Supplementary Information

A 2D Metal-Organic Framework with Wide Channels and Responsive Turn-On Fluorescence for the Chemical Sensing of Volatile Organic Compounds

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Materials and equipments

All of the reagents used were obtained from commercial suppliers and were used without further purification. NMR data were collected on a Bruker Avance 400 MHz NMR Spectrometer (DRX400). FT-IR spectra were obtained with a Bio-Rad FTS-3500 ARX FTIR Spectrometer. Elemental analyses (C, H, and N) were performed on a Vario MICRO series CHNOS Elemental Analyzer. Powder X-ray diffraction patterns were obtained on a Bruker D8 Advance X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at a scan rate of 0.02 deg s^{-1}. UV/visible spectra were collected in the solid state on a Shimadzu UV-3150 UV-Vis-Near-IR Spectrometer using $BaSO_4$ reflectance standards at room temperature. Fluorescent microscopy images were acquired at an excitation wavelength of 370 nm using a Nikon Ti-U Fluorescence Microscope equipped with 430 nm LP filter.

Synthesis of 4,4'-(2,2-diphenylethene-1,1-diyl)dibenzoic acid (DPEB)

4,4'-(2,2-Diphenylethene-1,1-diyl)bis(bromobenzene) (DPBB) was synthesized according to a previous report.[1] To a solution of DPBB (6 mmol, 2.94 g) in distilled THF, 7.5 mL of n-butyllithium solution (1.6 M in cyclohexane) was added dropwise under a positive N_2 pressure and cooled with dry ice-acetone bath (−78 °C). The reaction mixture was stirred and kept at −78 °C for two hours. Then excess dry ice was added in one portion, followed by stirring over six hours at room temperature. The resulting solution was diluted with dichloromethane (100 mL) and the pH of aqueous layer was adjusted to about 2.0 with dilute hydrochloric acid. The product was extracted with dichloromethane (200 mL × 3) and the combined organic layer was dried by $MgSO_4$. The solvent was removed under reduced pressure and the residue was re-dissolved using a small amount of dichloromethane/methanol mixed solvent. The obtained solution was added dropwise into hexane (300 mL) with stirring. The precipitates were isolated by suction filtration and washed with hexane for several times. The final product was obtained after drying under vacuum as pale yellow powder (2.27g, 90%). ^{1}H NMR (400 MHz, DMSO): δ (TMS, ppm) 7.71–7.69 (d, 4H), 7.18–7.07 (m, 10H), 6.99–6.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (TMS, ppm) 166.81, 147.09, 142.83, 142.17, 138.69, 130.67, 130.42, 128.80, 128.70, 127.82, 126.95. MS (MALDI–TOF): m/z Calcd for $C_{28}H_{20}O_4$: 420.1362. Found: 420.1 (M^+).

Preparation of NUS-1

DPEB (16.6 mg, 0.039 mmol) and $Zn(NO_3)_2$•$4H_2O$ (13.8 mg, 0.053 mmol) were dissolved in 10 mL of DEF in a vial. The vial was tightly capped and placed in a 100 °C oven for 72 h to yield 8.3 mg of colorless plate crystals of NUS-1 (yield: 21% based on DPEB). The crystal has a formula of $Zn_4O(C_{28}H_{18}O_4)_3(H_2O)_3$•12DEF•$8H_2O$, which was derived from crystal data and elemental analysis (% calc/found: C 58.73/58.88, H 7.12/5.21, N 5.71/5.66). FT-IR (neat, cm^{-1}): 2979 (w), 2937 (w), 2877 (w), 1628 (s), 1605 (m), 1559 (w), 1510 (w), 1439 (w), 1399 (s), 1363 (m), 1307 (w), 1262 (w), 1213 (w), 1177 (w), 1120 (w), 1101 (w), 1071 (w), 1020 (w), 648 (m), 586 (w), 577(w), 511 (m), 500 (m).

Preparation of NUS-1a

The obtained NUS-1 crystals were soaked in methanol for 3 days at room temperature, during which time the extract was decanted and fresh methanol was added every day. Then the sample was treated with dichloromethane similarly for another 3 days. This process was carried

out to wash out DEF and residual reagents in the pores. After removal of dichloromethane by decanting, the sample was dried under a dynamic vacuum at 100 °C for 3 h to give NUS-1a, which has a formula of $Zn_4O(C_{28}H_{18}O_4)_3$•2DEF•$4H_2O$ derived from crystal data and elemental analysis (% calc/found: C 62.47/62.05, H 4.68/3.64, N 1.55/1.51). FT-IR (neat, cm^{-1}): 2979 (w), 2937 (w), 2877 (w), 1628 (s), 1605 (m), 1559 (w), 1510 (w), 1439 (w), 1399 (s), 1363 (m), 1307 (w), 1262 (w), 1213 (w), 1177 (w), 1120 (w), 1101 (w), 1071 (w), 1020 (w), 648 (m), 586 (w), 577(w), 511 (m), 500 (m).

Preparation of NUS-1a⊃guests

To obtain the samples of NUS-1a⊃guests, NUS-1a crystals were soaked in individual liquid analytes for 2 days. The crystals were then collected and dried with tissue for further characterization.

X-ray crystallography

Single crystal X-ray diffraction data of DPEB, NUS-1, and NUS-1a were collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystals were kept at 100.0(2) K during data collection. The data were collected with a ω-scan technique and an arbitrary φ-angle. Data reduction was performed with the CrysAlisPro package, and an analytical absorption correction was performed. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package. The non-H atoms were treated anisotropically, whereas the aromatic and hydroxy-hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon or oxygen atoms. In these structures, free solvent molecules were highly disordered, and the attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these residual solvent molecules in NUS-1 and NUS-1a were removed from the data sets using the SQUEEZE routine of PLATON and refined further using the data generated. The contents of the solvent region are not represented in the unit cell contents in these crystal data. The details for data collection and refinement are listed in Table S3. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: 986066-986068. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Gas sorption measurements

Gas sorption isotherms of NUS-1a were measured up to 1 bar using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, NUS-1a (~50 mg) was degassed under reduced pressure (< 10^{-2} Pa) at 150 °C for 12 h. UHP grade N_2, He, H_2, Ar, O_2, CH_4 and CO_2 were used for all the measurements. Oil-free vacuum pumps and oil-free pressure regulators were used to prevent contamination of the samples during the degassing process and isotherm measurement. The temperatures at 77 K, 87 K, 195 K, and 273 K were maintained with a liquid nitrogen bath, liquid argon bath, acetone-dry ice bath, and ice water bath, respectively. Pore size distribution data were calculated from the Ar sorption isotherms at 87 K based on non-local density functional theory (NLDFT) model in the Micromeritics ASAP2020 software package (assuming cylinder pore geometry).

Thermal analyses

TGA were performed using a Shimadzu DTG–60AH Thermal Analyzer under flowing N_2 gas, with a heating rate of 10 °C min^{-1}. DSC analyses were carried out with a Mettler Toledo DSC822e Differential Scanning Calorimeter under N_2 atmosphere with a cooling/heating rate of 20 °C min^{-1}. All of the DSC measurements were carried out in the following four steps with 15 min intervals: 1) cooling the samples (4-6 mg) to −150 °C; 2) heating to room temperature; 3) cooling again down to −150 °C; 4) heating to 600 °C. Only the curves obtained through step 3 and 4 are shown and discussed in the main text.

Measurements of fluorescent emission spectra, quantum yield, and lifetime

Corrected solid-state fluorescent emission spectra were collected on a FLSP920 fluorescence spectrophotometer at room temperature. Lifetime data were obtained using a 405 nm laser excitation light source, which were then fitted using a second-order biexponential model with better fitting qualities. Quantum yields were determined according to published procedures.[2] Solid-state tetraphenylethylene (TPE) was used as a calibration reference.[3]

Since DPEB can be readily dissolved in THF while is non-soluble in water, the fluorescence behavior of DPEB under different aggregation stage can be studied by checking the fluorescence of DPEB dissolved in THF/H_2O mixed solvents with different volume ratios (100/0, 75/25, 50/50, 25/75, 10/90, 5/95, 1/99). The concentration of DPEB solutions was kept at 1.0×10^{-4} M.

Reference

(1) Zhou, X.; Li, H. Y.; Chi, Z. G.; Zhang, X. Q.; Zhang, J. Y.; Xu, B. J.; Zhang, Y.; Liu, S. W.; Xu, J. R. *New J. Chem.* **2012**, *36*, 685.

(2) Manna, B.; Chaudhari, A. K.; Joarder, B.; Karmakar, A.; Ghosh, S. K. *Angew. Chem. Int. Ed.* **2013**, *52*, 998.

(3) Zhao, Z. J.; Chen, S. M.; Lam, J. W. Y.; Jim, C. K. W.; Chan, C. Y. K.; Wang, Z. M.; Lu, P.; Deng, C. M.; Kwok, H. S.; Ma, Y. G.; Tang, B. Z. *J. Phys. Chem. C* **2010**, *114*, 7963.

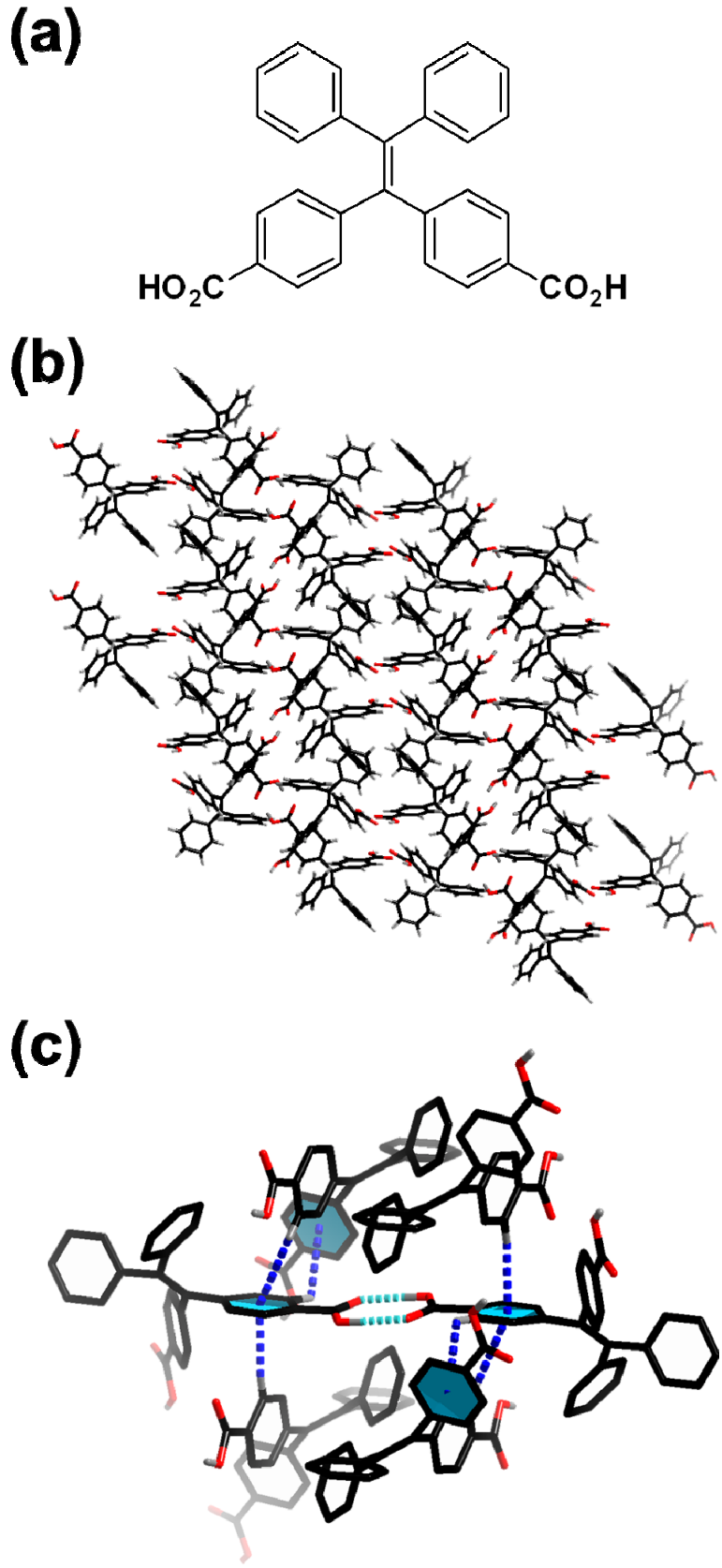

Figure S1. (a) Chemical structure of DPEB. (b) Crystal packing of DPEB viewed along [100] direction. (c) Hydrogen bonding interactions (azure dotted lines, distance: 1.78 Å, measured between H and O) and C-H···π interactions (blue dotted lines, distance: 2.72-3.51 Å, measured between H and adjacent phenyl ring centroids) of DPEB.

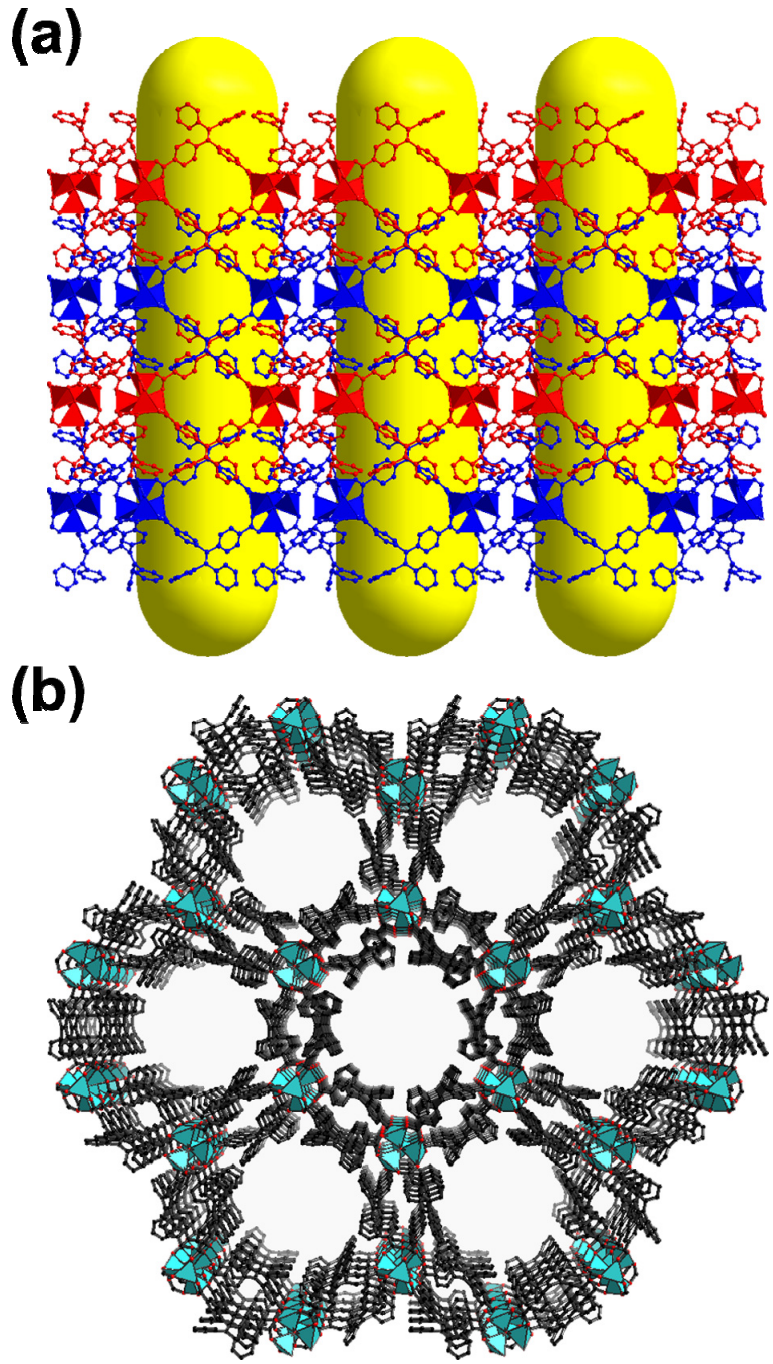

Figure S2. (a) Crystal structure of NUS-1a viewed along [010] direction, red and blue colors represent two neighboring layers, yellow capsules represent hollow channels. (b) Crystal structure of NUS-1a viewed along [001] direction.

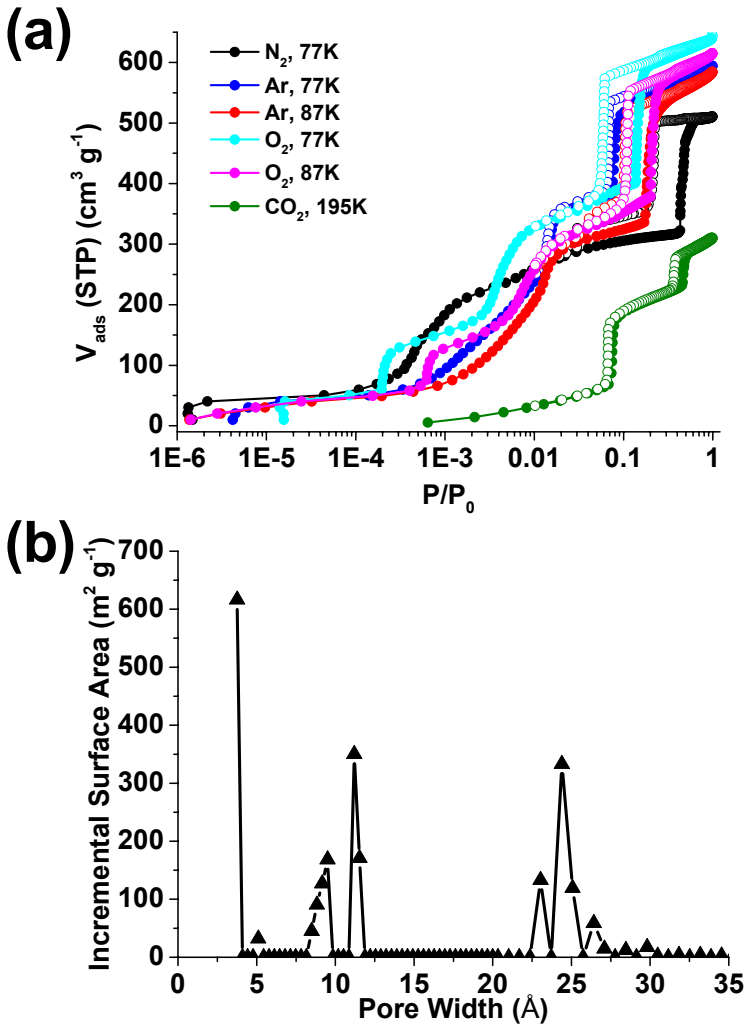

Figure S3. (a) Logarithmic scale of adsorption (filled) and desorption (open) isotherms of various gases under their condensable temperatures in NUS-1a. (b) Pore size distribution of NUS-1a calculated using non-local density functional theory (NLDFT) based on Ar sorption data at 87 K.

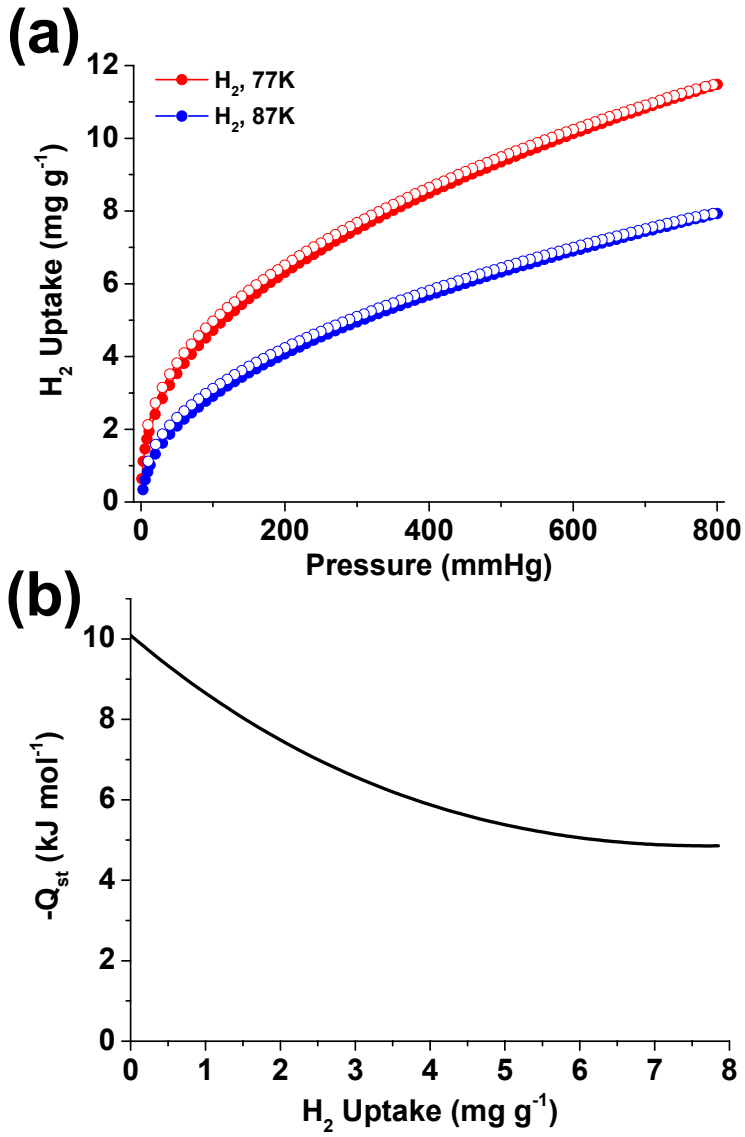

Figure S4. (a) Adsorption (filled) and desorption (open) isotherms of H_2 under various temperatures in NUS-1a. (b) Isosteric heat of adsorption (Q_{st}) of H_2 in NUS-1a.

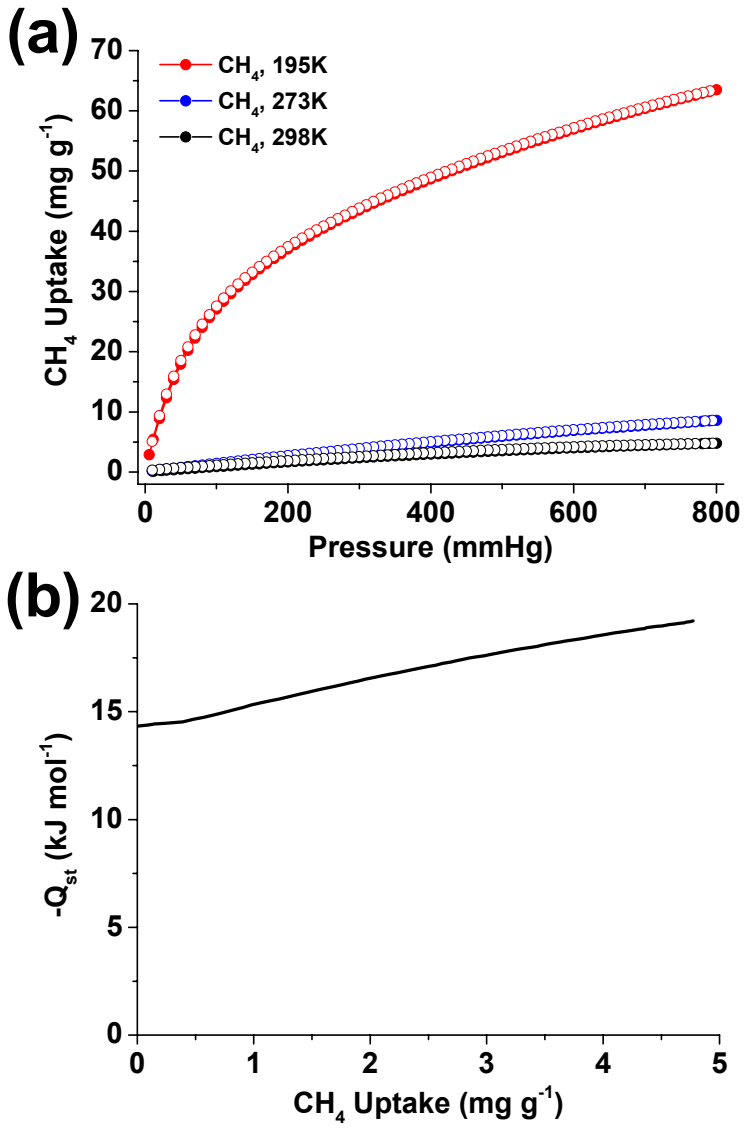

Figure S5. (a) Adsorption (filled) and desorption (open) isotherms of CH_4 under various temperatures in NUS-1a. (b) Isosteric heat of adsorption (Q_{st}) of CH_4 in NUS-1a.

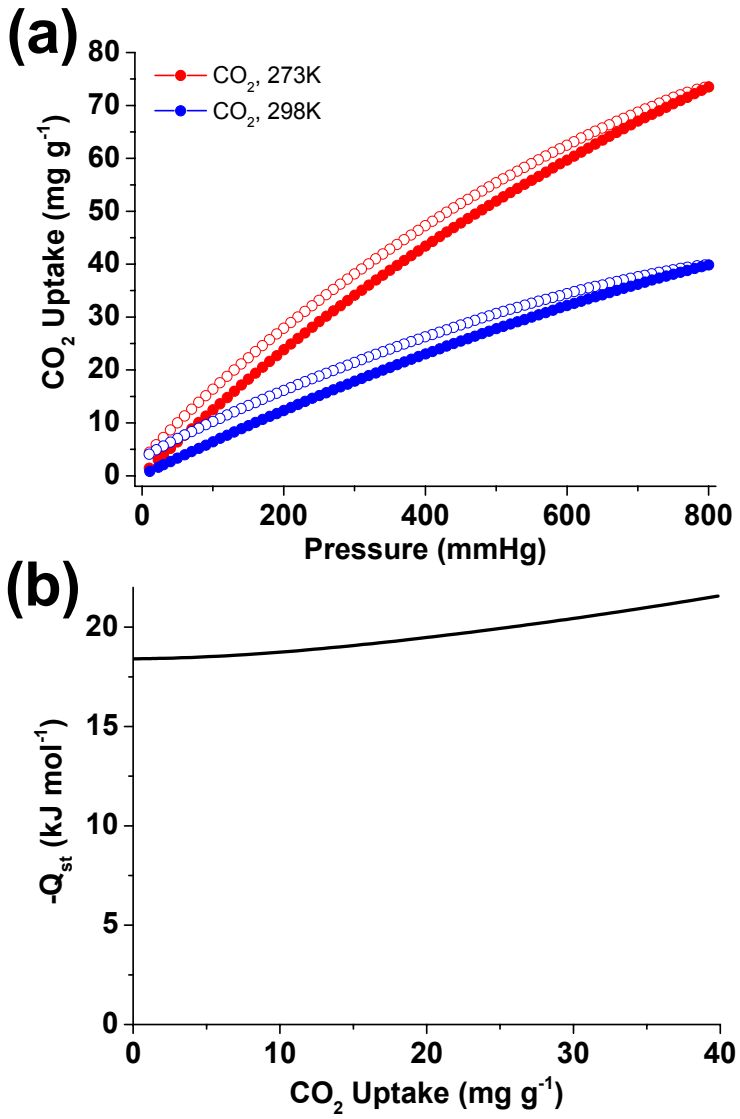

Figure S6. (a) Adsorption (filled) and desorption (open) isotherms of CO_2 under various temperatures in NUS-1a. (b) Isosteric heat of adsorption (Q_{st}) of CO_2 in NUS-1a.

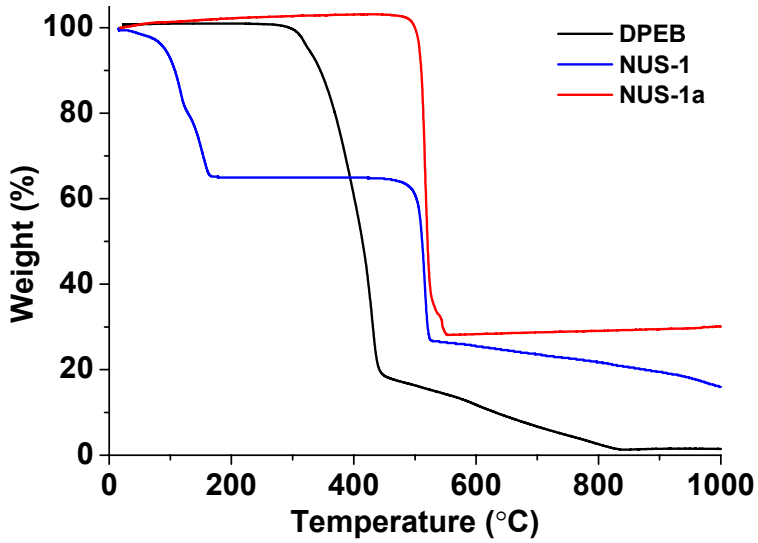

Figure S7. Thermogravimetric analysis (TGA) curves of DPEB, NUS-1, and NUS-1a.

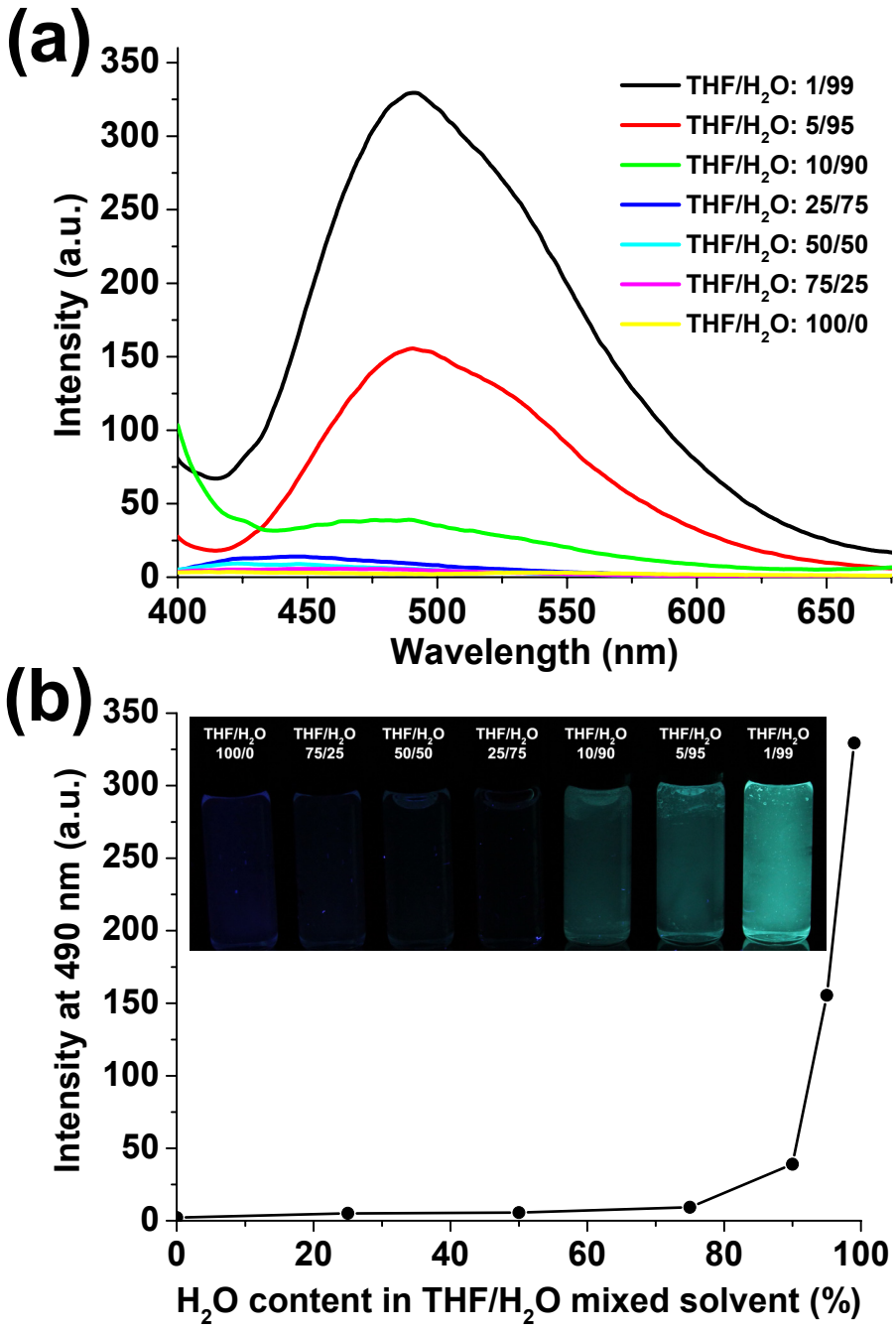

Figure S8. (a) Fluorescent emission spectra of DPEB in THF/H_2O mixed solvents with different volume ratios. (b) Intensity of DPEB fluorescent emissions at 490 nm versus H_2O content in THF/H_2O mixed solvents (imbedded: fluorescent images of DPEB solutions).

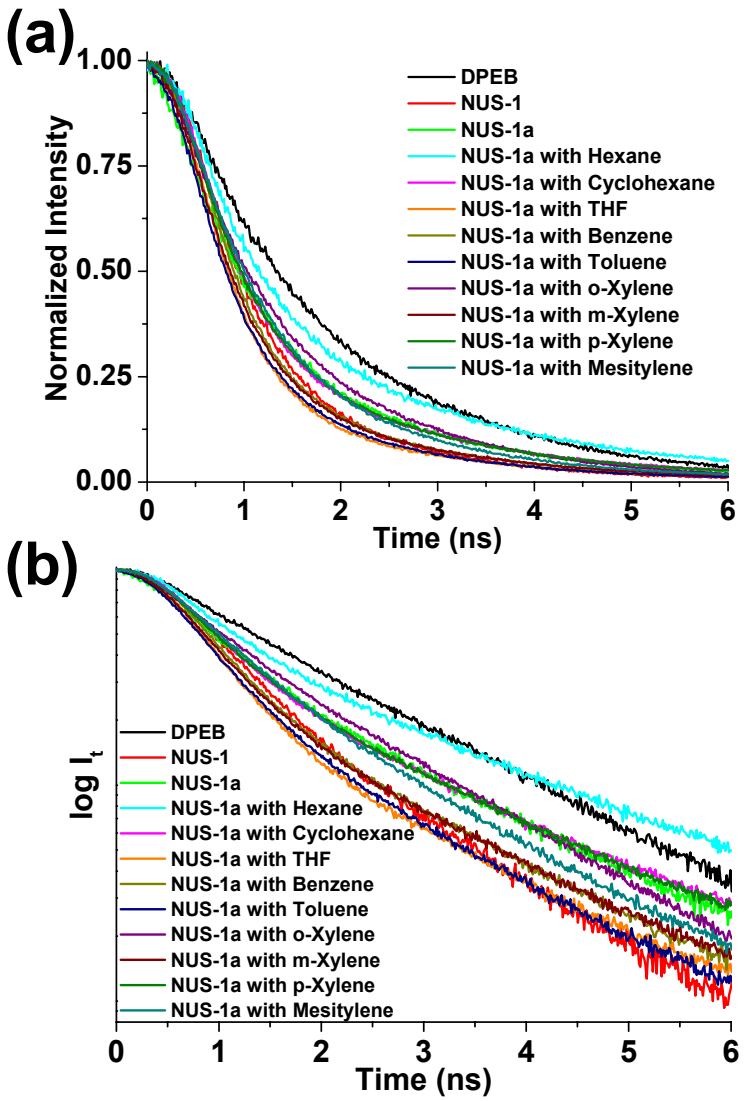

Figure S9. (a) Fluorescence decay curves of DPEB, NUS-1, NUS-1a, and NUS-1a⊃guests. (b) Logarithmic scale of fluorescence decay curves.

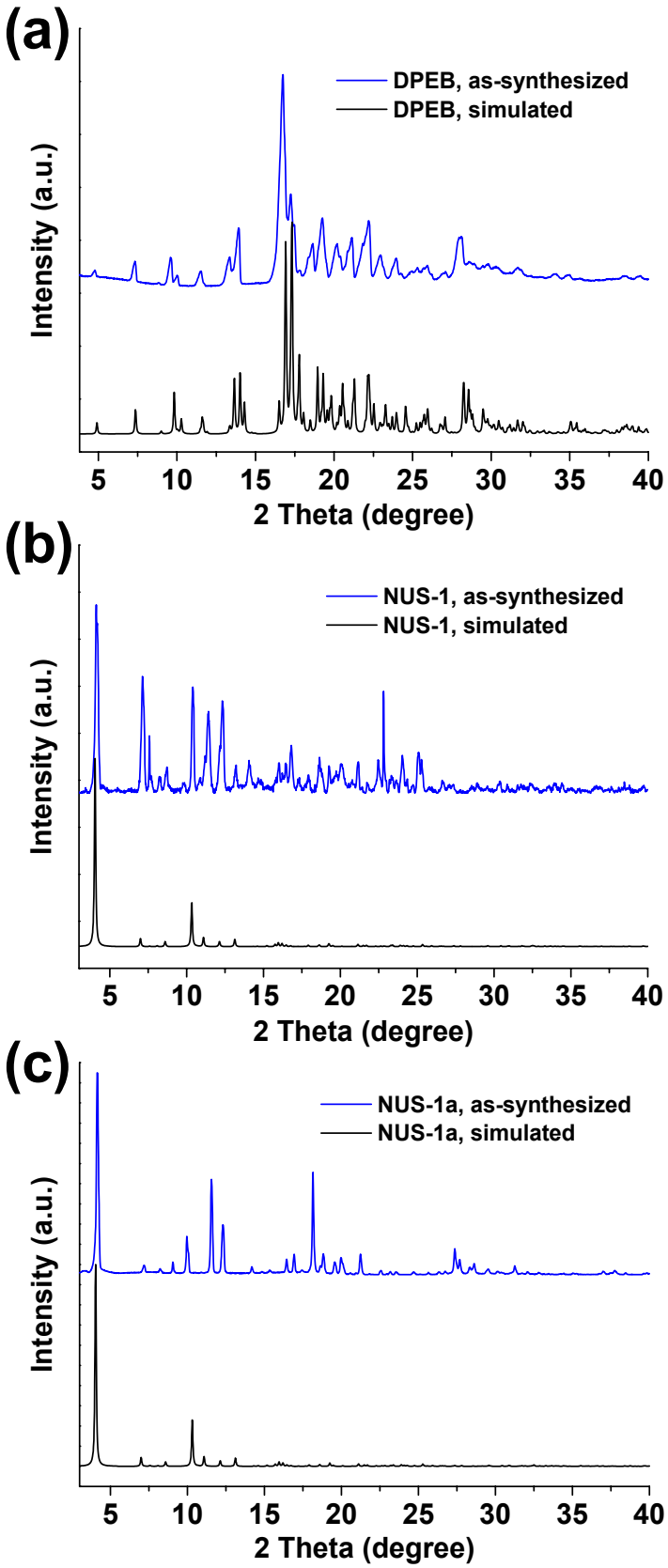

Figure S10. Simulated and measured PXRD patterns of (a) DPEB, (b) NUS-1, and (c) NUS-1a.

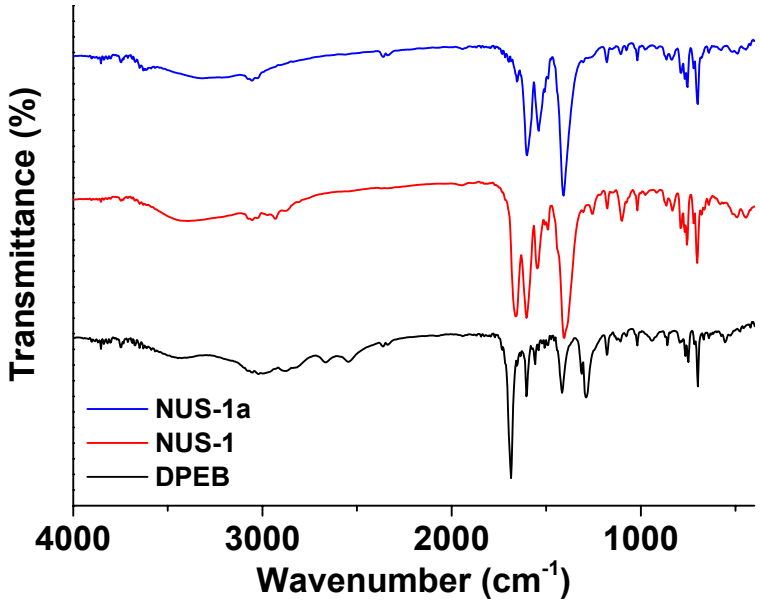

Figure S11. FT-IR spectra of DPEB, NUS-1, and NUS-1a.

Table S1. Summary of DSC results.

Sample	Mode	Peak Position (°C)	Enthalpy (J g^{-1})
DPEB	Heating	323.3	122.3
		461.3	78.9
NUS-1	Cooling	−13.7	−1.9
	Heating	−101.3	2.7
		13.7	1.5
		115.7	23.8
		174.7	30.5
		222.3	76.3
		547.3	117.4
NUS-1a	Heating	−132.7	2.3
		97.0	14.8
		237.0	5.3
		531.7	25.9

Table S2. Photoluminescent properties of DPEB, NUS-1, NUS-1a, and NUS-1a⊃guests.

Sample	DPEB	NUS-1	NUS-1a	NUS-1a+ Hexane	NUS-1a+ Cyclohexane	NUS-1a+ THF	NUS-1a+ Benzene	NUS-1a+ Toluene	NUS-1a+ o-Xylene	NUS-1a+ m-Xylene	NUS-1a+ p-Xylene	NUS-1a+ Mesitylene
λ_{fl} (nm)	487	467	486	489	492	467	504	468	481	473	484	458
Φ_{fl} (%)	79.5	16.7	14.6	17.3	37.5	33.5	49.5	32.6	17.0	22.1	14.5	32.9
τ_1, ns (%)	1.63 (86.22)	0.85 (77.55)	1.06 (67.75)	1.16 (52.65)	1.11 (47.45)	0.66 (52.84)	0.70 (50.15)	0.72 (58.53)	0.77 (25.94)	0.90 (50.58)	0.88 (52.57)	0.99 (71.82)
τ_2, ns (%)	2.71 (13.78)	2.63 (22.45)	3.08 (32.25)	3.40 (47.35)	3.46 (52.55)	2.69 (47.16)	2.47 (49.85)	2.53 (41.47)	1.75 (74.06)	2.97 (49.42)	3.04 (47.43)	3.04 (28.18)

Table S3. Crystal data and structural refinement of DPEB, NUS-1, and NUS-1a.

Sample	DPEB	NUS-1	NUS-1a
Molecular formula	$C_{56}H_{40}O_8$	$C_{84}H_{54}O_{14}Zn_4$	$C_{84}H_{54}O_{13}Zn_4$
M (g/mol)	840.88	1548.75	1532.75
Crystal system	triclinic	trigonal	trigonal
Temperature (K)	100.0 (2)	100.0 (2)	100.0 (2)
Space group	P–1	P–3	P–3
a (Å)	9.8296 (4)	25.2432 (6)	25.2435 (4)
b (Å)	12.6283 (6)	25.2432 (6)	25.2435 (4)
c (Å)	18.9578 (8)	11.6336 (3)	11.6675 (6)
α (°)	71.769 (4)	90	90
β (°)	86.991 (4)	90	90
γ (°)	88.723 (4)	120	120
Volume ($Å^3$)	2232.0 (2)	6420.0 (3)	6438.8 (6)
Z	2	2	2
D_x (g/cm^3)	1.251	0.801	0.791
Reflections collected	15345	16258	16447
Independent reflections	8632	8347	8310
R_{int}	0.023	0.020	0.088
R,[a] R_w[b] [$I > 2\sigma(I)$]	0.0397, 0.1019	0.0723, 0.1986	0.0949, 0.2400
Goodness-of-fit	1.074	1.108	0.923

[a] $R = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$ [b] $R_w = [\Sigma w(|F_0|-|F_c|)^2/\Sigma w(|F_0|)^2]^{1/2}$