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 Kusaka[b] 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^{TM} 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 oC, and to tis 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 Br_2 (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%. ^{1}H NMR [400 MHz, $(CD_3)_2SO$]: 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); ^{13}C NMR: δ_C 167.89, 144.82, 144.68, 130.34, 128.90, 126.69, 121.33, 36.88.

Synthesis and structure of $[(CH_3)_2NH_2]_2[Zn_8O_3(FDC)_6]\cdot7DMF$

$Zn(NO_3)_2\cdot6H_2O$ (60 mg, 2 mmol), H_2FDC (50 mg, 2 mmol), DMF (10 mL), and H_2O (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 $[(CH_3)_2NH_2]_2[Zn_8O_3(FDC)_6]\cdot7DMF$ (**Zn$_8$-as**) were heated at 120°C under vacuum for 24 h to obtain **Zn$_8$-de**.

For **Zn$_8$-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).

^{1}H NMR [400 MHz, $(CD_3)_2SO$]: 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, $(CH_3)_2NH_2^+$); ^{13}C 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 **Zn$_8$-de:**

IR (cm^{-1}, KBr): 1617.15 (s), 1552.4 (m), 1478.3 (m), 775.1 (s), 472.2 (s).

^{1}H NMR [400 MHz, $(CD_3)_2SO$]: δ = 8.14 (12H, s, FDC$^-$), 8.06-8.04 (12H, d, FDC$^-$),

7.98-7.96 (12H, d, FDC$^-$), 5.84 (DCl), 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 **Zn$_8$-*as*** and **Zn$_8$-*de***

	Zn$_8$-*as*	**Zn$_8$-*de***
Empirical formula	$C_{90}H_{48}O_{27}Zn_8$	$C_{90}H_{48}O_{27}Zn_8$
Formula weight	2084.24	2084.24
Crystal system	trigonal	trigonal
Space group	*R*-3/c	*R*-3/c
a	23.159(3)	19.3732(9)
b	23.159(3)	19.3732(9)
c	70.110(14)	78.804(3)
V	32565(12)	25614(3)
Z	12	12
ρ_{calcd} (g cm^{-3})	1.275	1.621
μ (mm^{-1})	1.799	2.287
F(000)	12528	12528
Data collected	69953	55272
Independent data	6382	5212
Goodness-of-fit	1.10	1.21
R_1, [a] wR_2 (*I*>2σ(*I*)) [b]	0.1464, 0.3804	0.1275, 0.3326
R_1, wR_2 (all data)	0.1521, 0.3839	0.2269, 0.3693
GOF [c]	1.10	1.21

[a] $R_1 = \Sigma\|F_o\|-\|F_c\|/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$, and [c] $GOF = \{\Sigma[\omega(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections, and *p* the total number of parameters refined.

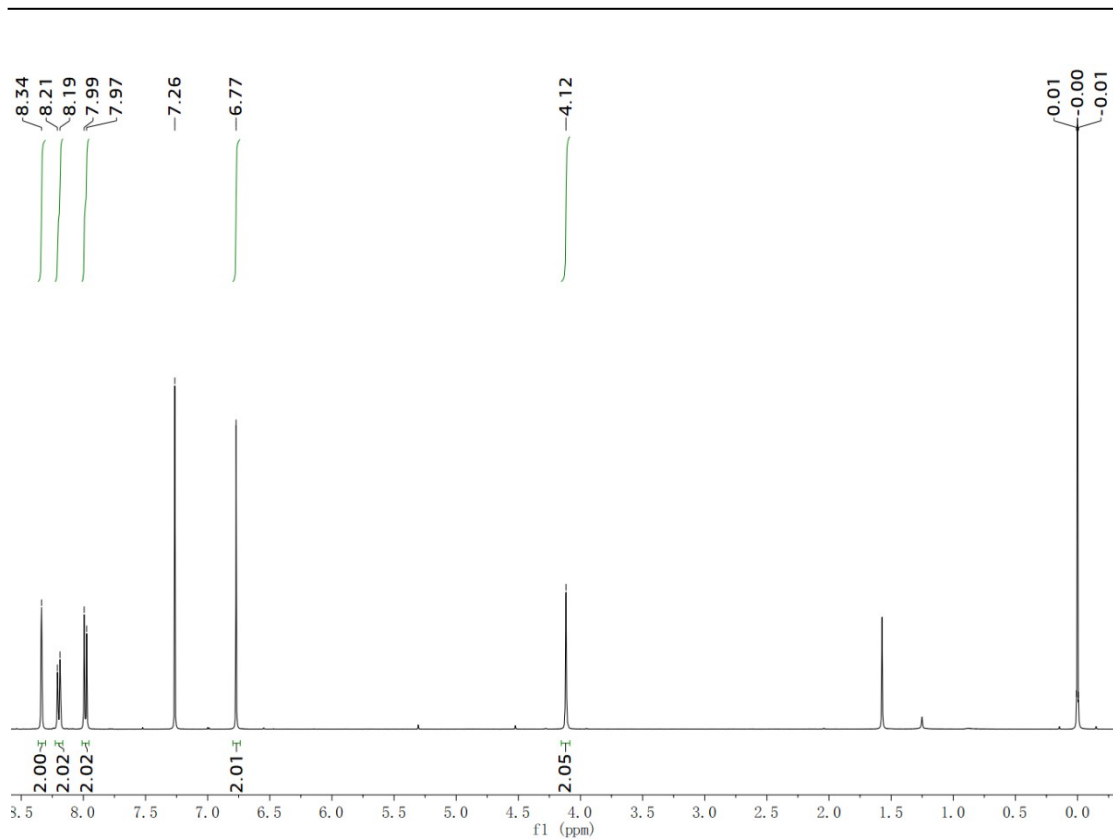## Supplementary Figures
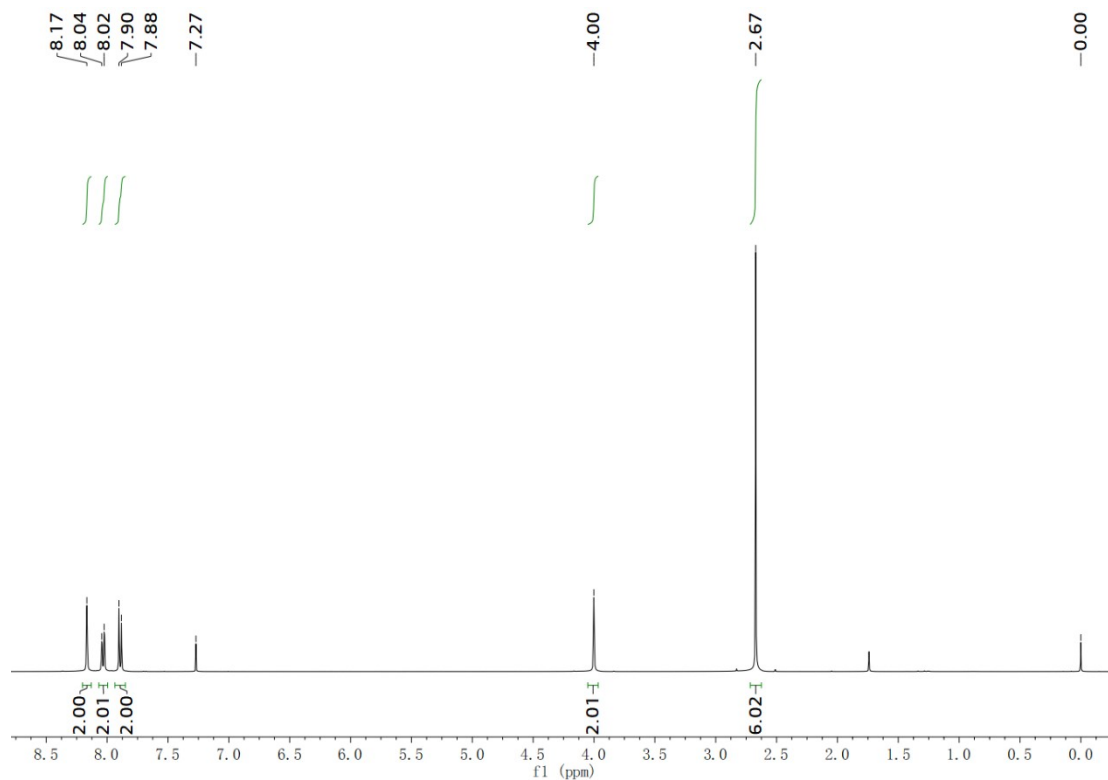
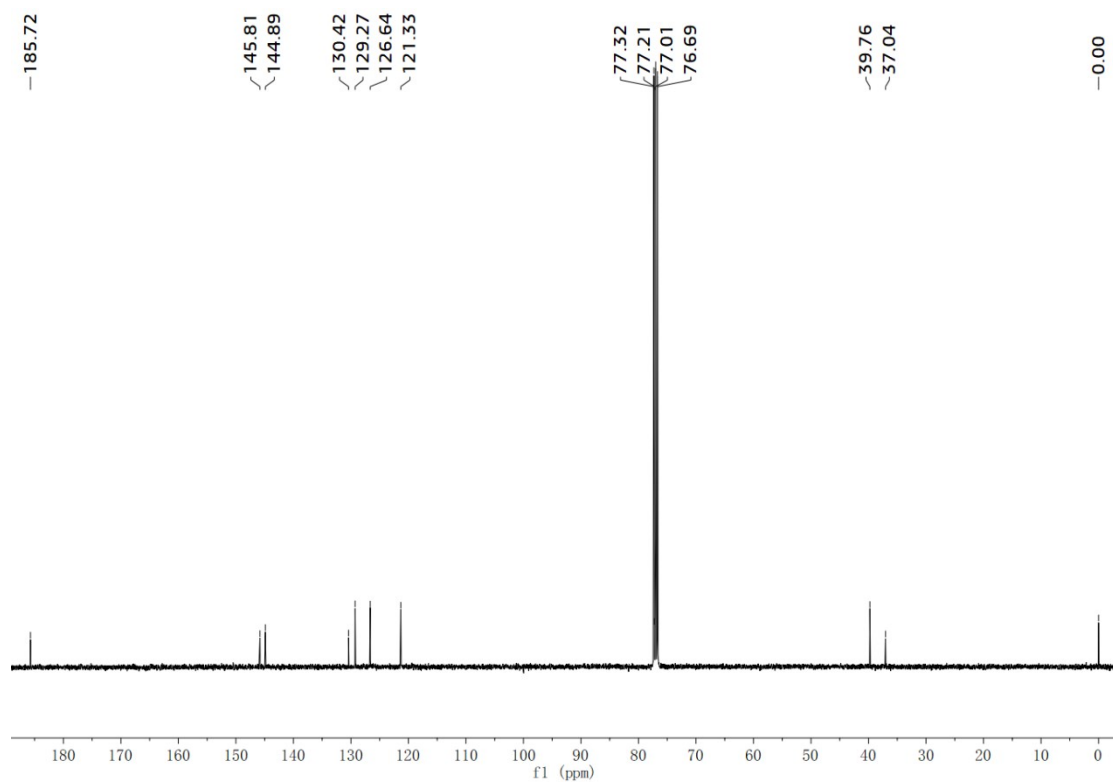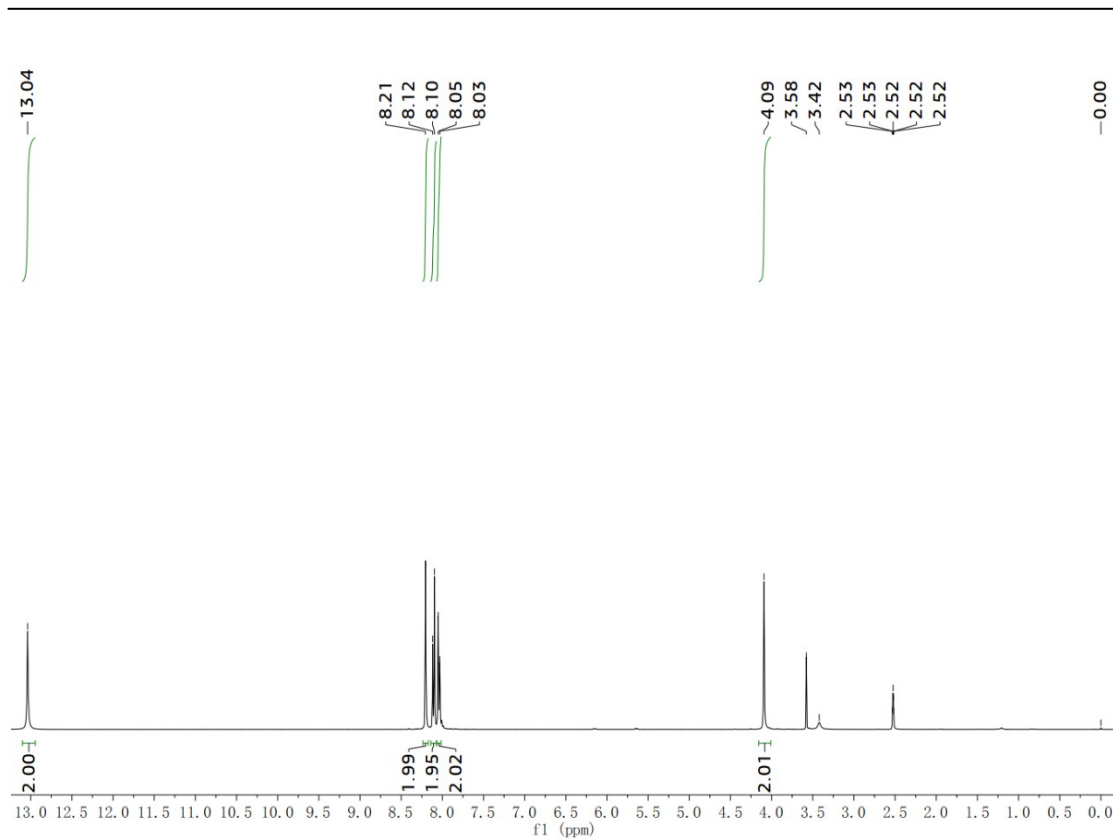**Fig. S1** The ^{1}H NMR spectrum of 2,7-diacetylfluorene with CDCl$_3$ as solvent.
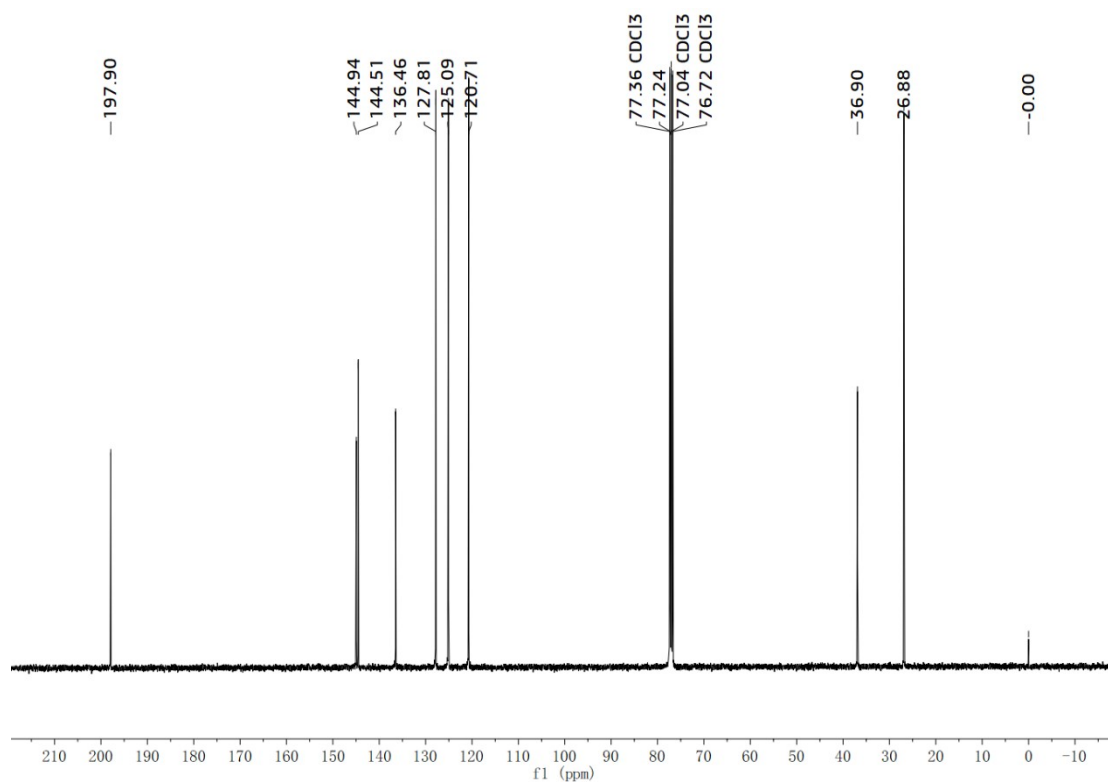
Fig. S2 The ^{13}C NMR spectrum of 2,7-diacetylfluorene with CDCl$_3$ as solvent.
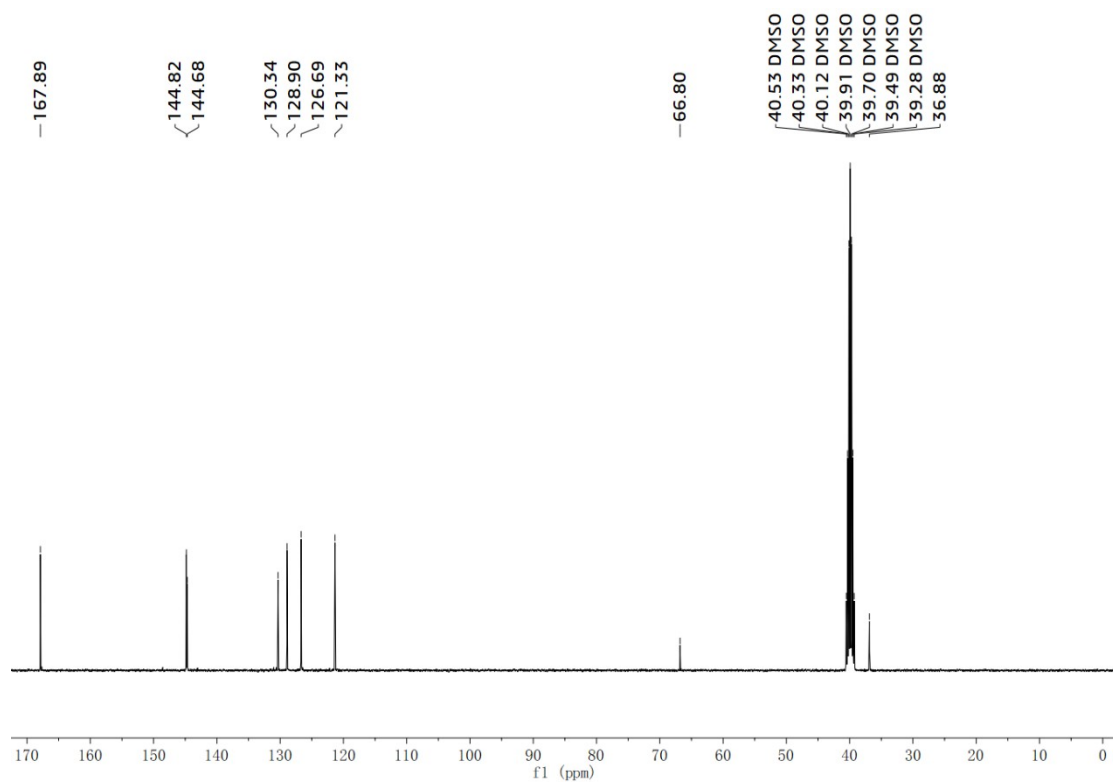
Fig. S3 The ^{1}H NMR spectrum of bis(dibromoacetyl)fluorene with CDCl$_3$ as solvent.

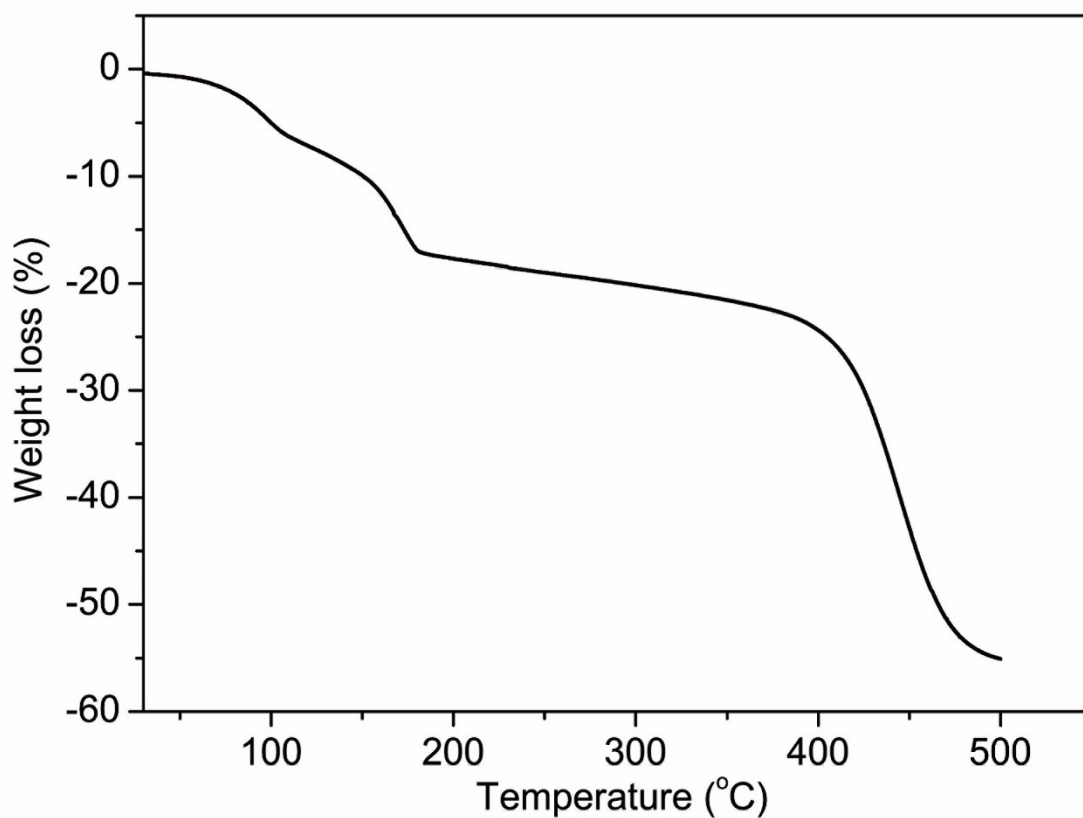**Fig. S4** The ^{13}C NMR spectrum of bis(dibromoacetyl)fluorene with CDCl$_3$ as solvent.

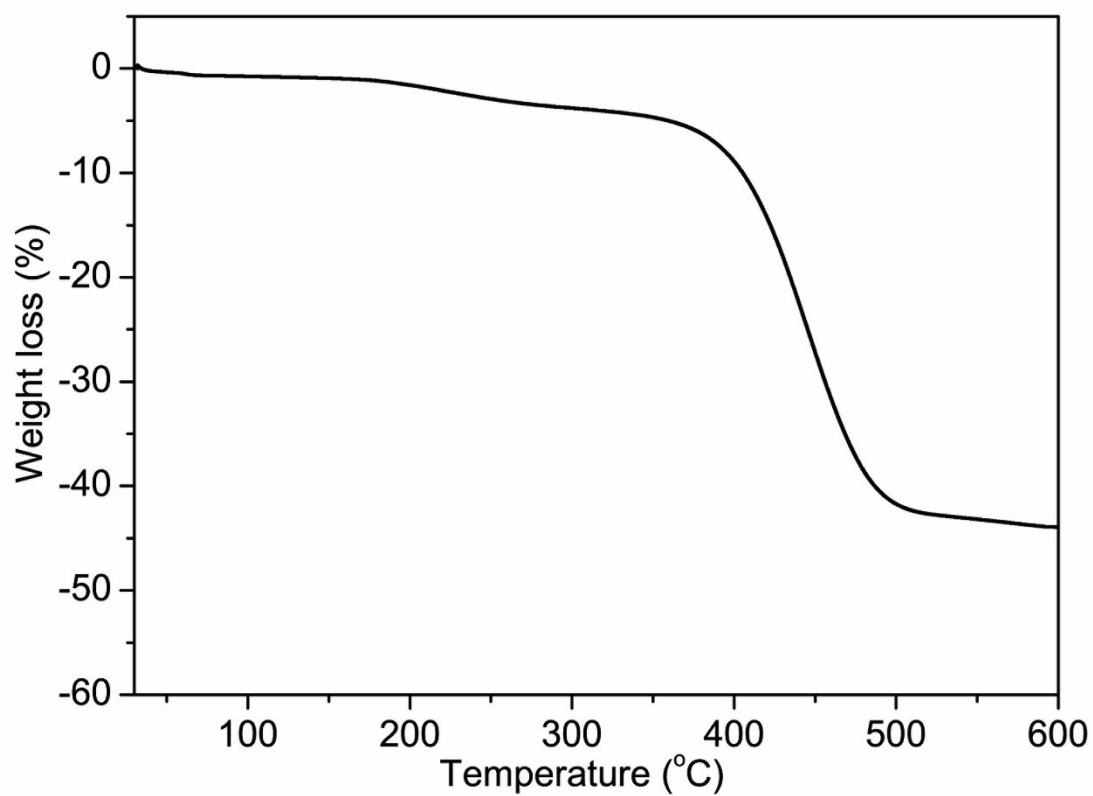**Fig. S5** The ^1H NMR spectrum of fluorene-2,7-dicarboxylic acid with DMSO-d_6 as solvent.

Fig. S6 The ^{13}C NMR spectrum of fluorene-2,7-dicarboxylic acid with DMSO-d_6 as solvent.

Fig. S7 Thermogravimetric curve of **Zn₈-*as*** under N₂.

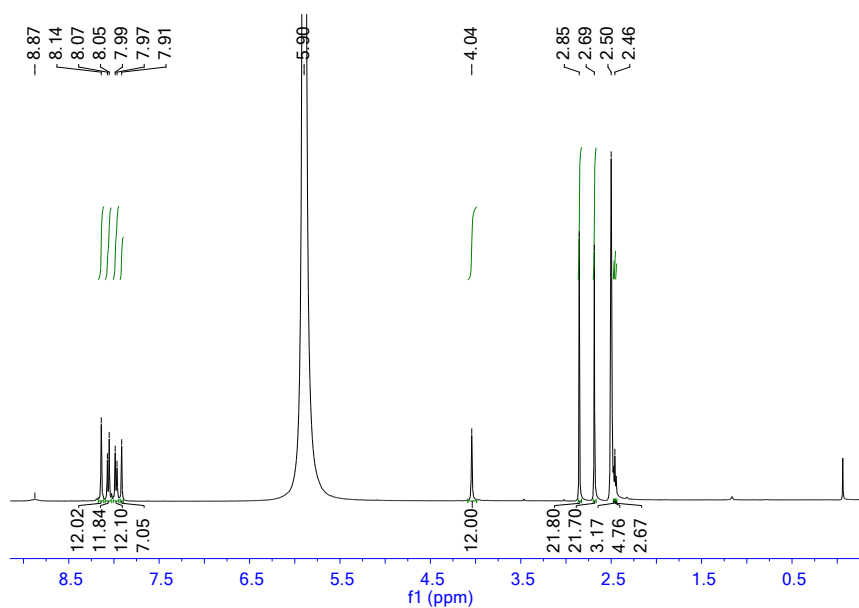**Fig. S8** Thermogravimetric curve of **Zn₈-*de*** under N₂.

Fig. S9 The ^1H NMR spectrum of **Zn₈-*as*** with DMSO-d_6 as solvent.
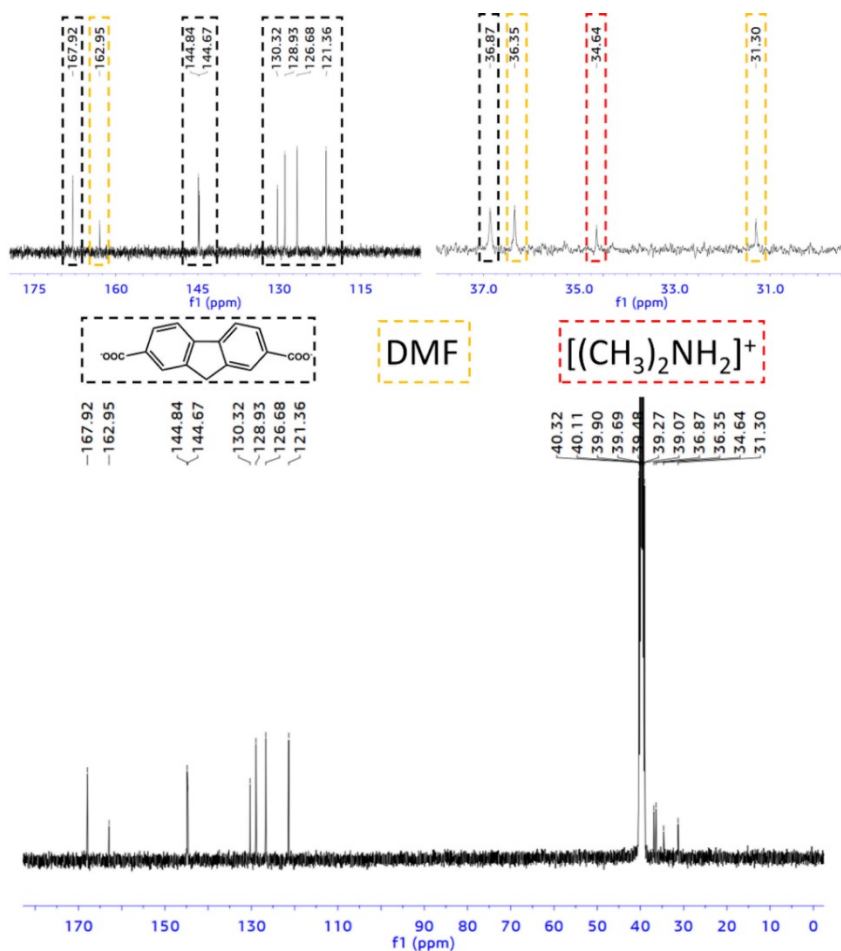
Fig. S10 The ^{13}C NMR spectrum of **Zn₈-*as*** with DMSO-d_6 as solvent.
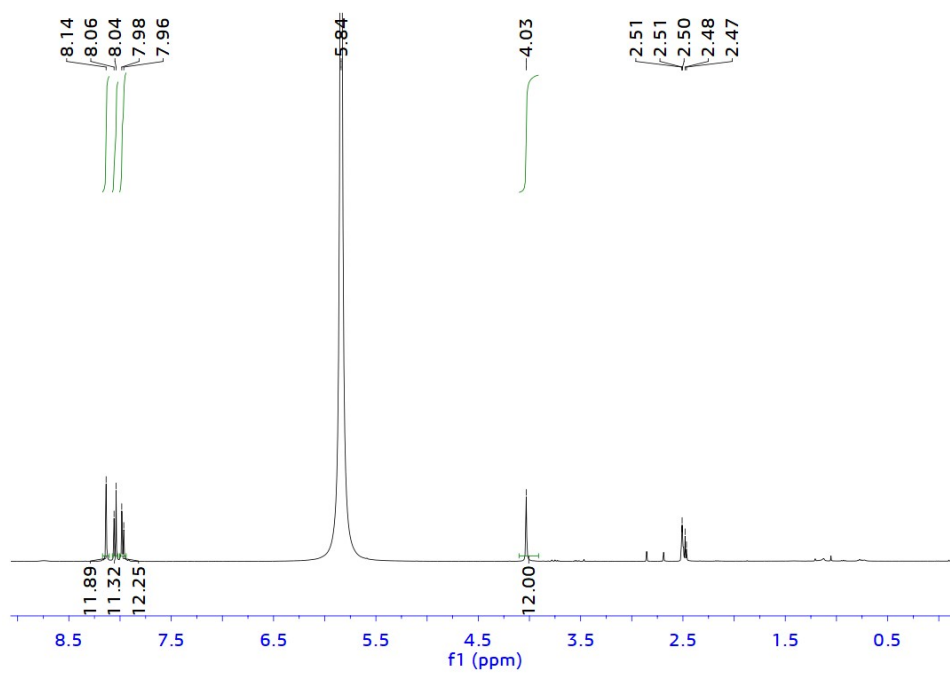
Fig. S11 The ^{1}H NMR spectrum of **Zn$_8$-*de*** with DMSO-d_6 as solvent.
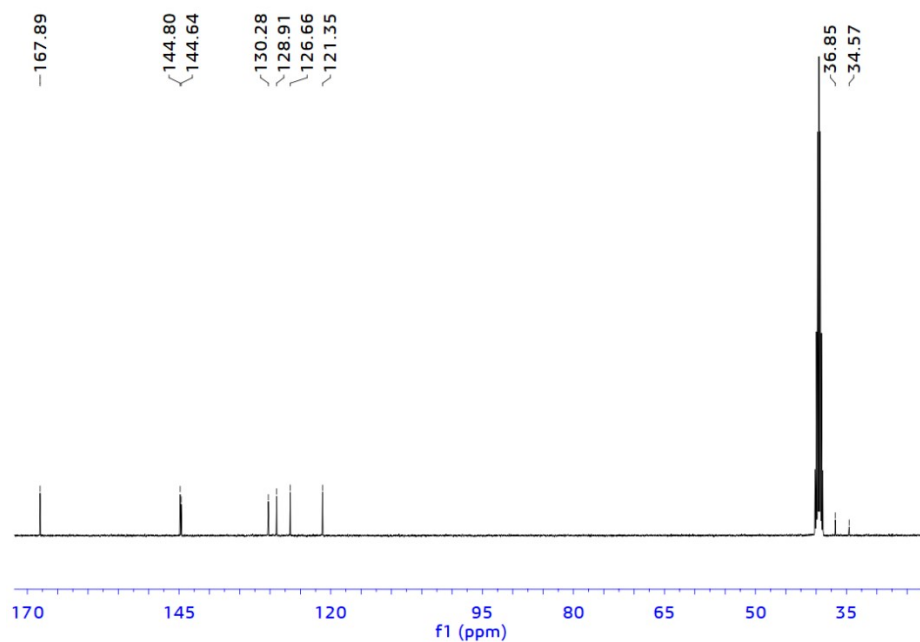
Fig. S12 The ^{13}C NMR spectrum of **Zn$_8$-*de*** with DMSO-d_6 as solvent.
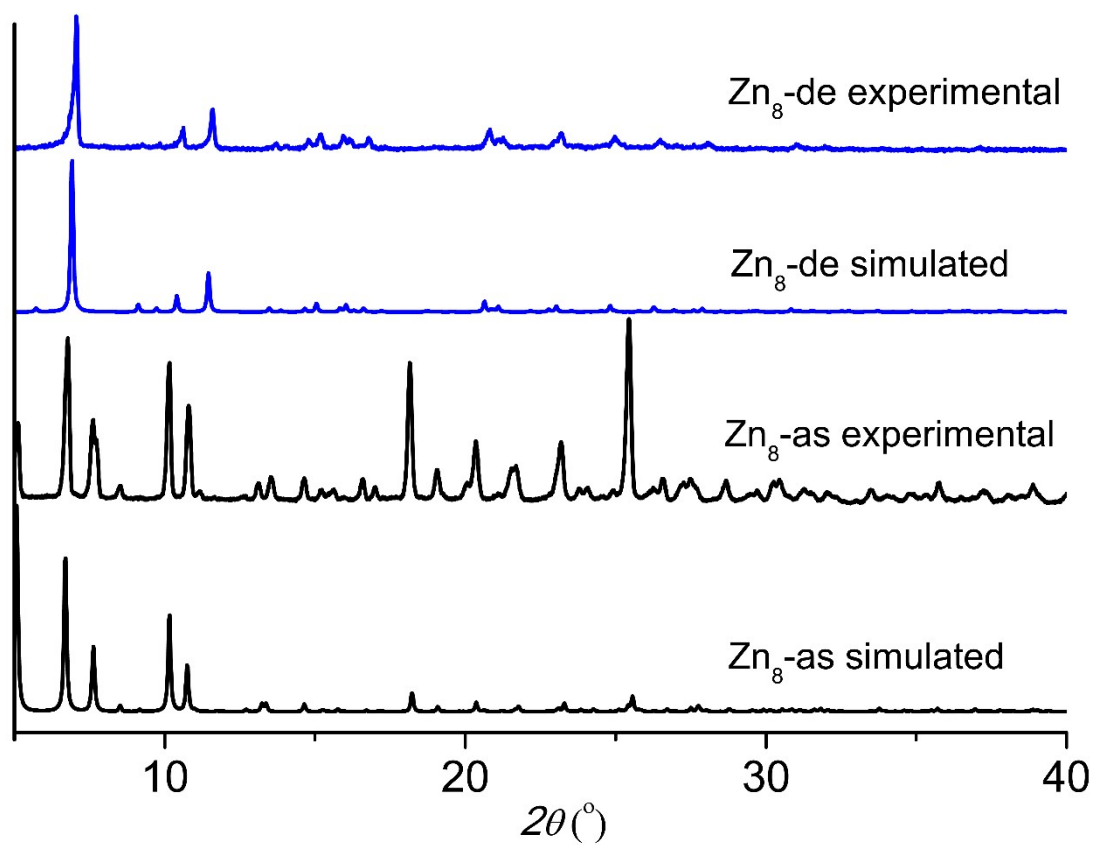
Fig. S13 PXRD patterns for **Zn₈-as** and **Zn₈-de**.
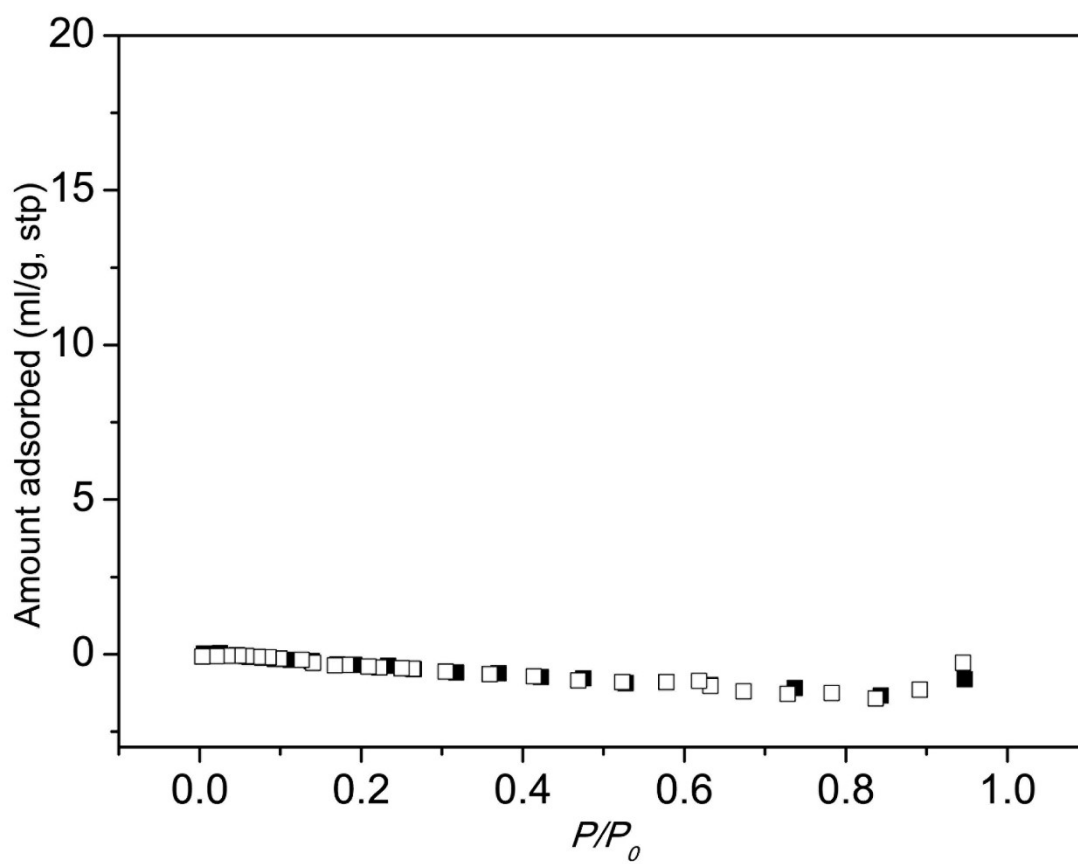
Fig. S14 N_2 adsorption (■) and desorption (□) profiles of **Zn$_8$-*de*** at 77 K.
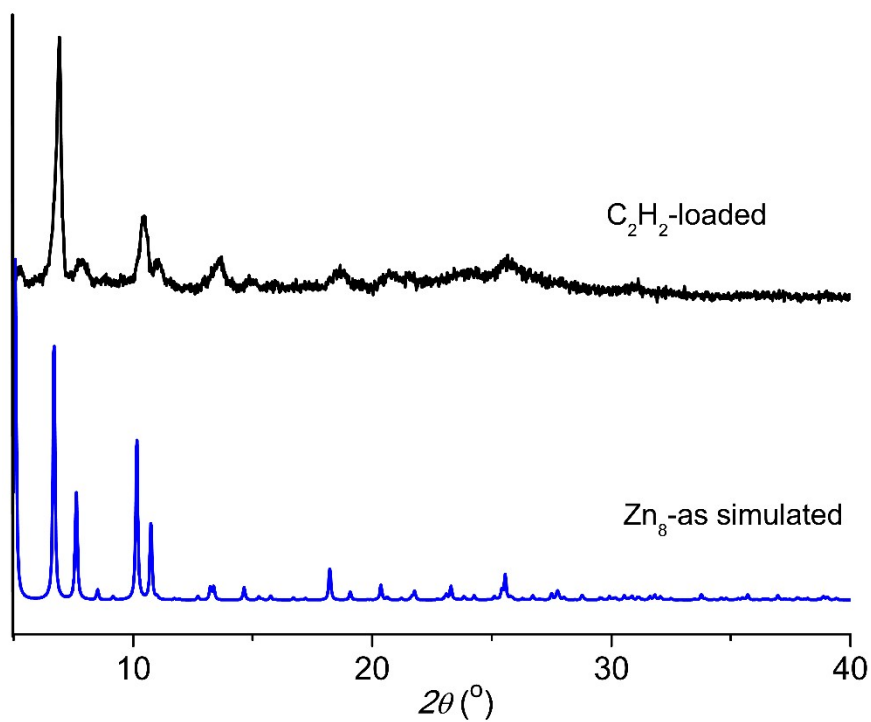

Fig. S15 PXRD patterns for **Zn$_8$-as** and C_2H_2 loaded form.

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).[S6] DFT-D3(BJ) was implanted to compensate the Van de Waals dispersion.[S7] During the geometric optimizations of the gas particles, positions of framework atoms and $(CH_3)_2NH_2^+$ anions were constrained.

The binding energy of C_2H_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_2H_2 or CO_2. To find the global minimum E_{A+B}, multiple initial configurations of the gas molecules were attempted.

Before the C_2H_2 and CO_2 DFT binding energy calculation, Monte Carlo (MC) simulation was performed using RASPA package[S8] to locate the $(CH_3)_2NH_2^+$ cations that could diffuse inside the pores as counter ions. The computational model of $(CH_3)_2NH_2^+$ was taken from the work of Nagys[S9] and Maria.[S10] Computational model of **Zn$_8$-*as*** and **Zn$_8$-*de*** were described using Universal Forcefield (UFF),[S11] where the partial charges were computed using Density-Derived Electrostatic Charges method (DDEC): DDEC3 protocols.[S12]
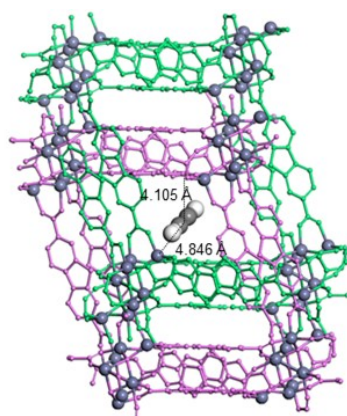
C$_2$H$_2$ in **Zn$_8$-as**
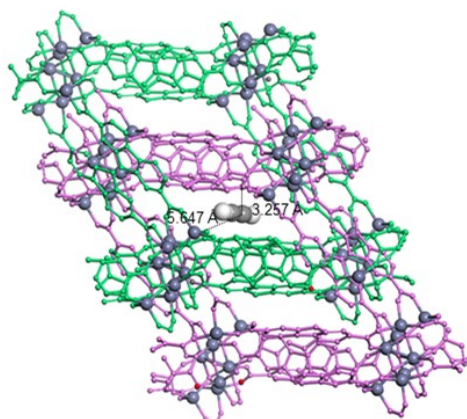
C$_2$H$_2$ in **Zn$_8$-de**
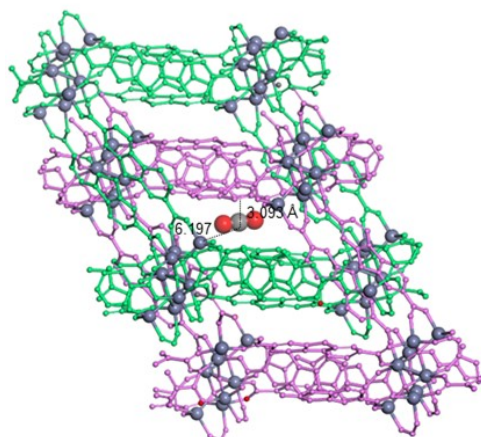
CO$_2$ in **Zn$_8$-de**

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

S1 Sulzberg, T.; Cotter, R. J. Electron acceptors derived from fluorenecarboxylic acids and their charge-transfer complexes. *J. Org. Chem.* 1970, **35**, 2762−2769.

S2 P.J. Skabara, R. Berridge, I.M. Serebryakov, A.L. Kanibolotsjy, L. Kanibolotskaya, S. Gordeyev, I.F. Perepichka, N.S. Sariciftci, C. Winder, *J. Mater. Chem.*, 2007, **17**, 1055-1062.

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

S4 Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Cryst.* 2003, **36**, 7−13.

S5 Spek, A. L. PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr., Sect. C,* 2015, **71**, 9−18.

S6 (a) G. Kresse, J. Non. Cryst. Solids, 1995, 192–193, 222–229; (b) G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.

S7 (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

S8 D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, *Mol. Simul.*, 2016, **42**, 81–101.

S9 M. C. Bernini, D. Fairen-Jimenez, M. Pasinetti, A. J. Ramirez-Pastor and R. Q. Snurr, *J. Mater. Chem. B*, 2014, **2**, 766–774.

S10 P. I. Nagy, *Phys. Chem. Chem. Phys.*, 2012, **14**, 849–857.

S11 A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035

S12 D. Nazarian, J. S. Camp and D. S. Sholl, *Chem. Mater.*, 2016, **28**, 785–793.