Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Superior perrhenate anion recognition in water by a halogen bonding acyclic receptor

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S1. Synthesis and Characterisation

S1.1 General Procedure

All commercially available chemicals and solvents were used as received without further purification. All dry solvents were thoroughly degassed with N_2, dried through a Mbraun MPSP-800 column and used immediately. Water used was deionized and passed through a Milli-Q® Millipore machine for microfiltration. TBTA (tris(benzyltriazolemethyl)amine) was prepared according to reported procedures.[1] Amberlite® was prepared by washing the commercial resin beads sequentially with 10 % NaOH (aq), water, 0.1 M NH_4PF_6 (aq), further water, and finally loaded with 0.1 M NH_4NO_3 (aq) before any anion exchange to the nitrate salt occurred.

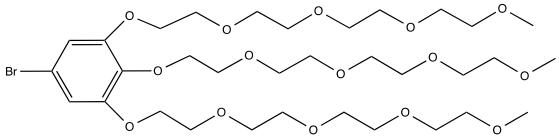
NMR spectra were recorded on Bruker AVIII HD Nanobay 400 MHz, Bruker AVIII 500 MHz and Bruker AVIII 500 MHz (with ^{13}C cryoprobe) spectrometers. Electrospray ionisation mass spectrometry (ESI-MS) was performed using the Waters Micromass LCT and Bruker microTOF spectrometers.

S1.2 Synthesis of Compounds

(2,5,8,11-tetraoxatridecan-13-yl) *p*-toluenesulfonate (TsO-TEG-OMe) was synthesized from tetraethylene glycol[2] and 5-bromo-1,2,3-trihydroxybenzene was obtained from 5-bromo-1,2,3-trimethoxybenzene[3] by following literature protocols.

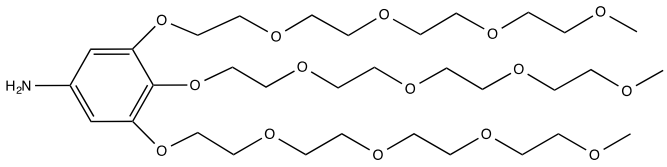
5-bromo-1,2,3-tris(tetraethylene glycol methyl ether)benzene

Procedure modified from a literature protocol.[4]



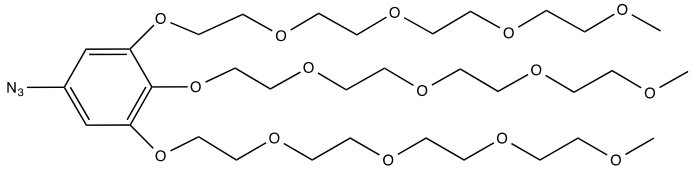
5-bromo-1,2,3-trihydroxybenzene (609 mg, 2.97 mmol) was mixed with anhydrous potassium carbonate (2.05 g, 14.9 mmol) and degassed and filled with N_2 thrice. Acetonitrile (20 mL) was degassed by bubbling with N_2 for 30 minutes before TsO-TEG-OMe (3.34 g, 9.22 mmol) was dissolved in it and added to the solid mixture. The reaction was stirred for 3 days under N_2 at 70 ^oC. After which, the reaction was cooled to ambient temperature and solvent removed *in vacuo* before chloroform (10 mL) and water (20 mL) was added. The aqueous layer was extracted with chloroform (5 x 20 mL) and the combined organics were dried with $MgSO_4$. Removal of solvent gave a brown liquid which was purified by silica gel chromatography (4 % CH_3OH in CH_2Cl_2) to give the product as a yellow liquid (1.91 g, 83 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.74 (s, 2H, Ar*H*), 4.13 (t, 6H, ^3J = 5.0 Hz, Ar-OCH_2), 3.54-3.84 (m, 42H, TEG alkyl groups), 3.38 (s, 9H, OCH_3); **^{13}C-NMR** (100 MHz, d_6-DMSO) δ 153.3, 137.9, 115.7, 111.5, 72.3, 71.9, 70.9, 70.7, 70.6, 70.6 (repeat), 70.5, 70.4, 69.6, 69.1, 59.0; **MS (ESI)** *m/z* calc. for $[M + H]^+$ = 775.3, found 775.2.

5-amino-1,2,3-tris(tetraethylene glycol methyl ether)benzene



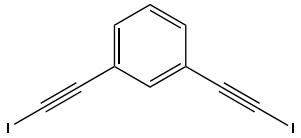
5-bromo-1,2,3-tris(tetraethylene glycol methyl ether)benzene (245 mg, 0.319 mmol) was dissolved in 28 % aqueous ammonia (6.0 mL) before ethylene glycol (0.18 mL, 3.19 mmol) and copper(I) iodide (61.0 mg, 0.319 mmol) were added portionwise. The mixture was stirred to mix before being heated in a microwave reactor at 150 ^{o}C for 1 hour. Upon cooling to ambient temperature, the brown aqueous mixture was diluted with water (10 mL) before extraction by chloroform (5 x 15 mL) till the organic layer was no longer coloured. The combined organics were dried with $MgSO_4$ and dried *in vacuo* to give the product as a brown liquid in good purity (221 mg, 98 %). The product was used without further purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 5.97 (s, 2H, Ar*H*), 4.11 (t, 4H, ^{3}J = 5.2 Hz, *meta*-ArOC*H*$_2$-), 4.04 (t, 4H, ^{3}J = 5.2 Hz, *para*-ArOC*H*$_2$-), 3.82 (t, 4H, ^{3}J = 5.2 Hz, *meta*-ArOCH$_2$C*H*$_2$-), 3.76 (t, 4H, ^{3}J = 5.2 Hz, *para*-ArOCH$_2$C*H*$_2$-), 3.55-3.71 (m, 36H, dendrimer alkyl-C*H*$_2$), 3.38 (s, 9H, OC*H*$_3$); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.2, 142.9, 131.1, 95.6, 72.5, 72.4, 71.9, 70.8, 70.6, 70.5, 70.4, 70.3, 69.7, 68.7, 61.7, 59.0; **MS** (ESI +ve) *m/z* 712.4096 ($[M + H]^+$, $C_{33}H_{62}NO_{15}$, calc. 712.4114).

5-azido-1,2,3-tris(tetraethylene glycol methyl ether)benzene)



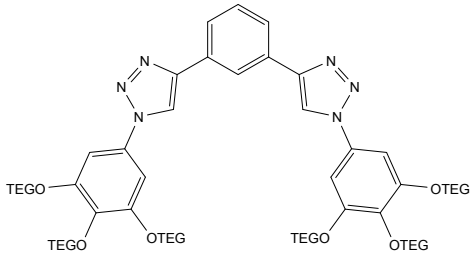
5-amino-1,2,3-tris(tetraethylene glycol methyl ether)benzene (500 mg, 0.702 mmol) was dissolved in 25 % sulfuric acid (10 mL) and chilled to 0 ^{o}C in an ice bath. A saturated solution of sodium nitrite (97.0 mg, 1.40 mmol) was then added and the reaction stirred at 0 ^{o}C for 1 hour. An aqueous solution of sodium azide (228 mg, 3.51 mmol) was then added carefully dropwise and the reaction was warmed up to ambient temperature and stirred for 4 hours. The dark red aqueous solution was then extracted with chloroform till the organic phase was no longer coloured. After drying with $MgSO_4$, removal of solvent gave the product as a red-brown liquid in sufficient purity without requiring further purification (492 mg, 95 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.26 (s, 2H, Ar*H*), 4.12 (t, 4H, ^{3}J = 4.8 Hz, *meta*-ArOC*H*$_2$-), 4.08 (t, 4H, ^{3}J = 5.1 Hz, *para*-ArOC*H*$_2$-), 3.82 (t, 4H, ^{3}J = 5.0 Hz, *meta*-ArOCH$_2$C*H*$_2$-), 3.76 (t, 4H, ^{3}J = 5.2 Hz, *para*-ArOCH$_2$C*H*$_2$-), 3.51-3.71 (m, 36H, dendrimer alkyl-C*H*$_2$), 3.36 (s, 9H, OC*H*$_3$); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.5, 135.8, 135.4, 99.0, 72.6, 72.4, 71.9, 70.8, 70.6, 70.5, 70.3, 69.6, 69.0, 61.7, 59.0; **MS** (ESI +ve) *m/z* 760.3809 ($[M + Na]^+$, $C_{33}H_{59}N_3O_{15}Na$, calc. 760.3838).

1,3-bis(iodoethynyl)benzene



1,3-diethynylbenzene (0.05 mL, 0.376 mmol) was dissolved in dry THF (1 mL) and the resulting yellow solution was cooled to -78 °C. 1.6 M *n*-butyllithium (0.72 mL, 1.13 mmol) was then added dropwise to the reaction which was stirred at -78 °C for 30 minutes before a solution of I_2 (0.286 g, 1.13 mmol) in dry THF (2 mL) was added. After stirring for 15 minutes at -78 °C, the reaction was warmed up slowly to ambient temperature and stirred for a further 1 hour. A saturated solution of sodium thiosulfate (5 mL), followed by chloroform (10 mL), was then added to the brown solution and the organic layer was separated. The aqueous layer was washed with chloroform (2 x 5 mL), and the combined organics were dried with brine and $MgSO_4$. Purification by recrystallisation with hexane gave the product as pale yellow needles (102 mg, 72 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H, Ar*H*), 7.37 (d, 2H, ^3J = 1.6 Hz, Ar*H*), 7.25-7.28 (m, 1H, Ar*H*); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 136.1, 132.5, 128.3, 123.7, 93.1, 7.6; **MS (EI)** *m/z* calc. for $[M]^+$ = 377.84, found 377.84.

1,3-bis(prototriazole)benzene receptor precursor

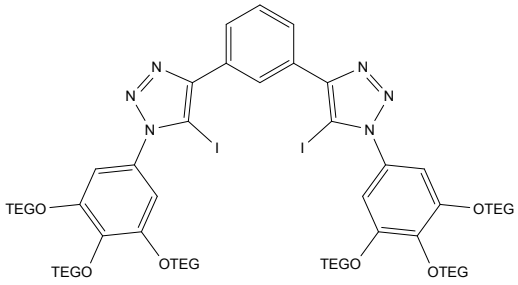


OTEG = $(OCH_2CH_2)_4OCH_3$

1,3-diethynylbenzene (4.5 µL, 0.034 mmol) and 5-azido-1,2,3-tris(tetraethylene glycol methyl ether)benzene) (50 mg, 0.068 mmol) were dissolved in dry, degassed CH_2Cl_2 (2 mL). To this mixture was added diisopropylethylamine (23 µL, 0.136 mmol), TBTA (9 mg, 0.017 mmol) and $Cu(MeCN)_4PF_6$ (6.3 mg, 0.017 mmol) and the reaction was stirred for 3 days at room temperature in a N_2 atmosphere. Subsequently, the reaction was washed with 10 % aqueous ammonia (2 x 5 ml), and the aqueous layer was back-extracted with chloroform (3 x 5 ml). The combined organics were dried with brine and $MgSO_4$ before the solvent was removed to yield a brown oil. Silica gel chromatography (6 % CH_3OH in CH_2Cl_2 as eluent) gave the product as a sticky yellow liquid (41 mg, 76 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H, spacer Ar*H*), 8.37 (s, 2H, triazole-*H*), 7.93 (d, 2H, ^3J = 7.6 Hz, spacer Ar*H*), 7.55 (t, 1H, ^3J = 7.6 Hz, spacer Ar*H*), 7.10 (s, 4H, dendrimer Ar*H*), 4.26 (t, 8H, ^3J = 4.8 Hz, *meta*-ArOCH_2-), 4.20 (t, 4H, ^3J = 4.8 Hz, *para*-ArOCH_2-), 3.86 (t, 8H, ^3J = 4.8 Hz, *meta*-ArOCH$_2$CH_2-), 3.79 (t, 4H, ^3J = 4.8 Hz, *para*-ArOCH$_2$CH_2-), 3.51-3.72 (m, 72H, dendrimer alkyl-CH_2), 3.36 (s, 6H, *para*-dendrimer terminal OCH_3), 3.33 (s, 12H, *meta*-dendrimer terminal OCH_3); **^{13}C-NMR** (100 MHz,

$CDCl_3$) δ 153.3, 147.8, 138.7, 132.5, 130.9, 129.5, 125.6, 123.0, 118.3, 100.7, 72.5, 71.8, 70.6, 70.5, 70.4, 70.3, 69.6, 69.3, 61.7, 58.9; **MS** (ESI +ve) *m/z* 1601.8441 ($[M + H]^+$, $C_{76}H_{125}N_6O_{30}$, calc. 1601.8435).

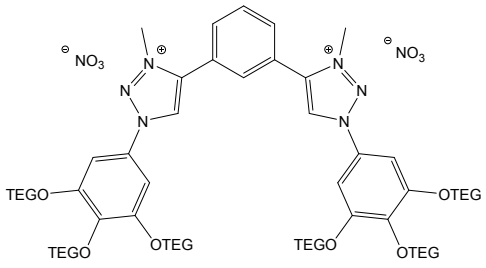
1,3-bis(iodotriazole)benzene receptor precursor



OTEG = $(OCH_2CH_2)_4OCH_3$

1,3-bis(iodoethynyl)benzene (25.6 mg, 0.068 mmol) and dendrimer aryl azide (100 mg, 0.136 mmol) was dissolved in degassed THF (2 mL). TBTA (7.2 mg, 0.014 mmol) and $Cu(MeCN)_4PF_6$ (10 mg, 0.027 mmol) was then added portionwise and the reaction stirred under N_2 for 2 days. Following which, the solvent was removed *in vacuo* and chloroform (10 mL) was added. After washing with 10 % aqueous ammonia (2 x 5 mL) and water (5 mL), the organic layer was dried with brine and $MgSO_4$. Purification by silica gel chromatography (5 % CH_3OH in CH_2Cl_2) gave the product as a bright yellow viscous liquid (112 mg, 89 %). **^{1}H-NMR** (400 MHz, CDCl) δ 8.68 (s, 1H, spacer-Ar*H*), 8.10 (d, 2H, ^3J = 7.6 Hz, spacer Ar*H*), 7.65 (t, 1H, ^3J = 7.6 Hz, spacer Ar*H*), 6.81 (s, 4H, dendrimer-Ar*H*), 4.21-4.27 (m, 12H, dendrimer-O*CH*$_2$), 3.84-3.90 (m, 12H, dendrimer-OCH$_2$*CH*$_2$), 3.54-3.75 (m, 72H, dendrimer alkyl-*CH*$_2$), 3.38 (s, 6H, *para*-dendrimer terminal O*CH*$_3$), 3.37 (s, 12H, *meta*-dendrimer terminal O*CH*$_3$), **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 152.8, 149.8, 139.8, 132.0, 130.5, 129.0, 128.0, 126.6, 106.5, 78.6, 72.6, 72.5, 71.9, 70.8, 70.6, 70.5, 70.4, 70.2, 69.6, 69.5, 69.3, 69.2, 61.7, 59.0; **MS** (ESI +ve) *m/z* 1853.6406 ($[M + H]^+$, $C_{76}H_{123}N_6O_{30}I_2$, calc. 1853.6368).

1,3-bis(prototriazole)benzene dendrimer receptor.2NO_3^- salt (**1a**)

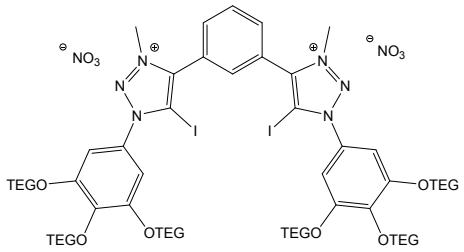


OTEG = $(OCH_2CH_2)_4OCH_3$

1,3-bis(prototriazole)benzene receptor precursor (40 mg, 0.025 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and added to trimethyloxonium tetrafluoroborate (8.1 mg, 0.055 mmol). The reaction was stirred under N_2 for 2 days, before MeOH (2 mL) was added to quench the reaction. The solvent was removed

in vacuo before preparatory thin layer chromatography (7.5 % CH_3OH in CH_2Cl_2) afforded the purified product as a sticky pale yellow liquid. Anion exchange was then carried out by dissolving the purified product in 9:1 CH_3OH/ H_2O and passing it through a nitrate-loaded Amberlite® anion exchange column twice. The solvent was removed *in vacuo* to afford the bis-nitrate salt of the compound as a sticky yellow liquid (28 mg, 64 %). **^{1}H-NMR** (400 MHz, d_4-CD_3OD) δ 9.64 (s, 2H, triazolium-Ar*H*), 8.25 (s, 1H, spacer-Ar*H*), 8.16 (d, 2H, ^3J = 6.0 Hz, spacer Ar*H*), 8.02 (t, 1H, ^3J = 6.0 Hz, spacer Ar*H*), 7.40 (s, 4H, dendrimer-Ar*H*), 4.54 (s, 6H, triazolium-NCH_3), 4.24-4.30 (m, 12H, dendrimer-OCH_2), 3.80-3.91 (m, 12H, dendrimer-OCH_2CH_2), 3.48-3.75 (m, 72H, dendrimer alkyl-CH_2), 3.32 (s, 6H, *para*-dendrimer terminal OCH_3), 3.30 (s, 12H, *meta*-dendrimer terminal OCH_3); **^{13}C-NMR** (100 MHz, d_4-CD_3OD) δ 153.6. 142.5, 140.4, 132.4, 130.8, 130.4, 127.5, 124.1, 100.7, 72.5, 71.5, 70.3, 70.2, 70.1, 69.9, 69.3, 57.7, 54.5, 42.4, 38.6; **MS** (ESI +ve) *m/z* 815.4419 ($[M]^{2+}$, $C_{78}H_{130}N_6O_{30}$, calc. 815.4410).

1,3-bis(iodotriazolium)benzene receptor.2NO_3^- salt (**1b**)



OTEG = $(OCH_2CH_2)_4OCH_3$

1,3-bis(iodotriazole)benzene receptor precursor (50 mg, 0.027 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and added to trimethyloxonium tetrafluoroborate (10 mg, 0.068 mmol), and the reaction was left to stir in the dark for 3 days under N_2. Following which, CH_3OH (1 mL) was added and stirred for 30 minutes before the solvent was removed *in vacuo*. Following purification by alumina column chromatography (CH_2Cl_2, gradually increasing methanol content to 3 %), anion exchange was then carried out by dissolving the purified product in 9:1 CH_3OH/ H_2O and passing it through a nitrate-loaded Amberlite® anion exchange column twice. Removal of solvent furnished the product as a sticky white solid (43 mg, 79 %). **^{1}H-NMR** (400 MHz, d_4-CD_3OD) δ 8.17 (s, 1H, spacer-Ar*H*), 8.08 (m, 3H, spacer Ar*H*), 7.17 ((s, 4H, dendrimer-Ar*H*), 4.43 (s, 6H, triazolium-NCH_3), 4.23-4.30 (m, 12H, dendrimer-OCH_2), 3.78-3.89 (m, 12H, dendrimer-OCH_2CH_2), 3.48-3.71 ((m, 72H, dendrimer alkyl-CH_2), 3.32 (s, 6H, *para*-dendrimer terminal OCH_3), 3.30 (s, 12H, *meta*-dendrimer terminal OCH_3); **^{13}C-NMR** (100 MHz, d_4-CD_3OD) δ 153.2, 145.6, 141.1, 133.7, 132.4, 131.0, 130.4, 124.7, 105.8, 93.8, 72.5, 71.6, 71.5, 70.5, 70.4, 70.3, 70.2, 69.9, 69.3, 69.2, 57.7, 38.8; **MS** (ESI +ve) *m/z* 941.3355 ($[M]^{2+}$, $C_{78}H_{128}N_6O_{30}I_2$, calc. 941.3377).

S1.3 Spectral Characterisation

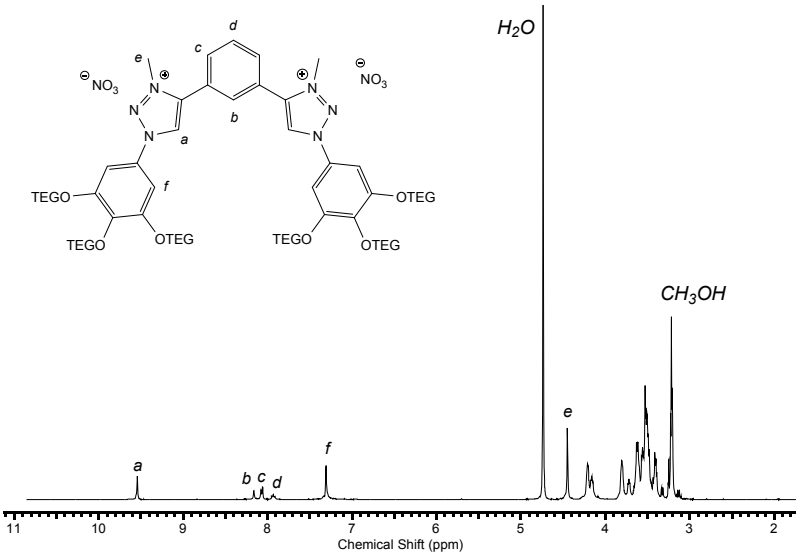


Fig S1-1. ^{1}H NMR of HB receptor **1a** in d_4-CD_3OD at 298 K (400 MHz). Triazolium H_a is acidic and was found to undergo deuterium exchange in CD_3OD.

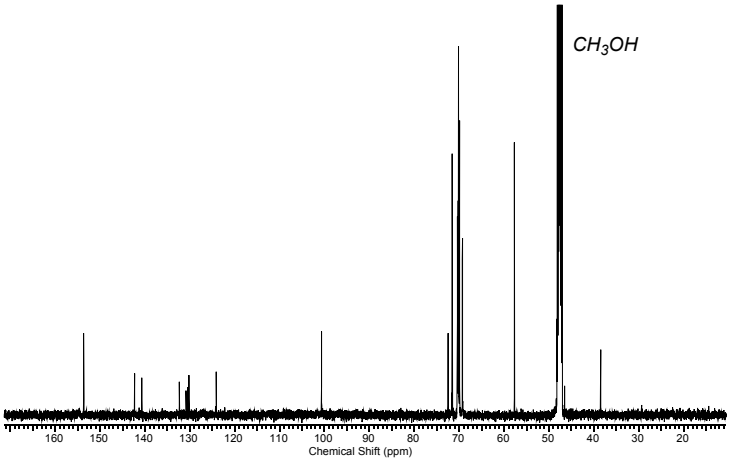
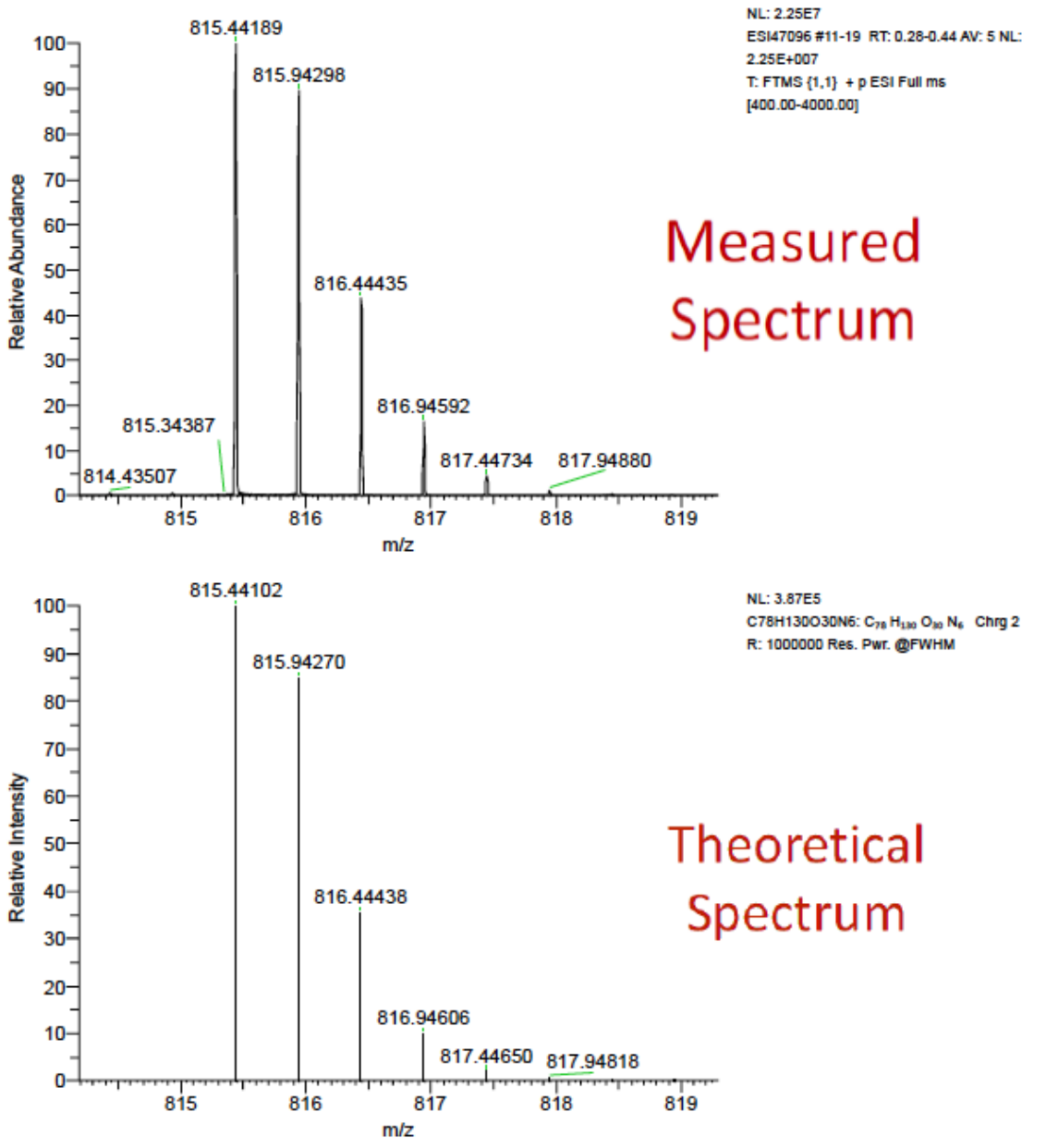


Fig. S1-2. ^{13}C NMR of HB receptor **1a** in d_4-CD_3OD at 298 K (100 MHz).



m/z	Formula	RDB	Delta ppm	Theo. Mass
815.44189	$C_{78}H_{130}O_{30}N_6$	17	1.07	815.44102

Fig. S1-3. High-resolution mass spectrum of HB receptor **1a**.

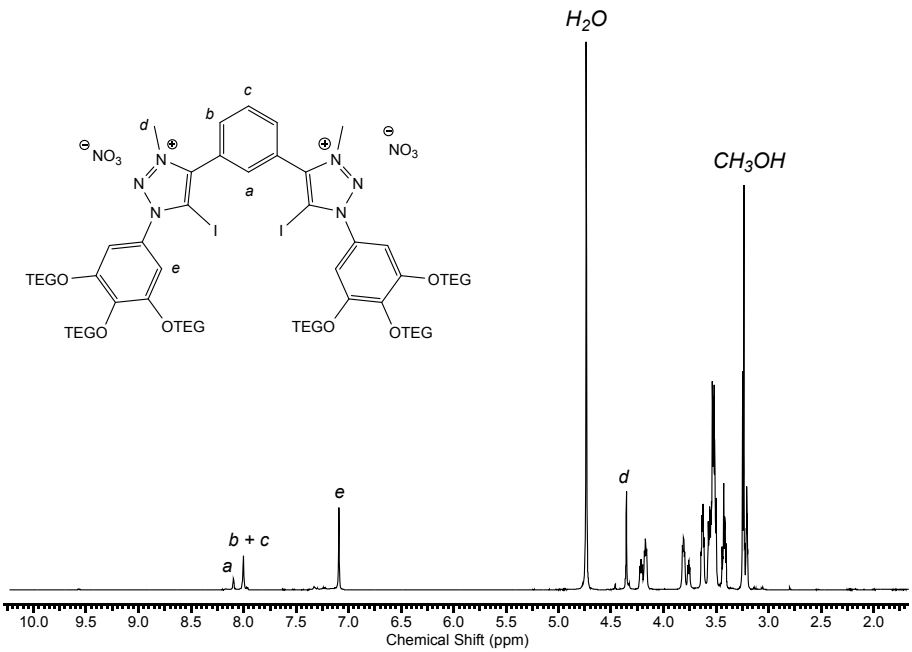


Fig S1-4. ^{1}H NMR of HB receptor **1a** in d_4-CD_3OD at 298 K (400 MHz)

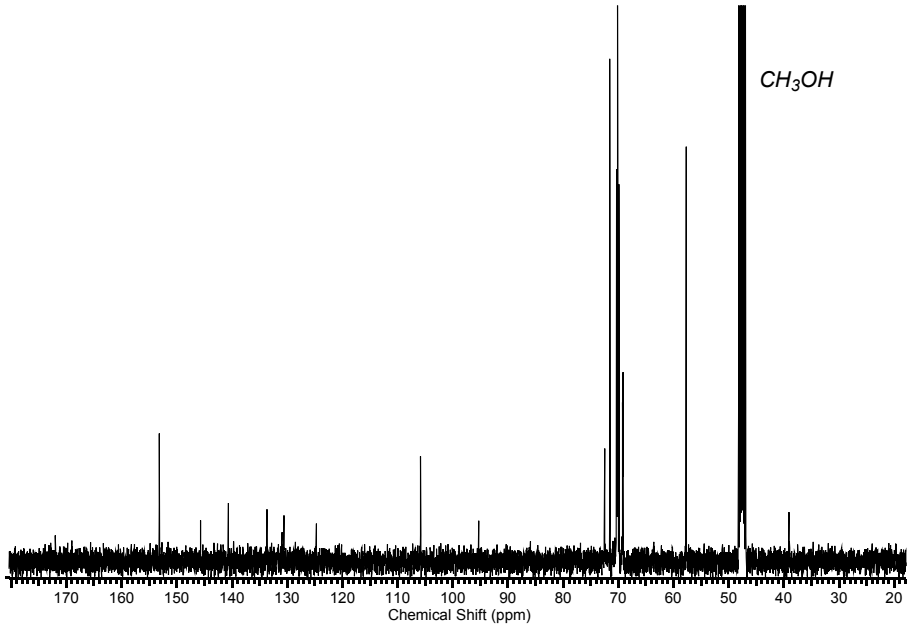
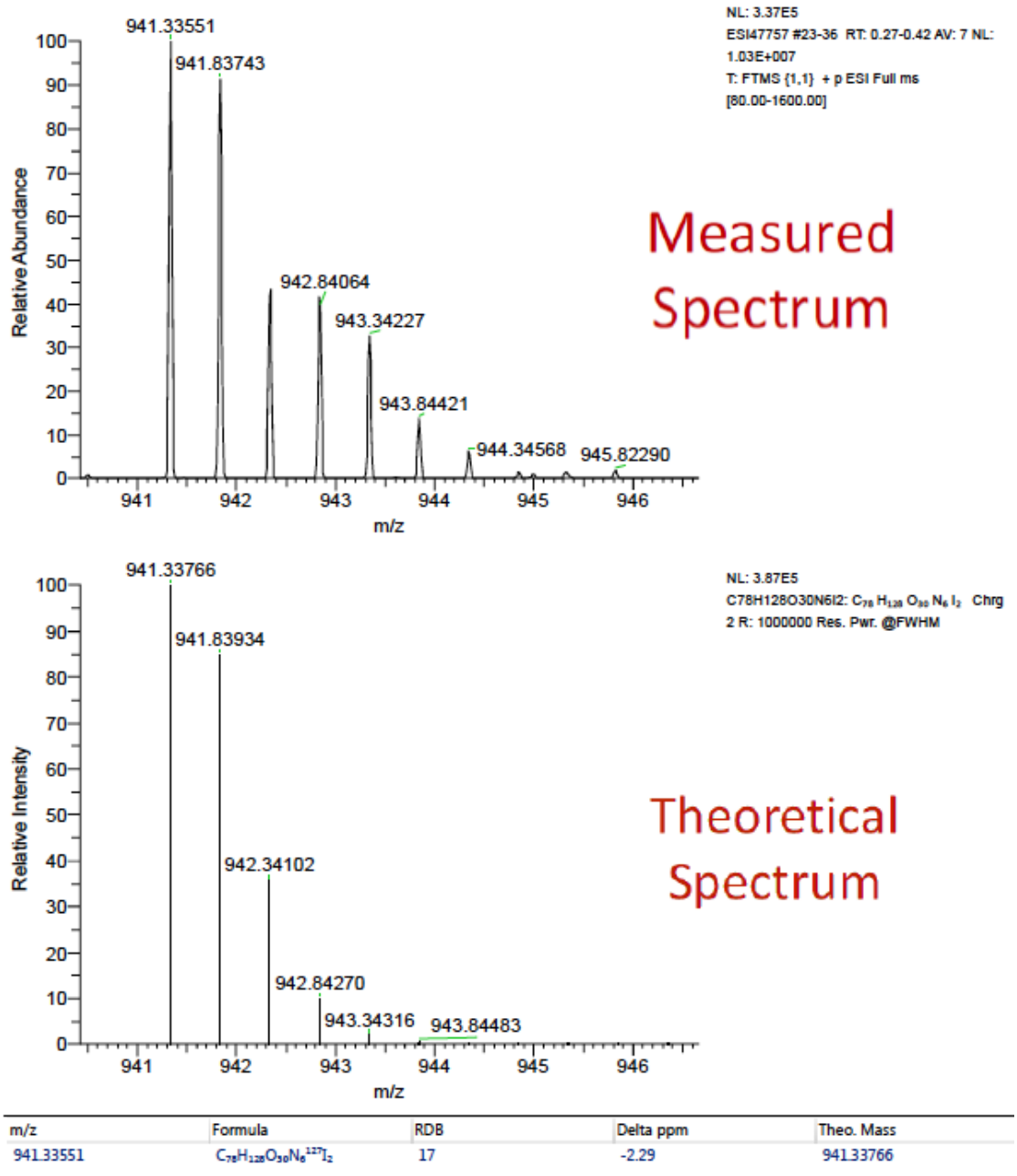


Fig. S1-5. ^{13}C NMR of HB receptor **1a** in d_4-CD_3OD at 298 K (100 MHz).



m/z	Formula	RDB	Delta ppm	Theo. Mass
941.33551	$C_{78}H_{128}O_{30}N_6{}^{127}I_2$	17	-2.29	941.33766

Fig. S1-6. High-resolution mass spectrum of HB receptor **1a**. **Top:** theoretical isotope model; **Bottom:** measured spectrum.

S2. Anion Recognition Studies of Receptors 1a and 1b by ^{1}H NMR titrations

S2.1 General Protocol

^{1}H NMR titration experiments were performed on a Bruker AVIII 500 MHz spectrometer. In a typical experiment, a solution of the appropriate sodium salt was added to a solution of the receptor molecule at 298 K. Both sodium salt and receptor were dissolved in pure D_2O unless otherwise stated. Sodium was chosen as the counter-cation due to its strongly hydrated and non-coordinating nature. A 0.75 M solution of the salt was added to 0.50 mL of a 1.5 mM solution of receptor, where 1.0 equivalent of salt added corresponds to 1.0 μL of the salt solution. The chemical shift of the tris-TEG aromatic *ortho*-proton was monitored for receptors **1a** and **1b** to ensure consistency. 17 data points corresponding to 0.0, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20.0, 25.0, 30.0, 40.0, 50.0, 60.0, 80.0, 100.0 and 120.0 equivalents of added guest anion were obtained.

The binding of anions with receptors **1a** and **1b** were found to be fast on the NMR timescale. The values of the observed chemical shift and concentration of anion were entered into the WinEQNMR2[7] computer programme for every titration point. From initial estimates made of the binding constants and limiting chemical shifts, these parameters were refined using non-linear least-squares analyses to obtain the best fit between empirical and calculated chemical shifts based on a 1:1 binding stoichiometry. The input parameters were varied till convergence of the best fit values of the binding constants and their errors were obtained. Despite the dicationic nature of the receptors, a 1:1 binding stoichiometry was found with the anions (all investigated are singly charged except for sulfate).

S2.2 ^{1}H NMR titration data for Receptors 1a and 1b

All titrations were carried out in D_2O at 298 K unless otherwise stated. In Figures S2-1, S2-2 and S2-4, empirical data points are represented by the filled dots, while continuous lines represent the calculated binding curves.

Hydrogen-bonding Receptor **1a**

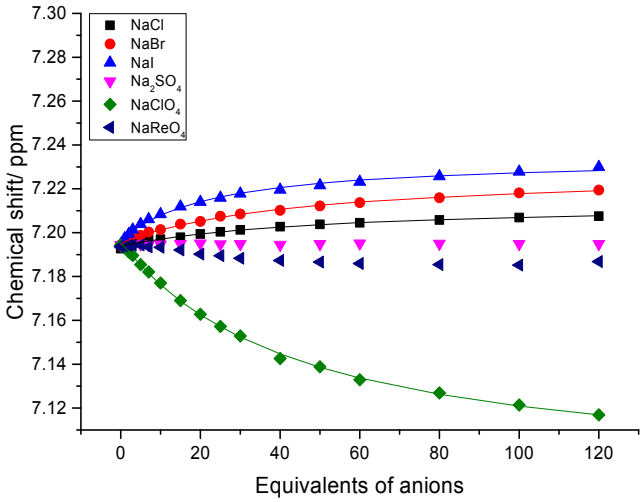


Figure S2-1. Plot of chemical shift of tris-TEG aromatic *ortho*-proton of hydrogen-bonding receptor **1a** against equivalents of anions added in D_2O (500 MHz, T = 298 K). The triazolium protons were not followed as they are highly acidic and found to undergo quick deuterium exchange with D_2O during the NMR titration experiment.

Halogen-bonding Receptor **1b**

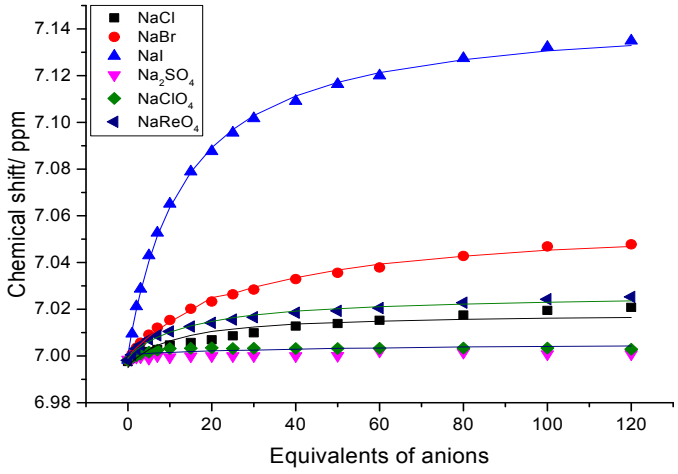


Figure S2-2. Plot of chemical shift of tris-TEG aromatic *ortho*-proton of hydrogen-bonding receptor **1b** against equivalents of anions added in D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K). Although ReO_4^- showed an overall smaller perturbation of the proton signal than I^- and Br^-, saturation (and hence

plateauing) of the ReO_4^- binding isotherm was observed in the presence of c.a. 80 equivalents of anion, while flattening of the binding curve did not occur for Br^- and I^- even at 120 equivalents.

S2.3 Control ^{1}H NMR Titration of Receptor 1a with $NaNO_3$

To confirm that the nitrate anion is non-coordinating, anion exchange of receptor **1a** to the hexafluorophosphate (PF_6^-) salt was performed using an Amberlite® column pre-loaded with ammonium hexafluorophosphate. A solution of **1a.2PF$_6$** in D_2O (1.5 mM) was prepared, and a ^{1}H NMR titration was performed with $NaNO_3$ using an identical protocol as described above.

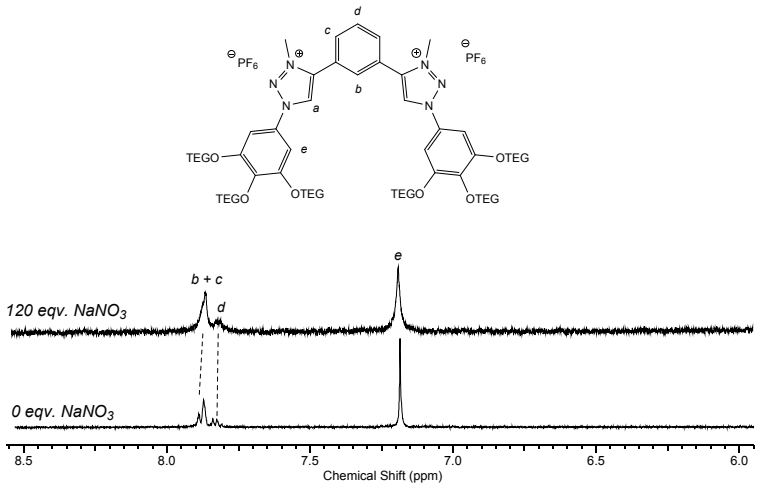


Figure S2-3. Partial NMR spectrum of the titration of **1a.2PF$_6$** with $NaNO_3$ in D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K). No significant perturbation of the H_e signal was observed even after 120 equivalents of $NaNO_3$.

S2.4 ^{1}H NMR Titration of Receptor 1b with $NaReO_4$ in 10 mM HEPES solution (pD = 7.4)

To investigate whether the presence of a dissolved buffer will influence the binding properties of receptor **1b** with $NaReO_4$ in D_2O, an analogous ^{1}H NMR titration experiment was performed. Analysis of the data with the WinEQNMR2 software (1:1 binding) gave an association constant of 45 $\pm$ 4 M^{-1}, which is consistent with that obtained in pure D_2O (Table 1, main paper).

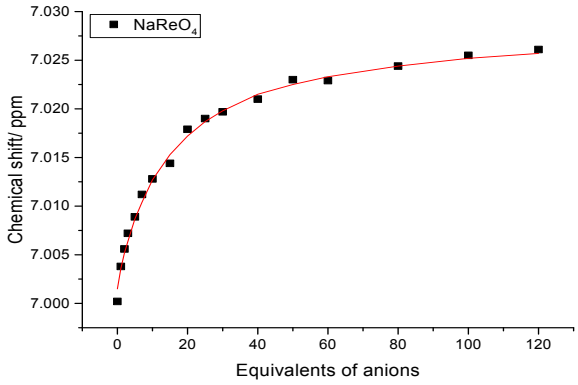


Figure S2-4. Plot of chemical shift of tris-TEG aromatic *ortho*-proton of hydrogen-bonding receptor **1b** against equivalents of $NaReO_4$ added in 10 mM HEPES solution in D_2O (pD = 7.4, [host] = 1.5 mM, 500 MHz, T = 298 K).

S2.5 VT NMR studies

VT NMR studies of Receptor **1b** with $NaReO_4$

^1H NMR titrations of **1b** with $NaReO_4$ in D_2O were performed at four different temperatures (T = 298, 308, 318 and 338 K).

Table S1. Association constants K_a (M^{-1}) of Receptor 1b with $NaReO_4$ at different temperatures.

T / K	K_a (M^{-1})
298	44(2)
308	38(3)
318	34(3)
338	24(2)

[a] 1:1 association constants were calculated from ^1H NMR titrations in D_2O using the WinEQNMR2 software.[7] Errors < 10 % ([host] = 1.5 mM).

A van't Hoff analysis was performed by plotting $R\ln K_a$ against $1/T$. The values of ΔH and ΔS were obtained from the gradient and the ordinate intercept of the best-fit line according to the following equation:

$$R\ln K_a = -\frac{\Delta H}{T} + \Delta S$$

VT NMR studies of Receptor **1a** with $NaReO_4$

A VT NMR titration was performed with receptor **1a** at 318 K in pure D_2O. As seen from **Figure S2-5** below, no binding was observed at 120.0 equivalents of $NaReO_4$.

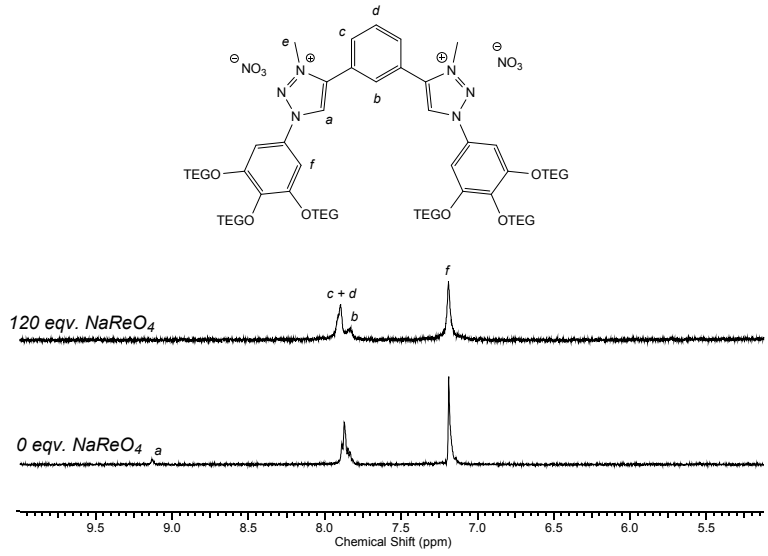


Figure S2-5. Partial NMR spectrum of the titration of **1a.2PF$_6$** with $NaNO_3$ in D_2O ([host] = 1.5 mM, 500 MHz, T = 318 K).

S3. Perrhenate Binding Studies by Luminescence Spectroscopy

Luminescence titrations were performed using a HORIBA Fluorolog, and the data was processed using the FluorEssence software. For each titration, 2.0 mL of a 10 μM solution of the receptor (**1a** or **1b**) was used initially in a 10 mM HEPES solution in water (pH = 7.4). $NaReO_4$ was dissolved in a 10 μM solution of the receptor in 10 mM HEPES so that the concentration of the receptor remains constant throughout the titration. The $NaReO_4$ solution was added in known aliquots using a microliter syringe, and the sample was thoroughly shaken before the spectra was recorded. An excitation wavelength of λ_{ex} = 320 nm was used for both receptors **1a** and **1b**.

S4. References

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