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Supplementary Material

Dye Displacement Assay for Saccharide Detection with Boronate Hydrogels

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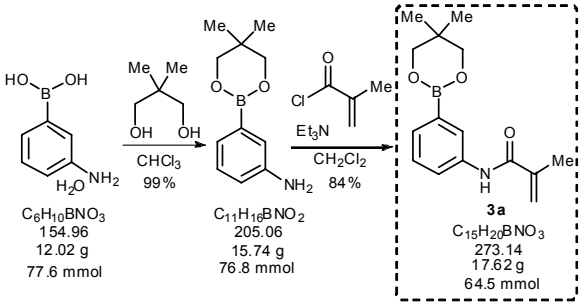
1. Synthetic Procedures:

(i). Large scale preparation of N-*(3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)methacrylamide* ***3a****: Step 1:* 2,2-Dimethylpropanediol (8.02 g , 77.0 mmol) was added to a 1 L round-bottomed flask containing 3-aminophenylboronic acid monohydrate (12.02 g, 77.6 mmol) in chloroform (500 mL). The resulting suspension was stirred for 12 h, after which time the reaction mixture was filtered and evaporated to dryness *in vacuo* yielding the intermediate 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)aniline as a white solid (15.74g, 99% yield): ^{1}H NMR (δ; 300 MHz; $CDCl_3$) 0.93 (6H, s, 2 × CH_3), 3.72 (4H, s, 2 × OCH_2), 6.71(1H, ddd, Ar C*H*), 7.12 (3H, m, Ar C*H*); ^{13}C{^{1}H} NMR (δ; 75 MHz; $CDCl_3$) 22.29 (2 × *C*H_3), 32.26 (*C*q), 72.70 (2 × O*C*H_2), 118.12 (Ar *C*H), 120.97(Ar *C*H), 124.82 (Ar *C*H), 128.99 (Ar *C*H), 145.69 (Ar *C*N), (*C*B not detected); ^{11}B{^{1}H} NMR (δ; 96 MHz; $CDCl_3$) 27.29 bs.



Step 2: The entire sample of 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)aniline (15.74 g, 76.8 mmol) was dissolved in dichloromethane (950 mL), to which triethylamine (10.7 mL, 76.8 mmol) was added. The obtained solution was stirred at 0 °C under nitrogen. A solution of methacryloyl chloride (7.5 mL, 77.2 mmol) in dichloromethane (50 mL) was added slowly over two hours. The solution was allowed to warm to room temperature and stirred for a further 30 min. The organic solution was then washed with water (3 x 100 mL), dried over magnesium sulphate, filtered and evaporated to dryness *in vacuo*. It is important to ensure that the temperature does not exceed 30 °C during any stage of the process in order to limit potential polymerisation side products. Compound **3** was thus obtained as an off white solid (17.62g, 84%). ^{1}H NMR (δ; 300 MHz; $CDCl_3$) 0.93 (6H, s, 2 × CH_3), 1.93 (3H, s, CH_3), 3.72 (4H, s, 2 × OCH_2), 5.35 (1H, m, C=C*H*H), 5.70 (1H, m, C=CH*H*), 7.25 (1H, t, Ar C*H*), 7.41(1H, dt, Ar C*H*), 7.82 (1H, ddd, Ar C*H*); ^{13}C{^{1}H} NMR (δ; 75 MHz; $CDCl_3$) 19.15 (methacryl *C*H_3), 22.28 (2 × *C*H_3), 32.29 (*C*q), 72.72 (2 × O*C*H_3), 120.06 (methacryl *C*H_2), 122.90 (Ar *C*H), 125.44 (Ar *C*H), 128.85 (Ar *C*H), 130.25 (Ar *C*H), 137.59 (methacryl *C*q), 141.35 (Ar *C*N), 166.80 (*C*=O amide) (*C*B not detected); ^{11}B{^{1}H} NMR (δ; 96 MHz; $CDCl_3$) 27.18 bs.

(ii). Synthesis of ***3b, 3c*** *and* ***3d****:* Our previously reported syntheses were used as described in *Polymer*, 2008, **49**, 3362,[1] NMR spectrums and mass spectroscopy were consistent with previous samples.

2. General Procedures:

General Procedure 1: Preparation of blank gels.[2] Freshly prepared aqueous ammonium persulphate (APS) stock solution (10%wt/vol) was kept cool (<4 °C) until required. Methylene bisacrylamide (0.1 g) and acrylamide (3.9 g) were stirred in water (10 mL). An aliquot (2 mL) of this mixture was further diluted two-fold with distilled water (2 mL). To this diluted aliquot tetramethylethylenediamine (TMEDA) (10 μL) was added along with an aliquot of APS stock solution (30 μL). The mixture was then poured into the chosen mould and allowed to set. After the mixture was set (15 to 60 min judged by visual inspection) the gels could be carefully removed (weight recorded if desired). Gels may be stored in phosphate buffer,[3, 4] in order to prevent gels drying.

General Procedure 2: Preparation of borogels. Borogels were prepared following the same procedure as the blank gels except boro-additives **3a-d** (0.1 g) were added in place of the same mass of acrylamide.

3. General Uptake and Release Experiment Protocols Employing 5 mm Gel Spheres:

i. Alizarin red-S uptake: Individual 5mm diameter gel spheres were placed in phosphate buffered ARS solution (1 mL, 2.5 x 10^{-4} M) and gently rotated (60 rpm). The solution's absorbance was recorded at defined intervals (see Fig. 3, main text). The decrease in absorbance of the ARS solution with time corresponds to amount of dye uptake.

ii. Removal of non-specifically bound ARS: After following the "uptake" procedure above, gel spheres were removed from buffered ARS solution, briefly dried on tissue paper, placed into fresh phosphate buffer solution (1 mL) and gently rotated (60 rpm). The solution's absorbance was recorded at defined intervals (see Fig. S-3, supporting information). The increase in observed absorbance is due to release of ARS dye retained within the gel from the "uptake" experiments. Both boro- and blank gels gave up the same amount of ARS in these experiments.

iii. Fructose titrations: After completion of steps i) and ii), gel spheres (both borogel and blank balls) were briefly dried on tissue paper, placed into fresh phosphate buffer solution (1 mL) and gently rotated (60 rpm), portions of solid fructose were added and the solution's absorbance recorded 30 min after each fructose addition (see Fig. 4, main text), 30 min was selected although change in absorbance after ~10 min was minimal. The increase in absorbance observed corresponds to ARS competitively displaced from boron by fructose.

4. Sphere Moulds:

Designs for the moulds were created using the computer-aided design program Rhinoceros (Version 3.0, Robert McNeel & Associates). There were two moulds. Each mould consisted of an upper part and a lower part. Both cast gel balls approximately 5 mm in diameter. The first mould cast single gel balls; the second mould cast nine gel balls. Files 5mmballmold(uppr).stl, 5mmballmold(lwr).stl, 5mmballx9(uppr).stl and 5mmballx9(lwr).stl allow part of the mould to be "printed" in three dimensions using rapid prototyping techniques. The parts contained in the .stl files may be inspected using SolidView (www.solidview.com). The parts for the moulds were made by Laser Lines Ltd., Banbury, UK from the .stl files listed above by fused deposition modelling, using a copolymer of acrylonitrile, butadiene and styrene.

The mould thus manufactured was filled with freshly prepared pre-mixed solution (general procedures) before rapidly fitting the top half (Fig. S-2). Vent holes allow excess solution to purge and be collected in reservoir on reverse, when excess gel is set (15 to 45 min) inner balls are also set.

5. Fig. S-1: UV/vis absorption spectra of gel slabs prepared with and without boronate in presence of alizarin red-S (ARS).

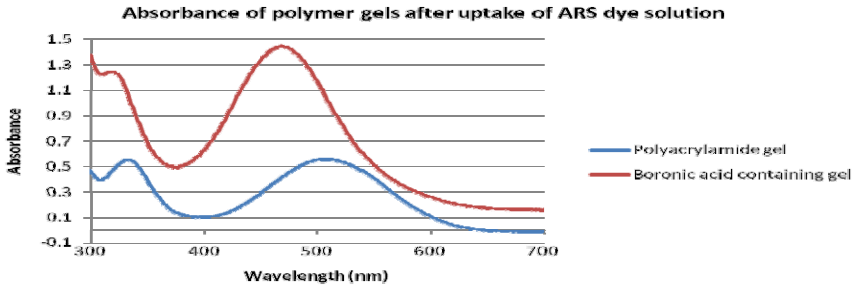


Fig. S-1

6. Fig. S-2: Schematic of mould for casting spheres. Left: Top half. Right: Bottom half. This mould prepares nine 5mm diameter spheres per casting.

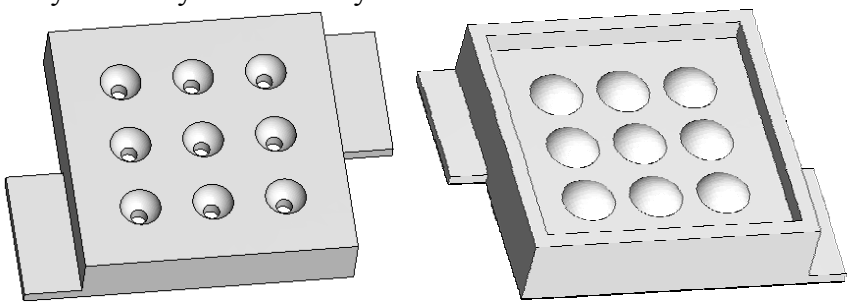


Fig. S-2

7. Fig S-3: Graph to show dye displaced from gel balls on washing in phosphate buffer. Graph depicts absorbance of supernatant solution per gram of gel, and suggests that all balls give up the same amount of non-specifically bound alizarin red-S.

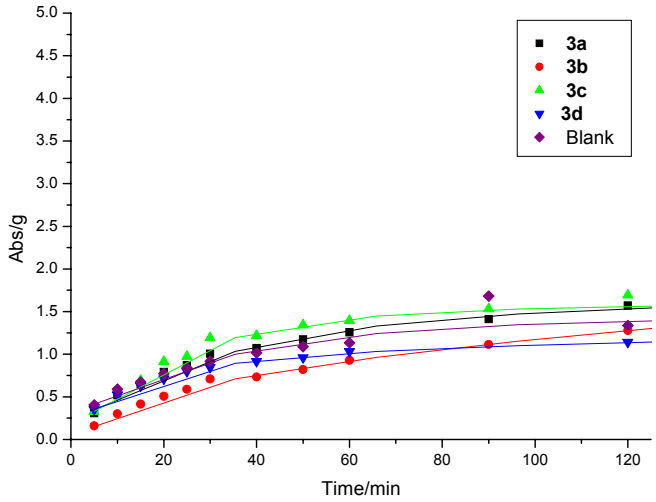


Fig. S-3

8. Table S-1: Fruit juice analysis data. A_0 = Abs of Juice solution before gel ball addition. A = Abs Juice solution 15 min after gel ball addition

Entry	Fruit Juice	Blank Mass (mg)	Blank (A_0)	Blank (A)	(i)Blank ($A-A_0$)/g	Boro gel (mg)	Boro gel (A_0)	Boro gel (A)	(ii) Boro gel ($A-A_0$)/g	Enhancement ratio (ii)/(i)
1	apple	90	0.072645	0.079192	0.072744	64	0.014814	0.055282	0.632313	8.692245
2	cranberry	89	0.016702	0.024711	0.089989	66	0.017008	0.030743	0.208106	2.312578
3	grape	81	0.086055	0.093176	0.087914	60	0.11548	0.160266	0.746433	8.490535
4	orange	80	0.380103	0.508502	1.604988	69	0.512393	0.525854	0.195087	0.12155
5	pineapple	88	0.378278	0.382133	0.043807	62	0.294369	0.36942	1.2105	27.63268
6	tomato	86	0.349569	0.357727	0.09486	63	0.291034	0.365894	1.188254	12.52634

1. F. D'Hooge, D. Rogalle, M. J. Thatcher, S. P. Perera, J. M. H. van den Elsen, A. T. A. Jenkins, T. D. James and J. S. Fossey, *Polymer*, 2008, **49**, 3362–3365.
2. N. Gao and M. A. Lehrman, *Glycobiology*, 2003, **13**, 1G-3G.
3. pH 7.4, 0.05 M, phosphate buffer was prepared as described in ref 4. The solution thus obtained had a measured pH of 7.2 and is referred to as "phosphate buffer" in the communication.
4. R. M. C. Dawson, D. C. Elliot, W. H. Elliot and K. M. Jones, *Data for Biochemical Research*, Clarendon Press, Oxford, 1986, p. 432.