Electronic Supplementary Information for CrystEngComm
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Supporting Information For

A highly stable dimethyl-functionalized Ce(IV)-based UiO-66 metal-organic framework material for gas sorption and redox catalysis

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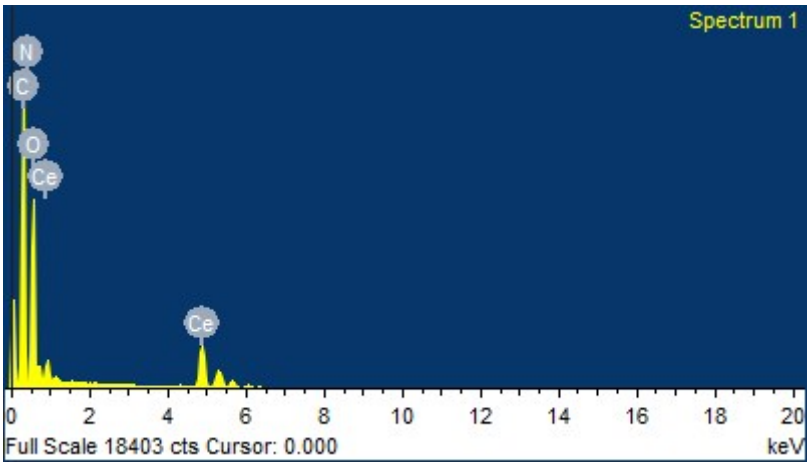

Figure S1. EDX spectrum of **1'**.

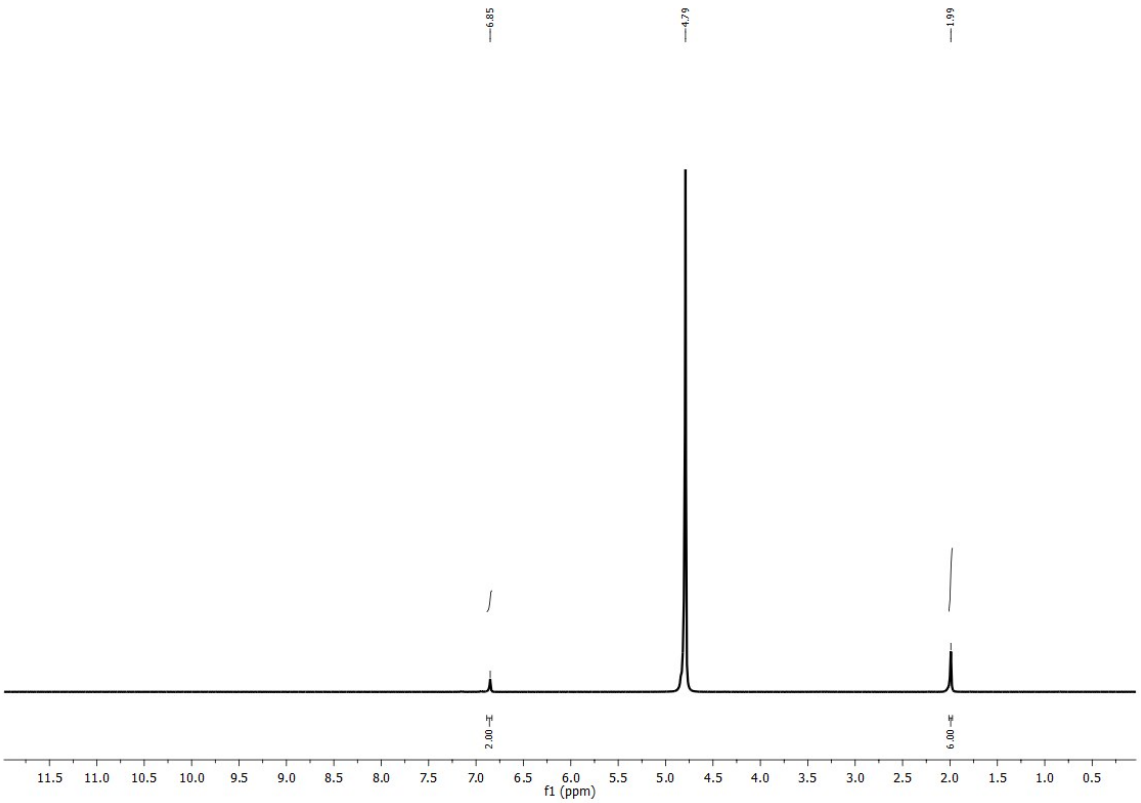

Figure S2. ^{1}H-NMR spectra of $H_2BDC\text{-}(CH_3)_2$ ligand recorded in 500 µL of 1M NaOH in D_2O. The peaks at δ values of 6.85 and 1.99 ppm correspond to the ligand. The peak at δ value of 4.79 ppm correspond to HDO (NMR solvent).

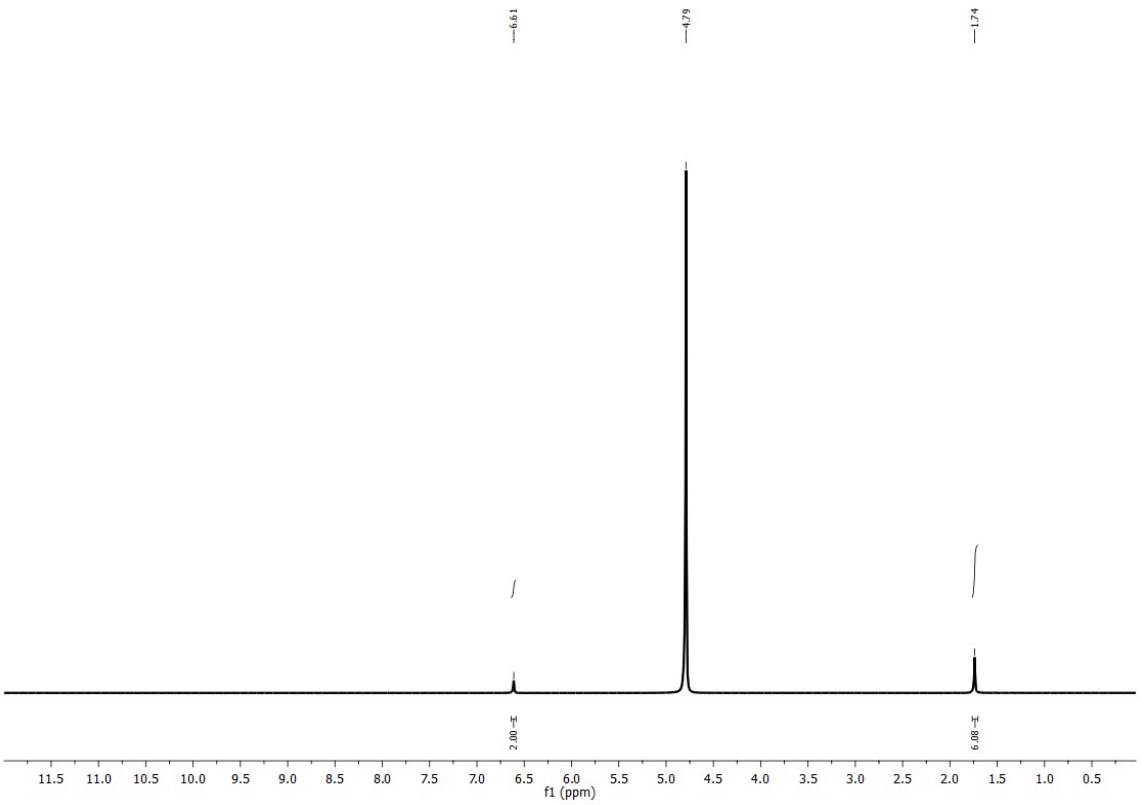

Figure S3. ^{1}H-NMR spectra of **1'** recorded in 500 µL of 1M NaOH in D_2O. The peaks at δ values of 6.61 and 1.74 ppm correspond to the ligand. The peak at δ value of 4.79 ppm correspond to HDO (NMR solvent).

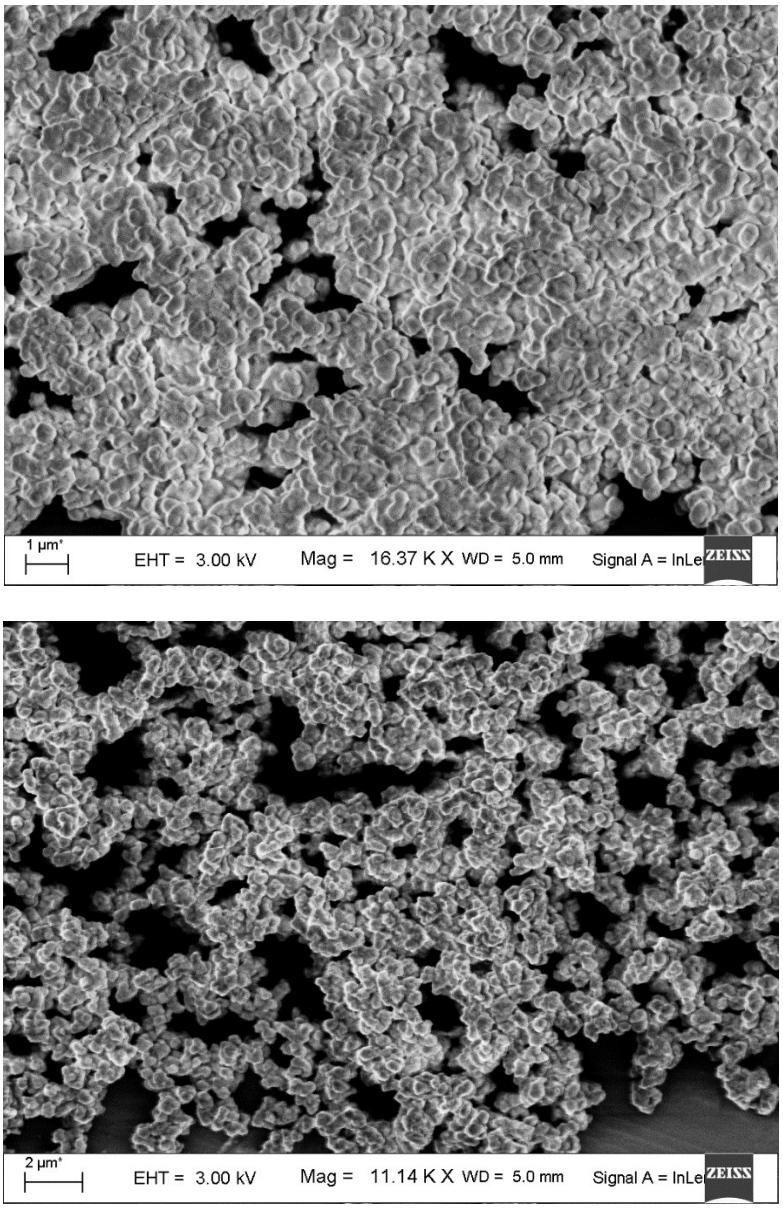

Figure S4. FE-SEM images of as-synthesized **1'**.

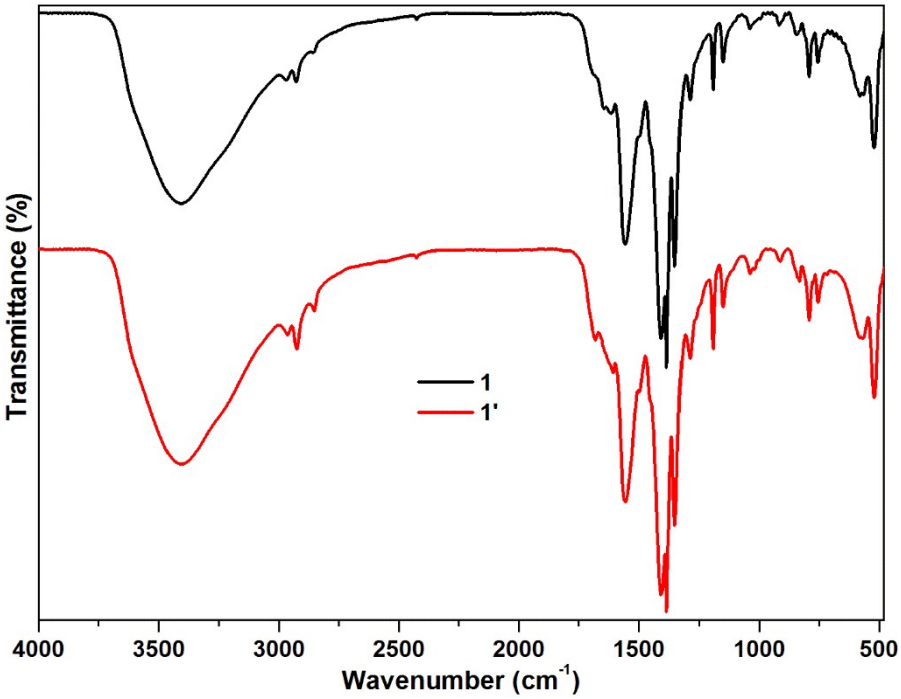

Figure S5. FT-IR spectra of as-synthesized **1** (black) and activated (red) **1'**.

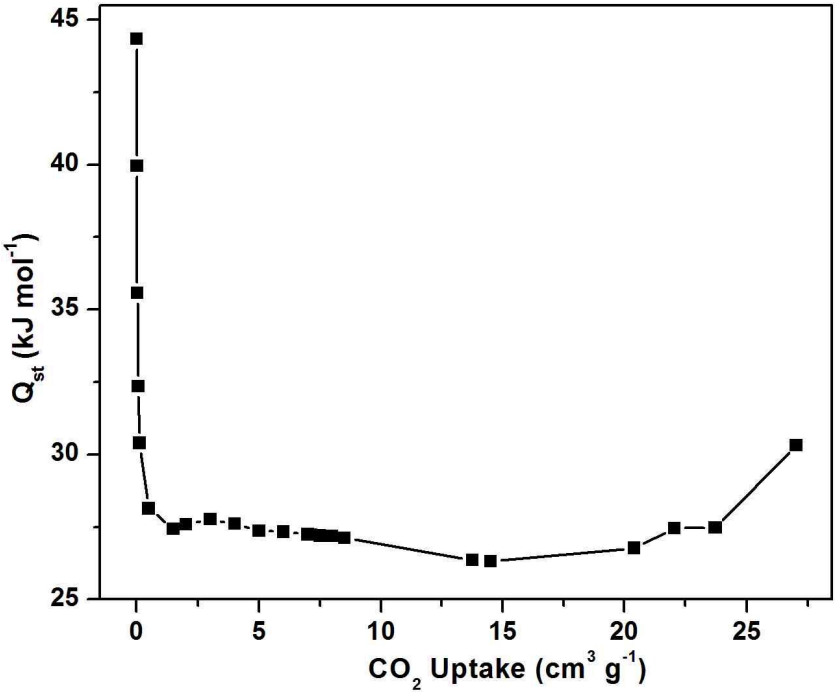

Figure S6. Calculated isosteric heats of adsorption as a function of CO_2 uptake for **1'**.

Table S1. Lattice parameters of as-synthesized **1** having cubic unit cell. The values are compared with those of the formerly reported, isostructural, parent and functionalized Zr(IV) and Ce(IV)-based UiO-66 compounds.

Compound	*a* (Å)	*V* (Å^3)
1	21.427(7)	9837.7(13)
Ce-UiO-66[1]	21.4727(3)	9900.6(4)
Ce-UiO-66-F[1]	21.5241(8)	-
Ce-UiO-66-CH_3[1]	21.4842(2)	-
Ce-UiO-66-Cl[1]	21.4904(2)	-
Ce-UiO-66-NO_2[1]	21.5194(2)	-
Ce-UiO-66-COOH[1]	21.4718(7)	-
Zr-UiO-66[2]	20.7004(2)	8870.3(2)
Zr-UiO-66-SO_3H[3]	20.824(1)	9029.8(6)
Zr-UiO-66-COOH[3]	20.8202(3)	9025.1(1)
Zr-UiO-66-I[3]	20.8076(5)	9008.8(2)
Zr-UiO-66-CF_3[4]	20.43(5)	8524.5(34)
Zr-UiO-66-$(COOH)_2$[4]	20.54(6)	8662.9(27)
Zr-UiO-66-F_2[4]	20.33(5)	8401.9(32)
Zr-UiO-66-Cl_2[4]	20.27(13)	8325.7(48)
Zr-UiO-66-Br_2[4]	20.23(3)	8276.5(36)

Table S2. Oxidation of styrene using various oxidants in the presence of **1'**.

S.No.	Substrate	Oxidant	T (^{o}C)	Time (h)	Conv. (%)	Selectivity (%)		
						2	**3**	Others
1	Styrene	TBHP in decane	40	1	3.5	5	80	15
2	Styrene	TBHP in decane	40	3	6.3	6	81	13
3	Styrene	TBHP in decane	40	5	10.1	6	74	20
4	Styrene	TBHP in decane	40	7	12.6	7	72	21
5	Styrene	TBHP in decane	70	1	17.2	37	47	16
6	Styrene	TBHP in decane	70	3	31	35	44	21
7	Styrene	TBHP in decane	70	5	48	32	45	23
8	Styrene	TBHP in	70	7	58.8	29	42	29

		decane						
9	Styrene	TBHP in water	70	1	15	16	68	16
10	Styrene	TBHP in water	70	3	29	21	61	18
11	Styrene	TBHP in water	70	6	62	19	50	31
12	Styrene	TBHP in water	70	9	72	17	44	39

Reaction conditions: styrene (1 mmol), oxidant (1 mmol), **1'** (20 mg), CH_3CN (2 mL).

Table S3. Conversion of cyclohexene in the presence of **1'** using TBHP as oxidant.

S.No.	Time (h)	Conv. (%)	Selectivity (%)			
			4	**5**	**6**	**7**
1	1	21	17	10	30	43
2	3	42	10	11	33	46
3	5	51	7	10	33	50
4	7	56	7	12	33	48

Reaction conditions: cyclohexene (1 mmol), TBHP in decane (1 mmol), **1'** (20 mg), CH_3CN (2 mL), 70 ^oC.

References:

1. M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. De Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578-12581.
2. M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, *J. Am. Chem. Soc.*, 2009, **131**, 10857-10859.
3. S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Grzywa, L. Sun, D. Volkmer and P. Van Der Voort, *Dalton Trans.*, 2013, **42**, 4730-4737.
4. S. Biswas and P. Van Der Voort, *Eur. J. Inorg. Chem.*, 2013, **2013**, 2154-2160.