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The facile self-assembly of nanoscale boronate ester rectangles from linear bis-catechols and 1,4-benzene diboronic acid is described. Spectroscopic and computational analyses reveal the influence of extended π -conjugation on the rectangles' absorption and fluorescence properties. The rectangles represent a new class of discrete, organic soluble covalent organic polygons.

The thermodynamically driven, dynamic covalent¹ condensation of boronic acids² with catechols to give boronate esters has proven to be a highly efficient means of preparing complex molecular and macromolecular structures. Boronate ester-based covalent organic frameworks^{3,4} (COFs) in particular have attracted significant interest on account of their well-defined porosity, high thermal stabilities, low densities, and applications in gas storage, 4a,b optoelectronics, 4c-f,h and heterogeneous catalysis.^{4g} While multiple examples of infinitely periodic 2- and 3-dimensional boronate ester COFs have been reported since their discovery⁵ in 2005 there have been few examples⁶ of their discrete analogues: i.e. porous, highly unsaturated covalent organic polygons or polyhedra (COPs) built from boronic acids and oligo-catechols.7 Herein we report the synthesis and dynamic selfassembly of two shape-persistent,1c alkyl-functionalized covalent organic boronate ester rectangles. Spectroscopic investigations reveal the dynamic nature of their self-assembly as well as their structuredependent absorption and fluorescence properties.

Linear bis-catechols **1** and **2** containing at their core 2,3-bis-(hexyloxy)phenylene or diethynyl-2,3-bis(hexyloxy)phenylene, respectively, were designed to function as 0° secondary building units in accordance with the directional-bonding⁸ approach to molecular self-assembly. Hexyloxy groups were found to be essential for the current study as neither unsubstituted nor methoxy substituted linear bis-catechols were sufficiently soluble to allow adequate solution phase assembly and characterization. There is literature precedent^{6b,d,9} for the dynamic assembly of discrete and oligomeric boronate esters in hydrophobic solvents such as CHCl₃ and CH₂Cl₂.

Discrete, soluble covalent organic boronate ester rectangles[†]

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1,4-Benzene diboronic acid (BDBA), however, is insoluble in CDCl₃ where it self-condenses into boroxine anhydride species, thus preventing assembly with either 1 or 2 in CDCl₃. We found that the addition of CD₃OD catalyses the dissociation of boroxine anhydride species and, likewise, the dynamic self-assembly of BDBA with 1 and 2. Indeed, within 10 min of mixing 1 or 2 with BDBA (10:1 CDCl₃-CD₃OD, 50 °C) the ¹H NMR spectrum of both assemblies become substantially disordered as dynamic covalent exchange between BDBA and 1 or 2 initially results in the formation of various kinetic intermediate assemblies. Within 3 h these dynamic libraries of oligomers have largely collapsed to their most thermodynamically favoured structures, as indicated by considerable sharpening of their ¹H NMR spectra. Full conversion to rectangles 3 and 4, however, is not complete until H₂O and CD₃OD are removed by stirring over 4 Å molecular sieves,¹⁰ providing rectangles 3 and 4 in near quantitative yield (Scheme 1). In addition to increasing the rectangles' solubility, the alkyl chains of 3 and 4 likely aid in rendering both assemblies highly resistant to hydrolysis¹¹ as hydrolytic disassembly could only be achieved by refluxing in a 1:1 mixture of D₂O-CD₃OD.



Scheme 1 Solution-phase synthesis of boronate ester rectangles **3** and **4** from the dynamic self-assembly of linear bis-catechols **1** and **2** with **BDBA**.

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Fig. 1 Partial ¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of bis-catechol **1** (a) and boronate ester rectangle **3** (b) indicating diagnostic shifts of proton signals H_a-H_d upon self-assembly.

The formation of rectangles **3** and **4** is supported by key shifts of diagnostic signals in their ¹H NMR spectra. Catechol Ar–OH signals at 7.61 and 6.01 ppm for tetraol **1**, for example, are no longer present in the ¹H NMR spectrum of rectangle **3** (Fig. 1). Catechol protons H_a – H_c shift collectively downfield by 0.3 ppm while the proton signal H_d of the central aromatic unit of **1** shifts from 7.33 ppm in the free tetraol to 7.41 ppm in assembly **3**. A new singlet corresponding to the aromatic protons of the central boronate unit is observed at 8.25 ppm. Analogous changes occur in the ¹H NMR spectrum of rectangle **4** (ESI,[†] Fig. S1). The sharp signals observed in the CDCl₃ spectra of **3** and **4** suggest assemblies of high symmetry rather than collections of oligomers.

Further characterization of covalent organic rectangles 3 and 4 is provided by infrared (IR) spectroscopy. The IR spectra of linear catechols 1 and 2 (ESI,[†] Fig. S2 and S3) reveal broad catechol CO-H stretching bands at 3272 and 3311 cm⁻¹, respectively, while the IR spectrum of BDBA shows a BO-H band centred at 3286 cm⁻¹. IR spectra of rectangles 3 and 4, however, contain no stretching bands above 3000 cm⁻¹, indicating full dehydration of each species. New B-O stretching bands at and 1326 cm⁻¹ (rectangle 3) and 1333 cm⁻¹ (rectangle 4) support the formation of boronate esters, but cannot rule out the formation of anhydrides. Boronate anhydrides display a characteristic¹² absorption band between 570-580 cm⁻¹, however neither the IR spectra of 3 nor 4 contains a peak in this region providing more definitive evidence that boronate esters rather than anhydrides are formed. Furthermore, rectangles 3 and 4 display bands at 660 and 656 cm⁻¹, respectively, corresponding to boronate ester out of plane bending modes.13

NMR and IR spectroscopic analyses, while supportive of the formation of boronate ester assemblies, cannot rule out the possibility that alternative, highly symmetric boronate ester oligomers have formed or are present. Accurate mass MALDI mass spectrometry was therefore used to investigate the molecularity of assemblies 3 and 4. The MALDI mass spectrum of rectangle 3 reveals a peak of m/z = 1199.565 [M + Na]⁺, which is in agreement with the calculated value of 1199.560. The MALDI mass spectrum of rectangle 4 shows a peak of m/z = 1272.572 [M]⁺ compared to a calculated value of 1272.571. MALDI mass spectrometry results quantitatively establish the molecularity of covalent organic rectangles 3 and 4 as being discrete species rather than oligomers.



Fig. 2 Absorption (solid lines) and normalized fluorescence (dashed lines) spectra of boronate ester rectangles **3** and **4**. All spectra were recorded in CHCl₃ (1.0×10^{-5} M). Excitation wavelengths: $\lambda_{ex} = 270$ nm (**3**), $\lambda_{ex} = 320$ nm (**4**).

The most prominent structural difference between linear biscatechols 1 and 2, and likewise rectangles 3 and 4, is the presence of ethynyl moieties in 2 and 4. These ethynyl groups have two noteworthy effects: (i) catechol moieties of 2 are able to adopt synperiplanar and anti-periplanar conformations while those of 1 cannot due to steric interactions at its biaryl C–C bonds, and (ii) π -conjugation is increased in 2 relative to 1. UV/Vis and fluorescence spectroscopy were used to investigate the effects of increased conjugation on the absorption and emission properties of rectangles 3 and 4. Plotted in Fig. 2 are the UV/Vis and fluorescence spectra of rectangles 3 and 4 $(1.0 \times 10^{-5} \text{ M}, \text{CHCl}_3)$ ¹⁴ The absorption of rectangle 3 (λ_{abs} = 264 nm, $\varepsilon = 3.0 \times 10^4 \,\mathrm{M^{-1} \, cm^{-1}})$ is almost identical to that of the boronate ester obtained by condensation of **BDBA** with catechol ($\lambda_{abs} = 282 \text{ nm}$, $\varepsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁵ underscoring the fact that conjugation is broken at the twisted biaryl bonds of 3. Absorption of rectangle 4, by contrast, is red-shifted by 93 nm relative to 3 (λ_{abs} = 357 nm, ε = 2.5 × 10⁴ M⁻¹ cm⁻¹) reflecting the increased conjugation provided by the ethynyl spacers. The effect of extended π -conjugation is again observed, though to a lesser extent, in the fluorescence spectra of 3 $(\lambda_{em} = 383 \text{ nm})$ and 4 $(\lambda_{em} = 400 \text{ nm})$. Stokes shifts of 119 nm and 43 nm are observed for rectangles 3 and 4, respectively, indicating the more conformationally flexible rectangle 3 undergoes greater relaxation upon excitation than the planar, more conjugated rectangle 4. Both boronate ester rectangles show significant emission in the blue region of the spectrum, making them possible candidates for soluble, stable blue emitters for organic light emitting diode (OLED) applications.¹⁶

Additional insight into increased π -conjugation in rectangle **4** relative to **3** was obtained through density functional theoretical calculations. Models of both rectangles with hexyloxy functionalities replaced with methoxy groups were constructed and fully conformational searched using molecular mechanics. The lowest energy structure of each rectangle was then optimized to full convergence at the B3LYP/6-31+g(d,p) level¹⁷ in a PCM¹⁸ solvent model for CHCl₃ using the program Gaussian 09.¹⁹ As can be seen in Fig. 3, the lowest energy conformation of **3** is non-planar, with dihedral angles of 129° between its conjugated boronate ester aromatic units and its central alkoxy-substituted aromatic rings. Rectangle **4**, however, does adopt a planar conformation. NBO analysis reveals that the HOMO orbitals of rectangles **3** and **4** are quite similar: both predominantly localized



Fig. 3 (a) Top views of the highest-occupied and lowest-unoccupied molecular orbitals of boronate ester rectangles 3 and 4 computed at the B3LYP/6-31+g(d,p) level (CHCl₃ solvent) along with computed HOMO-LUMO gaps (eV). (b) Edge views of both rectangles highlighting the non-planar structure of 3 and planar structure of 4.

on their more electron-rich catechol-based units. Their LUMO orbitals, however, differ considerably. The LUMO of 3 is entirely localized on its central, electron-poor boronate moieties. The LUMO of 4 is fully delocalized across the entire π -conjugated rectangle. Increased conjugation is also reflected in calculated HOMO-LUMO gaps of 4.29 and 3.52 eV for rectangles 3 and 4, respectively.

Soluble, shape-persistent covalent organic polygons bearing alkyl functionalities are likely to allow for the design and fabrication of new boronate ester materials - e.g. porous boronate ester mesogens, the organized assembly of covalent organic polygons into selfassembled monolayers, and the use of soluble covalent organic polygons as sensors for halide anions. The violet-blue emission of rectangles 3 and 4 opens possibilities for these and related assemblies to be used as soluble, thermally robust²⁰ components of OLEDs. Furthermore, we anticipate soluble COPs will play an important role in understanding and optimizing structure-function relationships of related COFs by providing valuable solution phase analysis that cannot otherwise be easily obtained given the insoluble nature of rigid, infinitely periodic frameworks. We are actively investigating the solution phase assembly and sensing applications of rectangles 3 and 4 as well as the synthesis and self-assembly of additional soluble, discrete covalent organic polygons.

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