Electronic Supplementary Information for Dalton Transactions

Supporting Information

for

The Interaction of Rare Earth Chlorides with 4,4'-Bipyridine for the Reversible Formation of Template Based Luminescent Ln-N-MOFs

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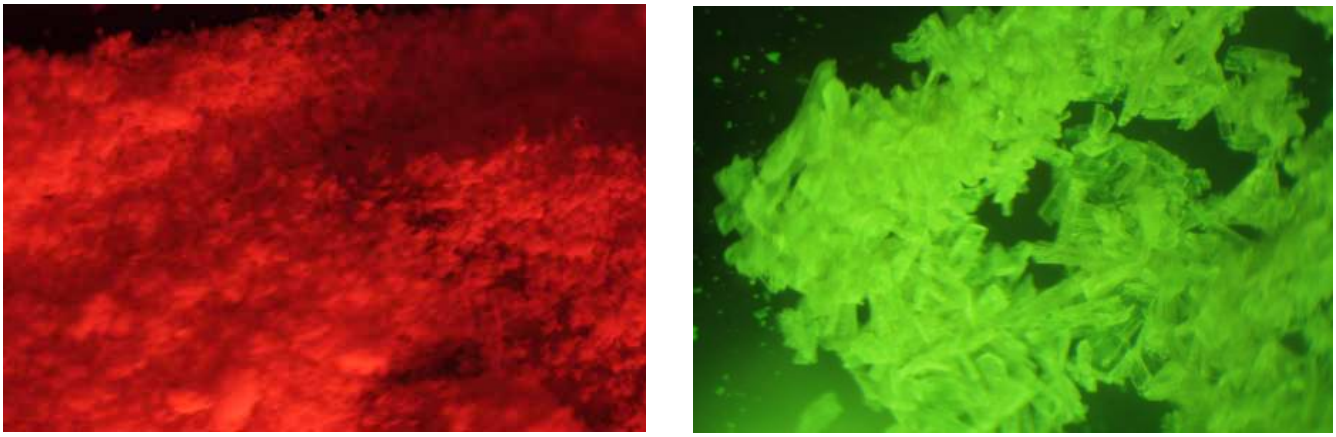

Fig. S1. Intensive red luminescence of $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ (**left**, ext. wavelength: 302 nm). Intensive green luminescence of $^{2}_{\infty}[Tb_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ (**right**, ext. wavelength: 302 nm).

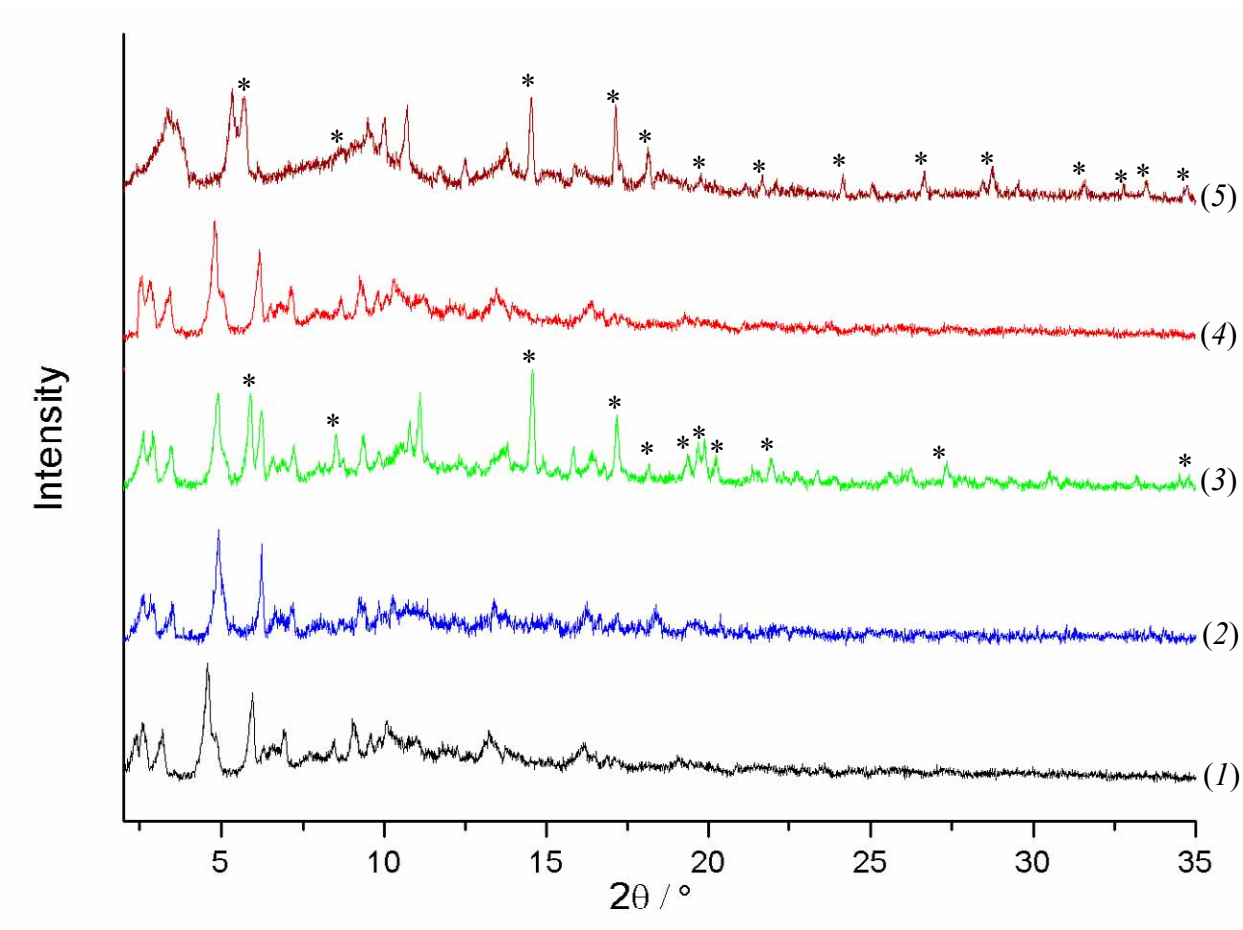

Fig. S2. : Observed X-ray powder diffraction patterns of the bulk materials of the reactions giving $^{2}_{\infty}[Ln_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$. Diffractograms *(1), (2)* and *(4)* depict the result of the annealed syntheses, *(3)* and *(5)* of the rapid treatment, as described in the experimental section. Only the annealed synthesis result in high yields and phase pure samples with no $LnCl_3$ reflections.

(*1*) $^{2}_{\infty}[Nd_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$
(*2*) $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$
(*3*) $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ * = $EuCl_3$
(*4*) $^{2}_{\infty}[Tb_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$
(*5*) high temperature compound after heating $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ up to 300 °C * = $EuCl_3$

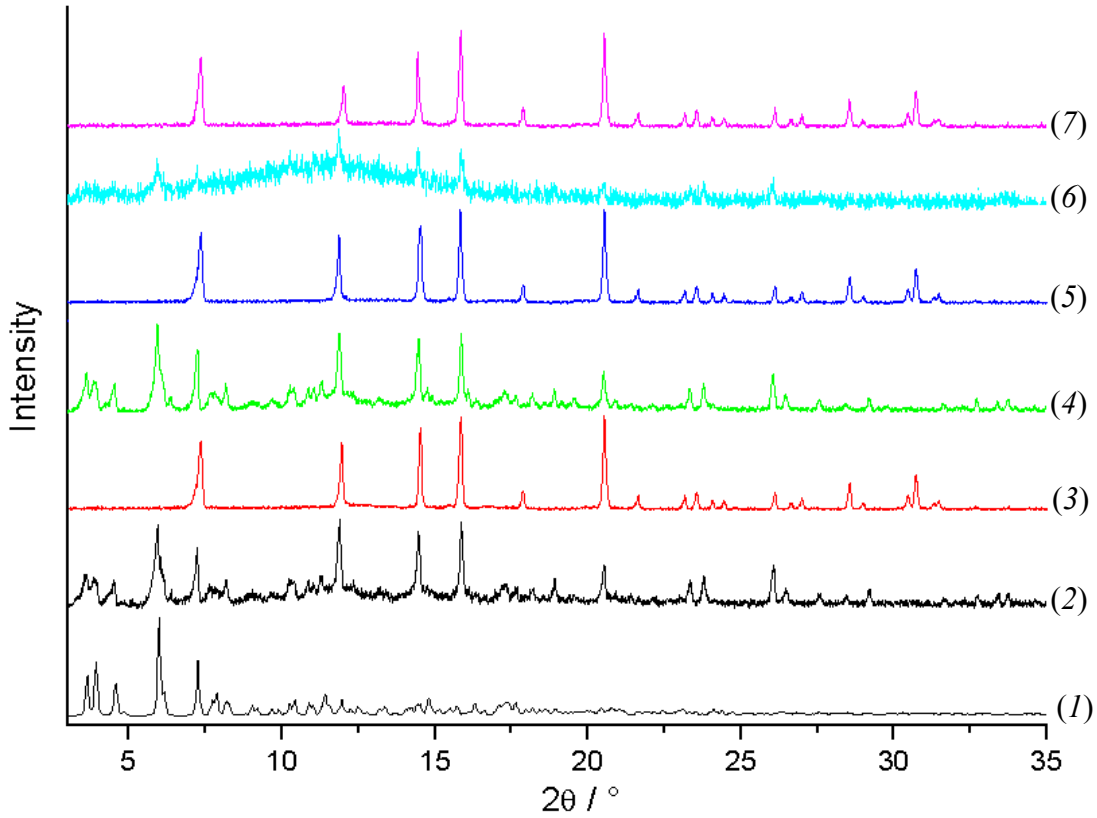

Fig. S3. : X-ray powder diffraction patterns for the reversible formation and decomposition of $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ (**3**) within several cycles.
(*1*) simulated powder diffraction pattern of $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$
(*2*) formation reaction of $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$, with an amount of excess $SmCl_3$
(*3*) re-formation reaction of $SmCl_3$ after heating the MOF up to 500 °C
(*4*) formation reaction of $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$, with an amount of excess $SmCl_3$
(*5*) re-formation reaction of $SmCl_3$ after heating the MOF up to 500 °C
(*6*) formation reaction of $^{2}_{\infty}[Sm_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$ with a double heating rate and half annealing time, with an amount of excess $SmCl_3$
(*7*) re-formation reaction of $SmCl_3$ after heating the MOF up to 500 °C

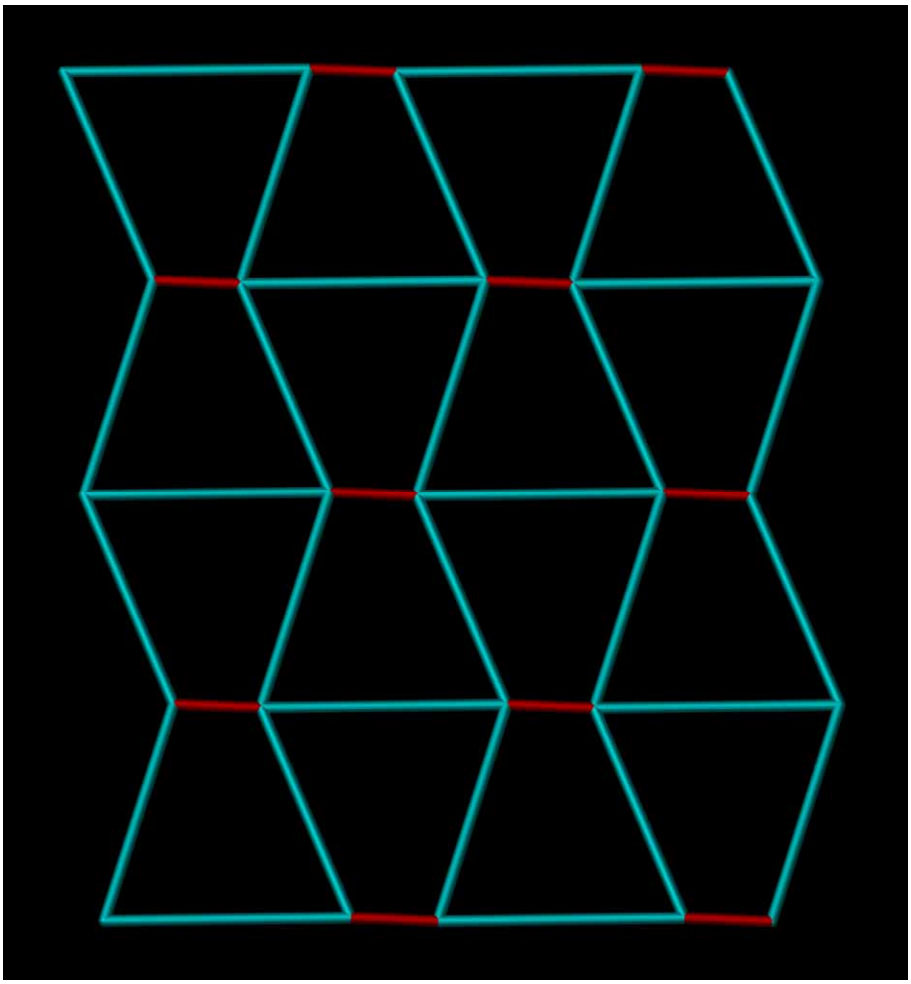

Fig. S4. Depiction of the connectivity and topology of $^{2}_{\infty}[Ln_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$. Red lines represent "Cl-double-bridges". Within a full connectivity description of the topology the double bridges count twice resulting in a 4,5 topology of the 2D-network. Without double bridges the simple topology of each layer is 4,4.

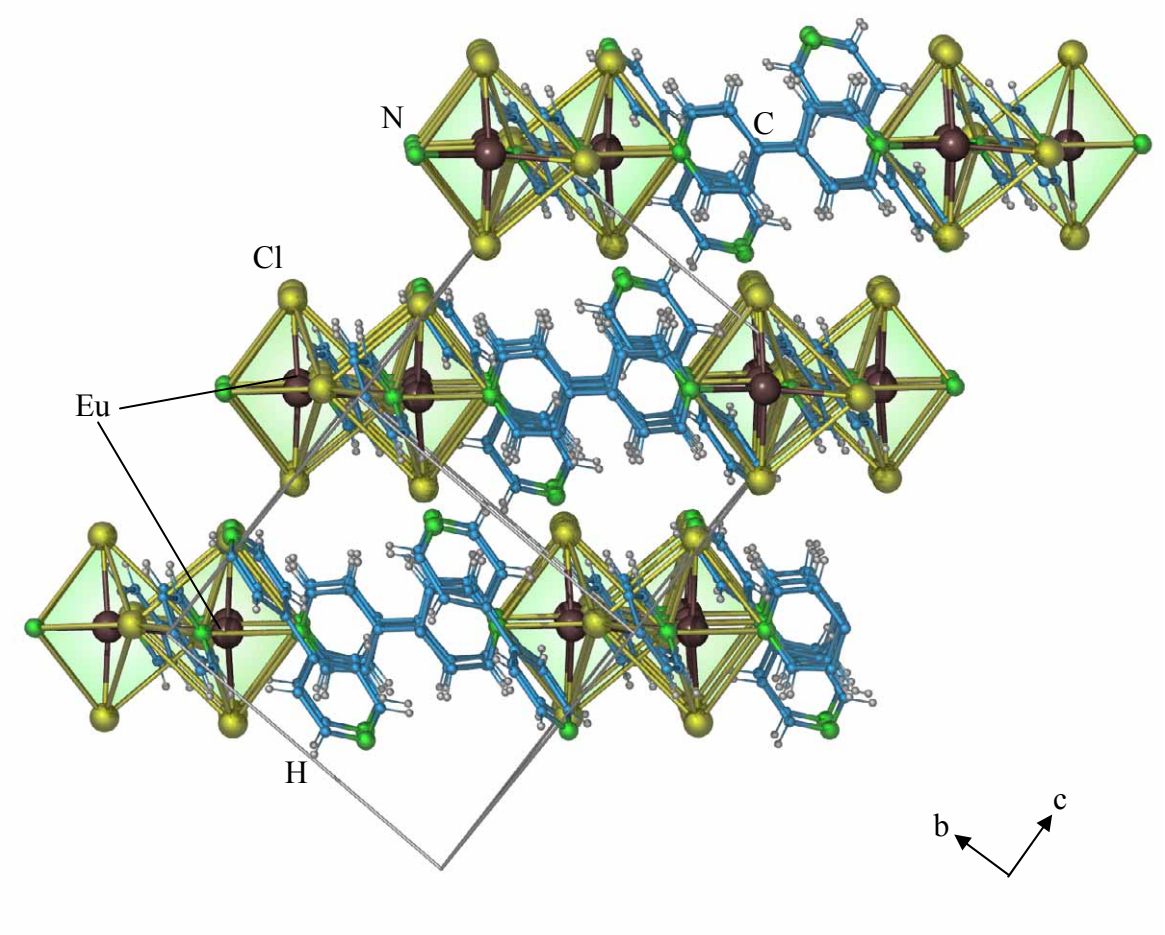

Fig. S5. Crystal structure of $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3)]\cdot 2(4,4'\text{-bipy})$. The two-dimensional net is build up by Ln-Cl dimers which are connected via bipyridine molecules to 2D-sheets.

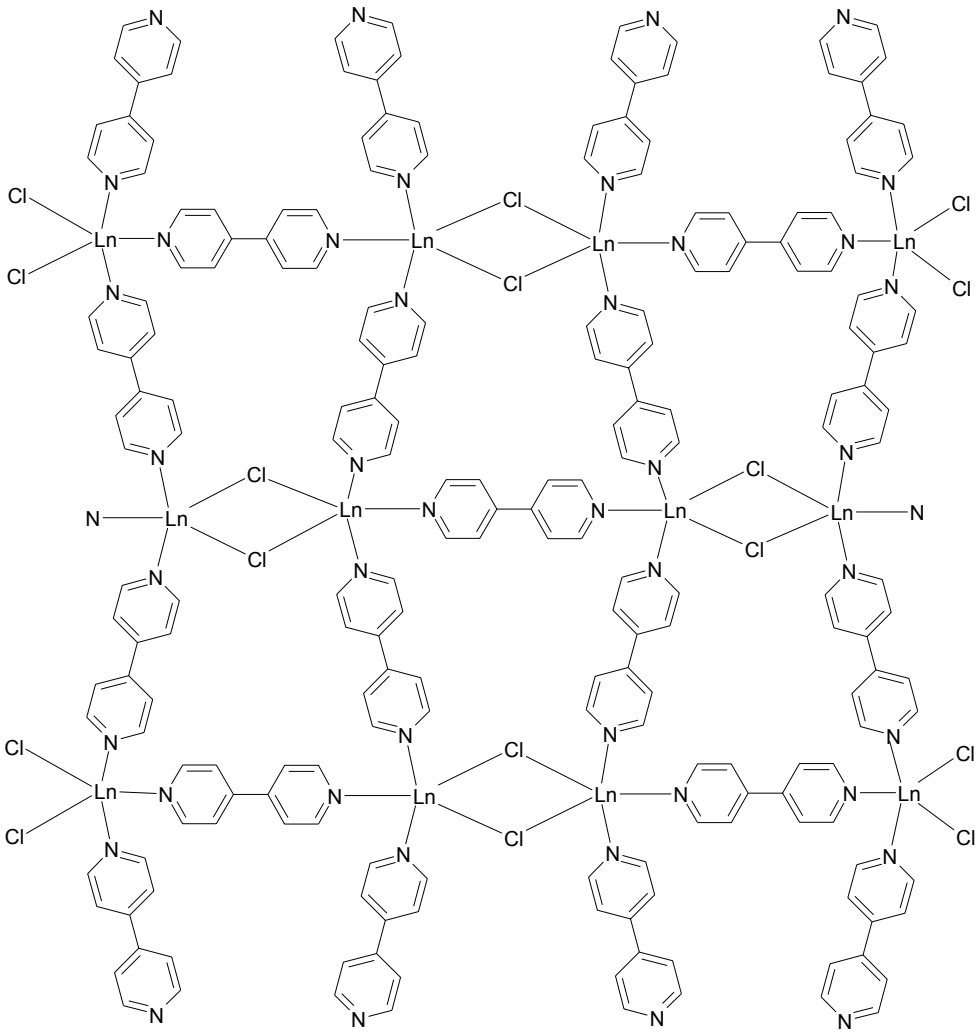

Fig. S6. Connectivity of a layer sheet of $^{2}_{\infty}[Ln_2Cl_6(4,4'\text{-bipy})_3]\cdot 2(4,4'\text{-bipy})$ (**1** - **5**). The layers exhibit a 4,4 topology.

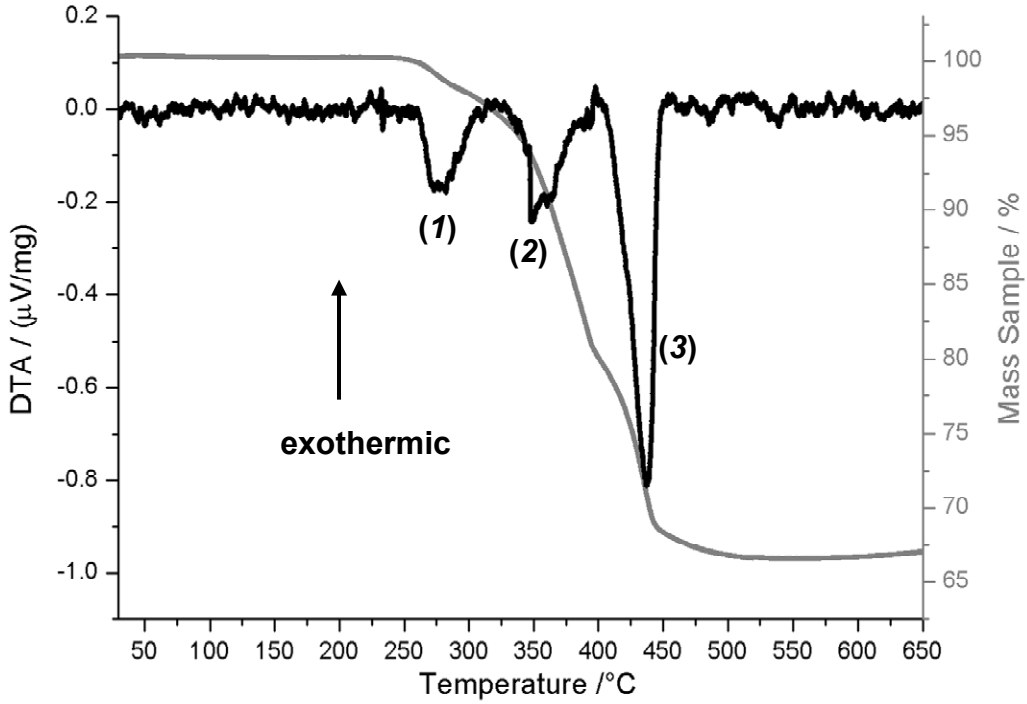

Fig. S6. Figure S6 shows the thermal behaviour of the high temperature product of $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3]\cdot 2(4,4'\text{-bipy})$ with an estimated formula "$[Eu_2Cl_6(4,4'\text{-bipy})_2]$". In order to get the high temperature compound, $^{2}_{\infty}[Eu_2Cl_6(4,4'\text{-bipy})_3]\cdot 2(4,4'\text{-bipy})$ **4** was first purified by evaporating excess 4,4'-bipyridine at 120 °C under vacuum and then heated to 300 °C for two hours. 21.5 mg of the high temperature compound were then investigated on the thermal analyzer in a constant He-flow of 50 ml/min with a heating rate of 10 ^{o}C/min.
As the simultaneous DTA/TG shows, the formation of the high temperature compound "$[Eu_2Cl_6(4,4'\text{-bipy})_2]$" was almost complete: Signal (*1*) exhibits only a slight amount of 2 % of 4,4'-bipyridine release from the remaining MOF phase **4**. Further heating of "$[Eu_2Cl_6(4,4'\text{-bipy})_2]$" above 320 °C then follows the course of degradation observed for **4** already: Signals (*2*) and (*3*) depict the release of the remaining equivalents of bipy from the MOF. The melting point of $EuCl_3$ (850 °C) is not observed in figure S6 as the investigation was stopped at 650 °C.

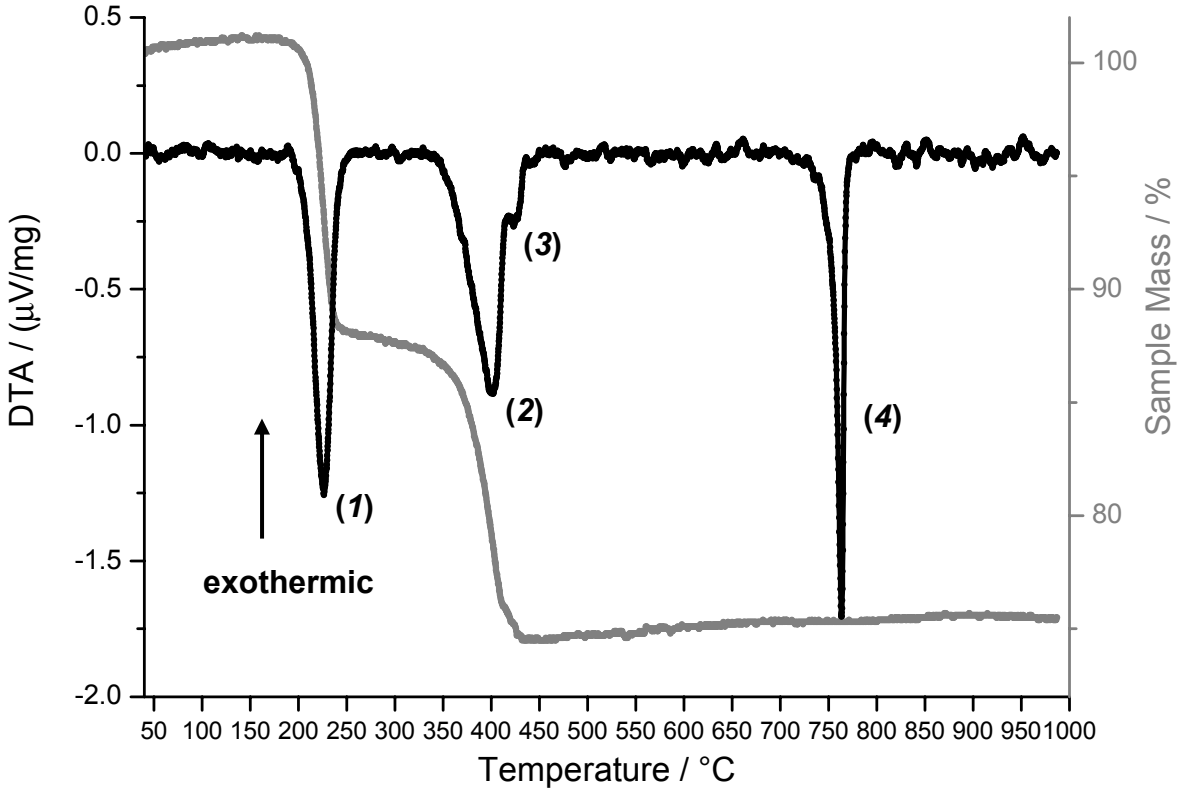

Fig. S7 Simultaneous DTA/TG investigation of the praseodymium containing MOF **1** with a heating rate of 10 °C/min. and a He flow of 50 ml/min. resulting in complete reformation of the reagents bipyridine (steps (*1*-*3*) and $PrCl_3$ (signal (*4*), melting point).

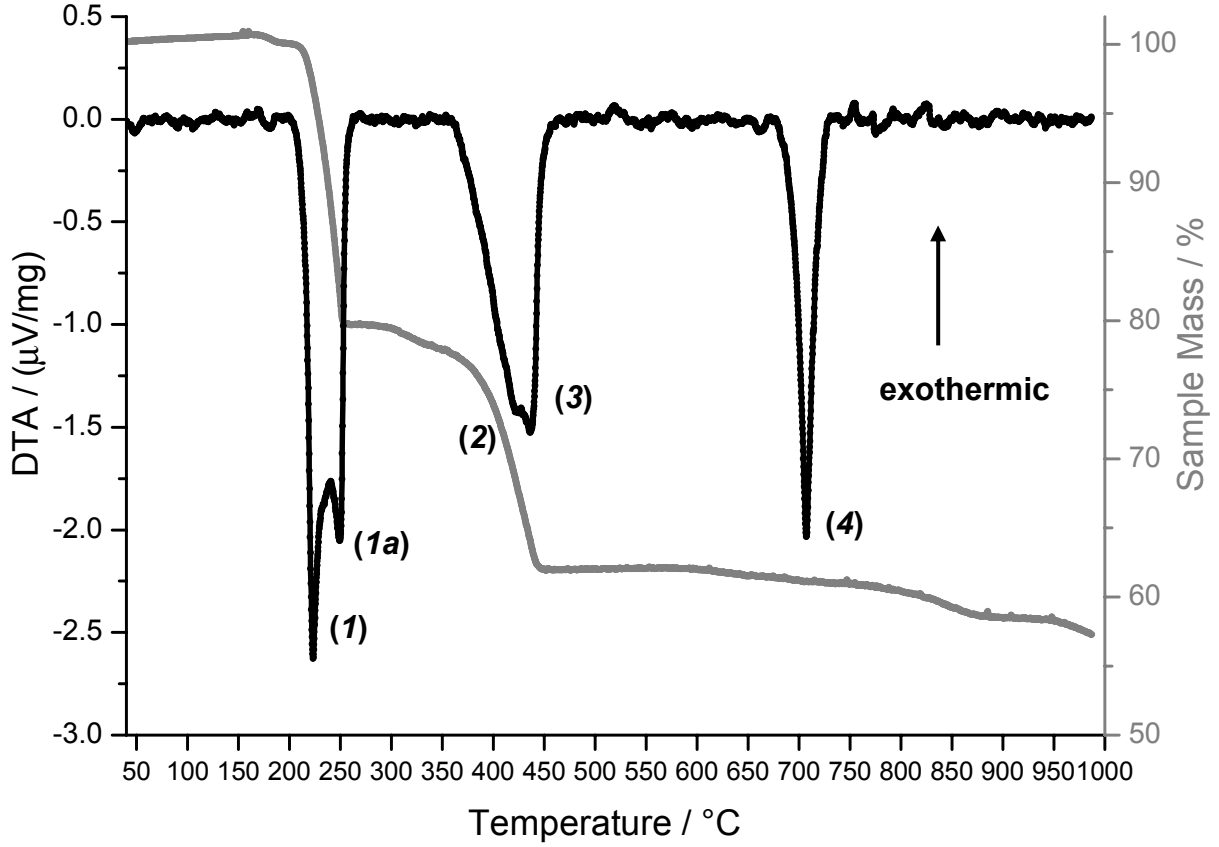

Fig. S8 Simultaneous DTA/TG investigation of the neodymium containing MOF **2** with a heating rate of 10 °C/min. and a He flow of 50 ml/min. resulting in complete reformation of the reagents bipyridine (steps (*1*-*3*)) and $NdCl_3$ (signal (*4*), melting point). Signal (*1a*) indicates that for the neodymium compound release of the template molecules and one of the linking molecules are two subsequent steps. For the other lanthanides only one signal is observed.

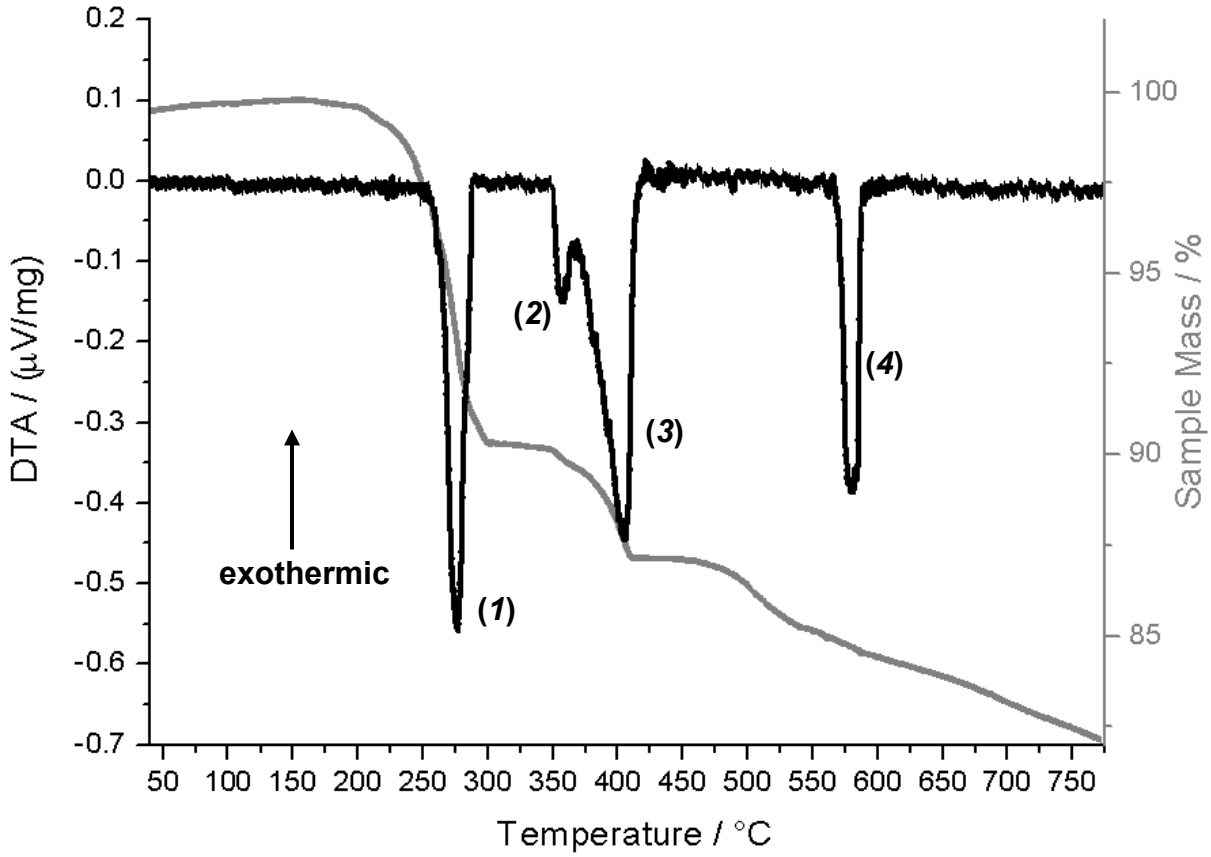

Fig. S9 Bulk product investigation of the terbium containing MOF **5** with simultaneous DTA/TG with a heating rate of 10 °C/min. and a He flow of 50 ml/min. resulting in complete reformation of the reagents bipyridine (steps (*1-3*)) and $TbCl_3$ (signal (*4*), melting point).

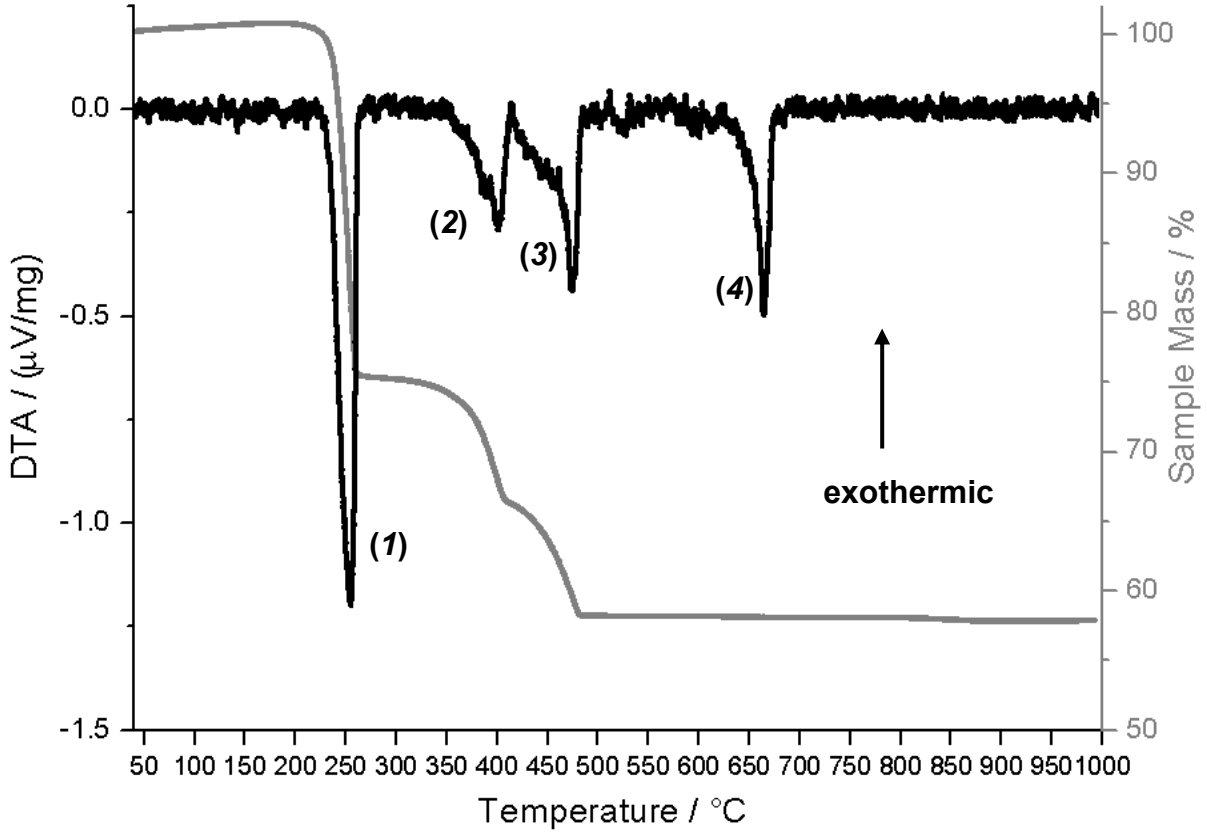

Fig. S10 Simultaneous DTA/TG investigation of the samarium containing MOF **3** with a heating rate of 3 °C/min. and a He flow of 50 ml/min. resulting in complete reformation of the reagents bipyridine (steps (*1*-*3*)) and $SmCl_3$ (signal (*4*), melting point).