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Supporting Information for:

Fluorescent chemosensors of carbohydrate triols exhibiting TICT emissions

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I. DFT calculations

Molecular orbital plots and energies were calculated from DFT-optimized geometries using B3LYP/6-31G* and Spartan 10.

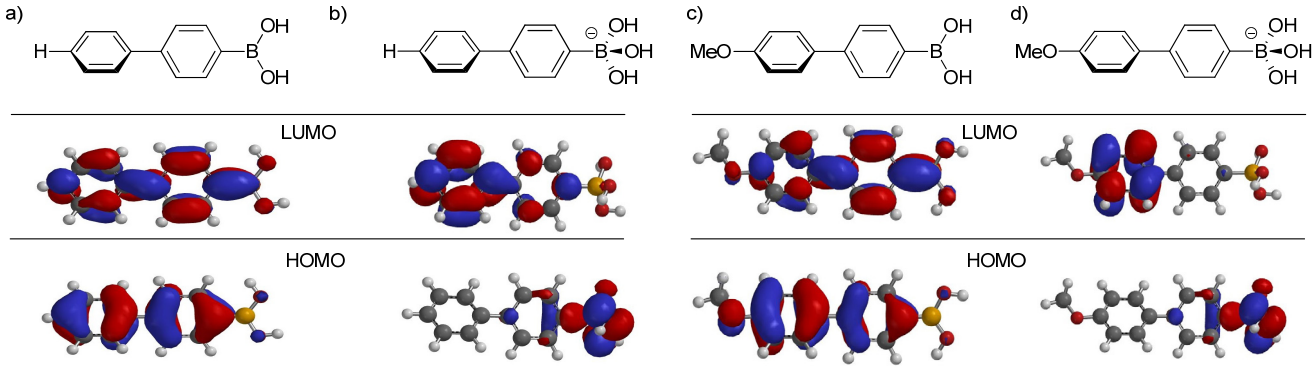


Figure S1: Structures and molecular orbitals of BBA (a) and its hydroxide complex (b), and MBBA (c) and its hydroxide complex (d) as calculated from DFT-optimized geometries using B3LYP/6-31G* in vacuum.

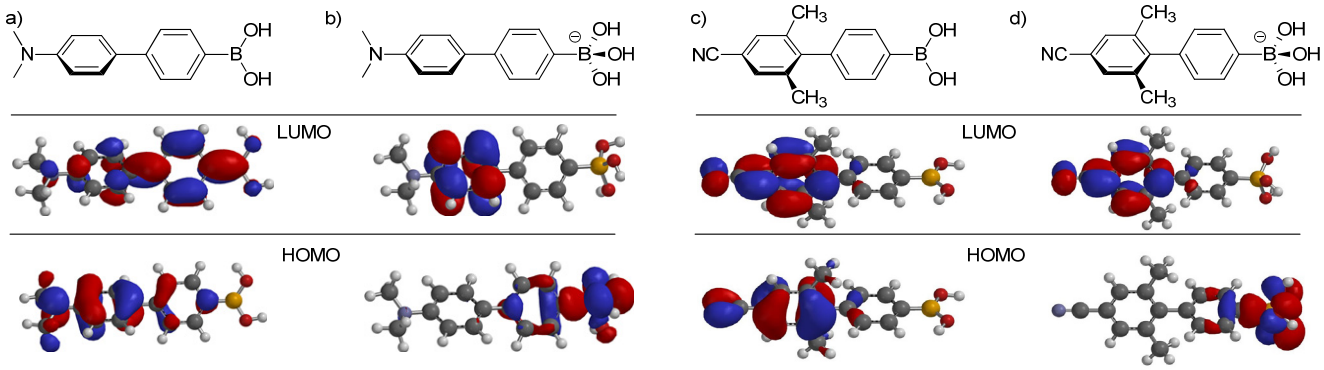


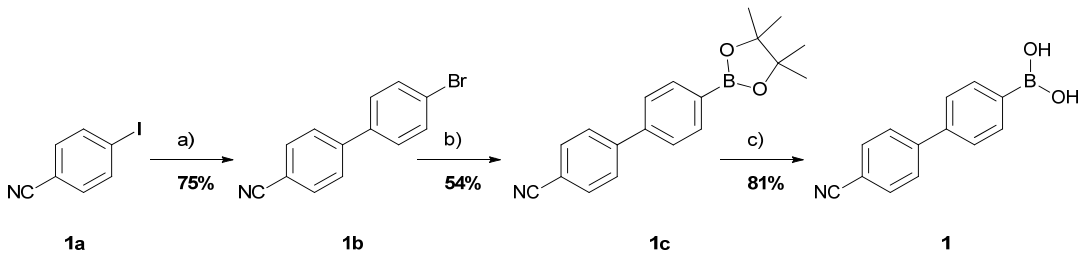
Figure S2: Structures and molecular orbitals of DBBA (a) and its hydroxide complex (b), and DM-CBBP (c) and its hydroxide complex (d) as calculated from DFT-optimized geometries using B3LYP/6-31G* in vacuum.

Table S1: DFT-calculated orbital energies (eV)

	Neutral	**Neutral**	**Neutral**	**Hydroxide complex**	**Hydroxide complex**	**Hydroxide complex**
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
CBBA (**1**)	-6.58	-1.84	4.74	-2.00	1.06	3.06
BBA (**2**)	-6.11	-1.05	5.06	-1.66	2.34	4.00
MBBA (**3**)	-5.63	-0.90	4.73	-1.62	2.45	4.07
DBBA (**4**)	-4.98	-0.73	4.25	-1.56	2.64	4.20
DM-DBBA (**5**)	-6.89	-1.29	5.60	-1.89	1.13	3.02

II. Synthesis and characterization of 4-4'-disubstituted biphenyl boronic acids

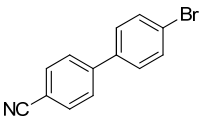
General synthetic methods and reagents. 4-Biphenylboronic acid (**2**) was obtained from *Sigma Aldrich*. 4-Bromo-3,5-dimethyl-benzonitrile was purchased from *Carbosynth*. 1,2,5-Pentanetriol and 1,2,6-hexanetrol were purchased from *TCI Chemicals.* All other reagents were purchased in the highest available grades from *Sigma Aldrich*. All non-aqueous reactions were conducted under argon using anhydrous solvents. Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F_{254}. ^{1}H-NMR spectra were recorded on a Bruker AV-300 (300MHz), AV-400 (400 MHz) or AV-500 (500 MHz) spectrometer. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents using as internal standards: $CDCl_3$ (*s*, δ = 7.27 ppm), DMSO (quint, δ = 2.50 ppm), THF (*s*, δ = 3.58 ppm). ^{13}C-NMR spectra were recorded on a Bruker AV-300 (75MHz) or AV-400 (100 MHz) spectrometer. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{13}C signals of the solvents using as internal standards: $CDCl_3$ (*s*, δC = 77.00 ppm), DMSO (*quint*, δC = 39.51 ppm). Multiplicities are abbreviated as follows: singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), doublet-doublet (*dd*), quintet (*quint*), septet (*sept*), multiplet (*m*), and broad (*br*). Mass spectrometry (MS): Hewlett Packard 5971; electron ionisation MS (EI-MS); Esquire-LC_00028; electrospray ionization MS (ESI-MS); high-resolution electrospray mass spectra (HR-ESI MS): Burker maXis HD. Absorbance and emission spectra were collected using a *Molecular Devices Spectra Max M5* instrument. Infrared spectra (IR): *Brechbühler JASCO;* FT/IR-4100 Fourier Transform Infrared Spectrometer, 1/λ in cm^{-1}. pH: *Thermo Orion310*.



1a **1b** **1c** **1**

Scheme S1: Synthesis of 4'-Cyanobiphenyl-4-yl-boronic acid (CBBA, 1) from 4-iodobenzonitrile (1a) in three steps with an overall yield of 33%. *a*) 4-Bromophenylboronic acid, $Pd(PPh_3)_4$, 2M aq. Na_2CO_3, MeOH, Toluene (1:1:4), N_2, 80 °C, 22h; *b*) bis(pinacolato)diboron, $Pd(dppf)Cl_2$, KOAc, DMF, N_2, 80 °C, 2.5h; *c*) $NaIO_4$, NH_4OAc, H_2O, Acetone, N_2, 23 °C, 48h.

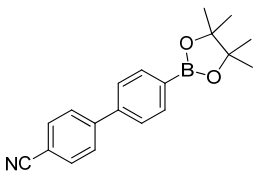
4-Bromobiphenylcarbonitrile (**1b**).[1]



4-Bromophenylboronic acid (**1a**) (2.00 g, 9.96 mmol) was dissolved in degassed MeOH (10 mL). 4-Iodobenzonitrile (1 eq, 2.28 g, 9.96 mmol) and $Pd(PPh_3)_4$ (145 mg, 0.13 mmol, 1.25 %) were dissolved in degassed toluene (40 mL). The two solutions were combined and aq. Na_2CO_3 (2M, 10 mL) was added. The solution was stirred at 80 °C for 22 h under argon. The reaction was cooled to 23 °C and the solvent were removed. The crude solid was dissolved in EtOAc (120 mL) and extracted with aq. Na_2CO_3 (2M, 50 mL) containing aq. NH_3 (25 %, 10 mL). The water phase was extracted with EtOAc (2 x 120 mL). The organic phases were combined and dried over $MgSO_4$. The solvent was removed under vacuum

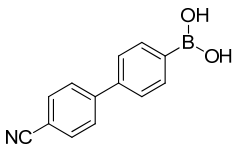
and the crude product purified by silica gel column chromatography using Hex:EtOAc (8.5:1.5) to give **1b** (1.94 g, 7.55 mmol, 76%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67-7.72 (*m*, 2H), 7.69-7.60 (*m*, 4H), 7.49-7.44 (*m*, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 138.0, 132.7, 132.3, 128.8, 127.5, 123.2, 118.7, 111.3; EI-MS (positive mode): *m/z*: $[M]^{\bullet+}$ calc. for $C_{13}H_8BrN^{\bullet+}$: 257.0; found: 256.9; IR: 2363*w*, 2357*w*, 2225*m*, 2157*w*, 1606*m*, 1482*m*, 1387*m*, 1070*m*, 1003*m*, 854*m*, 815*s*, 734*w*, 565*m*, 522*m*, 510*w*, 495*w*, 431*w*, 406*s*.

2-(4'-Cyano-4-biphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1c**).[2,3]

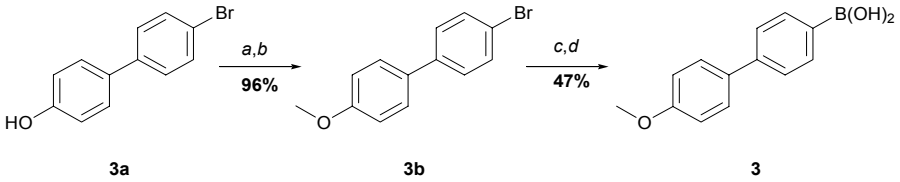


1b (1.60 g, 6.20 mmol), bis(pinacolato)diboron (1.1 eq, 1.73 g, 6.81 mmol) and potassium acetate (1.52 g, 15.5 mmol) were dissolved in anhydrous, degassed DMF (28 mL). Pd(dppf)Cl_2·DCM (308 mg, 0.38 mmol, 6 %) was added and the reaction was stirred at 80 °C for 2.5 h under argon. The solvent was removed under vacuum. Purification by silica gel column chromatography using Hex:EtOAc (8.5:1.5) followed by recrystallization from acetone (14 mL) gave **1c** (1.01 g, 3.32 mmol, 54%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (*d*, *J* = 8.2, 2H), 7.73 (*m*, 4H), 7.61 (*d*, *J* = 8.2, 2H), 1.38 (*s*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 141.7, 135.5, 132.6, 127.8, 126.5, 118.9, 111.2, 84.0, 24.9; ESI-MS (positive mode): *m/z*: $[M + Na]^+$: calc. for $C_{19}H_{20}BNNaO_2^+$: 328.2; found: 328.1; IR: 2981*m*, 2931*w*, 2870*m*, 2359*s*, 2341*m*, 2228*w*, 1607*w*, 1394*s*,1361*s*, 1330*m*, 1307*w*, 1278*w*, 1213*w*, 1143*s*, 1093*s*, 1021*w*, 964*w*, 858*m*, 819*s*, 808*w*, 669*w*, 656*m*, 568*w*, 529*w*, 522*w*, 504*w*, 480*w*, 468*w*, 452*w*, 417*m*.

4'-Cyanobiphenyl-4-yl-boronic acid (**1**).[3]

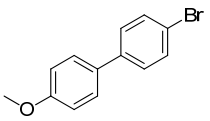


1c (700 mg, 2.29 mmol) was dissolved in acetone (23.5 mL). $NaIO_4$ (3.0 eq, 1.49 g, 6.95 mmol) and ammonium acetate (2.2 eq, 0.40 g, 5.14 mmol) were suspended in H_2O (23.5 mL) and slowly added. The reaction was stirred at 23 °C for 48 h. Acetone was removed under reduced pressure. Aqueous NaOH (2M, 23 mL, and 1 M, 100 mL) was added and extracted with DCM (120 mL). The organic phase was discharged. The aqueous phase was acidified to pH = 4 with concentrated, aq. HCl and chilled on an ice bath for 2 h. Filtration afforded **1** (414 mg, 1.86 mmol, 81%) as a colorless solid. ^{1}H NMR (400 MHz, THF-d_8): δ = 7.90 (*d*, *J* = 7.7, 2H), 7.80 (*m*, 4H), 7.56 (*d*, *J* = 7.7, 2H), 7.23 (*s*, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6, 139.6, 134.9, 132.8, 127.6, 126.0, 118.8, 110.1; ESI-MS (positive mode): *m/z*: $[M + Na]^+$ calc. for $C_{13}H_{10}BNNaO_2^+$: 246.1; found: 245.9; IR: 3408*brm*, 2238*m*, 1603*m*, 1394*s*, 1368*s*, 1334*s*, 1306*m*, 1167*w*, 1116*m*, 1094*w*, 1059*w*, 1005*m*, 822*s*, 751*m*, 724*m*, 707*w*, 662*w*, 652*m*, 641*m*, 631*w*, 611*w*, 565*m*, 520*m*, 489*w*, 423*w*.



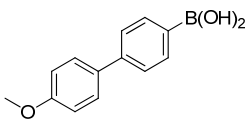
Scheme S2: Synthesis of 4'-Methoxy-4-yl-boronic acid (MBBA, 3) from 4-Bromo-4'-hydroxybiphenyl (3a) in two steps with an overall yield of 45%. *a*) NaH, DMF, N_2, 5 to 50 °C, 2h, *b*) MeI, N_2, 30 °C, 1h, *c*) *n*-BuLi, THF, N_2, -78 °C, 2h, 2) $B(O^iPr)_3$, N_2, -78 to 66 °C, 17h, *d*) HCl (10%), N_2, 23 °C, 2h.

4-Bromo-4'-methoxybiphenyl (**3b**).[4,8]



4-Bromo-4'-hydroxybiphenyl (**3a**) (4.88 g, 19.6mmol) was dissolved in dry DMF (100 mL). The solution was cooled to 5 °C in an ice bath. NaH (60% dispersion in mineral oil, 1.2 eq, 0.94 g, 22.7 mmol) was added. The reaction was allowed to warm to 23 °C and stirred for 1 h. The reaction was then heated to 50 °C and stirred for another hour, and cooled to 30 °C. MeI (1.3 eq, 1.60 mL, 3.63 g, 25.6 mmol) was added dropwise and the reaction was stirred for 1 h at 30 °C. The reaction was cooled to 23 °C and poured into ice water (150 mL). Colorless crystals were formed. After 30 minutes, the crystals were filtered off and washed with ice water (50 mL) and cold hexane (40 mL). The product was dried on high vacuum to afford **3b** (4.96 g, 18.9 mmol, 96 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (*d*, *J* = 8.7, 2H) 7.5 (*d*, *J* = 8.9, 2H), 7.42 (*d*, *J* = 8.7, 2H), 6.99 (*d*, *J* = 8.9, 2H), 3.86 (*s*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 139.8, 132.5, 131.8, 128.3, 128.0, 120.8, 114.3, 55.4; EI-MS (positive mode): *m/z*: $[M]^{\bullet+}$ calc. for $C_{13}H_{11}BrO^{\bullet+}$: 262.0, found: 262.0; IR: 2360*s*, 2348*w*, 2341*m*, 1605*w*, 1524*w*, 1483*m*, 1392*w*, 1366*w*, 1289*m*, 1255*m*, 1201*w*, 1180*w*, 1132*w*, 1038*m*, 810*s*, 493*w*, 480*m*, 471*m*, 459*m*, 445*w*, 426*w*.

4'-Methoxybiphenyl-4-yl)boronic acid (**3**).[4,5]



3b (5.40 g, 20.5 mmol) was dissolved in dry THF (205 mL) and cooled down to -78 °C. *n*-BuLi (1,6 eq, 2.5 M, 13.18 mL, 32.9 mmol) was slowly added and stirred for 2 h. Triisopropyl borate (2.8 eq, 13.3 mL, 10.8 g, 57.6 mmol) was slowly added. The reaction was allowed to warm up to 23 °C and then heated to 66 °C for 17 h. The reaction was then cooled to 23 °C. Aqueous HCl (10 %, 136 mL) was added and stirred for 2 h. The reaction was extracted with DCM (200 mL, 150 mL, 100 mL). The organic phases were combined and dried over $MgSO_4$ and the solvents were removed by rotavap. Recrystallization from chloroform (30 mL) gave **3** (2.22 g, 9.73 mmol, 47%) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (*s*, 2H), 7.85 (*d*, *J* = 8.0, 2H), 7.63 (*d*, *J* = 5.0, 2H) 7.59 (*d*, *J* = 8.2, 2H), 7.02 (*d*, *J* = 4.9, 2H), 3.79 (*s*, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 142.1, 135.4, 133.0 128.5, 125.9, 115.1, 55.8; ESI-MS (positive mode): *m/z*: $[M + Na]^+$ calc. for $C_{15}H_{13}BNaO_3^+$: 251.1, found: 251.1; IR: 3378*brm*, 2360*s*, 2340*m*, 1605*m*, 1531*m*, 1394*s*, 1339*s*, 1316*m*, 1285*s*, 1256*m*, 1210*w*, 1183*m*, 1154*w*, 1123*w*, 1092*w*, 1036*m*, 1022*w*, 1012*w*, 993*m*, 816*s*, 767*w*, 743*w*, 668*w*, 655*m*, 647*m*, 635*m*, 619*m*, 492*m*, 446*m*, 439*w*, 427*m*, 410*m*.

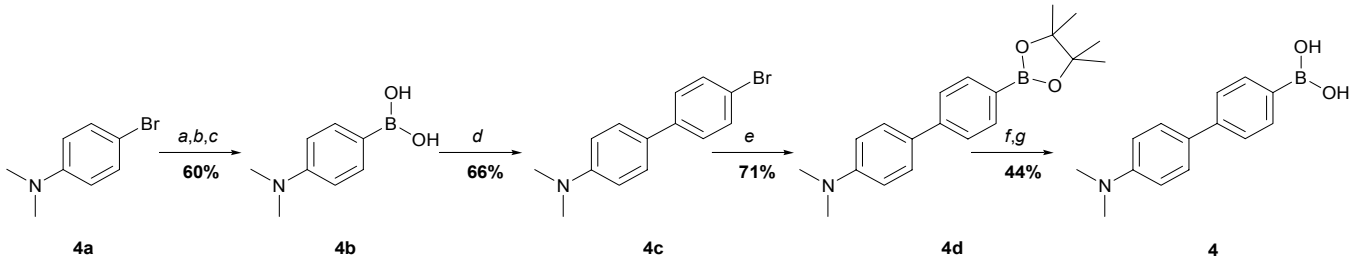
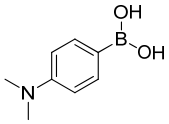


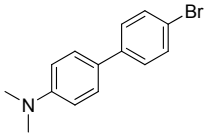
Figure S3: Synthesis of 4'-*N*,*N*-dimethylamine-biphenyl-4-yl-boronic acid (DBBA, 4) from 4-bromo-*N*,*N*-dimethylaniline (4a) in four steps with an overall yield of 12%. *a*) *n*-BuLi, THF, N_2, -78 °C, 1.5h, *b*) $B(OMe)_3$, N_2, -78 to 23 °C, 2h, *c*) NH_4Cl, N_2, 23 °C, 1.5h, *d*) 1-Bromo-4-iodobenzene, $Pd(PPh_3)_4$, Na_2CO_3, THF:H_2O (3.2:2), N_2, 60°C, 17h, *e*) bis(pinacolato)diboron, $Pd(PPh_3)_4$, KOAc, DMF, N_2, 80 °C, 17h; *f*) KHF_2, MeOH:H_2O (1:1), N_2, 23 °C, 1h, *g*) TMS-Cl, H_2O, CH_3CN, N_2, 23 °C, 15h.

4-(*N*,*N*-Dimethylamino)phenylboronic acid (**4b**).[6]



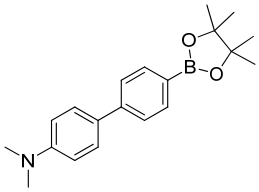
4-Bromo-*N*,*N*-dimethylaniline (**4a**) (3.50 g, 17.5 mmol) was dissolved in dry THF (70 mL) and cooled down to -78 °C. *n*-BuLi (1.1eq, 2.5M in hexane, 7.7 mL, 19.3 mmol) was slowly added over 5 minutes. The mixture was stirred for 1.5 h at -78 °C. $B(OMe)_3$ (2.3 eq, 4.55 mL, 40.8 mmol) was slowly added to the mixture. The reaction was stirred for another 40 min at -78 °C, and for 1.5 h at 23 °C. After quenching with saturated aq. NH_4Cl (70 mL), the reaction was stirred for another 1.5 h at 23 °C. The organic phase was collected and the water phase was extracted with DCM (4 x 140 mL). The combined organic phases were dried over $MgSO_4$ and solvents removed by rotavap. The crude was washed with a mixture of Hex:EtOAc (1:1) to deliver **4a** (1.75 g, 10.59 mmol, 60 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =8.11 (*d*, *J* = 8.7, 2H), 6.80 (*d*, *J* = 8.9, 2H), 3.07 (*s*, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 137.0, 111.1, 40.1; ESI-MS (positive mode):*m/z*: $[M + H]^+$ calc. for $C_9H_{13}BNO_2^+$: 166.1; found: 166.1; IR: 3208*brm*, 2363*m*, 2338*w*, 1605*s*, 1447*m*, 1424*m*, 1411*m*, 1339*s*, 1311*s*, 1227*w*, 1189*s*, 1167*m*, 1125*w*, 1086*w*, 945*w*, 816*w*, 746*w*, 687*w*, 676*w*, 513*w*, 504*w*, 486*w*, 441*w*, 419*m*;

4'-Bromo-*N*,*N*-dimethyl-[1,1'-biphenyl]-4-amine (**4c**).



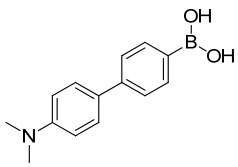
4-Iodo-1-bromobenzene (2.33 g, 8.23 mmol), **4b** (0.9 eq, 1.50 g, 9.14 mmol), Na_2CO_3 (3.12 g, 29.4 mmol), $Pd(PPh_3)_4$ (285 mg, 0.24 mmol, 3.0 %) were dissolved in a mixute of THF (49 mL) and H_2O (30 mL). The solution was degassed by bubbling argon through it for 1.5 h. The reaction was stirred at 60 °C for 17 h under argon, and cooled to 23 °C. The mixture was poured into DCM (220 mL) and extracted with H_2O (2 x 220 mL) and saturated aq. NaCl (150 mL). The organic phase was dried over Na_2SO_4 and the solvent was removed by rotavap. Purification by silica gel column chromatography using using Hex:EtOAc (19:1) gave **4c** (1.50 g, 5.4 mmol, 66 %) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (*dt*, *J* = 8.8, 2.1, 2H), 7.47 (*dt*, *J* = 9.0, 2.3, 2H), 7.42 (*dt*, *J* = 8.7, 2.4, 2H), 6.80 (*dt*, *J* = 8.9, 2.1, 2H), 3.01 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 140.1, 131.7, 127.8, 127.5, 119.9, 112.7, 40.5; ESI-MS (positive mode): *m/z*: $[M + H]^+$ calc. for $C_{14}H_{15}BrN^+$: 276.0; found: 276.0; IR: 2925*w*, 2885*w*, 2851*w*, 2806*w*, 2360*w*, 2337*w*, 1609*m*, 1528*w*, 1486*m*, 1444*w*, 1390*w*, 1355*m*, 1282*w*, 1221*m*, 1171*w*, 1077*w*, 1062*w*, 1004*w*, 804*s*, 499*w*;

2-(4'-*N*,*N*-Dimethylamine-4-biphenyl-4-yl)4,4,5,5-tetramethyl-1.3,2-dixoaborolane (**4d**)



4d (390 mg, 1.41 mmol), bis(pinacolato)diboron (1.1 eq, 394 mg, 1.55 mmol), and potassium acetate (345 mg, 3.52 mmol) were dissolved in anhydrous, degassed DMF (6.5 mL). Pd(dppf)Cl_2·DCM (69 mg, 0.08 mmol, 6 %) was added and the reaction was stirred at 80 °C for 17 h under argon. The solvent was removed under vacuum and the residue purified by silica gel column chromatography using Hex:EtOAc (19:1 to 15:1) to give **4d** (323 mg, 1.00 mmol, 71 %) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (*d*, *J* = 8.2, 2H), 7.59 (*d*, *J* = 8.2, 2H), 7.56 (*d*, *J* = 8.8, 2H), 6.82 (*d*, *J* = 7.9, 2H), 3.01 (*s*, 6H), 1.37 (*s*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 143.9, 135.2, 127.8, 125.4, 112.7, 83.7, 40.5, 24.9; ESI-MS (positive mode): *m/z*: $[M + H]^+$ calc. for $C_{20}H_{27}BNO_2^+$: 324.2; found: 324.2; IR: 2981*w*, 2925*w*, 2362*w*, 2355*w*, 1604*s*, 1537*m*, 1396*m*, 1361*s*, 1319*m*, 1287*w*, 1270*w*, 1209*m*, 1167*w*, 1141*s*, 1093*s*, 1016*w*, 962*w*, 945*w*, 858*m*, 814*s*, 746*w*, 718*w*;

4'-*N*,*N*-dimethylamine-biphenyl-4-yl-boronic acid (**4**)



4d (147 mg, 0.45 mmol) was dissolved in THF (4.1 mL). KHF_2 (12.1 eq, 426 mg, 5.45 mmol) dissolved in H_2O (1.4 mL) was added dropwise. The resulting suspension was stirred for 1 h. The reaction was concentrated by evaporation of the THF. The colorless solid was filtered off and washed in sequential order with cold H_2O (8 mL), cold acetone (3 mL) and cold diethylether (20 mL), and dried on high vacuum. The resulting solid (73 mg) was dissolved in acetonitrile (2.9 mL). Trimethylsilyl chloride (78 mg, 0.72 mmol) and H_2O (13 µl, 0.72 mmol) were added and stirred for 15 h. EtOAc (15 mL) were added and extracted with H_2O (3 x 30 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum to afford **4** (48 mg, 0.20 mmol, 44 %) as a colorless solid. ^{1}H NMR (400 MHz, THF-d_8): δ = 7.79 (*d*, *J*= 8.3, 2H), 7.53-7.50 (*m*, 4H), 7.03 (*s*, 2H), 6.76 (*d*, *J* = 8.9, 2H), 2.96 (*s*, 6H); ^{13}C NMR (100 MHz, THF-d_8): 151.3, 143.7, 135.5, 130.0, 128.2, 125.7, 113.6, 40.7; ESI-MS (positive mode): *m/z*: $[M + H]^+$ calc. for $C_{14}H_{17}BNO_2^+$: 242.1; found: 242.1 IR: 3421*brw*, 2360*s*, 2341*s*, 1604*m*, 1541*w*, 1416*w*, 1400*m*, 1362*m*, 1341*m*, 1326*m*, 1225*w*, 1138*m*, 1055*w*, 812*m*, 759*m*, 744*m*, 719*w*;

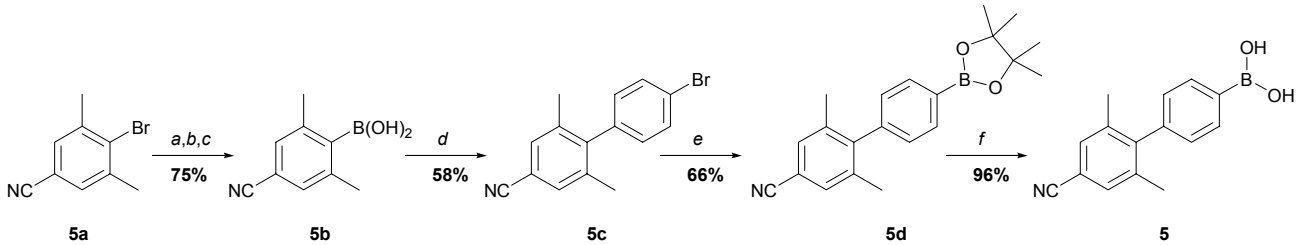
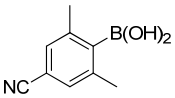


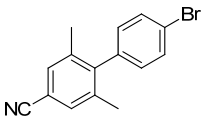
Figure S4: Synthesis of 4'-cyano-2',5'-dimethyl-biphenyl-4-yl-boronic acid (5) from 4-bromo-3,5-dimethylbenzonitrile (5a) in four steps with an overall yield of 28%. *a*) *n*-BuLi, THF, N_2, -100 °C, 2h, *b*) $B(OMe)_3$, N_2, -100 to 23 °C, 12h, *c*) HCl (15%), N_2, 23 °C, 1h, *d*) 1-bromo-4-iodobenzene, $Pd(PPh_3)_4$, $Ba(OH)_2$, dioxane:H_2O (3:1), N_2, 100°C, 3h, *e*) bis(pinacolatodiboron), $Pd(PPh_3)_4$, KOAc, DMF, N_2, 80 °C, 1h; *f*) $NaIO_4$, NH_4OAc, H_2O, Acetone, N_2, 23 °C, 72h.

2,5-Dimethyl-4-cyanophenylboronic acid (**5b**)



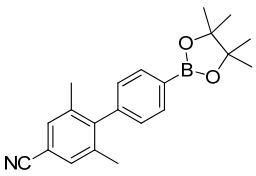
4-Bromo-3,5-dimethylbenzonitrile (**5a**) (1.40 g, 6.66 mmol), was dissolved in anhydrous THF and cooled down to -100 °C. *n*-BuLi (1.0 eq , 2.5M in Hexane, 2.70 mL, 6.75 mmol) was slowly added and the reaction stirred for 2 h. $B(OMe)_3$ (1.8 eq, 1.30 mL, 11.66 mmol) was slowly added at -100 °C and the reaction stirred at 23 °C for 12 h. The reaction was quenched with H_2O (20 mL) and acidified with aq. HCl (15 %, 3 mL) until pH = 2. The reaction was stirred for 1 h at 23 °C. The organic phase was separated from the aqueous phase. The aqueous phase was further extracted with EtOAc (2 x 20mL). The combined organic phases were dried over $MgSO_4$ and concentrated to a residue by rotavap. The crude was dissolved in EtOAc (100 mL) and extracted with H_2O (100 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed by rotavap. The residue was washed with hexane (4 x 28 mL) to give **5b** (0.88 g, 5.04 mmol, 75 %) as a pale orange solid. ^{1}H NMR (500 MHz, DMSO-*d*6): δ = 8.39 (*s*, 2H), 7.38 (*s*, 2H), 2.30 (*s*, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 140.0, 128.7, 119.3, 109.9, 21.4; ESI-MS (positive mode): m/z: $[M + Na]^+$ calc. for $C_9H_{10}BNNaO_2^+$: 198.1; found: 198.1; IR: 3344*brs*, 2926*w*, 2333*w*, 2234*m*, 1655*s*, 1603*w*, 1552*w*, 1431*s*, 1409*s*, 1363*s*, 1327*s*, 1286*s*, 1255*m*, 1170*m*, 1101*m*, 1030*m*, 872*m*;

4-(3,5-Dimethyl)-[4'-bromophenyl]benzonitrile (**5c**)



5b (495 mg, 2.83 mmol), 1-bromo-4-iodobenzene (1.1 eq, 878 mg, 3.10 mmol), $Ba(OH)_2{*}H_2O$ (1.78 g, 9.40 mmol) $Pd(PPh_3)_4$ (65 mg, 0.06 mmol, 2 %) were dissolved in degassed dioxane (7.5 mL) and degassed H_2O (2.5 mL). The reaction was heated to 100 °C for 3 h. The solvent was removed by rotavap and aq. HCl (1M, 50 mL) was added and extracted with DCM (3 x 50 mL). The organic phases were combined and washed with brine and dried over Na_2SO_4. The crude was purified by silica gel column chromatography using Hex:EtOAc (70:1 to 19:1) to give **5c** (469 mg, 1.64 mmol, 58 %) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (*dt*, *J* = 8.5, 2.3, 2H), 7.42 – 7.39 (*m*, 2H), 6.99 (*dt*, *J* = 8.7, 2.3, 2H), 2.05 (*s*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 138.1, 137.5, 132.1, 130.8, 130.0, 121.7, 119.0, 111.2, 20.7; ESI-MS (positive mode): m/z: $[M + Na]^+$ calc. for $C_{15}H_{12}BrNNa^+$: 308.0; found: 308.0; IR: 3083*w*, 3047*w*, 2949*m*, 2924*m*, 2854*m*, 2361*s*, 2342*m*, 2237*m*, 2207*w*, 1678*w*, 1558*w*, 1494*m*, 1471*s*, 1437*s*, 1408*w*, 1379*m*, 1294*w*, 1181*w*, 1120*w*, 1101*m*, 1070*s*, 1033*w*, 1002*s*, 895*m*, 873*s*, 841*s*, 829*s*, 764*w*, 750*m*, 725*m*;

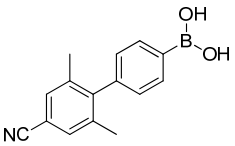
2-(4'-Cyano-3',5'-dimethyl-4-biphenyl-4-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5d**)



5c (300 mg, 1.05 mmol), bis(pinacolato)diboron (1.1 eq, 292 mg, 1.15 mmol) and potassium acetate (256 mg, 2.61 mmol) were dissolved in anhydrous, degassed DMF (4.8 mL). $Pd(dppf)Cl_2{\cdot}DCM$ (51 mg, 0.06 mmol, 6 %) was added and the reaction was stirred at 80 °C for 1 h under argon. The solvent was removed under vacuum. Purification by silica gel column chromatography using Hex:EtOAc (19:1) gave **5d** (230 mg, 0.62 mmol, 66 %) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (*d*, *J* = 8.1, 2H), 7.40 (*s*, 2H), 7.12 (*d*, *J* = 8.3, 2H), 2.04 (*s*, 6H), 1.39 (*s*, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 142.2, 137.4, 135.2, 130.7, 127.6, 119.2, 110.8, 83.9,

24.9, 20.6; ESI-MS (positive mode): m/z: $[M + Na]^+$ calc. for $C_{21}H_{24}BNNaO_2^+$: 356.2; found: 356.2; IR: 2978*m*, 2927*m*, 2226*w*, 1613*m*, 1603*m*, 1521*m*, 1447*w*, 1396*m*, 1359*s*, 1321*m*, 1271*m*, 1255*m*, 1213*w*, 1166*m*, 1144*s*, 1091*s*, 1025*w*, 1011*w*, 962*m*, 876*m*, 859*m*, 839*m*;

4'-Cyano-2',5'-dimethyl-biphenyl-4-yl)boronic acid (**5**)



5d (220 mg, 0.66 mmol), $NaIO_4$ (3.0 eq, 430 mg, 2.01 mmol) and ammonium acetate (2.3 eq, 115 mg, 1.49 mmol) were dissolved in H_2O (6.6 mL) and acetone (6.8 mL) and stirred at 23 °C for 72 h. H_2O (50 mL) was added and the mixture was extracted with EtOAc (2 x 50 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under vacuum to obtain **5** (159 mg, 0.63 mmol, 96 %) as a colorless solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.10 (*s*, 2H), 7.89 (*d*, *J* = 7.9, 2H), 7.61 (*s*, 2H), 7.11 (*d*, *J* = 7.9, 2H), 1.99 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.7, 140.3, 137.2, 134.5, 130.7, 127.1, 118.9, 109.8, 20.2; ESI-MS (positive mode): m/z: $[M + Na]^+$ calc. for $C_{15}H_{14}BNNaO_2^+$: 274.1; found: 274.1; IR: 3416*brs*, 2956*w*, 2926*m*, 2360*m*, 2339*w*, 2227*m*, 1657*s*, 1610*s*, 1601*s*, 1550*w*, 1518*w*, 1396*s*, 1338*s*, 1255*s*, 1106*s*, 1037*s*, 1010*s*, 876*s*, 838*s*, 742*m*, 702*m*;

III. Photophysical properties and titrations

For all photophysical experiments, compounds **1** – **5** were prepared as DMSO stock solutions and stored at -20 °C. All samples were prepared in two or more independent trials and measurements conducted using a *Molecular Devices* Spectra spectrophotometer. Solvatochromic measurements were performed in a quartz cuvette (l = 1 cm). All other measurements were performed in 96 well *Greiner* well plates for absorbance and 384 well *Corning* black, flat clear bottom microplates for fluorescence. Measurements were performed with spectrophotometric grade dioxane, deionized H_2O or aq. 0.1M sodium phosphate buffer. For all values reported, final DMSO concentrations after dilution were always less than 0.5%. E_T^{30} values for dioxane / water mixtures were determined by dissolving a small amount of Reichardt's dye in each solution and measuring the most red-shifted absorption maximum (Table S2).[9]

Quantum yield measurements were performed at the absorbance maximum of each BBA using optical densities of 0.1 ± 0.05. 2-Aminopyridine (φ = 0.60 at λ_{ex} = 300 nm) in 0.1 N H_2SO_4 (n = 1.333) was used as the fluorescent standard for the relative quantum yields measurements (Φ) of compounds **1** – **5**. Quantum yields were calculated as described,[10] according to the following equation (eq. 1):

$$\phi = \phi_R \frac{F}{F_R} \frac{A_R}{A} \frac{n^2}{n_R^2}$$

where Φ_R is the quantum yield of the reference, F and F_R are the integrated emission intensities of the probe and the reference, respectively. A and A_R are the optical densities of the probe and the reference, respectively. n and n_R are the refractive indices of the solvent for the sample and reference, respectively.

Hydroxide binding experiments were conducted in 0.1M sodium phosphate buffer solutions at various pH values in a final volume of 1 mL. The pH was varied by mixing 500 µL 0.2M NaH_2PO_4 buffer with various amounts of 1M NaOH and H_2O. The pH of each sample was measured using a *Thermo Orion310* pH-meter. D-(-)-Fructose and D-sorbitol binding experiments were conducted in 0.1M sodium phosphate buffer solutions (pH = 7.4) in final volumes of 1 mL. The carbohydrate concentrations were varied by mixing 500 µL of 0.2M NaH_2PO_4 buffer solution containing the fluorescent probe, with one volume of aqueous carbohydrate solutions to a final volume of 0.1 mL. Samples were read at multiple time points to ensure that equilibrium had been reached. 1,3,5-Pentanetriol was synthesized by a procedure published by *V.B. Riatto et al* from diethyl-1,3-acetonedicarboxylate.[7] All other diols, triols and carbohydrates were obtained in the highest possible grade from commercial sources.

Table S2: Photophysical properties of compounds 1 – 5.

Compound	Solvent (dioxane:H_2O)	λ_{abs} [nm]	λ_{em} [nm]	Stokes [cm^{-1}]	Φ	E_T^{30} [kcal*mol^{-1}]
CBBA (**1**)	90:10	276	329	5837	0.41	48.46
	60:40	276	331	6020	0.49	52.82
	30:70	276	332	6111	0.42	57.04
	H_2O	272	333	6735	0.33	63.10[a)]
	D_2O	273	332	6510	0.30	62.80[a)]
BBA(**2**)	90:10	258	312	6708	0.14	48.46
	60:40	257	314	7063	0.19	52.82
	30:70	259	313	6661	0.19	57.04
	H_2O	258	313	6811	0.19	63.10[a)]
	D_2O	257	313	6962	0.18	62.80[a)]
MBBA(**3**)	90:10	273	333	6600	0.58	48.46
	60:40	271	339	7402	0.57	52.82
	30:70	273	350	8059	0.72	57.04
	H_2O	271	360	9123	0.82	63.10[a)]
	D_2O	269	361	9474	0.81	62.80[a)]
DBBA(**4**)	90:10	314	393	6402	0.85	48.46
	60:40	313	415	7852	0.76	52.82
	30:70	307	420	8764	0.88	57.04
	H_2O	295	444	11376	0.80	63.10[a)]
	D_2O	295	443	11325	0.74	62.80[a)]
DM-CBBA(**5**)	90:10	242	316	9677	0.01	48.46
	60:40	238	317	10471	0.02	52.82
	30:70	240	318	10220	0.02	57.04
	H_2O	239	319	10493	0.01	63.10[a)]
	D_2O	239	319	10493	0.01	62.80[a)]

a) E_T^{30} taken as reported by C. Reichhardt.[9]

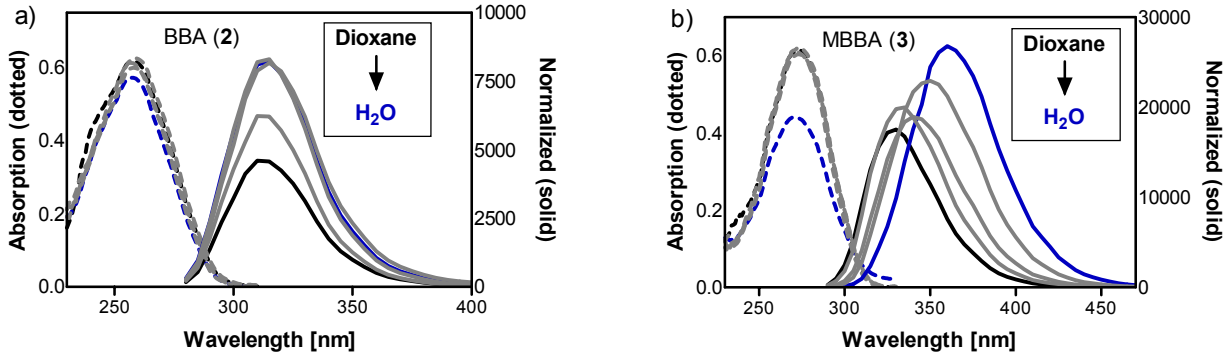


Figure S3: Absorption and emission spectra of BBA (a) and MBBA (b) in neutral dioxane-water mixtures. Absorption samples contained 5 µM of 2 or 3, and fluorescence samples contained 25 µM of 2 or 3. Excitation wavelengths were set to the absorption maximum of each compound (Table S2, ESI).

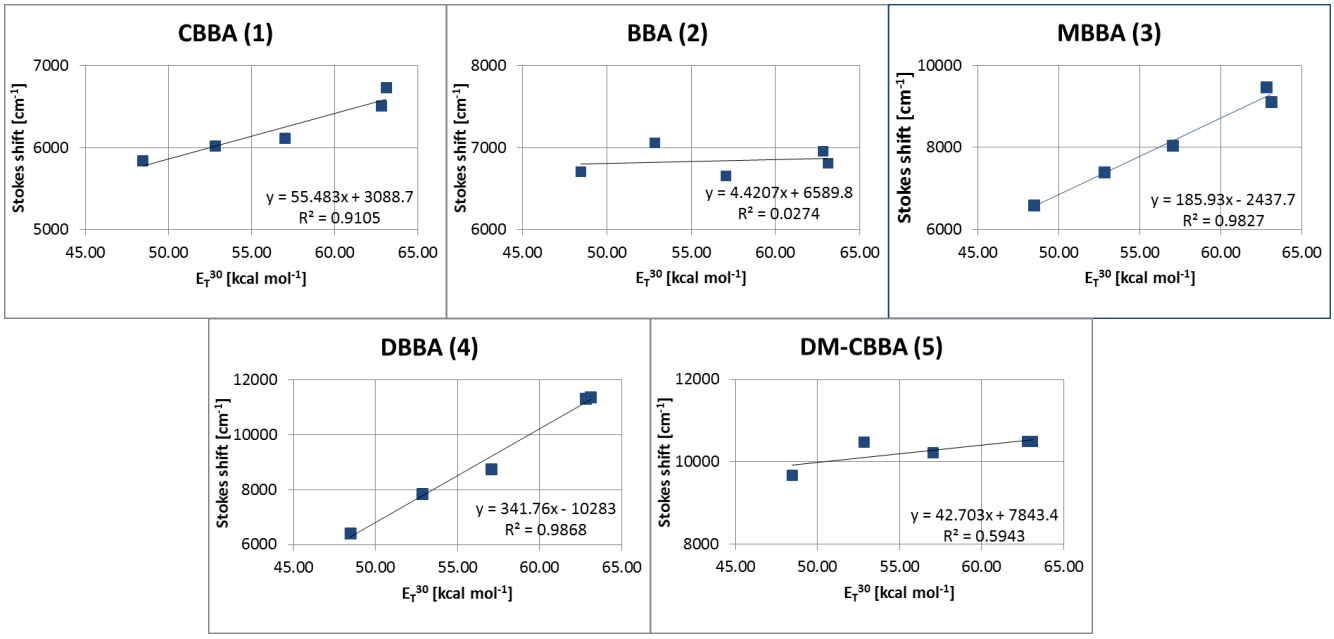


Figure S4: Plots between Stoke's shifts of compounds 1 – 5 versus E_T^{30} values.

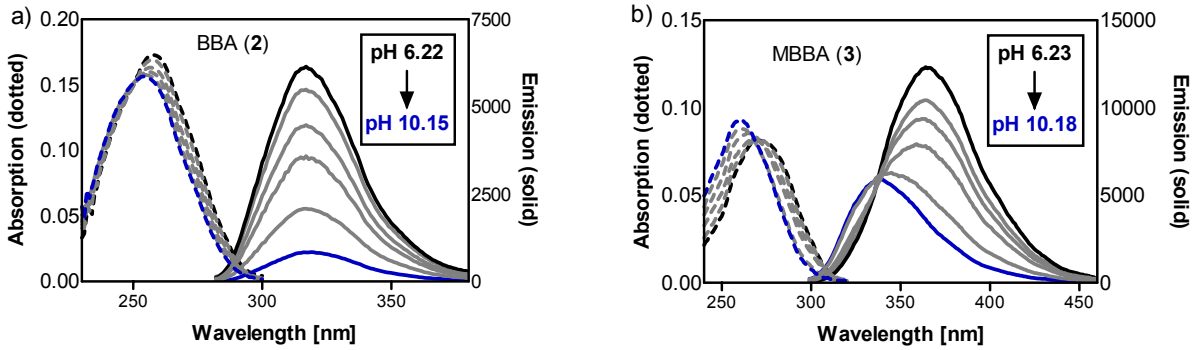


Figure S5: a) Absorption and emission spectra of BBA (2). b) absorption and emission spectra of MBBA (3) at different pH values measured in aqueous sodium phosphate buffer (100 mM). Absorption samples contained 10 µM of 2 or 6.25 µM 3. Excitation wavelengths were set to the absorption maximum of each compound (Table S2, ESI).

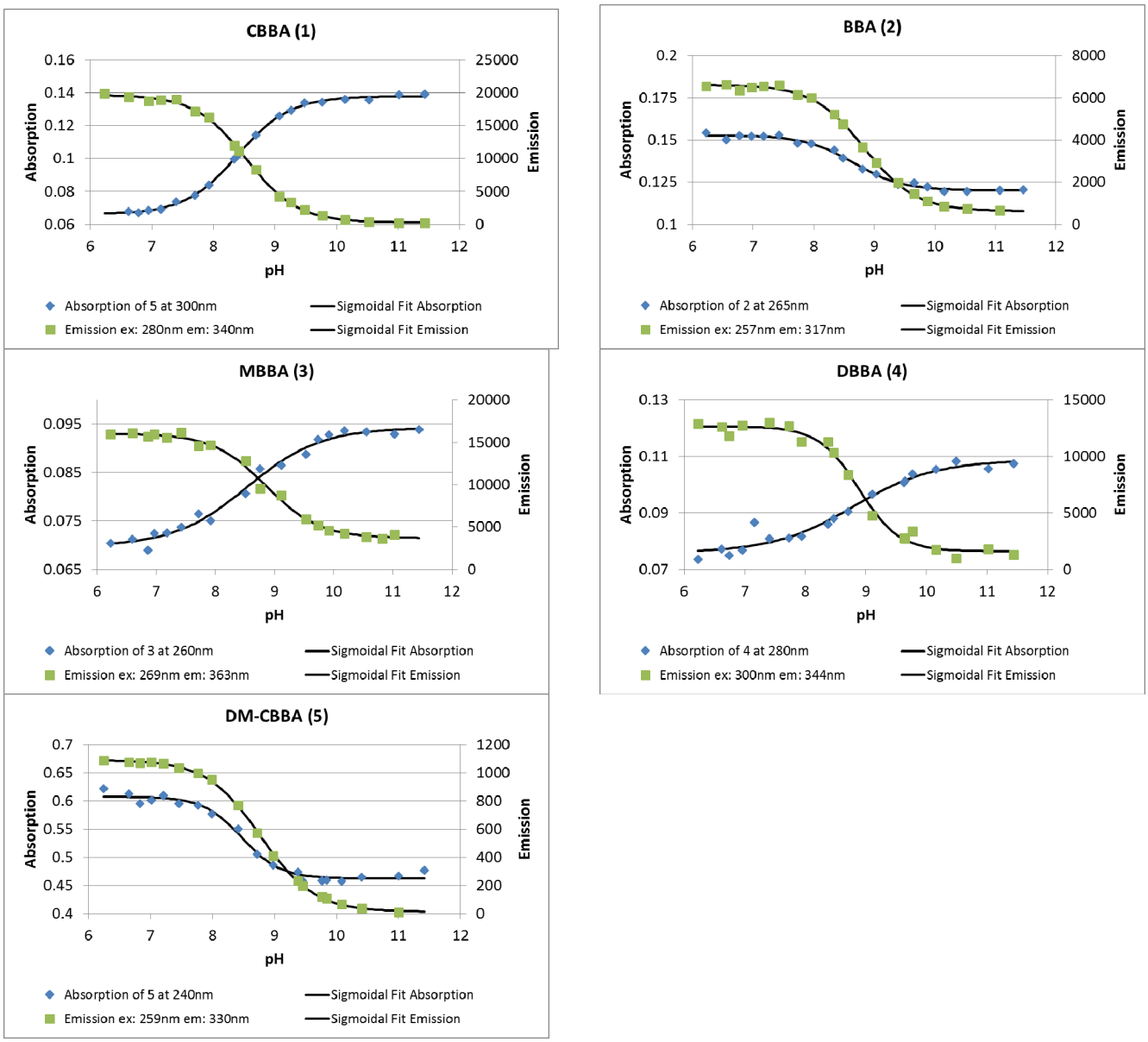


Figure S6: Changes in fluorescence and absorption of solutions containing compounds 1 – 5 versus pH. Samples contained 100 mM phosphate buffer and 10 µM of CBBA, 10 µM of BBA, 6.25 µM of MBBA, 6.25 µM of DBBA, or 50 µM of DM-CBBA.

Table S3: pK_a of BBA's measured in 100 mM phosphate buffer according to fluorescence (a) or absorbance (b) changes.

Compound	pK_a (fluorescence)	R^2	pK_a (absorbance)	R^2
CBBA (1)	8.53	0.999	8.50	0.999
BBA (2)	8.83	0.999	8.66	0.992
MBBA (3)	8.86	0.993	8.54	0.983
DBBA (4)	8.88	0.988	8.80	0.957
DM-CBBA (5)	8.77	1.000	8.47	0.985

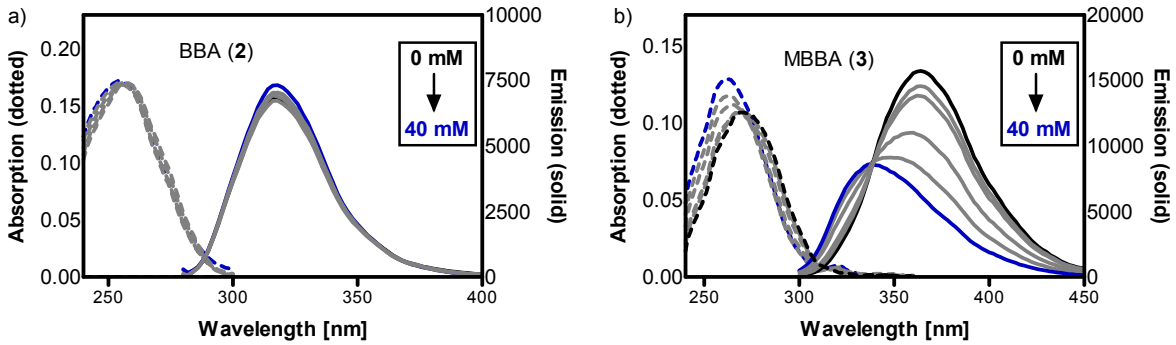


Figure S7: Absorption and emission spectra of 10 µM solutions of compound of 2 (a) or 3 (b) upon addition of D-(-)-fructose in aqueous sodium phosphate buffer (100 mM, pH = 7.4); Absorption: 10 µM of 2 (a) or 3 (b); Fluorescence: excitation wavelengths: 257 nm (2), 275 nm (3), and emission normalized to OD = 0.10.

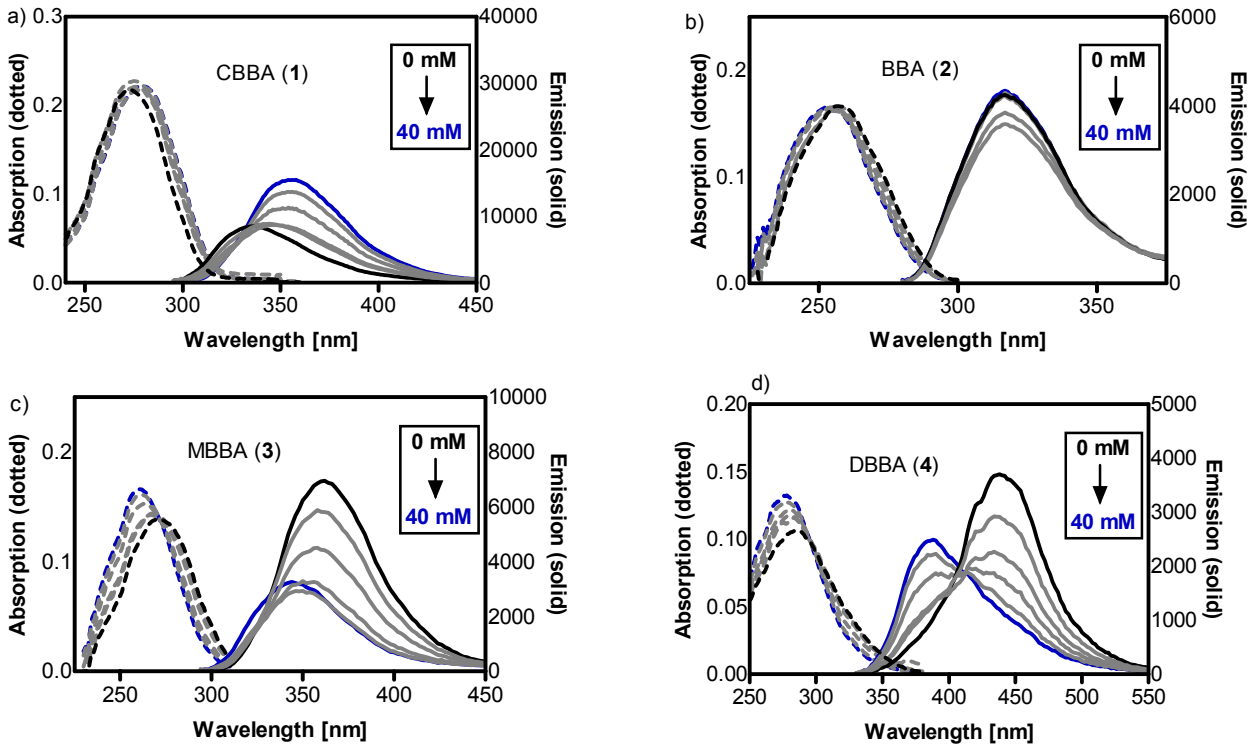


Figure S8: Absorption and emission spectra of 10 µM solutions of compounds 1 (a), 2 (b), 3 (c) and 4 (d) at upon addition of D-sorbitol in aqueous sodium phosphate buffer (100 mM, pH = 7.4); Absorption: 10 µM of 1, 2, 3 or 4; Fluorescence: excitation wavelength: 277 nm (1), 257 nm (2), 275 nm (3), 300 nm (4), and emission normalized to OD = 0.10.

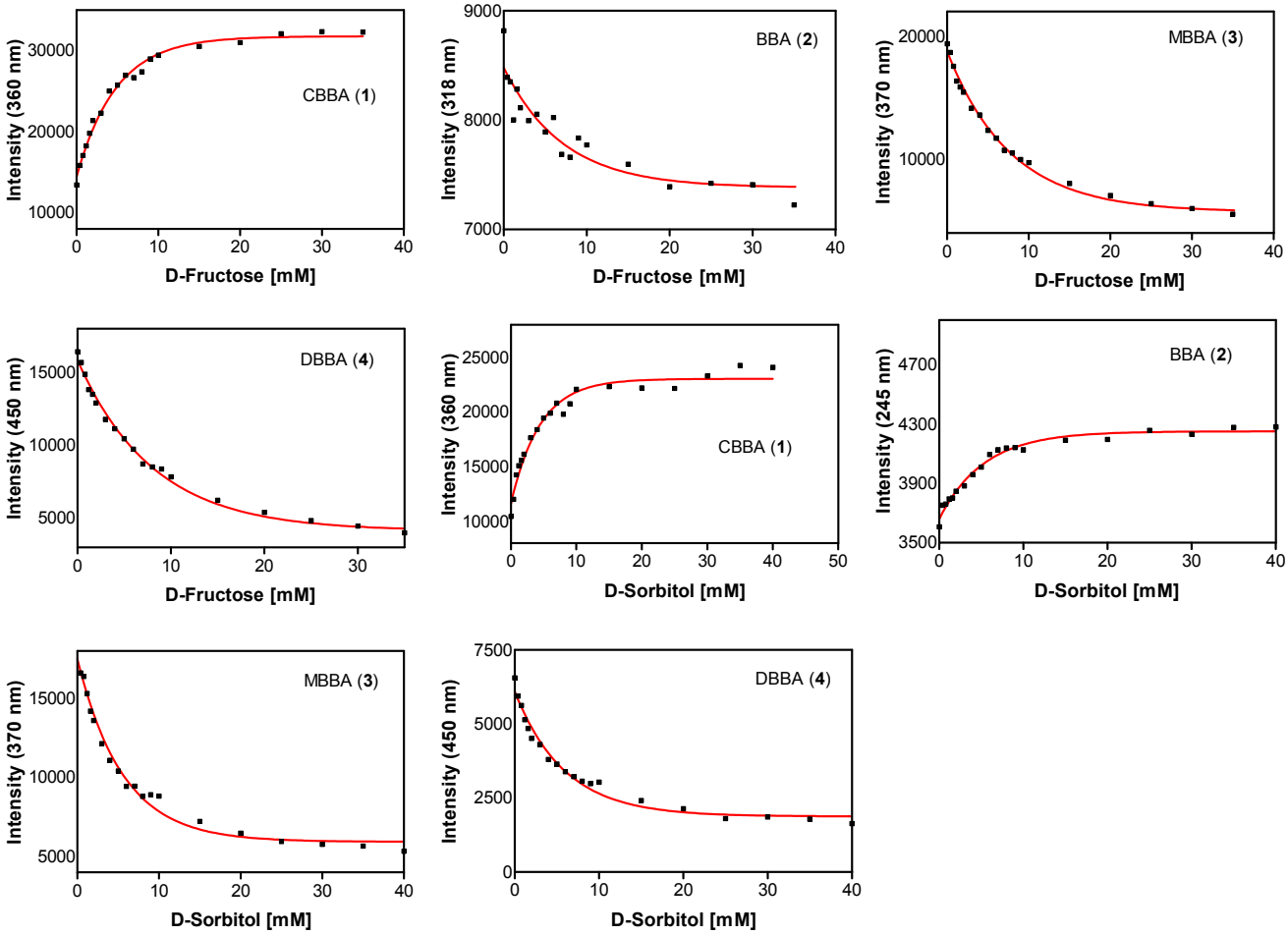


Figure S9: Binding isotherms of 10 μM solutions of compounds 1 – 4 upon addition of D-fructose or D-sorbitol in aqueous sodium phosphate buffer (100 mM, pH = 7.4). Excitation wavelengths: 277 nm (1), 257 nm (2), 272 nm (3), or 295 nm (4).

Table S4: K_d values determined from fluorescence changes in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4).

Compound	D-fructose K_d [mM]	D-sorbitol K_d [mM]
CBBA (1)	4.8	4.5
BBA (2)	7.2	5.3
MBBA (3)	7.8	5.6
DBBA (4)	8.2	5.9

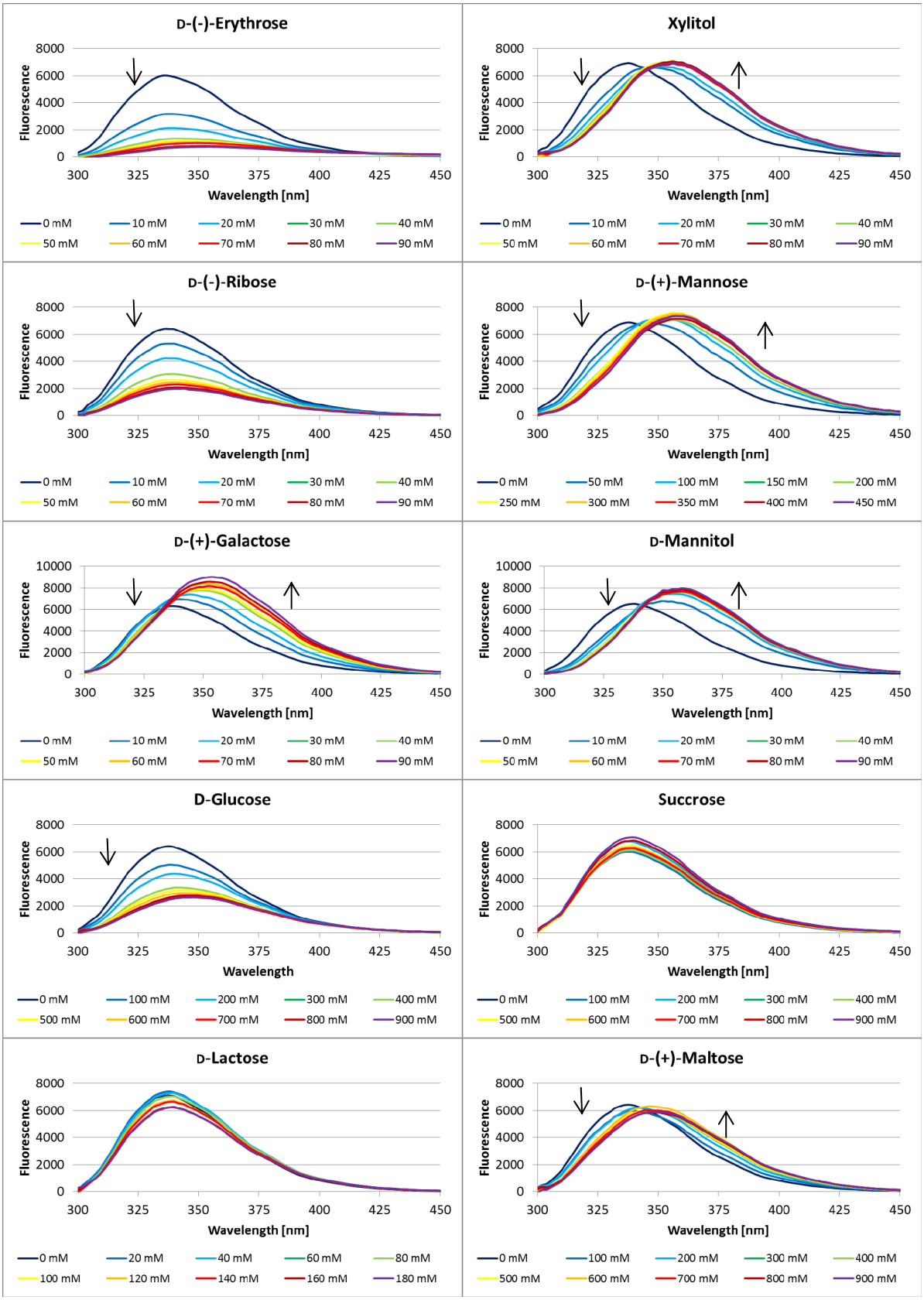
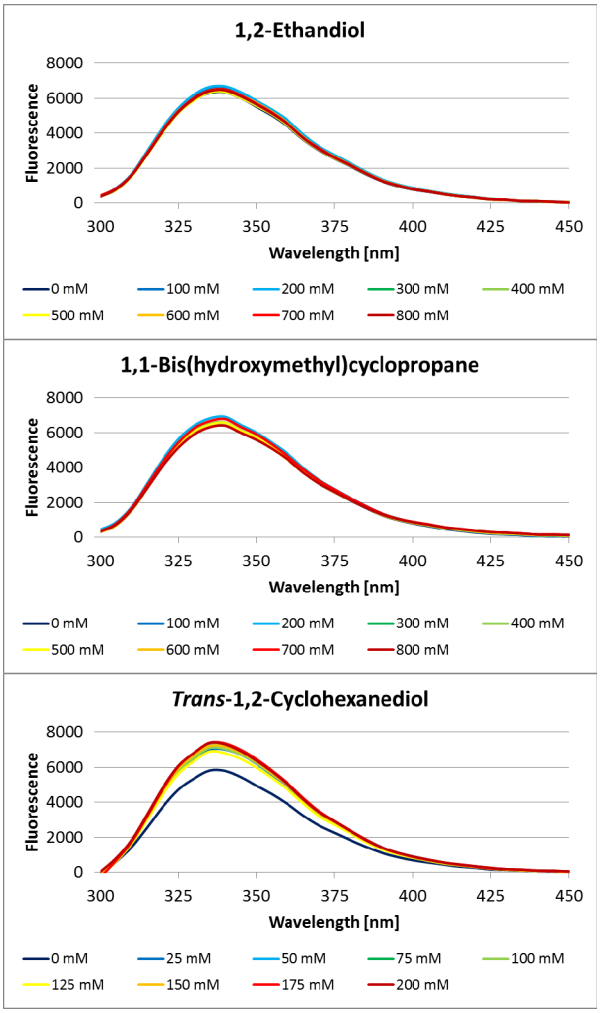


Figure S10: Fluorescence emission spectra (λ_{ex} = 277 nm) of a 2 µM solution of CBBA (1) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of carbohydrates.



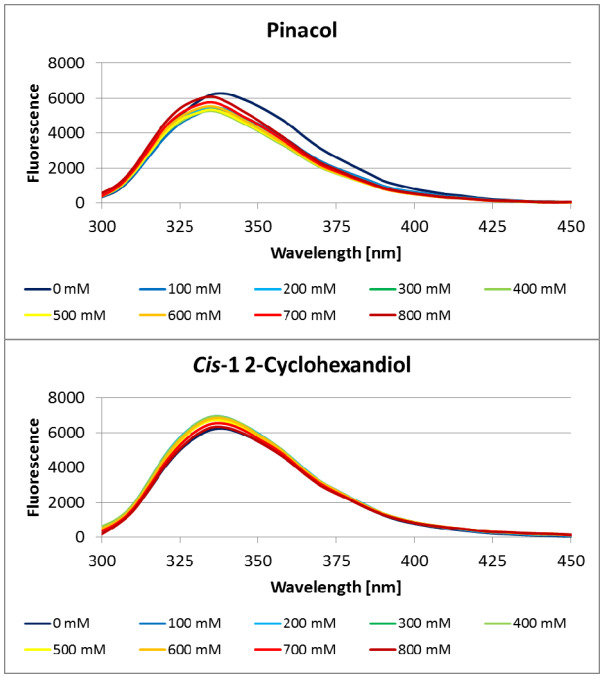


Figure S11: Fluorescence emission spectra (λ_{ex} = 277 nm) of a 2 µM solution of CBBA (1) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of non-carbohydrate diols.

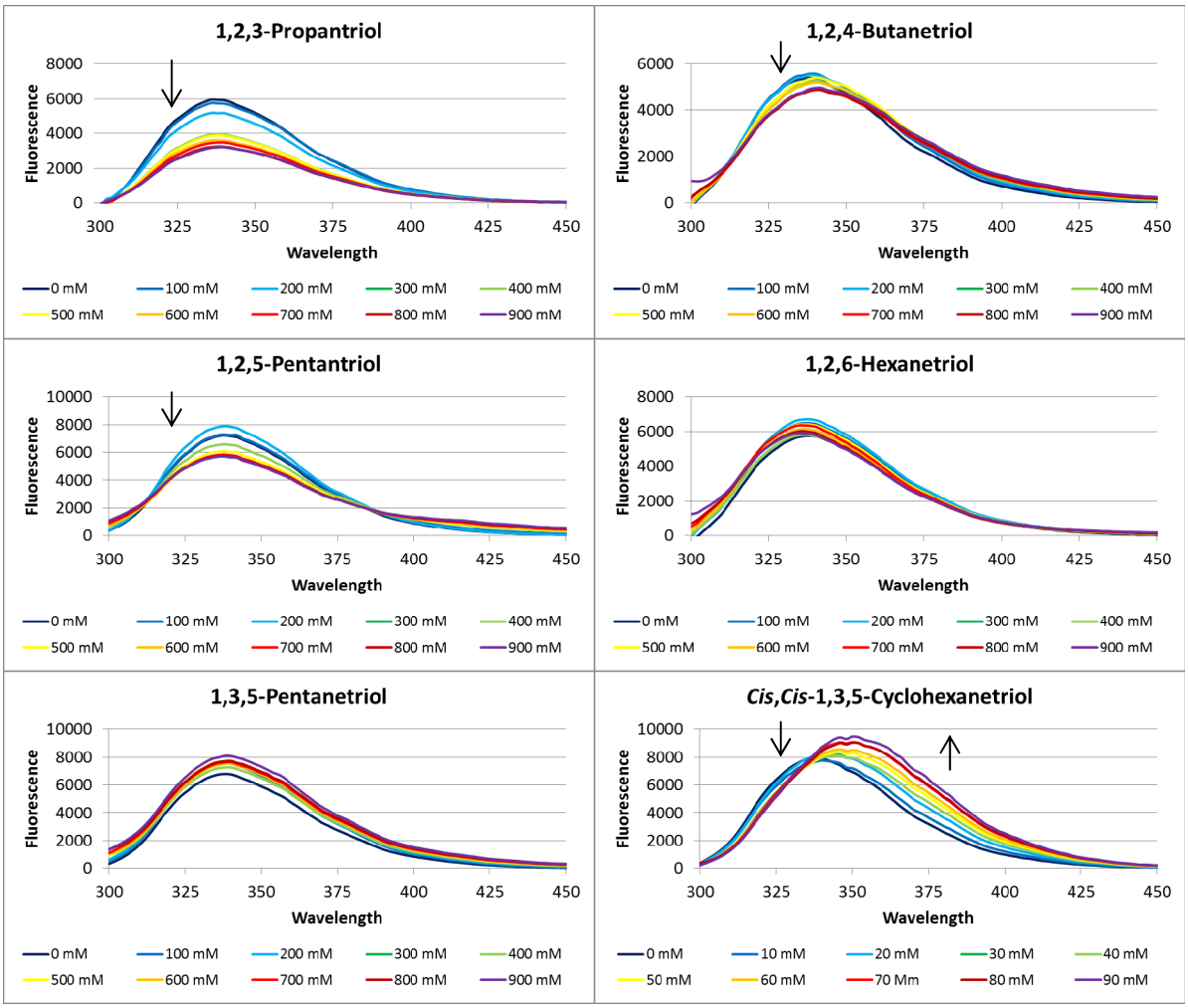


Figure S12: Fluorescence emission spectra (λ_{ex} = 277 nm) of a 2 µM solution of CBBA (1) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of non-carbohydrate triols.

Table S5: K_d values determined from fluorescence changes in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4).

Ligand	CBBA (**1**) K_d (mM)	CBBA (**5**) K_d (mM)
D-fructose	4.8	4.8
D-sorbitol	4.5	5.8
1,2,3-propantriol	490	n.d.
D-erythrose	14	36
Cis,*cis*-1,3,5-cyclohexanetriol	> 45	> 45
D-ribose	30	120
D-glucose	260	330
D-galactose	55	96
D-mannose	77	170

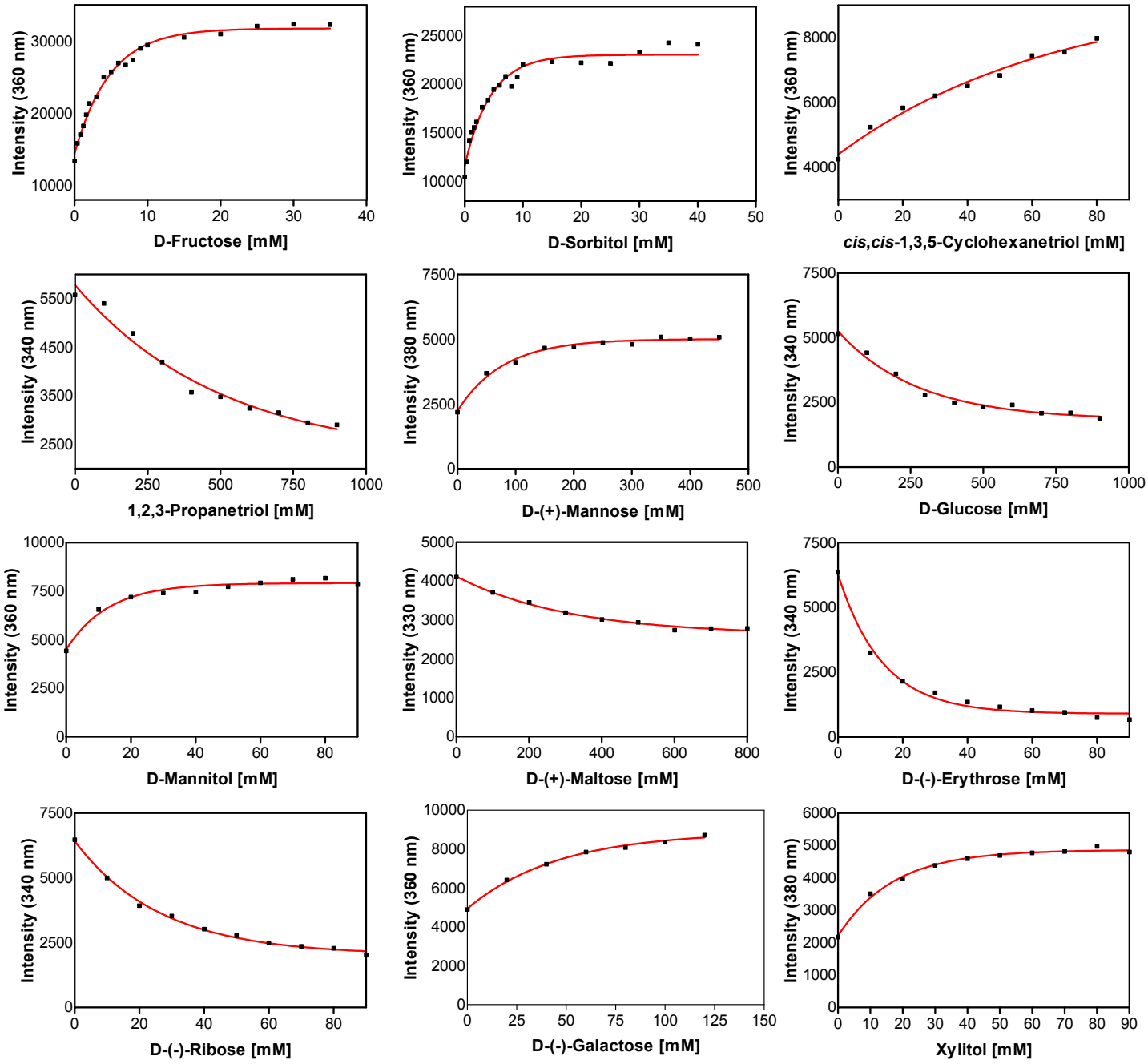


Figure S13: Binding isotherms according to fluorescence intensity (λ_{ex} = 277 nm) of CBBA (1, 2 – 10 µM solutions) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of various carbohydrates.

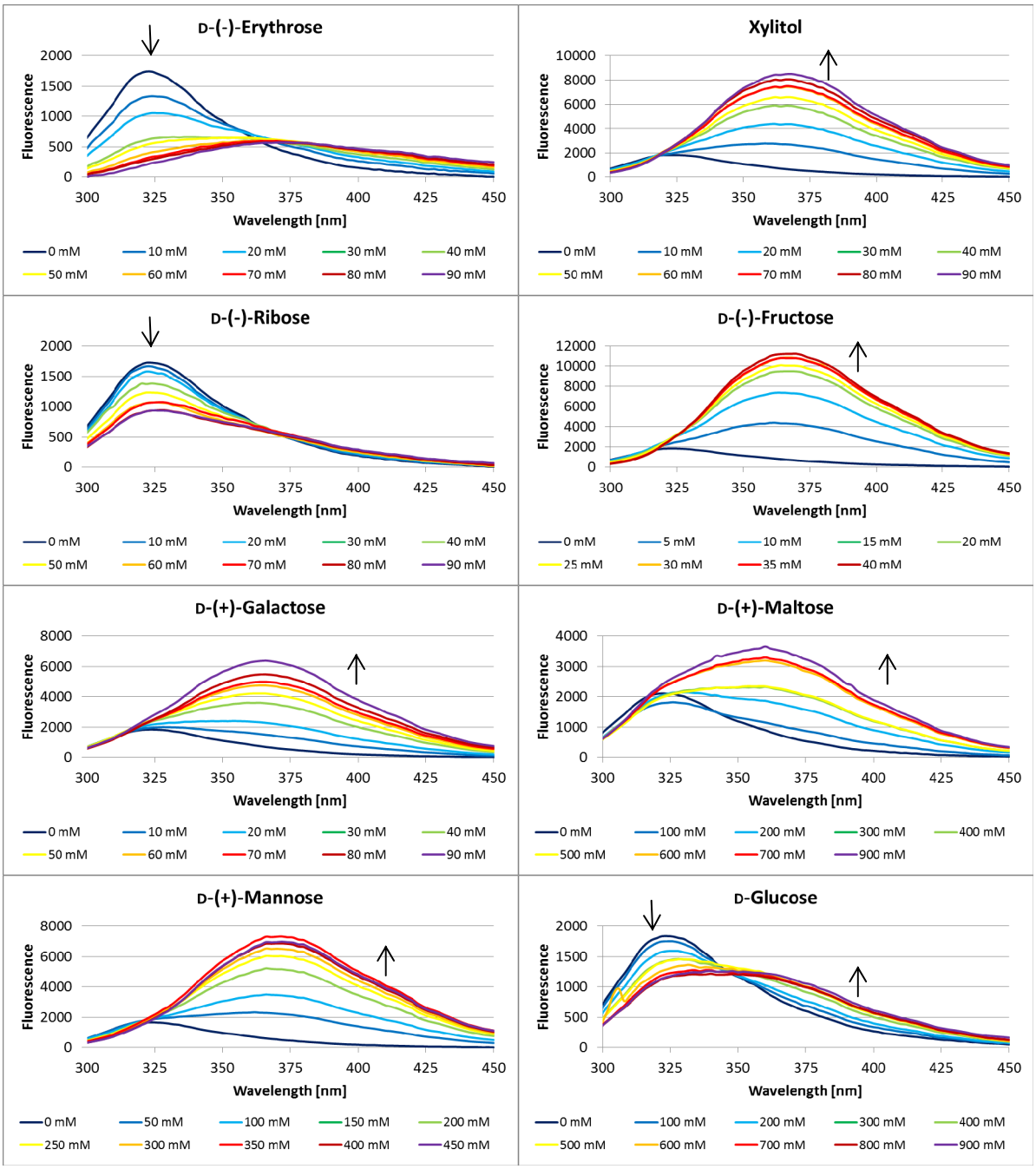


Figure S14a: Fluorescence emission spectra (λ_{ex} = 250 nm) of a 50 µM solution of DM-CBBA (5) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of carbohydrates.

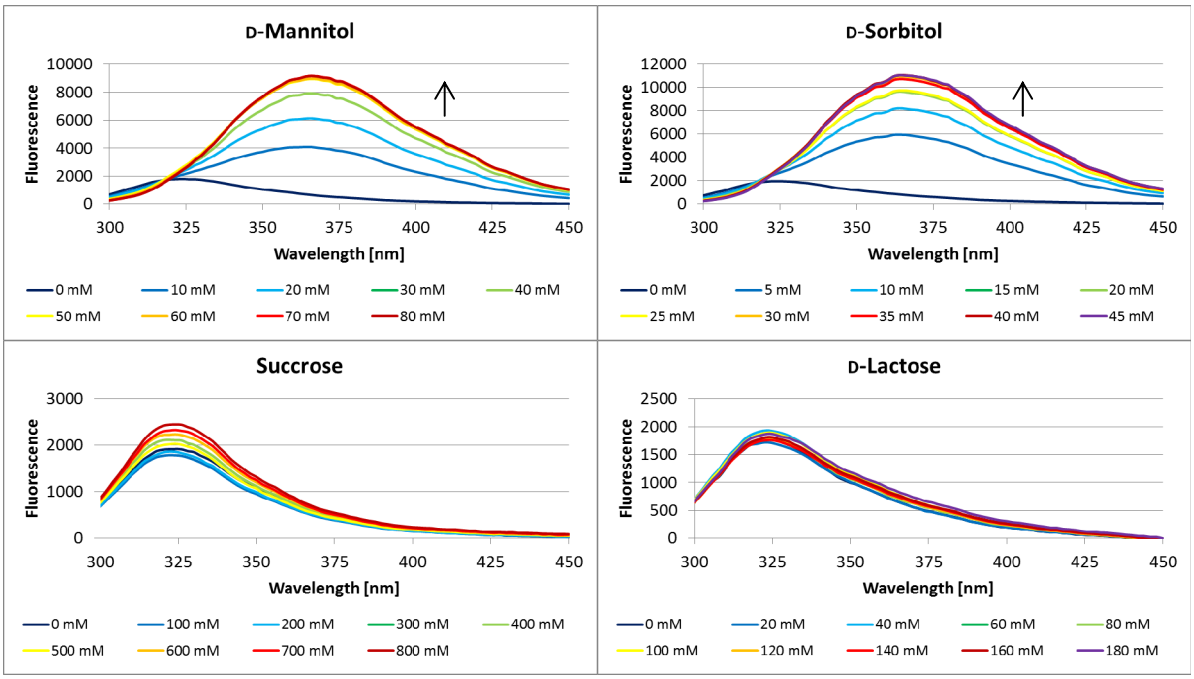


Figure S14b: Fluorescence emission spectra (λ_{ex} = 250 nm) of a 50 µM solution of DM-CBBA (5) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of carbohydrates.

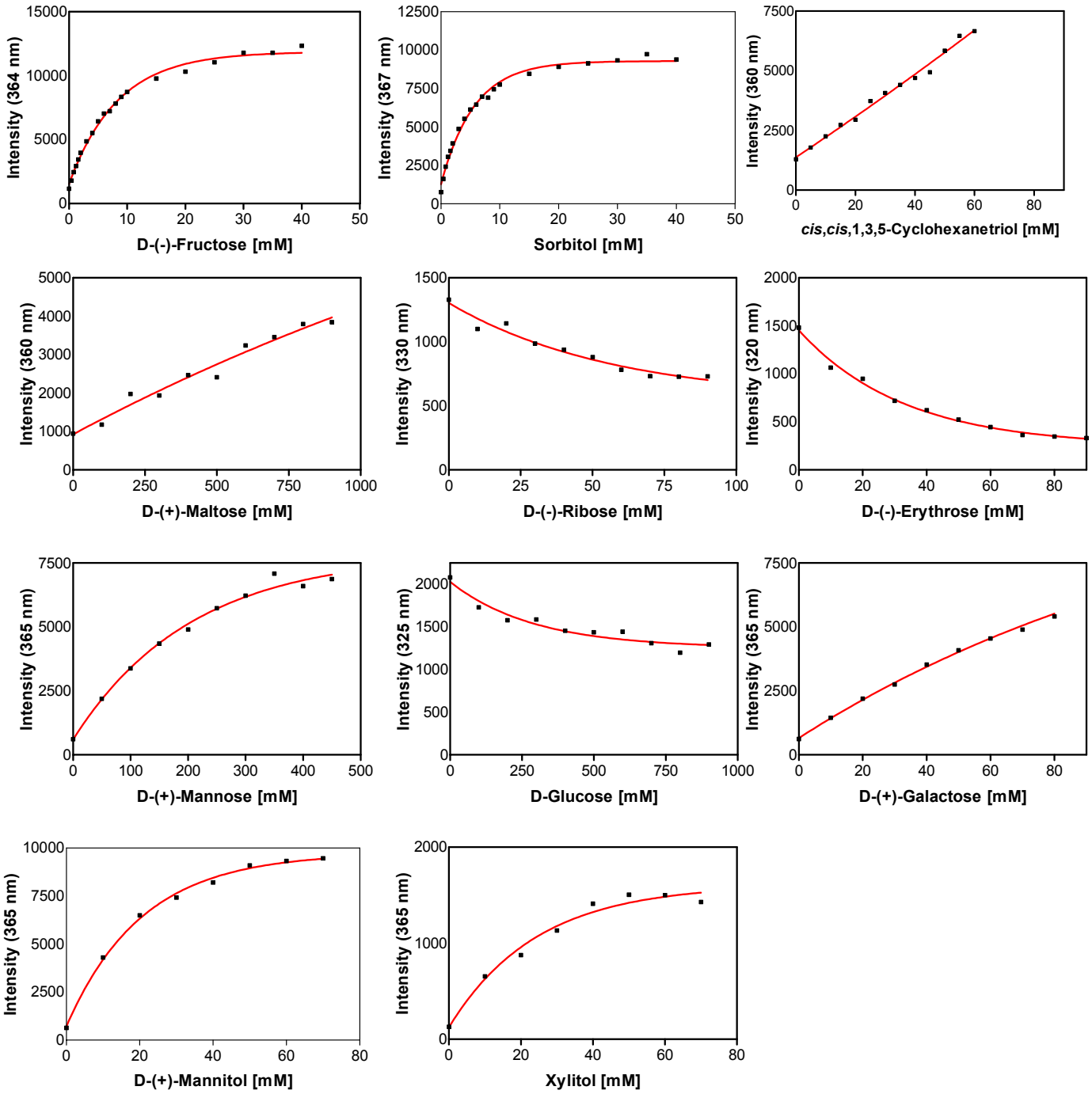


Figure S15: Binding isotherms according to fluorescence intensity (λ_{ex} = 250 – 256 nm) of DM-CBBA (5, 50 μM solutions) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of various carbohydrates.

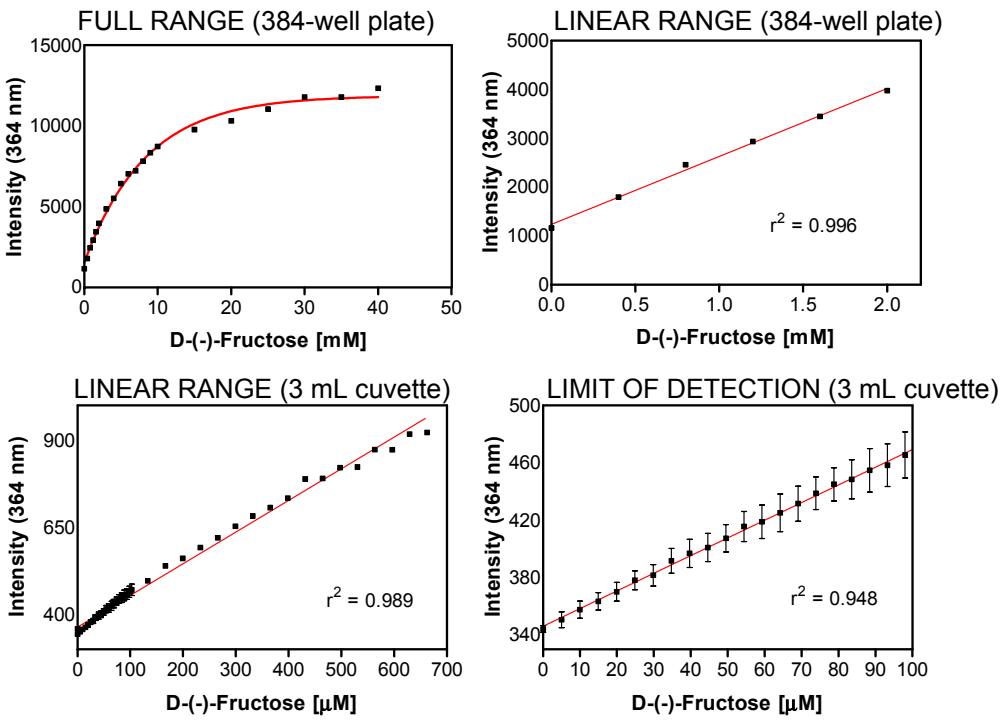


Figure S16: Binding isotherms according to fluorescence intensity (λ_{ex} = 256 nm) of DM-CBBA (5, 50 µM solution) in aqueous buffer containing 100 mM phosphate buffer (pH = 7.4) upon the addition of fructose. The limit of detection, according to the standard IUPAC definition, is the minimal concentration where the mean change (in fluorescence intensity) is at least three-fold larger than the standard deviation of the change.[11] The limit of detection is of fructose is therefore 5 µM. The limit of quantification is 15 µM.[11] Experiments reaching saturation for the purpose of K_d measurements were conducted using two or more independent titrations in 384-well plates. Experiments to determine the limit of detection were conduced using four independent titrations in a 3 mL cuvette.

IV. References

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