Supporting Information:

Enantioselective Adsorption in Homochiral Metal-Organic Frameworks: The Pore Size Influence

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SI1: 1,4-bis(4-pyridyl)benzene (BiPyB)

The synthesis of 1,4-bis(4-pyridyl)benzene (BiPyB) has been described in the literature.[1]

![Figure SI1. Synthesis of BiPyB.](image)

1,4-di(pyridin-4-yl)benzene. To a 50 mL three-necked round-bottom flask equipped with a reflux condenser were added 1,4-dibromobenzene (0.55 g, 2.33 mmol), 4-pyridylboronic acid (1.00 g, 8.17 mmol), Pd(dppf)Cl₂ (0.19 g, 0.23 mmol), and Na₂CO₃ (0.50 g, 4.67 mmol) in a degassed mixture of toluene/water (1:1 v/v, 16 mL). The mixture was allowed to reflux for 48h under argon atmosphere. The solvents were evaporated, and the black-brown residue was extracted with ethyl acetate (200 mL) followed by washing with water (3 x 120 mL), then with brine. The organic phase was dried over MgSO₄, concentrated under reduced pressure and the residue was purified by silica gel column chromatography (eluent: 20% to 50% ethyl acetate in dichloromethane) to give pure 1,4-bis(4-pyridyl)benzene (0.39 g, 72%) as a white solid. Rf(EA/DCM:70/30) = 0.18. ¹H-NMR (300 MHz, CDCl₃): δ = 8.71 (d, 4H, J = 6.0 Hz, CHPy), 7.77 (s, 4H, CIVH), 7.56 (d, 4H, J = 6.0 Hz, CIVH) ppm. ¹³C-NMR (75 MHz, CDCl₃): δ = 150.5 (CIVPy), 147.5 (CIVPy), 138.9 (CIVH), 127.9 (CHPy), 121.7 (CHH) ppm. MS (EI) m/z = 232 (100) [M⁺], 154 (5) [M⁺-C₃H₆N].

SI2: Synthesis of homochiral isoreticular SURMOFs

The gold-coated QCM sensors functionalized by MUD SAMs were used as substrate. The pure ethanol was used for the baseline. 1mM ethanolic Cu(OAc)$_2$ solution and 0.2mM equimolar H$_2$Dcam and L (Dcam = (1R,3S)-(+) -Camphoric acid; L = dabco:1,4-diazabicyclo[2.2.2] octane, BiPy:4,4'-bipyridine or BiPyB: 4-(4-pyridin-4-ylphenyl) pyridine) were successively pumped through the QCM cell. In between, the sample was purged with ethanol to remove unreacted, weakly absorbed reactants. The synthesis was repeated for 50 cycles. The temperature was set to 50ºC and the flow rate was set to 100 mL min$^{-1}$. A Q-Sense E4 QCM was used to monitor the SURMOF growth in situ, see Figure SI2.

![Graphs](a) (b) (c)

Figure SI2. The layer-by-layer syntheses of the isoreticular chiral SURMOFs, a) Cu$_2$(Dcam)$_2$(dabco), b) Cu$_2$(Dcam)$_2$(BiPy) and c) Cu$_2$(Dcam)$_2$(BiPyB), monitored in situ by QCM.
SI3: X-ray diffraction of SURMOFs

The out-of-plane and in-plane X-ray Diffraction (XRD) experiments were carried out using Cu-Kα (\(\lambda = 1.5405 \text{ Å}\)) in a \(\theta-2\theta\) geometry. All out-of-plane and in-plane data coincide perfectly with the XRD of the calculated structure verifying the synthesized structures (Fig.SI3). For all three SURMOF structures, the (100) and (010) lattice plane distances are 0.95 nm. The (001) lattice plane distances changes with the used pillar linker. It is 0.95 nm, 1.4 nm and 1.8 nm for \(\text{Cu}_2(\text{Dcam})_2(\text{dabco})\), \(\text{Cu}_2(\text{Dcam})_2(\text{BiPy})\) and \(\text{Cu}_2(\text{Dcam})_2(\text{BiPyB})\), respectively.

![XRD data of SURMOFs](image)

**Figure SI3.** The XRD data of a) \(\text{Cu}_2(\text{Dcam})_2(\text{dabco})\), b) \(\text{Cu}_2(\text{Dcam})_2(\text{BiPy})\) and c) \(\text{Cu}_2(\text{Dcam})_2(\text{BiPyB})\) grown on MUD SAMs on gold.
**SI4: Infrared reflection absorption spectroscopy (IRRAS) of SURMOF**

IRRAS spectra of the SURMOFs, Figure SI4, were measured with a FTIR spectrometer Bruker VERTEX 80. The absorption bands at about 3000 cm\(^{-1}\) are assigned to the methyl and methylene group, respectively. The absorption bands at roughly 1600 cm\(^{-1}\) and at 1467–1401 cm\(^{-1}\) are assigned to the \(\nu_{as}\) and \(\nu_{s}\) stretching bands of COO- groups.

Figure SI4. The IRRAS data of a) Cu\(_2\)(Dcam)\(_2\)(dabco), b) Cu\(_2\)(Dcam)\(_2\)(BiPy) and c) Cu\(_2\)(Dcam)\(_2\)(BiPyB) grown on MUD SAMs on gold.
SI5: Enantiopure (S) and (R)-limonene uptake by Cu$_2$(Lcam)$_2$(BiPy)

**Figure SI5.** QCM curves of (S)-limonene (black) and (R)-limonene (red) uptake by Cu$_2$(Lcam)$_2$(BiPy) grown on MUD SAMs on gold. From 4 uptake experiments each, the relative R- and S-limonene uptakes were determined to be 0.061 +/- 0.017 and 0.031 +/- 0.0052, respectively. This results in an enantiomeric excesses ($ee_{R vs.S}$) of 33%.