**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** ($C_{64}H_{64}O_8Br_4N_4 \cdot CHCl_3$): 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.

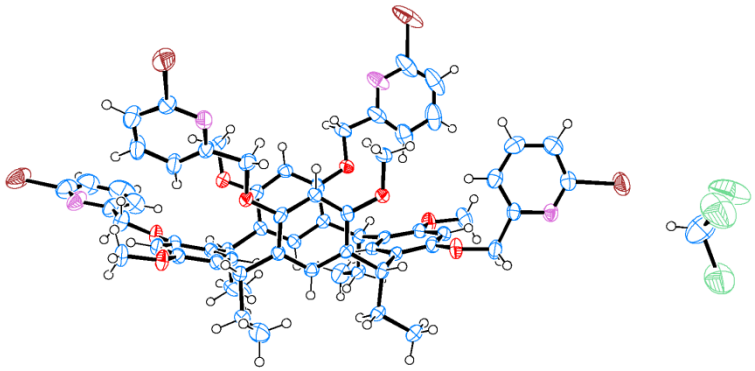


**Fig S1.** Ellipsoid plot at 50 % probability for structure **I** of compound **3**.

Structure **II** ($C_{64}H_{64}Br_4N_4O_8 \cdot 2.5\ CH_2Cl_2$): 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.

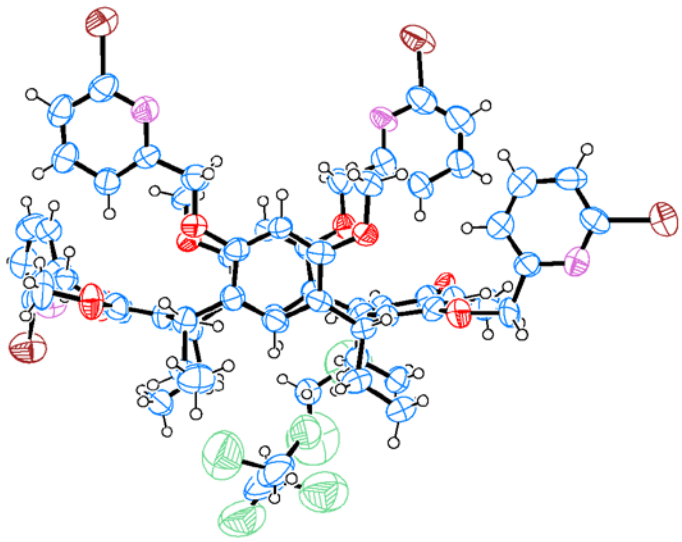


**Fig S2.** Ellipsoid plot at 50 % probability for structure **II** of compound **3**.

Structure **III** ($C_{64}H_{64}O_8Br_4N_4 \cdot 3\ CHCl_3$): Colorless block crystals (0.35 × 0.20 × 0.15 mm) were grown from methanol-chloroform solution of **3** that contained excess amount of $Cu(Cl_4O)_2 \cdot 6\ H_2O$ during few months.

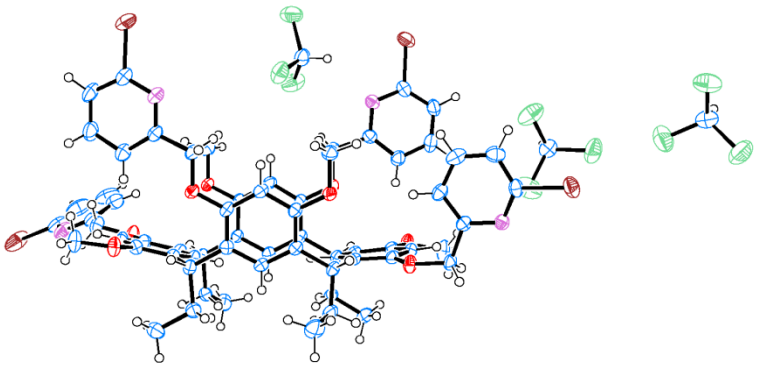


**Fig S3.** Ellipsoid plot at 50 % probability for structure **III** of compound **3**.

Structure **IV** ($C_{68}H_{68}O_8Br_4 \cdot CH_3CN$): 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.

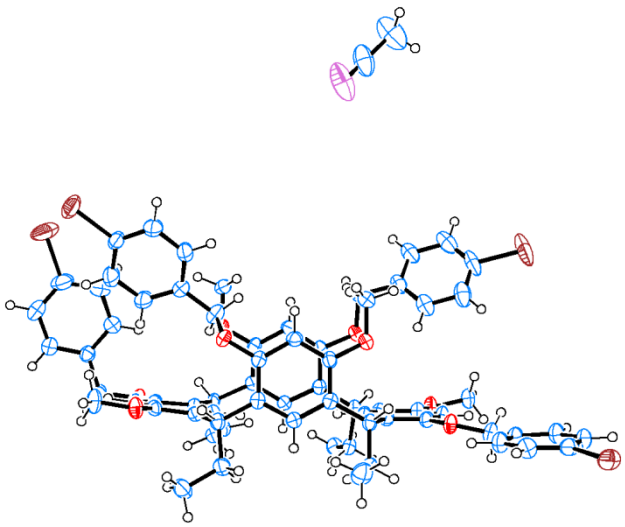


**Fig S4.** Ellipsoid plot at 50 % probability for structure **IV** of structure **4**.

## Conformational properties of the resorcinarene derivatives 3 and 4

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

| | **I** | **II** | **III** | **IV** |
|---|---|---|---|---|
| Dihedral angle[a]/° | 97.21/106.77, 167.18/170.64 | 103.44/103.81, 167.25/174.30 | 103.81/103.44, 167.59/169.94 | 87.04/83.82, 174.60/179.30 |
| Angle[b]/° | 24.23/157.85 | 27.46/157.82 | 27.25/161.80 | -8.91/174.09 |
| Tilt/° | 6.67 | 8.71 | 0.05 | 2.39 |
| Twist/° | 5.42 | 8.13 | 0.22 | 2.02 |
| Distance[c]/Å | 5.532/7.953 | 5.610/7.929 | 5.593/7.972 | 4.834/8.028 |

[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.

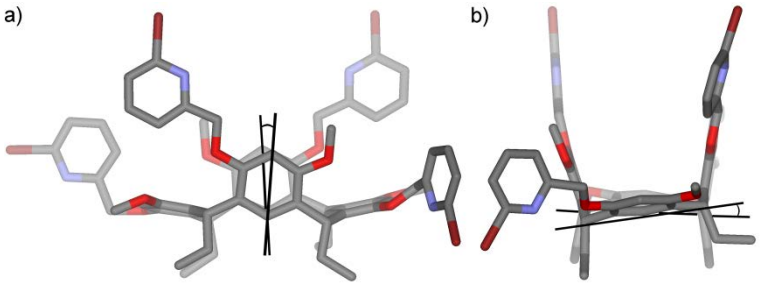



**Fig S5.** a) Tilt and b) twist angles of the pyridine and the benzyl functionalized resorcinarene tetrapodands (shown for structure **II**). Hydrogen atoms have been omitted for clarity.

**Additional figures for the structures of the bromopyridine- and pyridine derivatives of tetramethoxy resorcinarene**

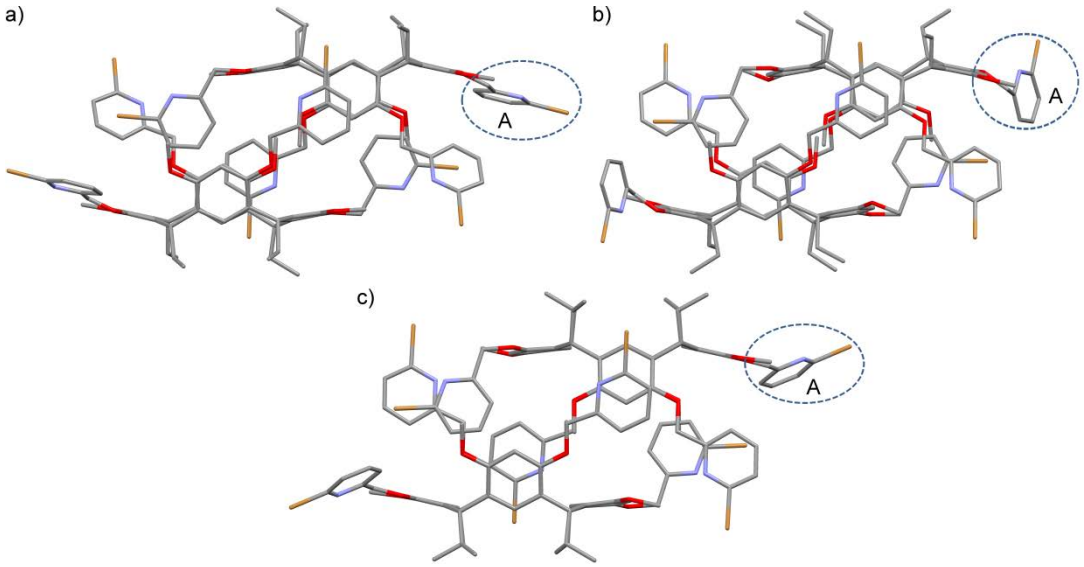



**Fig S6.** Front views of dimer pairs of a) structure **I**, b) structure **II** and c) structure **III** of compound **3**. The differently positioned pyridine rings (A) of the right-handed isomers have been circled and hydrogen atoms have been omitted for clarity.

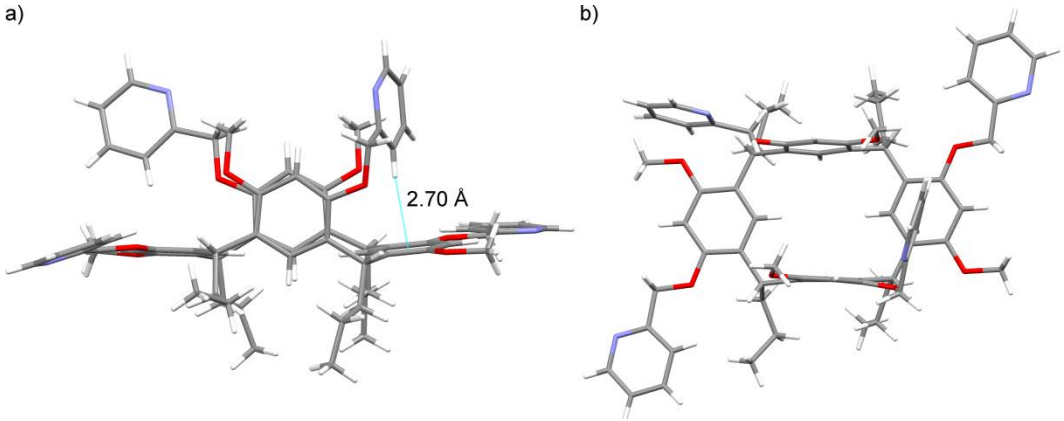
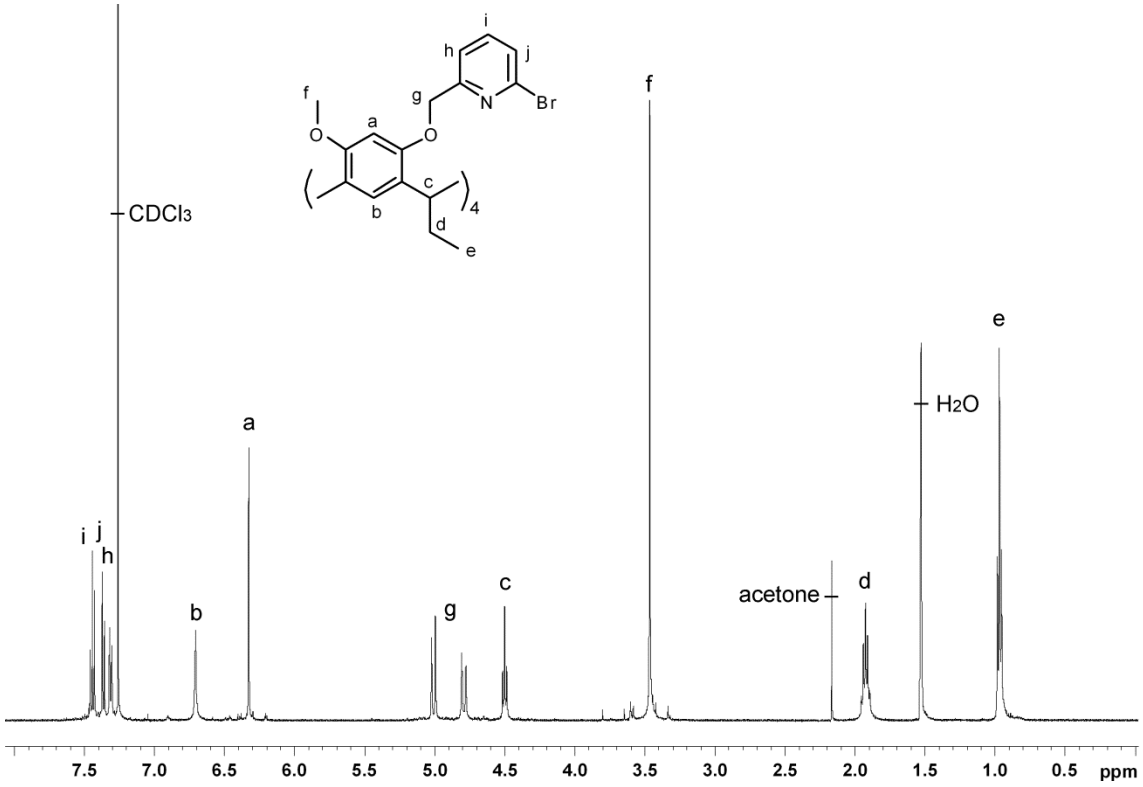


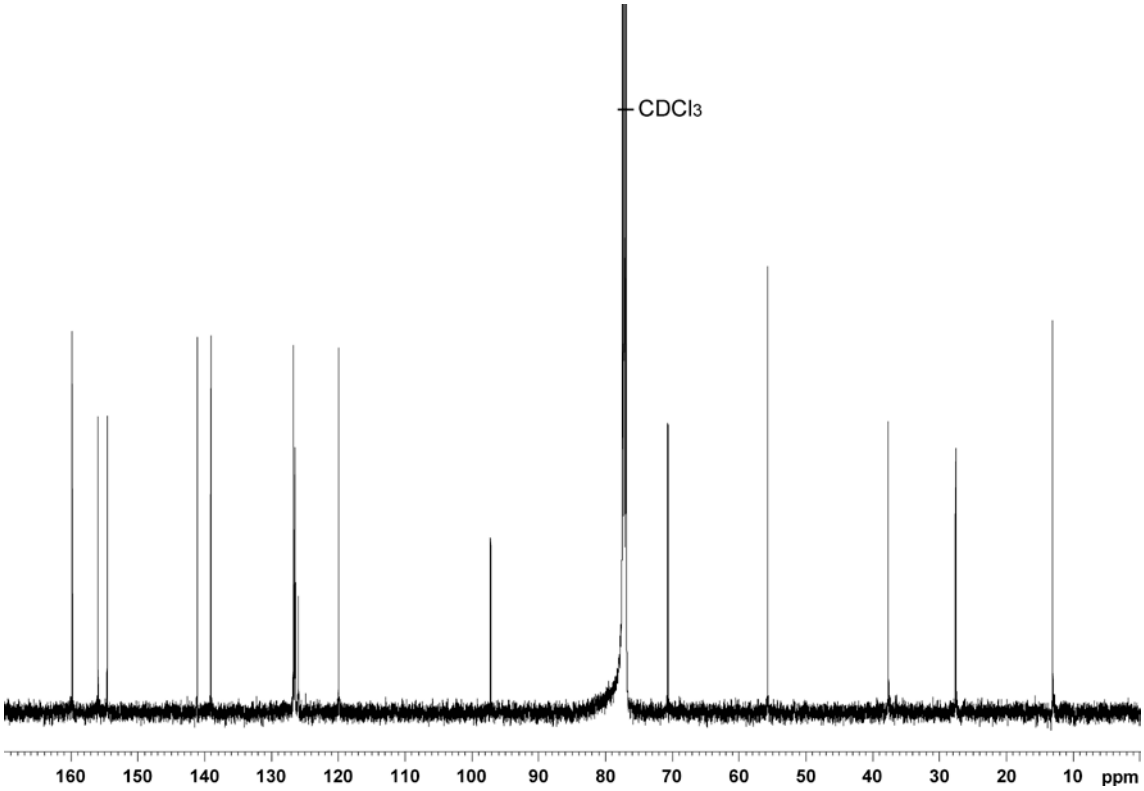

**Fig. S7** a) Front and b) top views of the structure CCDC 666176 published by McIldowie *et al.*[1] The aromatic edge-to-face interaction (2.70 Å) between the pyridine ring and the horizontal aromatic ring is shown with blue line.

[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)



**$^{1}$H and $^{13}$C NMR spectra of compound 4**

(in $CDCl_3$ at 30 °C)