Systematic Investigations on Bismuth Tri- and Tetraarylcarboxylates:

Crystal Structures - in situ X-ray Diffraction - Intermediates - Luminescence

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Abstract: The systematic investigation of the systems $\text{Bi}^{3+}$/ carboxylic acid / $\text{HNO}_3$ using the tri- and tetracarboxylic acids pyromellitic ($\text{H}_2\text{Pyrr}$), trimellitic ($\text{H}_2\text{Tri}$) and trimesic ($\text{H}_2\text{BTC}$) acid led to the discovery of five new bismuth carboxylates. The structural characterisation allows the establishment of the influence of the linker geometry and the $\text{Bi}^{3+}$ : linker molar ratio in the starting solution on the crystal structure. The crystallization of three selected compounds was investigated by in situ energy dispersive X-ray diffraction. Three new crystalline intermediates were observed within minutes and two of them could be isolated by quenching of the reaction mixture. Their crystal structures were determined from laboratory and synchrotron X-ray powder diffraction data which allowed us to establish a possible reaction pathway. In depth characterisation of the luminescence properties of the three bismuth pyromellate compounds was carried out. Fluorescence and phosphorescence could be assigned to (mainly) ligand and metal based transitions. The polymorphs $\text{BiHPyr}$ exhibit different luminescence properties although their structures are very similar. Surprisingly, doping of the three host structures with $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ ions was only successful for one of the polymorphs.

Keywords: Bismuth, inorganic-organic hybrid compounds, EDXRD, in situ, crystallization.

Introduction

Inorganic-organic hybrid compounds are in the focus of recent research activities due to their interesting sorption,[1-2] optical,[3-4] catalytic,[7-8] or magnetic properties.[9] While over the last decade most metal ions have been incorporated in this class of materials, only in the last few years bismuth carboxylate based compounds have been reported.[10-15] These show interesting optical [10-13, 15] or catalytic properties [14] and it is surprising that studies dealing with the synthesis of new bismuth carboxylates are very scarce.

Since the synthesis of metal carboxylates from reactants of low solubility can successfully be carried out under solvothermal conditions, leading to a great variety of different products, this method has also been applied to synthesize bismuth carboxylates.[10-11, 14-16] The reactions are carried out in sealed reactors under autogenous pressure at elevated temperatures above the boiling point of the solvent. It is well known that the synthesis parameters such as temperature, pH or molar ratio of the starting materials have a strong influence on the product formation. The inter-relationship of these parameters is very complex and thus structure prediction is rarely possible. Hence, extensive explorative synthetic work is necessary to obtain highly crystalline and pure compounds. High-throughput (HT) methods have been proven to allow the systematic and efficient investigation of parts of this complex parameter space.[17-18] Thus, these methods have been used for the systematic study of the influence of the $\text{pH}$,[19-22] temperature,[23-24] linker geometry and size,[25-26] concentration[21-22] or ionic radii.[27] In addition to the discovery of new compounds, the systematic variation of synthesis parameters allowed the establishment synthesis-structure relationships. Although HT methods are very valuable in finding new compounds, no information about the crystallization is obtained and thus a deeper understanding of the processes leading to the final product is not possible.

Recently, numerous methods have been developed to gain more information about the solvothermal crystallization mechanisms of materials.[28-29] The detection and structural characterization of crystalline intermediates is especially important because their crystal structures represent a local minimum on the energy hypersurface. These minima represent one step of the reaction mechanism and will...
help to understand the crystallization. Energy dispersive X-ray diffraction (EDXRD) has widely been applied to follow the crystallization of zeolites, metal phosphonates, metal-organic frameworks or thioantimonates under solvothermal reaction conditions.\textsuperscript{[26, 30-35]} Thus, it was possible to extract kinetic parameters,\textsuperscript{[20, 34, 36]} detect crystalline intermediates \textsuperscript{[26, 37]} or observe phase transformations.\textsuperscript{[19, 26, 36]}

Here we present the systematic high-throughput investigation of the synthesis of new bismuth carboxylates using pyromellitic, trimellitic and trimesic acid. To obtain a deeper understanding of the crystallisation processes, \textit{in situ} EDXRD studies on three new bismuth carboxylates were carried out.

**Results and Discussion**

**Results of the high-throughput experiments.**

In a systematic high-throughput study the three linker molecules pyromellitic acid (H\textsubscript{4}Pyr, 1,2,4,5-benzenetetracarboxylic acid), trimellitic acid (H\textsubscript{3}Tri, 1,2,4-benzenetricarboxylic acid) and trimesic acid (H\textsubscript{3}BTC, 1,3,5-benzenetricarboxylic acid) were used in combination with Bi(NO\textsubscript{3})\textsubscript{3}∙5H\textsubscript{2}O to synthesize new bismuth carboxylates. The Bi\textsuperscript{3+}: linker molar ratios were varied from 2:1-0.5:1 with and without the addition of 5 mol equivalent of HNO\textsubscript{3}. All the ratios are based on the amount of the linker, which was kept constant (15 mg). The results of the HT experiment and the results which are based on X-ray powder diffraction measurements, are shown in Fig. 1 and the important inorganic building units are shown in Fig 2. The use of pyromellitic acid leads to two new compounds. At the molar ratio of 2:1 the compound Bi\textsubscript{2}(O)(Pyr)(H\textsubscript{2}O) (1) is formed while at the lower ratio of 0.5:1 the compound Bi(HPyr) (3) is observed. The addition of HNO\textsubscript{3} has no influence on the phases formed. At intermediate molar ratios a mixture of both compounds is observed. The use of trimellitic acid leads to the new compound Bi(Tri)(H\textsubscript{2}O) (4). The Bi\textsuperscript{3+}:Tri molar ratio has no influence on the formed product. While in the absence of HNO\textsubscript{3} an unknown impurity with low crystallinity is observed, the addition of 5 mol equivalents of HNO\textsubscript{3} leads to the phase-pure compound 4. Changing the linker to trimesic acid, the new compound Bi\textsubscript{6}O\textsubscript{5}(BTC)\textsubscript{2}(HBTC) (8) is formed as a phase-pure product at the Bi\textsuperscript{3+}:BTC molar ratios of 2:1 in the absence of HNO\textsubscript{3} and 2:1:1:1 with additional HNO\textsubscript{3}. In the absence of additional acid and at molar ratios 1.5-0.5:1 the compound Bi\textsubscript{2}O\textsubscript{3}(BTC):2(HBTC) (7) is formed as a side-product.

The syntheses of all compounds except of 7 were successfully scaled-up and the crystal structures could be determined by single
crystal X-ray diffraction. Suitable crystals were isolated from the HT experiments or the scale-up syntheses. All compounds were characterized by thermogravimetric (TG) analysis, IR-spectroscopy, elemental analysis and X-ray powder diffraction. Details about the structure determination and the crystal structures are given in the experimental section and the supporting information, respectively.

**Structural trends and results of the HT experiments**

Using H$_2$Pyr or H$_2$BTC as the linker molecules and molar ratios of Bi$^{3+}$ : linker ≥ 2 : 1 lead to structures containing Bi-O-layers (compounds 1 and 8), while at Bi$^{3+}$ : linker molar ratios < 2 : 1 chains of BiO$_6$-polyhedra are observed (compounds 3 and 7). A similar inorganic chain of edge-sharing BiO$_6$-polyhedra is observed when the linker H$_3$Tri is employed (compound 4). Thus, the higher molar ratios lead to the incorporation of more Bi$^{3+}$ ions in the crystal structure. This is also reflected in the higher densities of 4.140 and 3.275 g/cm$^3$ for 1 and 3 and 4.021 and 3.568 g/cm$^3$ for 8 and 7, while compound 4 exhibits a density of 3.174 g/cm$^3$ (calculated from the crystal structures).

**In situ EDXRD studies**

To get a better understanding of product formation the crystallization of compounds 3, 4 and 8 was investigated by EDXRD at 150 °C. For all reactions water was used as the solvent without the addition of HNO$_3$. More details about the reaction conditions are given in the experimental section. In EDXRD studies intense white beam synchrotron radiation is employed to achieve a good time resolution (≤1 minute) while using conventional reaction vessels in the experiments. The white beam is sufficiently intense to penetrate steel autoclaves and thus reactions can be investigated without imposing an external influence on the reaction mixture provided no beam sensitive solvents are used.$^{[39]}$ In addition no scanning is needed due to the fixed angle of the solid state detector. For all experiments detector angles of about 2° were used. More details about identification of the phases observed in the EDXRD experiments are given in Table S8. A more quantitative evaluation of the EDXRD measurements including integration of the peaks in order to obtain crystallization curves or to determine kinetic parameter could not be carried out due to the high reaction rates and the overlap of the Bragg peaks of different compounds.

**Bi(NO$_3$)$_3$ / pyromellitic acid / H$_2$O (compound 3)**

The reaction system was investigated at 150 °C by *in situ* EDXRD using a molar ratio Bi$^{3+}$ : H$_2$Pyr = 1:2. The obtained spectra are represented as a three-dimensional plot in Figure 3. The homogenisation of the reaction mixture leads to an X-ray amorphous precipitate. Immediate upon heating, 1 is observed in the EDXRD spectra. The intensity of the most strongest signal (at 29.54 keV) starts to increase after 10 minutes and two peaks at 38.12 and 48.64 keV are detected. This transformation is completed after 60 minutes without any further changes during the investigated 8 h of reaction time. *Ex situ* experiments for the synthesis of compound 2 resulted in a highly crystalline phase-pure sample of Bi(HPyr) (2). As an additional result of the study, we were able to isolate the polymorphic compound 3 after a reaction time of 18 - 60 h. *Ex situ* studies showed that without an excess of the linker H$_2$Pyr, i.e. Bi$^{3+}$ : H$_2$Pyr ≤ 2 : 1, compound 1 is the final product after a reaction time of one week.

The crystal structures of 1 and 3 were determined from X-ray single crystal diffraction, but only a microcrystalline product of 2 could be obtained. Thus, the crystal structure had to be determined from X-ray powder diffraction data. The crystal structure determination was accomplished using real space methods as implemented in the program FOX$^{[40]}$ and the structure was refined by the Rietveld method using Topas Academic.$^{[41]}$ The final Rietveld plot is shown in Figure 4. Details about the structure determination and refinement are given in the experimental section and in the supporting information.

The inorganic building units of the three compounds obtained during the crystallization experiments are shown in Fig. 5 whilst the crystal structures of the two polymorphs are shown in Fig. 6. More details of the crystal structures are given in the supporting information. Bi$_2$(O)(Pyr)(H$_2$O) (1) (Fig. S1) crystallizes immediately upon heating. The crystal structure of 1 is built-up from face-sharing BiO$_6$ polyhedra which form Bi$_2$O$_2$ tetrameric units. Edge-sharing of these units by the oxygen atoms of carboxylate groups lead to the formation of layers. The presence of additional linker (H$_2$Pyr) in the reaction mixture allows the transformation from 1 to Bi(HPyr) (2) to take place. After 18 h the polymorphic compound Bi(HPyr) (3) is observed. The structures of compound 2 and 3 (Fig. S3-S8 and Fig. S7-S9, respectively) contain both chains of face-sharing BiO$_6$ polyhedra. These chains are connected by the aromatic rings of the pyromellitate ions to form a three-dimensional network, while one carboxylate group is protonated and forms CO-H···OC hydrogen bonds. The Bi-O-chains in 2 and 3 differ in the angle of the interconnection of the polyhedra.
after one minute a crystalline intermediate forms in black, the calculated powder pattern as an overlay in grey and the difference (observed-calculated) of both is given by the lower lack line. The allowed positions of the Bragg peaks are given as tick marks. A wavelength of 1.5406 Å was used.

The density of the 1, 2 and 3 increases from 2.749 to 3.207 and 3.275 g/cm³, respectively, while the space group symmetry decreases from C2/c to P2₁/a and P-1. According to Ostwald’s step rule compound 3 should be the thermodynamically most stable product. Compound 1 with an FO³ connectivity[38], which contains a more condensed inorganic building unit than compound 2 and 3 (FO² connectivity), is less stable under these reaction conditions and transforms into 2.38 In contrast, the transformation from a less to a higher condensed inorganic building unit has been observed for open-framework zinc phosphates.[42] The transformation of 1 into 2 may occur due to the release of H₂O from the structure on reaction with the ligand, leading to an entropy gain for the system due to the increased degrees of freedom of the H₂O molecule in the solution.

Fig. 5. Inorganic building units of the compounds obtained in the time dependent formation of 3.

Fig 6. Crystal structure of the polymorphic compounds 2 and 3. View along the b-axis. The carbon and oxygen atoms are shown as grey and black spheres, respectively. The BiO₆ polyhedra are given in grey.

Bi(NO₃)₃ / trimellitic acid / H₂O (compound 4)

The crystallization of Bi(Tri)(H₂O) (4) was investigated at 150 °C by in situ EDXRD (Fig. 7). Compound 4 starts to crystallize after 10 minutes and the reaction is already completed after about 20 minutes. During the first 10 minutes a slightly higher background compared to the final spectra in the region of 35-40 keV is observed that could be explained by the presence of an X-ray amorphous intermediate or precursor. This observation correlates well with the fact that in ex situ experiments a white X-ray amorphous precipitate is formed upon mixing of the starting materials at room temperature. Compound 4 persist as the final product even after one week of reaction time.

Dehydration properties

The crystal structure of 4 was determined by single crystal X-ray diffraction. One molecule of water per formula unit is observed (Fig. S17-S19), which coordinates in a terminal manner to the Bi³⁺ ion in the structure. Thermogravimetric measurements (Fig. S23) demonstrate that the water can be removed at 150 °C. The irreversible dehydration at 200 °C for 12 h results in the crystalline compound Bi(Tri) (5). The powder pattern (Fig. S21) was successfully indexed using Topas academics and the lattice parameters were refined using the Pawley method (a = 6.7135(6), b = 19.558(2), c = 6.6422(4) Å and α = 90, β = 90.23(2), γ = 90 °, chosen space group P2₁). The Pawley fit is shown in the supporting information (Fig S22). The structure could not be solved from X-ray powder diffraction data.

Bi(NO₃)₃ / trimesic acid / H₂O (compound 8)

The three-dimensional representation of the crystallization of 8 as studied by EDXRD at a reaction temperature of 150 °C is shown in Figure 8. Already after one minute a crystalline intermediate [Bi(BTC)(H₂O)]·H₂O (6) (FO², chains of corner-sharing BiO₆ polyhedra) is observed. Compound 6 transforms after 10 minutes into a second intermediate which could not be isolated. This compound is further transformed after 20 minutes into Bi₂(NO₃)₃·(BTC)₃(HBTC) (7) (FO², chains of corner- and face-sharing
BiOx polyhedra, x = 7-9) which was previously isolated from HT experiments. No further transformation to compound 8 was detected during the in situ EDXRD study. Surprisingly quenching of the reaction mixture led to phase-pure product of 8 (FeO), layers of XXX corner- and face-sharing BiOx polyhedra, x = 6, 8). Apparently upon cooling, 7 transforms into 8 under these reaction conditions.

Intermediate 6 was successfully isolated by quenching of the reaction mixture while similar experiments for the second intermediate exclusively resulted in yet another new phase in mixtures with compound 6 or 8. The crystal structure of the [Bi(BTC)(H₂O)]·H₂O (6) was determined from high resolution X-ray powder diffraction data measured at beamline P08 at PETRA, HASYLAB, DESY. The structure determination was accomplished by using real space methods as implemented in the program FOX. The crystal structure was refined by the Rietveld method as implemented in Topas Academics. The final Rietveld plot is shown in Fig. 9 and detailed structural description of compounds 6, 7 and 8 are given in the supporting information in the Figures S25-S27, S28-S30 and S32-S34, respectively. The inorganic building units of 6 - 8 are given in Fig. 10.

Fig. 8. Three-dimensional representation of the crystallization in the system Bi(NO₃)₃ / H₂BTC / H₂O at 150 °C. See Table S8 in the supporting information for the indexing of the signals.

Fig. 9. Final Rietveld plot of compound [Bi(BTC)(H₂O)]·H₂O (6). The observed powder pattern is shown in black, the calculated powder pattern as an overlay in grey and the difference (observed-calculated) of both is given by the lower black line. The allowed positions of the Bragg peaks are given as tick marks. A wavelength of 0.825986 Å was used.

Summary of the in situ experiments

The in situ EDXRD experiments have shown that bismuth carboxylates crystallize with very short reaction times. In addition, crystalline intermediates are often observed. Our results suggest that due to the long reaction times - usually days, up to a week – commonly used in the synthesis of bismuth carboxylates, metastable intermediates have been overlooked. Re-investigation of these systems should therefore be undertaken.

Characterization of compound 1-8

In order to learn more about the thermal stability, TG analyses were carried out. The TG measurements and their interpretation for compound 1-4, 6-8 are given in the supporting information (Fig. S11-S13, S23 and S36-S37). The observed weight losses are summarized in Table 1. All compounds containing water molecules show a weight loss at temperatures between 40 °C and 200 °C and all compounds start to decompose between 340 °C and 380 °C.

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<th>compound</th>
<th>loss of water</th>
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All compounds were also characterized by IR-spectroscopy. The IR-spectra and their interpretation are given in the supporting information (Fig. S14-S16, S24 and S38-S39). All compounds show characteristic broad bands in the region of 2500-3400 cm⁻¹ which can be assigned to O-H vibrations of the water molecules. Between 1550 to 1560 cm⁻¹ the asymmetric stretching vibrations of the carboxylate groups and in the range of 1400-1480 cm⁻¹ the symmetric stretching vibration are observed. The aromatic C-C stretching vibrations are observed in the range of 1480-1500 cm⁻¹ and the symmetric and asymmetric aromatic C-H deformation vibrations are observed in the range between 760-870 cm⁻¹.

**Luminescence properties and doping experiments of 1 - 3**

Bi³⁺ containing solids are well known as materials with distinct luminescence properties. The physical reasons for the large Stokes shifts that are highly dependent on the crystal structure and the composition of the host lattice, the unique temperature dependences of the emission lifetimes, typically on the order of 10⁻³ s at low and 10⁻²-10⁻⁵ s at high temperatures, as well as the spectroscopic assignment of the two distinct often observed emission bands in the visible luminescence spectra have been thoroughly discussed in the literature.[43-47] Usually, the spectroscopy of Bi³⁺ with ⁴S³/₂ in the ground and ⁴P³/₂ configuration in the first excited state is discussed in terms of Russell-Saunders type electronic energy terms. The energetically lowest possible ⁴P₀ ← ⁴S₀ excitation is strongly forbidden. Therefore, the ⁴P₁ ← ⁴S₀ transition, which is possible due to spin-orbit coupling of the ⁴P₁ and ⁴P₃ states, is observed as the so-called A band. Following absorption, fast non-radiative relaxation and equilibration of the Bi³⁺ system into the ⁴P₀ and ⁴P₁ levels is assumed with the ⁴P₀ level acting as a metastable trapping state.[43, 48] The ratio of the population of both states strongly depends on the temperature, and emission from both states is possible. Typically, at high temperatures the fast ⁴P₁ → ⁴S₀ emission dominates, however, at lower temperatures the observed excited state lifetimes steadily increase and reach plateau values on the order of 10⁻¹ s. The corresponding slow emission component can be assigned to the highly forbidden ⁴P₀ → ⁴S₀ transition. In most cases, due to broad bands and the rather small ⁴P₀-⁴P₁ energy splitting, the two emission bands are not resolved in the spectra. Nevertheless two separate luminescence bands are often observed. These two bands exhibit similar luminescence decay behaviour and have been frequently ascribed to result from rather complex Jahn-Teller effects.[45, 48-50]

The three pyromellitic acid based compounds 1-3 were selected for the detailed investigation of their photoluminescence characteristics in order to study the influence of the crystal structure. Especially the properties of 2 and 3 in comparison with 1 were of interest since the former two compounds are polymorphs with very similar crystal structures. Therefore, excitation and emission spectra of the observed short-lived (as of now termed fluorescence) and long-lived (as of now termed phosphorescence) spectral components have been recorded. Upon excitation with a standard UV lamp at a wavelength of 254/366 nm, 1 and 2 show strong blue luminescence colour and 3 a pale green. The resolved luminescence spectra are illustrated in Figures 11-13.

In all three cases, a short-lived fluorescence band centred at 430-470 nm and a second red-shifted long-lived phosphorescence band centred at 490-530 nm was observed. The splitting will be discussed below. The respective, markedly different fluorescence and phosphorescence excitation spectra of 1 and 2 suggest that two different emission centres are responsible for the two luminescence components. Note that the maxima of the two excitation spectra are shifted by approximately 20 nm for 1 and that the two-peak phosphorescence excitation feature of 2 can in fact be explained by a single broad absorption band of the one luminescent centre peaking around 340 nm with a pronounced intensity reduction arising from the strongly interfering absorption of the other luminescent centre at 330 nm. Due to the overall lower luminescence of 3 and the much stronger spectral overlap of the fluorescence and phosphorescence band, the temporal and spectral separation of the bands was experimentally more demanding and the interpretation of the obtained spectra is less clear. Both fluorescence and phosphorescence excitation spectra are very similar, nevertheless a good quality phosphorescence spectrum could be obtained by excitation at 275 nm and detection at 560 nm.

The phosphorescence bands have been further analyzed by recording intensity decay curves (see Figures S40-S44 in the supporting information) and luminescence lifetimes have been extracted by fitting biexponential functions. The fast decay component with lifetimes of 49-113 µs were close to the time resolution of the applied spectrophotometer and may be ascribed to residual signal from the underlying fluorescence band. The long decay components yielded lifetimes of τ = 1.1 ms, 0.84 ms and 1.80 ms for 1, 2 and 3, respectively.

We attribute the short-lived components peaking at 430-470 nm to intraligand luminescence from (π*-π) or (n→π*) transitions of the pyromellate ions. Both the maxima of the fluorescence excitation spectra at 320-340 nm and the observed Stokes shifts of 110-130 nm are consistent with the 320 nm maximum and 115 nm Stokes shift measured for alkaline aqueous solutions of the pure pyromellitic acid (Fig. S45). Bi³⁺ ions give rise to the second luminescent centre causing the long-lived luminescence peaking at 490-530 nm. Again, both the maxima of the phosphorescence excitation spectra at 320-360 nm (A band absorption) and the large observed Stokes shifts of 170-190 nm are consistent with observations in other Bi³⁺ containing systems.[43, 47-48, 51] According to the literature, the measured long luminescence decay times on the order of τ_duro = 1 ms reflect

![Figure 11. Luminescence spectra of compound 1. The fluorescence (0) excitation and emission spectra were measured with λ_excitation = 310 nm and λ_emission = 460 nm, respectively. The phosphorescence excitation and emission spectra were measured with λ_excitation = 360 nm and λ_emission = 515 nm, respectively. L refers to the luminescence of the linker ion.](image-url)
fluorescence.

The amount of...

and a long...

The MIR spectra were recorded on a Bruker ALPHA...

The luminescence spectra of the doped compound...
High-throughput (HT) experiments: The system Bi^{3+} / L / HNO_{3} with L = pyromelitic acid or trimellitic acid or trimesic acid was investigated by using HT methods. A custom-made HT reactor containing 24 PTFE liners, each with a maximum volume of 2 ml, was used.\[^{17, 21}\] The amount of the respective organic linker molecule was fixed at 15 mg each. Eight reactions with different molar ratios of Bi^{3+} / L were carried out for each linker and with and without the addition of 5 mol equiv. of 2 M HNO_{3}. The solids were added to the reactors and 1 ml of water and the HNO_{3} solution were added to the reaction mixture, homogenized by shaking, and heated in 1 h at 150 °C.\[^{25}\] The mixture was quenched after 150 °C in 1 h, the temperature was held for 48 h and subsequently cooled down to room temperature in 12 h. The reaction mixture was filtered and washed with 10 ml of DMF and 10 ml of water. A white powder was obtained with a yield of 757 mg (79%) based on H-Pyr. The phase-purity was confirmed by elemental analyses (obs. C 26.09%, H 0.43% calc. based on Bi(C_{5}H_{8}O_{4}) C 26.10%, H 0.66% yield 28.9 mg (32% based on H-Pyr)).

Synthesis of Bi(HPyr)\(^{3+}\): 30 mg (0.984 mmol) pyromelitic acid (H-Pyr) and 954 mg (1.96 mmol) of Bi(NO_{3})_{3}·5H_{2}O were combined in a 23 ml Teflon lined steel reactor and 9.5 ml of distilled water were added. The mixture was heated up to 150 °C in 1 h, the temperature was held for 48 h and subsequently cooled down to room temperature in 12 h. The product was filtered and washed with 10 ml of DMF and 10 ml of water. A white powder was obtained with a yield of 577 mg (79%) based on H-Pyr. The phase-purity was confirmed by elemental analyses (obs. C 26.10%, H 0.66% and X-ray powder diffraction (Fig. S10)).

Synthesis of Bi(Tri)(H_{2}O)\(^{2+}\): 150 mg (0.714 mmol) 1,3,5-benzenetricarboxylic acid (H-BHTC) and 346.2 mg (0.714 mmol) of Bi(NO_{3})_{3}·5H_{2}O were added to a 23 ml Teflon lined steel reactor. 8.21 ml distilled water and 1.79 ml 2M HNO_{3} were added and the reaction mixture was cooled to room temperature in 12 h. After cooling to room temperature the resulting product was filtered and washed with DMF and water. 237.5 mg of a white powder was obtained yield 76.6% based on H-BHTC. The phase-purity was confirmed by X-ray powder diffraction (Fig. S20) and elemental analysis (obs. C 24.90 %, H 1.16 % calc. based on Bi(C_{5}H_{8}O_{4})·H_{2}O C 25.26 %, H 1.16 %).

Synthesis of Bi(Tri)(F): Compound 5 was obtained by heating compound 4 at 200 °C for 15 h. A comparison of the powder patterns of 4 and 5 is given in the supporting information in Fig. S21.

Synthesis of (Bi(BTC)/H)(H_{2}O): 5: Compound 6 was obtained by quenching the reaction mixture of the in situ experiments of the system Bi(NO_{3})_{3} / trimesic Acid / H_{2}O after 5 minutes at 150°C. The precipitate was filtered of and washed with DMF and water.

Synthesis of Bi(BTC)/OH(HBTC)(NO)\(^{3+}\): 150 mg (0.714 mmol) 1,3,5-benzenetricarboxylic acid (H-BHTC) and 346.2 mg (0.714 mmol) of Bi(NO_{3})_{3}·5H_{2}O were combined in a 23 ml Teflon lined steel reactor with 9.64 ml of distilled water and 0.357 ml 2 M NaOH. The reactor was sealed and the mixture was heated up to 150 °C in 24 h, the temperature was held for 60 h and the reaction mixture was cooled down to room temperature in 48 h. The product was filtered and washed with 10 ml of DMF and 10 ml of water. 239.7 mg of a white powder was obtained purity was confirmed by X-ray powder diffraction (Fig. S21) with the presence of a unique impurity (Fig. S31)).

Synthesis of Bi(O)\(^{2+}\)(OH)(HBTC)(NO)\(^{3+}\): Larger amounts of 8 could be obtained by using 150 mg (0.714 mmol) 1,3,5-benzenetricarboxylic acid (H-BHTC) and 692 mg (1.43 mmol) Bi(NO_{3})_{3}·5H_{2}O in 10 ml water in a 23 ml Teflon lined steel reactor. The mixture was heated up to 150 °C in 24 h. The temperature was held for 48 h and the reaction mixture was cooled to room temperature in 12 h. The precipitate was filtered and washed with DMF and water. Phases-purity was confirmed by XRPD (Fig. S35) and elemental analyses. (obs. C 14.99 %, H 0.70 %, N 1.94 % calc. based on Bi(O)\(^{2+}\)(OH)(C_{5}H_{8}O_{4}) C 15.23 %, H 0.60 %, N 2.03 %) The compound could also be obtained quenching the reaction mixture of the in situ experiments of the system Bi(NO_{3})_{3} / trimetric Acid / H_{2}O after 20 minutes.

Synthesis of the doped compound 3: 250 mg (0.984 mmol) pyromelitic acid (H-Pyr) , 233.8 mg (1.96 mmol) of Bi(NO_{3})_{3}·5H_{2}O and 98 µL of 0.1 M Tm(NO_{3}) or Eu(NO_{3})_{3} solution were combined in a 23 ml Teflon lined steel reactor and 9.9 ml of distilled water were added. The mixture was heated at 150 °C for 12 h. The product was filtered and washed with 10 ml of DMF and 10 ml of water.

Crystal structure determination

The crystal structures of 1, 3, 4, 7, 8 were determined from single crystal X-ray data. X-ray diffraction measurements were performed on a Stoe IPDS diffractometer equipped with an image plate detector using Mo Kα radiation (λ = 71.037 pm). The crystal structures were solved by direct methods with the program SHELXS-97 and refined using the program SHELXL-97.\[^{25}\] H-atoms connected to carbon atoms were placed onto calculated positions. H-atoms of the water molecules could not be located in the difference Fourier maps. The OH and O\(^{2-}\) ions were distinguished by comparison of the bond geometry and the bond lengths with the literature known crystal structure of the basic bisnuth nitrate ([Bi(H_{2}O)(NO)(O(OH))(NO))\(^{3+}\)]. For all compounds numerical absorption correction were carried out using X-SHAPE and XRED.\[^{25}\] The crystals of compound 4 and 7 were merohedrally twinned and were refined using the RASF and Dمون command and implemented in SHELXL.\[^{25}\] The crystal structures of 2 and 6 were determined from X-ray powder diffraction data. The powder patterns were measured on a Panalytical empyrean diffractometer equipped with a ProCell detector system using Cu Kα\(^{2+}\) radiation and at beamline P08, PETRA, DESY, Hamburg with a wavelength of λ = 0.2898 Å using a Mythen 4K detector. The powder patterns were indexed using Topas.
We thank Dr. Michael Wharmby for the assistance with the powder data analyses and revision of the manuscript. Dr Christian Nather and Inke Jess for the single crystal X-ray diffraction measurements and the helpful discussions, Prof. Bensch and group for the support in the in situ experiments, the Ralph Norwid Schindler Stiftung for making available the fluorescence spectrophotometer, the Land Schleswig-Holstein and the SPP 1415 “Kristalline Nichtgleichgewichtsphasen” for the financial support.

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