

Supporting information for

Low-dimensional materials facilitate the conjugation between fluorogenic boronic acids and saccharides

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S1. Additional figures

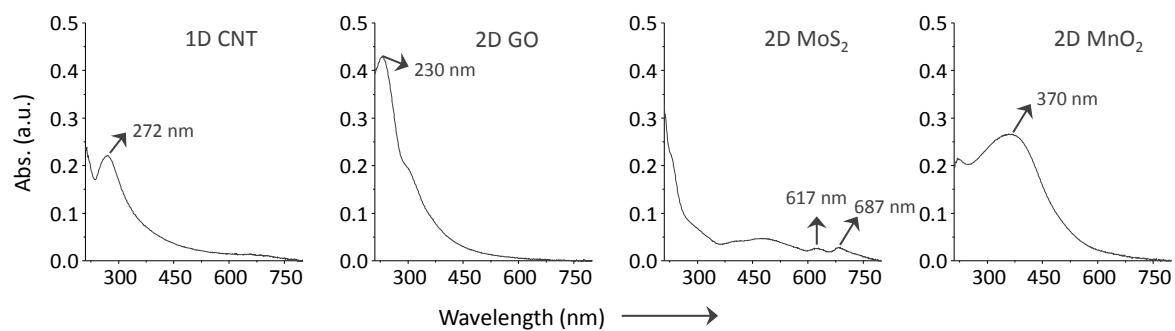


Figure S1. UV-vis spectrum of 1D carbon nanotube (CNT, $0.2 \mu\text{g mL}^{-1}$), 2D graphene oxide (GO, $0.3 \mu\text{g mL}^{-1}$), 2D molybdenum disulphide (MoS₂, $0.5 \mu\text{g mL}^{-1}$) and 2D manganese dioxide (MnO₂, $0.5 \mu\text{g mL}^{-1}$) recorded in Tris-HCl (0.01 M, pH 7.4).

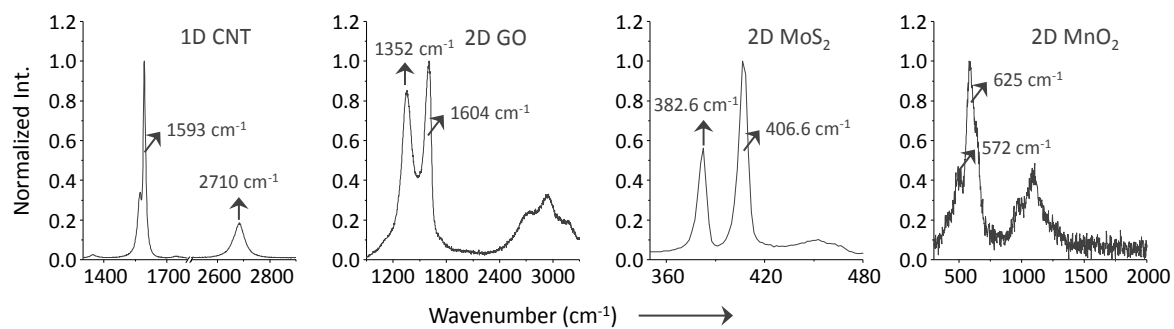


Figure S2. Raman spectrum of 1D carbon nanotube (CNT), 2D graphene oxide (GO), 2D molybdenum disulphide (MoS₂) and 2D manganese dioxide (MnO₂).

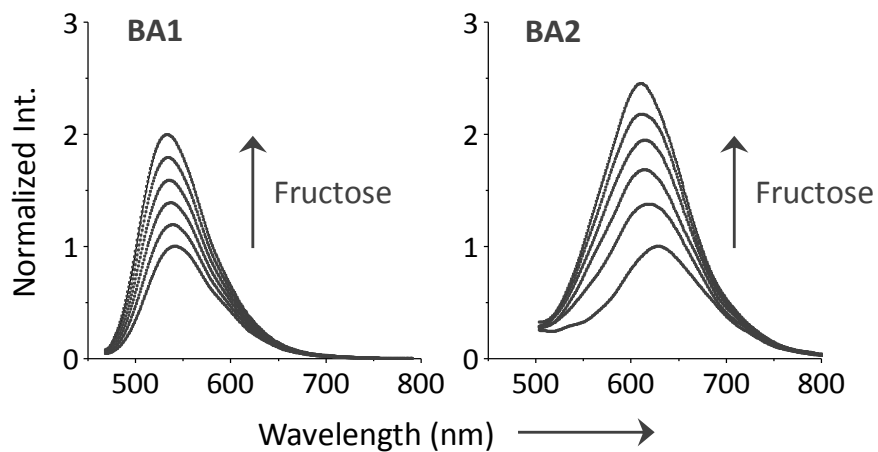


Figure S3. Fluorescence titration of **BA1** (20 μM) and **BA2** (20 μM) in the presence of increasing D-fructose (0-30 mM) in Tris-HCl (0.01 M, pH 7.4). Excitation wavelength: 450 nm and 470 nm for **BA1** and **BA2**, respectively.

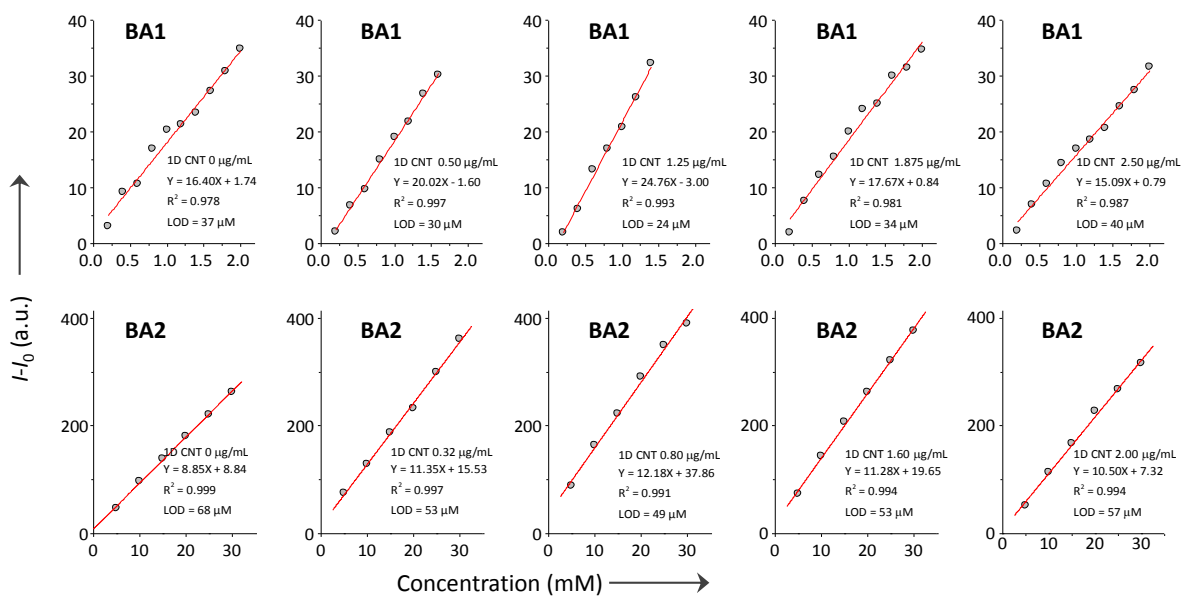


Figure S4. Plotting the fluorescence intensity change (where I and I_0 are the intensity of BA with and without D-fructose, respectively) of **BA1** and **BA2** (20 μM) in the presence of 1D CNT of different concentrations with increasing D-fructose in Tris-HCl (0.01 M, pH 7.4).

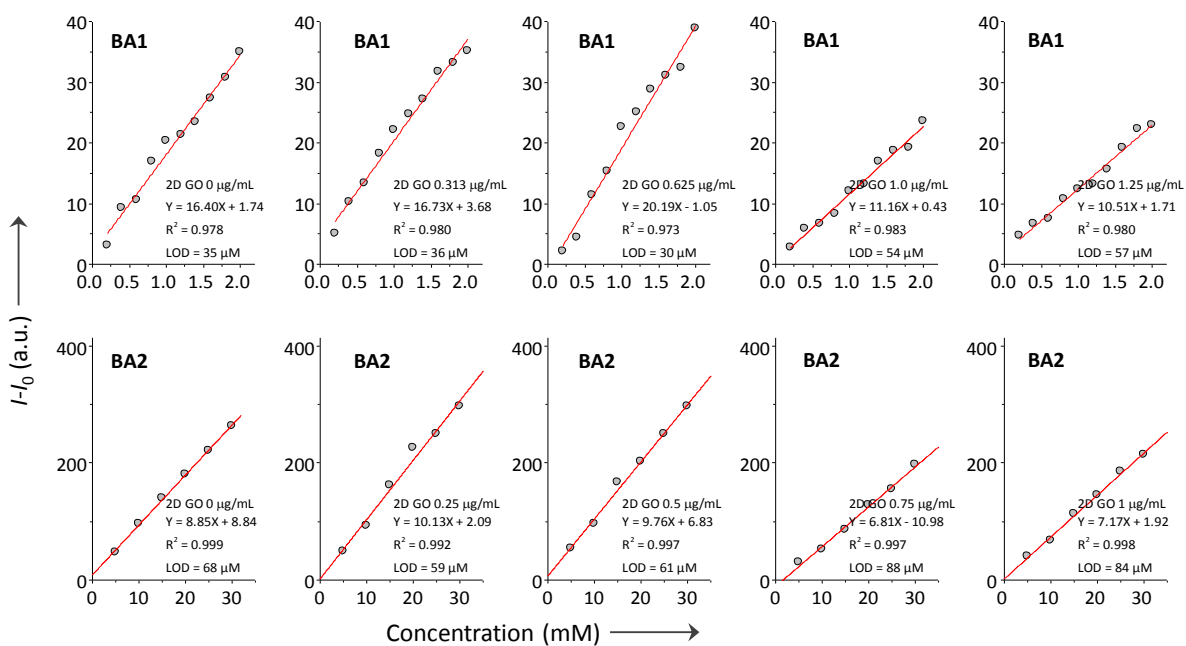


Figure S5. Plotting the fluorescence intensity change (where I and I_0 are the intensity of BA with and without D-fructose, respectively) of **BA1** and **BA2** (20 μM) in the presence of 2D GO of different concentrations with increasing D-fructose in Tris-HCl (0.01 M, pH 7.4).

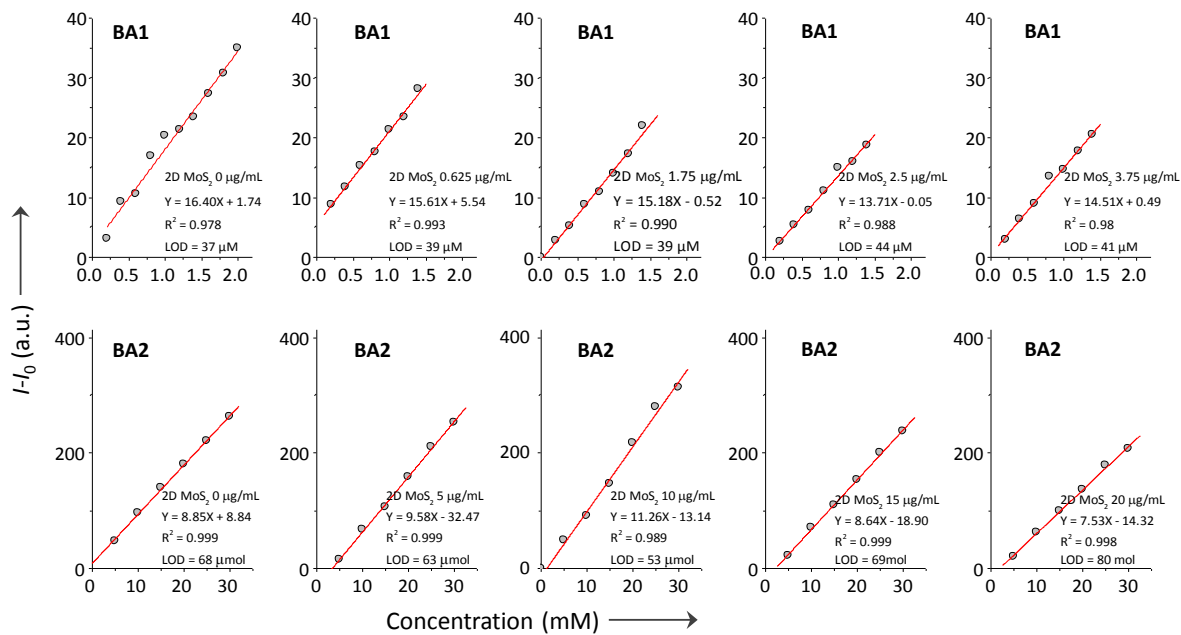


Figure S6. Plotting the fluorescence intensity change (where I and I_0 are the intensity of BA with and without D-fructose, respectively) of **BA1** and **BA2** (20 μ M) in the presence of 2D MoS₂ of different concentrations with increasing D-fructose in Tris-HCl (0.01 M, pH 7.4).

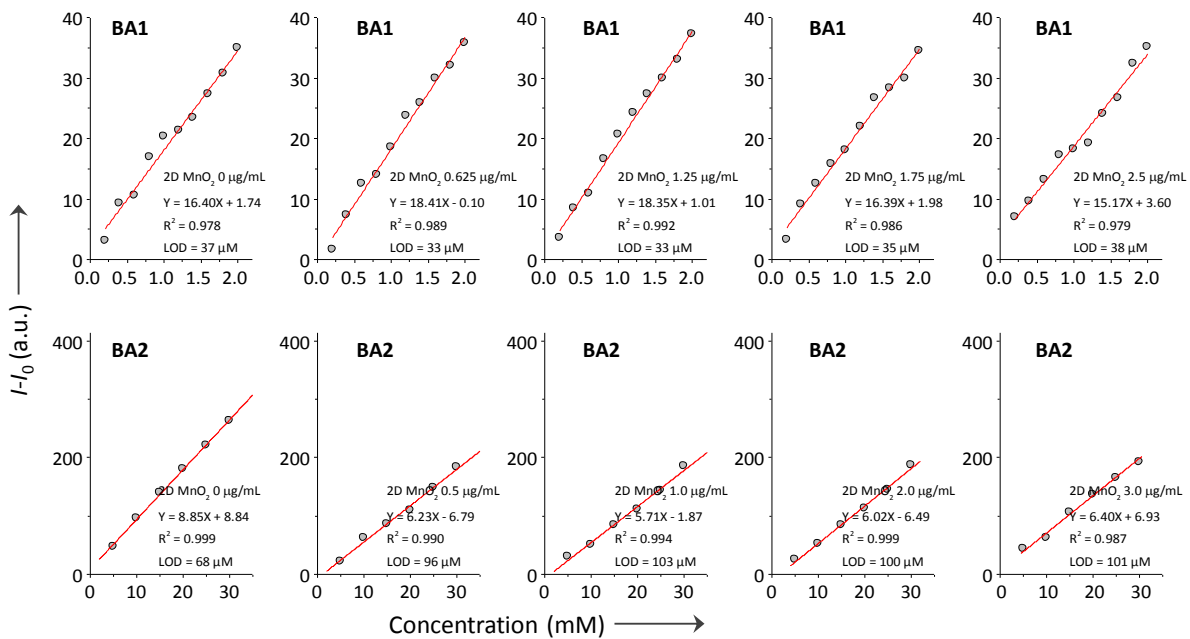
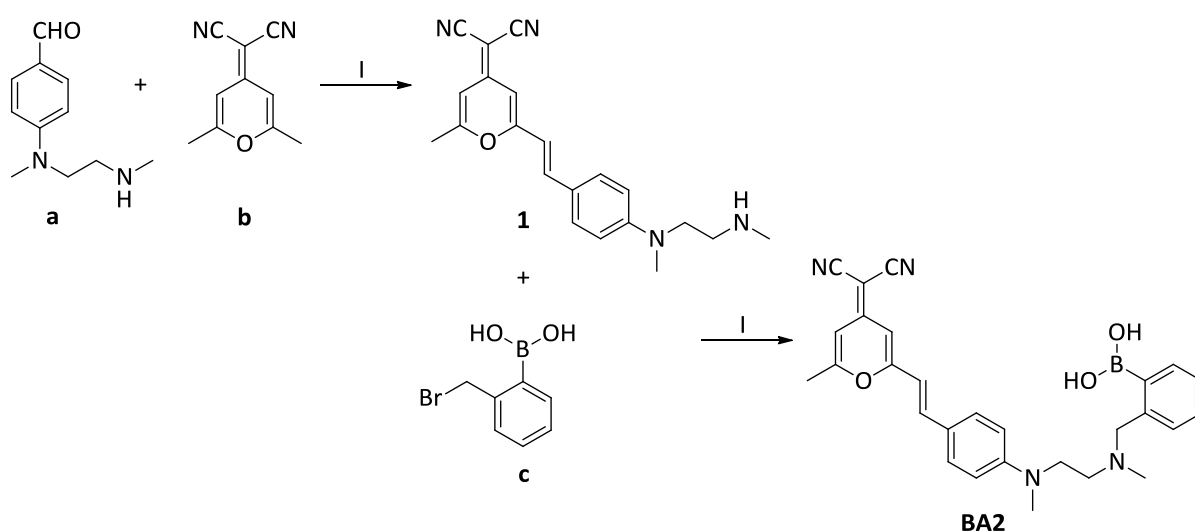


Figure S7. Plotting the fluorescence intensity change (where I and I_0 are the intensity of BA with and without D-fructose, respectively) of **BA1** and **BA2** (20 µM) in the presence of 2D MnO₂ of different concentrations with increasing D-fructose in Tris-HCl (0.01 M, pH 7.4).

S2. Experimental section

General. All chemicals used were of analytical grade or of the highest purity available. Ultrapure water were obtained from a Milli-Q integral Pure/Ultrapure Water Production unit. ^1H and ^{13}C NMR spectra were obtained with a Bruker Model AM 400 spectrometer (relative to tetramethylsilane [TMS]). High-resolution mass spectra (HRMS) were obtained using a Waters LCT Premier XE spectrometer. High performance liquid chromatography (HPLC) was carried out on an Agilent 1100 Series equipment. UV-vis spectra were obtained using a Varian Cary 500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Transmissin electron microscopy was carried out on JEOL 1400 equipped with a Gatan Orius charged-coupled device camera and Tridiem energy filter operating at 200 kV. Raman spectroscopy was carried out on a Renishaw InVia Reflex Raman system (Renishaw plc, Wotton-under-Edge, UK) employing a grating spectrometer with a Peltier-cooled charge-coupled device (CCD) detector coupled to a confocal microscope. Dynamic light scattering (DLS) was carried out with DelsaTM Nano.

Synthesis of BAs. The synthesis of **BA1** has been described previously (*ACS Appl. Mater. Interfaces*, 2014, **6**, 10078) and that of **BA2** shown below.



Scheme S1. Reagents and conditions: (I) Piperidine, Acetic acid in EtOH, 80 °C for **1**, and K_2CO_3 , KI in acetonitrile, reflux for **BA2**.

Synthesis of **1**

A solution of 4-fluoroacetophenone (5.0 g, 40 mmol), *N,N'*-dimethylethylenamine (5.0 g, 56 mmol), and K_2CO_3 (6.68 g, 0.4 mol) in dry DMF (20 mL) was refluxed under an argon atmosphere for 18 h. Then, the solvent was removed in vacuum and the resulting residue **a** (837 mg, 3.5 mmol) was dissolved in ethanol (30 mL), followed by addition of 2-(2,6-dimethyl-4H-pyran-4-ylidene)-malononitrile (**b**) (500 mg, 2.9 mmol). Then, piperidine (0.5 mL) and acetic acid (0.8 mL) were added into the mixture, and the resulting mixture was stirred for 12 h at 80

°C. After cooling down the solution to room temperature, the solvent was removed in vacuum. Then, ethyl acetate (50 mL) was added to the resulting residue and the mixture was washed with H₂O twice. The organic layer was removed in vacuum, and the residue dried over anhydrous magnesium sulfate, filtered and then evaporated to dryness. The crude product was purified by column chromatography to afford **1** as a red solid (0.42 g, two-step yield 14.3%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 6.78–6.71 (m, 3H), 6.61 (s, 1H), 3.51 (t, *J* = 6.9 Hz, 2H), 2.99 (s, 3H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.89 (s, 1H); ¹³C NMR (101 MHz, DMSO) δ 163.7, 161.1, 156.6, 150.6, 138.5, 129.9, 122.0, 120.3, 115.8, 112.7, 111.7, 105.4, 105.1, 104.1, 99.5, 54.0, 50.6, 35.5, 21.4, 19.3. HR-ESI-MS: *m/z* [M + H]⁺ calcd for C₂₁H₂₂N₄O 347.1872, found 347.1858.

Synthesis of **BA2**

To a solution of **1** in acetonitrile were added (2-bromomethylphenyl)boronic acid (**c**) (75 mg, 3.5 mmol), K₂CO₃ (100 mg) and KI (50 mg). The mixture was stirred at reflux overnight. Then, solvent was removed in vacuum and ethyl acetate (50 mL) was added to the resulting residue. The mixture was washed with H₂O twice. The organic layer was removed in vacuum and the resulting residue dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The crude product was purified by column chromatography to afford **BA2** as a red solid (132 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 6.7 Hz, 1H), 7.39–7.28 (m, 5H), 7.18 (d, *J* = 7.1 Hz, 1H), 6.59–6.52 (m, 3H), 6.49 (s, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 3.70 (s, 2H), 3.54 (s, 2H), 2.98 (s, 3H), 2.68 (s, 2H), 2.38 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 161.6, 161.3, 160.42, 156.5, 150.3, 138.5, 136.4, 131.0, 130.6, 130.3, 129.8, 127.7, 122.6, 115.6, 112.7, 111.8, 106.2, 105.5, 64.6, 57.4, 49.8, 38.7, 29.7, 20.0. HR-ESI-MS: *m/z* [M+H]⁺ calcd for C₂₈H₃₀N₄O₃B 481.2411, found 481.2415. HPLC (*t*_R 4.98 min over 15 min of 0.8 mL/min mobile phase [95% methanol and 5% water], purity 97.3%).

S3. Original spectral copies of new compounds

