#### Supporting Information:

# Chiral Recognition in Metal-Organic Frameworks by Solid-State NMR Spectroscopy Using Chiral Solvating Agents

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### **Sample preparation**<sup>1</sup>

The 1,4-benzenedicarboxylate-linker (BDC-linker) molecules are modified by the organochemical addition of enantiomerically pure chiral side groups, resulting in (S)-2-(4-isopropyl-2-oxooxazolidin-3-yl)terephthalic acid or (S)-2-(4-benzyl-2-oxooxazolidin-3-yl)terephthalic acid linkers, respectively. The as-synthesized solids<sup>1</sup> were washed with *N*,*N*-diethylformamide, and the solvent was exchanged with dichloromethane. The compounds were dried in vacuum at room temperature to get activated samples, which were further handled under inert gas (argon) atmosphere in a glove box.

### **NMR experiments**

For NMR measurements, an activated sample of each compound was homogenized and divided into two aliquots. The <sup>13</sup>C cross polarization (CP) MAS NMR spectra of these two unloaded samples were measured in order to further ensure the identity of the aliquots. Afterwards, the samples were loaded with (*R*)-or (*S*)-TFPE. An advantage of TFPE is its liquid state at room temperature. This allows loading the MOFs with TFPE in large excess and without using any additional solvent in order to ensure maximal effects. The MOF particles soak up TFPE from the surrounding solution until their pore system is filled. Afterwards, the samples were stored for 24 hours under inert atmosphere for equilibration. Furthermore, the equilibration process also encompassed at least 1 hour of preliminary magic angle sample spinning at 16 kHz before the measurements were started. Solid-state <sup>13</sup>C NMR experiments were performed on a Bruker Avance 300 spectrometer operating at 75.47 MHz for <sup>13</sup>C using a commercial double resonance 2.5 mm MAS NMR probe. Ramped <sup>1</sup>H-<sup>13</sup>C CP<sup>2,3</sup> was used with 8 ms mixing time.

Small phase incremented alternation (SPINAL) <sup>1</sup>H-decoupling<sup>4</sup> was applied during the signal acquisition.

## **Supplementary figures**



Figure S1: Schematic representation of synthesis procedure<sup>1</sup>

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Figure S2: <sup>13</sup>C CP MAS NMR spectra of achiral MOF UMCM-1.

- A) Top (red): Loaded with (*R*)-TFPE, Middle (blue): Loaded with (*S*)-TFPE). Bottom (black): Unloaded sample. Stars denote signals due to TFPE.
- B) Superposition of the spectra of achiral UMCM-1 loaded with the two different enantiomers ((R)-TFPE = red; (S)-TFPE = blue). Note the almost ideal agreement of the two spectra. Stars denote signals due to TFPE.



Figure S3: <sup>13</sup>C CP MAS NMR spectra of the chiral MOF Bn-UMCM-1. Top (red): Loaded with (*R*)-TFPE, Middle (blue): Loaded with (*S*)-TFPE). Bottom (black): Unloaded sample. Stars denote signals due to TFPE.



Figure S4: <sup>13</sup>C CP MAS NMR spectra of Bn-UMCM-1 in the side group signal and linker carboxylate region loaded with (R)-TFPE (red) and (S)-TFPE (blue).

#### References

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