Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Electronic Supplementary Information for

Computational screening, synthesis and testing of Metal-Organic Frameworks with a bithiazole linker for carbon dioxide capture and its green conversion into cyclic carbonates

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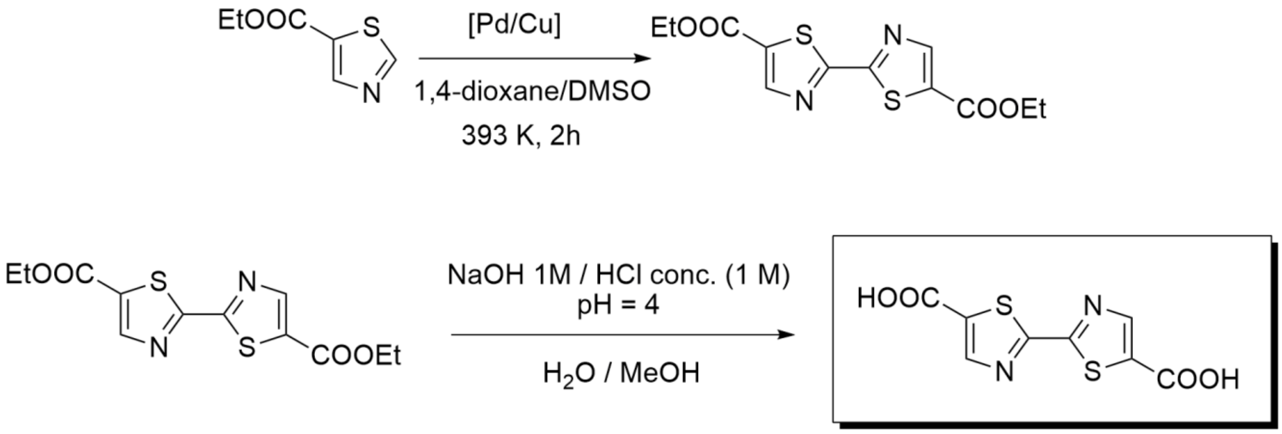


Scheme S1. Synthesis of H_2TzTz.

Single-crystal X-ray Diffraction Structure Determination of H_2TzTz

Single crystal X-Ray data were collected at low temperature (T = 100 K) on an Oxford Diffraction XcaliburPX diffractometer equipped with a CCD area detector using a Cu Kα radiation (λ = 1.5418 Å). The program used for the data collection was CrysAlis CCD 1.171.[1] Data reduction was carried out with the program CrysAlis RED 1.171[2] and the absorption correction was applied with the program ABSPACK 1.17. Direct methods implemented in Sir97[3] were used to solve the structures and the refinements were performed by full-matrix least-squares against F^2 implemented in SHELX2014.[4] All the non-hydrogen atoms were refined anisotropically while the hydrogen atoms of the aromatic rings were fixed in calculated positions and refined isotropically with the thermal factor depending on the one of the atom to which they are bound. The water and –COOH hydrogen atoms were located on the residual density maps and then included with fixed bond distances and U_{iso} values constrained at the level of 1.5×U_{eq} of the carrier oxygen atom. The geometrical calculations were performed by PARST97[5] and molecular plots were produced by the program ORTEP3.[6] CCDC-1883496 contains the supplementary crystallographic data for H_2TzTz · $2H_2O$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* ccdc.cam.ac.uk/community/requestastructure.Table S1 collects the main experimental details and crystallographic data.

Table S1. Main crystallographic data, experimental details and structure refinement details for H_2TzTz ·2 H_2O.

Formula	$C_8H_8N_2O_6S_2$
M [g mol^{-1}]	292.28
T [K]	100(2)
Color, habit	Light yellow plates
Size [mm^3]	0.002 x 0.01 x 0.01
Crystal system	Monoclinic
a [Å]	18.266(8)
b [Å]	3.694(14)
c [Å]	18.297(8)
β [°]	114.624(5)
V [Å^3]	1122.3(8)
D_{calc} [g cm^{-3}]	1.730
Space group	$P\ 2_1/n$
Z	4
θ range for collection [°]	4.478 - 72.313
Measured reflns	10613
Unique reflns	2172
Completeness [%]	99.8 % (to θ= 67.680°)
R_{int}	0.0385
Data/restraints/parameters	2172 / 4 / 173
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.1338, 0.3259
$R1$, w$R2$ (all data)	0.1573, 0.3351
Gof on F^2	1.321
Max, min peak [e Å^{-3}]	1.460, -1.265

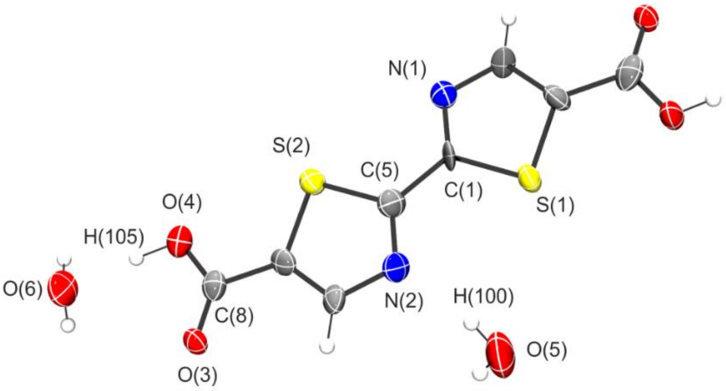


Figure S1. ORTEP drawing of the [2,2'-bithiazole]-5,5'-dicarboxylic acid molecule (dihydrate) at 50% probability level. Selected bond lengths (Å) and angles (°): C(1)-N(1) = 1.322(16); C(1)-S(1) = 1.709(11); C(5)-N(2) = 1.333(16); C(5)-S(2) = 1.727(12); C(8)-O(3) = 1.170(14); C(8)-O(4) = 1.319(15); O(4)-H(105) = 0.96(15); S(2)-C(5)-C(1)-S(1) = -179.7(3); N(2)-C(5)-C(1)-N(1) = 178.5(6). Hydrogen bonds [D---A distances (Å)]: O(4)-H(105)···O(6) = 2.567(13); O(5)-H(100)···N(2) = 2.859(15).

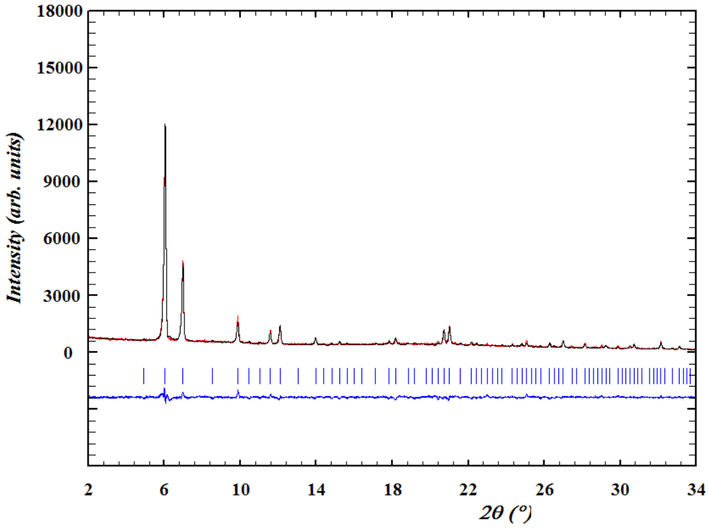
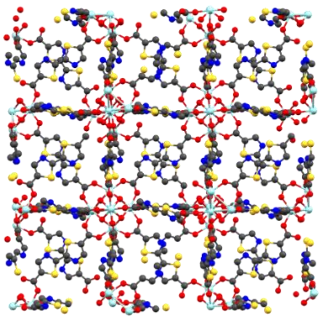
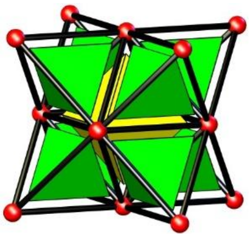


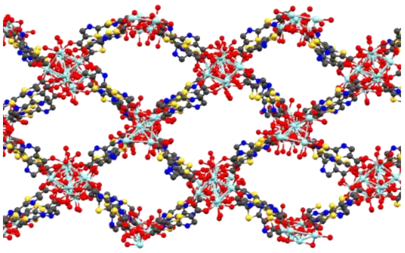
Figure S2. Graphical result of the final Rietveld refinement carried out on **1·DMF** in terms of experimental, calculated and difference traces (black, red and blue, respectively). The blue markers indicate the positions of the Bragg reflections.



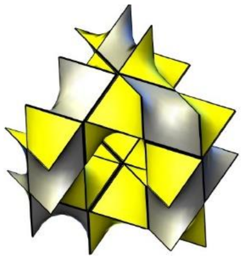
fcu $[Zr_6O_4(OH)_4]$



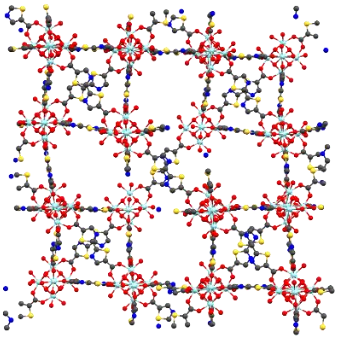
fcu



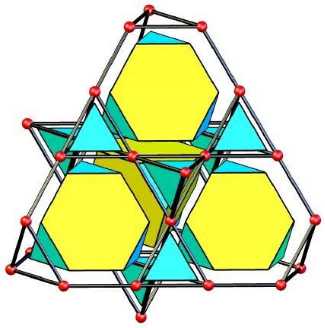
bcs $[Zr_6O_4(OH)_{10}(H_2O)_6]$



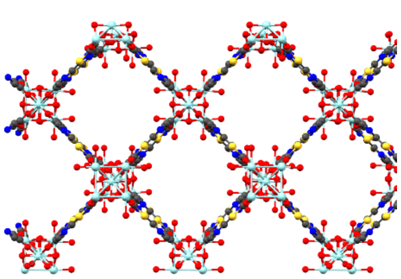
bcs



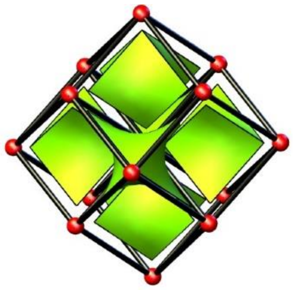
crs $[Zr_6O_4(OH)_{10}(H_2O)_6]$



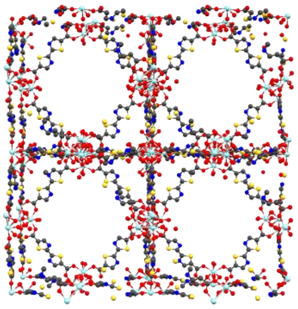
crs



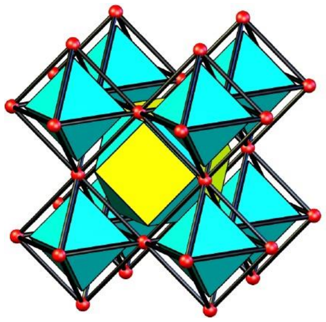
bcu $[Zr_6O_4(OH)_8(H_2O)_4]$



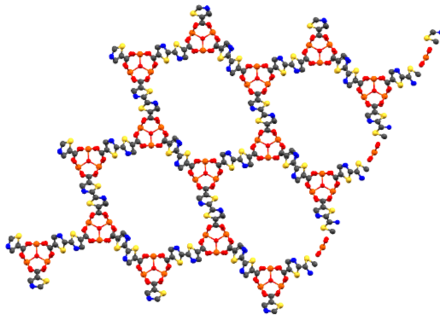
bcu



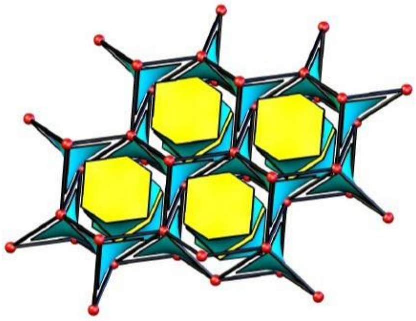
reo [$Zr_6O_4(OH)_8(H_2O)_4$]



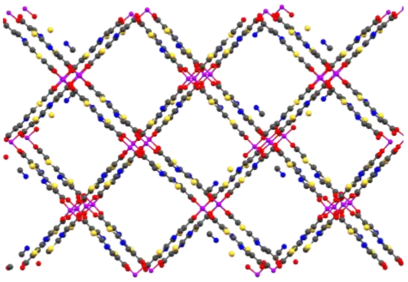
reo



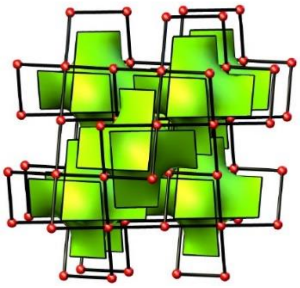
acs [Cr_3O]



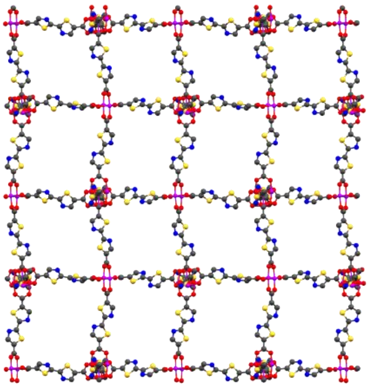
acs



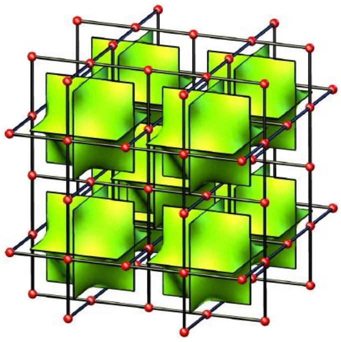
lvt [$Cu_2(RCOO)_4$] paddlewheel



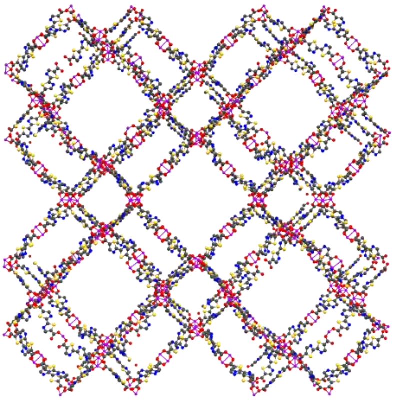
lvt



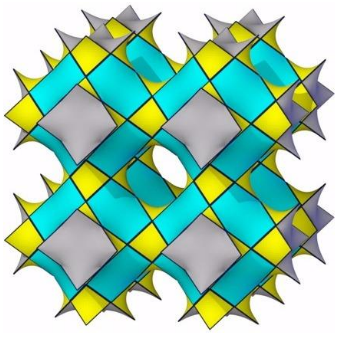
nbo [$Cu_2(RCOO)_4$] paddlewheel



nbo



rhr $[Cu_2(RCOO)_4]$ paddlewheel



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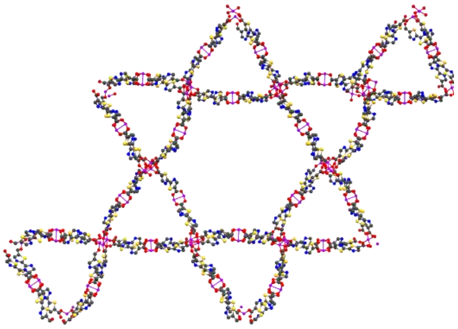
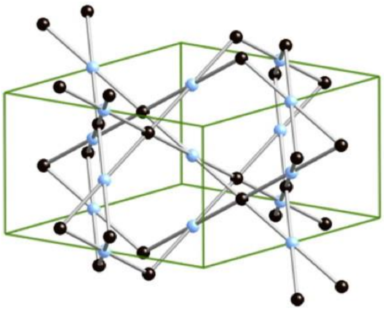


ssa $[Cu_2(RCOO)_4]$ paddlewheel



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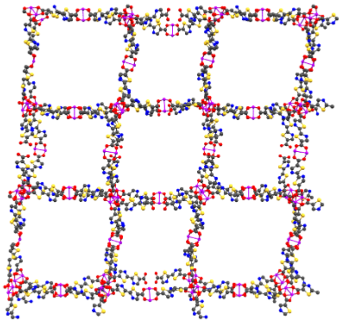
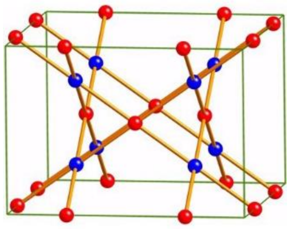
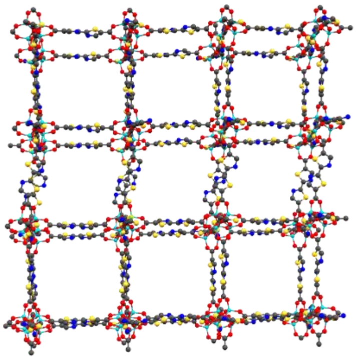


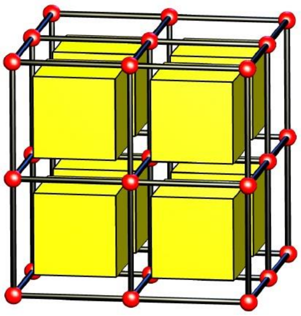
ssb $[Cu_2(RCOO)_4]$ paddlewheel



ssb



pcu $[Zn_4O]$



pcu

Figure S3. Crystalline networks and related net topology of the 12 optimized MOF structures built through the ToBaCCo algorithm starting from H_2TzTz. The net topology representations have been taken from the website of the Reticular Chemistry Structure Resource (RCSR: http://rcsr.anu.edu.au/). The **fcu** MOF is the synthesized sample.

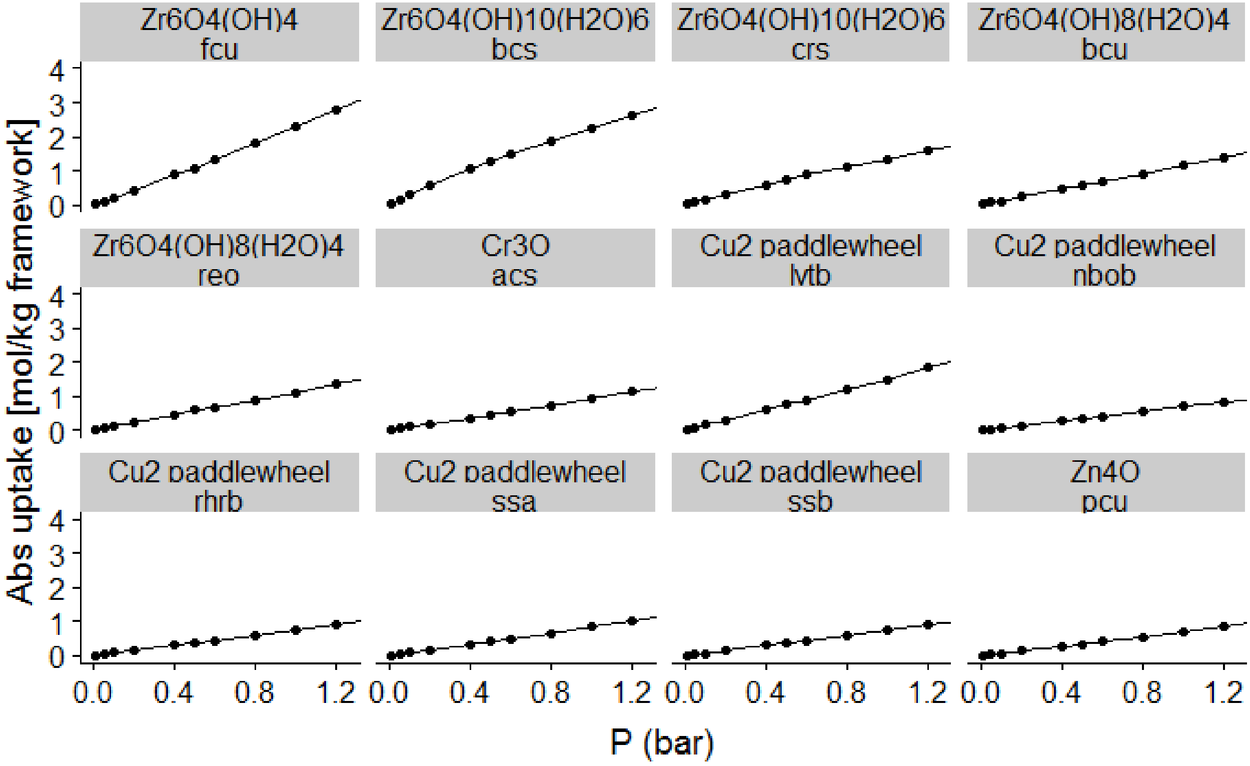


Figure S4. GCMC-simulated (RASPA code) CO_2 adsorption isotherms at T = 298 K and p_{max} = 1.2 bar for the 12 hypothetical MOF structures shown in Figure S3.

Table S2. Lennard-Jones parameters for MOF and adsorbate atoms in GCMC simulations.

Atom type	ε/k_B [K]	σ [Å]	q [e]	Forcefield
C	52.83	3.43	See CIFs for CO_2 simulations	UFF (framework) [7]
Cu	2.52	3.11		
H	22.14	2.57		
N	34.72	3.26		
O	30.19	3.12	No MOF charges for N_2 simulations	
S	137.86	3.59		
Zr	34.72	2.78		
N_n2	36.0	3.31	-0.482	TraPPE (guests) [8]
N_com	0.0	0.0	0.964	
C_co2	27.0	2.80	0.70	
O_co2	79.0	3.05	-0.35	

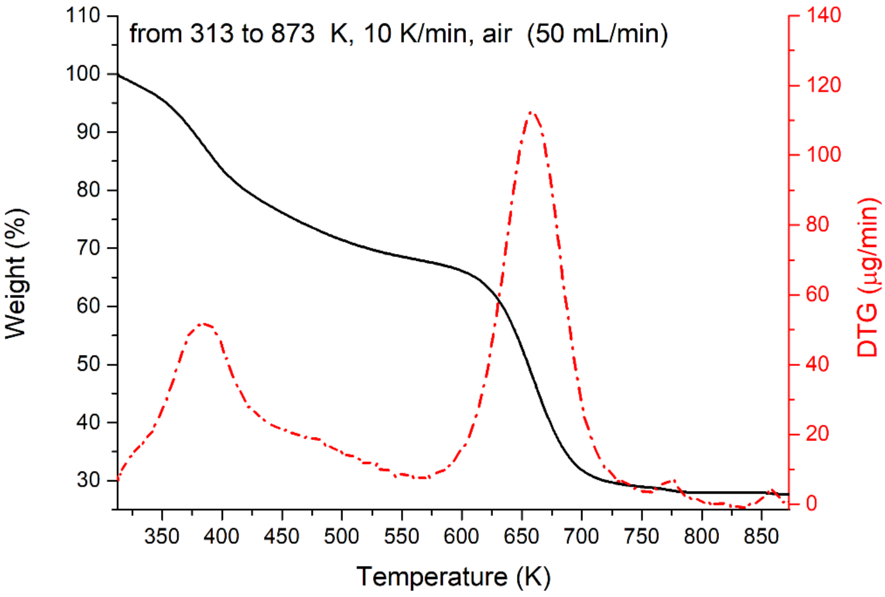


Figure S5. Thermogravimetric analysis of **1·DMF** under air.

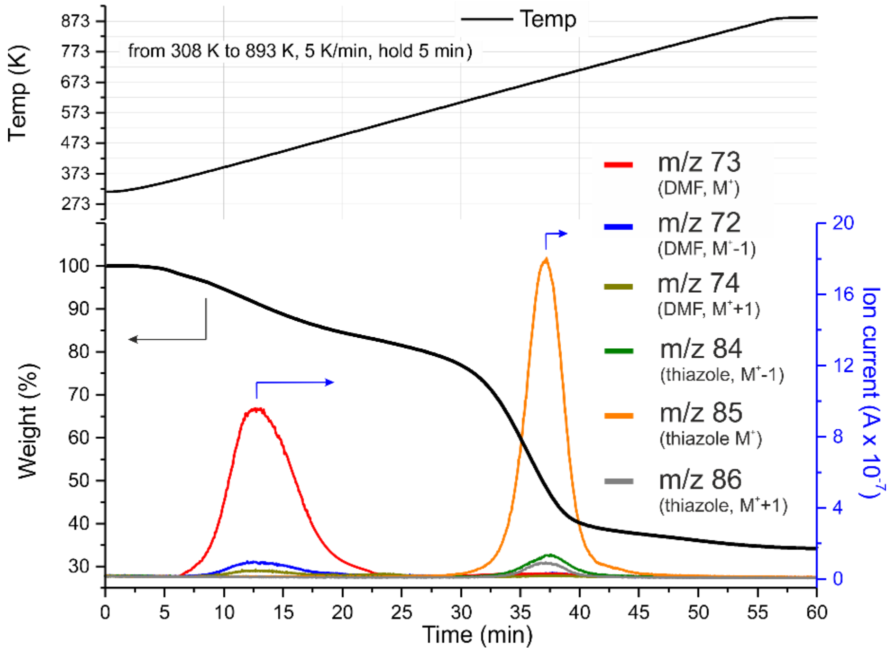


Figure S6. Thermogravimetric analysis coupled with mass analysis of volatiles *vs.* time profile of **1·DMF**. The corresponding temperatures can be inferred from the temperature *vs.* time graph on the upper part of the picture.

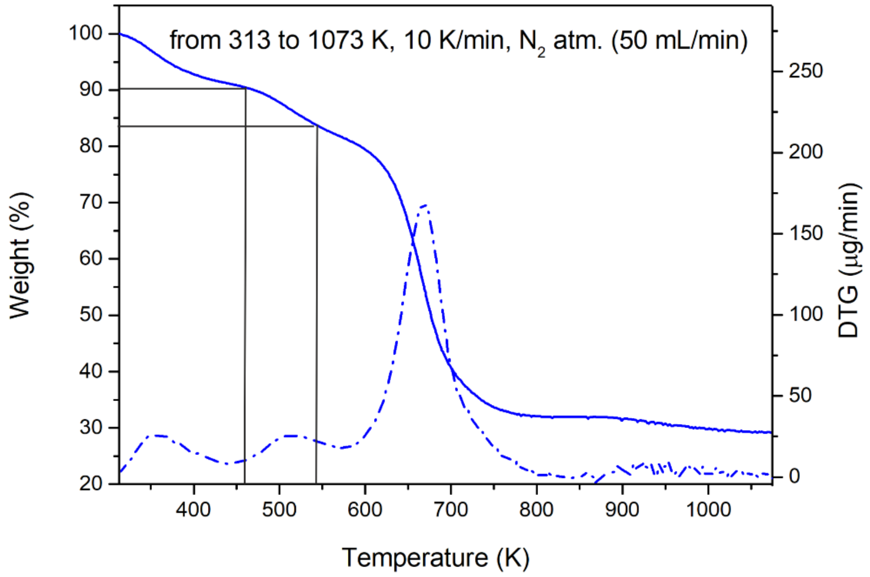
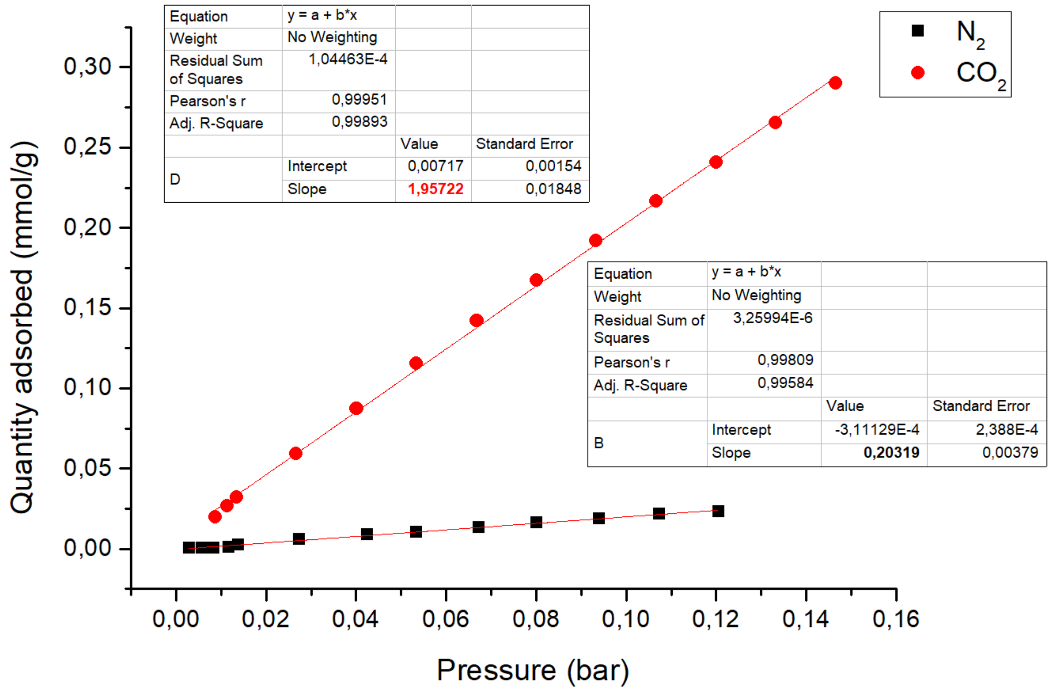


Figure S7. TG-DTG profile of the activated material (**1**). The black lines highlight the weight loss of *ca*. 6.5% corresponding to the residual DMF inside the material's pores after activation.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1,04463E-4		
Pearson's r	0,99951		
Adj. R-Square	0,99893		
		Value	Standard Error
D	Intercept	0,00717	0,00154
	Slope	1,95722	0,01848

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	3,25994E-6		
Pearson's r	0,99809		
Adj. R-Square	0,99584		
		Value	Standard Error
B	Intercept	-3,11129E-4	2,388E-4
	Slope	**0,20319**	0,00379

Figure S8. Comparison of the N_2 (black) and CO_2 (red) isotherms at 298 K in the 0-0.16 bar interval for the estimation of the CO_2 *vs.* N_2 selectivity of **1** through the Henry method.

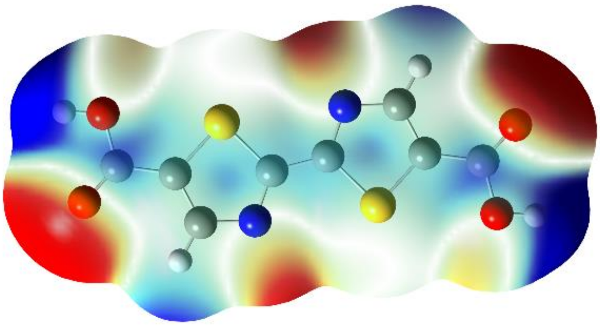


Figure S9. Electrostatic potential of H_2TzTz. Negatively charged regions are coloured in red, neutral in white, and positive in blue.

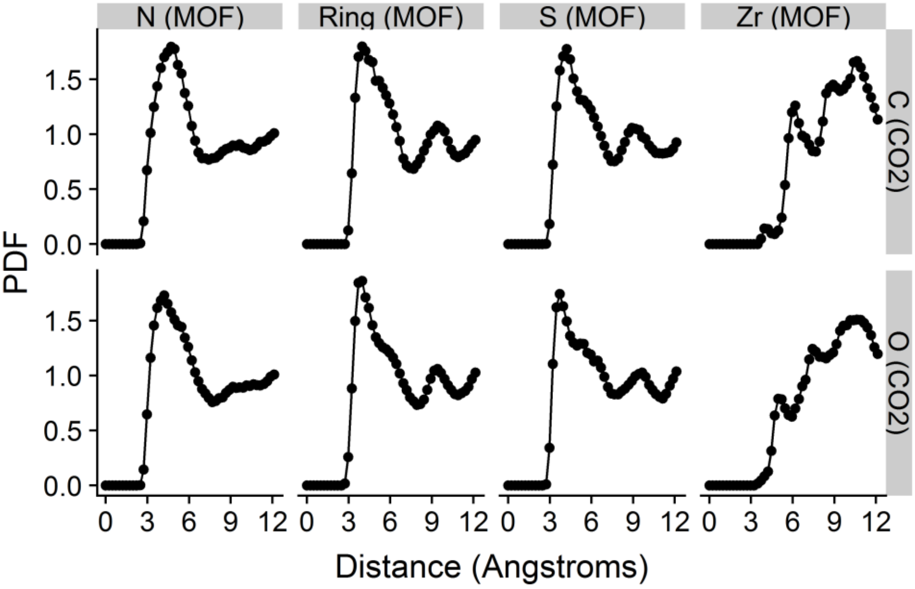


Figure S10. RDF plots for selected atomic distances for the computed [CO_2@**1**] structures.

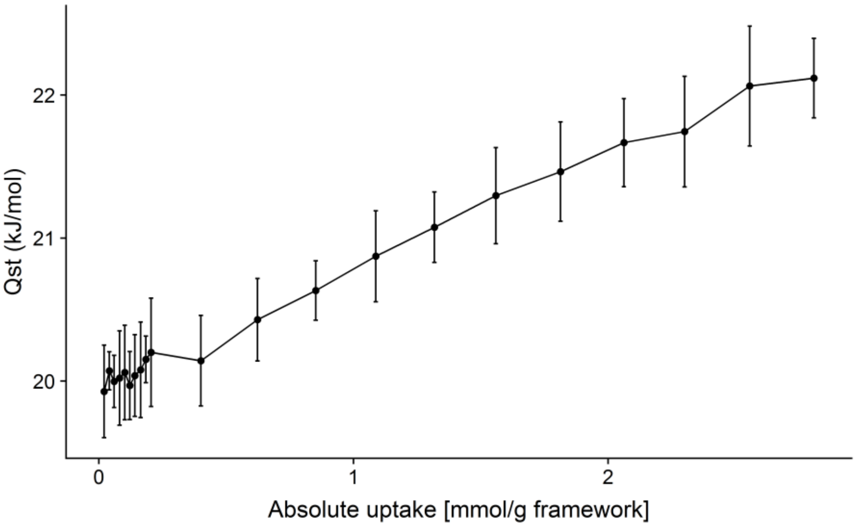


Figure S11. Simulated heat of adsorption for CO_2 in **1** calculated using the fluctuation method for GCMC simulations with 50.000 production cycles.

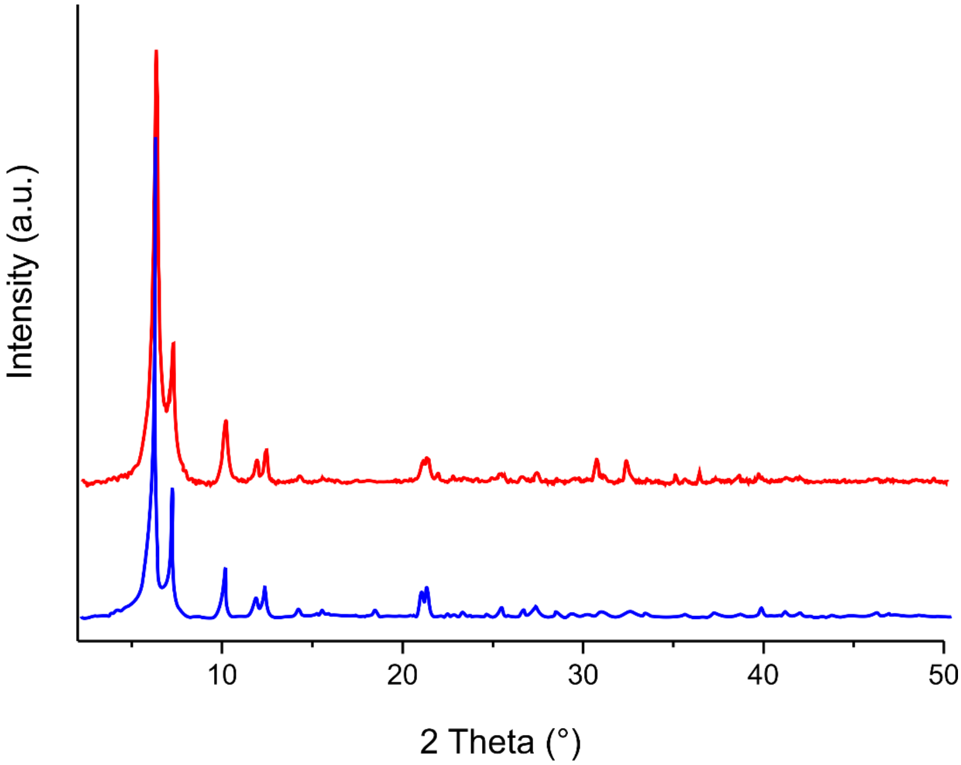


Figure S12. PXRD pattern of **1** before (blue) and after (red) three recycling runs in the catalytic transformation of epichlorohydrin into its cyclic carbonate.

References

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[1] CrysAlis CCD 1.171.31.2 (release 07-07-2006), CrysAlis171.NET, Oxford Diffraction Ltd.

[2] CrysAlis RED 1.171.31.2 (release 07-07-2006), CrysAlis171.NET, Oxford Diffraction Ltd.

[3] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, SIR97: a New Tool for Crystal Structure Determination and Refinement. *J. Appl. Crystallogr.* 1999**, 32**, 115-119.

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[8] J. J. Potoff and J. I. Siepmann, *AlChE J.* 2001, **47**, 1676-1682.