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#### COMMUNICATION

## Planar-chiral building blocks for metal-organic frameworks<sup>†</sup>

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The first example of a planar-chiral building block being used for chiral metal-organic frameworks (MOFs) is presented. The porous MOF structure combined with the chiral properties of the planar linker allows a selective adsorption, demonstrated for an unpolar terpene limonene in thin surface-mounted MOF films.

The creation of chiral surfaces and porous materials is an important tool in the development of separation and sensing of chiral molecules. Particularly high potential shows the material class with the highest specific surface areas,<sup>1</sup> metal-organic frameworks (MOFs),<sup>2-4</sup> which are crystalline solids self-assembled from metal complexes and chiral or achiral organic ligand molecules. Due to the option of tailoring the structure and the properties by choosing appropriate components, chiral MOFs are especially attractive and enable an efficient enantiomer separation.<sup>5</sup> Recently, surfacemounted MOFs (SURMOFs) have been used for constructing designed porous surfaces with different pore sizes and chiral $^{6,7}$  (and achiral<sup>6, 8-15</sup>) structures. The drawback of most central chiral MOF and SURMOF structures which have been presented so far is the use of non- $C_2$ -symmetric building blocks as the direction of incorporation is in most cases random and therefore regioisomers could be created (for a system with  $C_2$ -symmetry, see<sup>16</sup>). An interesting material that has the possibility of planar-chiral properties combined with C<sub>2</sub>-symmetry are 4,7-substituted paracyclophanes.

Since the first studies on [2.2]paracyclophanes by Brown<sup>17</sup> and Cram,<sup>18-20</sup> the interest in this class of compounds is constantly growing. Due to their unique structural, physical and electronic properties,<sup>21-25</sup> they find wide applications in material science<sup>26, 27</sup> and as ligands in asymmetric syntheses.<sup>28-35</sup> We recently established a route to 4,7-disubistuted paracyclophanes<sup>36</sup> which might serve as linker for metal-organic frameworks. To obtain the required starting material (*S*<sub>*P*</sub>)-**1-H**, the procedure starts from formyl paracyclophane (Scheme 1).<sup>36-38</sup>



Scheme 1 Syntheses of PcTPDC (*S<sub>P</sub>*)-1-H; *Reagents and conditions:* (i) 1) Cl<sub>2</sub>CHOMe (1.05 equiv.), TiCl<sub>4</sub> (2.0 equiv.); CH<sub>2</sub>Cl<sub>2</sub>, rt, 8 h, 99%; 2) Resolution with (*R*)-phenylethylamine; 3) H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, rt, 16 h, 81% (gram scale); 4) a) N<sub>2</sub><sup>+-</sup>C<sub>6</sub>H<sub>4</sub>-4-SO<sub>3</sub>H, NaOH/MeOH; b) SnCl<sub>2</sub>/HCl; c) Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; 67% over 3 steps (ii) 1) a) H<sub>2</sub>NNH<sub>2</sub>.H<sub>2</sub>O (2.5 equiv.), ethanol, reflux, 2 h; b) Tf<sub>2</sub>O(4 equiv.), DMAP (6 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 2 h; 68% plus 30% starting material; 2) 4-carboxyphenylboronic acid (4.0 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (6 mol%), K<sub>2</sub>CO<sub>3</sub> (3.0 equiv.); dioxane, 48 h, under argon; 88%; 3) aq. 1 M KOH; THF, reflux, 16 h, 94%



Figure 1 Molecular structures of (S)-4,7-bis(4-methoxycarboxyphenyl)-[2.2]paracyclophane (1-Me) (displacement parameters are drawn at 50% probability level) (see also <sup>36</sup>)

To demonstrate the high potential of planar-chiral building blocks, thin films of metal-organic frameworks (MOFs) containing **1-H** were prepared by liquid-phase epitaxy in a well-defined layer-by-layer fashion directly on the solid substrate, resulting in surface-mounted MOFs (SURMOFs).<sup>8</sup> The SURMOF synthesis was performed by exposing the functionalized substrate surface successively to the solution of the metal-complex (here: 0.5mM ethanolic solution of zinc acetate 2-hydrate) and to the solution of the organic linker Published on 10 February 2015. Downloaded by University of Sussex on 11/02/2015 14:26:15.

molecules (here: 0.1 mM solution of PcTPDC, i.e. (S)-1) by employing a spray method.<sup>9</sup> After each step, the sample was purged with pure ethanol to remove the unreacted, weakly adsorbed reactants. To support the growth and to increase the crystallinity of the chiral SURMOF-2 of type Zn(PcTPDC) an achiral SURMOF of Cu(DMTPDC)<sup>13</sup> type (DMTPDC: 2',5'-dimethyl-[1,1':4',1"terphenyl]-4,4"-dicarboxylic acid) was used as seeding layer. The seeding-layer SURMOF, which has the same lattice parameters as the Zn(PcTPDC) SURMOF on top, was prepared by successively exposing the functionalized substrate surface to 0.5 mM ethanolic solution of copper(II) acetate and 0.1 mM ethanolic solution of DMTPDC. The gold substrate was functionalized with a 16mercaptohexadecanoic acid self-assembled monolayer (MHDA SAM). The seeding-layer SURMOF was prepared in twelve spray cycles and the chiral SURMOF on top in 25 cycles. The crystallinity of the thin MOF film was checked by X-ray diffraction (XRD, Figure 2), where crystalline growth in [100] direction was found for the seeding and for the top layer. The smooth morphology of the MOF film can be seen from the SEM images in the supporting information.



**Figure 2: X-ray diffractogram of thin MOF film.** The XRDs of the Cu(DMTPDC) seeding layer (black) and of the Zn(PcTPDC) SURMOF on top of the seeding layer (red) show crystalline growth in (100) orientation.<sup>13</sup> The areas of the diffraction peaks increase approximately by 1/3 when the Zn(PcTPDC) is grown on top of the Cu(DMTPDC) seeding layer. An X-ray diffractometer of type Bruker D8 Advance with an X-ray radiation of 0.154 nm wavelength was used.

The chiral character of the two-layered SURMOF film was investigated by circular dichroism (CD), see Figure 3. <sup>5,13</sup> A rotation of the polarization direction, i.e. a different absorption of left-hand and right-hand circular polarized light, can be observed, verifying the chiral character of the SURMOF film. Furthermore, the CD spectrum of the two-layered SURMOF is similar to the CD spectrum of the chiral PcTPDC linker molecule.

The chiral character of the thin MOF film was further investigated by studying the enantioselectivity. For this purpose, the enantiopure uptakes of chiral probe molecules, (*S*)- and (*R*)-limonene, were investigated by using a quartz crystal microbalance (QCM). <sup>12,39</sup>After activating the samples at 338 K in a flow of pure argon for several hours, the uptakes of the enantiopure guest molecules were studied at a temperature of 303 K. The initial pure argon flow was switched to an argon flow passing over (*R*)- or (*S*)-limonene at room temperature (298 K), resulting in an argon flow enriched with the vapor of the chiral guest molecules and the guest molecule uptake by the two-layered SURMOF grown on the gold-coated sensor was measured by QCM. The uptakes of (*R*)- or (*S*)-limonene were investigated three times each in an alternate manner to guarantee reproducible results. Typical uptake curves are shown in Figure 4. The average uptake amount of R-limonene is  $0.041\pm0.004$  g per g SURMOF, while it is  $0.024\pm0.003$  g (*S*)-limonene per g SURMOF. Therewith, a (theoretical) enantiomeric excess (ee) R vs. S of 26% follows.



**Figure 3: Circular dichroism.** The CD spectra of the chiral PcTPDC linker in ethanolic solution (black) and of the SURMOF (red) are measured in transmission. For this purpose the two-layered SURMOF was grown on a quartz glass substrate. <sup>5,13</sup>

It should be mentioned that the enantiomeric excess in the pure Zn(PcTPDC) layer is larger than the here determined value, which is the average value for the two-layered film, i.e. of the chiral top layer and the achiral seeding layer with an enantiomeric excess of 0. By assuming that the amount of (*R*)- or (*S*)-limonene adsorbed in the seeding layer is about half of the total adsorbed amount of *S*-limonene, an enantiomeric excess (ee) R vs. S of 41% is estimated for the pure Zn(PcTPDC) phase.



**Figure 4: Uptake of enantiopure (***R***)- or (***S***)-limonene.** The uptake of R- or S-limonene from the gas phase by the two-layered chiral SURMOF is measured with a quartz crystal microbalance. The relative uptake amount denotes the limonene uptake relative to the mass of the SURMOF ( $39 +/-2 \mu g \text{ cm}^{-2}$ ), which is determined by comparing the resonance frequencies of the QCM sensor with (4.98637MHz) and without (4.98853MHz) the SURMOF on top and by using the Sauerbrey equation.<sup>40</sup>

In conclusion a novel  $C_2$ -Symmetric building block was used for the generation of chiral surface-mounted MOF structures. The selective incorporation of limonene is demonstrated. We are presently working on substituted derivatives allowing modified binding motifs.

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†Electronic Supplementary Information (ESI) available: crystallographic data of 4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane (**1-Me**) in cif-format. Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1042413 (4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk). See DOI: 10.1039/c000000x/

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