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Synthesis, structure and characterization of two solvatochromic Metal-organic Frameworks for chemical sensing application

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1. Synthesis procedure

Materials and methods

Commercially available reagents are used as received without further purification. Powder X-ray diffraction (PXRD) patterns were measured within the 2θ range of 2-40° on an Ultima IV X-ray diffractometer using Cu-Kα radiation. Thermogravimetric analyses (TGA) were carried out with a Netzsch TG 209 TG-DTA analyzer under a nitrogen atmosphere. ^{1}H nuclear magneticresonance (NMR) spectra were recorded on a 400 MHz Systems Spectrometers. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. Infrared (IR) spectra were recorded on a Nicolet iS 50 ATR-FTIR form. IR spectra were recorded over a spectral range of 4000-500 cm^{-1}. The UV−Vis spectrum for the solid state sample was obtained on an Agilent Cary 100 UV/Vis spectrophotometer with background correction. Solid state and liquid state fluorescence spectra were recorded on an Agilent Cary Eclipse Fluorescence spectrophotometer at room temperature. The gas adsorption isotherm was collected on the surface area analyzer ASAP 2020 PLUS.

Synthesis of Ethyl 4-vinyl benzoate: Ethyl 4-vinyl benzoate was synthesized according to a reported modified procedure.[1]

^{1}H NMR match previously reported data. Under a nitrogen atmosphere, 4-vinyl benzoic acid (1.00 g, 6.75 mmol), 1,3-dicyclohexyl-carbodiimide (1.67g, 8.10 mmol), and 4-dimethylaminopyridine (82.5 mg, 0.675 mmol) were added to a 100 mL round-bottom flask equipped with a magnetic stir bar. To this mixture were added CH_2Cl_2 (50 mL) and ethanol (2.90 g, 67.5 mmol). The resulting solution was stirred under nitrogen for 12h at RT, filtered through a Celite pad, and evaporated to near dryness under vacuum. Chromatography of the crude product on silica (Hexane: EtOAc=30:1), followed by concentration gave a primrose yellow oil (0.98 g, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 2H, J=8.5 Hz, ArH), 7.24 (d, 2H, J = 8.0 Hz, ArH), 6.51 (dd, 1H, J_1 = 11 Hz, J_2 = 18 Hz, $CH=CH_2$), 5.63 (d, 1H, J = 18 Hz, $CH=CH_2$), 5.16 (d, 1H, J = 11 Hz, $CH=CH_2$), 4.16 (q, 2H, J = 7.5 Hz, CH_2CH_3), 1.19 (t, 3H, J = 7.0 Hz, CH_2CH_3)

Synthesis of Diethyl 4,4'-((1E,1'E)-anthracene-9,10-diylbis (ethene-2,1-diyl)) dibenzoate(L′): 9,10-Dibromoanthracene (126 mg, 0.376 mmol), ethyl 4-vinyl benzoate (166 mg, 0.94 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (45.1 mg, 0.04 mmol), $[(t\text{-}Bu)_3PH]BF_4$ (52.2 mg, 0.18 mmol), Cy_2NMe (300 mL) in THF (5 mL) were heated at reflux overnight. The THF was removed under reduced pressure, the crude product purified using flash chromatography with CH_2Cl_2 as the eluent. Additional recrystallization from CH_2Cl_2 and EtOH, gave the yellow crystal **L′** (148.2 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, J=7.1, 6H), 4.39 (q, J=7.1, 4H), 6.95 (AB, J=16.3, 2H, vinyl CH), 7.48(dd, J=8.1, 4H), 8.02 (AB, J=16.3, 2H, vinyl CH), 7.71 (dd, J=8.1, 4H), 8.01 (d, J =8.1, 4H), 8.04 (d, J=8.1, 4H), 8.35(dd, J=8.1, 4H)

Synthesis of 4,4'-((1E,1'E)-anthracene-9,10-diylbis(ethene-2,1-diyl)) dibenzoic acid (L): L′ (252.1 mg, 0.42 mmol), LiOH·H_2O (112.0 mg, 2.7 mmol) and 1:9 H_2O / ethanol (20 mL) was added to a round flask, reaction at 100℃ for 17h. After cooling to room temperature the solvent was removed under reduced pressure, the remaining solution diluted with H_2O, cooled in an ice-bath and the pH adjusted to 3 by the addition of HCl (1 M). The precipitate was collected filtered and product dried under vacuum, gave a gelatinous precipitate that was collected and recrystallized from THF/H_2O and dried to give the **L** as a pale yellow powder (211 mg, 92 %). ^{1}H NMR (400 MHz, DMSO): δ 7.03 (AB, J=16.3, 2H, vinyl CH), 7.59 (dd, J=8.1, 4H), 7.95 (dd, J=8.1, 4H), 8.03 (d, J =8.1, 4H), 8.40 (d, J=8.1, 4H), 8.34 (AB, J=16.3, 2H, vinyl CH), 8.40(dd, J=8.1, 4H)

Synthesis of PU-1: $ZrCl_4$ (4.3 mg, 0.018 mmol), ligand L (7.12 mg, 0.015 mmol), and benzoic acid (36.6mg, 0.3mmol) were ultrasonically dissolved in N, N′-dimethylformamide (DMF, 1 mL) in a 4 mL glass tube. The tube was sealed and then heated at 100 °C for 72 h in an oven. After cooling to room temperature, the yellow crystal was separated from the mother liquor via centrifugation (70% yield based on the ligand L). IR: 3060 (w), 3017 (w), 1730 (w), 1606 (m), 1410 (s), 1177 (m), 1024 (s), 965(w), 767 (s).

Synthesis of PU-2: $HfCl_4$ (5.3 mg, 0.018 mmol), ligand L (7.12 mg, 0.015 mmol), and trifluoroacetic acid (TFA) (0.022 mL, 0.3 mmol) were ultrasonically dissolved in N, N′-dimethylformamide (DMF, 1 mL) in a 4 mL glass tube. The tube was sealed and then heated at 120 °C for 48 h in an oven. After cooling to room temperature, the brown crystal was separated from the mother liquor via centrifugation (62% yield based on the ligand L). IR: 3084 (w), 3029 (w), 1750 (w), 1621 (m), 1415 (s), 1179 (m), 1032 (s), 972(w), 770 (s).

2. Ligand ^{1}H-NMR Characterization

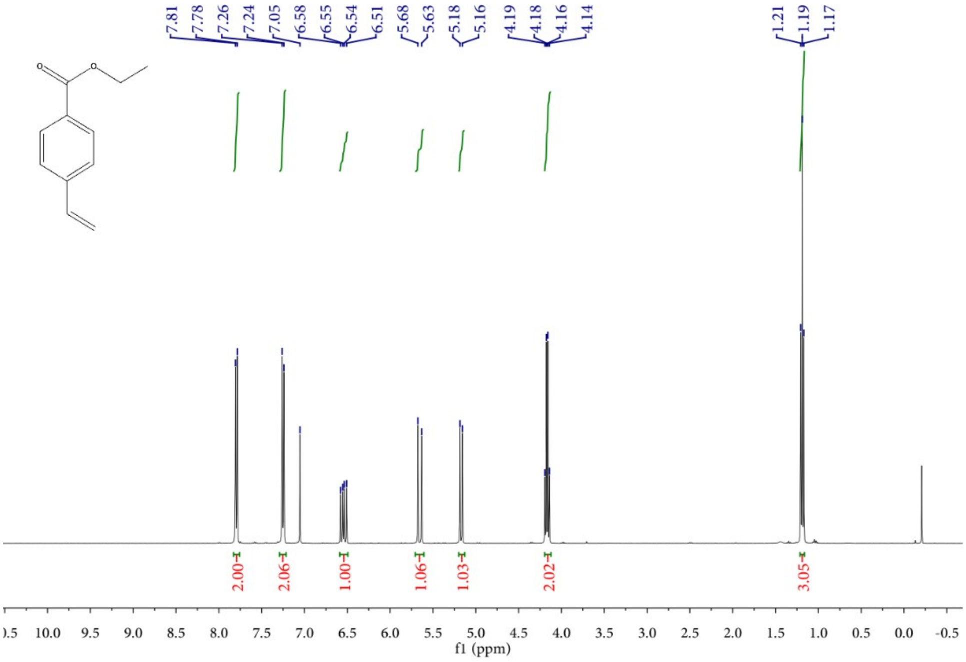

Figure S1: ^{1}H-NMR of Ethyl 4-vinyl benzoate

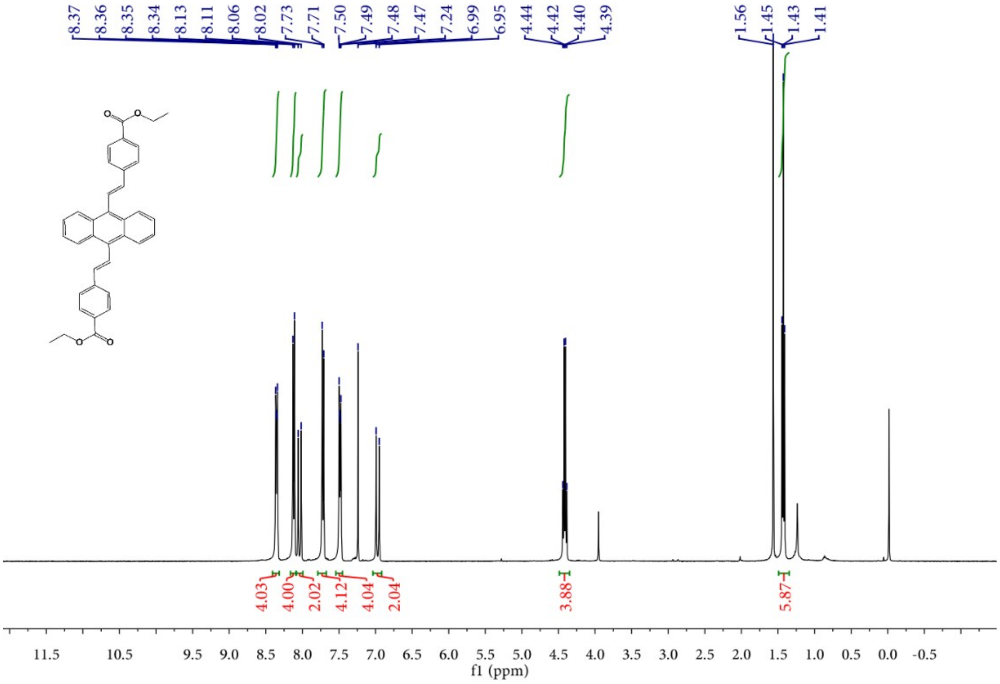

Figure S2: ^{1}H-NMR of L´

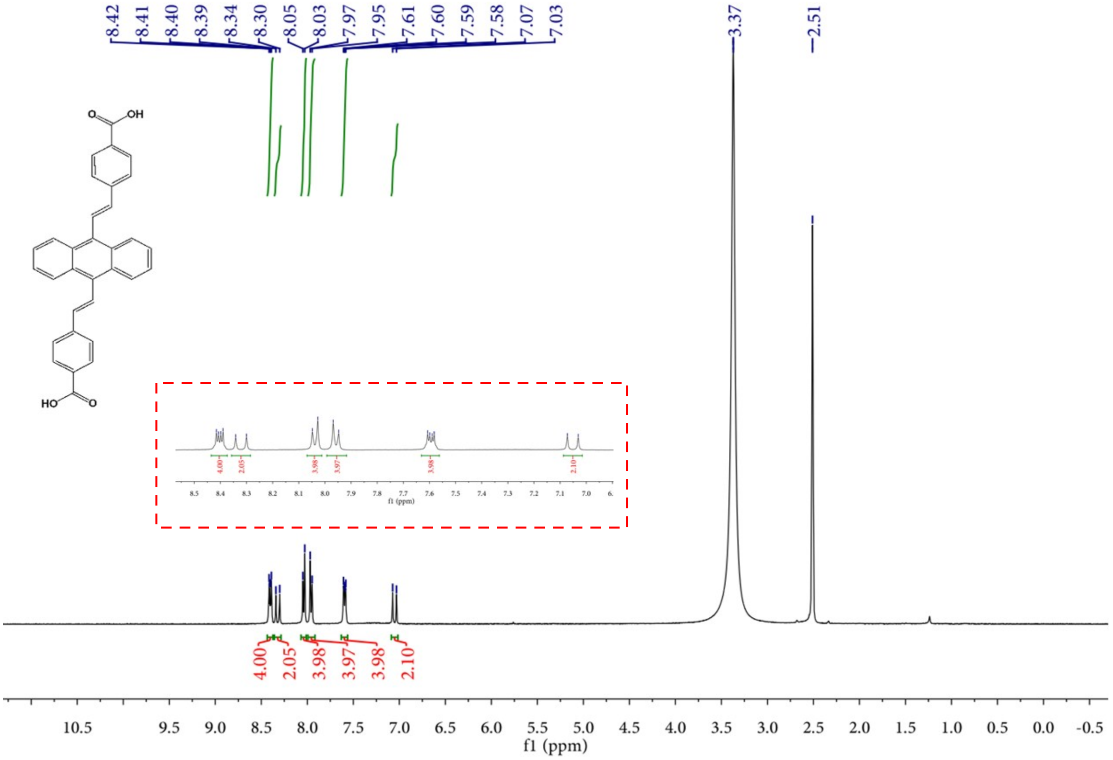

Figure S3: ^{1}H-NMR of ligand L

3. Crystallography

Suitable crystal PU-1 and PU-2 was paced in a cooled N_2 gas stream at about 120 K for crystallographic data collection on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å). Data reduction included absorption was performed by using the SAINT program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with SHELXTL. All the hydrogen atoms were placed geometrically and refined using a riding model. Because of disordered solvent molecules in compound, their diffraction contribution was removed by using the PLATON/SQUEEZE, and the guest molecules can be determined by the TGA and elemental analyses. Detailed crystal data and structure refinement for PU-1 and PU-2 are shown in Table S1.

Table S1. Crystal data and structure refinement for PU-1 and PU-2

Compound	**PU-1**	**PU-2**
CCDC number	1819073	1819074
Formula	$C_{96}H_{48}O_{16}Zr_3$	$C_{192}H_{156}Hf_6O_{32}$
M, g/mol	1730.65	4046.75
Crystal	Cubic	Cubic
Space group	Fd-3m	Fd-3m
T, K	120K	120K
a, Å	39.1912(4)	39.11982(15)
b, Å	39.1912(4)	39.11982(15)
c, Å	39.1912(4)	39.11982(15)
α, degree	90°	90°
β, degree	90°	90°
γ, degree	90°	90°
Z	16	8
V, Å^3	60195.8(11)	59867.4(4)
Final R indices [I > 2σ(I)]	$R_1 = 0.0790$, $wR_2 = 0.1867$	$R_1 = 0.0370$, $wR_2 = 0.0863$
Final R indexes [all data]	$R_1 = 0.0853$, $wR_2 = 0.1915$	$R_1 = 0.0410$, $wR_2 = 0.0889$
GOF	1.050	1.089

Tab. S2. Representation of selected bond lengths and bond Angles of PU-1

Atom	Atom	Bond Lengths(Å)	Atom	Atom	Atom	Bond Angles(°)
Zr1	O1	2.226(3)	O2	Zr1	O1	140.09(9)
Zr1	O2	2.222(3)	O3	Zr1	O1	142.46(8)
Zr1	O3	2.0648(17)	O3	Zr1	O2	70.29(14)
O1	C1	1.271(4)	C2	O1	Zr1	132.7(3)
C1	C2	1.475(10)	O1	C1	C2	116.7(3)
C2	C3	1.380(8)	C3	C2	C1	120.5(4)
C3	C4	1.410(10)	C2	C3	C4	120.6(8)
C4	C5	1.383(9)	C5	C4	C3	120.4(8)
C5	C6	1.480(14)	C4	C5	C6	120.5(5)
C6	C7	1.406(13)	C7	C6	C5	121.5(7)
C7	C8	1.457(16)	C6	C7	C8	121.1(11)
C8	C9	1.452(16)	C9	C8	C7	119.3(11)
C8	C12	1.426(18)	C12	C8	C7	123.6(12)
C9	C10	1.411(15)	C12	C8	C9	117.1(11)
C10	C11	1.453(15)	C10	C9	C8	121.5(11)
C12	C13	1.50(2)	C9	C10	C11	122.3(11)
C13	C14	1.34(2)	C8	C12	C13	118.2(14)

Tab. S3. Representation of selected bond lengths and bond Angles of PU-2

Atom	Atom	Bond Lengths(Å)	Atom	Atom	Atom	Bond Angles(°)
Hf1	O1	2.216(3)	O2	Hf1	O1	142.70(8)
Hf1	O2	2.0531(16)	O3	Hf1	O1	139.83(9)
Hf1	O3	2.214(3)	O3	Hf1	O2	70.55(13)
O1	C1	1.259(4)	C1	O1	Hf1	132.1(3)
C1	C2	1.492(10)	O1	C1	C2	116.2(3)
C2	C3	1.385(11)	C3	C2	C1	120.7(5)
C3	C4	1.391(15)	C2	C3	C4	122.1(10)
C4	C5	1.367(14)	C5	C4	C3	118.0(12)
C5	C6	1.566(19)	C4	C5	C6	118.8(8)
C6	C7	1.446(17)	C7	C6	C5	118.0(9)
C7	C8	1.59(4)	C6	C7	C8	122.1(15)
C8	C9	1.48(4)	C9	C8	C7	113(3)
C8	C12	1.32(6)	C12	C8	C7	119.7(14)
C9	C10	1.447(15)	C12	C8	C9	119.7(14)
C10	C11	1.417(15)	C10	C9	C8	120.2(18)
C12	C13	1.59(6)	C9	C10	C11	122.1(11)
C13	C14	1.29(6)	C8	C12	C13	127(4)

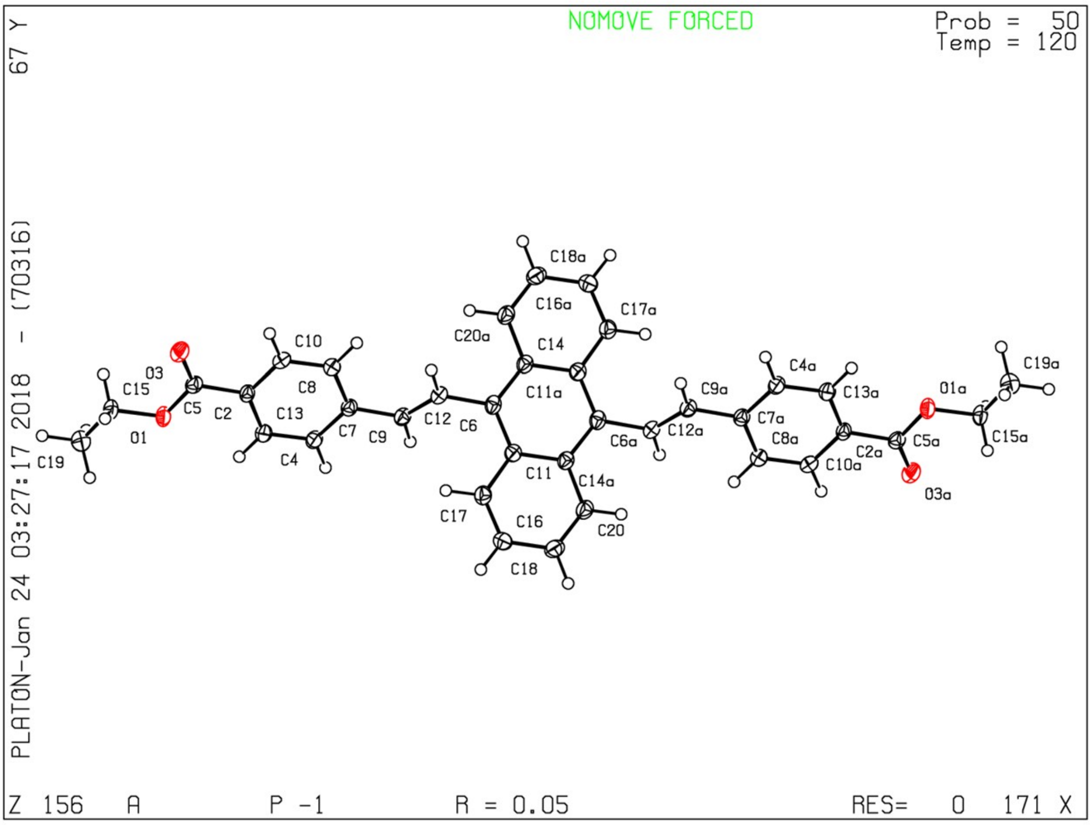

Figure S4: Single crystal structure of ligand L´

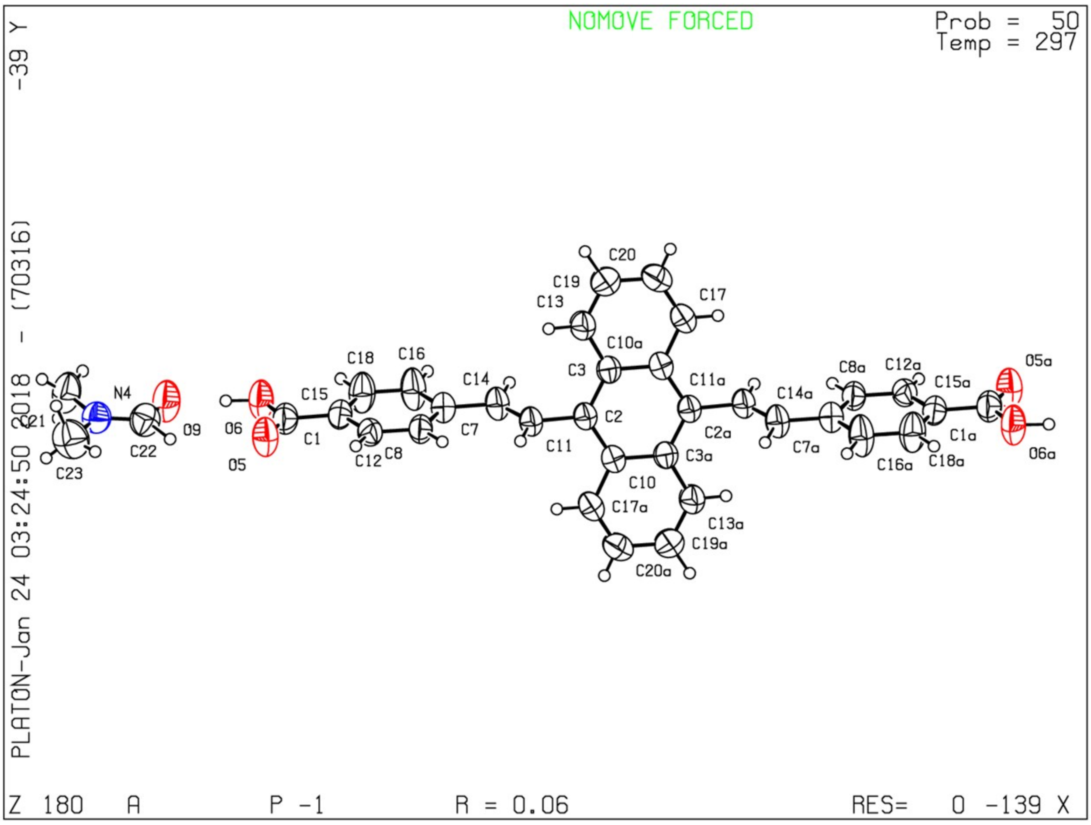

Figure S5: Single crystal structure of ligand L

4. Powder X-ray diffraction

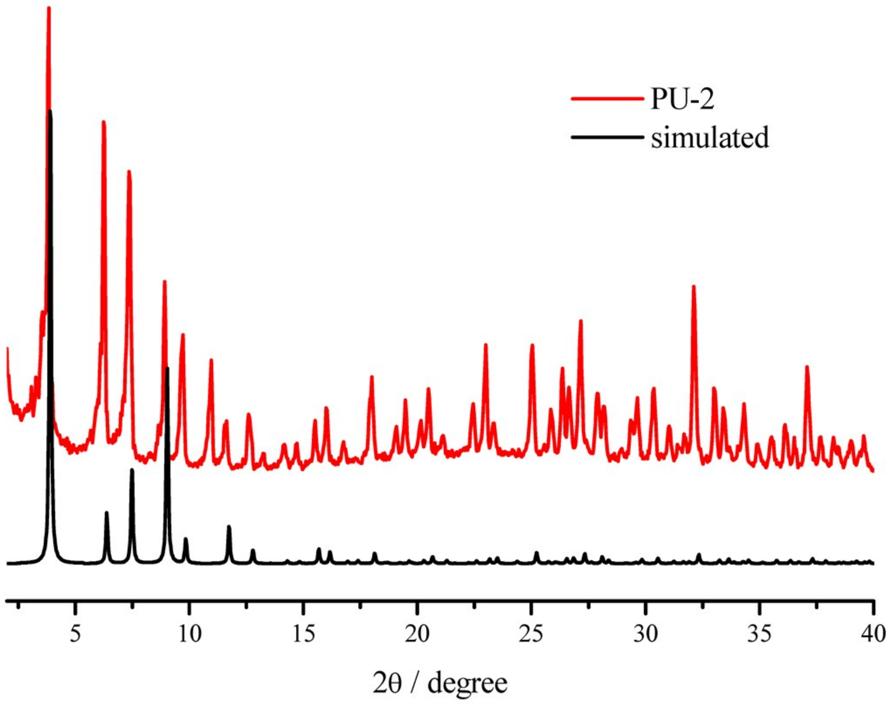

Figure S6: PXRD pattern of PU-2

5. CO_2 sorption

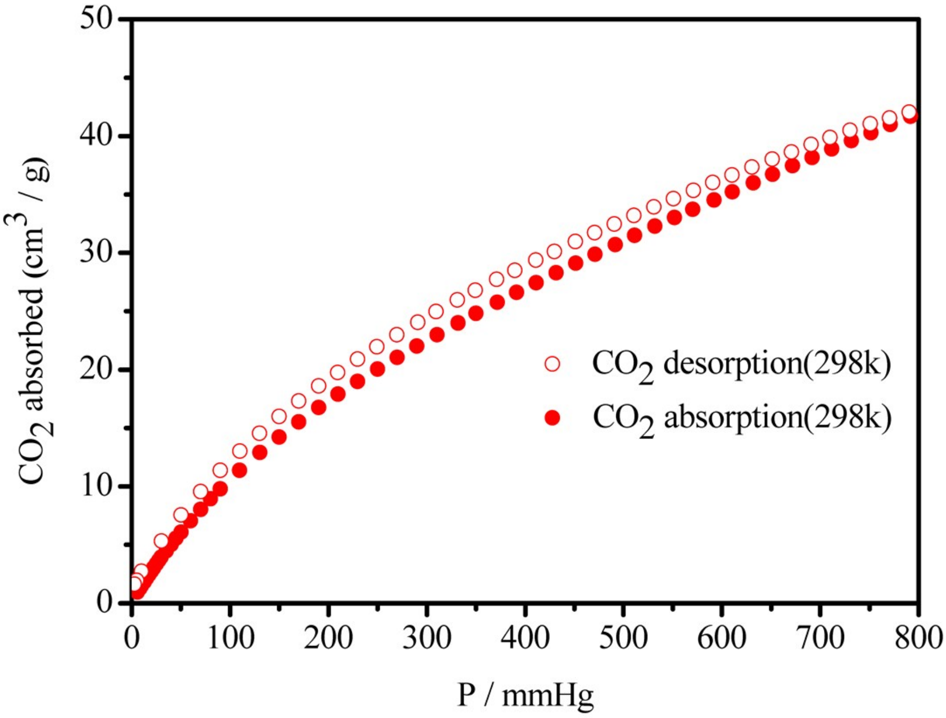

Figure S7: The CO_2 sorption isotherms at 298 K

6. Solvatochromic

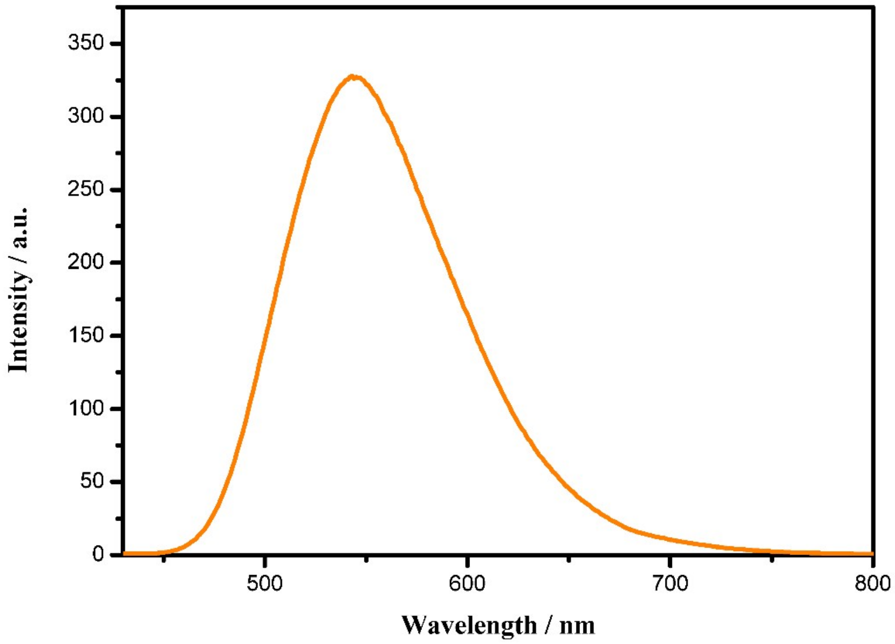

Figure S8: Solid-state fluorescence emission spectra of desolvated PU-1 for emission at 545 nm.

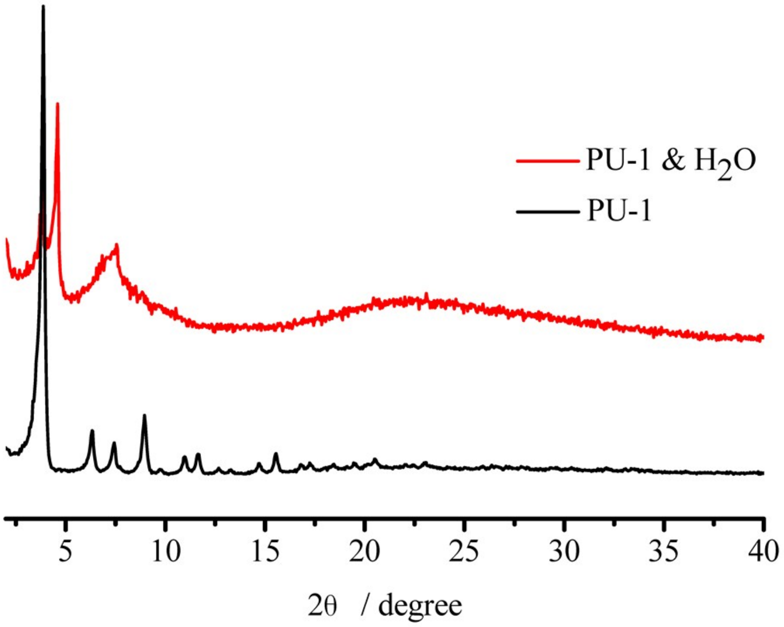

Figure S9: PXRD diffraction patterns of PU-1 after soaking in water

Figure S10: Optical microscope image of PU-1 crystal: as-synthesized(left), water treatment(right)

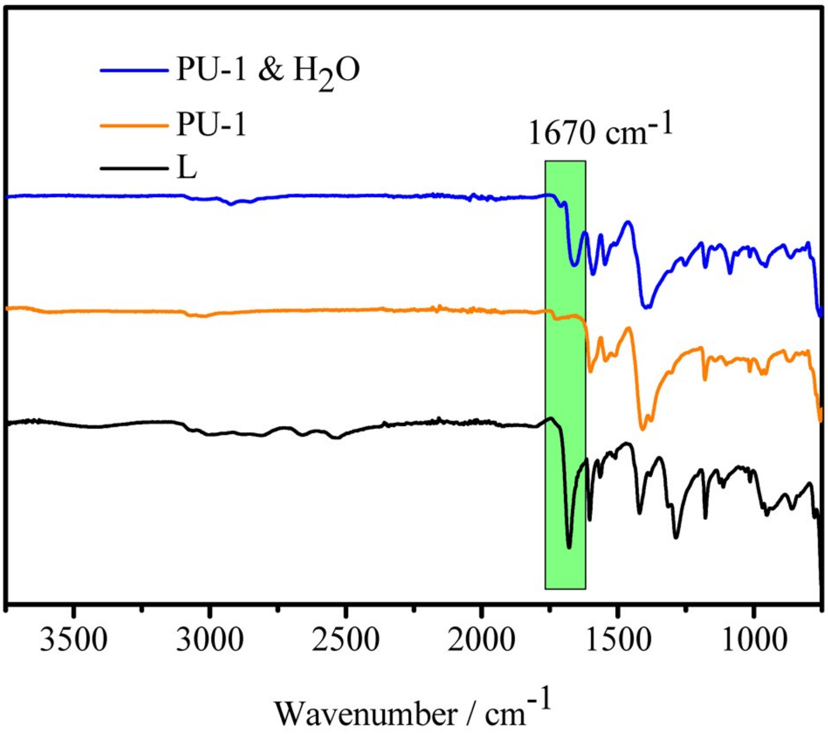

Figure S11: The IR spectrum of PU-1 & H_2O, PU-1, and the ligand L

1. S. H. Cho, B. Ma, S. B. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chemical communications*, 2006, **37**, 2563.