A robust near infrared luminescent ytterbium metal-organic framework for sensing of small molecules

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Experimental Section

Materials and Measurements. All reagents and solvents were used as received from commercial suppliers without further purification. Elemental analyses (C, H, N) were carried out on a VarioEL analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer using CuKα radiation (λ = 0.15405 nm). TGA (thermal gravimetric analysis) was performed under a nitrogen atmosphere with a heating rate of 3 °C/min using a Shimadzu TGA-50 thermogravimetric analyzer. N_2, H_2, C_2H_2, CH_4 and CO_2 adsorption isotherms were measured on ASAP 2020. A Coulter Omnisorp 100cx analyzer was used to measure methanol, ethanol, propanol, isopropanol sorption isotherm for activated 1a formed by heating of the as-synthesized MOF 1a at the temperature of 200 °C under high vacuum overnight.

Fluorescence Measurements. The fluorescence properties of MOF **1** and solvent included MOF **1a** were investigated in various solvent emulsions at room temperature. The **1a**–solvent emulsions were prepared by introducing 5 mg of **1a** powder into 5.00 mL of methanol, ethanol, 2-propanol, acetone, acetonitrile, chloroform, DMF, or THF. For sensing properties with respect to acetone, different amounts of acetone were added into a standard 1a emulsion in 2-propanol, while the concentration of Yb^{3+} was kept constant. The fluorescence spectra were measured on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrophotometer, equipped with a 450W Xe-lamp as the excitation source

and a monochromator iHR320 equipped with a liquidnitrogen-cooled R5509-72 PMT as detector.

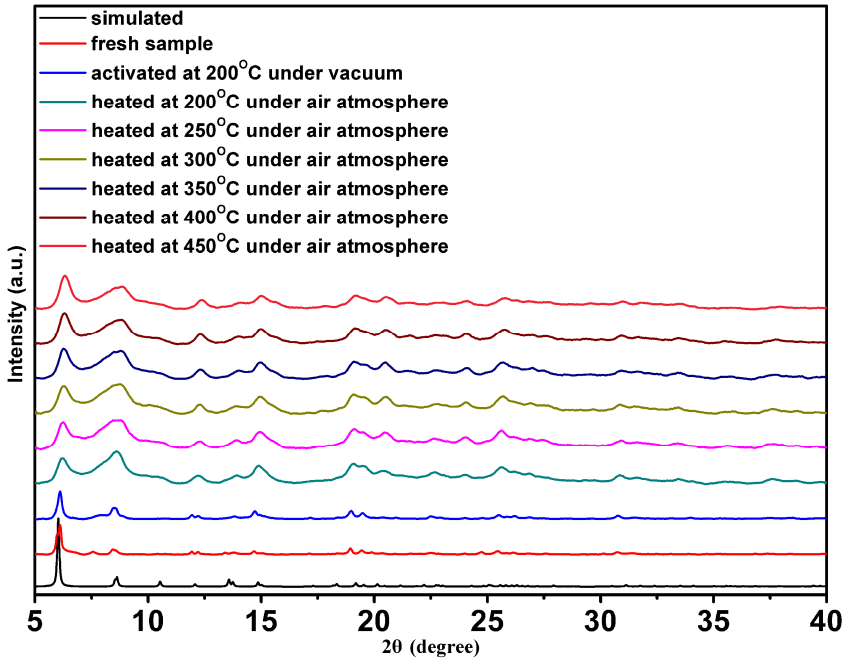

Figure S1. PXRD patterns of the as-synthesized (red), the simulated from single X-ray crystal structure (black) and thermally activated MOF **1** at different temperatures.

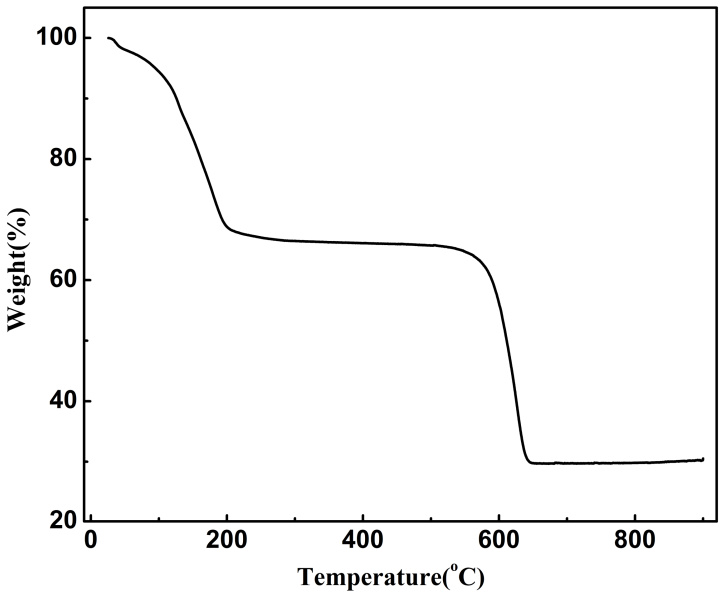

Figure S2. TGA traces of MOF **1** ranging from room temperature to 900 °C.

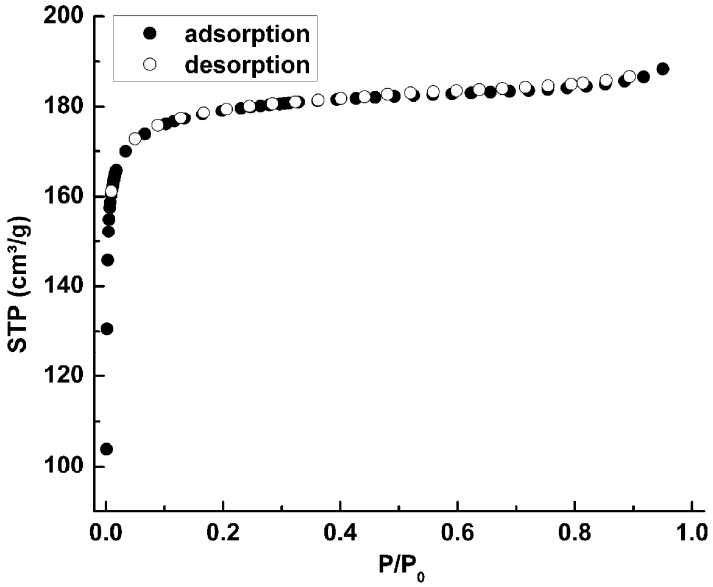

Figure S3. Gas sorption isotherm of MOF **1a** for N_2 at 77 K.

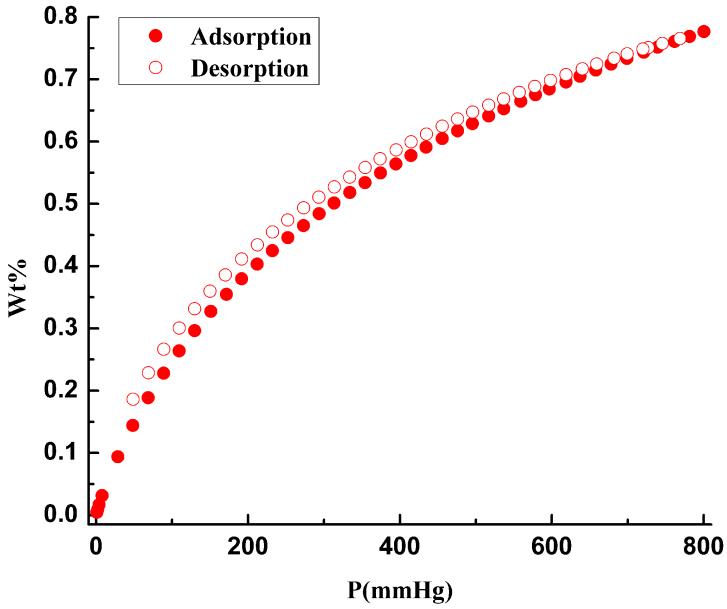

Figure S4. Gas sorption isotherm of MOF **1a** for H_2 at 77 K.

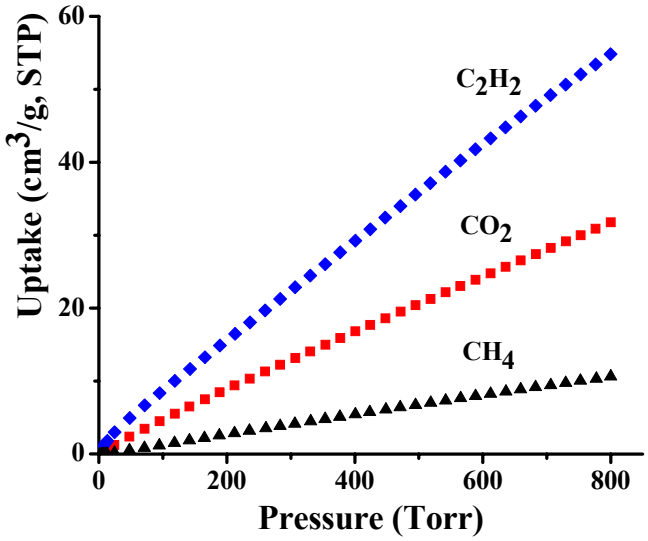

Figure S5. Gas sorption isotherms of MOF **1a** for C_2H_2, CO_2 and CH_4 at 273K.

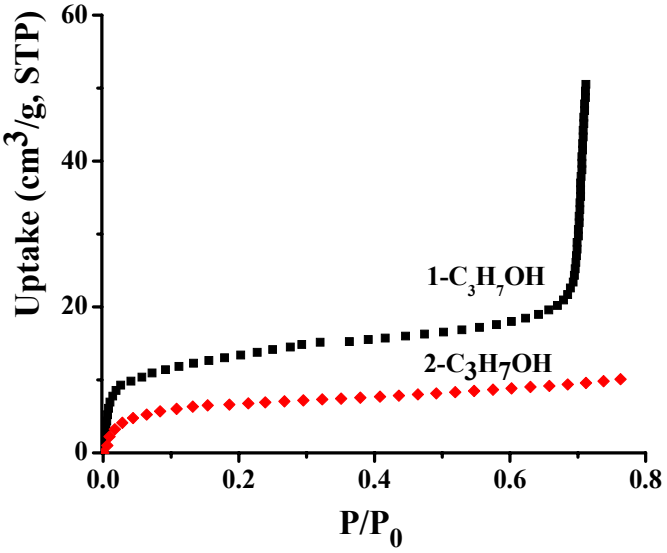

Figure S6. Vapor sorption isotherms of MOF **1a** for propanol and isopropanol at room temperature.

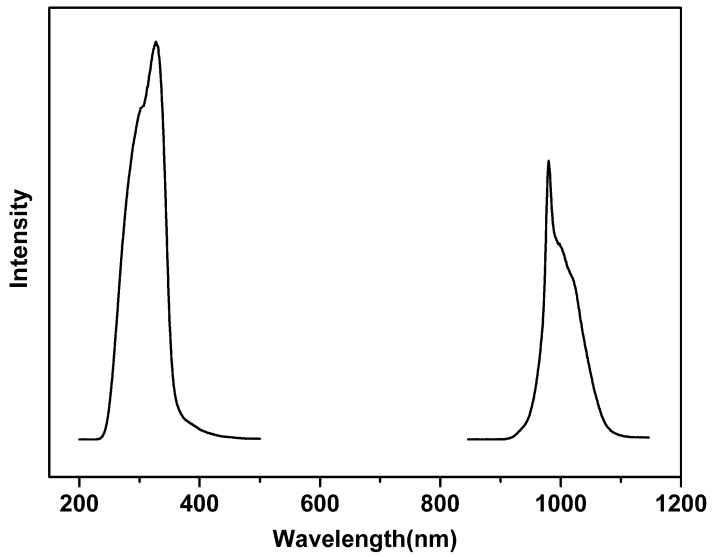

Figure S7. The excitation and PL spectrum of solid MOF **1a** (monitored and excited at 980 and 326 nm, respectively).

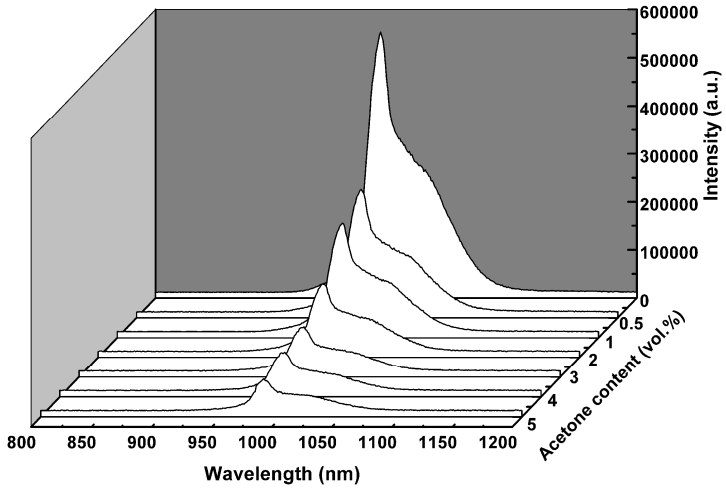

Figure S8. The PL spectra of MOF **1a** 2-propanol emulsion in the presence of various content acetone solvent (excited at 309 nm).

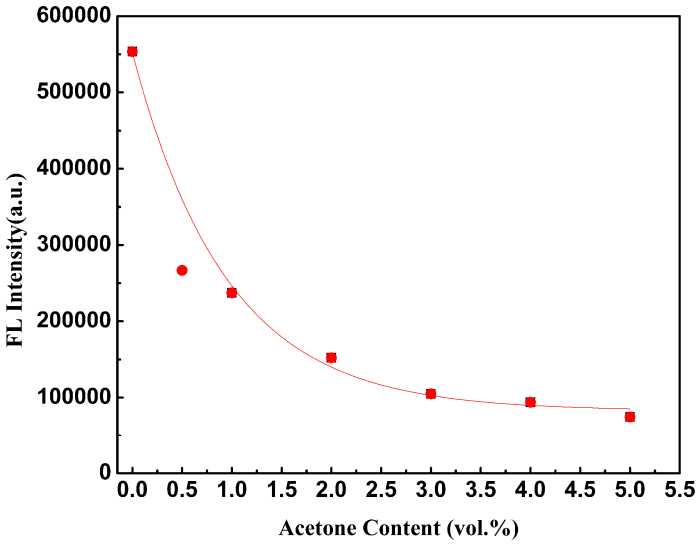

Figure S9. The PL intensity of MOF **1a** 2-propanol emulsion as a function of acetone content.

Derivation of the Isosteric Heats of Adsorption: A virial type expression of the following form was used to fit the combined isotherm data for a given material at 296.0 and 273.2 K.[1]

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1).$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represents the number of coefficients required to adequately describe the isotherms. The equation was fit using the statistical software package ***SPSS*** 16.0. m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, as determined using the average value of the squared deviations from the experimental values was minimized. In all cases, $m \leq 6$ and $n \leq 3$. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2).$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J $K^{-1}mol^{-1}$.

From these results, the Henry's constant (K_H) is calculated from where T is temperature.[2]

$$K_H = \exp(-b_0) \cdot \exp(-a_0 / T)$$

CGD file to rationalize the topology of MOF-**1**

```
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  NODE 3 3  0.41664 0.02740 0.41191
  NODE 4 5  0.02811 0.24229 0.70898
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  EDGE  0.02811 0.24229 0.70898   0.05101 0.26196 0.95119
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  EDGE  0.41664 0.02740 0.41191   0.26196 -0.05101 0.20119
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# EDGE_CENTER  0.03956 0.25212 0.83008
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# EDGE_CENTER  1.07282 0.94676 -0.02051
# EDGE_CENTER  0.74335 0.94711 -0.04404
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References

1. J. Roswell, O. M.Yaghi, *J. Am. Chem. Soc.,* 2006, **128**, 1304.
2. R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi*, J. Am. Chem. Soc.,* 2009, **131**, 3875.