Supporting Information

An anion receptor with NH and OH groups for hydrogen bonds

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Contents

1. Syntheses of receptor 2

Synthesis and physical properties of **2**: A dry Schlenk flask was charged with **1**[1] (0.74 g, 1.2 mmol), CuI (4.5 mg, 0.02 equiv), $PdCl_2(Ph_3P)_2$ (17 mg, 0.02 equiv). The flask was capped with a rubber septum, and degassed with nitrogen and vacuum two times prior to the addition in 25 mL dry Et_3N/THF(3:2) were added to a Schlenk tube. 2-Methyl-but-3-yn-2-ol (0.35 mL, 3.0 equiv) were added to a Schlenk tube by gastight syringe. After charged from rubber septum to cock, the degassed mixture was stirred under nitrogen at 60~61 °C for 15 h. The reaction mixture was cooled to ambient temperature, the catalysts was filtered through celite with CH_2Cl_2 and evaporated. The residue was dissolved in CH_2Cl_2, and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (CH_2Cl_2/ Hexane= 1:2) to give **2** as white solid (0.51 g, 80%) : mp 319-320 °C; IR (KBr): 3354 (OH and NH overlapped), 2214(C≡C), 1160 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 2H; NH), 8.22 (s, 2H), 7.99 (s, 2H), 7.47 (s, 2H), 5.67 (s, 2H, OH), 1.99 (s, 12H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.7, 125.8, 124.9, 124.0, 121.6, 117.3, 104.4, 97.4, 80.1, 77.0, 67.1, 34.8, 32.0. Anal. Calcd for $C_{36}H_{40}N_2O_2$: C, 81.17; H, 7.47; N, 5.21. Found: C, 81.15; H, 7.66; N, 5.31.

2. Binding Studies

Titrations were conducted using the UV-visible spectroscopy ($K_a > 5\times 10^3$ M^{-1}) and ^{1}H NMR spectroscopy ($K_a < 5\times 10^3$ M^{-1}) at 24 ±1 °C.

1) Titrations

a) UV-Visible titration: A stock solution of **2** (2.0×10^{-5} M) in 1% v/v H_2O/CH_3CN (50 mL) was first prepared for the UV/visible titration. Using this solution as a solvent, a stock solution of an anion (0.3-10 mM) was prepared. Small portions of the anion solution were added to the solution of **2** (2.0 mL), and the spectrum was recorded after each addition and 12-15 data points were obtained. Upon addition of the anion solution, the UV/Vis spectra were gradually changed, showing clear isosbestic points at three or four wavelengths as shown below. The association constants (K_a) were determined by nonlinear curve fitting of the titration curves,[2] plotting absorbance at 340 and 385 nm against equivalents of the anion added. All of the titration curves were well fitted to the expression of a 1:1 binding isotherm.

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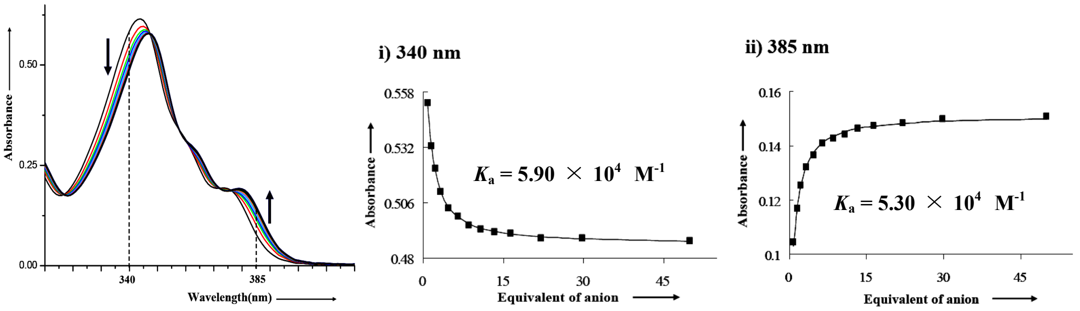
[1] (a) K.-J. Chang, D. Moon, M. S. Lah and K.-S. Jeong, *Angew. Chem. Int. Ed.,* 2005, **44**, 7926-7929; (b) N.-K. Kim, K.-J. Chang, D. Moon, M. S. Lah and K.-S. Jeong, *Chem. Commun.,* 2007, 3401-3403.

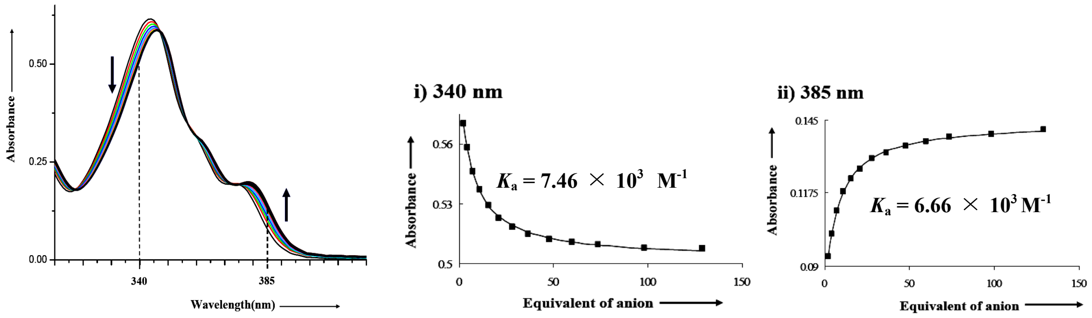
[2] J. R. Long, R. S. Drago, *J. Chem. Edu.* **1982**, *59*, 1037-1089 b) K. A. Connors, *Binding Constants*; John Wiley & Sons: New York, 1987.

b) ^{1}H NMR titration: A stock solution (2.0-3.0 mM) of **1** (or **2**) and a stock solution (9-100 mM) of an anion as a tetrabutylammonium in 1% (v/v) H_2O/CD_3CN (1.5 -2.0 mL) were separately prepared. A 500 μL portion of **1** (or **2**) was transferred to a NMR tube, and an initial NMR spectrum was taken to determine the initial chemical shift of free host. Aliquots of the anion solution were added to the solution of **1** (or **2**) and the spectrum was recorded after each addition. The association constants (K_a) were determined by using the non-linear least squares fitting of the titration curves plotting the chemical shift changes of the host NH, OH, and/or CH signals against the molar equivalent of the anion. All of the titration curves were well fitted to the expression of a 1:1 binding isotherm.

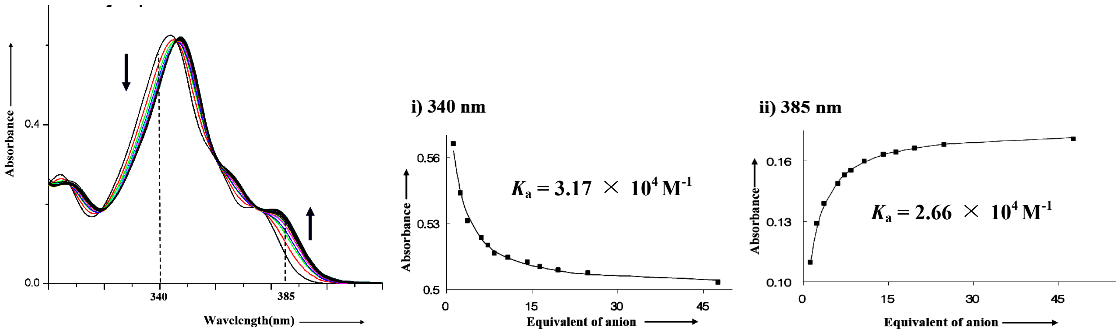
a) **2** + TBA^+Cl^-



b) **2** + TBA^+Br^-



c) **2** + $TBA^+H_2PO_4^-$



d) **2** + TBA^+AcO^-

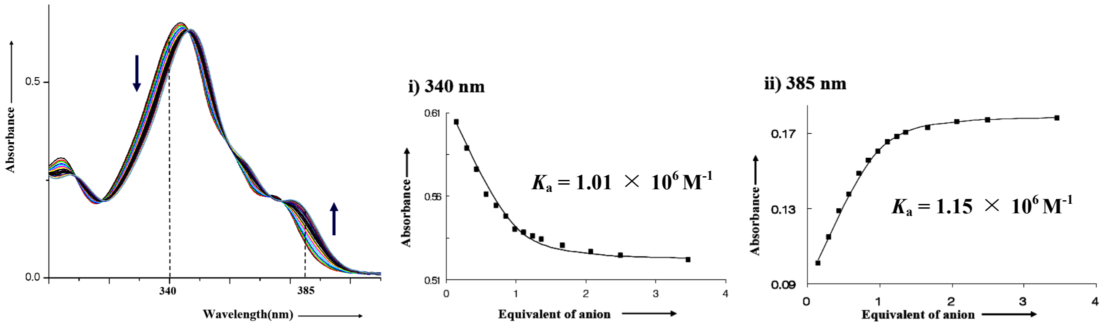
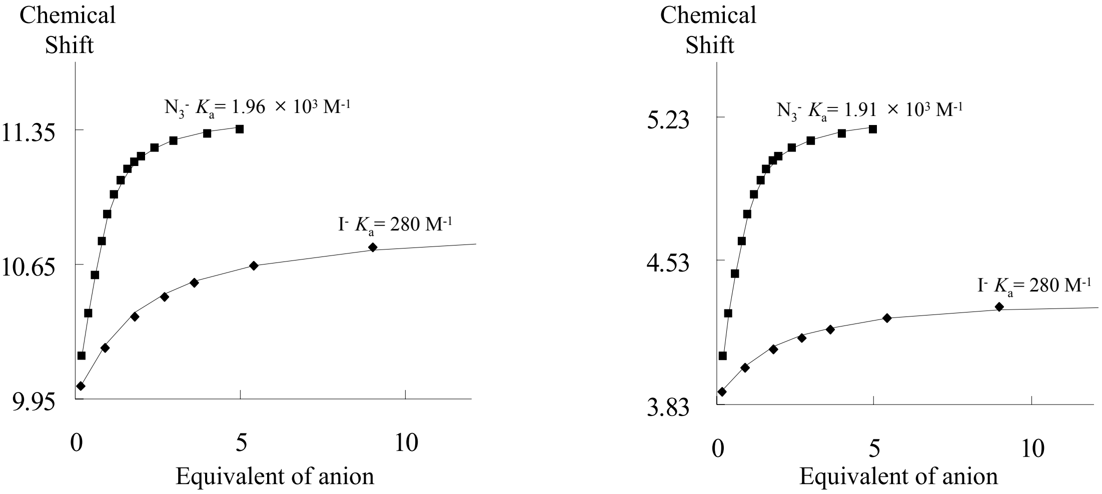
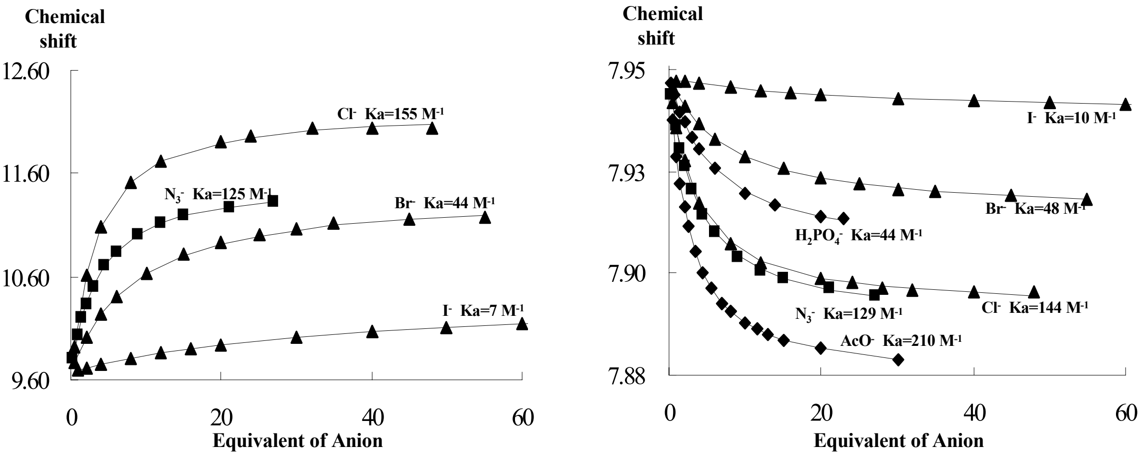


Figure S1. The UV/Vis spectra of **2** upon addition of an anion (left), and experimental (dots) and theoretical (lines) titration curves between **2** and anions (middle, right).


a) NH resonance

b) OH resonance

Figure S2. The ^1H NMR titration curves (dot: experimental, line: theoretical) based on chemical shift changes in the NH and OH signals of **2** (1% H_2O/CD_3CN, 24 ±1 °C).



a) NH resonance

b) CH resonance

Figure S3. Experimental (dots) and theoretical (lines) titration curves between **1** and anions (left: NH peak, right: aromatic CH) in 1% H_2O/CD_3CN at 24 ±1 °C

2) Job's plots:[3]

a) UV/Visible spectroscopy: Stock solutions of host (80 μM) and guest (80 μM) in 1% H_2O/CH_3CN were prepared in separate volumetric flasks. To an UV/visible cell, a total 2.00 mL solution of a host and guest was added in the following ratios:10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 and each other spectrum was recorded. Job's plots were constructed by plotting $[HG]\cdot\alpha$ against mol fraction.

$$A = A_H + A_{HG}$$

Here, A is the observed UV absorbance of the each solution, and A_H and A_{HG} are corresponding to the UV absorbance of the free host and its complex, respectively. According to Beer-Lambert's law and by substituting $\alpha = \frac{\varepsilon_{HG}}{\varepsilon_H} - 1 = \frac{\Delta\varepsilon_{HG}}{\varepsilon_H}$, the above equation becomes

$$[HG]\alpha = \frac{A}{b\varepsilon_H} - [H]_0$$

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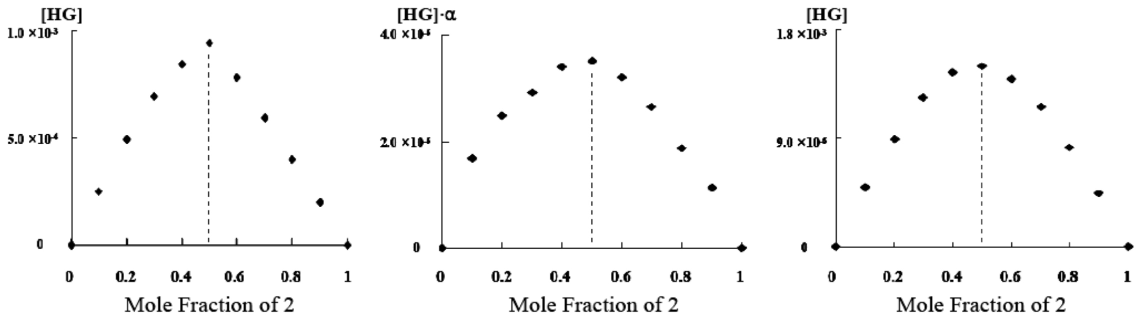
[3] K. A. Connors, *Binding Constants*; John Wiley & Sons: New York, 1987.

b) ^{1}H NMR spectroscopy: Stock solutions of host (2.0 mM) and guest (2.0 mM) in 1% H_2O/CH_3CN (5.0 mL) were prepared in separate volumetric flasks. Ten 5mm-o.d. NMR tubes were separately filled with total 500 μL solution of the host and guest in the following ratios (μL, host/guest) at 297±1 K: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. The ^{1}H NMR spectra were obtained for each tube and the host NH signal was used to calculate the complex concentration, $[HG] = [H]_t \times (\delta_{obsd} - \delta_{free})/(\delta_{com} - \delta_{free})$. This value was plotted again the mole fraction**.**


a) **2** + TBA^+Cl^-

b) **2** + $TBA^+H_2PO_4^-$

c) **2** + $TBA^+N_3^-$

Figure S4. Job's plots between **2** and $Bu_4N^+Cl^-$ (^{1}H NMR), $Bu_4N^+H_2PO_4^-$ (UV/vis), and $Bu_4N^+N_3^-$ (^{1}H NMR)

3. X-ray crystallographic Analysis

X-ray crystallographic analysis of [(tetrabutylammonium)$_2$(**2**Cl)$_2$]·0.5(methylene chloride): A crystal freshly harvested from the mother liquor was coated with paratone oil and the diffraction data were collected at 173 K with a Bruker Smart CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using SMART and SAINT software packages.[4] Empirical absorption corrections were applied by use of SADABS program.[5] The crystal structure was solved by direct method and refined by full-matrix least-squares calculations with SHELXTL-PLUS software package. [6]

Crystal data: $C_{52.25}H_{76.5}Cl_{1.5}N_3O_2$, fw = 831.84 g mol^{-1}, triclinic, space group P-1, a =16.103(2), b = 17.066(2), c = 22.027(3) Å, α = 112.499(2)°, β = 90.721(3)°, γ = 111.326(2)°, V = 5128.2(13) Å^3, T = 173(2) K, Z = 4, μ(Mo Kα, λ = 0.71073 Å) = 0.140 mm^{-1}, 26506 reflections were collected, 17623 were unique [R_{int} = 0.0229]. Two **2**s, two chlorides, two tetrabutylammonium cations, and a methylene chloride of a half occupancy were found as an asymmetric unit. Some electron densities around a crystallographic inversion center were found in a difference Fourier map and assigned as a non-coordinating methylene chloride molecule with a half occupancy. All non-hydrogen atoms except the minor occupancy sites of a tert-butyl group of **2** and a tetrabutylammonium cation were refined anisotropically; all hydrogen atoms involved in hydrogen bonds could be found in a difference Fourier map and were refined with assigned isotropic displacement coefficients U(H) = 1.2 (N) or 1.5U (O), while the remaining hydrogen atoms were allowed to ride on their respective atoms with assigned isotropic displacement coefficients U(H) = 1.2 (C) or 1.5U (C_{methyl}). The disordered tert-butyl group and the disordered parts of the tetrabutyl-ammonium cation were restrained in ideal geometries during the least squares refinement. Refinement of the structure converged at a final R1 = 0.0655, wR2 = 0.1571 for 12486 reflections with I > 2σ(I), R1 = 0.0921, wR2 = 0.1708, GOF = 1.042 for all 26506 reflections. The largest difference peak and hole were 0.669 and -0.443 e·Å^{-3}, respectively.

X-ray crystallographic analysis of [(tetrabutylammonium)$_2$(**2**H_2PO_4)$_2$]·3(methylene chloride): A crystal freshly harvested from the mother liquor was coated with paratone oil. The diffraction data were measured at 89 K with synchrotron radiation (λ = 0.70000 Å) on a 4AMXW ADSC Quantum-210 detector with a Pt-coated Si double crystal

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[4] SMART and SAINT, *Area Detector Software Package and SAX Area detector Integration Program*; Bruker Analytical X-ray: Madison, WI, **1997**.

[5] SADABS, Area Detector Absorption Correction Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

[6] G. M. Sheldrick, *SHELXTL–PLUS*, *Crystal Structure Analysis Package*; Bruker Analytical X-ray, Madison, WI, **1997**.

monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (Ver. 0.98.694)[7] was used for data collection, cell refinement, reduction, and absorption correction. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.

Crystal data: $C_{107}H_{162}Cl_6N_6O_{12}P_2$, fw = 1999.07 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 15.618(3), b = 25.838(5), c = 30.105(5) Å, β = 101.50(3)°, V = 11905(4) Å^3, T = 90(2) K, Z = 4, μ(Mo Kα, λ = 0.70000 Å) = 0.226 mm^{-1}, 80737 reflections were collected, 21000 were unique [R_{int} = 0.0595]. Two **2**s, two dihydrogen phosphates, two tetrabutylammonium cations, four disordered methylene chloride sites were found as an asymmetric unit. Refinement of the structure converged at a final R1 = 0.0880, wR2 = 0.2519 for 13091 reflections with $I > 2\sigma(I)$. Although four disordered solvent sites were identified, the PLATON SQUEEZE calculation for the disordered solvent region (2432 Å^3, 20.4% of the crystal volume)[8] shows there are 510 solvent electrons per unit cell, which approximately correspond to three CH_2Cl_2 molecules per formula. The structure refinement after modification of the data led to better refinement and data convergence. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms involved in hydrogen bonding could be found in a difference Fourier map and were refined with assigned isotropic displacement coefficients U(H) = 1.2 (N) or 1.5U (O), while the remaining hydrogen atoms were allowed to ride on their respective atoms with assigned isotropic displacement coefficients U(H) = 1.2 (C) or 1.5U (C_{methyl}). The C-C distances of the minor occupancy sites in a disordered tetrabutylammonium cation were restrained in ideal distance during the least-squares refinement. Refinement of the structure converged at a final R1 = 0.0664, wR2 = 0.1843 for 12812 reflections with $I > 2\sigma(I)$, R1 = 0.0975, wR2 = 0.2006 for all 21000 reflections. The largest difference peak and hole were 0.433 and -0.578 e·Å^{-3}, respectively.

CCDC 674972 and 679730 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

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[7] Z.Otwinowski and W.Minor, In *Methods in Enzymology*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, *Vol.* **276**, *part A*, 1997, pp. 307-326.

[8] A. L. Spek, Acta Crystallogr. Sect. A 1990, **46,** 194-201.

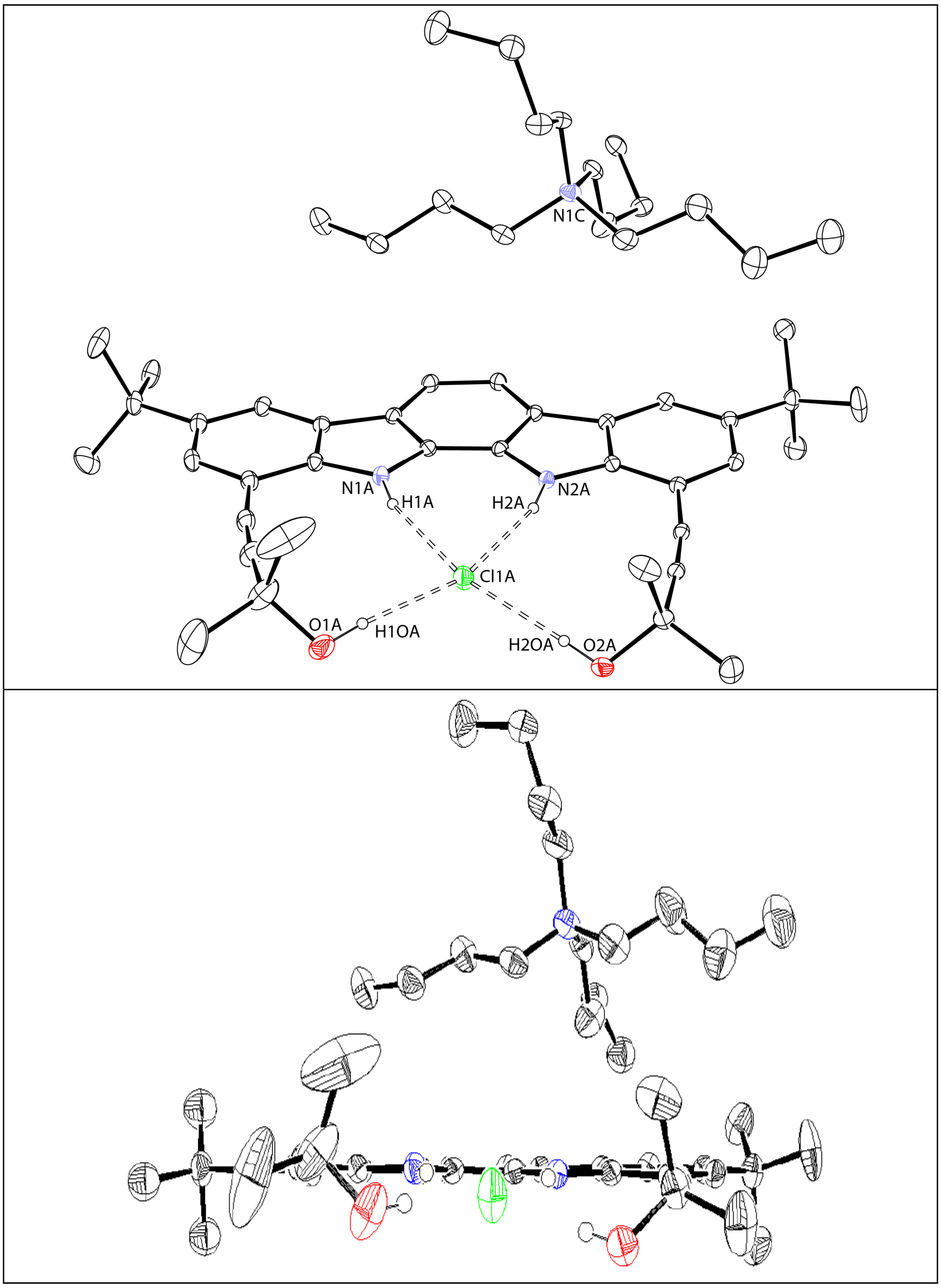

Figure S9 Two different views of ORTEP plots for the crystal structure of **2**·$Bu_4N^+Cl^-$ with 20% probability ellipsoids.

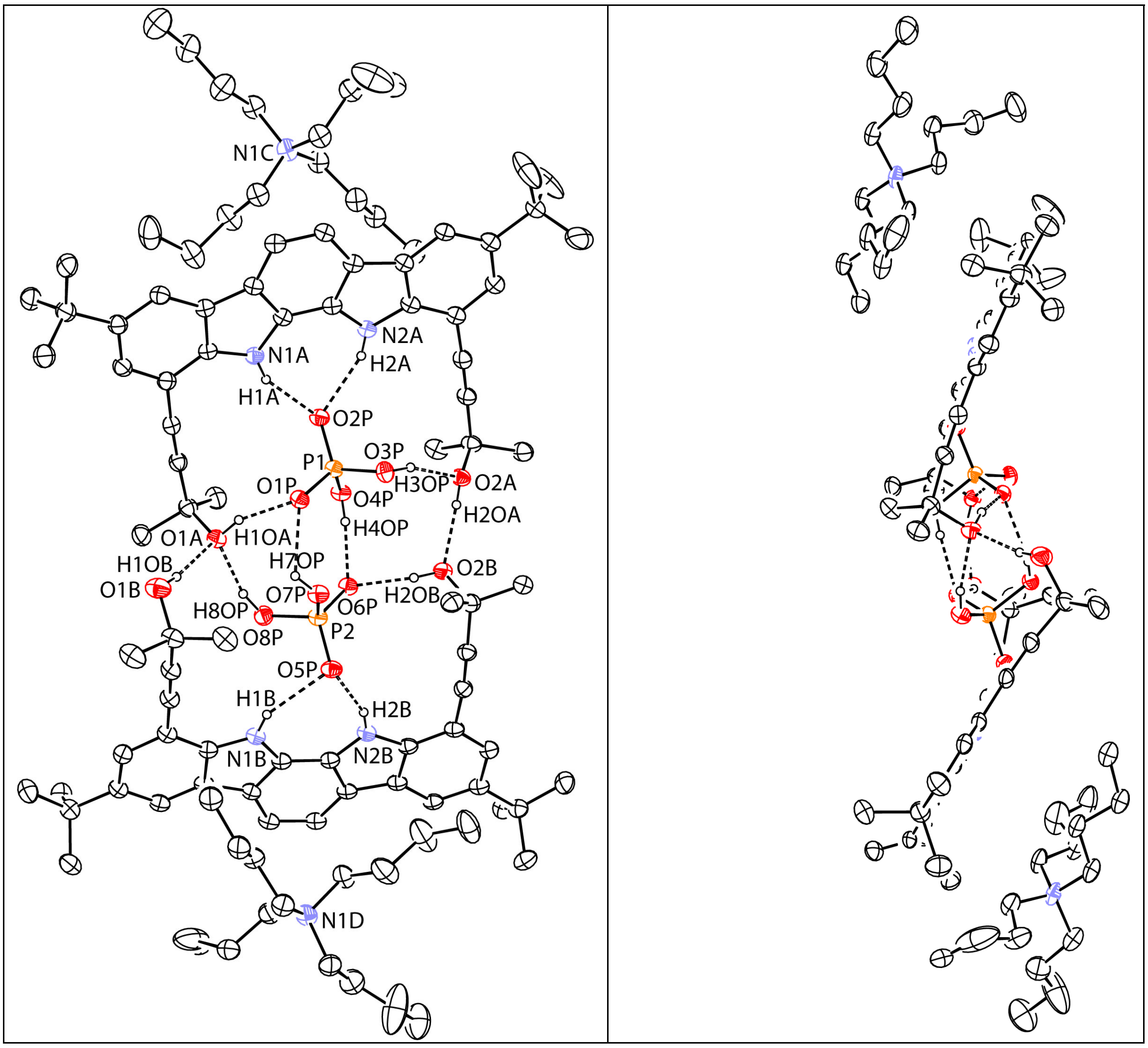

Figure S10 Two different views of ORTEP plots for the crystal structure of $(\mathbf{2}\cdot \mathrm{Bu_4N^+H_2PO_4^-})_2$ with 30% probability ellipsoids.

Table S1. Crystal data and structure refinement for [(tetrabutylammonium)$_2$(**2**Cl)$_2$]$^{\cdot}$0.5(methylene chloride).

Empirical formula	C52.25 H76.50 Cl1.50 N3 O2	
Formula weight	831.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 16.103(2) Å	α= 112.499(2)°.
	b = 17.066(2) Å	β= 90.721(3)°.
	c = 22.027(3) Å	γ = 111.326(2)°.
Volume	5128.2(13) Å^3	
Z	4	
Density (calculated)	1.077 Mg/m^3	
Absorption coefficient	0.140 mm^{-1}	
F(000)	1810	
Crystal size	0.95 x 0.75 x 0.43 mm^3	
Theta range for data collection	1.35 to 25.00°.	
Index ranges	-12<=h<=19, -20<=k<=18, -25<=l<=26	
Reflections collected	26506	
Independent reflections	17623 [R(int) = 0.0229]	
Completeness to theta = 25.00°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9424 and 0.8788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17623 / 10 / 1160	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0655, wR2 = 0.1571	
R indices (all data)	R1 = 0.0921, wR2 = 0.1708	
Largest diff. peak and hole	0.669 and -0.443 e.Å^{-3}	

Table S2. Crystal data and structure refinement for [(tetrabutylammonium)$_2$(**2**H_2PO_4)$_2$]$^\cdot$3(methylene chloride).

Empirical formula	C107 H162 Cl6 N6 O12 P2	
Formula weight	1999.07	
Temperature	90(2) K	
Wavelength	0.70000 Å	
Crystal system	Monoclinic	
Space group	*P*2$_1$/*n*	
Unit cell dimensions	a = 15.618(3) Å	α= 90°.
	b = 25.838(5) Å	β= 101.50(3)°.
	c = 30.105(6) Å	γ = 90°.
Volume	11905(4) Å^3	
Z	4	
Density (calculated)	1.138 Mg/m^3	
Absorption coefficient	0.226 mm^{-1}	
F(000)	4296	
Crystal size	0.25 x 0.22 x 0.12 mm^3	
Theta range for data collection	1.35 to 25.00°.	
Index ranges	-18<=h<=18, -29<=k<=29, -36<=l<=36	
Reflections collected	80737	
Independent reflections	21000 [R(int) = 0.0595]	
Completeness to theta = 25.00°	95.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9734 and 0.9457	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21000 / 10 / 1204	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1843	
R indices (all data)	R1 = 0.0975, wR2 = 0.2006	
Extinction coefficient	0.0048(4)	
Largest diff. peak and hole	0.433 and -0.578 e.Å^{-3}	

Table S3. Hydrogen bonds for [(tetrabutylammonium)$_2$(**2**Cl)$_2$]·0.5(methylene chloride) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2A)-H(2A)...Cl(1A)	0.91(3)	2.31(3)	3.186(2)	162(2)
N(1A)-H(1A)...Cl(1A)	0.88(3)	2.36(3)	3.206(3)	161(3)
O(2A)-H(2OA)...Cl(1A)	0.87(4)	2.26(4)	3.124(2)	178(3)
O(1A)-H(1OA)...Cl(1A)	0.90(5)	2.22(5)	3.114(3)	175(4)
N(2B)-H(2B)...Cl(1B)	0.87(3)	2.46(3)	3.303(2)	162(3)
N(1B)-H(1B)...Cl(1B)	0.84(3)	2.46(3)	3.264(2)	161(3)
O(2B)-H(2OB)...Cl(1B)	0.91(4)	2.27(4)	3.172(2)	177(3)
O(1B)-H(1OB)...Cl(1B)	0.88(4)	2.32(4)	3.192(3)	178(4)

Table S4. Hydrogen bonds for [(tetrabutylammonium)$_2$(**2**H_2PO_4)$_2$]·3(methylene chloride) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1A)-H(1OA)...O(1P)	0.857(18)	1.81(2)	2.627(3)	158(4)
O(2A)-H(2OA)...O(2B)	0.833(18)	1.89(2)	2.683(3)	160(3)
N(1A)-H(1A)...O(2P)	0.87(3)	1.96(3)	2.758(3)	152(3)
N(2A)-H(2A)...O(2P)	0.81(3)	2.09(3)	2.845(3)	155(3)
O(3P)-H(3OP)...O(2A)	0.858(18)	1.83(2)	2.656(3)	162(3)
O(4P)-H(4OP)...O(6P)	0.817(18)	1.806(19)	2.616(3)	172(3)
O(1B)-H(1OB)...O(1A)	0.865(19)	2.04(2)	2.895(3)	170(4)
O(2B)-H(2OB)...O(6P)	0.850(18)	1.85(2)	2.669(3)	161(4)
N(1B)-H(1B)...O(5P)	0.81(3)	2.25(3)	2.967(3)	148(3)
N(2B)-H(2B)...O(5P)	0.84(3)	1.89(3)	2.690(3)	158(3)
O(7P)-H(7OP)...O(1P)	0.821(18)	2.12(3)	2.640(3)	122(3)
O(8P)-H(8OP)...O(1A)	0.859(18)	1.86(2)	2.688(3)	160(3)