Supporting information for

# INSIGHT OF THE THERMAL DECOMPOSITION OF AMMONIUM HEXAHALOGENOIRIDATES(IV) AND HEXACHLOROIRIDATE(III)

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**Table S1.** Thermal decomposition parameters for $(NH_4)_3[IrCl_6]\cdot H_2O$, $(NH_4)_2[IrCl_6]$ and $(NH_4)_2[IrBr_6]$.

| Compound | Atmosphere | Step | $\square T_{step}$(°C) | T(°C) | Δm (wt.%) | Δm (a.e.m.) | gaseous products |
|---|---|---|---|---|---|---|---|
| $(NH_4)_3[IrCl_6]\cdot H_2O$ | $H_2$ | 2 | 90-160<br>160-300 | 111<br>274 | 4.2<br>52.9 | 19.8<br>251.2 | $H_2O$<br>HCl, $N_2$, $NH_3$ |
| $(NH_4)_3[IrCl_6]\cdot H_2O$ | He | 3 | 50-150<br>150-270<br>270-400 | 118<br>221<br>354 | 3.76<br>8.94<br>47.2 | 17.9<br>42.5<br>224.1 | $H_2O$<br>HCl<br>$N_2$, HCl, $NH_3$ |
| $(NH_4)_2[IrCl_6]$ | $H_2$ | 3 | 150-215<br>215-310<br>310-350 | 188<br>290<br>322 | 11.6<br>31.4<br>12.3 | 51.1<br>137.8<br>54.0 | $N_2$, HCl<br>HCl<br>HCl, $NH_3$ |
| $(NH_4)_2[IrCl_6]$ | He | 1 | 345-430 | 406 | 55.3 | 242.7 | HCl, $N_2$, $NH_3$ |
| $(NH_4)_2[IrBr_6]$ | $H_2$ | 3 | 160-340 | 235<br>287 | 16.8<br>53.2 | 117.8<br>373.9 | HBr, $N_2$, $NH_3$ |
| $(NH_4)_2[IrBr_6]$ | He | 3 | 355-480<br>480-525<br>525-575 | 457<br>514<br>555 | 35.8<br>15.1<br>18.9 | 251.8<br>105.9<br>132.9 | HBr, $N_2$, $NH_3$ |

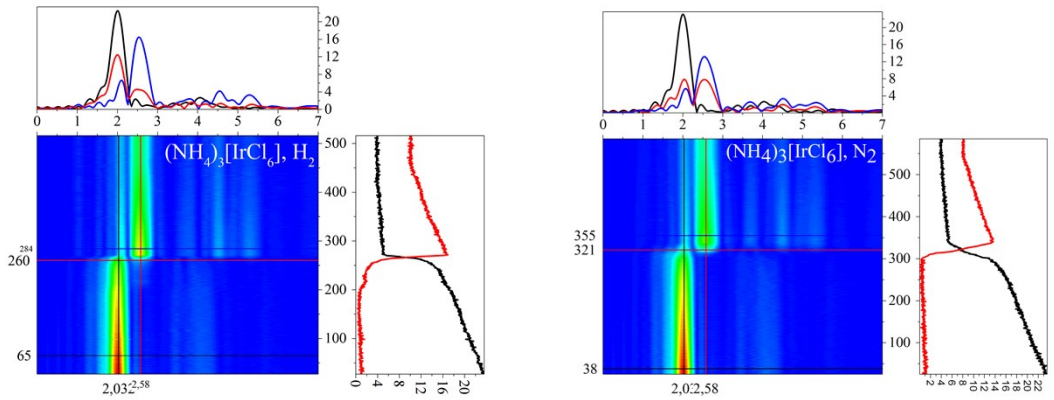


**Figure S1**. 2D-FT map with magnitude profiles of FT corresponding to Ir–Cl (black curve) and Ir–Ir (red curve) FT peaks and FTs at 65, 260 and 284 °C in $H_2$ (left) and 38, 321 and 355 °C in $N_2$ (right).

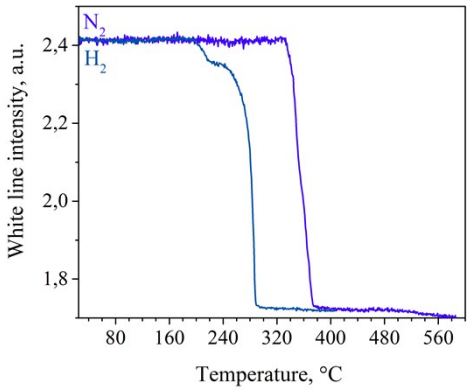


**Figure S2**. Temperature behavior of the White line intensity at Ir $L_{III}$-edge for $(NH_4)_3[IrCl_6]\cdot H_2O$ in $N_2$ and $H_2$ atmospheres.

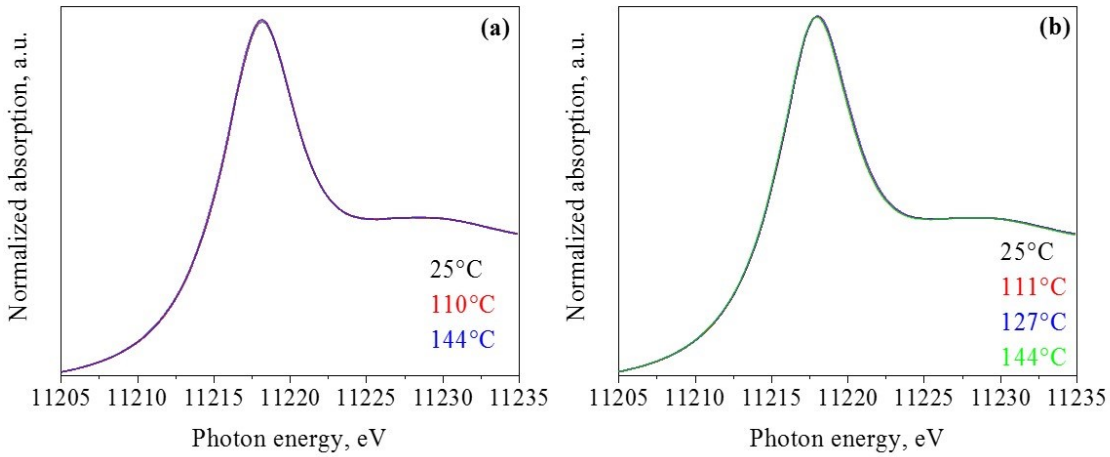


**Figure S3**. XANES spectra at Ir $L_{III}$-edge for $(NH_4)_3[IrCl_6]\cdot H_2O$ at room temperature and above 100 °C, where there is no crystalline water.