Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Salt Loading in MOFs: Solvent-Free and Solvent-Assisted Loading of NH_4NO_3 and $LiNO_3$ in UiO-66

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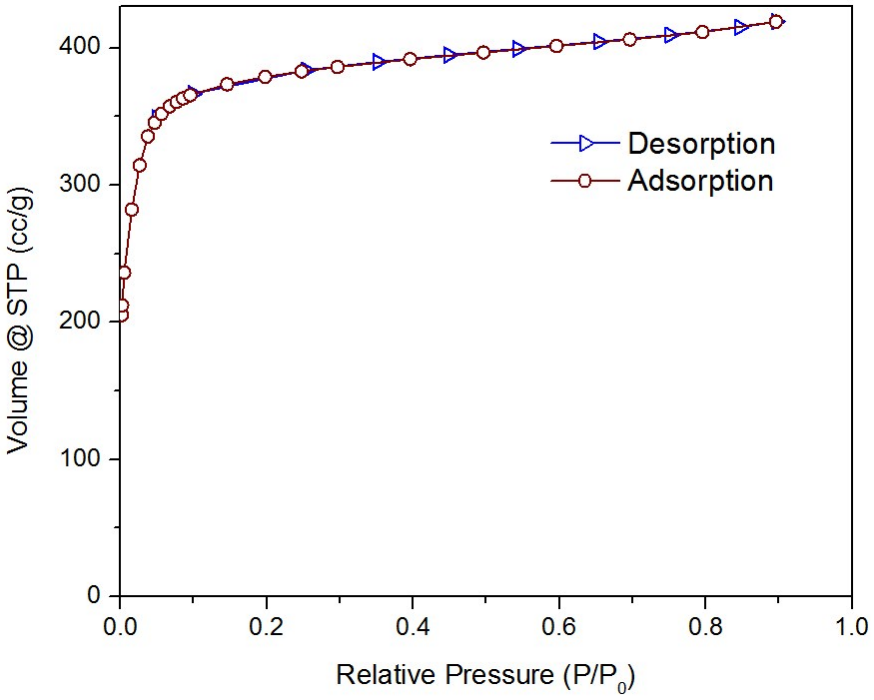

Fig. S1. Nitrogen sorption isotherm of UiO-66 at 77 K. BET surface area of the material is calculated to be 1530 $m^2 g^{-1}$.

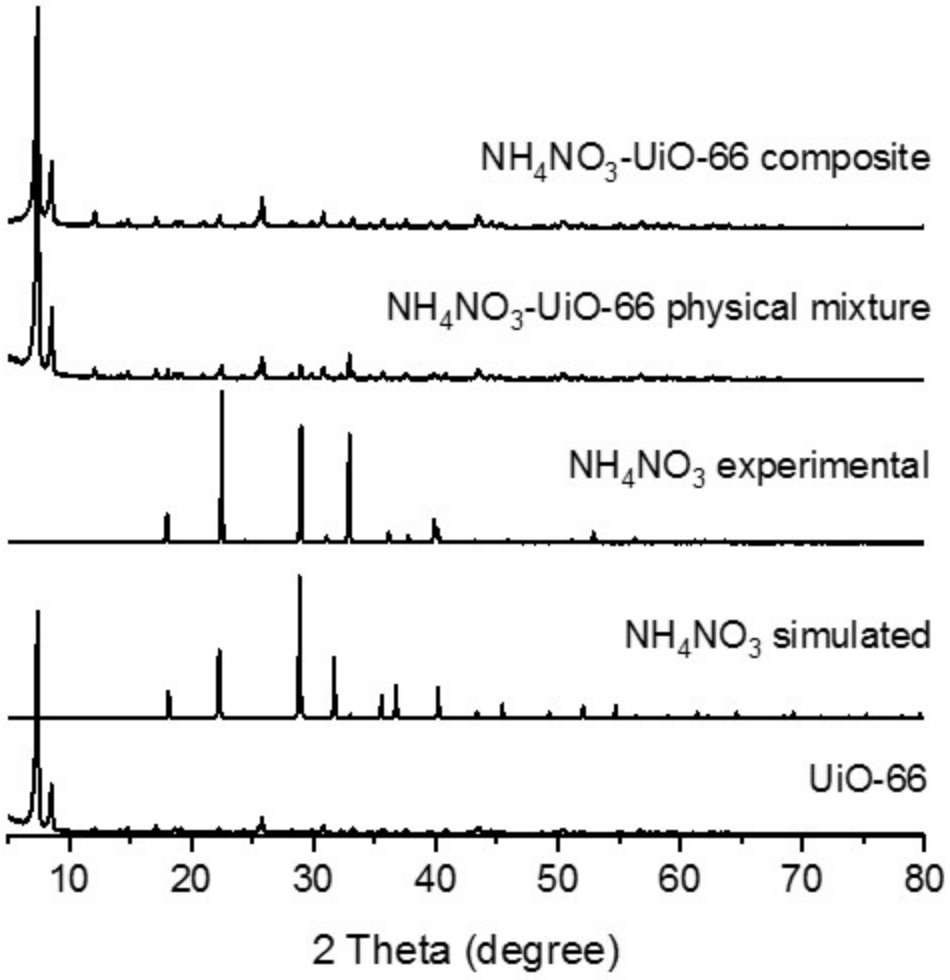

Fig. S2. Powder X-ray diffraction patterns of UiO-66, NH_4NO_3, a physical mixture of the two, and the UiO-66-NH_4NO_3 composite.

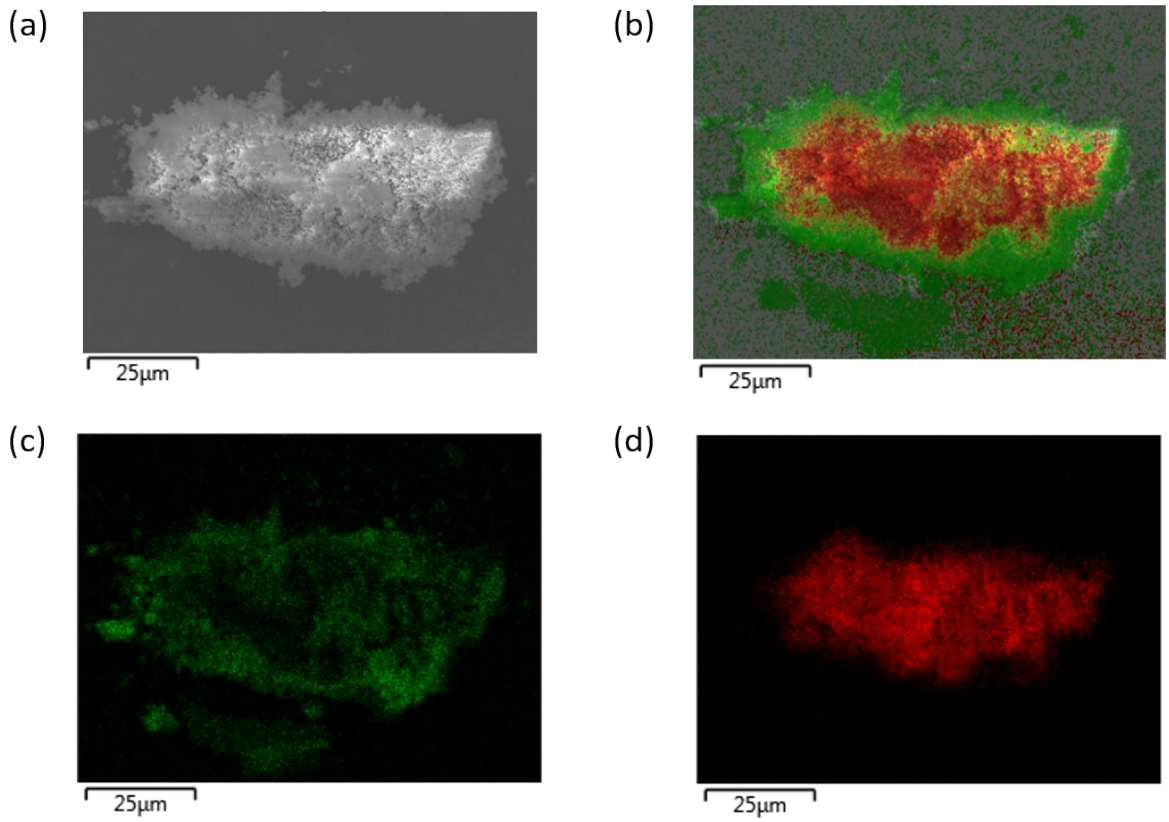

Fig. S3. (a) SEM image of a ground mixture of NH_4NO_3 and UiO-66 and elemental mapping of (c) zirconium (green), (d) nitrogen (red) and (b) both elements based on EDS analysis.

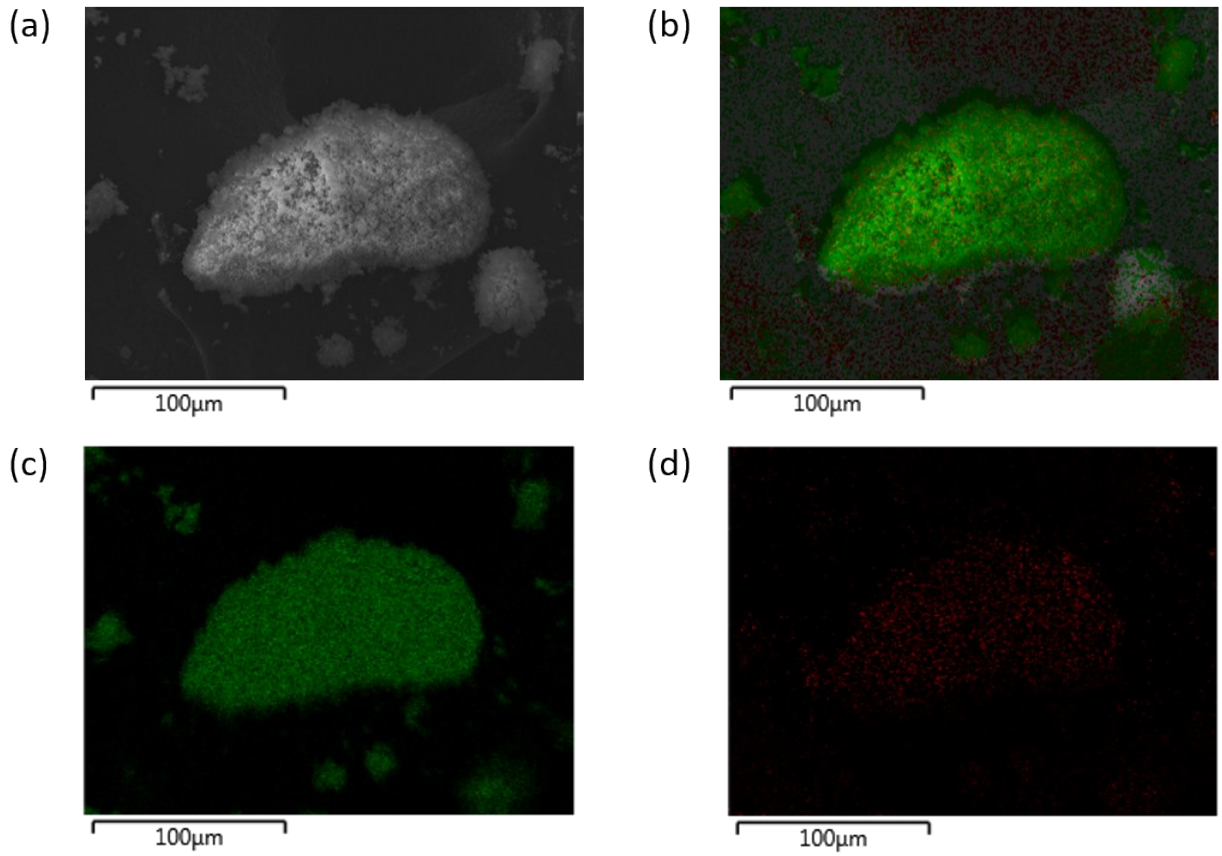

Fig. S4. (a) SEM image of NH_4NO_3-UiO-66 composite and elemental mapping of (c) zirconium (green), (d) nitrogen (red) and (b) both elements based on EDS analysis.

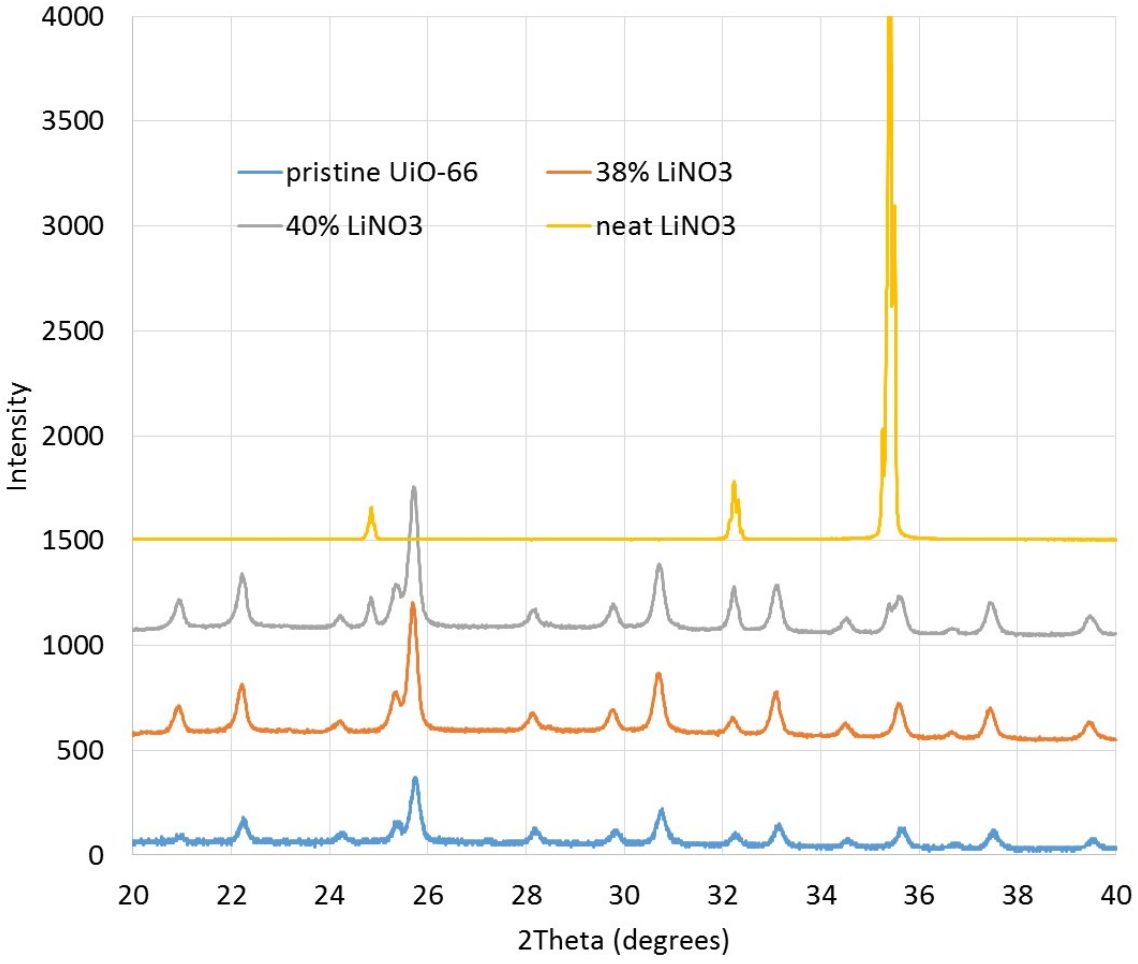

Fig. S5. PXRD patterns of (bottom to top) UiO-66, $LiNO_3$-UiO-66 composite with 38 wt% $LiNO_3$, $LiNO_3$-UiO-66 composite with 40 wt% $LiNO_3$, and neat $LiNO_3$. Peaks at $2\theta = 24.8°$ and 35.4° due to crystalline $LiNO_3$ are evident in the 40 wt% $LiNO_3$ composite (meaning there is unloaded, crystalline $LiNO_3$ on the exterior of the MOF) but not in the 38 wt% $LiNO_3$ composite.

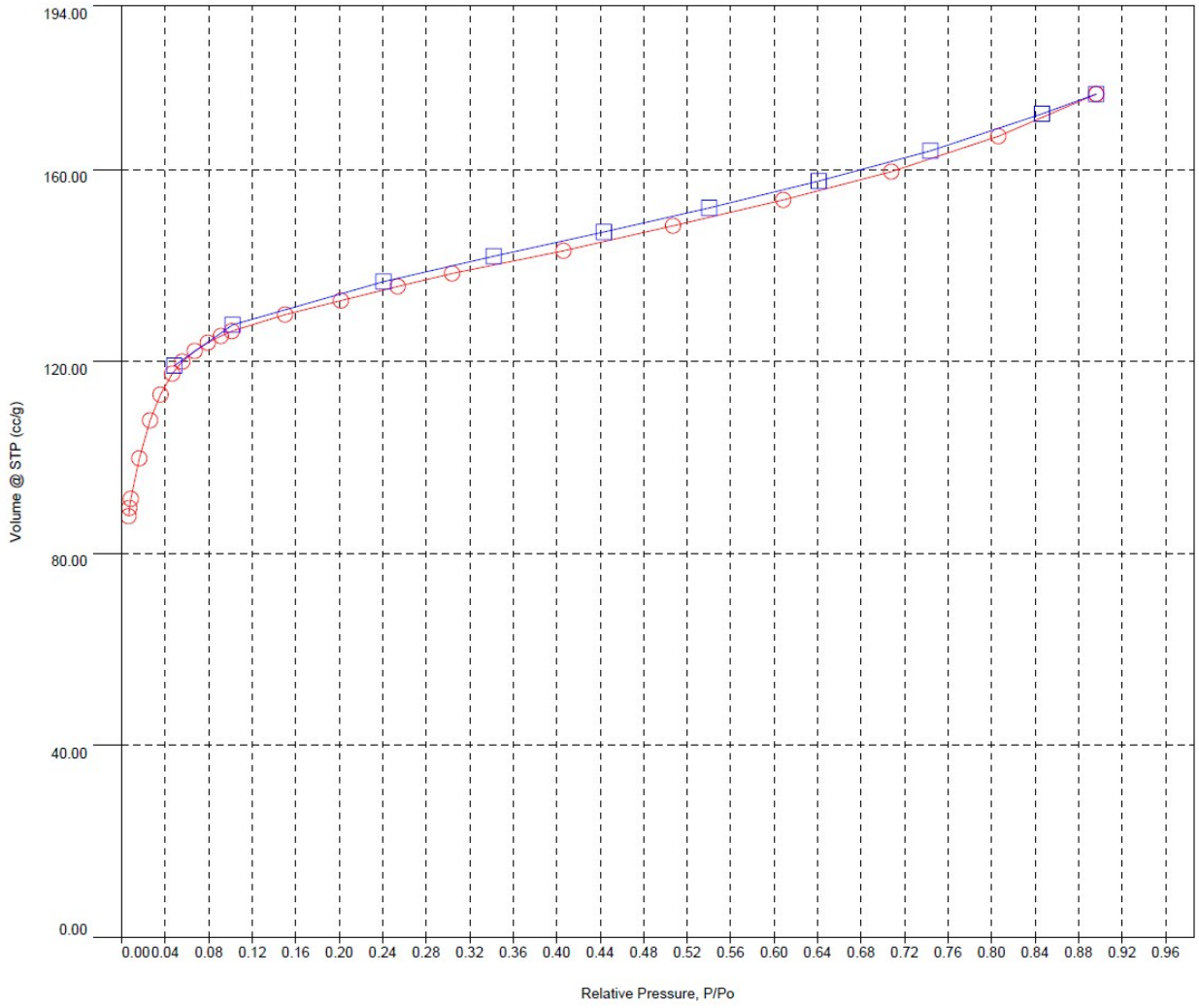

Fig. S6. Nitrogen sorption isotherm of $LiNO_3$-UiO-66 (20 wt% $LiNO_3$) at 77 K. BET surface area of the material is calculated to be 528 $m^2\ g^{-1}$, compared to 1098 $m^2\ g^{-1}$ for this sample of UiO-66 in its pristine state.

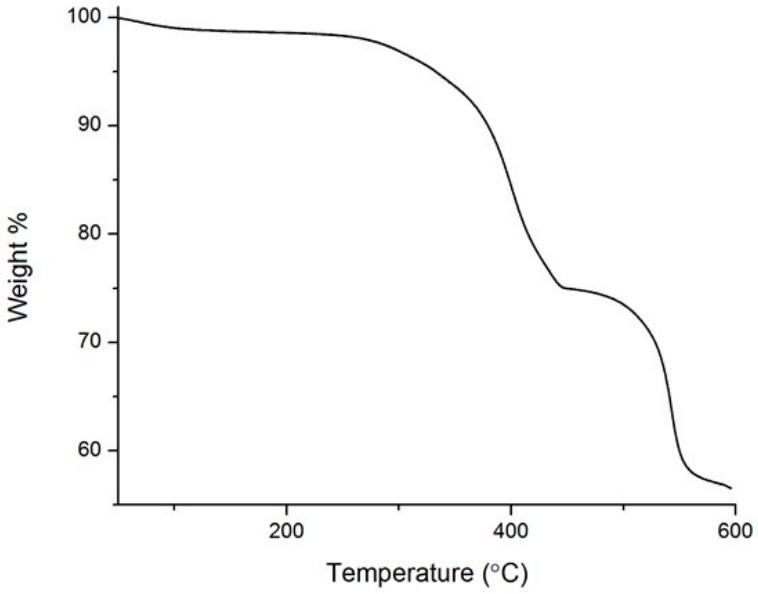

Fig. S7. TGA thermogram of $LiNO_3$-UiO-66 composite.

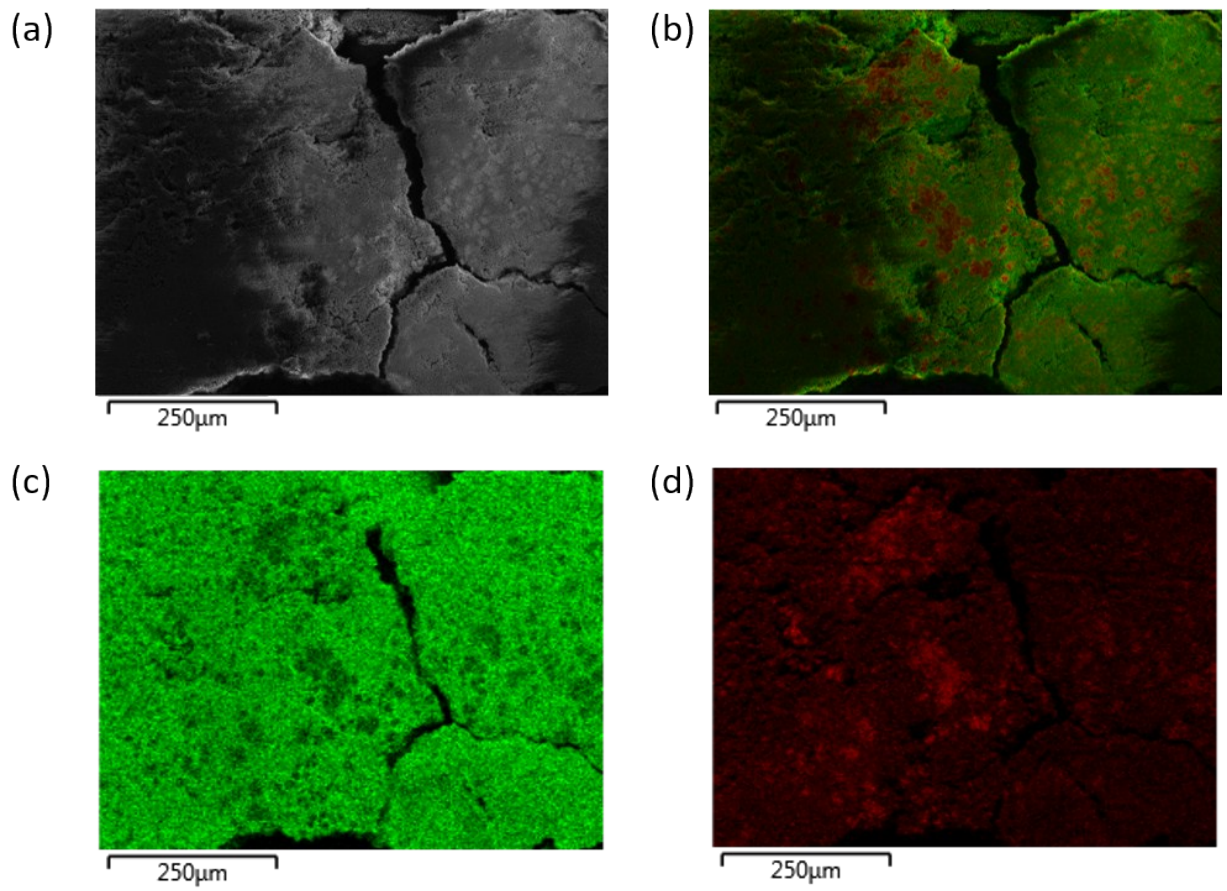

Fig. S8. (a) SEM image of a ground mixture of $LiNO_3$ and UiO-66 and elemental mapping of (c) zirconium (green), (d) nitrogen (red) and (b) both elements based on EDS analysis.

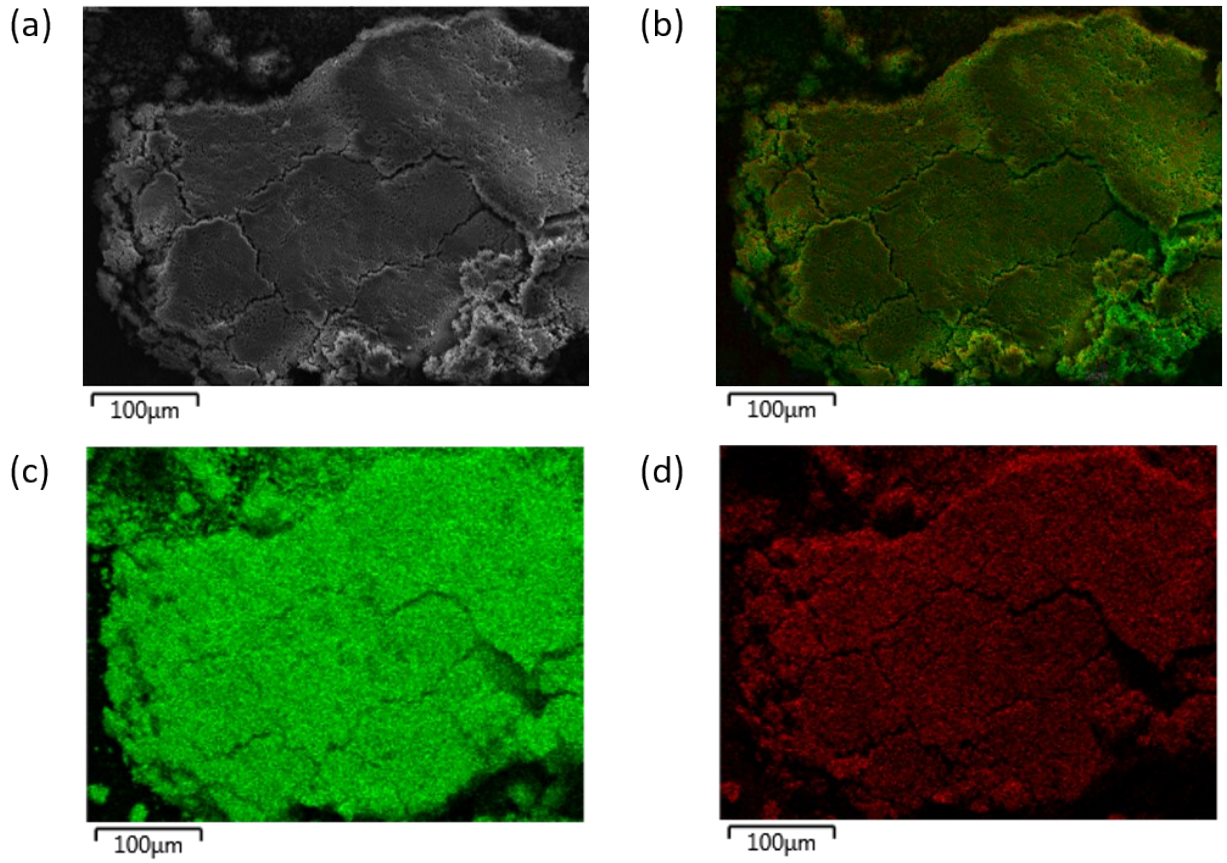

Fig. S9. (a) SEM image of $LiNO_3$-UiO-66 composite and elemental mapping of (c) zirconium (green), (d) nitrogen (red) and (b) both elements based on EDS analysis.

Energetic Properties of NH_4NO_3-UiO-66 and $LiNO_3$-UiO-66 Composites

The crystallographic density of pristine UiO-66 is 1.218 g cm^{-3}. A 32 wt% loading of NH_4NO_3 indicates an uptake of ~38 oxidizer molecules per unit cell of the MOF ($Zr_{24}O_{120}C_{192}H_{96}$) and the PXRD indicates no significant changes in the unit cell size (sum formula of the composite: $C_{192}H_{248}O_{234}N_{76}Zr_{24}$). Therefore, the NH_4NO_3-UiO-66 composite has a relatively high density of 1.787 g cm^{-3}. Whereas UiO-66 is non-energetic with a highly negative oxygen balance of -88.2 %, loading of NH_4NO_3 in UiO-66 results in composite with an oxygen balance of -53.9 %.

The $LiNO_3$-UiO-66 composite can be prepared with 38 wt% loading of the $LiNO_3$, which corresponds to about 58 molecules of the oxidizer per unit cell of the MOF (sum formula: $C_{192}H_{96}N_{76}O_{294}Li_{58}Zr_{24}$), The composite has a high density of 1.967 g cm^{-3} and an oxygen balance of -32.7 %. In fact, both energetic composites NH_4NO_3-UiO-66 and $LiNO_3$-UiO-66 have oxygen balances far superior to TNT (-74.0 %).

Sensitivity of the energetic composites to impact was investigated by the small scale drop test method.[1] The salt-MOF composites NH_4NO_3-UiO-66 and $LiNO_3$-UiO-66 are insensitive with drop height higher than 217 cm, which is the maximum height for the apparatus used in our laboratory. The results indicate that, unlike the case of organic oxidizers, loading of inorganic oxidizers leads to impact insensitive energetic composites. Nonetheless, both energetic composites can be thermally initiated as evidenced from exothermic peaks in the DSC profiles of the composites (see Figs. 4 and 7 in the primary manuscript). To test the thermal sensitivities further, sealed in DSC pans containing ~12 mg $LiNO_3$-UiO-66 composites were placed in glass tubes and heated with a propane torch, and high-speed imaging of the thermal decomposition was carried out at 10000 frames per second. The $LiNO_3$-UiO-66 composite indeed undergoes rapid

decomposition with rapid gas release and sharp emission of sound (c.f. movie provided separately in the ESI). Therefore, the salt-MOF composites are impact insensitive and thermally stable energetics that may find applications such as drilling of deep oil wells.[2]

References

(1) Landenberger, K. B.; Bolton, O.; Matzger, A. J. Energetic–Energetic Cocrystals of Diacetone Diperoxide (DADP): Dramatic and Divergent Sensitivity Modifications via Cocrystallization. *J. Am. Chem. Soc.* **2015**, *137* (15), 5074–5079. https://doi.org/10.1021/jacs.5b00661.

(2) Agrawal, J. P. Some New High Energy Materials and Their Formulations for Specialized Applications. *Propellants Explos. Pyrotech.* **2005**, *30* (5), 316–328. https://doi.org/10.1002/prep.200500021.