Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Supramolecular Forces and Their Interplay in Stabilizing Complexes of Organic Anions: Tuning Binding Selectivity in Water.

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Table S1. Ligands and anions protonation constants determined at 298.1 ± 0.1 K in 0.1 M NMe_4Cl aqueous solution. Figures in parentheses are standard deviations on the last significant figure.

Equilibrium	***log K***
$H^+ + L1 = HL^+$	*4.45(3)*[a]
$H^+ + HL1^+ = H_2L1^{2+}$	*3.45(3)*[a]
$H^+ + L2 = HL^+$	*6.19(1)*[a]
$H^+ + HL2^+ = H_2L^{2+}$	*5.37(1)*[a]
$H^+ + CH_3COO^- = CH_3COOH$	*4.51(1)*
$H^+ + C_6H_5COO^- = C_6H_5COOH$	*4.15(3)*
$H^+ + Pht^{2-} = HPht^-$	*5.10(3)*
$H^+ + HPht^- = H_2Pht$	*2.78(3)*
$H^+ + IPht^{2-} = HIPht^-$	*4.32(1)*
$H^+ + HIPht^- = H_2IPht$	*3.28(1)*

[a] taken from ref. 9.

Table S2. Crystal data and structure refinement for $(H_2L)(HPhthalate)_2{\cdot}2H_2O$ (a), $(H_2L)(HIsophthalate)_2$ (b) and $H_2L2(C_6H_5SO_3)_2{\cdot}H_2O$ (c).

	(a)	(b)	(c)
Empirical formula	$C_{30}H_{40}N_6O_{12}$	$C_{30}H_{36}N_6O_{10}$	$C_{26}H_{38}N_6O_9S_2$
Formula weight	676.68	640.65	642.74
Temperature (K)	100	100	100
space group	*C 2/c*	$P\ 2_1/n$	$P\ na2_1$
a (Å)	27.337(3)	6.8698(1)	15.1627(5)
b (Å)	6.1593(4)	14.4541(3)	6.4915(4)
c (Å)	20.343(2)	14.7842(3)	29.4057(9)
α (°)	90	90	90
β (°)	106.22(1)	95.204(2)	90
γ (°)	90	90	90
Volume (Å^3)	3289.0(5)	1461.97(5)	2894.4(2)
Z	4	2	4
Independent reflections / R(int)	2918 / 0.0476	2719 / 0.0672	4695 / 0.0398
μ (mm^{-1})	0.901/ (Cu-kα)	0.930/ (Cu-kα)	2.222/ (Cu-kα)
R indices [$I>2\sigma(I)$]*	R1 = 0.0466	R1 = 0.0513	R1 = 0.0287
	wR2 = 0.1386	wR2 = 0.1411	wR2 = 0.0741
R indices (all data)*	R1 = 0.0568	R1 = 0.0702	R1 = 0.0311
	wR2 = 0.1599	wR2 = 0.1714	wR2 = 0.0755

* $R1 = \Sigma \,||Fo| - |Fc|| / \Sigma |Fo|$; $wR2 = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma wFo^4]^{½}$

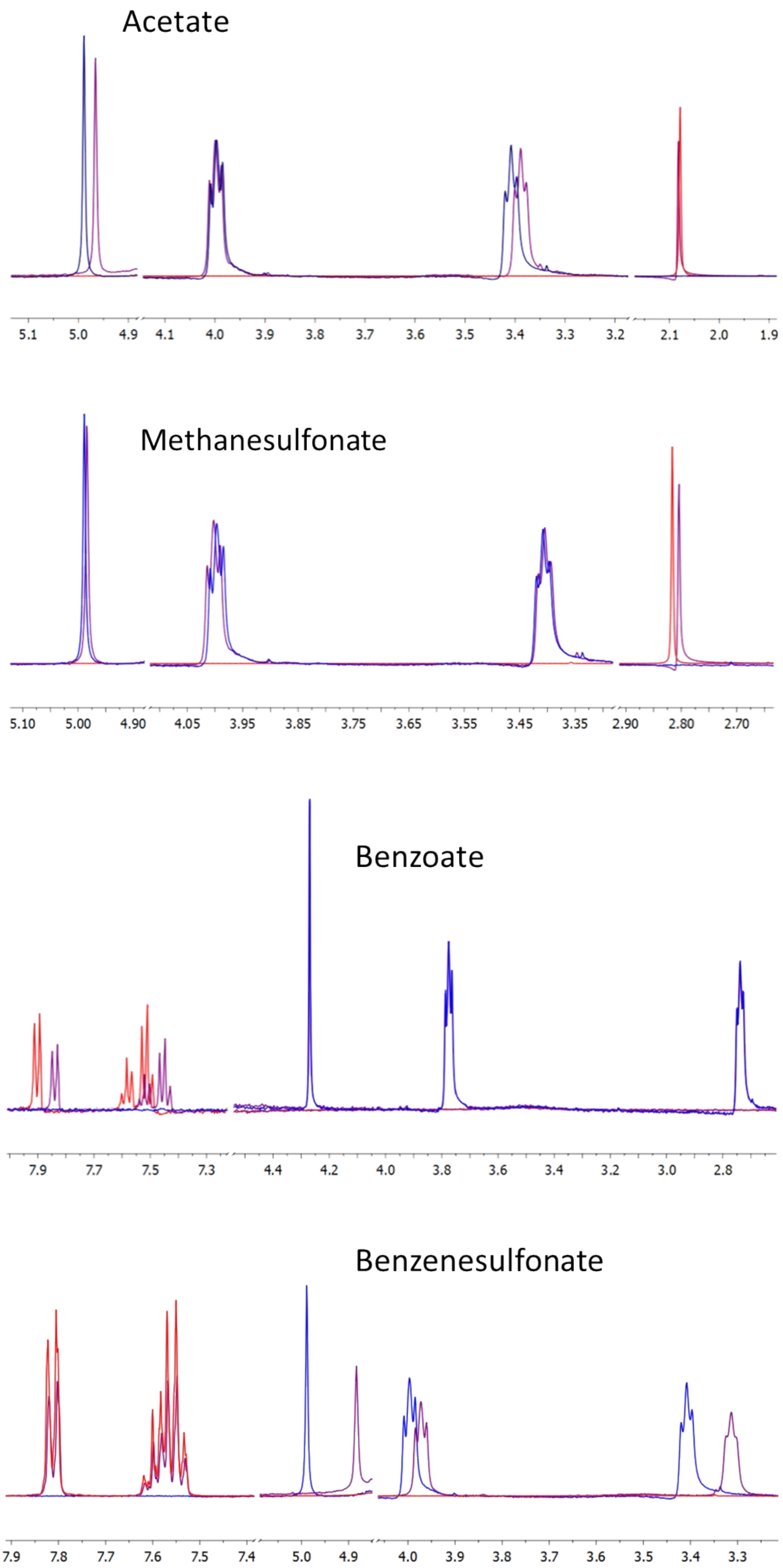

Figure S1. ^{1}H NMR spectra of studied anions with L1. Colour code: blue: L1 only; red: Substrate only; violet: 1:5 L1:Substrate solution. Working pH as reported in Table 4 for each spectrum. Sample concentrations as reported in the Experimental Section.

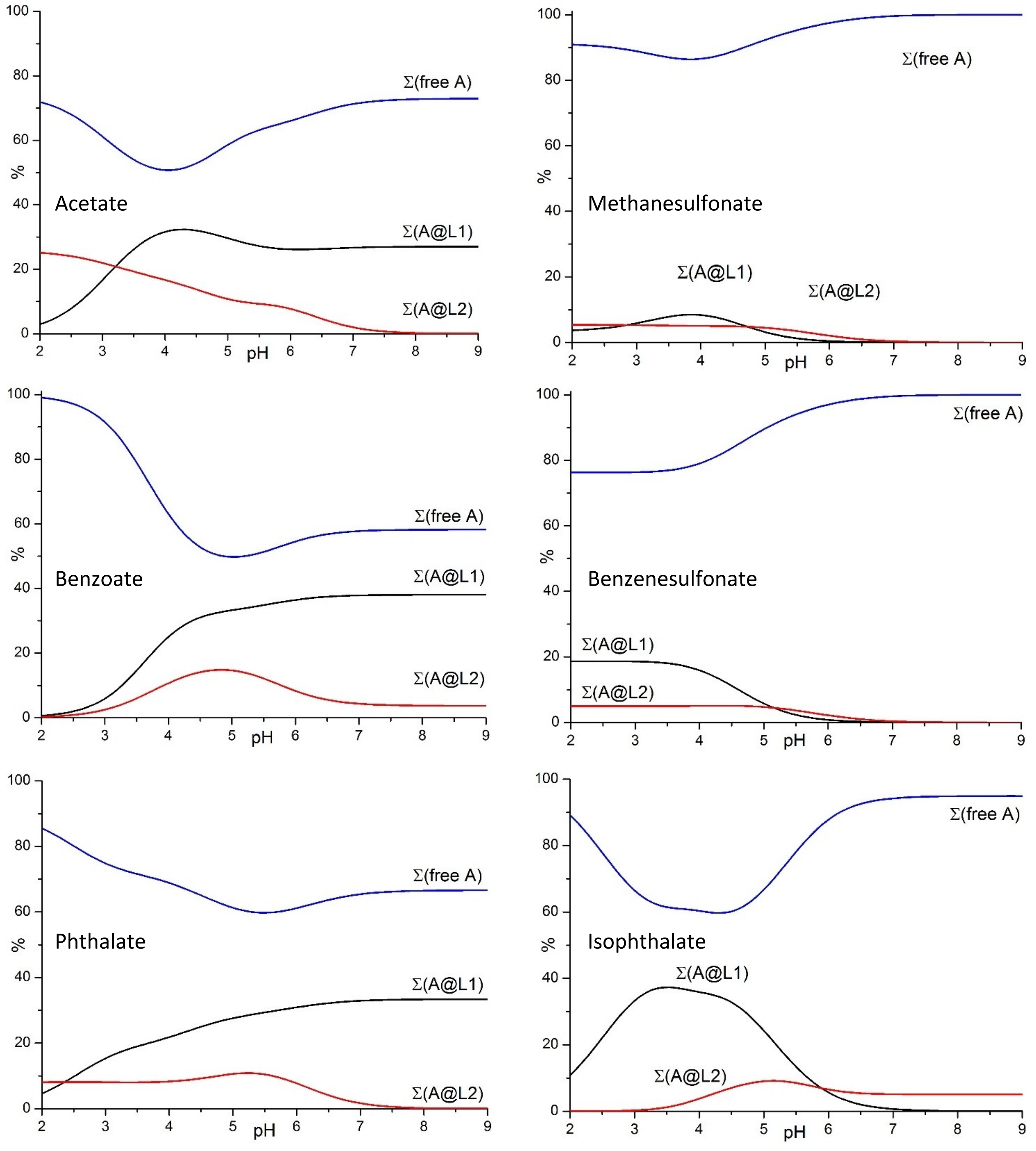

Figure S2. Selectivity diagrams showing the percentage of free and bound anion to each ligand as a function of pH: ΣA@L1 = total abundance (%) of L1-A complexes, ΣA@L2 = total abundance (%) of L2-A complexes (sums run over all the possible complex species reported in Tables 2 and 3, for L1 and L2 respectively). Concentration of all reagents is set to 1 mM. Percentages are referred to total anion concentration.

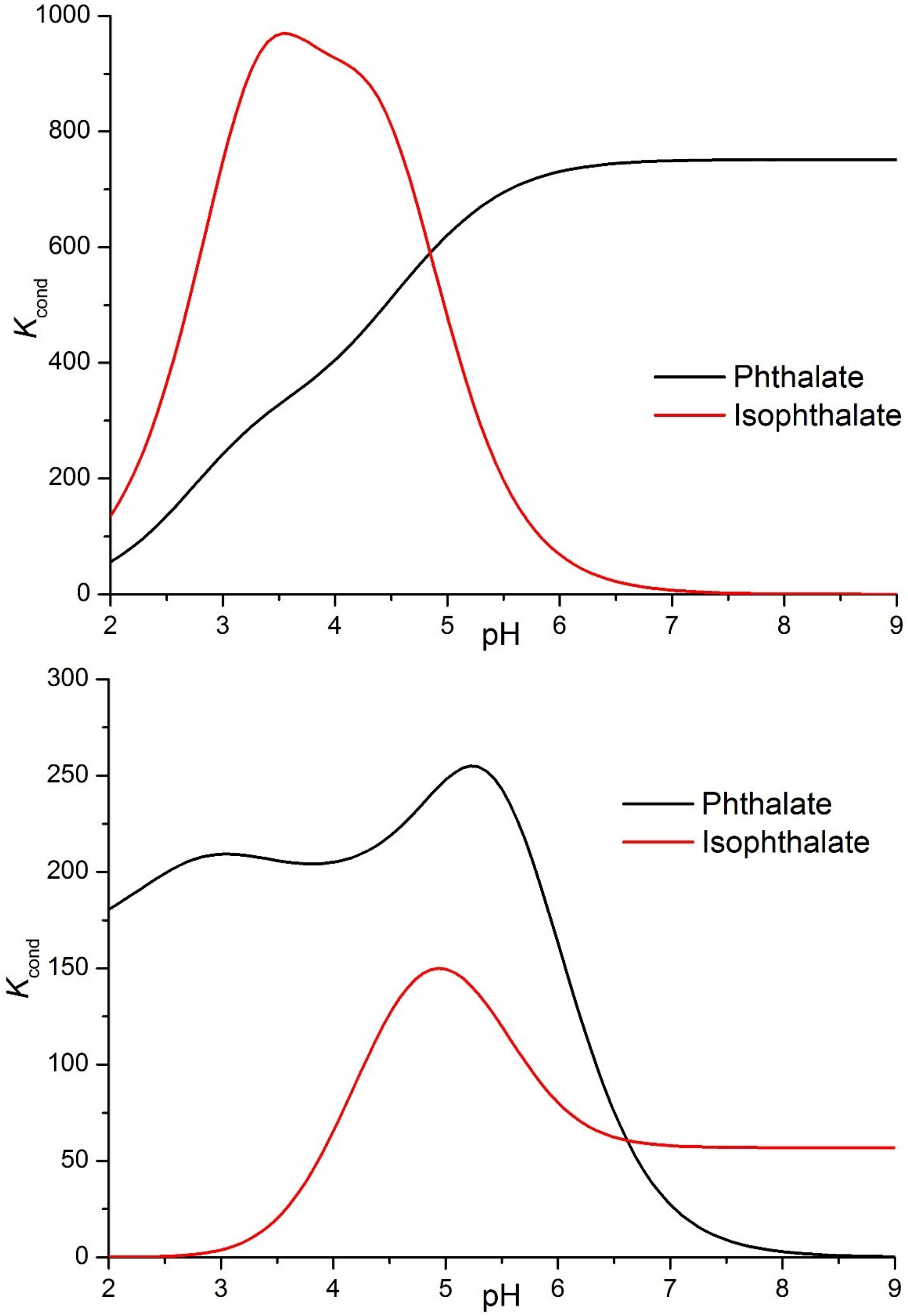

Figure S3. Conditional stability constants for complexes of L1 (top) and L2 (bottom) with phthalate and isophthalate anions. $K_{cond} = \Sigma[H_{i+j}LA]/(\Sigma[H_iL]\times \Sigma [H_jA])$, with *i* and *j* number of acidic protons on the ligand and on the anion, respectively.

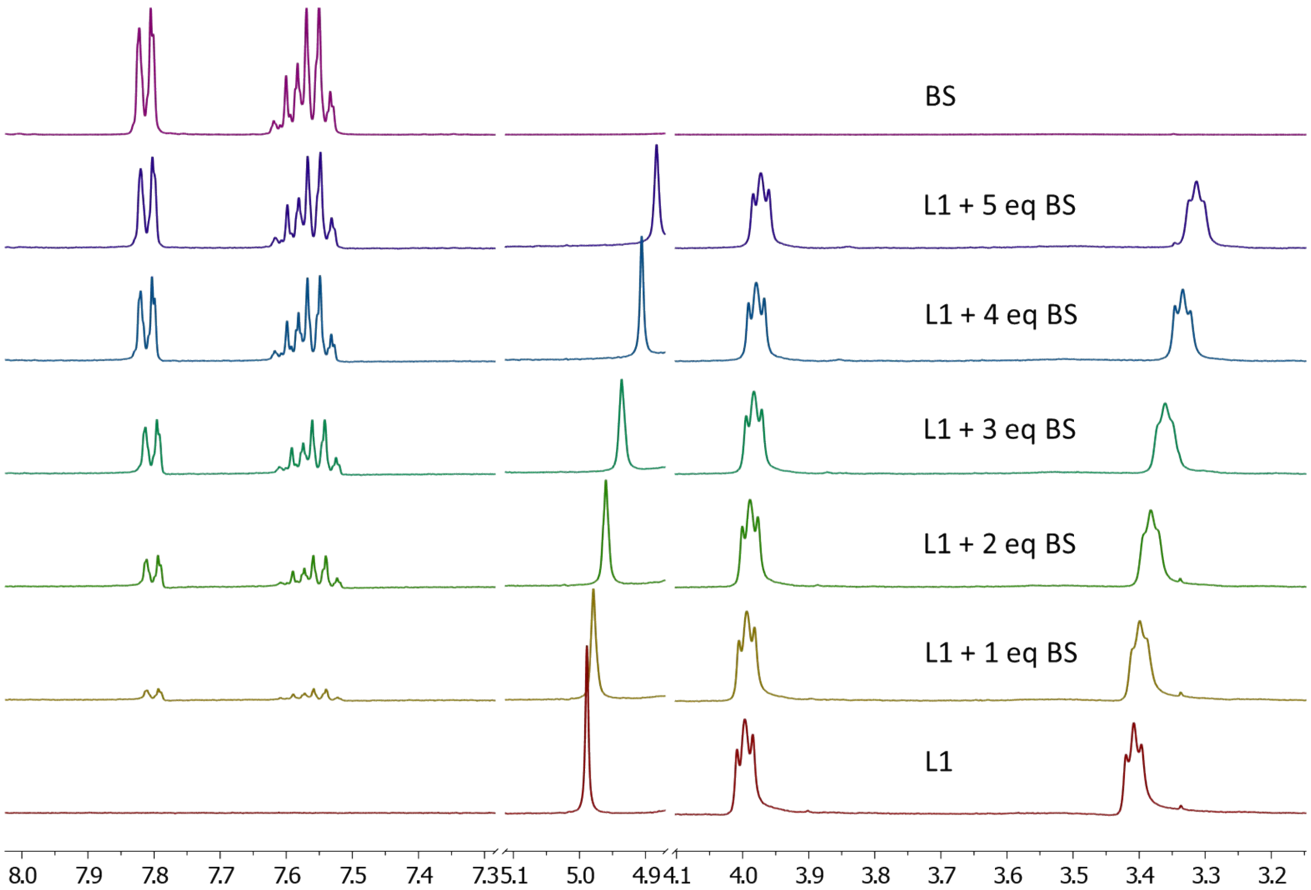

Figure S4. ^{1}H NMR titration performed by adding benzenesulfonate (BS) to L1. Conditions are given in the Experimental Section.