Supporting Information

Halogen Bonded Polypseudorotaxanes Based on
Pillar[5]arene Host

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Experimental details

All solvents and 1,2,4,5-tetrafluoro-3,6-diiodobenzene (4) was purchased from Sigma Aldrich and used without further purification. Permethylated pillar[5]arene (MeP5A)\textsuperscript{1}, 1,4-di(1H-imidazol-1-yl)butane (1)\textsuperscript{2}, 1,4-bis(iodoethynyl)benzene (2)\textsuperscript{3} and 1,4-diiodobuta-1,3-diyne (3)\textsuperscript{4} were obtained according to the reported literatures. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR were recorded on Bruker Avance III HD 400 MHz at ambient temperature.

MeP5A·1
40 mg (53,27 mmol; 1 eq.) of MeP5A and 20,3 mg (106,54 mmol; 2 eq.) of 1 were dissolved in 5 ml of hot chloroform. After dissolution of all the components 2 ml of toluene was added. The solution was left cool and within 3 days X-ray quality crystals of MeP5A·1 complex were obtained (mp 229–231°C).

MeP5A·1-2
35 mg of MeP5A·1 (37,19 mmol; 1 eq.) and 14 mg of 2 (37,19 mmol; 1 eq.) were dissolved in hot dichloromethane (4 ml). After cooling carbon tetrachloride (2 ml) was added. Single, transparent crystals were obtained after 1 week (mp >240°C (dec.))

MeP5A·1-3
33 mg of MeP5A·1 (35,06 mmol; 1 eq.) 10,6 mf of 3 (35,06 mmol; 1 eq.) were heated in 1:1 (v/v) mixture of toluene and dichloromethane. Upon standing for 4 days single crystals were obtained (mp > 240°C (dec.)).

MeP5A·1-4
27 mg of MeP5A·1 (28,69 mmol; 1 eq.) and 11,5 mg of 4 (28,69 mmol; 1 eq.) were dissolved in hot dichloromethane (4 ml). After cooling carbon tetrachloride (2 ml) was added. X-ray quality crystals of MeP5A·1·4 were grown within few days (mp 192–196°C (dec.)).

\textsuperscript{1}H and \textsuperscript{13}C NMR spectra of MeP5A·1, MeP5A·1-2, MeP5A·1-3, MeP5A·1·4 (400 MHz, CDCl\textsubscript{3} / CD\textsubscript{3}SOCD\textsubscript{3}) reflect complex equilibrium between the complexed and uncomplexed components indicating a slow exchange in solution on NMR timescale.\textsuperscript{5}
**Figure S1.** The two symmetry independent molecules of 2 are located around inversion centers making the polypseudorotaxane in MeP5A·1·2 (top) achiral. In contrary, the polypseudorotaxane in MeP5A·1·3 (bottom) shows exclusively translational symmetry implying that the MeP5A beads are homochiral.
Table S1. Geometry of halogen and hydrogen bonds

<table>
<thead>
<tr>
<th></th>
<th>X···Y (Å)</th>
<th>D–X···Y (°)</th>
<th>Symmetry code i</th>
</tr>
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<tr>
<td><strong>MeP5A-1·2·2(CCl₄)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>C46–I1···N1A'</td>
<td>2.75(1)</td>
<td>171.5(4)</td>
<td>1–x, –y, 1–z</td>
</tr>
<tr>
<td>C46–I1···N1'</td>
<td>2.784(7)</td>
<td>175.3(02)</td>
<td>1–x, –y, 1–z</td>
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<tr>
<td>C51–I2···N3'</td>
<td>2.792(4)</td>
<td>176.3(2)</td>
<td>1–x, 1–y, –z</td>
</tr>
<tr>
<td><strong>MeP5A-1·3·1.5(toluene)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C49–I2···N1</td>
<td>2.753(2)</td>
<td>172.9(1)</td>
<td></td>
</tr>
<tr>
<td>C46–I1···N3'</td>
<td>2.734(2)</td>
<td>174.11(8)</td>
<td>–1+x, y, 1+z</td>
</tr>
<tr>
<td><strong>MeP5A-1·4₂·2(H₂O)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1W–H1W···N3A'</td>
<td>3.11(5)</td>
<td>156</td>
<td>x, y, 1+z</td>
</tr>
<tr>
<td>O1W–H1W···N3B'</td>
<td>3.32(4)</td>
<td>165</td>
<td>1–x, y, 1.5–z</td>
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<tr>
<td>O2W–H2W···N3B'</td>
<td>2.82(6)</td>
<td>171(8)</td>
<td>x, y, –1+z</td>
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<td>C27–I2···O1W'</td>
<td>2.89(1)</td>
<td>173.8(2)</td>
<td>1–x, 1–y, 1–z</td>
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<td>C27–I2···N12A'</td>
<td>3.31(6)</td>
<td>158(2)</td>
<td>1–x, 1–y, 1–z</td>
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<tr>
<td>C24–I1···O2W'</td>
<td>2.978(5)</td>
<td>171.6(2)</td>
<td>0.5–x, 0.5–y, –0.5+z</td>
</tr>
</tbody>
</table>

The crystal structure of MeP5A·1·4₂·2(H₂O)

MeP5A·1·4₂·2(H₂O) crystallizes in the Pbcn space group. The asymmetric part of the unit cell contains one molecule of 4, one half of MeP5A molecule that is situated around twofold symmetry axis, one molecule of 1 having half occupancy due to disorder and two halves of water molecules – one molecule is disordered (O1W) and the other (O2W) is located at the twofold axis. The molecules of 1 and water molecules are accommodated within channels formed by Me5PA and 4. The crystallographic symmetry of the empty channel is higher than the symmetry of the molecular assembly formed by 1 and water molecules enclosed within the channel. As a result there are two possible arrangements of the molecules within the channel that are mutually related by a dyad perpendicular to the channel axis. A closer inspection shows that the molecules within the channel are ordered and the observed disorder arises from a statistical distribution of the two different channels over the crystal. The arrangement of molecules of 1 and water molecules within the ordered channel is shown in Fig. S2. The imidazolyl N3A atom is hydrogen bonded to the water molecule O1w that is also involved in halogen bond with the I2 atom of 4. The O2W molecule that is situated at the twofold axis forms two halogen bonds with I1 and very weak hydrogen bond with N3B. This N3B atom is additionally involved in halogen bonding with I2. Geometry of intermolecular interactions in MeP5A·1·4₂·2(H₂O) is given in Table S1. The halogen and hydrogen bond
interactions of the pseudorotaxane MeP5A-1 with water molecules and iodine atoms of 4 assemble these entities into a 3D framework. The crystal structure of MeP5A-1.4\textsubscript{2}·2(H\textsubscript{2}O) is formed by a mutual interpenetration of two such 3D frameworks what is schematically shown in Fig. S3 where the two frameworks are presented in different colors and the content of the channel that is oriented perpendicular to the plane of the drawing is represented by a circle. Interestingly, the 3D polypseudorotaxane framework is chiral and the interpenetrating frameworks are of the opposite chirality.

Figure S2. Hydrogen bonds and halogen bonds in MeP5A-1.4\textsubscript{2}·2(H\textsubscript{2}O). MeP5A and O2W are located on a twofold symmetry axis, whereas 1 and O1W are disordered over two sides related by twofold axis (disorder is not shown).

Figure S3. Two interpenetrated chiral 3D frameworks generated via O–H···N hydrogen bonds and C–I···O and C–I···N halogen bonds in MeP5A-1.4\textsubscript{2}·2(H\textsubscript{2}O). The channels comprising the molecules of 1 and water molecules are represented schematically by circles.
References
