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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A pentadecanuclear boroxine-cage has been generated through a single-component self-assembly process, and serves as a twofold concave–convex self-complementary tecton for the assembly of a complex 3D molecular network.

The advances achieved in metal-directed and molecular self-assembly during the last few years indicate that supramolecular architectures such as metal–organic macrocycles, cages, capsules, and infinite 1D, 2D and 3D assemblies will be of significant relevance for applications in the fields of separation, storage, sorption, sensing, and catalysis.[1] Such finite or infinite assemblies can be generated either from single self-complementary or multiple complementary tectons.[2]

Albeit HCNO-based organic chemistry has been employed successfully for the generation of molecular networks through non-covalent interactions,[2a] so far it lacks the capability to create crystalline materials of covalently bound 2D and 3D infinite structures, an exception being only the modifications of elemental carbon. The reason is that covalent C–(HNO) bonds are kinetically and thermodynamically too stable to undergo the reversible bond-cleavage required for the self-repairing capability during the self-assembly process.[3] Among the second-row elements boron has unique features required for self-assembly: (i) with amines, it forms complexes with reversible, but still relatively strong coordinative N→B bonds, (ii) with hydroxyl-bearing reagents reversible ester functions are generated, in particular in trigonal boron complexes, and (iii) boron can have either tri- or tetra-coordinate environments, which provides it with the capability of functioning either as a triginal-planar or a tetrahedral node in molecular assemblies.[4]

Using trivalent boron atoms macrocycles,[5] polymers,[6] cages[7] and porous covalent organic frameworks (COFs)[8] have been prepared. With the hydrolytically more stable tetravalent boron atoms macrocycles,[9,10] helicoidal structures,[11] cages[9h,12] and rotaxanes[13] are known. There are also some reports on assemblies in which boronate building blocks have been employed in combination with metal-ion nodes.[5d,14]

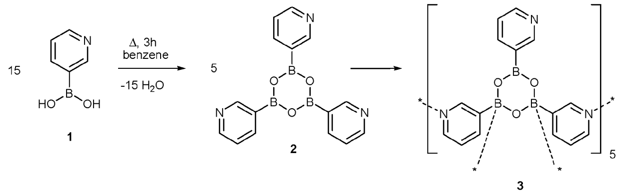
The above-mentioned assemblies have been created mostly from two or more complementary tectons,[2] and belong therefore to the class of multi-component systems.[2b] Boron assemblies generated from a single component (self-complementary tecton) are very rare so far,[5a,12b] albeit it is evident that simpler structural motifs have the advantage of facilitating the predictability and tunability of higher-order structures.

Herein, we report on the single-component self-assembly of a pentameric boroxine cage, which has the unique property to serve as a twofold concave–convex tecton for the generation of a complex 3D molecular network. The reaction sequence involves two levels of self-complementary self-assembly.

Compound **3** was prepared in a one-pot reaction from a total of 15 molecules of 3-pyridineboronic acid (3-pyba) in benzene. Recrystallization from ethanol gave crystalline material of the title compound in >95% yield in a form suitable for single-crystal X-ray diffraction analysis.‡ From known boron chemistry it can be assumed that the compound was formed in a two-step reaction, consisting (i) in the condensation reaction of three molar equivalents of 3-pyba (**1**) to give tris(3-pyridyl)boroxine **2** that (ii) further assembled in a self-complementary way through coordinative N→B boron interactions to the boroxine-pentamer **3** (Scheme 1).[9a,15,16]

The perspective views of the molecular structure given in Fig. 1, 2a–c and S1, S2† show that in compound **3** five boroxine molecules are linked through a total of ten N→B bonds to a pentadecanuclear boron cage with pseudo C_2-symmetry. Thus, each boroxine molecule acts simultaneously as a twofold donor and acceptor unit in the assembly, in which ten boron atoms have distorted tetrahedral geometry and five boron atoms are trigonal planar. Each tetra-coordinate boron atom is chiral; however, since the assembly has been obtained from an achiral tecton, the racemate has been formed. The enantiomers have the boron atom configurations (1*S*,2*S*,4*R*,5*R*,7*R*,8*R*,10*R*,11*R*,13*R*,14*R*)-**3** and *ent*-**3** (atom numbers are given in Fig. S1†), and coexist within the crystal lattice at the same crystallographic site.‡

The molecular cage has *pseudo*-C_2-symmetry with an overall dimension of 16.6 × 19.1 × 19.4 Å^3, and resembles the shape



Scheme 1 Proposed two-step self-assembly of the boroxine-pentamer **3** from a single component (3-pyridineboronic acid).

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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, ^{11}B NMR spectrum, additional figures and schemes. CCDC 695836. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814918f

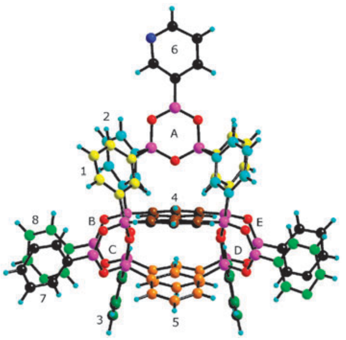

Fig. 1 Perspective view of the molecular structure of the boroxine-pentamer **3**. Boron and oxygen are represented as pink and red spheres, respectively. The 3-pyridyl groups are shown in different colors in order to highlight those having different chemical environments in solution.

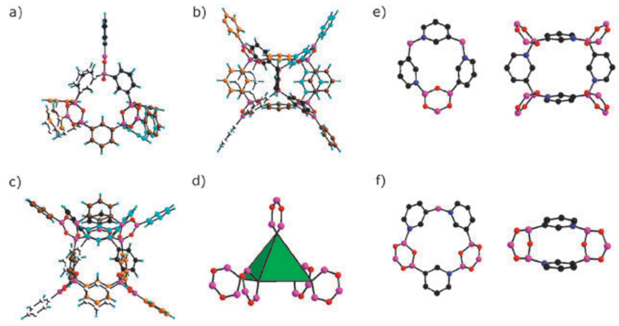

Fig. 2 Different perspective views of the boroxine-pentamer **3** (a–c), representation of the molecular topology (d), and presentation of the boron macrocycles present in the assembly (e–f).

of an approximate square-pyramidal polyhedron (Fig. 2d). This topology is unusual, since building blocks with C_3-symmetry frequently give assemblies corresponding to the Platonic and Archimedean solids.[17] The faces of the assembly consist of four different calixarene-type macrocyclic rings (Fig. 2e–f), of which only the tetramer (Fig. 2e on the right) has been found previously in a boron-containing discrete molecule.[18,19]

Interestingly, the largest and the smallest macrocycle (Fig. 2f) are complementary concave and convex units for the formation of a supramolecular synthon (Fig. S3†), which is formed through a combination of intermolecular C–H···O (2.5–2.6 Å) and C–H···π (2.8–2.9 Å) interactions.‡ Since there are four macrocycles that are located alternately around the base of the approximate square pyramid, the boroxine-pentamers can serve as twofold self-complementary tectons,[2b] thus allowing for the formation of a molecular network. A detailed analysis of the supramolecular architecture of compound **3** shows that the tecton adopts three different orientations within the crystal lattice, thus giving a 3D molecular arrangement (Fig. 3 and S4, Scheme S1†) with cavities that are occupied by solvent molecules (EtOH and H_2O; calculated accessible solvent volume: 21.7%).

In non-polar solvents such as CD_2Cl_2 and $CDCl_3$ the ^1H and ^{11}B NMR spectra show single sets of resonances that are in agreement with the boroxine-pentamer structure observed in the solid state.

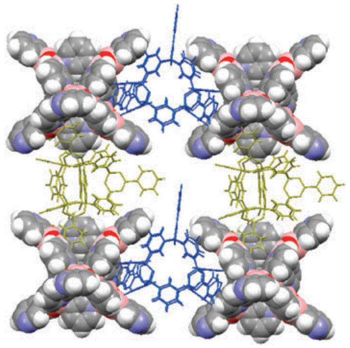

Fig. 3 Fragment of the crystal lattice of **3**, showing the connectivity of the self-complementary boroxine-pentamer tectons to an approximate rectangular 3D molecular network. Different types of representation and color have been used to highlight the three different tecton orientations.

As shown in Fig. 4 and S5,† the signals for the four different hydrogen atoms in the pyridyl rings (H_a–H_d) are distributed over three regions: (i) the singlet region from δ = 10.54 to 9.31 ppm for hydrogens H_a, (ii) the doublet region from δ = 8.90 to 7.80 ppm for hydrogens H_b and H_d, and (iii) the doublet of doublet (dd) region from δ = 7.43 to 6.86 ppm for hydrogens H_c. The ^1H NMR spectrum integrates for 60 hydrogen atoms in the expected proportion of 15 : 30 : 15 for the three regions described above. A comparison with the shift displacements for the monomeric boroxine **2** (δ = 8.62 ppm for H_a, δ = 8.55 and 8.45 ppm for H_b and H_d, and δ = 7.74 ppm for H_c, in CD_3OD)[20] shows that the signals of the singlet region, in particular those for H1, H2, H3, H4 and H5 (Fig. 1), are shifted to higher frequencies, while those of the doublet and dd regions are generally shifted to lower frequencies (see Table S1†). This can be attributed to a series of 16 close hydrogen–hydrogen contacts in the range from 2.3 to 3.5 Å within the molecule center, which could also be evidenced by NOESY experiments (Fig. S5c†).

According to the C_2-symmetry of the boroxine-pentamer, the ^{11}B NMR spectrum (Fig. S6†) shows five signals, two in the region for tri-coordinate (δ = 35.3 and 32.5 ppm), and three in the region for tetra-coordinate boron atoms (δ = 5.4, −1.9 and −19.3 ppm).[10] Interestingly, one of the signals is shifted to an unusually low frequency for boronates with a $\{BCNO_2\}$ }environment (δ = −19.3 ppm), which can be

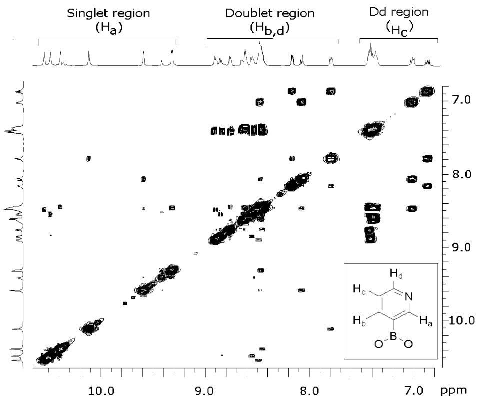

Fig. 4 COSY spectrum for the boroxine-pentamer **3** (in CD_2Cl_2).

explained by anisotropic shielding effects within the macromolecular entity.

Further evidence for the existence of the cage-assembly in solution is provided by the mass spectrum (ESI^+) that shows peaks corresponding to the molecular ion (1574.61, 2%) and fragments having tetrameric (1260.49, 13%), trimeric (945.37, 43%), dimeric (630.25, 13%) and monomeric (316.13, 100%) composition (Fig. S7†).

In polar solvents such as methanol only signals for the previously reported tris(3-pyridyl)boroxine **2** are detected (*vide supra*),[20] thus indicating either dissociation of the cage or a dynamic dissociation–recombination exchange process which is fast on the NMR time scale (Fig. S8†).

In conclusion, the synthetic strategies following either of the two sequences (i) *heteroarylboronic acid → boroxine → N–B linked supramolecular architecture* and (ii) *heteroarylboronic acid → boroxine → N–B linked assembly → supramolecular network* are unexplored so far and promise to be powerful tools for the generation of 0D, 1D, 2D and 3D polyboroxine assemblies and networks.

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Notes and references

‡ Crystal data for **3**: $C_{75}H_{60}B_{15}N_{15}O_{15}\cdot 2EtOH\cdot 3.67H_2O$, M_r = 1731.72, 0.42 × 0.49 × 0.51 mm, trigonal, space group $R\bar{3}$, a = 34.535(3), c = 39.198(4) Å, V = 40 486(6) Å^3, Z = 18, ρ_{calcd} = 1.278, $2\theta_{max}$ = 23.00°, 12 527 independent reflections, R_1 = 0.1210 for 9194 reflections with $I > 2\,\sigma(I)$ and wR_2 = 0.3087 for all data, 1140 parameters, GOF = 1.192. Although relatively large crystals could be grown, the R values are elevated. This can be attributed to the disorder of the molecular structure, the partial disorder of the solvent molecules, the large unit cell and the weak diffraction at theta angles >20°. The low resolution of the data affects the reliability of the bond lengths and angles and the refinement of the anisotropic thermal parameters (for details see ESI†). CCDC 695836.

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