

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

2-Iodo-Imidazolium Receptor Binds Oxoanions via Charge-Assisted Halogen Bonding

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Synthetic procedures

General

Commercial HPLC-grade solvents were used without further purification. Starting materials were purchased from Sigma–Aldrich and used without further purification. Reactions in solution were carried out in oven-dried glassware under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature with a Bruker 400 MHz spectrometer. DMSO- d_6 was used as both solvent and internal standard in ^1H and ^{13}C NMR spectra. All chemical shift values are given in ppm. The mass spectra were recorded on a GC-MS AGILENT GC-MSD5975. Differential Scanning Calorimetry (DSC) analysis was performed on a Mettler Toledo DSC823e instrument, aluminium light 20 μl sample pans and Mettler STARe software for calculation. Melting points were also determined with Reichert instrument by observing the melting process through an optical microscope. ATR-FTIR spectra were obtained with a Nicolet Nexus FTIR spectrometer. The values were given in wave numbers and were rounded to 1 cm^{-1} upon automatic assignment (s-strong, m-medium, w-weak, br-broad).

Synthesis of compound 1·I: Compound **2·I** (0.200 g, 0.48 mmol) is added to 20 mL of MeCN at 25°C . 0.110 g (2eq) of potassium *tert*-butoxide is added. A significant change from light yellow to gray-green colour is noted. After 30 min, 0.250 g of iodine (2 eq.) is added and a brown-red precipitate is formed. During the operation the vessel is maintained under argon atmosphere. The solution is left under stirring for 12-18 h. The precipitate is filtered. Crystallization by slow evaporation produce single crystals of **1**. Yield 58 %. ^1H -NMR (400MHz, DMSO- d_6): δ 8.876 (s, 1H), δ 8.22 (m, 4H), δ 7.79 (d, 1H, $J=2$ Hz), δ 7.65 (m, 4H), δ 6.76 (d, 1H, $J=2$ Hz), δ 6.28 (s, 2H), δ 4.258 (q, 2H), δ 1.42 (t, 3H); ^{13}C -NMR (100 MHz, DMSO- d_6): δ 131.5, 130.8, 129.9, 128.3, 126.0, 124.9, 124.1, 123.8, 122.8, 104.8, 48.8, 47.5, 15.4. ESI-Mass: m/z calcd for $[\text{C}_{20}\text{H}_{18}\text{IN}_2]^+$: 413.05; found : 413.

Synthesis of compound 3·I: Compound **2·I** (125 mg, 0.302 mmol) was added to a solution of N-bromosuccinimide (110 mg, 0.618 mmol) in acetonitrile (5 mL). The solution was stirred at ambient temperature for 12 h whereupon the solution was concentrated by solvent evaporation to a volume of ca. 2 mL, from which **3** crystallized out as orange prisms. Yield 98 mg (66 %). ^1H -NMR (400MHz, CD_3CN): δ 8.82 (s, 1H), δ 8.21 (d, 2H, $J_1=8.3\text{Hz}$), δ 8.14 (d, 2H, $J=8.8$ Hz), δ 7.62 (m, 4H), δ 7.35 (d, 1H, $J=2.3$), δ 6.57 (d, 1H, $J=2.3$ Hz), δ 6.20 (s, 2H), δ 4.24 (q, 2H), δ 1.48 (t, 3H); (400 MHz, DMSO- d_6) = δ 8.89 (s, 1H), δ 8.25 (t, 4H), δ 7.79 (d, 1H, $J=2$), δ 7.64 (m, 4H), δ 6.80 (d, 1H, $J=2$ Hz), δ 6.28 (s, 2H), δ 4.24 (q, 2H), δ 1.41 (t, 3H); ^{13}C -NMR (100 MHz, CD_3CN): δ 132.6, 132.4, 130.7, 129.2, 129.1, 126.8, 126.7, 124.4, 123.9, 123.8, 121.3, 48.1, 47.2, 14.6. ESI-Mass: m/z calcd for $[\text{C}_{20}\text{H}_{18}\text{BrN}_2]^+$: 365.07, 367.06; found : 365, 367.

NMR titration experiments

Typical NMR titration experimental procedure: Solution of Receptor **1·I⁻**, **2·I⁻**, and **3·I⁻** in DMSO-d₆, (concentration in the range 0.0075-0.010 M) were prepared. 0.6 ml of fresh receptor solution was placed in the NMR tube. Addition of small volumetric (1-2 μL) aliquots of concentrated solution of the (TBA)X salts were then added via Hamilton syringe. All spectra were recorder on Bruker 400 and 500 MHz at 300 K. Relaxation delay = 5 sec; SW= 12 ppm; LB = 1 Hz; NS= 32. RG is adjusted at high TBA salt concentration.

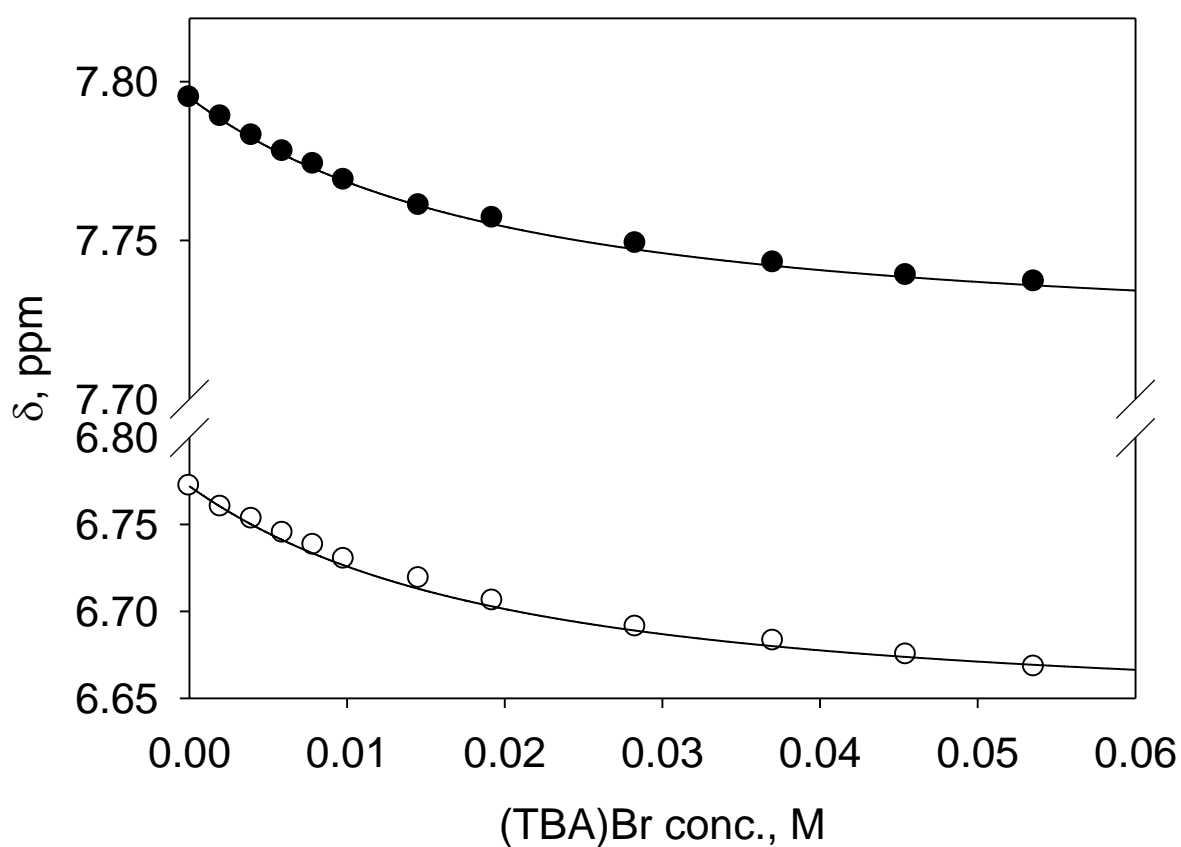
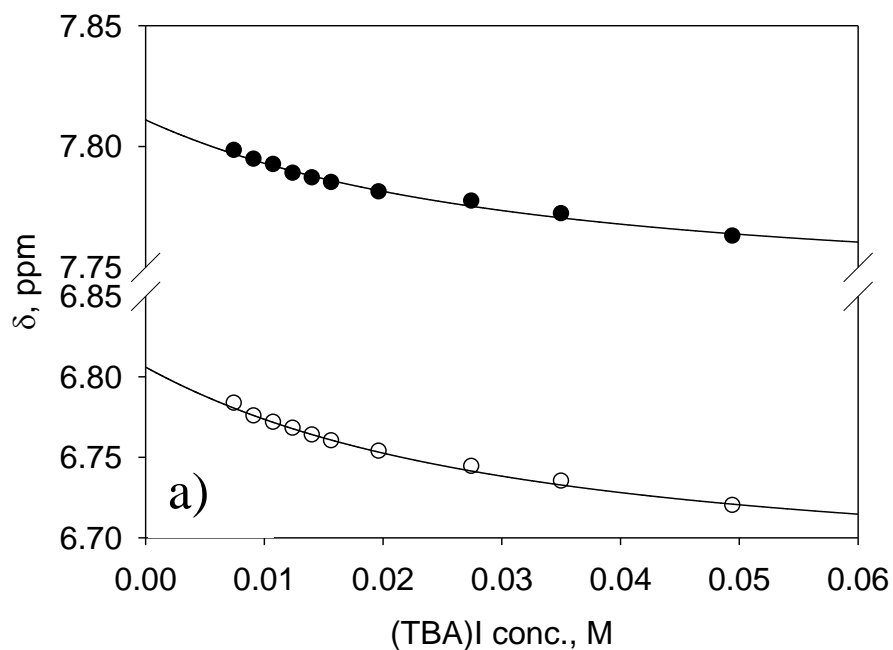
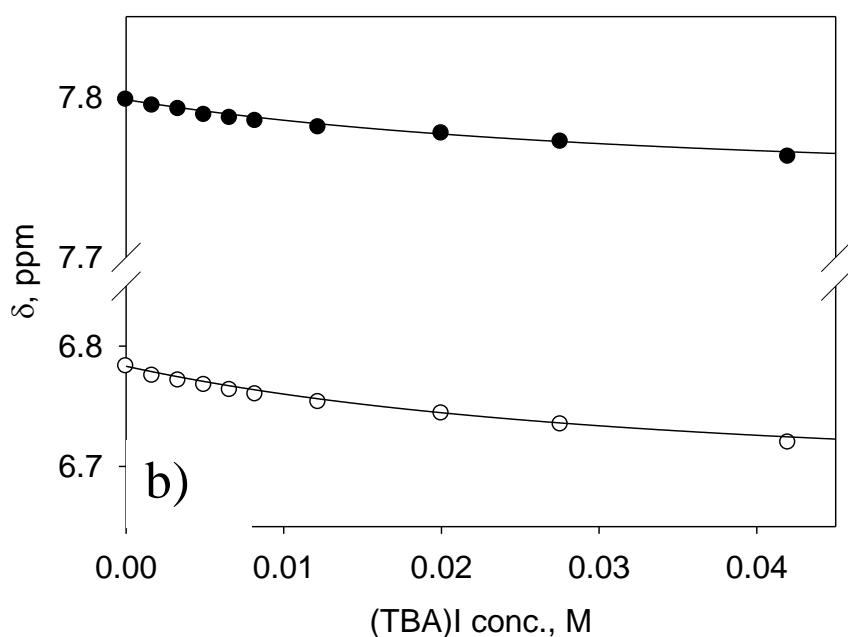


Figure 1S. ¹H-NMR titration plot for receptor **1·I⁻** (0.010 M solution in DMSO-d₆) with (TBA)Br at 300 K. Best fitting curves are shown as full lines. (data: full circle = H4; empty circle = H5)



Parameter	Value	StdErr	CV(%)	Dependencies
$\Delta\delta_{\infty}$ H4	-7.418e-2	4.697e-3	6.332e+0	0.9365273
$\Delta\delta_{\infty}$ H5	-1.340e-1	6.820e-3	5.089e+0	0.9698927
δ H4 [I]=0	7.811e+0	2.108e-3	2.698e-2	0.9514397
δ H5 [I]=0	6.806e+0	3.251e-3	4.777e-2	0.9795941
K	3.887e+1	7.843e+0	2.017e+1	0.9939726



Parameter	Value	StdErr	CV(%)	Dependencies
$\Delta\delta_{\infty}$ H4	-5.751e-2	3.517e-3	6.117e+0	0.7931977
$\Delta\delta_{\infty}$ H5	-1.039e-1	5.883e-3	5.661e+0	0.9260622
K	3.442e+1	3.455e+0	1.004e+1	0.9423977

Figure 2S. $^1\text{H-NMR}$ titration plot for receptor $\mathbf{1}\cdot\text{I}^-$ (0.010 M solution in DMSO-d_6) with (TBA)I at 300 K. a) the initial concentration of iodide is considered explicitly; b) the initial concentration of iodide anion is not considered explicitly. Best fitting curves are shown as full lines. (data: full circle = H4; empty circle = H5). Best fit parameters (K , $\Delta\delta_{\infty}$ and extrapolated δ at $[\text{I}] = 0$ are also shown on the right side of the plot.

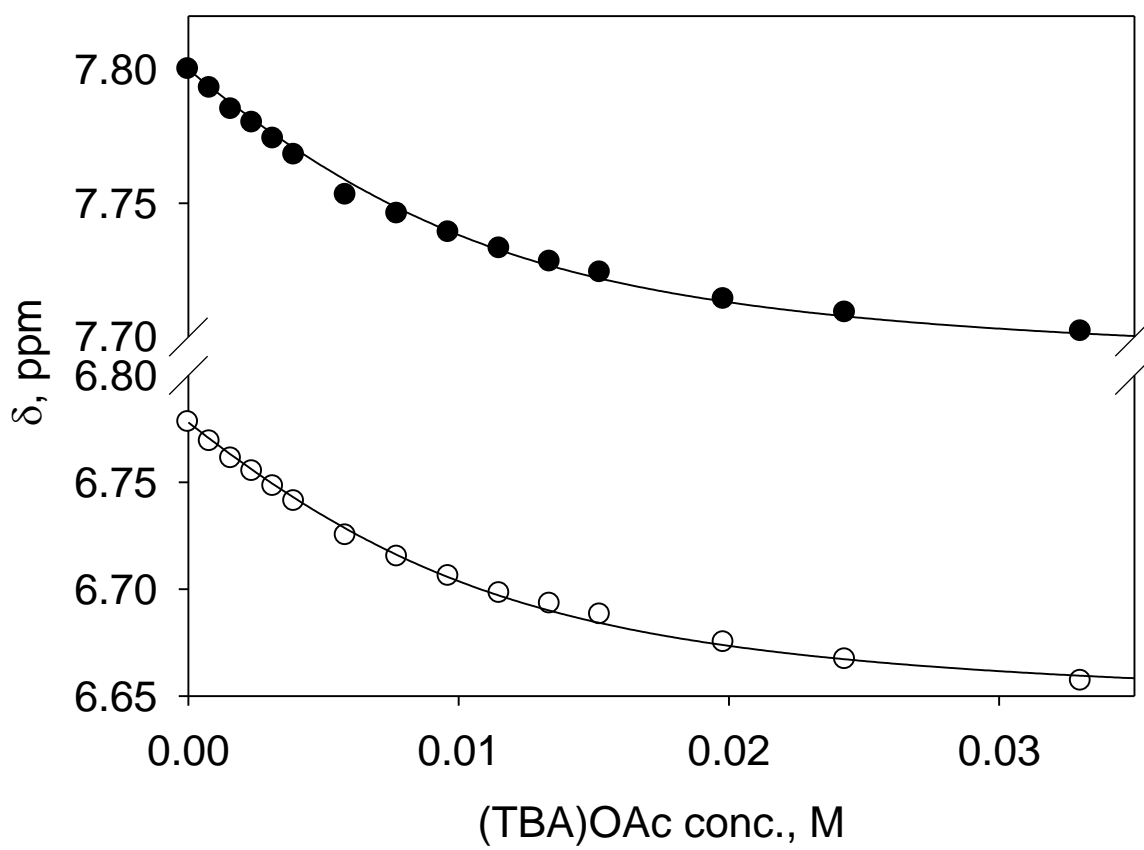


Figure 3S. $^1\text{H-NMR}$ titration plot for receptor $\mathbf{1}\cdot\text{I}^-$ (0.010 M solution in DMSO- d_6) with (TBA)AcO at 300 K. Best fitting curves are shown as full lines. (data: full circle = H4; empty circle = H5).

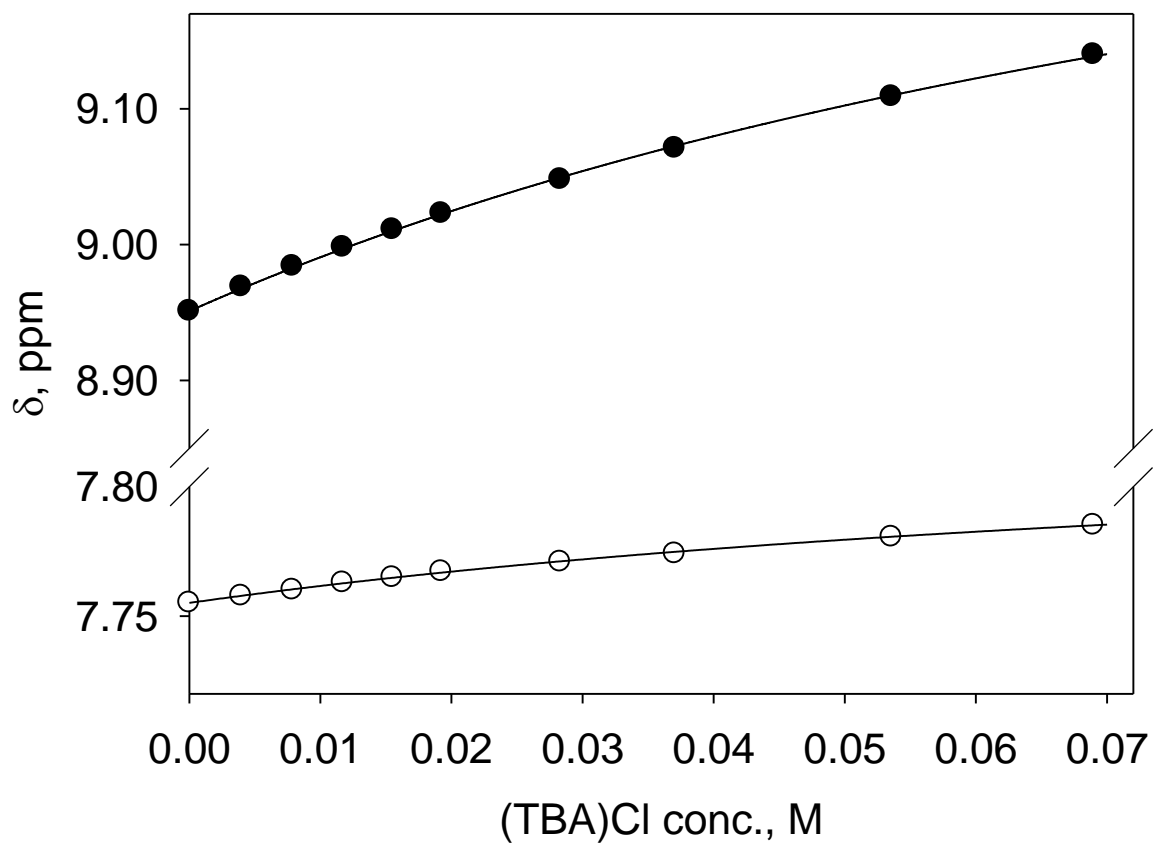


Figure 4S. $^1\text{H-NMR}$ titration plot for receptor $2\cdot\text{I}^-$ (0.010 M solution in DMSO-d_6) with (TBA)Cl at 300 K. Best fitting curves are shown as full lines. (data: full circle = H2; empty circle = H4).

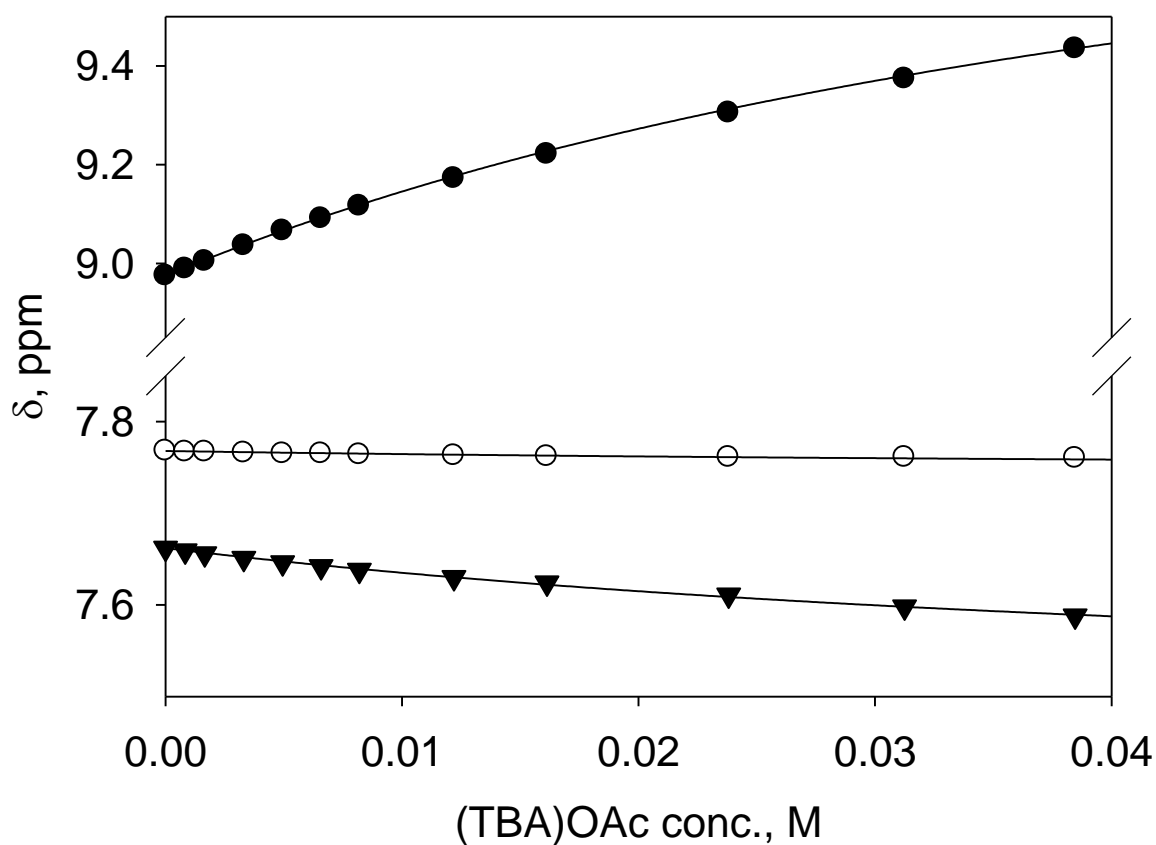


Figure 5S. ^1H -NMR titration plot for receptor $2\cdot\text{I}^-$ (0.010 M solution in DMSO- d_6) with (TBA)OAc at 300 K. Best fitting curves are shown as lines. (data: full circle = H2; empty circle = H4; triangle = H5).

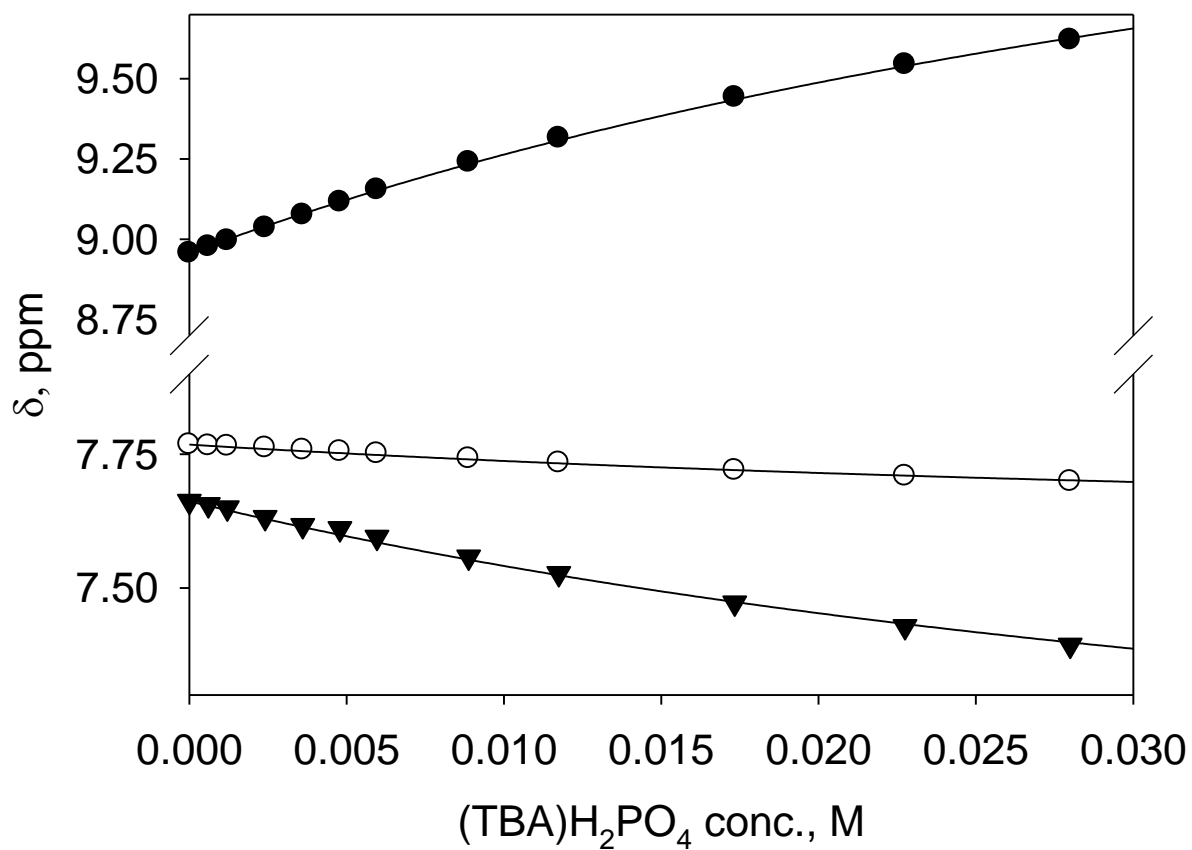


Figure 6S. ^1H -NMR titration plot for receptor $2\cdot\text{I}^-$ (0.010 M solution in DMSO- d_6) with $(\text{TBA})\text{H}_2\text{PO}_4$ at 300 K. Best fitting curves are shown as lines. (data: full circle = H2; empty circle = H4; triangles = H5)

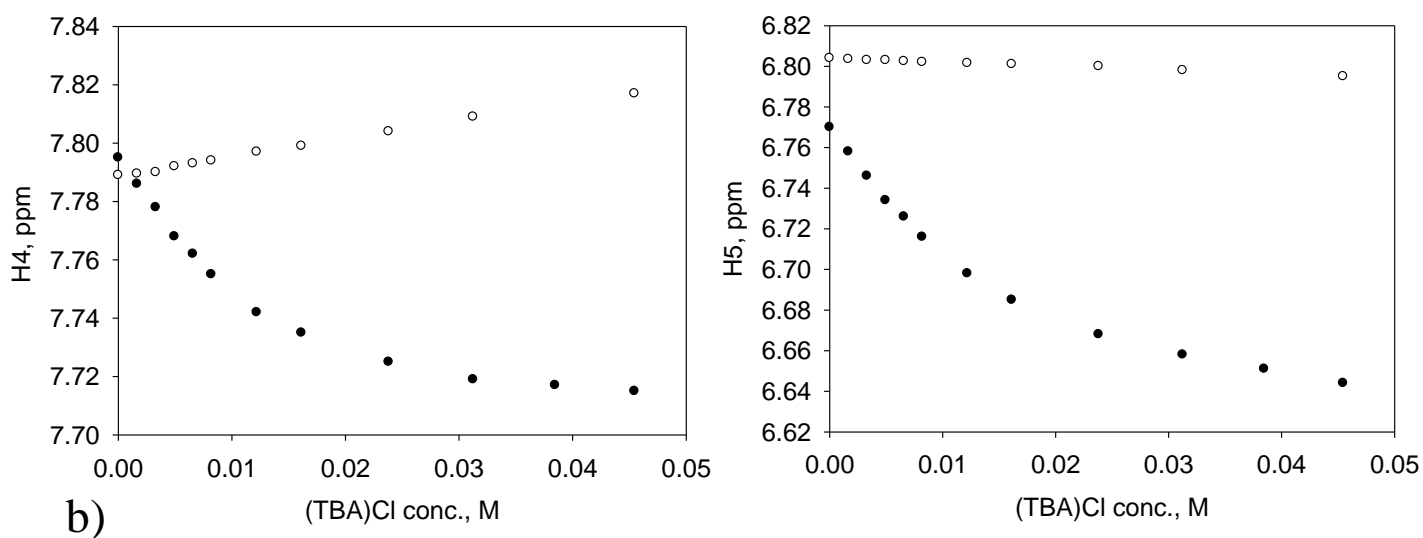
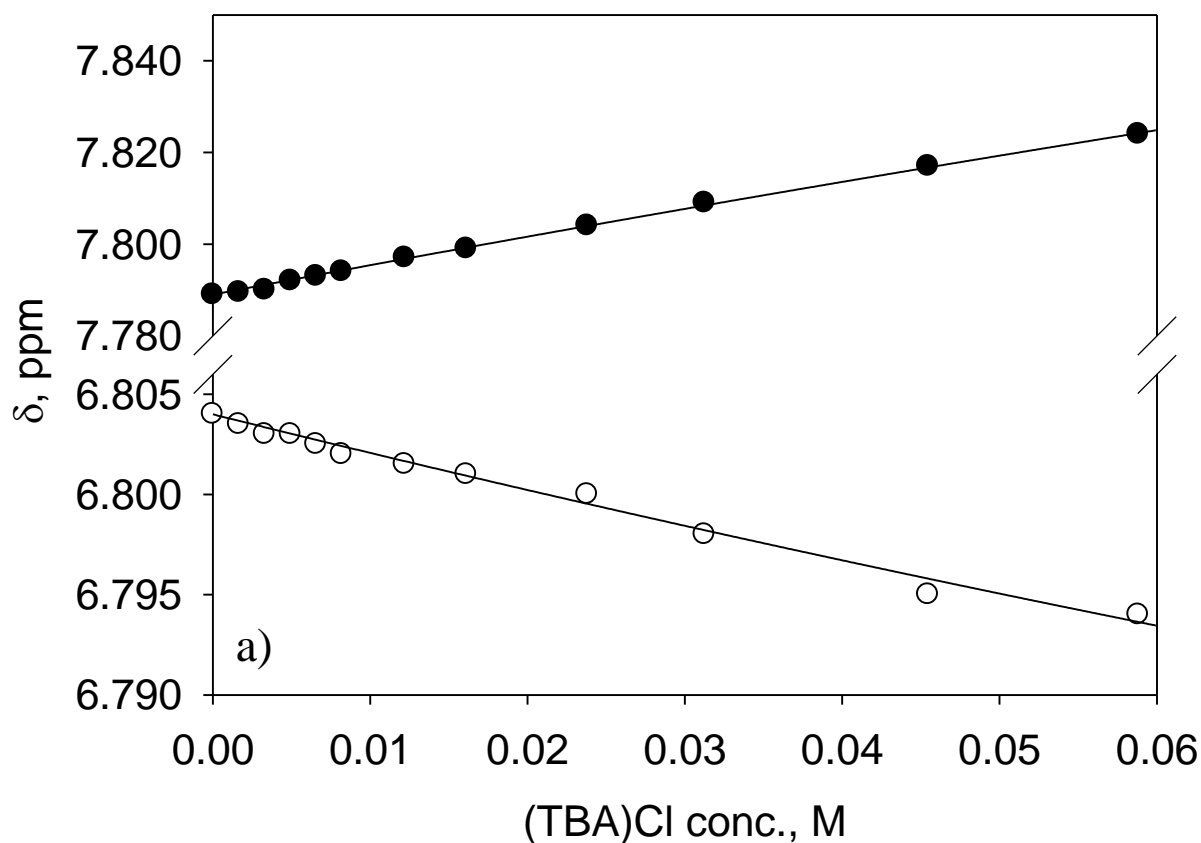


Figure 7S. a) ^1H -NMR titration plot for receptor **3-I** (0.010 M solution in DMSO- d_6) with (TBA)Cl at 300 K. Best fitting curves are shown as full lines. (data: full circle = H4; empty circle = H5); b) Comparison between the chemical shift changes of **1** (full circles) and **3** (empty circle) upon addition of (TBA)Cl in DMSO at 300K (^1H -NMR, 400MHz). As far as the Cl $^-$ binding properties with respect to **1** is concerned, **3** displays an association constant of approximately two order of magnitude less. The precision of the data is limited due to the small shift observed. Most importantly, given the downfield shift variation of H4 (figure which compares well with that of 2H in **2**), the small associative forces responsible for the feeble binding most probably is H-bonding with the H4.

List of references for XB in 2-halo-imidazolium systems

a) N. Kuhn, T. Kratz, G. Henkel, *Chem. Commun.* **1993**, 1778; b) E. Fooladi, B. Dalhus, M. Tilset *Dalton Trans.* **2004**, 3909; c) N. Kuhn, A. Abu-Rayyan, K. Eichele, S. Schwarz, M. Steimann *Inorg. Chim. Acta* **2004**, 357, 1799; d) G. Laus, A. Schwarzler, P. Schuster, G. Bentivoglio, M. Hummel, K. Wurst, V. Kahlenberg, T. Lorting, J. Schutz, P. Peringer, G. Bonn, G. Nauer, H. Schottenberger, *Z. Naturforsch., B: Chem. Sci.* **2007**, 62, 295; e) M. L. Cole, C. Jones, P. C. Junk, *New J. Chem.* **2002**, 26, 1296; f) N. Kuhn, M. Richter, M. Steimann, M. Strobele, K. Sweidan, *Z. Anorg. Allg. Chem.* **2004**, 630, 2054; g) N. Kuhn, J. Fahl, R. Fawzi, C. Maichle-Mossmer, M. Steimann, *Z. Naturforsch., B: Chem. Sci.* **1998**, 53, 720; h) A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha; *J. Am. Chem. Soc.* **1997**, 119, 12742; i) N. Kuhn, A. Abu-Rayyan, M. Gohner, M. Steimann, *Z. Anorg. Allg. Chem.* **2002**, 628, 1721; j) A. J. Arduengo III, M. Kline, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1991**, 113, 9704; k) N. Kuhn, A. Al-Sheikh, S. Schwarz, M. Steimann *Z. Naturforsch., B: Chem. Sci.* **2004**, 59, l) 129; N. Kuhn, A. Abu-Rayyan, M. Strobele *Z. Anorg. Allg. Chem.* **2002**, 628, 2251.

Crystallographic data

Single crystal data collection, structure solution and refinement.

Data were collected on a Bruker KAPPA APEX II diffractometer with Mo-K α radiation and CCD detector. The structures were solved by SIR2002¹ and refined by SHELXL-97² programs, respectively. The refinement was carried on by full-matrix least-squares on F². Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Single crystal data collection, structure solution and refinement.

Structure	1·I ⁻	1·Cl ⁻	1·Br ⁻	2·Cl ⁻	1·H ₂ PO ₄ ⁻
Chemical formula (moiety)	C ₂₀ H ₁₈ N ₂ I ⁺ ·I ⁻	C ₂₀ H ₁₈ N ₂ I ⁺ ·Cl ⁻ , H ₂ O	C ₂₀ H ₁₈ N ₂ I ⁺ ·Br ⁻ , CHCl ₃	C ₂₀ H ₁₉ N ₂ ⁺ ·Cl ⁻ , H ₂ O	C ₂₀ H ₁₈ N ₂ I ⁺ ·H ₂ PO ₄ ⁻ , C ₃ H ₇ NO
Chemical formula (total)	C ₂₀ H ₁₈ I ₂ N ₂	C ₂₀ H ₂₀ ClIN ₂ O	C ₂₁ H ₁₉ BrCl ₃ IN ₂	C ₂₀ H ₂₁ ClIN ₂ O	C ₂₃ H ₂₇ IN ₃ O ₅ P
Formula weight	540.16	466.73	612.54	340.84	583.35
Temperature [K]	103(2)	103(2)	296(2)	90(2)	90(2)
Radiation, wavelength [Å]	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
Crystal system, space group	Monoclinic, <i>P</i> 21/ <i>c</i>	Monoclinic, <i>P</i> 21/ <i>c</i>	Monoclinic, <i>P</i> 21/ <i>c</i>	Monoclinic, <i>P</i> 21/ <i>c</i>	Monoclinic, <i>P</i> 21/ <i>c</i>
<i>a</i> [Å]	8.2333(4)	12.3454(12)	7.0749(6)	9.7188(5)	16.8192(13)
<i>b</i> [Å]	10.2275(6)	10.2075(10)	12.5777(15)	19.4850(5)	16.3863(13)
<i>c</i> [Å]	21.9756(12)	15.1939(15)	26.548(3)	9.1908(5)	8.5845(6)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	92.507(2)	91.473(10)	90.531(12)	95.994(5)	90.086(3)
γ [°]	90.00	90.00	90.00	90.00	90.00
Cell volume [Å ³]	1848.71(17)	1914.0(3)	2362.3(4)	1201.1(3)	2365.9(3)

¹ M.C. Burla, M. Camalli, B. Carrozzini, G.L. Casciarano, C. Giacovazzo, G. Polidori, R. Spagna. SIR2002: *J. Appl. Cryst.* **2003**, *36*, 1103.

² Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112-122.

ρ_{calc} [g cm ⁻³]	1.941	1.620	1.722	1.308	1.638
<i>Z</i>	4	4	4	4	4
dimension [mm ³]	0.05 x 0.16 x 0.36	0.08 x 0.14 x 0.20	0.15 x 0.26 x 0.42	0.02 x 0.12 x 0.20	0.02 x 0.05 x 0.35
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	3.406	1.823	3.396	0.229	1.461
Tmin, Tmax	0.6092, 0.7468	0.6581, 0.7057	0.2463, 0.3171	0.66, 0.746	0.905, 1
<i>F</i> (000)	1032	928	1192	720	1176
Crystal colour and shape	Brown Elongated Table	Brown Block	Yellow Block	Colourless Plate	Colourless Needle
θ_{max} [°]	34.49	34.36	33.48	28.76	27.5
Data collected	55642	31778	23152	13942	29610
Unique data	6886	6582	6948	4394	29610
<i>R</i> _{int}	0.0267	0.0281	0.0203	0.078	0.0388
No. obs. data <i>I</i> _o > 2σ(<i>I</i> _o)	6520	5842	5282	2517	22598
no. parameters	219	306	254	230	204
No. Restrains.	0	21	0	2	175
<i>R</i> _{all}	0.0561	0.0277	0.0530	0.1043	0.0896
<i>R</i> _{obs}	0.0532	0.0237	0.0354	0.042	0.0617
<i>wR</i> _{all}	0.1482	0.0710	0.0989	0.0901	0.1559
<i>wR</i> _{obs}	0.1467	0.0692	0.0904	0.0781	0.1398
Goodness-of-fit on <i>F</i> ²	1.316	1.075	1.049	0.913	1.02
$\Delta\rho_{\text{min,max}}$ [e Å ⁻³]	-2.434; 3.775	-0.577; 1.224	-1.157, 1.016	-0.255, 0.055	-2.143, 3.375
<i>CCDC</i>	828713	828715	828714	828716	828717

Table S2. Halogen bonding and hydrogen bonding distances and angles in halide and phosphate salts of **1** and **2**.

Co-crystal name	XB C-donor(D)⋯acceptor(A)	Distance D⋯A (Å)	Angle C-D⋯A (deg)
1 ·I ⁻	C16-I2⋯I1	3.2828(6)	171.93(18)
1 ·Cl ⁻	C1-I1⋯Cl1 ^a	3.0233(5)	174.14(10)
1 ·Br ⁻	C16-I1⋯Br2 ^b	3.0994(5)	178.46(13)
2 ·Cl ⁻	C1-H1⋯Cl1	2.643(21)	158.89(10)
1 ·H ₂ PO ₄ ⁻	C2-I1⋯O3 ^c	2.6024(23)	177.84(17)

a: 1-x, -0.5+y, 1.5-z; b: -x, -0.5+y, 0.5-z; c: 1-x, -0.5+y, 0.5-z

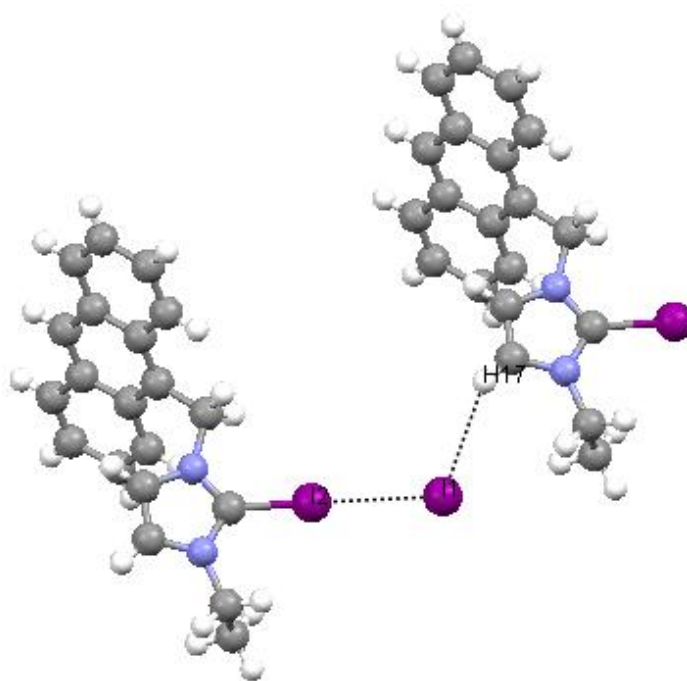


Figure 8S. Halogen bonding and hydrogen bonding geometrical parameters for **1·I**: distance [I1 \cdots H17 x, 1+y, z]: 3.051(3) Å. Colour code: carbon: gray; nitrogen: blue; iodine: purple; and hydrogen: white. Interactions are highlighted as black dotted line.

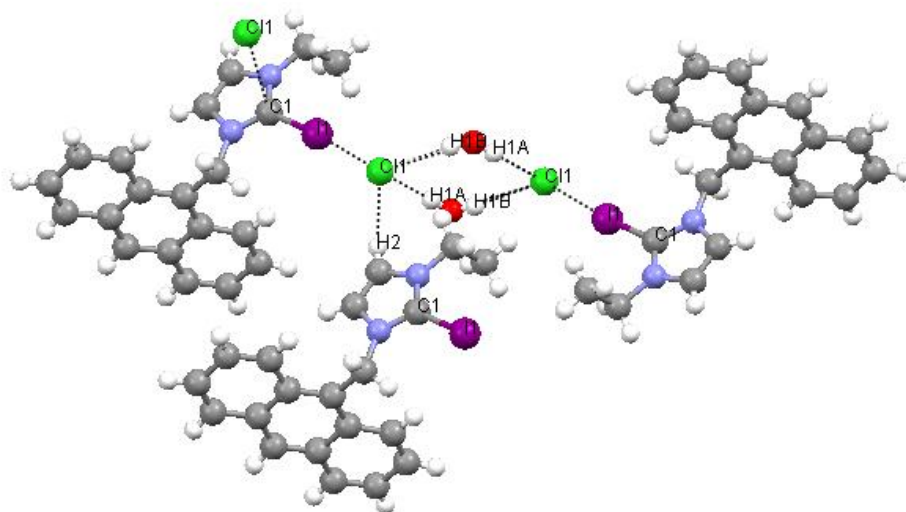


Figure 9S. Halogen bonding, hydrogen bonding and other non covalent interactions geometrical parameters for **1·Cl**: distance [H1A \cdots Cl1(-x+1, -y+1, -z+1)]: 2.392(4) Å and [H1B \cdots Cl1(x, y+1, z)]: 2.413(3) Å; angle [O1-H1A \cdots Cl1]: 169.91° and [O1-H1B \cdots Cl1]: 168.64°, distance [Cl1 \cdots Cl1]: 3.4186(16) Å; distance [Cl1 \cdots H2(1-x, -0.5+y, 1.5-z)]: 2.7804(228) Å. Colour code: carbon: gray; nitrogen: blue; oxygen: red; iodine: purple; chlorine: green and hydrogen: white. Interactions are highlighted as black dotted line.

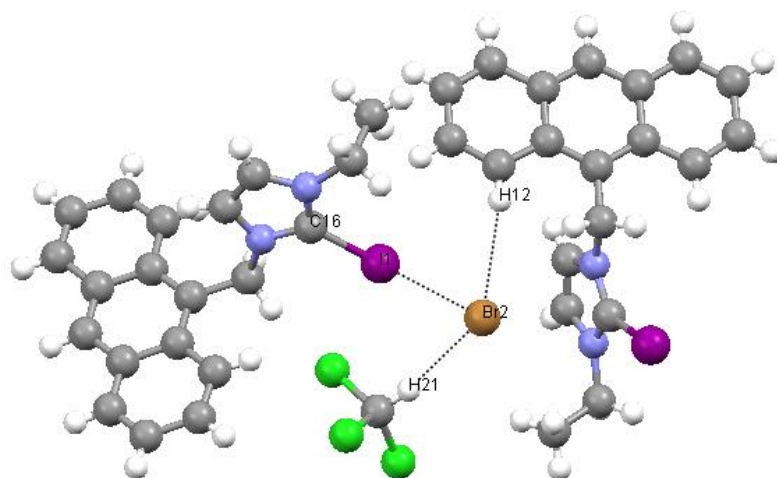


Figure 10S. Halogen bonding and hydrogen bonding interaction geometrical parameters for $\mathbf{1} \cdot \text{Br}^-$: distance [H21 \cdots Br2(-1-x, -0.5+y, 0.5-z)]: 2.726(4) Å and [H12(-x,0.5+y, 0.5-z) \cdots Br2(-1-x, -0.5+y, 0.5-z)]: 2.413(2) Å; angle [C-H21 \cdots Br2(-1-x, -0.5+y, 0.5-z)]: 170.47° and [C-H12(-1-x, -0.5+y, 0.5-z) \cdots Br2(-1-x, -0.5+y, 0.5-z)]: 165.45°. Colour code: carbon: gray; nitrogen: blue; iodine: purple; chlorine: green; bromine: light brown and hydrogen: white. Interactions are highlighted as black dotted line.

X-ray structure of 2·Cl⁻. X-ray study revealed same rectangular shaped HB pattern between two water molecules and chloride anion observed in **5**, while the hydrogen atom 2H on imidazolium ring was found hydrogen bonded to chloride atom (see Figure S12). Further weak hydrogen bonds, mainly due to the crystal packing requirements, complete the coordination sphere of the Cl⁻.

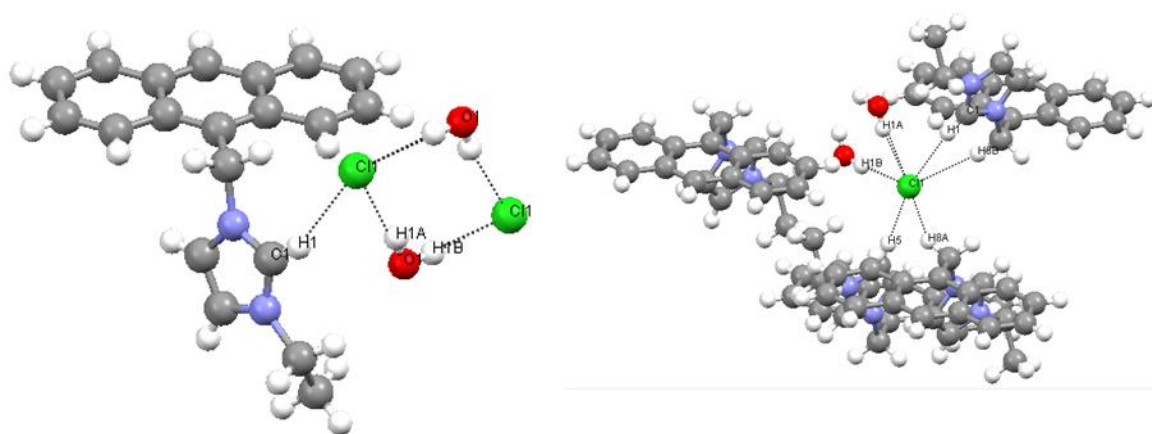


Figure 11S. Hydrogen bonding geometrical parameters for **6**. Left: distance [H1A[⋯]Cl1]: 2.366(20) Å and [H1B[⋯]Cl1]: 2.370(20) Å; angle [O1-H1A[⋯]Cl1]: 169.28(20)° and [O1-H1B[⋯]Cl1]: 174.03(20)°. Right: [H5[⋯]Cl1]: 2.635(5) Å, [H8A[⋯]Cl1]: 2.725(4) Å, [H8B[⋯]Cl1]: 2.857(5) Å. Colour code: carbon: gray; nitrogen: blue; oxygen: red; chlorine: green and hydrogen: white. Interactions are highlighted as black dotted line.

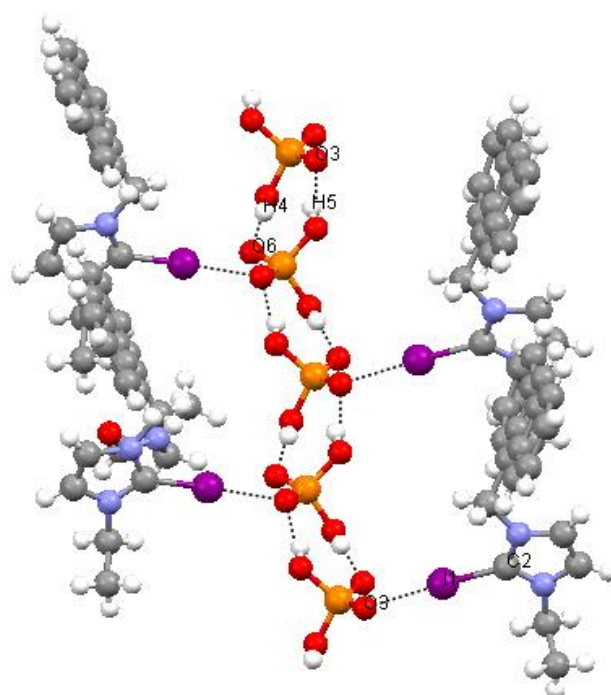


Figure 12S. Halogen bonding and hydrogen bonding interactions geometrical parameters for $\mathbf{1} \cdot \mathbf{H}_2\mathbf{PO}_4^-$ distance [H4 \cdots O6(x, -y+0.5, z+0.5)]: 1.726(3) Å and [H5 \cdots O3(x, -y+0.5, z-0.5)]: 1.784(4) Å; angle [O4-H4 \cdots O6(x, -y+0.5, z+0.5)]: 164.87(4)° and [O5-H5 \cdots O3(x, -y+0.5, z-0.5)]: 164.22(3)°. Colour code: carbon: gray; nitrogen: blue; iodine: purple; oxygen: red; phosphorous: light brown and hydrogen: white. Interactions are highlighted as black dotted line. DMF molecule is omitted for clarity.

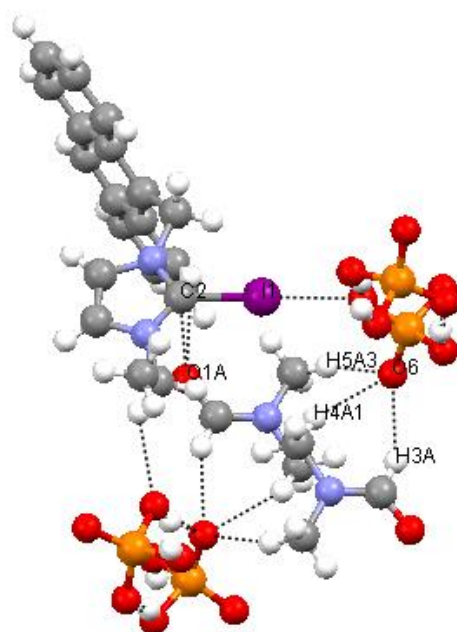


Figure 13S. Hydrogen bonding and other non covalent interactions geometrical parameters for DMF molecule in $1 \cdot \text{H}_2\text{PO}_4^-$. Distance [H3A...O6]: 2.515(3) Å, [H4A1...O6]: 2.568(3) Å, [H5A3...O6]: 2.561(3) Å, [O1A...H12]: 2.678(3) Å and [O1A...C2]: 3.143(7) Å; angle [C3A-H3A...O6]: 164.2(3)°, [C4A-H4A1...O6]: 155.3(4)°, [C5A-H5A3...O6]: 155.3(4)° and [C12-H12...O1A]: 123.4(2). Colour code: carbon: gray; nitrogen: blue; iodine: purple; oxygen: red; phosphorous: light brown and hydrogen: white. Interactions are highlighted as black dotted line.