A new strongly paramagnetic cerium containing microporous MOF for CO_2 fixation under ambient conditions

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Table S1. Crystal data and structure refinement for Ce_2NDC_3

Empirical formula	$C_{48}H_{46}Ce_2N_4O_{16}$
Formula weight	1215.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a=11.4988 (12) Å, b=11.5886 (12) Å, c = 23.465 (2) Å, α =78.702 (2)° β= 87.143 (2)° γ = 62.144(2)°
Volume	2707.8(5) $Å^3$
Z, Calculated density	2, 1.490 Mg/m^3
Absorption coefficient	1.727 mm-1
F (000)	1212
Crystal size	0.18× 0.16× 0.14 mm
Theta range for data collection	0.89 to 31.86°
Limiting indices	-15<=h<=14, -15<=k<=14, -30<=l<=34
Reflections collected / unique	33546 / 14754
Absorption correction	Semi-empirical from equivalents
Max. And min. Transmission	0.785 and 0.740
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	14754 / 0 / 639
Goodness-of-fit on F2	1.015
Final R indices [I> 2σ (I)]	R1 = 0.0382, wR2 = 0.1626
R indices (all data)	R1 = 0.0843, wR2 = 0.1801

Table S2. Bond distance and bond angles obtained from CIF of Ce_2NDC_3

Ce(1)-O(3)	2.626	Ce(1)-O(4)	2.684
Ce(1)-O(10)	2.469	Ce(1)-O(8)	2.530
Ce(1)-O(1)	2.563	Ce(1)-O(2)	2.503
Ce(1)-O(7)	2.501	Ce(2)-O(14)	2.520
Ce(2)-O(15)	2.512	Ce(2)-O(16)	2.581
Ce(2)-O(9)	2.701	Ce(2)-O(18)	2.460
Ce(2)-O(4)	2.484	Ce(1)-O(9)	2.469
Ce(1)-O(11)	2.480	Ce(2)-O(52)	2.438
O(1)-Ce(1)-O(2)	51.61	O(2)-Ce(1)-O(3)	150.56
O(1)-Ce(1)-O(3)	141.44	O(7)-Ce(1)-O(1)	71.82
O(7)-Ce(1)-O(2)	95.06	O(7)-Ce(1)-O(3)	74.34
O(7)-Ce(1)-O(4)	118.88	O(1)-Ce(1)-O(4)	142.29
O(2)-Ce(1)-O(4)	145.38	O(3)-Ce(1)-O(4)	48.91
O(8)-Ce(1)-O(1)	112.36	O(8)-Ce(1)-O(2)	78.05
O(8)-Ce(1)-O(3)	72.55	O(8)-Ce(1)-O(4)	105.16
O(8)-Ce(1)-O(7)	71.26	O(10)-Ce(1)-O(1)	125.67
O(10)-Ce(1)-O(2)	79.64	O(10)-Ce(1)-O(3)	92.72
O(10)-Ce(1)-O(4)	69.08	O(10)-Ce(1)-O(7)	143.66
O(10)-Ce(1)-O(8)	72.48	O(9)-Ce(2)-O(14)	105.94
O(9)-Ce(2)-O(15)	118.53	O(9)-Ce(2)-O(16)	49.09
O(14)-Ce(2)-O(15)	72.04	O(14)-Ce(2)-O(16)	73.98
O(15)-Ce(2)-O(16)	73.73	O(18)-Ce(2)-O(9)	71.50
Ce(2)-O(9)-Ce(1)	106.42	Ce(2)-O(4)-Ce(1)	106.49

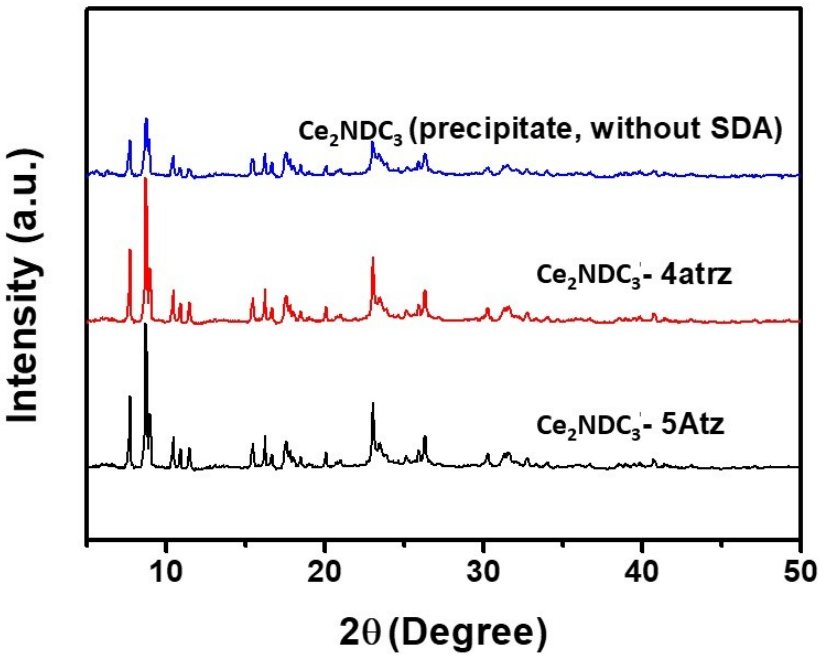

Figure S1: PXRD pattern of Ce_2NDC_3 in presence of 5-Atz (black coloured), 4atrz (red coloured) and Ce_2NDC_3 (precipitate without SDA, blue coloured)

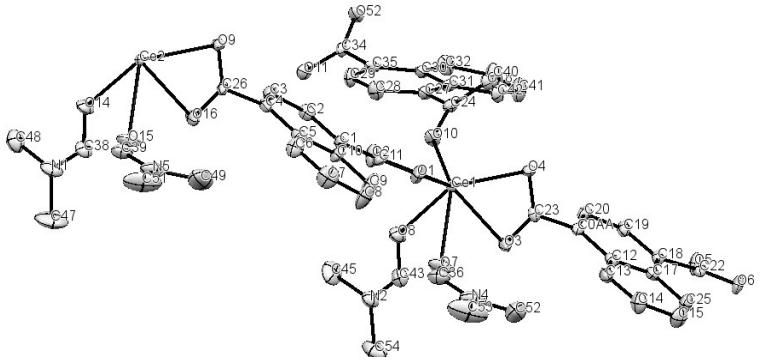

Figure S2: Asymmetric unit of Ce_2NDC_3 (ORTEP view)

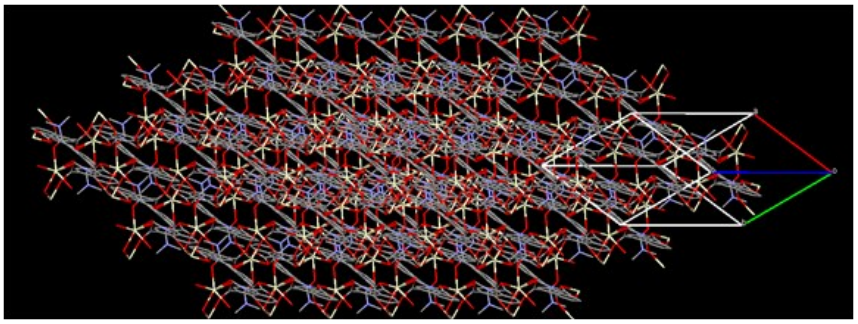

Figure S3: Wireframe model of Ce_2NDC_3.

Table S3. Comparison of Q_{st} values for CO_2 uptake between some MOFs containing saturated and unsaturated metal sites with Ce_2NDC_3.

Entry	MOFs	Q_{st} value ($-\Delta H_{ads}$ (CO_2) kJ mol^{-1})	Referances
1	HKUST-1	35	1
2	$Cr_3(BTC)_2$	26.7	2
3	$Ni_3(BTC)_2(Me_2NH)_2(H_2O)$	36.8	2
4	$Mo_3(BTC)_2(DMF)_{0.5}$	25.6	2
5	$[Ru_3(BTC)_2][BTC]_{0.5}$	32.6	2
6	Ce_2NDC_3	36.43	This work
7	UiO-66-DM	46.8	3
8	$(In_2X)(Me_2NH_2)_2(DMF)_9(H_2O)_5$	21.14	**4**
9	Mg_2(dobdc)	43.5	5
10	Mn_2(dobdc)	31.7	5
11	Fe_2(dobdc)	33.2	5
12	Cu-BTTri-mmen	96	6
13	Cu-BTTri-en	90	7
14	NH_2-MIL-53(Al)	50	8
15	CAU-1	48	9
16	bio-MOF-11	45	10
17	MIL-100(Cr)	62	11
18	HKUST-1	45	12
19	CuBTTri,	21	7

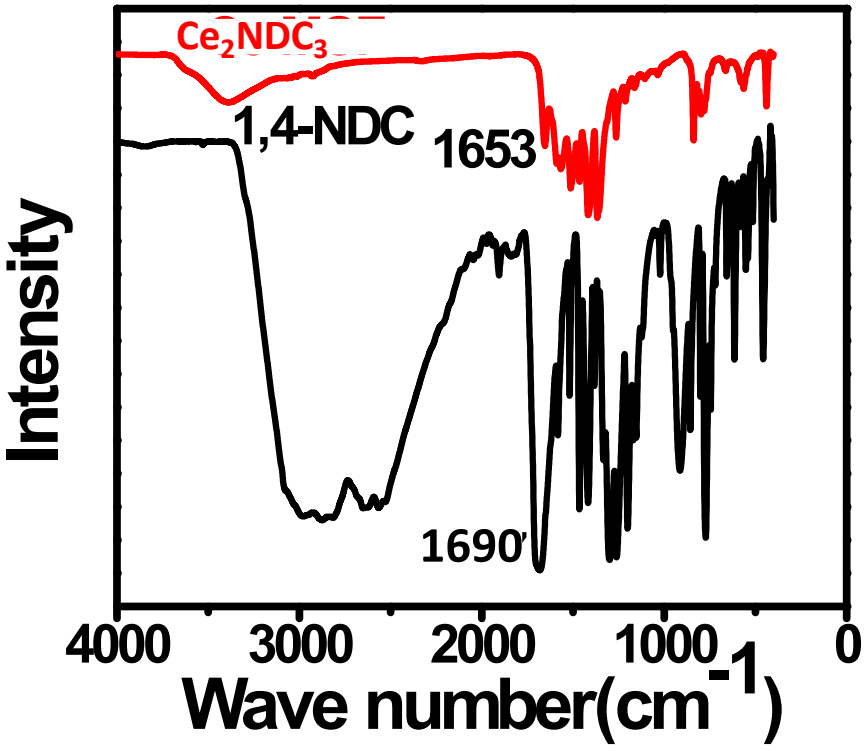

Figure S4: FTIR spectra of NDC ligand and Ce_2NDC_3

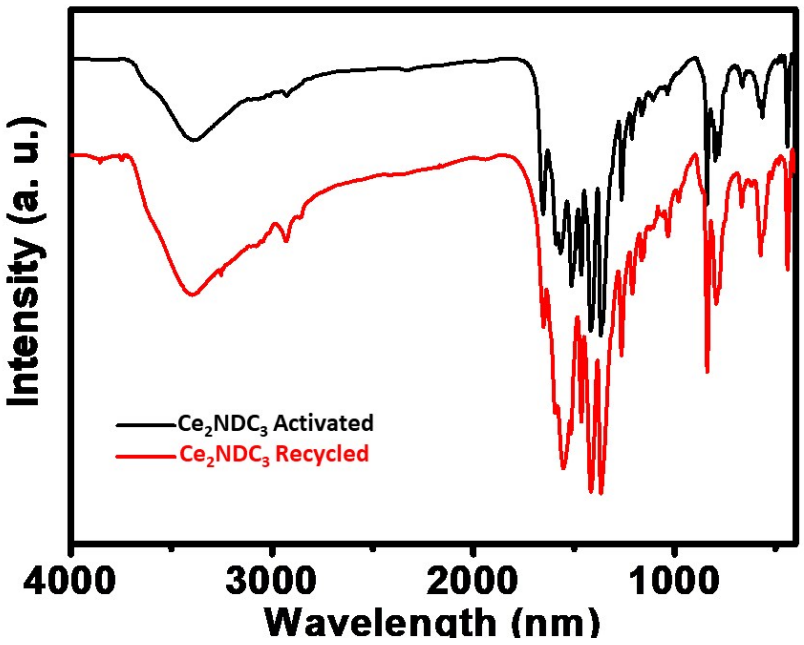

Figure S5: FTIR spectra of Ce_2NDC_3 before and after recycle of catalyst

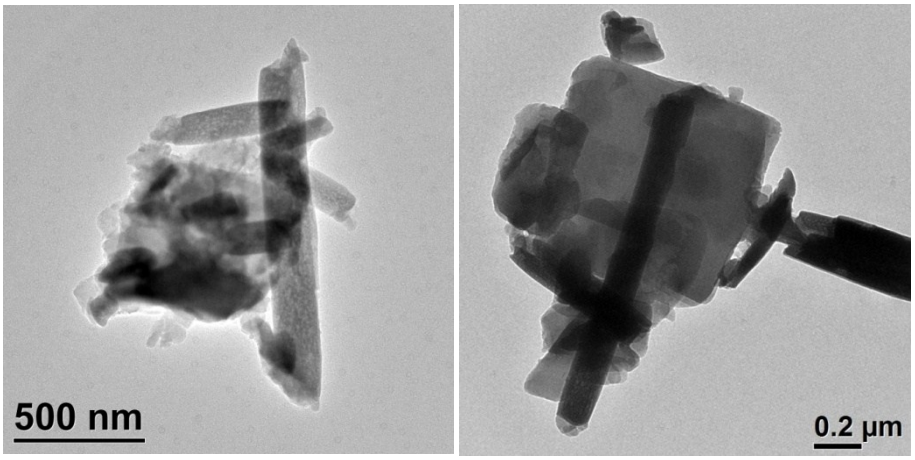

Figure S6: UHR TEM images of Ce_2NDC_3 after recycling of the catalyst.

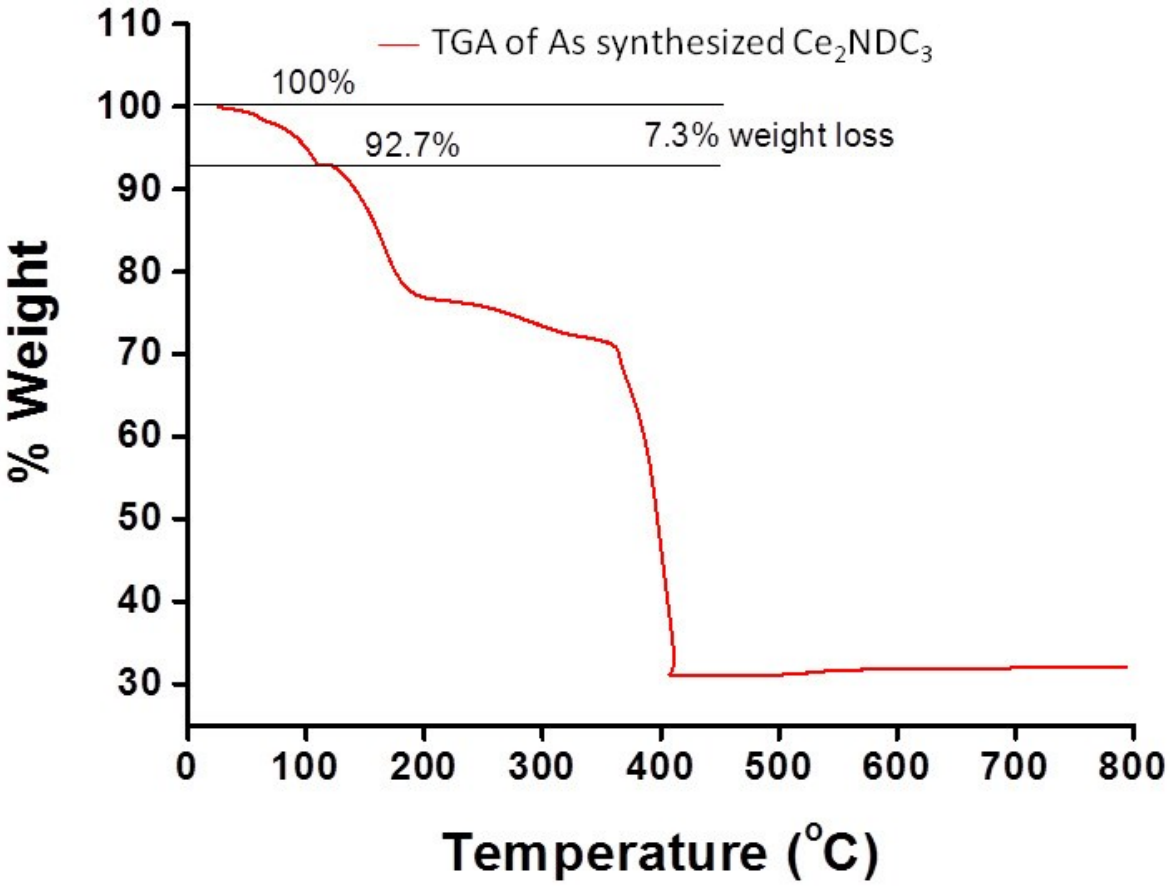

Figure S7: TGA plot in air of Ce_2NDC_3 (without vacuum dry).

Section 1. Validation of masked solvent molecules during refinement from TGA

Ce_2NDC_3

Triclinic, $P\bar{1}$ space group, Z = 2

Therefore,

FW = 1215.13

Squeezed electron density =118.

Then weight loss for water molecule is 118/2=59/10=5.9*18= 106.2 [Where electron density for H_2O=10 & MW of H_2O=18]

i.e. Total weight including squeezed water = 1215.13+106.2=1321.33

Weight loss for about 7 water molecules

= 106.2/1321.33 X 100%

= 8.04 % Experimental Value (7.3 %) (ESI. Fig. S7)

Section 2. Experimental part for magnetic studies:

The magnetic susceptibility measurements were obtained with the use of MPMS-XL Quantum Design SQUID magnetometer. These magnetometer works between 1.8 and 300 K for dc applied fields ranging from -5 to 5 T. For this sample *M* versus *H* measurements was performed at 100 K to confirm the absence of ferromagnetic impurities. The magnetic data were corrected for the sample holder, paratone oil and the intrinsic diamagnetic contributions. Measurements were performed on a polycrystalline sample. The mass of the sample was estimated at about 20.00 mg.

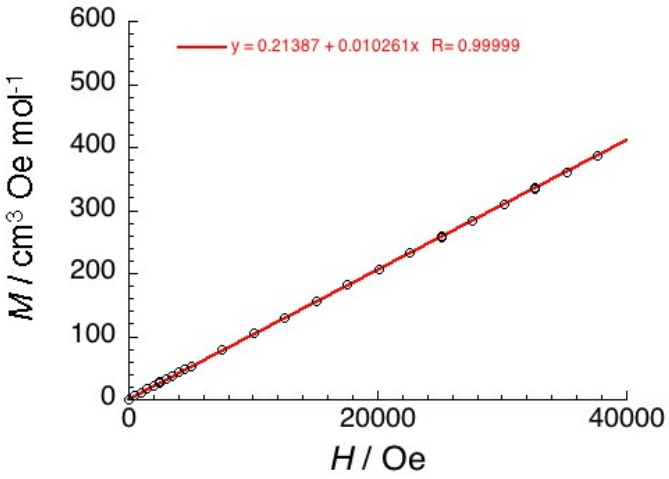

Figure: S8. Field dependence of magnetization for Ce_2NDC_3, collected at 100 K. The red line represents the linear fit to the data

Table S4. Optimization of catalytic activity of Ce_2NDC_3 under different pressure, temperature and reaction time with SO = 10mmol, 1.8 mol% TBAB and 20 mL DCM.

Catalyst weight (Ce_2NDC_3)	**Pressure (Mpa)**	**Temp (^oC)**	**Time (h)**	**Yield (%)**
25 mg	1.2	120	24	98
25 mg	1.2	90	24	98
25 mg	1.2	60	24	95
25 mg	1.2	RT	24	94
25 mg	0.5	60	24	94
25 mg	0.2	RT	24	94
25 mg	0.5	120	8	98
25 mg	0.1	60	24	92
25 mg	0.1	RT	24	90
20 mg	0.1	RT	12	89
20 mg	0.1	RT	8	89
15 mg	**0.1**	**RT**	**8**	**89**
15 mg	0.1	RT	4	85
10 mg	0.1	RT	8	76

Table S5. Comparison of catalytic activity of Ce_2NDC_3 with other catalysts

Catalyst	**Pres. (Mpa)**	**Temp (^oC)**	**Time (h)**	**Yield (%)**	**Ref.**
UMCM-1-NH_2	0.4	RT	4	78	13
Cr-MIL-101	0.8	RT	24	82	14
MOF-5	0.4	RT	4	57	15
Hf-Nu-1000	0.1	RT	26	100	16
Ni-saldpen-MOF	2	RT	4	-	17
MMCF-2	0.1	RT	48	95.4	18
MMPF-9	0.1	RT	48	87.4	19
UMCM-1	1.2	RT	24	85	13
UMCM-1-NH_2	1.2	RT	24	90	13
Ce_2NDC_3	**0.1**	**RT**	**8**	**89**	**This work**

Proton NMR of the 4,5-Tetramethylene-1,3-dioxolan-2-one and cyclohexane epoxide

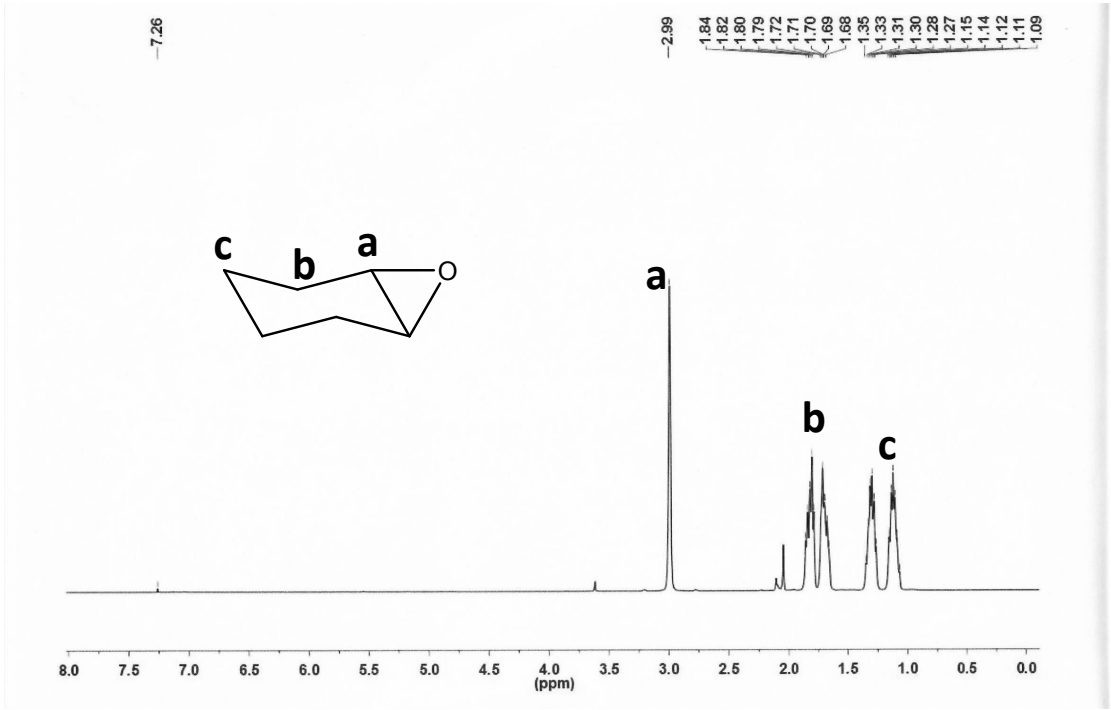

Figure S9a: NMR spectra of cyclohexane epoxide

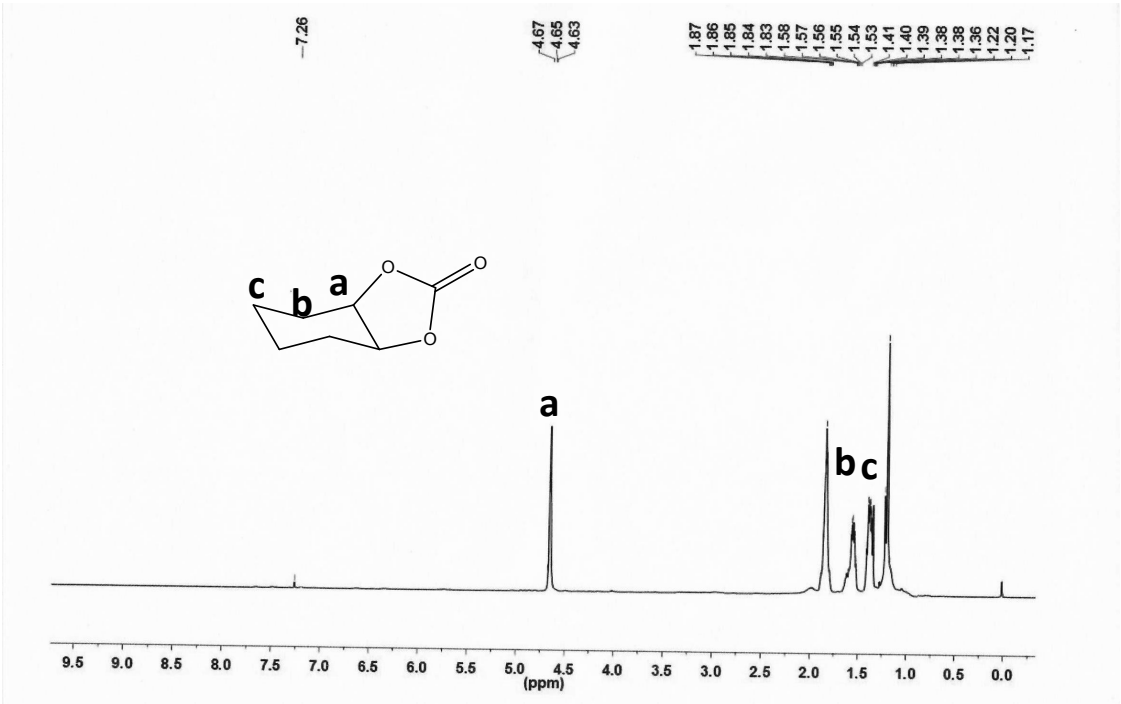

Figure S9b: NMR spectra of 4,5-Tetramethylene-1,3-dioxolan-2-one (signal at 4.6 ppm indicates formation of cyclic carbonate)

Section 3. NMR of collected cyclic carbonate:

1. 4-Chloromethyl-1,3-dioxolan-2-one: Colorless liquid; 92% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.00–4.95 (m, 1H), 4.59 (dd, J=9.1, 8.8 Hz, 1H), 4.40 (dd, J=9.1, 8.8 Hz, 1H), 3.80-3.69 (m, 2H).

2. 4-Phenyl-1,3-dioxolan-2-one: White solid; 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.40-7.37 (m, 3H), 7.31-7.26 (m, 2H), 5.59 (t, J=7.9 Hz, 1H), 4.77 (dd, J=8.3, 7.9 Hz, 1H), 4.30 (dd, J=8.3, 7.9 Hz, 1H).

3. 4-Allyloxymethyl-1,3-dioxolan-2-one: Colourless liquid, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.73 (ddt, J=17.4, 10.5, 5.7 Hz, 1H), 5.16(dd, J=17.4, 1.5 Hz, 1H), 5.02(dd, J=10.5, 1.5 Hz, 1H), 4.78-4.70 (m, 1H), 4.49 (t, J=8.4 Hz, 1H), 4.20 (t, J=8.4 Hz, 1H), 3.83 (d, J=5.7 Hz, 2H), 3.51-3.40 (m, 2H).

4. 4-(hydroxymethyl)-1,3-dioxolan-2-one: yellow liquid, 79% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72-5.77(br s, 1H), 4.70-4.75 (m, 1 H), 4.36 - 4.41 (m, 2 H), 4.25 (dd, J = 12.4, 3.4Hz, 1 H), 3.52 (dd, J = 12.4, 3.4 Hz, 1 H).

5. 4,5-Tetramethylene-1,3-dioxolan-2-one: pale yellow liquid, 44% yield; ^{1} H NMR (500 MHz, $CDCl_3$) δ=4.63-4.67 (m, 2 H), 1.87-1.80 (m, 4 H), 1.61-1.54 (m, 2 H), 1.40-1.34 (m, 2 H).

References

1. Q. M. Wang, D. Shen, M. Bulow, M. L. Lau, S. Deng, F. R.; Fitch, N. O. Lemcoff and J. Semanscin, Microporous Mesoporous Mater. 2002, **55**, 217.

2. C. R. Wade and M. Dincă, Dalton Trans., 2012, **41**, 7931-7938.

3. H. Jasuja and K. S. Walton, J. Phys. Chem. C, 2013, **117**, 7062-7068.

4. Z. J. Lin, Y. B. Huang, T. F. Liu, X. Y. Li and R. Cao, Inorg. Chem., 2013, **52**, 3127-3132.

5. W. L. Queen, M. R. Hudson, E. D. Bloch, J. A. Mason, M. I. Gonzalez, J. S. Lee, D. Gygi, J. D. Howe, K. Lee, T. A. Darwish, M. James, V. K. Peterson, S. J. Teat, B. Smit, J. B. Neaton, J. R. Long and C. M. Brown, *Chem. Sci*., 2014, **5**, 4569-4581.

6. T. M. McDonald, D. M. D'Alessandro, R. Krishna and J. R. Long, *Chem. Sci*. 2011, **2**, 2022-2028.

7. A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc*. 2009, **131**, 8784-8786.

8. B. Arstad, H. Fjellvag, K.O. Kongshaug, O. Swang and R. Blom, *Adsorption*, 2008, **14**, 755-762.

9. X. Si, C. Jiao, F. Li, J. Zhang, S. Wang, S. Liu, Z. Li, L. Sun, F. Xu, Z. Gabelica and C. Schick, *Energy Environ. Sci.* 2011, **4**, 4522-4527.

10. J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.* 2010, **132**, 38-39.

11. P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G.D. Weireld, J. S. Chang, D. Y. Hong, Y. K. Hwang, S. H. Jhung and G. Ferey, *Langmuir*, 2008, **24**, 7245-7250.

12. Q. M. Wang, D. Shen, M. Bulow, M. L. Lau, S. Deng, F. R.; Fitch, N. O. Lemcoff and J. Semanscin, Microporous *Mesoporous Mater*. 2002, **55**, 217-230.

13. R. Babu, A. C. Kathalikkattil, R. Roshan, J Tharun, D. Kim and D. Park, *Green Chem.* 2016, **18**, 232-242;

14. O. V. Zalomaeva, A. M. Chibiryaev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev and V. P. Fedin, *J. Catal*. 2013, **298**, 179-185.

15. J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.* 2009, **11**, 1031-1036.

16. J. Martinez, J. A. C. Osma, A. Earlam, C. A. Moreno, A. Otero, A. L. Sanchez, M. North and A. R. Dieguez, *Chem. Eur. J*. 2015, **21**, 9850-9862.

17. Y. Ren, X. Cheng, S. Yang, C. Qi, H. Jiang and Q. Mao, *Dalton Trans*. 2013, **42**, 9930-9937.

18. W. Y. Gao, H. Wu, K. Leng, Y. Sun, and S. Ma, *Angew Chem. Int. Ed*., 2016, **55**, 5472-5476

19. W. Y. Gao, L. Wojtas and S. Ma, *Chem. Commun*. 2014, **50**, 5316-5218.