Solvent templating and structural dynamics of fluorinated 2D Cu-carboxylate MOFs derived from the diffusion-controlled process

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Supplementary Information (15 pages)

Table of contents:

1. Crystal structure images – Figure S1 .................................................................................. 2
2. Glass reactor picture – Figure S2 .................................................................................. 3
3. IR spectra – Figures S3 – S7 ...................................................................................... 4
4. PXRD studies – Figures S8 – S11 and S13 – S19 ......................................................... 7
5. SEM image – Figure S12 .......................................................................................... 9
6. Gas adsorption isotherms – Figures S20 – S22 .......................................................... 13
7. Optical microscope images – Figure S23 ...................................................................... 15
Figure S1. Crystal structures of 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e): [Cu$_2$(OOR)$_4$] paddlewheel units (top), views parallel (middle) and perpendicular (bottom) to the MOF layers. MOFs were indexed as follows: [Cu(hfipbb)∙R]$_{XX}$, where R represents solvent molecules coordinated to the [Cu$_2$(OOR)$_4$] clusters and XX is a stacking type of the MOF layers (either I-x or I-xy). Note: interlayer stacking distances in studied 2D MOFs are dependent on temperature (values reported here for 100 K).
**Figure S2.** Picture of the glass reactor after the diffusion-controlled synthesis of 1.
Figure S3. FTIR (ATR) spectrum of material 1.

Figure S4. FTIR (ATR) spectrum of material 2.
Figure S5. FTIR (ATR) spectrum of material 3.

Figure S6. FTIR (ATR) spectrum of material 4.
Figure S7. FTIR (ATR) spectrum of material 5.
Figure S8. PXRD diffractograms demonstrating patterns: experimental (red), simulated (preferred orientation, black) and simulated (no preferred orientation, blue) for 1, 2, 3, 4 and 5.
Figure S9. VTPXRD study of 1 in the temperature range from 25 °C to 200 °C.

Figure S10. VTPXRD patterns of 2 collected in the temperature range from 25 °C to 200 °C.
Figure S11. PXRD pattern of materials 2-P and 2-G compared to the simulated pattern of 2.

Figure S12. SEM image of the sample 2-P. The estimated crystal size is 9.8 ± 1.8 μm.
Figure S13. VTPXRD patterns of 3 collected in the temperature range from 25 °C to 200 °C. The simulated pattern of 3 was calculated by accounting for both preferred orientation of crystallites as well as thermal expansion of 3 (single crystal data were collected at 100 K).

Figure S14. VTPXRD patterns of 4 collected in the temperature range from 25 °C to 200 °C.
Figure S15. VTPXRD patterns of 5 collected in the temperature range from 25 °C to 200 °C.

Figure S16. PXRD study of post-synthetic modification of material 1.
Figure S17. PXRD study of post-synthetic modification of material 2.

Figure S18. PXRD study of post-synthetic modification of material 3. The simulated pattern of 3 was calculated by accounting for both preferred orientation of crystallites as well as thermal expansion of 3 (single crystal data were collected at 100 K).
**Figure S19.** PXRD study of post-synthetic modification of material 4.

**Figure S20.** N\textsubscript{2} adsorption isotherms of 1 (blue), 2 (red), 3 (green) and 4 (orange) measured at 77 K. Open symbols denote desorption.
Figure S21. H₂ adsorption isotherms of 1 (blue), 2 (red), 3 (green) and 4 (orange) measured at 77 K. Open symbols denote desorption.

Figure S22. CO₂ adsorption isotherms of 1 (blue), 2 (red), 3 (green) and 4 (orange) measured at 273 K. Open symbols denote desorption.
Figure S23. Microscope images of samples 2 (top, scale bar = 500 μm), 2-G (middle, scale bar = 100 μm) and 2-P (bottom, scale bar = 100 μm).