

Supporting Information

Naphthalimide-based optical turn-on sensor for monosaccharide recognition using boronic acid receptor

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S1.General

The absorption of the synthesized dye and GO in PBS solution was measured using CECIL-CE9200 spectrophotometer. Fluorescence emission changes were examined by spectral Perkin-Elmer LS55 fluorescence spectrophotometer. Functional groups were evaluated using FTIR technique by SPECTRUM ONE spectrometer. ¹H NMR and ¹³C NMR spectra were measured by Bruker DRX AVANCE NMR spectrophotometer at two frequencies 500 MHz and 125 MHz, respectively in DMSO.

S2.Synthesis

The intermediate 3 was synthesized using acenaphthene according to the references mentioned [1,2,3]. Compound 4 (NO) was synthesized according to previously reported procedure [4]. 4-Bromo-1,8-naphthalic anhydride (36 mmol) was reacted with o-phenylenediamine (55 mmol) in glacial acetic acid (120 ml) for 7h under reflux and then washed with water to obtain the desired product. After recrystallization with acetic acid, needle yellow powders were obtained, yield 73%; m.p. 215-216 °C, FTIR (KBr) cm⁻¹:1691, 1390, 764.

Compound 5 (NOP): Compound 4 (10 mmol), piperazine (80 mmol), hydrated CuSO₄ (1.6 mmol) and 2-methoxyethanol (100 ml) were reacted under reflux and nitrogen gas for 7h. After raw material exhausted the resulting mixture was poured by water. Crystallized from ethanol then purified on silica gel yielded the orange needles (20%). m.p.235-236 °C, FTIR (KBr) cm⁻¹: 3431, 2346, 1676, 1362. ¹H NMR (DMSO, 500MHz) δppm: 8.7-7.44 (m,9H), 3.31 (t, j=5 ,4H), 2.46 (t, j=5 ,4H). ¹³C NMR (DMSO, 125 MHz) : 156.7, 154.9, 141.4, 138.8, 134.6, 133.5, 133.3, 131.2, 130.0, 128.2, 123.4, 123.3,123.0, 115.2, 114.1, 49.7, 42.8. Elemental analysis: Anal. Calcd. (%) for: C₂₂H₁₈N₄O: C, 87.42; H, 5.96; N, 18.54. Found (%): C, 87.48; H, 5.88; N, 18.42.

Compound 6 (NOPB): The intermediate 5 (0.47 mmol) was reacted with (2-bromo methyl phenyl) boronic acid pinacol ester (0.64 mmol) under reflux for 7h. The solvent used in this part of synthesis was a 40 ml mixed solution of THF: CH₃OH (v:v=1:1). During the reaction, 2ml of tri ethylamine was added dropwise to the reaction mixture. After tracing reaction with TLC, the extra solvent

was removed from the system under reduced pressure and the resulting product was purified on silica gel using [5:1 CH₂Cl₂: CH₃OH] to obtain orange powders (0.064g, 25%). FTIR (KBr) cm⁻¹: 3430, 2326, 1656, 1335, 1094. ¹H NMR (DMSO, 500MHz) δppm: 8.45(d, j=25, 1H), 8.36(d, j= 25, 1H), 8.3(d, j=25, 1H), 7.26-8.25 (m, 10H), 3.83 (s ,2H), 3.4 (t, j=5 ,4H), 2.5 (t, j=5,4H). ¹³C NMR (DMSO, 125 MHz) δppm: 157.2, 155.5, 146.5, 135.3, 134.3, 134.1, 133.9, 133.3, 133.1, 132, 131.9, 127.2, 126.6, 126.1, 125.7, 125.1, 122.8, 122, 116, 115.7, 115.5, 62.2, 53.7, 51.6. Elemental analysis: Anal. Calcd. (%) for: C₂₉H₂₅N₄O₃B: C, 71.46; H, 5.13; N, 11.5. Found (%): C, 71.44; H, 5.15; N, 11.7.

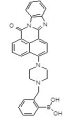

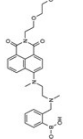


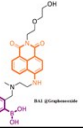
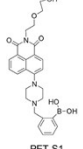
S3. Additional Tables

Table S3-1 The association constants (K_{as}) between NOPB and NOPB-GO with fructose and their detection limits (LOD), quantum yield in the absence and presence of fructose

Probe	K _{as} (M ⁻¹)	LOD (mM)	ϕ _{fa}	FE
NOPB-Fructose	94.33	0.040	0.157	3
NOPB Blank	-	-	0.052	-
NOPB-GO-Fructose	196.07	0.023	0.009	15
NOPB-GO	-	-	0.0006	-

^a Fluorescein (ϕ =0.95 in ethanol) was used as the reference, [NOPB] =5×10⁻⁵ M, ,[NOPB-GO]= 5×10⁻⁵ M with 40 µg/mL GO , [Fructose] = 100 mM, 50 mM PBS, pH 7.4.^b Fluorescent enhancement (FE) is the ratio of quantum yield with sugar and that without sugar.

Table S3-2 Naphthalimide fluorescence probes for fructose detection

Structure	Stock Shift (nm)	Mechanism of detection	pH	Association constant ($K_a(M^{-1})$)	Linear range (mM)	ΔI_f	LOD(mM)	year	Ref.
	50	Flourescence enhancement	7.4	94.33	0.13-50	6.5	0.040	2019	Present study
	50	Flourescence enhancement	7.5	196.07	0.07-30	35	0.023	2019	Present study
	120	Flourescence enhancement	7.5	170	1-20	2	0.1mM	2006	[5]
	77	Flourescence enhancement	7.4	57	N R	2.5	2-2.3 M	2007	[6]
	77	Flourescence enhancement	7.4	28	N R	2.5	-	2008	[7]
	85	Flourescence enhancement	9	-N R	0-50mM	2.8	2.7	2014	[8]
	130	Flourescence enhancement	7.4	75.8	0-2000	50	0.045	2015	[9]

NR=no report

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