Supporting Information

# Fluorescent detection of carbon disulfide with a highly emissive and robust isoreticular series of Zr-based luminescent metalorganic frameworks (LMOFs)

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# Section 1. Synthesis of Organic Ligands and MOFs

Synthesis of both organic ligands was carried out from modified conditions previously reported including the synthesis of precursor 1 [1], [2].

Synthesis of tetramethyl 4',4''',4''''',4''''''(ethene-1,1,2,2-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylate) Briefly, 9.15 g (14.23 mmol) of Br<sub>4</sub>-TPE, 15.45 g (85.85 mmol) of 4-(H<sub>4</sub>-tcbpe-ester, C1). Methoxycarbonylphenylboronic acid, 0.64 g (0.55mmol) of tetratris(triphenylphosphine) palladium (0) and 19.89g (144 mmol) of K<sub>2</sub>CO<sub>3</sub> were placed in a 1 L three-neck round bottom flask and cycled with vacuum / nitrogen cycles. Simultaneously, 320 mL of THF and 50 mL of DI H2O was bubbled with nitrogen flow in a separate round bottom flask. After 15 minutes of bubbling, the solvent was transferred over to the main reaction vessel through cannula and refluxed for 36 hours at 120 °C. After reaction completion, monitored by TLC, the reaction was cooled to RT and concentrated under reduced pressure to remove THF. The crude product was then extracted with several portions of dichloromethane, washed with water and finally brine. The organic layer was thoroughly dried with sodium sulfate, filtered and concentrated under reduced pressure. The crude product was then transferred to a 500 mL round bottom flask to which was added 300 mL of acetone and refluxed for 15 minutes. While still hot, the product was filtered and collected. The process was repeated a total of 3 times and the bright green-yellow powder was dried overnight in a vacuum oven. The product was then run through a short column to remove palladium impurity using a mixture of DCM:EtOAc (29:1, V:V). The solution was concentrated under reduced pressure to provide 7.7 g (8.87 mmol) of the bright yellow green ester (62% yield). <sup>1</sup>H NMR data (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, 8H, J = 8.1Hz), 7.64(d, 8H, J = 8.0Hz), 7.45(d, 8H, J = 7.9Hz), 7.21(d, 8H, J = 8.0Hz), 3.93(s, 12H).

**Synthesis of 4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carboxylic acid)) (H4tcbpe, C2)**. The resulting ester above was transferred into a 500 mL flask with 150 mL of 3M NaOH and 150 mL of tetrahydrofuran and refluxed overnight. The reaction vessel was cooled and an additional 100 mL of water was added to the solution. The organic solvent was removed under reduced pressure to provide a clear, bright yellow solution. Upon removal of tetrahydrofuran, the solution was transferred to a large addition funnel and added dropwise under constant stirring to 175 mL of a 3M HCl solution. The bright yellow precipitate was collected by centrifugation and washed with water until the pH of the aqueous solution turned neutral. The collected sample was then dried overnight in a vacuum oven to produce our final product in a 95% yield. <sup>1</sup>

**Synthesis of 4',4''',4'''',4''''',4'''''''-(ethene-1,1,2,2-tetrayl)tetrakis(3-fluoro-[1,1'-biphenyl]-4-carboxylic acid)** (H<sub>4</sub>-tcbpe-F, C5). The resulting purified ester from the Suzuki coupling was transferred into a 500 mL flask with 150 mL of 3M NaOH and 150 mL of tetrahydrofuran and refluxed overnight. Once cooled, 150 mL of water was added to the reaction and the organic solvent was removed under reduced pressure. Addition of this solution, under constant stirring, to 175 mL of 3M HCl caused the precipitation of our final product. The sample was collected by centrifugation, washed with water until the aqueous solution was of neutral pH and dried in a vacuum oven with a 94% yield. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO, 300 MHz): δ 7.19 (d, J = 8.22 Hz, 8H), 7.51 - 7.76 (m, 16H), 7.89 (t, J = 8.22 Hz, 4H), 13.24 (s, 4H).

Optical image of crystals of compound 1:



Optical image of crystals of compound **2**:



# Section 2. Crystallographic Data

Empirical Formula	$Zr_6O_{32}C_{108}H_{80}$
Formula Weight	2437.04
Crystal System	Orthorhombic
Space Group	Cmcm
a/Å	26.266 (2)
b/Å	42.046 (3)
c/Å	16.4816 (6)
$\alpha /^{\circ}$	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	18202 (2)
Z	4
Q <sub>calc</sub> $g/cm^3$	0.889
Rint	0.0703
Data/restraints/parameters	8877/381/487
Goodness-of-fit on F <sup>2</sup>	1.031
$R_1, wR_2[I>2\sigma(I)]$	0.0437/0.1314
R <sub>1</sub> , wR <sub>2</sub> [All data]	0.0577/0.1457

Table S1. Crystal Data and refinement details for 1





Fig. S1 The chemical stability of **2** under various pH conditions for 36 hours.



Section 4. Thermogravimetric Analysis Results of 1 and 2

Fig. S2 a) Thermogravimetric analysis for **1** under a constant nitrogen flow. b) The PXRD pattern of **1** after being heated at 200 °C for 6 hours.



Fig. S3 a) Thermogravimetric analysis for **2** under a constant nitrogen flow. b) The PXRD pattern of **2** after being heated at 150 °C and 200 °C respectively for 6 hours.

#### Section 5. Photoluminescence Measurements of 1 and 2



Fig. S4 Emission profiles for as-made 1 (solid black) and outgassed 1 (solid blue) under 360 nm and 455 nm excitation. Excitation profiles for as-made 1 (dashed black) and outgassed 1 (dashed blue) under 455 and 531 nm, respectively.



Fig. S5 Emission profiles for as-made **2** (solid black) and outgassed **2** (solid blue) under 360 nm and 455 nm excitation. Excitation profiles for as-made **2** (dashed black) and outgassed **2** (dashed blue) under 491 and 557 nm, respectively.



Fig. S6 Emission and excitation profiles for both H<sub>4</sub>tcbpe (black) and H<sub>4</sub>tcbpe-F (blue) under 365 and 535 nm, respectively.

# Section 6. Optical Absorption Data of 1 and 2



Fig. S7 The optical absorption spectra of **1**: as-made (black) and outgassed (red).



Fig. S8 The optical absorption spectra for **2**: as-made (black) and outgassed (red).



Fig. S9 A comparison of the optical absorption spectra of **2** in the as-made, outgassed and carbon disulfide loaded state.

### Section 7. Porosity Analysis

#### Activation of 1

The activation of compound one was performed through a previously reported method. Briefly, approximately 120 mg of **1** was placed inside of a 20 mL scintillation vial and solvent exchanged with 20 mL of DMA 3x, Dichloromethane 3x and Hexane 3x. Prior to nitrogen uptake measurements, the sample was outgassed under vacuum at 70 °C for 12hrs.



Fig. S10 TGA profile for each step of the multi-solvent exchange process for 1.



Fig. S11 a) Nitrogen isotherms for **1** with different solvents for solvent exchange. b) pore size distribution of **1** with a pore size of approximately 6Å.



Fig. S12 PXRD patterns of  ${\bf 1}$  after thermally activating the sample and  $N_2$  adsorption experiment.

### Section 8. Stern-Volmer Analysis



Fig. S13 The fluorescence emission profile of **1** under different concentrations of carbon disulfide in DMA.



Fig. S14 The fluorescence emission profile of **2** under different concentrations of carbon disulfide in DMA.

Stern-Volmer analysis was used in order to determine the quenching efficiencies of **1** and **2** upon exposure to carbon disulfide. The Stern-Volmer plots show a linear relationship with regards to quenching intensity and concentration of quencher thus allowing us to calculate the quenching efficiency by using the slope of the plots.

$$\frac{I_o}{I} = 1 + K_{SV}[Q]$$

Equation 1: I<sub>0</sub> is defined as the maximum fluorescence intensity of the MOF prior to exposure to the analyte, I is the maximum intensity of the fluorescence spectrum at a given concentration of the analyte, [Q] is the known concentration of exposure to the analyte and K<sub>sv</sub> is the quenching efficiency.

The Limit of Detection (LOD) is defined as the concentration of carbon disulfide is greater than the average standard deviation of multiple FL experiments, standard deviation values for **1** and **2** were 0.0188 and 0.0133, respectively. Using the S-V curves in Fig. S16 and Fig. S17, we determined the limit of detection to be 2.89 and 2.59 ppm based on  $3\sigma/m$ .



Fig. S15 Stern-Volmer plot of **1** upon exposure to carbon disulfide in DMA with a quenching efficiency of 1,488 M<sup>-1</sup>.



Fig. S16 Stern-Volmer plot of 2 upon exposure to carbon disulfide in DMA with a quenching efficiency of 1,176 M<sup>-1</sup>.

### Section 9. Luminescence Quenching Mechanism



Fig. S17 The absorption spectra of pure CS<sub>2</sub> compared to the emission profile of **2** in various different states.

#### Section 10. In-situ Infrared Measurement



Fig. S18 (a) IR difference spectra of **2** during adsorption (~ 5 min, top) and desorption (middle three) of carbon disulfide, referenced to activated MOF in vacuum (bottom).

Section 11. Mechanochromic Behavior



Fig. S19 Optical images demonstrating the mechanochromic behavior of **1**: a) before grinding, b) after partial grinding and c) after prolonged grinding.

Section 12. Exposure to other common VOCs



Fig. S20. PL spectra of 5 mg of MOF samples taken after being suspended in common volatile organic compounds (VOC's). Inset (left to right) are samples in dimethylformamide, dichloromethane, acetone, ethyl ether, ethyl acetate, benzene and toluene.

# References

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