## Lewis Acid–Base Interactions

# Highly Lewis Acidic Arylboronate Esters Capable of Colorimetric Turn-On Response

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Dedicated to Professor Dr. Christian Reichardt on the occasion of his 80th birthday

**Abstract:** A series of boronate- $\pi$ -acceptor compounds containing different types of  $\pi$  bridges (1,4-phenylen or thien-2,5-diyl or furan-2,5-diyl) that link the switchable boronate ester group with the efficient TCF acceptor group (TCF = 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-di-

hydrofuran) has been synthesized. A TCF chromophore of this type undergoes transition to a donor- $\pi$ -acceptor compound upon coordination of Lewis bases at the Lewis acidic boron center, which is accompanied by an enhanced intramolecular charge-transfer interaction. The Lewis acid character has been investigated by spectroscopic measurements (UV/Vis, NMR spectroscopies) as well as DFT and ab initiobased calculations. It is shown that the TCF acceptor group and thiophene or furan  $\pi$ -bridges directly bound to the boron atom cooperatively increase the Lewis acidity. UV/Vis titration experiments confirm fluoride binding constants in the range of up to  $10^8 \text{ M}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>. In addition to the strong boron fluoride binding motif, Lewis interactions also occur with weaker Lewis bases, such as pyridine or aliphatic alcohols. The unique combination of chromophoric and Lewis acidic properties is responsible for the intense colorimetric turn-on response detectable after complex formation.

# Introduction

Organoboron compounds featuring a highly Lewis acidic boron center have become very important in the fields of frustrated Lewis pairs,<sup>[1]</sup> anion sensing,<sup>[2,3]</sup> and carbohydrate recognition.<sup>[4]</sup> Strategies that have been considered to increase the Lewis acidity of triarylboranes include linking of perfluorinated aryl residues<sup>[5]</sup> or other electron-withdrawing groups to the boron atom,<sup>[3,6]</sup> assisting coulombic interaction with peripheral cationic substituents,<sup>[2a,7]</sup> incorporation of the boron center in antiaromatic  $\pi$  systems,  $^{\scriptscriptstyle [8]}$  and extension of the  $\pi\text{-electron}$ system that contains the boron atom.<sup>[9]</sup> It has also been shown that the affinity toward Lewis basic anions can be effectively enhanced by using chelating organoboron receptors.<sup>[2a, 10]</sup> Some of these strategies can also be applied to arylboronic acids and arylboronate esters. However, less attention has been paid to increasing the Lewis acidic nature of chromophoric compounds.<sup>[2c]</sup> In triarylboranes, such as trianthrylborane, the extended  $\boldsymbol{\pi}$  conjugation is interrupted by the coordination of Lewis bases at the vacant p-orbital of the boron

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center, which results in an increase in the HOMO–LUMO energy gap together with a blueshift in the UV/Vis absorption.<sup>[2f]</sup> As a consequence, the interaction of Lewis bases with various triarylboranes typically gives a turn-off response.<sup>[2]</sup> To achieve a colorimetric turn-on response that involves arylboronic acids or arylboronate esters, several concepts have been reported.<sup>[11-13]</sup> In our current study, a Lewis base-triggered turn-on response was envisaged by using changes in the electronic character upon coordination at the boron center. Thus, the boron moiety develops a significant electron-donating ability when changing from trigonal-planar to tetrahedral coordination.<sup>[12,13]</sup> In combination with electron-accepting groups attached to a polarizable  $\pi$ -system, a donor- $\pi$ -acceptor chromophore was formed that shows enhanced intramolecular charge-transfer interactions (Scheme 1).<sup>[7a, 12, 13]</sup>

Previous studies on nitrostilbeneboronate esters demonstrate that the Lewis acidity at the boron atom is dependent on the strength of the electron-withdrawing group.<sup>[12a]</sup> Herein,



**Scheme 1.** Influence of Lewis acid–base interaction at the boron atom on the intramolecular charge transfer (ICT) behavior of a polarizable  $\pi$  system directly bound to boron (EWG = electron withdrawing group).

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the strong electron-withdrawing ability of the TCF acceptor group (TCF = 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran)<sup>[14]</sup> is utilized to achieve a further increase in the Lewis acidity at the boron atom. It is shown that the Lewis acidic character can be increased by heterocyclic  $\pi$ -bridges, such as thien-2,5-diyl or furan-2,5-diyl, which are directly attached to the boron center.

## **Results and Discussion**

The Knoevenagel reaction of formylated boronate esters 1 a-c with TCF gave new borylated TCF chromophores 2 a-c (Scheme 2).



Scheme 2. Synthesis of 2 a-c (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl).

Starting arylboronate esters **1a**–**c** can easily be obtained by a reaction of the corresponding arylboronic acids with pinacol under anhydrous conditions.<sup>[12]</sup> Target compounds **2a**–**c** were fully characterized by using multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B), IR, and UV/Vis spectroscopies. The observed <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic resonances of **2a**–**c** are consistent with the structures shown in Scheme 2. The central C=C double bond is in a *trans* configuration, as shown by the observed <sup>3</sup>*J*(H,H) coupling constants (**2a**: <sup>3</sup>*J*(H,H) = 16.4 Hz; **2b**: <sup>3</sup>*J*(H,H) = 16.1 Hz; **2c**: <sup>3</sup>*J*(H,H) = 16.3 Hz). The <sup>11</sup>B NMR spectroscopic resonances of **2a**–**c** observed in CDCl<sub>3</sub> (**2a**:  $\delta$  = 31.5 ppm; **2b**:  $\delta$  = 28.4 ppm; **2c**:  $\delta$  = 27.6 ppm) indicate the presence of a three-coordinated boron atom typically found in arylboronate esters.<sup>[12,15]</sup>

The UV/Vis absorption spectra of  $2\mathbf{a}-\mathbf{c}$  in  $CH_2CI_2$  show structured absorption bands (see Figure 1). Instead of the peak wavelength ( $\lambda_{max}$ ), the centroid wavelength ( $\lambda_c$ ) was used to determine the position of the lowest-energy UV/Vis absorption bands of  $2\mathbf{a}-\mathbf{c}$  ( $\lambda_c$  is the center of the full-width-at-half-maximum boundary). Whereas the maximum UV/Vis absorption band of  $2\mathbf{a}$  is found at  $\lambda_c$ =403 nm, that of  $2\mathbf{b}$  ( $\lambda_c$ =441 nm) and  $2\mathbf{c}$  ( $\lambda_c$ =442 nm) are shifted to longer wavelengths, according to an increased push-pull character mediated by the electron-rich thiophene and furan  $\pi$  bridges present in  $2\mathbf{b}$  and  $2\mathbf{c}$ , respectively.

The structures of TCF chromophores **2a–c** and the corresponding fluoroboronate adducts (BF adducts) **2a·F<sup>-</sup>**, **2b·F<sup>-</sup>**, and **2c·F<sup>-</sup>** were optimized at the B3LYP/TZVP level of theory. The influence of the polar solvent environment of CH<sub>2</sub>Cl<sub>2</sub> was considered by using the COSMO solvation model ( $\varepsilon$  = 8.9) denoted as B3LYP/TZVP-COSMO.<sup>[16]</sup> The calculated structures of **2a–c** each show the existence of a trigonal-planar geometry for the boronate ester group. RI-CC2 response calculations



**Figure 1.** UV/Vis absorption spectra of **2a–c** and **2a–c·F<sup>–</sup>** measured in CH<sub>2</sub>Cl<sub>2</sub>, values of the centroid wavelength  $\lambda_c$  are given in parenthesis.

clearly indicate that the maximum UV/Vis absorption band of **2 a–c** is dominated by HOMO–LUMO excitation (Table S1 in the Supporting Information), as reported previously for other TCF-based chromophores.<sup>[14d]</sup> A summary of the calculated values for  $E_{\rm HOMO}$  and  $E_{\rm LUMO}$  is given in Table 1. Although the  $E_{\rm LUMO}$ 

Table 1. HOMO and LUMO energies of $2a-c$ , $2a\cdot F^-$ , $2b\cdot F^-$ , and $2c\cdot F^-$ calculated at the B3LYP/TZVP-COSMO level of theory.					
	E <sub>HOMO</sub> [eV]	$E_{\rm LUMO}$ [eV]	$E_{\rm gap}$ [eV]		
2a	-6.55	-3.42	3.13		
2b	-6.37	-3.46	2.91		
2c	-6.32	-3.41	2.91		
2 a·F⁻	-5.70	-2.87	2.83		
2 b·F⁻	-5.54	-2.79	2.75		
2 c·F⁻	-5.49	-2.76	2.73		

values of 2a-c are all at a similar level, the  $E_{HOMO}$  values of 2b and 2c are increased compared with that of 2a due to the  $\pi$ -excessive nature of the heterocyclic thiophene and furan bridges. The shift in  $E_{gap}$  values calculated for 2a-c is consistent with the shift in UV/Vis absorption bands measured for 2a-c.

The coordination of Lewis bases at the boron center results in the alteration of the electronic properties of the boron center and thus changes the UV/Vis absorption behavior of **2a-c**. Complex formation studies were carried out with the fluoride ion as a strong Lewis base. Addition of TBAF (*n*Bu<sub>4</sub>NF, 0.1  $\bowtie$  in THF) to freshly prepared solutions of **2a-c** in CH<sub>2</sub>Cl<sub>2</sub> generates the corresponding BF adducts **2a-F<sup>-</sup>**, **2b-F<sup>-</sup>**, and **2c-F<sup>-</sup>**. The formation of these complexes is demonstrated by an upfield shift in the <sup>11</sup>B NMR resonance (**2a-F<sup>-</sup>**:  $\delta$ =5.3 ppm; **2b-F<sup>-</sup>**:  $\delta$ =5.9 ppm; **2c-F<sup>-</sup>**:  $\delta$ =4.9 ppm) that is typically found in four-coordinate aryl boronate esters.<sup>[12,15]</sup> Upon addition of TBAF, the intensity of the UV/Vis band of the arylboronate ester is decreased and a new absorption band that corresponds to the BF adduct appears at longer wavelengths (see Figure 1). A series of UV/Vis absorption spectra obtained upon



**Figure 2.** UV/Vis absorption spectra series of **2c** in CH<sub>2</sub>Cl<sub>2</sub> ( $3.5 \times 10^{-5}$  M) upon incremental addition of TBAF (a) and spectral changes monitored at  $\lambda$  = 525 nm (b).

incremental addition of TBAF to 2c is given in Figure 2. The bathochromic shift in the UV/Vis band upon formation of the BF adduct is increased in the presence of thiophene and furan bridges in **2b** and **2c** (**2a**:  $\Delta\lambda_c = 49 \text{ nm}$ ;  $\tilde{\nu} = 2690 \text{ cm}^{-1}$ ; **2b**:  $\Delta \lambda_c = 77 \text{ nm}; \ \tilde{\nu} = 3370 \text{ cm}^{-1}; \ \mathbf{2c}: \ \Delta \lambda_c = 84 \text{ nm}; \ \tilde{\nu} = 3610 \text{ cm}^{-1})$ owing to an overlap of the electron-donating effects of the tetrahedral boron moiety<sup>[12b]</sup> and the electron-rich heterocyclic  $\pi$ bridges.<sup>[17]</sup> A distinct color change from yellow to red arises for **2b** and **2c** in CH<sub>2</sub>Cl<sub>2</sub> after addition of TBAF, which correspond to a colorimetric turn-on response upon formation of the BF adduct (see TOC graphic and Figure S3 in the Supporting Information). In contrast, addition of TBAF to 2a in CH<sub>2</sub>Cl<sub>2</sub> merely increases the intensity of the yellow color. The results of RI-CC2 response calculations demonstrate that the maximum UV/Vis absorption bands of BF adducts 2a-c·F<sup>-</sup> are mainly dominated by HOMO-LUMO excitations, as already shown for free arylboronate esters 2a-c (Table 1). The shifts observed in the UV/Vis absorption spectrum are in agreement with the narrowed HOMO-LUMO energy gap upon fluoride ion binding.

Although a redshift in the UV/Vis absorption band of 2ac in CH<sub>2</sub>Cl<sub>2</sub> is observed upon addition of F<sup>-</sup>, the presence of a tenfold excess of halides Cl<sup>-</sup>, Br<sup>-</sup>, or l<sup>-</sup> added as  $nBu_4N^+$ salts did not change the UV/Vis absorption profiles.

To evaluate the strength of the Lewis acidic nature of 2a-c, we determined the fluoride-binding capability in  $CH_2CI_2$  by using UV/Vis titration experiments with incremental addition of TBAF (for 2c see Figure 2 and Figures S4–S6 in the Supporting Information).

Table 2. Calculated gas-phase fluoride ion affinities (FIA) and experimen-					
tal fluoride ion binding constants (K) for $2a-c$ determined in $CH_2CI_2$ . All					
structures have been optimized at the B3LYP/TZVP level of theory.					

	$FIA^{[a]}$ [kJ mol <sup>-1</sup> ]	$FIA^{[b]} [kJmol^{-1}]$	$FIA^{[c]}$ [kJ mol <sup>-1</sup> ]	<i>K</i> [M <sup>-1</sup> ]	
2a 2b 2c	330.0 355.7 359.0	355.1 376.7 378.4	341.5 366.1 367.8	$\begin{array}{c} 4.0(0.7) \times 10^6 \\ 1.9(0.8) \times 10^7 \\ > 1 \times 10^8 \end{array}$	
[a] Calculated at the B2LVP/T7\/P level of theory. [b] Single point calcula					

tion at the RI-MP2/TZVPP level of theory. [c] Calculated at the RI-BP86/ SV(P) level of theory according to a isodesmic approach.<sup>[20]</sup>

The fluoride binding constants (K) of 2a-c have been obtained from the 1:1 binding isotherm according to a method described by Gabbaï and co-workers.<sup>[10a]</sup> A comparison of experimental and calculated values is given in Table 2. The fluoride binding constant (K) for **2a** ( $K = 4.0 \times 10^6 \,\text{m}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>) already exceeds values typically found for arylboronate esters.<sup>[2c,12]</sup> The strong electron-withdrawing ability of the TCF acceptor group is the origin of the enhanced electrophilicity of the arylboronate group in 2a. Compared with 2a, the Lewis acidity of **2b** ( $K = 1.9 \times 10^7 \,\mathrm{m}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>) is further increased by the thiophene  $\pi$  bridge bound to the boron atom. Enhancement of the Lewis acidity of the boron center by thiophene moieties was already reported for triarylboranes.<sup>[7a,9]</sup> The fluoride binding constant of 2c exceeded the measurable range  $(K > 10^8 \,\mathrm{m}^{-1})$  in CH<sub>2</sub>Cl<sub>2</sub>, which reveals that the Lewis acidic character of 2c is substantially increased compared with 2a (see Table 2). Thus, the fluoride ion affinity of 2c is comparable to that of mono- and even some bidentate receptors based on triarylboranes.<sup>[2]</sup> The furan-2,5-diyl bridge directly bound to boron and the TCF acceptor group both cooperatively increase the electrophilicity of the boron atom in 2a to a remarkably high value. Although some 2-furylboranes have been described in the literature,<sup>[19]</sup> the impact of a furyl group on the Lewis acidity of the boron atom has not been studied. To the best of our knowledge, this is the first study to report that the Lewis acidity of an organoboron compound is increased by a furan-2-yl moiety directly bound to the boron atom.

The increased Lewis acidity of the boron center in **2b** and **2c** is still a surprising observation because electron-rich  $\pi$  bridges and other electron-donating groups tend to reduce the electron deficiency at the boron atom and thus diminish the Lewis acidity.<sup>[2c,3c,18]</sup>

To support the experimental findings concerning the Lewis acidic nature, the fluoride-ion affinity (FIA) of **2***a*–*c* was calculated by using the gas-phase reaction according to Equation (2).<sup>[16]</sup> Additionally, the FIA was also obtained by means of single-point calculations at the RI-BP86/SV(P) level of theory according to the isodesmic approach [Eq. (3)] by considering the experimental FIA of CF<sub>2</sub>O (FIA = 209 kJ mol<sup>-1</sup>).<sup>[20]</sup> Calculated FIA values are summarized in Table 2.

$$\mathbf{2} + \mathbf{F}^{-} \to \mathbf{2} \cdot \mathbf{F}^{-} \tag{2}$$

$$\mathsf{CF}_3\mathsf{O}^- + \mathbf{2} \to \mathsf{CF}_2\mathsf{O} + \mathbf{2} \cdot \mathsf{F}^- \tag{3}$$

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In all calculations, it was found that the FIA increases in the order 2a < 2b < 2c, which is in agreement with the experimentally determined fluoride-ion binding constants. The results demonstrate that the FIA of 2a is in the same order of magnitude as the FIA of triphenylborane (BPh<sub>3</sub>), which has been reported to be 342 kJ mol<sup>-1.[20b]</sup>

Further understanding of the Lewis acidic character can be obtained by analyses of the electron-density distribution. A summary of relevant natural bond orbital (NBO) charges calculated for 2a-c by using natural population analysis is given in Table 3.

Table theory	<b>Table 3.</b> NBO charges in <b>2a–c</b> calculated at the B3LYP/TZVP level of theory (pin = $C_6H_{12}O_2$ ; EWG = $C_{12}H_6N_3O$ ).						
$\begin{array}{c} \begin{array}{c} & & & \\ & & $							
	pin	В	(B)—C	(B)—aryl	Х	EWG	
2a 2b 2c	-0.78 -0.75 -0.74	+ 1.07 + 1.05 + 1.01	-0.34 -0.49 -0.01	-0.22 -0.18 -0.16	+0.10 + 0.45 - 0.36	-0.07 -0.11 -0.11	

For 2a-c, minor trends in the charge-density distribution have been found at the pinacol ester (denoted as pin) and the TCF-based acceptor group (denoted as EWG, including the central C=C double bond). The electron density at the boron atom increases in the order 2a < 2b < 2c. However, from the order of the Lewis acidity (2a < 2b < 2c) the lowest electron density at the boron atom would be expected in 2c. At the aryl group directly bound to the boron atom, denoted as (B)aryl, major differences are apparent. Overall, the charge density located at (B)–aryl is diminished in the order  $2\,a\!>\!2\,b\!>\!2\,c.$  In 2b, a positive partial charge is located at the sulfur atom, which can provide attractive coulombic interactions with Lewis bases. In 2c, the electron density at the carbon atom directly bound to the boron center, denoted as (B)--C, is reduced due to the -I effect of the electronegative furan oxygen atom. The loss of charge density reduces repulsive interactions to Lewis bases and thus increases the Lewis acidity of the boron atom in **2 c**.

NBO calculations also show that coordination of a fluoride ion to 2a-c induces a charge transfer from the electron-releasing four-coordinate boron moiety ( $-BpinF^-$ ) to the TCF acceptor group (see Figures S7–S9 in the Supporting Information). In addition, DFT calculations show that a distinct bond-length alternation (BLA) is found for 2a-c, which in turn is noticeably reduced upon fluoride-ion coordination. The decrease in the BLA is in agreement with the intramolecular charge transfer that occurs upon formation of the BF adducts (for details, see Figures S10 and S11 in the Supporting Information).

The enhanced Lewis acidity of  $2\,b$  and  $2\,c$  facilitates the interaction with Lewis bases weaker than  $F^-.$  In this way, compounds  $2\,b$  and  $2\,c$  are able to interact with electron-

pair-donating solvents, such as pyridine or aliphatic alcohols, through the formation of Lewis acid-base adducts.

The UV/Vis absorption of **2b** and **2c** measured in pyridine (Figures 3 and 4) is shifted to longer wavelengths compared with that measured in CH<sub>2</sub>Cl<sub>2</sub> (**2b**:  $\lambda_c$ (pyr)=476 nm;  $\Delta\lambda_c$ = 35 nm;  $\tilde{\nu}$ =1700 cm<sup>-1</sup>; **2c**:  $\lambda_c$ (pyr)=488 nm;  $\Delta\lambda_c$ =46 nm;



Figure 3. Selected UV/Vis absorption spectra of 2 b in solvents of different polarity (TMU = 1,1,3,3-tetramethylurea; TCE = 1,1,2,2-tetrachloroethane).



Figure 4. Selected UV/Vis absorption spectra of 2 c in solvents of different polarity (TMU = 1,1,3,3-tetramethylurea; TCE = 1,1,2,2-tetrachloroethane).

 $\tilde{\nu} = 2100 \text{ cm}^{-1}$ ). Similar measurements with **2a** exhibit a very small redshift on changing the solvent from CH<sub>2</sub>Cl<sub>2</sub> to pyridine ( $\lambda_c(\text{pyr}) = 408 \text{ nm}$ ;  $\Delta \lambda_c = 5 \text{ nm}$ ;  $\tilde{\nu} = 300 \text{ cm}^{-1}$ ), which indicates the presence of a trigonal-planar boron atom in **2a** under these conditions (Figure 5).

<sup>11</sup>B NMR spectroscopy measurements in  $[D_s]$ pyridine confirm the formation of a tetrahedral boron species for **2b** ( $\delta$  = 12.8 ppm) and **2c** ( $\delta$  = 7.5 ppm). The <sup>11</sup>B signal of **2c** at higher field is in agreement with the increased Lewis acidity of **2c** compared with **2b**. In contrast, adduct formation with pyridine was not observed for **2a**, as shown by the <sup>11</sup>B resonance at

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**Figure 5.** Selected UV/Vis absorption spectra of 2a in solvents of different polarity (TMU = 1,1,3,3-tetramethylurea; TCE = 1,1,2,2-tetrachloroethane).

 $\delta$  = 28.0 ppm. Accordingly, steric strain, which is similar around the boron center in **2a**-**c**, can be overcome due to the highly Lewis acidic boron center in **2b** and **2c**.

Remarkably, the strong Lewis acidic character of **2b** and **2c** even enables interactions with aliphatic alcohols. These interactions can be monitored by using UV/Vis spectroscopy. A compilation of the UV/Vis absorption spectra of **2a**–**c** measured in HFIP, TFE, MeOH, EtOH, 1-PrOH, 2-PrOH and 1-BuOH (HFIP= 1,1,1,3,3,3-hexafluoroisopropanol; TFE=2,2,2-trifluoroethanol) is given in Figures 6–8.

A redshift in the UV/Vis absorption can be observed for **2b** and **2c**, which is dependent on the electron-pair-donating ability of the alcohol and the Lewis acidity of the boron compound (Figures 7 and 8). In contrast, no redshift in the UV/Vis absorption band is observed for the less Lewis acidic **2a**. The UV/Vis absorption profiles of **2b** measured in EtOH and 2-PrOH and that of **2c** measured in MeOH, EtOH, 1-PrOH, 2-PrOH, and BuOH are very similar compared to that of BF adducts **2b**·F<sup>-</sup> and **2c**·F<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>. With the UV/Vis spec-



Figure 6. UV/Vis absorption profiles of 2a measured in common alcohols. The UV/Vis spectra of 2a and  $2a \cdot F^-$  measured in CH<sub>2</sub>Cl<sub>2</sub> are included for comparison.

1.0 CH<sub>2</sub>Cl<sub>2</sub> HEIP TFF 0.8 MeOH **FtOH** 1-PrOH 0.6 2-PrOH 1-BuOH Α 2b·F<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> 0.4 0.2 0.0 300 350 400 450 500 550 600 650 700  $\lambda / nm$ 

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Figure 7. UV/Vis absorption profiles of 2b measured in common alcohols. The UV/Vis spectra of 2b and 2b-F<sup>-</sup> measured in CH<sub>2</sub>Cl<sub>2</sub> are included for comparison.



Figure 8. UV/Vis absorption profiles of 2c measured in common alcohols. The UV/Vis spectra of 2c and 2c-F<sup>-</sup> measured in CH<sub>2</sub>Cl<sub>2</sub> are included for comparison.

tral shifts upon complex formation with  $F^-$  or pyridine in mind, we conclude that a four-coordinate boron species is formed in which an alkoxide is coordinated at the boron center. A possible interaction scenario is suggested in Scheme 3. The formation of a similar boron-methanol complex was previously described for the highly Lewis acidic thiophene-based bis(benzo-[*b*]-thien-2-yl)mesitylborane, however, the authors do not explain the fundamental aspects of the interaction in detail.<sup>[9]</sup>

The stoichiometry of this equilibrium is difficult to determine because manifold interactions are possible between the excess alcohol and the starting compound as well as the formed adduct. The generation of Brönsted acidity of **2b** and **2c** by interaction with alcohols is supported by the result that addition of the sterically hindered base 2,6-di-*tert*-butylpyridine (DTP) increases the intensity of the UV/Vis absorption band of the suggested boron–alkoxide complex in **2b** or **2c**. Thus, DTP traps mobile protons in the alcoholic solution and shifts the overall equilibrium to the adduct side of the formula given in Scheme 3. This feature is clearly observed for TFE as a solvent that reacts incompletely with **2b** or **2c** due to its reduced ba-

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Scheme 3. Suggested interaction of 2b and 2c with alcohols R–OH that induce Brönsted acidity. The uptake of the liberated proton is possible by the alcohol R–OH itself, similar to autoprotolysis of the alcohol, or by addition of the noncoordinating base DTP.

sicity compared with methanol or ethanol, which are moderately basic and can abstract a proton. DTP itself is unable to form any complexes with 2a-c as shown by reference experiments. In HFIP, which has a weak electron-pair-donating ability, a redshift is not observed for 2b and 2c, which indicates that the free arylboronate ester is predominantly present in this solvent.<sup>[21]</sup>

Lewis basic impurities, such as alkaline traces left from drying of the alcohols, can be excluded as the origin of the shift observed for 2b and 2c because these traces would also interact with 2a, which was not observed.

The solubility of **2a**–**c** in pure alcohols is too low to confirm complex formation by using <sup>11</sup>B NMR spectroscopy. However, <sup>11</sup>B NMR spectroscopic measurements of **2c** in a CDCl<sub>3</sub>/EtOH (50:50 v/v) mixture reveal a shift to higher field (in CDCl<sub>3</sub>:  $\delta$  = 27.6 ppm; in CDCl<sub>3</sub>/EtOH:  $\delta$ =23.1 ppm), which indicates that four-coordinate boron species are present. In contrast, adduct formation with fluoride can be confirmed for **2c** by the <sup>11</sup>B resonance at  $\delta$ =4.9 ppm.

The UV/Vis absorption of **2***a*–**c** was measured in 20 noncoordinating solvents to show the influence of specific effects on the solvatochromic redshift of the UV/Vis absorption measured in pyridine or aliphatic alcohols. In this context, solvatochromic effects seem to be of minor importance because the position of the UV/Vis absorption band is only slightly shifted by a change in solvent polarity from Et<sub>2</sub>O to dimethyl sulfoxide (**2a**:  $\tilde{\nu} = 250 \text{ cm}^{-1}$ ; **2b**:  $\tilde{\nu} = 420 \text{ cm}^{-1}$ ; **2c**:  $\tilde{\nu} = 520 \text{ cm}^{-1}$ , Figure 3–5).<sup>[21]</sup>

It is notable that each of the long wavelength UV/Vis absorption energies of 2a-c is a function of the solvent-polarizability parameter SP<sup>[21c]</sup> (see Table S2 in the Supporting Information). Thus, different dependencies of the UV/Vis absorption energies on SP are found for chlorinated and non-chlorinated solvents (Figure 9).

With increasing solvent parameter SP, the UV/Vis absorption band is shifted to longer wavelengths, which is in line with a positive solvatochromic shift.<sup>[22]</sup> This result underlines the fact that polarizable solvents do nonspecifically induce a weak



**Figure 9.** Correlation of the measured UV/Vis absorption maxima ( $\tilde{v}_{cr}$  centroid wavenumber) of **2a-c** as a function of the polarizability (SP parameter) in 20 solvents (excluding alcohols and pyridine).  $\blacksquare = 2a; \land = 2b;$  and  $\bullet = 2c$ . Closed symbols represent nonchlorinated solvents. Open symbols represent chlorinated solvents. Data taken from Table S2 in the Supporting Information.

electron displacement of the chromophore from the boron center to the EWG, according to Scheme 1.

It should be noted that the direct coordination of pyridine or aliphatic alcohols onto the boron center does not correspond to the concept of solvatochromism because a chemical alteration takes place.<sup>[22]</sup>

#### Conclusion

We report on the synthesis and properties of new D- $\pi$ -A-type TCF chromophores with a boronate pinacol ester group. It is shown that the Lewis acidity of the boron atom can be dramatically enhanced by the combination of the strongly electron-withdrawing TCF acceptor group together with the electron-rich thiophene and furan  $\pi$  bridges. We note that a 2-furyl moiety directly bound to the boron atom extraordinarily increases the Lewis acidity of the boron center. The high Lewis acidity of the boron atom in 2b and 2c enables interaction not only with strong Lewis bases, such as fluoride ions, but also with weaker Lewis bases, such as pyridine and common aliphatic alcohols. Lewis acid-base interactions at the boron atom decrease the HOMO-LUMO energy gap of the chromophore and shift the UV/Vis absorption band to longer wavelengths. In the presence of electron-rich thiophene and furan  $\pi$  bridges, Lewis acid-base interactions at the boron atom induce a distinct color change that results in a colorimetric response visible with the naked eye.

#### **Experimental Section**

#### Synthesis of 2 c

2-Formyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (0.382 g, 1.72 mmol), TCF (0.343 g, 1.72 mmol), and piperidine

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(20 µL) were dissolved in a mixture of anhydrous toluene (5 mL) and anhydrous THF (2 mL). After heating to reflux for 2 h, the solvent was removed under vacuum. The resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and flushed through a short plug of silica gel. The solvent was removed under vacuum and the resulting solid was further purified by recrystallization from ethyl acetate to afford 2c as orange-red crystals (0.397 g, 57%). M.p. (EtOAc): 279°C (decomp); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 1.37$  (s, 12 H, CH<sub>3</sub>), 1.74 (s, 6H, CH<sub>3</sub>), 6.92 (d,  ${}^{3}J = 16.3$  Hz, 1H, CH), 6.98 (d,  ${}^{3}J = 3.6$  Hz, 1H, CH), 7.18 (d,  ${}^{3}J = 3.6$  Hz, 1H, CH), 7.59 ppm (d,  ${}^{3}J = 16.3$  Hz, 1H, CH); <sup>1</sup>H NMR (250 MHz, [D<sub>5</sub>]pyridine):  $\delta = 1.25$  (s, 12 H, CH<sub>3</sub>), 1.67 (s, 6 H, CH<sub>3</sub>), 6.94 (d, <sup>3</sup>*J*=15.9 Hz, 1 H, CH), 7.33 (d, <sup>3</sup>*J*=3.6 Hz, 1 H, CH), 7.55 (d, <sup>3</sup>*J*=3.6 Hz, 1 H, CH), 8.15 ppm (d, <sup>3</sup>*J*=15.9 Hz, 1 H, CH); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 24.7 (CH<sub>3</sub>), 26.2 (CH<sub>3</sub>), 57.7 (C), 85.0 (C), 97.6 (C), 98.6 (C), 110.5 (CN), 110.9 (CN), 111.7 (CN), 113.6 (CH), 119.8 (CH), 126.1 (CH), 132.1 (CH), 154.5 (C), 173.2 (C), 175.4 ppm (C);  $^{11}\text{B}$  NMR (80 MHz, CDCl\_3):  $\delta\!=\!27.6\,\text{ppm}$  (brs);  $^{11}\text{B}$  NMR (80 MHz,  $[D_{s}]$ pyridine):  $\delta = 7.5$  ppm (brs); IR (KBr):  $\tilde{\nu} = 3121$  (m), 3055 (w), 2983 (m), 2232 (s), 1585 (s), 1346 (s), 1317 (m), 1142 (m), 1024 cm<sup>-1</sup> (m); UV/Vis (CH\_2Cl\_2):  $\lambda_{\rm max}$  ( $\!\varepsilon\!$ )  $\!=\!$  442 nm (42400); elemental analysis calcd (%) for C<sub>22</sub>H<sub>22</sub>BN<sub>3</sub>O<sub>4</sub>: C 65.53, H 5.50, N 10.42; found: C 65.67, H 5.49, N 10.46.

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