Supporting Information

The Design of Novel and Resistant Zn(PZDC)(ATZ) MOF Catalyst for Chemical Fixation of CO_2 under solvent-free Conditions

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Single-crystal X-ray diffraction analysis

Data were collected with a (Cu-Kα, λ = 1.54184 Å) on an Agilent Technology SuperNova Eos Dual system microfocus source and focusing multilayer mirror optics at a temperature of 293 K and processed using CrysAlis^{Pro}. Using Olex2,[1] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.[2] All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the organic ligands were localized in their calculated positions and refined using the riding model. The free solvent molecules in Zn(PZDC)(ATZ) could not be modeled due to highly disordered, thus the diffraction contributions from the solvent molecules were removed by the SQUEEZE routine.[3] The SQUEEZE routine indicated the large solvent accessible voids accounting for 21.7% of the unit-cell volume. The final formula for MOFs was determined by combining single-crystal structures, elemental microanalyses and TGA data. Further details of the X-ray structural analyses were given in Table S1. Selected bond lengths and bond angles of Zn(PZDC)(ATZ) were listed in Table S2.

Table S1 Crystallographic data for Zn(PZDC)(ATZ).

Empirical formula	$C_6H_7N_7O_6Zn_2$
Formula weight	403.93
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	*P*nnm
a/Å	11.5016(3)
b/Å	17.0121(4)
c/Å	14.7070(4)
V/Å^3	2877.68(13)
Z	8
ρ_{calc}g/cm^3	1.865
μ/mm^{-1}	4.492
F(000)	1600.0
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	9.282 to 134.158
Index ranges	$-13 \leq h \leq 10$, $-20 \leq k \leq 15$, $-17 \leq l \leq 14$
Reflections collected	6406
Independent reflections	2679 [R_{int} = 0.0285, R_{sigma} = 0.0334]
Data/restraints/parameters	2679/0/200
Goodness-of-fit on F^2	1.071
Final $R^{a,b}$ indexes [I>=2σ (I)]	R_1 = 0.0369, wR_2 = 0.0977
Final *R* indexes [all data]	R_1 = 0.0421, wR_2 = 0.1009
Largest diff. peak/hole / e Å^{-3}	0.59/-0.57

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = |\sum w(|F_o|^2 - |Fc|^2)^2/\sum|w(F_o^2)_2|^{1/2}$.

Table S2 Selected bond lengths [Å] and angles [°] for Zn(PZDC)(ATZ).

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Zn1-O2[1]	2.347(2)	Zn2-O1	2.035(3)
Zn1-O2	2.110(2)	Zn2-O3[3]	2.092(2)
Zn1-O4[2]	2.070(2)	Zn2-O4[2]	2.283(2)
Zn1-O6	2.200(3)	Zn2-O5	2.189(3)
Zn1-N1[1]	2.063(3)	Zn2-N2[2]	2.062(3)
Zn1-N6	2.095(3)	Zn2-N3	2.104(3)
Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O2-Zn1-O2[1]	75.93(10)	O1-Zn2-O3[3]	98.39(11)
O2-Zn1-O6	84.31(11)	O1-Zn2-O4[2]	93.91(10)
O4[2]-Zn1-O2[1]	163.55(10)	O1-Zn2-O5	84.53(13)
O4[2]-Zn1-O2	94.33(10)	O1-Zn2-N2[2]	166.99(12)
O4[2]-Zn1-O6	85.84(11)	O1-Zn2-N3	91.36(13)
O4[2]-Zn1-N6	95.11(11)	O3[3]-Zn2-O4[2]	166.16(10)
O6-Zn1-O21	80.09(10)	O3[3]-Zn2-O5	89.46(11)
N1[1]-Zn1-O2	149.26(11)	O3[3]-Zn2-N3	91.56(11)
N1[1]-Zn1-O2[1]	73.59(10)	O5-Zn2-O4[2]	85.40(11)
N1[1]-Zn1-O4[2]	114.23(11)	N2[2]-Zn2-O3[3]	91.19(11)
N1[1]-Zn1-O6	86.59(11)	N2[2]-Zn2-O4[2]	75.72(10)
N1[1]-Zn1-N6	100.62(12)	N2[2]-Zn2-O5	86.79(13)
N6-Zn1-O2	87.23(12)	N2[2]-Zn2-N3	97.18(12)
N6-Zn1-O2[1]	97.58(11)	N3-Zn2-O4[2]	94.49(11)
N6-Zn1-O6	171.53(12)	N3-Zn2-O5	175.87(13)

Symmetry codes: (1) X,-Y,+Z; (2) -1/2-X,1/2+Y,1/2-Z; (3)-1-X,-Y,+Z; (4) +X,+Y,1-Z; (5) +X,+Y,-Z

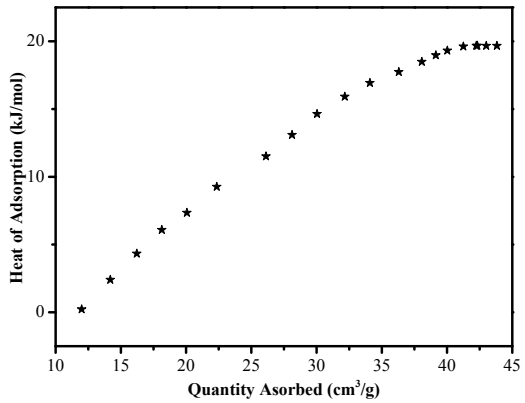

Fig. S1 Isosteric heat of adsorption for CO_2 in Zn(PZDC)(ATZ).

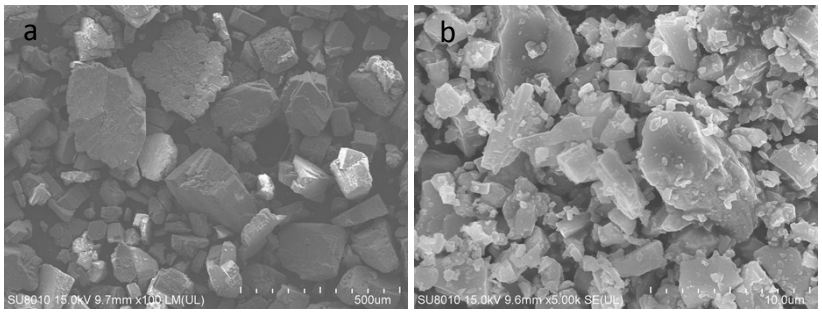

Fig. S2 SEM images of Zn(PZDC)(ATZ) (a) fresh catalyst, (b) after seven recycles.

References

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3 A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7-13.