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Electronic Supplementary Information

Electronic and Fluorescent Dual Mode Room-Temperature Ammonia Sensor Achieved by Decorating Hydroquinone into Metal-Organic Framework

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Materials and Methods

TPP was prepared according to literature methods,[1] other chemicals were obtained from commercial sources and used without further purification. The powder X-ray diffraction patterns (PXRD) were recorded on a Rigaku DMAX 2500 powder diffractmeter at 40 kV and 100 mA using Cu-Kα (λ = 1.54056Å), with a scan speed of 0.2 s/step at room temperature. Scanning electron microscope (SEM) characterization was performed using an FEI Quanta 200 field emission SEM (accelerating voltage: 20 kV). Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 449C thermal analyzer at a heating rate of 5 ^{o}C/min under nitrogen. N_2 sorption isotherms were measured on a Micromeritics ASAP 2020 HD88 surface-area and pore-size analyzer up to 1 bar of gas pressure by the static volumetric method. All used gases were of 99.99% purity. The fluorescence spectra were measured with a Fluorolog Horiba Jobin Yvon Fluoromax-4 spectrophotometer at room temperature.

Synthesis of SNNU-88

In a 20 mL glass vial, 102.6 mg of $Mg(NO_3)_2{\cdot}6H_2O$, 39.6 mg of DHBDC, 31.2 mg of TPP were dissolved in a mixture of 4.0 g of DMA and 2.0 g of DMPU. After addition of 0.3 g 85% formic acid, the vial was sealed and placed in a 130 ^{o}C oven for 5 days. Large colorless hexagon crystals were obtained after cooling to room temperature. Pure sample was obtained by filtering and washing the raw product with hot DMA/DMPU mixtures. The yield was about 34% based on DHBDC. The phase purity of compound was checked by powder X-ray diffraction. TG analyse indicated that the sample starts to collapse at above 250 ^{o}C (Figure S2b). N_2 sorption isotherm at 77 K indicate typical type I sorption behavior, confirming its microporous nature, and the main pore width is 4.6 Å by Horvath-Kawazoe (H-K) method (Figure S2c). The BET surface area was calculated to be 1010 m^2/g.

The films of the SNNU-88 were prepared by placed a ceramic substrate of Ag-Pd substrate inside the vial. The Ag-Pd electrode was collected and washed with acetonitrile and immersed in 10 mL of acetonitrile for 3 days, during which the acetonitrile solution was refreshed everyday.

X-ray Crystallograpic Determination

Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on $|F|^2$ with anisotropic displacement using *SHELXTL*.[2] All non-hydrogen atoms in the framework were refined with anisotropic displacement parameters. Crystal data as well as details of data collection and refinements were summarized in Tables S1.

Electronic Ammonia Gas Sensing Measurement of SNNU-88

The electronic gas-sensing measurements of as-prepared porous SNNU-88 films were carried out on a CGS-1TP chemical gas sensor-1 temperature pressure intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China). The analysis system offered an external temperature control, which could adjust the sensor temperature with a precision of 1 ^{o}C. In this case, the operating temperature was remained at 25 ^{o}C (defined as the room temperature) and the as-fabricated sensor was finally plugged into a measurement board of the sensor measuring system. Before testing, the sensor was aged in air for 24 h at room temperature to achieve the device stabilization. After that, the detected gas (ammonia, dichloromethane, trichloromethane, methanol, ethanol, ethylene glycol, isopropanol, n-propanol, acetone, formaldehyde, acetaldehyde, nitromethane, ethyl ether, n-hexane, pyridine, tetrahydrofuran) was introduced by injecting a certain volume of liquid analytes with a microsyringe onto a metal-plate heater in the test chamber, and the concentrations of the detected gas were calculated according to the total volume (18 L) of gas chamber. The dynamic sensing tests were carried out by repeatedly exposing the sensors to the detected gas in closed chamber and to air by opening the chamber. The gas-sensing sensitivity of sensors are defined as the ratio Rair/Rgas, where Rair and Rgas are the electrical resistance of the sensor in air and in the tested gas at the operating temperature, respectively. In our measurement system, The response time and recovery time were defined as the time taken for the sensor to reach 90% of its maximum response and decrease to 10% of its minimum response, respectively.[3]

Luminescent Detection of $NH_3{\cdot}H_2O$

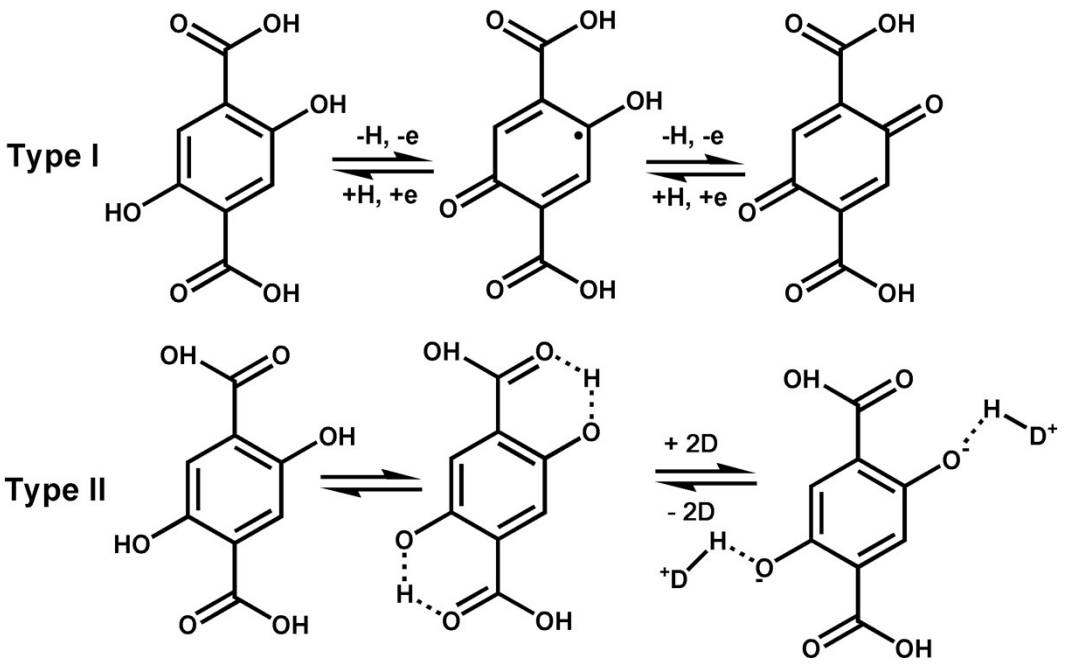
Micrometer-size SNNU-88 sample (5 mg) was well-dispersed in 5 mL DMA by ultrasound for about 20 min to ensure even dispersion, and then diverse amounts of $NH_3{\cdot}H_2O$ were added to a quartz cuvette containing 3 mL of DMA suspension of SNNU-88 for the luminescent detection experiment. The emission intensity was monitored after each addition. For all the fluorescence titration experiments, the excitation wavelength was 362 nm and the emission spectra were recorded in the range of 410–700 nm. The sensing of ammonia vapor was carried out using SNNU-88 solid phase. The original crystals were dried by flowing nitrogen, then the drying

crystals were placed in a 5 mL vial which was placed in a 20 mL vial containing 1 mL of ammonia, and then they were sealed at 50 ℃ for 2 hours. The luminescent colors of the crystal changed from blue to yellow green under the irradiation of UV light of 365 nm. After response SNNU-88 were subjected to solvent exchange by soaking into fresh DMA for 2 days and exchanged for 5 times, and then the sample was N_2-dried again. Under the irradiation of UV light of 365 nm, the luminescent colors of the sample get back to original color, which also can response to NH_3 similar the first time by our naked eyes distinguishing the colors.

Table S1. Crystal data and structure refinements for **SNNU-88**.

Compound	**SNNU-88**
Empirical formula	$C_{44}H_{18}Mg_3N_4O_{19}$
Formula weight	979.55
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a(Å)	16.9671(5)
b(Å)	16.9671(5)
c(Å)	15.3079(10)
α (deg)	90
β (deg)	90
γ (deg)	120
Volume(Å^3)	3816.5(3)
Z	2
$d_{calcd.}$ (g·cm^{-3})	0.852
μ(mm^{-1})	0.090
F(000)	996
Reflections collected/unique	13059/1318
R_{int}	0.0705
Data/restraints/parameters	1318/0/74
GOF on F^2	1.053
R_1[a], wR_2[b] [I > 2σ(I)]	0.0438, 0.1099
R_1[a], wR_2[b] (all data)	0.0586, 0.1147

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.



Scheme S1. Two typical proton-involved processes for DHBDC: redox-active transformation of enol and keto isomers (Type I) and intramolecular and intermolecular proton transfer (Type II). D represents the electron donor.

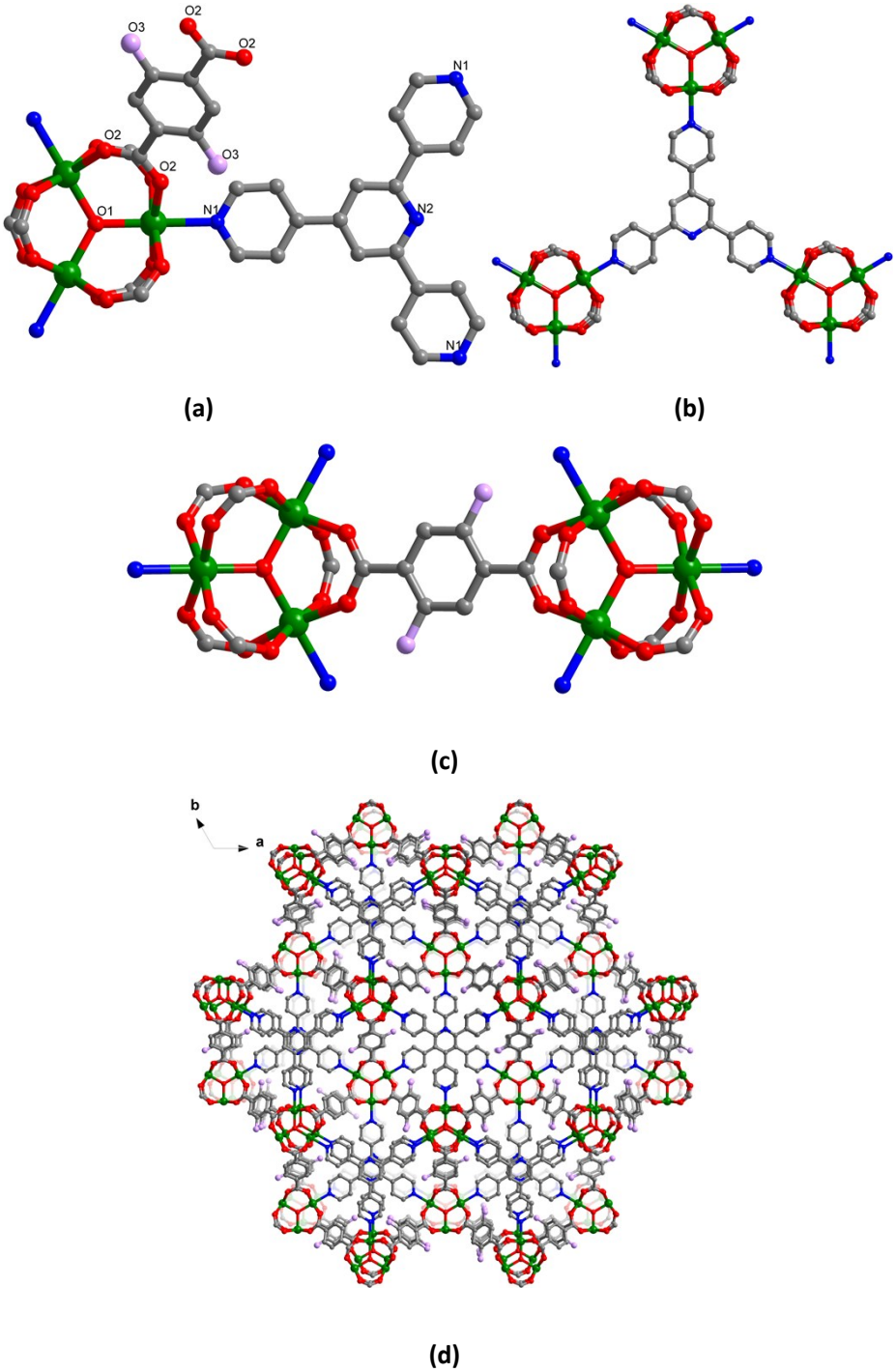
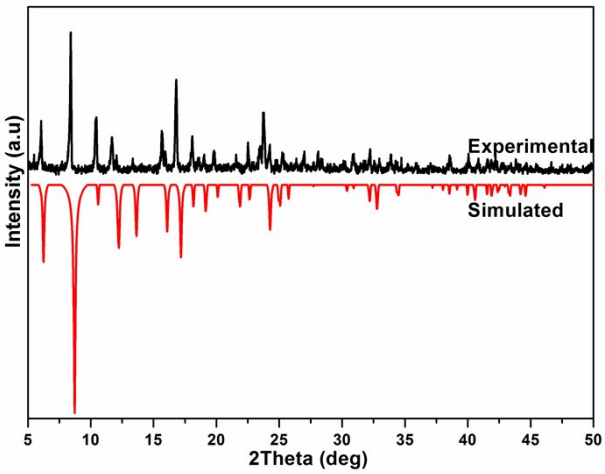
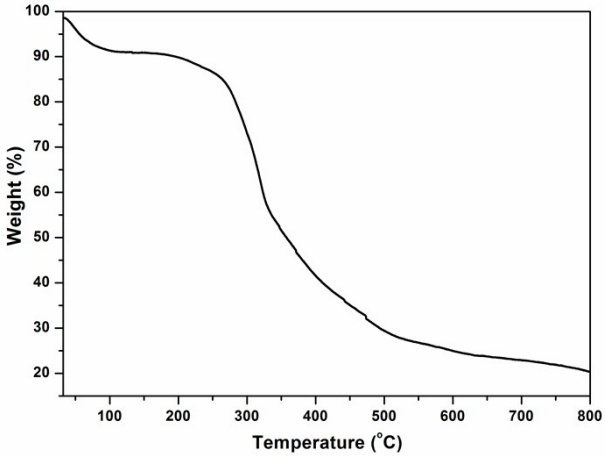


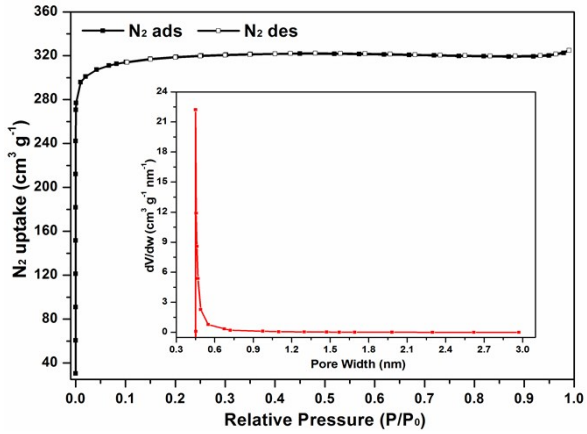
Figure S1 Linkage between Mg3-trinuclear cluster, DHBDC and TPP (a-c) and 3-D framework of SNNU-88 viewed along the *c*-axis direction (d).



(a)

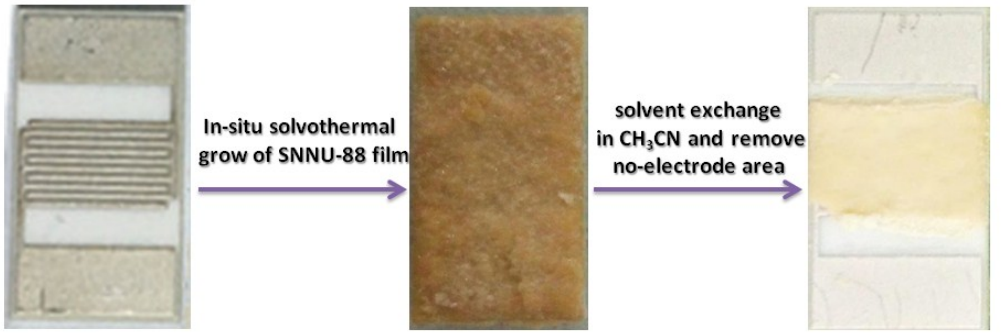


(b)

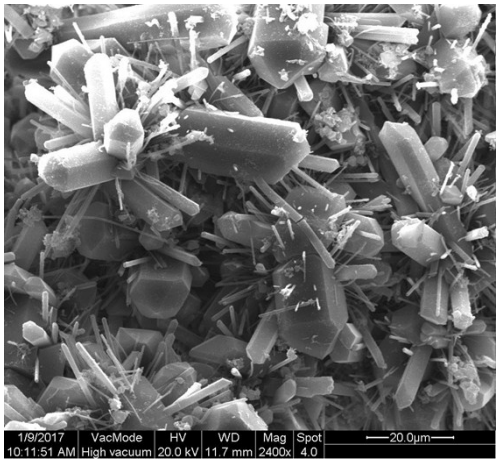


(c)

Figure S2 (a) Experimental and simulated PXRD patterns for SNNU-88; (b) TGA curves for SNNU-88; (c) N_2 adsorption and desorption isotherms of SNNU-88 (the inset shows the pore size distribution calculated by the Horvath-Kawazoe method).



(a)



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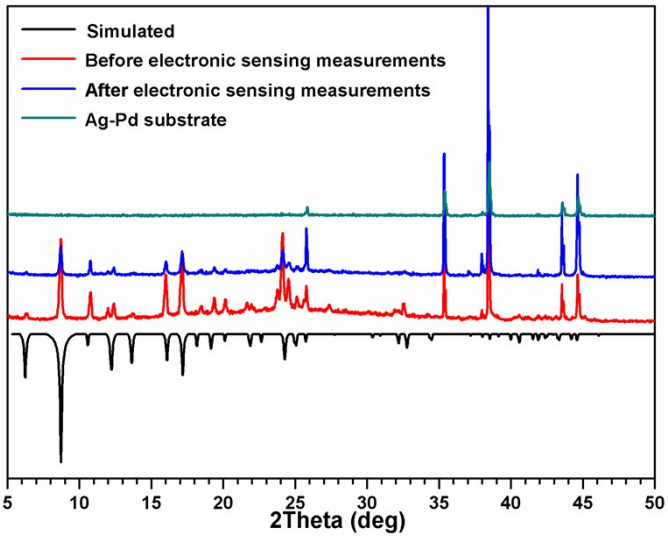
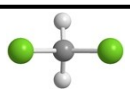
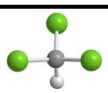
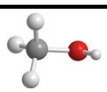
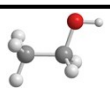
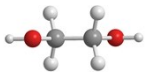
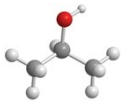
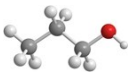
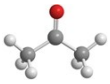
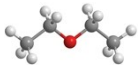
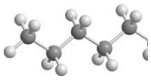
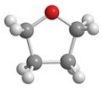


(c)

Figure S3 (a) Optical microscope image of the in-situ fabricated SNNU-88 film on Ag-Pd substrate; (b) SEM image of SNNU-88 film; (c) Powder X-ray diffraction patterns: black, simulated; red, the fabricated film on the substrate before test; blue, the fabricated film on the substrate after test; green, the Ag-Pd substrate.

Table S2. Summary of semiconductor responses of SNNU-88 film toward 16 common VOCs (50 ppm) at room temperature.

VOCs						
(R_{air}/R_{gas})-1	1.51	0.25	0.41	0	0	0
VOCs						
(R_{air}/R_{gas})-1	0.23	0.20	0	0.30	0	0
VOCs						
(R_{air}/R_{gas})-1	0.38	0.39	0.32	0.16		

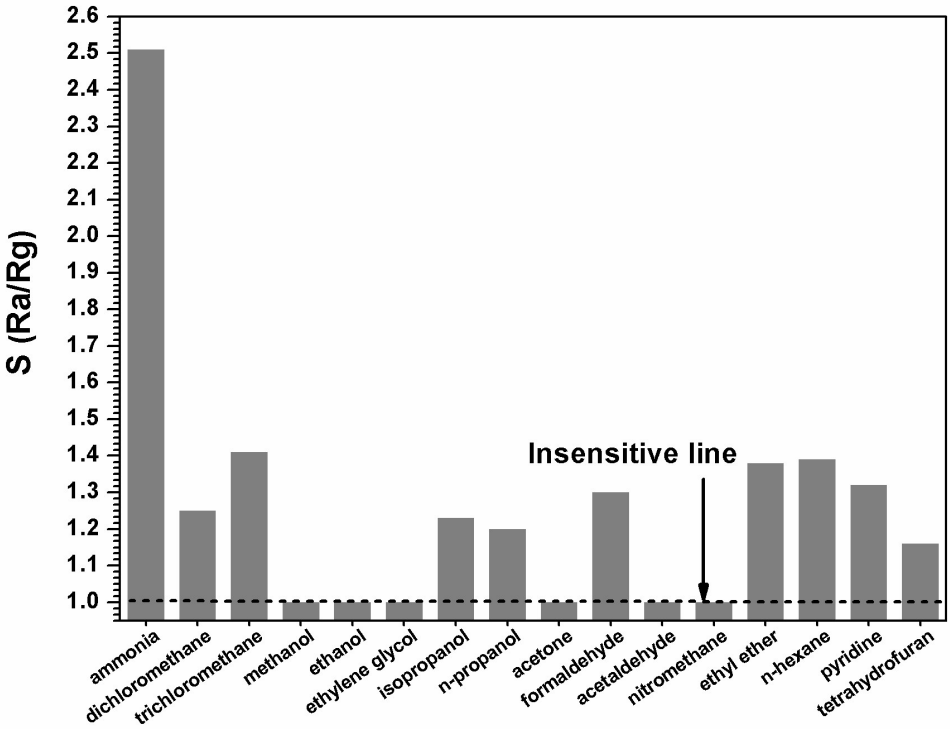


Figure S4. Summary of semiconductor responses of SNNU-88 film toward 16 common VOCs (50 ppm) at room temperature.

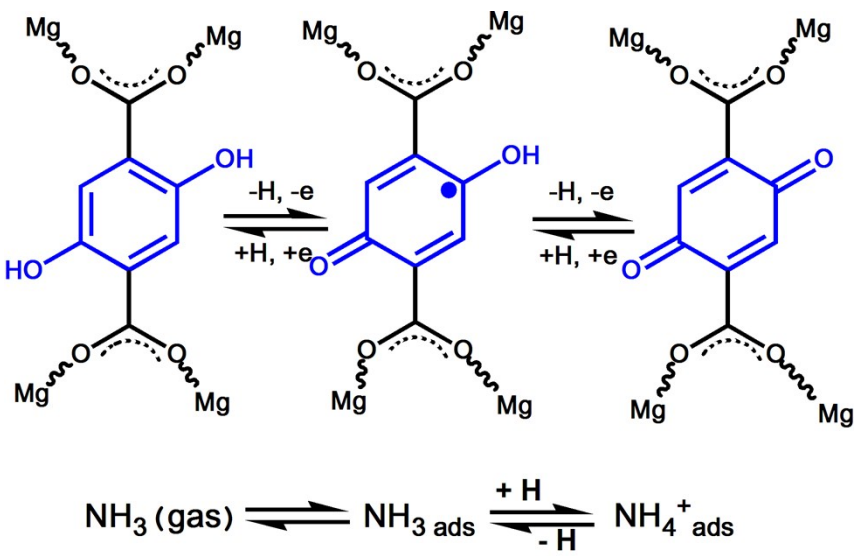


Figure S5 The proposed electronic ammonia sensing mechanism for SNNU-88.

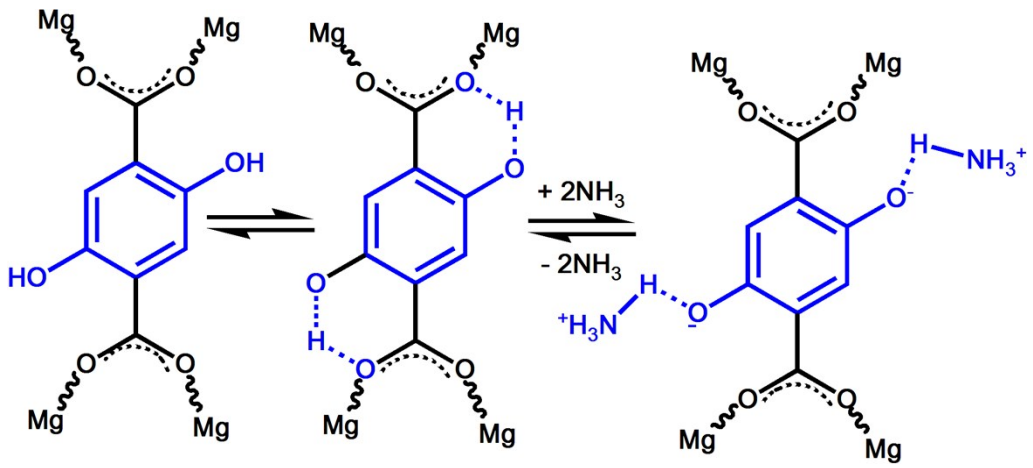


Figure S6 The proposed intramolecular and intermolecular proton transfer for DHBDC.

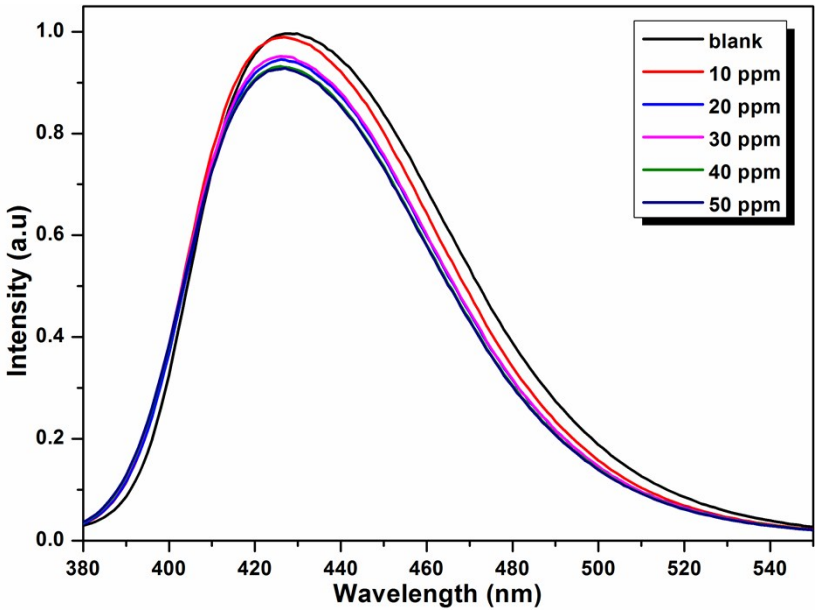


Figure S7. The emission spectra of SNNU-88-BDC MOF in DMA with the presence of diffferet ammonut of $NH_3 \cdot H_2O$ (0 -50 ppm) in DMA.

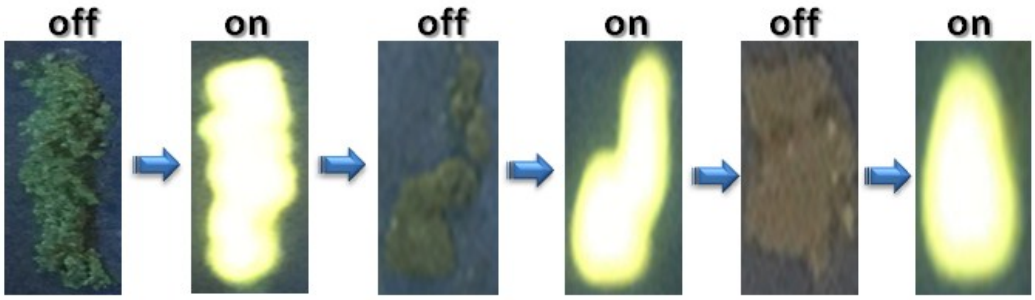


Figure S8 The turn-off and turn-on luminescence of solid-state SNNU-88 crystals by repeated remove and contact with ammonia gas.

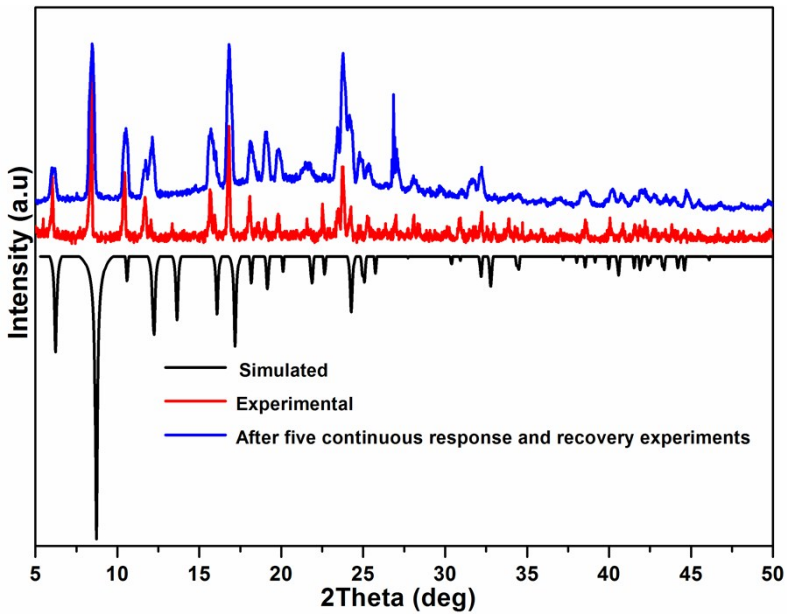
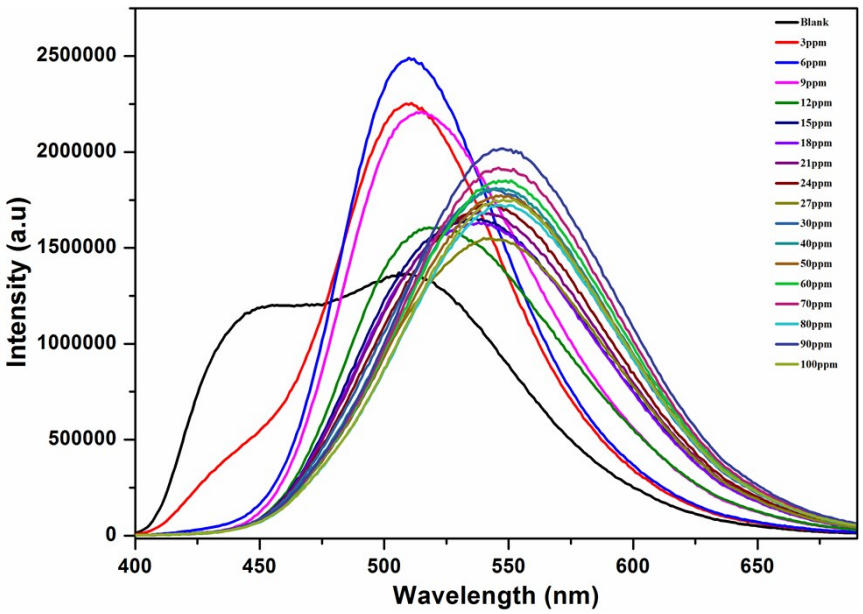
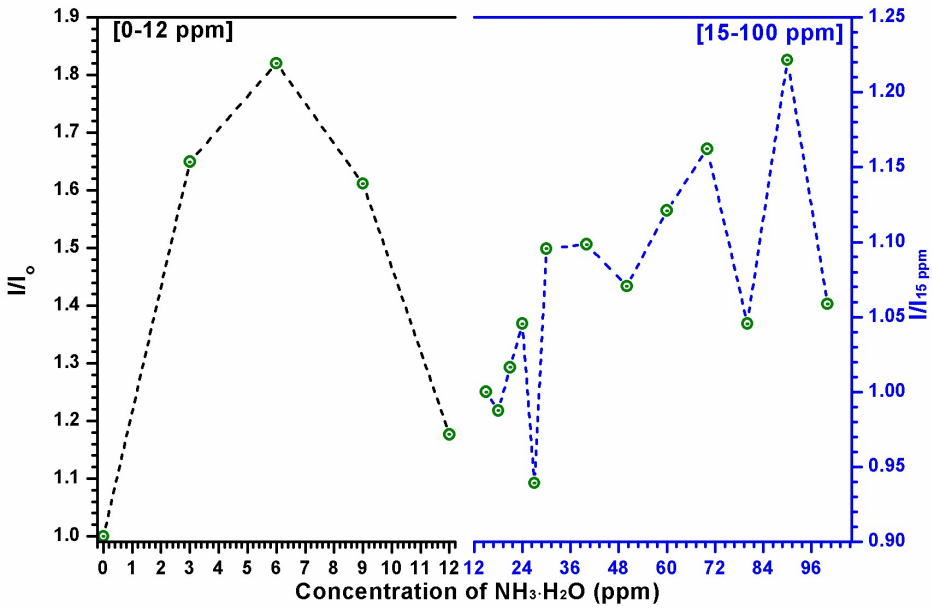


Figure S9 Powder X-ray diffraction patterns: black, simulated; red, before the ammonia sensing experiments; blue, after five continuous response and recovery experiments.



(a)



(b)

Figure S10 The fluorescent response of DHBDC to varing concentration (0 -100 ppm) of $NH_3 \cdot H_2O$ in DMA: (a) the fluorescent spectra; (b) the irregular relationship between the intensity and $NH_3 \cdot H_2O$ concentration.

References

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3. H. Xu, J. Ju, W. Li, J. Zhang, J. Wang and B. Cao, *Sens. Actuators B*, 2016, **228**, 634.