

SUPPORTING INFORMATION

Investigation of the Effect of polar Functional Groups on the Crystal Structures of Indium MOFs

Martin Krüger,^a Martin Albat,^a A. Ken Inge,^b and Norbert Stock^a

^a Institut für Anorganische Chemie, Christian-Albrechts-Universität, Max-Eyth-Straße 2, 24118 Kiel, Germany.

^b Department of Materials and Environmental Chemistry, Stockholm University, Stockholm SE-106 91, Sweden.

Table of Content

Fig. S1 Reaction scheme for the synthesis of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$).	3
Fig. S2 1H -NMR spectrum of 2-aminoterephthalic acid.	4
Fig. S3 1H -NMR spectrum of 2-formamidoterephthalic acid.	4
Fig. S4 1H -NMR spectrum of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$) measured in $DMSO-D_6$	5
Fig. S5 1H -NMR spectrum of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$) measured in 5% $NaOD/D_2O$	6
Table S1 Crystal structure data of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$).	6
Table S2 Selected bond lengths of $H_2BDC-NH_2$	7
Fig. S6 Asymmetric unit of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$).	7
Fig. S7 Crystal structure of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$). Above the hydrogen bonding model is shown, whereas the unit cell along [010] is shown below. Carbon atoms are shown in grey, nitrogen in blue and oxygen in red. Hydrogen bonds are marked in dashed lines.	8
Table S3 Selected bond lengths of $In-BDC-NH_2$ (1).	9
Table S4 Selected bond lengths of $In-BDC-NH_2/NO_2$ (3).	9
Fig. S8 Asymmetric unit of $In-BDC-NH_2$ (1) with numbering scheme as used in Table S3. ...	10
Table S5 Overview of the bands visible in The IR spectrum of $In-BDC-NH_2$ (1) discussed in the manuscript.	10
Fig. S9 Thermogravimetric measurement of $In-BDC-NH_2$ (1). The calculated values based on the assumed sum formula are given in brackets.	11
Fig. S10 Comparison of the PXRD pattern recorded for granulated crystals of $In-BDC-H/NH_2$ and the simulated pattern of $In-BDC-NH_2$	11
Fig. S11 Comparison of the PXRD pattern recorded for the sample using the same synthesis conditions as used for 1 with linker molecule replaced by $H_2BDC-NH_2/NO_2$ and the simulated pattern of dimethylammonium 2-amino-5-nitroterephthalate hemihydrate obtained from single crystal XRD measurements. ²	12
Fig. S12 Comparison of the PXRD pattern recorded for $In-BDC-NH_2/NO_2$ and the simulated pattern of $In-BDC-NH_2/NO_2$ obtained from single crystal XRD measurements.	12
Fig. S13 Asymmetric unit of $In-BDC-NH_2/NO_2$ with numbering scheme as used in Table S4.	13
Fig. S14 Crystal structure of $In-BDC-NH_2/NO_2$. Trinuclear clusters composed of three InO_6 octahedra bridged by an μ_3-O atom (left) are interlinked by a disordered tetradentate $BDC-NH_2/NO_2^{2-}$ ions (middle) to form a super-tetrahedron (right).	13
Fig. S15 Crystal structure of $In-BDC-NH_2/NO_2$. To each super-tetrahedron (left) four additional trinuclear $In-O$ -clusters are attached via tridentate carboxylate ions (middle). Thus, four additional super-tetrahedra are formed (right; only two face-sharing super-tetrahedra are displayed), face-sharing with the central one (left).	14
Fig. S16 1H -NMR spectrum of $In-BDC-NH_2/NO_2$. The MOF was dissolved in 5% $NaOD/D_2O$. Signals of DMF as well as $HCOO^-$ and dimethylammonium ions (DMA), the hydrolysis products of DMF, are visible.	14
Table S6 Overview of the bands visible in The IR spectrum of $In-BDC-NH_2/NO_2$ (3) discussed in the manuscript.	15
Fig. S17 Thermogravimetric measurement of $In-BDC-NH_2/NO_2$. A clear assignment of decomposition steps was not possible.	15

Synthesis of 2-amino-5-nitroterephthalic acid

The synthesis was accomplished by following the literature procedure reported by Skibo et al.¹ The reaction scheme is shown in Figure 1.

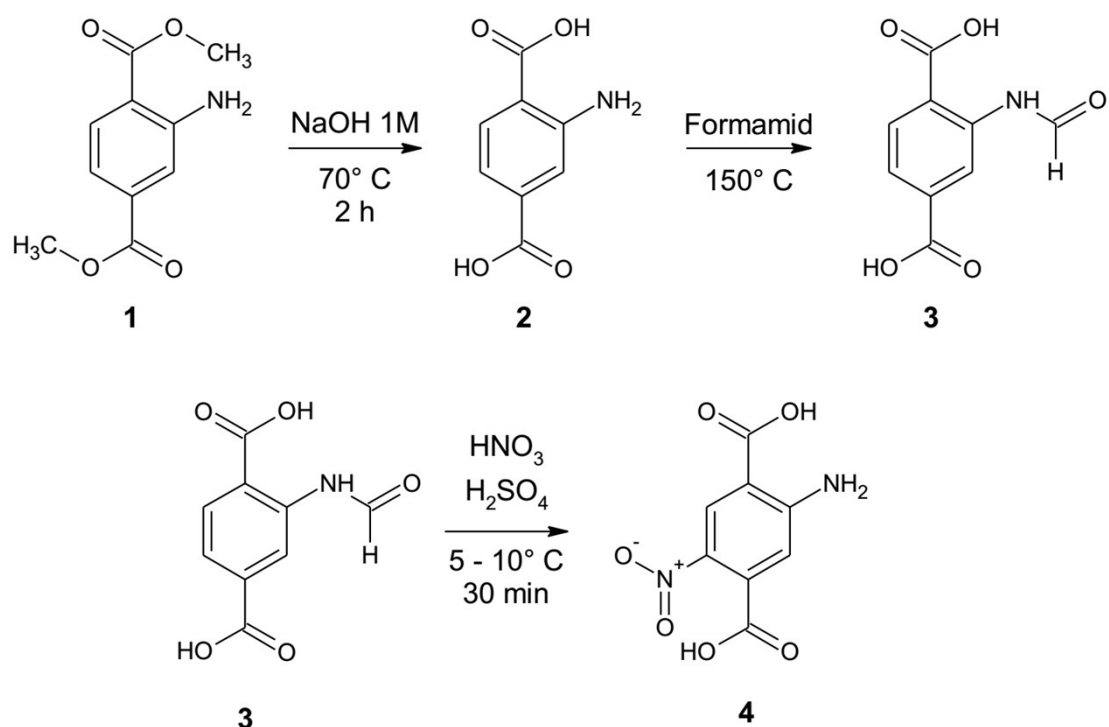


Fig. S1 Reaction scheme for the synthesis of 2-amino-5-nitroterephthalic acid (H₂BDC-NH₂/NO₂).

Step 1: A mixture of 87g (416 mmol) of dimethyl aminoterephthalate and 800 mL of a 1M NaOH solution was heated in a 1 L flask to 70 °C until the solid was solved completely. After cooling down to room temperature conc. HCl was added until a yellow solid precipitated which was filtered and washed with water. The ¹H-NMR spectrum of the final product is displayed in Figure S2.

Yield: 67 g (370 mmol, 89%)

¹H-NMR: (200 MHz, DMSO-D₆, 300 K): δ [ppm]: 7.77 (1H, d, J = 8.3 Hz, H3), 7.39 (1H, d, J = 1.4 Hz, H1), 7.02 (1H, dd, J = 8.3 Hz, J = 1.6 Hz, H2).

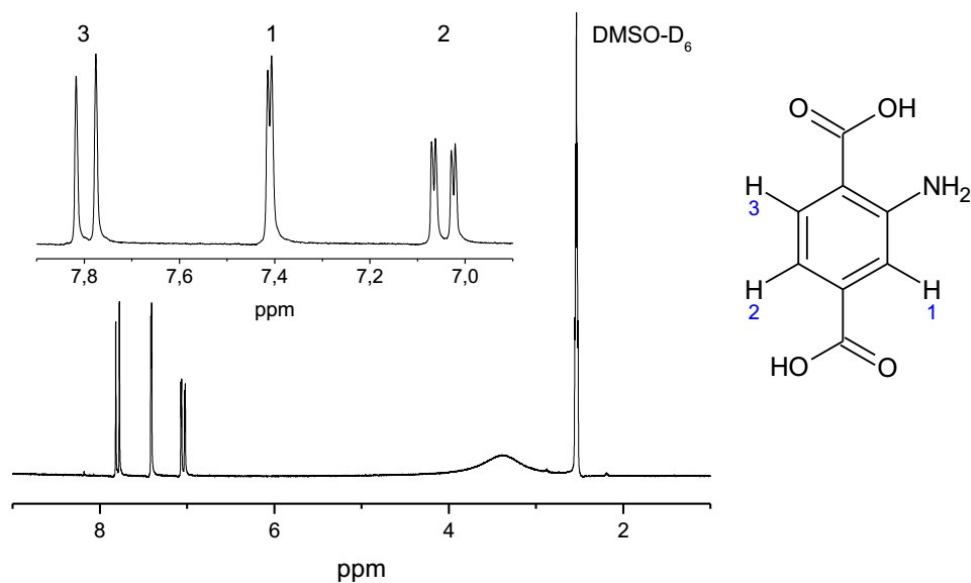


Fig. S2 ¹H-NMR spectrum of 2-aminoterephthalic acid.

Step 2: A suspension of 20.8 g 2-aminoterephthalic acid (114 mmol) and 100 mL formamide was heated rapidly to 150 °C until the solid was solved. During cooling down to room temperature a brown solid precipitated which was filtered of and dissolved in a saturated aqueous Na(HCO₃) solution. While acidifying this solution with conc. acetic acid a white solid precipitated which was filtered off, washed with water and dried completely. The ¹H-NMR spectrum of the final product is displayed in Figure S3.

Yield: 9.7 g (53 mmol, 48%)

¹H-NMR: (200 MHz, DMSO-D₆, 300 K): δ [ppm]: 9.1 (1H, s H1), 8.54 (1H, s H2), 8.07 (1H, d, J = 8.2 Hz, H4), 7.69 (1H dd, J = 8.2 Hz, J = 1.7 Hz, H3)

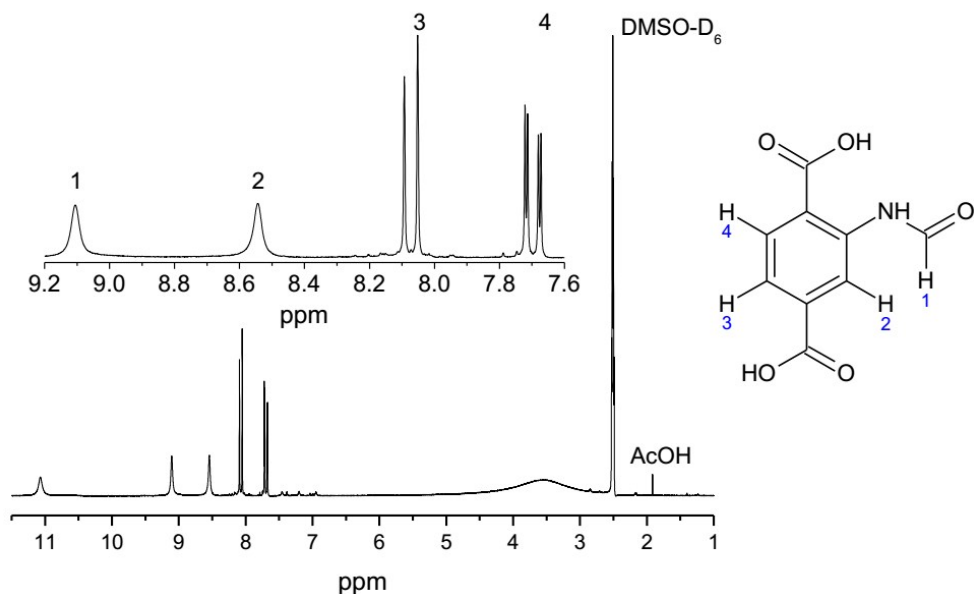


Fig. S3 ¹H-NMR spectrum of 2-formamidoterephthalic acid.

Step 3: To 20 mL of fuming nitric acid, cooled in an ice bath, 5.1 g (24 mmol) of formamidoterephthalic acid was added under stirring. To this suspension 10 mL of conc. sulfuric acid, which was also cooled in an ice bath, was added slowly within 15-20 minutes keeping the temperature between 5-10°C. After addition, the solid was dissolved and the solution was poured on 100 g of ice and stored in a refrigerator overnight. The precipitated solid was filtered off and recrystallized from hot water. Orange-brown crystals of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$) were obtained. The 1H -NMR spectrum of the final product is displayed in Figure S4 and S5. Detailed information of the crystal structure of $H_2BDC-NH_2/NO_2$ can be found in Table S1 and Figures S6 and S7.

Yield: 1.5 g (6.6 mmol, 27%)

1H -NMR: (200 MHz, DMSO- D_6 , 300 K): δ [ppm]: 8.49 (1H, s, H1), 6.89 (1H, s, H2).

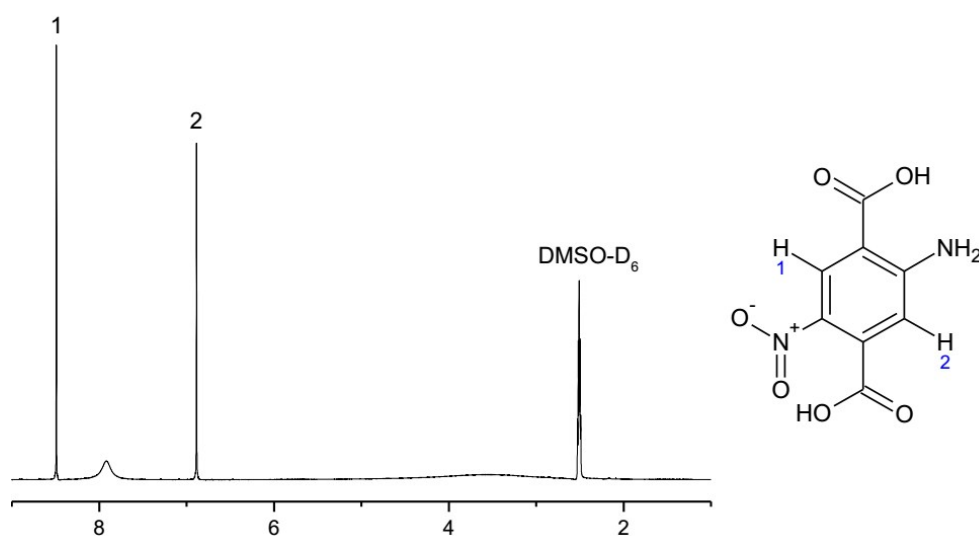


Fig. S4 1H -NMR spectrum of 2-amino-5-nitroterephthalic acid ($H_2BDC-NH_2/NO_2$) measured in DMSO- D_6 .

¹H-NMR: (200 MHz, NaOD/D₂O, 300 K): δ [ppm]: 8.36 (1H, s, H1), 6.41 (1H, s, H2).

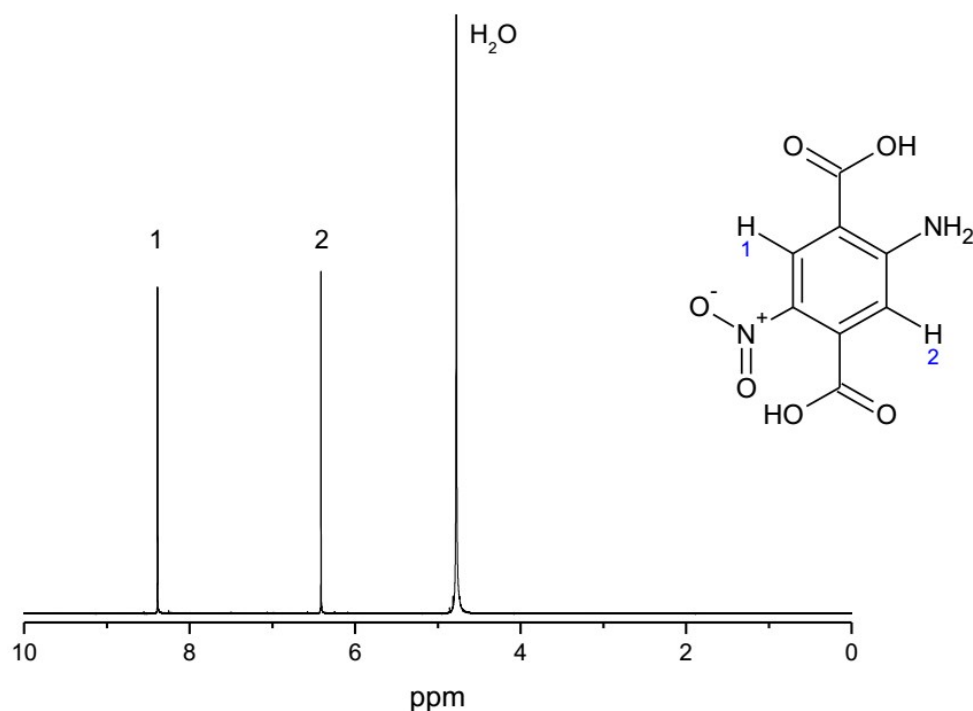


Fig. S5 ¹H-NMR spectrum of 2-amino-5-nitroterephthalic acid (H₂BDC-NH₂/NO₂) measured in 5% NaOD/D₂O.

Table S1 Crystal structure data of 2-amino-5-nitroterephthalic acid (H₂BDC-NH₂/NO₂).

	H ₂ BDC-NH ₂ /NO ₂
structure determination	single crystal data
formula sum	C ₈ H ₆ N ₂ O ₆
Z	4
crystal system	triclinic
<i>a</i> / Å	6.7000(13)
<i>b</i> / Å	9.2100(18)
<i>c</i> / Å	15.040(3)
<i>α</i> / °	78.47(3)
<i>β</i> / °	78.31(3)
<i>γ</i> / °	89.31(3)
<i>V</i> / Å ³	890.1(3)
space group	P-1
solution method	direct methods
range / °2θ	2.3 – 28.0
wavelength / Å	MoK _α
GOF	1.026
tot., uniq. data, R _{int}	4159, 4159, 0.0
observed data [I > 2σ(I)]	2818
R ₁ , wR ₂	0.059, 0.180
Δe min./max (e/Å ³)	-0.53, 0.39
calc. density / g/cm ³	1.17352

Table S2 Selected bond lengths of H₂BDC-NH₂.

atom 1	atom 2	distance / Å	atom 1	atom 2	distance / Å
C1	C2	1.408(3)	C10	C11	1.386(3)
	C6	1.368(3)	C10	N3	1.438(3)
	C7	1.510(3)	C11	C12	1.387(3)
C2	C3	1.390(3)	C12	C13	1.427(3)
	N1	1.443(3)		C16	1.487(3)
C3	C4	1.395(3)	C13	C14	1.428(3)
C4	C5	1.426(3)		N4	1.341(3)
	C8	1.476(3)	C15	O7	1.293(3)
C5	C6	1.428(3)		O8	1.233(3)
	N2	1.342(3)	C16	O9	1.316(3)
C7	O1	1.293(3)		O10	1.223(3)
	O2	1.228(3)	N1	O5	1.247(3)
C8	O3	1.311(3)		O6	1.230(3)
	O4	1.228(3)	N3	O11	1.228(2)
C9	C10	1.407(3)		O12	1.243(2)
	C14	1.371(3)			
	C15	1.506(3)			

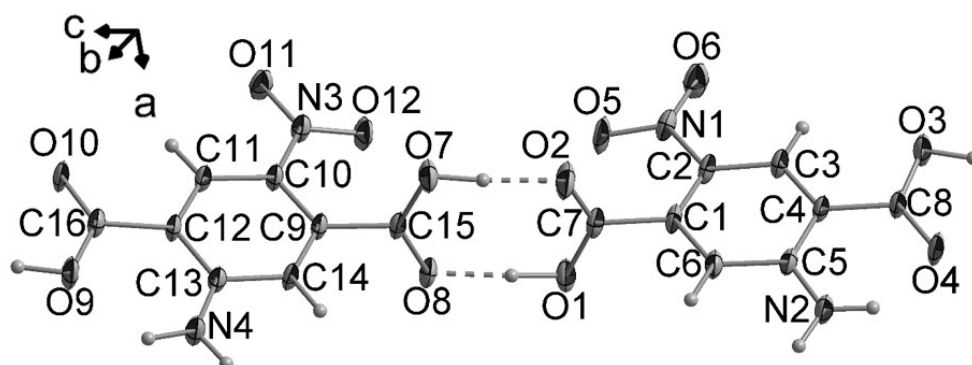


Fig. S6 Asymmetric unit of 2-amino-5-nitroterephthalic acid (H₂BDC-NH₂/NO₂).

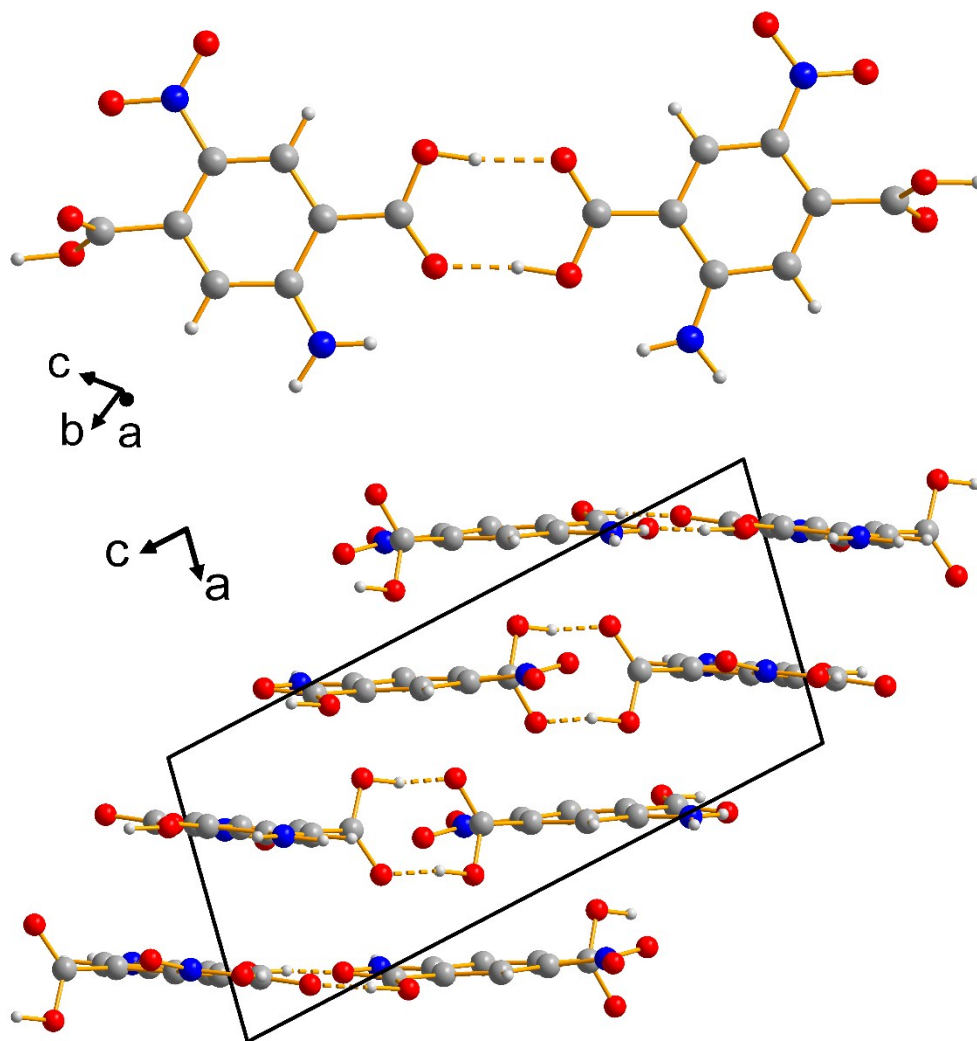


Fig. S7 Crystal structure of 2-amino-5-nitroterephthalic acid ($\text{H}_2\text{BDC-NH}_2/\text{NO}_2$). Above the hydrogen bonding model is shown, whereas the unit cell along $[010]$ is shown below. Carbon atoms are shown in grey, nitrogen in blue and oxygen in red. Hydrogen bonds are marked in dashed lines.

Table S3 Selected bond lengths of In-BDC-NH₂ (**1**).

atom 1	atom 2	distance / Å
In1	O1	2.261(2)
	O2	2.292(2)
C1	O1	1.266(5)
C1	O2	1.277(5)
C1	C4	1.491(4)
C2	N1	1.367(10)
C2	C2	1.430(8)
C3	C4	1.386(6)

Table S4 Selected bond lengths of In-BDC-NH₂/NO₂ (**3**).

atom 1	atom 2	distance / Å	atom 1	atom 2	distance / Å
In1	O1	2.0355(4)	C1	C2	1.511(15)
	O2	2.087(6)	C2	C3	1.358(13)
	O4	2.152(4)	C3	C4	1.392(18)
	O5	2.168(4)		N1	1.64(3)
O2	C1	1.221(17)	C4	C5	1.325(19)
O3	C1	1.268(18)		N2	1.36(3)
O4	C6	1.234(6)	C5	C6	1.509(10)
O5	C7	1.224(6)	C7	C8	1.499(11)
O6	N1	1.18(3)	C8	C9A	1.365(16)
O7	N1	1.39(4)		C9B	1.43(3)
O8	N3	1.41(3)	C9A	N3	1.51(2)
O9	N3	1.35(2)	C9B	N4	1.412(14)

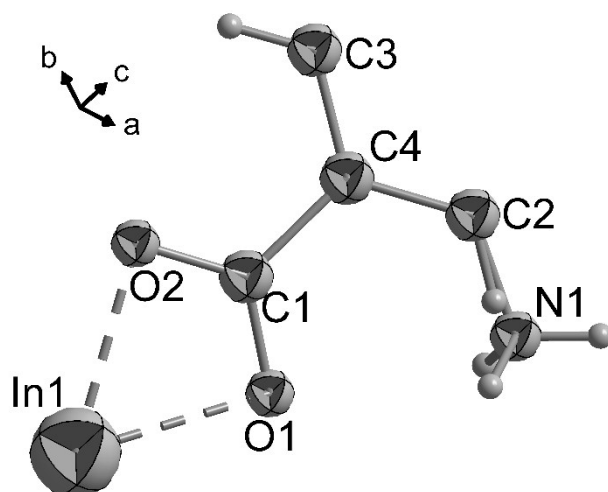


Fig. S8 Asymmetric unit of In-BDC-NH₂ (**1**) with numbering scheme as used in Table S3.

Table S5 Overview of the bands visible in The IR spectrum of In-BDC-NH₂ (**1**) discussed in the manuscript.

wavenumber / cm ⁻¹	vibration	wavenumber / cm ⁻¹	vibration
3438	asym. -NH ₂ stretching	1254	-NH ₃ ⁺ rocking
3336	sym. -NH ₂ stretching	1151	C-N stretching
3183	asym. N-H stretching	1099	-NH ₃ ⁺ rocking
2780	sym. N-H stretching	1019	-NH ₃ ⁺ rocking
1661	C-O stretching	861	arom. ring
1623	sym. carboxylate stretching	832	arom. ring
1551	asym. -NH ₃ ⁺ deformation	765	N-H out of plane
1498	sym. -NH ₃ ⁺ deformation	700	C-N deformation
1426	asym. carboxylate stretching	662	arom. ring
1330	C-N stretching		

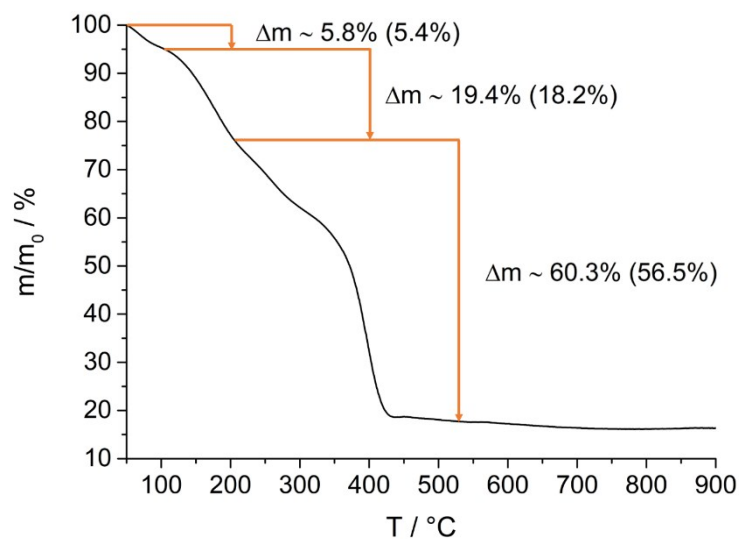


Fig. S9 Thermogravimetric measurement of In-BDC-NH₂ (**1**). The calculated values based on the assumed sum formula are given in brackets.

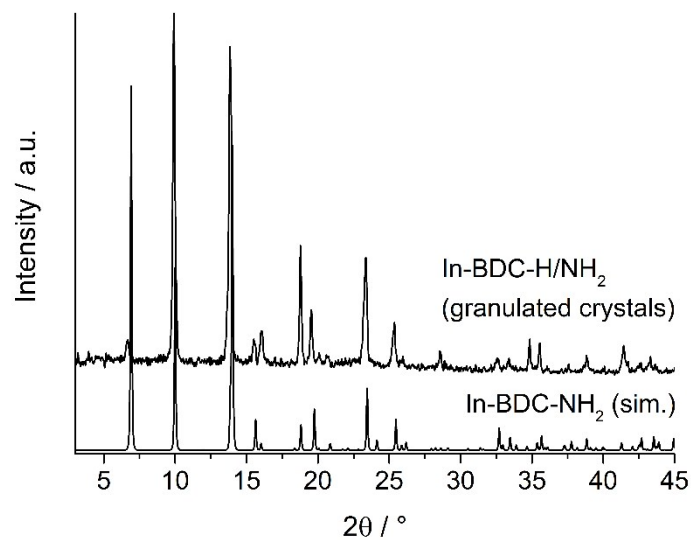


Fig. S10 Comparison of the PXRD pattern recorded for granulated crystals of In-BDC-H/NH₂ and the simulated pattern of In-BDC-NH₂.

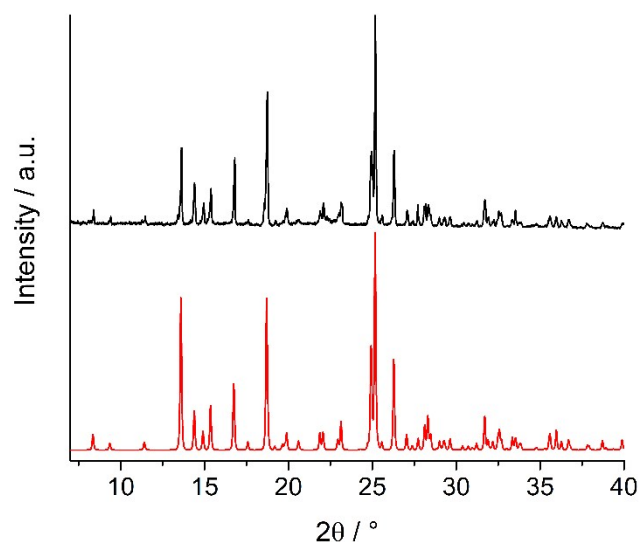


Fig. S11 Comparison of the PXRD pattern recorded for the sample using the same synthesis conditions as used for **1** with linker molecule replaced by H₂BDC-NH₂/NO₂ and the simulated pattern of dimethylammonium 2-amino-5-nitroterephthalate hemihydrate obtained from single crystal XRD measurements.²

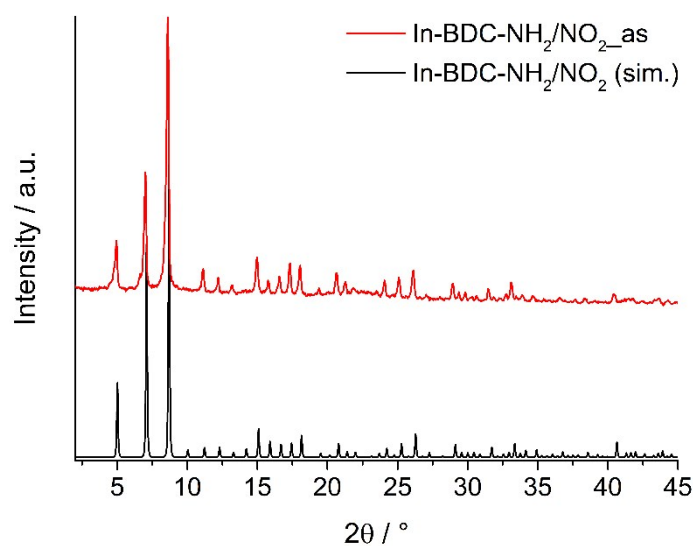


Fig. S12 Comparison of the PXRD pattern recorded for In-BDC-NH₂/NO₂ and the simulated pattern of In-BDC-NH₂/NO₂ obtained from single crystal XRD measurements.

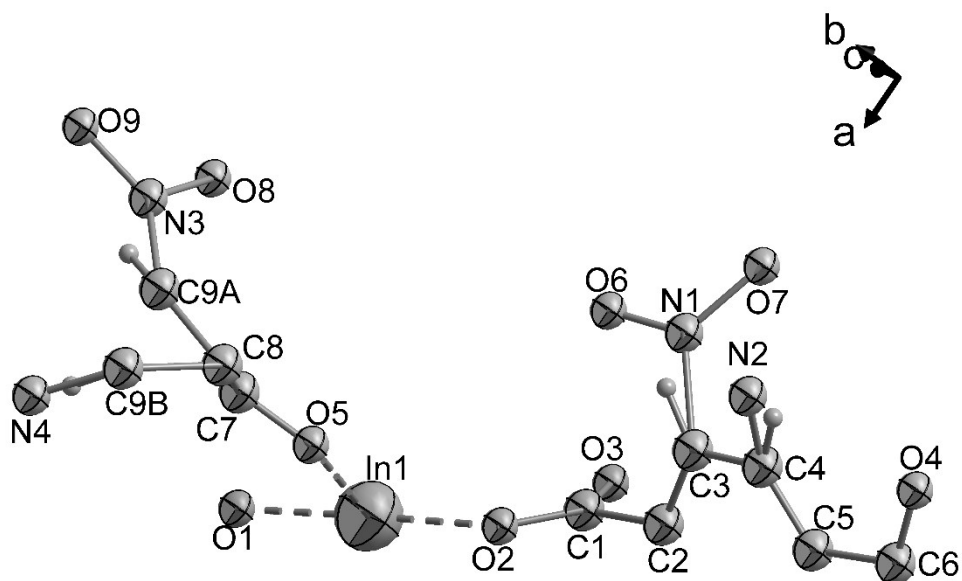


Fig. S13 Asymmetric unit of In-BDC-NH₂/NO₂ with numbering scheme as used in Table S4.

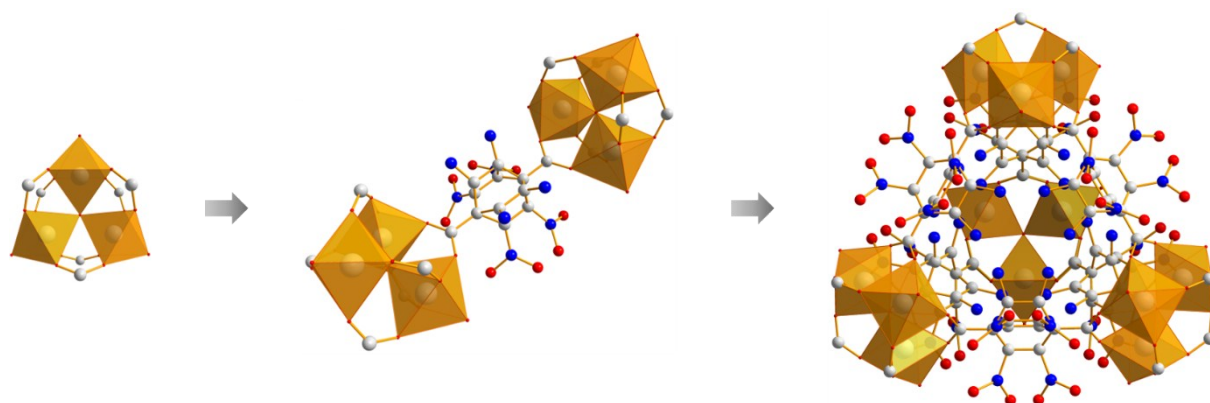


Fig. S14 Crystal structure of In-BDC-NH₂/NO₂. Trinuclear clusters composed of three InO₆ octahedra bridged by an μ_3 -O atom (left) are interlinked by a disordered tetradentate BDC-NH₂/NO₂²⁻ ions (middle) to form a super-tetrahedron (right).

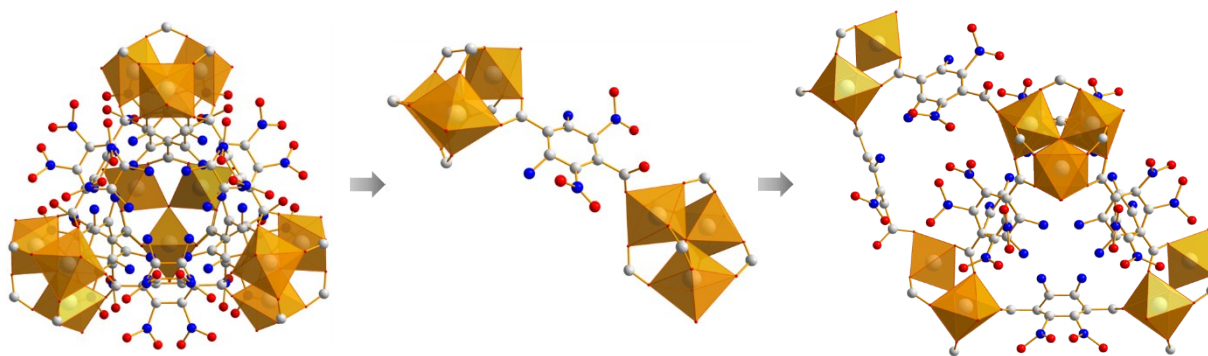


Fig. S15 Crystal structure of In-BDC-NH₂/NO₂. To each super-tetrahedron (left) four additional trinuclear In-O-clusters are attached via tridentate carboxylate ions (middle). Thus, four additional super-tetrahedra are formed (right; only two face-sharing super-tetrahedra are displayed), face-sharing with the central one (left).

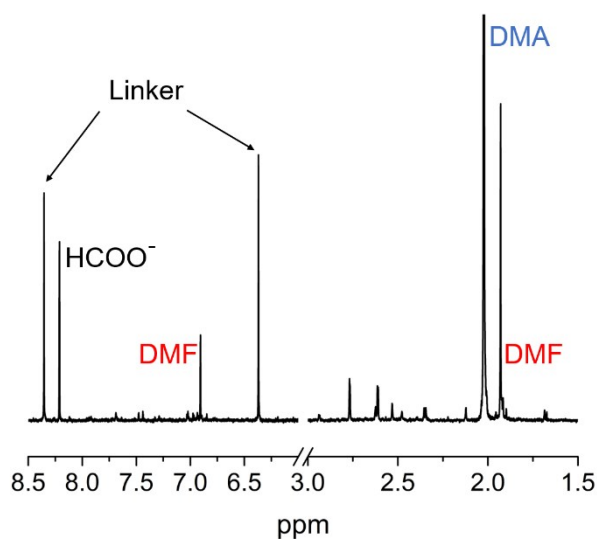


Fig. S16 ¹H-NMR spectrum of In-BDC-NH₂/NO₂. The MOF was dissolved in 5% NaOD/D₂O. Signals of DMF as well as HCOO⁻ and dimethylammonium ions (DMA), the hydrolysis products of DMF, are visible.

Table S6 Overview of the bands visible in The IR spectrum of In-BDC-NH₂/NO₂ (**3**) discussed in the manuscript.

wavenumber / cm ⁻¹	vibration	wavenumber / cm ⁻¹	vibration
3430	asym. -NH ₂ stretching	1254	Ar-N stretching
3316	sym. -NH ₂ stretching	1159	asym. carboxylate stretching
3193	asym. C-H stretching	1096	N-H stretching
3065	ammonium stretching vibration	1023	C-H stretching
2923	C-H stretching	871	arom. ring
2801	sym. C-H stretching	784	N-H deformation
1644	C-O stretching	761	N-H out of plane
1620	sym. carboxylate stretching	660	arom. ring
1577	C=C stretching	501	N-H out of plane
1299	C-N stretching		

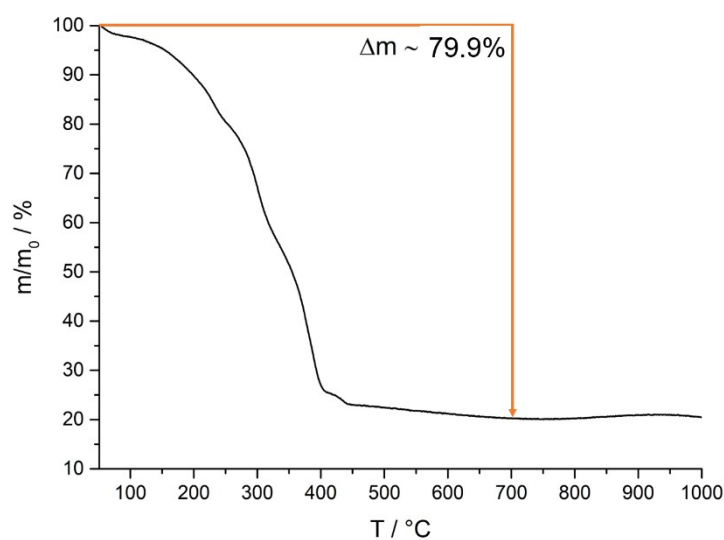


Fig. S17 Thermogravimetric measurement of In-BDC-NH₂/NO₂. A clear assignment of decomposition steps was not possible.

References

1. E. B. Skibo and J. H. Gilchrist, *The Journal of Organic Chemistry*, 1988, **53**, 4209-4218.
2. M. Krueger, M. Albat, F. Pieper and N. Stock, *IUCrData*, 2016, **1**, x160048.