Electronic Supplementary Material (ESI) for Analyst.

Supporting information

Development of a new *in-situ* analysis technique applying luminescence of local coordination sensors: principle and application for monitoring metal-ligand exchange processes

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Contents

1. Additional *in-situ* and *ex-situ* results for assembly 1

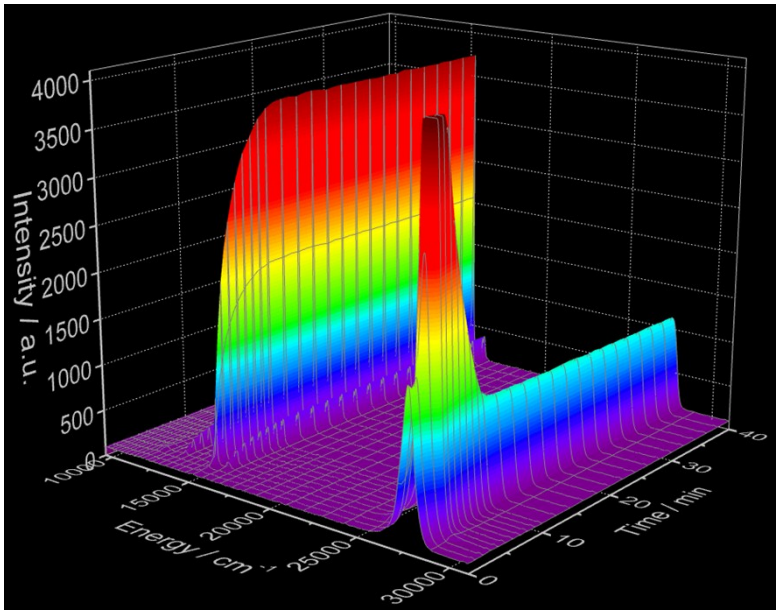

Figure S1. *In-situ* luminescence measurements for assembly 1 (λ_{ex} = 365 nm), presenting the characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 1-4) Eu^{3+} transitions [1] besides the intensity profile of the excitation light.

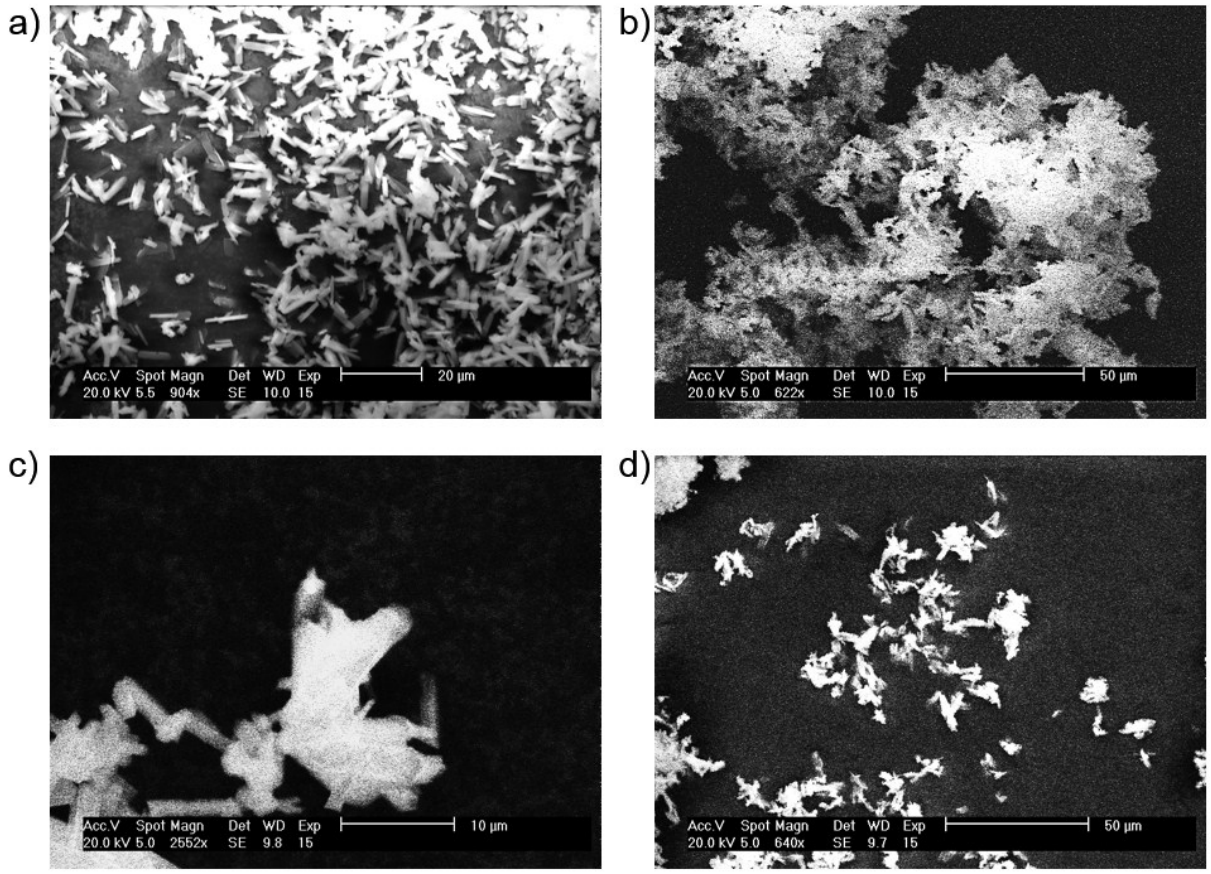

Figure S2. *Ex-situ* scanning electron microscopy images of $[Eu(phen)_2(NO_3)_3]$ after a) 5 min, b) 20 min, c) 60 min and d) 90 min after the addition of the phen to the $Eu(NO_3)_3$ solution.

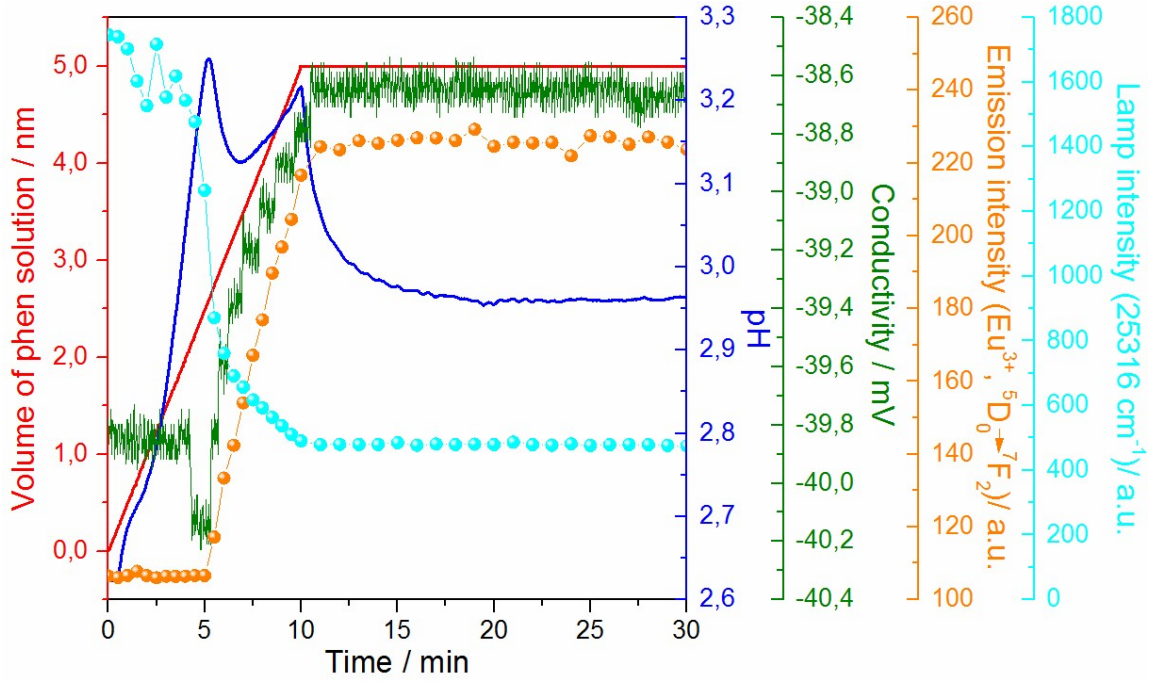

Figure S3. Time dependence of addition of phen to $Eu(NO_3)_3$ solution (red curve) in comparison to pH (dark blue curve), conductivity (green curve), intensity of $^5D_0 \rightarrow {}^7F_2$ Eu^{3+} transition [1] (orange curve) and intensity of excitation source (λ_{ex} = 395 nm, light blue curve).

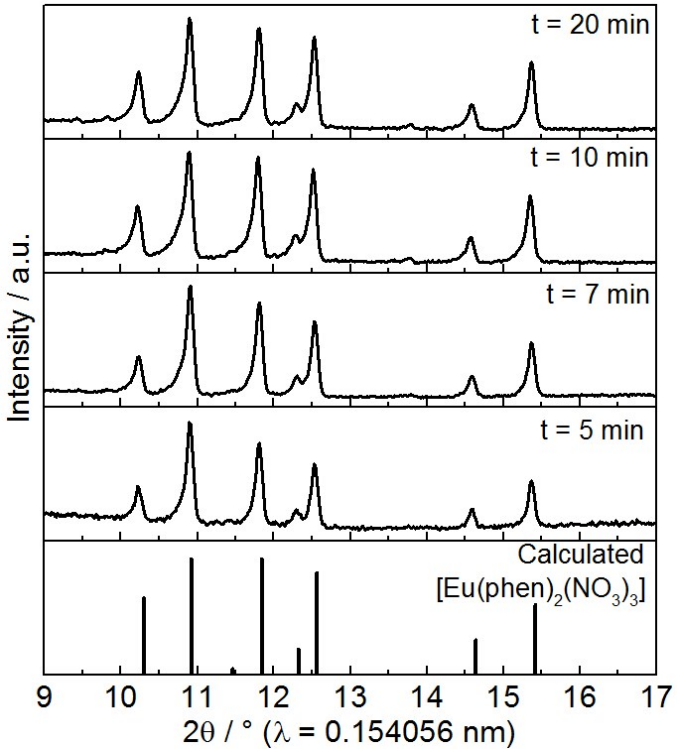

Figure S4. *Ex-situ* X-ray diffraction pattern for different reaction times in comparison to the calculated pattern for $[Eu(phen)_2(NO_3)_3]$ [2]. These samples have been removed and dried at 80°C for 2 h without washing.

2. Additional in-situ and ex-situ results for assembly 2

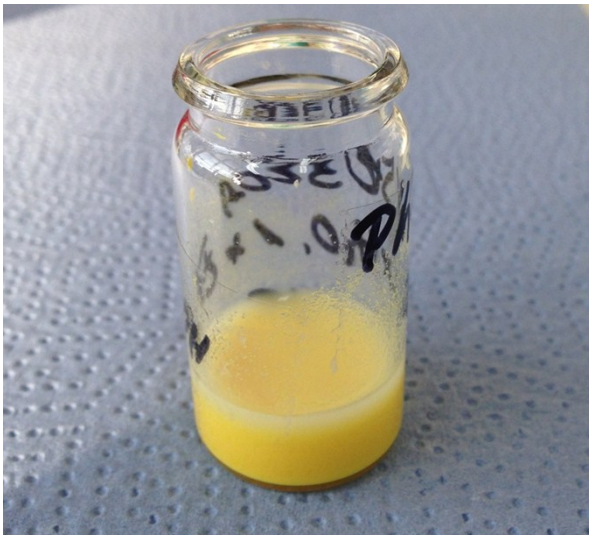

Figure S5. Yellow color of [Sn(phen)Cl_4] converted from [Eu(phen)$_2$(NO_3)$_3$] upon addition of $SnCl_2$.

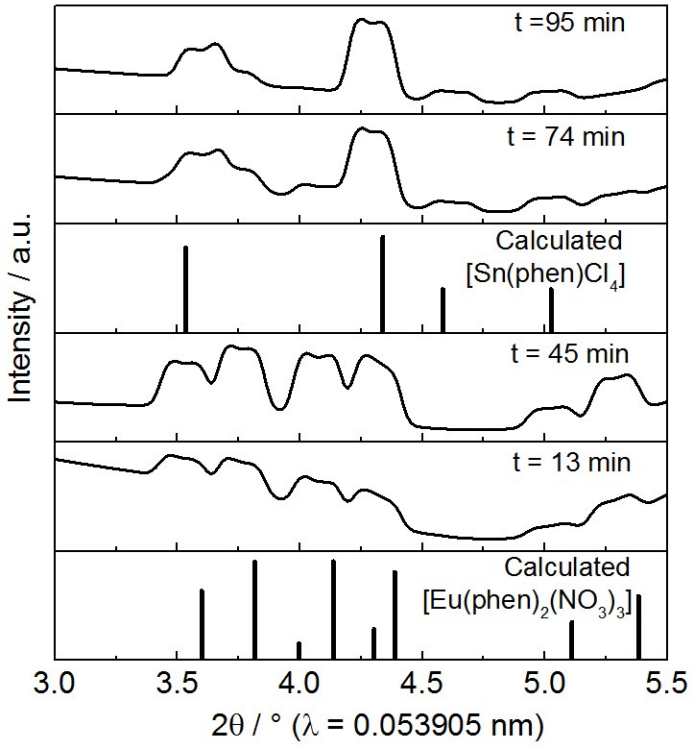

Figure S6. *In-situ* XRD patterns for different reaction times of the assembly **2** in comparison to calculated patterns for $[Eu(phen)_2(NO_3)_3]$ [2] and $[Sn(phen)Cl_4]$ [3]. Broadening effect of the single reflexes caused by the large measurement volume displayed on Figure S9.

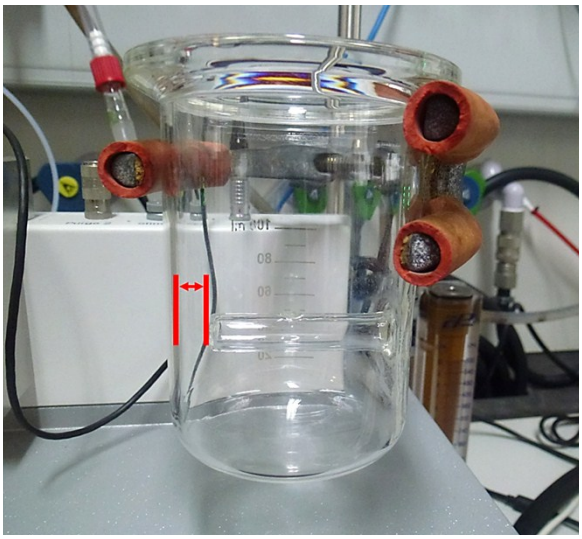

Figure S7. Modification of glass reactor with introduction of a glass tube for allowing *in-situ* analyses applying synchrotron radiation. Red arrow shows the portion of the reaction system available for the XRD measurements.

3. References

[1] G. H. Dieke, in Spectra and energy levels of RE ions in crystals, Wiley, New York, **1968**.

[2] A. G. Mirochnik, B. V. Bukvetskii, P. A. Zhikhareva, V. E. Karasev, *Russ. J. Coord. Chem.* **2001**, 27, 443-448.

[3] D. L. Perry, R. A. Geanangel, *J. inorg, nucl. Chem.* **1974**, 36, 205-206.