Base catalytic activity of alkaline earth MOFs: a (micro)spectroscopic study of active site formation by controlled transformation of structural anions

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Supporting information

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Experimental and theoretical procedures

Chemicals

Malononitrile was purchased from Fluka; *N*,*N*-dimethylformamide, benzaldehyde, *p*-nitrobenzaldehyde, trimesic acid and barium nitrate from Acros; toluene and acetonitrile from VWR; ethyl cyanoacetate, ethyl acetoacetate and *p*-methoxybenzaldehyde from Aldrich; methyl vinyl ketone from Sigma Aldrich; diethyl malonate, cyclopentanone, cyclohexanone and *o*-nitrobenzaldehyde from Janssen Chimica; nitric acid (65%) from Chemlab, *p*-bromobenzaldehyde from Alfa Aesar and strontium nitrate from Merck. All chemicals were of the highest grade available and were used without further purification.

Material synthesis and activation

$Ba_2(BTC)(NO_3)(DMF)$ was synthesized according to the procedure reported by Foo *et al.*:[1] $Ba(NO_3)_2$ (104.5 mg) was added to a solution of 1,3,5-benzenetricarboxylic acid (H_3BTC) (42.0 mg) in DMF (20 ml) in a glass bottle. The bottle was sealed and heated to 140°C for 24 h. Afterwards, the needle shaped crystals were recovered by vacuum filtration, washed with DMF and air dried.

$Sr_2(BTC)(NO_3)(DMF)$ was synthesized according to a procedure based on that by Lee *et al.*:[2] $Sr(NO_3)_2$ (0.539 g), H_3BTC (0.210 g) and nitric acid (0.5 ml of a 65 % solution) were added to 10 ml DMF in a Teflon lined steel autoclave. The autoclave was sealed and heated to 180°C for 3 days. Afterwards, the crystals were recovered by vacuum filtration, washed with DMF and air dried.

Prior to catalytic testing, the materials were activated overnight under vacuum (<1 mbar) at elevated temperature (ranging from 200 to 320 °C) with a heating ramp of 5 °C. After activation, the materials were kept under inert atmosphere.

Catalytic testing

In a typical reaction, 1 mmol of each reactant was combined with 2 ml of solvent, toluene or acetonitrile. The mixture was added to 50 mg of activated catalyst. The reaction mixture was heated

to 70 °C and aliquots of sample were removed for analysis at set intervals. The identity of the reaction products was verified by GC-MS (Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer) and the product yields were determined via GC-analysis. Evaluation of the substrate scope was performed in reactions in which 1 mmol of each reactant was combined with 2 ml of toluene. This mixture was added to 50 mg of catalyst and stirred at the reaction temperature.

Physicochemical characterization

Thermogravimetric analyses of the samples were performed using a TA Instruments Q500 thermogravimetric analyzer. To simulate the activation procedure, the measurements were performed under He flow with a linear heating ramp of 5 °C/min to 320 °C, after which the temperature remained constant, and a Pfeiffer Omnistar mass spectrometer with a QME 200 quadrupole was positioned downstream of the TGA to analyze the gases released in the TGA experiment.

Fourier transform infrared spectroscopy measurements (FTIR) were performed on a Nicolet 6700 spectrometer. Thin self-supporting wafers (± 10 mg cm^{-2}) were prepared and introduced in an *in situ* cell. The cell was brought under vacuum (p < 1 mbar); the temperature was raised at a rate of 5 °C/min until the desired temperature was reached and FTIR spectra were recorded after different time intervals.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a S-Probe monochromatized XPS spectrometer from Surface Science Instruments (VG) with an Al Kα X-ray (1486.6 eV) monochromatic source. The take-off angle was 45° with a voltage and power of the source of 10 kV and 200 W respectively. A base pressure of 2 10^{-9} mbar was obtained in the measuring chamber and the pass energy was 107 eV. The analysis surface was 250 x 1000 µm² with a flood gun (neutralizer) setting of 4 eV on the sample with Ni grid. The accumulation time was approximately 2 h for each spectrum.

The ^{13}C CP MAS NMR spectra were recorded on a Bruker Avance400 spectrometer (9.4 T). 22000 scans were accumulated with a recycle delay of 10 s. The length of the proton $\pi/2$-pulse was 2.5 μs. The contact time was 4.0 ms. The samples were packed in 4 mm zirconia rotors. The spinning frequency of the rotor was 6000 or 8000 Hz. Tetramethylsilane was used as chemical shift reference.

The crystallinity and structure of the synthesized materials were confirmed via powder X-ray diffraction (PXRD). Reflection patterns were recorded on a STOE STADI MP in Bragg-Brentano mode (2θ - θ geometry; CuKα1, 1.54060 Å) using a linear position sensitive detector.

EPR spectra were recorded using a Bruker 300E continuous wave spectrometer, with a rectangular cavity cooled to 115 K. The sample was irradiated with a microwave frequency of 9.59 GHz and the measurement with a sweep width of 800 G was centered at 3415 G. The data were analyzed and the spectra were simulated using the EasySpin software package.[3]

Scanning electron microscopy (SEM) micrographs were recorded using a Philips XL30 FEG after coating with Au, coupled with energy-dispersive X-ray spectroscopy (EDX) at 15 kV.

N_2 sorption measurements were performed on a Micromeritics 3Flex surface analyser at 77 K. Prior to measurements, the samples were activated under vacuum at either 200 or 320°C.

To determine the nitrate to metal ratio in the samples, the MOFs were dissolved in an aqueous solution of trifluoroacetic acid. The nitrate content of these solutions was subsequently determined via a colorimetric assay using a Skalar Continuous Flow Analyser. The metal contents of these solutions were determined after dilution using a ICP-MS using an Agilent ICP-MS 7700X.

Fluorescence microscopy measurements

For the microscopic measurements a $Ba_2(BTC)(NO_3)$ suspension in ethanol was spincoated on a cleaned glass cover slip. Liquid phase base catalyzed transesterification experiments, using 3 ml of an ethanolic fluorescein diacetate (FDA) solution, were performed using a specially designed Teflon container sealed to the glass cover slip via a silicone rubber gasket which can be directly used on an

inverted epifluorescence microscope. Confocal fluorescence images were acquired using an Olympus FluoView™ FV1000 with an oil immersion objective lens (Olympus, 100X, 1.4 NA) and λ_{exc} = 491 nm, λ_{em} = 505-605 nm. For the NASCA[4] ('Nanometer Accuracy by Stochastic Chemical reAction') experiments a wide-field fluorescence setup based on an inverted microscope Olympus IX71 platform equipped with an oil immersion objective lens (Olympus, 100X,1.4 NA) and a 491 nm diode laser (Cobolt Calypso 100) was used providing 20 W/cm^2 power on the sample. Fluorescence imaging (505 – 1000 nm) was done with EM-CCD camera (ImagEM Enhanced C9100-13) and further single molecule identification, localization and generation of the NASCA images were performed with IgorPro v.6.34A software and dedicated routines (http://sushi.chem.kuleuven.be/localizer). For confocal measurements a 100 μM FDA solution was used and a 420 nM solution for the NASCA microscopy. Purification of the commercial FDA (Acros Organics, 99%) via preparative HPLC (Waters 996 PDA) followed by freeze-drying was performed prior to the measurements.

Theoretical modeling

Proton affinities (PAs) of various (modified) $Ba_2(BTC)(NO_3)$ materials and BaO clusters were computed using hybrid Density Functional Theory (DFT) methods, in order to rationalize the experimentally observed catalytic activity. A two-step procedure was followed: first, the materials' structures were optimized using a periodic Density Functional Theory code and next, clusters were cut from the periodic structure to calculate the PAs.

Periodic DFT-D calculations were carried out on three different Ba-MOF structures with the Vienna Ab Initio Simulation Package (VASP 5.2.12).[5-8] The 1x1x1 unit cells were optimized with a plane wave kinetic energy cutoff of 600 eV, employing the PBE exchange-correlation functional [9, 10] with D3-dispersion corrections of Grimme and coworkers[11]. The projector augmented wave approximation (PAW) [12] was used and Brillouin zone sampling was restricted to the Γ-point. A Gaussian smearing [6] of 0.05 eV was applied to improve convergence. For the cell optimizations, the convergence criterion for the electronic self-consistent field (SCF) problem was set to 10^{-6} eV while the atomic forces were

converged below 0.01 eV/ Å. The Ba-MOF unit cells were constructed starting from a Crystallographic Information File (CIF) in which $Ba_2(BTC)(NO_3)$ is fully solvated by DMF.[13] A unit cell containing 216 atoms was used for $Ba_2(BTC)(NO_3)(DMF)$. Subsequently, the MOF material without DMF ($Ba_2(BTC)(NO_3)$) was constructed. Further activation leads to a structure wherein chains of alternating defect sites ($*$) and O^{2-} ions are formed within the MOF ($Ba_2(BTC)(*)_{0.5}O_{0.5}$). The optimized Ba-MOF structures and their unit cell characteristics are presented in the supporting information. Notably, the unit cell volume of the Ba-MOF model containing defect sites exhibits a volume expansion of approximately 4%. This might lead to internal stress within the material or to loss of crystallinity upon activation of the material.

Various Ba-MOF clusters were then cut from the periodically optimized structure to investigate the PA. Use of finite clusters is advisable since periodic calculations fail in reproducing accurate PAs, due to the additional charge induced in the unit cell when adding a proton to the framework. The manipulation of the periodic structure files and cluster models was done using ZEOBUILDER, an in-house developed software tool for building complex molecular structures.[14] All cluster simulations were carried out using Gaussian09.[15] In all cluster simulations, the carboxylic units of the linkers were kept fixed during the optimizations to maintain the rigidity of the model as in the crystal. Clusters of varying size were investigated and various levels of theory were assessed (see supporting information); only the most accurate values are reported hereafter. Small BaO clusters ($(BaO)_n$, n=4, 6, 8 and 16) were constructed to mimic the BaO bulk material, exhibiting a cubic crystal structure. These BaO-clusters were optimized and protonation was considered. The cluster optimizations were performed with the hybrid B3LYP functional[16, 17] including D3 corrections for van der Waals interactions[11] and combined with the 6-311G(d,p) basis set for C, O and H atoms and the def2-tzvp [18] core potential for Ba. The resulting energies (without D3 corrections) and vibrational contributions were applied to compute PAs according to:

$$PA = \frac{5}{2}RT - \left[\Delta E_{SCF} + \Delta E_{vib}\right],$$

with ΔE_{SCF} the SCF energy difference, ΔE_{vib} the zero point energy difference and the (5/2)RT term contains the translational energy and the pressure-volume term of the gas phase proton. PAs have previously been used to assess the base character of MOF materials.[19, 20]

Additional figures

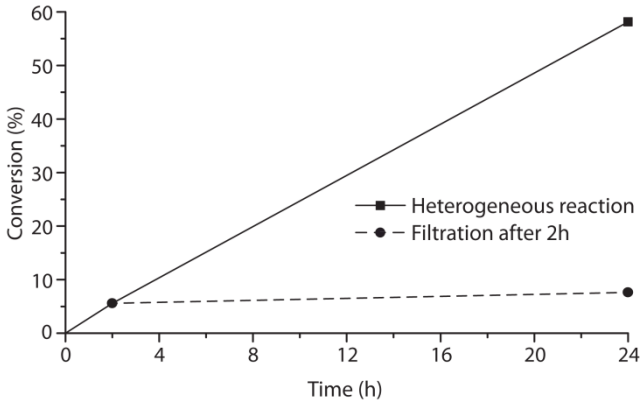


Fig. S1: Hot filtration test for the Ba-MOF activated overnight at 320 °C in the Michael addition of ethyl cyanoacetate to methyl vinyl ketone in toluene at 70 °C.

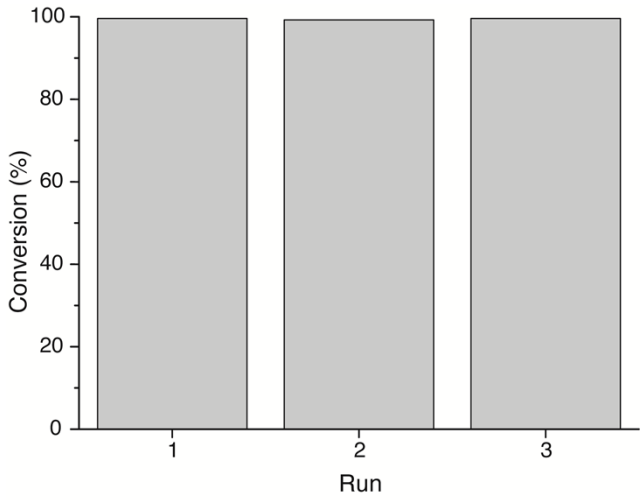


Fig. S2: Recycle test for the Ba-MOF activated overnight at 320 °C in the Knoevenagel condensation of malononitrile and benzaldehyde in toluene at 70 °C.

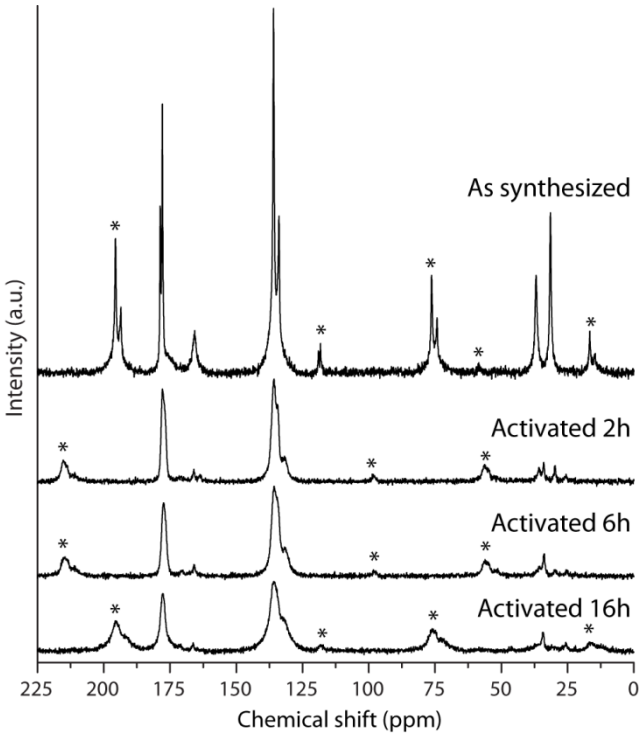


Fig. S3: ^{13}C CP MAS NMR of $Ba_2(BTC)(NO_3)$ after different activation times at 320 °C. Spinning sidebands are marked with *.

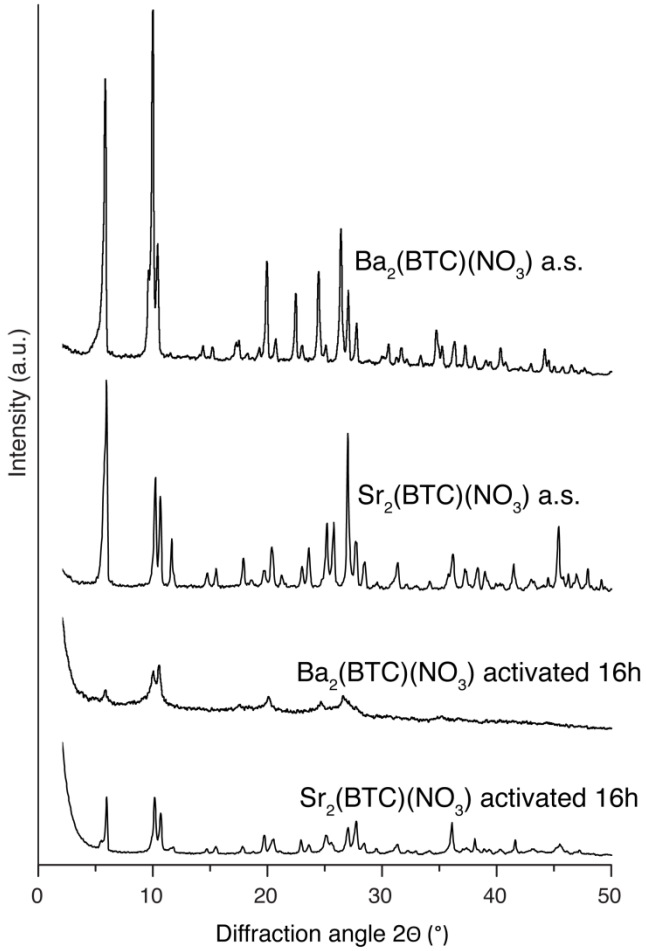


Fig. S4: X-ray diffraction patterns of the Sr and Ba $M_2(BTC)(NO_3)$ MOFs before and after activation at 320 °C.

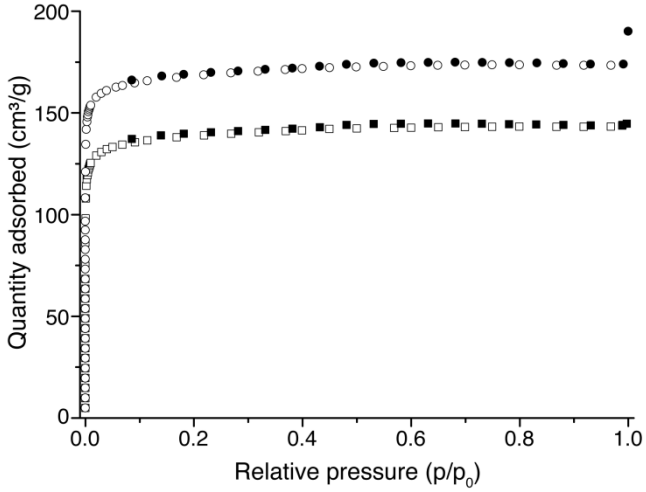


Fig. S5: Nitrogen gas adsorption isotherms at 77 K for $Sr_2(BTC)(NO_3)$ activated at 200°C (□/■) and 320°C (○/●). Empty and filled characters represent adsorption and desorption, respectively.

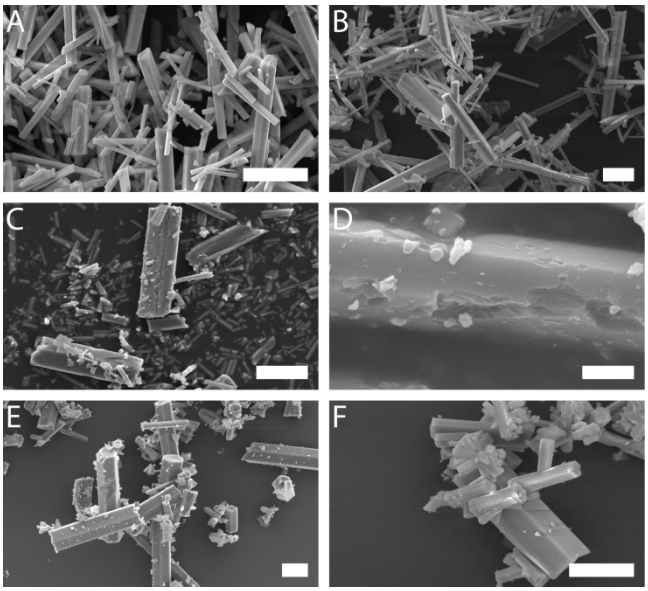


Fig. S6: SEM micrographs: $Ba_2(BTC)(NO_3)$ as synthesized (A) and after activation at 320°C (B-D), $Sr_2(BTC)(NO_3)$ before (E) and after activation at 320°C (F). Scale bar 10µm (A, B, C, E, F) and 1µm (D).

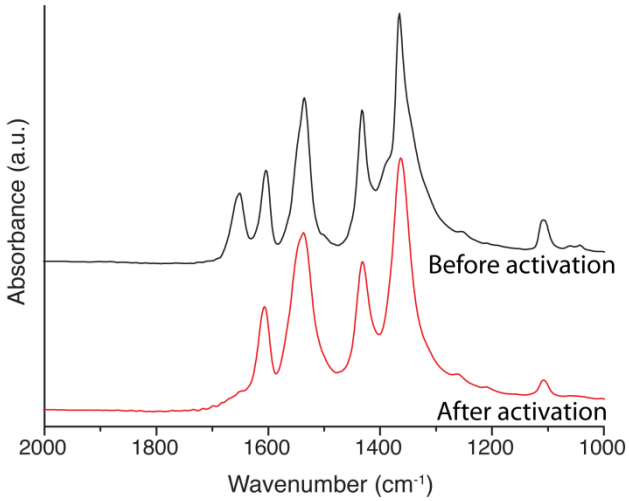


Fig. S7: FTIR spectrum of $Ba_2(BTC)(NO_3)$ before and after activation at 320°C. Loss of the absorption band at 1652 cm^{-1} illustrates the removal of DMF from the framework upon activation.

Screening of different alkaline earth MOFs

Materials

Table S1: Overview of the different alkaline earth metal MOFs screened in this study and their references.

Material	Reference
$Ba_2(BTC)(NO_3)(DMF)$	[1]
$Ba_3(BTC)_2(H_2O)_4$	[21]
$Sr_2(BTC)(NO_3)(DMF)$	[2]
Sr(BDC)(DMF)	[22]
Sr-CPO-22	[23]

Catalytic activity of the tested materials

Table S2: Conversion of benzaldehyde in the Knoevenagel condensation with ethyl cyanoacetate in the presence of different alkaline earth metal MOFs activated at different temperatures.[a]

Catalyst	$T_{activation}$	X_{24h}	$T_{activation}$	X_{24h}
$Ba_2(BTC)(NO_3)(DMF)$	200	**15**	320	**99**
$Ba_3(BTC)2(H_2O)_4$	200	1	320	-
$Sr_2(BTC)(NO_3)(DMF)$	200	**16**	320	**61**
Sr(BDC)(DMF)	200	3	320	2
Sr-CPO-22	150	1	320	2

[a] Reaction conditions: 1 mmol of each reactant; 2 ml toluene, 70 °C, 50 mg MOF.

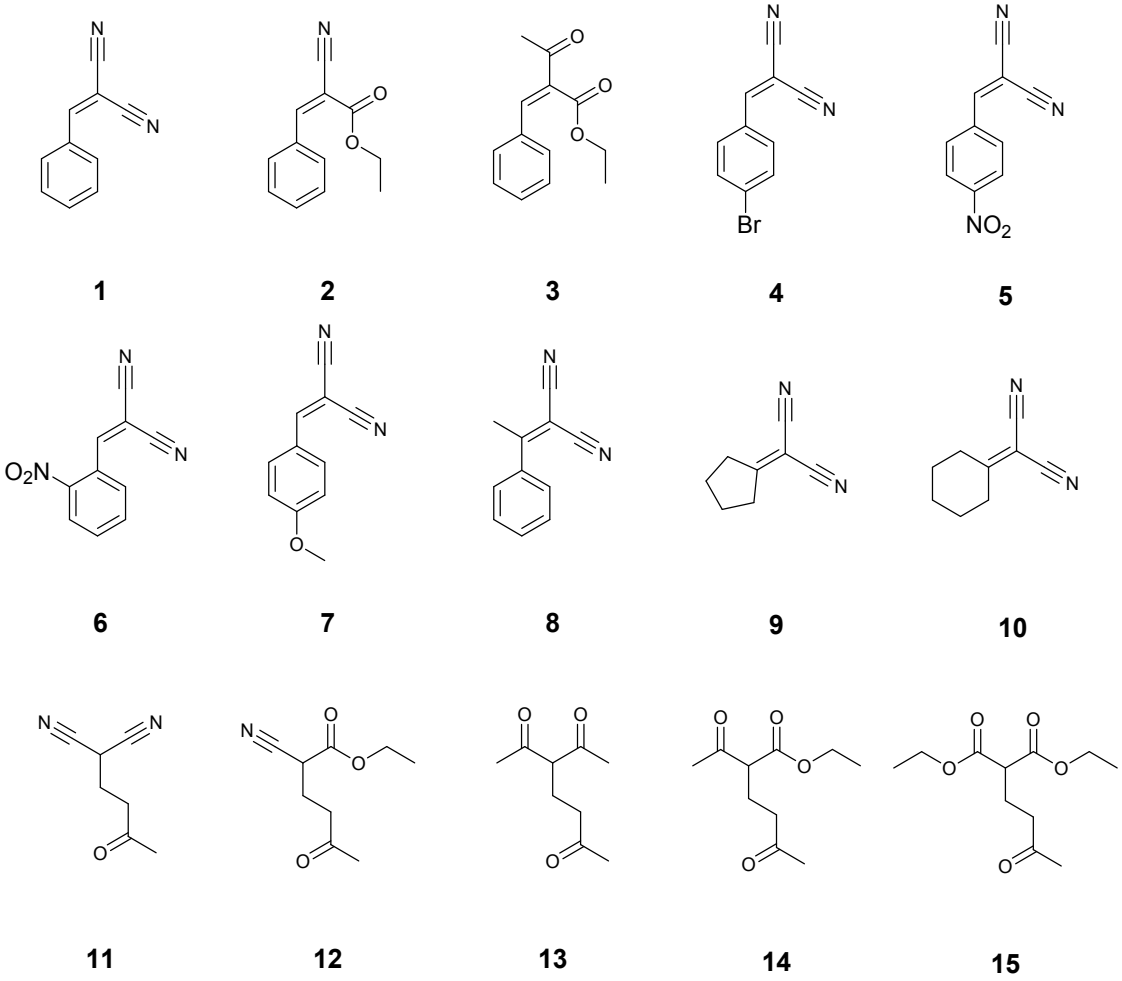
Table S3: Conversion of benzaldehyde in the Knoevenagel condensation with malononitrile in the presence of different alkaline earth metal MOFs activated at different temperatures.[a]

Catalyst	$T_{activation}$	X_{24h}	$T_{activation}$	X_{24h}
$Ba_2(BTC)(NO_3)(DMF)$	200	**15**	320	**99**
$Ba_2(BTC)(NO_3)(DMF)$	650[b]	**10**		
$Ba_3(BTC)_2(H_2O)_4$	200	44	320	31
$Sr_2(BTC)(NO_3)(DMF)$	200	**16**	320	**61**
Sr(BDC)(DMF)	200	37	320	30
Sr-CPO-22	150	14	320	11

[a] Reaction conditions: 1 mmol of each reactant; 2 ml toluene, 70 °C, 50 mg MOF.

[b] Calcination in air rather than activation under vacuum.

Mass spectra of the reaction products



Compound 1: α-cyanocinnamonitrile: *m*/*z* 154 (M^+, 100%), 127 (77), 103 (60), 76 (15), 61 (9), 50 (15), 39 (7).

Compound 2: ethyl α-cyanocinnamate: *m*/*z* 201 (M^+, 80%), 172 (77), 156 (100), 128 (80), 102 (61), 77 (51), 51 (36).

Compound 3: ethyl α-acetylcinnamate: *m*/*z* 218 (M^+, 91%), 217 (100), 203 (19), 189 (20), 173 (31), 147 (20), 131 (67), 103 (42), 77 (29), 51 (14), 43 (79).

Compound 4: 4-bromobenzalmalononitrile: *m*/*z* 234 (M^+, 66%), 232 (M^++2, 67%), 207 (8), 183 (7), 153 (100), 126 (29), 99 (12), 75 (8).

Compound 5: 4-nitrobenzalmalononitrile: *m*/*z* 199 (M^+, 100%), 169 (35), 153 (71), 141 (65), 126 (78), 114 (35), 99 (21), 75 (13).

Compound 6: 2-nitrobenzalmalononitrile: *m*/*z* 199 (M^+, 65, M^+), 182 (17), 169 (19), 144 (45), 126 (88), 114 (59), 99 (100), 75 (25).

Compound 7: 4-methoxybenzalmalononitrile: *m*/*z* 184 (M^+, 100%), 169 (12), 141 (48), 114 (29), 88 (6).

Compound 8: β,β-Dicyano-α-methylstyrene: *m*/*z* 168 (M^+, 100%), 153 (7), 140 (63), 128 (63), 114 (34), 103 (28), 89 (20), 77 (54), 63 (51), 51 (68), 39 (39), 32 (60).

Compound 9: Cyclopentylidenemalononitrile: *m*/*z* 132 (M^+, 10%), 104 (11), 77 (9), 67 (15), 51 (10), 41 (100), 39 (33), 32 (3).

Compound 10: Cyclohexylidenemalononitrile: *m*/*z* 146 (M^+, 12%), 131 (20), 118 (11), 105 (14), 92 (13), 77 (17), 64 (16), 55 (100), 51 (23), 39 (80).

Compound 11: 2-(3-oxobutyl)malononitrile: *m*/*z* 136 (M^+, 12%), 121 (10), 93 (8), 66 (45), 52 (15), 43 (100), 39 (27).

Compound 12: Ethyl 2-cyano-5-oxohexanoate: *m*/*z* 183 (M^+, 1%), 168 (1), 155 (2), 138 (9), 110 (9), 85 (3), 71 (5), 58 (10), 43 (100).

Compound 13: 3-acetyl-2,6-heptanedione: *m*/*z* 152 (M^+-18, 2%), 128 (35), 113 (13), 95 (26), 85 (16), 71 (46), 43 (100).

Compound 14: Ethyl 2-acetyl-5-oxohexanoate: *m*/*z* 158 (M^+-42, 6%), 139 (2), 130 (2), 111 (6), 101 (6), 84 (14), 55 (9), 43 (100).

Compound 15: Ethyl 2-ethoxycarbonyl-5-oxohexanoate: *m*/*z* 230 (M^+, 1%), 215 (1), 185 (10), 160 (21), 139 (7), 133 (7), 127 (7), 111 (8), 86 (9), 55 (21), 43 (100).

Theoretical simulations: periodic geometry optimizations

Table S4: Summary of the cell characteristics of the optimized unit cells using PBE-D3.

	Volume (Å^3)	a	b	c	α	β	γ
$Ba_2(BTC)(NO_3)(DMF)$	2861.43	17.869	17.868	10.347	90.000	90.019	119.993
$Ba_2(BTC)(NO_3)$	2867.16	17.872	17.873	10.364	90.000	90.000	119.999
$Ba_2(BTC)(*)_{0.5}O_{0.5}$[a]	2979.00	18.213	18.469	10.373	89.998	90.001	121.360

[a] (*) represents a vacancy between two Ba atoms. For the investigated unit cell, there were 8 different possibilities for vacancy creation. One possibility was considered and modeled.

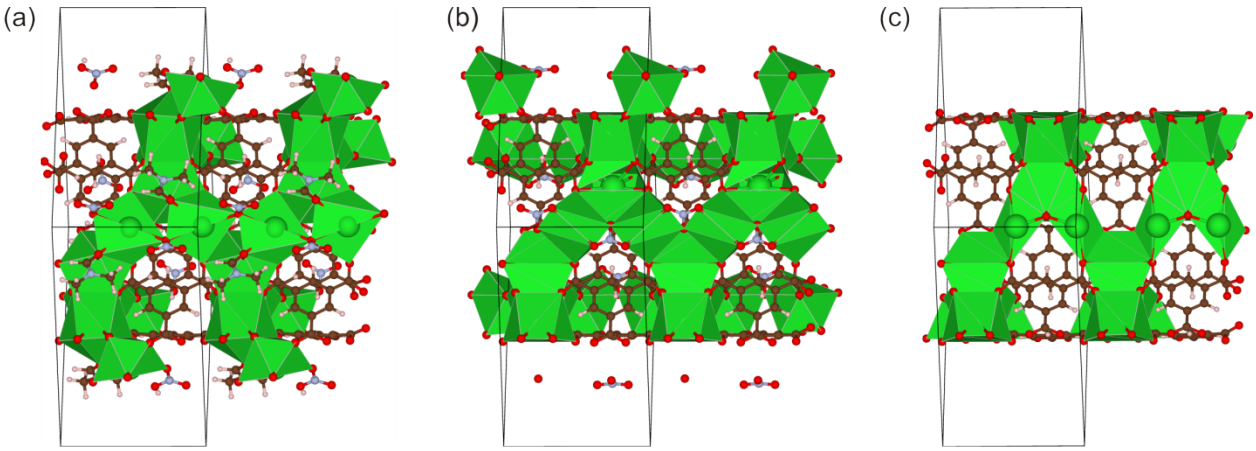


Fig. S5: View of the PBE-D3 optimized Ba-MOFs: (a) $Ba_2(BTC)(NO_3)(DMF)$, (b) $Ba_2(BTC)(NO_3)$, (c) $Ba_2(BTC)(*)_{0.5}O_{0.5}$.

Theoretical simulations: calculating proton affinities using finite clusters

Clusters were cut out from the PBE-D3 periodically optimized structure and further refined to compute **proton affinities (PAs)**, defined as:

$$PA = \frac{5}{2}RT - [\Delta E_{SCF} + \Delta E_{vib}]$$

The computed PA value serves as a measure for basicity :[19] the larger the PA, the larger the basicity. Various Ba-MOF clusters were investigated, as depicted below.

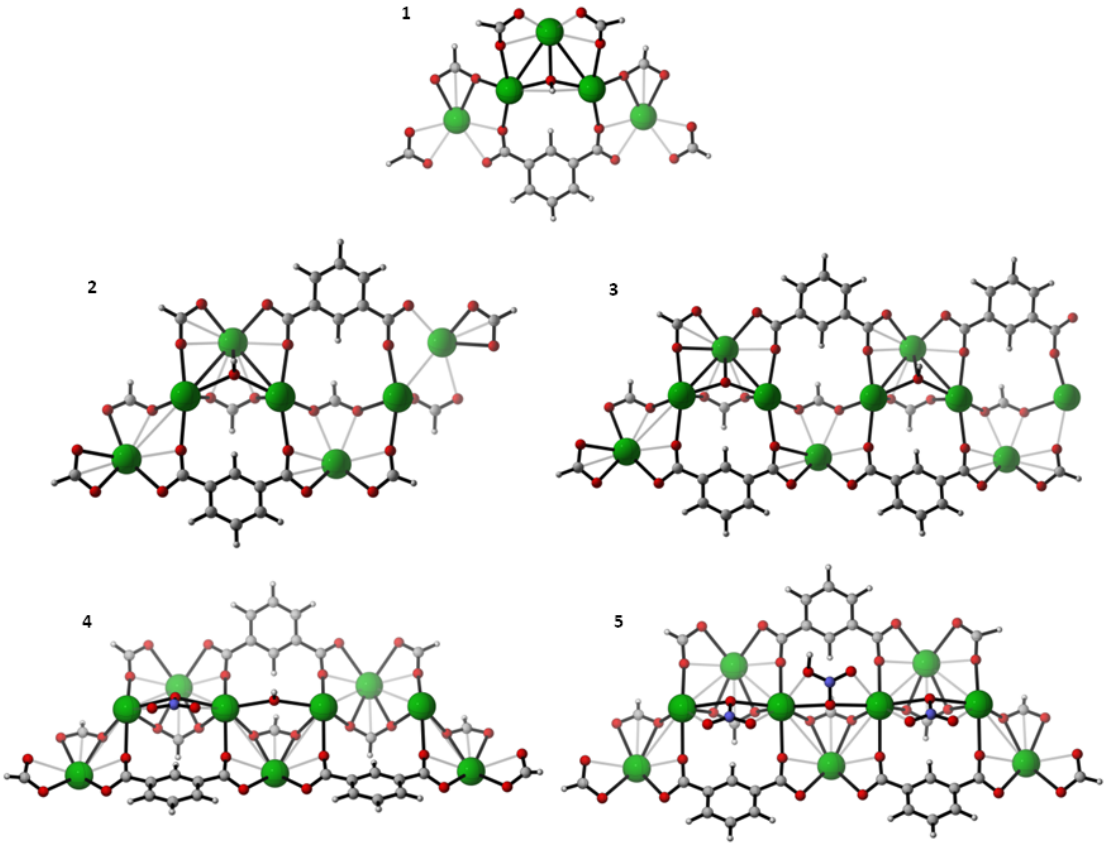


Fig. S6: Representation of investigated Ba-MOF clusters. **1.** Small cluster of the Ba-MOF structure with 2 NO_3^- anions replaced by an O^{2-} anion; **2-3.** Larger Ba-MOF clusters with NO_3^- anions replaced by O^{2-}; **4.** Ba-MOF cluster defect site with residual NO_3^- anion adjacent to an O^{2-} ion; **5.** Ba-MOF

cluster representative of the original material $Ba_2(BTC)(NO_3)$. For all clusters the protonated form is shown.

The hybrid B3LYP functional is used throughout for the optimizations, during which the carboxylic (CO_2) units of the linkers were kept fixed to maintain the periodic structure.

- **Influence of localized basis set size and core potential:**

Cluster 1 was used to investigate the influence of basis set and core potential on the computed PA values. Various basis sets (BS) were assessed for the C, O and H atoms, whereas for Ba the LanL2dz and def2-tzvp core potentials are used; the latter one being more extended.

Table S5: Influence of localized basis set size and core potential.

	PA [kJ/mol]	
BS	LanL2dz	Def2-tzvp
3-21G	1169	988
6-31G(d,p)	1149	1021
6-311G(d,p)	1124	1012

The effect of BS size and core potential is substantial; therefore the largest BS (6-311G(d,p)) was used for further validation.

- **Influence of cluster size and presence of defect site/NO_3 units:**

Table S6: Computed PA values of clusters **1-5**.

	PA [kJ/mol]	
	6-311G(d,p) and LanL2dz	6-311G(d,p) and def2-tzvp
1	1124	1012
2	1330	1181
3	1310	1153
4	1371	1233
5	847	876

Comparison of **1** with **2** and **3** suggests that the small cluster is not sufficient to capture the effects of the periodic system, whereas clusters **2** and **3** lead to comparable PA values.

Comparison of cluster **5** with the other clusters suggests that introduction of a defect leads to a much more basic cluster (PA increases substantially). Cluster **4** (exhibiting a O^{2-} type defect next to a residual nitrate) exhibits an even larger PA value.

- **Comparison with BaO**

Small BaO clusters ($(BaO)_n$, n=4, 6, 8 and 16, shown below, Fig. S7) were constructed to mimic the BaO bulk material exhibiting a cubic crystal structure. Kwapien et al. reported that small gas-phase clusters of MgO can display unusual structural diversity and flexibility.[24] Similar observation was made for the BaO clusters. Nevertheless, we selected the clusters exhibiting a cubic like structure and in these cases; the geometrical deformations are rather modest.

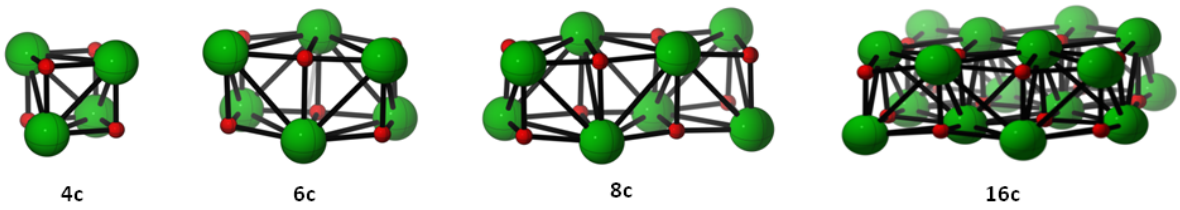


Fig. S7: BaO clusters of different size, $(BaO)_n$, n=4, 6, 8 and 16.

The computed PA values of a diatomic BaO molecule are 1391 and 1226 kJ/mol, using the LanL2dz and def2-tzvp core potential, respectively. The latter one is close to the value of 1215 kJ/mol (see NIST, http://webbook.nist.gov/chemistry/), supporting the choice for def2-tzvp.

Table S7: Computed PA values of the BaO clusters.

	PA [kJ/mol]	
	6-311G(d,p) and LanL2dz	6-311G(d,p) and def2-tzvp
4c	1430	1277
6c	1423	1305
8c	1429	1321
16c	-[a]	1312

[a] The LanL2dz simulations did not reach convergence.

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Structures in POSCAR format

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0.6632811642530594 0.9938659877887647 0.3364988665032245 T T T
0.3305655187742024 0.3360492308248329 0.3363835180067650 T T T

0.0530160816439837 0.7049504106939728 0.0931988052136363 T T T
0.6515958998775992 0.9470133486549118 0.0936630685969279 T T T
0.2959595712122883 0.3479765240534008 0.0936689485322793 T T T

$Ba_2(BTC)(NO_3)$

Ba O N C H
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17.8724558160276317 0.0009244822102274 0.0000258284153347
-8.9368378714506882 15.4777401453683705 -0.0001017828853057
-0.0000180170450663 -0.0000365592816568 10.3644718554148874
Ba O N C H
12 54 6 54 18
Selective dynamics
Direct
0.8202750271449615 0.3823575490563416 0.7500121195758896 T T T
0.6176791287222627 0.4378934796951354 0.7500181369119620 T T T
0.5621487996149009 0.1797846572656281 0.7500089107107200 T T T
0.3823715746754020 0.8202479360990668 0.2500204471637712 T T T
0.4379123882321158 0.6176472737469653 0.2500071058357465 T T T
0.1798028503368186 0.5621299333623770 0.2500154624112362 T T T
0.0000227739813474 0.3553091522546020 0.5000088503281148 T T T
0.6447389474043188 0.6447140038275669 0.5000160358585313 T T T
0.3553423791174192 0.0000252234658829 0.5000273799890248 T T T
0.0000259781299649 0.3553048764020254 0.0000079854145895 T T T
0.6447269949958431 0.6447174299268699 0.0000350662676243 T T T
0.3553376334358460 0.0000067794920895 0.0000159146438411 T T T
1.0080425998843068 0.3091899440534471 0.2500136219247953 T T T
0.6908764338891022 0.6989036877688198 0.2500232077266162 T T T
0.3012186503116490 -0.0080058172723047 0.2500225694594478 T T T
0.3092196873366752 1.0080358194849879 0.7500262410493973 T T T
0.6988214128208626 0.6908214632530161 0.7500387611525863 T T T
-0.0080438214819865 0.3011052944302260 0.7500044596353785 T T T
0.8321405257569843 0.3106968275604852 0.5026998531712309 T T T
0.6893366688884864 0.5214307536726123 0.5026907813154670 T T T
0.4785969128511648 0.1678986907067700 0.5027145873585129 T T T
0.8321378424994245 0.3106782437895825 -0.0026875448862917 T T T
0.6893372345132858 0.5214349479926704 -0.0026749823961953 T T T
0.4786094827832676 0.1678914431375965 -0.0026858691142224 T T T
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0.8913528478032886 0.4921889513817462 0.4568915959436405 T T T
0.6008671817077040 0.1086697221519352 0.0431348831569439 T T T
0.5078419699685661 0.3991494584706409 0.0431241516357898 T T T
0.8913684270192601 0.4922075081155390 0.0431272672353619 T T T

$Ba_2(BTC)(*)_{1/2}O_{1/2}$

Ba O C H
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18.2107583241284701 -0.2899452319848149 0.0004202499003332
-9.3592844745798782 15.9222075833104384 -0.0000149632056879
-0.0004322161478319 0.0001435264132934 10.3731419637933477
Ba O C H
12 39 54 18
Selective dynamics
Direct

0.8194708196422711 0.3892419952781153 0.7460477336857856 T T T
0.6122597617331322 0.4324926200269502 0.7458433593183929 T T T
0.5585675571170786 0.1787316363142210 0.7458331727289443 T T T
0.3922917496649569 0.8192222989705903 0.2451690076477814 T T T
0.4489064816127524 0.6228783925828214 0.2452775377888297 T T T
0.1842705225443575 0.5600555437472778 0.2452323121875299 T T T
0.0088591988762161 0.3940255983720484 0.4599139522119504 T T T
0.6166192993888611 0.6192626132404140 0.4591794690820103 T T T
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0.6168391810558506 0.6193958455422207 1.0318180413014508 T T T
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