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Supplementary Information

Inverse CO_2/C_2H_2 Separation Assisted by Coordinated Water in a Dysprosium (III) Metal–Organic Frameworks

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Materials and Methods

1.1 Generals

All chemicals and solvents used were commercially available and used without further purifications. Powder X-ray diffraction (PXRD) data were collected with a Rigaku-Miniflex-600 X-ray powder diffractometer or a Rigaku SmartLab using Cu Kα radiation (λ = 1.5406Å nm). Field emission scanning electron microscope (FE-SEM) experiments were characterized by FEI Verios G4 SEM. Thermogravimetric analysis (TGA) was carried out in a flow of nitrogen using a TGA-2 (METTLER TOLEDO) with a heating rate of 10 °C/min.

1.2 Preparation of Dy-F-oxa

The powder sample of **Dy-F-oxa** were prepared according to the literature report with some modifications[1,2]. To a 100 mL Teflon vial, 20 mL $Dy(NO_3)_3 \cdot 6H_2O$ (0.02 M), 20 mL NaF (0.02 M) and 20 mL $Na_2C_2O_4$ (0.02 M) aqueous solutions were added and heated to *ca*. 60 °C under stirring. The precipitate was collected by filtration and washed with distilled water. Yield (based on Dy): 90.5%.

1.3 Gas adsorption

A Micromeritics 3Flex instrument was used for recording all gas sorption isotherms, CO_2 (195, 273 and 298 K) and C_2H_2 (273 and 298 K). For N_2 adsorption isotherms, the temperature was controlled at 77 K using a Dewar containing 4 L liquid N_2. Precise control of 273 K and 298 K temperatures was implemented by a dc-2006 from Ningbo Scientz Biotechnology, which contained a cyclic control system of ethylene glycol and water mixture (*v*/*v* = 1:1). Helium was used for the estimation of dead space for gas and water adsorption measurements. The activation of the **Dy-F-oxa** sample was achieved by degassing for 4 h at 80 ^{o}C under a dynamical vacuum using a degassing station.

1.4 Isosteric heat of adsorption

A virial-type expression of the below form was used to fit the combined isotherm data of CO_2 and C_2H_2 at 273 and 298 K, where *P* is the pressure described in Pa, *N* is the adsorbed amount in mmol/g, *T* is the temperature in K, a_i and b_i are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

$$Q_{\mathrm{st}} = -R\sum_{i=0}^{5} a_i N^i$$

1.5 Langmuir-Freundlich fitting

The isothermal for different gases at 298 K were fitted using the Langmuir-Freundlich model as following:

$$q = q_{sat}\frac{b_A p^n}{1 + b_A p^n}$$

where q and q_{sat} are gas loading at a specific pressure and saturation respectively, b_A is Langmuir-Freundlich constant at A site, n is Freundlich exponent and p is pressure.

1.6 IAST calculations of adsorption selectivity

The selectivity of equimolar CO_2/C_2H_2 binary mixtures at 298 K was calculated using ideal adsorption solution theory (IAST) method[3], and the selectivity is defined as following:

$$S = \frac{x_{\mathrm{A}}/x_{\mathrm{B}}}{y_{\mathrm{A}}/y_{\mathrm{B}}}$$

where S is the selectivity of A towards B, x_{A} and x_{B} are the molar fractions of A and B in the adsorbent respectively, y_{A} and y_{B} are the molar fractions of A and B in the gas mixture respectively.

1.7 Computational details

To understand the host-guest interactions between the framework and CO_2 and C_2H_2 molecules, the Grand Canonical Monte Carlo (GCMC) simulations were performed using the Sorption module in Material Studio software package. The simulation box for **Dy-F-oxa** was built from the single-crystal

structure with 1 × 1 × 1 supercell after making *P*1 and the CIF files were adapted from Cambridge Crystallographic Data Centre (CCDC) for free. All the frameworks and gas molecules were both treated as rigid bodies and the Q_{eq} fitted charge and the ESP charge were assigned to the hosts and guests respectively. The loading steps, equilibration steps, and production steps were all set to 2.0×10^7. The Metropolis method was applied during the simulation[4]. All the host-guest interaction behavior was described using Universal force field (UFF[5]). The cut-off radius used for the Lennard–Jones interactions is 18.5 Å.

1.8 Breakthrough experiments

The breakthrough curves were recorded on a homemade apparatus. Activated **Dy-F-oxa** 3.2g particles were prepared and packed into a stainless-steel column. An equimolar gas mixture of CO_2 and C_2H_2 (total gas pressure and flow: 100 kPa and 1 cm^3/min) passes through the packing column at 298 K, and the outlet gas concentration was monitored by a gas chromatography analyzer (TCD-Thermal Conductivity Detector, detectionS5 limit 0.1 ppm). During gas breakthrough cycling tests, the sample in the column was regenerated under He flow of 20 cm^3/min at 80 °C for 8 hours, after each breakthrough experiment.

Productivity of C_2H_2 is derived from breakthrough experiments following this definition:

$$p = \frac{F \times y_{C2H2} \times \int_{t_1}^{t_2} \frac{C(t)}{C_0} dt}{V_m}$$

where P is the C_2H_2 productivity in mmol/g, t_1 is the C_2H_2 breakthrough time in min/g, t_2 is the breakthrough time of other gas, F is the inlet gas volume flow rate, $y_{C_2H_2}$ is the volume fraction of C_2H_2 in mixed gas, $C_{(t)}$ is the C_2H_2 concentration in the outlet gas, C_0 is the C_2H_2 concentration in the inlet gas, V_m is molar volume of gas.

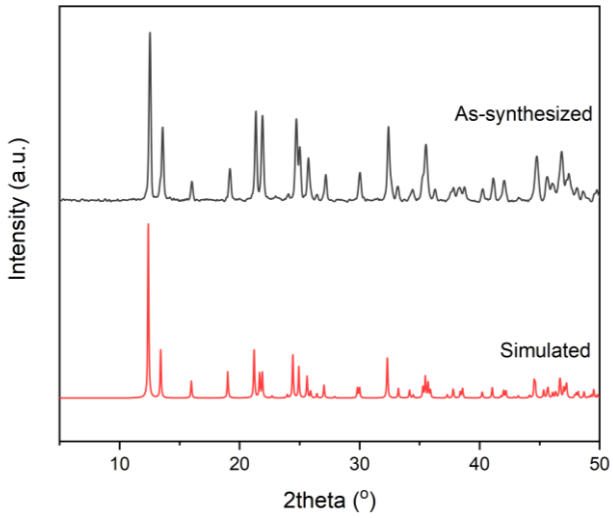


Fig. S1 As-synthesized (black) and simulated (red) PXRD patterns of **Dy-F-oxa**.

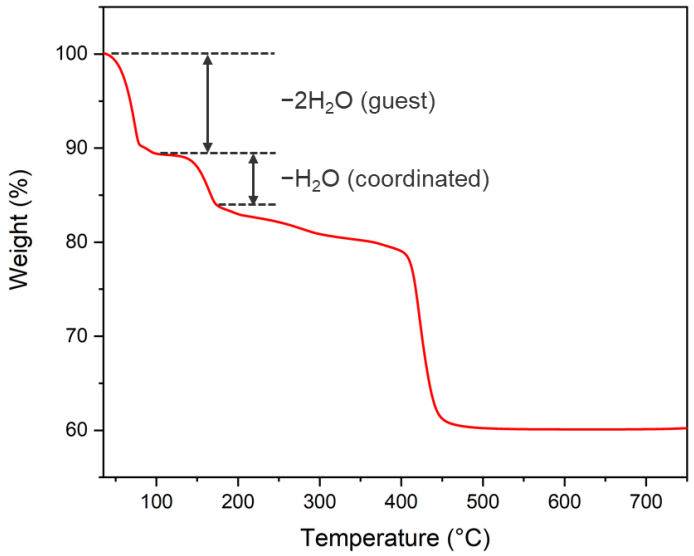


Fig. S2 TGA curve of **Dy-F-oxa**.

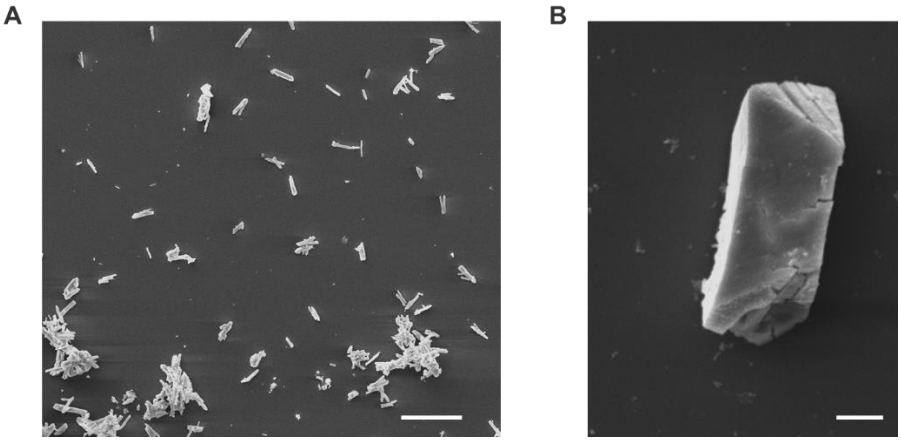


Fig. S3. The FESEM images of **Dy-F-oxa** samples. Scale bars on the image (A) and (B) are 10 and 2 μm, respectively.

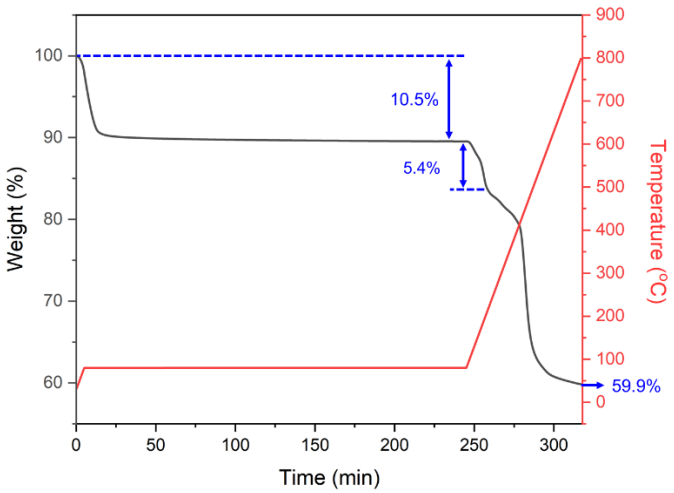


Fig. S4 TGA curve of activated **Dy-F-oxa**. With the heating rate of 10 °C/min, the sample was heated to 80 °C and keep this temperature for 4 hours. Then the activated sample was heated to 800 °C.

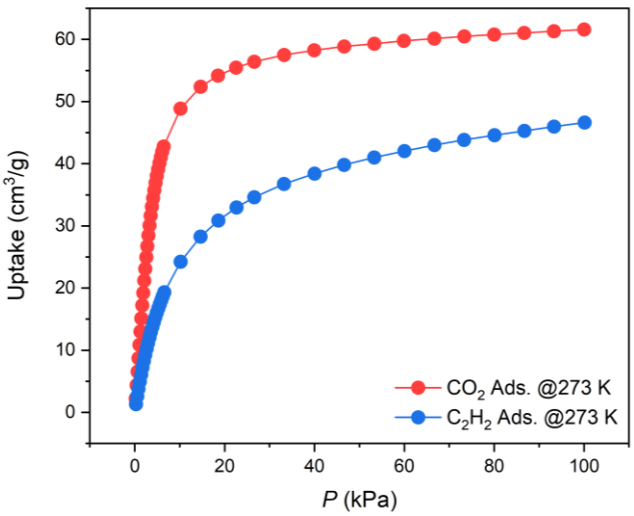


Fig. S5 CO_2 and C_2H_2 adsorption isotherms at 273 K of **Dy-F-oxa**.

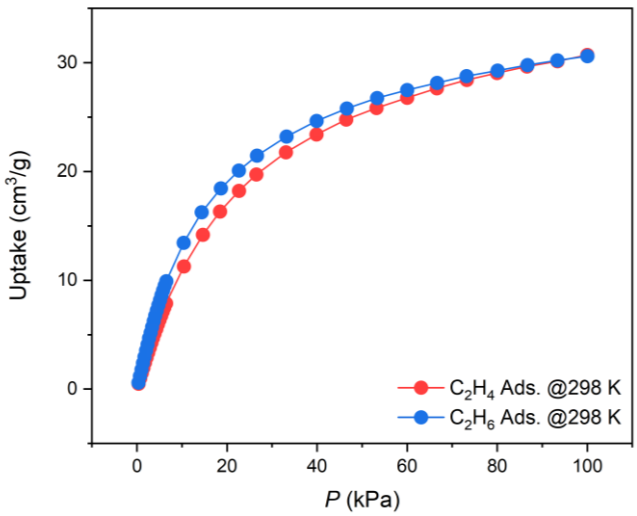
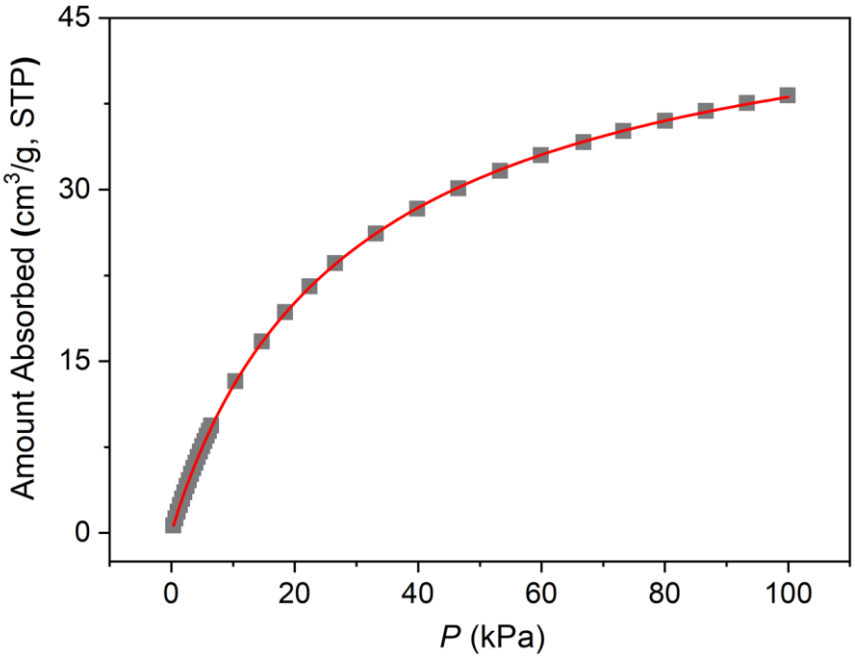
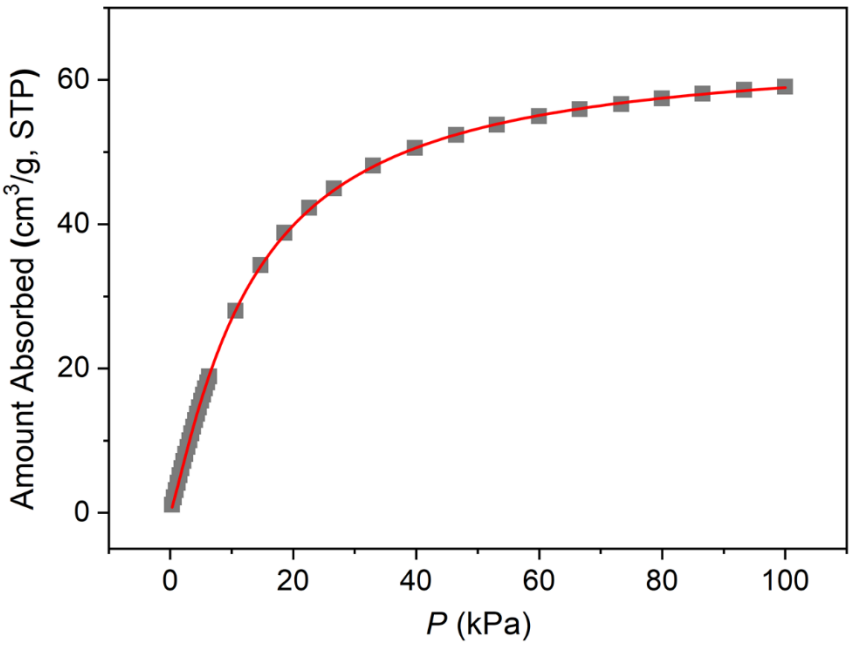


Fig. S6 C_2H_4 and C_2H_6 adsorption isotherms at 298 K of **Dy-F-oxa**.



Equation	A1*B1*x^C1/(1+B1*x^C1)	
Reduced Chi-Sqr	0.00395	
Adj. R-Square	0.99998	
	Value	Standard Error
A1 (q_{sat})	50.07238	0.16576
B1 (b_A)	0.03721	1.64328E-4
C1 (n)	0.96589	0.00297

Fig. S7 The Langmuir-Freundlich fitting details of C_2H_2 adsorption isotherm at 298 K for **Dy-F-oxa** and the solid lines are the best fit for the data.



Equation	A1*B1*x^C1/(1+B1*x^C1)	
Reduced Chi-Sqr	0.03952	
Adj. R-Square	0.99991	
	Value	Standard Error
A1 (q_{sat})	64.42253	0.18893
B1 (b_A)	0.04785	4.83903E-4
C1 (n)	1.17589	0.00635

Fig. S8 The Langmuir-Freundlich fitting details of CO_2 adsorption isotherm at 298 K for **Dy-F-oxa** and the solid lines are the best fit for the data.

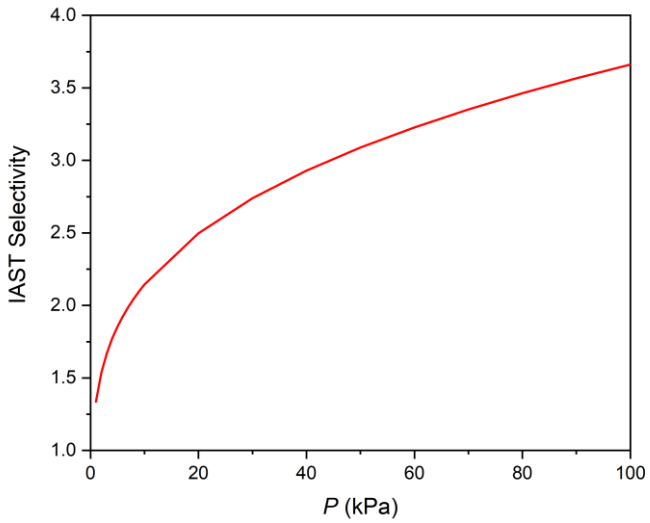
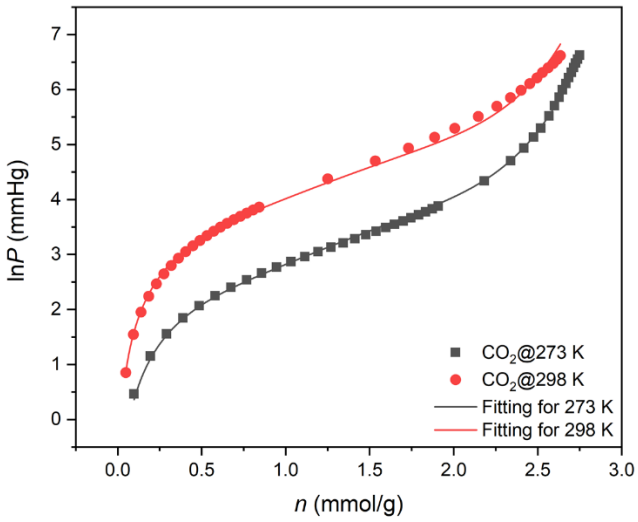
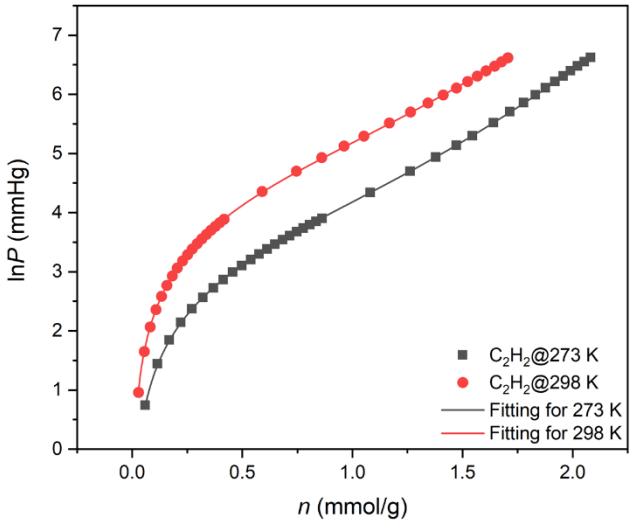


Fig. S9 Calculated IAST selectivity of **Dy-F-oxa** for CO_2/C_2H_2 with 1:1 ratio at 298 K.



Model	virial2 (User)	
Equation	ln(x)+1/K*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5+a6*x^6+a7*x^7+a8*x^8+a9*x^9)+(b0+b1*x+b2*x^2)	
Plot	273 K	298 K
a0*	-4081.44336 ± 101.58683	-4081.44336 ± 101.58683
a1*	472.08771 ± 117.91103	472.08771 ± 117.91103
a2*	-822.0564 ± 234.91307	-822.0564 ± 234.91307
a3*	863.01979 ± 209.7007	863.01979 ± 209.7007
a4*	-385.26848 ± 81.42897	-385.26848 ± 81.42897
a5*	64.68606 ± 11.45142	64.68606 ± 11.45142
a6*	0 ± 0	0 ± 0
a7*	0 ± 0	0 ± 0
a8*	0 ± 0	0 ± 0
a9*	0 ± 0	0 ± 0
b0*	17.53463 ± 0.34965	17.53463 ± 0.34965
b1*	-0.46848 ± 0.20906	-0.46848 ± 0.20906
b2*	0 ± 0	0 ± 0
K	273 ± 0	298 ± 0
Reduced Chi-Sqr*	0.00422	
R-Square (COD)	0.99938	0.99744
R-Square (COD)*	0.99852	
adj. R-Square*	0.99838	

Fig. S10 Virial equation (lines) fitting of the experimental CO_2 adsorption data (symbols) for **Dy-F-oxa**.



Model	virial2 (User)	
Equation	ln(x)+1/K*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5+a6*x^6+a7*x^7+a8*x^8+a9*x^9)+(b0+b1*x+b2*x^2)	
Plot	273 K	298 K
a0*	-3290.05916 ± 15.56158	-3290.05916 ± 15.56158
a1*	24.51663 ± 26.68188	24.51663 ± 26.68188
a2*	-60.66684 ± 59.67348	-60.66684 ± 59.67348
a3*	66.74638 ± 74.01187	66.74638 ± 74.01187
a4*	7.04742 ± 39.68621	7.04742 ± 39.68621
a5*	-4.67162 ± 7.62763	-4.67162 ± 7.62763
a6*	0 ± 0	0 ± 0
a7*	0 ± 0	0 ± 0
a8*	0 ± 0	0 ± 0
a9*	0 ± 0	0 ± 0
b0*	15.5606 ± 0.05296	15.5606 ± 0.05296
b1*	0.55093 ± 0.05493	0.55093 ± 0.05493
b2*	0 ± 0	0 ± 0
K	273 ± 0	298 ± 0
Reduced Chi-Sqr*	1.04496E-4	
R-Square (COD)	0.99997	0.99995
R-Square (COD)*	0.99996	
adj. R-Square*	0.99996	

Fig. S11 Virial equation (lines) fitting of the experimental C_2H_2 adsorption data (symbols) for **Dy-F-oxa**.

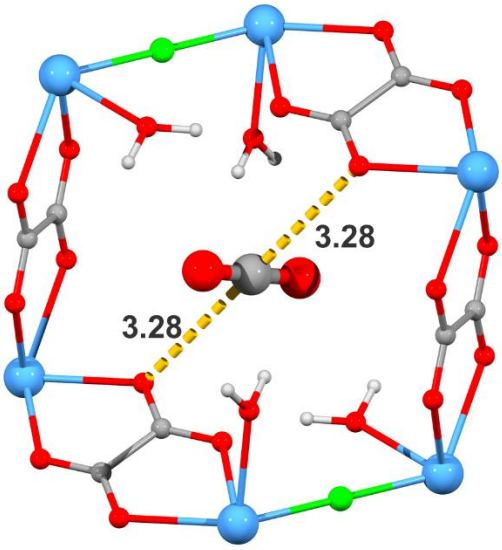


Fig. S12 Interactions between electropositive $C^{\delta+}$ atom of CO_2 and nearby O atoms of two carboxyl groups in **Dy-F-oxa**. Distances are given in Å.

References.

1. L.-L. Li, Y.-F. Fang, S. Liu, S.-S. Chen and W.-Z. Wang, *Inorg. Chim. Acta*, 2022, **538**, 120979.
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