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Supplementary information for

Frustrated Lewis pair-mediated fixation of CO₂ within a metalorganic framework

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Experimental section

General considerations

All of the chemicals are commercially available and were used without any further purification. ¹H (400.13 MHz), ¹⁹F (376.60 MHz) and ¹³C (100.62 MHz) NMR spectra were recorded on a Bruker Avance II 400 spectrometer at 298 K. High-resolution mass spectra were recorded on a Micromass Q-TOF Ultima API (ESI). Infrared spectra were collected on a Perkin Elmer FT-IR/FIR Frontier Spectrometer from 400 to 4000 cm⁻¹. Thermogravimetric analysis (TGA) was performed under N₂ on a TGA Q 500, V20.13 with a balance gas flow of 10 mL/min and a sample gas flow of 25 mL/min. Powder X-ray diffraction data were collected on a Bruker D8 Advance using Cu *Ka* radiation ($\lambda = 1.5418$ Å, 50 kW/40mA). Sorption data were acquired using the Intelligent Gravimetric Analyzer (IGA).

MOF-545 synthesis

MOF-545 was synthesized according to the known procedure.¹ Zirconyl chloride octahydrate (37.5 mg, 0.111 mmol) was added to DMF (10 mL) and sonicated for thirty minutes. Following sonication, tetrakis(4-carboxyphenyl)porphyrin (6.5 mg, 0.037 mmol) was added to the solution. After a further ten minutes of sonication, formic acid (7 mL) was added to the solution. The solution was placed in two 20 mL scintillation vials and heated at 130 °C for three days. The crystals were collected by filtration and washed with DMF (5 × 10 mL) over a three-hour period. The DMF was then replaced with acetone (5 × 30 mL) over a five-day period, after which acetone was removed by heating at 150 °C under vacuum for 48 h.

BCF adsorption in MOF-545

MOF-545 (25 mg) was dispersed in 6 mL of dry toluene, containing 50 mg of BCF, and left for three hours. Then, the solution was centrifuged, and an aliquot was taken from the supernatant solution. The concentration of BCF in the aliquot was determined by ¹⁹F NMR with 1,4-dibromotetrafluorobenzene as an internal standard.

CO₂ reduction experiment with MOF-545 under pressure

Mixing of the reagents was made in a glovebox, under nitrogen atmosphere. MOF-545 (25 mg) was placed in a glass vial, equipped with a magnetic stirring bar. Then $B(C_6F_5)_3$ (50 mg, 0.097 mmol) were added and the resulting mixture was dispersed in 6 mL of dry toluene. The vial was placed in a 20 mL steel reactor. The reactor was filled with H₂ (20 bars) and left for 1 h at rt with stirring, with consequent charging with CO₂ (20 bars) and vigorous stirring for additional 20 h under 100°C. After the reaction an aliquot was taken and analyzed by mass spectrometry and NMR. For the next cycle, the filtered MOF solid after the reaction was dispersed in a solution containing 50 µL of TEA in 10 mL of acetone, stirred for 30 min, centrifuged, washed with acetone three times and dried under vacuum at 150°C overnight.



Figure S1. ¹⁹F NMR spectra of BCF solution in toluene (1,4-dibromotetrafluorobenzene as an internal standard) before adsorption by MOF-545 (upper spectrum) and after (lower spectrum)

Synthesis of tetraphenylporphyrin (TPP)

To a refluxing solution of benzaldehyde (1.06 g, 10 mmol) in propionic acid (10 mL) a solution of pyrrole (0.67 g, 10 mmol) in propionic acid (10 mL) was added dropwise. After refluxing for 2 h under stirring, the mixture was cooled to rt and left for 12 h. The mixture was filtered, then the precipitate washed with methanol, dried in vacuum, and subjected to column chromatography (silica gel, 50% CHCl₃/hexane) to obtain TPP (0.21 g, 13%) as purple crystals; m.p.: >250 °C. ¹H NMR (400.13 MHz, CDCl₃) δ : -2.78 (broad s, 2H), 8.84 (s, 8H), 8.21 (m, 8H), 7.76 (m, 12H). ¹³C NMR (100.62 MHz, CDCl₃) δ : 142.32, 134.71, 130.99, 128.17, 127.85, 126.83, 120.29. ESI MS m/z 615.2560 (calcd 615.2549 [M+H]⁺).

CO₂ reduction experiment with TPP under high pressure

Mixing of the reagents was performed in a glovebox under a nitrogen atmosphere. TPP (60 mg, 0.097 mmol) were placed in a glass vial, equipped with a magnetic stirring bar. Then $B(C_6F_5)_3$ (50 mg, 0.097 mmol) was added and the resulting mixture was dissolved in dry toluene (6 mL), giving a purple solution. The vial was placed in a 20 mL steel reactor. The reactor was filled with H₂ (20 bars) and left for 1 h under rt and stirring, with consequent charging with CO₂ (20 bars) and vigorous stirring for additional 20 h under 100°C. After the reaction the green liquor was filtered and analyzed by mass spectrometry and NMR without any further purification steps.



CH₃OH

Figure S2. a) Schematic representation of the reaction of CO_2 reduction by hydrogen in the presence of MOF-545; b) Proposed mechanism for frustrated Lewis pair-mediated CO_2 reduction.^{2,3}



Figure S3. ESI MS spectrum of the reaction mixture for CO₂ reduction with MOF-545 ($H_2 - 20$ bars, CO₂ - 20 bars, 100°C, 20 h); negative mode.



Figure S4. IR spectra of the MOF-545 before and after the reaction of CO_2 reduction (H₂ – 20 bars, CO_2 – 20 bars, 100°C, 20 h).



Figure S5. TGA for the MOF-545 before and after the reaction of CO_2 reduction (H₂ – 20 bars, CO_2 – 20 bars, 100°C, 20 h).



Figure S6a. ESI MS spectrum of the reaction mixture for CO_2 reduction experiment with TPP (H₂ – 20 bars, CO_2 – 20 bars, 100°C, 20 h); positive mode.



Figure S6b. ESI MS spectrum of the reaction mixture for CO_2 reduction experiment with TPP (H₂ – 20 bars, CO_2 – 20 bars, 100°C, 20 h); negative mode.

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