Supramolecular gels based on boronate esters and imidazolyl donors

Soft Matter

Supramolecular gels based on boronate esters and imidazolyl donors

N. Luisier,[a] R. Scopelliti[a] and K. Severin[a]*

Dative boron-nitrogen bonds can be used for the controlled assembly of boronate esters and N-donor ligands. So far, most investigations have focused on crystalline assemblies. In contrast, there are very few reports about soft materials based on dative B−N bonds. Here, we describe the formation of gels by aggregation of diboronate esters and ditopic bisimidazolyl donor ligands. Analyses of low molecular weight model compounds by NMR spectroscopy, isothermal titration calorimetry, and X-ray crystallography reveal that imidazolyl ligands form particularly strong dative bonds with boronate esters. The strong interaction allows gel formation in competitive polar solvents such as THF and acetone. In less polar solvents, very low critical gel concentrations of down to 0.02 wt% are observed. By using a diboronate ester linked by an azobenzene group, it is possible to form a photoresponsive gel.

Introduction

Lewis acidic boronate esters can form dative bonds with N-donor ligands such as pyridines. This interaction leads to a change of the geometry around the boron from trigonal planar to approximately tetrahedral.[1] While Lewis acid-base adducts between boronate esters and N-donor ligands are known for a long time, it is only recently that dative boron-nitrogen bonds have been used more extensively in the context of structural supramolecular chemistry.[2,3] Complex assemblies can be obtained by combining (poly)boronate esters **A** with polytopic N-donor ligands **B** to give assemblies of type A_xB_y. Alternatively, boronate esters have been attached covalently to N-donors to give monomers of type **A−B**, which can assemble to form $(A-B)_x$ aggregates. Different types of structures have been obtained using these strategies, including macrocycles,[4] cages,[5] rotaxanes,[6] and polymers.[4a-c,7] In 2011, our group has reported the formation of crystalline, two-dimensional networks by reaction of triboronate esters with bipyridyl ligands.[8] During the course of these investigations, we observed unexpectedly the formation of a gel for one particular ester/N-donor ligand combination.[8] Subsequently, the group of Iwasawa has reported the formation of a gel upon addition of 1,3-diaminopropane to an oligomeric boronic ester.[9] These first reports demonstrate that dative B−N bonds can in principle be used to induce gel formation. In the meantime, we have and others studied numerous other combinations of boronate esters and pyridyl donor ligands.[4a-c,5,7b] Aggregation via B−N bonds gave soluble, molecularly defined nanostructures, or solid precipitates, but
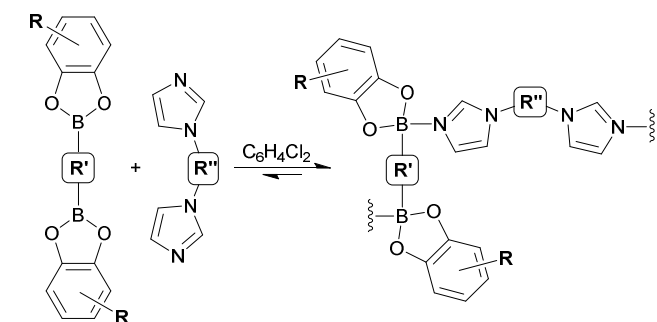
additional examples of gels were not found for pyridyl-based N-donors. However, when we combined a diboronate ester with a bisimidazole ligand instead of a bipyridyl ligand, we observed again the formation of a gel.[10] Below, we describe a detailed study about these kind of supramolecular gels.[11] It is shown that the combination of diboronate esters with bisimidazolyl ligands allows preparing a variety of gels, some of which are characterized by a very low critical gel concentration (down to 0.02 wt%). These studies are supplemented by investigations of low molecular weight model compounds, which provide a better understanding of the interaction of imidazolyl donors and boronate esters.

Results and discussion

As mentioned in the introduction, we have recently observed the formation of a gel upon combination of a diboronate ester with a bisimidazolyl ligand.[10] This finding suggested that the utilization of imidazolyl donors, as opposed to pyridyl donors, might be a better way to obtain soft materials based on dative B−N bonds. Therefore, we initiated a screening of different combinations of diboronate esters and bisimidazolyl ligands for possible gel formation (Table 1). The screening was performed by adding equimolar amounts (10 μmol each) of a diboronate ester and a bisimidazolyl ligand in 1,2-dichlorobenzene or toluene to give a 1.0 wt% solution. This mixture was heated to dissolve the solids and allowed to cool to room temperature. The capability to induce gelation was then examined by a simple tube-inversion test over 5 minutes. For the samples able to form a gel, the critical gel concentration

(CGC) and the sol-gel temperature were determined (Table 1, for additional data see ESI, Table S2). Toluene and 1,2-dichlorobenzene were selected as solvents because low polarity aromatic solvents result in stronger dative B−N bonds.[12]

Table 1 Gelation capability for different combinations of diboronate esters and bisimidazolyl ligands in 1,2-dichlorobenzene.

Entry	R	R'	R"	Gel	$T_{sol\text{-}gel}$ [°C]
1	H	p-C$_6$H$_4$	CH$_2$	yes^a	105
2	H	p-C$_6$H$_4$	CMe$_2$	yes^a	105
3	H	p-C$_6$H$_4$	p-C$_6$H$_4$	no^c	-
4	H	p-C$_6$H$_4$	1,4-C$_4$H$_8$	no^c	-
5	H	4,4'-Biphenylene	CH$_2$	yes^b	65
6	H	4,4'-Biphenylene	CMe$_2$	yes^b	45
7	H	4,4'-C$_6$H$_4$CCC$_6$H$_4$	CMe$_2$	yes^b	80
8	H	2,6-Naphthalene	CMe$_2$	no^c	-
9	4,5-Cl	p-C$_6$H$_4$	CH$_2$	no^c	-
10	4,5-Cl	p-C$_6$H$_4$	CMe$_2$	yes^b	55
11	4-Me	p-C$_6$H$_4$	CMe$_2$	yes^a	90
12	4-Me	p-C$_6$H$_4$	CH$_2$	yes^a	95
13	4-tBu	p-C$_6$H$_4$	CMe$_2$	yes^b	50
14	3,5-tBu	p-C$_6$H$_4$	CMe$_2$	no^d	-
15	3-OMe	p-C$_6$H$_4$	CMe$_2$	yes^a	100

^{a} transparent gel; ^{b} opaque gel; ^{c} a precipitate was observed; ^{d} a solution was obtained.

Initially, we tested the combination of the ester derived from 1,4-phenylenediboronic acid and catechol with bisimidazolyl ligands having different spacer groups R'' (Table 1, entries 1−4). Strong gels with a sol-gel temperature of above 100 °C were obtained for R'' = CH$_2$ and CMe$_2$, and those N-donor ligands were then used for further studies. In total, we observed the formation of a gel for 10 out of the 15 different combinations that we have tested. In the remaining five cases, we mostly observed the formation of solid precipitates, and only one mixture gave rise to a slightly viscous solution (entry 14). Extending the spacer lengths of the diboronate ester from R' = 1,4-phenylene to 4,4'-biphenylene or 4,4'-C$_6$H$_4$C≡CC$_6$H$_4$ was possible without compromising gel formation, even though the sol-gel temperature was lower (entries 5−7). For R' = 2,6-naphthalene and R'' = CMe$_2$, however, we observed a precipitate (entry 8).

Variations of the catecholate groups resulted in pronounced differences of the macroscopic properties. Although electron-withdrawing substituents on the boronate ester should increase the binding strength of a Lewis base, 4,5-dichloro-substituted bis(dioxaboroles) afforded either a gel with a low $T_{sol\text{-}gel}$ or a precipitate (entry 9 and 10). For R = 4-Me, stronger gels were obtained, but for R = 4-tBu, or R = 3,5-tBu, weak gels or a viscous liquid were observed (entries 11−14). Surprisingly, for R = 3-OMe we observed a gel with a high $T_{sol\text{-}gel}$ of 100 °C (entry 15), even though the electron-donating methoxy group should result in weaker dative B−N bonds. All these gels are thermoreversible, as they could be melted and reformed for several cycles without noticeable changes in macroscopic properties. During these cycles, solubilisation upon heating and gelation upon cooling occurred at the same temperature.

For the combination of 1,4-bis(benzodioxaborole)benzene (R = H, R' = p-C$_6$H$_4$) and bisimidazolylpropane (R'' = CMe$_2$), the CGC and the sol-gel temperature were measured in 17 different solvents.[13] All of the low polarity aromatic and chlorinated solvents which we tested afforded gels with very low CGCs and sol-gel temperatures close to the boiling points of the corresponding solvent. Noteworthy is the very low critical gel concentration of 0.02 wt% which was obtained for chlorinated benzenes.[14]

Table 2 Gelation capability in different solvents.

Solvent	$T_{sol\text{-}gel}$ [°C]	CGC [wt%]
1,2-Dichlorobenzene	105	0.02
Toluene	105	0.05
1,2,4-Trichlorobenzene	100	0.02
Benzene	80	0.04
Chloroform	50	0.05
1,1,2,2-Tetrachloroethane	85	0.05
Mesitylene	105	0.05
Xylenes	100	0.04
Chlorobenzene	95	0.02
Nitrobenzene	60	0.05
Dimethyl sulfoxide^a	-	-
Methanol^a	-	-
Dioxane^a	-	-
Tetrahydrofuran	50	1
Acetonitrile	35	1
Acetone	40	0.33
Ethyl Acetate	60	0.2

^{a} a solution was obtained.

We also tested a series of rather polar solvents (DMSO, MeOH, dioxane, THF, CH₃CN, acetone, and EtOAc). Normal, synthesis-grade solvents were employed which all contain traces of water. Therefore, one may observe a partial hydrolysis and/or solvolysis (in the case of MeOH) of the diboronate ester. Furthermore, all of these solvents contain Lewis basic donor groups, which can compete with the bisimidazolyl ligand for coordination to the Lewis acidic boronate esters. Despite these limiations, we observed gelation for tetrahydrofuran, acetone, acetonitrile, and ethyl acetate. As expected, the gels show a lower $T_{\text{sol-gel}}$ and a higher CGC. Still, it is remarkable that gels based on dative B−N bonds can be formed is such a polar environment.

To further characterize the physical properties of the gels, rheology measurements were carried out with oscillatory frequency sweep, and the elastic (G') and viscous moduli (G'') were recorded. The measurements were performed using 1,2-dichlorobenzene or 1,2,4-trichlorobenzene as solvent with concentrations of 1.0 and 3.0 wt%. In all cases, the value of G' was exceeding G'', which is in line with the definition of a gel: the elastic (solid) component is higher than the viscous part, and thus the overall behaviour of the sample is solid-like. Even though the dative B−N bond is a reversible interaction in solution, no self-healing behaviour was observed for this family of gel. The values of elastic moduli are for all samples in the kilopascal range, which is a typical value for a low molecular weight organic gelator at a low concentration.[15]
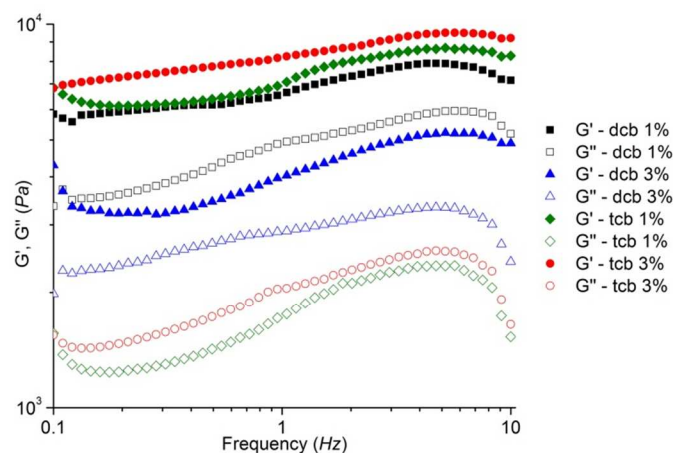
Fig. 1 Frequency stress sweep profile of gels derived from 1,4-bis(benzodioxaborole)benzene and bisimidazolylpropane at different concentrations in 1,2-dichlorobenzene (dcb) or 1,2,4-trichlorobenzene (tcb). The measurements were performed at room temperature.

Scanning electron microscopy was used to determine the network morphology of two selected xerogels, which were obtained by freeze drying. As gel components, we have used 1,4-bis(benzodioxaborole)benzene in combination with bisimidazolylmethane (R'' = CH₂) or bisimidazolylpropane (R'' = CMe₂). These combinations had given rise to particularly stable gels (Table 1, entry 1 and 2). For both samples, a typical fibrilar network was observed, with an average fibril diameter below

100 nm (Fig. 2). The small diameter of the fibril is in line with the transparency of those gels.
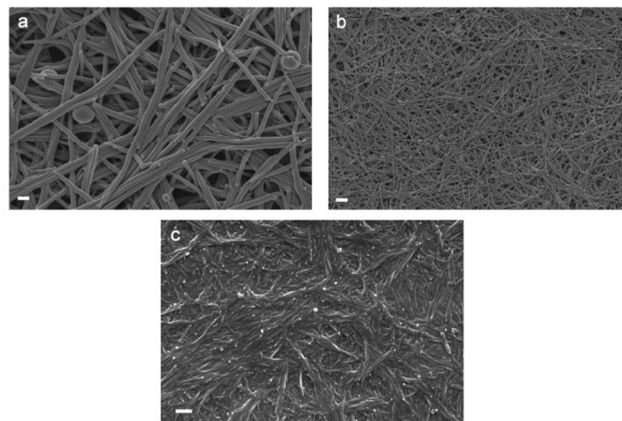
Fig. 2 Scanning electron microscopy images of xerogels derived from 1,4-bis(benzodioxaborole)benzene and bisimidazolylmethane in 1,2-dichlorobenzene (**a** and **b**), or 1,4-bis(benzodioxaborole)benzene and bisimidazolylpropane in toluene (**c**). Scale bars: 200 nm (**a**, **c**), 1 μm (**b**).

^{1}H NMR measurements of gel samples at room temperature showed no signals corresponding to the gel precursors, confirming the presence of polymeric aggregates before removal of the solvent. We also analysed the composition of the solid gel component which was obtained by filtration. Digestion of these solids in MeOD and subsequent analysis by ^{1}H NMR spectroscopy confirmed the expected 1:1 stoichiometry of boronate ester and N-donor ligand.

The diboronate ester 1,4-bis(benzodioxaborole)benzene is formed by condensation of 1,4-benzenediboronic acid and catechol. We were interested if we could make the gel directly from the diboronic acid and catechol, thereby avoiding one synthetic step. To examine this point, we added a solution of the bisimidazolyl ligand (116.9 mg) in THF (10 g) to a solution of catechol (73.1 mg) and the diboronic acid (110.0 mg) in THF (20 g). Less than 10 seconds were needed for the complete gelation of the mixture (Scheme 1). The CGC and the $T_{\text{sol-gel}}$ values of the resulting 1.0 wt% gel were identical to those obtained by using the pre-synthesized diboronate ester.
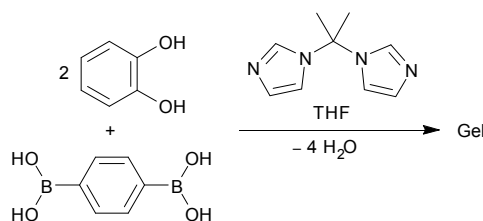
Scheme 1 Formation of a gel in THF from 1,4-benzenediboronic acid, catechol, and a bisimidazolyl ligand.

The fast and efficient gel formation was unexpected, because boronate ester condensation is not favored in a polar, water-miscible solvent such as THF. This was evidenced by an NMR study with the model compounds phenylboronic acid and catechol. The ^{1}H NMR spectrum of an equimolar mixture of these two compounds in THF-d8 (200 mM each) showed that the condensation reaction is not favored (no shift for the CH protons of catechol; see Fig. 3a and 3b). A different situation was encountered when one equivalent of N-methylimidazole was added to the mixture. Significant differences in chemical shift were observed for the signals of N-methylimidazole and catechol (Fig. 3c and 3d), suggesting the nearly quantitative formation of the tetrahedral B−N adduct. The fact that N-methylimidazole is able to promote the condensation reaction between phenylboronic acid and catechol was not unexpected, because it is known that N-donors can stabilize boronate esters.[7a,16] The magnitude of the effect, however, was surprising. In fact, when a similar experiment was performed with pyridine instead of N-methylimidazole, a less complete condensation reaction was observed (See ESI, Fig. S1).
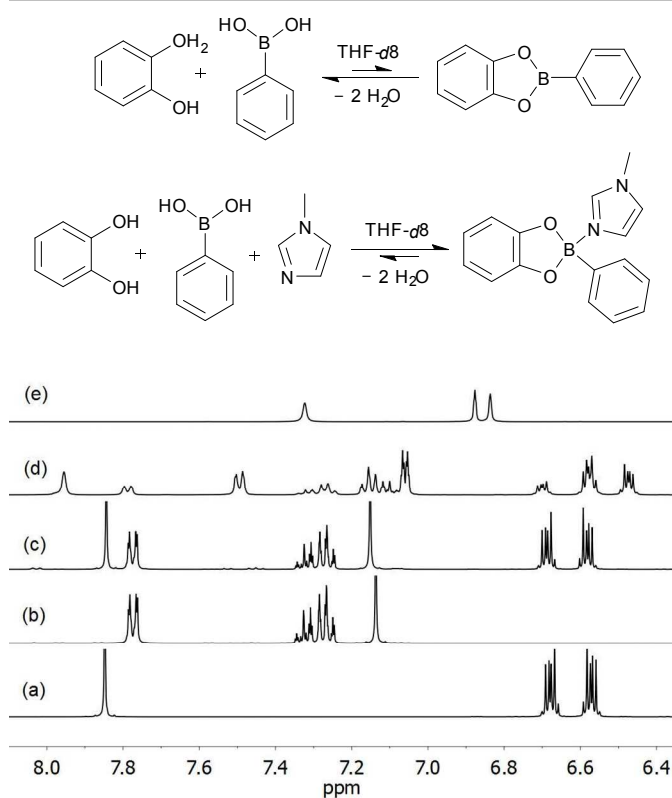
Fig. 3 Aromatic region of the ^{1}H-NMR spectra (THF-d8) of catechol (**a**), phenylboronic acid (**b**), an equimolar mixture of catechol and phenylboronic acid (**c**), an equimolar mixture of catechol, phenylboronic acid, and N-methylimidazole (**d**), and N-methylimidazole (**e**). The spectra were recorded after an equilibration time of 4 h using a concentration of 200 mM for each compound.

As a first step towards the development of functional materials based on gels with B−N linkages, we have examined the preparation of a photoresponsive gel. One possibility to prepare a photoresponsive gel is the incorporation of azobenzene groups.[17] We thus synthetized an azobenzene-containing diboronate ester from the corresponding boronic acid[18] (for details see ESI). In combination with bisimidazolylpropane, we were able to form a gel in aromatic solvents such as chlorobenzenes (mono, di or tri substituted), xylenes or toluene (Scheme 2, ESI Table S1). In 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, the CGC of the gel was as low as 0.05 wt%. Upon UV-irradiation of gel samples at λ = 366 nm, a rupture of the gel state was observed after a few minutes. The likely cause of this transformation is a photochemically induced *trans-cis* isomerization of the azobenzene moiety. At the moment, we can only speculate about what is happening on the molecular level after the isomerization of the ester. One possible reason for the disruption of the gel state could be the preferential formation of macrocycles and/or shorter oligomers instead of linear polymers. Re-gelation could be induced by a heating cooling cycle.
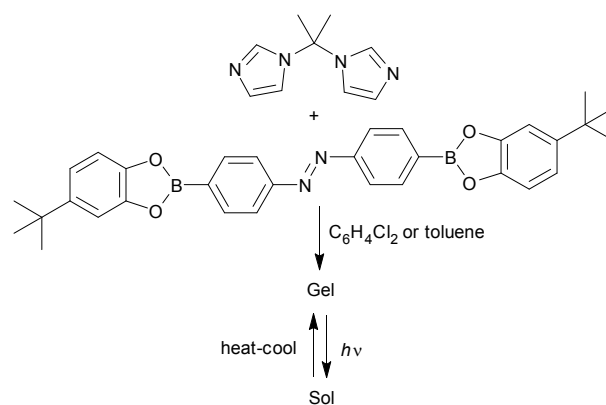

Scheme 2 Formation of a photoresponsive gel by utilization of a diboronate ester with an azobenzene group.

The low CGC values of the gels and the efficient adduct formation in polar solvents such as THF prompted us to further investigate the thermodynamics of the imidazolyl-boronate ester interaction. The binding strength of N-methylimidazole to different monoboronate esters was investigated by isothermal titration calorimetry (ITC). The association constants K_a, which were obtained from these measurements, are listed in Table 3 (for additional data see Table S4).

For the complexation of N-methylimidazole to the simple 2-phenylbenzodioxaborole (R1 = H, R2 = H), association constants between 10^3 M^{-1} (CHCl$_3$, toluene and benzene) and 10^4 M^{-1} (*o*-dichlorobenzene) were obtained (Table 3, entries 1−4). These values are approximately two orders of magnitude higher than what was observed for the adduct of 2-phenylbenzodioxaborole and pyridine.[12] The ability of N-methylimidazole to form more stable B−N adducts compared to pyridine is likely related to its increased basicity, but the reduced steric bulk of the 5-membered heterocycle might contribute as well. As expected, it was possible to further increase the stability of the B−N adduct by functionalization of the boronate ester with electron-withdrawing groups. In these

cases, association constants of more than 10^5 M^{-1} were obtained (Table 3, entries 7−9).

Table 3 Association constants of adducts between 2-phenylbenzodioxaborole and N-methylimidazole as determined by isothermal titration calorimetry (ITC). The values are averages of three independent measurements.
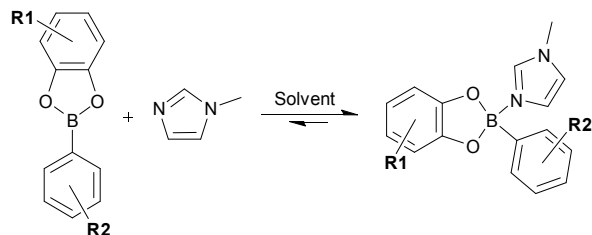
| Entry	R1	R2	Solvent	K_a [M^{-1}]
1	H	H	Chloroform	1.2(±0.3) x 10^3
2	H	H	Benzene	8.9(±0.6) x 10^3
3	H	H	o-Dichlorobenzene	1.1(±0.1) x 10^4
4	H	H	Toluene	7.6(±0.3) x 10^3
5	4-Me	H	Toluene	3.3(±0.3) x 10^3
6	4-Ph	H	Toluene	6.6(±0.4) x 10^3
7	H	4-CN	Toluene	1.2(±0.1) x 10^5
8	H	4-NO$_2$	Toluene	2.1(±0.1) x 10^5
9	3,4-Cl	H	Toluene	1.8(±0.4) x 10^5

In order to evaluate the stability of the B−N adducts at higher temperatures, we have examined toluene solutions of 2-phenylbenzodioxaborole and N-methylimidazole (20 mM each) at temperatures between 25 and 100 °C by ^{1}H NMR spectroscopy. The resulting spectra were then compared to the spectra of the individual compounds at the same temperature and concentration (see ESI, Fig. S11−S13). This study revealed that even at 100 °C, a substantial amount of the N-donor is bound to the boronate ester. For the gels based on diboronate esters and ditopic N-donors, it can thus be concluded that above the gel-sol temperature we still have the presence of short oligomers.

To complement the solution based investigation by ITC and NMR spectroscopy, we have determined the solid state structure of six N-methylimidazole-boronate ester adducts by single crystal X-ray crystallography. Some key structural parameter are listed in Table 4, and ball and stick representations of the adducts are shown in Fig. 4. The B−N bond lengths of the six adducts vary between 1.588 and 1.633 Å. These values are slightly smaller than what has been observed for crystalline adducts between boronate ester and pyridyl donors (typically, B−N$_{py}$ > 1.65 Å).[4a-c,19] In line with the results obtained by Höpfl,[1] we were able to observe a correlation between the B−N bond length and the tetrahedral character (THC) of the adducts (see ESI, Fig. S14). However, no correlation could be established between the free energy of binding as determined by ITC in solution, and the THC or the B−N bond length (see ESI, Fig. S15 and S16). Apparently, packing effects are able to obliterate the small structural

differences that one would expect purely based on thermodynamic considerations.

Table 4 Tetrahedral character (THC) and selected bond lengths of the B−N adducts shown in Fig. 4 as determined by single crystal X-ray crystallography.

R1	R2	THC [%]	B−N [Å]	B-O(1) [Å]	B-O(2) [Å]
H	4-CN	80.2	1.608(2)	1.489(2)	1.500(2)
H	H	73.4	1.633(8)	1.498(7)	1.476(7)
H	4-NO$_2$	79.3	1.609(2)	1.484(2)	1.495(2)
H	4-Ph	85.4	1.588(5)	1.506(5)	1.496(5)
4-CH$_3$	H	80.9	1.601(3)	1.501(2)	1.494(2)
3,4-Cl	H	78.8	1.590(2)	1.495(2)	1.497(2)
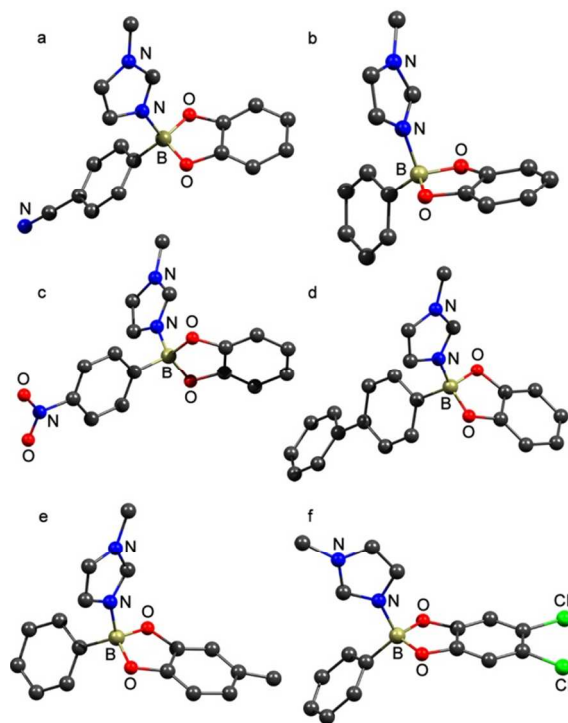
Fig. 4 Molecular structure of N-methylimidazole-boronate ester adducts in the solid state.

Conclusions

We have shown that gels can be obtained by aggregation of diboronate esters and ditopic bisimidazolyl donor ligands via dative B−N bonds. For some combinations, very low critical gel concentrations of down to 0.02 wt% were observed. Furthermore, we could demonstrate gel formation in competitive polar solvents such as THF and acetone. The high propensity of bisimidazolyl donors to from gels is in contrast to what has been overserved for reactions with polytopic pyridyl ligands. Analyses of low molecular weight model compounds by NMR spectroscopy, isothermal titration calorimetry, and X-ray crystallography have revealed that imidazolyl ligands form

stronger dative bonds to boronate esters than normal pyridyl ligands. The increased binding strength is likely a key factor for the high propensity of bisimidazolyl ligands to from gels. By using a diboronate ester with an azobenzene bridge, we were able to generate a photoresponsive gel. This result represents a first step towards the development of functional soft materials based on dative B−N bonds.

Acknowledgements

Notes and references

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Graphic for the TOC: