Supramolecular Chemistry

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Molecular Networks Based on Dative Boron–Nitrogen Bonds**

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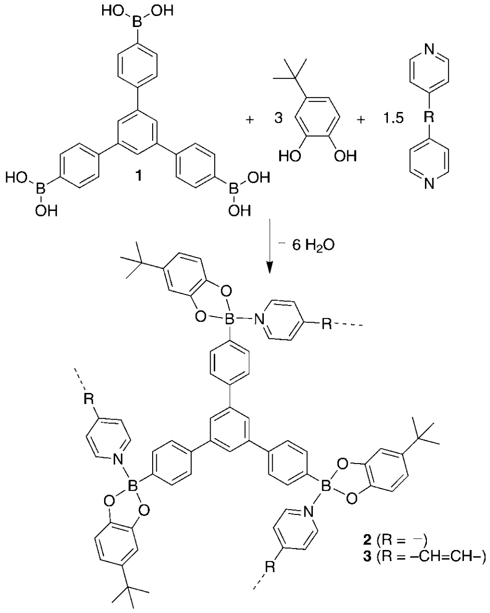
The controlled synthesis of crystalline polymers with two- or three-dimensional network structures (crystal engineering) can be achieved by connection of molecular building blocks through noncovalent interactions.[1] Hydrogen bonds[2] and coordination bonds[3] are most commonly used in this context, but halogen bonds,[4] metal–metal,[5] CH–π,[6] and π–π interactions[7] have been employed as well. Noncovalent interactions are also crucial for the creation of gels from low-molecular-weight gelators (LMGs).[8] In fact, the crystal engineering approach of using supramolecular synthons[9] has been an inspiration for the design of LMGs.[10] Crystalline and soft molecular networks show a vast number of potential applications. Novel strategies to generate such structures are thus of high interest. Herein we describe crystalline organic networks and an organogel that were obtained by connection of triboronate esters with bipyridyl linkers. A unique feature of these supramolecular polymers is the presence of dative boron–nitrogen bonds as crucial structure-directing elements.

Boronate esters are Lewis acidic compounds, which can form adducts with N-donor ligands.[11] This interaction results in a distinct structural change from trigonal-planar to tetrahedral geometry at the boron atom. The strength of the B−N interaction depends on the steric and electronic characteristics of the reaction partners as well as on the solvent.[11,12] Dative bonds between boronate esters and N-donor groups have been employed in the context of materials chemistry and structural supramolecular chemistry.[13] For example, B−N bonds were used to make molecularly defined macrocycles[14] and linear polymers.[15,16] The utilization of B−N bonds for the creation of molecular networks is, to best of our knowledge, unprecedented.

Two-dimensional polymers can be accessed by connection of tritopic building blocks with ditopic linkers. To implement such a synthetic strategy with boronate esters, we used the triboronic acid **1** along with 4-*tert*-butylcatechol[17] and 4,4′-bipyridine or 1,2-di(4-pyridyl)ethylene (Scheme 1). The triboronic acid **1** was expected to undergo a triple condensation reaction with the catechol to give a triboronate ester, which is then linked by the bipyridyl linker.



Scheme 1. Synthesis of the two-dimensional networks **2** and **3** by polycondensation reactions.

When a mixture of **1**, 4-*tert*-butylcatechol, and 4,4′-bipyridine (ratio 2:6:3; [**1**] = 3.3 mM) was heated in toluene/THF (2:1) under reflux using a Dean–Stark trap, a homogeneous colorless solution was obtained. Upon cooling, polymer **2** precipitated in the form of an orange powder in 65 % yield.[18] Polymer **3** was obtained in a similar fashion using the extended linker 1,2-di(4-pyridyl)ethylene (yield: 71 %).

The polymers can be dissolved in organic solvents such as chloroform or toluene upon heating. In solution, the B−N bonds are broken. This was shown by NMR spectroscopy: the signals observed in the ^{1}H NMR spectra are identical to those of the corresponding triboronate ester and the free bipyridyl linker (see the Supporting Information). In the solid state, however, the boron centers are tetrahedral, as evidenced by signals in the ^{11}B NMR spectrum (cross-polarization magic angle spinning) at $\delta = 14$ ppm (**3**).[19]

The polymers can be crystallized by slow cooling of toluene solutions or by vapor diffusion of pentane into toluene solutions. Crystallographic analyses were performed

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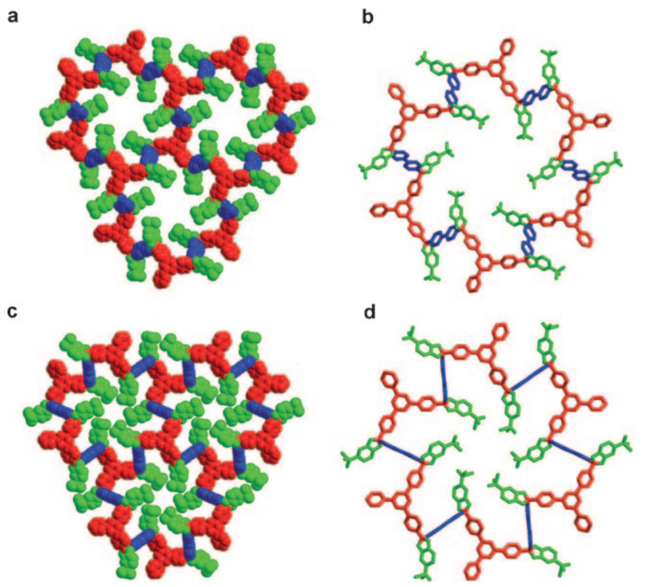


Figure 1. Parts of the two-dimensional network structures of **2** (a, b) and **3** (c, d) as determined by single-crystal X-ray diffraction. Space-filling (a, c) and wireframe views (b, d) along the crystallographic *z* axis. Catechol groups in green, bipyridyl linker in blue, and triphenylbenzene in red.

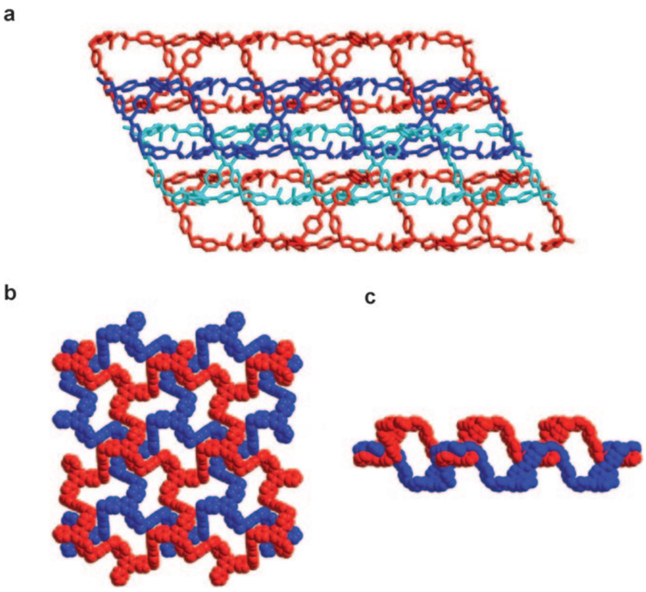


Figure 2. The (A-B-C)$_n$ layer structure of **3** in the solid state. a) Wireframe view along the crystallographic *x* axis. b,c) Space-filling representation of two adjacent layers viewed along the crystallographic *z* and *y* axes. The layers are tightly interwoven, but there is no catenation. For clarity, the catechol groups have been removed in (b) and (c).

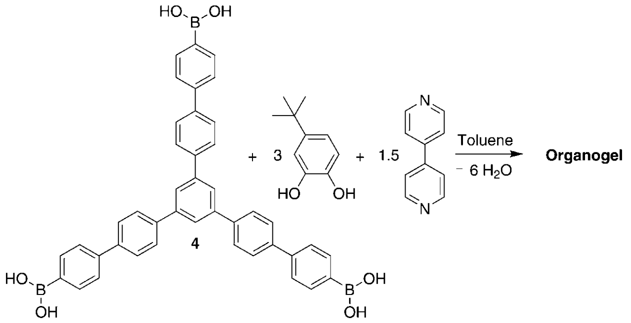
for both compounds,[20] and graphic representations of the solid-state structures are shown in Figure 1. The polymers form two-dimensional networks in which the triboronate esters act as nodes that are connected by the bipyridyl linkers. The compounds are related to some covalent organic frameworks (COFs), as they feature boronate esters as integral components of their framework.[21] In contrast to COFs, however, network formation is achieved through dative boron–nitrogen bonds. The B−N bond lengths are 1.676(5) Å for **2** and 1.678(7) Å for **3**. These values are similar to what has been observed for the 4-picoline adduct of phenylcatecholborane (1.651(3) Å).[22] The trigonal triphenylbenzene core of the boronate ester shows a propeller-like conformation, with a torsion angle between the peripheral and the central benzene rings of 45° (**2**) and 32° (**3**).

The individual layers of the networks can be described as connections of large macrocyclic structures with ring sizes of 126 (**2**) or 138 (**3**) atoms. The macrocycles of **3** appear more compact when viewed along the crystallographic *z* axis (Figure 1d vs. Figure 1b). However, the diameter of the macrocycles, as defined by the longest B···B distance, is rather similar (36.6 Å for **2** and 37.2 Å for **3**).

The polymer layers of **2** and **3** show an (A-B-C)$_n$ repeat pattern (Figure 2a). The individual layers are tightly interwoven, but there is no catenation of adjacent layers (Figure 2b,c).[23]

Crystalline **2** and **3** contain voids, which are filled with disordered toluene molecules. Thermogravimetric analysis (TGA) indicates that the solvent can be removed under vacuum at room temperature for 12 h (see the Supporting Information). However, removal of the solvent leads to a loss of crystallinity, as evidenced by powder X-ray diffraction analysis. Furthermore, N_2 sorption measurements with solvent-free polymer **3** did not show significant permanent porosity (ca. 13 $m^2 g^{-1}$). The structural collapse seems to occur in two steps. Upon careful removal of solvent from crystalline **3** at ambient conditions (room temperature, no vacuum), the diffraction peaks at $10° \leq 2\Theta \leq 20°$ disappear, but a dominant low-angle peak at $2\Theta \approx 5°$ remains. The latter is attributed to the d spacing of 15.75 Å of the (101) plane, which is slightly smaller ($d = 16.68$ Å) than the interchain spacing in the original **3**. This first step can be reversed by addition of toluene, which results in the re-formation of crystalline **3** (see the Supporting Information). However, more forcing conditions (prolonged standing after removal of solvent, or application of vacuum) irreversibly produce an amorphous material (step 2). A similar behavior was observed for **2**.

We have also investigated condensation reactions with the extended triboronic acid **4** (Scheme 2). This compound was obtained from 1,3,5-tris(4′-bromobiphenyl)benzene using a standard procedure (see the Supporting Information). Contrary to what was observed for the smaller building block **1**,



Scheme 2. Synthesis of an organogel with B−N linkages.

reaction of **4** with 4-*tert*-butylcatechol and 4,4′-bipyridine in toluene resulted in the formation of an orange gel. All three components are necessary for gel formation, as evidenced by control reactions in which one of the reactants was omitted. The system thus represents an example of a multicomponent gel.[24,25] Gel formation was expected to proceed by condensation of the triboronic acid **4** with 4-*tert*-butylcatechol to give the corresponding triester **5**, which is then linked by 4,4′-bipyridine through dative B–N bonds. This assumption was verified by reaction of preformed **5** (1 equiv) with 4,4′-bipyridine (1.5 equiv), which likewise resulted in gel formation.

Gelation of toluene can be achieved with as low as 0.5 wt % of the two components. The system thus qualifies as a supergelator.[26] Gel formation with **5** and 4,4′-bipyridine was also observed in benzene and THF but not in mesitylene. Additional evidence for the formation of a 3-dimensional network was obtained by scanning electron microscopy (SEM). SEM images of the xerogel obtained from toluene show a network of entangled nanofibers with diameters less than 40 nm. This observation is consistent with the transparency of the gel.[27]

A gel obtained by mixing **5** and 4,4′-bipyridine in [D$_8$]toluene (1.0 wt %) was examined by ^{1}H NMR spectroscopy at variable temperatures (25 to 90 °C). A line-width analysis indicated a gelation temperature of approximately 60 °C (see the Supporting Information). The well-resolved spectrum obtained at 90 °C showed signals corresponding to the free boronate ester **5** and 4,4′-bipyridine, thus indicating rupture of the dative B–N bonds. As expected,[18] the gel–sol transition was accompanied by a loss of the orange color (thermochromic behavior). The gelation temperature derived from the UV/Vis spectra recorded at variable temperatures (Figure 3) is in line with what has been determined by NMR spectroscopy.

In summary, we have demonstrated that crystalline and soft molecular networks can be obtained by connection of boronate esters through dative B–N bonds. The polymers are either obtained in one-step, three-component condensation reactions or by linking preformed boronate esters with bipyridyl linkers. Polymer formation can be reversed by increasing the temperature, a feature which could be of interest from a processing point of view. It appears likely that related two- and three-dimensional networks can be obtained by variation of the building blocks. Furthermore, it should be possible to tune the stability of the networks by modulating the strength of the dative B–N interaction through steric and electronic effects.[28] Investigations in this direction are currently being performed in our laboratory.

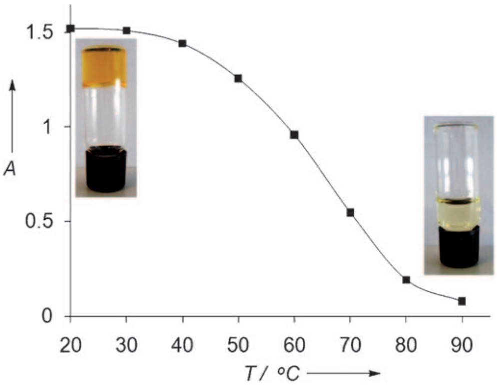


Figure 3. Change in absorbance of the organogel in toluene (1 wt %) at 425 nm. Temperature was increased from 20 to 90 °C in increments of 10 °C. Images of the gel below (left) and above (right) the gelation temperature are shown.

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[1] a) C. B. Aakeröy, N. R. Champness, C. Janiak, *CrystEngComm* **2010**, *12*, 22–43; b) G. R. Desiraju, *Angew. Chem.* **2007**, *119*, 8492–8508; *Angew. Chem. Int. Ed.* **2007**, *46*, 8342–8356; c) D. Braga, L. Brammer, N. R. Champness, *CrystEngComm* **2005**, *7*, 1–19; d) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.

[2] a) M. D. Ward, *Struct. Bonding (Berlin)* **2009**, *132*, 1–23; b) I. A. Baburin, V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *Cryst. Growth Des.* **2008**, *8*, 519–539; c) K. E. Maly, N. Malek, J.-H. Fournier, P. Rodríguez-Cuamatzi, T. Maris, J. D. Wuest, *Pure Appl. Chem.* **2006**, *78*, 1305–1321; d) G. R. Desiraju, *Acc. Chem. Res.* **2002**, *35*, 565–573.

[3] C. Janiak, J. K. Vieth, *New J. Chem.* **2010**, *34*, 2366–2388, and references therein.

[4] a) M. Fourmigué, *Curr. Opin. Solid State Mater. Sci.* **2009**, *13*, 36–45; b) P. Metrangolo, T. Pilati, G. Terraneo, S. Biella, G. Resnati, *CrystEngComm* **2009**, *11*, 1187–1196; c) L. Brammer, G. M. Espallargas, S. Libri, *CrystEngComm* **2008**, *10*, 1712–1727; d) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem.* **2008**, *120*, 6206–6220; *Angew. Chem. Int. Ed.* **2008**, *47*, 6114–6127.

[5] M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.* **2008**, *37*, 1884–1895.

[6] M. Nishio, *CrystEngComm* **2004**, *6*, 130–158.

[7] C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc. Perkin Trans. 2* **2001**, 651–669.

[8] a) A. Dawn, T. Shiraki, S. Haraguchi, S.-i. Tamaru, S. Shinkai, *Chem. Asian J.* **2011**, *6*, 266–282; b) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, *Chem. Soc. Rev.* **2008**, *37*, 109–122; c) A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem.* **2008**, *120*, 8122–8139; *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018; d) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489–497; e) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836; f) X. Y. Liu, *Top. Curr. Chem.* **2005**, *256*, 1–37; g) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159.

[9] G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327;.

[10] a) J. H. van Esch, *Langmuir* **2009**, *25*, 8392–8394; b) P. Dastidar, *Chem. Soc. Rev.* **2008**, *37*, 2699–2715.

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

[12] a) B. E. Collins, S. Sorey, A. E. Hargrove, S. H. Shabbir, V. M. Lynch, E. V. Anslyn, *J. Org. Chem.* **2009**, *74*, 4055–4060; b) L. Zhu, S. H. Shabbir, M. Gray, V. M. Lynch, S. Sorey, E. V. Anslyn, *J. Am. Chem. Soc.* **2006**, *128*, 1222–1232; c) W. Ni, G. Kaur, G. Springsteen, B. Wang, S. Franzen, *Bioorg. Chem.* **2004**, *32*, 571–581.

[13] a) R. Nishiyabu, Y. Kubo, T. D. James, J. S. Fossey, *Chem. Commun.* **2011**, *47*, 1124–1150; b) A. L. Korich, P. M. Iovine, *Dalton Trans.* **2010**, *39*, 1423–1431; c) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985–4022; d) K. Severin, *Dalton Trans.* **2009**, 5253–5264; e) N. Fujita, S. Shinkai, T. D. James, *Chem. Asian J.* **2008**, *3*, 1076–1091.

[14] a) N. Christinat, R. Scopelliti, K. Severin, *J. Org. Chem.* **2007**, *72*, 2192–2200; b) N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.* **2004**, 1158–1159.

[15] N. Christinat, E. Croisier, R. Scopelliti, M. Cascella, U. Röthlisberger, K. Severin, *Eur. J. Inorg. Chem.* **2007**, 5177–5181.

[16] For one-dimensional polymers featuring dative B–N bonds between boranes and N-donor ligands, see: a) Y. Qin, C. Cui, F. Jäkle, *Macromolecules* **2007**, *40*, 1413–1420; b) R. E. Dinnebier, M. Wagner, F. Peters, K. Shankland, W. I. F. David, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1400–1405; c) M. Grosche, E. Herdtweck, F. Peters, M. Wagner, *Organometallics* **1999**, *18*, 4669–4672; d) M. Fontani, F. Peters, W. Scherer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* **1998**, 1453–1465.

[17] 4-*tert*-Butylcatechol was used instead of simple catechol to increase solubility.

[18] The color is likely due to charge-transfer transitions from the electron-rich catecholate to the electron-deficient bipyridyl linkers (see Ref. [14]).

[19] N. Farfán, R. Contreras, *J. Chem. Soc. Perkin Trans. 2* **1987**, 771–773.

[20] X-ray data for **2**: $C_{28.25}H_{27}BNO_2$, $M = 423.32$ g mol^{-1}, space group $R\bar{3}$, $a = b = 29.9203(12)$, $c = 17.0275(15)$ Å, $V = 13201.2(14)$ Å^3, $Z = 18$, $\rho = 0.958$ g cm^{-1}, $\mu = 0.059$ mm^{-1}, $F(000) = 4041$, crystal size $0.23 \times 0.20 \times 0.15$ mm^3, 39206 reflections collected, 5972 independent reflections, $R_{int} = 0.0872$, R_1 $[I > 2\sigma(I)] = 0.0950$, wR_2 (all data) $= 0.2740$, largest difference peak 0.389 e Å^{-3}, largest difference minimum -0.323 e Å^{-3}. X-ray data for **3**: $C_{38}H_{38}BNO_2$, $M = 551.50$ g mol^{-1}, space group $R\bar{3}$, $a = b = 28.036(6)$, $c = 22.600(4)$ Å, $V = 15384(6)$ Å^3, $Z = 18$, $\rho = 1.072$ g cm^{-1}, $\mu = 0.065$ mm^{-1}, $F(000) = 5292$, crystal size $0.30 \times 0.25 \times 0.19$ mm^3, 277448 reflections collected, 5989 independent reflections, $R_{int} = 0.1245$, R_1 $[I > 2\sigma(I)] = 0.1333$, wR_2 (all data) $= 0.3899$, largest difference peak 0.473 e Å^{-3}, largest difference minimum -0.439 e Å^{-3}. For both structures, scattering contributions from diffuse solvent were removed using the SQUEEZE routine in PLATON (see the Supporting Information). CCDC 800644 (**2**) and 800645 (**3**) contain 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.

[21] For COFs with boronate ester linkages, see: a) E. L. Spitler, W. R. Dichtel, *Nat. Chem.* **2010**, *2*, 672–677; b) S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang, *Angew. Chem.* **2008**, *120*, 8958–8962; *Angew. Chem. Int. Ed.* **2008**, *47*, 8826–8830; c) W. R. Tilford, S. J. Mugavero III, P. J. Pellechia, J. J. Lavigne, *Adv. Mater.* **2008**, *20*, 2741–2746; d) N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin, L. Porte, *J. Am. Chem. Soc.* **2008**, *130*, 6678–6679; e) 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; f) R. W. Tilford, W. R. Gemmill, H.-C. zur Loye, J. J. Lavigne, *Chem. Mater.* **2006**, *18*, 5296–5301.

[22] W. Clegg, A. J. Scott, F. E. S. Souza, T. B. Marder, *Acta Crystallogr. Sect. C* **1999**, *55*, 1885–1888.

[23] For a discussion of catenation in metal–organic frameworks, see: O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 950–952.

[24] For examples, see: a) Y. Li, J. Liu, G. Du, H. Yan, H. Wang, H. Zhang, W. An, W. Zhao, T. Sun, F. Xin, L. Kong, Y. Li, A. Hao, J. Hao, *J. Phys. Chem. B* **2010**, *114*, 10321–10326; b) D. G. Velázquez, D. D. Díaz, Á. G. Ravelo, J. J. M. Tellado, *J. Am. Chem. Soc.* **2008**, *130*, 7967–7973; c) B. Jonganurakkun, Y. Nodasaka, N. Sakairi, N. Nishi, *Macromol. Biosci.* **2006**, *6*, 99–103; d) S. H. Um, J. B. Lee, N. Park, S. Y. Kwon, C. C. Umbach, D. Luo, *Nat. Mater.* **2006**, *5*, 797–801; e) W. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowen, *J. Am. Chem. Soc.* **2006**, *128*, 11663–11672; f) S. J. Rowan, J. B. Beck, *Faraday Discuss.* **2005**, *128*, 43–53; g) Y. Zhao, J. B. Beck, S. J. Rowan, A. M. Jamieson, *Macromolecules* **2004**, *37*, 3529–3531; h) J. B. Beck, S. J. Rowan, *J. Am. Chem. Soc.* **2003**, *125*, 13922–13923.

[25] For a review on two-component gels, see: A. R. Hirst, D. K. Smith, *Chem. Eur. J.* **2005**, *11*, 5496–5508.

[26] K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664–6676.

[27] B. Xing, M.-F. Choi, B. Xu, *Chem. Eur. J.* **2002**, *8*, 5028–5032.

[28] Preliminary results show that the stability constants of boronate ester–pyridyl interactions can be altered by more than three orders of magnitude using electronic effects.