Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

UiO-67-derived bithiophene and bithiazole MIXMOFs for luminescence sensing and removal of contaminants of emerging concern in wastewater

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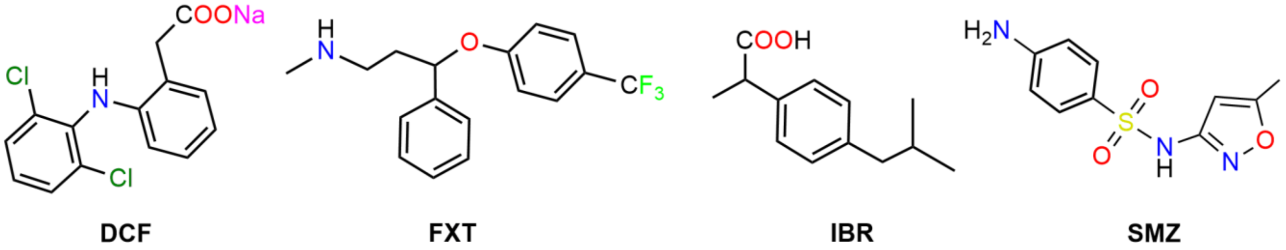

Scheme S1. Molecular formulae of the CECs used in this work: Diclofenac Sodium (DCF), Fluoxetine (FXT), Ibubrofen (IBR) and Sulfametoxazole (SMZ).

Ligand quantification in the MIXMOFs UiO-67-TpTp·DMF and UiO-67-TzTz·DMF

The approximate linkers composition in the two MIXMOFs has been assessed through ^{1}H NMR analysis of the digested samples in acidic solutions (48% aqueous HF, Sigma Aldrich/DMSO-d_6). In a typical procedure, 10 mg of sample was dissolved in three drops of aqueous hydrofluoric acid and 0.6 mL of DMSO-d_6 directly into an NMR tube. The mixture was heated at T = 343 K for 12 h, to complete the sample digestion. The as-obtained clear yellow solution was analysed *via* ^{1}H NMR (400 MHz, relaxation delay τ = 15 s, 512 scans).

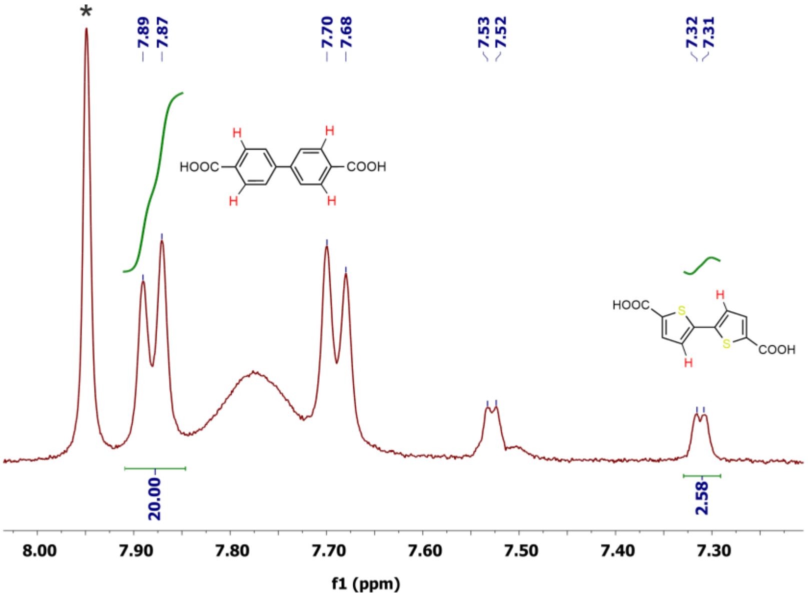

Figure S1. Zoom of the aromatic region used for the quantification of the ligands ratio from the ^{1}H NMR spectrum (400 MHz, HF$_{aq}$/DMSO-d_6, 298 K) of digested **UiO-67-TpTp·DMF**. * Clathrated DMF solvent signal.

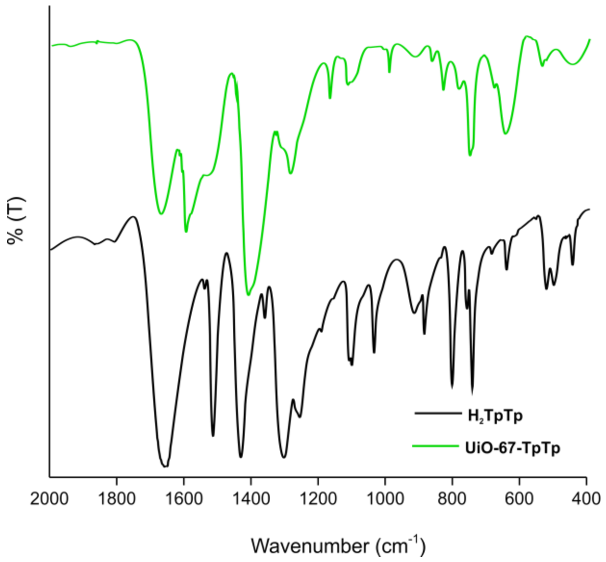

Figure S2. Infrared spectra (KBr, T = 298 K) of **UiO-67-TpTp·DMF** and **H_2TpTp·DMF** at comparison.

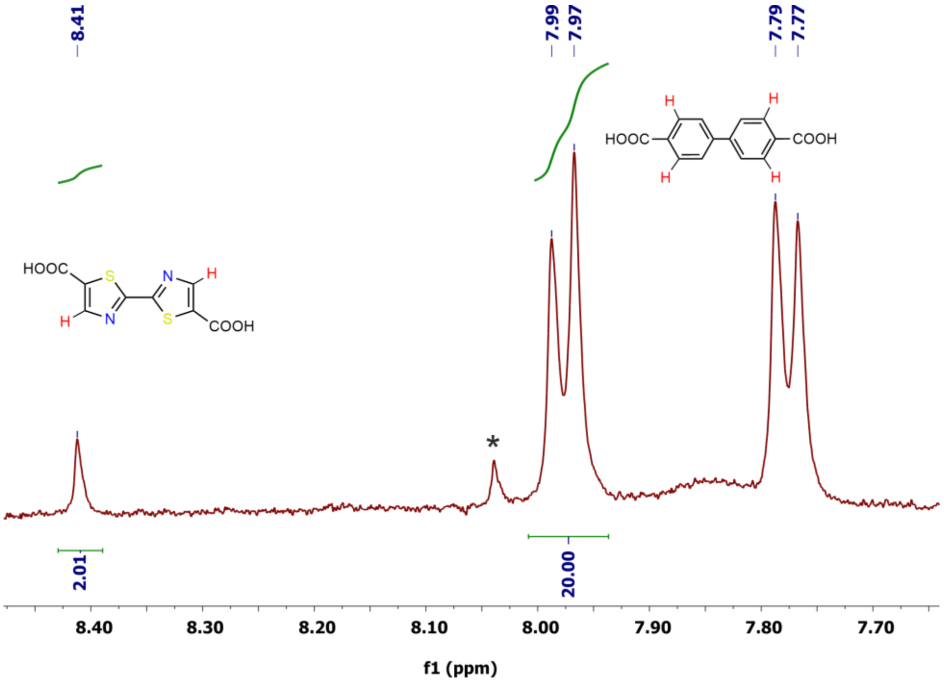

Figure S3. Zoom of the aromatic region used for the quantification of the ligands ratio from the ^{1}H NMR spectrum (400 MHz, HF_{aq}/DMSO-d_6, 298 K) of digested **UiO-67-TzTz·DMF**. * Clathrated DMF solvent signal.

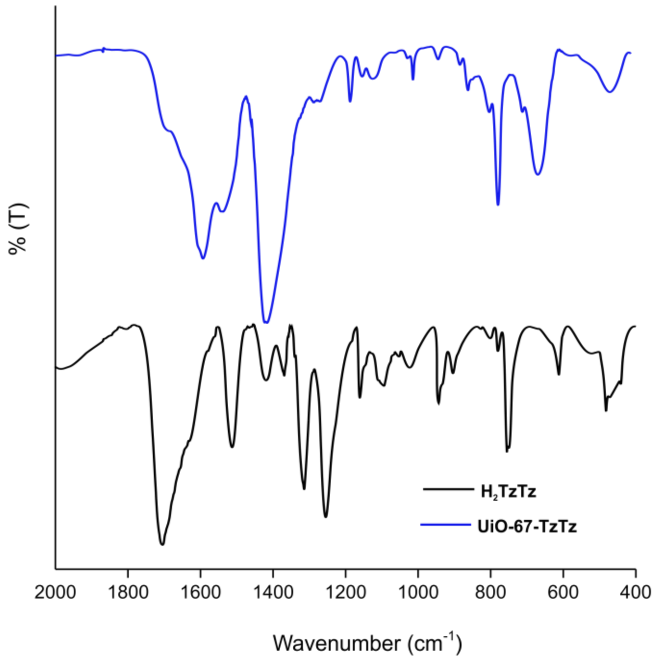

Figure S4. Infrared spectra (KBr, T = 298 K) of **UiO-67-TzTz·DMF** and **H$_2$TzTz** at comparison.

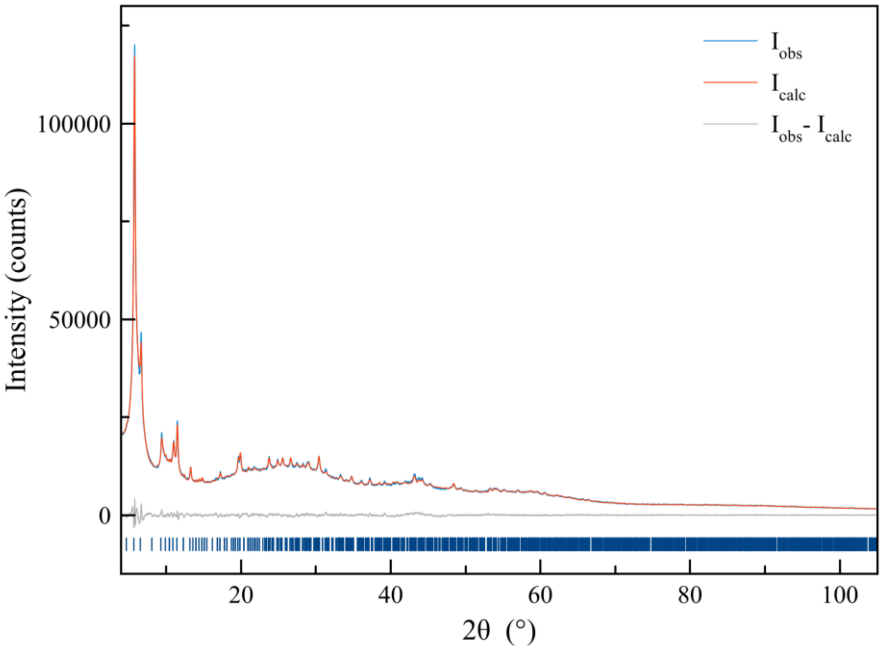

Figure S5. Graphical result of the final structure refinement carried out with the Rietveld method on the PXRD pattern of **UiO-67-TzTz·DMF** in terms of experimental, calculated and difference traces (blue, red and grey, respectively). The violet markers at the bottom indicate the positions of the Bragg reflections.

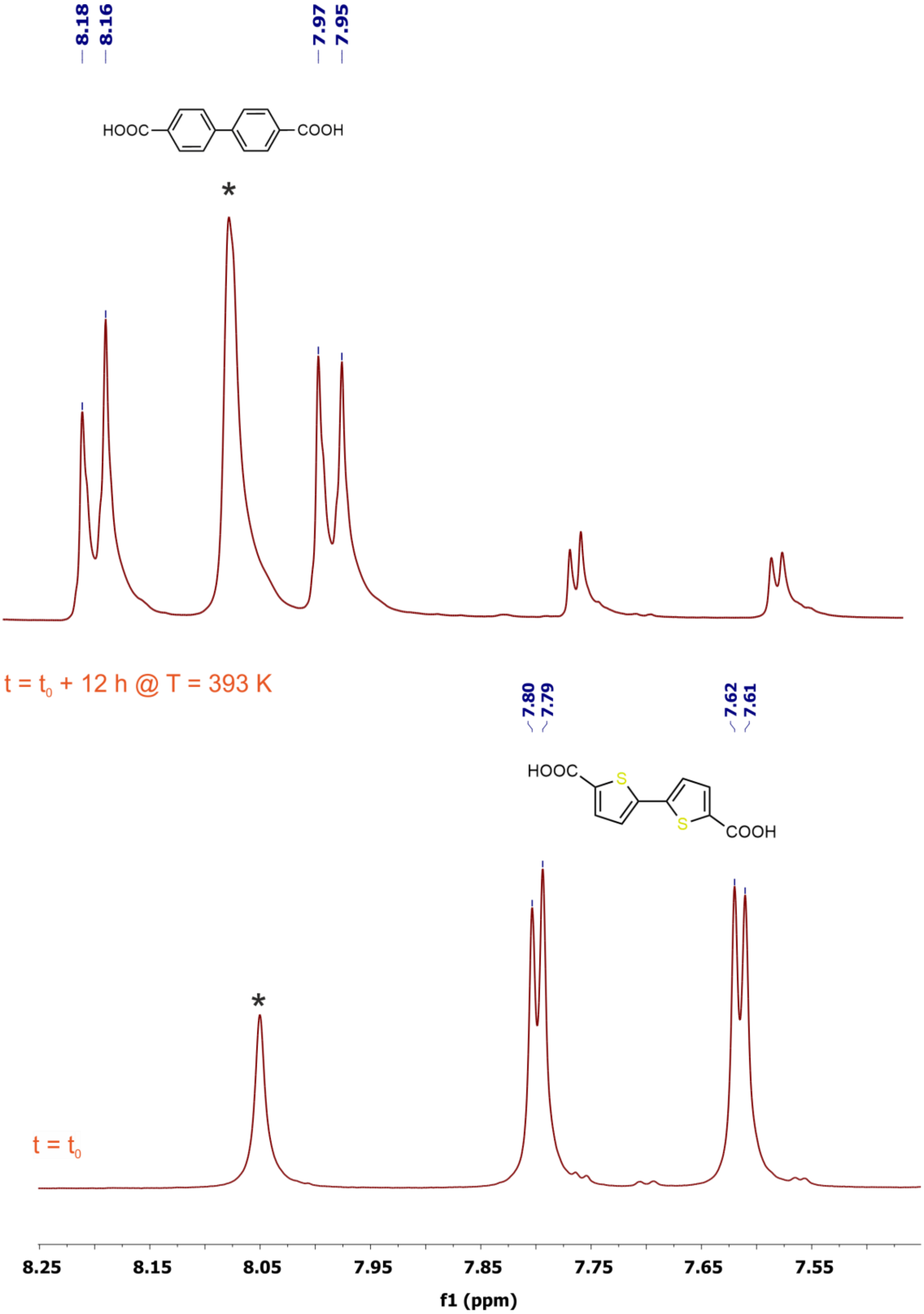

Figure S6. SALE for the synthesis of **UiO-67-TpTp·DMF** monitored through ^{1}H NMR spectroscopy in DMF-d_7 solution (400 MHz, T = 298 K). Bottom: spectrum of **H_2TpTp** initial solution at t = t_0. Top: spectrum recorded after keeping the NMR tube with added **UiO-67** for 12 h at T = 393 K. The new signals ascribed to the biphenyl linker coming from a partial **$PhPh^{2-}$/$TpTp^{2-}$** exchange are clearly visible in the supernatant. * DMF residual solvent signal.

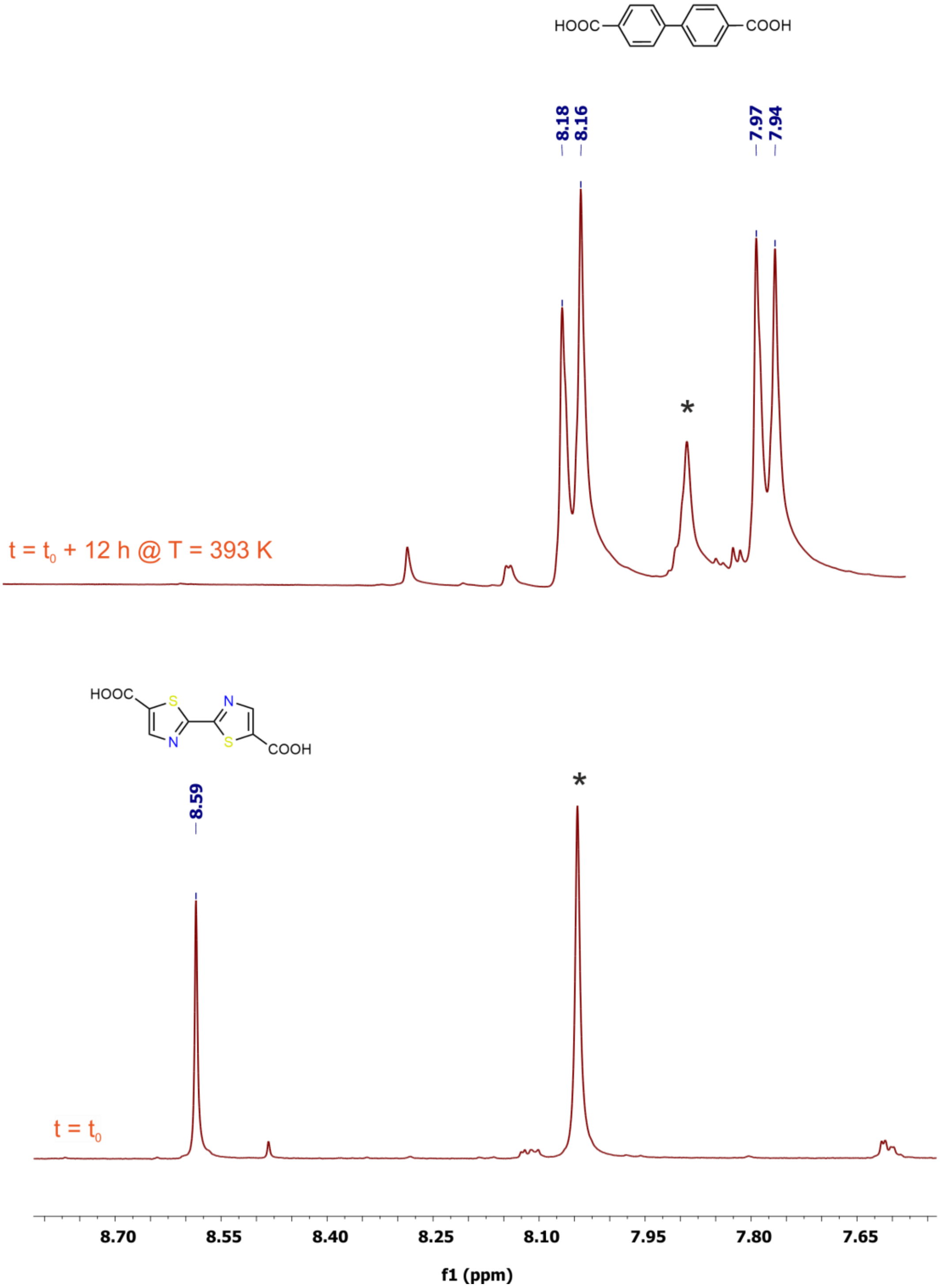

Figure S7. SALE for the synthesis of **UiO-67-TzTz·DMF** monitored through ^{1}H NMR spectroscopy in DMF-d_7 solution (400 MHz, T = 298 K). Bottom: spectrum of **H_2TzTz** initial solution at t = t_0. Top: spectrum recorded after keeping the NMR tube with added **UiO-67** for 12 h at T = 393 K. The new signals ascribed to the biphenyl linker coming from a partial **PhPh^{2-}/TzTz^{2-}** exchange are clearly visible in the supernatant. * DMF residual solvent signal.

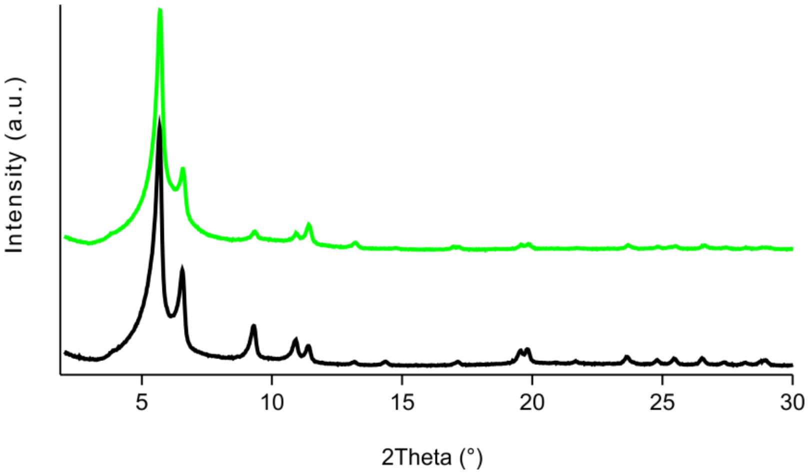

Figure S8. PXRD pattern of **UiO-67-TpTp·DMF** before (black) and after (green) soaking in water at ambient temperature for 12 h.

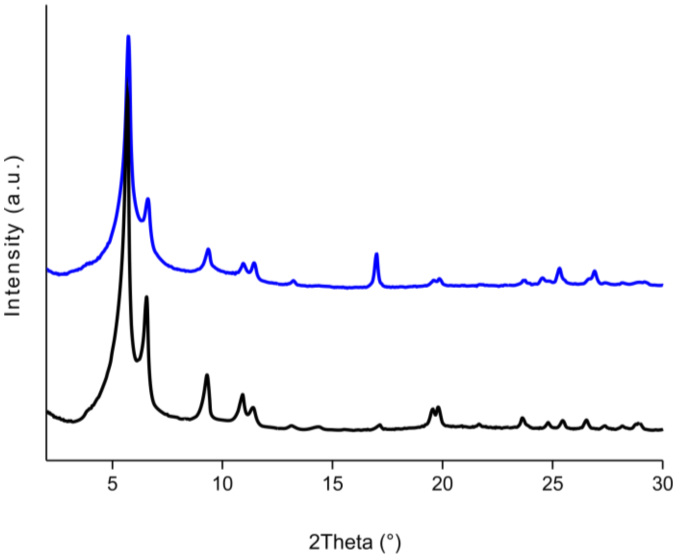

Figure S9. PXRD pattern of **UiO-67-TzTz·DMF** before (black) and after (blue) soaking in water at ambient temperature for 12 h.

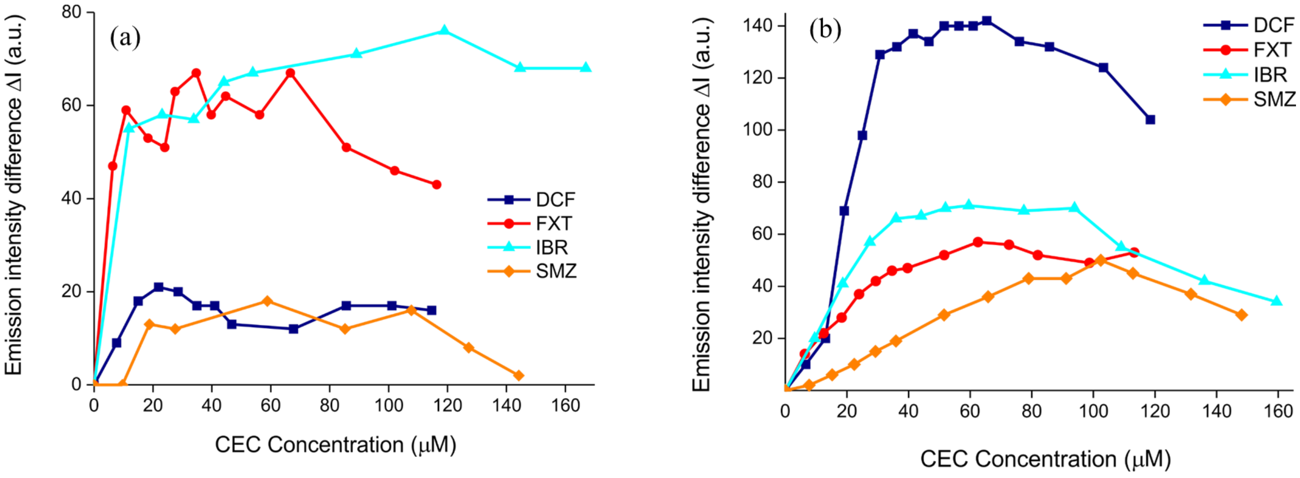

Figure S10. Emission intensity variation *vs.* CEC concentration in the luminescent response of **UiO-67-TpTp·DMF** (a) and **UiO-67-TzTz·DMF** (b).

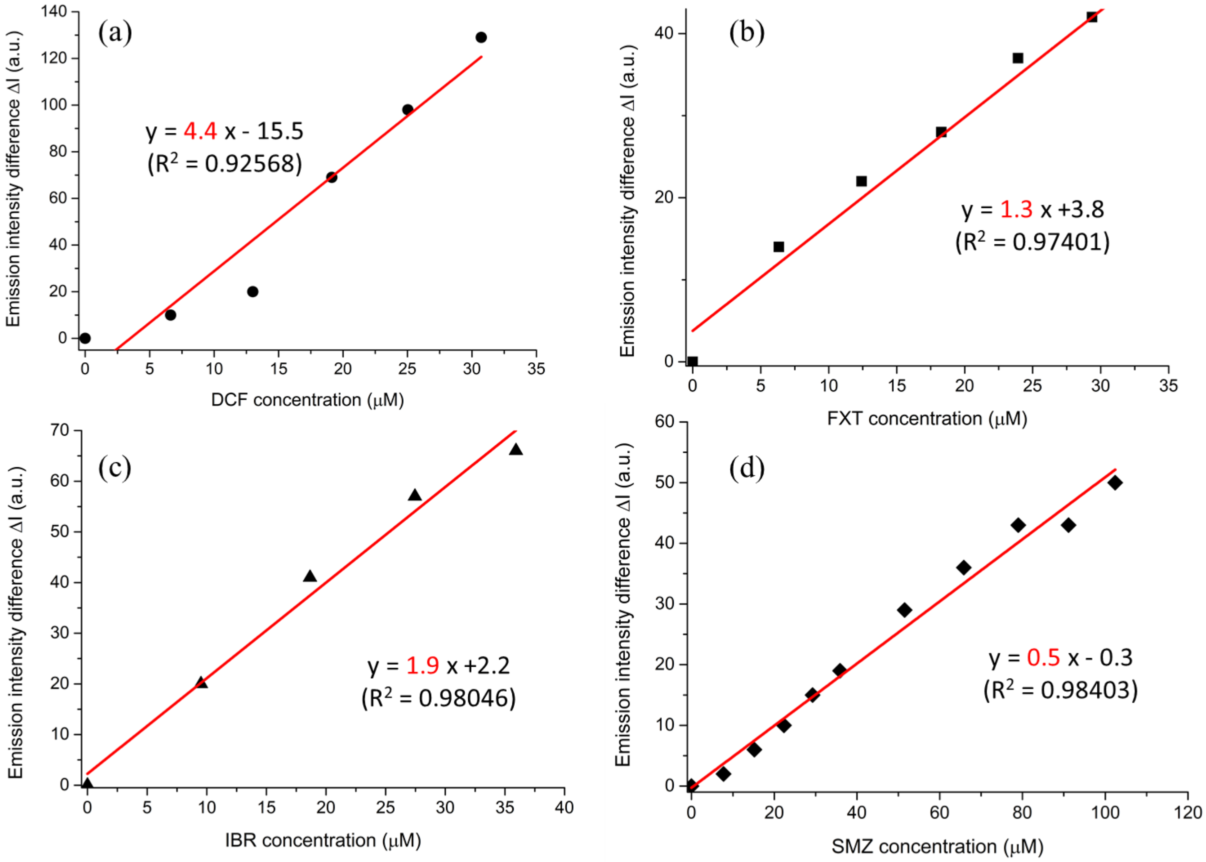

Figure S11. Linear data fitting for the dependence of the emission intensity from the CEC concentration for **UiO-67-TzTz·DMF**. (a) Diclofenac sodium, (b) fluoxetine, (c) ibuprofen and (d) sulfamethoxazole.

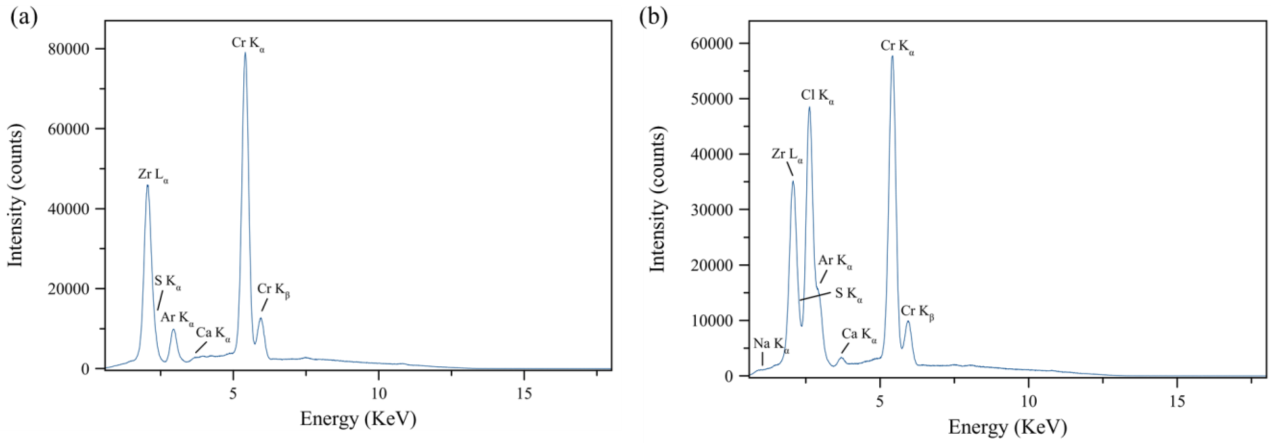

Figure S12. X-ray fluorescence spectra of **UiO-67-TzTz·DMF** (a) and [DCF@**UiO-67-TzTz**] (b) measured in air. The characteristic lines of argon come from air, those of chromium from the anode of the X-ray source and those of calcium from the sample-holder.

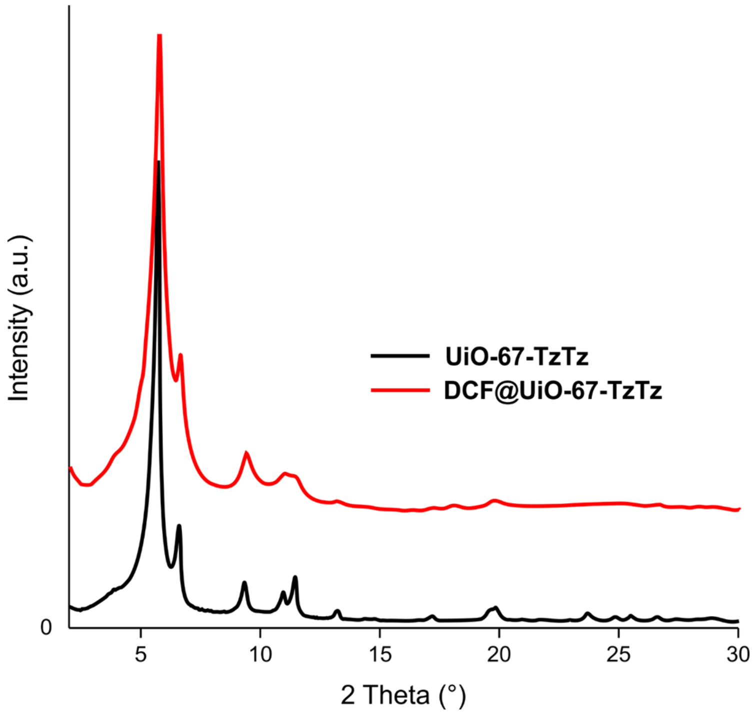

Figure S13. PXRD patterns of **UiO-67-TzTz·DMF** and [DCF@**UiO-67-TzTz**] at comparison.

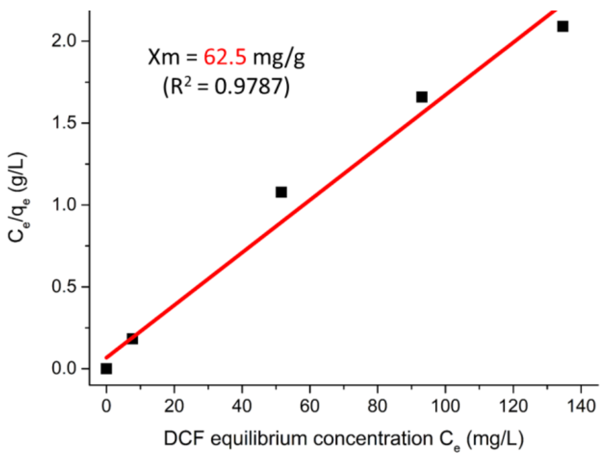

Figure S14. Linear data fitting according to a Langmuir model of the DCF adsorption isotherm of **UiO-67-TzTz·DMF**.