

Cite this: *Chem. Sci.*, 2011, **2**, 1719

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EDGE ARTICLE

## Dative boron–nitrogen bonds in structural supramolecular chemistry: multicomponent assembly of prismatic organic cages†

Burcak Icli,<sup>a</sup> Erin Sheepwash,<sup>a</sup> Thomas Riis-Johannessen,<sup>a</sup> Kurt Schenk,<sup>a</sup> Yaroslav Filinchuk,<sup>b</sup> Rosario Scopelliti<sup>a</sup> and Kay Severin<sup>\*a</sup>

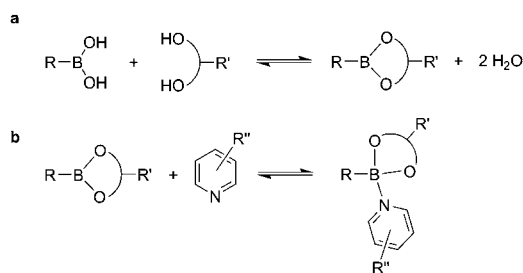
Received 25th May 2011, Accepted 7th June 2011

DOI: 10.1039/c1sc00320h

The multicomponent reaction of diboronic acids with a catechol and a tripyridyl linker results in the formation trigonal prismatic cages. The cages feature six dative boron–nitrogen bonds as structure-directing elements. The size of the cages can be varied by changing the diboronic acid building block. The cages are able to encapsulate polyaromatic molecules such as triphenylene or coronene.

### Introduction

Boronic acids are versatile building blocks for the assembly of molecular and polymeric nanostructures.<sup>1</sup> A key reaction in this context is the condensation of boronic acids with 1,2- and 1,3-diols (Scheme 1a). This reaction is reversible, and the equilibrium between boronic acid, diol and boronate ester is rapidly established.<sup>2</sup> Complex structures can be accessed by using polyboronic acids in combination with polyalcohols. Molecular cages, for example, have been obtained by condensation of a cavitand-type tetraboronic acid with a dicatechol linker<sup>3</sup> or by condensation of triboronic acids with tetra-<sup>4</sup> and hexaols.<sup>5</sup> The dynamic nature of the boronate ester allows for error correction processes to occur. Quantitative yields in thermodynamically controlled reactions are thus possible.



**Scheme 1** Reversible reactions involving boronate esters.

<sup>a</sup>Institut des Sciences et Ingénierie Chimiques and Institut de Physique des Systèmes Biologiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. E-mail: kay.severin@epfl.ch

<sup>b</sup>Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

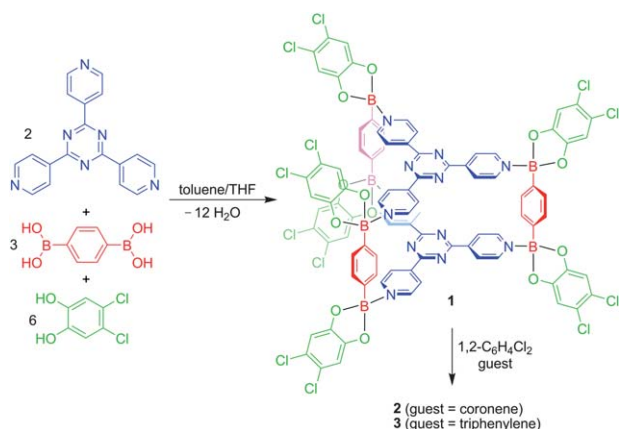
† Electronic supplementary information (ESI) available: Experimental procedures and crystallographic data for the cages **1–4** in cif format. CCDC reference numbers 827248–827251. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1sc00320h

Boronate esters are Lewis-acidic compounds which can form dative bonds to N-donor ligands such as pyridines (Scheme 1b). Dative B–N bonds have been investigated extensively for different reasons,<sup>2,6</sup> but their utilization in structural supramolecular chemistry is largely unexplored.<sup>1</sup> Below we demonstrate that dative B–N bonds can be used in conjunction with boronate esters to construct prismatic cages in multicomponent condensation reactions. The cages are able to act as hosts for polyaromatic molecules such as triphenylene and coronene.

### Results and discussion

We have recently shown that dative B–N bonds between boronate esters and pyridyl ligands can be used to build macrocycles,<sup>7</sup> rotaxanes,<sup>8</sup> and 1-<sup>9</sup> and 2-dimensional polymers.<sup>10</sup> These results prompted us to explore the possibility to assemble cages *via* B–N interactions. Cage-like structures can be obtained by connection of tritopic building blocks with ditopic linkers. As tritopic building block we chose 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt), a pyridyl ligand which has been used with high success in supramolecular coordination chemistry.<sup>11</sup> To connect the tpt ligands we employed a diboronate ester, which was prepared *in situ* by condensation of 1,4-benzenediboronic acid with 4,5-dichlorocatechol. The chlorinated catechol was chosen instead of plain catechol to increase the Lewis-acidity of the boronate ester, which was expected to strengthen the dative B–N bond. The cage synthesis was performed as follows: a mixture of tpt (2 equiv.), 1,4-benzenediboronic acid (3 equiv.) and 4,5-dichlorocatechol (6 equiv.) in a mixture of toluene and THF (2 : 1) was heated under reflux using a Dean Stark trap to remove water. Upon cooling, cage **1** precipitated in form of an orange powder, which was isolated in 94% yield (Scheme 2).

At room temperature, compound **1** could not be dissolved in common organic solvents such as chloroform and toluene. However, recrystallisation was possible from hot 1,2-dichlorobenzene (~180 °C). The crystallisation likely involves a rupture of the cage structure by breakage of the dative B–N bonds and

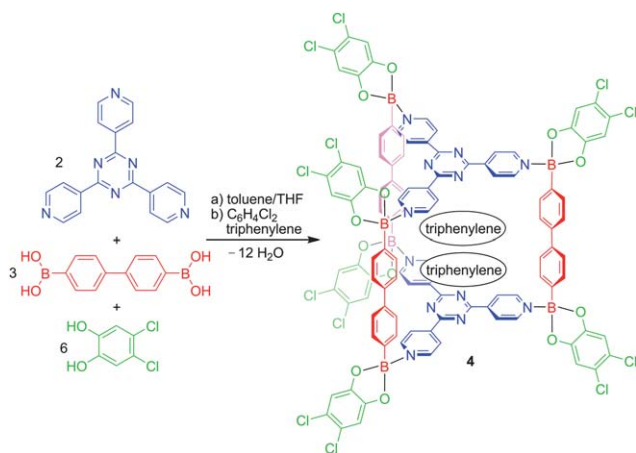


**Scheme 2** Multicomponent assembly of the cages 1–3.

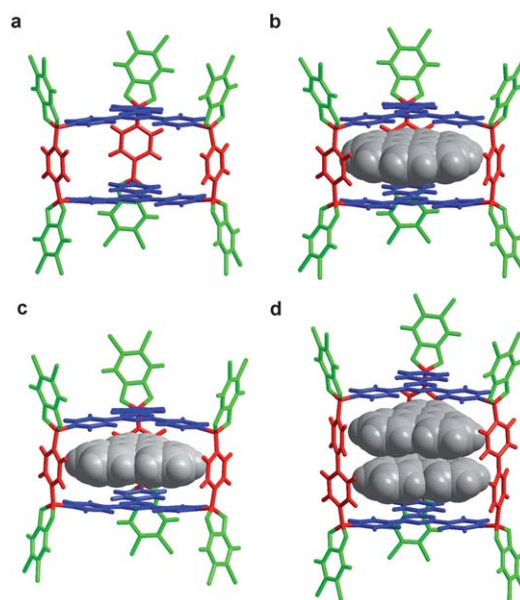
reassemble during slow cooling. This assumption is supported by the fact that the hot solution was nearly colourless, whereas cage **1** is an orange solid.<sup>12</sup>

Transition-metal based cages based on tpt ligands display a very rich host–guest chemistry.<sup>11</sup> In particular, it was found that prismatic tpt cages are potent receptors for planar polyaromatic molecules.<sup>11,13</sup> Inspired by these results, we recrystallised cage **1** in the presence of coronene and triphenylene. The resulting crystalline compounds **2** and **3** indeed contained aromatic guests as evidenced by crystallographic analyses (see below). Furthermore, UV/vis measurements of the filtered solutions indicated that cage **1** had fully extracted coronene and >90% of triphenylene from the organic solutions. To extend the size of the cage, we have performed a multicomponent reaction with 4,4'-biphenyldiboronic acid instead of 1,4-benzenediboronic acid. The latter was crystallised from hot 1,2-dichlorobenzene in the presence of triphenylene to give cage **4** (Scheme 3).

The very low solubility of **1–4** prevented characterisation by solution-based analysis methods.<sup>14</sup> Crystallographic analyses were therefore performed on all four compounds and graphic representations of the solid-state structures are shown in Fig. 1. The cages have the expected trigonal prismatic geometry in which the diboronate ester struts hold the tpt ligands together in an essentially eclipsed fashion. The compounds are close structural analogues of coordination cages described by the group of



**Scheme 3** Multicomponent assembly of cage **4**.



**Fig. 1** Molecular structures of the cages **1** (a), **2** (b), **3** (c), and **4** (d) as determined by single crystal X-ray diffraction. The colour coding follows the descriptions given in Scheme 2 and 3.

Fujita.<sup>11a</sup> Instead of diboronate esters, they have used dinuclear Pd<sup>II</sup> and Pt<sup>II</sup> complexes to bridge tpt ligands. A major difference is the charge of the cages: the metal-based cages have a total charge of 12+ whereas our organic analogues are neutral.

Both the struts and the tritopic tpt ligands of **1–4** are slightly buckled outwards with respect to the cage interiors. Such distortions are likely due to strain imposed by the tetrahedral boron centres at the vertices of the cages. No significant change in tpt⋯tpt distance is observed on going from empty cage **1** to filled cages **2** or **3**. It is worth noting that residual electron density was observed in the interior of **1**, suggesting its partial occupation by co-crystallised solvent. However, the electron density was too diffuse to be meaningfully modelled and its scattering contributions were removed using the SQUEEZE routine in PLATON.<sup>15</sup>

As shown by host–guest complexes **2** and **3**, respectively, coronene and triphenylene are complementary in size and shape to the cage interiors. The planar aromatic guests are located centrally between the two tpt walls at distances of c.a. 3.5 Å from each, typical for  $\pi$ -stacking interactions, and their anisotropic displacement parameters evidence some minor rotational disorder about the three-fold symmetry axis. The larger volume of cage **4**, achieved by using longer biphenyl struts, allows it to accommodate two aromatic guests. In the latter case, two triphenylene moieties are stacked on top of each other within the cage, both being located marginally closer to the nearest tpt wall (tpt⋯triphen: 3.5 Å) than to the mutually adjacent guest (triphen⋯triphen: 3.8 Å). The triphenylenes are well ordered this time, and they lie with the three protruding phenyl rings oriented towards the boronate ester struts as opposed to the open faces of the cage. Each is rotated by a shallow angle (c.a. 5°), in opposite directions with respect to the three-fold symmetry axis, ensuring that neither the guests nor the tpt walls adopt a fully eclipsed conformation.

## Conclusions

We have reported the assembly of tpt-based molecular cages from purely organic building blocks. To best of our knowledge, **1–4** are the first examples of molecular cages which contain dative B–N bonds to boronate esters as an integral part of their structure.<sup>16</sup> A limitation with respect to potential applications is the low stability and solubility in organic solvents. However, molecular cages can also display interesting behaviour in the solid state.<sup>17</sup> It will be interesting to see whether the concept to replace coordinative M–N bonds by dative B–N bonds can be extended to other types of cage structures. Investigations in this direction are ongoing in our laboratory.

## Acknowledgements

The work was supported by the Swiss National Science Foundation and by the EPFL. We thank the Swiss-Norwegian Beam Lines (ESRF) for beamtime allocation.

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