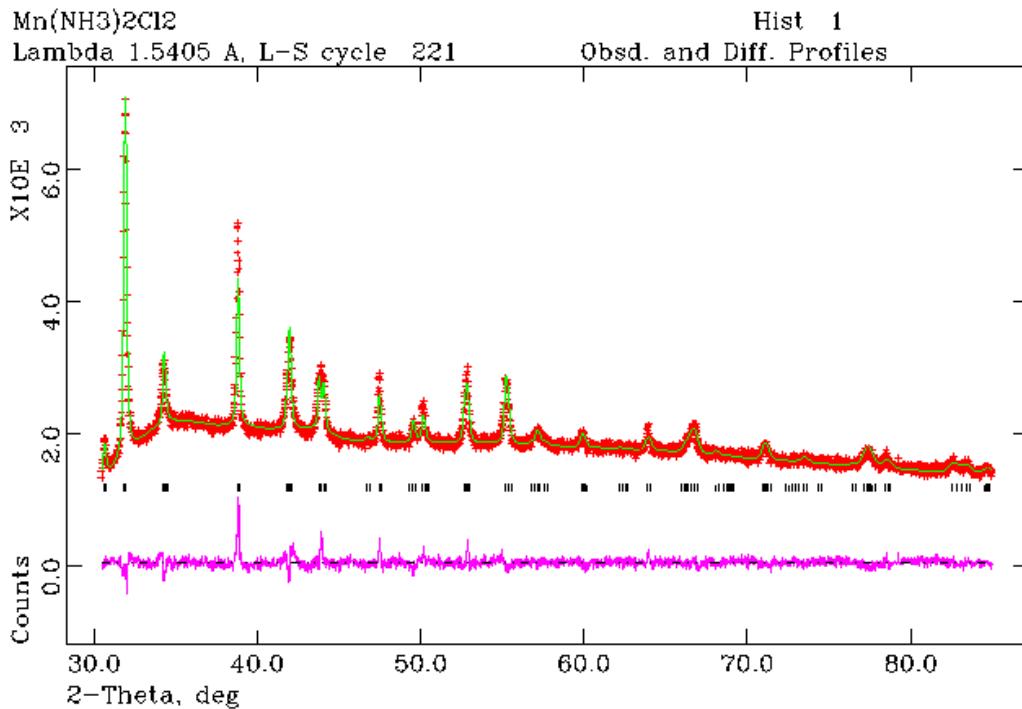
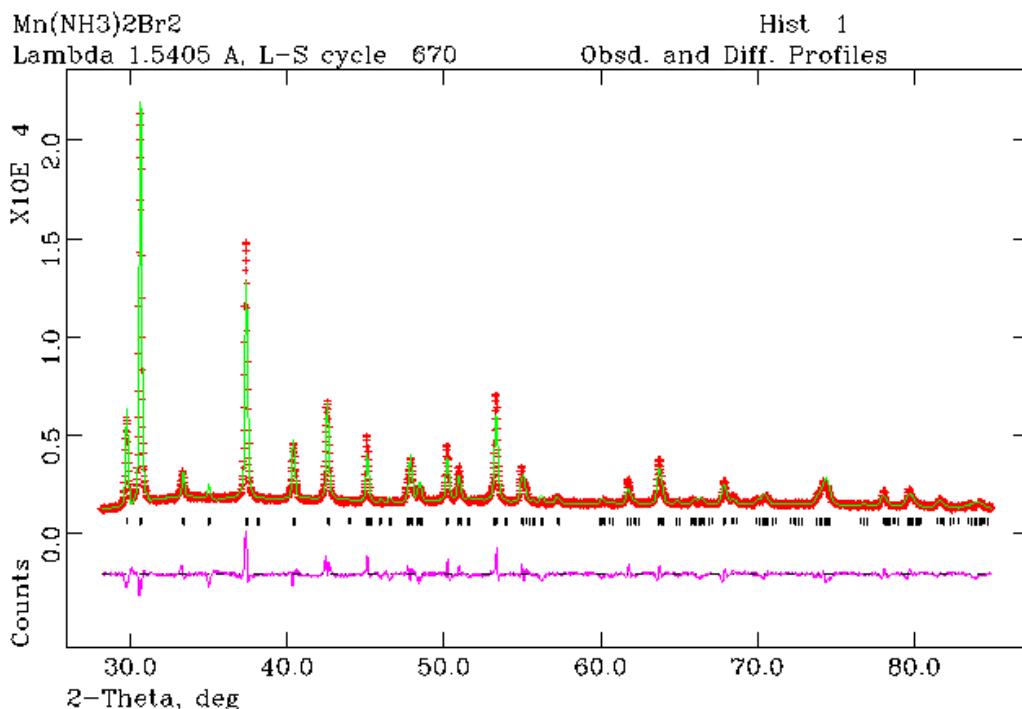


Supplementary Information

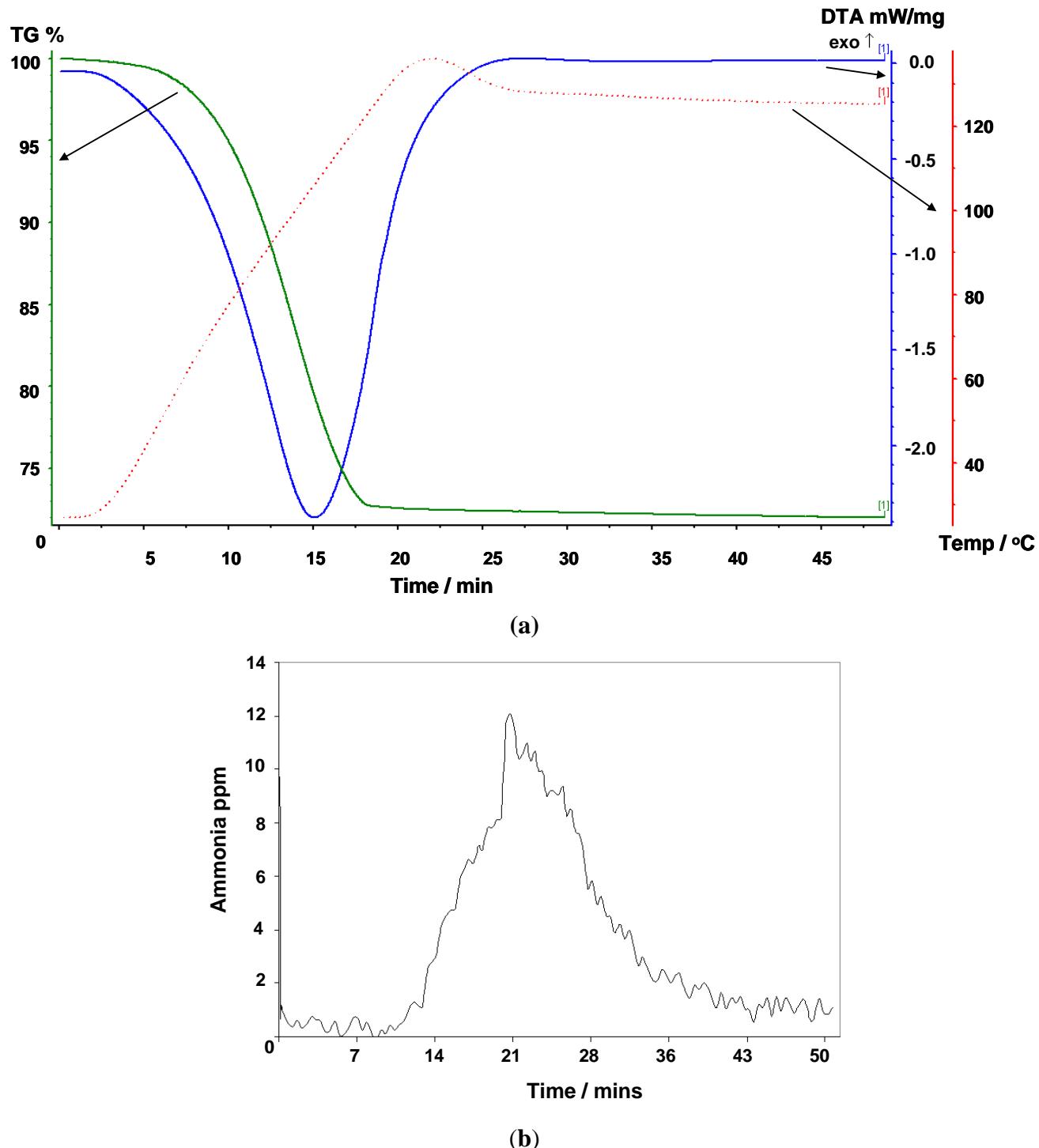
S1. Rietveld refinement profile for **3** from PXRD data. Crosses indicate the observed data, the upper continuous line shows the calculated profile and the lower continuous line the difference profile. Tick marks show reflection positions for orthorhombic $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$.



S2. Rietveld refinement profile for **4** from PXRD data. Crosses indicate the observed data, the upper continuous line shows the calculated profile and the lower continuous line the difference profile. Tick marks show reflection positions for orthorhombic $\text{Mn}(\text{NH}_3)_6\text{Br}_2$.



S3. (a) TG-DTA data, and (b) corresponding MS data for the thermal decomposition of $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ to $\text{Mn}(\text{NH}_3)_2\text{Cl}_2$.



S4. (a) TG-DTA data, and (b) corresponding MS data for the thermal decomposition of $\text{Mn}(\text{NH}_3)_6\text{Br}_2$ to $\text{Mn}(\text{NH}_3)_2\text{Br}_2$.

