Supporting Information for

The Effect of Halogen Bonding on the Packing of Bromine Substituted Pyridine and Benzyl Functionalized Resorcinarene Tetrapodands in the Solid State

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Details of the crystallization experiments

Structure I (C_{64}H_{64}O_{8}Br_{4}N_{4}·CHCl_{3}): Colorless plate crystals (0.15 × 0.05 × 0.05 mm) were grown from methanol-chloroform solution of 3 by slow evaporation at room temperature within a couple of days.

![Ellipsoid plot at 50% probability for structure I of compound 3.](image)

Structure II (C_{64}H_{64}Br_{4}N_{4}O_{8}·2.5 CH_{2}Cl_{2}): Colorless thin plate crystals (0.16 × 0.10 × 0.03 mm) were grown from methanol-dichloromethane solution of 3 by slow evaporation at 2–8 °C within a couple of days.
Fig S2. Ellipsoid plot at 50 % probability for structure II of compound 3.

**Structure III** (C_{64}H_{64}O_{8}Br_{4}N_{4}·3 CHCl_{3}): Colorless block crystals (0.35 × 0.20 × 0.15 mm) were grown from methanol-chloroform solution of 3 that contained excess amount of Cu(Cl_{4}O)_{2}·6 H_{2}O during few months.

Fig S3. Ellipsoid plot at 50 % probability for structure III of compound 3.

**Structure IV** (C_{68}H_{68}O_{8}Br_{4}·CH_{3}CN): Colorless block crystals (0.20 × 0.15 × 0.05 mm) were grown from acetonitrile-chloroform solution of 4 by slow evaporation within a couple of days.
Conformational properties of the resorcinarene derivatives 3 and 4

Table S1 Conformational properties of the resorcinarene core in the structures I–IV

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihedral angle(^{a}/°)</td>
<td>97.21/106.77, 167.18/170.64</td>
<td>103.44/103.81, 167.25/174.30</td>
<td>103.81/103.44, 167.59/169.94</td>
<td>87.04/83.82, 174.60/179.30</td>
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<tr>
<td>Angle(^{b}/°)</td>
<td>24.23/157.85</td>
<td>27.46/157.82</td>
<td>27.25/161.80</td>
<td>-8.91/174.09</td>
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<tr>
<td>Tilt/°</td>
<td>6.67</td>
<td>8.71</td>
<td>0.05</td>
<td>2.39</td>
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<tr>
<td>Twist/°</td>
<td>5.42</td>
<td>8.13</td>
<td>0.22</td>
<td>2.02</td>
</tr>
<tr>
<td>Distance(^{c}/Å)</td>
<td>5.532/7.953</td>
<td>5.610/7.929</td>
<td>5.593/7.972</td>
<td>4.834/8.028</td>
</tr>
</tbody>
</table>

\(^{a}\) Dihedral angles between the methine plane (C7-C14-C21-C28) and the upright and horizontal aromatic rings. \(^{b}\) Between the opposite aromatic ring planes. \(^{c}\) Between the opposite aromatic ring centroids.

Fig S4. Ellipsoid plot at 50 % probability for structure IV of structure 4.

Fig S5. a) Tilt and b) twist angles of the pyridine and the benzyl functionalized resorcinarene tetrapodands (shown for structure II). Hydrogen atoms have been omitted for clarity.
Additional figures for the structures of the bromopyridine- and pyridine derivatives of tetramethoxy resorcinarene

**Fig S6.** Front views of dimer pairs of a) structure I, b) structure II and c) structure III of compound 3.
The differently positioned pyridine rings (A) of the right-handed isomers have been circled and hydrogen atoms have been omitted for clarity.

**Fig. S7** a) Front and b) top views of the structure CCDC 666176 published by McIldowie et al. The aromatic edge-to-face interaction (2.70 Å) between the pyridine ring and the horizontal aromatic ring is shown with blue line.

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1 M. J. McIldowie, M. Mocerino, M. I. Ogden, B. W. Skelton, Tetrahedron, 2007, 63, 10817–10825. See structure: CCDC 666176
$^1$H and $^{13}$C NMR spectra of compound 3

(in CDCl$_3$ at 30 °C)
\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of compound 4

(in CDCl\(_3\) at 30 °C)