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Formation of Boronate Ester Polymers with Efficient Intrastrand Charge-Transfer Transitions by Three-Component Reactions

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The three-component reaction of aryl boronic acids with 1,2,4,5-tetrahydroxybenzene and 1,2-bis(4-pyridyl)ethylene or 4,4′-bipyridine leads to the formation of dark-purple boronate ester polymers. Crystallographic analyses show that the polymer strands have a zig–zag geometry, and the bis(dioxaborole) units are connected by dipyridyl linkers through dative B–N interactions. Upon dissolution of the polymers in hot chloroform, most of the B–N connections are broken, which indicates that polymer formation is a reversible process. A computational study provides evidence that the strong color of the polymers is due to efficient intrastrand charge-transfer excitations from the tetraoxobenzene to the dipyridyl linker.

Introduction

Boronic acids are known to easily and reversibly condense with diols to form boronate esters. This type of reaction has been exploited extensively in carbohydrate chemistry where boronic acids are used as an integral part of receptors and sensors or as protecting groups.[1] The reversible formation of boronic esters has also been employed to build complex structures such as macrocycles,[2] dendrimers,[3] helicates,[4] nanotubes,[5] or porous covalent organic frameworks.[6] The labile boron–oxygen bonds are used here in a similar fashion to metal–ligand interactions in supramolecular coordination chemistry. Constitutional dynamic polymers[7] with boronate ester backbones represent another interesting class of compounds. Lavigne and coworkers showed that poly(dioxaborolane)s[8] and poly(dioxaborole)s[9] can be obtained by the condensation of diboronic acids with pentaerythritol or 1,2,4,5-tetrahydroxybenzene.[10] An interesting feature of these polymers is that hydrolytic degradation can be reversed by annealing under vacuum ("self-repairing polymers").[8] The polycondensation of diboronic acids with sugar derivatives as linkers has been investigated by the groups of Shinkai[11] and Shimizu.[12] Again it was found that the polymerization is a reversible process, which depends on the conditions.

An alternative way to generate dynamic polymers with boron centers in the backbone is the polymerization by dative B–N bonds. This was demonstrated by Wagner and coworkers who made polymers by the reaction of the borylated ferrocene [$(C_5H_4BMe_2)_2Fe$] with 4,4′-bipyridine or pyrazine[13] and by the group of Jäkle who assembled polymers with borane end groups by the reaction with 4,4′-bipyridine.[14,15] In the following we show that boronic acid–diol condensations can be used *in parallel* with dative B–N interactions to generate novel polymer architectures by three-component reactions. The resulting crystalline polymers are deeply colored due to efficient intrastrand charge-transfer transitions.

Results and Discussion

To evaluate the possibility to generate boronate polymers with ditopic N-donor ligands, we heated a mixture of 1,2-bis(4-pyridyl)ethylene, two equivalents of 4-ethylphenylboronic acid, and one equivalent of 1,2,4,5-tetrahydroxybenzene in benzene with the use of a Dean–Stark trap. A slightly yellow solution was obtained, from which, upon cooling, a dark-purple solid (**1**) precipitated (Scheme 1). A similar behavior was observed when 4-*tert*-butylphenylboronic acid was employed: when the hot benzene solution was cooled, a dark precipitate formed (**2**).

At room temperature, products **1** and **2** were found to display low solubility in common organic solvents such as benzene, chloroform, acetonitrile, and tetrahydrofuran. Upon heating, however, it was possible to dissolve them in chloroform. This process was accompanied with a strong change in color: the dark-purple solids gave rise to weakly yellow solutions. When the hot chloroform solutions were cooled to room temperature, the purple polymers started to precipitate after a few minutes, which indicated that the color change was due to a reversible process.

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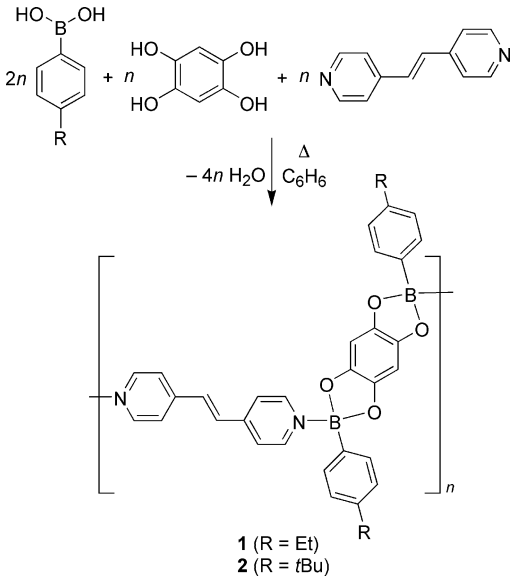
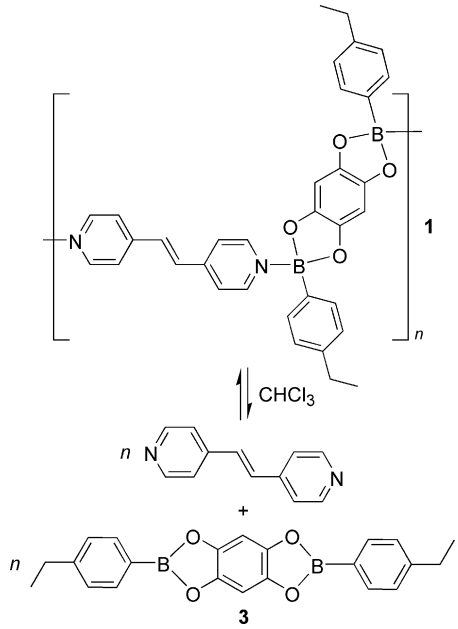
[‡] X-ray crystal structural analysis.



Scheme 1. Synthesis of polymers **1** and **2**.



Scheme 2. When dissolved in $CHCl_3$, polymer **1** splits into 1,2-bis(4-pyridyl)ethylene and bis(dioxaborole) **3**.

A $CDCl_3$ solution of polymer **1** was analyzed by ^1H NMR spectroscopy, and its spectrum was nearly a superposition to those of 1,2-bis(4-pyridyl)ethylene and bis(dioxaborole) **3** ($\Delta\delta < 0.15$ ppm). The latter compound was prepared for comparison by condensing 4-ethylphenylboronic acid with 1,2,4,5-tetrahydroxybenzene.[16] The ^{11}B NMR spectrum of **1** showed a peak at $\delta = 28.8$ ppm, which was similar to that of **3** ($\delta = 34.6$ ppm) and very distinct from the expected signal of a tetracoordinated boron center.[17] This data suggested that the chloroform solution of polymer **1** contained mainly dissociated 1,2-bis(4-pyridyl)-ethylene and bis(dioxaborole) **3** (Scheme 2). The small differences in chemical shifts can be explained by the formation of minor amounts of B–N adducts, which are in fast equilibrium with 1,2-bis(4-pyridyl)ethylene and **3**. A related situation was observed for the ferrocene polymers prepared by Wagner et al.: upon dissolution at high temperature, the polymer was split into its monomers, $[(C_5H_4BMe_2)_2Fe]$ and 4,4′-bipyridine.[13]

The reversible formation of **1** from 1,2-bis(4-pyridyl)-ethylene and **3** allowed single crystals to be obtained from $CHCl_3$/pentane solutions, and crystallographic analysis confirmed the polymeric structure (Figure 1). The ditopic 1,2-bis(4-pyridyl)ethylene acts as a bridge between the boronate esters. The average boron–nitrogen bond length of 1.677 Å is long relative to what was observed for other crystallographically characterized adducts between sp^2-nitrogen donors and tetracoordinated boron centers.[18] Accordingly, the tetrahedral character (THC)[18] of the boron center is relatively low (THC_{av} = 72.5%). This data is in line with the results of the NMR spectroscopic experiments, which suggest that the dative B–N bond in **1** is weak. The B–O bonds ($B–O_{av}$ 1.479 Å) are, as expected, longer than what was observed for 1,2,4,5-tetrahydroxybenzene-based bis(dioxaborole)s with trigonal planar boron (B–O 1.388–1.395 Å).[14]

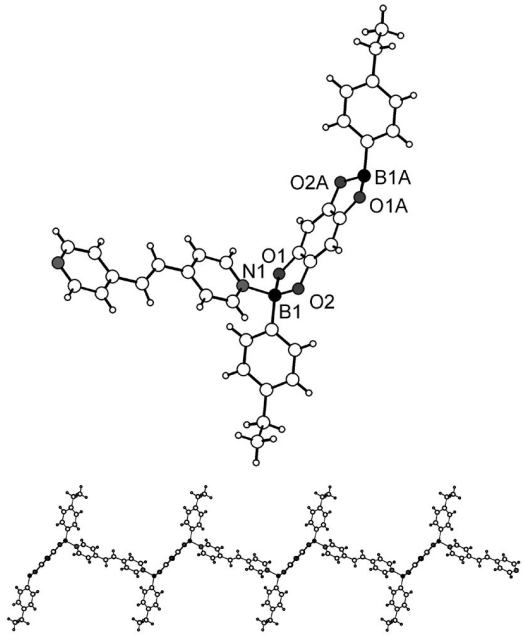
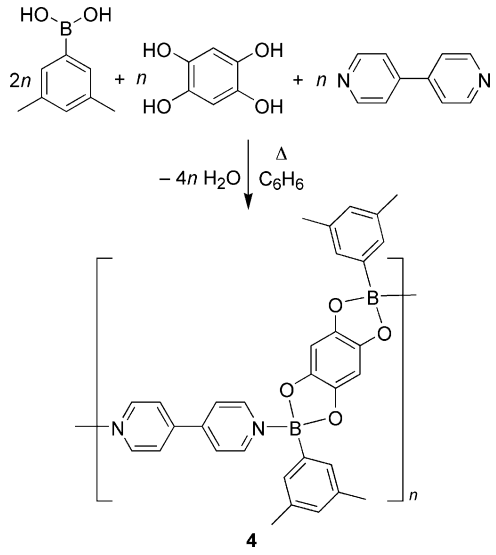


Figure 1. Molecular structure of polymer **1** in the crystal. Top: view of the repeating unit – only one of the two crystallographically independent subunits is shown; bottom: view of the polymer chain. The solvent molecule ($CHCl_3$) is not shown for clarity.

The modular nature of the three-component polymerization reactions offers structural flexibility as demonstrated by the formation of polymer **4**, which contains 4,4′-bipyridine instead of 1,2-bis(4-pyridyl)ethylene as the bridging N-donor ligand (Scheme 3). The physical properties of **4** are similar to those of **1** and **2**: the polymer has a dark-purple color and it splits into 4,4′-bipyridine and the respective boronate ester upon dissolution in hot chloroform.



Scheme 3. Synthesis of polymer **4**.

The molecular structure of polymer **4** in the crystal is depicted in Figure 2. As it was observed for **1**, a zig–zag chain is formed. With B1–N1 1.702(5) Å, B1–O1 1.470(4) Å, and B1–O2 1.479(4) Å, the bond lengths of **4** are very similar to those of **1**. Again, the long B–N bond correlates with a low tetrahedral character of 69.5%.

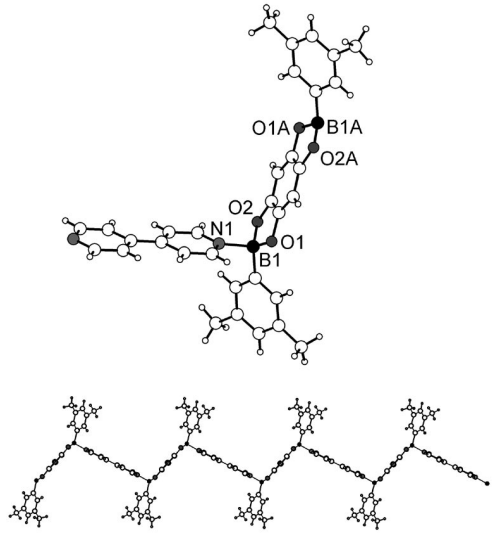


Figure 2. Molecular structure of polymer **4** in the crystal. Top: view of the repeating unit; bottom: view of the polymer chain.

The solid-state ^{11}B NMR spectra of polymers **1**, **2**, and **4** are in agreement with the depicted structures and show peaks around 10 ppm. An interesting difference was observed when we attempted to make a polymer from methyl boronic acid, 4,4′-bipyridine, and 1,2,4,5-tetrahydroxybenzene. Again, a dark-purple precipitate was formed (**5**), but its solid-state ^{11}B NMR spectrum showed two peaks at ca. 32 and ca. 9 ppm. The former peak is characteristic for a trigonal planar boron center.[16] We therefore propose that compound **5** is the monoadduct [MeB($C_6H_2O_4$)BMe(bipy)] with one trigonal and one tetragonal boron center. Apparently, the methyl boronate ester is not sufficiently Lewis acidic to promote extended polymerization.

A striking feature of polymers **1**, **2**, and **4** is their very dark-purple color. Because the color disappears upon dissolution in chloroform, it must be the fully assembled polymer, which gives rise to the strong absorption. To understand this phenomenon, we performed single-point second-order approximate coupled-cluster (CC2)[19] calculations of the electronic excitations on model systems of the acid and base pairs 1,2-bis(4-pyridyl)ethylene and 4,5-dihydroxyphenyl-4-ethylphenylborole and of their respective condensate in vacuo. Both the uncomplexed acid and base showed the first absorption peak in the near-UV region (4.2 and 3.8 eV, respectively), which is consistent with the finding that the solution containing nonassembled monomers is colorless. In contrast, the assembled acid–base complex showed one transition in the yellow-green region (2.2 eV), which is in agreement with the observed purple coloration of its crystals.

Decomposition of the optical excitation in the visible region onto a molecular orbital basis shows that it has an almost pure HOMO–LUMO π–π* character (88%). This transition corresponds to an intrastrand charge-transfer excitation from the hydroxy–phenyl ring of the dioxaborol moiety to the 1,2-bis(4-pyridyl)ethylene ring (Figure 3).[20] Charge-transfer transitions internal to the dioxaborol strand, specifically between the hydroxy–phenyl and the ethyl–phenyl rings, are not strongly affected by the presence of the pyridyl base; therefore, they do not contribute to the absorption in the visible region, and they remain confined in the UV region of the spectrum. Furthermore, it should be noted that there is no orbital contribution of boron and thus no extended conjugation as it was observed for polymers containing tricoordinate boron.[9b]

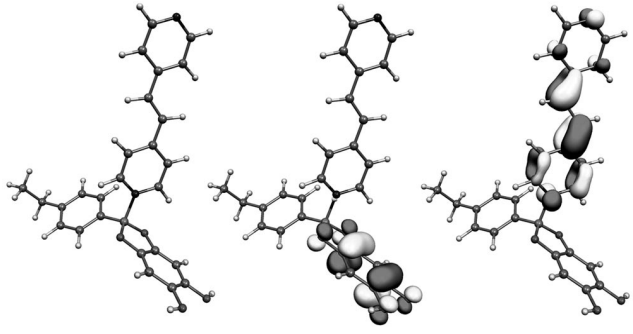


Figure 3. Left: Theoretical cluster-model of the polymeric acid–base pair. Center-right: HOMO–LUMO orbitals responsible for the charge-transfer optical transition in the yellow-green region.

Conclusions

We showed that condensation reactions of aryl boronic acids with 1,2,4,5-tetrahydroxybenzene can be used *in parallel* with dative B–pyridyl interactions to generate novel polymer architectures by three-component reactions. The

resulting crystalline polymers are deeply colored due to efficient intrastrand charge-transfer transitions. An intrinsic advantage of the multicomponent assembly strategy is its modular nature, which allows structural modifications to be easily incorporated. This was evidenced by utilizing different boronic acids and dipyridyl linkers. Because of the weak B–N interaction, the polymers are not stable in solution. However, the reversible formation of the polymer backbone could be interesting from a processing point of view. Furthermore, single crystals can be grown and thus structural information can be obtained. Overall, the work further highlights the potential of boronic acids as building blocks for the generation of polymers with interesting new structures and properties.

Experimental Section

General: 1,2-Bis(4-pyridyl)ethylene, 4,4′-bipyridyl, and the boronic acids were obtained from commercial sources. 1,2,4,5-Tetrahydroxybenzene was prepared as described in the literature.[21] All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk techniques. The ^{1}H, ^{13}C and ^{11}B spectra were recorded with a 400 MHz spectrometer by using the residual protonated solvents (^{1}H, ^{13}C) as internal standards or $BF_3{\cdot}OEt_2$ (^{11}B) as an external standard. ^{1}H NMR spectra of the polymers were obtained by dissolving the samples in hot chloroform and then rapidly measuring the solutions before the polymers started to precipitate. The solid-state NMR spectra were recorded with a Bruker DRX 400 spectrometer with a 7.0-widebore magnet by utilizing a 3-mm CPMAS probehead. A solution of boric acid in H_2O was used as the external standard (δ = 19.3 ppm).

Polymer 1: A suspension of 4-ethylphenylboronic acid (135 mg, 0.90 mmol), 1,2,4,5-tetrahydroxybenzene (64 mg, 0.45 mmol), and 1,2-bis(4-pyridyl)ethylene (82 mg, 0.45 mmol) in distilled benzene (90 mL) was heated under reflux with the use of a Dean Stark trap. After 8 h, the suspension was filtered hot, and the filtrate was cooled to room temperature. Upon cooling, a purple solid precipitated. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 196 mg, 79%. $(C_{34}H_{30}B_2N_2O_4)_n$ (552.24)$_n$: calcd. C 73.95, H 5.48, N 5.07; found C 74.25, H 5.47, N 5.16. Crystals were obtained by slow diffusion of pentane into a solution of **1** in chloroform.

Polymer 2: A suspension of 4-*tert*-butylphenylboronic acid (160 mg, 0.90 mmol), 1,2,4,5-tetrahydroxybenzene (64 mg, 0.45 mmol), and 1,2-bis(4-pyridyl)ethylene (82 mg, 0.45 mmol) in distilled benzene (90 mL) was heated under reflux with the use of a Dean Stark trap. After 8 h, the suspension was filtered hot, and the filtrate was cooled to room temperature. Upon cooling, a purple solid precipitated. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 222 mg, 81%. $(C_{38}H_{38}B_2N_2O_4)_n$ (608.34)$_n$: calcd. C 75.02, H 6.30, N 4.60; found C 75.18, H 6.39, N 4.39.

Boronate Ester 3: A suspension of 4-ethylphenylboronic acid (135 mg, 0.90 mmol) and 1,2,4,5-tetrahydroxybenzene (64 mg, 0.45 mmol) in distilled benzene (90 mL) was heated under reflux with the use of a Dean Stark trap. After 8 h, the suspension was filtered hot, and the filtrate was cooled to room temperature. Upon cooling, white crystals formed. The crystals were filtered, washed with pentane, and dried under vacuum. Yield: 93 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, ^{3}J = 7 Hz, 6 H, CH_3), 2.73 (q, ^{3}J = 8 Hz, 4 H, CH_2), 7.31 (s, 2 H, phenyl), 7.34 (d, ^{3}J = 8 Hz, 4 H, phenyl), 8.00 (d, ^{3}J = 8 Hz, 4 H, phenyl) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 15.45, 29.36, 98.36, 128.08, 135.15, 143.95, 149.18 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 34.6 ($h_{1/2}$ = 870 Hz) ppm. $C_{22}H_{20}B_2O_4$ (370.01): calcd. C 71.41, H 5.45; found C 71.25, H 5.57.

Polymer 4: A suspension of 3,5-dimethylphenylboronic acid (135 mg, 0.90 mmol), 1,2,4,5-tetrahydroxybenzene (64 mg, 0.45 mmol), and 4,4′-bipyridyl (70 mg, 0.45 mmol) in distilled benzene (90 mL) was heated under reflux with the use of a Dean Stark trap. After 1 h, the suspension was filtered hot, and the filtrate was cooled to room temperature. Upon cooling, a purple solid precipitated. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 176 mg, 74%. $(C_{32}H_{28}B_2N_2O_4)_n$ (526.20)$_n$: calcd. C 73.04, H 5.36, N 5.32; found C 72.62, H 5.43, N 5.45. Crystals were obtained by slow diffusion of pentane into a solution of **4** in chloroform.

Adduct 5: A suspension of methylboronic acid (54 mg, 0.90 mmol), 1,2,4,5-tetrahydroxybenzene (64 mg, 0.45 mmol), and 4,4′-bipyridyl (70 mg, 0.45 mmol) in distilled benzene (90 mL) was heated under reflux with the use of a Dean Stark trap. After 1 h, the suspension was filtered hot, and the filtrate was cooled to room temperature. Upon cooling, a purple solid precipitated. The precipitate was filtered, washed with pentane, and dried under vacuum. Yield: 110 mg, 71%. $C_{18}H_{16}B_2N_2O_4$ (345.95)$_n$: calcd. C 62.49, H 4.66, N 8.10; found C 62.03, H 4.46, N 7.82.

X-ray Crystallography: Details about the crystals and their structure refinement are listed in Table 1. Data collection was performed at 100(2) K by means of a Bruker APEX II CCD detector. Data reduction was carried out with EvalCCD.[22] Absorption correction

Table 1. Crystallographic data for polymers **1** and **4**.

	1·$CHCl_3$	**4**
Empirical formula	$C_{35}H_{31}B_2Cl_3N_2O_4$	$C_{16}H_{14}BNO_2$
Mol. weight / g mol^{-1}	671.59	263.09
Crystal size / mm	0.59 × 0.29 × 0.16	0.52 × 0.15 × 0.10
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a / Å	9.989(2)	8.104(5)
b / Å	12.797(4)	11.507(7)
c / Å	13.452(4)	14.356(8)
α / °	100.01(3)	90
β / °	91.234(17)	95.82(6)
γ / °	102.769(19)	90
Volume / Å^3	1648.3(8)	1331.8(14)
Z	2	4
Density / g cm^{-3}	1.353	1.312
Temperature / K	100(2)	100(2)
Absorption coeff. / mm^{-1}	0.320	0.085
Θ range / °	3.32 to 25.02	3.36 to 25.00
Index ranges	–11 → 11	–9 → 9
	–15 → 15	–13 → 13
	–16 → 16	–17 → 17
Reflections collected	28027	16398
Independent reflections	5765 (R_{int} = 0.0729)	2338 (R_{int} = 0.1178)
Absorption correction	semiempirical	semiempirical
Max. / min. transmission	1.0000 / 0.8119	1.0000 / 0.4708
Data / restraints / param.	5765 / 0 / 452	2338 / 0 / 181
Goodness-of-fit on F_2	1.127	1.118
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0564	R_1 = 0.0678
	wR_2 = 0.0860	wR_2 = 0.1207
R indices (all data)	R_1 = 0.1081	R_1 = 0.1249
	wR_2 = 0.1025	wR_2 = 0.1408
Larg. diff. peak/hole / e Å^{-3}	0.307 / –0.279	0.264 / –0.233

was applied to both data sets. Structure solution and refinement were performed with the SHELXTL software package, release 5.1.[23] The structures were refined by using the full-matrix least-squares on F^2 with all non-hydrogen atoms anisotropically defined. H atoms were placed in calculated positions by using the "riding model". CCDC-653486 and -653487 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Section: Vertical excitations for the 1,2-bis(4-pyridyl)ethylene, the (dioxaborole), and the Lewis condensate of the two species were computed at the single-point second-order approximate coupled-cluster (CC2)[17] level. Calculations were performed by using the TURBOMOLE 5.9 code,[24] within the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals.[25] For all calculations a cc-pVDZ[26] basis set was used.

Acknowledgments

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[1] a) T. D. James in *Topics in Current Chemistry Vol. 277: Creative Chemical Sensor Systems* (Ed.: T. Schrader), Springer, Berlin, **2007**, pp. 107–152; b) T. D. James in *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine* (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2005**, pp. 441–480; c) H. Fang, G. Kaur, B. Wang, *J. Fluoresc.* **2004**, *14*, 481–489; d) S. Striegler, *Curr. Org. Chem.* **2003**, *7*, 81–102; e) T. D. James, S. Shinkai in *Topics in Current Chemistry Vol. 218: Host–Guest Chemistry – Mimetic Approaches to Study Carbohydrate Recognition* (Ed.: S. Penadés), Springer, Berlin, **2001**, pp. 159–200; f) W. Wang, X. Gao, B. Wang, *Curr. Org. Chem.* **2003**, *7*, 81–102; g) T. D. James, K. R. A. S. Sandanayake, S. Shinkai, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1910–1922.

[2] For selected references, see: a) N. Iwasawa, H. Takahagi, *J. Am. Chem. Soc.* **2007**, *129*, 7754–7755; b) V. Barba, R. Villamil, R. Luna, C. Gogoy-Alcántar, H. Höpfl, H. I. Beltran, L. S. Zamudio-Rivera, R. Santillan, N. Farfán, *Inorg. Chem.* **2006**, *45*, 2553–2561; c) N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.* **2004**, 1158–1159; d) E. Barnea, T. Andrea, M. Kapon, M. S. Eisen, *J. Am. Chem. Soc.* **2004**, *126*, 5066–5067; e) M. Sánchez, H. Höpfl, M. E. Ochoa, N. Farfán, R. Santillan, S. Rojas-Lima, *Chem. Eur. J.* **2002**, *8*, 612–621; f) V. Barba, E. Gallegos, R. Santillan, N. Farfán, *J. Organomet. Chem.* **2001**, *622*, 259–264; g) N. Farfán, H. Höpfl, V. Barba, M. E. Ochoa, R. Santillan, E. Gómez, A. Gutiérrez, *J. Organomet. Chem.* **1999**, *581*, 70–81.

[3] N. Christinat, R. Scopelliti, K. Severin, *J. Org. Chem.* **2007**, *72*, 2192–2200.

[4] a) M. Albrecht, M. Fiege, M. Baumert, M. de Groot, R. Fröhlich, L. Russo, K. Rissanen, *Eur. J. Inorg. Chem.* **2007**, 609–616; b) H. Katagiri, T. Miyagawa, Y. Furusho, E. Yashima, *Angew. Chem. Int. Ed.* **2006**, *45*, 1741–1744.

[5] B. F. Abrahams, D. J. Price, R. Robson, *Angew. Chem. Int. Ed.* **2006**, *45*, 806–810.

[6] a) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268–272; b) R. W. Tilford, W. R. Gemmill, H.-C. zur Loye, J. J. Lavigne, *Chem. Mater.* **2006**, *18*, 5296–5301; c) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166–1170.

[7] J.-M. Lehn, *Prog. Polym. Sci.* **2005**, *30*, 814–831.

[8] W. Niu, C. O'Sullivan, B. M. Rambo, M. D. Smith, J. J. Lavigne, *Chem. Commun.* **2005**, 4342–4344.

[9] a) B. M. Rambo, J. J. Lavigne, *Chem. Mater.* **2007**, *19*, 3732–3739; b) W. Niu, M. D. Smith, J. J. Lavigne, *J. Am. Chem. Soc.* **2006**, *128*, 16466–16467.

[10] For reviews on boron-containing polymers, see: a) F. Jäkle, *Coord. Chem. Rev.* **2006**, *250*, 1107–1121; b) F. Jäkle, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 293–307; c) K. Ma, M. Scheibitz, S. Scholz, M. Wagner, *J. Organomet. Chem.* **2002**, *652*, 11–19.

[11] a) M. Mikami, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1995**, 153–154; b) M. Mikami, S. Shinkai, *Chem. Lett.* **1995**, 603–604.

[12] I. Nakazawa, S. Suda, M. Masuda, M. Asai, T. Shimizu, *Chem. Commun.* **2000**, 881–882.

[13] a) R. E. Dinnebier, M. Wagner, F. Peters, K. Shankland, W. I. F. David, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1400–1405; b) M. Grosche, E. Herdtweck, F. Peters, M. Wagner, *Organometallics* **1999**, *18*, 4669–4672; c) M. Fontani, F. Peters, W. Scheer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* **1998**, 1453–1465.

[14] Y. Qin, C. Cui, F. Jäkle, *Macromolecules* **2007**, *40*, 1413–1420.

[15] For the functionalization of polymer side chains by dative B–N bonds, see: P. M. Iovine, M. N. Fletcher, S. Lin, *Macromolecules* **2006**, *39*, 6324–6326.

[16] For structurally related compounds, see: W. Niu, M. D. Smith, J. J. Lavigne, *Cryst. Growth & Design* **2006**, *6*, 1274–1277.

[17] H. Nöth, B. Wrackmeyer in *NMR – Basic Principles and Progress Vol. 14: NMR Spectroscopy of Boron Compounds* (Eds.: P. Diehl. E. Fluck, R. Kosfeld), Springer, Berlin, **1978**.

[18] H. Höpfl, *J. Organomet. Chem.* **1999**, *581*, 129–149.

[19] O. Christiansen, H. Koch, P. Jørgensen, *Chem. Phys. Lett.* **1995**, *243*, 409–418.

[20] For charge-transfer excitations in tetracoordinate boron compounds, see ref.[13] and: a) Y. Qin, I. Kiburu, S. Shah, F. Jäkle, *Org. Lett.* **2006**, *8*, 5227–5230; b) Y. Cui, Q.-D. Liu, D.-R. Bai, W.-L. Jia, Y. Tao, S. Wang, *Inorg. Chem.* **2005**, *44*, 601–609.

[21] P. R. Weider, L. S. Hegedus, H. Asada, S. V. D'Andreq, *J. Org. Chem.* **1985**, *50*, 4276–4281.

[22] A. J. M. Duisenberg, C. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220–229.

[23] G. M. Sheldrick, *SHELXTL*, University of Göttingen, Germany, **1997**; Bruker AXS, Inc., Madison, Wisconsin, 53719, USA, **1997**.

[24] R. Ahlrichs, M. Bar, M. Haser, H. Horn, C. Kolmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.

[25] F. Weigend, M. Haser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152.

[26] D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358–1371.

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