

**Electronic Supplementary Information (ESI)**

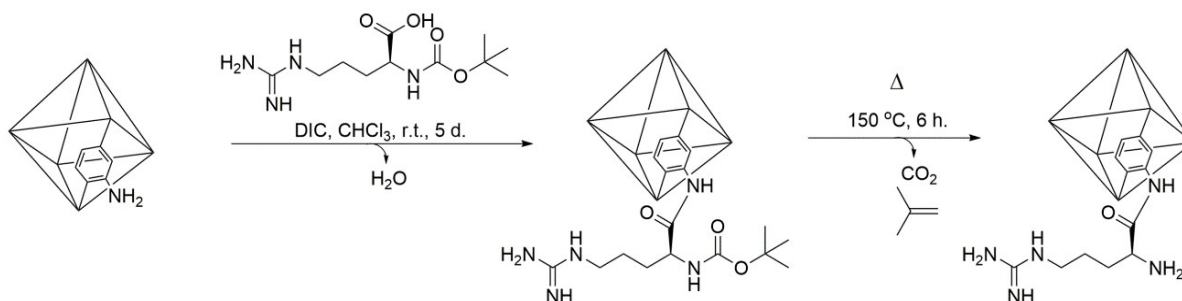
**A linear fluorescence-quenching response in an amidine-functionalised solid-state sensor for gas-phase and aqueous CO<sub>2</sub> detection**

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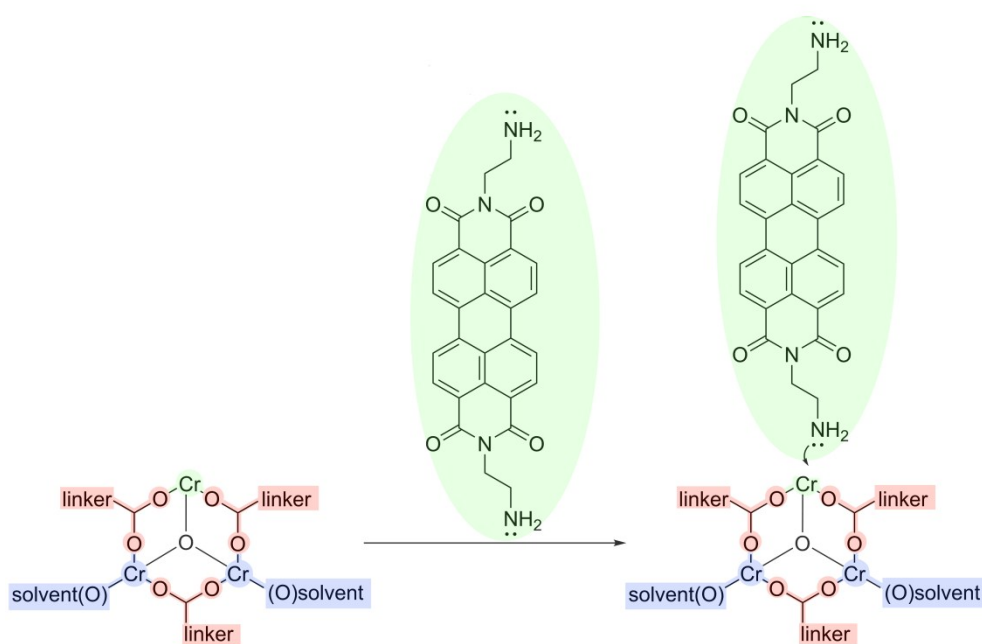
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## Synthesis



**Figure S1** Schematic diagram showing PSM with BOC-Arg-OH through a condensation reaction with DIC, followed by removal of the BOC group by thermolysis.



**Figure S2** Representation of a Cr-MIL-101 trimer of chromium octahedral centres sharing a common vertex  $\mu_3\text{-O}$ , connected *via* the organic linker (2-aminoterephthalic acid, red) and the presence of either terminal molecules (*e.g.*, solvent, blue) or coordinatively unsaturated (open) chromium sites (green). The open chromium sites may then be coordinated by the lone pair of the nitrogen on one side the penda moiety, leaving the other end free in the pore to interact with  $\text{CO}_2$ . Schematic adapted from reference [1].

All commercially available chemicals were of reagent grade and were used as received, unless otherwise specified. The synthesis of Cr-MIL-101- $\text{NH}_2$  was carried out according to literature procedure.<sup>[2, 3]</sup>

*2,2'-(1,3,8,10-tetrahydroanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9-diyl)bis(ethan-1-amine)* (peda)

The method was adapted from reference [4].

Ethylene diamine (1.7 mL, 25.6 mmol) was added to a suspension of 3,4,9,10-perylenetetracarboxylic dianhydride (1.00 g, 2.55 mmol) in toluene (40 mL). The mixture was refluxed for 16 h, and the resulting powder was filtered

and washed with hot toluene. The red solid was added to aqueous KOH (5 M, 40 mL) and stirred at room temperature for 6 h. The mixture was filtered and washed with water to give an ochre-coloured solid (830 mg, 68 %). Due to difficulties with solubility, the product was characterised by FTIR as being identical to that previously published.

*[Al<sub>2</sub>(bdc-NH<sub>2</sub>)<sub>3</sub>] (Al-MIL-101-NH<sub>2</sub>)*

The method was adapted from reference [5].

AlCl<sub>3</sub>·6H<sub>2</sub>O (170 mg, 0.706 mmol), 2-aminoterephthalic acid (187 mg, 1.03 mmol) and DMF (10 mL) were added to a 21 mL glass vial. The vial was heated in an aluminium heat block at 130 °C for 72 h, and the yellow powder that resulted upon cooling was isolated gravity filtration. PXRD confirmed that the structure was the same as that previously published.

*[Cr<sub>2</sub>(bdc-NH-arg)<sub>3</sub>] (1)*

The method was adapted from reference [6].

CHCl<sub>3</sub> (10 mL) was cooled in a round-bottom flask in an ice bath. *N*<sub>α</sub>-(*tert*-Butoxycarbonyl)-L-arginine (BOC-Arg-OH) (226 mg, 0.825 mmol) and *N,N'*-diisopropylcarbodiimide (DIC) (131 μL, 0.843 mmol) were added with stirring. The resulting solution was stirred in an ice bath for 5 min, then Cr-MIL-101-NH<sub>2</sub> (47mg, 0.17 eq. NH<sub>2</sub> sites) was added. The mixture was stirred at r.t. for 2 d. The resulting powder was isolated by trituration with CHCl<sub>3</sub> followed by centrifugation, and washed with EtOH:CHCl<sub>3</sub> (1:1, 2 × 30 mL). To activate the compound, the powder was steeped in ethanol for 72 h (exchanging every 24 h) before being evacuated at 150 °C under vacuum for 6 h. PXRD confirmed that the structure was retained through the PSM process. <sup>1</sup>H NMR of the product decomposed in NaOH/D<sub>2</sub>O solution (1 M) confirmed 100% conversion of the ligand. Anal. Calcd. for Cr<sub>3</sub>C<sub>42</sub>H<sub>58</sub>N<sub>15</sub>O<sub>21</sub> (MW = 1265.00 g/mol): C 39.88, H 4.62, N 16.61%. Found: C 39.61, H 4.88, N 16.13%. IR (cm<sup>-1</sup>) ν = 3310 (br), 1670 (s), 1625 (s), 1500 (m), 1435 (s), 1395 (s), 1340 (w), 1260 (w), 1165 (w), 770 (m), 600 (m).

*[Al<sub>2</sub>(bdc-NH-arg)<sub>3</sub>] (2)*

The method was adapted from reference [6].

DMF (6 mL) was cooled in a round-bottom flask in an ice bath. *N*<sub>α</sub>-(*tert*-Butoxycarbonyl)-L-arginine (BOC-Arg-OH) (150 mg, 0.548 mmol) and *N,N'*-diisopropylcarbodiimide (DIC) (131 μL, 1.04 mmol) were added with stirring. The resulting solution was stirred in an ice bath for 5 min, then Al-MIL-101-NH<sub>2</sub> (60 mg, 0.2 eq. NH<sub>2</sub> sites) was added. The mixture was stirred at r.t. for 2 d. The resulting powder was isolated by trituration followed by centrifugation, and washed with DMF (2 × 30 mL) and EtOH (2 × 30 mL). To activate the compound, the powder was steeped in ethanol for 72 h (exchanging every 24 h) before being evacuated at 150 °C under vacuum for 6 h. PXRD confirmed that the structure was retained through the PSM process. <sup>1</sup>H NMR of the product decomposed in NaOH/D<sub>2</sub>O solution (1 M) confirmed 100% conversion of the ligand. Anal. Calcd. for Al<sub>3</sub>C<sub>42</sub>H<sub>58</sub>N<sub>15</sub>O<sub>21</sub> (MW = 1189.95 g/mol): C 42.39, H 4.91, N 17.66%. Found: C 42.20, H 4.88, N 15.97%. IR (cm<sup>-1</sup>) ν = 3350 (br), 1655 (s), 1580 (s), 1500 (m), 1445 (s), 1405 (s), 1260 (w), 775 (m), 610 (w), 460 (w).

*[Cr<sub>2</sub>(bdc-NH<sub>2</sub>)<sub>3</sub>(peda)<sub>2</sub>] (3)*

The method was adapted from reference [1].

Cr-MIL-101-NH<sub>2</sub> (50 mg, 0.17 mmol Cr<sup>3+</sup> sites) and peda (84 mg, 0.20 mmol) were heated at reflux in toluene (10 mL) for 16 h. The powder was isolated by gravity filtration, and washed copiously with hot DMF (100 °C) until the filtrate turned clear. A red solid was yielded. To activate the compound, the powder was steeped in ethanol for 72 h (exchanging every 24 h) before being evacuated at 150 °C under vacuum for 6 h. PXRD confirmed that the structure was retained through the PSM process. Anal. Calcd. for Cr<sub>3</sub>C<sub>108</sub>H<sub>106</sub>N<sub>15</sub>O<sub>18</sub> (MW = 2058.11 g/mol): C 63.03,

H 5.15, N 10.10%. Found: C 60.82, H 5.30, N 8.60%. IR ( $\text{cm}^{-1}$ )  $\nu$  = 1775 (s), 1670 (w), 1620 (w), 1595 (s), 1510 (w), 1410 (s), 1300 (s), 1235 (w), 1150 (w), 1125 (w), 1020 (s), 940 (w), 860 (w), 810 (w), 735 (w).

## Methods

### *Powder X-ray diffraction (PXRD)*

PXRD data was collected over the 5–50° 2 $\theta$  range with a 0.02° step size and 2°/min scan rate on a PANalytical XPert Pro diffractometer fitted with a solid-state PIXcel detector (45 kV, 40 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation.

### *Elemental analyses*

Elemental analyses for C, H, N and S were conducted at the Chemical Analysis Facility at Macquarie University. All samples were sent dry and were redried by heating (110 °C) prior to analysis.

### *Thermogravimetric analysis (TGA)*

TGA measurements were carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyser. Dry N<sub>2</sub> flowed through the system (0.1 L min<sup>-1</sup>) during data collection. In order to identify the approximate temperatures of guest loss and thermal decomposition, the sample temperature was ramped at 0.75 °C min<sup>-1</sup> from 25 to 600 °C. In order to determine the uptake of guests in the vapour phase, the sample was activated *in situ* at temperatures specified in text, then cooled to room temperature and exposed to the vapour of interest for a period of 2 h.

### *Gas sorption*

Adsorption isotherms were measured using the Accelerated Surface Area & Porosimetry System (ASAP) 2020 or the 3Flex, both supplied by Micromeritics Instruments Inc. Approximately 50–100 mg of sample was loaded into a glass analysis tube and outgassed for 6–16 h under vacuum prior to measurement at temperatures as specified in the synthetic methods.

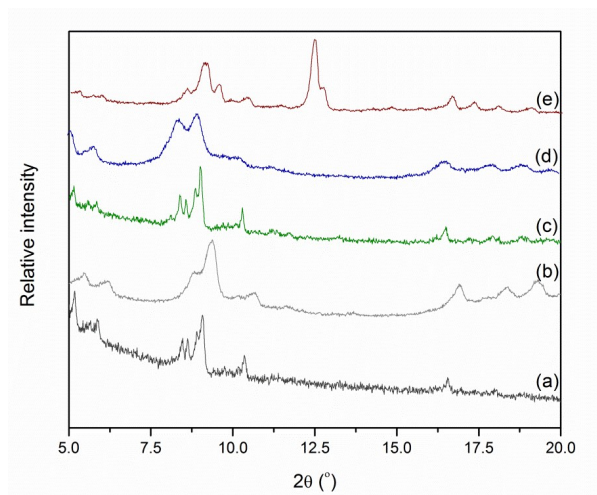
### *Ultraviolet-visible (UV-visible) spectroscopy*

UV-visible spectra were recorded using a CARY5000 UV-Visible spectrophotometer with a Praying Mantis attachment and Varian WinUV software. A baseline correction was undertaken with dry, finely ground BaSO<sub>4</sub>. *In situ* CO<sub>2</sub> dosing experiments were performed using the variable temperature and sample environment stages on the Praying Mantis attachment. Samples were heated to 100 °C for 2 h prior to CO<sub>2</sub> dosed spectra collection.

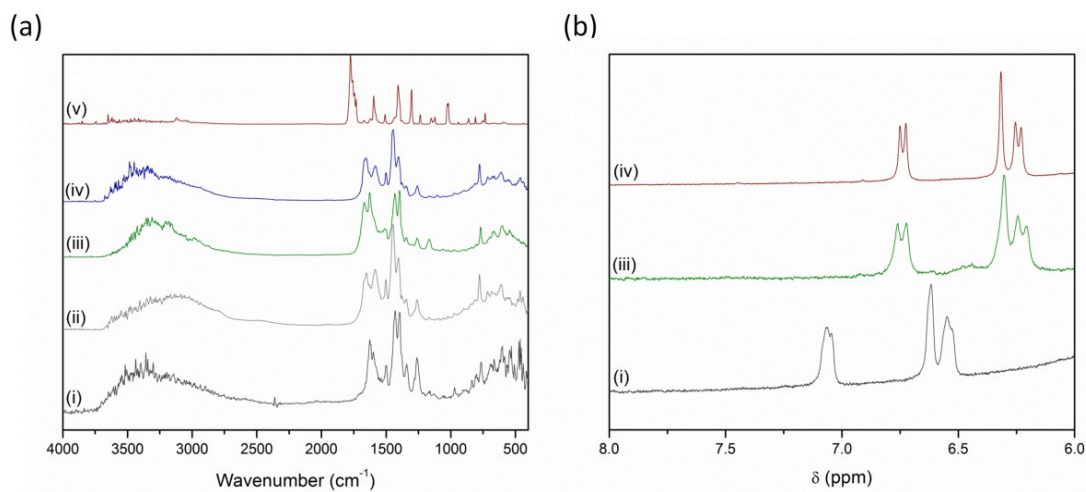
### *Fluorescence spectroscopy*

Fluorescence spectroscopy was conducted on a Cary Varian Eclipse Fluorescence Spectrophotometer using excitation wavelengths as determined from UV-visible spectra. Solid-state measurements were performed by flattening the solid on a quartz slide and slotting it into the cuvette diagonally. *In situ* CO<sub>2</sub> measurements were performed by sealing the quartz cell and purging with pure CO<sub>2</sub> for 1 min. Measurements on suspensions were performed by sonicating the MOF (ca. 10 mg) in solvent (1 mL) for 30 s and purging CO<sub>2</sub> through the mixture for 60 min total, with measurements taken every minute for the first 5 minutes, then every 5 min for the remaining time period. This was converted to volume of CO<sub>2</sub> by reacting the CO<sub>2</sub> being discharged from the cylinder at a given time period and pressure with limewater, and filtering off, drying and weighing the CaCO<sub>3</sub> that precipitated. This mass was used to back calculate the number of moles and therefore the volume of CO<sub>2</sub> (at RTP) that was dosed at several time points <10 min to give a linear trend which was extrapolated to the remaining time points.

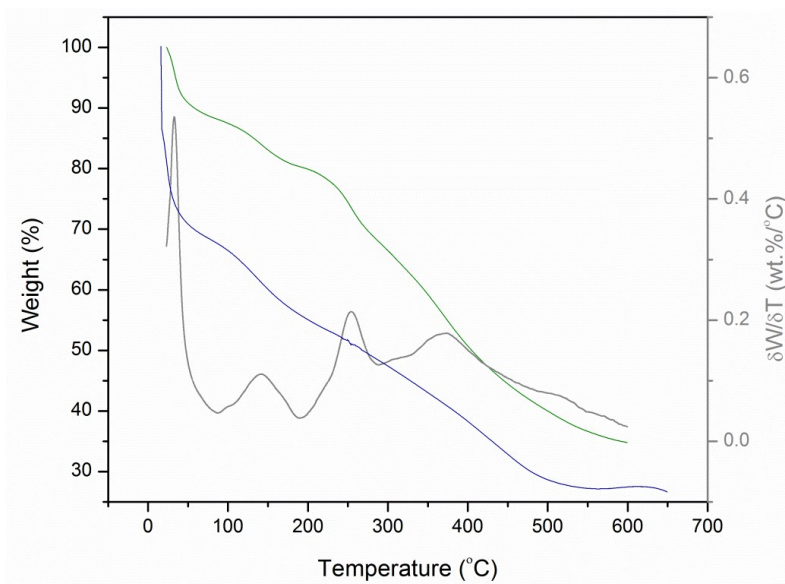
## Characterisation



**Figure S3** PXRD patterns of (a) Cr-MIL-101-NH<sub>2</sub>, (b) Al-MIL-101-NH<sub>2</sub>, and compounds (c) **1**, (d) **2** and (e) **3**. The additional peak 12.45° 2θ in compound **3** is attributed to either perylene ordering in the pore, or a slight disruption to the structure itself by virtue of the PSM.

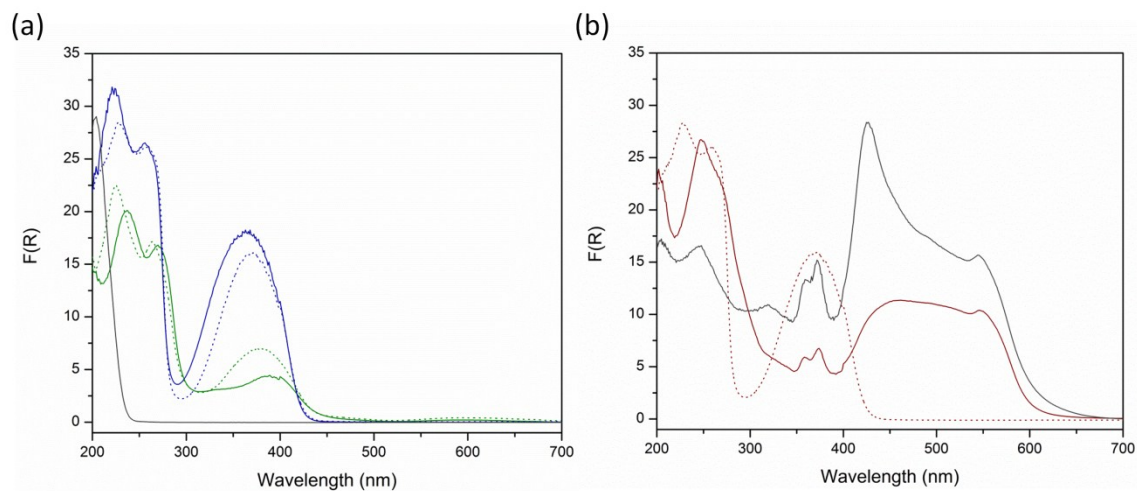


**Figure S4** (a) FTIR, and (b) <sup>1</sup>H NMR spectra of (i) Cr-MIL-101-NH<sub>2</sub>, (ii) Al-MIL-101-NH<sub>2</sub>, and compounds (iii) **1**, (iv) **2**, and (v) **3**. <sup>1</sup>H NMR spectrum of **3** was not carried out due to the insolubility of the perylene moiety.



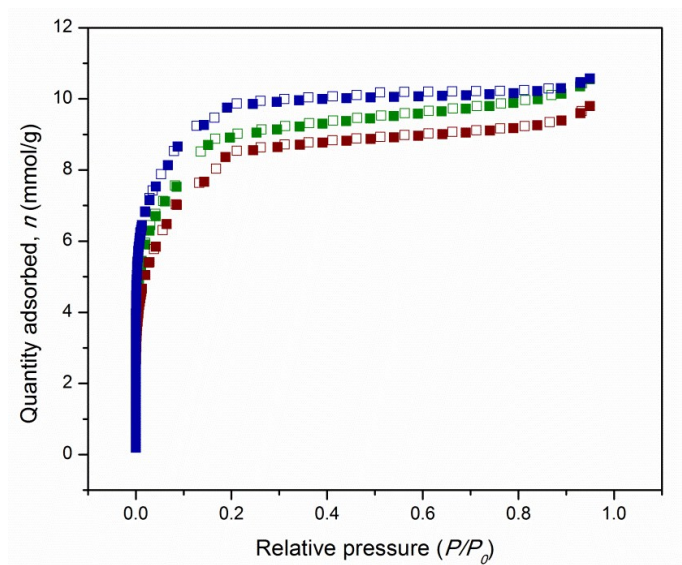
**Figure S5** TGA plots of compound **1** (green) and **2** (blue), and a representative first derivative plot for **1** highlighting the step at *ca.* 150 °C corresponding to the thermolysis of the BOC group.

### Optical properties

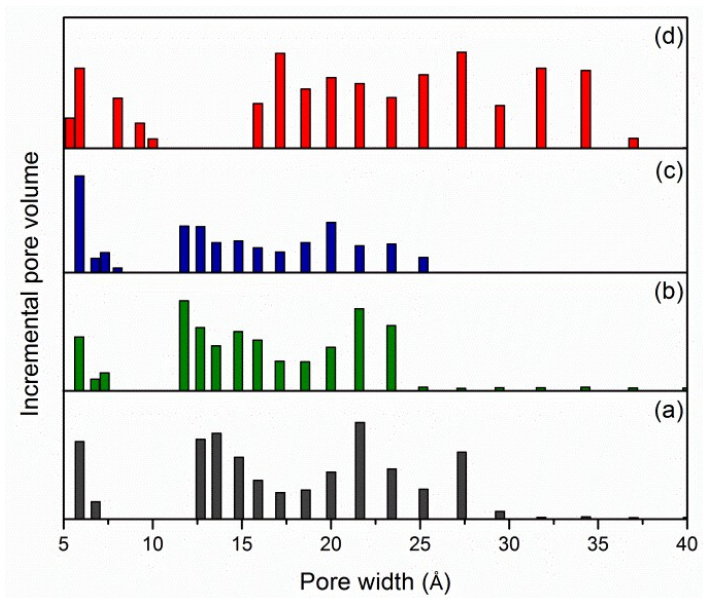


**Figure S6** UV-vis spectra of (a) compound **1** (green), compound **2** (blue), arginine (grey), Cr-MIL-101-NH<sub>2</sub> (green dotted), Al-MIL-101-NH<sub>2</sub> (blue dotted), and (b) compound **3** (red), peda (grey) and Cr-MIL-101-NH<sub>2</sub> (red dotted).

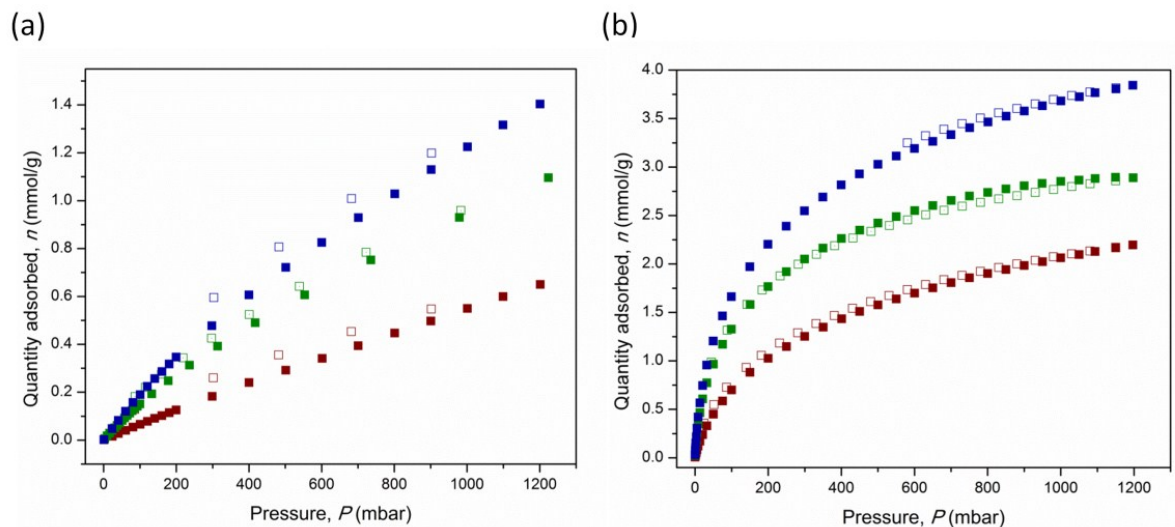
## Gas uptake



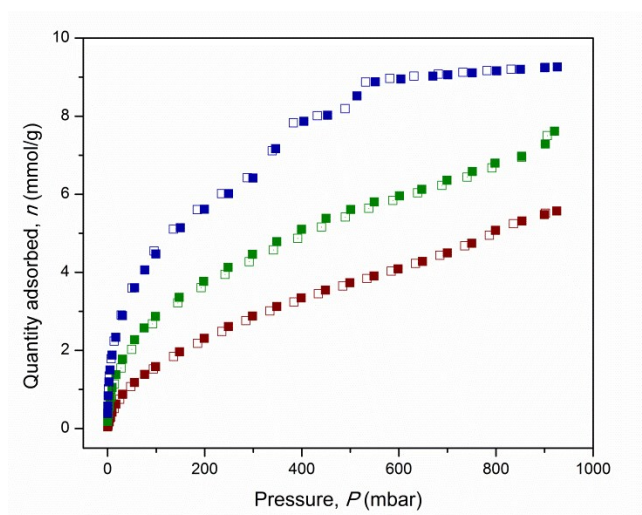
**Figure S7** 77 K  $N_2$  adsorption (filled symbols) and desorption (open symbols) isotherms for compounds **1** (green), **2** (blue), and **3** (red).



**Figure S8** DFT pore size distributions for (a) Cr-MIL-101-NH<sub>2</sub> (grey), and compounds (b) **1** (green), (c) **2** (blue), and (d) **3** (red).

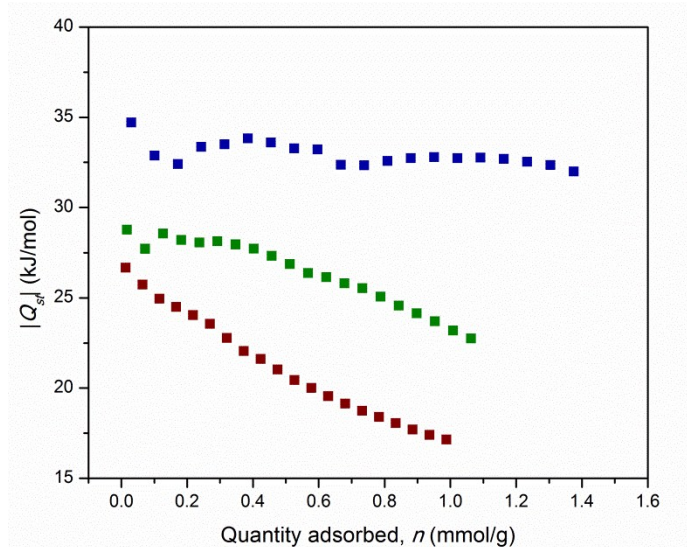


**Figure S9** Adsorption (closed symbols) and desorption (open symbols) isotherms of (a) 298 K  $\text{CO}_2$  and (b) 77 K  $\text{H}_2$  for compounds **1** (green), **2** (blue), and **3** (red).



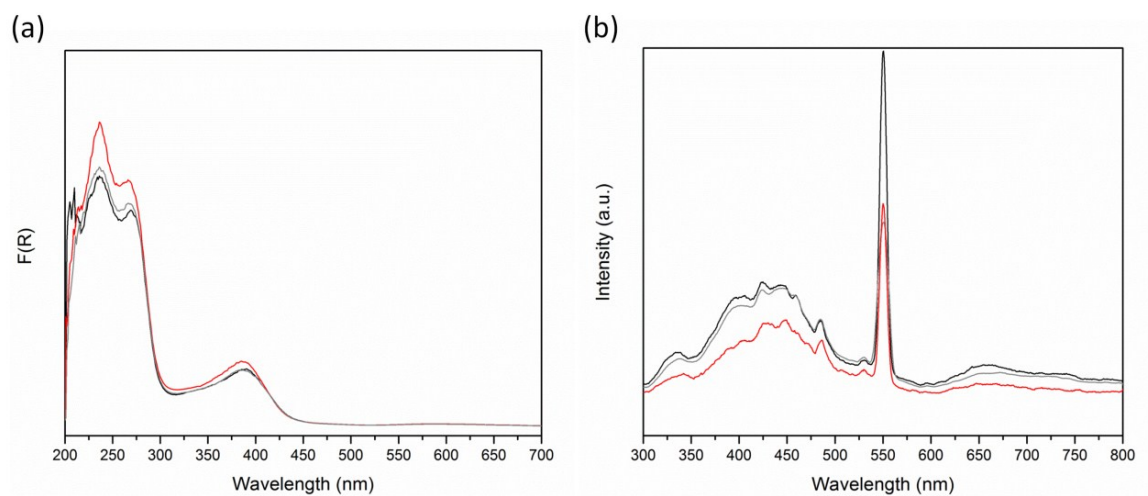
**Figure S10** Adsorption (closed symbols) and desorption (open symbols) isotherms of 195 K  $\text{CO}_2$  for compounds **1** (green), **2** (blue), and **3** (red).



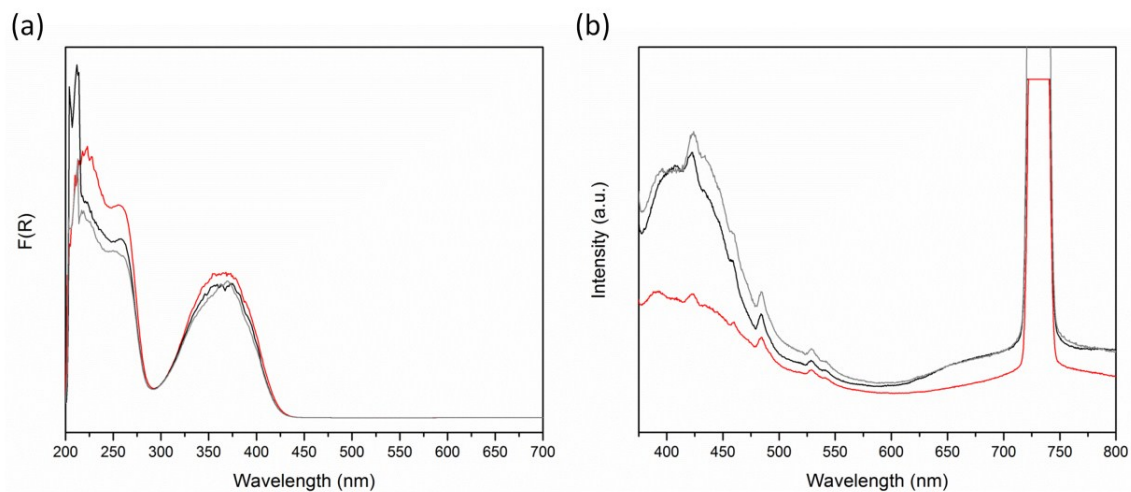


**Figure S11** The isothermic heat of adsorption profiles calculated from CO<sub>2</sub> isotherms at 298, 308 and 318 K by interpolation and the Clausius-Clapeyron equation for compounds **1** (green), **2** (blue) and **3** (red).

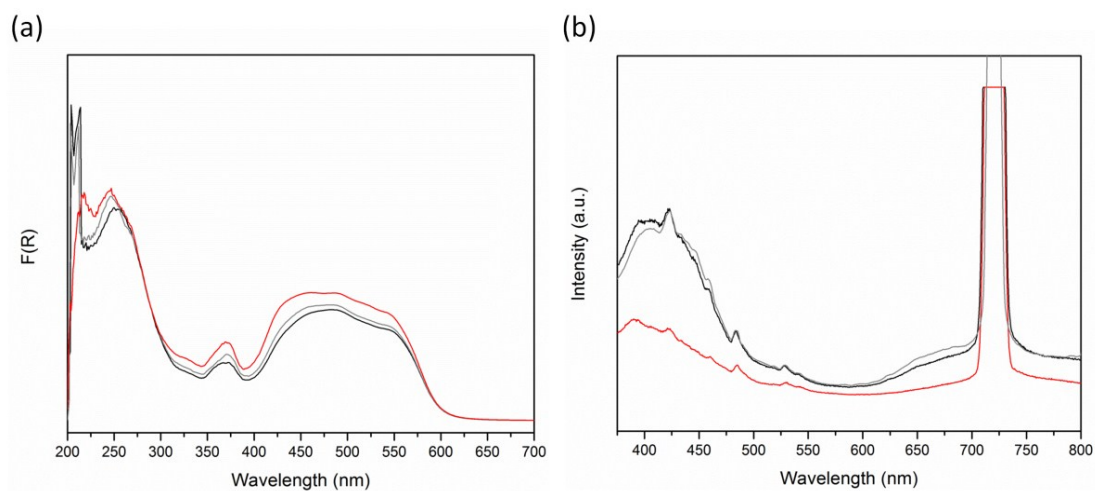
#### Interplay of optical and fluorescence properties with CO<sub>2</sub>



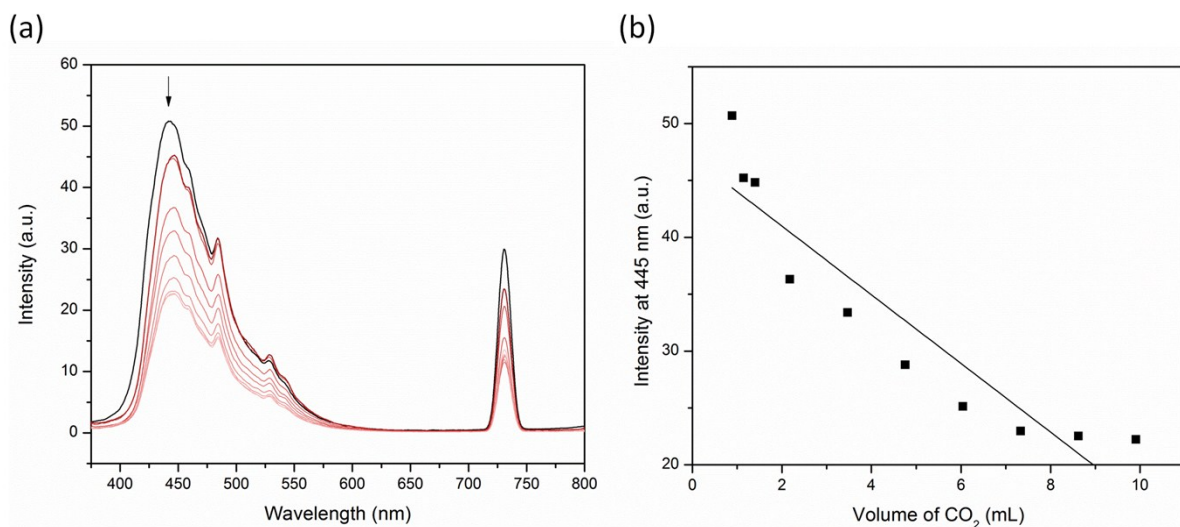
**Figure S12** (a) UV-visible spectra, and (b) fluorescence spectra following excitation at 275 nm of compound **1** under argon (black), under CO<sub>2</sub> (red), and re-purged with argon (grey). The peak at 550 nm in the emission spectrum is due to a second-order transmission through the emission monochromators.



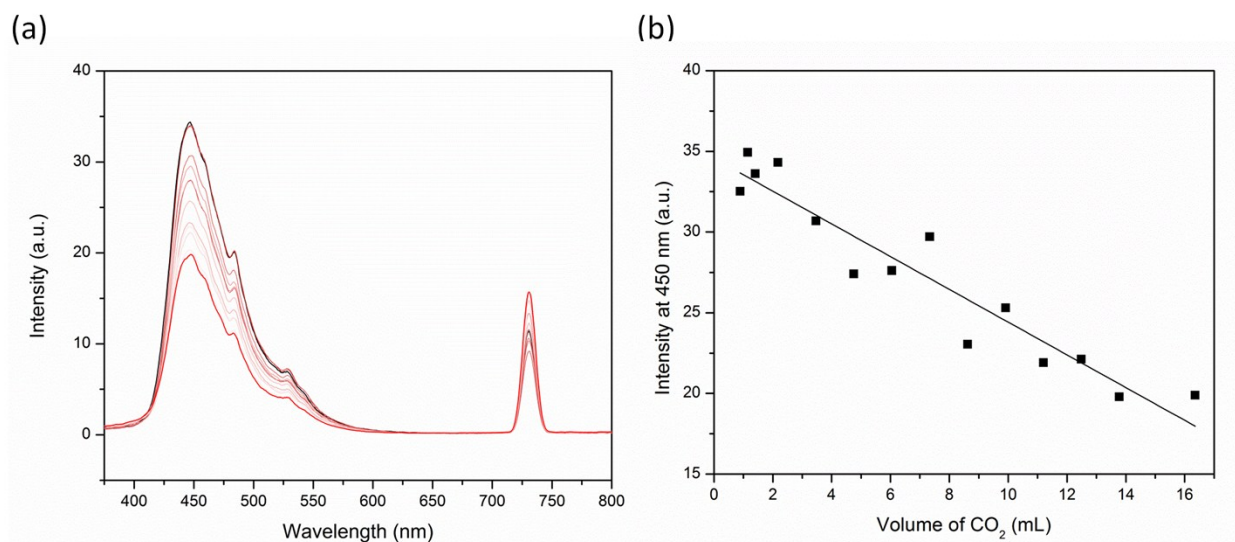
**Figure S13** (a) UV-visible spectra, and (b) fluorescence spectra following excitation at 365 nm of compound **2** under argon (black), under CO<sub>2</sub> (red), and re-purged with argon (grey). The peak at 730 nm in the emission spectrum is due to a second-order transmission through the emission monochromators.



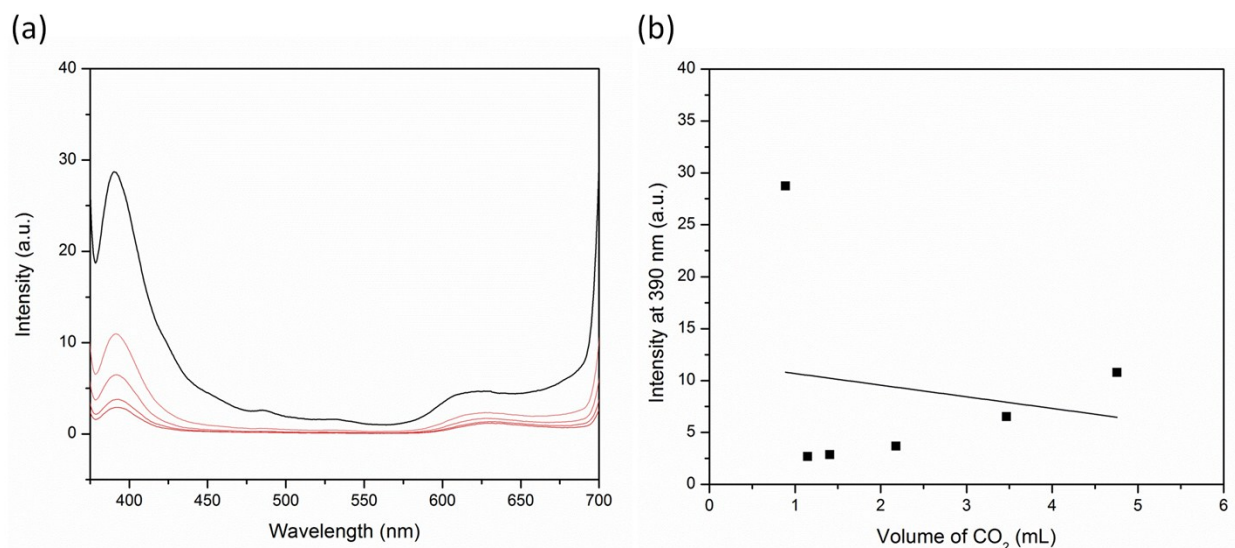
**Figure S14** (a) UV-visible spectra, and (b) fluorescence spectra following excitation at 360 nm of compound **3** under argon (black), under CO<sub>2</sub> (red), and re-purged with argon (grey). The peak at 720 nm in the emission spectrum is due to a second-order transmission through the emission monochromators.



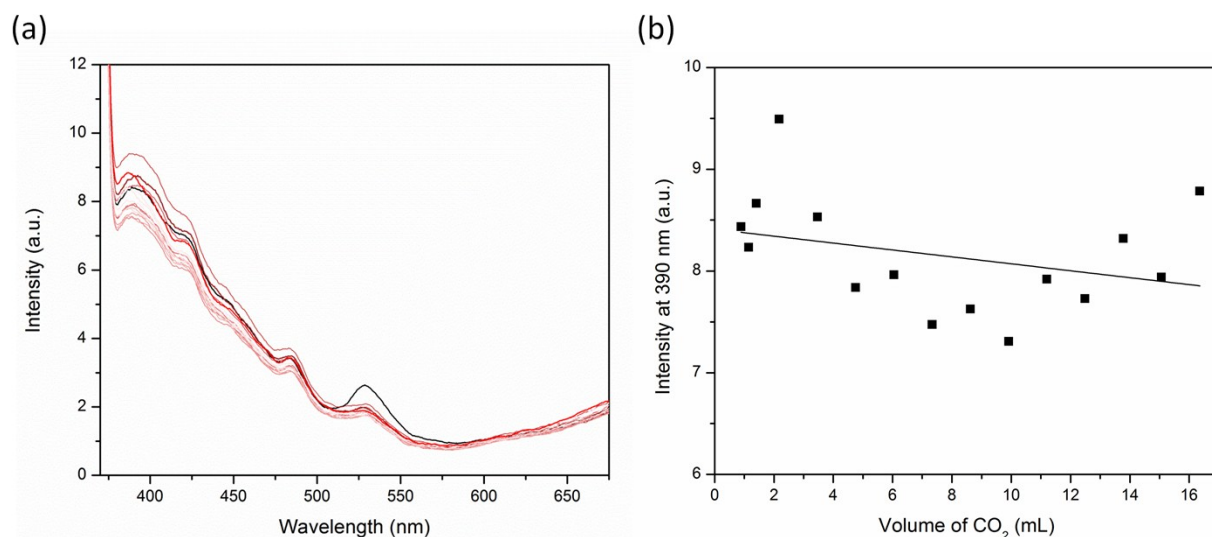
**Figure S15** (a) Fluorescence response of a suspension of compound **2** in water degassed with Ar (black) with incremental CO<sub>2</sub> dosing (red) following excitation at 365 nm, and (b) intensity at 460 nm vs. volume of CO<sub>2</sub> dosed.



**Figure S16** (a) Fluorescence response of a suspension of compound **2** in DMF degassed with Ar (black) with incremental CO<sub>2</sub> dosing (red) following excitation at 365 nm, and (b) intensity at 460 nm vs. volume of CO<sub>2</sub> dosed.



**Figure S17** (a) Fluorescence response of a suspension of compound **3** in water degassed with Ar (black) with incremental CO<sub>2</sub> dosing (red) following excitation at 360 nm, and (b) intensity at 460 nm vs. volume of CO<sub>2</sub> dosed.



**Figure S18** (a) Fluorescence response of a suspension of compound **3** in DMF degassed with Ar (black) with incremental CO<sub>2</sub> dosing (red) following excitation at 360 nm, and (b) intensity at 460 nm vs. volume of CO<sub>2</sub> dosed.

## References

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- [4] B. Roy, T. Noguchi, D. Yoshihara, Y. Tsuchiya, A. Dawn, S. Shinkai, *Organic & Biomolecular Chemistry* **2014**, *12*, 561-565.
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