Electronic Supplementary Information (ESI) for

Direct White-Light-Emitting and Near-Infrared Phosphorescence of Zeolitic Imidazolate Framework-8

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A. Experimental Section.

1. Materials and general procedures.

All of the chemicals are commercial available, and used without further purification. PXRD patterns were collected on a Rigaku Ultima-IV automated diffraction system with Cu Kα radiation (λ = 1.5406 Å). Measurements were made in a 2θ range of 5−50° at room temperature with a step of 0.02° (2θ) and a counting time of 0.2 s / step. The operating power was 40 Kv, 30 mA. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. Optical diffuse reflectance spectra were obtained on a Shimadzu UV-3600 spectrophotometer at room temperature. Data were collected in the wavelength range of 200−800 nm. $BaSO_4$ powder was used as a standard (100% reflectance). The C, H, N analyses were carried out using a Perkin–Elmer Elementarvario elemental analysis instrument.

Room temperature time-resolved photoluminescence (PL) experiments were conducted on an Edinburgh FLS980 fluorescence spectrometer equipped with a xenon arc lamp (Xe900) and a microsecond flash-lamp (uF900), respectively. The phosphorescence quantum yields (QY) at room temperature were estimated using an integrating sphere (F-M101, Edinburgh) accessary in FLS980 fluorescence spectrometer. The integrating sphere has a Teflon-lined, diameter of 150 mm and weight of 2 kg was used. Photographs of single crystals for ZIF-8 were taken under OLYMPUS IXTI fluorescence microscope.

2. Synthesis of ZIF-8

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.297 g), 2-methylimidazole (2 mmol, 0.164 g), 0.2 mL of concentrated HNO_3 and 15 mL of DMF was stirred for 10 min. The mixture was then transferred to and, sealed in, a Teflon reactor (23 ml) and heated at 120 °C for 24 h. After that, the mixture was cooled at a rate of 5 $°C \cdot h^{-1}$ to room temperature. The pale-yellow crystals of ZIF-8 were washed by DMF (3 × 10 mL) and stored in DMF until needed for experiments. To obtain the guest-free ZIF-8a, the as-synthesized ZIF-8 sample (ca. 50 mg) was soaked in absolute methanol at ambient temperature for 7days, during which the solvent was refreshed four times, and then

heating at 80 °C in vacuum for 24 h.

Elemental analysis: Calc. (%) for $C_{10}H_{16}N_{4.67}O_{1.33}Zn$ (ZIF-8): C, 41.66; H, 5.59; N, 22.69; found (%): C, 41.81; H, 5.68; N, 22.01. Calc. (%) for $C_8H_{10}N_4Zn$ (ZIF-8a): C, 42.22; H, 4.43; N, 24.62; found (%): C, 43.53; H, 4.55; N, 24.71.

It is worthwhile to note that, recently, a method of coordination modulation for fabricating porous coordination polymer (PCP) nanocrystals has been reported by Kitagawa.[1] Modulated nucleation can be induced by the addition of modulators with the same functionality as organic linkers to impede the coordination interaction between metal ions and organic linkers. In this work, the addition of modulator generates a competitive situation to impede the coordination interaction between metal ions and organic linkers, and then regulates the rate of framework extension and crystal growth. In addition, the modulator can also physically prevent the aggregation of crystals, which leads to anisotropic growth. In our work reported herein, the addition of large amounts of concentrated nitric acid modulator significantly decelerated the rate of crystal growth and facilitated the formation of large scale (micrometer) crystallites with highly crystalline of ZIF-8.

3. Electronic structure calculations

All calculations were performed with the density functional theory (DFT) method using Dmol3[2a,b] module in Material Studio software package.[2c] The initial configuration was fully optimized by Perdew-Wang (PW91)[2d] generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP). The core electrons for metals were treated by effective core potentials (ECP). The self-consistent field (SCF) converged criterion was within 1.0×10^{-5} hartree $atom^{-1}$ and the converging criterion of the structure optimization was 1.0×10^{-3} hartree $bohr^{-1}$. The Brillouin zone is sampled by $1 \times 1 \times 1$ *k*-points, and test calculations reveal that the increase of *k*-points does not affect the results.

B. Supporting Figures

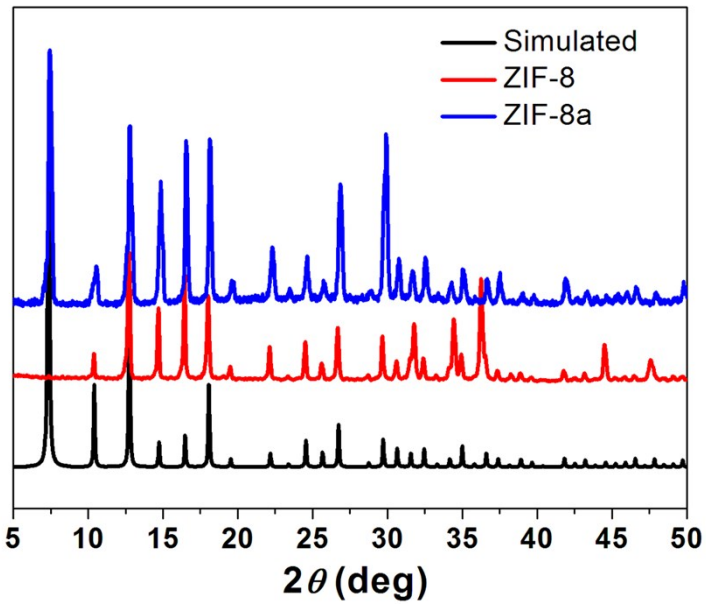


Figure S1. PXRD patterns of simulated (black) and as synthesized ZIF-8 (red) as well as the activated sample ZIF-8a (blue).

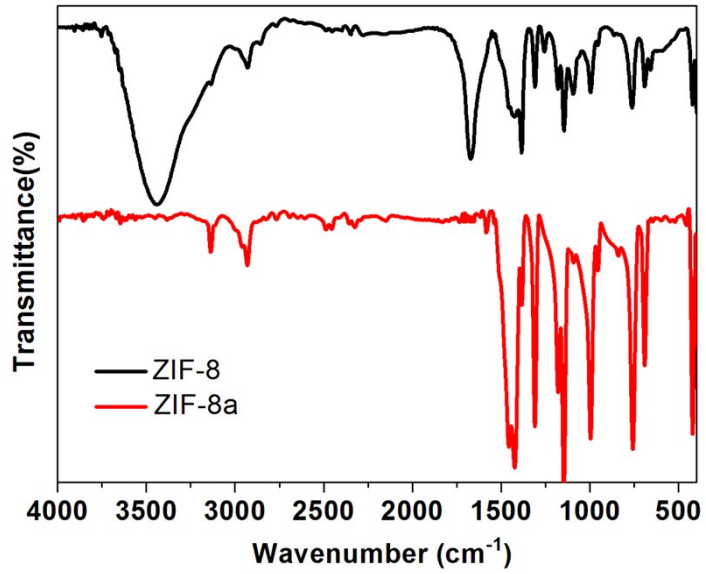


Figure S2. FT-IR spectra of ZIF-8 and the guest-free ZIF-8a.

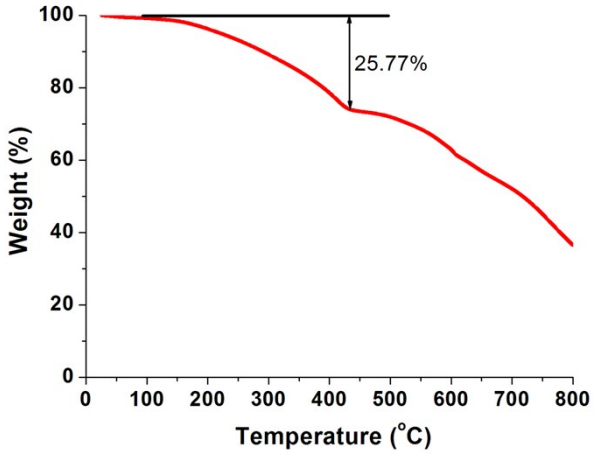
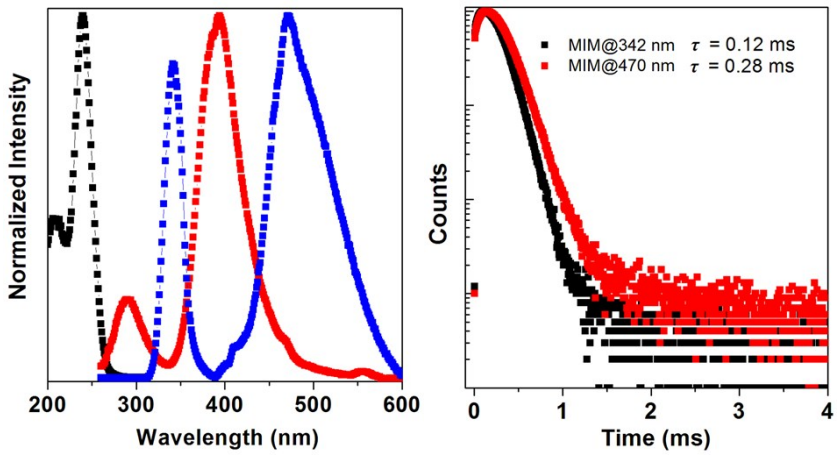


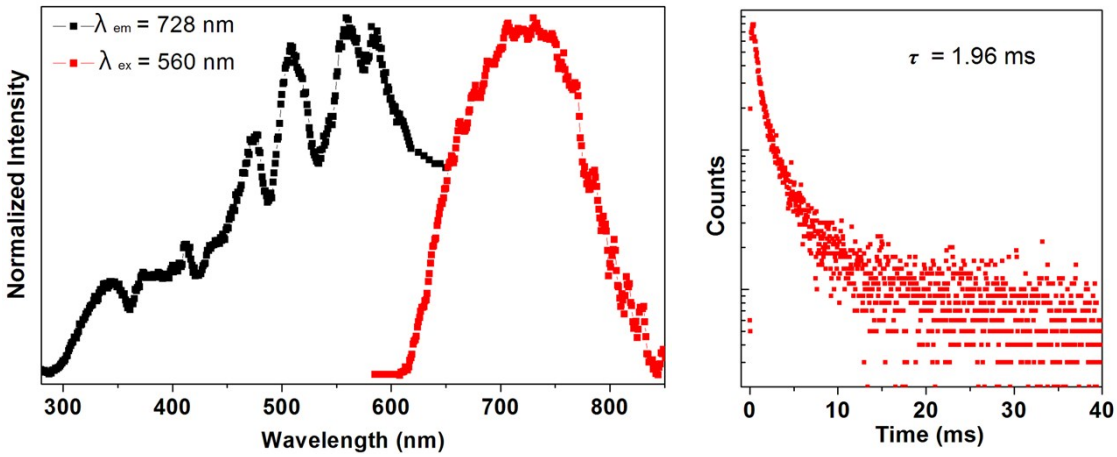
Figure S3. Thermogravimetric analysis (TGA) curves of ZIF-8.

The weight-loss step of 25.77% (96~430 °C) correspond to the escape of all guest molecules in as-synthesized ZIF-8 (2/3 DMF and 2/3 H_2O; calcd. 21.04 %). The weight loss of guest molecules (DMF and water) delayed up to high temperature (430 °C) can be attributed to relatively strong binding energy between guests and ZIF-8 host, thus the guests leave the restricted porous system slowly. Similar behavior can also be observed in other references about ZIF-8.[3]



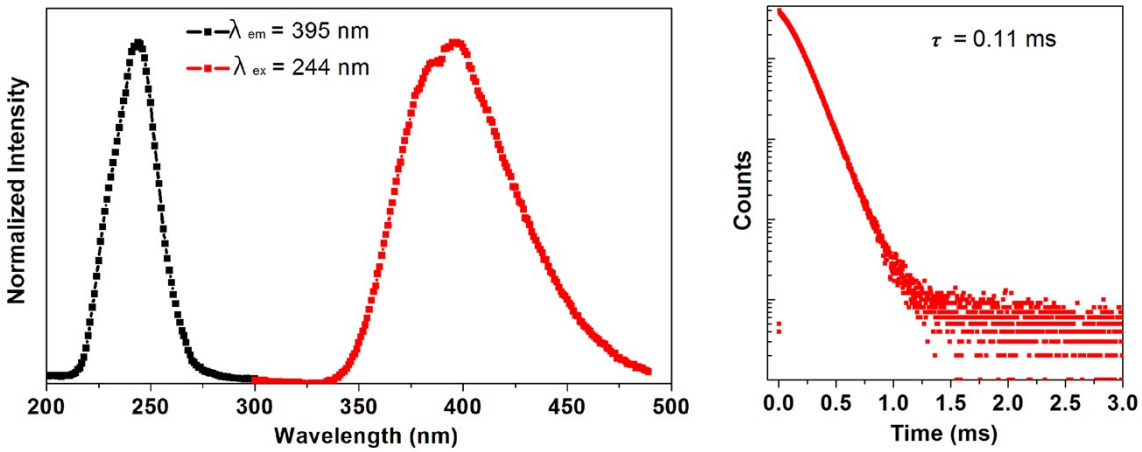
(a) (b)

Figure S4. (a) Normalized excitation (black line), fluorescence (red line), and phosphorescence (blue line) spectra of MIM. (b) Time-resolved phosphorescence decay curves of MIM.



(a) (b)

Figure S5. (a) Normalized excitation (black line) and phosphorescence (red line) spectra of ZIF-8. (b) Time-resolved phosphorescence decay curve of ZIF-8.



(a) (b)

Figure S6. (a) Normalized excitation (black line) and phosphorescence (red line) spectra of ZIF-8a. (b) Time-resolved phosphorescence decay curves of ZIF-8a.

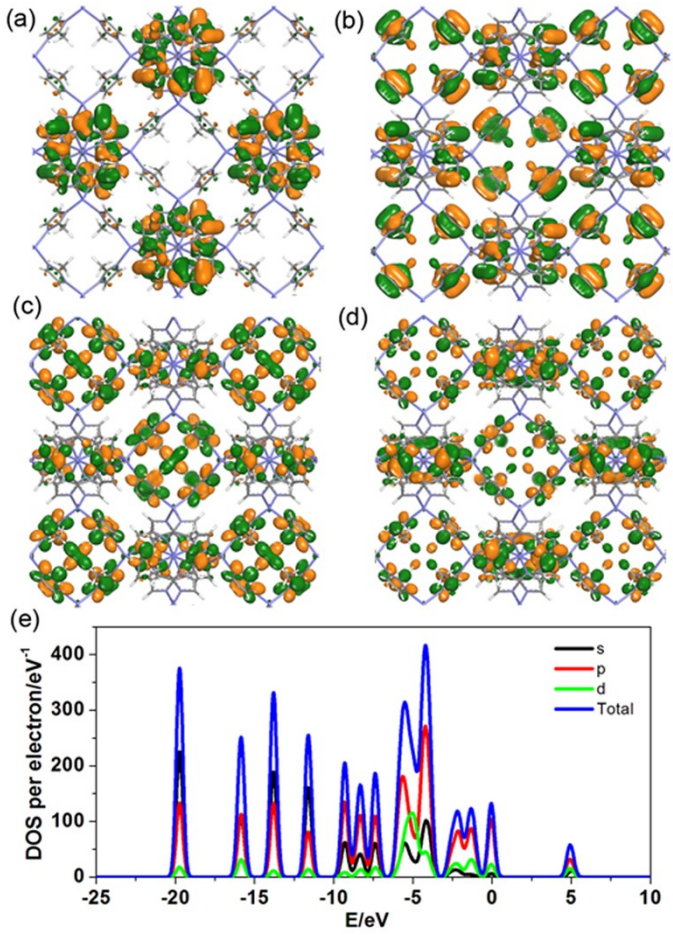


Figure S7. Frontier orbitals (HOMO (a), HOMO-1 (b), LUMO (c) and LUMO+1 (d)) profiles and total/partial electronic density of state (TDOS and PDOS, (e)) for the DFT-optimized structure for ZIF-8a (H: white; O: red; C: gray; Zn: blue-gray; N: blue).

C. Supporting References

1. T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda, S. Kitagawa, *Angew. Chem. Int. Ed*., 2009, **48**, 4739.
2. (*a*) B. Delley, *J. Chem. Phys*., 1990, **92**, 508; (*b*) B. Delley, *J. Chem. Phys*., 2000, **113**, 7756; (*c*) Dmol3 Module, MS Modeling, Version 2.2; Accelrys Inc.: San, Diego, 2003; (*d*) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B*., 1992, **46**, 6671.
3. (*a*) K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *PNAS* 2006, **103**, 10186; (*b*) X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, *Angew. Chem., Int. Ed. Engl*., 2006, **45**, 1557.