Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI)

Synthesis and click modification of an azido-functionalized Zr(IV) metal-organic framework and a catalytic study

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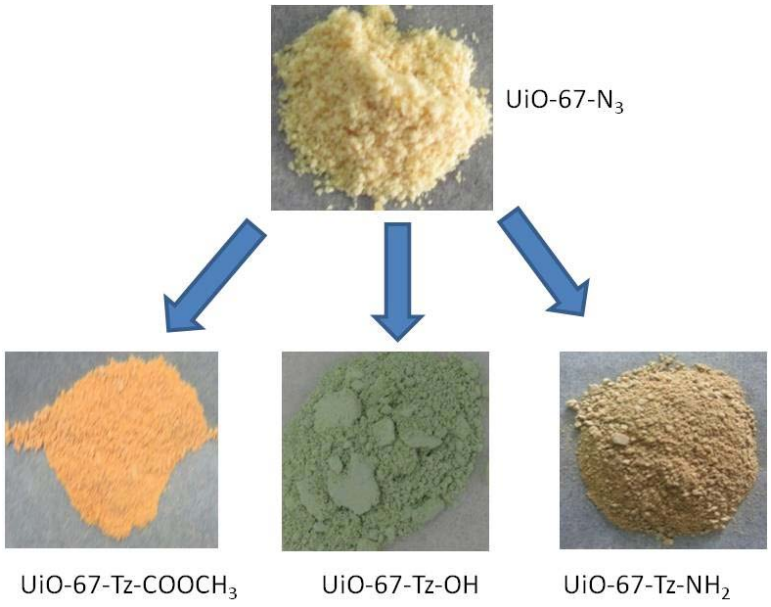

Fig. S1 Pictures showing the color changes after click PSM.

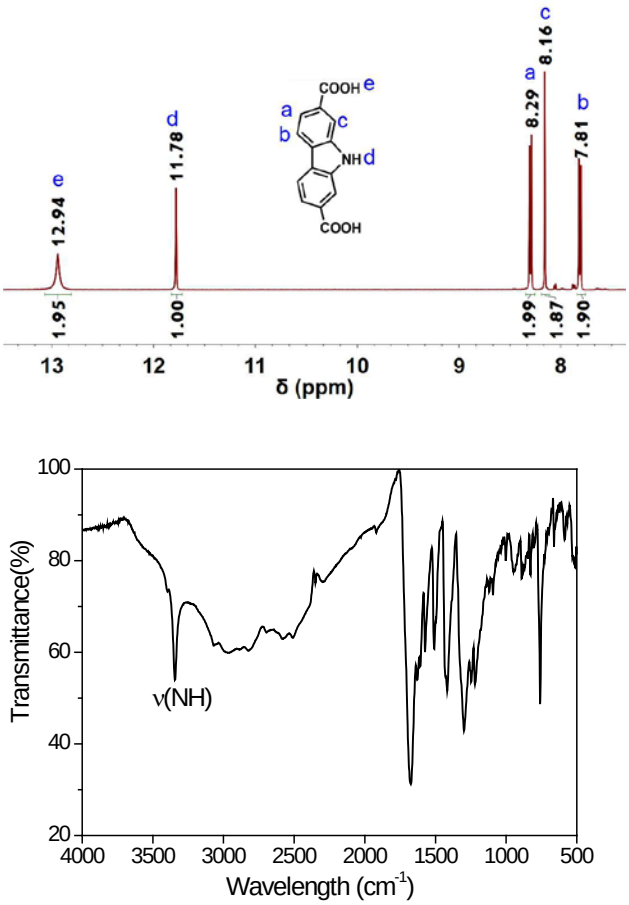

Fig. S2. ^{1}H NMR (DMSO-d_6) and IR spectra of the solid obtained by digesting the product (synthesized at 140 ^{o}C) with concentrated HCl(aq).

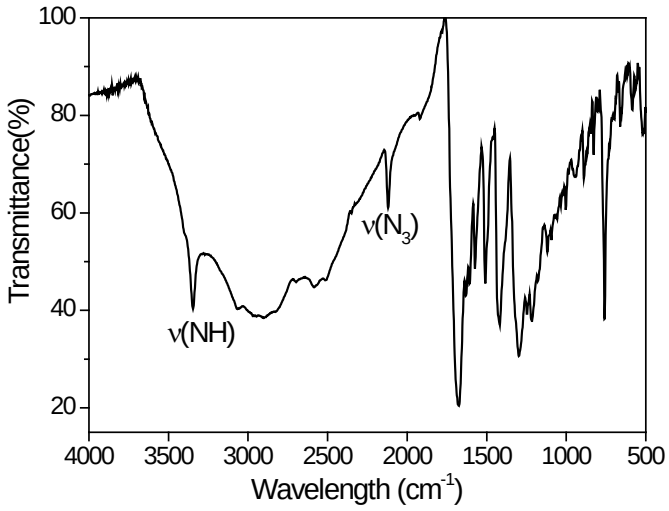

Fig. S3. IR spectrum of the solid obtained by digesting the product (synthesized at 110 ^{o}C) with concentrated HCl(aq).

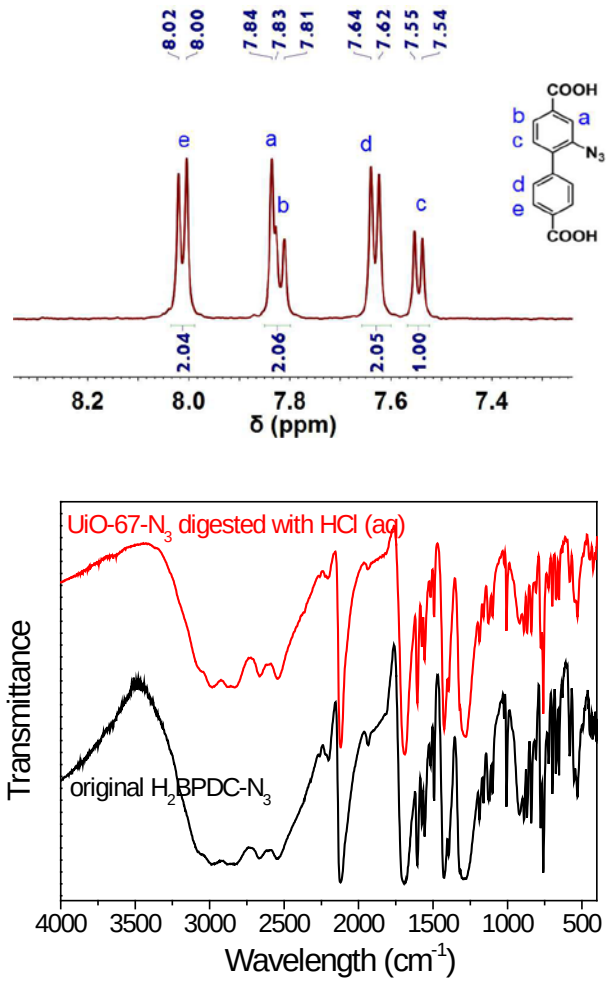

Fig. S4. ^{1}H NMR (DMSO-d_6) and IR spectra of the solid obtained by digesting UiO-67-N_3 (synthesized at 80 ^{o}C) with concentrated HCl(aq).

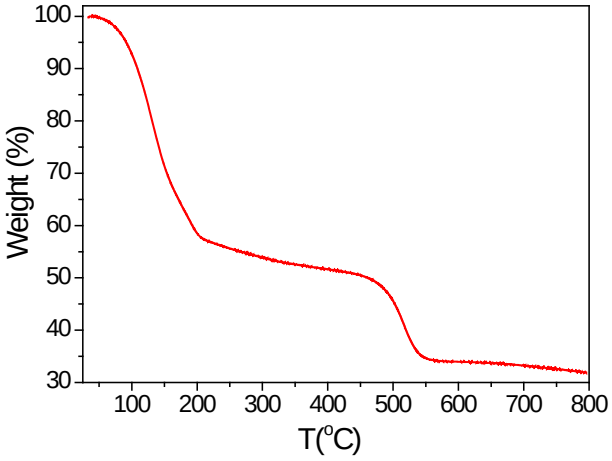

Fig. S5. Thermogravimetric plot of UiO-67-N_3.

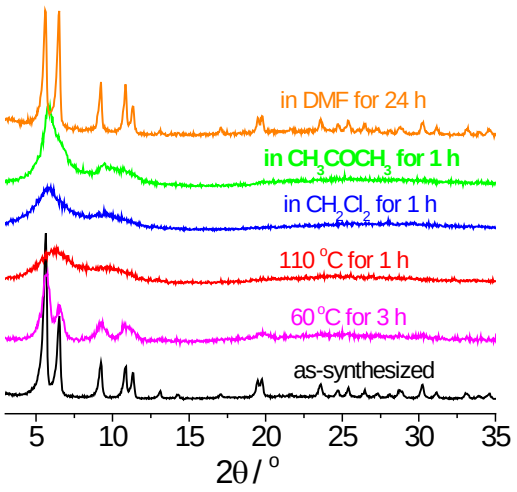

Fig. S6. XRD patterns of the samples of UiO-67-N_3 heated at different temperature and those immersed in different solvents.

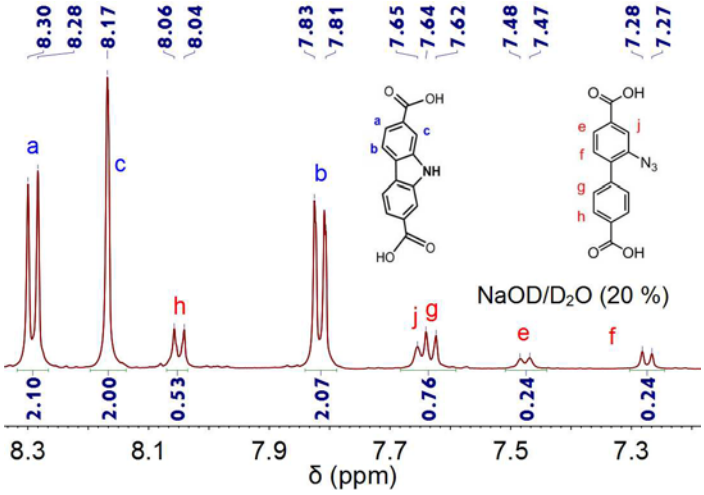

Fig. S7. ^{1}H NMR spectrum of a UiO-67-N_3 sample heated at heated at 110 °C for 1h and dissolved in 20% NaOD/D_2O.

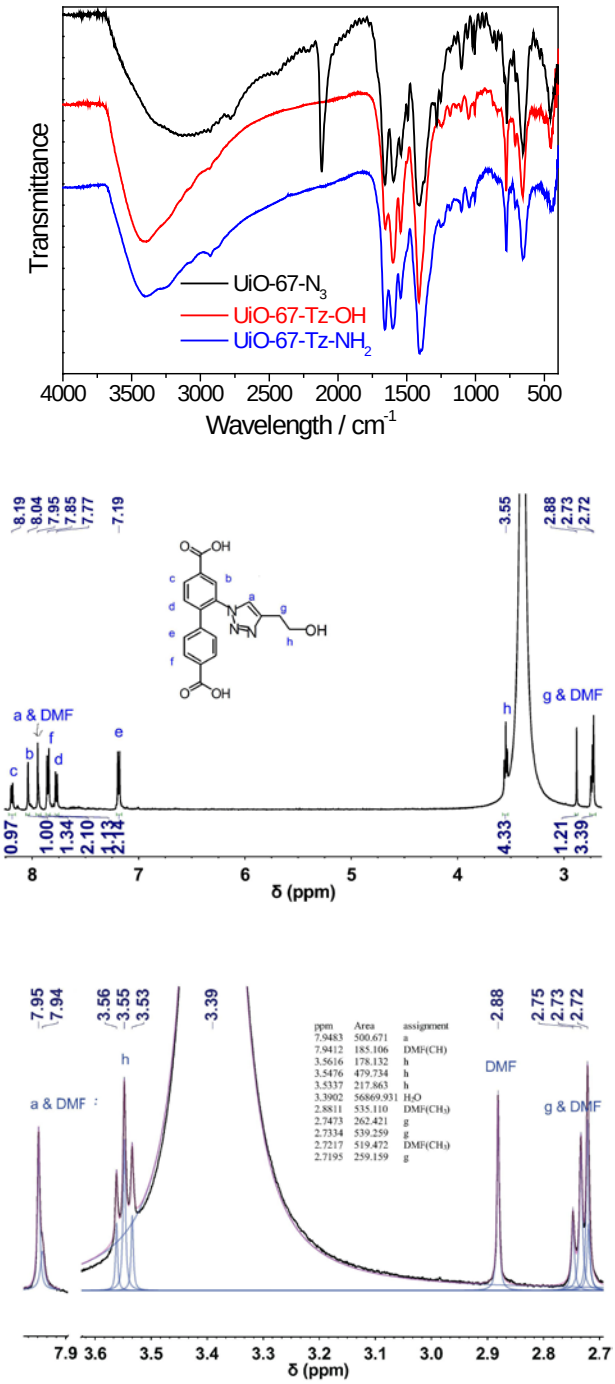

Fig. S8. Top: IR spectra of the click modified MOFs compared with that of UiO-67-N_3. Middle: ^{1}H NMR spectrum of UiO-67-Tz-OH dissolved in HF(aq, 40%)/DMSO-d_6. Bottom: the fit and assignment of overlapping peaks in the ^{1}H NMR spectrum. *NOTE*: For UiO-67-Tz-NH2, we failed to obtain an assignable NMR spectrum perhaps because the amino-bearing organic component could undergo some unidentified reaction during the digestion. This is not surprising for amino compounds. Nevertheless, the successful PSM of the MOF with propargylamine was evidenced by the IR spectra (the complete disappearance of azido adsorption at ~2117 cm^{-1}, the absence of alkyne absorption at ~2130 cm^{-1}, and the appearance of NH_2 adsorption at ~3400 and 3260 cm^{-1}).

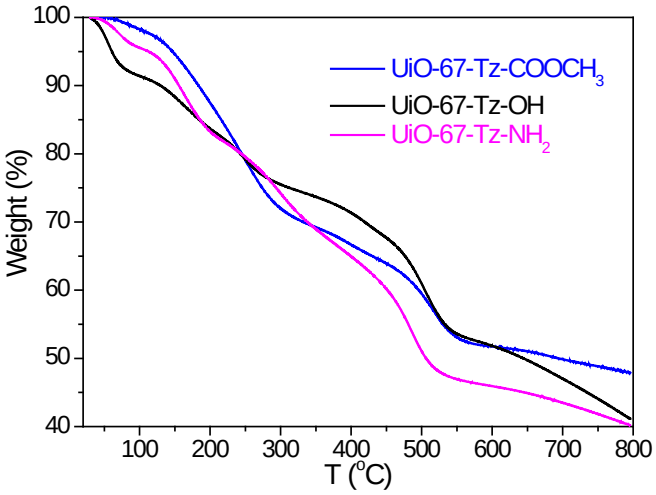

Fig. S9. Thermogravimetric plots of the post-synthetically modified MOFs.

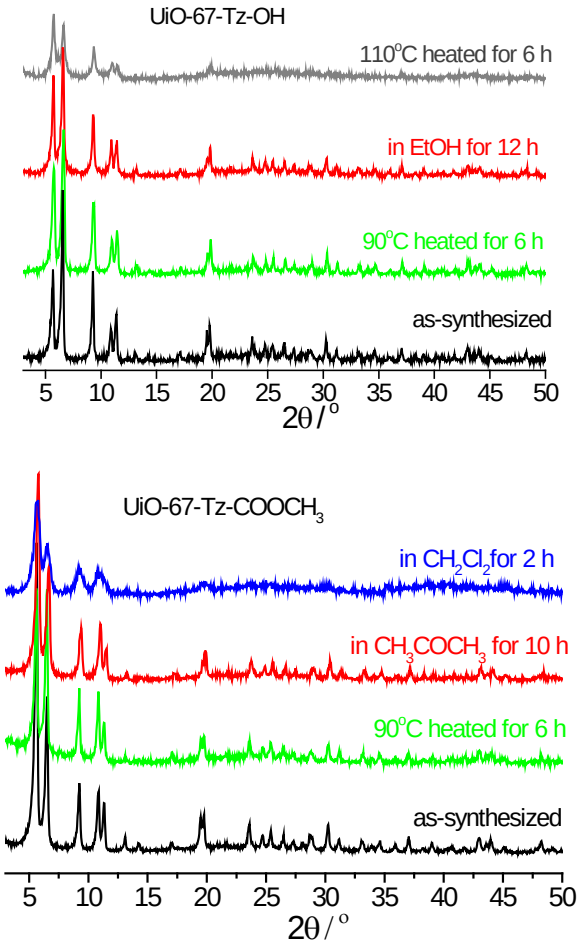

Fig. S10. XRD patterns of UiO-67-Tz-OH and UiO-67-Tz-$COOCH_3$ sample heated at different temperature or immersed in different solvents.

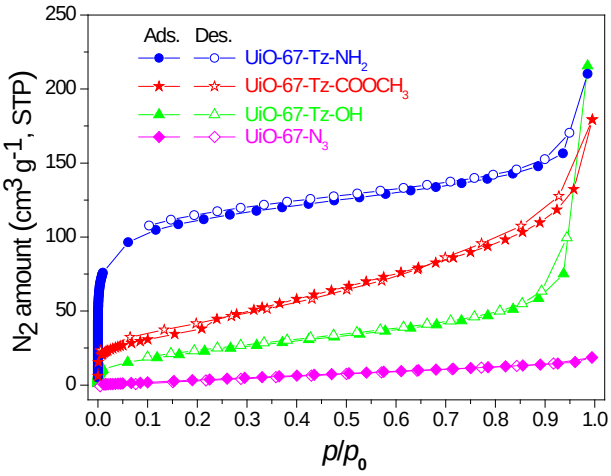

Fig. S11. Nitrogen adsorption-desorption isotherms of UiO-67-N_3 and the post-synthetically modified MOFs.

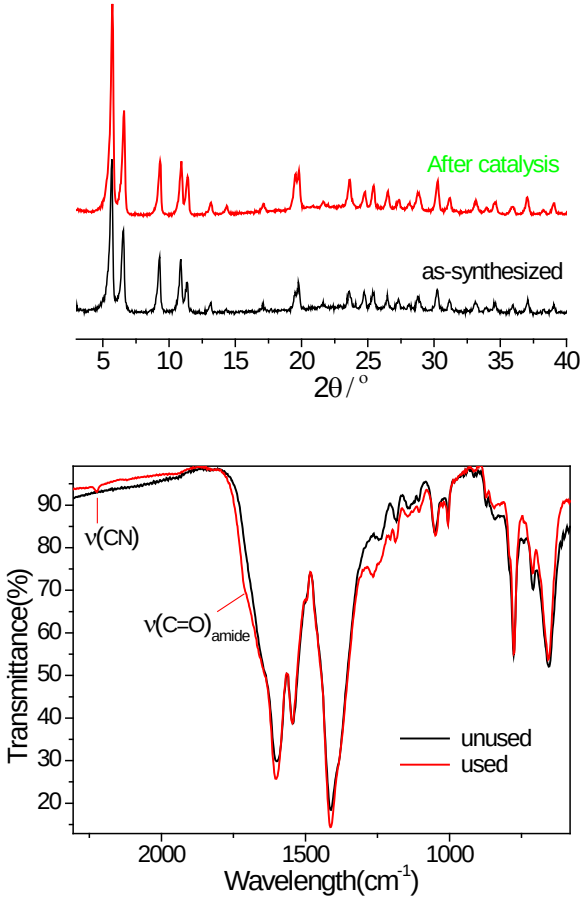

Fig. S12. XRD and IR spectra for UiO-67-Tz-NH_2 before and after a catalytic reaction between benzaldehyde and ethyl cyanoacetate. For IR measurements, both samples were treated with acetone several times and dried in vacuo to eliminate the influence of any adsorbed molecules (DMF, reactants and products).

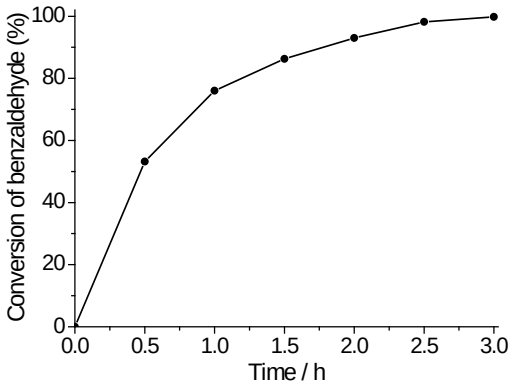

Fig. S13. Conversion vs. time plot for the Knoevenagel condensation between benzaldehyde (1 mmol) and malononitrile (2 mmol) in the presence of different UiO-67-Tz-NH_2 (0.012 mmol) in DMF (3 ml) at 40 ^{o}C.