Phase formation studies of Ca-terephthalate MOF-type materials

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Figure S1. Part of the Ca-BDC-*tric* (NICS-8) structure with labeled atoms showing the coordination environment of Ca^{2+} cation and location of partially occupied O atom belonging to adsorbed water molecule.

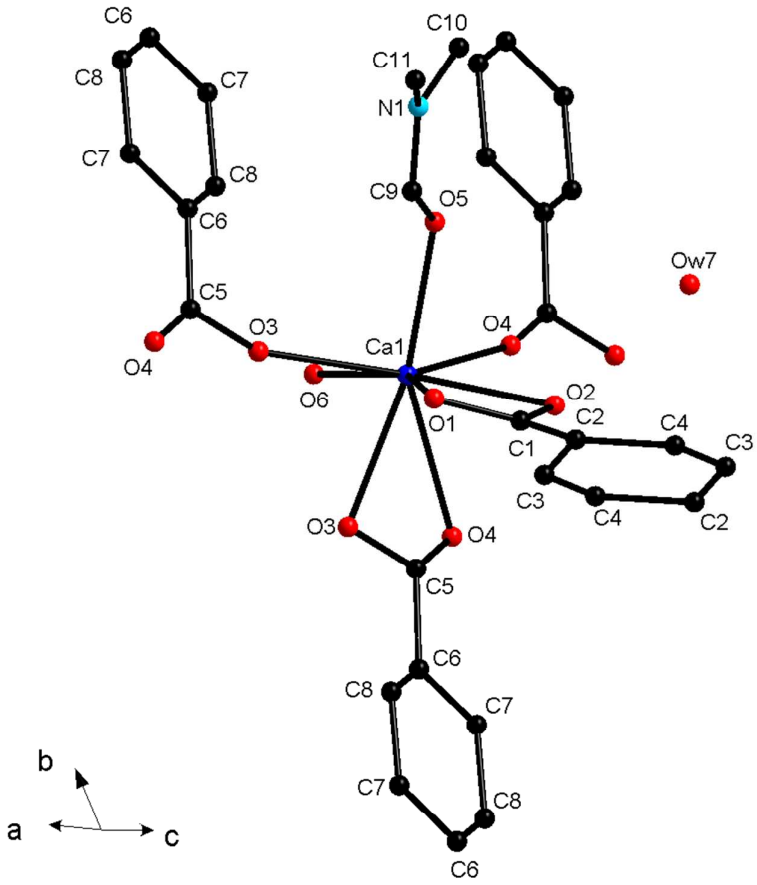

Figure S2. Rietveld plot of Ca-BDC- *tric* structure. Experimental plot – black line; calculated plot – red crosses; differential plot – blue line; calculated *d* values – black rods.

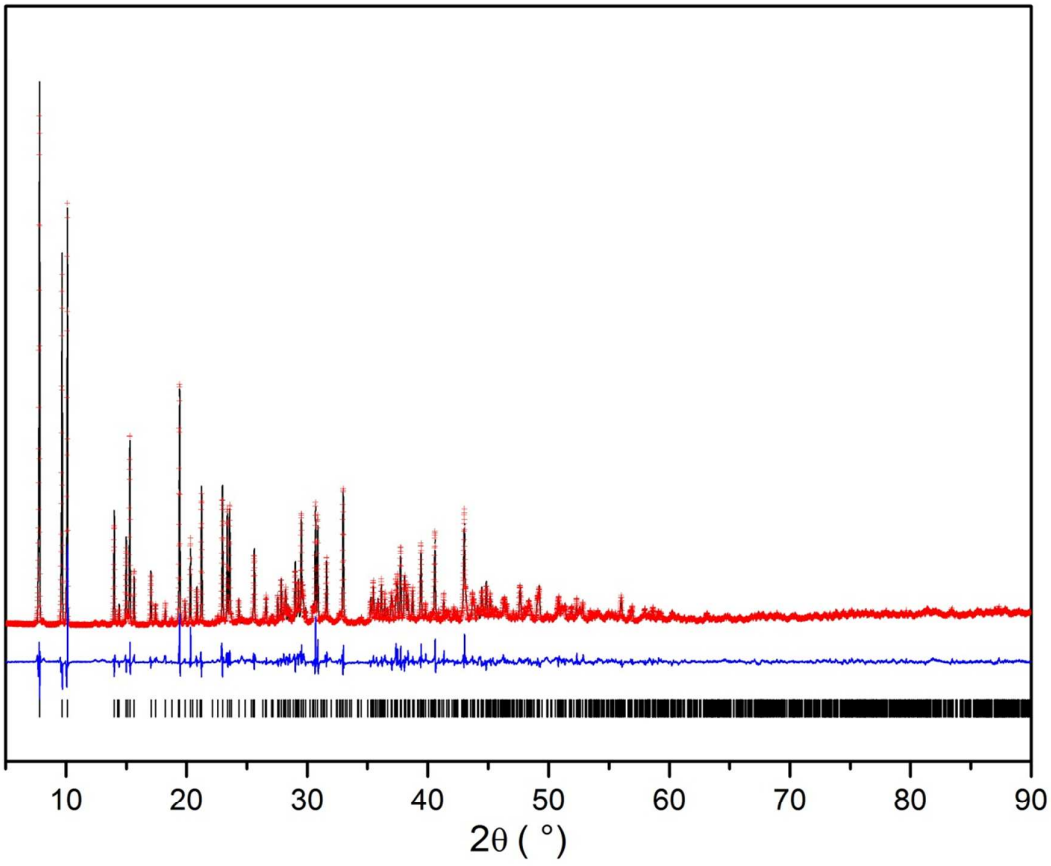

Table S1. Crystal structure and refinement data of Ca-BDC-*tric* (NICS-8) structure.

Chemical formula	$C_{11}H_{13}CaNO_{6.5}$
Formula weight (g/mol)	303.31
Temperature (°C)	25
Wavelength (Å)	1.5418
symmetry	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	12.4544(1)
b (Å)	10.2080(1)
c (Å)	6.7012(1)
α (°)	107.433(1)
β (°)	104.433(1)
γ (°)	66.7607(9)
V (Å^3)	738.36(2)
Z	2
calculated density (g/mL)	1.306
2θ range (°)	0 to 90.0
No Reflections	1211
No of structural parameters	113
GoF	1.38
R_{wp}, R_p	0.124, 0.092
R_{Bragg}	0.050

Table S2. Atomic coordinates for Ca-BDC-*tric* structure.

	x	y	z	Beq
Ca1	0.4442(3)	0.1094(3)	0.7715(7)	2.6(1)
O1	0.2587(6)	0.0891(7)	0.501(1)	2.2(1)
O2	0.2621(7)	0.0783(8)	0.820(1)	2.2(1)
O3	0.4903(7)	0.1410(7)	0.460(1)	2.2(1)
O4	0.4756(8)	0.1553(7)	0.155(2)	2.2(1)
O5	0.3088(7)	0.3641(8)	0.781(2)	2.2(1)
O6	0.6459(7)	0.0914(8)	0.871(2)	2.2(1)
Ow7	0.147(1)	0.287(1)	0.143(3)	2.2(1)
C1	0.2202(5)	0.0584(9)	0.629(1)	2.7(2)
C2	0.1099(5)	0.0375(8)	0.564(1)	2.7(2)
C3	-0.0690(7)	0.019(1)	0.647(2)	2.7(2)
C4	0.0482(5)	0.0407(9)	0.718(1)	2.7(2)
C5	0.4870(9)	0.2139(9)	0.343(1)	2.7(2)
C6	0.5145(9)	0.6364(7)	0.578(1)	2.7(2)
C7	0.5398(8)	0.5492(6)	0.719(1)	2.7(2)
C8	0.5388(9)	0.4015(7)	0.641(1)	2.7(2)
C9	0.238(2)	0.4312(9)	0.658(3)	2.7(2)
C10	0.211(1)	0.646(1)	0.863(2)	2.7(2)
C11	0.101(1)	0.601(1)	0.536(2)	2.7(2)
N1	0.1906(9)	0.5684(8)	0.685(1)	4.1(2)

Table S3. Selected bond lengths and angles for Ca-BDC-*tric* structure.

Contact distances (Å)		Angles (°)	
Ca1 – O6^{i}	2.380(9)	O6—Ca1—O4^{i}	75.8(4)
Ca1 – O4^{i}	2.43(1)	O6—Ca1—O3^{i}	77.0(3)
Ca1 – O3^{i}	2.44(1)	O6—Ca1—O5^{i}	112.5(3)
Ca1 – O5^{i}	2.471(7)	O6—Ca1—O2^{i}	152.6(4)
Ca1 – O2^{i}	2.52(1)	O6—Ca1—O1^{i}	154.0(3)
Ca1 – O1^{i}	2.593(8)	O4—Ca1—O3^{i}	146.8(4)
O1 – C1^{i}	1.24(1)	O4—Ca1—O5^{i}	91.3(3)
O4 – C5^{i}	1.22(1)	O4—Ca1—O2^{i}	81.1(3)
O2 – C1^{i}	1.24(1)	O4—Ca1—O1^{i}	129.9(4)
O3 – C5^{i}	1.22(1)	O3—Ca1—O5^{i}	81.8(3)
O5 – C9^{i}	1.19(2)	O3—Ca1—O2^{i}	129.4(3)
C9 – N1^{i}	1.26(1)	O3—Ca1—O1^{i}	79.6(3)
C10 – N1^{i}	1.25(1)	O5—Ca1—O2^{i}	82.4(3)
C11 – N1^{i}	1.30(1)	O5—Ca1—O1^{i}	74.6(3)
C5 – C6^{ii}	1.45(1)	O2—Ca1—O1^{i}	49.9(3)
C1 – C2^{i}	1.47(1)	O2—C1—O1^{i}	120.6(8)
C2 – C3^{ii}	1.41(1)	O3—C5—O4^{i}	114.6(9)
C2 – C4^{ii}	1.42(1)	O1—C1—C2^{i}	117.8(8)
C3 – C4^{i}	1.42(1)	O2—C1—C2^{i}	119.6(8)
C6 – C7^{i}	1.38(1)	C1—C2—C3^{i}	123.1(8)
C6 – C8^{ii}	1.45(1)	C1—C2—C4^{i}	119.5(7)
		O3—C5—C6^{i}	122.0(8)
		O4—C5—C6^{i}	123.2(9)
		C5—C6—C7^{i}	119.8(7)
		C5—C6—C8^{i}	116.2(7)
		O5—C9—N1^{i}	127.2(1)
		C9—N1—C10^{i}	118.7(1)
		C9—N1—C11^{i}	109(1)
		C10—N1—C11^{i}	128(1)

Symmetry codes: (i) x, y, z; (ii) -x,-y, -z.

Table S4. Weight contributions of Ca-BDC-*orth* phase in the products obtained after 1 day of crystallization at specified temperatures and TEA/Ca^{2+} molar ratios using $Ca(NO_3)_2.4H_2O$ as precursor. Results are based on the Rietveld quantification analyses with the uncertanties given in brackets. Quantities of Ca-BDC-*tric* correspond to 100 – wt.% (Ca-BDC-*orth*).

	TEA/Ca^{2+} molar ratio					
	0	0.30	0.63	1.00	1.30	1.63
60 °C	39(1)	0	0	0	0	0
70 °C	44(1)	0	0	0	0	0
80 °C	42(1)	0	0	0	0	0
90 °C	35(1)	0	0	0	0	8(1)
100 °C	43(1)	8(1)	0	0	7(1)	10(1)
110 °C	54(1)	11(1)	0	4(1)	7(1)	13(1)
120 °C	64(1)	17(1)	8(1)	6(1)	8(1)	58(1)
130 °C	90(2)	30(1)	80(2)	8(1)	20(1)	63(1)
140 °C	100	100	91(2)	80(2)	100	100
150 °C	100	100	100	100	100	100

Table S5. Weight contributions of Ca-BDC-*orth* phase in the products obtained after 3 days of crystallization at specified temperatures and TEA/Ca^{2+} molar ratios using $Ca(NO_3)_2.4H_2O$ as precursor. Results are based on the Rietveld quantification analyses with the uncertanties given in brackets. Quantities of Ca-BDC-*tric* correspond to 100 – wt.% (Ca-BDC-*orth*).

	TEA/Ca^{2+} molar ratio					
	0	0.30	0.63	1.00	1.30	1.63
60 °C	44(1)	0	0	0	0	0
70 °C	27(1)	0	0	0	0	0
80 °C	24(1)	0	0	0	0	0
90 °C	27(1)	0	0	0	0	2(1)
100 °C	61(1)	5(1)	0	0	2(1)	25(1)
110 °C	64(1)	8(1)	0	0	3(1)	26(1)
120 °C	90(2)	47(1)	7(1)	7(1)	44(1)	100
130 °C	100	90(2)	80(2)	64(1)	90(2)	100
140 °C	100	100	95(2)	95(2)	92(2)	100
150 °C	100	100	100	100	100	100

Table S6. Weight contributions of Ca-BDC-*orth* phase in the products obtained after 1 day of crystallization at specified temperatures and TEA/Ca^{2+} molar ratios using $CaCl_2.6H_2O$ as precursor. Results are based on the Rietveld quantification analyses with the uncertanties given in brackets. Quantities of Ca-BDC-*tric* correspond to 100 – wt.% (Ca-BDC-*orth*).

	TEA/Ca^{2+} molar ratio					
	0	0.30	0.63	1.00	1.30	1.63
60 °C	41(1)	0	0	0	0	0
70 °C	34(1)	0	0	0	0	0
80 °C	42(1)	0	0	0	0	3(1)
90 °C	35(1)	0	0	0	8(1)	3(1)
100 °C	43(1)	4(1)	0	0	12(1)	5(1)
110 °C	54(1)	80(2)	0	3(1)	68(1)	67(1)
120 °C	64(1)	100	8(1)	78(2)	100	100
130 °C	100	100	551)	100	100	100
140 °C	100	100	91(2)	100	100	100
150 °C	100	100	100	100	100	100

Table S7. Weight contributions of Ca-BDC-*orth* phase in the products obtained after 3 days of crystallization at specified temperatures and TEA/Ca^{2+} molar ratios using $CaCl_2.6H_2O$ as precursor. Results are based on the Rietveld quantification analyses with the uncertanties given in brackets. Quantities of Ca-BDC-*tric* correspond to 100 – wt.% (Ca-BDC-*orth*).

	TEA/Ca^{2+} molar ratio					
	0	0.30	0.63	1.00	1.30	1.63
60 °C	44(1)	0	0	0	0	0
70 °C	27(1)	0	0	0	0	0
80 °C	24(1)	0	0	0	9(1)	15(1)
90 °C	27(1)	4(1)	0	68(1)	55(1)	22(1)
100 °C	41(1)	55(1)	0	77(2)	100	91(2)
110 °C	60(1)	78(2)	13(1)	100	100	100
120 °C	90(2)	100	38(1)	100	100	100
130 °C	100	100	92(2)	100	100	100
140 °C	100	100	100	100	100	100
150 °C	100	100	100	100	100	100