Boronic acid based photoinduced electron transfer (PET) fluorescence sensors for saccharides†

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A simple three step synthesis was developed to provide six novel modular sensors, consisting of three *para* sensors, and three *meta* sensors with naphthalene, anthracene and pyrene fluorophores. The interaction of the six sensors with the saccharides: D-glucose, D-fructose, D-galactose, and D-mannose, were evaluated. All sensors displayed increasing fluorescence intensity upon the addition of these saccharides, with all of the sensors showing enhanced selectivity for D-glucose over D-galactose, D-fructose and D-mannose. High affinity (K_{obs}) was also observed for the *meta* sensors with respect to the *para* sensors. The naphthalene and anthracene *meta* sensors showed particularly high affinity (K_{obs}) for D-galactose. Circular dichroism spectroscopy was used to probe the structures of the complexes formed. Cyclic complexes were formed between all six sensors and D-glucose. Whilst naphthalene and anthracene *meta* sensors which displayed high affinity for D-galactose also formed cyclic complexes with that saccharide.

Introduction

"A *sensor* is a device that interacts with matter or energy and yields a measurable signal in response".[1] This definition bears witness to the extensive range of applications possible with sensors. We can distinguish *biosensors*, which utilise a biological element for analyte recognition, from *chemosensors*, in which the analyte interacts with a synthetically prepared entity.

In keeping with convention the term saccharide is used to refer broadly to polyhydroxylated carbohydrates.[2] The product of photosynthesis, carbohydrates single-handedly account for the most prolific class of organic compounds that can be found on the surface of the Earth. Within biology they are of fundamental significance. In their most ubiquitous roles they endow Nature with structural rigidity, in the form of cellulose, and function as the energy store that sustains life, in the forms of starch and glycogen.[3]

Not only are these compounds abundant they are also incredibly versatile. Oligo-saccharides are involved in protein targeting and folding, as well as controlling the cell recognition events for infection, inflammation and immunity.[4] From a medicinal perspective the monitoring of D-glucose has proved of particular importance. D-Glucose provides the metabolic energy for most cells of higher organisms. In humans a breakdown in the transport pathways of D-glucose has been linked to conditions such as cancer,[5] cystic fibrosis[6] and renal glycosuria,[7,8] but by far the most prevalent condition resulting from ineffective D-glucose transport is diabetes mellitus.[9]

Diabetes presents one of the largest health challenges to face us in the 21st century. Current reports indicate that diabetes affects 5% of the global population.[10] In the UK the increase in obesity, population age and a progressively more sedentary lifestyle has seen the prevalence of Type 1 diabetes double every 20 years since 1945.[11] Diabetes is associated with chronic ill health, disability and premature mortality. From a physiological perspective the debilitating long-term complications include heart disease,[12] blindness,[13] kidney failure,[14] stroke[15] and nerve damage leading to amputation.[16]

At an economic level the repercussions are also serious. Within the UK 5% of the National Health Service's budget is spent on treating diabetes and its complications.[17] This equates to £3.5 billion per year or £9.6 million per day. Following extensive and widespread trials, unequivocal evidence exists that monitoring and adjusting diabetic blood-sugar levels to maintain them within tight boundaries‡ dramatically reduces the health risks faced by diabetics.[18–20]

Since continuous and noninvasive systems are critical for the control of the disease status. Glucose chemosensors have become the focus of intense research, the ultimate aim is to provide diabetics simple more robust and less invasive methods of measuring blood glucose levels important for the long-term management of the disease. Towards that end one area of research of particular focus has been the development of boronic acid based saccharide receptors.[21–39]

With this research we set out to construct modular diboronic acid fluorescent photo induced electron transfer (PET) sensors for saccharides. The recognition of saccharides using the esterification with boronic acids is facilitated by the interaction with a proximal tertiary amine. The precise nature

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† Electronic supplementary information (ESI) available: Synthesis of **1**, **13** and **27**. Also: titration curves of sensors **1**, and **3** to **8**, fluorescence spectra and CD spectra of sensors **3** to **8** with selected saccharides. See DOI: 10.1039/c0nj00578a

‡ Non-diabetic blood glucose concentrations are usually in the range 4 mM to 7 mM.[18]

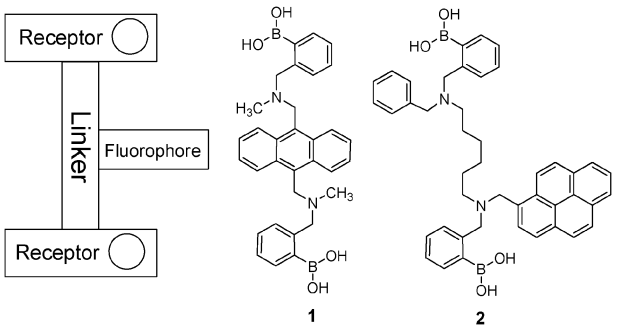
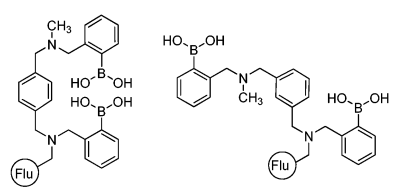


Fig. 1 Schematic representation of PET sensors **1** and **2**.

of the Lewis acid–base interaction (N···B) has been the subject of some controversy.[40–42] However, the fact that the proximal amine has a positive effect on the binding efficiency of boronic acids is not in debate. The interaction of the boron atom (Lewis acid) and neighboring nitrogen atom (Lewis base) is strengthened on saccharide binding, thus the photo induced electron transfer (PET) process, from nitrogen to the attached fluorophore is suppressed and the fluorescence of the fluorophore is switched on.[43]

The modular concept for the design of saccharide selective boronic acid sensors has been championed by us[44–52] and others.[53–59] A modular approach allows the linker and fluorophore units of a sensor to be varied independently. That way the dimensions of the binding pocket and emission wavelength could be altered in a controlled manner. We used the structure of sensors **1** as blue print for our design, schematically represented in Fig. 1.

Sensor **1** consists of a fluorophore (an anthracene unit) which is at the centre of the molecule and also acts as the linker, the two receptors (phenyl boronic acid units) are then arranged symmetrically either side of the anthracene unit.[60–62] The modular system **2** consists of a fluorophore, linker (hexamethylene) and two boronic acid receptors.[45–50] Sensor **2** is one of a series of modular sensors prepared by our group, this sensor with a hexamethylene linker and pyrene fluorophore had the largest observed binding constant amongst the sensors prepared for D-glucose with an observed binding constant of 962 dm^3 mol^{-1}. However, sensor **1** has an observed binding constant of 4000 dm^3 mol^{-1}.[61,62] Here, we propose that the larger binding constant observed for sensor **1** may be due in part to the greater rigidity of the linker connecting the two boronic acid receptor units as well as a stacking interaction between D-glucose and the extended aromatic surface of the anthracene unit. In order to explore the effect of linker rigidity on the saccharide selectivity we designed sensors **3–5** (*para series*) and **6–8** (*meta series*) (Fig. 2).



3 Flu = naphthalene
4 Flu = anthracene
5 Flu = pyrene

6 Flu = naphthalene
7 Flu = anthracene
8 Flu = pyrene

Fig. 2 Six target sensors.

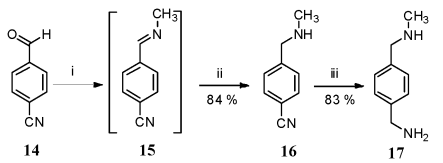
Results and discussion

The target sensors **3–8** can be prepared by dividing the synthesis into 3 different steps: the initial formation of the core unit, followed by the addition of the fluorophore and subsequent addition of the boronic acid units in the last stage of the synthesis. Therefore, one unique synthetic route to make a core molecule (the linker in this case) can be used to synthesise a variety of sensors with different fluorophores.

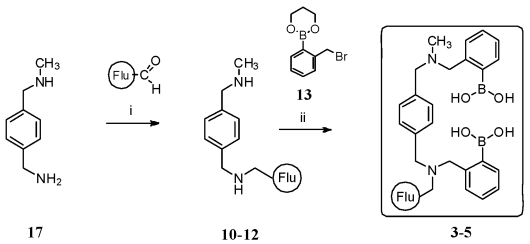
The *para* or *meta* diaminomethyl-benzyl represents the core unit of the sensors. Both boronic acid groups and fluorophore unit are added to this core structure *via* an amine group. Changing the nature of the fluorophore (naphthalene, anthracene, pyrene) and the position of the two aminomethyl groups (*para* for sensors **3–5** and *meta* for sensors **6–8**) quickly allows the synthesis of six sensors.

The synthesis of compounds **3**, **4** and **5** uses core unit **17** as a starting material. Synthesis of core unit **17** was achieved starting from commercial 4-cyanobenzaldehyde **14** Scheme 1. This involved the addition of methylamine to 4-cyanobenzaldehyde **14** to form 4-cyanomethylamine **16**, which can be reduced to the diamine **17** by treatment with $LiAlH_4$ (Scheme 1).

Treatment of the commercially available 4-cyanobenzaldehyde **14** with a solution of 6 equivalents of methylamine in methanol gave the intermediate imine **15**, which was not isolated. This was reduced *in situ* with sodium borohydride (5 equivalents) in methanol to give the amine **16** in 84% yield. The amine **16** was then treated with 5 equivalents of lithium aluminium hydride in dry THF to reduce the nitrile group to a primary amine.[63] This afforded the target amine **17** in a yield of 70% over 2 steps. The fluorophore and the two boronic acid groups are consecutively added onto the core unit **17**, as shown in Scheme 2.



Scheme 1 Synthetic route to core unit **17**. *Reagents and conditions*: (i) CH_3NH_2/methanol, rt; (ii) $NaBH_4$/methanol, rt; (iii) $LiAlH_4$/dry THF, Δ.



10 Flu = naphthalene 73%
11 Flu = anthracene 59 %
12 Flu = pyrene 90 %

3 Flu = naphthalene 82 %
4 Flu = anthracene 81 %
5 Flu = pyrene 82 %

Scheme 2 Addition of fluorophores and boronic acid receptors to core unit **17**. *Reagents and conditions:* (i) a, fluorophore/methanol, rt; b, $NaBH_4$/methanol, rt; (ii) **13**, K_2CO_3/dry acetonitrile, Δ.

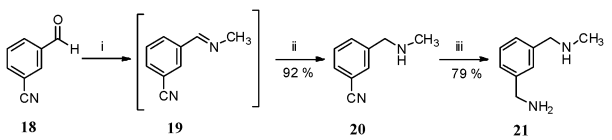
The fluorophore is added to diamine **17** *via* the reaction between the primary amine group of **17** and the aldehyde group of naphthalen-2-carbaldehyde, anthracen-9-carbaldehyde or pyren-1-carbaldehyde. The two boronic acid groups are finally added to the diamine compounds **10**, **11** and **12** by using a nucleophilic substitution with cyclic boronate ester **13**.

The addition of the fluorophores as arylaldehydes gave diamines **10**, **11** and **12** in 73%, 59% and 90% yield respectively. The addition of the two boronic acids by treatment with bromide **13** afforded the *para* series of sensors **3**, **4** and **5** in 82%, 81% and 82% yield, respectively, after purification (trituration with hexane and chloroform).

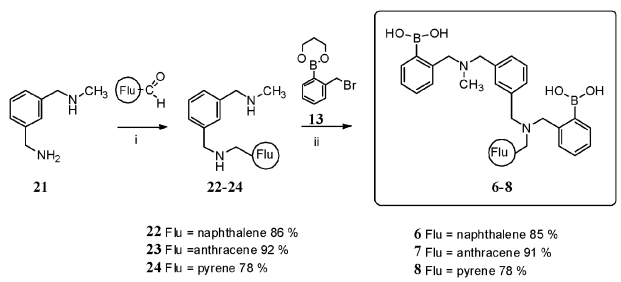
Core unit **21** was synthesised in a similar manner to core unit **17**, using 3-cyanobenzaldehyde **18** as starting material, Scheme 3.

Core unit **21** was then used for the synthesis of the *meta* sensors (**6–8**) in a similar manner to the way that core unit **17** was used for the preparation of sensors **3–5**. Accordingly diamines **22**, **23** and **24** were obtained in 86, 92 and 78% yield respectively. Treatment of **22–24** with cyclic boronate ester **13** gave the *meta* sensors **6**, **7** and **8** in 85%, 91% and 78% yield respectively (Scheme 4).

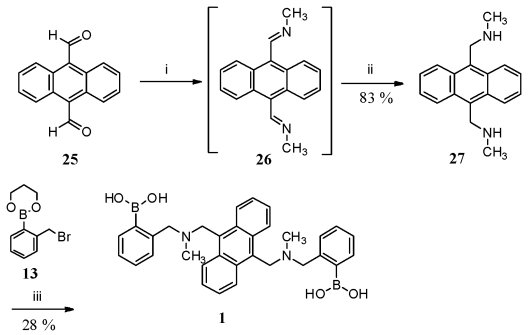
Sensor **1** was also synthesised in order to make it possible to directly compare all the sensors under identical conditions. The route used to prepare sensor **1** is different to the originally published method and is shown in Scheme 5. 9,10-Dialdehyde anthracene **25** was treated with a solution of methylamine (6 equivalents) in methanol at room temperature to give the intermediate imine **26** which was not isolated. The imine was then reduced *in situ* with sodium borohydride (5 equivalents) in methanol at room temperature to form the diamine **27**. Treatment of diamine **27** with 3 equivalents of aryl bromide **13** in alkaline dry acetonitrile afforded sensor **1** in 28% yield (23% over the two steps) (Scheme 5).



Scheme 3 Formation of core unit **21**. *Reagents and conditions*: (i) CH_3NH_2/methanol, rt; (ii) $NaBH_4$/methanol, rt; (iii) $LiAlH_4$/dry THF, Δ.



Scheme 4 Addition of the fluorophore and the two boronic acid receptors to core unit **21**. *Reagents and conditions*: (i) a, fluorophores/methanol, rt; b, $NaBH_4$/methanol; (ii) bromide **13**, K_2CO_3/dry acetonitrile, Δ.



Scheme 5 Synthesis of sensor **1**. *Reagents and conditions*: (i) CH_3NH_2/methanol, rt; (ii) $NaBH_4$/methanol, rt; (iii) bromide **13**, K_2CO_3/dry CH_3CN, Δ.

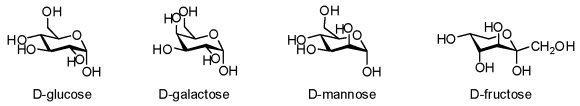


Fig. 3 Structures of D-glucose, D-galactose, D-mannose and D-fructose.

Fluorescence titrations of sensors **1** and **3–8** with D-glucose, D-fructose, D-galactose, and D-mannose (Fig. 3) were carried out in an aqueous methanolic buffer solution [52.1 wt% methanol at pH 8.21 (KCl, 0.01000 mol dm^{-3}; KH_2PO_4, 0.002752 mol dm^{-3}; Na_2HPO_4, 0.002757 mol dm^{-3})].[64] The fluorescence intensity of the sensors **1** and **3–8** increased with increasing saccharide concentration. The observed stability constants (K_{obs}) of sensors **1** and **3–8** were calculated by the fitting of emission intensity *versus* saccharide concentration curves using a 1 : 1 binding model (1 : 2 complexes were not needed to reproduce the data). The observed stability constants (K_{obs}) are shown in Table 1.

To help visualize the trends of the observed stability constants (K_{obs}) in Table 1, the stability constants of the diboronic acid sensors **3–8** are reported in Fig. 4 and 5.

From Table 1 and Fig. 4 and 5 it is clear that the observed stability constants are generally larger for the *meta* sensors (**6–8**) than for the *para* sensors (**3–5**). Also, increasing the size of the fluorophore for both the *para* and *meta* sensors in general reduces the observed stability constants; for the *para* sensors **4** (naphthalene) > **5** (anthracene) > **6** (pyrene) and for the *meta* sensors **6** (naphthalene) > **7** (anthracene) > **8** (pyrene). From Table 1 it is also apparent that the original sensor **1** has the highest observed stability constant for D-glucose. However, when we consider the observed stability constants for D-galactose the *meta* sensors (**6–8**) and *para* sensor **3** (naphthalene) all have a higher binding constant with that saccharide than sensor **1**. Clearly a smaller fluorophore and *meta* spacer favours the formation of a complex with D-galactose.

In order to probe the nature of the differences in observed stability constants we carried out circular dichroism (CD) spectroscopic analysis of the complexes, since it will be possible to gain information about the structure of the sensor:saccharide complexes. CD spectroscopy has been used with diboronic acid sensors to show the formation of cyclic complexes with certain saccharides. For example compound **1**, forms a cyclic complex with D-glucose Fig. 6.[61,62]

Table 1 Observed stability constants (K_{obs}) (coefficient of determination; r^2) for the saccharide complexes of sensors **1** and **3–8**

Sensor	D-Glucose K_{obs}/dm^3 mol^{-1}	D-Galactose K_{obs}/dm^3 mol^{-1}	D-Fructose K_{obs}/dm^3 mol^{-1}	D-Mannose K_{obs}/dm^3 mol^{-1}
3	320 ± 13 (0.99)	168 ± 22 (0.98)	154 ± 10 (0.99)	11 ± 2 (0.99)
4	282 ± 42 (0.98)	18 ± 7 (0.94)	112 ± 24 (0.96)	9 ± 3 (0.98)
5	157 ± 7 (0.99)	71 ± 3 (0.99)	84 ± 4 (0.99)	9 ± 1 (0.99)
6	452 ± 38 (0.99)	330 ± 26 (0.99)	124 ± 5 (0.99)	10 ± 2 (0.99)
7	428 ± 67 (0.97)	299 ± 25 (0.99)	107 ± 19 (0.98)	24 ± 6 (0.97)
8	299 ± 15 (0.99)	171 ± 14 (0.99)	131 ± 10 (0.99)	36 ± 5 (0.99)
1	1972 ± 176 (0.99)	114 ± 14 (0.99)	132 ± 7 (0.99)	19 ± 2 (0.99)

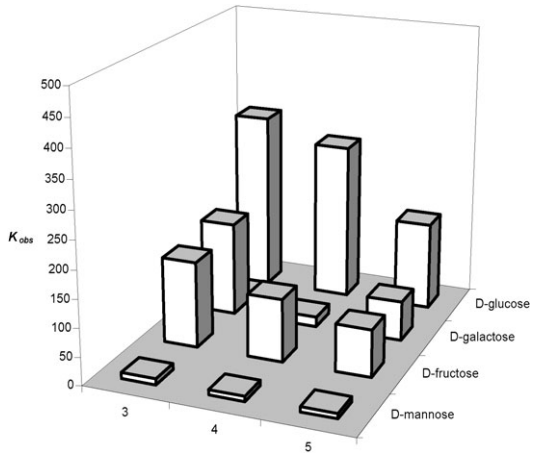


Fig. 4 Observed stability constants (K_{obs}) for the saccharide complexes of the *para* sensors **3–5**.

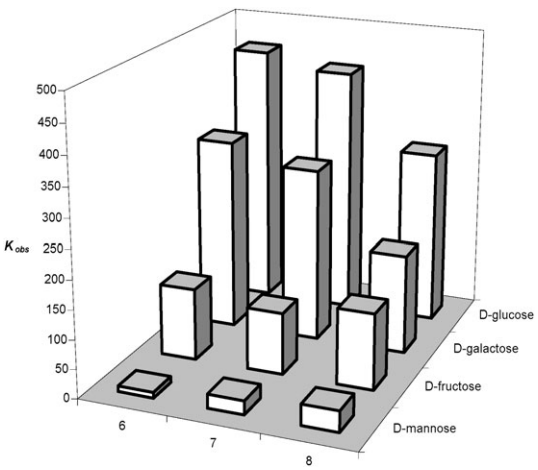


Fig. 5 Observed stability constants (K_{obs}) for the saccharide complexes of the *meta* sensors **6–8**.

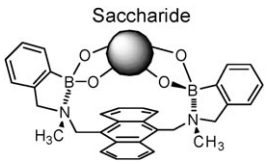


Fig. 6 Cyclic complex formed between sensor **1** and saccharides.

The formation of the cyclic complex between compound **1** and D-glucose produces a rigid structure freezing the molecular motion of the chromophoric anthracene unit and as a result a CD active species is formed. The complexes formed between compound **1** and D- and L-glucose produce mirrored symmetrical absorptions with opposite signs. The results of the CD spectroscopic measurements performed on sensors **3–8** are given in Tables 2 and 3. Fig. 8 shows the CD spectra of **7** in the presence of D-glucose and L-glucose and Fig. 9 represents the CD activity of **7** in the presence of D-galactose.

The results should help elucidate the structure of the complexes formed between sensors **3–8** and the saccharides D-glucose, D-galactose, D-mannose and D-fructose.

From Tables 2 and 3, we can see that all of the sensors produce CD-active complexes with D-glucose, but are CD-silent with D-fructose. This result indicates that all the sensors form a cyclic complex with D-glucose and a non-cyclic complex with D-fructose. However, D-galactose gave different results dependent on the structure of the diboronic acid sensor. Sensors **3**, **4**, **5** and **8** form CD-silent complexes with D-galactose,

Table 2 Absorption and CD maximum of **3–5** (*para* series) and its saccharide complexes

Sensor (*para* series)	Saccharide	Absorption maximum/nm	CD maximum wavelength(λ)/ellipticity (θ) (nm/deg cm^2 dmol^{-1})
3	D-Glucose	275	289/−452
	L-Glucose	275	289/+390
	D-Galactose	274	Silent
	D-Fructose	273	Silent
4	D-Glucose	380	393/+713
	L-Glucose	380	393/−944
	D-Galactose	378	Silent
	D-Fructose	379	Silent
5	D-Glucose	349	356/−329
	L-Glucose	349	356/+352
	D-Galactose	345	Silent
	D-Fructose	345	Silent

Table 3 Absorption and CD maximum of **6–8** (*meta* series) and their saccharide complexes

Sensors (*meta* series)	Saccharides	Absorption maximum/nm	CD maximum wavelength (λ)/ellipticity (θ) (nm/deg cm^2 dmol^{-1})
6	D-Glucose	273	289/+905
	L-Glucose	273	290/−967
	D-Galactose	273	290/−1052
	D-Fructose	275	Silent
7	D-Glucose	384	395/−948
	L-Glucose	384	395/+806
	D-Galactose	383	394/+824
	D-Fructose	384	Silent
8	D-Glucose	349	357/−934
	L-Glucose	349	357/+496
	D-Galactose	344	Silent
	D-Fructose	349	Silent

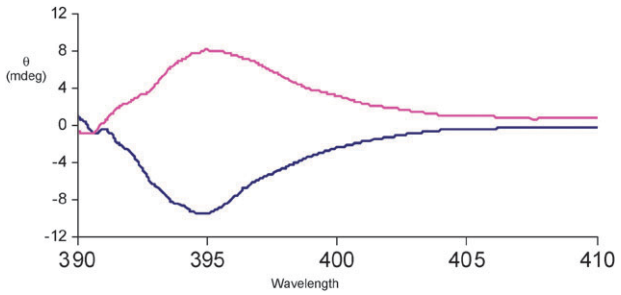


Fig. 8 CD spectra of sensor **7** in the presence of L- or D-glucose.

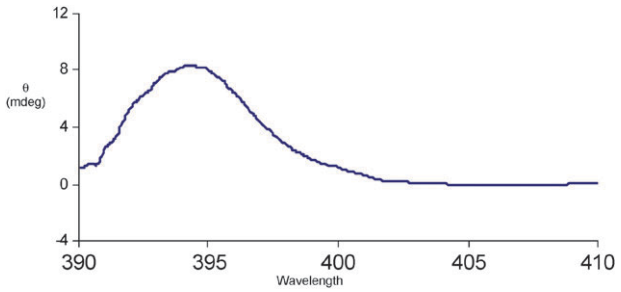


Fig. 9 CD spectra of sensor **7** in the presence of D-galactose.

while sensors **6** and **7** form a cyclic CD-active complex with D-galactose. This observation may help explain why sensors **6** and **7** gave higher K_{obs} values with D-galactose than sensors **3**, **4**, **5** and **8**.

From the CD data sensors **6** and **7** are able to form cyclic complexes with D-glucose and D-galactose. However, sensor **8** has the same basic structure as sensors **6** and **7** and the fact that it does not form the same complex is somewhat surprising. However, this could be due to the bulk of the fluorophore (pyrene unit), which could make the rotation of the C–N bonds difficult. The lack of flexibility may make it difficult for the two boronic acid groups to rearrange easily and form a cyclic complex. As expected, all of the sensors showed fluorescence enhancement on saccharide addition, with sensors belonging to the *meta* series (**6–8**) having larger observed stability constants K_{obs} than sensors of the *para* series (**3–5**). Also, all six sensors are D-glucose selective with the highest observed stability constants K_{obs} obtained with D-glucose. Sensors **6** and **7** have particularly high observed stability constants K_{obs} with D-galactose when compared with the other sensors.

To help explain the experimental CD spectra we have carried out calculations on model systems. In our computations an anthracene linker segment is represented by a phenyl group to reduce computational cost, however the remainder of the bound saccharide to the boron sensor is unchanged, see Fig. 7. The density functional PBE1PBE[65–67] was used in conjunction with Dunning–Woon cc-pVDZ[68–71] and Pople-type 6-31G(*d*) and 6-31 + G(*d*)[72] basis sets. This method in conjunction with these basis sets have been shown previously to be efficient alternatives to more rigorous methods when studying boronic acid compounds.[73–76] All computations were performed with the GAUSSIAN 03 program.[77]

In order to explain why galactose is CD silent with *para*-sensors **3–5** and CD active with *meta* sensors **6** and **7**, we

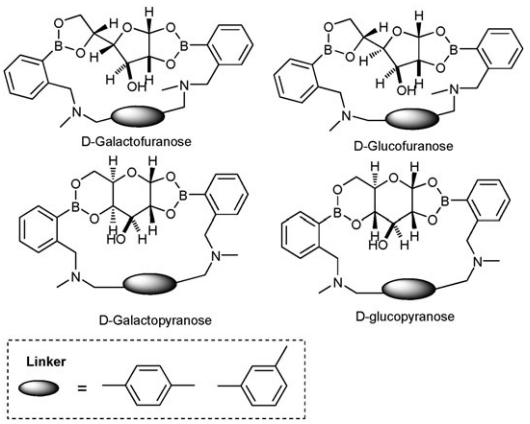


Fig. 7 Cyclic complexes for D-galactose and D-glucose bound to *para* and *meta* linkers in their furanose or pyranose forms.

Table 4 Relative energies of D-galactose and D-glucose bound to *para*- and *meta*-linkers in their furanose or pyranose forms

	Basis set	Linker	Furanose	Pyranose
D-Galactose	cc-pVDZ	*meta*	0.0	0.0
		para	+11.9	+11.0
D-Glucose	cc-pVDZ	*meta*	0.0	0.0
		para	+2.4	+5.4
D-Galactose	6-31G(*d*)	*meta*	0.0	0.0
		para	+10.5	+8.7
D-Glucose	6-31G(*d*)	*meta*	0.0	0.0
		para	+1.9	+5.3

optimized the geometries of both the pyranose and furanose forms of D-galactose and D-glucose with *meta* and *para* benzene linkers. In Table 4 the relative energies of two D-galactose and two D-glucose conformers with *meta*- and *para*-linkers are listed. In all instances, the *meta*-linked conformer is much lower in energy than the *para*-counterpart for D-galactose. The corresponding relative energies for glucose with both *meta* and *para* linkers show a much smaller difference, see Table 4. These differences in the relative energies help explain why the *meta* sensors **6** and **7** are CD active with D-galactose, while the *para* sensors **3–5** are CD silent with D-galactose. The energy differences also explain why both the *meta* and *para* sensors are CD active with D-glucose.

Conclusions

This research has shown that it is possible to synthesise modular PET fluorescent saccharide sensors using quick, easy and mild reaction conditions. Two series of sensors *para* **3–5** and *meta* series **6–8** were synthesised. The six sensors (**3–8**) prepared are different in the nature of the fluorophore (naphthalene, anthracene or pyrene) and/or geometry of the two boronic acids units (spacer), allowing us to investigate systematically the effect of the fluorophore and the spacer on the selectivity of the sensors. Previous research has shown that the selectivity of a sensor toward one particular saccharide can be explained by the formation of a cyclic complex between the sensor and that saccharide.[61,62] This was the case for the cyclic complex formed between sensor **1** and D-glucose. Here, the six sensors **3–8** showed selectivity towards D-glucose and form

cyclic complexes with D-glucose. Two *meta* sensors **6** and **7** showed particularly strong affinity for D-galactose, with K_{obs} of 330 dm^3 mol^{-1} and 299 dm^3 mol^{-1} respectively. This may suggest that the spacer used in the *meta* series of sensors was favourable for interactions with D-galactose. Although, *meta* sensor **8** did not seem to form a cyclic complex with D-galactose the K_{obs} of 171 dm^3 mol^{-1} was higher than that for sensor **1** which has a K_{obs} of 114 dm^3 mol^{-1}. Therefore the choice of the spacer is important for the selectivity of the sensor, but, structural factors can handicap the formation of the cyclic complex, for example the presence of sterically bulky groups.

It has also been shown that there is substantial variation in the values of the observed stability constants K_{obs}. Sensors **1** and **3–8** are all glucose selective. However, they all have very different stability constant K_{obs} values. The highest stability constant is seen for sensor **1** with K_{obs} of 1972 dm^3 mol^{-1}, the *meta* series of sensors **6–8** have a K_{obs} varying between 299 dm^3 mol^{-1} (**8**) and 452 dm^3 mol^{-1} (**6**). Whilst the *para* series of sensors have observed stability constant K_{obs} values varying between 157 dm^3 mol^{-1} (**5**) and 320 dm^3 mol^{-1} (**3**).

The results presented here have confirmed that PET diboronic acid sensors represent a powerful tool for the detection of saccharides. We believe that these results will aid further research in the development of saccharide selective sensors. For example, sensors **6** and **7** could be used as models for the design of D-galactose selective fluorescent sensors. We are currently exploring the development of these sensors incorporated into polymers and attached to fibre-optic devices, to facilitate continuous *in vivo* monitoring of saccharides for a variety of industrial and medicinal applications.

Experimental section

NMR spectroscopy

NMR spectra were recorded on a Bruker AC-300 or AM-300, a Varian Gemini 500, a Jeol 270-EX or a Jeol 400-EX spectrometer. All chemical shifts (δ) are described in parts per million relative to tetramethylsilane as the internal standard. The multiplicities of the spectroscopic data are presented in the following manner: s = singlet; d = doublet; t = triplet; m = multiplet and the values of the coupling constants J are given in Hz.

Mass spectrometry

Mass spectra and accurate mass were recorded on a Kratos Profile or VG ProSpec for Electron Impact (E.I.), a VG ProSpec for Chemical Ionisation (C.I.), a VG ZabSpec for Fast Atom Bombardment (F.A.B.), a micromass LCT for Electrospray Ionisation (E.I.) or a Micromass Autospec spectrometer with E.I., C.I., F.A.B. and Electrospray sources. Electrospray samples were prepared in a CH_3OH/H_2O 1 : 1 solution and F.A.B. spectra were recorded using *m*-nitrobenzyl alcohol or glycerol as a matrix.

Infrared spectra

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR or a Perkin-Elmer 1600 FT-IR spectrometer. The samples were prepared as Nujol mulls, solutions in chloroform or as neat samples. The frequencies (ν) as absorption maxima are given in wavenumbers (cm^{-1}).

Elemental analyses were performed at the University of North London, the University of Birmingham and the University of Bath.

Melting points were determined using a Gallenkamp melting point apparatus and are reported uncorrected.

Thin layer chromatography (TLC)

Precoated aluminium-backed silica plates were supplied by Fluka Chemie (Silica gel with fluorescent indicator 254 nm, thickness 0.2 mm). Ultraviolet light was employed for visualisation.

Column chromatography

Column chromatography was performed using silica gel 60 (0.063–0.200 mm) (E. Merck, 64 271 Darstadt, Germany) and the column fractions were collected and monitored by TLC.

Fluorescence experiments

Fluorescence measurements were recorded on a Perkin Elmer LS 50 B Fluorimeter using quartz cuvets with 10 mm path length.

Synthesis

4-Methylaminomethyl-benzonitrile (**16**). Methylamine (45.7 cm^3 of a 2.0 mol dm^{-3} solution in methanol, 91.4 mmol) was added under argon atmosphere to 4-cyanobenzaldehyde (2.00 g, 15.25 mmol) **14** in a stirred round-bottomed flask at room temperature. The reaction was left stirring overnight. A solution of sodium borohydride (5.64 g, 152.50 mmol) in dry methanol (100 cm^3) was added in one portion to the reaction mixture and the reaction mixture was stirred for 4 h and then concentrated under reduced pressure. Then water (50 cm^3) was added to the solution and the aqueous layer was extracted with dichloromethane (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the amine **16** as a yellow oil (1.88 g, 84.4%) (found: M^+, 146.0835. $C_9H_{10}N_2$ requires 146.0843); ν_{max} (Neat)/cm^{-1} 2229 (CN nitrile). δ_H(300 MHz; $CDCl_3$) 2.29 (3H, s, CH_3), 3.67 (2H, s, CH_2), 7.30 (2H, d, $J_{2,3}$ 8.1 Hz, 2-ArC*H* and 6-ArC*H*), 7.45 (2H, d, $J_{3,2}$ 8.1 Hz, 3-ArC*H* and 5-ArC*H*); δ_C(75 MHz; $CDCl_3$) 36.05 (CH_3), 55.43 (CH_2), 110.52 (4-Ar*C*), 119.09 (CN), 128.66 (2-Ar*C*H and 6-Ar*C*H), 132.13 (3-Ar*C*H and 5-Ar*C*H) and 145.17 (1-Ar*C*); m/z (EI^+) 146 (66%, M^+) and 44 (100, $[CH_3NHCH_2]^+$).

4-Methylaminomethyl-benzylamine (**17**). To a solution of 4-methylaminomethyl-benzonitrile **16** (1.22 g, 8.35 mmol) in dry THF (30 cm^3) at 0 °C was added $LiAlH_4$ (40 cm^3 of a 1.0 mol dm^{-3} solution in dry diethylether, 40.00 mmol) and the resultant reaction mixture heated under reflux for 3 h. After cooling, the solvent was removed under reduced pressure and water (50 cm^3) was added drop wise. The organic phase was extracted with DCM (3 × 50 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford the diamine **17** as a yellow oil (1.04 g, 83.0%).

(Found: M^+, 150.1148. $C_9H_{14}N_2$ requires 150.1156). δ_H(300 MHz; $CDCl_3$) 36.05 (3H, s), 3.71 and 3.82 (4H, s) and 7.20–7.30 (4H, m); δ_C(75 MHz; $CDCl_3$) 36.0, 46.2, 55.8, 127.2, 128.4, 138.7, 142.1; *m/z* (EI^+) 149 (28%, $[M - H]^+$), 133 (20, $[M - NH_3]^+$) and 120 (100, $[M - CH_3NH]^+$).

(4-Methylaminomethyl-benzyl)-naphthalen-2-ylmethyl-amine (**10**). To a solution of the diamine **17** (0.92 g, 6.10 mmol) in methanol (50 cm^3) was added 2-naphthaldehyde (0.95 g, 6.10 mmol). After 5 h stirring at room temperature, a solution of $NaBH_4$ (1.11 g, 30.00 mmol) in methanol (20 cm^3) was added and the reaction mixture was stirred for 4 h and then concentrated under reduced pressure. Water (50 cm^3) was added carefully and the organic phase was extracted with DCM (3 × 50 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford the diamine **10** as a yellow oil (1.30 g, 73.5%) (found: M^+, 290.1780. $C_{20}H_{22}N_2$ requires 290.1782). δ_H(300 MHz; $CDCl_3$) 2.43 (3H, s), 3.72 (2H, s), 3.81 (2H, s), 3.94 (2H, s), 7.29–7.76 (11H, m); δ_C(75 MHz; $CHCl_3$) 36.0, 53.0, 53.3, 55.8, 125.6, 125.9, 126.0, 126.5, 126.7, 127.3, 127.4, 127.7, 127.9, 128.2, 129.1, 132.7, 133.6, 137.9, 138.8, 139.1; *m/z* (EI^+) 289 (36%, $[M - H]^+$), 260 (9, $[M - (CH_3NH)]^+$), 170 (10, $[NaphCH_2NHCH_2]^+$) and 141 (100, $[NaphCH_2]^+$).

(4-{[(Anthracen-9-ylmethyl)-amino]-methyl}-benzyl)-methyl-amine (**11**). To a solution of diamine **17** (0.65 g, 4.30 mmol) in methanol (50 cm^3) was added 9-anthraldehyde (0.89 g, 4.30 mmol). After 5 h stirring, a solution of $NaBH_4$ (0.75 g, 20.00 mmol) in methanol (20 cm^3) was added. The reaction mixture was stirred for 4 h at room temperature and then concentrated under reduced pressure. Water (50 cm^3) was added carefully and the aqueous layer was extracted with DCM (3 × 50 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the diamine **11** as a yellow-orange oil (0.86 g, 58.8%) (found: M^+, 340.1995. $C_{24}H_{24}N_2$ requires 340.1992). δ_H(300 MHz; $CDCl_3$) 2.47 (3H, s), 3.77 (2H, s), 4.02 (2H, s), 4.68 (2H, s), 7.25–7.51 (8H, m), 7.99 (2H, d, *J* 7.5 Hz), 8.21 (2H, d, *J* 7.5 Hz), 8.39 (1H, s); δ_C(75 MHz; $CDCl_3$) 36.0, 44.9, 54.1, 55.8, 124.2, 124.9, 126.0, 127.2, 127.8, 128.3, 128.4, 128.6, 129.1, 129.3, 130.3, 131.5, 131.7, 138.9, 139.1; *m/z* (ES^+) 363 (100%, $[M + Na]^+$), 341 (49, $[M + H]^+$) and 310 (47, $[M - CH_3NH]^+$).

(4-Methylaminomethyl-benzyl)-pyren-1-ylmethyl-amine (**12**). To a stirred solution of diamine **17** (0.72 g, 4.80 mmol) in methanol (50 cm^3) was added 1-pyrenecarboxaldehyde (1.10 g, 4.80 mmol). After 5 h stirring, a solution of $NaBH_4$ (0.94 g, 25.00 mmol) in methanol (20 cm^3) was added, and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was concentrated under reduced pressure and water (50 cm^3) was added carefully. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined DCM extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the diamine **12** as a yellow oil (1.57 g, 89.8%) (found: $[M + H]^+$, 365.1999. $C_{26}H_{25}N_2$ requires 365.2017). δ_H(300 MHz; $CDCl_3$) 2.44 (3H, s), 3.73 (2H, s), 3.91 (2H, s), 4.44 (2H, s), 7.23–8.09 (13H, m); δ_C(75 MHz; $CDCl_3$) 36.1, 51.1, 53.5, 55.9, 123.3, 124.7, 125.0, 125.1, 125.9, 127.1, 128.3, 128.5, 129.2, 130.7, 130.9, 131.3, 133.9, 138.9, 139.1; *m/z* (ES^+) 365 (100%, $[M + H]^+$) and 334 (43, $[M - CH_3NH]^+$).

(2-Boronobenzyl)-(4-{[(2-boronobenzyl)-methyl amino] methyl}-benzyl)-naphthalen-2-ylmethyl-amine (**3**). To a stirred solution of diamine **10** (0.58 g, 2.00 mmol) in 50 cm^3 of dry acetonitrile was added 2-(2-bromomethyl-phenyl)-[1,3,2]-dioxaborinane **13** (1.52 g, 6.00 mmol), followed by K_2CO_3 (1.10 g, 8.00 mmol). The reaction mixture was heated and stirred under reflux for 5 h. The acetonitrile was then removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration, the solvent was removed under reduced pressure to afford the crude product as a dark yellow solid. Recrystallisation from $CHCl_3$/hexane afforded the boronic acid **3** as a pale yellow powder (0.92 g, 82.4%), mp 134–136 °C (decomp.). δ_H(300 MHz; $CHCl_3/CD_3OD$ 1 : 1) 2.13 (3H, s), 3.42 (2H, s), 3.47 (2H, s), 3.49 (2H, s), 3.52 (2H, s, 4), 3.60 (2H, s), 7.06–7.60 (19H, m); δ_C(75 MHz; $CHCl_3/CD_3OD$ 1 : 1) 39.6, 56.6, 56.8, 57.9, 58.2, 65.7, 125.5, 125.6, 126.5, 126.8, 127.1, 127.1, 127.3, 127.6, 127.8, 128.3, 128.97, 129.6, 130.5, 132.5, 132.5, 132.8, 138.8, 141.0, 142.9; *m/z* (ES^+) 633 (40%, $[M - 3 \times H_2O + 4 \times CH_3OH + H]^+$ and 619 (100, $[M - 2 \times H_2O + 3 \times CH_3OH + H]^+$).

Anthracen-9-ylmethyl-(2-boronobenzyl)-(4-{[(2-boronobenzyl)-methyl-amino] methyl}-benzyl)-amine (**4**). To a stirred solution of diamine **11** (0.34 g, 1.00 mmol) in dry acetonitrile (40 cm^3) was added 2-(2-bromomethyl-phenyl)-[1,3,2]dioxaborinane **13** (0.76 g, 3.00 mmol), followed by K_2CO_3 (0.55 g, 4.00 mmol). The reaction mixture was then heated and stirred under reflux for 5 h. The acetonitrile was removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$), filtered and removed under reduced pressure to afford the crude product as a yellow-orange solid. Recrystallisation from chloroform/hexane afforded the boronic acid **4** as a pale yellow powder (0.49 g, 80.5%), mp 154–155 °C (decomp.). δ_H(300 MHz; $CDCl_3/CD_3OD$ 1 : 1) 2.06 (3H, s), 3.49 (2H, s), 3.58 (2H, s), 3.74 (4H, s), 4.47 (2H, s), 7.05–8.37 (21H, m); δ_C(125 MHz; $CDCl_3/CD_3OD$ 1 : 1) 40.2, 59.2, 59.4, 59.8, 124.6, 124.7, 124.8, 124.9, 131.2, 131.5; *m/z* (ES^+) 727 (46%, $[M - 4 \times H_2O + 2 \times HO(CH_2)_3OH + K]^+$) and 799 (92%, $[M + 2 \times HO(CH_2)_3OH + K]^+$).

(2-Boronobenzyl)-(4-{[(2-boronobenzyl)-methyl-amino]-methyl}-benzyl)-pyren-1-ylmethyl-amine (**5**). To a stirred solution of diamine **12** (0.72 g, 2.00 mmol) in dry acetonitrile (40 cm^3) was added 2-(2-bromomethyl-phenyl)-[1,3,2]dioxaborinane **13** (1.52 g, 6.00 mmol), followed by K_2CO_3 (1.10 g, 8.00 mmol). The reaction mixture was then stirred and heated under reflux for 5 h. The acetonitrile was removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration, the filtrate was concentrated under reduced pressure to afford the crude product as a dark yellow solid. Recrystallisation from chloroform/hexane afforded the boronic acid **5** as a pale yellow powder (1.04 g, 82.3%), mp 174–175 °C (decomp.)

(found: C, 77.3; H, 6.2; N, 3.9%. Calc. for $C_{46}H_{46}B_2N_2O_4$ (protected compound): C, 77.5; H, 6.5; N, 3.9%). δ_H(300 MHz; $CDCl_3/CD_3OD$ 1 : 1) 1.79 (3H, s), 3.25 (2H, s), 3.46 (2H, s) 3.63 (4H, s), 4.05 (2H, s), 6.74–7.93 (21H, m); δ_C(125 MHz; $CDCl_3/CD_3OD$ 1 : 1) 40.2, 52.9, 54.9, 57.9, 58.0, 59.49, 123.1, 124.3, 124.7, 125.1, 125.8, 127.2, 127.3, 130.6, 131.1, 131.1; *m*/*z* (ES^+) 711 (100%, $[M - 4 \times H_2O + 4 \times CH_3OH + Na]^+$).

3-Methylaminomethyl-benzonitrile (**20**). Methylamine (60 cm^3 of a 2.0 mol dm^{-3} solution in CH_3OH, 120 mmol) was added under an argon atmosphere to a solution of 3-cyanobenzaldehyde **18** (2.62 g, 20.00 mmol) in methanol CH_3OH (30 cm^3). After 5 h stirring at room temperature, the reaction was complete as judged by TLC. A solution of $NaBH_4$ (3.78 g, 100 mmol) in methanol (30 cm^3) was then added in one portion, the reaction mixture stirred for 4 h at room temperature and then concentrated under reduced pressure. Water (50 cm^3) was then added and the aqueous layer was extracted with DCM (3 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the amine **20** as a yellow oil (2.69 g, 92.1%) (found: M^+, 146.0837. $C_9H_{10}N_2$ requires 146.0843); ν_{max} ($CHCl_3$)/cm^{-1} 2232 (CN nitrile). δ_H(270 MHz; $CDCl_3$) 2.38 (3H, s), 3.72 (2H, s) and 7.34–7.57 (4H, m); δ_C(67.5 MHz; $CDCl_3$) 35.9, 55.9, 112.0, 118.6, 128.81, 130.30, 131.24, 132.3, 141.5; *m*/*z* (EI^+) 145 (77%, $[M - H]^+$), 116 (49, $[M - CH_3NH]^+$) and 44 (100, $[CH_3NHCH_2]^+$).

3-Methylaminomethyl-benzylamine (**21**). To a solution of 3-methylaminomethyl-benzonitrile **20** (0.73 g, 5.00 mmol) in dry THF (30 cm^3) at 0 °C was added $LiAlH_4$ (25.0 cm^3 of a 1.0 mol dm^{-3} solution in dry diethylether, 25.00 mmol) and the resultant reaction mixture heated under reflux for 3 h. After cooling, the solvent was removed under reduced pressure and water (50 cm^3) was added drop wise. The aqueous phase was extracted with DCM (3 × 50 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure, to afford the diamine **21** as a yellow oil (0.59 g, 79.0%) (found: M^+, 150.1147. $C_9H_{14}N_2$ requires 150.1156). δ_H(270 MHz; $CDCl_3$) 2.45 (3H, s), 3.74 (2H, s), 3.85 (2H, s) and 7.18–7.38 (4H, m); δ_C(100 MHz; $CDCl_3$) 36.0, 46.3, 55.9, 125.5, 126.5, 126.7, 128.4, 140.1, 143.1; *m*/*z* (EI^+) 149 (34%, $[M - H]^+$), 133 (90, $[M - NH_3]^+$) and 120 (100, $[M - CH_3NH]^+$).

Methyl-(3-{[(naphthalene-2ylmethyl)amino]-methyl}-benzyl)-amine (**22**). To a stirred solution of diamine **21** (0.45 g, 3.00 mmol) in methanol (50 cm^3) was added 2-naphthaldehyde (0.47 g, 3.00 mmol). After 5 h stirring, a solution of $NaBH_4$ (0.56 g, 15.00 mmol) in methanol (20 cm^3) was then added and the reaction mixture stirred for 4 h, then concentrated under reduced pressure. Water (50 cm^3) was added carefully and the aqueous phase was extracted with DCM (3 × 50 cm^3). The combined DCM extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the diamine **22** as a yellow oil (0.75 g, 85.9%) (found: $[M + H]^+$, 291.1863. $C_{20}H_{23}N_2$ requires 291.1861). δ_H(270 MHz; $CDCl_3$) 2.40 (3H, s), 3.69 (2H, s), 3.79 (2H, s), 3.92 (2H, s), 7.14–7.79 (11H, m); δ_C(100 MHz; $CDCl_3$) 36.3, 53.5, 53.7, 56.3, 125.7, 126.2, 126.7, 126.8, 127.1, 127.1, 127.9, 127.9, 128.2, 128.3, 128.7, 132.9, 133.6, 137.9, 140.2, 140.6; *m*/*z* (ES^+) 291 (100%, $[M + H]^+$).

(3-{[(Anthracen-9-ylmethyl)-amino]-methyl}-benzyl)-methyl-amine (**23**). To a stirred solution of diamine **21** (0.45 g, 3.00 mmol) in methanol (50 cm^3) was added 9-anthraldehyde (0.61 g, 3.00 mmol). After 5 h stirring, a solution of $NaBH_4$ (0.56 g, 15.00 mmol) in methanol (20 cm^3) was added and the reaction mixture was stirred for 4 h and then concentrated under reduced pressure. Water (50 cm^3) was added carefully and the aqueous phase was extracted with DCM (3 × 50 cm^3). The combined DCM extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the diamine **23** as a yellow-orange oil (0.94 g, 92.2%) (found: $[M + H]^+$, 341.2010. $C_{24}H_{25}N_2$ requires 341.2017). δ_H(400 MHz; $CDCl_3$) 2.46 (3H, s), 3.77 (2H, s), 4.02 (2H, s), 4.69 (2H, s), 7.33–7.51 (8H, m), 7.99 (2H, d, *J* 8.0 Hz), 8.22 (2H, d, *J* 8.0 Hz), 8.39 (1H, s); δ_C(100 MHz; $CDCl_3$) 36.0, 45.0, 54.3, 56.0, 124.1, 124.8, 125.9, 126.9, 126.9, 127.1, 128.0, 128.4 and 129.0, 130.2, 131.4, 131.5, 140.0, 140.4; *m*/*z* (ES^+) 341 (100%, $[M + H]^+$).

Methyl-(3-{[(pyren-1-ylmethyl)-amino]-methyl}-benzyl)-amine (**24**). To a stirred solution of diamine **21** (0.45 g, 3.00 mmol) in methanol (50 cm^3) was added 1-pyrenecarboxaldehyde (0.69 g, 3.00 mmol). After 5 h stirring, a solution of $NaBH_4$ (0.55 g, 15.00 mmol) in methanol (20 cm^3) was added. The reaction mixture was stirred for 4 h and then concentrated under reduced pressure. Water (50 cm^3) was added carefully and the aqueous phase was extracted with DCM (3 × 50 cm^3). The combined DCM extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford the diamine **24** as a yellow oil (0.85 g, 77.8%) (found: $[M + H]^+$, 365.2008. $C_{26}H_{25}N_2$ requires 365.2017). δ_H(400 MHz; $CDCl_3$) 2.46 (3H, s), 3.76 (2H, s), 3.96 (2H, s), 4.47 (2H, s), 7.20–8.31 (13H, m); δ_C(100 MHz; $CDCl_3$) 35.9, 51.1, 53.7, 55.9, 123.1, 124.5, 124.8, 124.9, 125.7, 126.8, 126.8, 126.9, 127.2, 127.3, 127.9, 128.3, 128.9, 130.5, 130.6, 131.1, 133.6, 139.8, 140.3; *m*/*z* (ES^+) 365 (100%, $[M + H]^+$) and 334 (43, $[M - CH_3NH]^+$).

(2-Boronobenzyl)-(3-{[(2-boronobenzyl)naphthalen-2-ylmethyl-amino]-methyl}-benzyl)-methyl-amine (**6**). To a stirred solution of diamine **22** (0.58 g, 2.00 mmol) in dry acetonitrile (40 cm^3) was added 2-(2-bromomethyl-phenyl)-[1,3,2]dioxaborinane **13** (1.52 g, 6.00 mmol), followed by K_2CO_3 (1.10 g, 8.00 mmol). The reaction mixture was then stirred and heated under reflux for 5 h. After cooling, the acetonitrile was removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration, they were concentrated until dryness to afford the crude product as a dark yellow solid. Recrystallisation from chloroform/hexane afforded the boronic acid **6** as a pale yellow powder (0.95 g, 85.1%), mp 147–150 °C (decomp.). δ_H(300 MHz; $CDCl_3/CD_3OD$ 1 : 1) 2.28 (3H, s), 3.80 (2H, s), 3.83 (2H, s), 3.87 (2H, s), 3.92 (2H, s), 4.56 (2H, s), 7.06–7.81 (19H, m); δ_C(75 MHz; $CDCl_3/CD_3OD$ 1 : 1) 40.6, 57.1, 58.1, 60.6, 66.4, 124.6, 125.1, 125.2, 126.0, 126.2, 126.3, 126.7, 126.8, 126.9, 127.0, 127.3, 127.4, 128.0, 128.1, 128.4, 132.2, 136.5, 137.4; *m*/*z* (ES^+) 615 (30%, $[M - 4 \times H_2O + 4 \times CH_3OH + H]^+$) and 777 (100%, $[M - 2 \times H_2O + 2 \times HO(CH_2)_3OH + 2 \times CH_3OH + K]^+$).

(3-{[Anthracen-9-ylmethyl-(2-boronobenzyl)-amino]-methyl}-benzyl)-(2-borono benzyl)-methyl-amine (**7**). To a stirred

solution of diamine **19** (0.68 g, 2.00 mmol) in dry acetonitrile (40 cm^3) was added 2-(2-bromomethyl-phenyl)-[1,3,2]-dioxaborinane **13** (1.52 g, 6.00 mmol), followed by K_2CO_3 (1.10 g, 8.00 mmol). The reaction mixture was then stirred and heated under reflux for 5 h. After cooling, the acetonitrile was removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration, the filtrate was concentrated until dryness to afford the crude product as a dark yellow solid. Recrystallisation from chloroform/hexane afforded the boronic acid **7** as a pale yellow powder (1.11 g, 91.3%), mp 179–180 °C (decomp.). δ_H(300 MHz; $CDCl_3/CD_3OD$ 1 : 1) 2.21 (3H, s), 3.66 (2H, s), 3.68 (2H, s), 3.70 (2H, s), 3.73 (2H, s), 4.57 (2H, s), 6.99–8.38 (21H, m); *m*/*z* (ES^+) 665 (50%, $[M - 4 \times H_2O + 4 \times CH_3OH + H]^+$).

(2-Boronobenzyl)-(3-{[(2-boronobenzyl)-pyren-1-yl methyl-amino]-methyl}-benzyl)-methyl-amine (**8**). To a stirred solution of diamine **24** (0.72 g, 2.00 mmol) in dry acetonitrile (40 cm^3) was added 2-(2-bromomethyl-phenyl)-[1,3,2]dioxaborinane **13** (1.52 g, 6.00 mmol), followed by K_2CO_3 (1.10 g, 8.00 mmol). The reaction mixture was then stirred and heated under reflux for 5 h. After cooling, the acetonitrile was removed under reduced pressure and water (50 cm^3) was added. The aqueous phase was extracted with DCM (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration, the filtrate was concentrated until dryness to afford the crude product as a dark yellow solid. Recrystallisation from chloroform/hexane afforded the boronic acid **8** as a pale yellow powder (0.99 g, 78.3%), mp 173–174 °C (decomp.). δ_H(300 MHz; $CDCl_3/CD_3OD$ 1 : 1) 2.18 (3H, s), 3.69 (2H, s), 3.72 (2H, s), 3.82 (2H, s), 3.85 (2H, s), 4.30 (2H, s), 6.70–8.30 (21H, m); *m*/*z* (ES^+) 837 (90%, $[M - H_2O + 2 \times HO(CH_2)_3OH + CH_3OH + K]^+$) and 851 (100%, $[M - 2 \times H_2O + 2 \times HO(CH_2)_3OH + 2 \times CH_3OH + K]^+$).

Fluorescence measurements. The fluorescence spectra of **1** (1 × 10^{-7} mol dm^{-3}), **3** (5 × 10^{-6} mol dm^{-3}), **4** (1 × 10^{-7} mol dm^{-3}), **5** (1 × 10^{-7} mol dm^{-3}), **6** (5 × 10^{-6} mol dm^{-3}), **7** (1 × 10^{-7} mol dm^{-3}) and **8** (1 × 10^{-7} mol dm^{-3}) in a pH 8.21 buffer [0.01000 mol dm^{-3} KCl, 0.002752 mol dm^{-3} KH_2PO_4 and 0.002757 mol dm^{-3} Na_2HPO_4, in 52.1% methanol–47.9% water (w/w)][64] were recorded as increasing amounts of various saccharides (D-glucose, D-galactose, D-mannose and D-fructose) were added to the solution.

CD measurements. The CD spectra of **3** (1 × 10^{-3} mol dm^{-3}), **4** (1 × 10^{-3} mol dm^{-3}), **5** (1 × 10^{-3} mol dm^{-3}), **6** (1 × 10^{-3} mol dm^{-3}), **7** (1 × 10^{-3} mol dm^{-3}) and **8** (1 × 10^{-3} mol dm^{-3}) in a 90% methanol–10% water (v/v) were recorded in the presence of D-glucose (1 × 10^{-2} mol dm^{-3}), L-glucose (1 × 10^{-2} mol dm^{-3}), D-mannose (1 × 10^{-2} mol dm^{-3}) and D-fructose (1 × 10^{-2} mol dm^{-3}).

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