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Supramolecular polymers based on dative boron–nitrogen bonds†

Erin Sheepwash,[a] Nicolas Luisier,[a] Martin R. Krause,[b] Stefanie Noé,[b] Stefan Kubik[b] and Kay Severin*[a]

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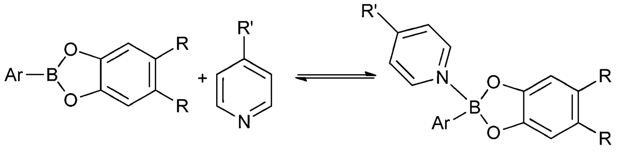
Heteroditopic monomers containing an arylboronate ester and a dialkyl-4-aminopyridine group aggregate *via* dative boron–nitrogen bonds to give main chain supramolecular polymers. The degree of polymerization can be tuned by changing the electronic and steric properties of the boronate ester.

Main-chain supramolecular polymers are formed by aggregation of monomers *via* directional and reversible non-covalent interactions.[1] A limiting factor is the strength of the non-covalent interaction: binding constants of $K_a \geq 10^6$ M^{-1} between the functional groups of the monomers are typically required to obtain polymers of significant molecular weight.[1,2] In this regard, dative bonds between Lewis-acidic arylboronate esters and nitrogen-donor ligands seem to be less suited as they have been described "to be of similar strength to a hydrogen bond".[3] The quantitative measurements which have been reported so far provide a slightly more optimistic picture with binding energies between −11 and −25 kJ mol^{-1} ($K_a \sim 10^2$–10^4 M^{-1}).[4,5] Below we report that it is possible to increase the strengths of dative B–N bonds substantially by using complementary electronic effects. This finding was the basis for the successful synthesis of main-chain supramolecular polymers with dative B–N bonds.

Dative B–N bonds between arylboronate esters and amines have been studied extensively in the context of boronic acid-based carbohydrate sensors.[3,4,6] Recently, it was shown that dative B–N interactions between dioxaboroles (condensation products of boronic acids and catechols) and pyridyl donor-ligands can be used for the construction of molecularly defined nanostructures[7] and polymeric materials.[8] In solution, these compounds display limited stability because of the weak B–N bond. In order to gain more insight into the factors which govern the binding strengths of dioxaboroles and pyridyl ligands, we decided to perform a quantitative study. ^1H NMR spectroscopic titration experiments were carried out with different dioxaboroles and pyridine donors. Benzene-d_6 and $CDCl_3$ solutions containing the dioxaborole and a variable amount of the *N*-donor ligand were analyzed by ^1H NMR spectroscopy (see ESI†, Fig. S1–S4). In all cases, the exchange between bound and free *N*-donors was found to be fast on the NMR time scale and averaged signals were observed. Numerical fitting[9] of the isotherms to a 1 : 1 binding model gave association constants (K_a), the values of which are summarized in Table 1.

Table 1 Association constants of adducts between dioxaboroles and pyridyl ligands



	Ar	R	R′	K_a [M^{-1}] C_6D_6	K_a [M^{-1}] $CDCl_3$
1[a]	Ph	H	H	$5.1(0.5) \times 10^1$	$3.6(0.3) \times 10^1$
2[a]	Ph	Cl	H	$1.1(0.7) \times 10^4$	$9.1(2.4) \times 10^2$
3[a]	2,4,6-F	H	H	$8.8(6.8) \times 10^4$	$9.8(1.1) \times 10^3$
4[a]	2,4,6-^{i}Pr	H	NMe_2	$4.4(0.5) \times 10^1$	$2.2(0.2) \times 10^0$
5[b]	Ph	H	NMe_2	$9.1(0.4) \times 10^4$	$6.0(0.2) \times 10^4$
6[b]	2,4,6-F	H	NMe_2	$1.3(0.2) \times 10^6$	$6.2(0.3) \times 10^5$
7[b]	Ph	Cl	NMe_2	$4.0(0.1) \times 10^6$	n.d.

[a] Determined by ^1H NMR spectroscopy. [b] Determined by ITC; the values are averages of three independent measurements.

The constants for the binding of pyridine to boronate esters were found to be in the range of 10^1–10^4 M^{-1} indicating a weak to moderate interaction, with electron withdrawing substituents on the ester increasing the K_a value. A significant improvement in binding was observed when dimethylaminopyridine (DMAP) was employed as the *N*-donor. The association constants were found to be 2 to 3 orders of magnitude higher than those observed with pyridine (Table 1, entry 1 *vs.* entry 5, entry 2 *vs.* entry 7, and entry 3 *vs.* entry 6). For the DMAP adducts of boronate esters containing a halogenated arylboronic acid or catecholate, binding constants of K_a = 1.3(0.2) × 10^6 M^{-1} (entry 6) and K_a = 4.0(0.1) × 10^6 M^{-1} (entry 7) were determined by isothermal titration calorimetry (ITC). To the best of our knowledge, these are the highest reported values for a dative B–N bond involving dioxaboroles. It is also possible to counterbalance electronic with steric effects. The utilization of a boronate ester with sterically demanding isopropyl groups resulted in weak binding of DMAP (entry 4).

It is evident from the data summarized above that it is possible to achieve binding constants of 10^6 M^{-1} by electronic tuning of the boronate ester and the pyridyl donor ligands.

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[a] *Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. E-mail: kay.severin@epfl.ch*
[b] *Fachbereich Chemie, Technische Universität Kaiserslautern, Germany*

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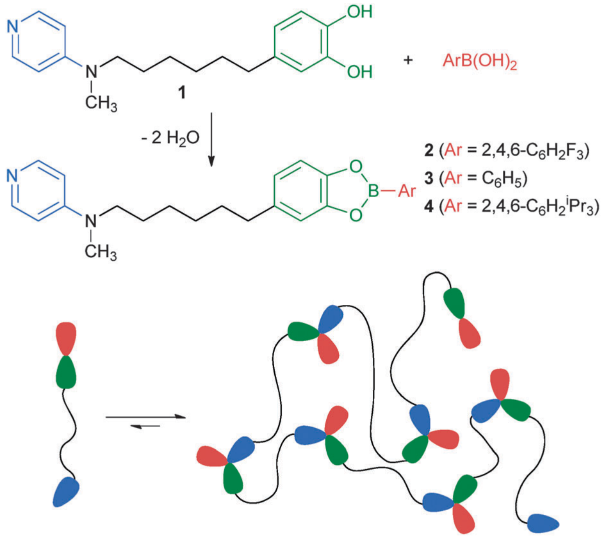

Scheme 1 Synthesis of the heteroditopic monomers **2–4** and aggregation *via* dative B–N bonds.

This finding prompted us to explore the possibility of creating main-chain supramolecular polymers with dative B–N bonds.

Three monomers were synthesized containing boronate ester and dialkylaminopyridyl end groups. The preparation of these monomers was achieved by condensation of the common precursor **1** with different arylboronic acids (Scheme 1, for details see ESI†). In organic solvents of low polarity, these monomers were expected to aggregate *via* dative B–N bonds. The strength of the B–N interaction, and thus the degree of polymerization, should increase in the order **4** < **3** < **2** (**4** features sterically demanding isopropyl groups, whereas **2** contains an electron withdrawing 2,4,6-$C_6H_3F_3$ group).

The aggregation of **2–4** in chloroform was investigated by concentration dependent viscosity measurements (Fig. 1). The steep, non-linear increase in the relative viscosities (η_r) with concentration gives clear evidence for polymer formation in the case of monomers **2** and **3**.[10] Further, the observed trends in viscosities are in line with the association constants measured for the simple esters (Table 1). A greater degree of polymerization was observed for the trifluoro-substituted monomer **2** whose corresponding simple ester in chloroform provided a K_a value of an order of magnitude higher than that of the related ester of monomer **3**. This difference in K_a values for B–N bond formation manifests a larger increase in relative viscosity for monomer **2** compared to **3**. The triisopropyl-substituted **4** gave a comparably shallow curve, with a viscosity at 100 mM of less than half that of **2**.

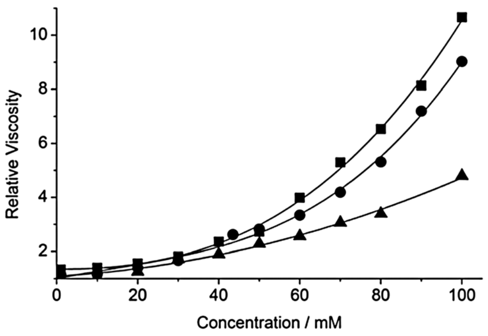

Fig. 1 Relative viscosities (η_r) of chloroform solutions containing different amounts of monomer **2** (■), **3** (●), or **4** (▲).

Assuming that the self-assembly of the monomers occurs with a K_a value in the range of that measured for the corresponding simple boronate ester–DMAP adducts (Table 1, entries 5 and 6), the average degree of polymerization can be calculated.[11,12] These calculations yielded values of about 500 (**2**) and 150 monomeric units (**3**), which translate into average molecular weights of 200 000 (**2**) and 60 000 g mol^{-1} (**3**).‡

The addition of a chain stopper to a supramolecular polymer should result in a pronounced decrease in solution viscosity, even at low mole fractions.[12] A solution of **2** (75 mM) was titrated with DMAP. The relative viscosity decreased rapidly to approximately $\eta_r = 1$ at 0.1 equivalents of DMAP (see ESI†, Fig. S10). The drop in viscosity upon addition of the chain stopper DMAP indicates that the observed viscosity of solutions of **2** is not due to unspecific aggregation, but is in fact due to the formation of boron–nitrogen dative bonds.

To further characterize the polymers, ^1H NMR spectra in $CDCl_3$ were taken at varying monomer concentrations. Solutions of **2** showed peak broadening of about 8 Hz when the concentration of the monomer was increased from 10 to 100 mM (see ESI†, Fig. S11). The peak broadening is consistent with the formation of oligomeric and/or polymeric species in solution.[13] Furthermore, diffusion ordered spectroscopy (DOSY) NMR experiments were carried out for **2** and **3**. In both cases, the diffusion coefficients increased significantly when the monomer concentration was raised from 10 mM to 100 mM (see ESI†, Fig. S12–S15). This result is in line with the expected concentration dependence of a supramolecular polymerization process.[14]

In summary, we have shown that it is possible to increase the binding strength of pyridyl ligands to boronate esters substantially by using electronic effects. Importantly, it is possible to achieve association constants of $\geq 10^6$ M^{-1}. This observation led to the successful development of main-chain supramolecular polymers based on dative B–N bonds. It is likely that the B–N binding motif can also be used for the formation of branched or cross-linked supramolecular polymers. Furthermore, it should be possible to combine dative B–N bonds with other supramolecular interactions such as hydrogen bonds to create complex polymer architectures *via* orthogonal self-assembly.[15] Studies in this direction are ongoing in our laboratory.

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Notes and references

‡ It is likely that macrocycles are formed along with polymers. The former are neglected for the calculations.

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