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Fluoride binding by an anionic receptor: tuning the acidity of amide NH groups for basic anion H-bonding and recognition

Riccardo Montis, Andrea Bencini, Simon Coles, Luca Conti, Luca Fusaro, Philip A. Gale, Claudia Giorgi, Peter Horton, Vito Lippolis, Lucy Mapp, Claudia Caltagirone

Electronic Supporting information

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1. Syntheses

1.1. Synthesis of H_2L1

A solution of L-tryptophan (1 g, 4.9 mmol) in 3mL of KOH 2M was cooled down to 0-5 °C in an ice bath. 10 mL of THF were added and the solution stirred vigorously. To this solution, were added simultaneously over 1 h, 1.6 mL of aqueous KOH 4M and4 mL of a solution of 2,6-bis(chlorocarbonyl)pyridine (500 mg, 2.45 mmol) in THF. After completion of the addition, the solution was warmed up to room temperature and stirred for 30 min. THF was removed by evaporation at low pressure and the aqueous phase diluted with 10 mL of H_2O and acidified with formic acid until complete precipitation of a white-yellow solid. The product was filtered, recrystallized from water and the solid phase dried under vacuum (0.8313, yield 63%).

^{1}H-NMR (600 MHz, DMSO- d_6, 298 K): δH: 12.87 (s, 2H); 10.70 (s, 2H); 9.34 (d, J = 8.1 Hz, 2H); 8.14 (m, 3H); 7.63 (d, J = 7.7 Hz, 2H); 7.21 (d, J = 8.1 Hz, 2H); 7.20 (d, J = 2.1 Hz, 2H); 7.03 (t, J = 8.0 Hz, 2H); 6.95 (t, J = 7.4 Hz, 2H); 4.74 (m, 2H); 3.46 (dd, J = 5.5, 15.0 Hz, 2H); 3.34 (dd, J = 9.4, 15.0 Hz, 2H);

^{13}C-NMR (100 MHz, DMSO- d_6, 298 K), δC: 173.03, 163.16, 148.49, 139.44, 136.11, 127.12, 123.63, 120.95, 118.43, 118.23, 111.41, 110.28, 53.63, 26.92.

Elemental Analysis: (Calc (found)): **H_2L1**·H_2O C% 62.47 (62.28), H% 4.88 (5.10), N% 12.56 (12.48).

MS (ESI+, m/z)): $[M+H]^+$ 540.2 .

1.2. Synthesis of H_2L2

A solution of L-tryptophan (1.02 g, 4.9 mmol) in 3mL of KOH 2M was cooled down to 0-5 °C in an ice bath. 10 mL of THF were added and the solution stirred vigorously. To this solution, were added simultaneously over 1 h, 1.6 mL of aqueous KOH 4M and4 mL of a solution of 2,6-bis(chlorocarbonyl)pyridine (498 mg, 2.45 mmol) in THF. After completion of the addition, the solution was warmed up to room temperature and stirred for 30 min. THF was removed by evaporation at low pressure and the aqueous phase diluted with 4 mL of H_2O and acidified with about 1 mL (pH approximately 3) of formic acid until complete precipitation of a white-yellow solid. The product was filtered, recrystallized from water and the solid phase dried under vacuum (0.9445 g 72%).

^{1}H-NMR (400 MHz,DMSO- d_6, 298 K): δH: 10.79 (s, 2H); 8.78 (d, J = 7.8 Hz, 2H); 8.27 (s, 1H); 7.93 (dd, J = 1.4, 7.8 Hz 2H); 7.58 (d, J = 7.9 Hz, 2H); 7.52 (t, J = 7.9 Hz, 2H); 7.31 (d, J = 7.9 Hz, 2H); 7.18 (td J = 2.0 Hz, 2H); 7.05 (t, J = 7.7 Hz, 2H); 6.97 (t, J = 7.2 Hz, 2H); 4.67 (m, 2H); 3.31 (dd, J = 4.7, 15.0 Hz, 2H); 3.20 (dd, J = 10.0, 15.0 Hz, 2H);

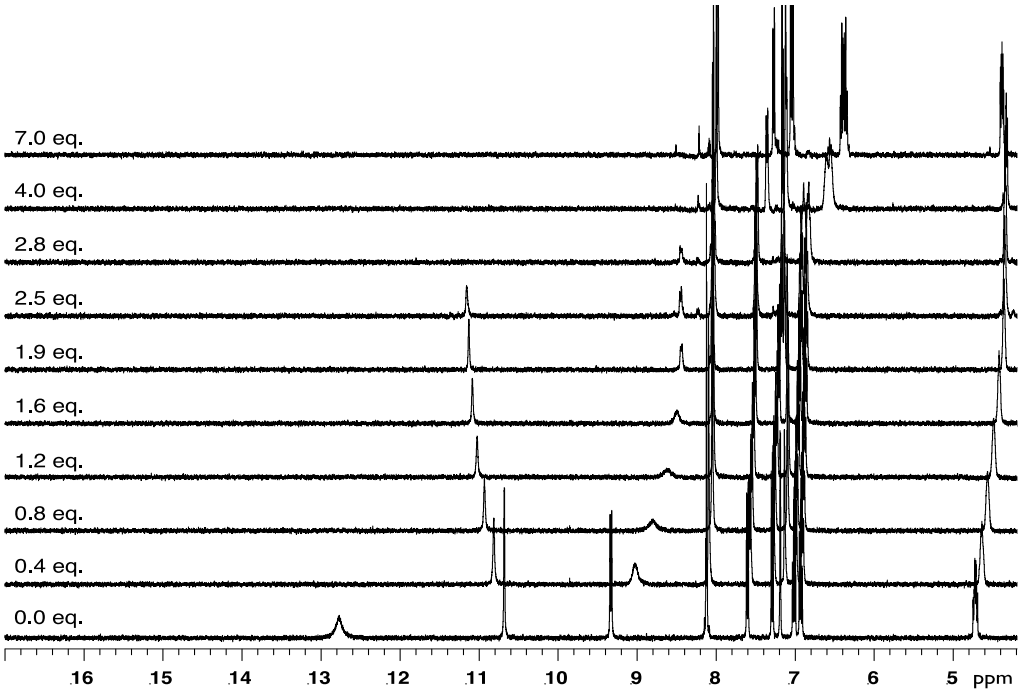
^{13}C-NMR (125 MHz, DMSO- d_6, 298 K), δC: 173.57, 166.03, 136.16, 134.23, 130.13, 128.28, 127.20, 126.82, 123.62, 121.03, 118.48, 118.20, 111.50, 110.46, 53.85, 26.73.

Elemental Analysis: (Calc (found)): **H_2L2**·H_2O C% 64.74 (64.07), H% 5.07 (5.11), N% 10.07 (10.38).

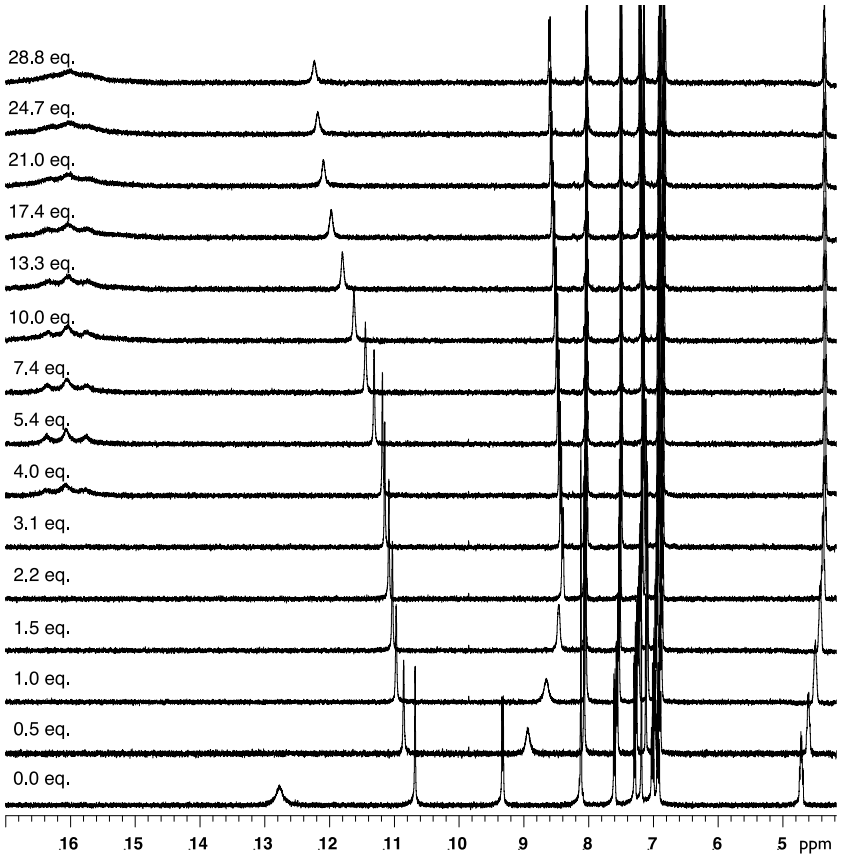
MS (ESI+, m/z)): $[M+H]^+$ 539.2 .

2. ^{1}H and $^{19}F^-$ NMR measurements

^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer at 400 and 377 MHz, respectively. ^{1}H and ^{19}F NMR peak positions in deuterated DMSO at 298 K were referred to TMS (internal standard) and FTEG (1H,1H,8H,8H-perfluoro-3,6-dioxaoctane-1,8-diol, external standard).[1]



A



B

Figure S1. Stack plot (between 4.5 and 17 ppm) of the ^{1}H-NMR spectra of **H_2L1** upon addition of increasing amount of TBAOH (A) and TBAF (B) in DMSO-d_6.

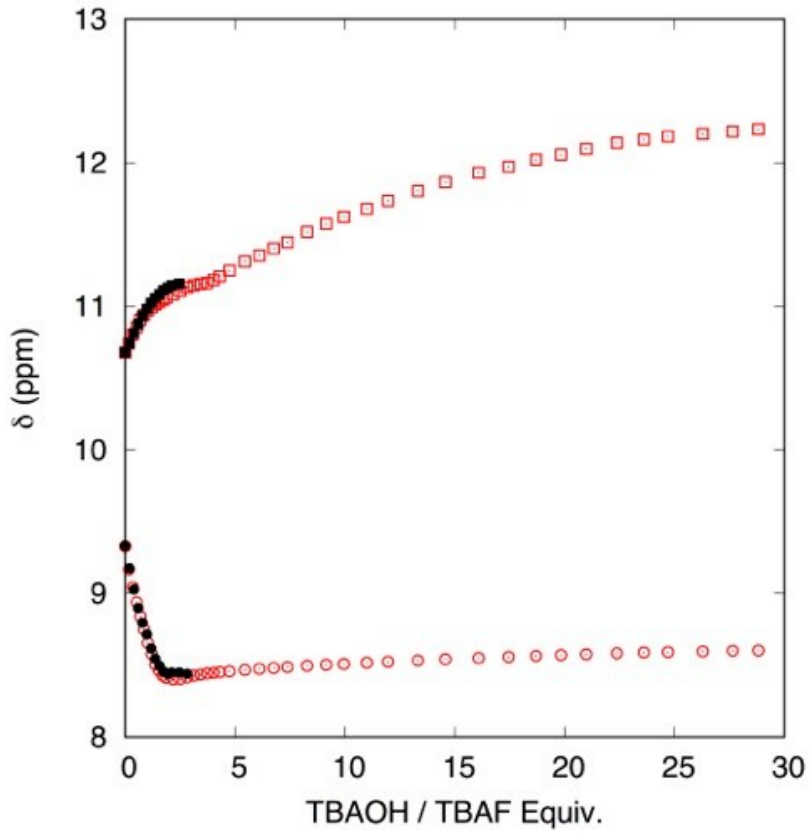


Figure S2. Variation of chemical shift values of NH1 and NH2 resonance lines of **H_2L1** as a function of TBAOH (black full dots) and TBAF (red empty dots) equivalents.

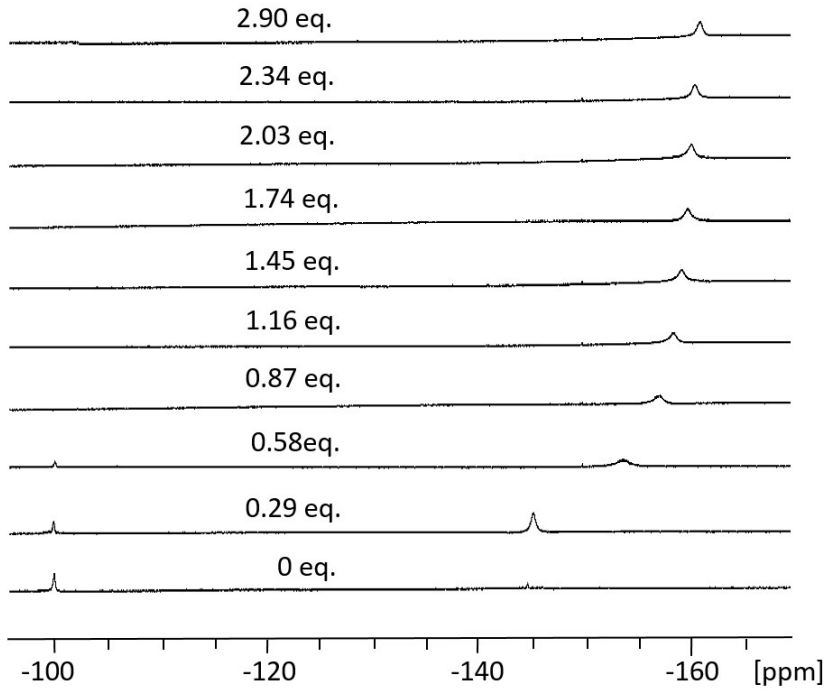


Figure S3. Stack plot of the ^{19}F-NMR titration of TBAF (0.012 M) with **H_2L1** in DMSO-d_6.

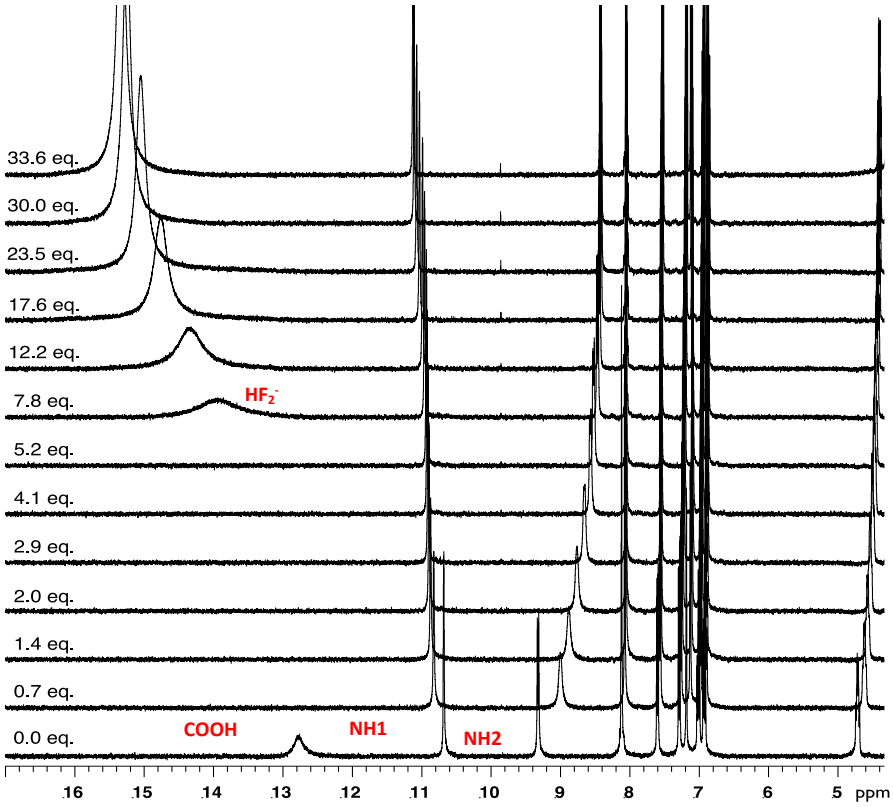


Figure S4. Stack plot of ^{1}H-NMR spectra recorded after the addition of increasing amounts of $TBAHF_2$ to H_2L1 (0.005M) in DMSO-d_6.

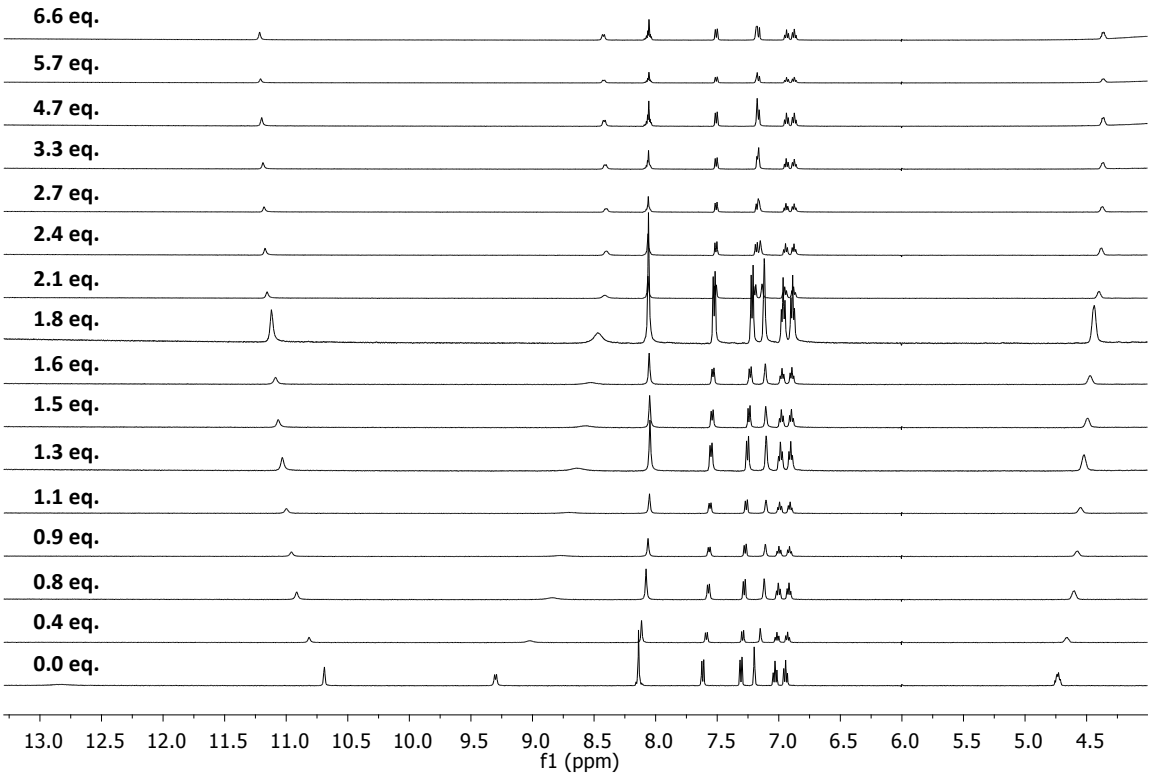


Figure S5. Stack plot of the ^{1}H-NMR titration of **H_2L1** (0.005M) with acetate as TBA salt (0.075M) in DMSO-d_6.

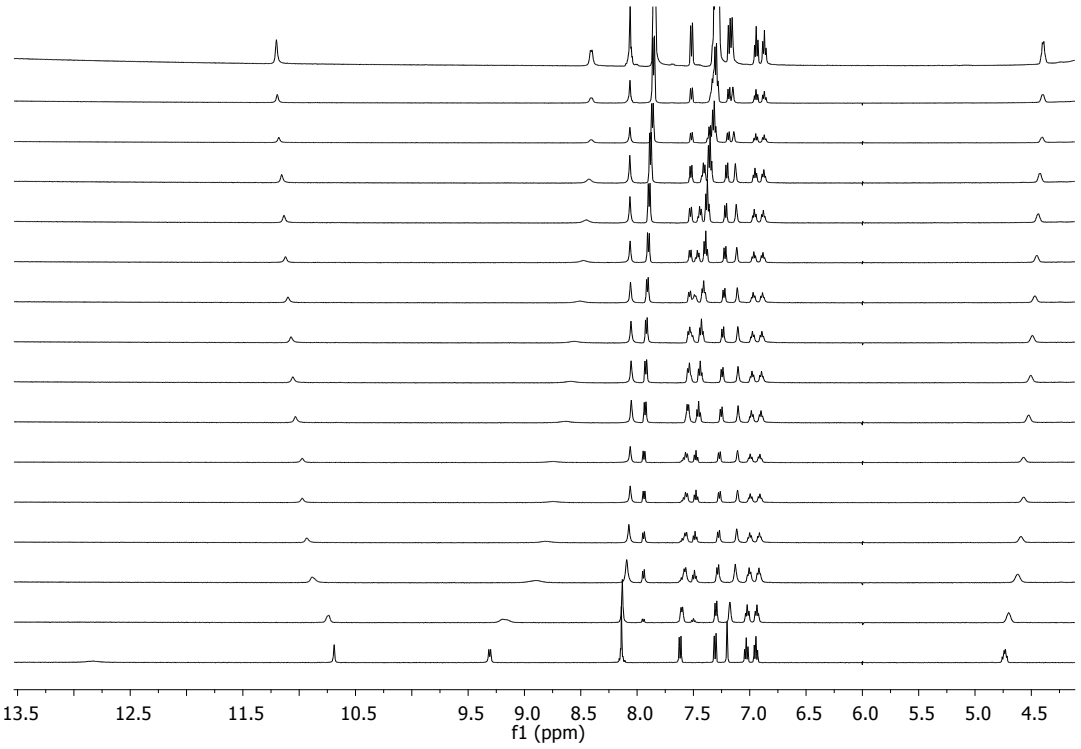


Figure S6. Stack plot of the^{1}H-NMR titration of **H_2L1** (0.005M) with benzoate as TBA salt (0.075M) in DMSO-d_6.

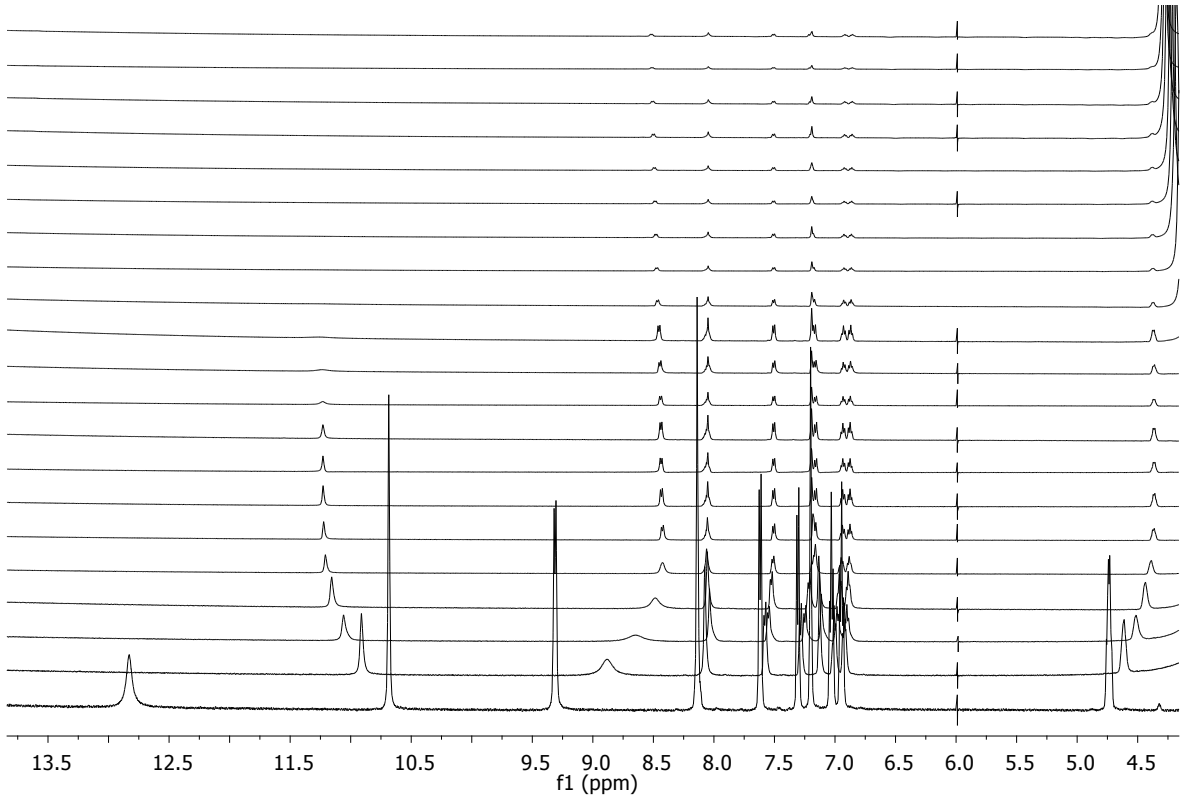


Figure S7. Stack plot of the ^{1}H-NMR titration of **H_2L1** (0.005M) with hydrogenpyrophosphate as TBA salt (0.075M) in DMSO-d_6.

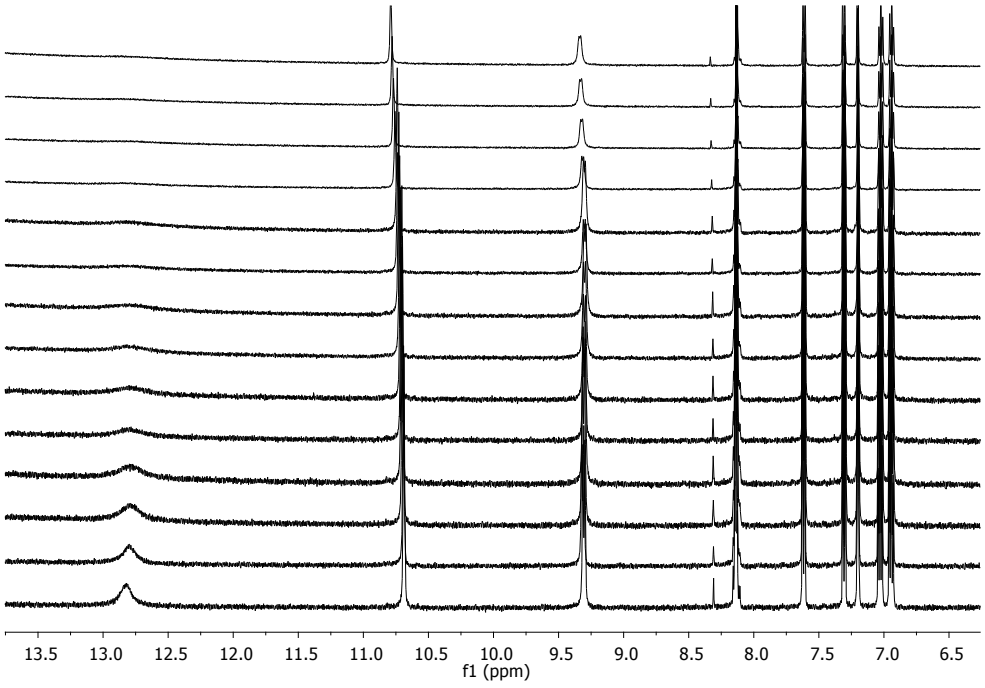


Figure S8. Stack plot of the ^{1}H-NMR titration of **H_2L1** (0.005M) with chloride as TBA salt (0.075M) in DMSO-d_6.

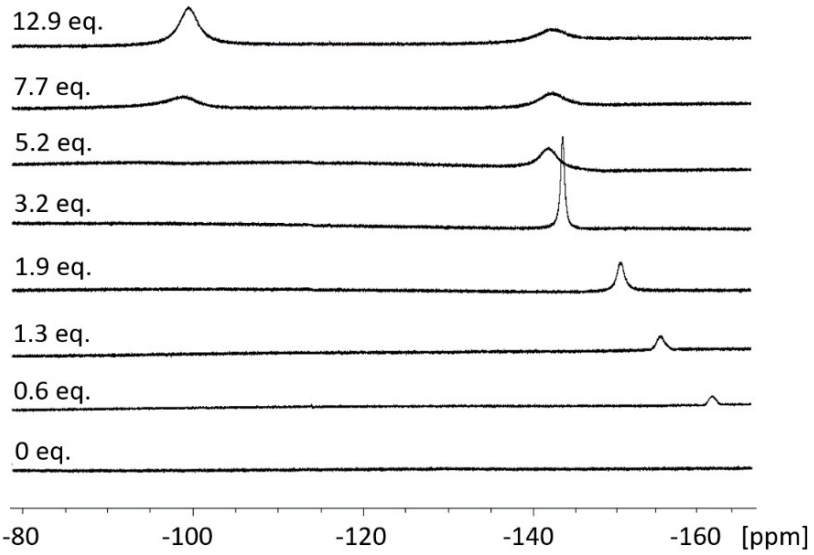


Figure S9. Stack plot of the ^{19}F-NMR titration of **H_2L2** (0.01M) with fluoride as TBA salt in DMSO-d_6

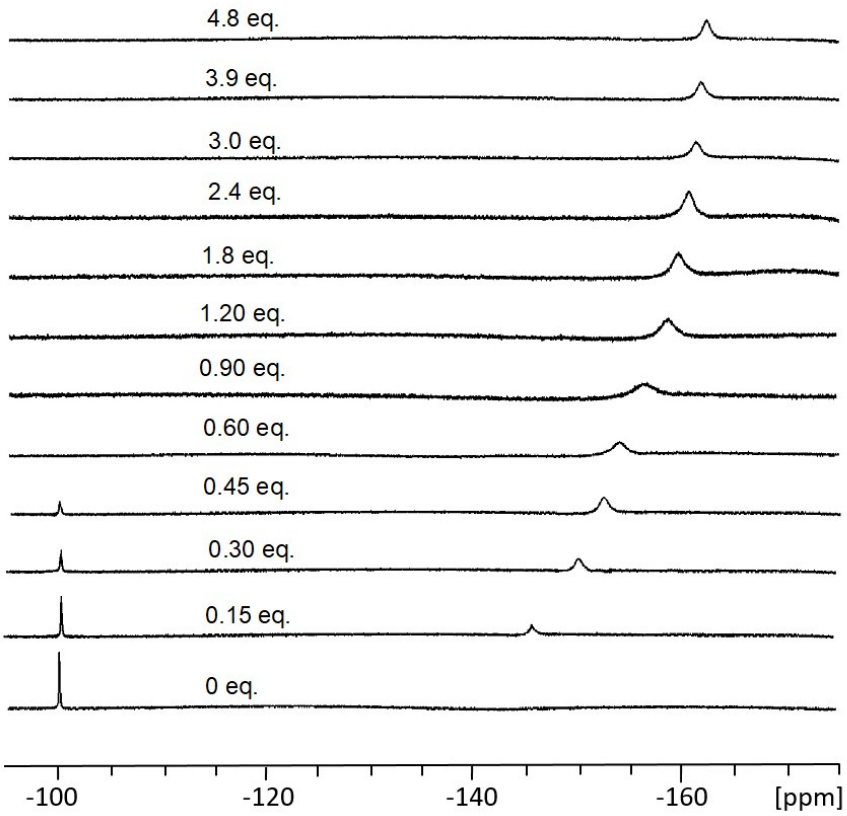


Figure S10. Stack plot of the ^{19}F-NMR titration of TBAF ((0.013M) with **H_2L2** in DMSO-d_6.

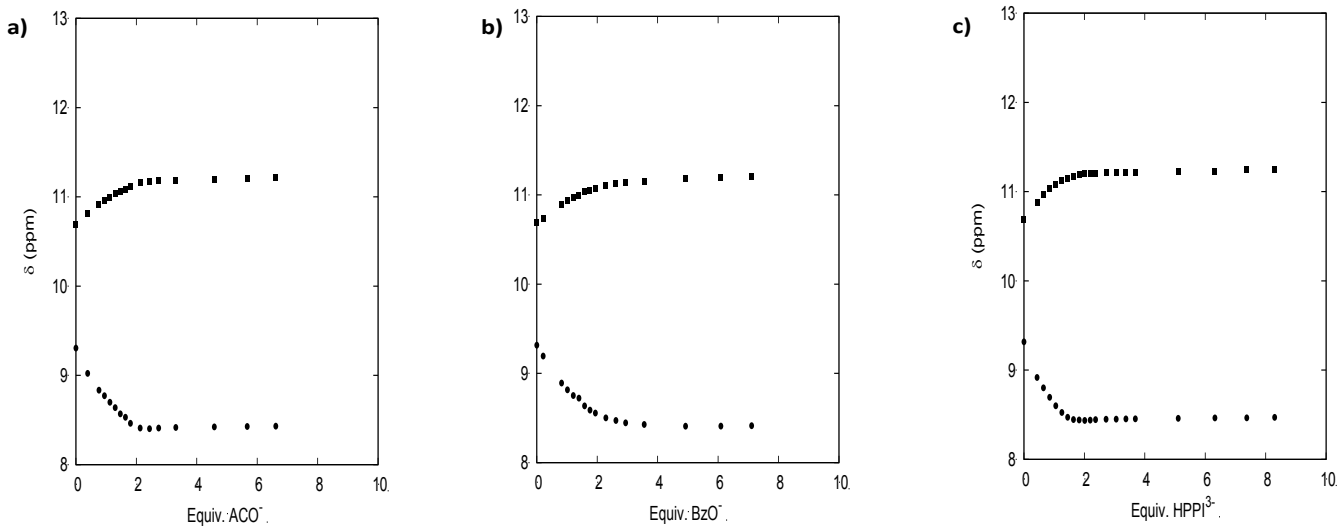


Figure S11. Variation of chemical shift values of NH1 and NH2 resonance lines of **H_2L1** as a function of TBAAcO (a), TBABzO (b) and $(TBA)_3HPpi$ (c) equivalents.

3. Potentiometric Measurements.

All the pH metric measurements (pH = -log $[H^+]$) were carried out in degassed 0.1 mol dm^{-3} $NaClO_4$ H_2O/EtOH (50/50 vol/vol) solutions, at 298.1 K by using equipment and procedure which have been already described.[2] The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of $HClO_4$ with CO_2-free NMe_4OH solutions and determining the equivalent point by the Gran's method,[3] which allows to determine the standard potential E^o, and the ionic product of water (pK_w = 13.83(1) at 298.1 K in 0.1 mol dm^{-3} $NaClO_4$). In the experiments to determine the stability of the anion complexes, the ligand concentration was generally 5 x 10^{-4} M, while the anion concentration was varied in the range 4 x 10^{-4} – 9 x 10^{-3} M. At least three measurements (about 100 data points each one) were performed for each system in the pH range 2-10.5 and the relevant e.m.f. data were treated by means of the computer program HYPERQUAD,[4] determining the protonation constants of both receptors (Table S1), fluoride and pyrophosphate (Table S2) and the overall stability constants (logβ) of the complexes (Tables S3 and S4), from which we calculated the stepwise association constants of the complexes (logK) also reported in Tables S3 and S4.

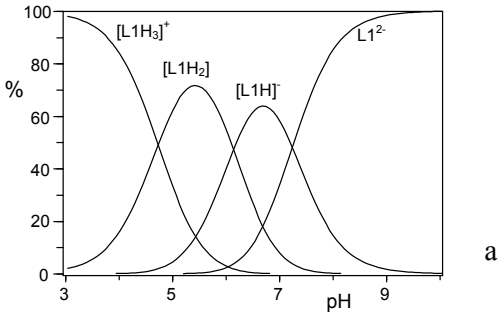
Table S1. Protonation constants of the receptors in H_2O/EtOH (50:50 v/v) (I = 0.1 M)

Equilibrium[a]	log K	
	H_2L1	**H_2L2**
$L^{2-} + H^+ = LH^-$	6.98(1)	6.7(1)
$LH^- + H^+ = LH_2$	5.95(1)	5.8(1)
$LH_2 + H^+ = LH_3^+$	4.57(6)	-

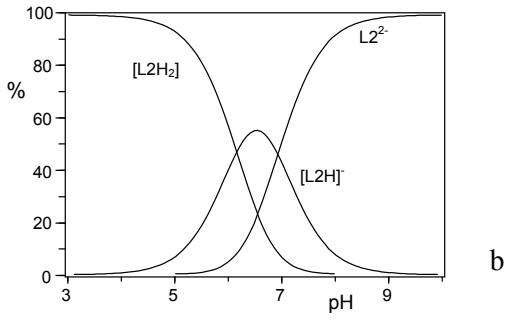
[a]The two first protonation constants of **H_2L1** are similar to those of **H_2L2**. In this case, however, a third protonation equilibrium occurs at more acidic pH values, Reasonably, protonation of the pyridine nitrogen gives rise to the three-protonated species [**L1**H_3]$^+$ species below pH 6.

Table S2. Protonation constants of fluoride in H_2O/EtOH (50:50 v/v) (I = 0.1 M)

Equilibrium	Log K
$F^- + H^+ = HF$	4.22(4)
$2F^- + H^+ = HF_2^-$	7.11(3)



a



b

Figure S12. Distribution diagrams of the protonated forms of **H_2L1** (a) and **H_2L2** (b).

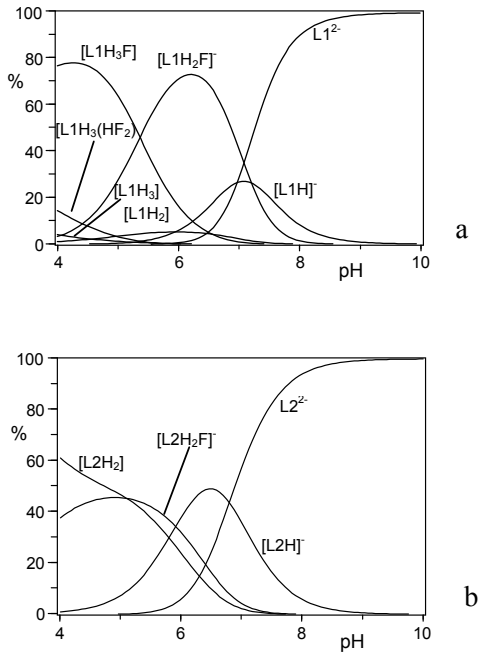


Figure S13. Distribution diagrams of the fluoride complexes formed by **H_2L1** (a), and **H_2L2** (b).

4. Single Crystal X-ray diffraction

Single crystal X-ray diffraction data for compounds **H_2L1·H_2O**, **(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O** are given in Table 1. The crystallographic data collection for compounds **(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O** were performed on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity HG Saturn 724+ detector mounted at the window on an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics at 100(2) K. For compound **H_2L1·H_2O** the data collection was performed on a Rigaku XtaLABmini fixed chi 2-circle diffractometer with a Mercury 375R detector at 170(2) K. Cell determinations and data collections were carried out using CrystalClear[5]. With the data reduction, cell refinement and absorption correction using CrysAlisPro[6] (**(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O** or CrystalClear[5] (**H_2L1·H_2O**). Using Olex2[7] the structures were solved using SHELXS[8] (**H_2L1·H_2O**) or SHELXT[9] (**(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O** and models refined with SHELXL[10]. All non-H atoms were refined anisotropically and difference Fourier syntheses were employed in positioning idealized hydrogen atoms and were allowed to ride on their parent C-atoms. Compounds **(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O** both have some disorder requiring the use of geometrical and thermal restraints.

It was not possible to accurately locate all the hydrogen atoms of the water and HF moieties in compound **(L1·HF)TBA_2·2.25 H_2O**. Their locations were determined and fixed based on given donor-acceptor distances and expected pKa's.

Table S3. Crystal data and structure refinement for compounds **$H_2L1{\cdot}H_2O$** , **(HL1)TBA·0.86 H_2O** and **(L1·HF)TBA_2·2.25 H_2O**

Compound	**$H_2L1{\cdot}H_2O$**	**(HL1)TBA·0.86 H_2O**	**(L1·HF)TBA_2·2.25 H_2O**
CCDC deposition N	CCDC1854630	CCDC1854632	CCDC1854631
Formula	$C_{29}H_{27}N_5O_7$	$C_{45}H_{61.72}N_6O_{6.86}$	$C_{183}H_{304}F_2N_{21}O_{26.5}$
$D_{calc.}$/ g cm^{-3}	1.399	1.206	1.153
m/mm^{-1}	0.102	0.082	0.078
Formula Weight	557.55	796.40	3260.45
Colour	colourless	colourless	colourless
Shape	plate	plate	needle
Size/mm^3	0.330×0.170×0.050	0.090×0.060×0.010	0.250×0.050×0.010
T/K	170	100(2)	100(2)
Crystal System	monoclinic	triclinic	monoclinic
Flack Parameter	2.2(10)	0.4(6)	-0.1(6)
Space Group	$P2_1$	$P1$	$P2_1$
a/Å	9.4201(16)	9.4112(3)	19.7262(8)
b/Å	13.601(2)	14.2754(5)	17.6337(6)
c/Å	10.9510(18)	16.4708(10)	28.3261(9)
a/°	90	84.157(4)	90
b/°	109.325(8)	88.236(4)	107.612(4)
g/°	90	85.515(3)	90
V/Å^3	1324.0(4)	2194.01(17)	9391.3(6)
Z	2	2	2
Z'	1	2	1
Wavelength/Å	0.71075	0.71075	0.71075
Radiation type	MoK_a	MoK_a	MoK_a
Q_{min}/°	2.995	1.993	1.568
Q_{max}/°	27.484	25.028	25.028
Measured Refl.	16382	23844	54455
Independent Refl.	6061	12127	26411
Reflections with I > 2(I)	3718	9130	14476
R_{int}	0.0828	0.0349	0.0675
Parameters	393	1202	2510
Restraints	3	1238	4364
Largest Peak	0.234	0.396	0.867

Deepest Hole	-0.216	-0.200	-0.254
GooF	1.027	1.008	1.009
wR_2 (all data)	0.1204	0.1249	0.2547
wR_2	0.1032	0.1122	0.2068
R_1 (all data)	0.1223	0.0826	0.1698
R_1	0.0634	0.0540	0.0896

4.1. Crystal structure of $H_2L1 \cdot H_2O$

Crystallization by slow evaporation from a solution of the receptor **H_2L1** in methanol resulted in the formation of colourless plates. **$H_2L1 \cdot H_2O$** crystallizes in the monoclinic crystal system (space group $P2_1$) with one independent receptor and one water molecule in the asymmetric unit. The receptor adopts a conformation with the amido NHs oriented approximately parallel with respect to the plane of the pyridine ring and pointing at the centre of the pseudo-cavity (Fig. S14 a). Apart from two intramolecular hydrogen bonds with the pyridine nitrogen [N(2)···N(3) and N(4)···N(3) distances are 2.672(5) Å and 2.655(6) Å respectively], no relevant interactions involving amido NHs are observed.

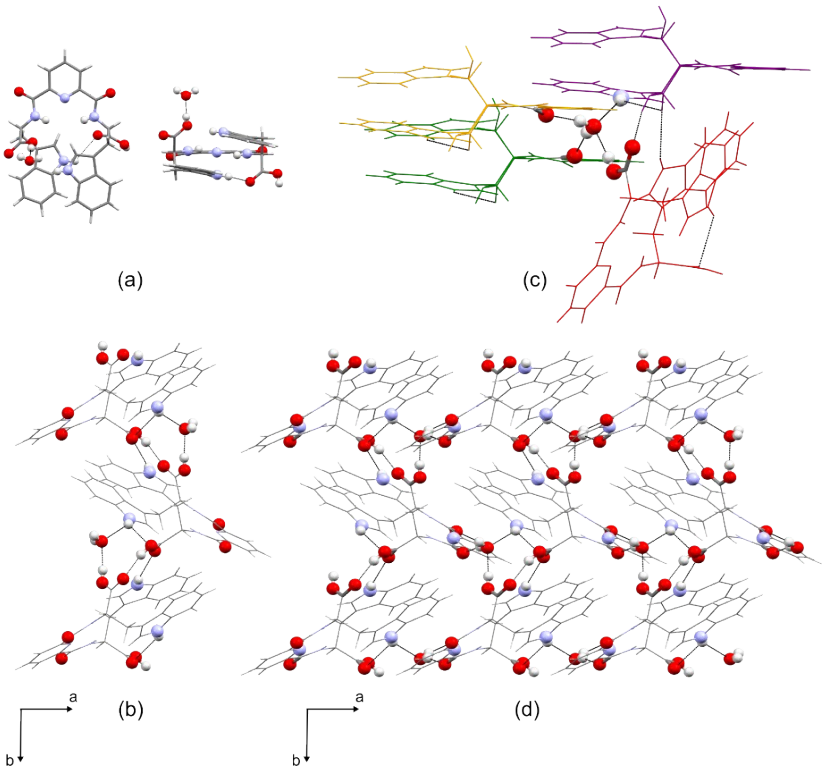


Fig.S14. (a) asymmetric unit of **$H_2L1 \cdot H_2O$** viewed along two perpendicular directions; (b) infinite 1-D chain of receptor molecule, viewed down the *c* direction; (c) tetrahedral coordination of one water molecule; (d) crystal packing of H_2L1, viewed down the *c* direction.

The size of the cavity is dramatically reduced by the conformation of the two tryptophan pendant arms. Both indole rings lie on distinct planes approximately parallel to the pyridine ring, with the NH donors pointing toward the carboxylic group of the opposite pendant arm. Adjacent receptor molecules interact each other via a set of O-H…O hydrogen bonds involving the two carboxylic groups [O(1)…O(5) distance is 2.650(5) Å] assisted by a N-H…O hydrogen bonding involving one of the indole NHs and one of the carboxylic groups [N(1)…O(2) distance is 3.137(6)Å]. These result in infinite herringbone chains propagating along the direction *b* of the unit cell, due to the 2_1 screw axis symmetry (Fig S14 b). Each independent water molecule interacts via set of O-H…O and N-H…O with four adjacent receptor molecules adopting a distorted tetrahedral geometry. As result of this coordination, water molecules are responsible for the propagation of adjacent receptor units along the three direction of the packing, contributing to the formation of the infinite chains mentioned above via O-H…O…H-N bridges [O(6)…O(1W) and N(5)…O(1W) distances are 2.553(6) Å and 3.180(5)Å respectively] and bridging receptors unit along the remaining two directions (Fig S14 d).

4.2. Crystal structure of (HL1)TBA·0.86H_2O

(HL1)TBA·0.86H_2O was crystallised by slow evaporation from a solution of **H_2L1** in DMSO/ $MeNO_2$ (approximately 1:10) in presence of excess of $(TBA^+)_3$ $HPpi^{3-}$, resulting in the formation of colourless plates. The crystal structure **(HL1)TBA·0.86H_2O** crystallises in the triclinic crystal system (space group *P*1). Surprisingly, though the system was crystallised in presence of a large excess of $(TBA^+)_3$ $HPpi^{3-}$, no $HPpi^{3-}$ ions are present in the crystal structure, with the asymmetric unit only composed of two independent receptor molecules, two tetrabutylammonium ions (TBA^+) and two independent water molecules (one partially occupied). The positive charge of the two TBA^+ cations is balanced by deprotonation of the carboxylic groups, one per each independent receptor unit. The absence of the $HPpi^{3-}$ anion in the crystal structure is consistent with the reduced size of the pseudo-cavity, which is not suitable to accommodate any guest. Like the case of **H_2L1·H_2O**, the amido NHs are parallel to the plane of the pyridine ring and oriented toward the centre of the pseudo-cavity which has a reduced size due to the orientation of the tryptophan pendant arms, differing in this case for the relative orientation of the imidazole rings with respect the pyridine ring (Fig S15 a). One of these is oriented approximately perpendicular to the pyridine ring for both independent receptors and the second imidazole rings are oriented to form with the plane of the pyridine ring angles of approximately 40° and 55° respectively. In both independent receptor units, the two carboxylic groups are oriented approximatively perpendicular to the pyridine ring but pointing in opposite directions (Fig. S15 a). L Like the structure of **H_2L1·H_2O**, tryptophan pendant arms and water molecules are responsible for the development of the crystal packing along the three directions of the unit cell. Along the shortest axis (direction *a* of the unit cell), the two independent receptors develop separately by translation symmetry to form two symmetrically independent infinite chains (Fig.S2 b). In one of them (chain 1), independent receptors interact each other by set of N-H…O and O-H…O hydrogen bonds (see Fig S15 b) involving

indole NHs and oxygens of both, carboxylate and carboxylic groups [N(5)…O(6), O(5)…O(2) and N(1)…O(1) distances are 3.321(6) Å, 2.484(4) Å and 2.771(5)Å respectively]. In the second type of chain (chain 2), adjacent identical receptor molecules are connected each other by the same set of N-H…O and O-H…O hydrogen bonds (see Fig S14 b), differing on for the replacement of one of the N-H…O with N-H…O-H…O water bridges involving the indole NH and one of the carboxylate oxygens [O(402)…O(36) and N(35)…O(402) distances are 2.688(8)Å and 2.877(11) Å respectively].

The two independent chains interact each other via set O…H-O-H…O water bridges involving the amido C=O groups and one molecule of water [O(401)…O(4) and O(401)…O(33) distances are 2.853(6) Å and 2.769(6) Å respectively] forming 2-D corrugated sheets that propagate along the -*bc* direction. Adjacent 2-D arrangements interact each other along the ab directions, forming channels which are fitted with TBA+ chains interacting with receptor units and water molecules via weak C-H…O hydrogen bonding (Fig. S15 c).

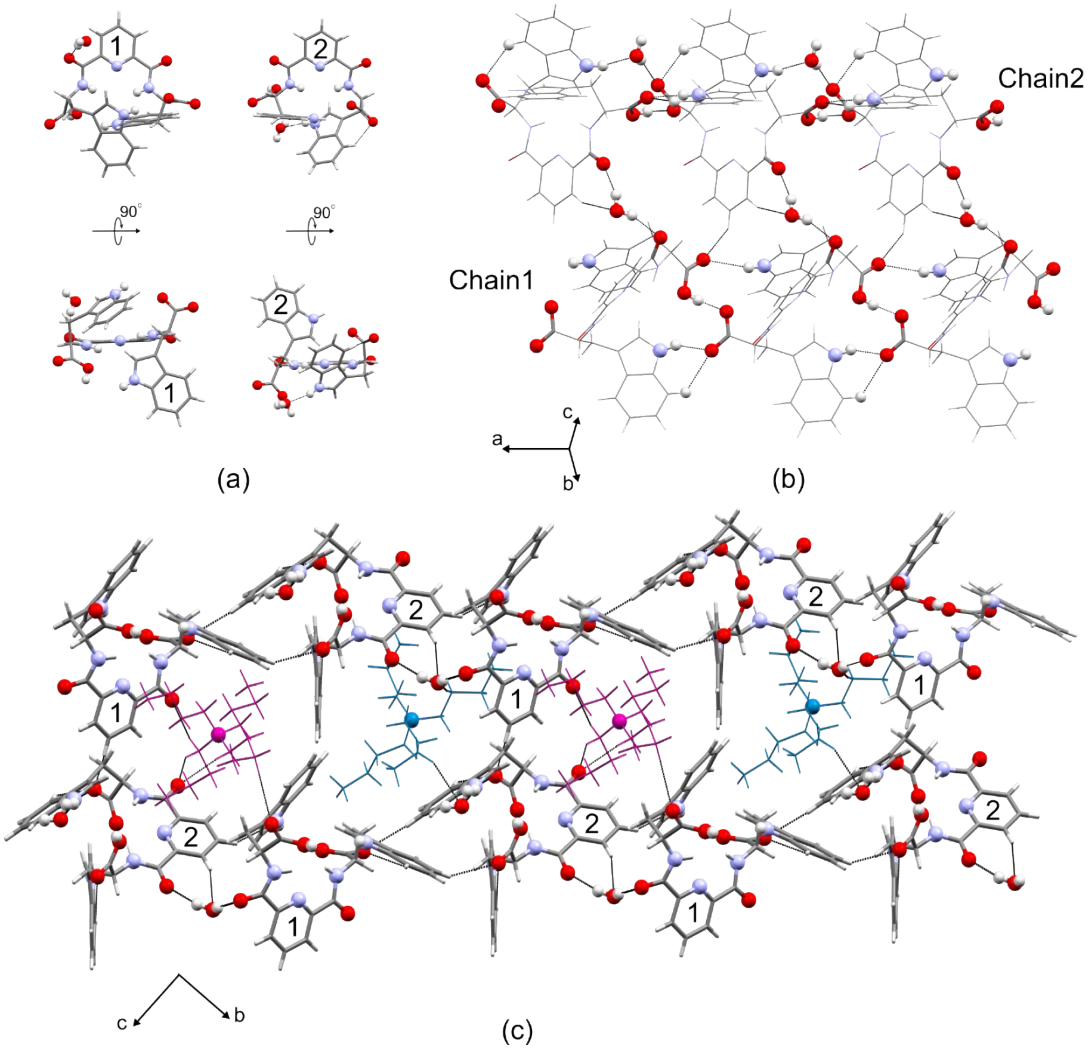


Fig.S15. (a) independent receptor units in **(HL1)TBA·0.86H_2O** viewed along two perpendicular directions; (b) infinite 1-D chains of receptor molecules 1 and 2, viewed down the *cb* direction; (c) crystal packing of **(HL1)TBA·0.86H_2O**, viewed down *a* direction. Independent receptor units are numbered as 1 and 2, independent TBA^+ cations are indicated as purple and teal.

4.3. Crystal structure of (L1·HF)TBA_2·2.25 H_2O

(L1·HF)TBA_2·2.25 H_2O was crystallised by slow evaporation from a solution of **HL1** in CH_3CN/DMSO 1:3 presence of an excess of TBA^+F^-. Evaporation of the solvent resulted in the formation of colourless needles. The crystal structure **(L1·HF)TBA_2·2.25 H_2O** crystallises in the monoclinic crystal system (space group $P2_1$).

The asymmetric unit consists of three independent fully deprotonated receptor molecules, six independent TBA^+ cations, nine molecule of water and two independent HF molecules. The quality of the data was not sufficiently good to identify the hydrogen atoms, consequently it was not possible to accurately locate all the hydrogen atoms of the water and HF moieties in compound **(L1·HF)TBA_2·2.25 H_2O**.

The two independent fluoro atom can only exist as HF or F^-. Considering the number of TBA^+ cations (six positive charges), the only possibility to have two F^- anions in the crystal structure and, at the same time, balance the charges, would involve the protonation of only two carboxylate groups, resulting in a total of six negative charges (two F^- and four COO- anions). This could be ascribed to the water adsorbed by the DMSO during the crystallization by solvent evaporation. A simpler description would involve the protonation occurring in the F^- anion to form two HF molecules, six COO^- anions and six TBA^+ cations. Accordingly, we believe that the two fluoro atoms must be HF instead F^-. This is also confirmed by the analysis of the donor-acceptor distances for potential hydrogen bonding, which also confirm that the pseudo-cavity of the third independent receptor unit is occupied by one molecule of water. In two of the three independent receptor units (Fig. S16 a and b), the HF guest specie is connected to the amide NHs via N-H···F hydrogen bonding (N···F distances lie in the range 2.911(9) -3.097(9) Å) and to one of the carboxylates via F-H···O interactions [F(2)···O(32) and F(1)···O(2) distances are 2.852(9) Å and 2.854(7) Å]. On the opposite side of the carboxylate, the HF molecules also interact with one water molecule via O-H···F hydrogen bonds [O(102)···F(2) and O(103)···F(1) distances are 2.785(11) Å and 2.804(10) Å]. The third independent receptor unit (Fig S17 c) has the cavity occupied by one molecule of water which interacts with the two amido NHs via N-H···O hydrogen bonds [N(64)···O(101) and N(62)···O(101) distances are 2.872(9) Å and 3.150(9) Å] and with the two carboxylate of the tryptophan pendant arms via O-H···.O hydrogen bonds [O(101)···O(65) and O(101))···O(62) distances are 2.816(10) Å and 2.818(10) Å]. Differently to the previous two structures, in which the molecular conformation adopted reduce the size of the pseudo-cavity and prevents any guest specie to be hosted, in this case the three receptor molecules adopt an open conformation, with the indole groups of the tryptophan oriented approximately perpendicular to the plane of the pyridine ring, pointing the indole NHs in opposite directions (Fig S16). The carboxylate groups are oriented parallel to the indole group pointing to the opposite direction with respect the indole NHs.

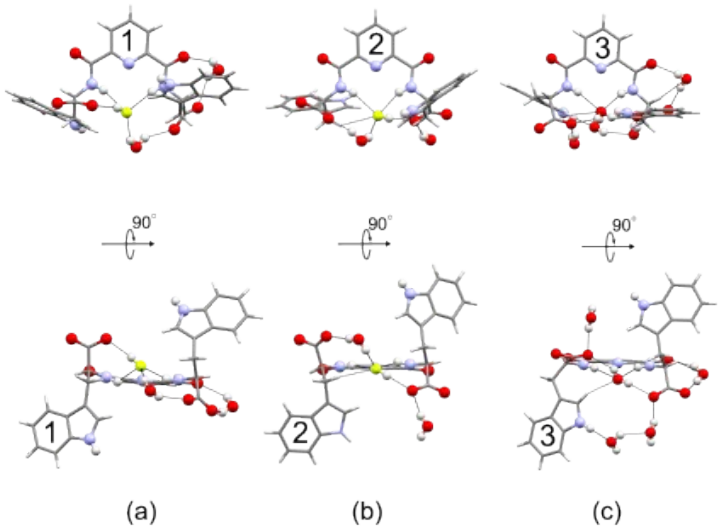


Fig S16. Molecular conformation and main intermolecular interactions observed for the three symmetry independent receptor units in the crystal structure **(L1·HF)TBA$_2$·2.25 H$_2$O**. The two symmetry independent HF molecule and the nine symmetry independent water molecules are also shown. TBA^+ are not displayed for clarity. Hydrogen bonds are indicated as black dashed lines.

This conformation favours N-H···O hydrogen bonds between carboxylate oxygens and indole NHs from adjacent receptor units (N···O distances are in the range 2.708(11)-2.850(8) Å), generating infinite chains of the three independent receptors that propagate along the *c* direction of the unit cell (Fig S17 a). These interactions are also assisted by N-H···H-O-H···O water bridges (O···O distances are in the range 2.818(10)-2.965(10) Å) which connect opposite carboxylate from adjacent receptor units. In one of the three independent receptors, the set of N-H···O hydrogen bonds occurs only in one side of the chain, being the other side only connected by N-H···H-O-H···O water bridges [N(63)···O(106) and O(106)···O(3) distances are 2.773(10)Å and 2.630(11) Å respectively]. Along the direction b, receptor molecules forming the 1-D chains described above, are related by 2_1 screw axis and are developby direct interactions between receptor molecules and TBA^+ units, which also operate along the a direction, generating the 3-D packing (Fig S17 b).

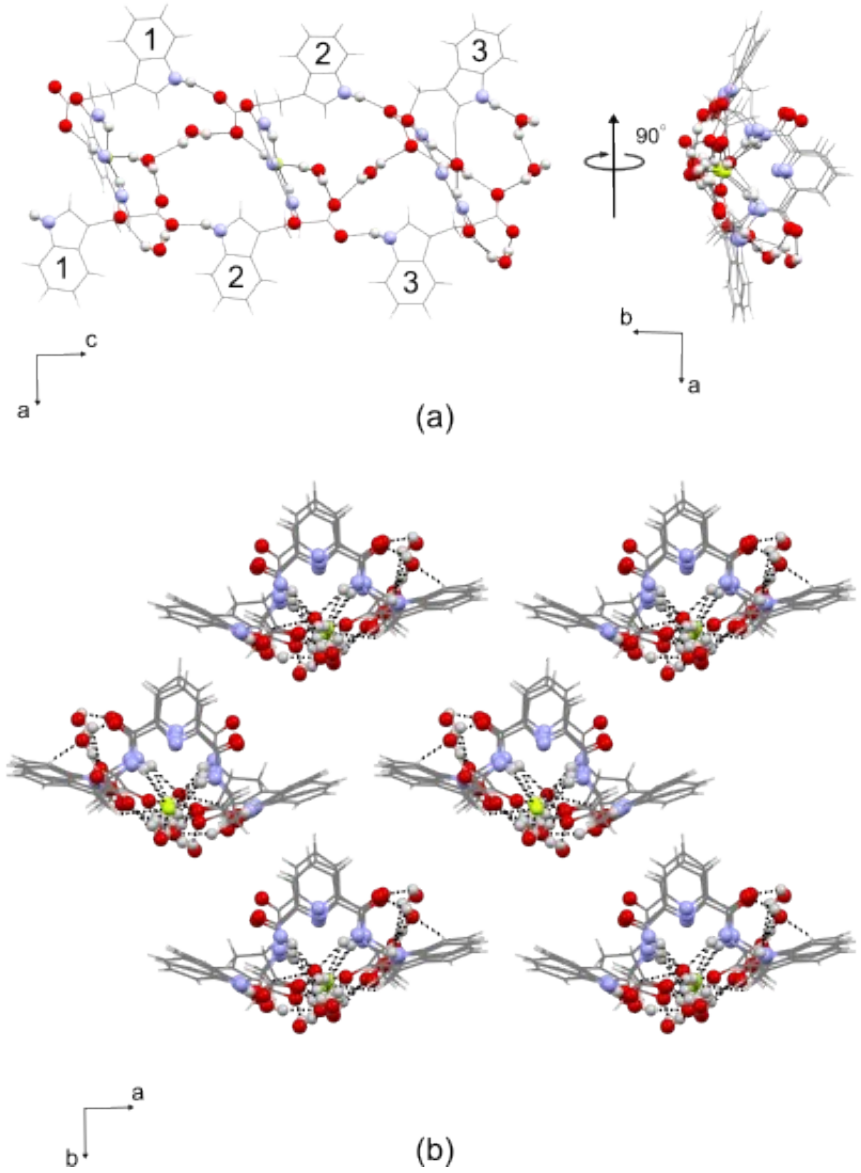


Fig. S17. Crystal packing of structure **(L1·HF)TBA$_2$·2.25 H$_2$O**. (a) Instance of 1-D chains of the connected three symmetry independent receptor molecules viewed along two perpendicular directions of the packing (directions b and c respectively); (b) packing of the 1-D chains along the a and b directions, viewed along the c direction of the unit cell. Main hydrogen bonds are indicated as black dashed lines. TBA+ cations are not displayed for clarity.

Table S4. Intermolecular Interactions. Hydrogen bonds (●) and intramolecular hydrogen bonds (●).

Structure	D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA)	Symmetry
H$_2$L1·H$_2$O	● O(1W)–H(1WA)···O(3)	0.85	1.87	2.694(5)	163	-x,-1/2+y,-2-z
	● N(1)–H(1N)···O(2)	0.80(5)	2.45(6)	3.137(6)	144(5)	1-x,-1/2+y,-2-z
	● O(1W)–H(1WB)···O(4)	0.85	1.87	2.712(5)	169	-x,-1/2+y,-3-z

	N(2)–H(2N)···N(3)	0.83(5)	2.26(4)	2.672(5)	111(4)	-
	N(4)–H(4N)···N(3)	0.87(4)	2.22(5)	2.655(6)	111(4)	-
	N(5)–H(5N)···O(1W)	0.87(5)	2.45(5)	3.180(5)	142(5)	1-x,1/2+y,-2-z
	O(1)–H(11)···O(5)	0.83(7)	1.84(6)	2.650(5)	165(6)	1-x,1/2+y,-2-z
	O(6)–H(61)···O(1W)	0.76(4)	1.80(4)	2.553(6)	173(8)	-
	C(10)–H(10)···O(3)	1.00	2.38	2.820(6)	106	-
	C(19)–H(19)···O(4)	1.00	2.39	2.803(6)	104	-
(HL1)TBA·0.86H_2O	N(1)-H(1)···O(1)	0.88	1.98	2.771(5)	149	-1+x,y,z
	N(2)-H(2)···N(3)	0.88	2.30	2.692(7)	107	-
	N(4)-H(4)···O(5)	0.88	2.33	2.631(6)	100	-
	N(4)-H(4)···N(3)	0.88	2.31	2.691(6)	106'	-
	O(5)-H(5)···O(2)	0.84	1.65	2.484(4)	174	-1+x,y,z
	N(5)-H(5A)···O(6)	0.88	2.48	3.321(6)	161	1+x,y,z
	N(31)-H(31)···O(31)	0.88	2.02	2.797(5)	147	1+x,y,z
	O(32)-H(32)···O(35)	0.84	1.64	2.464(6)	165	-1+x,y,z
	N(32)-H(32A)···N(33)	0.88	2.23	2.643(6)	109	-
	N(34)-H(34)···N(33)	0.88	2.26	2.659(6)	107	-
	N(35)-H(35A)···O(402)	0.88	2.04	2.877(11)	160	-
	N(35A)-H(35B)···O(36)	0.88	2.60	3.43(2)	158	-1+x,y,z
	N(35A)-H(35B)···O(402)	0.88	2.01	2.63(2)	127'	-
	O(401)-H(40A)···O(4)	0.87	2.03	2.853(6)	157	-
	O(401)-H(40B)···O(33)	0.87	1.93	2.769(6)	161	-
	O(402)-H(40D)···O(36)	0.87	1.94	2.688(8)	143	-1+x,y,z
	C(19) -H(19)···O(4)	1.00	2.50	2.846(6)	100	-
	C(50) -H(50)···O(34)	1.00	2.47	2.847(7)	102	-
	C(51) -H(51B)···O(36)	1.12	2.56	2.976(18)	101	-
	C(55) -H(55)···O(36)	0.95	2.42	3.201(10)	139	-
(L1·HF)TBA_2·2.25 H_2O	O(101)-H···O(62)	0.87	2.12	2.818(10)	137	-
	F(1)-H(1)···O(2)	0.87	2.01	2.854(7)	163	-
	F(1)-H(1)···N(2)	0.87	2.56	2.966(10)	110'	-
	O(109)-H(A)···O(66)	0.87	1.98	2.837(16)	170	-
	N(2)-H(2)···F(1)	0.88	2.31	2.966(10)	132	-
	N(2)-H(2)···N(1)	0.88	2.37	2.722(11)	104'	-
	O(104)-H(B)···O(32)	0.87	2.06	2.892(11)	159	-

F(2)-H(2B)···O(32)	0.87	1.99	2.852(9)	174	-
N(3)-H(3)···O(33)	0.88	1.98	2.798(11)	154	-
O108-H0AA···O62	0.87	2.11	2.965(10)	168	-
N4-H4···F1	0.88	2.26	3.079(9)	155	-
N4-H4···N1	0.88	2.36	2.734(10)	106'	-
O108-HC···O35	0.87	2.13	2.878(12)	144	-
N5-H5···O66	0.88	2.05	2.850(8)	152	x,y,1+z
O105-H1AA···O65	0.87	1.98	2.818(10)	161	-
O105-HD···O2	0.87	2.02	2.875(9)	166	x,y,-1+z
O106-H2AA···O105	0.87	2.14	2.875(9)	142	-
O106-HE···O3	0.87	1.85	2.630(11)	148	x,y,-1+z
O107-H3AA···O6	0.87	2.12	2.776(14)	132	-
O104-H10···O103	0.87	2.15	2.932(12)	149	-
O107-HF···O4	0.87	2.13	2.833(8)	138	-
O102-H10U···O35	0.87	1.81	2.664(14)	167	-
O102-H10V···F2	0.87	2.01	2.785(11)	148	-
O103-H10W···O5	0.87	2.01	2.764(11)	145	-
O103-H10X···F1	0.87	2.04	2.804(10)	146	-
O101-H10Y···O65	0.87	2.02	2.816(10)	151	-
O109-H10Z···O64	0.87	2.05	2.853(10)	154	-
N32-H32 ···F2	0.88	2.14	2.911(9)	146	-
N32-H32 ···N31	0.88	2.34	2.730(11)	107'	-
N33 -H33···O63	0.88	1.92	2.788(10)	169	-
N34 -H34···F2	0.88	2.26	3.097(9)	158	-
N34 -H34···N31	0.88	2.33	2.717(9)	107'	-
N35 -H35···O6	0.88	1.91	2.744(8)	156	-
N62 -H62···O101	0.88	2.29	3.150(9)	166	-
N62-H62···N61	0.88	2.35	2.709(10)	105'	-
N63-H63···O106	0.88	1.89	2.773(10)	177	-
N64-H64···O101	0.88	2.06	2.872(9)	153	-
N64-H64···N61	0.88	2.29	2.695(9)	108'	-
N65-H65···O36	0.88	1.89	2.708(11)	154	-
C19-H19 ···O4	1.00	2.40	2.807(10)	104	-
C37-H37···O31	1.00	2.50	2.846(15)	100	-
C49-H49···O34	1.00	2.38	2.783(11)	103	-
C79-H79···O64	1.00	2.46	2.838(10)	102	-

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