Electronic Supplementary Information

Facile synthesis and superior properties of a nitrogen-rich energetic Zn-MOF with 2D azide-bridged bilayer structure

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Experimental section

Caution

AP, CL-20 and 5-amino-1*H*-tetrazole (atz) are all energetic materials which are sensitive towards impact and friction. Necessary safeguard procedures must be adopted when handling them or mixtures containing them, including safety glasses, face shield, latex gloves, body armor and grounded equipments.

General methods

All reagents and solvents employed were commercially available and used without further purification. Infrared spectra were recorded in the range of 4000~400 cm^{-1} on a Perkin-Elmer FTIR spectrum 2000 spectrometer using KBr pellets. Raman spectra were recorded using a Horiba HR800 Raman spectrometer. Scanning electron microscopy (SEM) was carried out using a Hitachi SU-8010 FE-SEM. Elemental analyses were performed with a Perkin-Elmer model 240C instrument. Powder X-ray diffraction (PXRD) data were obtained using a Rigaku D/MAX 2500V/PC diffractometer with Cu $K\alpha_1$ (λ = 1.5056 Å) radiation. A step size of 0.05° and counting time of 1.2 s/step were applied in a 2θ range of 8.0°~60.0°. Thermogravimetric (TG) analyses were performed on a Delta Series TGA7 instrument in N_2 atmosphere with a heating rate of 10 °C min^{-1} from 30 to 550 °C. Differential scanning calorimetry (DSC) analyses were conducted on a Netzsch DSC 204 HP instrument in N_2 atmosphere. Gas adsorption isotherms towards N_2 and CO were acquired using a Quantachrome Autosorb-iQ automated gas sorption analyzer under a pressure of 0~0.1 MPa. The temperature was precisely controlled between 30 and 100 °C using an external circulator bath.

Synthesis of $[Zn_2(atz)_3(N_3)]_n$

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.149 g, 0.5 mmol), 5-amino-1*H*-tetrazole (0.085 g, 1.0 mmol), DMF (2 mL) and water (8 mL) was vigorously stirred at room temperature for 0.5 h, then sealed in a 15 mL Teflon autoclave and heated at 90 °C for 24 h. After the autoclave was cooled to room temperature at a rate of 10 °C h^{-1}, the mixture was filtered and washed with 10 mL of cold methanol. Finally, desired product was obtained as colorless crystals in ca. 90% yield based on Zn. Anal. calcd. for $C_3H_6N_{18}Zn_2$ (Mr = 424.96, %): C, 8.48; H, 1.42; N, 59.33; Found (%): C, 8.41; H, 1.43; N, 59.36. FT-IR spectra of atz and $[Zn_2(atz)_3(N_3)]_n$ are shown in Fig. S1.

X-ray crystallographic study

Single crystal X-ray experiment of $[Zn_2(atz)_3(N_3)]_n$ was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) using ω-φ scan modes. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods using SHELXS-97 and refined by means of full-matrix least-squares procedures on F^2 with SHELXL-97 program. All non-hydrogen atoms were located using subsequent Fourier-difference methods and refined anisotropically. In all cases, hydrogen atoms were placed in their calculated positions and thereafter allowed to ride on their parent atoms. CCDC 2141838 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

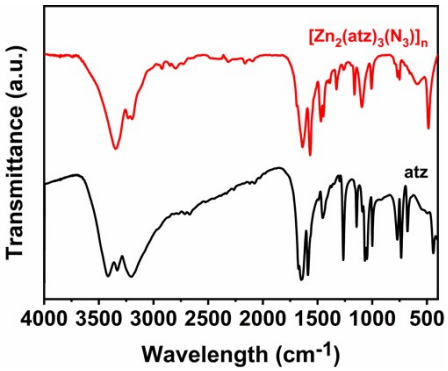

Fig. S1 FT-IR spectra of atz and $[Zn_2(atz)_3(N_3)]_n$.

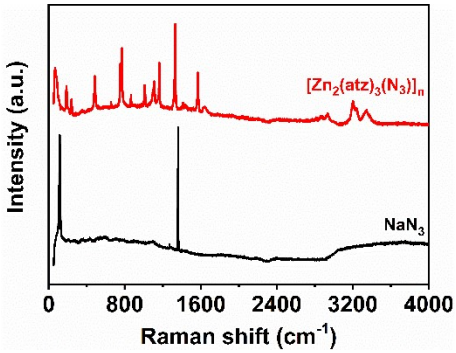

Fig. S2 Raman spectrum of $[Zn_2(atz)_3(N_3)]_n$ and NaN_3.

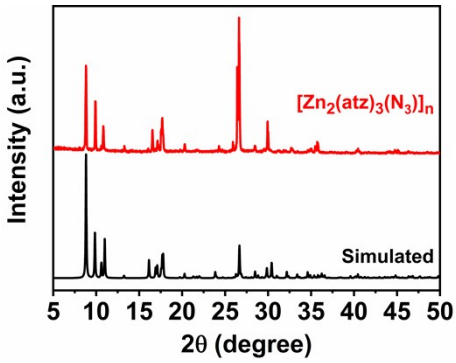

Fig. S3 Simulated and actual powder XRD patterns of $[Zn_2(atz)_3(N_3)]_n$.

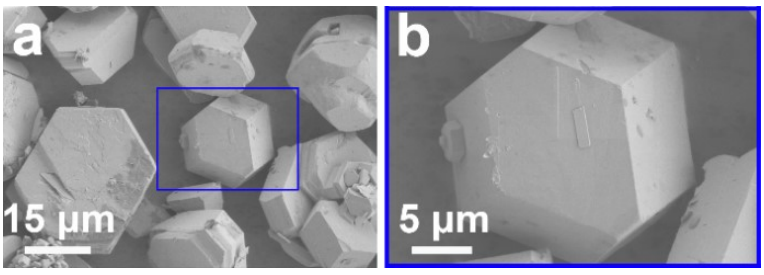

Fig. S4 SEM images of $[Zn_2(atz)_3(N_3)]_n$. Fig. S4b is the enlarged image of corresponding area in Fig. S4a.

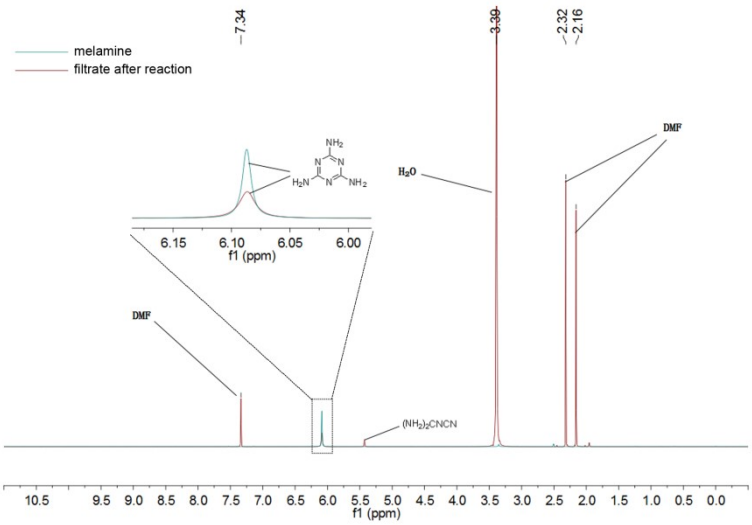

Fig. S5 H^1-NMR spectra of melamine and the filtrate after reaction.

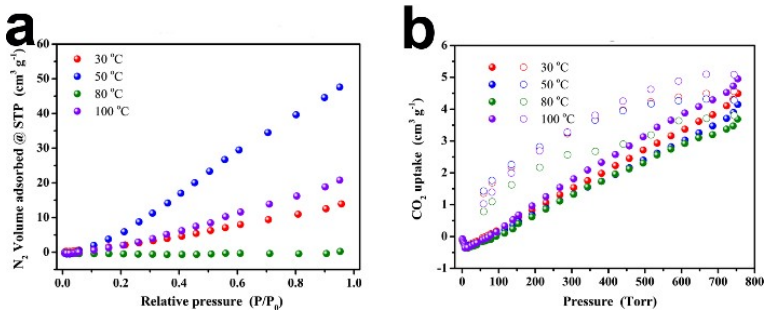

Fig. S6 Gas adsorption curves of $[Zn_2(atz)_3(N_3)]_n$ at different temperatures towards (a) N_2 and (b) CO_2.

Table S1 Thermodecomposition peak temperature of $[Zn_2(atz)_3(N_3)]_n$ under different heating rates and kinetic parameters estimated by Kissinger's and Ozawa's methods.

Heating rate (°C min^{-1})	T_p (°C)	E_k (kJ mol^{-1})	lnA_k (s^{-1})	R_k	E_o (kJ mol^{-1})	R_o
5	363.5	219.76	33.48	0.9999	219.20	0.9999
10	374.0					
15	380.1					
20	384.4					

Table S2 Calculated parameters used in the detonation reaction for $[Zn_2(atz)_3(N_3)]_n$.

	EMOF (hartree)	Zn (hartree)	NH_3 (hartree)	C (hartree)	N_2 (hartree)	ΔE_{det} (hartree)	ΔE_{det} (kcal g^{-1})	ΔH_{det} (kcal g^{-1})
$[Zn_2(atz)_3(N_3)]_n$	-1235.0341	-65.596	-56.505	-37.738	-109.448	2.0341	3.0036	3.4311

Table S3 Comparison of key physicochemical properties of energetic MOFs and some traditional energetic materials.

EMOFs	ρ[a] (g cm^{-3})	N[b] (%)	Ω[c] (%)	T_d[d] (°C)	Q[e] (kJ g^{-1})	v_D[f] (km s^{-1})	p[g] (GPa)	IS[h] (J)	FS[i] (N)
$[Zn_2(atz)_3(N_3)]_n$	**1.541**	**59.33**	**-32.50**	**362**	**14.36**	**8.034**	**25.96**	**>40**	**>360**
CHP[1]	1.948	14.71	-11.48	194	5.23	8.225	31.73	0.5	——
NHP[1]	1.983	33.49	-11.48	220	5.73	9.184	39.69	——	——
CHHP[2]	2.000	23.58	-13.05	231	3.14	6.205	17.96	0.8	——
ZnHHP[2]	2.117	23.61	-49.99	293	2.93	7.016	23.58	——	——
$[Cu(atz)(NO_3)(OH)]_n$[3]	2.41	30.91	-24.72	~280	3.16	7.459	29.71	11	180
[Zn(ata)(OH)][3]	2.54	54.1	-33.60	~325	2.55	8.628	39.67	>40	>360
$[Cu(atrz)_3(NO_3)_2]_n$[4]	1.680	53.35	-58.83	~225	15.14	9.160	35.68	22.5	——
$[Ag(atrz)_{1.5}(NO_3)]_n$[4]	2.160	43.76	-49.99	~250	5.78	7.773	29.70	30	——
$[Cu_4Na(Mtta)_5(CH_3CN)]_n$[5]	1.975	40.08	-71.97	335	9.90	7.225	24.43	36	>360
$[K_2Zn(bta)_{24}]_n$[6]	2.015	48.69	-32.44	349	——	——	——	>40	>360
$[Pb(bta)\cdot 2H_2O]_n$[7]	3.250	31.98	-22.32	~330	4.97	8.963	47.47	>40	——
$[Cu_2(to)(dns)]_n$[8]	2.458	15.42	-47.55	217	4.10	7.522	29.51	38.6	>360
$[Ag_{16}(BTFOF)_9]_n\cdot[2(NH_4)]_n$[9]	1.997	35.36	-34.16	221	3.57	11.81	65.29	>40	>360
KCPT[10]	1.98	39	-27.24	323	5.97	8.457	32.5	7.5	240
$[Pb(HBTI)]_n$[11]	3.186	34.22	-46.90	325	4.85	7.842	35.87	>40	>360
$[Co(HTATT)]_n$[12]	1.903	65.25	-58.00	~360	17.71	9.99	45.71	>40	>360
$[Ag_2(DTPZ)]_n$[13]	2.812	32.58	-52.10	346	10.15	8.355	38.89	>40	>360
$[Cu(tztr)]_n$[14]	2.216	49.36	-52.35	360	14.22	8.429	40.02	>40	>360
TNT[3]	1.65	18.5	-73.96	244	3.75	7.178	20.5	15	353
RDX[3]	1.81	37.8	-21.60	210	5.80	8.600	33.92	7.5	120
HMX[3]	1.95	37.8	-21.60	287	5.52	8.900	38.39	7.4	——
CL-20[3]	2.04	38.36	0	221	6.16	9.730	44.4	4	48

[a] Density. [b] Nitrogen content. [c] Oxygen balance. [d] Onset decomposition temperature. [e] Heat of detonation.

[f] Detonation velocity. [g] Detonation pressure. [h] Impact sensitivity. [i] Friction sensitivity.

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