Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for

Construction of nano-sized FOX-7/ZIF-8 composites for fast decomposition and reduced sensitivity

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Experimental Section

General

1,1-Diamino-2,2-dinitroethene ($C_2H_4N_4O_4$, FOX-7) was prepared according to the literature.[1] Zinc hydroxide [$Zn(OH)_2$] and 2-methylimidazole were purchased from Macklin.

Liquid-assisted mechanochemical synthesis were performed with horizontal planetary ball mill (MSK-SFM-1S, HF-Kejing, China) using ball-to-powder mass ratio of ~10 : 1. FT-IR spectra were recorded on a Fourier transform infrared spectrometer (Spectrum Two, L1600300, the United States), collected from 4000 cm^{-1} to 400 cm^{-1} with 4 cm^{-1} resolution. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (DX2700, Dandong Haoyuan Instrument, China) in steps of 0.03 2θ from 5 to 50° 2θ at room temperature. Elemental analysis was performed on an Elementar Vario EL cube elemental analyzer (Germany). The specific surface areas and pore properties were measured on physical adsorption instrument (ASAP 2460, Micromeritics, United States) by nitrogen adsorption-desorption. The morphology and microstructure of composites were analyzed by scanning electron microscopy (SEM, REGULUS 8230, Hitachi, Japan) at 15 kV. In order to obtain better conductivity, after being fixed on the aluminum plate with double-sided carbon tape, all the samples were coated with a layer of gold-palladium alloy. Differential scanning calorimetric analyses (DSC) were carried out on an HSC-1 instrument (HENVEN, China) in the Ar atmosphere with a heating rate of 5 $^oC\ min^{-1}$.

The impact sensitivity test was determined with a WL-1 type impact sensitivity instrument with a 5.0 kg drop weight according to GJB-772A-97 standard method 601.2.[2] Each sample (50 mg) was tested 25 times to obtain a H_{50} (The H_{50} value represents the drop height of 50% explosion probability). The friction sensitivity test was carried out by using a WM-1 type friction sensitivity instrument (pendulum angle: 90^o; relative pressure: 3.92 MPa) with a 1.5 kg pendulum weight according to GJB-772A-97 standard method 602.1.[2] Each sample (30 mg) was tested 25 times and an explosion probability P (%) was obtained.

Preparation of FOX-7/ZIF-8 composites and ZIF-8

In a typical synthesis, FOX-7 (0.296 g, 2.0 mmol) in DMF solution (2 mL), $Zn(OH)_2$ (0.1988 g, 2.0 mmol), 2-methylimidazole (1.314 g, 16.0 mmol) was sealed in a 100 mL corundum vial along with zirconia balls with diameters of 3.3 mm. Then the mixture was milled for 4 h at room temperature. The resulting yellow powder was washed with ethanol to remove excess 2-methylimidazole. After drying under vacuum, the desired sample was obtained and denoted as **FOX-7/ZIF-8 (I)**. The synthesis procedure of **FOX-7/ZIF-8 (II)** and **FOX-7/ZIF-8 (III)** was similar except $Zn(OH)_2$ (0.2982 g, 3.0 mmol) and 2-methylimidazole (1.971 g, 24.0 mmol), or $Zn(OH)_2$ (0.398 g, 4.0 mmol) and 2-methylimidazole (2.627 g, 32.0 mmol) were used, respectively.

The synthesis procedure of ZIF-8 was similar to **FOX-7/ZIF-8 (I)**, except FOX-7 was not used as reactant.

Table S1. Elemental analysis results of FOX-7/ZIF-8 composites.

Compound	Content (wt%)			
	C	H	N	O
FOX-7/ZIF-8 (I)	28.46	3.01	26.98	19.16
FOX-7/ZIF-8 (II)	33.56	3.06	26.70	13.48
FOX-7/ZIF-8 (III)	34.97	3.10	25.70	11.60

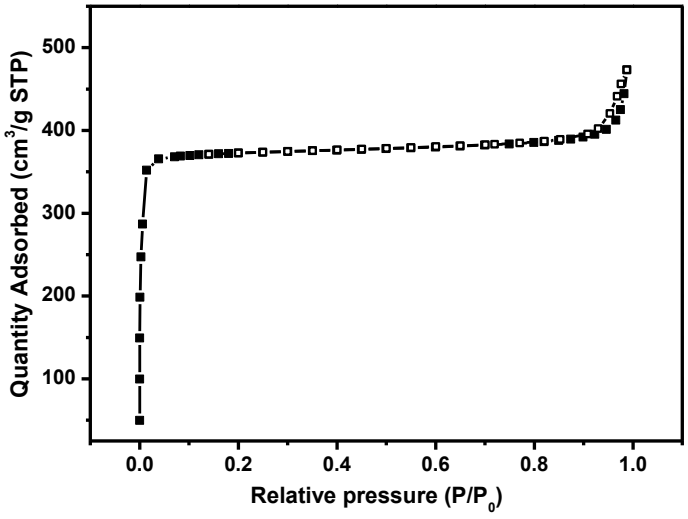

Fig. S1. Nitrogen adsorption/desorption isotherms of liquid-assisted mechanochemically prepared ZIF-8.

Table S2. Textural parameters of FOX-7/ZIF-8 composites and ZIF-8.

Compound	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
FOX-7/ZIF-8 (I)	659	0.322
FOX-7/ZIF-8 (II)	868	0.434
FOX-7/ZIF-8 (III)	921	0.732
ZIF-8	1110	0.548

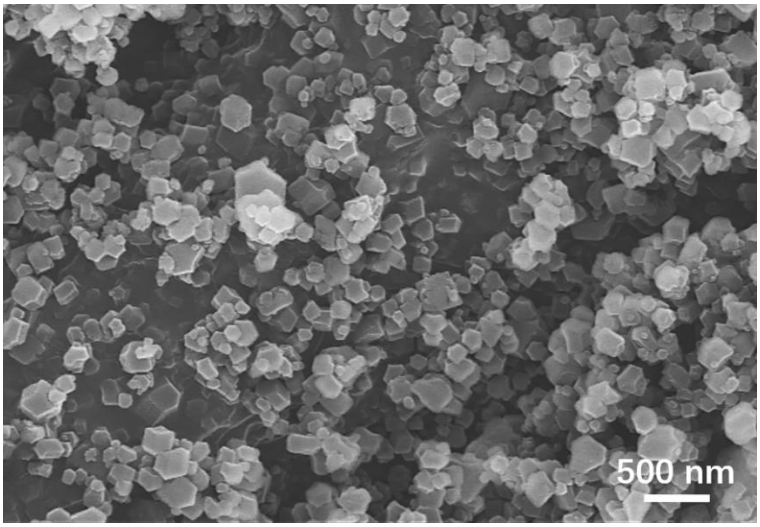

Fig. S2. SEM image of liquid-assisted mechanochemically prepared ZIF-8.

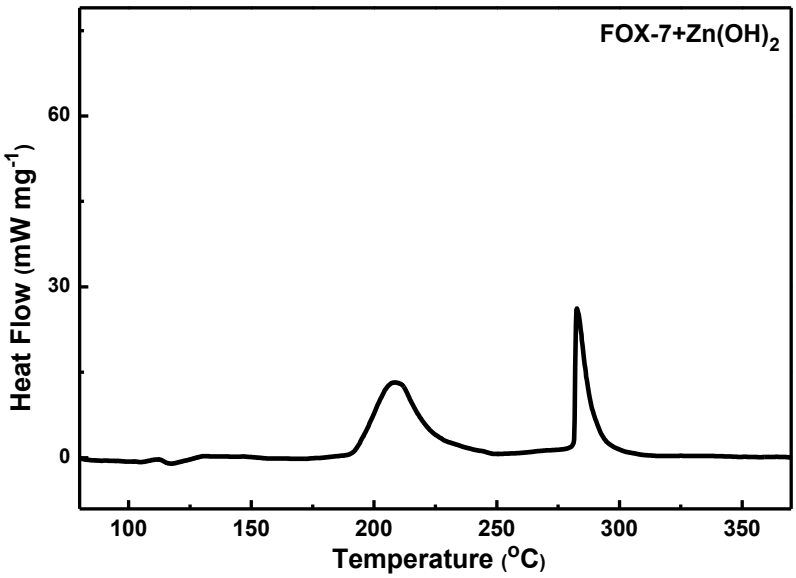

Fig. S3. DSC curve of equivalent physical mixture of FOX-7 and $Zn(OH)_2$ [denoted as FOX-7+$Zn(OH)_2$] at a heating rate of 5 °C min^{-1}.

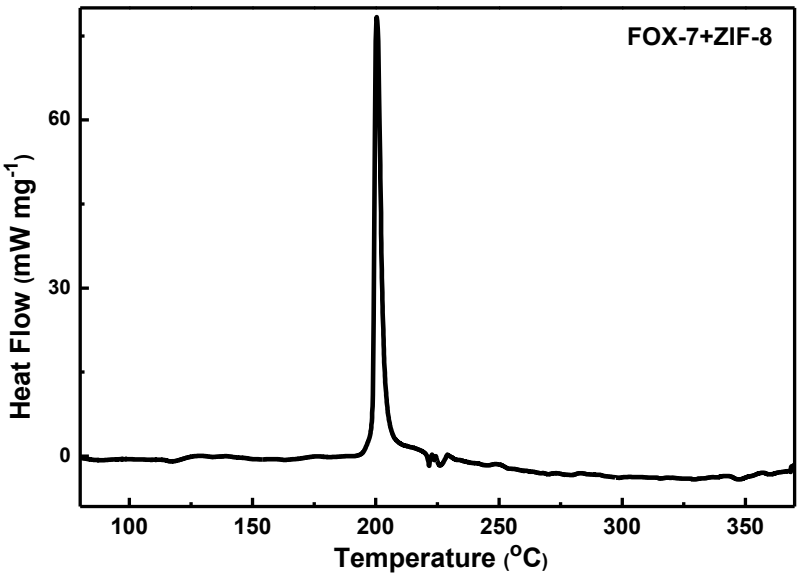

Fig. S4. DSC curve of equivalent physical mixture of FOX-7 and ZIF-8 (denoted as FOX-7+ZIF-8) at a heating rate of 5 ºC min^{-1}.

AIMD Section

Computational methods and details

The FOX-7/ZIF-8 model was built using Materials Studio 17.2, and the forcite module was used to adjust the position of the FOX-7 in the cages. AIMD simulations of FOX-7/ZIF-8 and α-FOX-7 were carried out using VASP[3-5] within the PBE-GGA method.[6] Because the cell size of FOX-7/ZIF-8 is large enough, no supercell is used for FOX-7/ZIF-8. α-FOX-7 used the 2×2×2 supercell. The total time of simulation was 45 ps with each time step setting to 1.0 fs. The first 5 ps was the relaxation in 300 K, and the next 40 ps was the program temperature from 300 K to 1000 K. The plane wave energy cut-off was set to 500 eV. We set the Nosé–Hoover thermostat[7] to control the temperature within the canonical ensembles (NVT). For the consistency with DFT calculations, we also employed the DFT-D3 correction method to describe the van der Waals interactions.[8, 9]

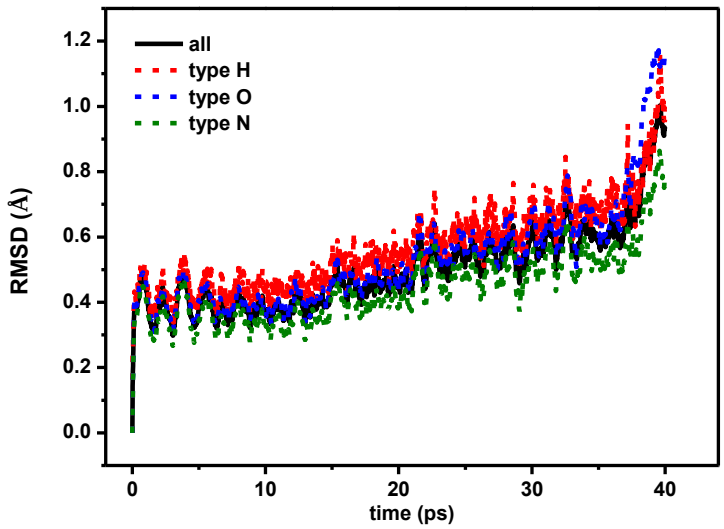

Fig. S5. Root Mean Square Deviation (RMSD) of atomic position shift in α-FOX-7 model when temperature rises to 1000 K. Blue dotted line represents oxygen atom, red dotted line represents hydrogen atom, green dotted line represents nitrogen atom, and black solid line represents all atoms.

References

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