Supplementary Information

Selective Recognition of Tetrahedral Dianions by a Hexaaza Cryptand Receptor

Pedro Mateus,[a] Rita Delgado,[a,b]* Paula Brandão,[c] Sílvia Carvalho[d] and Vítor Félix[d]

[a]*Instituto de Tecnologia Química e Biológica, UNL, Av. da República – EAN, 2780–157 Oeiras, Portugal. Fax: (+351) 21 441 12 77, e-mail: delgado@itqb.unl.pt.* [b]*Instituto Superior Técnico, DEQB, Av. Rovisco Pais, 1049–001 Lisboa, Portugal.* [c]*Departamento de Química, CICECO, Universidade de Aveiro, 3810–193 Aveiro, Portugal,* [d]*Departamento de Química, CICECO and Secção Autónoma de Ciências da Saúde, Universidade de Aveiro, 3810–193 Aveiro, Portugal.*

Contents: Figures and Tables not shown in the main text **Page**

Fig. S1	^{1}H and ^{13}C NMR spectra of the hexaimine in $CDCl_3$.	S2
Fig. S2	HMQC spectra of the hexaimine in $CDCl_3$.	S2
Fig. S3	^{1}H and ^{13}C NMR spectra of xyl in $CDCl_3$.	S3
Fig. S4	COSY spectra of xyl in $CDCl_3$.	S3
Fig. S5	HMQC spectra of xyl in $CDCl_3$.	S4
Fig. S6	NOESY spectra of xyl in $CDCl_3$.	S4
Fig. S7	ESI mass spectra of xyl in MeOH.	S5
Fig. S8	^{1}H NMR spectra of solutions of the H_6xyl$(TsO)_6$ receptor (A) and of the receptor with each anionic substrate in equimolar amounts, Cl^- (B), NO_3^- (C), AcO^- (D), $H_2PO_4^-$ (E) and SO_4^{2-} (F), respectively, in D_2O at pD = 3.80 and 298.2 K.	S5
Fig. S9	ESI mass spectra of a solution of 1:1 receptor to sulfate stoichiometry in H_2O/MeOH (50:50 v/v) at pH = 3.80.	S5
Fig. S10	ESI mass spectra of a solution of 1:1:1 receptor/sulfate/nitrate stoichiometry in H_2O/MeOH (50:50 v/v) at pH = 3.80.	S6
Fig. S11	Evolution of the six S···N distances over 15 ns long simulation	S6
Fig. S12	Rdfs for O–H···C_N and O–H···Cl distances between the water (blue) and methanol (in red) molecules and the centre of mass of the receptor (left) and the anion (right). The Rdfs were calculated over the 15 ns of simulation.	S6
Table S1	Stepwise protonation (K_i^H) constants of the anions in H_2O/MeOH	S7

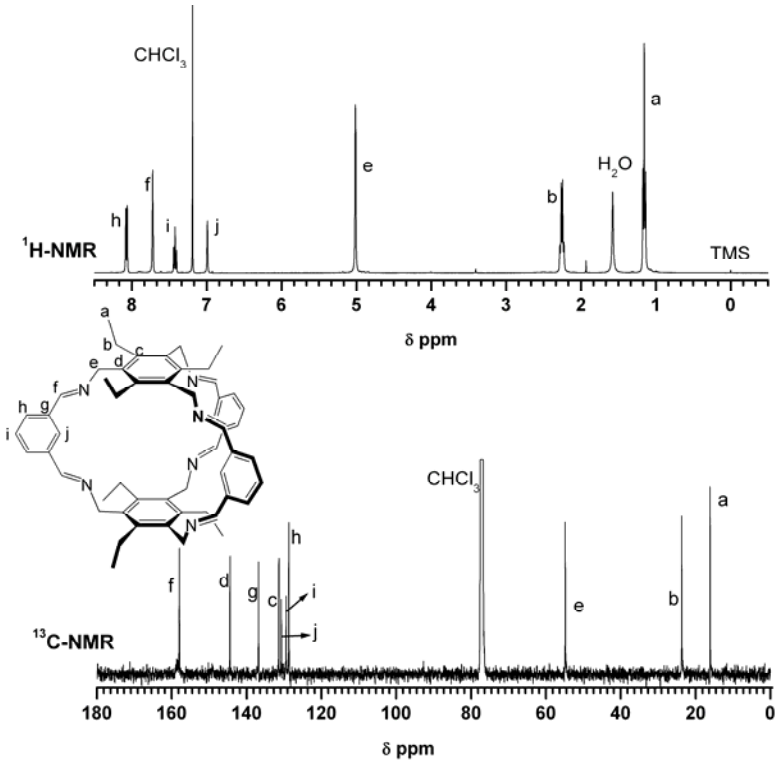

Fig. S1 ^{1}H and ^{13}C NMR spectra of the hexaimine in $CDCl_3$.

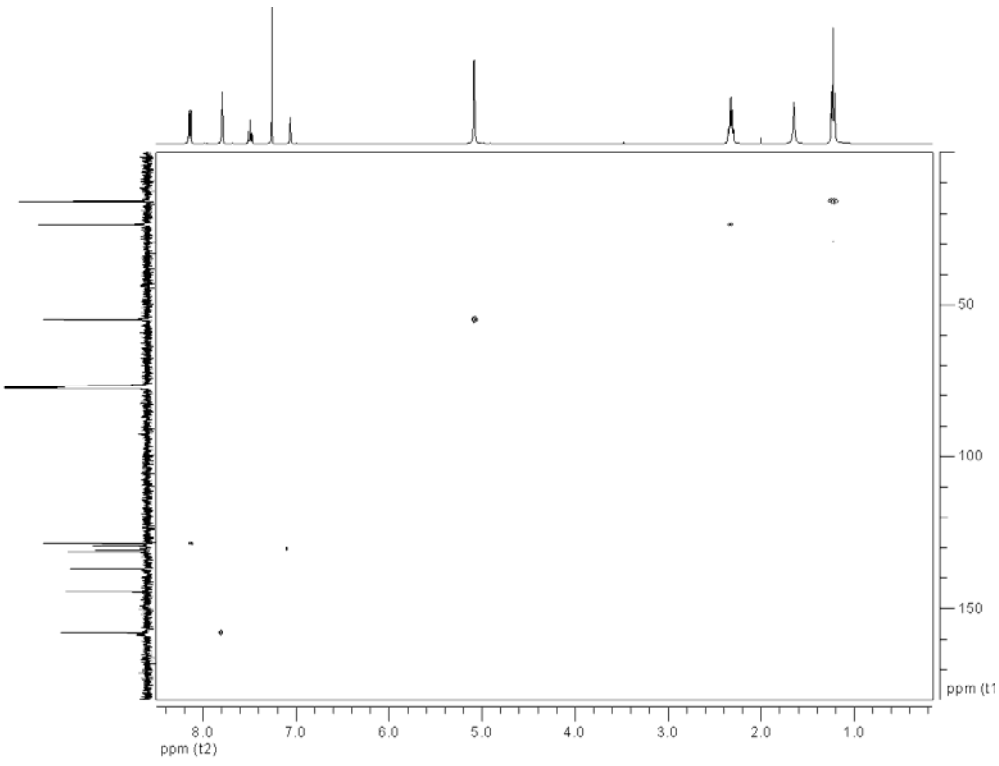

Fig. S2 HMQC spectra of the hexaimine in $CDCl_3$.

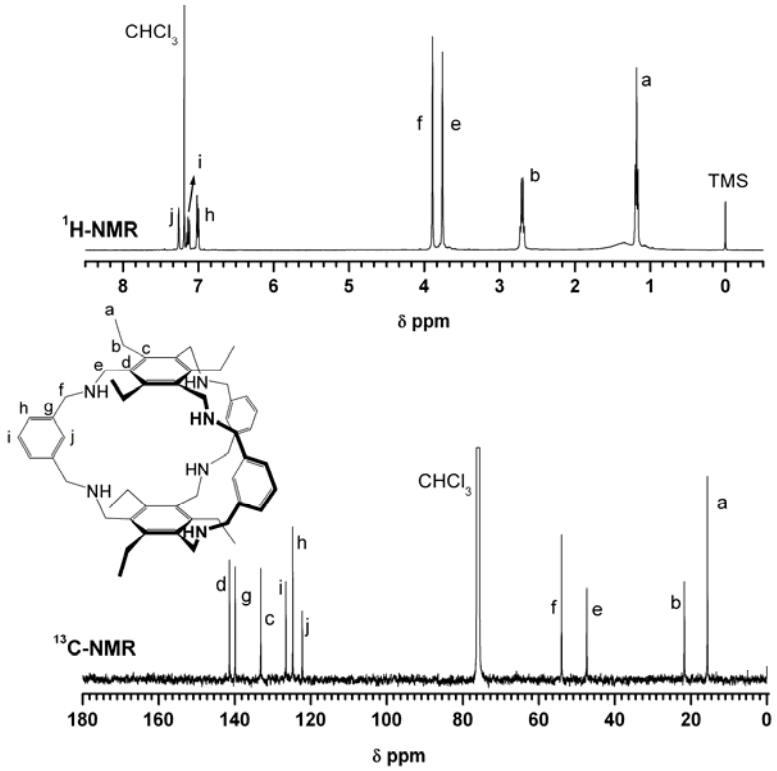

Fig. S3 ^{1}H and ^{13}C NMR spectra of xyl in $CDCl_3$.

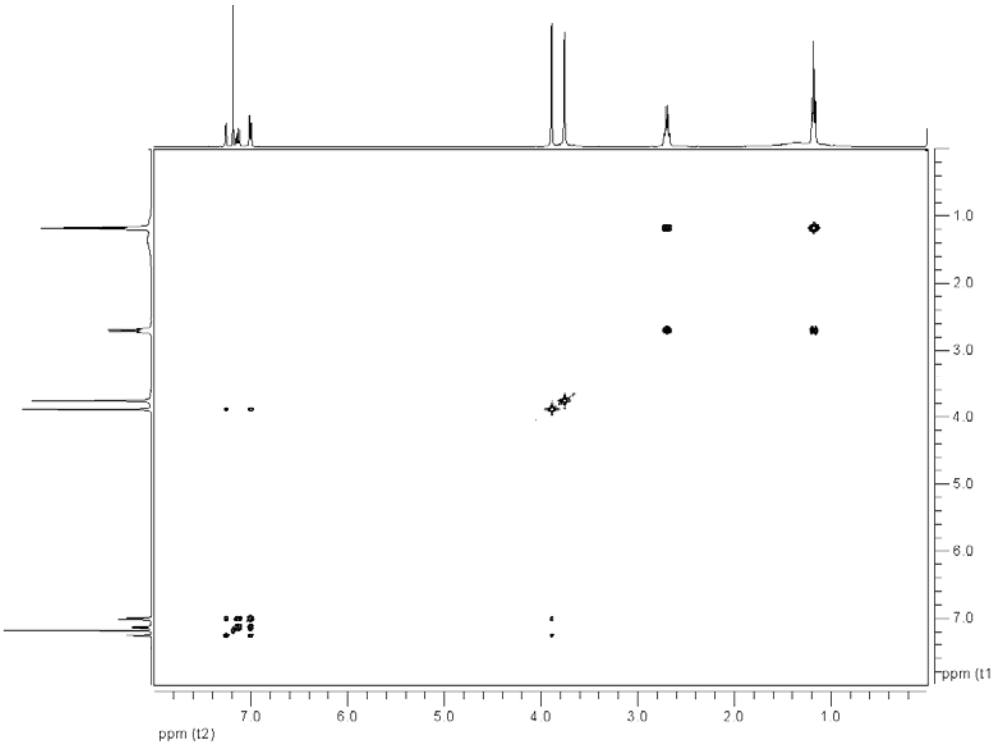

Fig. S4 COSY spectra of xyl in $CDCl_3$.

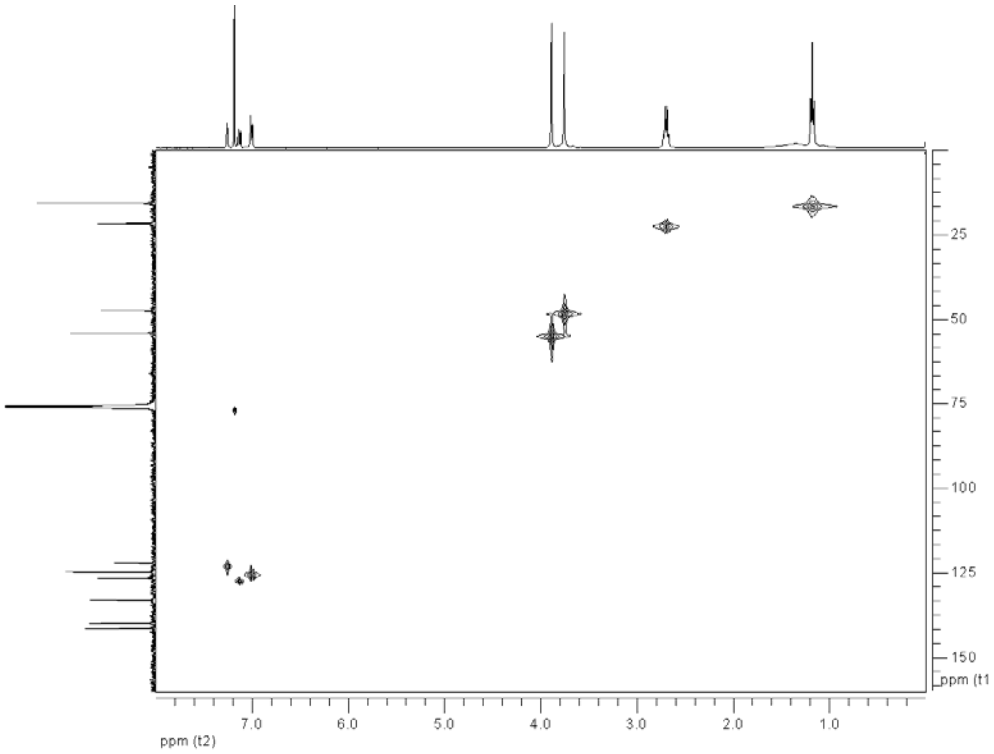

Fig. S5 HMQC spectra of xyl in $CDCl_3$.

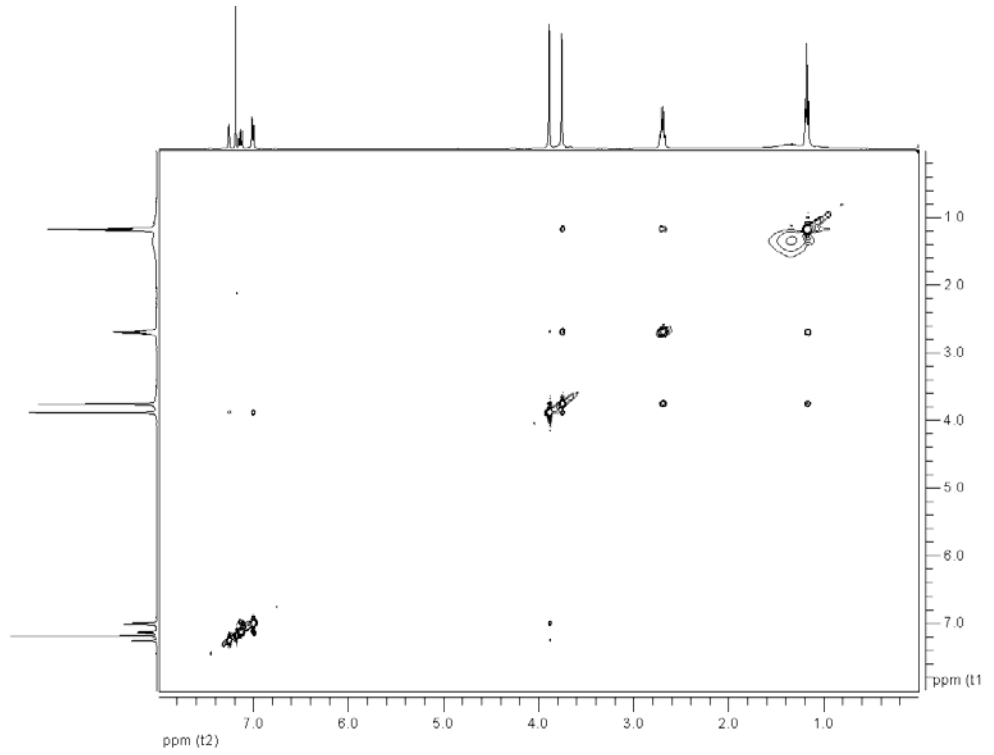

Fig. S6 NOESY spectra of xyl in $CDCl_3$.

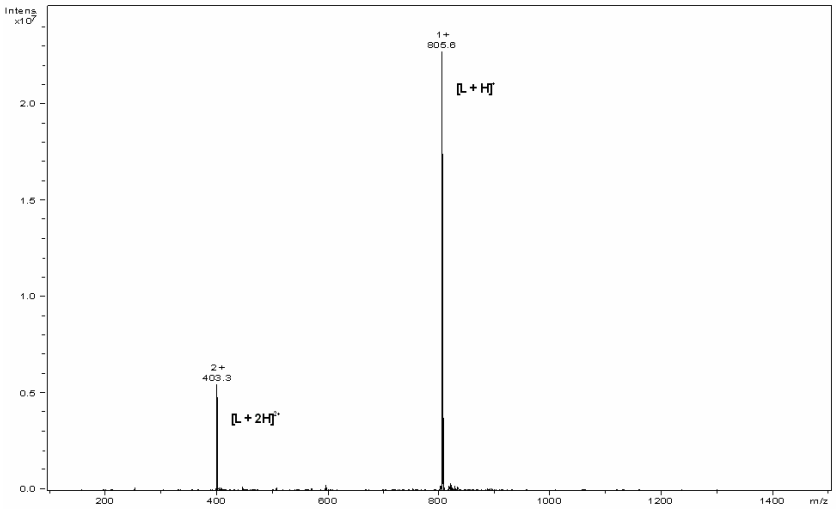

Fig. S7 ESI mass spectra of xyl in MeOH.

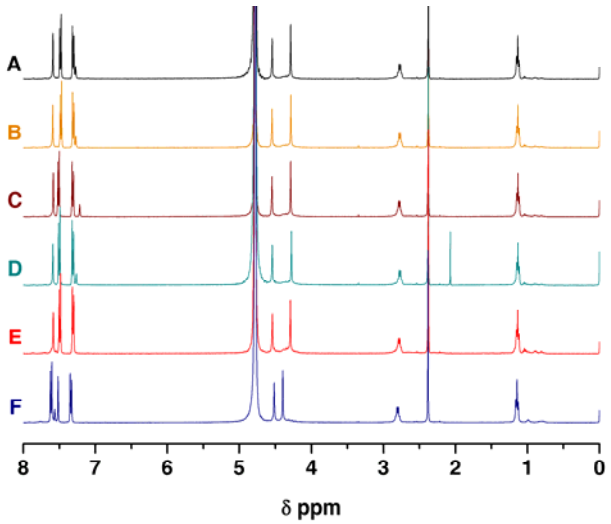

Fig. S8 ^{1}H NMR spectra of solutions of the H_6xyl$(TsO)_6$ receptor (A) and of the receptor with each anionic substrate in equimolar amounts, Cl^- (B), NO_3^- (C), AcO^- (D), $H_2PO_4^-$ (E) and SO_4^{2-} (F), respectively, in D_2O at pD = 3.80 and 298.2 K.

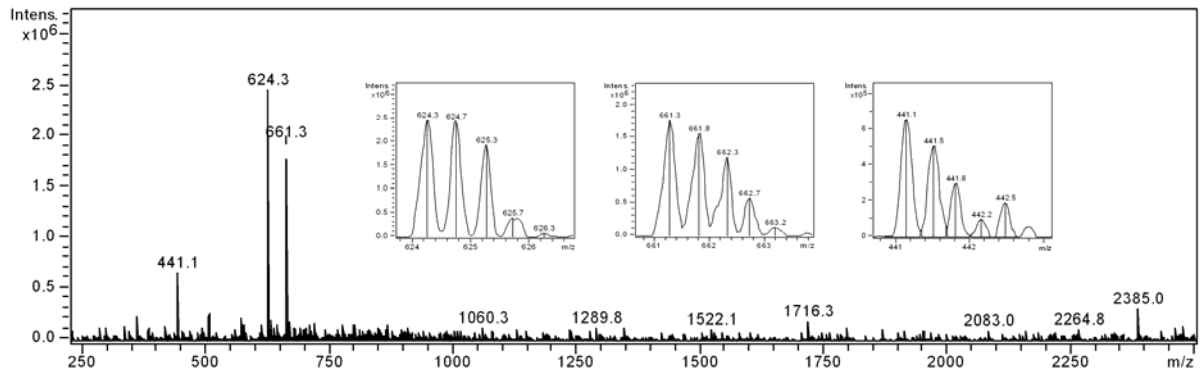

Fig. S9 ESI mass spectra of a solution of 1:1 receptor to sulfate stoichiometry in H_2O/MeOH (50:50 v/v) at pH = 3.80.

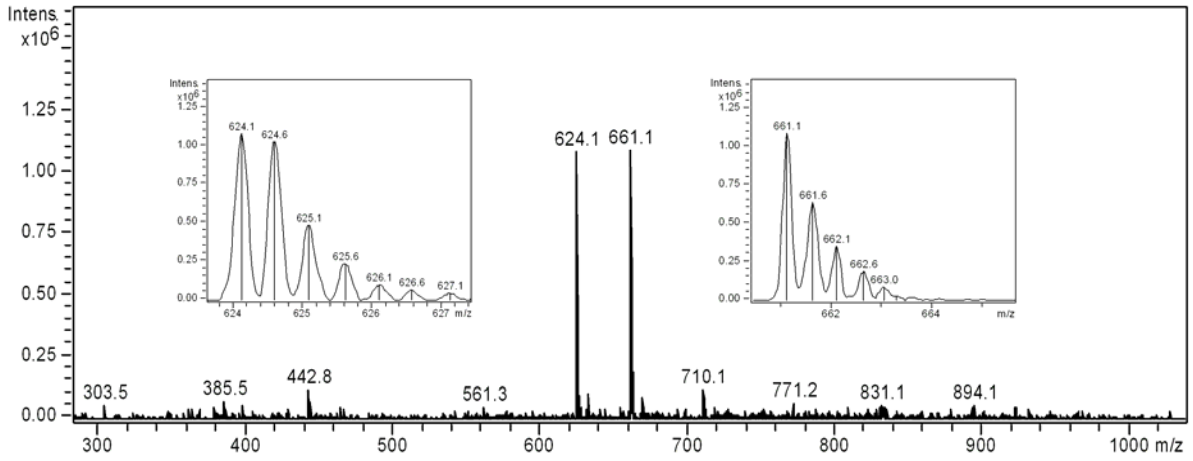

Fig. S10 ESI mass spectra of a solution of 1:1:1 receptor/sulfate/nitrate stoichiometry in H_2O/MeOH (50:50 v/v) at pH = 3.80.

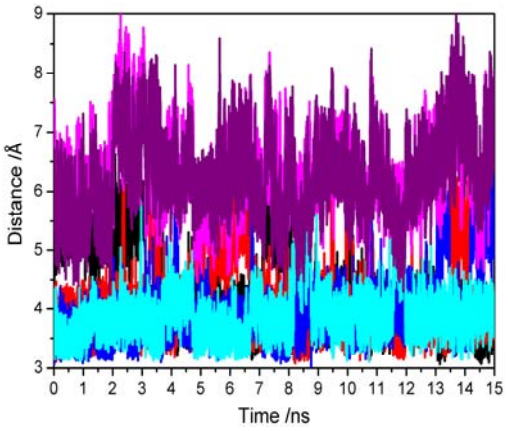

Fig. S11 Evolution of the six S···N distances over 15 ns long simulation

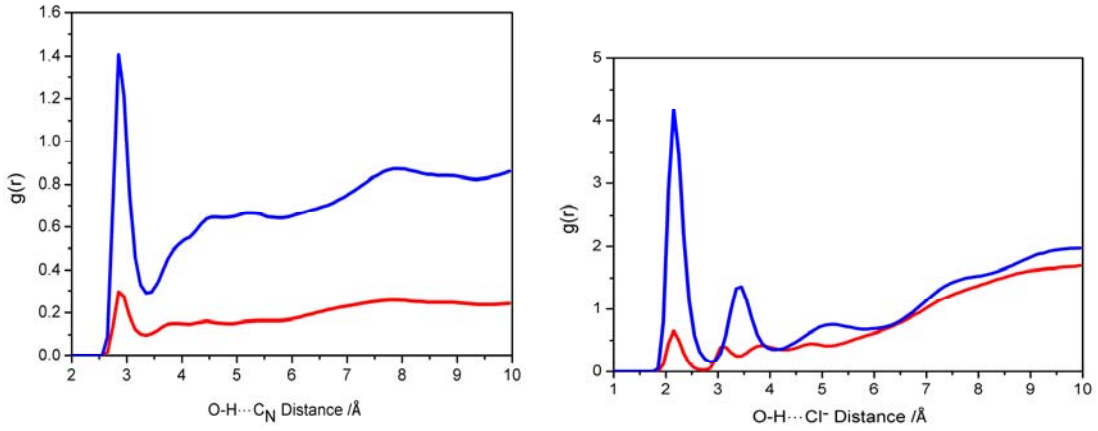

Fig. S12 Rdfs for O–H···C_N and O–H···Cl distances between the water (blue) and methanol (in red) molecules and the centre of mass of the receptor (left) and the anion (right). The Rdfs were calculated over the 15 ns of simulation.

Table S1 Stepwise protonation (log K_i^H) constants of the anions in H_2O/MeOH (50:50 v/v); T = 298.2 ± 0.1 K; I = 0.10 ± 0.01 mol dm^{-3} in KTsO.

Equilibrium quotient[a]	SO_4^{2-}	SeO_4^{2-}	$S_2O_3^{2-}$	AcO^-	PO_4^{3-}
[HA]/[A][H]	2.51(1)	2.36(1)	2.04(1)	5.28(1)	n.d.[b]
$[H_2A]/[HA][H]$	–	–	–	–	7.46(1)
$[H_3A]/[H_2A][H]$	–	–	–	–	2.82(1)

[a] A is the anion. [b] Too high to be accurately determined by potentiometry