Design of a MOF based on octa-nuclear zinc clusters realizing both thermal stability and structural flexibility

Yunsheng Ma,*a,b,‡ Xiaoyan Tang,a,b,‡ Ming Chen,a Akio Mishima,b Liangchun Li,c Akihiro Hori,b Xiaoyu Wu,d Lifeng Ding,d Shinpei Kusakab and Ryotaro Matsuda*,b

a School of Materials Engineering, Jiangsu Key Laboratory of Advanced Functional Materials, Changshu Institute of Technology, Changshu, Jiangsu 215500, PR China
b Department of Materials Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan
c Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, PR China
d Department of Chemistry, Xi’an Jiaotong-Liverpool University, 111 Ren’ai Road, Suzhou Dushu Lake Higher Education Town, Jiangsu Province, 215123, China
Experimental
Materials and general procedures
All the starting materials were of reagent grade and used as purchased. The ligand 9H-fluorene-2,7-dicarboxylic acid (H$_2$FDC) was prepared according to the literature methods.$^{S1,S2}$ The powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV diffractometer with Cu-Kα radiation. The thermal gravimetric analyses (TGA) data were recorded on a Rigaku Thermo plus TGA 8120 apparatus in the temperature range 25–500°C under nitrogen atmosphere at a heating rate of 5 °C min$^{-1}$. The $^1$H nuclear magnetic resonance (NMR) spectra were measured on a Bruker Fourier™ 300 NMR spectrometer.

Synthesis of 2,7-diacetylfluorene
To an ice-cooled mixture of AlCl$_3$ (40 g, 0.3 mol) and 50 mL anhydrous 1,2-dichloroethane, acetic anhydride (15.3 g, 0.15 mol) was added dropwise with stirring. Thirty minutes later, fluorene (7.3 g, 0.044 mol) in 50 mL 1,2-dichloroethane was added dropwise to the above gray-green solution. The reaction was kept at 0 °C for 5 h. Then solvent 1,2-dichloroethane was distilled off. After pouring onto ice-HCl, the aqueous phase was decanted. The remainder was recrystallized with acetone to give 2,7-diacetylfluorene in 60% yield. $^1$H NMR [400 MHz, CDCl$_3$]: δ$_H$ 8.17 (2H, s), 8.04-8.02 (2H, d), 7.90-7.88 (2H, d), 4.00 (2H, s), 2.67 (6H, s); $^{13}$C NMR: δ$_C$ 197.90, 144.94, 144.51, 136.46, 127.81, 125.09, 120.71, 36.90, 26.88.

Synthesis of bis(dibromoacetyl)fluorene
2,7-diacetylfluorene (1.05 g, 4.22 mmol) was dissolved in acetic acid (40 mL) at 50 °C, and to this solution 0.95 mL of Br$_2$ (18.6 mmol) was added on vigorous stirring in one portion. The mixture was stirred at 100 °C for 10 min, cooled to 50 °C and diluted with water. The crude product was collected by filtration and dried under vacuum. Block crystals of bis(dibromoacetyl)fluorene can be obtained by recrystallized method with dichloromethane. Yield: 92%. $^1$H NMR [400 MHz, CDCl$_3$]: δ$_H$ 8.34 (2H, s), 8.21-8.19 (2H, d), 7.99-7.97 (2H, d), 6.77 (2H, s), 4.12 (2H, s); $^{13}$C NMR: δ$_C$ 185.72, 145.81, 144.89, 130.42, 129.27, 126.64, 121.33, 39.76, 37.04.

Synthesis of fluorene-2,7-dicarboxylic acid
In a 3-neck flask, equipped with mechanical stirrer, bis(dibromoacetyl)fluorene (1.15 g, 2.1 mmol) was dissolved in 30 mL of 1,4-dioxane at 70 °C and to this solution on vigorous stirring was added warm (80 °C) solution of sodium carbonate (2 g, 18.9 mmol) in 10 mL of water immediately followed by Br₂ (0.31 mL, 6.1 mmol). In 30 sec, 15 mL of water (80 °C) was added, followed in 1 min intervals by portions of 15, 15 and 30 mL of hot water. The mixture was boiled for 5 h to remove bromoform. After cooled down, most of 1,4-dioxane was evaporated under reduced pressure. White solid of fluorene-2,7-dicarboxylic acid could precipitate after acidify the above pale-yellow solution with condensed HCl. The white product was centrifuged and washed with distilled water to remove excess HCl. Fluorene-2,7-dicarboxylic acid was dried under vacuum at 80 °C. Yield: 85%. 

**1H NMR [400 MHz, (CD₃)₂SO]:** δ H 13.04 (2H, s), 8.21 (2H, s), 8.12-8.10 (2H, d), 8.05-8.03 (2H, d), 4.07 (2H, s); 

**13C NMR:** δ C 167.89, 144.82, 144.68, 130.34, 128.90, 126.69, 121.33, 36.88.

**Synthesis and structure of [(CH₃)₂NH₂]₂[Zn₈O₃(FDC)₆]·7DMF**

Zn(NO₃)₂·6H₂O (60 mg, 2 mmol), H₂FDC (50 mg, 2 mmol), DMF (10 mL), and H₂O (0.2 mL) were mixed in a 20 mL glass viral, which was capped, heated to 80 °C for 72 h, and cooled to room temperature. The pale-yellow cubic crystals were collected and washed with DMF. The crystals of [(CH₃)₂NH₂]₂[Zn₈O₃(FDC)₆]·7DMF (Zn₈-as) were heated at 120°C under vacuum for 24 h to obtain Zn₈-de.

**For Zn₈-as:**

IR (cm⁻¹, KBr): 1668.98 (s), 1611.63 (s), 1559.28 (m), 1536.84 (m), 1481.99 (m), 1442.11 (m), 1397.23 (vs), 778.95 (s), 492.24 (s), 457.34 (s).

**1H NMR [400 MHz, (CD₃)₂SO]:** δ H 8.14 (12H, s, FDC⁻'), 8.07-8.05 (12H, m, FDC⁻'), 7.99-7.97 (12H, m, FDC⁻'), 7.91 (7H, s, DMF), 5.90 (DCl), 4.04 (12H, s, FDC⁻'), 2.85 (21H, s, DMF), 2.69 (21H, s, DMF) and 2.46 (12H, m, (CH₃)₂NH₂⁺); 

**13C NMR:** δ C 167.92, 162.95, 144.84, 144.67, 130.32, 128.93, 126.68, 121.36, 36.86, 36.35, 34.63 and 31.30.

**For Zn₈-de:**

IR (cm⁻¹, KBr): 1617.15 (s), 1552.4 (m), 1478.3 (m), 775.1 (s), 472.2 (s).

**1H NMR [400 MHz, (CD₃)₂SO]:** δ = 8.14 (12H, s, FDC⁻'), 8.06-8.04 (12H, d, FDC⁻'),
7.98-7.96 (12H, d, FDC), 5.84 (DCI), 4.03 (12H, s, FDC), 2.47 (12H, m, (CH$_3$)$_2$NH$_2^+$);

$^{13}$C NMR: δ$_C$ 167.89, 144.80, 144.64, 130.28, 128.91, 126.66, 121.35, 36.85 and 34.57.

**Gas adsorption measurement**

Before measurement, the solvent-exchanged sample (about 100 mg) was prepared by immersing the as-synthesized sample in methanol to remove non-volatile solvents. The completely activated sample was obtained by heating the solvent-exchanged sample at 120 °C under reduced pressure (<10$^{-2}$ Pa) for more than 20 h.

Gas adsorption isotherms were obtained using a Belsorp-max adsorption instrument from BEL Japan Inc. using the volumetric technique. The coincident PXRD/adsorption measurements were carried out using a Rigaku Ultima IV with CuKα radiation ($λ$ = 1.5406 Å) connected with BELSORP-18 volumetric adsorption equipment (Bel Japan Inc.). Those apparatuses were synchronized with each other and each PXRD pattern was obtained at each equilibrium point of the sorption isotherms.

**Single-crystal X-ray diffraction analyses**

Single-crystal X-ray diffraction measurement was performed at 103 K with Rigaku Saturn 70 CCD system and 'XtaLAB Pro: Kappa single' with MoKα optic ($λ$ = 0.71075 Å) and a confocal monochromator. Data were processed using CrystalClear TM-SM (version 1.4.0). The structures were solved by directed methods and refined using the full-matrix least-squares technique using the SHELXL-2018/3 package.$^{S3}$ All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were refined isotropically, with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. While we are fully aware that the charged entities, such as [((CH$_3$)$_2$NH)$_2]^+$ reported herein, are not recommended to be ‘SQUEEZED’, we are however not able to locate the [((CH$_3$)$_2$NH)$_2]^+$ cation due to the high symmetry of the framework that induces severe disorder. The electron densities ascribed to [((CH$_3$)$_2$NH)$_2]^+$ cation and other unidentified solvates are removed by SQUEEZE function of the PLATON program.$^{S4,S5}$ Crystallographic and refinement details of Zn$_8$-as and Zn$_8$-de are listed in Table S1.
Table S1 Crystal data and structure refinements for Zn₈-as and Zn₈-de

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[a] R₁ = Σ||Fₒ||−|F_c||Σ|Fₒ||, [b] wR₂ = {Σ[ω(Fₒ²−F_c²)²]/Σ[ω(F₀²)]}¹/², and [c] GOF = {Σ[ω(Fₒ²−F_c²)²]/(n−p)}¹/², where n is the number of reflections, and p the total number of parameters refined.
Supplementary Figures

Fig. S1 The $^1$H NMR spectrum of 2,7-diacylfluorene with CDCl$_3$ as solvent.

Fig. S2 The $^{13}$C NMR spectrum of 2,7-diacylfluorene with CDCl$_3$ as solvent.
Fig. S3 The $^1$H NMR spectrum of bis(dibromoacetyl)fluorene with CDCl$_3$ as solvent.

Fig. S4 The $^{13}$C NMR spectrum of bis(dibromoacetyl)fluorene with CDCl$_3$ as solvent.
Fig. S5 The $^1$H NMR spectrum of fluorene-2,7-dicarboxylic acid with DMSO-$d_6$ as solvent.

Fig. S6 The $^{13}$C NMR spectrum of fluorene-2,7-dicarboxylic acid with DMSO-$d_6$ as solvent.
Fig. S7 Thermogravimetric curve of Zn$_8$-as under N$_2$.

Fig. S8 Thermogravimetric curve of Zn$_8$-de under N$_2$. 
Fig. S9 The $^1$H NMR spectrum of Zn$_8$-as with DMSO-$d_6$ as solvent.

Fig. S10 The $^{13}$C NMR spectrum of Zn$_8$-as with DMSO-$d_6$ as solvent.
Fig. S11 The $^1$H NMR spectrum of $\text{Zn}_8$-de with DMSO-$d_6$ as solvent.

Fig. S12 The $^{13}$C NMR spectrum of $\text{Zn}_8$-de with DMSO-$d_6$ as solvent.
Fig. S13 PXRD patterns for $\text{Zn}_8$-as and $\text{Zn}_8$-de.
**Fig. S14** N$_2$ adsorption (■) and desorption (□) profiles of Zn$_8$-de at 77 K.

**Fig. S15** PXRD patterns for Zn$_8$-as and C$_2$H$_2$ loaded form.
**Computational Methodology**

Density functional theory (DFT) calculations with the plane-wave pseudopotential formalism and Perdew-Burke-Ernzerhof exchange-correlation functional cut-off at 500 eV were performed using Vienna ab initio simulation package (VASP). DFT-D3(BJ) was implanted to compensate the Van de Waals dispersion. During the geometric optimizations of the gas particles, positions of framework atoms and (CH$_3$)$_2$NH$_2^+$ anions were constrained.

The binding energy of C$_2$H$_2$ and CO$_2$ was calculated by the following equation:

$$E_C = E_{A+B} - E_A - E_B$$

Where $E_A$ is the energy of the optimized MOF structure. $E_B$ is the energy of the gas molecules. $E_{A+B}$ is the energy of the optimized binding complex of the MOFs with either C$_2$H$_2$ or CO$_2$. To find the global minimum $E_{A+B}$, multiple initial configurations of the gas molecules were attempted.

Before the C$_2$H$_2$ and CO$_2$ DFT binding energy calculation, Monte Carlo (MC) simulation was performed using RASPA package to locate the (CH$_3$)$_2$NH$_2^+$ cations that could diffuse inside the pores as counter ions. The computational model of (CH$_3$)$_2$NH$_2^+$ was taken from the work of Nagys and Maria. Computational model of Zn$_8$-as and Zn$_8$-de were described using Universal Forcefield (UFF), where the partial charges were computed using Density-Derived Electrostatic Charges method (DDEC): DDEC3 protocols.
**Fig. S16** DFT optimized binding positions (a) C$_2$H$_2$ in Zn$_8$-as; (b) C$_2$H$_2$ in Zn$_8$-de; (c) CO$_2$ in Zn$_8$-de (Color scheme: Brown, Zn; C, grey; O, red. [(CH$_3$)$_2$NH$_2$]$^+$ cations and hydrogen atoms were omitted for clarity)
References


S3 Sheldrick, G. SHELXL-2018/3, Program for the Solution and Refining of Crystal structures. **2018**.


