Electronic Supplementary Material (ESI) for Dalton Transactions

Programmed functionalization of SURMOFs via heteroepitaxial growth and post-synthetic modification

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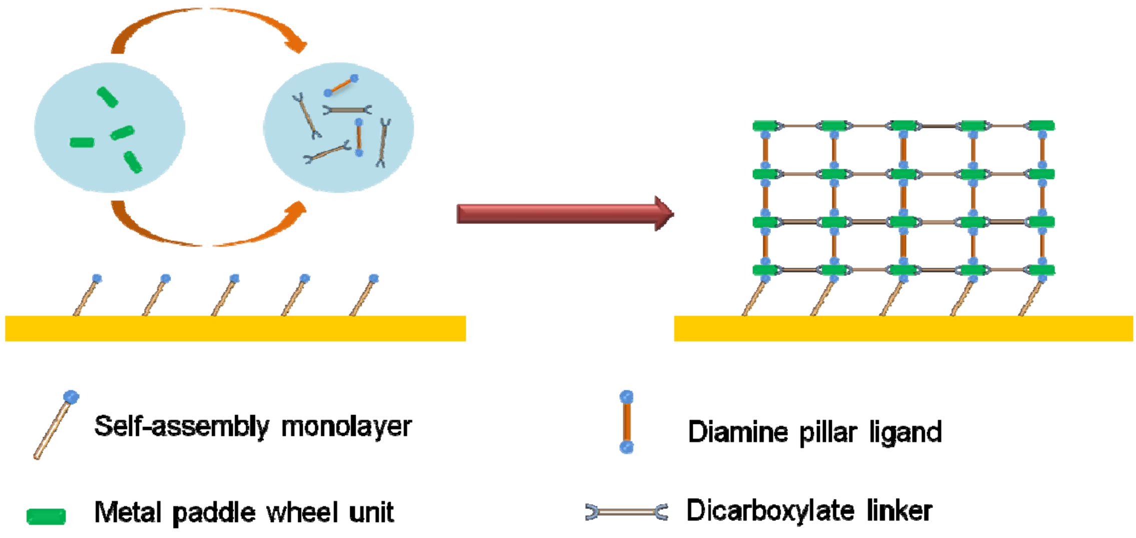
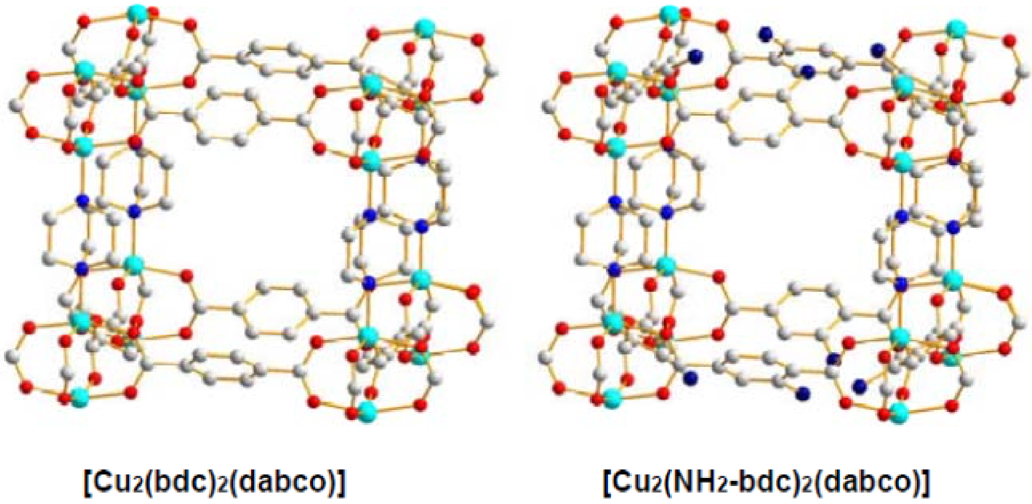


Fig. S1 Schematic illustration of step-by-step liquid epitaxial growth of metal-organic frameworks on self-assembly monolayers.


$[Cu_2(bdc)_2(dabco)]$

$[Cu_2(NH_2\text{-}bdc)_2(dabco)]$

Fig. S2 Crystal structures of MOF **A** $[Cu_2(bdc)_2(dabco)]$ and **B** $[Cu_2(NH_2\text{-}bdc)_2(dabco)]$

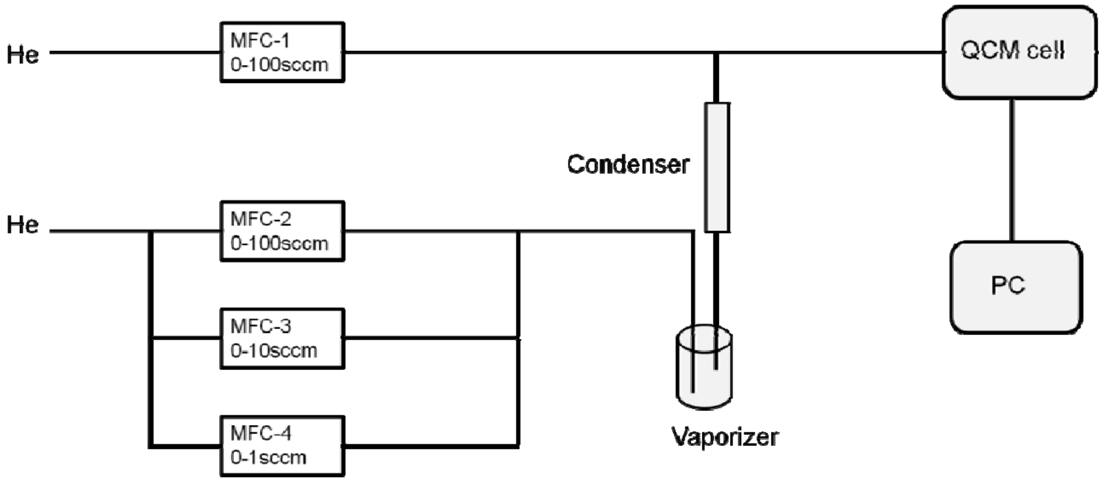


Fig. S3 Experimental setup for adsorption of organic vapors in SURMOFs deposited on QCM substrates.

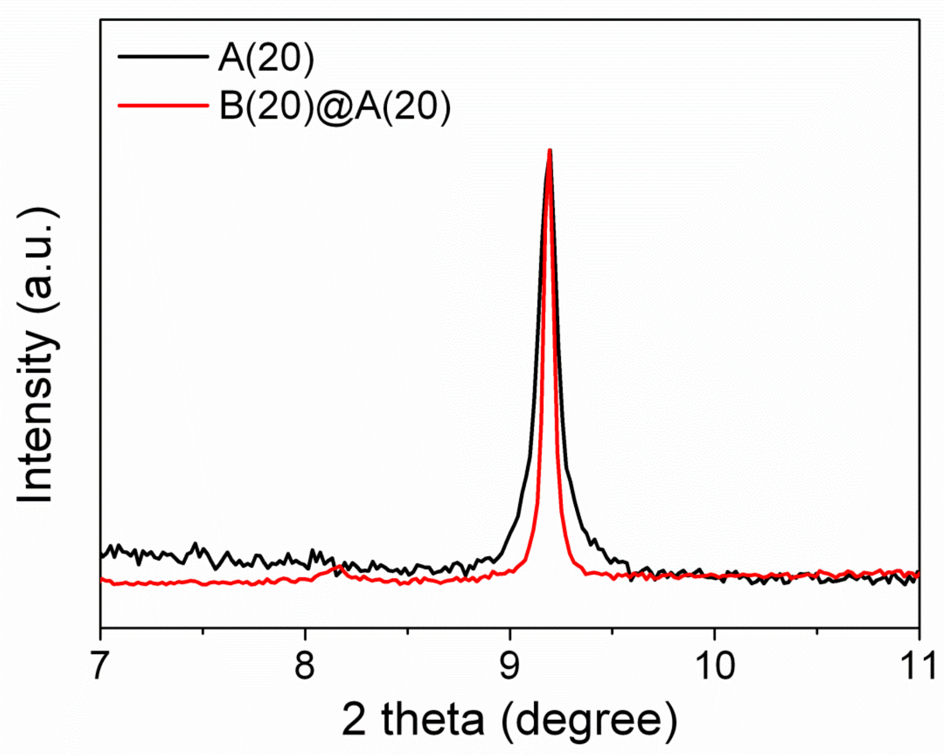


Fig. S4 Normalized out-of-plane XRD patterns of SURMOF **A**(20) and **B**(20)@**A**(20) centered at 9.2º.

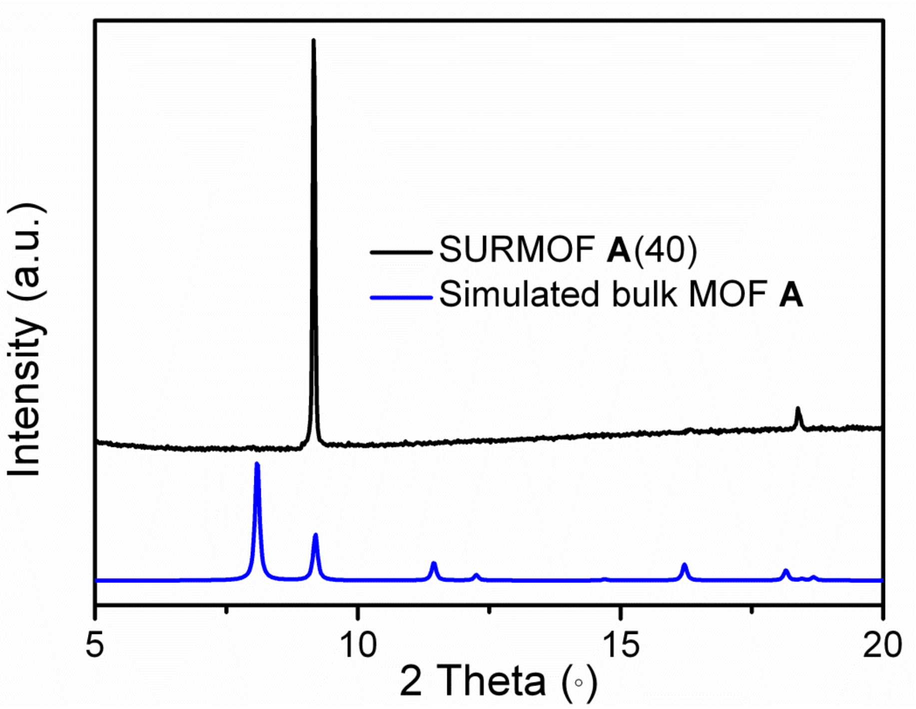


Fig. S5 Out-of-plane XRD patterns of SURMOF **A**(40) compared with simulated bulk MOF **A**.

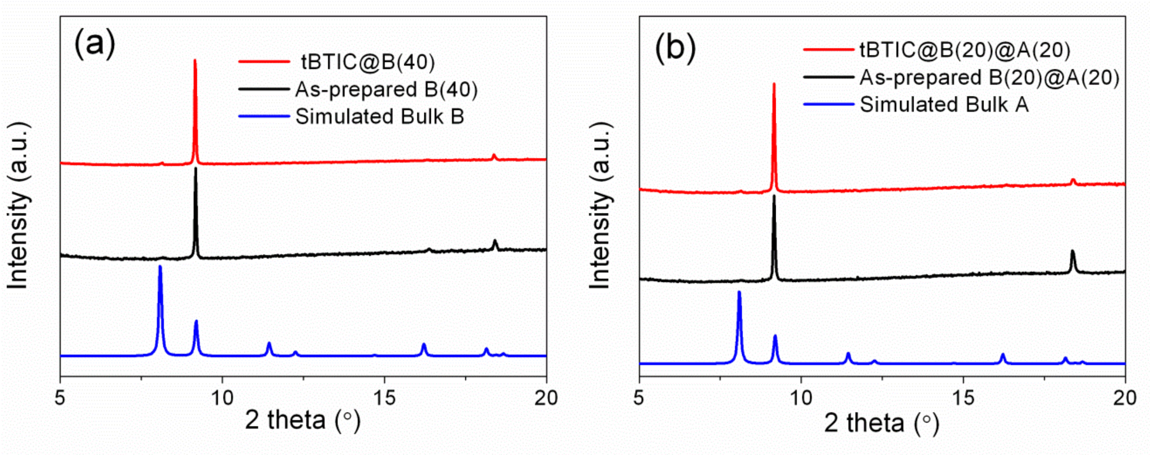


Fig. S6 Out-of-plane XRD patterns of SURMOFs before and after post-synthetic modification: (a) **B**(40) and (b) **B**(20)@**A**(20).

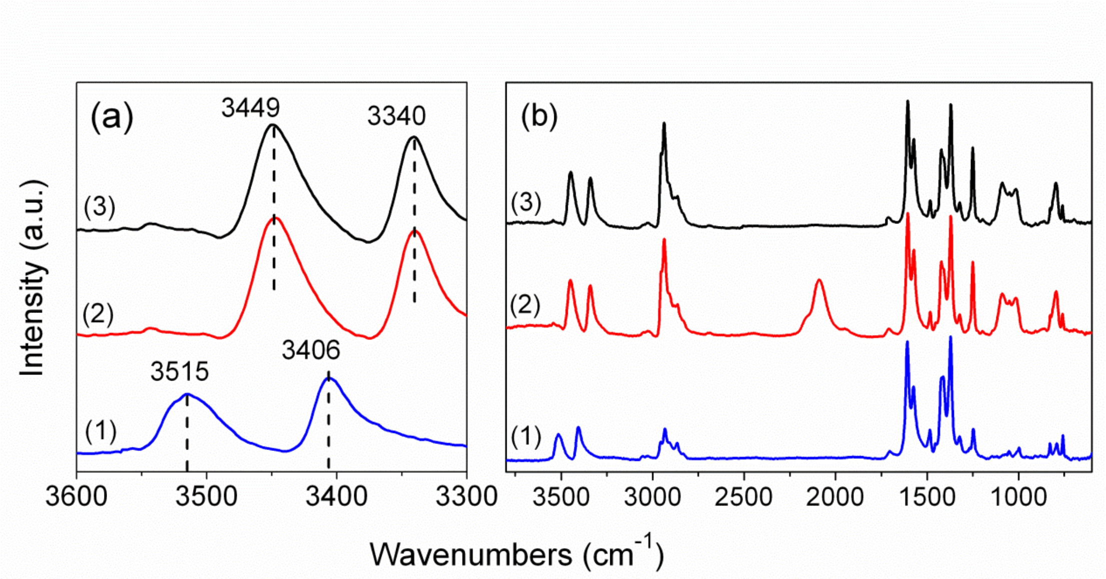


Fig. S7 IRRAS spectra for (1) as-prepared SURMOF **B**(40), (2) tBITC loaded SURMOF **B**(40) and (3) vacuum treated tBITC loaded SURMOF **B**(40) overnight (denoted as SURMOF tBITC@**B**(40)).

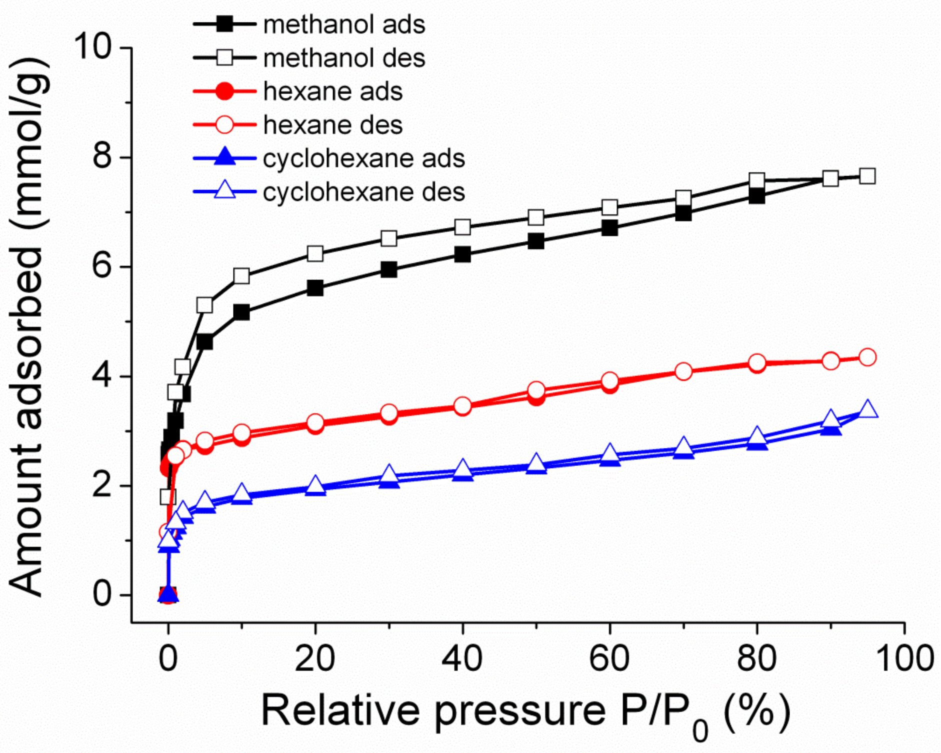


Fig. S8 Adsorption and desorption isotherms of organic vapors (methanol, hexane and cyclohexane) in SURMOF **A**(40) at 293K.

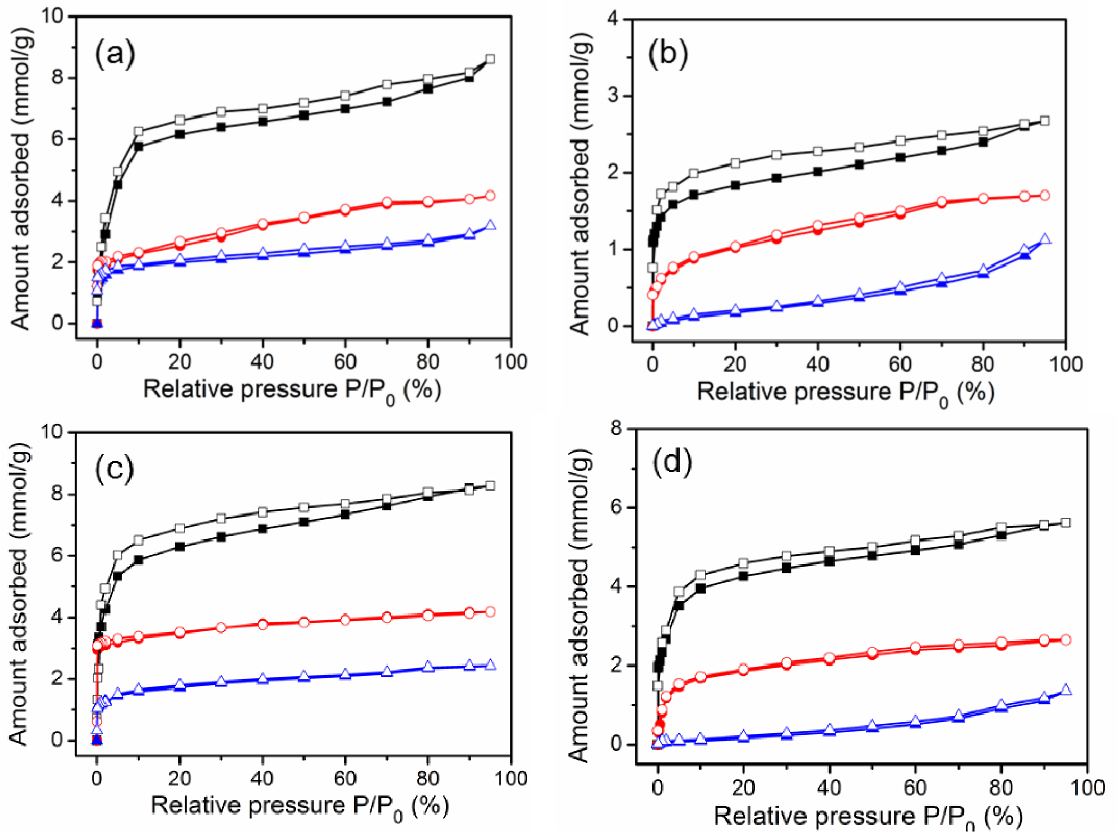


Fig. S9 Adsorption (open) and desorption (solid) isotherms of methanol (black), hexane (read) and cyclohexane (blue) in SURMOFs at 293K: (a) **B**(40); (b) tBITC@**B**(40); (c) **B**(20)@**A**(20); (d) tBITC@**B**(20)@**A**(20). The adsorption and desorption branches of isotherms of hexane and cyclohexane overlapped perfectly. However, the sorption isotherms of methanol in all samples show apparent hysteresis, which are similar to the results studied by K. Uemura et al.[1] They attributed the hysteresis to the hydrogen bonds formation between hydroxyl groups of methanol molecules and the carboxylate groups in the pores.

Reference:

1 K. Uemura, Y. Yamasaki, F. Onishi, H. Kita and M. Ebihara, *Inorg. Chem.*, 2010, **49**, 10133-10143.