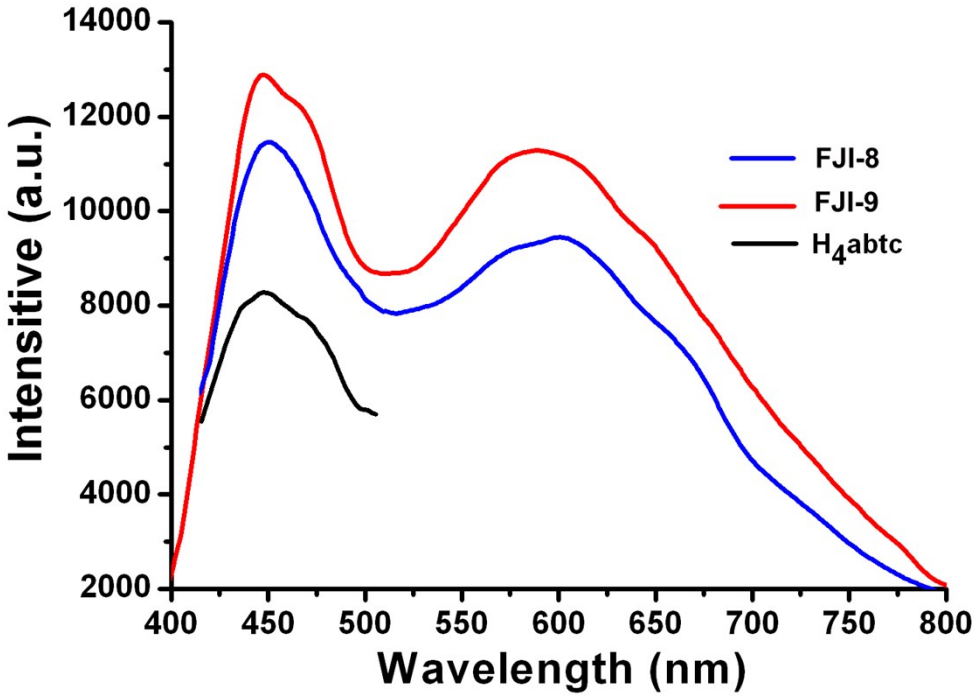


Fig S4 The solid-state spectra of H_4abtc ligand, **FJI-8** and **FJI-9** at room temperature (λ_{ex} = 375 nm)