

Supporting Information

Nitrogen-Enriched Flexible Metal-Organic Framework for CO₂ Adsorption

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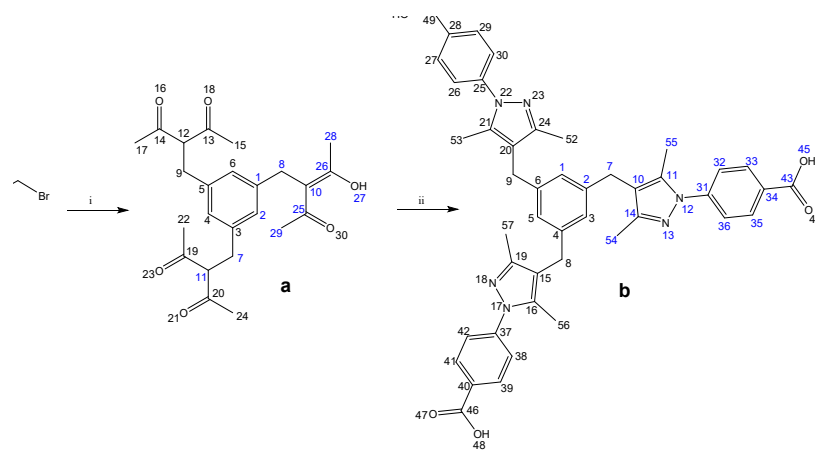
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Synthesis and characterization of the linker

The linker was synthesized according to the reaction shown in scheme 1.



- i) acac, KOt-Bu, THF dry, KI, N₂, 24 h, reflux
ii) AcOH, EtOAc, 4-hydrazinobenzoic acid, 24 h, reflux

Scheme 1. Synthesis of the linker

Step 1. Synthesis of (Z)-3,3'-((5-(2-acetyl-3-hydroxybut-2-en-1-yl)-1,3-phenylene)bis(methylene))bis(pentane-2,4-dione) (Precursor-a)

In a 250 mL two-necked round-bottomed flask with a magnetic stir bar and reflux condenser under nitrogen atmosphere was added potassium (1.72 g, 0.044 mol) and dry tert-butyl alcohol (57.15 mL). The mixture was heated to reflux and stirring for three hours until complete dissolution of the potassium. Next, acetylacetone (6.43 g, 0.064 mol) was added dropwise to the stirred, refluxing solution. After 1 hour, the solution of 1,3,5-tris(bromomethyl)benzene (5.00 g, 0.014 mol) in dry tetrahydrofuran (72 mL) was added dropwise, it was left for another hour and then potassium iodide (0.43 g) was added. The reaction mixture was stirred and heated at reflux temperature for 24 hours. Three-fourths of the solvent was extracted by distillation and then washed with water and extracted with benzene. The organic phase was dried over magnesium sulfate anhydrous, solvent and excess acetylacetone was removed in vacuum obtaining a dark-yellow oil. Finally, the product was purified by column chromatography on silica gel (acetone/hexane 1:4 v/v) to afford a light-yellow oil.

^1H NMR assignments for C_i correspond to mono and dienol molecules involved in the tautomeric equilibrium, so the number of H is the sum of the moiety in both of them.

Yield: 47.36%. **^1H NMR** (400 MHz, CDCl_3 , 298K): δ/ppm = 16.77 (s, 18H, H_{27}), 6.73 (s, 6H, H_2), 3.92 (t, $J_{\text{HH}}=7.55$ Hz, 3H, H_{11}), 3.57 (s, 6H, H_8), 3.08 (q, 7.55 $J_{\text{HH}}=7.55$ Hz, 6H, H_7), 2.10 (s, 18H, H_{29}), 2.04 (s, 18H, H_{28}). **^{13}C NMR { ^1H }** (100 MHz, CDCl_3 , 298K): δ/ppm = 203.32 (C_{25}), 191.94(C_{26}), 140.96 (C_3), 139.09 (C_1), 125.74 (C_2), 108.22 (C_{10}), 69.93 (C_{11}), 34.04 (C_7), 32.89 (C_8), 29.70 (C_{29}), 23.41 (C_{28}). **DEPT-135** (100 MHz, DMSO-d_6 , 298 K): δ/ppm =125.62 (C_2), 69.80 (C_{11}), 33.97(C_7), 32.76 (C_8), 29.65 (C_{29}), 23.28 (C_{28}). **$^1\text{H},^{13}\text{C}$ -HSQC** (400 MHz/100 MHz, CDCl_3 , 298 K): $\delta(^1\text{H})/\delta(^{13}\text{C})$ = 6.72/125.75 (H_2/C_2), 3.89/69.91 ($\text{H}_{11}/\text{C}_{11}$), 3.54/32.88 (H_8/C_8), 3.03/34.03 (H_7/C_7), 2.07/29.72 ($\text{H}_{29}/\text{C}_{29}$), 2.00/23.40 ($\text{H}_{28}/\text{C}_{28}$). **$^1\text{H},^{13}\text{C}$ -HMBC** (400 MHz/100 MHz, CDCl_3 , 298 K): $\delta(^1\text{H})/\delta(^{13}\text{C})$ = 3.54/108.22, 125.75, 140.96, 191.94 ($\text{H}_8/\text{C}_{10/2/3/26}$), 3.03/125.75 (H_7/C_2), 2.07/203.32 ($\text{H}_{29}/\text{C}_{25}$), 2.00/191.94 ($\text{H}_{28}/\text{C}_{26}$). **FT-IR (Nujol):** ν/cm^{-1} = 3530 (w), 3410 (w), 3010 (w), 2924 (m), 2853 (w), 1727 (s), 1605 (m), 1450 (m), 1358 (m), 1257 (w), 1149 (s), 956 (s), 841 (w), 748 (m), 710 (w), 625 (w), 525 (m), 447 (w), 301 (s), 270 (s). **HRMS(HESI):** m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{24}\text{H}_{30}\text{O}_6$ (415.21), found 415.21. **UV-Vis** (nm): 292.

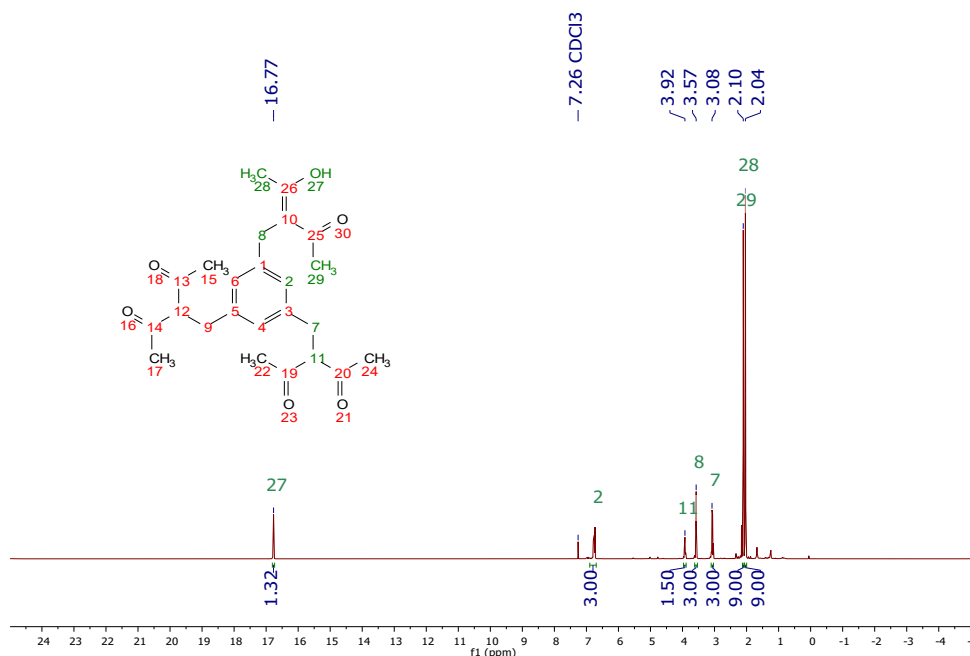


Figure S1. 400 MHz ^1H NMR spectrum of the precursor in CDCl_3

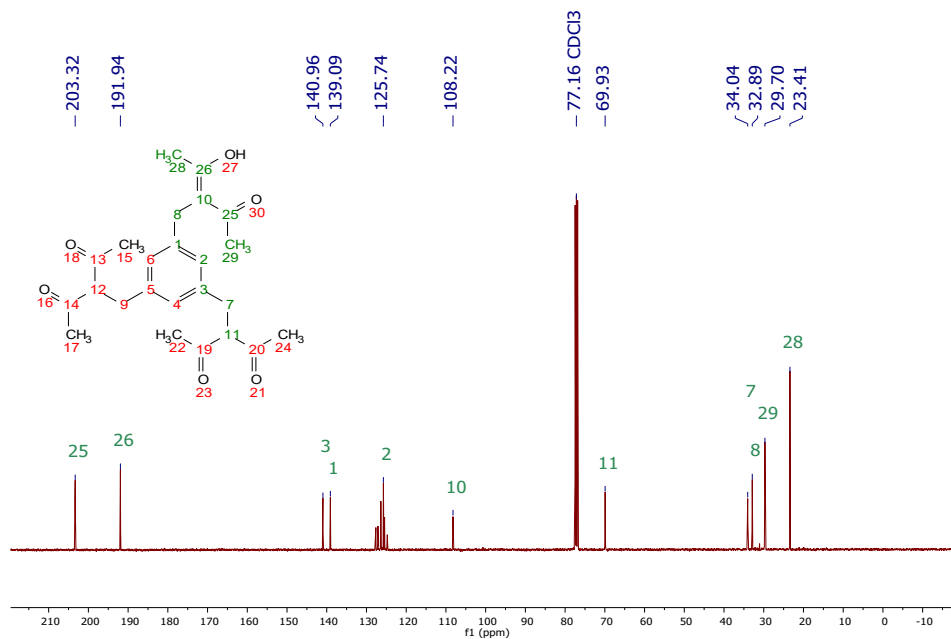


Figure S2. 400 MHz ¹³C NMR spectrum of the precursor in CDCl₃

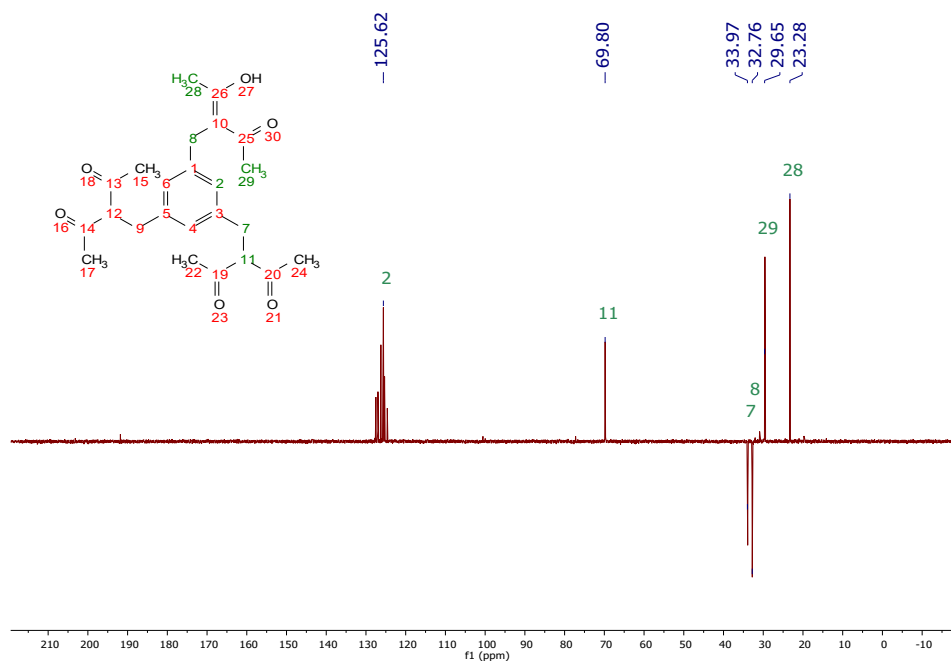


Figure S3. DEPT-135 NMR spectrum of the precursor in CDCl₃

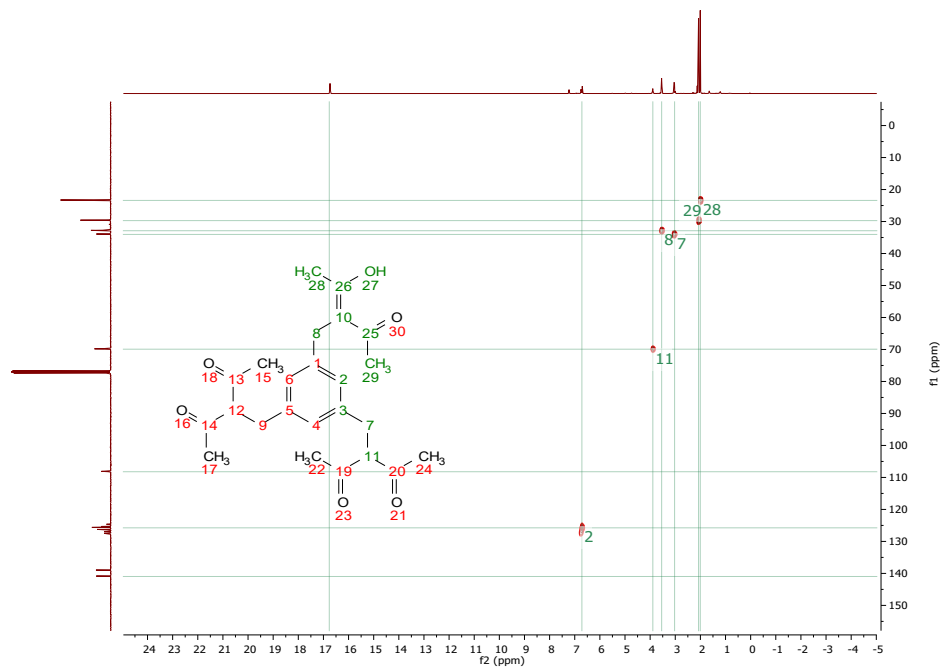


Figure S4. 400 MHz HSQC NMR spectrum of the precursor in CDCl_3

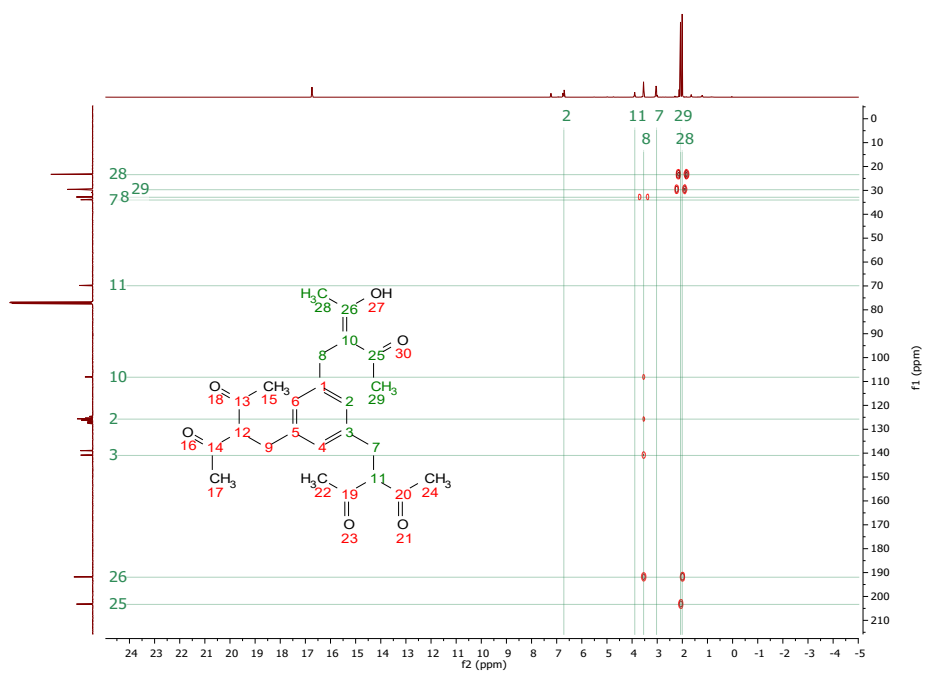


Figure S5. 400 MHz HMBC NMR spectrum of the precursor in CDCl_3

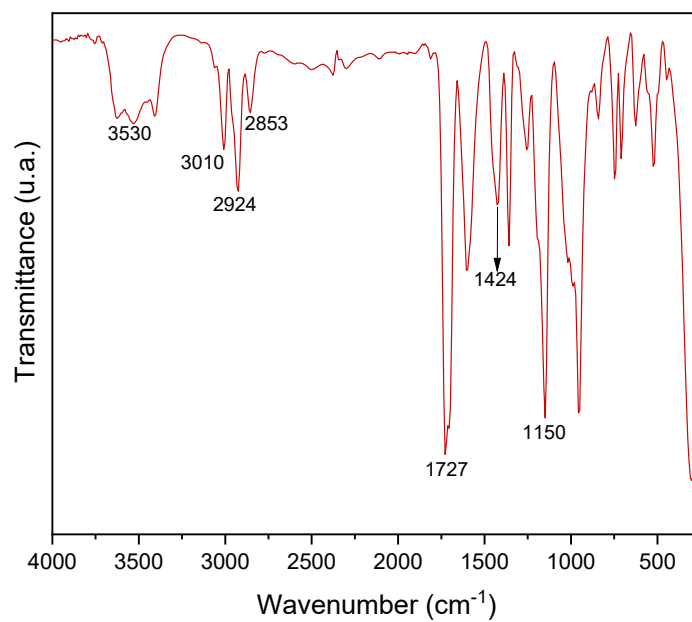


Figure S6. FT-IR Spectrum of the precursor in KBr

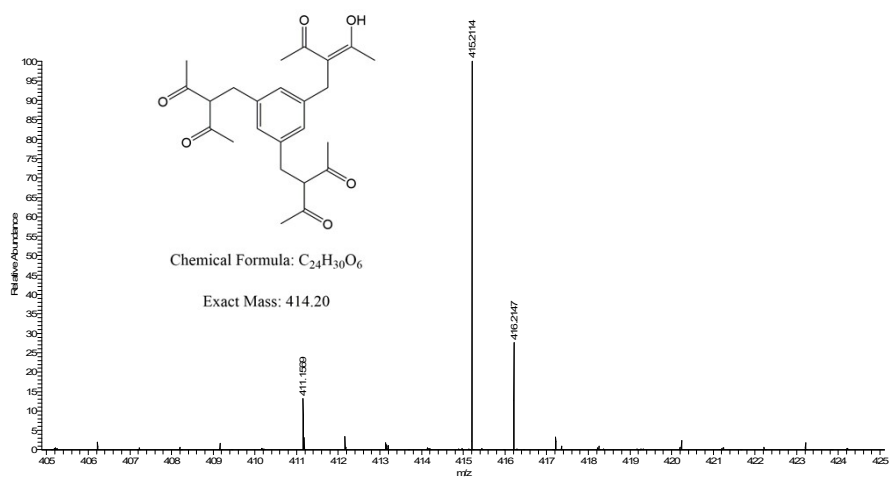


Figure S7. HRMS Spectrum of the precursor

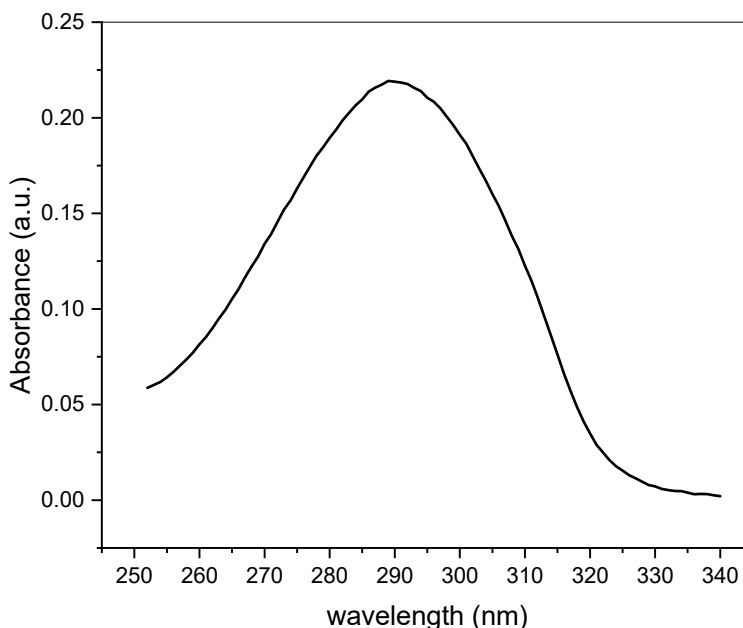


Figure S8. UV-Vis Spectrum of the precursor in CHCl_3 [0.001 M]

Step 2. 4,4',4''-(4,4',4''-(benzene-1,3,5-triyltris(methylene))tris(3,5-dimethyl-1H-pyrazole-4,1-diyl))tribenzoic acid (Linker)

The precursor a (1.60 g, mmol), ethyl acetate (75 mL) and acetic acid (15 mL) were added to a 500 mL two-neck round bottom flask with a magnetic stir bar and a reflux condenser. It was heated to reflux to dissolve the mixture and stirred for 1 hour. Then, to the dissolution, 4-hydrazinobenzoic acid (1.71 g, 11.238 mmol) was added and kept under reflux and stirring for 24 hours. The product obtained was filtrated and washed with water and ethyl acetate (x3). Finally, it was dried in a vacuum oven at 60 °C for 12 hours.

^1H NMR (400 MHz, CDCl_3 , 298K): δ /ppm= 13.01 (s, 1H, H_{45}), 8.00 (d, $J_{\text{HH}}=8.62$ Hz, 2H, $\text{H}_{33,35}$), 7.58 (d, $J_{\text{HH}}=8.62$ Hz, 2H, $\text{H}_{32,36}$), 6.79 (s, 1H, H_3), 3.69 (s, 2H, H_7), 2.25 (s, 3H, H_{55}), 2.04 (s, 3H, H_{54}). **^{13}C NMR** (^1H) (100 MHz, CDCl_3 , 298K): δ /ppm= 166.68 (C_{43}), 148.24 (C_{14}), 143.16 (C_{31}), 140.80 (C_2), 136.46 (C_{11}), 130.29 ($\text{C}_{33,35}$), 128.42 (C_{34}), 125.37 (C_1), 123.01 ($\text{C}_{32,26}$), 117.94 (C_{10}), 28.57 (C_7), 11.87 (C_{54}), 11.18 (C_{55}). **DEPT-135** (100 MHz, DMSO-d_6 , 298 K): δ /ppm = 130.03 ($\text{C}_{33,35}$), 125.11 (C_3), 122.75 ($\text{C}_{32,26}$), 28.31 (C_7), 11.62 (C_{54}), 10.92 (C_{55}). **$^1\text{H},^{13}\text{C}$ -HSQC** (400 MHz/100 MHz, CDCl_3 , 298 K): $\delta(^1\text{H})/\delta(^{13}\text{C})$ = 8.01/130.73 ($\text{H}_{33,35}/\text{C}_{33,35}$), 7.59/123.46 ($\text{H}_{32,36}/\text{C}_{32,36}$), 6.79/125.83 (H_3/C_3), 3.70/29.02 (H_7/C_7), 2.25/11.62 ($\text{H}_{55}/\text{C}_{55}$), 2.04/12.37 ($\text{H}_{54}/\text{C}_{54}$). **$^1\text{H},^{13}\text{C}$ -HMBC** (400 MHz/100 MHz, CDCl_3 , 298 K): $\delta(^1\text{H})/\delta(^{13}\text{C})$ = 8.01/143.43, 166.63 ($\text{H}_{33,35}/\text{C}_{34/43}$), 7.59/128.42 ($\text{H}_{32,36}/\text{C}_{31}$), 6.79/28.55, 140.69 ($\text{H}_3/\text{C}_{7/2}$), 3.69/117.90, 125.38, 136.43, 140.69, 148.20 ($\text{H}_7/\text{C}_{10/3/11/2/14}$), 2.25/117.90, 136.43 ($\text{H}_{55}/\text{C}_{10/11}$), 2.04/117.90, 148.20 ($\text{H}_{54}/\text{C}_{10/14}$). **FT-IR (KBr)**: ν/cm^{-1} = 3485 (w), 3169 (w), 2917 (w), 2517 (w), 2517 (w), 1929 (w), 1721 (s), 1603 (s), 1510 (m), 1427 (m), 1373 (m), 1263 (m), 1172 (w), 1103 (m), 1041 (m), 1018 (m), 957 (w), 918 (w), 864 (m), 810 (w), 779 (s), 548 (m), 517 (m), 409 (w). **HRMS(HESI)**: m/z $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{45}\text{H}_{42}\text{N}_6\text{O}_6$ (763.32), found 763.32. **UV-Vis** (nm): 292.

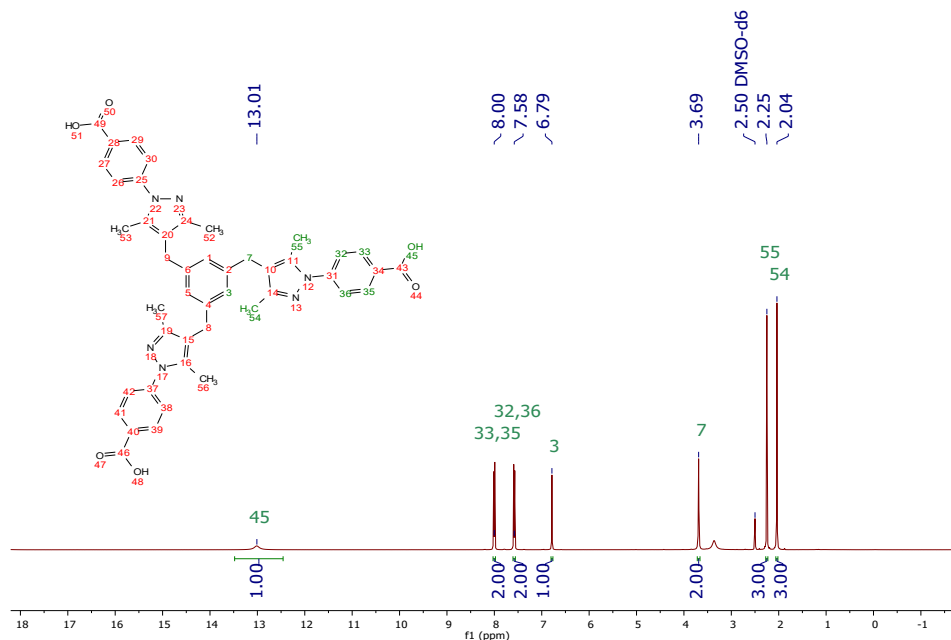


Figure S9. 400 MHz ^1H NMR spectrum of the linker in DMSO-d_6

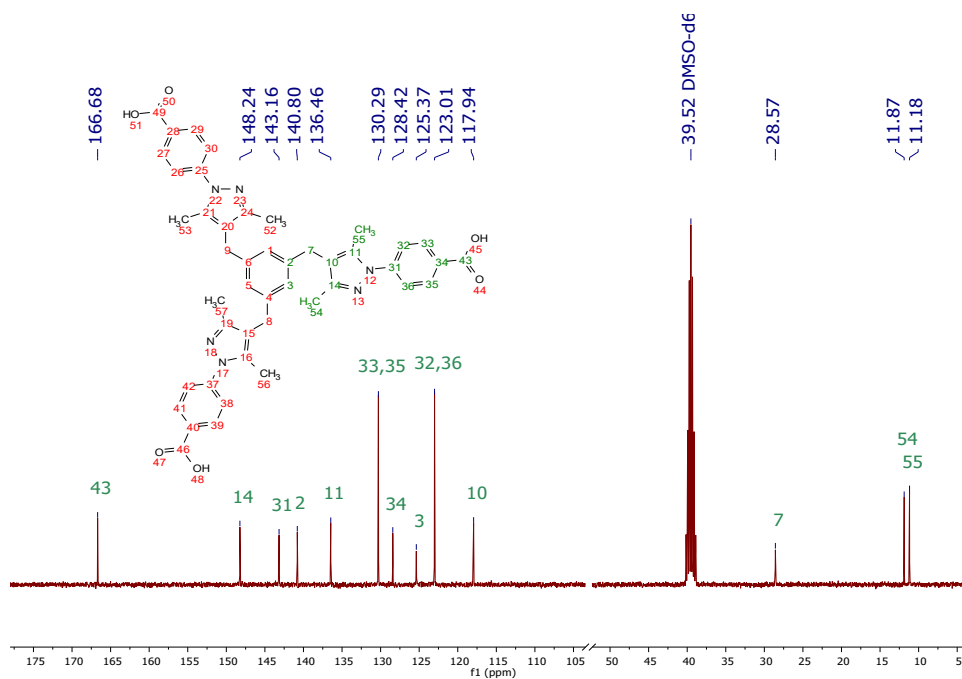


Figure S10. 400 MHz ^{13}C NMR spectrum of H_2L in DMSO-d_6

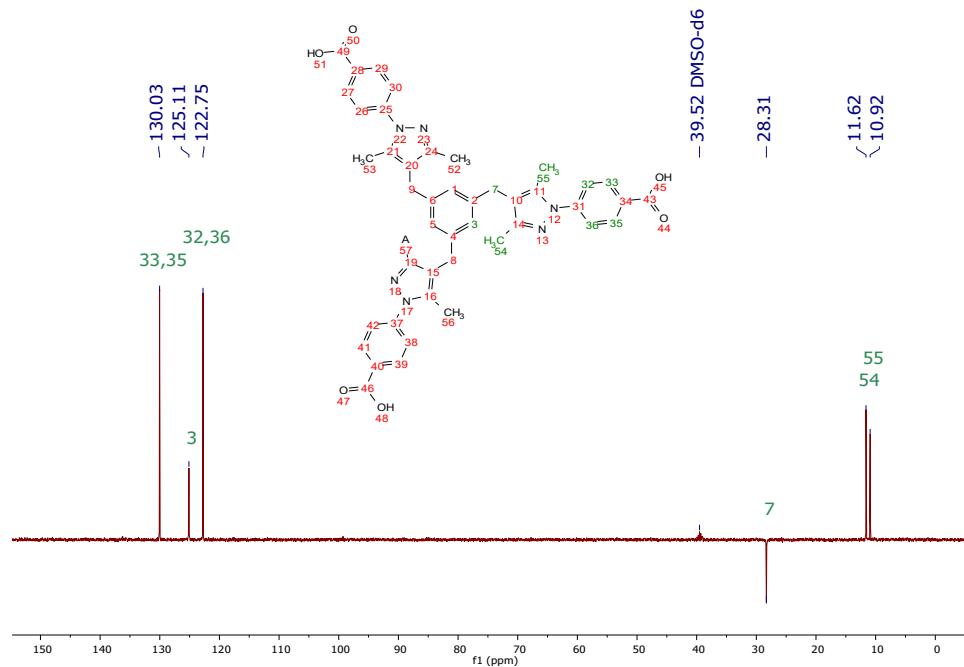


Figure S11. DEPT-135 NMR spectrum of the linker in DMSO-d₆

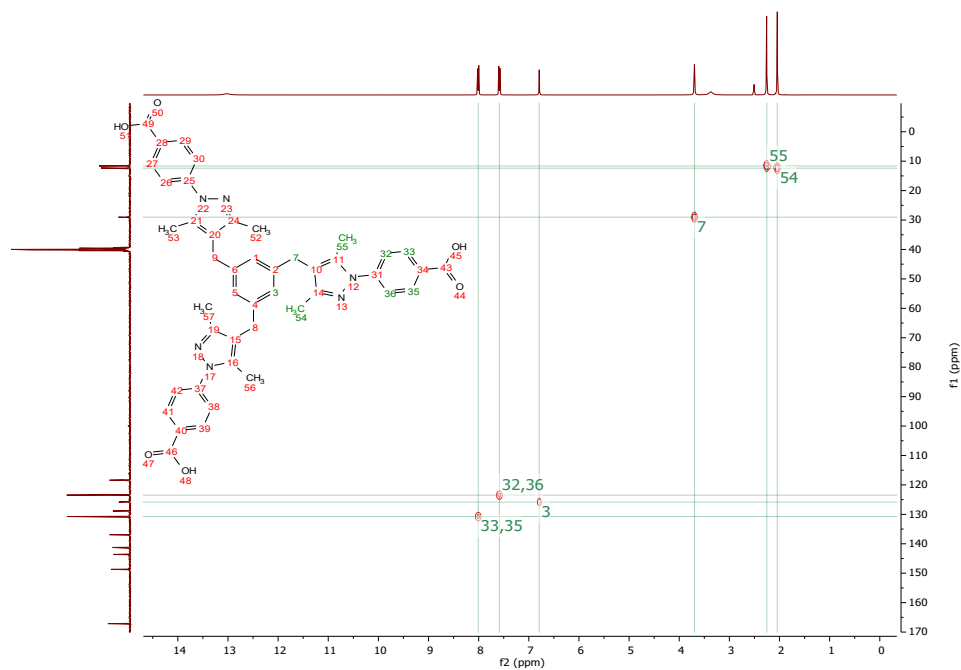


Figure S12. 400 MHz HSQC NMR spectrum of the linker in DMSO-d₆

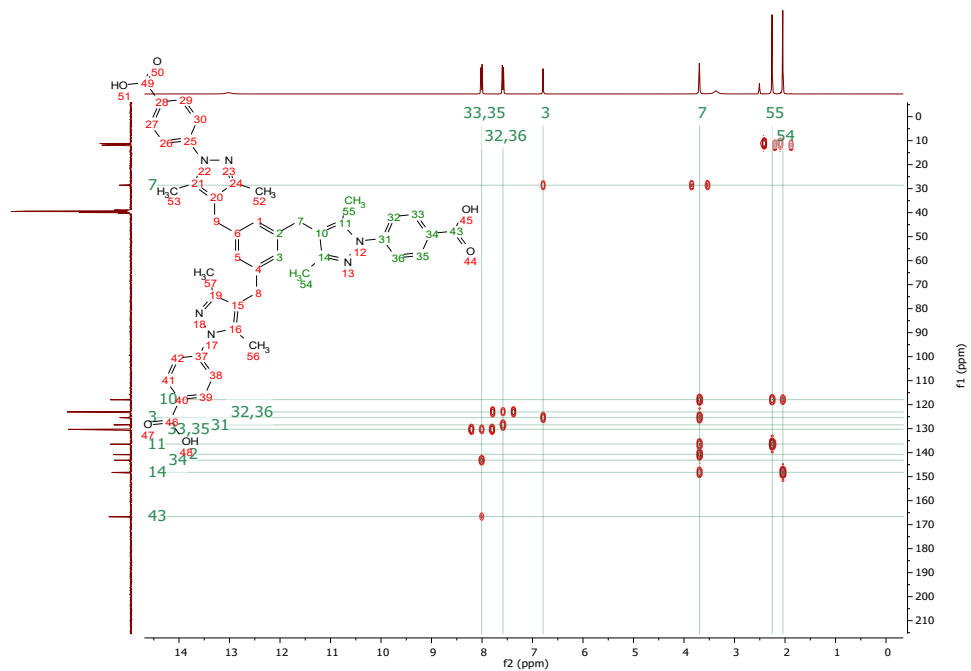


Figure S13. 400 MHz HMBC NMR spectrum of the linker in DMSO-d₆

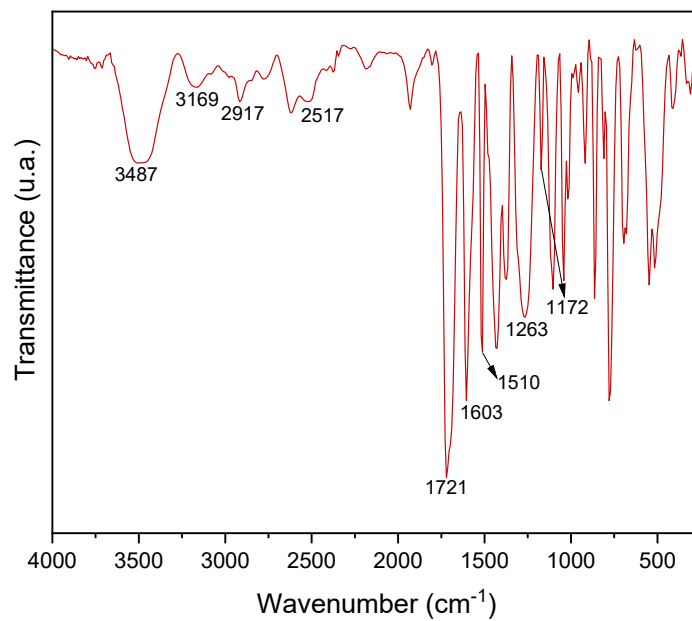


Figure S14. FT-IR Spectrum of the linker

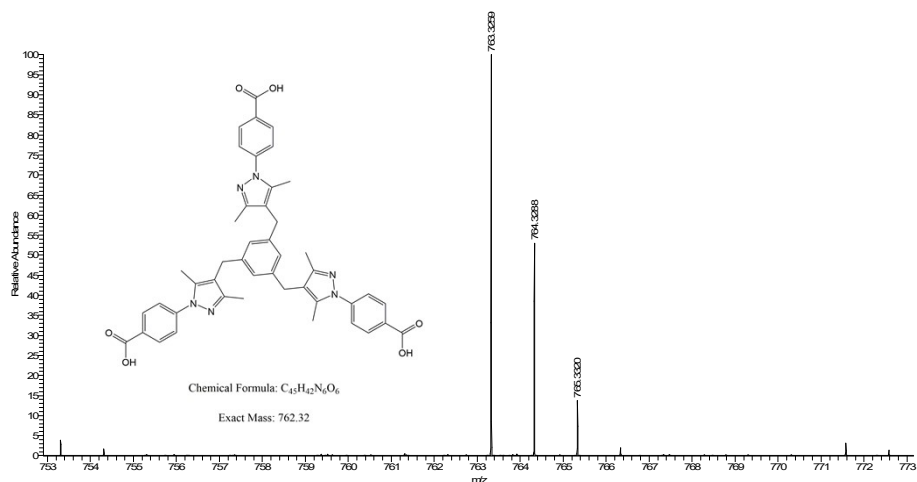


Figure S15. HRMS Spectrum of the linker

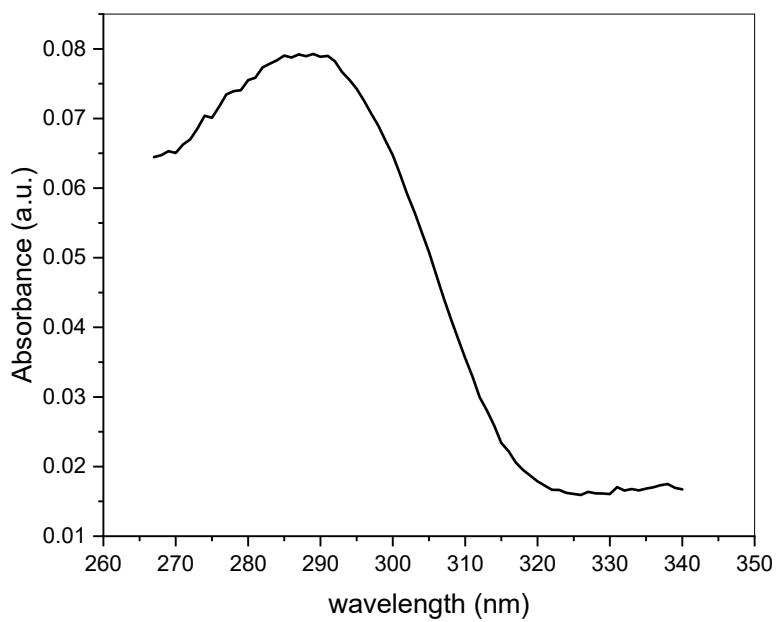


Figure S16. UV-Vis Spectrum of the linker in DMSO [0.001 M]

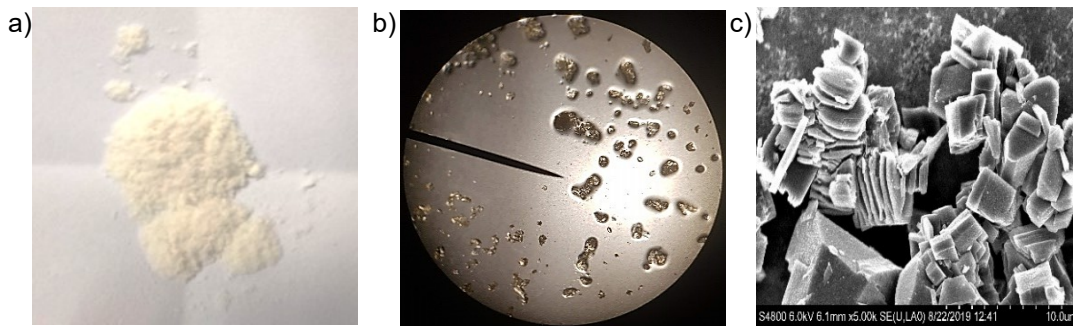
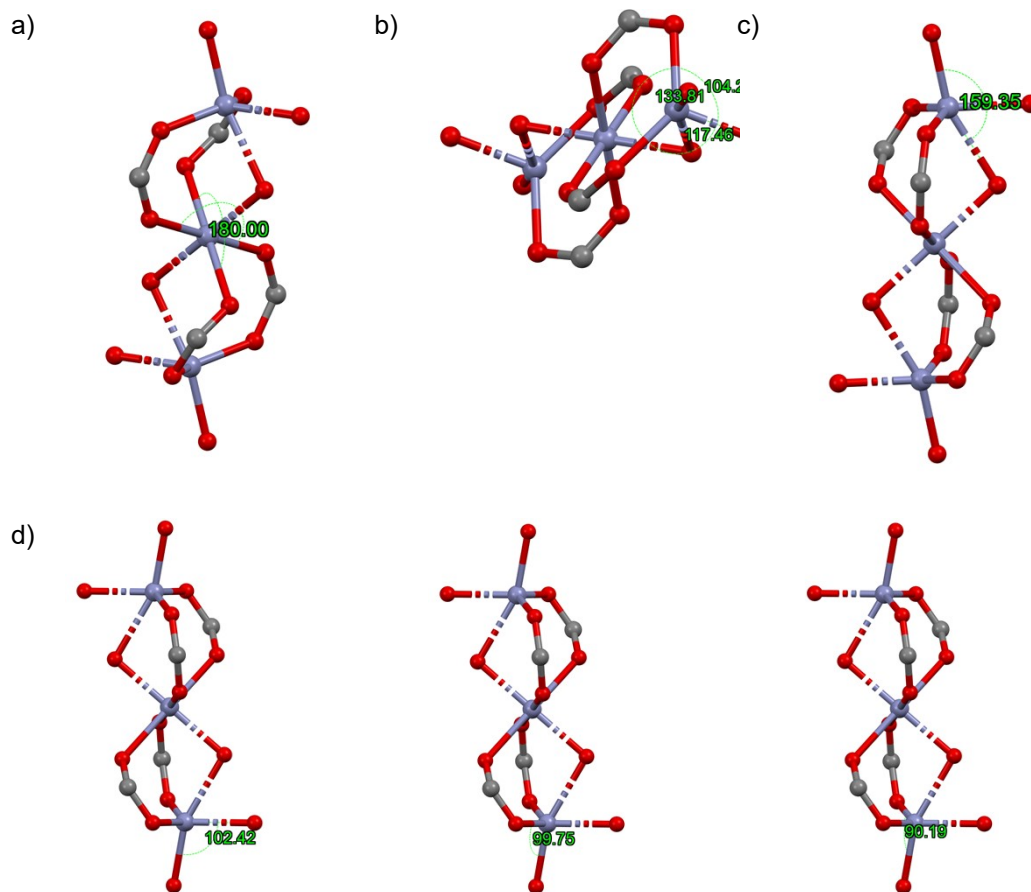


Figure S17. For $[Zn_2(L)(DMF)]$, a) Physical aspect b) Crystals images using an optical microscope (100x), and c) SEM image



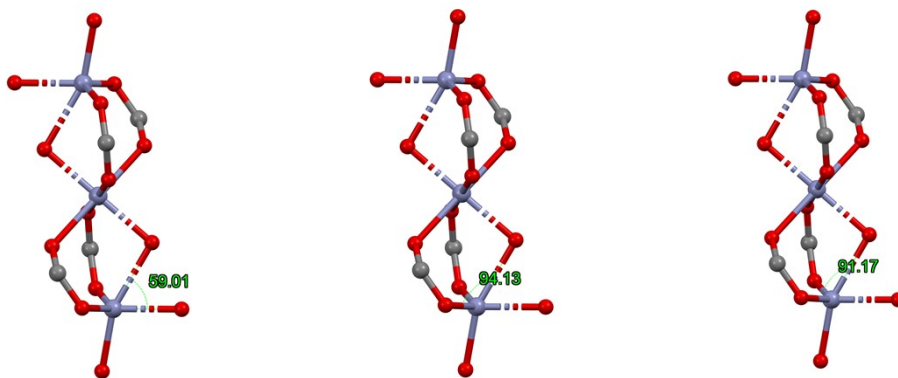


Figure S18. Angles O–Zn–O in the node of $[Zn_2(L)DMF]$ in a) octahedral structure, b) trigonal bipyramidal in axial position, c) trigonal bipyramidal in equatorial positions, and d) between oxygens of axial and equatorial positions

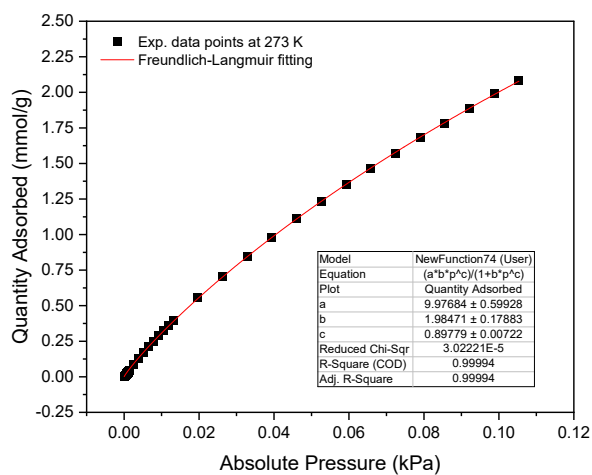


Figure S19. Freundlich–Langmuir fit for CO_2 adsorption isotherm on $[Zn_2(L)DMF]$ at 273 K.

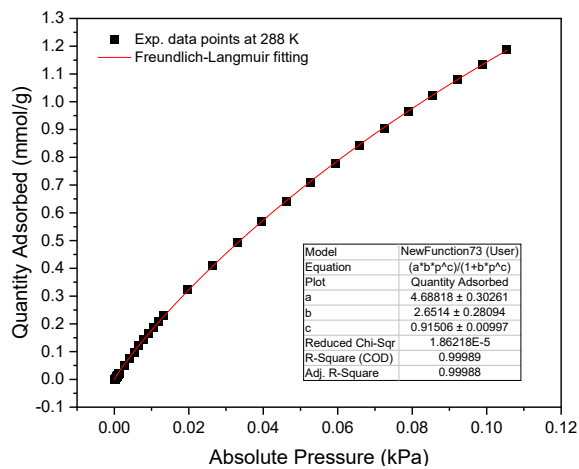


Figure S20. Freundlich–Langmuir fit for CO_2 adsorption isotherm on $[Zn_2(L)DMF]$ at 288 K.

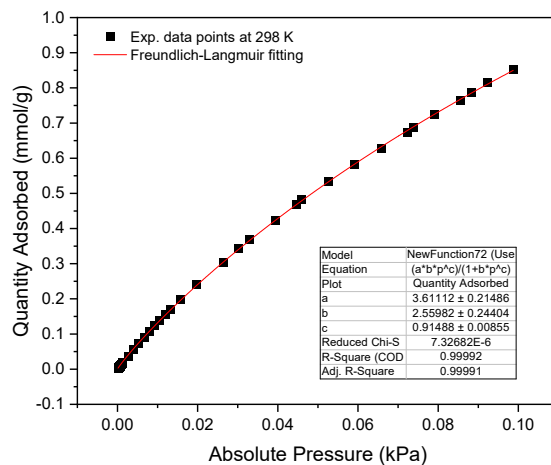


Figure S21. Freundlich–Langmuir fit for CO₂ adsorption isotherm on [Zn₂(L)DMF] at 298 K.

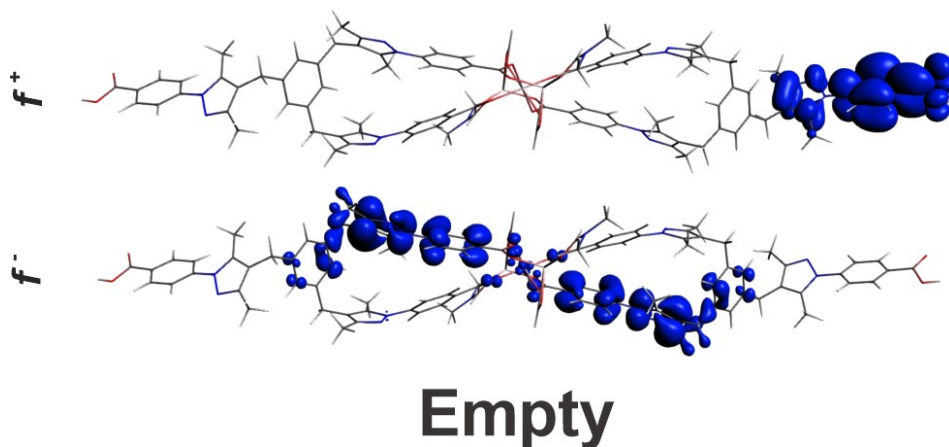


Figure S22. Frontier molecular orbital diagrams for the CO₂ system studied theoretically

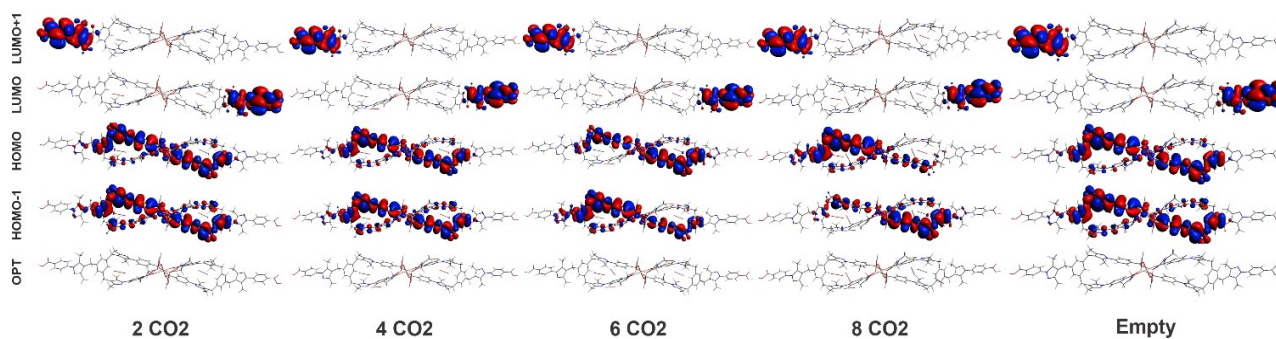


Figure S23. Fukui function plot for the empty MOF

Table S1. Crystal data and structure refinement for [Zn₂(L)DMF]

MOF	[Zn ₂ (L)DMF]
Empirical formula	C ₁₀₂ H ₁₀₆ N ₁₆ O ₁₆ Zn ₃
Formula weight	2008.13
Temperature/K	100.01(11)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	14.2475(3)
b/Å	10.38151(15)
c/Å	33.0497(5)
α/°	90
β/°	94.7685 (17)
γ/°	90
Volume/Å ³	4871.48 (15)
Z	2
ρ _{calc} (g/cm ³)	1.369
μ.mm ⁻¹	0.807
F(000)	2096
Crystal size (mm ³)	0.241 × 0.115 × 0.052
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.114 to 67.738°
Index ranges	-20 ≤ h ≤ 21, -15 ≤ k ≤ 15, -51 ≤ l ≤ 50
Reflections collected	112588
Independent reflections	17776 [R _{int} = 0.0416]
Data/restraints/parameters	17776/180/675
Goodness-of-fit on F ²	1.066
Final R indexes [>=2σ] _{eters}	R ₁ = 0.0652, wR ₂ = 0.1723
Final R indexes [all data]	R ₁ = 0.0879, wR ₂ = 0.1834
Largest diff. peak/hole / e Å ⁻³	1.636/-0.831