

**3-Pyridineboronic Acid → Boroxine → Pentadecanuclear Boron Cage → 3D
Molecular Network: A Sequence Based on two Levels of Self-Complementary Self-
Assembly**

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Supplementary Information

1. Experimental Procedure

A solution of 3-pyridineboronic acid (0.200 g, 1.63 mmol) in benzene (120 mL) was heated to reflux with the use of a Dean Stark trap. After 3 h the solvent was partially evaporated (\approx 80 mL) and the reaction mixture was allowed to cool to room temperature. A white solid precipitated that was separated by filtration and recrystallized from ethanol to give crystals that were suitable for single-crystal X-ray diffraction analysis. Yield: 180 mg, 96 %. M.p. 240 °C (dec.).

2. Single-crystal X-ray diffraction analysis

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$, monochromator: graphite). Frames were collected at $T = 293 \text{ K}$ via ω/ϕ -rotation at 10 s per frame (Bruker-SMART, Version 5.618, 2000). The measured intensities were reduced to F^2 and corrected for absorption with SADABS (Bruker-SAINT-NT, Version 6.04, 2001). Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the Bruker-SHELXTL-NT program package (version 6.10, 2000). Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. Although relatively large crystals could be grown, the R

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values are somewhat elevated. This can be attributed to the disorder of the molecular structure (vide infra), the partial disorder of the solvent molecules, the large unit cell and the weak diffraction at theta angles $> 20^\circ$. The low resolution of the data affects the reliability of the bond lengths and angles, intermolecular distances and the refinement of the anisotropic thermal parameters.

Since the space group is centrosymmetric ($R\bar{3}$) and since asymmetric tectons have been used for the assembly, the boroxine-pentamer **3** crystallized in form of the racemate. Interestingly, the enantiomers are disordered around the same crystallographic site within the crystal lattice, which can be attributed to the apparent C_2 -symmetry of the bridging 3-pyridyl fragments. The difference between the two enantiomers lies in the mirror-reflected N \rightarrow B and B-C bond distribution between the boroxine rings within the pentameric cage. The occurrence of the disorder is not surprising, if it is considered that the two enantiomers have the same periphery (Figure S1 shows one of the two enantiomers). EXYZ and EADP instructions have been used for the definition of the boron-coordinated nitrogen and carbon atoms (occ = 0.5). Therefore, the B-C and N \rightarrow B bond lengths given in the CIF file are average values for the two bond types.

The unit cell contains 18 boroxine-pentamer cages, 36 ethanol molecules and 66 water molecules. Of the ethanol molecules, one fraction is located on crystallographic C_3 axes (occ = 0.33; 6 molecules) and the remaining are disordered over three positions in a single type of crystallographic solvent cavity (occ = 0.66, 0.33 and 0.66; 30 molecules). Of the 66 water molecules, the first fraction is located on crystallographic C_3 axes (occ = 0.33 and 0.33; 12 molecules), the second fraction is disordered over two positions (occ = 0.41 and 0.59; 18 molecules), and the remaining part is located at general positions (occ = 1.00; 36 molecules). Hydrogen atoms could only be calculated for those ethanol molecules that were not localized on crystallographic C_3 axes. However, the O(31B)-H(31D) and O(31C)-H(31G) O-H groups do not form hydrogen bonds, indicating that the riding model used to model these hydrogen atoms might have placed them not correctly because of the low resolution of the data. Hydrogens have not been included for the water molecules.

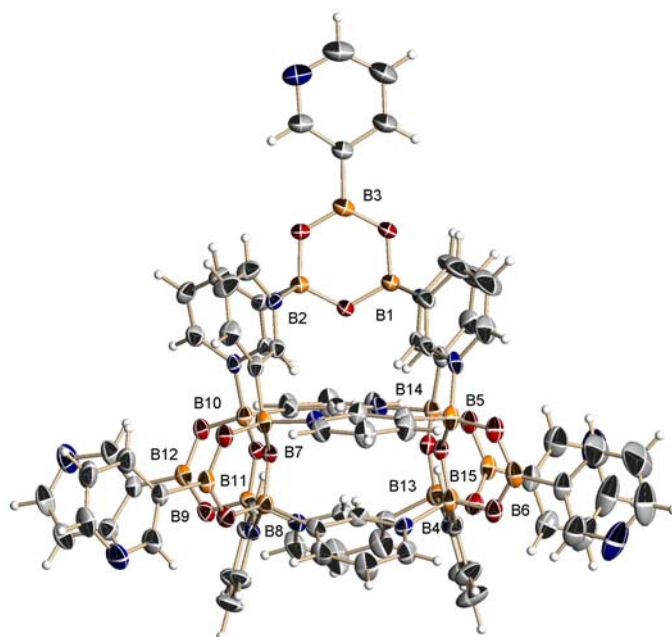


Figure S1 Perspective view of the molecular structure of one of the enantiomers present in the crystal lattice of compound **3**: (*1S,2S,4R,5R,7R,8R,10R, 11R,13R,14R*)-**3** (ellipsoids at 30 % level). Consecutive numbering for the boron atoms is given.

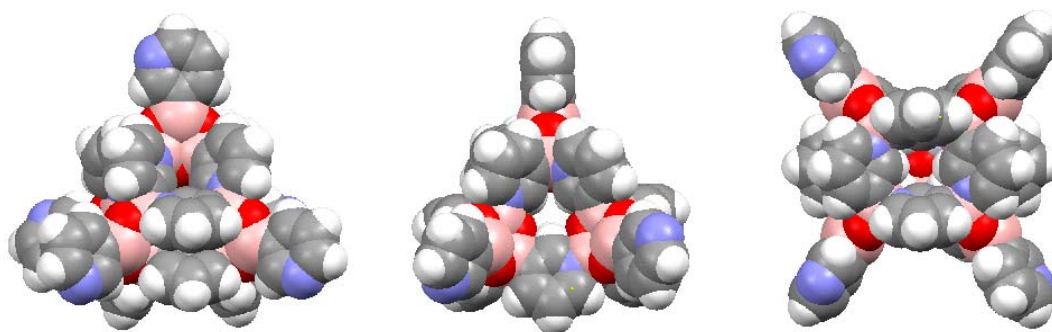


Figure S2 Different perspective views of the boroxine-pentamer **3** (space-filling models).

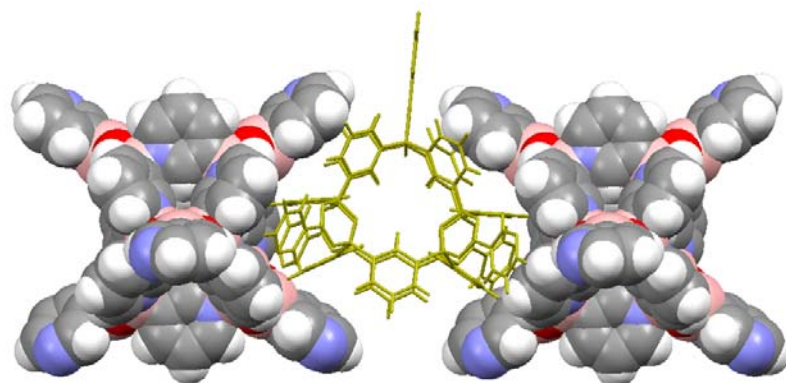
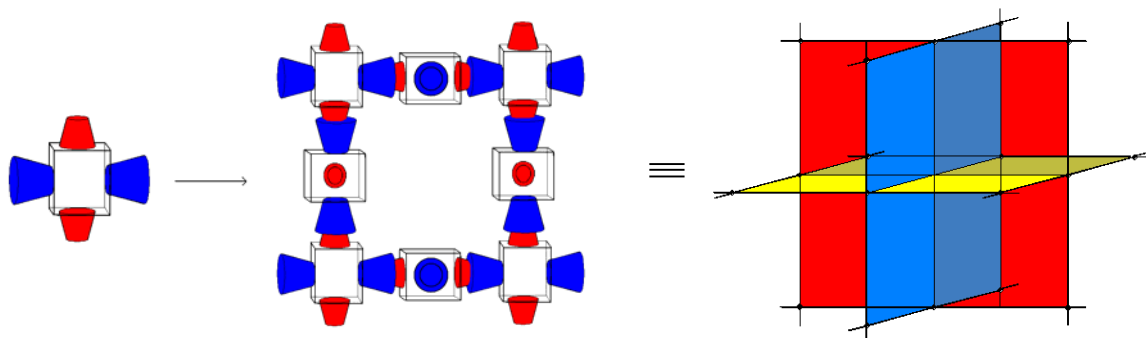


Figure S3 Fragment of the crystal lattice of compound **3**, showing the supramolecular synthon formed between the concave and convex macrocycles described in Figure 2f (main text).



Scheme S1 Graphic representation of the 3D molecular network generated from the self-complementary boroxine-pentamer tectons described in Figures 1, 2, S1 and S2. The blue cones represent the larger concave macrocycles, the red ones the smaller convex macrocycles.

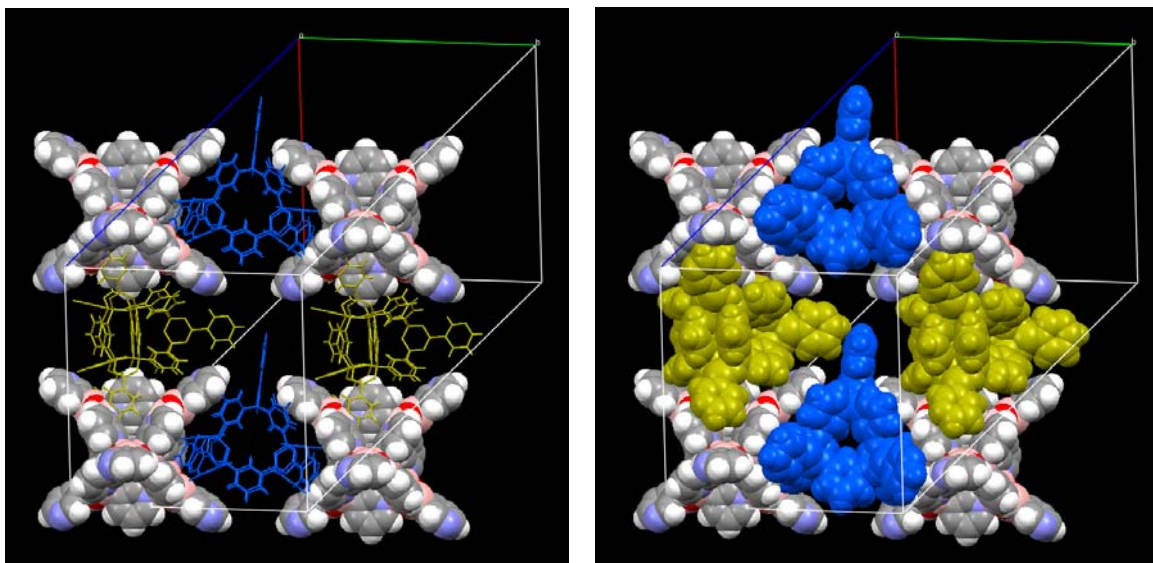


Figure S4 Different views of the crystal lattice of compound **3**, showing the connectivity of the self-complementary boroxine-pentamer tectons that gives rise to an approximate rectangular 3D molecular network. Different types of representation (spacefill and stick) and colors have been used to highlight the three different tecton orientations.

3. Spectroscopic data for the boroxine-pentamer **3**

IR (KBr) $\tilde{\nu}_{\max}$: 3391 (br, w), 3085 (w), 3031 (w), 2959 (w), 2926 (w), 1609 (m), 1587 (m), 1477 (m), 1421 (s), 1359 (s), 1312 (s), 1258 (m), 1201 (m), 1157 (m), 1084 (s), 999 (m), 861 (m), 806 (m), 755 (m), 714 (s), 639 (m), 590 (m), 479 (w) cm^{-1} .

^1H NMR (400 MHz, CD_2Cl_2 , 20 °C, TMS): see Table S1. **^{11}B NMR** (128 MHz, CD_2Cl_2 , 20 °C, $\text{BF}_3\cdot\text{OEt}_2$, external standard) δ = 35.3, 32.5, 5.4 -1.9 and -19.3 ppm.

Elemental Analysis: Calcd for $\text{C}_{75}\text{H}_{60}\text{B}_{15}\text{N}_{15}\text{O}_{15}\cdot 2\text{EtOH}\cdot 3.67\text{H}_2\text{O}$ (1731.82 g/mol) (%): C, 54.78, H, 4.63, N, 12.13; found: C, 54.58 H, 4.50, N, 11.50. This result is also in agreement with the TGA spectrum, which, in the temperature range from 20 to 210 °C, showed an initial weight loss of 8.90 % (calculated: 9.14 %) that can be attributed to the evaporation of the solvent molecules.

MS (ESI⁺): m/z (%): 1574.61 ($[M+H]^+$, 2), 1260.49 (tetramer, 13%), 945.37 (trimer, 43), 630.25 (dimer, 13) and 316.13 (monomer, 100).

MS (FAB⁺): *m/z* (%): 1258.84 (tetramer, 1), 944.13 (trimer, 3), 629.42 (dimer, 3) and 314.71 (monomer, 92).

From the NOESY experiment the signals for the H_a hydrogens in the pyridyl rings labeled 4 (Figures 1 and 2 shown in the main text) could be located. A further analysis of the COSY spectrum allowed for the assignment of the whole spectrum (Table S1).

According to the pseudo C₂-symmetry of the cage observed in the solid state, of the total of fifteen pyridyl rings eight have different chemical environments (labeled 1-8 in Figure 1) in a stoichiometry of 2:2:2:2:2:1:2:2, thus giving a total of 60 hydrogen atoms (4 for each of the 15 pyridyl rings). As mentioned in the manuscript, the signals for the 60 hydrogen atoms are distributed over three regions and integrate in the expected proportion of 15:30:15 (see Figure S5a). The full assignment of the spectrum could be achieved considering the following:

- a) Pyridyl ring 6 integrates only for one hydrogen in the singlet region.
- b) Within the center of the cavity, the H_a hydrogen of pyridyl ring 4 interacts with H_a of pyridyl rings 1,2 and 5 (as seen from the intermolecular distances in the solid state that are furthermore evidenced by the NOESY experiment, Figure S5c). Please see also Figures 2b and 2c in the manuscript, which are views from the top and the bottom.
- c) Pyridyl rings 1 and 2 as well as 7 and 8 should have very similar chemical environments and therefore chemical shifts.
- d) The signal shape allows for the distinction of the singlets (H_a), doublets (H_b and H_d) and triplets (H_c).
- e) The intensity of the crosspeaks in the COSY and NOESY spectra helps to identify the nearest neighbors within the pyridyl group and within the molecule center, respectively.

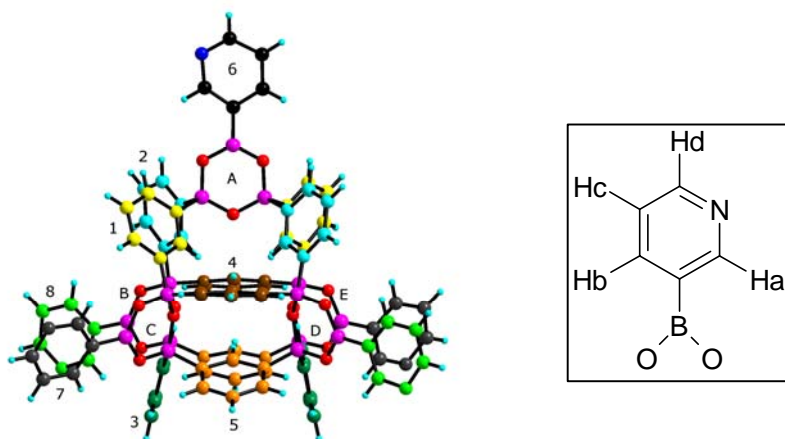
The ¹¹B NMR spectrum (Figure S5) shows five signals, two in the region for tri-coordinate boron atoms ($\delta = 35.3$ and 32.5 ppm), and three in the region for tetra-coordinate boron atoms ($\delta = 5.4, -1.9$ and -19.3 ppm). Two of the five signals are relatively sharp and have been assigned to the boron atoms located at the apical position of the

pyramidal-shaped cage (boroxine A in Figure 1, $\delta = 32.5$ and 5.4 ppm). The remaining three signals are broadened and have been assigned to the boron atoms located at the basal positions of the molecular skeleton (boroxines B-E, $\delta = 35.3$, -1.9 and -19.3 ppm), considering that intramolecular contacts enhance the velocity of relaxation of excited boron nuclei. It should be noticed that ^{11}B has a nucleus with a quadrupolar moment ($I = 3/2$).

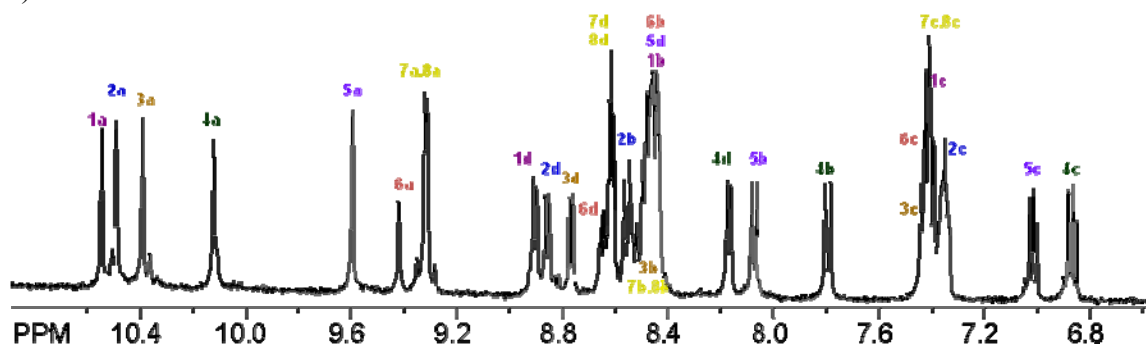
Table S1. ^1H NMR (400 MHz) chemical shifts (reference TMS, in ppm) for the boroxine-pentamer **3** (in CD_2Cl_2). For numbering of the pyridyl rings see Figure 1 (main text).

Pyridyl ring	δH_a (m, i)	δH_b (m, i)	δH_c (m, i)	δH_d (m, i)
1 ^a	10.54 (s, 2)	8.49 (m, 2)	7.41 (m, 2)	8.90 (dd, 2)
2 ^a	10.48 (s, 2)	8.55 (dt, 2)	7.34 (m, 2)	8.86 (dd, 2)
3	10.39 (s, 2)	8.43 (m, 2)	7.43 (m, 2)	8.76 (dd, 2)
4	10.11 (s, 2)	7.80 (dt, 2)	6.86 (dd, 2)	8.17 (dd, 2)
5	9.59 (s, 2)	8.07 (dt, 2)	7.02 (dd, 2)	8.46 (m, 2)
6	9.41 (s, 1)	8.55 (dt, 1)	7.36 (m, 1)	8.65 (dd, 1)
7 ^b	9.32 (s, 2)	8.44 (m, 2)	7.43 (m, 2)	8.60 (m, 2)
8 ^b	9.31 (s, 2)	8.46 (m, 2)	7.36 (m, 2)	8.62 (m, 2)

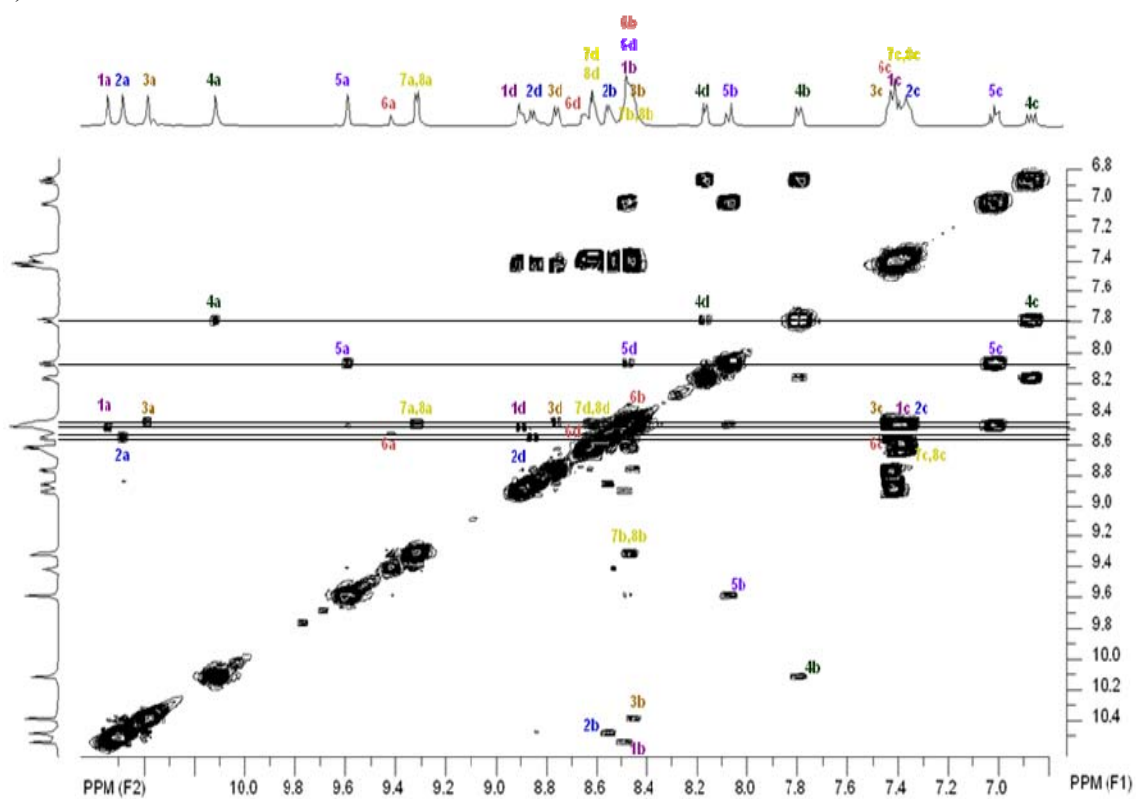
^{a, b} Signals may be interchanged.



a)



b)



c)

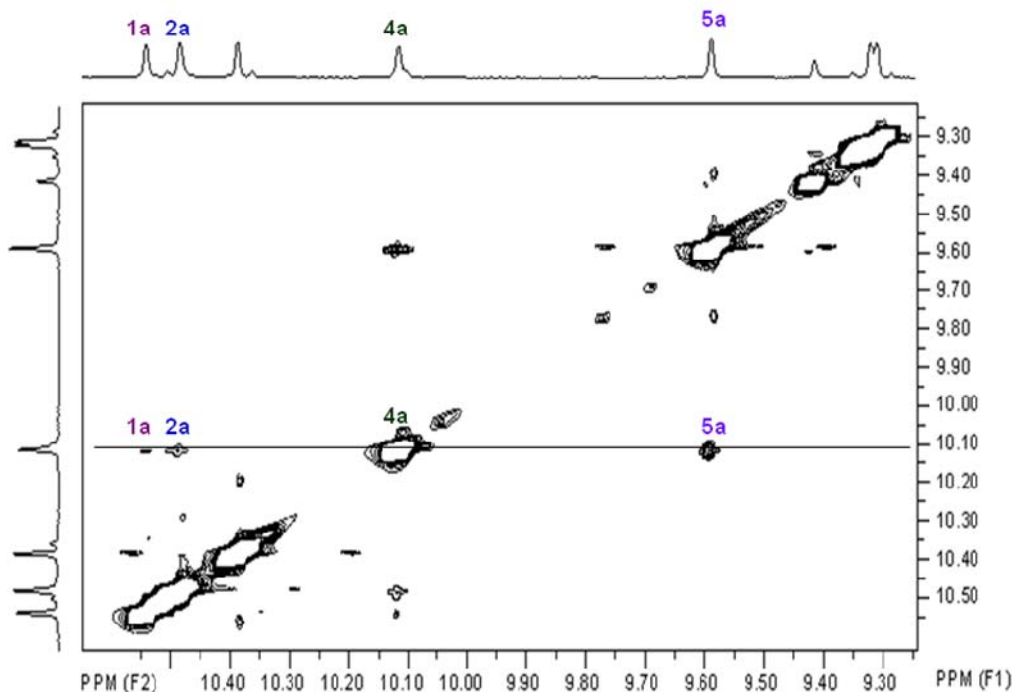


Figure S5 ^1H NMR (a), COSY (b) and NOESY (c) spectrum for the boroxine-pentamer **3**.

Important notes: Different colors have been used to highlight the assignment of the eight pyridyl groups having different chemical environments (1-8 in the molecular structure given above). The horizontal lines in (b) indicate the coupling interactions of the H-atoms belonging to the same pyridyl ring (H_a , H_b , H_c and H_d). As indicated in Table S1, the assignment for the pyridyl rings labeled 1 and 2 as well as 7 and 8 might be interchanged, since the chemical environment is very similar.

The NOESY spectrum evidences the close contacts between the H_a hydrogen atoms directed into the molecule center (pyridyl groups labeled 1, 2, 4 and 5).

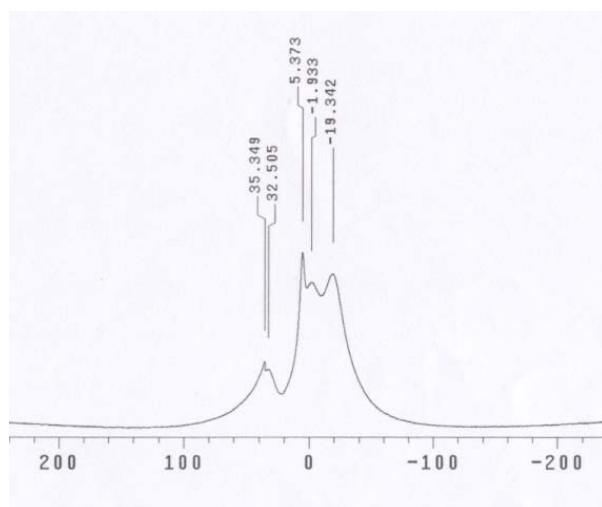


Figure S6 ^{11}B NMR (128 MHz, external reference $\text{BF}_3\cdot\text{OEt}_2$) spectrum of compound **3** (in CD_2Cl_2).

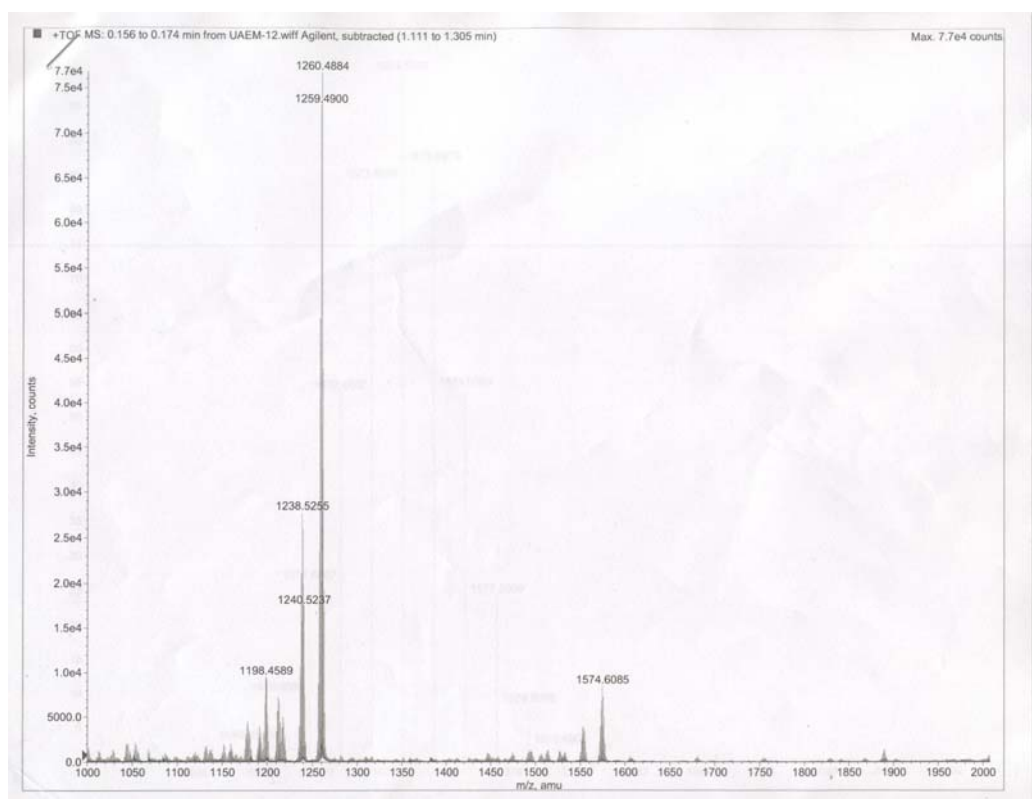
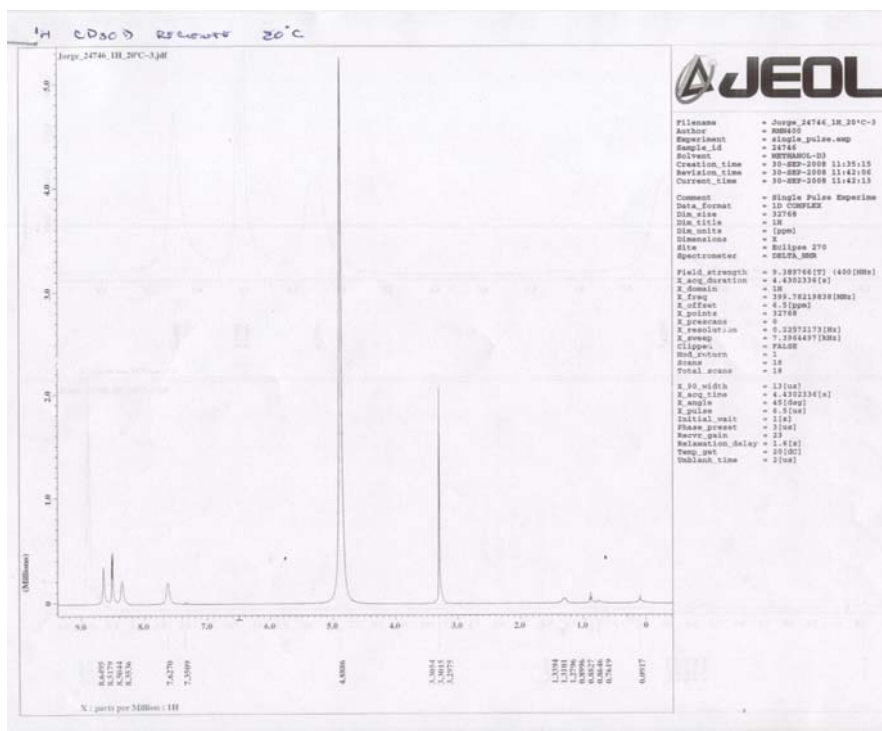


Figure S7 Mass spectrum (ESI^+) of compound **3** showing peaks corresponding to the molecular ion (1574.61, 2%) and a fragment having tetrameric (1260.49, 13%), composition.

a)



b)

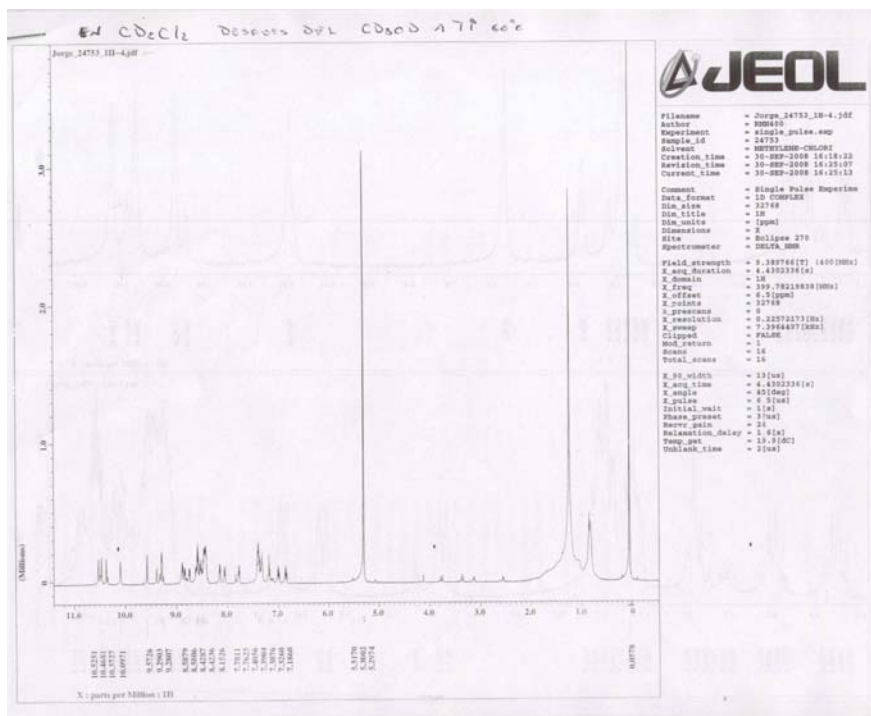


Figure S8 ¹H NMR spectrum of compound **3** a) in CD₃OD (20 °C). b) in CD₂Cl₂ after evaporation of the solvent used for the first experiment (CD₃OD).

Important notes

The spectra shown in Figure S8 correspond to the following experiment: First, a sample of the boroxine-pentamer was dissolved in CD₃OD and the ¹H NMR spectrum was measured. It agreed with the spectrum reported for the tris(3-pyridyl)boroxine **2** (please see page S6 in reference 20), thus indicating dissociation or a dynamic dissociation-recombination exchange process in this solvent, in which, however, the equilibrium is shifted to the dissociated species. Then we evaporated the methanol and re-dissolved the solid in CD₂Cl₂, giving a ¹H NMR spectrum that was identical to that given in Figures 4 and S5a, thus showing that the boroxine molecules reassembled again to the cage.

These results and the literature^[9a,15-16] are therefore in full agreement with the reaction sequence proposed in Scheme 1.