SUPPLEMENTARY MATERIAL

Hierarchically structured mixed-linker HKUST-1 Metal Organic Frameworks as catalysts: One-pot synthesis of quinazolines

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Sample compositions.

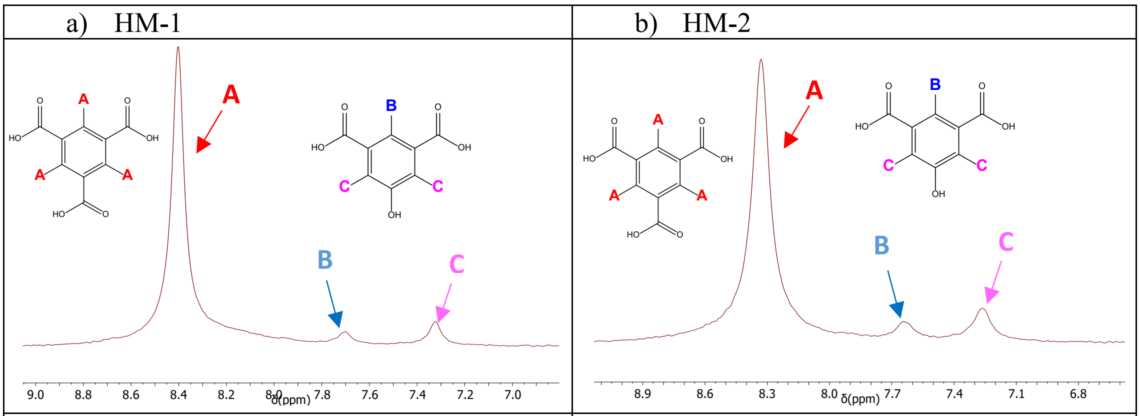
Results obtained from ICP (Cu) and Elemental analysis (C, H, N) of samples **M1**, **HM-1** and **HM-2**. The calculated values of Cu, C, H and N given in the Table below are based on the empirical formulas considering the measured BTC:OH-IP molar ratios determined from the ^1H NMR spectra of the digested samples, and the Metal-to-Ligand ratios determined from TGA. According to FTIR spectroscopy of adsorbed CO at 77 K, the amount of Cu^+/Cu^{2+} mixed-valence sites is very low in all samples, so we assume that charge compensation upon OH-IP linkers incorporation into the lattice is mainly achieved through residual nitrate anions coming from the copper salt used in the synthesis. Therefore, the experimental data are adjusted to general formulas $[Cu_3(BTC)_x(OH\text{-}IP)_y(NO_3)_y]$ (with $x + y \leq 2$).

	Formula	Cu		C		H		N	
		Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp
M1	$[Cu_3(BTC)_{1.94}]$	32.2	31.9	35.4	35.0	0.98	1.02	0.00	0.08*
HM-1	$[Cu_3(BTC)_{1.73}(OH\text{-}IP)_{0.19}(NO_3)_{0.19}]$	32.0	31.8	34.5	34.4	1.00	1.04	0.45	0.47
HM-2	$[Cu_3(BTC)_{1.54}(OH\text{-}IP)_{0.27}(NO_3)_{0.27}]$	33.2	32.8	33.4	33.1	0.99	1.02	0.66	0.69

* The N content of the samples can originate from both, nitrate anions (needed to compensate mixed-valence Cu^+/Cu^{2+} centers) and any residual DMF used in the syntheses.

Figure S1. Determination of the amounts of OH-IP substitution in **HM-1** and **HM-2** by ^{1}H NMR spectroscopy of the solids previously digested in d_2-H_2SO_4 in d_6-DMSO.

a) HM-1 b) HM-2



Substitution level : **10%** of OH-isophthalic

Substitution level : **15%** of OH-isophthalic

Figure S2. TGA curves (*left*) and first derivative (*right*) of samples **M-1**, **HM-1** and **HM-2**.

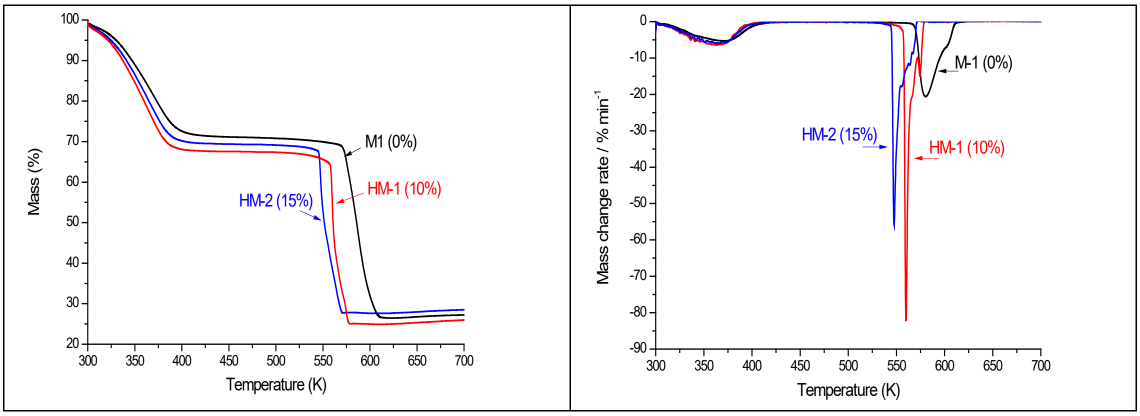
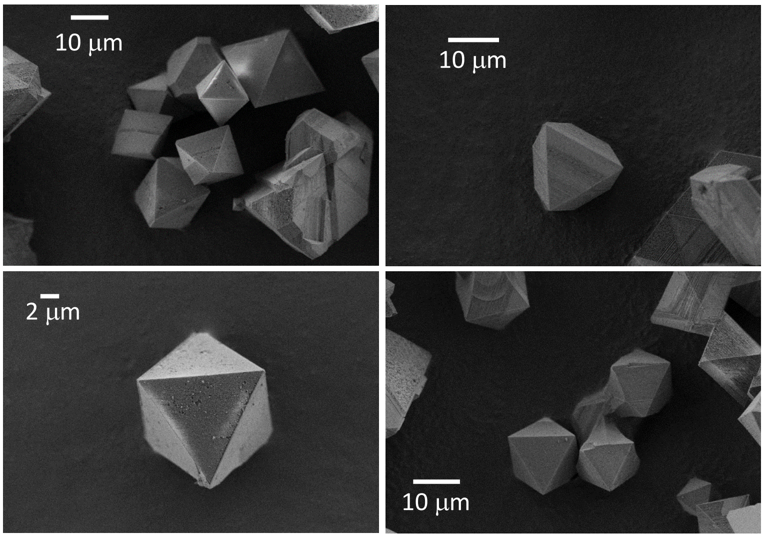
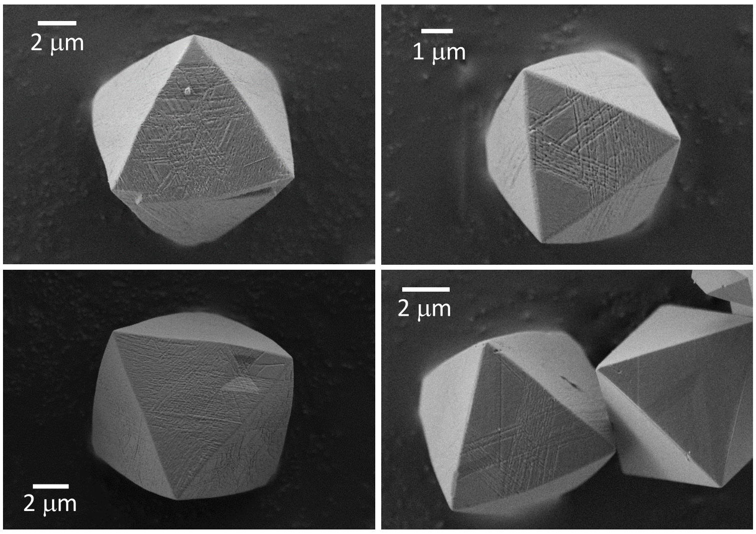


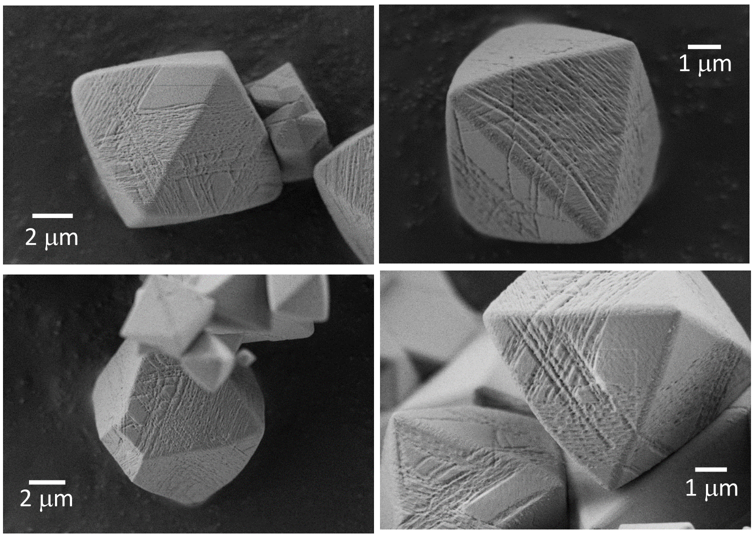
Figure S3. Representative FESEM images of (from *top* to *bottom*): **M-1**, **HM-1** and **HM-2**.



M-1

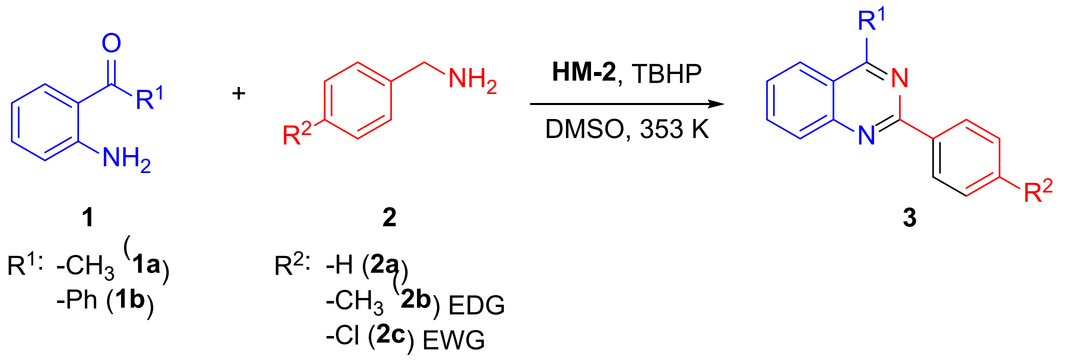


HM-1



HM-2

Table S1. Scope of the one-pot synthesis of quinazolines (**3**) by oxidative coupling of 2-aminobenzoketones (**1**) and benzylamines (**2**)



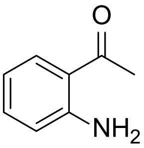
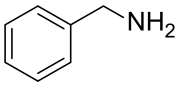
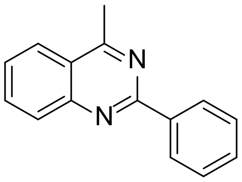
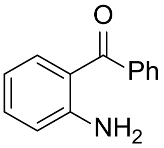
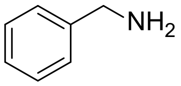
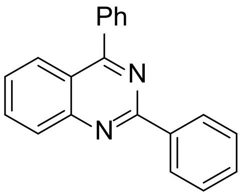
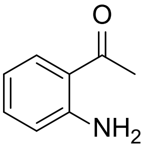
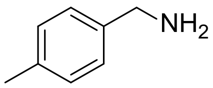
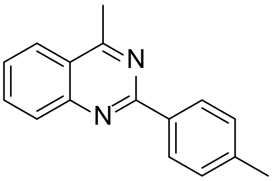
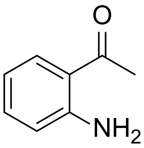
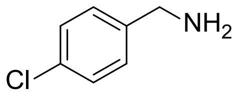
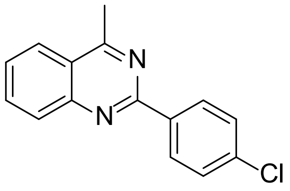
Entry	2-aminobenzoketone	Benzylamine	Quinazoline Product	Yield	
				1 h	5 h
1				55	100
2				39	98
3				48	97
4				52	99

Figure S4. Hot filtration test of **HM-2** during the synthesis of quinazoline

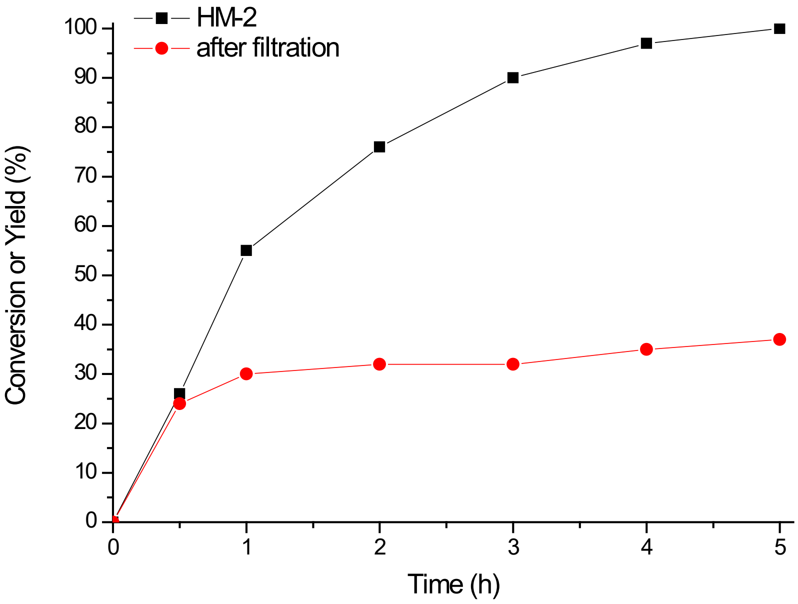


Figure S5. XRD pattern of fresh **HM-2** and the solid recovered after 4 catalytic cycles.

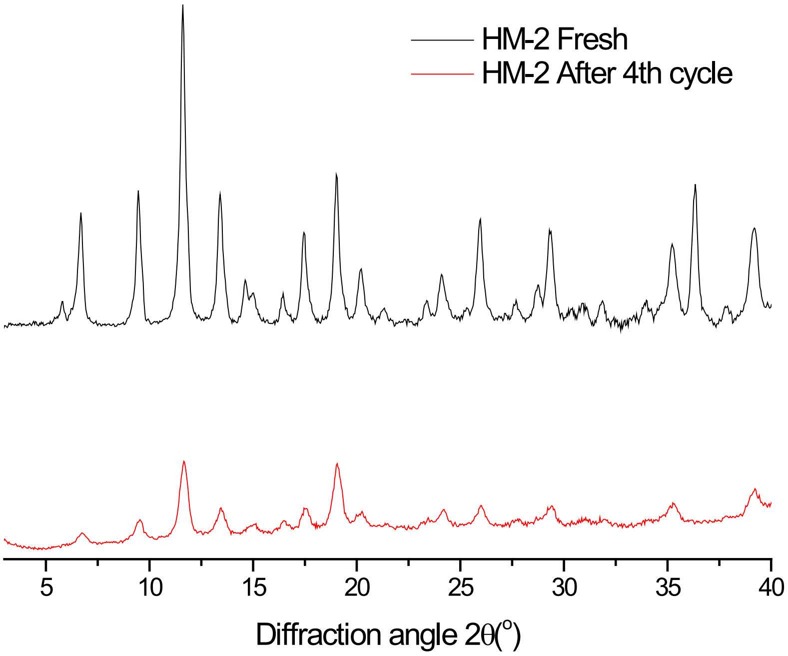


Figure S6. FTIR spectra of adsorbed CO at 77 K over **M-1** (*left*) and **HM-2** (*right*). For the sake of clarity, the spectra at higher equilibrium pressures of CO have been upward shifted to appreciate better the details at low CO doses (up to ca. 1 mbar)