## Electronic Supplementary Information (ESI) for

# The first ionothermal synthesis of a 3D ferroelectric metal-organic framework with colossal dielectric constant

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### **Materials and Methods**

All reagents of A. R. grade employed were commercially available and used without further purification. The FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FT-IR Spectrometer in the range of 4000–400 cm<sup>-1</sup>. The Raman spectra were recorded using an ALMEGA Dispersive Raman spectrometer with the laser wavelength of 532 nm. C, H, and N elemental analyses were determined on an Elementar Vario EL III elemental analyzer. Thermal stability studies were carried out on a NETSCHZ STA–449 C thermoanalyzer under nitrogen atmosphere (40–1000 °C range) at a heating rate of 10 °C min<sup>-1</sup>.

The solid-state and solution fluorescence spectra were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer. The excitation slit and emission slit both were 2.5 nm.

Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX 2500 powder diffractmeter at 40 kV and 100 mA using Cu-K $\alpha$  ( $\lambda = 1.54056$  Å), with a scan speed of 0.2 s/step and a step size of 0.02°. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury 2.3 program provided by the Cambridge Crystallographic Data Centre.

The UV-vis spectrum was recorded at room temperature on computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength range 200 – 1600 nm. A BaSO<sub>4</sub> plate was used as a reference, on which finely ground powder of the sample was coated. The absorption spectrum was calculated from reflection spectra by the Kubelka-Munk function:<sup>[1]</sup>  $\alpha/S = (1-R)^2/2R$ , where  $\alpha$  is the absorption coefficient, *S* is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5 µm, and *R* is the reflectance. The band gap value was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the  $\alpha/S$  versus *E* (eV) plot.

The measurements of electric hysteresis loop and dielectric performance were carried out using a powdery sample in the form of a pellet after the parallel surfaces coated with gold (area =  $0.3651 \text{ cm}^2$ ). The electric hysteresis loop and dielectric response of the specimens were measured using a precision LCR meter (model E4980A, Agilent, USA) in a temperature range of -125 – 125 °C under different frequencies (100 Hz, 1k Hz, 10k Hz, and 100k Hz).

Suitable single crystals of **1** were carefully selected under an optical microscope and glued to thin glass fibers. Crystallographic data for all compounds were carried out on a Siemens Smart CCD Diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at T = 293(2) K. All absorption corrections were performed using the SADABS.<sup>[2]</sup> The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares analysis with SHELXTL-97 software.<sup>[3]</sup> All non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon and nitrogen atoms were fixed at their ideal positions. Crystal data as well as details of data collection and refinement for **1** are summarized in Table S1 and Table S2. Selected bonded lengths and angles for **1** are listed in Table S3.

#### The Topological Analysis for Compound 1

A better insight into the 3D network of **1** can be achieved by application of a topological approach. As depicted in Fig. S4, three 4-coordianted Zn centers and two  $\mu_6$ -1,2,4,5-BTC ligands can be regarded as 4-connected and 6-connected nodes, which lead to a (4, 6)-connected  $(4^46^2)(4^46^2)(4^56)(4^66^28^{6}10)(4^46^48^{6}10)$  topology, representing the nodes Zn1, Zn2, Zn3, and two ligands, respectively. On the other hand, if the trinuclear [Zn<sub>3</sub>] motifs mentioned above are taken into account, a simple (4, 6)-connected network will be obtained as depicted in Fig. S5. The Schläfli symbol for this net is  $(4^25^96^4)(4^25^26^7)$  (the first symbol for 6-connected trinuclear [Zn<sub>3</sub>] motifs, the second for the 4-connected 1,2,4,5-BTC ligands). Furthermore, according to the concept of infinite rodlike secondary building units,<sup>[4]</sup> the 3D net of **1** can be reduced to a very concise topological framework based on 1D helices and  $\mu_6$ -1,2,4,5-BTC linkers (Fig. S6). It is undoubtedly that the unprecedented topology of **1** is useful at the basic level in the crystal engineering of inorganic networks or coordination frameworks.

#### The Solid-State PL Spectrum, Diffuse Reflection Spectrum and TGA

The solid-state PL spectrum study at room temperature shows that compound 1 emits a blue light centered at 437 nm upon photo-excitation at 385 nm. This emission is intensively enhanced when 1 was dissolved in water (Fig. S7). The fluorescence spectrum of 1 may be assigned as an intraligand  $n \rightarrow \pi^*$  transition due to the similar emissions of pure 1,2,4,5-BTC

ligand,<sup>[5, 6]</sup> as well as the d<sup>10</sup> configuration of Zn(II). The diffuse reflection spectrum of **1** reveals the presence of an optical gap of 3.55 eV (Fig. S8), which is consistent with its color. Thermogravimetric analysis shows that compound **1** is thermally stable up to *ca*. 300 °C (Fig. S9). The high thermal stability, strong emission, as well as the CDC behavior of **1** makes it a fine candidate for photoactive and ferroelectric bifunctional materials.

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- [2] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, 1996.
- [3] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.
- [4] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc. 2005, 127, 1504.
- [5] J. D. Lin, X. F. Long, P. Lin and S. W. Du, Cryst. Growth Des., 2010, 10, 146.
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Empirical formula	$Zn_{3}C_{20}O_{16}H_{4}^{\ a}$
Formula weight	696.40
Temperature (K)	293(2)
Crystal system, Space group	Orthorhombic, <i>Fdd</i> 2
	a = 25.807(5) Å
TT '4 11 1'	b = 29.405(6) Å
Unit cell dimensions	c = 19.637(4) Å
	$V = 14902(5) \text{ Å}^3$
Z, Density(cal.)	16, 1.242 g/cm <sup>3</sup>
Absorption coefficient	2.00 mm <sup>-1</sup>
F(000)	7744
Crystal Size (mm)	$0.59 \times 0.40 \times 0.30$
Theta range for data collection	3.16 to 25.36
Limiting indices	- 31 <= h <= 30, - 34 <= k <= 35, - 23 <= 1 <= 21
Reflections collected / unique	35902 / 6765
Observed Reflection	6202 ( <i>I</i> >2 <i>σ</i> ( <i>I</i> ))
Data Completeness measured	0.997
Relative Transmission Factor	0.5852 and 0.3849
Refinement Method	Full-matrix least-squares on F <sup>2</sup>
Parameter/Restraints/Data(obs.)	372 / 14 / 6765
Goodness-of-fit	1.054
Final R indices $(I \ge 2\sigma(I))^{b}$	R1 = 0.0616, wR2 = 0.1577
R indices (all)	R1 = 0.0670, wR2 = 0.1622
Largest difference peak	1.469 and -1.548 e·A <sup>-3</sup>

 Table S1. Crystal data and structure refinement for 1.

<sup>a</sup> The program SQUEEZE was used to model the electron density in the pores from the disordered [EMI]<sup>+</sup> cations and crystalline water molecules.

<sup>b</sup> R1 =  $\sum (|F_o| - |F_c|) / \sum |F_o|$ , wR2 =  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$ .

atom	x	У	Z	U(eq)	atom	x	У	Z	U(eq)
Zn1	0.82822 (3)	0.45123 (3)	0.33569 (4)	0.0298 (2)	C19	0.7181 (3)	0.4311 (2)	0.3628 (3)	0.0297 (16)
Zn2	0.68569 (3)	0.43536 (3)	0.08611 (4)	0.0296 (2)	C20	0.9127 (4)	0.7192 (4)	0.3047 (4)	0.059 (3)
Zn3	0.75457 (4)	0.49665 (4)	0.46695 (6)	0.0577 (3)	01	0.5103 (2)	0.3148 (2)	0.3473 (3)	0.0461 (15)
C1	0.8970 (5)	0.6523 (5)	0.1987 (5)	0.068 (3)	02	0.5511 (2)	0.2805 (2)	0.2621 (3)	0.0471 (15)
C2	0.8180 (3)	0.5491 (2)	0.3696 (4)	0.0349 (18)	03	0.6762 (3)	0.4642 (2)	0.2317 (3)	0.0594 (18)
C3	0.8567 (3)	0.6029 (3)	0.2897 (4)	0.0404 (19)	O4	0.6650 (3)	0.4029 (2)	0.1660 (3)	0.0549 (17)
C4	0.8387 (3)	0.5960 (3)	0.3540 (3)	0.0331 (16)	05	0.8418 (3)	0.5935 (3)	0.5064 (3)	0.073 (2)
C5	0.8378 (3)	0.6307 (2)	0.4013 (4)	0.0323 (16)	O6	0.7839 (5)	0.6481 (3)	0.4959 (4)	0.109 (4)
C6	0.8193 (3)	0.6243 (3)	0.4738 (4)	0.0363 (17)	07	0.7802 (3)	0.5454 (2)	0.4101 (4)	0.067 (2)
C7	0.6194 (3)	0.3380 (3)	0.3887 (3)	0.0308 (16)	08	0.8392 (3)	0.5161 (2)	0.3391 (4)	0.0601 (17)
C8	0.6047 (3)	0.3078 (3)	0.4484 (3)	0.0300 (16)	O9	0.9090 (10)	0.6958 (9)	0.1827 (10)	0.087 (7)
С9	0.6523 (3)	0.3937 (3)	0.2823 (3)	0.0314 (16)	O18	0.8972 (10)	0.6243 (9)	0.1646 (14)	0.104 (8)
C10	0.6583 (3)	0.3709 (3)	0.3997 (3)	0.0330 (16)	O9'	0.8809 (8)	0.6815 (9)	0.1671 (10)	0.068 (5)
C11	0.6151 (3)	0.3615 (2)	0.2728 (3)	0.0298 (16)	O18'	0.9266 (8)	0.6178 (6)	0.1729 (9)	0.069 (4)
C12	0.5968 (3)	0.3346 (2)	0.3250 (3)	0.0280 (14)	O10	0.6109 (2)	0.32511 (19)	0.5073 (2)	0.0367 (12)
C13	0.6668 (3)	0.4236 (3)	0.2220 (4)	0.0380 (18)	011	0.7573 (2)	0.4291 (2)	0.3241 (3)	0.0463 (15)
C14	0.8581 (3)	0.6720 (3)	0.3833 (4)	0.0401 (19)	012	0.7131 (2)	0.4552 (2)	0.4139 (3)	0.0443 (14)
C15	0.8775 (3)	0.6453 (3)	0.2708 (4)	0.048 (2)	O13	0.9038 (5)	0.7533 (2)	0.3274 (6)	0.106 (4)
C16	0.8800 (4)	0.6783 (3)	0.3195 (4)	0.055 (3)	O14	0.9496 (4)	0.7118 (3)	0.2738 (5)	0.101 (3)
C17	0.5484 (3)	0.3062 (2)	0.3105 (4)	0.0308 (16)	O17	0.5888 (3)	0.2692 (2)	0.4365 (3)	0.0503 (16)
C18	0.6750 (3)	0.3984 (3)	0.3473 (3)	0.0292 (15)					

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters  $(\text{\AA}^2)$  for **1**.

Zn1—O10 <sup><u>i</u></sup>	1.919(5)	Zn2—O4	1.913(6)	Zn3—O14 <sup><u>ii</u></sup>	1.922(7)
Zn1—O8	1.930 (6)	$Zn2-O5^{iii}$	1.916(6)	Zn3—O12	1.928(5)
Zn1—O9 <sup><u>ii</u></sup>	1.939(18)	Zn2—O1 <sup><u>i</u></sup>	1.939(5)	Zn3—O7	1.934(7)
Zn1—O11	1.955(5)	Zn2—O13 <sup><u>iv</u></sup>	1.990(8)	$Zn3-O2^{\underline{v}}$	1.960(5)
Zn1—O9' <sup><u>ii</u></sup>	2.00(2)				
O10 <sup><u>i</u></sup> —Zn1—O8	111.2(3)	011—Zn1—O9' <u><sup>ii</sup></u>	119.3(7)	O14 <sup><u>ii</u></sup> —Zn3—O12	108.6(4)
O10 <sup><u>i</u></sup> —Zn1—O9 <sup><u>ii</u></sup>	132.8(9)	O4—Zn2—O5 <sup>iii</sup>	110.2(3)	O14 <sup><u>ii</u></sup> —Zn3—O7	121.3(4)
O8—Zn1—O9 <sup>ii</sup>	91.3(8)	$O4$ —Zn2— $O1^{\underline{i}}$	100.6(3)	O12—Zn3—O7	110.3(3)
O10 <sup><u>i</u></sup> —Zn1—O11	100.6(2)	$O5^{\underline{i}\underline{i}\underline{i}}$ —Zn2— $O1^{\underline{i}}$	117.3(3)	$O14^{\underline{ii}}$ —Zn3— $O2^{\underline{v}}$	117.3(4)
O8—Zn1—O11	118.1(3)	O4—Zn2—O13 <sup><u>iv</u></sup>	114.0(4)	O12—Zn3—O2 $^{\underline{v}}$	99.1(3)
O9 <sup><u>ii</u></sup> —Zn1—O11	104.2(7)	$O5^{\underline{i}\underline{i}\underline{i}}$ —Zn2—O13 $^{\underline{i}\underline{v}}$	100.3(4)	$O7$ —Zn3— $O2^{\underline{v}}$	97.8(3)
O10 <sup><u>i</u></sup> —Zn1—O9' <u><sup>ii</sup></u>	107.0(6)	$O1^{\underline{i}}$ —Zn2—O13 $^{\underline{iv}}$	115.0(4)		
O8—Zn1—O9' <u><sup>ii</sup></u>	100.5(8)				

Table S3. Selected bond lengths (Å) and bond angles (°) for 1.

.

Symmetry transformations used to generate equivalent atoms: (i) x+1/4, -y+3/4, z-1/4; (ii) -x+7/4, y-1/4, z+1/4; (iii) -x+3/2, -y+1, z-1/2; (iv) x-1/4, -y+5/4, z-1/4; (v) -x+5/4, y+1/4, z+1/4.



Fig. S1 X-ray powder diffraction patterns for 1.



**Fig. S2** The 3D anionic MOF of **1** entrapped by the charge-balanced  $[EMI]^+$  cations viewed along the *c*-axis direction.

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Left-handed

**Right-handed** 

**Fig. S3** The detailed 3D porous framework of **1** constructed from alternant 2D sheets formed by left- and right-handed helical chains, respectively.

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**Fig. S4** The (4, 6)-connected topology with three 4-coordianted Zn centers and two  $\mu_6$ -1,2,4,5-BTC ligands acting as 4-connected and 6-connected nodes.

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**Fig. S5** The (4, 6)-connected topology with the trinuclear [Zn<sub>3</sub>] motif as 6-coordianted node and one unique 1,2,4,5-BTC ligand as 4-connected node (the other unique 1,2,4,5-BTC ligand acts as linker).

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Fig. S6 A concise topological net of 1 based on 1D helices and 1,2,4,5-BTC linkers.



Fig. S7 Solid state and water solution excitation and emission spectra of 1 at room temperature.

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Fig. S8 Diffuse reflection spectrum of 1.

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Fig. S9 TG/DTA curves of compound 1.



Fig. S10 IR (black) and Raman (blue) spectra for 1.