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Full Paper

# Using Quenching Kinetics and Thermodynamics of Amino-Fluorophores as Empirical Tools for Predicting Boronic Acid Sensors Suitable for Use in Physiological Conditions

*Nicholas McGregor,*[A] *Christophe Pardin,*[A,B] *and W. G. Skene*[A,C]

[A]Laboratoire de caractérisation photophysique des matériaux conjugués, Department of Chemistry, Pavillon JA Bombardier, Université de Montréal, CP 6128, succ. Centre-ville, Montreal, Quebec, H3C 3J6, Canada.
[B]Department of Chemistry, D'Iorio Hall, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada.
[C]Corresponding author. Email: w.skene@umontreal.ca

A series of water-soluble 1-amino-naphthalenes and 2-amino-fluorenes are prepared. These serve as model fluorophores for measuring the thermodynamics and kinetics of fluorescence quenching with phenylboronic acids and aliphatic amines. Steady-state and time-resolved fluorescence quenching kinetics are investigated using the Stern–Volmer method. Diffusion limited quenching constants and exergonic thermodynamics of electron transfer are derived for the 5-amino-1-napthol and 2-aminofluorene derivatives with phenylboronic acid and/or an aliphatic imine. No quenching and endergonic thermodynamics or electron transfer are observed for 5-sulfonamide, 5-sulfonic acid, or 5-hydroxy-7-sulfonic acid aminonaphthalene derivatives. Boronic acid sensors synthesized from these aminofluorophores by reductive amination with 2-formylphenylboronic acid undergo fluorescence revival in the presence of saccharides only when the fluorophore demonstrates diffusion limited quenching kinetics and exergonic thermodynamics of electron transfer with the boronic acid or imine quenchers. Thus, these two properties are suitable empirical tools for predicting saccharide-induced fluorescence revival of boronic acid sensors.

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## Introduction

Fluorescent molecular sensors have attracted much attention in part because of their sensitivity compared with their colourimetric counterparts.[1] Boronic acid derivative fluorophores are of no exception.[2–4] These sensors undergo significant fluorescence changes upon binding of polyols, notably saccharides.[5] The selective sensor properties of boronic acid fluorophores for biologically relevant saccharides have led to their use as non-invasive diagnostic tools.[6–8] In particular, they have been extensively applied as glucose sensors for monitoring saccharide levels in diabetics.[9–15]

A notable advent to the field of boronic acid sensors was the incorporation of an amine fluorophore in proximity to the boronic acid.[16] The inclusion of the nitrogen leads to B–N interactions that quench the fluorophore's fluorescence. This interaction is perturbed upon binding of either a 1,2 or 1,3-periplanar diol that causes revival of the fluorophore's fluorescence.[3,17] This leads to a versatile off/on chemofluorescence sensor with both a high sensitivity and low limit of detection.[18] This is in contrast to their amine-free boronic acid counterparts that do not benefit from B–N interactions and simply undergo variable changes in fluorescence intensity.[19]

The added benefit of the B–N interaction is a reduction in the p$K_a$ for boron ester formation with diols.[20,21] The p$K_a$ is reduced to ~7.5 and significantly favours boron ester formation under physiological conditions. Saccharide sensing of biological samples is, therefore, possible without sample treatment or additional solution preparation, providing that the fluorophore is water soluble. This is in contrast to fluorophores that do not contain the proximal amine-boronic acid. These require aqueous solutions with pH ≥ 10 and the extreme pH potentially can lead to sample and fluorophore degradation. Another potential undesired side effect of measurements at extreme conditions is the pH-induced fluorescence changes that compete with the desired binding signalling events.[22]

Water-soluble boronic acid sensors are desired for homogeneous saccharide analyte–fluorophore sample preparation and analysis. However, this is often problematic because the required fluorescence properties necessitate polyaromatic systems that have limited water solubility. Many strategies have been adopted, including calixarene encapsulation, to increase the water solubility of the aryl fluorophores.[23] Functionalization of the boronic acid fluorophores with either carboxylic or sulfonic acids is an alternate means of obtaining

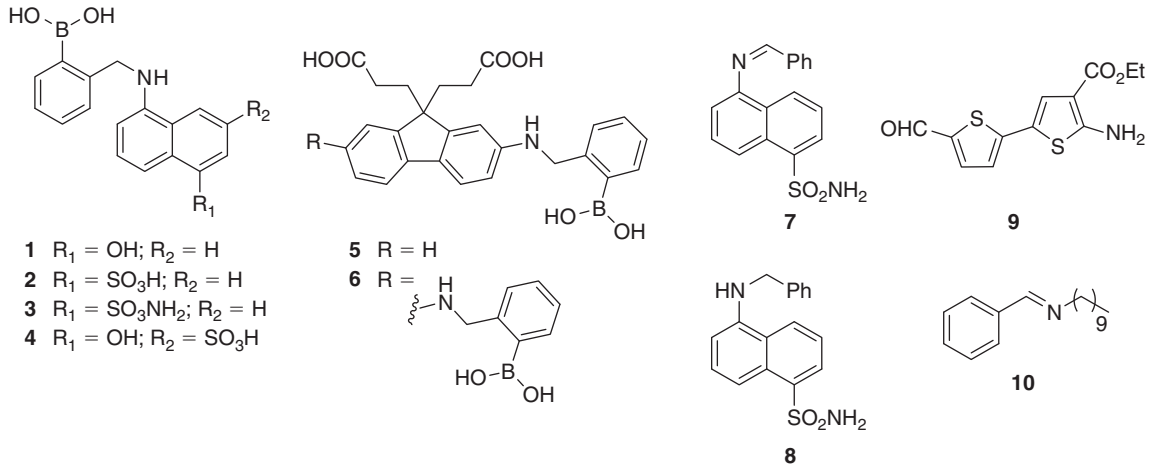
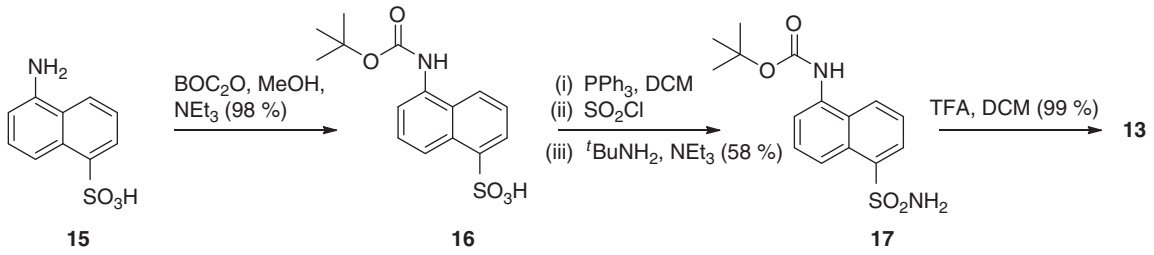



**Fig. 1.** Water-soluble boronic acid-based saccharide sensors and fluorophores prepared.




**Scheme 1.** Synthetic scheme of **13**.

water-soluble derivatives.[24,25] Meanwhile, amine incorporation for the desired B–N interactions is normally done by a two-step reductive amination of an amino-fluorophore with 2-formylphenylboronic acid. Although the required imine formation and its subsequent reduction are straightforward, certain functional groups cannot tolerate the reaction conditions. Moreover, undesired side products including boroxines and aldehyde decomposition can occur.[26,27] Taking into account these drawbacks coupled with the additional functionalization step with water solubilizing groups and a hit-or-miss fluorescence quenching/revival of the sensor, it would be beneficial to have a simple and reliable means of predicting a good sensor before undertaking its multistep synthesis. We, therefore, investigated both the quenching kinetics and thermodynamics of amino-fluorophores as empirical tools for predicting the fluorescence quench/rival of their boronic acid derivatives. The preparation of water-soluble naphthalene (**1**–**4**) and fluorene (**5**–**6**) boronic acid sensors reported in Fig. 1 are herein presented. The operating pH range of these sensors is also demonstrated. The fluorescence quenching/revival of these sensors were further correlated with the fluorescence quenching kinetics ($k_q$) and thermodynamics of their amino-fluorophore precursors (**11**–**14** and **20**–**21**) to demonstrate that both the $k_q$ constant and Rehm–Weller data are viable means of screening for sensors whose fluorescence can be triggered with saccharide binding.

## Results and Discussion

Naphthalene and fluorene were chosen for preparing water-soluble saccharide sensors because they are known to have high fluorescence quantum yields ($\Phi_f$). Furthermore, the required amine derivatives are stable and commercially available. They can also be easily modified with water solubilizing functional groups. For example, the sulfonamide **13** was prepared from the corresponding sulfonic acid **15** in 56 % overall yield as outlined in Scheme 1. The naphthalene fluorescence sensors were subsequently prepared stepwise by imination with 2-formylphenylboronic acid followed by reduction (Scheme 2) in high yields.

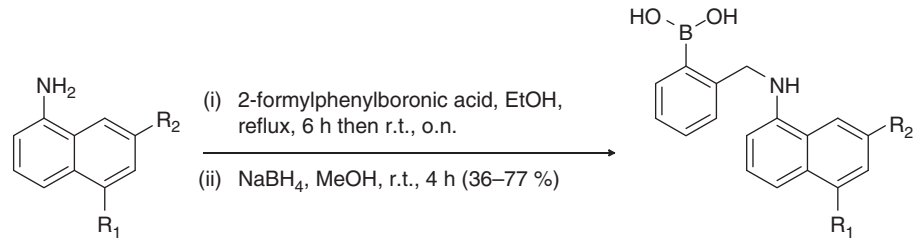
The fluorene series was prepared by 9,9′-dialkylation with *t*-butylacrylate followed by a one-pot stepwise reductive amination and immediate deprotection (Scheme 3). In contrast to the naphthalene series, the reductive amination yields for the fluorenes are much lower with overall poor chemical yields (<15 %).

Given the low chemical yields of the fluorene sensors, it would be beneficial to accurately predict their fluorescence sensing capacity and favourable B–N interactions for desired off/on fluorescence. Predictive tools would further be advantageous for optimizing the design and preparation of efficient sensors and to avoid a hit-or-miss approach. For this reason, we investigated the quenching kinetics and thermodynamics of the amino-fluorophore precursors **11**–**14** and **20**–**21** for correlation of the fluorescence quenching/revival of their corresponding boronic acid sensors **1**–**6**.

The quenching of the amino-fluorophores was first done with the imine **10**. This was chosen as a benchmark for fluorescence quenching because imines are known to be efficient excited singlet state quenchers.[28–39] Moreover, the imine is the intermediate product in the reductive amination of the sensors and it would give important fluorescence quenching information. Steady-state fluorescence quenching was by done by the Stern–Volmer method according to:

$$\frac{\Phi_o}{\Phi} = \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_o[Q], \qquad (1)$$

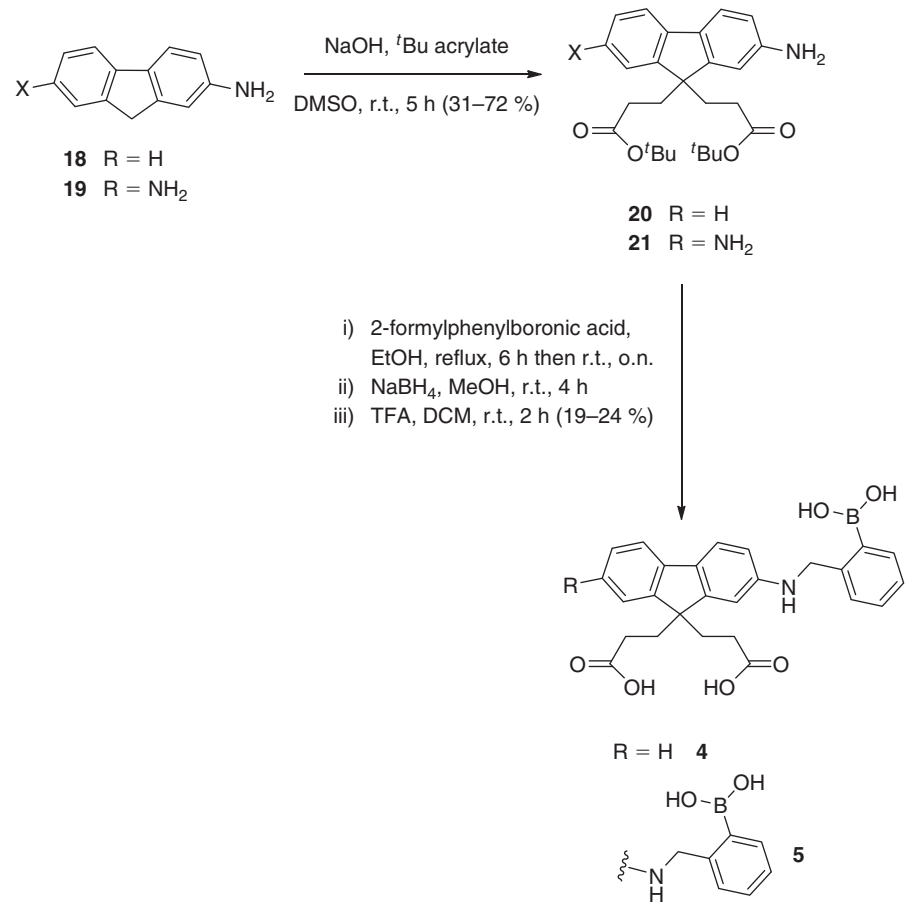
where $\Phi_o$ is the fluorescence in the absence of quencher, $\Phi$ is the fluorescence with quencher, $K_{SV}$ is the Stern–Volmer quenching constant, $k_q$ is the bimolecular quenching rate constant, $\tau_o$ is the fluorescence lifetime in the absence of quencher, $\tau$ is the fluorescence lifetime with quencher, and [Q] is the quencher concentration. The fluorescence of the amino-fluorophores was investigated as a function of the concentration of **10**. As seen in Fig. 2a, the fluorescence is significantly quenched with **10**. However, there is a marked difference in the quenching between **12** and **20**, according to the inset of Fig. 2a. The quenching difference can quantitatively be derived from the $k_q$ by taking into account the amino-fluorophore's fluorescence lifetime. As seen in Table 1, the calculated $k_q$ values are diffusion controlled ($\approx 10^{10}\,M^{-1}\,s^{-1}$) for **11**, **20**, and **21**, confirming that their fluorescence can be efficiently quenched with a small amount of **10**. Conversely, no fluorescence quenching was measured with **12** and **14**, regardless of quencher concentration. Meanwhile, a slower than diffusion controlled quenching was measured for both **9** and **13**. Although the quenching kinetics is for intermolecular excited state quenching, they nonetheless provide relevant information for intramolecular quenching. This is possible by assuming the concentration of excited species produced when irradiated with the fluorimeter lamp is in the micromolar range while the ground state concentration of the quencher covalently bonded to the fluorophore is $\approx 0.1$ mM. In this case, an intermolecular quenching of $K_{SV} \geq 5\,M^{-1}$ would




**11** $R_1 = OH$; $R_2 = H$
**12** $R_1 = SO_3H$; $R_2 = H$
**13** $R_1 = SO_2NH_2$; $R_2 = H$
**14** $R_1 = OH$; $R_2 = SO_3H$

**1** $R_1 = OH$; $R_2 = H$
**2** $R_1 = SO_3H$; $R_2 = H$
**3** $R_1 = SO_3NH_2$; $R_2 = H$
**4** $R_1 = OH$; $R_2 = SO_3H$

**Scheme 2.** Synthetic scheme of naphthalene boronic acid derivatives.




**18** R = H
**19** $R = NH_2$

**20** R = H
**21** $R = NH_2$

R = H **4**

**5**

**Scheme 3.** Synthetic scheme of fluorene boronic acid derivatives.

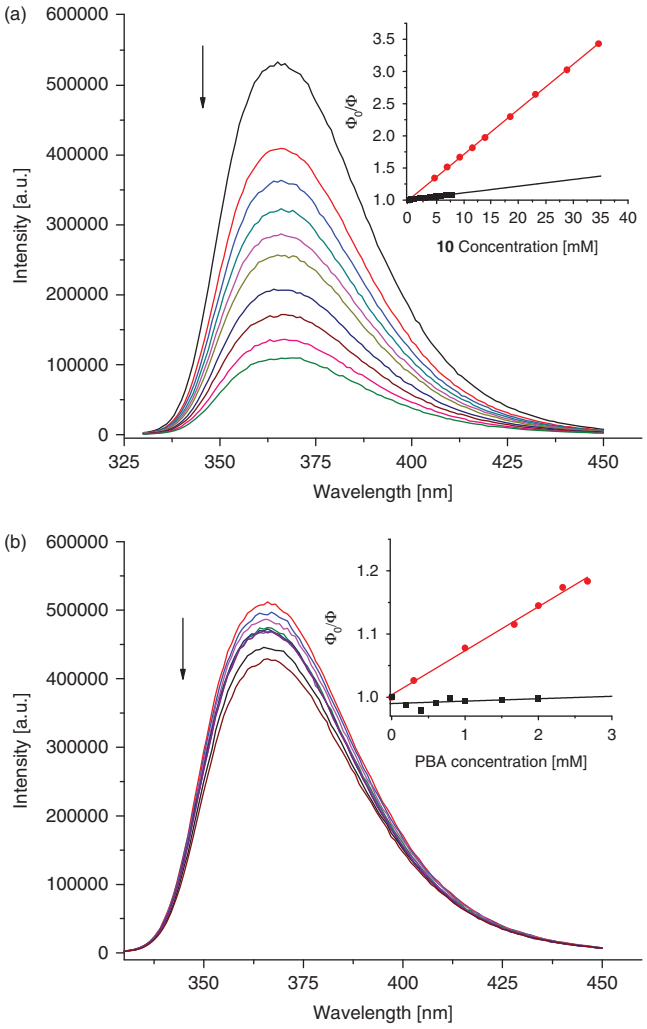



**Fig. 2.** (a) Fluorescence quenching of **20** with **10** in degassed anhydrous acetonitrile and excited at 314 nm. Inset: Stern–Volmer quenching plot of **20** (●) and **13** (■) with **10**, excited at 314 and 370 nm, respectively. (b) Fluorescence quenching of **11** with phenylboronic acid in degassed anhydrous acetonitrile with excitation at 332 nm. Inset: Stern–Volmer quenching plot of **11** (●) and **12** (■) with phenylboronic acid. Stern–Volmer quenching of **12** was done in degassed pH 7.4 phosphate buffered solution and excited at 338 nm.

imply that more than 95 % of the fluorophore's singlet excited states would be quenched by intramolecular deactivation when the imine is covalently bonded to the fluorophore. Both **7** and **8** were prepared and investigated to confirm that the intermolecular quenching data can be used for predicting intramolecular quenching of the fluorophore when conjugated to the imine. As can be seen in Table 1, the fluorescence of **7** is completely quenched, as predicted by the measured $K_{SV}$ of 5 $M^{-1}$ for the quenching of **13** by **10**. The fluorophore's quenched fluorescence is revived when the imine is reduced to its corresponding secondary amine **8**. The quenched and revived fluorescence observed with **7** and **8**, respectively, confirm definitively that the imine is responsible for fluorescence quenching. They further confirm that the intermolecular quenching measured with **10** can be used to reliably predict intramolecular fluorescence quenching.

The fluorescence quenching was further investigated with the naphthalene fluorophores using phenylboronic acid as the quencher. This would provide more relevant fluorescence deactivation information of the boronic acid sensor. The intermolecular quenching of a fluorophore with phenylboronic acid would further provide sound evidence that the fluorescence of its boronic acid derivative would also be quenched, similar to **7**. Quenched fluorescence of the boronic acid fluorophore and fluorescence revival with saccharide binding are desired properties. The quenching of the naphthalene fluorophores was subsequently investigated. The quenching was done in acetonitrile instead of phosphate buffered solution (PBS). This was in part owing to the limited solubility of phenylboronic acid in PBS. More importantly, the boronic acid maintains its uncharged, $sp^2$ state in anhydrous acetonitrile. This is the hybridization that leads to B–N interactions and fluorescence quenching in boronic acid sensors. The same quenching trend for the fluorophores was observed with phenylboronic acid as with **10** (Fig. 2b). Time-resolved fluorescence quenching with **11** and phenylboronic acid was also investigated. In this case, no quenching was observed. Only a decrease in signal intensity proportional to the quencher concentration was observed (see Accessory Publication). This implies that the fluorescence quenching occurs by a ground state complex between the boronic acid and the fluorophore.

Based on the kinetic quenching data, boronic acid sensors derived from fluorophores **1**, **20**, and **21** would possess the

**Table 1. Photophysical, kinetic, and thermodynamic data of amino-fluorophores**

| Fluorophore | $\varepsilon$ [$mM^{-1}\cdot cm^{-1}$] | $\lambda_{ex}^{A}$ [nm] | $\lambda_{em}^{B}$ [nm] | $\tau_0^C$ [ns] | $k_q^D$ [$10^{10}\ M^{-1}\cdot s^{-1}$] | $k_q^E$ [$10^{10}\ M^{-1}\cdot s^{-1}$] | $E_{pa}^{F}$ [V] | $\Delta G_{PET}^{G}$ [kJ mol$^{-1}$] | $\Delta G_{PET}^{H}$ [kJ mol$^{-1}$] |
|---|---|---|---|---|---|---|---|---|---|
| **11** | 5.4 | 332 | 414 | 5.2 | 2.1 | 1.4 | 0.72 | −68 | −58 |
| **12** | 4.3 | 338 | 507 | 6.9 | – | 0 | 1.02 | 19 | 10 |
| **13** | 3.2 | 370 | 514 | 8.4 | 0.1 | 0 | 1.09 | 39 | 29 |
| **14** | 4.4 | 345 | 445 | 4.2 | – | 0 | – | – | – |
| **20** | 4.6 | 325 | 365 | 3.8 | 2.2 | – | 1.06 | −68 | −58 |
| **21** | 3.2 | 314 | 388 | 3.3 | 1.9 | – | 0.66 | −87 | −87 |
| **9** | 47.4 | 405 | 512 | 2.3 | 0.5 | – | 0.63 | −10 | −2 |

[A]Excitation wavelength used for fluorescence measurements.
[B]Emission wavelength.
[C]Fluorescence liftetime.
[D]For **10** in acetonitrile.
[E]For phenylboronic acid in pH 7.4 phosphate buffered solution.
[F]Oxidation potential versus Ag/AgCl (sat'd).
[G]Rehm–Weller energetics for photoinduced electron transfer quenching with **10**.
[H]Rehm–Weller energetics for photoinduced electron transfer quenching with phenylboronic acid.

**Table 2. Absolute quantum yields of boronic acid fluorescence sensors and their corresponding amino-fluorophores precursors**

| Compound | Quantum yield[A] | | |
|---|---|---|---|
| | Amino-fluorophore[B] | Without fructose | With fructose[C] |
| **1** | 0.35 (**11**) | 0.06 | 0.33 |
| **2** | 0.56 (**12**) | 0.47 | 0.41 |
| **3** | 0.56 (**13**) | 0.45 | 0.36 |
| **4** | 0.53 (**14**) | 0.48 | 0.45 |
| **5** | 0.43 (**20**) | 0.05 | 0.43 |
| **6** | 0.25 (**21**) | 0.02 | 0.26 |
| **7** | 0.56 (**13**) | < 0.01 | N/D |
| **8** | 0.56 (**13**) | 0.51 | N/D |
| **9** | 0.83 (**9**) | N/D | N/D |

[A]Absolute quantum yield measured with an integrating sphere. N/D is not determined.
[B]Values in parentheses are the corresponding amino-fluorophore precursors.
[C]Fructose concentration 50 mM.

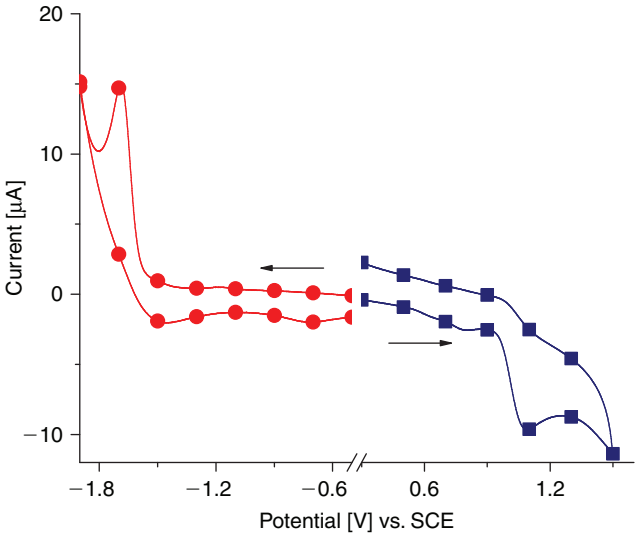



**Fig. 3.** Cyclic voltammogram of **13** (■) and **10** (●) measured in degassed *N,N*-dimethylformamide at 100 mV $s^{-1}$. Arrow indicates scan direction.

desired fluorescence quenching/revival properties. Conversely, the fluorescence of the boronic acid derivatives of fluorophores **2**–**4** and **9** would not be quenched. The absolute quantum yields of the amino-fluorophore precursors and their corresponding boronic acids were subsequently measured using an integrating sphere. The advantage of using the integrating sphere is that quantum yields independent of a reference are possible. This results in precise quantum yield measurements that are not limited to the excitation or emission wavelengths of the fluorescence reference (actinometer). It is obvious from the absolute $\Phi_{fl}$ data found in Table 2 that the measured $\Phi_{fl}$ correlate with the quenching data. More specifically, when the phenylboronic acid moiety is added to each fluorophore, the fluorescence of **2**–**4** is decreased by only 10–20 %, meanwhile the fluorescence of **1**, **5**, and **6** are quenched significantly.* Based on the good correlation between the fluorescence quenching of the amino-fluorophores and the measured $\Phi_{fl}$ of the boronic acid sensor the $k_q$ is a good empirical parameter for predicting quenched fluorescence in boronic acid sensors. In fact, diffusion controlled fluorescence quenching with either phenylboronic acid or an imine can be used to rapidly assess the fluorescence quenching of the boronic acid sensor based on its corresponding amino-fluorophore precursor.

Although the exact mechanism responsible for fluorescence quenching remains contentious,[13,18,40] we nonetheless examined the thermodynamics of photoinduced electron transfer (PET) as an additional tool for screening amino-fluorophores and for predicting their boronic acid sensor properties. The thermodynamics can be calculated according to the Rehm–Weller equation: $\Delta G^{\circ}_{PET} = E_{pa}$ (fluorophore) $- E_{pc}$ (quencher) $- \Delta E_{0,0} - \lambda$.[41] The equation accounts for the fluorophore's capacity to be oxidized ($E_{pa}$), the quencher's capacity to be reduced ($E_{pc}$) by accepting the transferred electron from the fluorophore, and the solvent reorganization energy ($\lambda$). The energy gap ($\Delta E_{0,0}$) between the ground and excited singlet states of the fluorophore accounts for electron transfer from its excited state. The energy gap is calculated from the intercept of the normalized plot of the absorption and fluorescence spectra of the fluorophore. The $E_{pa}$ and $E_{pc}$ values were measured by cyclic voltammetry and correspond to the oxidation and reduction potential of the fluorophore and quencher, respectively. A typical voltammogram showing the one-electron oxidation and reduction process is represented in Fig. 3. Exergonic energies for PET quenching with phenylboronic acid and **10** were calculated for **11**, **20**, and **21**, while endergonic energies were found for the other naphthalenes. The exergonic energies calculated for **11**, **20**, and **21** predict that the fluorescence of their corresponding boronic acids (**1**, **5**, and **6**) would be quenched, which is the case. The good agreement between the predicted and actual quenched fluorescence of the sensors suggest that the fluorescence quenching thermodynamics and kinetics offer the possibility of predicting suitable boronic acid fluorophores with quenched/revival fluorescence. Based on this assumption, the boronic acid derivative of **9** would be an ideal saccharide sensor. Unfortunately, the reductive amination of **9** was not possible, regardless of the reaction conditions used.

The saccharide fluorescence sensing of the water-soluble fluorophores was done first with fructose. This saccharide was chosen because it is stable, non-absorbing in the UV-visible range, and is known to strongly bind to boronic acids in a 1:1 complex. It should be noted that the fluorophores are extremely soluble in PBS at pH 6–10, making them suitable for use as sensors under physiological conditions. The sensors' fluorescence was examined as a function of pH both in the absence and presence of fructose. This was done primarily to determine the optimal working pH of the sensors. As seen in Fig. 4, **5** exhibits the desired fluorescence increase with fructose at physiological conditions, with a working pH range from 7 to 9.5. Similarly, both **1** and **5** exhibit fluorescence increases with fructose binding at physiological pH. The ideal sensing pH, the pH at which the greatest change in fluorescence upon fructose binding is observed, for each of the fluorophores is 7.5, 8.0, and 7.8 for **1**, **5**, and **6**, respectively.

The saccharide on/off fluorescence sensing of the water-soluble fluorophores was also done with fructose. For **1**, **5**, and **6**, the fluorescence is restored to the same value as their amino-fluorophore precursor, within error, upon fructose binding. The fluorescence increase and revival for **4** are clearly seen in Fig. 5

*Quantum yields less than 0.1 cannot be accurately measured with the integrating sphere.

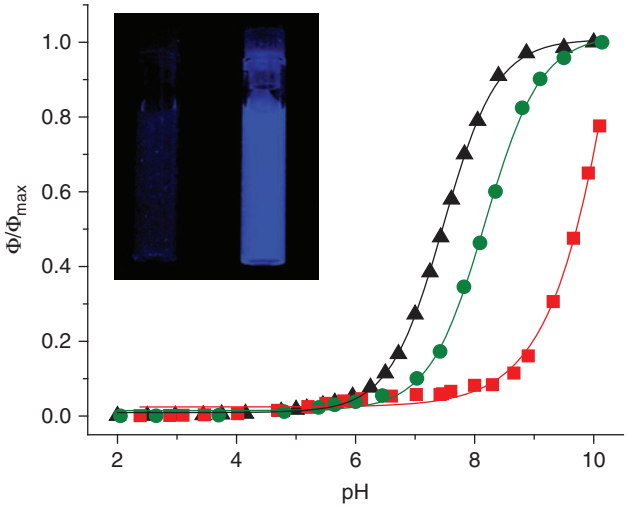



**Fig. 4.** Fluorescence of **5** as a function of pH without (■) and with 10 (●) and 100 (▲) mM fructose. Inset: pictures of **5** without (left) and with 100 (right) mM of fructose at pH 8.0 irradiated with a 350 nm UV lamp.

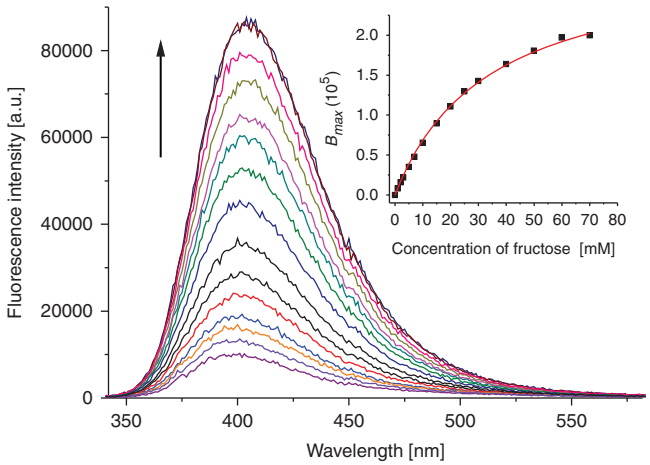



**Fig. 5.** Fluorescence spectra of **6** in pH 7.4 PBS with added fructose demonstrating the fluorescence revival of **6** upon saccharide addition. Inset: Plot of [**6**:fructose] versus [fructose] with a two-site binding fit, used to determine the binding constants of **6** with fructose, overlayed.

and the inset of Fig. 4, respectively. As predicted by the quenching kinetics and thermodynamics, the remaining naphthalenes do not exhibit any fluorescence enhancement with fructose addition. The fluorescence increase as a function of fructose for the sensors leads to binding constants of 170, 53, and 30 $M^{-1}$ for **1**, **5**, and **6**, respectively. The high water solubility combined with the quantitative fluorescence revival and the strong binding constant for fructose at physiological conditions make the naphthol (**1**) and fluorene boronic acids (**4** and **5**) interesting candidates for sensing saccharides in biological conditions without sample preparation or pH adjustment.

## Conclusion

A series of water-soluble 1-amino-naphthalenes and 2-amino-fluorenes served as model compounds for empirically predicting suitable boronic acid fluorophores with desired fluorescence off/on properties based on fluorescence quenching and thermodynamics. It was found that amino-fluorophores that exhibited diffusion controlled $k_q$ and exergonic PET energetics with phenylboronic acid were quenched when reductively aminated with 2-formylphenylboronic acid. The fluorescence could also be quantitatively restored in the presence of fructose, making them good saccharide sensors. It was found that either fluorescence kinetics or PET thermodynamics can be used as an empirical tool for predicting the suitability of boronic acid as saccharide sensors by investigating their amino-fluorophore precursor. It was further found that carboxylic acid fluorenyl derivatives are ideal saccharide sensors under physiological conditions owing to their quantitative fluorescence turn-on response towards fructose combined with their water solubility and good sensing pH range. These predictive tools are currently being applied to identify new water-soluble ratiometric boronic acid fluorescence sensors that emit at different wavelengths upon saccharide binding.

## Experimental

### *General Methods*

All chemicals and solvents were used as received unless specified. NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HR-MS) were recorded on a LC-MSD-TOF instrument from Agilent technologies in positive or negative electrospray mode. Either protonated molecular ions $(M + H)^+$ or the molecular anion $(M - H)^-$ were used for empirical formula confirmation. All fluorescence measurements were performed in an Edinburgh Instruments FLS920 sample chamber with a Xe900 xenon light source unless otherwise specified. Absorbance measurements were performed on a Cary 500 Scan UV-Vis-IR spectrophotometer. Quartz cuvettes from NSG Precision Glass were use for all spectroscopic measurements. All pH measurements performed using a VWR SB20 pH meter. Column chromatography was performed on silica gel (230–400 mesh) unless otherwise specified. Anhydrous solvents were obtained from a Glass Contour solvent system.

### *Synthesis*

The reagents **11**, **12**, **14**, **18**, and **19** were purchased from Sigma–Aldrich and were used as received.

#### *5-((Tert-butoxycarbonyl)amino)naphthalene-1-sulfonic acid (**16**)*

Into anhydrous methanol (20 mL) were added 5-aminonaphthalene-1-sulfonic acid (2.43 g, 10.9 mmol) and triethylamine (1.74 mL, 2.5 mmol). To this dark purple solution was added di-*tert*-butyl dicarbonate (4.75 g, 21.8 mmol). The solution was allowed to react for 3 h under $N_2$ atmosphere. The solvent was then removed under vacuum and the resulting light pink solid was taken up into water (100 mL). The aqueous phase was then washed with ethyl acetate (3 × 35 mL) and dried by lyophilization to yield the triethylamine salt adduct as a light pink solid (4.52 g, 98 %). $\delta_H$ (400 MHz, $CDCl_3$) 8.62 (d, 1H, *J* 8.8), 8.41–8.36 (m, 2H), 7.98 (d, 1H, *J* 7.6), 7.78 (t, 1H, *J* 4), 7.64 (t, 1H, *J* 8), 6.91 (s, 1H), 1.58 (s, 9H). $\delta_C$ (400 MHz, $CDCl_3$) 157.2, 138.8, 129.2, 127.6, 126.9, 126.8, 125.4, 124.1, 46.9, 27.9, 8.8. HR-MS (ESI) Calc. for $C_{15}H_{16}NO_5S$ $[M - H]^-$: 322.0755. Found: 322.0759.

#### *Tert-butyl (5-sulfamoylnaphthalen-1-yl)carbamate (**17**)*

Triphenyl phosphine (3.14 g, 12.0 mmol) was dissolved in dichloromethane (150 mL) and cooled to 0°C. To this was added

thionyl chloride (950 μL, 13.2 mmol) drop wise. After 20 min of stirring and warming to room temperature, **16** (2.50 g, 6.00 mmol) was added and the reaction mixture was stirred for 1.5 h. The solution was then cooled to 0°C and *tert*-butyl amine (1.75 mL, 16.5 mmol) was added followed by triethylamine (2.30 mL, 16.5 mmol). The mixture was stirred for 6 h and it was then quenched with water (200 mL). The product was extracted into dichloromethane and dried with $Na_2SO_4$. The solvent was removed under reduced pressure to yield the title compound as a solid (1.15 g, 58 %). $\delta_H$ (400 MHz, $CDCl_3$) 8.6 (d, 1H, *J* 8.8), 8.41–8.36 (m, 2H), 7.98 (d, 1H, *J* 7.6), 7.78 (t, 1H, *J* 4), 7.64 (t, 1H, *J* 8), 6.91 (s, 1H), 1.58 (s, 9H). $\delta_C$ (400 MHz, $CDCl_3$) 153.8, 140.5, 134.7, 130.5, 129.5, 129.9, 129.8, 128.5, 124.3, 121.3, 81.9, 28.7. MS (ESI) Calc. for $C_{15}H_{15}NO4SCl$ $[M-H]^-$: 340.0. Found: 340.0.

### *5-Aminonaphthalene-1-sulfonamide (**13**)*

In dichloromethane (100 mL) was dissolved **17** (600 mg, 1.59 mmol) to which was then added trifluoroacetic acid (15 mL, 0.19 mol). The reaction mixture was left to stir overnight at room temperature. Both the acid and solvent were removed under reduced pressure. The resulting solid was recrystallized from ethyl acetate by adding dichloromethane to afford the product as a white solid (351 mg, 99 %). $\delta_H$ (400 MHz, $D_2O/CD_3CN$) 8.24–8.19 (m, 2H), 7.99 (d, 1H, *J* 4.4), 7.54–7.49 (m, 2H), 6.99 (d, 1H, *J* 4 Hz).

### *Representative Procedure for the Reductive Amination of **1**–**4***

In absolute ethanol (20 mL) was dissolved **11** (159 mg, 1 mmol) to which was added 2-formylphenylboronic acid (232 mg, 1.55 mmol). The reaction mixture was refluxed for 6 h under $N_2$. The solvent was then removed under reduced pressure and the resulting Schiff base was dissolved in anhydrous methanol (10 mL). Sodium borohydride (151 mg, 4 mmol) was then added and the reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with water (80 mL) and the aqueous fraction was washed with dichloromethane (3 × 25 mL). The product **1** was obtained as a white powder (211 mg, 36 %) after purifying the organic layer on silica flash column chromatography using dichloromethane/methanol eluent. $\delta_H$ (400 MHz, $CD_3OD$) 7.56 (t, 2H, *J* 8.8), 7.43 (d, 1H, *J* 7.6), 7.34 (t, 1H, *J* 8.2), 7.27–7.22 (m, 3H), 7.10 (t, 1H, *J* 8.0), 6.81 (d, 1H, *J* 7.0), 6.49 (d, 1H, *J* 7.4), 4.49 (s, 2H). HR-MS (ESI) Calcd. for $C_{17}H_{17}BNO_3$ $[M+H]^+$: 294.1296. Found 294.1298.

The crude product **2** was crystallized from the aqueous layer by acidification and cooling to 4°C. The resulting crystals were collected by vacuum filtration and washed with ice-cold water. The product was dried overnight in a desiccator to give the product as a light purple solid (273 mg, 76 %). $\delta_H$ (400 MHz, $CD_3OD + Et_3N$) 8.22 (t, 2H, *J* 8.7), 8.16 (d, 1H, *J* 7.2), 7.44–7.42 (m, 2H), 7.31 (q, 2H, *J* 7.3), 7.23 (t, 1H, *J* 7.8), 6.67 (d, 1H, *J* 7.1), 4.53 (s, 2H). HR-MS (ESI) Calc. for $C_{15}H_{16}BNO_3$ $[M+H]^+$: 294.1296. Found: 294.1298.

The crude product **3** was obtained by extracting with ethyl acetate (3 × 25 mL) followed by drying with $Na_2SO_4$. The product was recrystallized from ethyl acetate upon adding diethyl ether to yield a yellow solid (168 mg, 47 %). $\delta_H$ (400 MHz, $CD_3OD$) 8.40 (d, 1H, *J* 8.5), 8.23 (d, 1H, *J* 7.3), 7.99 (d, 1H, *J* 8.6), 7.52 (t, 1H, *J* 8.0), 7.46 (d, 1H, *J* 7.7), 7.35 (t, 2H, *J* 8.1), 7.25–7.23 (m, 2H), 6.61 (d, 1H, *J* 7.8), 4.53 (s, 2H). HR-MS (ESI) Calc. for $C_{15}H_{16}BNO_3$ $[M+H]^+$: 294.1296. Found: 294.1298.

The crude product **4** was crystallized from the aqueous layer by acidification and cooling to 4°C. The resulting crystals were collected by vacuum filtration and washed with ice-cold water. The product was dried overnight in a desiccator to give the product as a light purple solid (257 mg, 69 %). $\delta_H$ (400 MHz, $CD_3OD$) 8.11 (s, 1H), 7.80 (d, 1H, *J* 8), 7.45 (d, 1H, *J* 8), 7.35–7.20 (m, 5H), 6.00 (d, 1H, *J* 8), 4.54 (s, 2H). HR-MS (ESI) Calc. for $C_{17}H_{16}BNO_6S$ $[M+H]^+$: 374.0864. Found: 374.0882.

### *5-(Benzylideneamino)naphthalene-1-sulfonamide (**7**)*

To 2-methylpropan-2-ol (10 mL) was added **13** (100 mg, 0.45 mmol). The mixture was stirred to dissolve and then benzaldehyde (0.059 mL, 0.58 mmol) was added. The reaction was stirred under nitrogen at room temperature overnight. A yellow precipitate formed that was collected by vacuum filtration and then washed with ice-cold ethanol to yield the title product (49 mg, 35 %). $\delta_H$ (400 MHz, $CD_3OD$) 8.76 (s, 1H), 8.60 (d, 1H, *J* 8), 8.37 (d, 1H, *J* 8), 8.20 (d, 1H, *J* 6.4), 8.10 (s, 2H), 7.70–7.60 (m, 7H), 7.39 (d, 1H, *J* 6). HR-MS (ESI) Calc. for $C_{17}H_{16}BNO_6S$ $[M+H]^+$: 311.0849. Found: 311.0854.

### *5-(Benzylamino)naphthalene-1-sulfonamide (**8**)*

To a 70/30 volume mixture of toluene/ethanol (20 mL) was added **7** (49 mg, 0.16 mmol). To this was added $NaBH_4$ (50 mg, 0.76 mmol) and the reaction was left to stir at room temperature for 4 h. The reaction mixture was then partitioned between water (50 mL) and ethyl acetate (50 mL). The aqueous layer was washed with ethyl acetate (3 × 15 mL). The combined organic layer was then washed with brine (2 × 10 mL), dried with magnesium sulfate, filtered, and the solvent then evaporated. Purification over a silica column using hexanes/ethyl acetate yielded a yellow solid (28 mg, 58 %). $\delta_H$ (400 MHz, $CD_3OD$) 8.56 (d, 1H, *J* 8), 8.09 (d, 1H, *J* 6.8), 7.55–7.20 (m, 10H), 6.48 (d, 1H, *J* 8), 4.53 (d, 2H, *J* 4). HR-MS (ESI) Calc. for $C_{17}H_{16}BNO_6S$ $[M+H]^+$: 313.1005. Found: 313.1011.

### *N-Benzylidenedecan-1-amine (**10**)*

To benzaldehyde (510 μL, 5 mmol) was added *n*-decylamine (1.01 mL, 5.05 mmol). The mixture was heated to 80°C under nitrogen atmosphere in the presence of molecular sieves for 15 min. The reaction mixture was then allowed to cool to room temperature and the product was obtained as a light yellow oil (1.21 g, 99 %). $\delta_H$ (400 MHz, $CDCl_3$) 8.30 (s, 1H), 7.74 (m, 2H), 7.43 (m, 3H), 4.14 (q, 1H), 3.62 (t, 2H), 1.72 (t, 2H), 1.35–1.25 (m, 16H).

### *Di-tert-butyl 3,3′-(2-Amino-9H-fluorene-9,9-diyl) dipropanoate (**20**)*

In dimethyl sulfoxide (5 mL) was dissolved **18** (362 mg, 2 mmol). Tetrabutylammonium bromide (19 mg, 0.06 mmol) was added followed by 50 % aqueous sodium hydroxide (800 μL, 15.5 mmol). After 20 min of stirring, the solution of **18** turned red and to this was added drop wise *tert*-butyl acrylate (1.17 mL, 8 mmol). The reaction mixture was stirred at room temperature for 5 h. Water (50 mL) was then added to quench the reaction and the product was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were then washed with brine (20 mL) and dried with $MgSO_4$. The solvent was then removed under reduced pressure and the crude product was purified by silica flash column chromatography using hexanes/ethyl acetate eluent to yield **20** (630 mg, 72 %). $\delta_H$ (400 MHz,

$CDCl_3$) 7.55 (d, 1H, *J* 3.6), 7.48 (d, 1H, *J* 3.6), 7.32–7.22 (m, 3H), 6.71–6.68 (m, 2H), 2.32–2.25 (m, 4H), 1.54–1.48 (m, 4H), 1.32 (s, 18H). $\delta_C$ (400 MHz, $CDCl_3$) 173.5, 150.4, 147.5, 146.9, 152.1, 132.7, 127.7, 126.3, 123.2, 121.2, 118.9, 114.9, 110.1, 80.4, 53.5, 35.3, 30.4, 28.4, 14.6. ES-MS Calc. for $C_{27}H_{35}NNaO_4$: 460.2458. Found: 460.2472.

### *Di-tert-butyl 3,3′-(2,7-Diamino-9H-fluorene-9,9-diyl) dipropanoate (**21**)*

The same procedure as **18** was used to afford the title product (282 mg, 31 %) $\delta_H$ (400 MHz, $CDCl_3$) 7.33 (d, 2H, *J* 8), 6.66–6.63 (m, 4H), 3.72 (s, 4H), 2.21 (t, 4H, *J* 8), 1.54 (t, 4H, *J* 8), 1.33 (s, 18H). $\delta_C$ (400 MHz, $CDCl_3$) 173.6, 149.3, 145.4, 133.4, 119.8, 114.9, 110.4, 80.4, 53.3, 35.4, 30.4, 28.4. ES-MS calcd for $C_{27}H_{37}N_2O_4$: 453.2749. Found: 453.2748.

### *3,3′-(2-((2-Boronobenzyl)amino)-9H-fluorene-9,9-diyl) dipropanoic acid (**5**)*

In absolute ethanol (10 mL) was dissolved **20** (100 mg, 0.23 mmol). The reaction mixture was then refluxed under dry nitrogen for 6 h. The solvent was removed under reduced pressure and the crude reaction mixture was redissolved in anhydrous methanol (5 mL). Sodium cyanoborohydride (116 mg, 1.84 mmol) was then added to the Schiff base and the reaction mixture was stirred under nitrogen at room temperature overnight. The solvent was removed under reduced pressure and the product was redissolved in a minimal amount of dichloromethane. Trifluoroacetic acid (5 mL, 65.3 mmol) was then added and the reaction mixture was stirred overnight under nitrogen. Both the acid and solvent were removed under reduced pressure and the product (20.3 mg, 19 %) was obtained by reverse-phase HPLC purification using a MeOH/$H_2O$ solvent system. $\delta_H$ (400 MHz, $CD_3OD$) 7.57–7.19 (m, 9H), 6.96 (s, 1H), 6.88 (s, 1H), 4.43 (s, 2H), 2.35 (m, 4H), 1.46 (m, 4H). ES-MS Calc. for $C_{26}H_{27}BNO_6$: 460.1926. Found: 460.1940.

### *3,3′-(2-((2-Boronobenzyl)amino)-7-((3-boronobenzyl) amino)-9H-fluorene-9,9-diyl)dipropanoic acid (**6**)*

Similar to the procedure for **5**, **21** (100 mg, 0.22 mmol) yielded **6** (31.7 mg, 24 %). $\delta_H$ (400 MHz, $CD_3OD$) 7.62–7.19 (m, 11H), 6.96–6.69 (m, 4H), 4.36 (s, 2H), 2.23 (m, 4H), 1.28 (m, 4H). ES-MS Calc. for $C_{33}H_{33}B_2N_2O_8$: 607.2429. Found: 607.2438.

### *Solubility*

The solubility values were determined by two methods: 1) stock solutions were prepared of each compound in either acetonitrile or DMSO in a concentration of 1–100 mg $mL^{-1}$. With these stock solutions, increasingly concentrated solutions of boronic acid derivatives in 0.1 M, pH 7.4 PBS were prepared with a maximum of 5 % acetonitrile or DMSO until a precipitate was observed by UV-visible absorbance by comparing the baseline absorbance in non-absorbing regions referenced to solvent of the same mixture; 2) PBS (pH 7.4, 0.1 M) was slowly added to precisely weighed samples of boronic acid derivatives with continuous stirring for 2–3 min between solvent additions until the compound was completely dissolved. A compound was considered water soluble if soluble at $>1$ mg $mL^{-1}$.

### *Fluorescence Measurements*

Samples were prepared with spectroscopic grade solvents and were thoroughly degassed with nitrogen. Absolute quantum yield values were determined using an integrating sphere. Emission and scattering spectra were measured with samples whose absorbances ranged between 0.2 and 0.4 at the corresponding excitation wavelength. The quantum yields (QYs) were calculated using the following formula:

$$QY = \frac{\int \text{sample emission}}{\int \text{blank scatter} - \int \text{sample scatter}} \quad (2)$$

Lifetime measurements were done with deoxygenated solutions with absorbances ranging between 0.2 and 0.4 at the excitation wavelength using a nF900 nanoflash lamp with a reference solution of colloidal silica.

Molar absorptivities of the boronic acid derivatives were determined by titrating an analytically prepared stock solution of the compound into PBS (3 mL, 0.1 M).

Fluorimetric saccharide binding titrations were performed by preparing the desired concentration of the boronic acid derivative (3 mL) in PBS (0.1 M). The fluorescence spectrum of the unbound sensor was measured in a 1 cm path length quartz cuvette from NSG Precision Glass. Saccharide from a stock solution (1 M) in PBS (0.1 M) was then titrated. Spectra were taken at regular intervals until the signal saturated. The integrated fluorescence was related to the boronic acid bound fraction by the following equation: $\Phi_{obs} - \Phi_{apo}/\Phi_{holo} - \Phi_{apo}$, where $\Phi_{obs}$ is the observed integrated fluorescence intensity, $\Phi_{holo}$ is the integrated fluorescence intensity of the fluorophore at saturation, and $\Phi_{apo}$ is the integrated fluorescence intensity of the fluorophore without any saccharide present. The bound fraction was then plotted against the saccharide concentration and either a non-linear one-site or two-site binding fit was done using Origin Pro 8 software for determining the binding constant. $B_{max}$ values, the maximum possible concentrations of saccharide present in the sensor-bound state, were fixed using the known concentration of sensor present and binding stoichiometry.

### *Fluorescence pH Titration*

PBS (2 mL, 0.5 M) was titrated to pH ~2 with 1 M HCl. The solution was then diluted to 10 mL by adding the given boronic acid derivative stock solution and water to give a PBS solution (0.1 M) of pH ~2.5 with the desired concentration of boronic acid derivative and saccharide. This was then titrated with 50/50 v/v NaOH (0.1 M)/PBS (0.2 M) solution with the boronic acid derivative and saccharide. At a given pH, a volume (3 mL) was pipetted into a quartz cuvette and the fluorescence emission spectrum was recorded.

### *Cyclic Voltammetry*

Cyclic voltammetry was performed with a BASi EC Epsilon potentiostat. Compounds were dissolved in anhydrous and deoxygenated *N,N*-dimethylformamide containing tetrabutylammonium hexafluorophosphate (0.1 M). A platinum electrode and a saturated Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively.

## Accessory Publication

Absorbance and fluorescence spectra, cyclic voltammograms, $^1H$ and $^{13}C$-NMR spectra, and ESI-MS of the compounds are available on the Journal's website.

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## References

[1] C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. O. P. Gabbaî, *Chem. Rev.* **2010**, *110*, 3958. doi:10.1021/CR900401A

[2] S. Jin, Y. Cheng, S. Reid, M. Li, B. Wang, *Med. Res. Rev.* **2010**, *30*, 171. doi:10.1002/MED.20155

[3] C. D. Geddes, J. R. Lakowicz, J. S. Fossey, T. D. James, in *Reviews in Fluorescence 2007* **2009**, p. 103 (Ed. C. D. Geddes) (Springer: New York, NY).

[4] R. W. Sinkeldam, N. J. Greco, Y. Tor, *Chem. Rev.* **2010**, *110*, 2579. doi:10.1021/CR900301E

[5] J. Yoon, A. W. Czarnik, *J. Am. Chem. Soc.* **1992**, *114*, 5874. doi:10.1021/JA00040A067

[6] Y. Zou, D. L. Broughton, K. L. Bicker, P. R. Thompson, J. J. Lavigne, *ChemBioChem* **2007**, *8*, 2048. doi:10.1002/CBIC.200700221

[7] D. Luvino, D. Gasparutto, S. Reynaud, M. Smietana, J.-J. Vasseur, *Tetrahedron Lett.* **2008**, *49*, 6075. doi:10.1016/J.TETLET.2008.07.173

[8] T. Zhang, E. V. Anslyn, *Org. Lett.* **2007**, *9*, 1627. doi:10.1021/OL070280O

[9] E. A. Moschou, B. V. Sharma, S. K. Deo, S. Daunert, *J. Fluoresc.* **2004**, *14*, 535. doi:10.1023/B:JOFL.0000039341.64999.83

[10] G. J. Worsley, G. A. Tourniaire, K. E. S. Medlock, F. K. Sartain, H. E. Harmer, M. Thatcher, A. M. Horgan, J Pritchard, *Clin. Chem.* **2007**, *53*, 1820. doi:10.1373/CLINCHEM.2007.091629

[11] D. B. Cordes, J. T. Suri, F. E. Cappuccio, J. N. Camara, S. Gamsey, Z. Sharrett, P. Thoniyot, R. A. Wessling, B. Singaram, in *Glucose Sensing* **2006**, p. 47 (Eds C. D. Geddes, J. R. Lakowicz) (Springer: New York, NY).

[12] J. C. Pickup, F. Hussain, N. D. Evans, O. J. Rolinski, D. J. S. Birch, *Biosens. Bioelectron.* **2005**, *20*, 2555. doi:10.1016/J.BIOS.2004.10.002

[13] H. Fang, G. Kaur, B. Wang, *J. Fluoresc.* **2004**, *14*, 481. doi:10.1023/B:JOFL.0000039336.51399.3B

[14] R. Badugu, J. R. Lakowicz, C. D. Geddes, *J. Fluoresc.* **2004**, *14*, 617. doi:10.1023/B:JOFL.0000039349.89929.DA

[15] T. James, S. Shinkai, in *Host-Guest Chemistry – Mimetic Approaches to Study Carbohydrate Recognition* **2002**, Volume 215, p. 159 (Ed. S. Penadés) (Springer: New York, NY).

[16] T. D. James, K. R. A. S. Sandanayake, S. Shinkai, *Chem. Commun.* **1994**, *477*. doi:10.1039/C39940000477

[17] W. Ni, G. Kaur, G. Springsteen, B. Wang, S. Franzen, *Bioorg. Chem.* **2004**, *32*, 571. doi:10.1016/J.BIOORG.2004.06.004

[18] T. James, in *Creative Chemical Sensor Systems* **2007**, Volume 277, p. 107 (Ed. T. Schrader) (Springer: Berlin).

[19] H. Cao, M. D. Heagy, *J. Fluoresc.* **2004**, *14*, 569. doi:10.1023/B:JOFL.0000039344.34642.4C

[20] S. L. Wiskur, J. J. Lavigne, H. Ait-Haddou, V. Lynch, Y. H. Chiu, J. W. Canary, E. V Anslyn, *Org. Lett.* **2001**, *3*, 1311. doi:10.1021/OL0156805

[21] H. S. Mader, O. S. Wolfbeis, *Microchim. Acta* **2008**, *162*, 1. doi:10.1007/S00604-008-0947-8

[22] J. Wang, S. Jin, B. Wang, *Tetrahedron Lett.* **2005**, *46*, 7003. doi:10.1016/J.TETLET.2005.08.053

[23] H. Cao, M. D. Heagy, *J. Fluoresc.* **2004**, *14*, 569. doi:10.1023/B:JOFL.0000039344.34642.4C

[24] Z. Cao, P. Nandhikonda, M. D. Heagy, *J. Org. Chem.* **2009**, *74*, 3544. doi:10.1021/JO9002008

[25] Y. Cheng, N. Ni, W. Yang, B. Wang, *Chemistry* **2010**, *16*, 13528. doi:10.1002/CHEM.201000637

[26] J. C. Norrild, I. Søtofte, *J. Chem. Soc., Perkin Trans. 2* **2002**, *303*. doi:10.1039/B107457A

[27] A. L. Korich, P. M. Iovine, *Dalton Trans.* **2010**, *39*, 1423. doi:10.1039/B917043J

[28] S. Dufresne, W. G. Skene, *J. Phys. Org. Chem.* **2011**, in press. doi:10.1002/POC.1894

[29] S. Dufresne, T. Skalski, W. G. Skene, *Can. J. Chem.* **2011**, *89*, 173. doi:10.1139/V10-089

[30] Y. Dong, A. a. Bolduc, N. McGregor, W. G. Skene, *Org. Lett.* **2011**, *13*, 1844. doi:10.1021/OL200353K

[31] S. Barik, S. Bishop, W. G. Skene, *Mater. Chem. Phys.* **2011**, *129*, 529. doi:10.1016/J.MATCHEMPHYS.2011.04.060

[32] S. Dufresne, A. Bolduc, W. G. Skene, *J. Mater. Chem.* **2010**, *20*, 4861. doi:10.1039/C0JM00557F

[33] A. Bolduc, S. Dufresne, W. G. Skene, *J. Mater. Chem.* **2010**, *20*, 4820. doi:10.1039/B923821B

[34] S. Barik, S. Friedland, W. G. Skene, *Can. J. Chem.* **2010**, *88*, 945. doi:10.1139/V10-080

[35] S. Dufresne, S. A. P. Guarìn, A. Bolduc, A. N. Bourque, W. G. Skene, *Photochem. Photobiol. Sci.* **2009**, *8*, 796. doi:10.1039/B819735K

[36] S. Dufresne, L. Callaghan, W. G. Skene, *J. Phys. Chem. B* **2009**, *113*, 15541. doi:10.1021/JP907391Y

[37] A. N. Bourque, S. Dufresne, W. G. Skene, *J. Phys. Chem. C* **2009**, *113*, 19677. doi:10.1021/JP907263P

[38] S. Dufresne, W. G. Skene, *J. Org. Chem.* **2008**, *73*, 3859. doi:10.1021/JO8002503

[39] D. Tsang, M. Bourgeaux, W. G. Skene, *J. Photochem. Photobiol. A* **2007**, *192*, 122. doi:10.1016/J.JPHOTOCHEM.2007.05.013

[40] Y. Ooyama, A. Matsugasako, K. Oka, T. Nagano, M. Sumomogi, K. Komaguchi, I. Imae, Y. Harima, *Chem. Commun.* **2011**, *47*, 4448. doi:10.1039/C1CC10470E

[41] A. Gilbert, J. Baggott, *Essentials of Molecular Photochemistry* **1991** (CRC Press: Boca Raton, FL).