New insights into the crystallization of polymorphic materials: from real-time serial crystallography to luminescence analysis

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Electronic supplementary information

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1. Supplementary synthesis description



Figure S1: Adaptation of *in situ* reactor for experiments at synchrotron facilities. X-ray beam enters the empty glass tube and exits the unmodified side of the reactor, minimizing the solution volume passed by the beam before reaching the detector.



Figure S2: Experimental setup at P09 (DESY) for simultaneous performance of *in situ* X-ray diffraction analysis and the ILACS technique. Inset: Reactor irradiated with UV light (λ_{ex} = 395 nm).



Figure S3: In situ setup used at the SOLEIL synchrotron facility.



Figure S4: *In situ* reactor setup at the University of Kiel for monitoring the synthesis of [Eu(phen)₂(NO₃)₃] applying time-resolved measurements of pH value, besides infrared and luminescence spectroscopy, dosing system and temperature control.

2. Complementary results to experiments I and II



Figure S5: Time-dependence of the addition of the ligand solution (phen, green curve), in comparison to the XRD intensity at 4.3 °20 (blue curve), luminescence intensity at 615 nm (λ_{ex} = 395 nm, red curve) and intensity of the light source at 386 nm (pink curve) during synthesis of [Eu(phen)₂(NO₃)₃] Phase **1** (exp. *II*, Table 1).



Figure S6: Time-dependence of the addition of the ligand solution (phen and acac, green curve), in comparison to the XRD intensity at 4.3 °20 (blue curve), luminescence intensity at 615 nm (λ_{ex} = 395 nm, red curve) and intensity of the light source at 386 nm (pink curve) during synthesis of [Eu(phen)₂(NO₃)₃] Phase **2** (exp. *II*, Table 1).



3. Complementary results to experiments III-VII

Figure S7: a) *In situ* emission intensity (λ_{ex} = 395 nm) of the ⁵D₀→⁷F₁ Eu³⁺ transition recorded during synthesis of **2** under presence of acac for T = 60 °C (exp. *III*) and 25 °C (exp. *IV*). b) *In situ* emission intensity (λ_{ex} = 395 nm) of the ⁵D₀→⁷F₁ Eu³⁺ transition recorded during synthesis of **1** without acac for T = 60 °C (exp. *VI*) and 25 °C (exp. *VII*). Figures c)-f) present the respective *in situ* emission spectra under these synthesis conditions. The intensity of the emission spectra at Figures S7 a) and b) has been normalized for improving the comparability between experiments and overcome the artifact of the detector saturation at 4000 counts, as demonstrated on Figures S7c)-f).



Figure S8: a) 3D *in situ* IR spectra measured during synthesis of 2 with acac at 60 °C (exp. *III*). b) Comparison of the time-dependent *in situ* IR measurements with *ex situ* measured IR spectra of Eu(NO₃)₃, (green curve), phen (red curve) and acac (blue curve) solutions. The asterisk (*) signs mark negative IR values due to air bubbles on the sensor, especially during the measurement period at t < 60 min, at 60 °C.



Figure S9: Time dependence of the volume of ligand solution (acac and phen, green curve) during synthesis of **2** at 60 °C (exp. *III*) in comparison to the time dependence of the IR absorption at 1365 cm⁻¹ (acac, red curve)^[X] and 1420 cm⁻¹ (phen, orange curve). ^[X] The result of the simultaneously measured in situ emission intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ Eu³⁺ transition (λ_{em} = 395 nm) is shown in red.



Figure S10: X-ray diffraction measurement of $[Eu(phen)_2(NO_3)_2]$ synthesized with acac at 60 °C (black curve, exp. *III*), in comparison to the calculated diffraction pattern for Phase **2**. [1]



Figure S11: Emission (a and b, $\lambda_{ex} = 340$ nm) and excitation ($\lambda_{em} = 616$ nm) spectra of [Eu(phen)₂(NO₃)₂] Phases **1** (green curves) and **2** (pink curves), accompanied by their respective X-ray diffraction patterns (c).



Figure S12: Time dependence of the intensity of the emission peak assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ Eu³⁺ transition during the addition of the ligand (green curve) to europium solution for the synthesis of [Eu(phen)₂(NO₃)₂] Phase **2** with acac at 60 °C, excited at 365 nm (blue curve, exp. *IV*) and at 395 nm (red curve, exp. *III*).



Figure S13: Time dependence of *in situ* measurements of pH values during the addition of the ligand (green curve) to europium solution for the synthesis of $[Eu(phen)_2(NO_3)_2]$. Phase **1** is synthesized without acac at 25 °C (blue curve, exp. *VII*) and at 60 °C (violet curve, exp. *VI*). Phase **2** is synthesized with acac at 25 °C (red curve, exp. *V*) and at 60 °C (orange curve, exp. *III*).

4. Supplementary results to experiments *VIII-X*



Figure S14: Comparison of measured X-ray diffraction patterns of $[Eu(phen)_2(NO_3)_3]$ prepared without H₂O with the Eu:phen:acac ratios 1:1:0 (green curve, exp. *VIII*) and 1:2:0 (blue curve, exp. *IX*) as well as prepared with H₂O in the reaction medium (pink curve, exp.

X), in comparison to calculated patterns of Phases 1 and 2. [1]



Figure S15: Comparison of measured X-ray diffraction patterns of [Eu(phen)₂(NO₃)₃] Phases
1 and 2 after stirring in ethanol for 1 h as well of Phases 1 (exp. *VIII*) and 2 (exp. *X*) after three years, in comparison to calculated diffraction patterns. [1]

5. Supplementary results to experiment XII



Figure S16: Emission spectrum ($\lambda_{ex} = 365$ nm) recorded parallel to serial crystallography experiment during synthesis of [Eu(phen)₂(NO₃)₃] in flow regime (exp. *XII*). The atheistic (*) sign indicates the saturation of the detector at 4000 counts.

6. References

[1] G. G. Sadikov, A. S. Antsyshkina, I. A. Kuznetsova, M. N. Rodnikova, Crystallogr. Rep. 51 (2006) 47-52.