Supporting Information

A novel cage-like MOF showing gas separation, CO_2 conversion and selective adsorption of organic dye

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Contents

1. IR spatra, TGA and PXRD

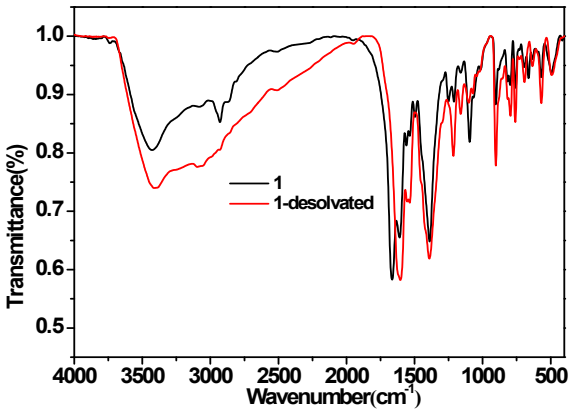


Fig. S1 IR spectra of as-synthesized and desolvated samples of **1**.

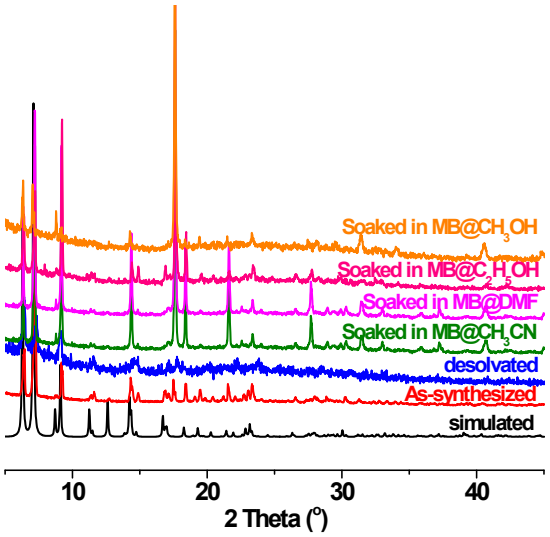


Fig. S2 PXRD patterns of **1**.

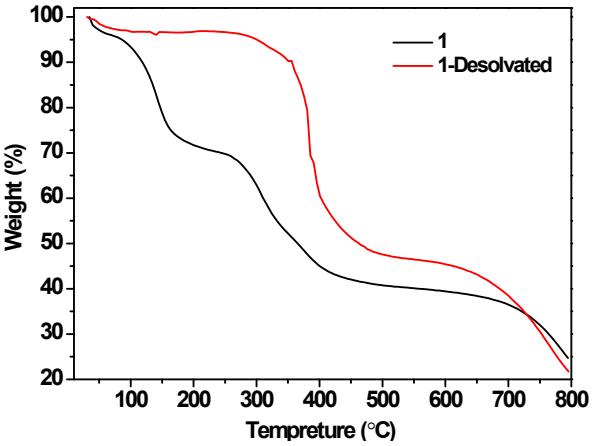


Fig. S3 TGA curves of as-synthesized and desolvated samples of **1**.

2. Pore size distribution

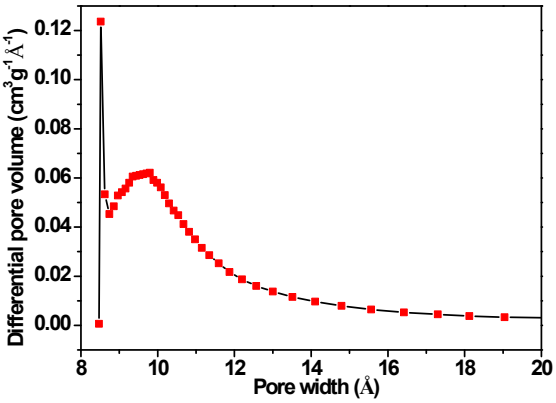


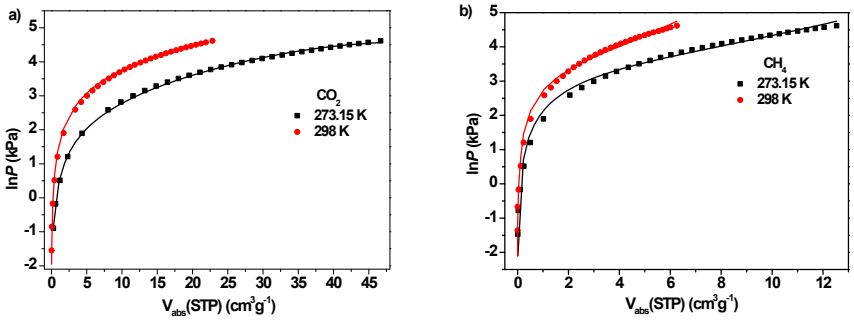
Fig. S4 Differential pore volume as a function of pore width calculated from the N_2 adsorption isotherm at 77 K for **1a** using the Horvath-Kawazoe model.

3. Calculation of sorption heat

Calculation of sorption heat for gas using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad\qquad Q_{\mathrm{st}} = -R \sum_{i=0}^{m} a_i N^i$$

Above virial expression was used to fit the combined isotherm data for **1a** at 273.15 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, 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.



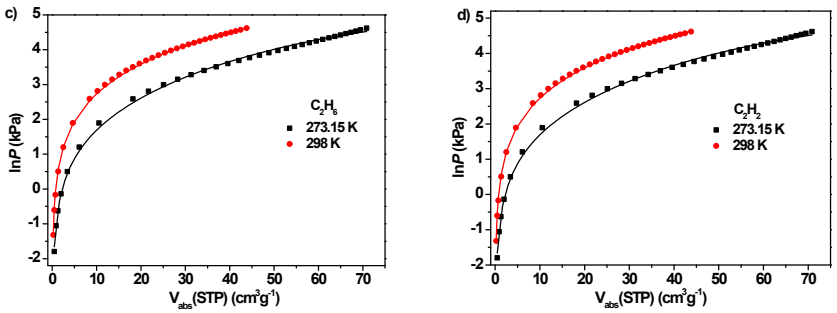


Fig. S5 a) CO_2, a0 = -3625.22439, a1 = 40.95674, a2 = 0.13977, a3 = -0.00268, a4 = 0, b0 = 13.65941, b1= -0.1453, Chi^2 = 0.00842, R^2 = 0.99663. b) CH_4, a0 = -2336.61614, a1 = -25.23567, a2 = 2.04559, b0 = 10.75778, Chi^2 = 0.07768, R^2 = 0.96708. c) C_2H_6, a0 = -2600.59554, a1 = -0.19665, a2 = 0.09197, b0 =9.18033, Chi^2 = 0.00105, R^2 = 0.99958. d) C_2H_2, a0 = -3639.71088, a1 = 22.88615, a2 = -0.04456, b0 = 12.45357, b1 = -0.05622, Chi^2 = 0.00312, R^2 = 0.99895.

4. Selectivity prediction

Selectivity prediction via IAST

The experimental isotherm data for pure gas A, and gas B were fitted at 298 K using a dual Langmuir-Freundlich (L-F) model (Figure S4):

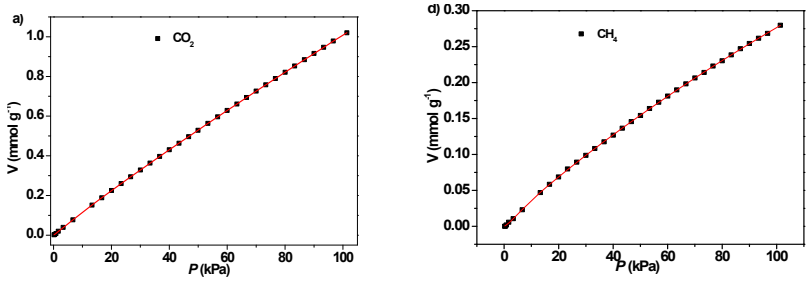
$$q = \frac{a_1 * b_1 * P^{c_1}}{1 + b_1 * P^{c_1}} + \frac{a_2 * b_2 * P^{c_2}}{1 + b_2 * P^{c_2}}$$

Where q and p are adsorbed amounts and the pressure of component i, respectively.

The adsorption selectivities for binary mixtures of gas A/gas B, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j / y_i}$$

were respectively calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz. Where xi is the mole fraction of component i in the adsorbed phase and yi is the mole fraction of component i in the bulk.



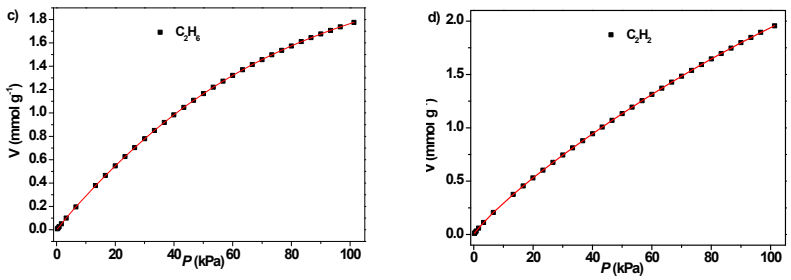


Fig. S6 a) CO_2, a1 = 20.48025, b1 = 0.0006, c1 = 0.96726, a2 = 0.00395, b2 = 0.00005, c2 = 4.00808, Chi^2 = 7.9592E-7, R^2 = 0.99999; b) CH_4, a1 = 1.01474, b1 = 0.00131, c1 = 1.18893, a2 = 0.03755, b2 = 0.03155, c2 = 1.35039, Chi^2 = 2.9957E-7, R^2 = 0.99997; c) C_2H_6, a1 = 3.10479, b1 = 0.00649, c1 = 1.14774, a2 =0.0258, b2 = 0.64603, c2 =1.99087, Chi^2 =8.9404E-7, R^2 = 0.99998; d) C_2H_2, a1 = 10.33455, b1 = 0.00322, c1 = 0.92469, a2 =0.02585, b2 = 0.18064, c2 = 1.33497, Chi^2 =3.9685E-6, R^2 =0.99999.

5. UV-Vis absorption spectra and adsorption pictures of MB

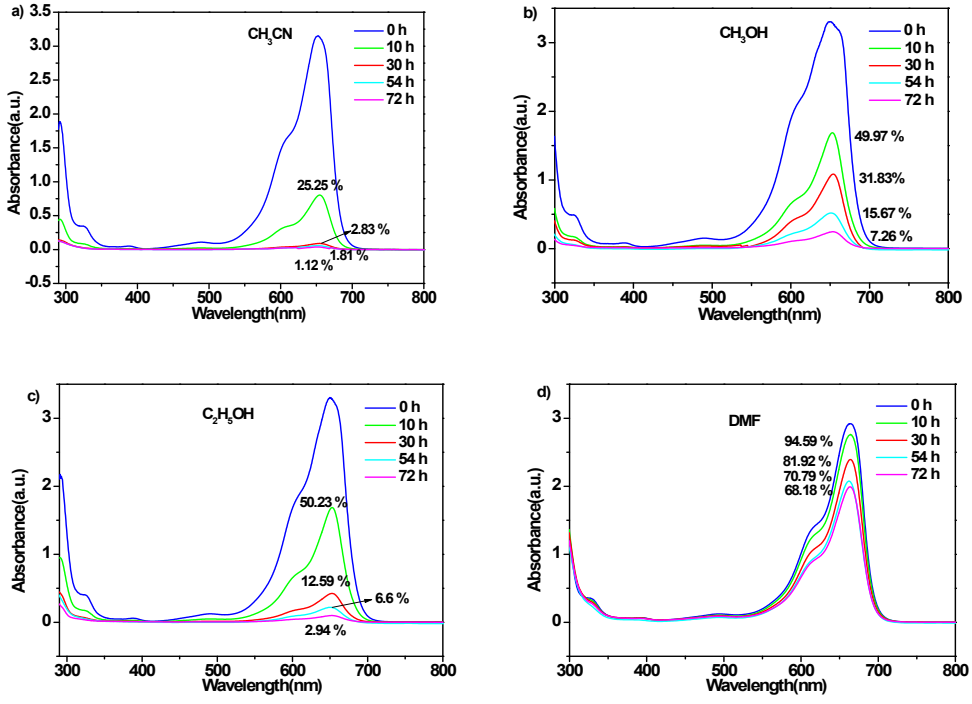


Fig. S7 UV-Vis absorption spectra of MB in different solvents (a, b, c, d).

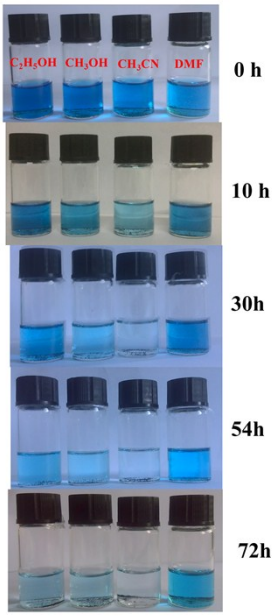


Fig. S8 Adsorption picture of MB in different solvents.

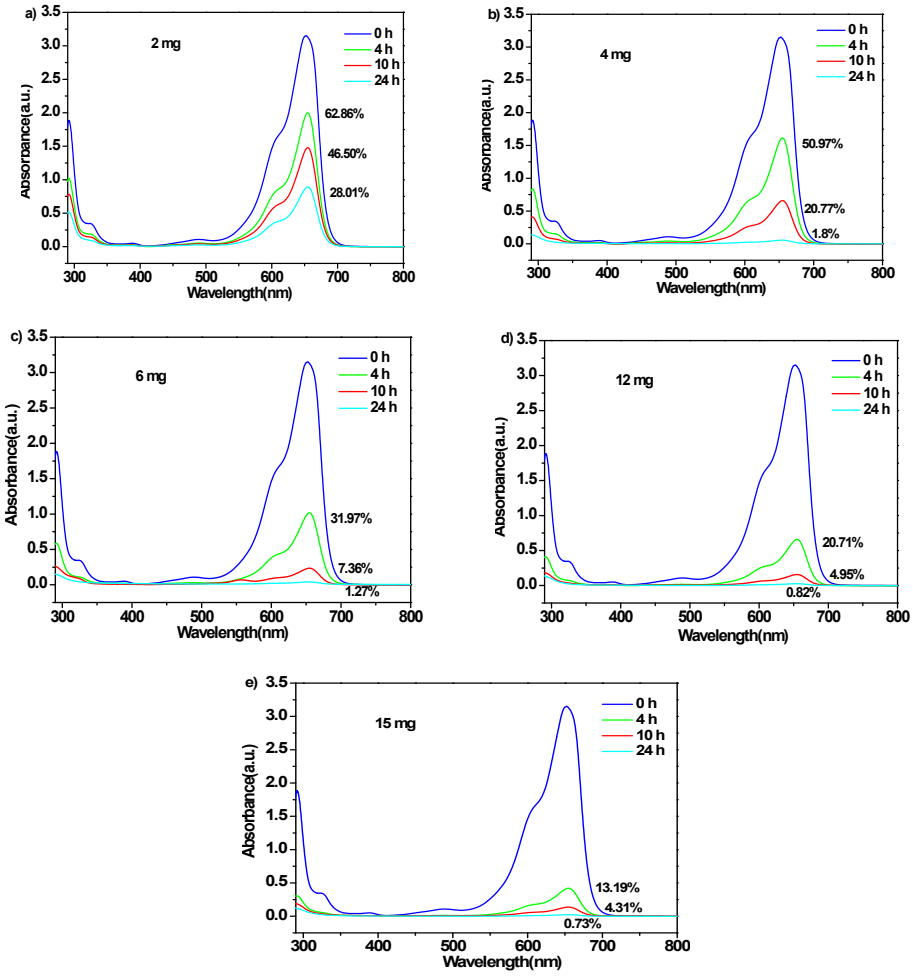


Fig. S9 UV-Vis absorption spectra of MB with different masses of **1** in CH_3CN.

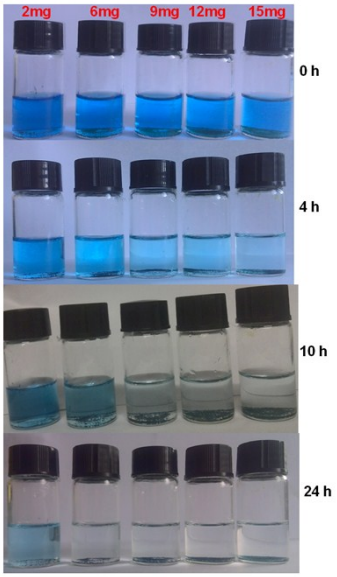
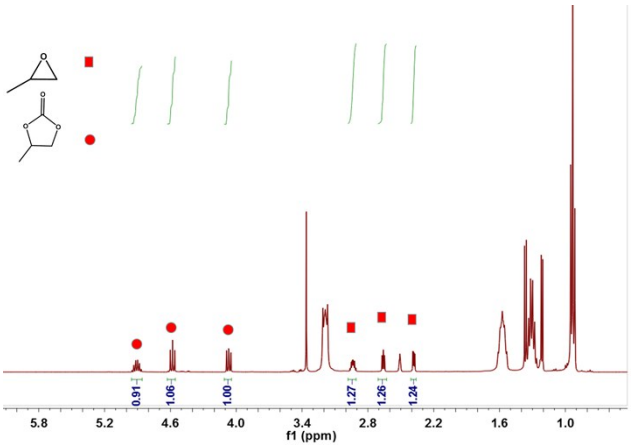


Fig. S10 Picture of adsorbing MB with different masses of **1** in CH_3CN.

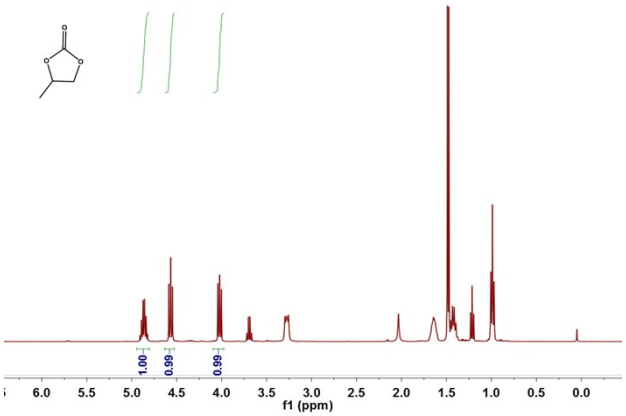
6. GCMC Simulation Methodlody

Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of gas in **1a** by the Sorption module of Material Studio. The framework and gas molecule were considered to be rigid. The partial charges for atoms of **1a** were derived from QEq method and QEq_neutral1.0 parameter (Table S3). One unit cell was used during the simulations. The interaction energies between gas and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for gas molecule and atoms of **1a** were modeled with the universal forcefield (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 1×10^6 maximum loading steps and 1×10^6 production steps were employed.

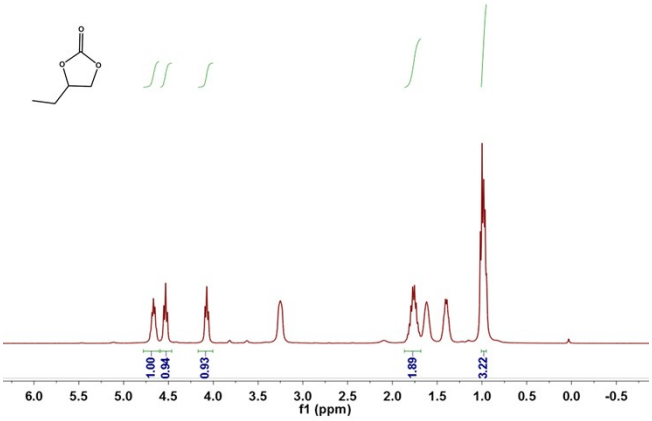
7. ^{1}H NMR Spectra Characterization



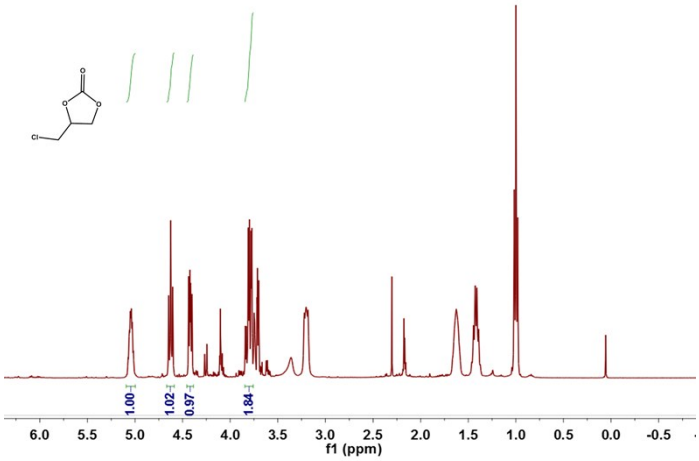
^{1}H NMR spectrum of propylene carbonate in $CDCl_3$.



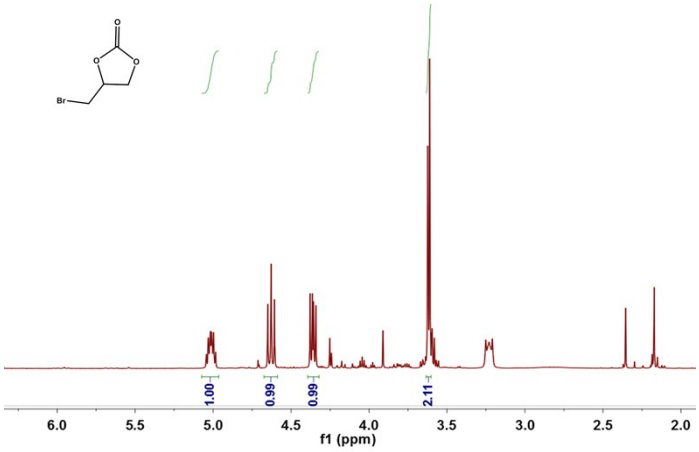
^{1}H NMR spectrum of propylene carbonate in $CDCl_3$.



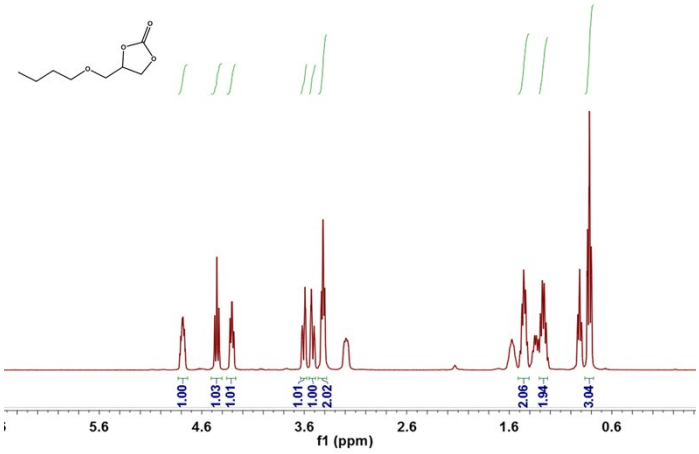
H NMR spectrum of 1,2-butylene carbonate in $CDCl_3$.



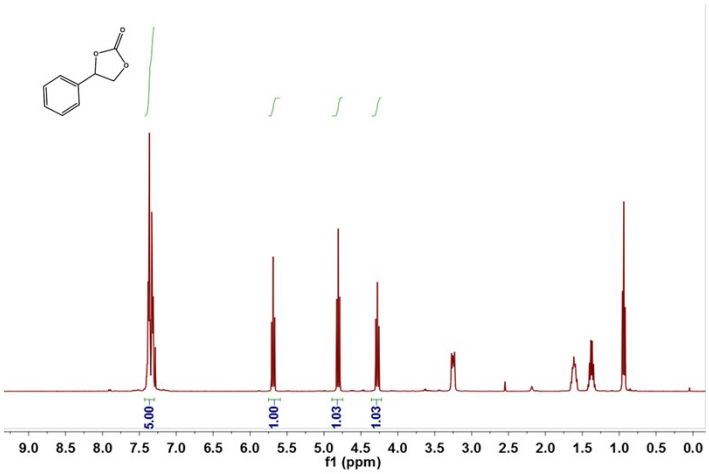
^{1}H NMR spectrum of 4-cloromethyl-1,3-dioxolan-2-one in $CDCl_3$.



^{1}H NMR spectrum of 4-bromomethyl -1,3-dioxolan-2-one in $CDCl_3$.



^{1}H NMR spectrum of 3-butoxy-1,2-propylene carbonate in $CDCl_3$.



H NMR spectrum of styrene carbonate in $CDCl_3$.

8. Table of crystallographic data

Table 1. Crystallographic data for **1**.

Chemical formula	$C_{14.5}H_{13.75}F_{1.75}N_{6.5}O_3Zn_{1.5}$
Formula weight	458.37
T (K)	296(2)
Crystal system	Orthorhombic
Space group	*I*222
a (Å)	16.196(2)
b (Å)	19.408(2)
c (Å)	20.285(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	6375.9(14)
Z	8
$D_{calcd.}$[g·cm^{-3}]	0.955
μ (mm^{-1})	1.164
Reflns collected/unique/R_{int}	17202/6234/0.0563
Goof	1.057
R_1[a], wR_2[b] [I > 2σ]	0.0522, 0.1348
R_1[a], wR_2[b] (all data)	0.0829, 0.1571

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

Table S2. Selected bond lengths [Å] and angles [º].

Zn(1)-O(2)#1	2.076(10)	O(2)#1-Zn(1)-O(2)#2	179.0(6)	F(3)-Zn(2)-O(4)	85.9(4)
Zn(1)-O(2)#2	2.076(10)	O(2)#1-Zn(1)-O(4)	90.5(3)	O(1)#2-Zn(2)-O(4)	90.3(3)
Zn(1)-O(4)	2.081(5)	O(2)#2-Zn(1)-O(4)	90.5(3)	N(3)-Zn(2)-O(4)	86.5(3)
Zn(1)-N(7)	2.129(6)	O(2)#1-Zn(1)-N(7)	89.5(3)	N(5)-Zn(2)-O(4)	169.4(4)
Zn(1)-N(2)	2.147(9)	O(2)#2-Zn(1)-N(7)	89.5(3)	O(3)-Zn(2)-O(4)	173.5(7)
Zn(1)-N(2)#3	2.148(9)	O(2)#1-Zn(1)-N(2)#3	90.2(3)	F(3)-Zn(2)-F(3')	35.1(5)
Zn(2)-F(3)	1.848(5)	O(2)#2-Zn(1)-N(2)#3	89.9(3)	O(1)#2-Zn(2)-F(3')	159.7(6)
Zn(2)-O(1)#2	1.995(9)	F(3')-Zn(2)-F(3')#4	69.1(7)	N(3)-Zn(2)-F(3')	97.3(6)
Zn(2)-N(3)	2.054(9)	O(4)-Zn(1)-N(2)#3	86.0(3)	N(5)-Zn(2)-O(3)	14.6(7)
Zn(2)-N(5)	2.060(19)	N(7)-Zn(1)-N(2)#3	94.0(3)	N(5)-Zn(2)-F(3')	84.2(8)
Zn(2)-O(3)	2.10(2)	N(2)-Zn(1)-N(2)#3	172.1(5)	O(3)-Zn(2)-F(3')	98.5(6)
Zn(2)-O(4)	2.1574(16)	F(3)-Zn(2)-O(1)#2	124.7(3)	O(4)-Zn(2)-F(3')	87.2(4)
F(3)-Zn(2)#4	1.848(5)	F(3)-Zn(2)-N(3)	132.0(3)	F(3)-Zn(2)-F(3')#4	34.1(4)
F(3')-Zn(2)#4	2.25(2)	O(1)#2-Zn(2)-N(3)	102.6(3)	O(1)#2-Zn(2)-F(3')#4	90.7(5)
Zn(2)-F(3')	2.20(2)	F(3)-Zn(2)-N(5)	83.5(5)	N(3)-Zn(2)-F(3')#4	165.5(5)
Zn(2)-F(3')#4	2.25(2)	O(1)#2-Zn(2)-N(5)	95.7(9)	N(5)-Zn(2)-F(3')#4	83.3(8)
O(4)-Zn(2)#3	2.1573(16)	N(3)-Zn(2)-N(5)	100.7(9)	O(3)-Zn(2)-F(3')#4	91.2(7)
O(4)-Zn(1)-N(7)	180	F(3)-Zn(2)-O(3)	97.0(5)	O(4)-Zn(2)-F(3')#4	87.9(4)
O(2)#1-Zn(1)-N(2)	89.9(3)	O(1)#2-Zn(2)-O(3)	83.3(7)	N(3)-Zn(2)-O(3)	95.9(7)
O(2)#2-Zn(1)-N(2)	90.2(3)	N(7)-Zn(1)-N(2)	94.0(3)	O(4)-Zn(1)-N(2)	86.0(3)

Symmetry codes: #1 = x+1/2, -y+1/2, -z+1/2; #2 = -x+1/2, y-1/2, -z+1/2; #3 = -x+1, -y, z; #4 = x, -y, -z.

9. Atomic partial charges in the framework 1a

Table S3. Atomic partial charges (e) in the framework **1a**.

Zn1	0.463492	F3’	-0.314872	C9	0.180851	H8A	0.323214
Zn2	0.646675	O1	-0.422078	C11	-0.0300926	H8B	0.309540
N1	-0.239425	O2	-0.455675	C10	0.213167	H11	0.0693988
N2	-0.0176036	O3	-0.392697	C12	-0.410933	H12	1.00000
N3	0.0397788	O4	-0.132092	C13	0.768540	H14	0.246278
N4	-0.210486	C1	0.317824	C14	0.106087	H15	0.103829
N5	0.132041	C2	-0.0241229	C15	-0.123840	H17A	0.204279
N6	-0.296053	C3	-0.150858	C16	0.0142409	H17B	0.197615
N7	-0.267429	C4	-0.177181	C17	-0.379681	H17C	0.200845
N8	-0.768312	C5	0.0460924	C18	-0.411445	H18A	0.185242
F1	-0.685014	C6	0.379198	H3	0.160832	H18C	0.208401
F2	-1.00000	C7	-0.0641322	H4	0.165928	H18D	0.170989
F3	-0.201721	C8	0.674272	H7	0.151571		