Non-symmetric substituted ureas locked in (*E*,*Z*) conformation: an unusual anion binding *via* supramolecular assembly

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Electronic Supplementary Information

S1 General procedures

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen. 2-quinolinecarbonyl azide,[1] and 7-aminoindole[2] were synthesised following a literature procedure. ^{1}H-NMR (400 MHz) and ^{13}C NMR (100 MHz, 126 MHz) spectra were determined on a Varian INOVA-400 spectrometer, and Varian INOVA-500 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet . Chemical shifts for ^{13}C NMR are reported in ppm, relative to the central line of a septet at δ = 39.52 ppm for deutero-dimethylsulfoxide. Infrared (IR) spectra were recorded on a NICOLET 5700 FT-IR spectrophotometer and reported in wavenumbers (cm^{-1}). Microanalytical data were obtained using a Fisons EA CHNS-O instrument (T = 1000 °C). Fluorescence spectra were recorded on a Cary Eclypse spectrofluorimeter. All solvents and starting materials were purchased from commercial sources where available.

^{1}H spectra were acquired using a 6.7 μs pulse (90°), 1 s delay time, 1 s acquisition time and a spectral width of 5 kHz. ^{1}H-^{1}H correlation TOCSY experiments were recorded over the same spectral window as ^{1}H one-dimensional spectra, using 2048 complex points and sampling each of the 512 increments with 64 scans with 250 ms spin-lock using the MLEV-17 mixing scheme. The same acquisition parameters have been applied for the acquisition of the NOESY experiments with 200 ms mixing time. Selective DPFGSE (Double Pulse Field Gradient Spin-Echo) one-dimensional noesy[3] has been performed with the same acquisition parameters as for simple ^{1}H spectra with 512 scans and 200 ms mixing time. In order to correct for sources of relaxation other than the dipolar one giving the noe enhancement, the so-called PANIC (Peak Amplitude Normalization for Improved Cross-relaxation) method was applied.[4] The intensity of each noe peak was divided by that of the inverted resonance in the same spectrum, thus providing a normalized noe enhancement. Generally speaking, this kind of transient NOE experiments, on the whole, usually give smaller NOE enhancements than are normally observed in the steady-state like experiments. However, this

was the method of choice since it has been shown how the artefacts typically generated by difference NMR spectroscopy are eliminated, and how it is possible to measure NOE enhancements of as little as 0.02%.[3]

Proton NMR titrations were performed by adding aliquots of the putative anionic guest (as the TBA salt, 0.075 M) in a solution of the receptor (0.005M) in DMSO-d_6/0.5% water to a solution of the receptor (0.005M).

Structure calculations were performed using the simulated annealing molecular dynamics algorithm implemented in DYNAMO (http://spin.niddk.nih.gov/NMRPipe/dynamo). The temperature was increased to 4000 K in 1000 initialization steps, then kept constant for 4000 steps, and finally slowly decreased to 0 K during the 20000 steps cooling stage. Gromos-53a6 force field parameters were obtained through the ProDrg server (http://davapc1.bioch.dundee.ac.uk/prodrg/).

The radial distribution functions have been computed through the software VMD[5] by selecting each of the aromatic ring protons of one **L**^{1} molecule involved in the duplex, on one hand, and all of the aromatic carbons of the other molecule, on the other. Results for the two proposed supramolecular assemblies (Fig. 8b and 8c) are shown in Figure S10.

S1.1. Synthesis of 1-(1H-indol-7-yl)-3-(quinolin-2-yl)urea (**L**^{1})

A solution of 2-quinolinecarbonyl azide (0.1 g, 0.505 mmol) in anhydrous toluene (20 ml) was refluxed under N_2 for 4h to induce rearrangement into isocyanate. 7-aminoindole (0.06 g, 0.454 mmol) was then added and the resulting mixture was refluxed for 24h. A grey precipitate was formed, filtered and was left stirring in CH_2Cl_2 overnight. The solution was then filtered and the filtrate was concentrated in vacuum to give a light brown solid which was washed with MeOH to give the desired compound as a white solid. Yield 29% (0.04g, 0.132 mmol) M.p.: 220°C; ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K): δH 6.47-6.49 (m, 1H); 7.01 (t, J=7.6 Hz, 1H); 7.20 (d, J = 7.2, 1H); 7.30-7.50 (m, 4H); 7.70 (t, J = 7.6 Hz, 1H); 7.84 (d, J= 8.4 Hz, 1H); 7.89 (d, J=8 Hz, 1H);8.32 (d, J=8.8 Hz, 1H); 10.12 (s, 1H, NH); 10.89 (s, 1H, NH); 11.67(s, 1H, NH). ^{13}C-NMR (100 MHz, DMSO-d_6, 298 K) δC 101.65, 113.60, 115.14, 116.84, 119.06, 122.73, 124.39, 124.51, 125.63, 126.51, 127.76, 129.49, 129.73, 130.20, 138.73, 144.98, 152.46, 152.89. IR (KBr, cm^{-1}) ν = 3382 (br, NH indole stretching), 3255 (br, NH urea stretching),1649 (s, CO stretching). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a 1:1 mixture of DCM and MeOH resulting in a solvate phase (**L**^{1}α). Elemental analysis found (calculated for $C_{21}H_{26}N_4O_4$): C 63.45 (63.30); H 6.52 (6.58); N 14.11 (14.06). A further crystallization experiment carried out in the presence of tetrabutylammonium acetate from MeOH/THF 2:1 resulted in a non-solvated phase of the free receptor **L**^{1} (**L**^{1}β).

Elemental analysis found (calculated for $C_{18}H_{14}N_4O$): C 71.49 (71.51); H 4.66 (4.67); N 18.55 (18.53).

S1.2. Synthesis of (1-(quinolin-2-yl)-3-(quinolin-8-yl)urea) (L^2)

A solution of 2-quinolinecarbonyl azide (0.1 g, 0.505 mmol) in toluene anhydrous (20 ml) was refluxed under N_2 for 4h to induce rearrangement into isocyanate. 8-aminoquinoline (0.65 g, 0.454 mmol) was then added and was refluxed overnight. The reaction mixture was filtered to give the desired product as a white solid. Yeld 63% (0.09g, 0.286 mmol). M.p. <250°C; ^{1}H-NMR (400 MHz, DMSO-d_6, 298 K): δH 7.29 (d, J= 8.8 Hz, 1H); 7.50 (t, J=7.2 Hz, 1H); 7.58-7.72 (m, 3H); 7.83-7.90 (m, 2H); 8.31 (d, J=8.4 Hz, 2H); 8.44 (d, J= 8.4 Hz, 1H); 8.76 (d, J= 6.8 Hz, 1H); 9.18-9.21 (m, 1H); 10.30 (s, 1H, NH); 13.96 (s, 1H, NH). ^{3}C-NMR (126 MHz, DMSO-d_6, 298 K) δC 113.29, 115.80, 120.80, 122.03, 124.25, 124.48, 126.43, 127.17, 127.70, 128.06, 130.35, 136.29, 136.50, 138.53, 138.67, 145.13, 148.71, 151.97, 152.47. IR (KBr, cm^{-1}) ν = 3358 (br, NH indole stretching), 3220 (br, NH urea stretching),1685 (s, CO stretching).

Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from DMSO. Elemental analysis: found (calculated for $C_{19}H_{14}N_4O$): C 72.59 (72.60); H 4.51 (4.49); N 17.81 (17.77).

S2. Crystallographic Data

S2.1. $L^1\alpha$.

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit*). Cell determination: DirAx[5] **Data collection:** Collect[6]. **Data reduction and cell refinement:** *Denzo*[7]. Absorption correction: Sheldrick, G. M. SADABS - Bruker Nonius area detector scaling and absorption correction - V2.10 **Structure solution:** *SHELXS97*[8]. **Structure refinement:** *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Special details: Hydrogens were located in the difference map and then placed in idealised positions and refined using a riding model. PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of 101 A^3. Electron density peaks centred around the 3-fold axes could not be sensible modelled as solvent and the SQUEEZE algorithm was applied[9] from within the platon software[10]. The solvents used for crystallisation were DCM and MeOH.

S2.2. $L^1\beta$ and L^2

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode

generator with HF *Varimax* optics (100µm focus). **Cell determination, Data collection, Data reduction and cell refinement & Absorption correction**: CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011) , **Structure solution**: SHELXS97[8]. S**tructure refinement**: SHELXL97 (G. M. Sheldrick (1997), University of Göttingen, Germany).

Special details: All hydrogen atoms were placed in idealised positions and refined using a riding model.

Table S1. Crystal data and structure refinement details.

	L^{1}α	**L^{1}β**	**L^2**
Empirical formula	$C_{21}H_{26}N_4O_4$	$C_{18}H_{14}N_4O$	$C_{19}H_{14}N_4O$
Moiety formula	$C_{18}H_{14}N_4O$,3(CH_3OH)	$C_{18}H_{14}N_4O$	$C_{19}H_{14}N_4O$
Formula weight	302.33	302.33	314.34
Crystal system	Trigonal	Orthorhombic	Monoclinic
Space group	*R*–3	*Pna*2$_1$	*P2$_1$/c*
a /Å	32.989(7)	22.003(4)	8.0410(17)
b /Å	32.989(7)	7.1308(14)	19.459(4)
c /Å	7.098(2)	18.677(4)	18.998(4)
α / °	90.00	90.00	90.00
β / °	90.00	90.00	94.696(3)
γ / °	90.00	90.00	90.00
V /Å^3	6689(3)	2930.5(9)	2962.6(11)
T / K	100(2)	100(2)	100(2)
Crystal shape	Needle	Slab	Plate
Crystal size / m^3	0.20 × 0.03 × 0.02	0.22 × 0.10 × 0.03	0.12 × 0.10 × 0.04
Colour	colourless	colourless	colourless
Z	18	8 (Z' = 2)	8 (Z' = 2)
θ range for data collection	2.96 – 25.02°	3.00 – 25.03°	2.54 – 31.28
Index ranges	–38 ≤ *h* ≤ 18, 0 ≤ *k* ≤ 39, 0 ≤ *l* ≤ 8	–19 ≤ *h* ≤ 26, –5 ≤ *k* ≤ 8, –22 ≤ *l* ≤ 21	–11 ≤ *h* ≤ 11, –27 ≤ *k* ≤ 27, –13 ≤ *l* ≤ 27
Reflections collected	2613	12023	16289
Independent reflections	2613 [R_{int} = 0.0000]	2677 [R_{int} = 0.1016]	8526 [R_{int}=0.0333]
Completeness	99.6 % (θ = 25.02°)	99.7 % (θ = 25.03°)	99.0 % (θ = 27.50°)
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	0.9982 and 0.9826	0.9973 and 0.9806	0.9964 and 0.9891
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2613 / 0 / 208	2677 / 1 / 415	8526 / 0 / 433
Goodness-of-fit on F^2	1.164	1.044	1.119
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0712, *wR2* = 0.1314	*R1* = 0.0624, *wR2* = 0.1016	*R1 = 0.0793,* *wR2 = 0.1604*
***R* indices (all data)**	*R1* = 0.0990, *wR2* = 0.1421	*R1* = 0.0859, *wR2* = 0.1085	*R1 = 0.1121, wR2 = 0.1788*
Largest diff. peak and hole	0.256 and –0.227 e Å^{-3}	0.239 and –0.302 e Å^{-3}	0.294 and –0.243 e Å^{-3}

Table S2. Hydrogen bonds [Å and °].

Phase	*D*–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
	N2–H2A···O1[i]	0.88	1.98	2.845(3)	169
L[1]α	N3–H3A···N1	0.88	1.90	2.657(3)	143
	N4–H4A···O1	0.88	1.98	2.686(3)	136
	N102–H102···O201	0.88	2.13	2.997(5)	169
	N103–H103···N101	0.88	1.90	2.654(6)	142
L[1]β	N104–H104···O101	0.88	1.97	2.687(5)	137
	N202–H202···O101	0.88	1.97	2.848(5)	172
	N203–H203···N201	0.88	1.92	2.682(6)	143
	N204–H204···O201	0.88	2.00	2.703(5)	137
	N2–H902...N4	0.88	1.98	2.697(2)	138
L[2]	N3–H903...O2	0.88	1.95	2.830(2)	175
	N6–H906...N8	0.88	1.98	2.694(3)	137
	N7–H907...O1	0.88	2.03	2.888(2)	166

i (-x+5/3, -y+1/3, -z- 2/3)

S2.3 XPac Analysis

The XPac methodology[11] enables the comparison of structures of related molecules. The analysis is carried out by using the XPac software which allow the identification of any geometrically similar assemblies of molecules occurring in two or more structures. These common molecular arrangements are referred to as Supramolecular Constructs (SCs), and may have different dimensions: 0-D (discrete molecular assemblies), 1-D (similar stacks or rows of molecules), 2-D (similar sheets, packed differently) and 3-D (isostructurality, isomorphism and pseudo-isostructurality).

The analysis was carried out using all the atoms of the quinoline substituted group as Corresponding Ordered Set of Points (COSP) (see Figure S1), and medium filter parameters (a:10, p:14, d:1.5).

For each similarity identified the software provide a dissimilarity index (χ)[12] (see table S3).

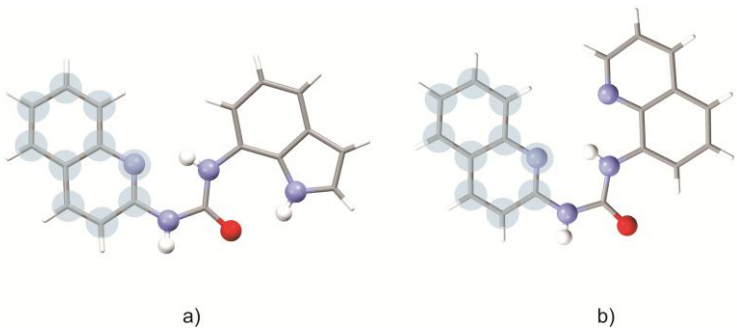


Figure S1. Corresponding Ordered Set of Points (COSP) chosen for the analysis and represented for L[1](a) and L[2] (b).

	$L^1\alpha$	$L^1\beta$	L^2
$L^1\alpha$	-	1D $\chi = 8.9$	1D $\chi = 8.3$
$L^1\beta$	-	-	1D $\chi = 12.7$

Table S3. Dissimilarity index (χ) for the three comparisons $L^1\alpha$- $L^1\beta$, $L^1\alpha$- L^2 and $L^1\beta$- L^2.

S2.4 Methanol solvate $L^1\alpha$

The analysis of the crystal packing of **$L^1\alpha$** viewed along the *001* direction reveals the presence of channels which have not any potential strong hydrogen bond donor or acceptor (Fig S2 and S3).

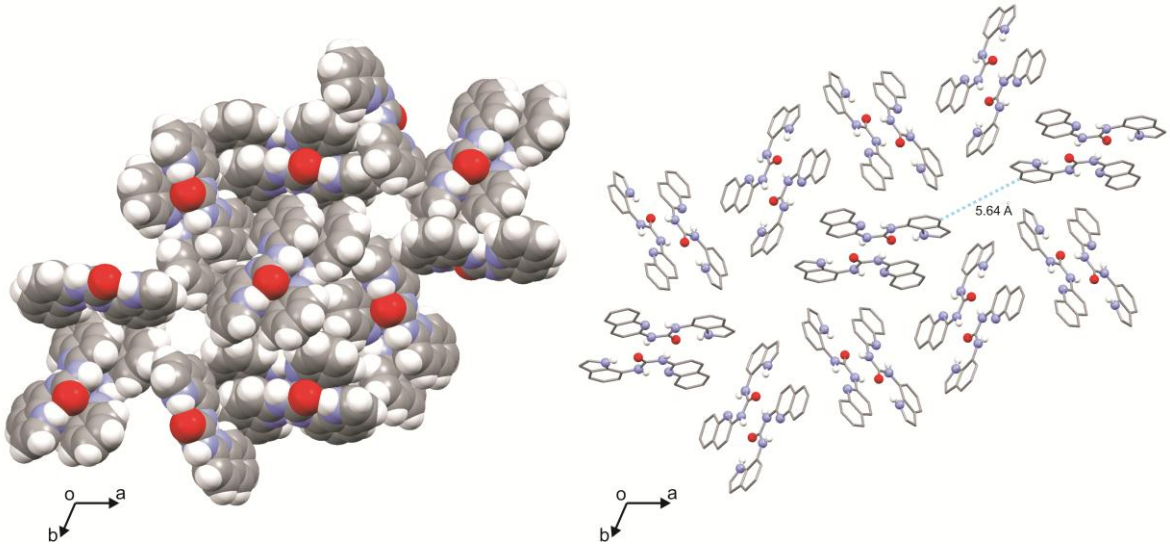


Figure S2. 1-D channels for **$L^1\alpha$** viewed along the *001* direction: spacefill representation (left), capped sticks representation (right). An estimation of the diameter (Å) measured as (quin)H-(quin)H distances is also reported.

A calculation of the solvent accessible void for **$L^1\alpha$** (probe radius 1.2 Å)[10, 13] gives a value of 101.4 Å^3 for each channel.

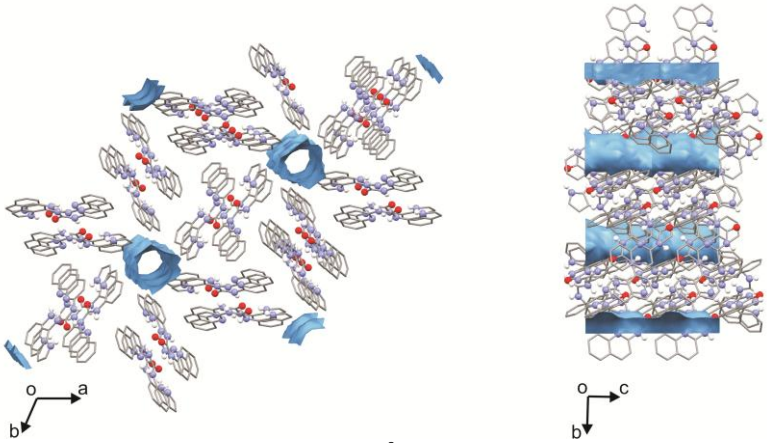


Figure S3. Solvent accessible surface (probe radius 1.2 Å) calculated for **$L^1\alpha$**, respectively viewed along the *001* direction (left) and the *100* direction (right).

This value is consistent with the expected volume for solvent molecules such as H_2O (40 Å^3) and generally small molecules (100-300 Å^3). At this stage it is not possible to discriminate which solvent, MeOH or DCM, initially co-crystallised with, but from volume and electron density considerations (methanol has an electron count of 18; squeeze suggests an electron count of 47 per cell which would give 3 molecules of this solvent per unit cell) methanol is assumed the most likely. This is also confirmed by elemental analysis (

S3. L^1 Dimerisation constant determination by ^1H dilution experiment and variable temperature experiments in $CDCl_3$

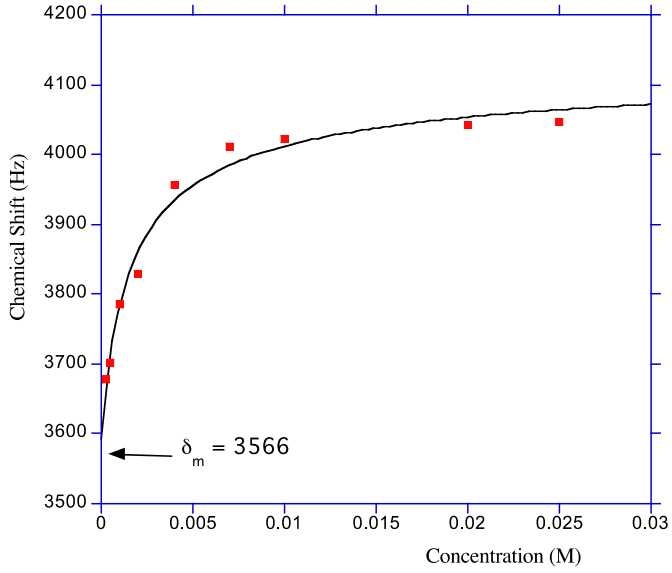


Figure S4. Determination of the dimerisation constant (K_{dim}) of **L¹** in $CDCl_3$ at 298 K, experimental data square points. Standard nonlinear least-squares regression analysis of the concentration-dependent chemical shift changes of proton N2-H2A The equation used for fitting the data had the form $\delta_{obsd} = \delta_m + (\delta_{dim} - \delta_m)\,[1 + 8K_{dim}[A_0]]^{½} - 1] / [1 + 8K_{dim}[A_0]]^{½} + 1]$ where $[A_0]$ is the total concentration, δ_{obsd} , δ_m , δ_{dim}, are the observed, monomer, and dimer chemical shift, respectively.[15]

$K_{dim} = 430 \pm 37\ M^{-1}$

R = 0.98923

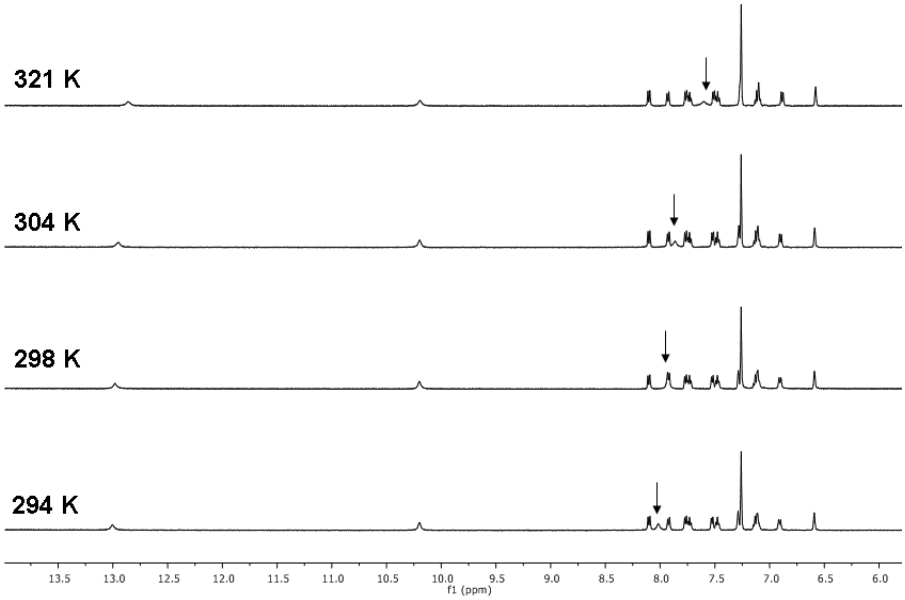
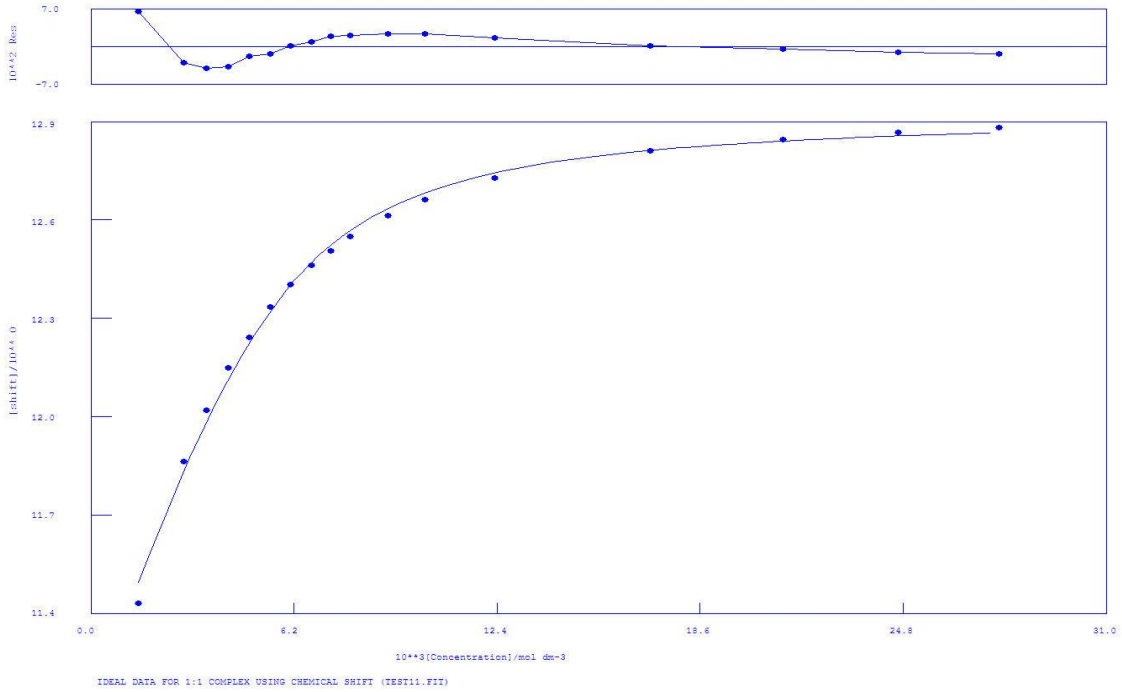


Figure S5 ^{1}H-NMR stack plot of solutions of **L^{1}** in $CDCl_3$ at 298 K at variable temperature. The arrows indicate the N2–H2A signal moving upfield upon increasing the temperature.

S4. Proton NMR titration fitting

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 FILE: TEST11.FIT
 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
 File prepared by M. J. Hynes, October 22 2000
NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  1.20340E+03 2.000E-01 1.244E+02 7.581E+00    K1
   2  1  1.10926E+01 2.000E-01 3.048E-02 2.313E+00   SHIFT M
   3  1  1.29822E+01 1.000E+00 2.099E-02 5.323E+00    SHIFT ML
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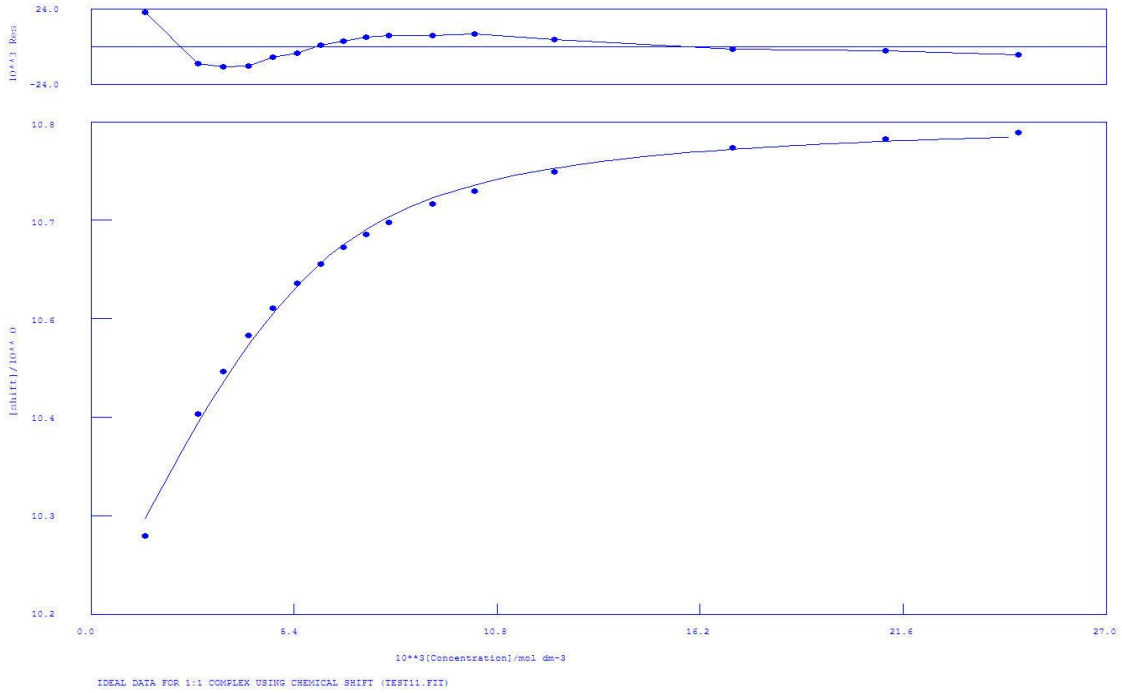
Figure S6. ^{1}H-NMR of **L^1** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the indolic NH.

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 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
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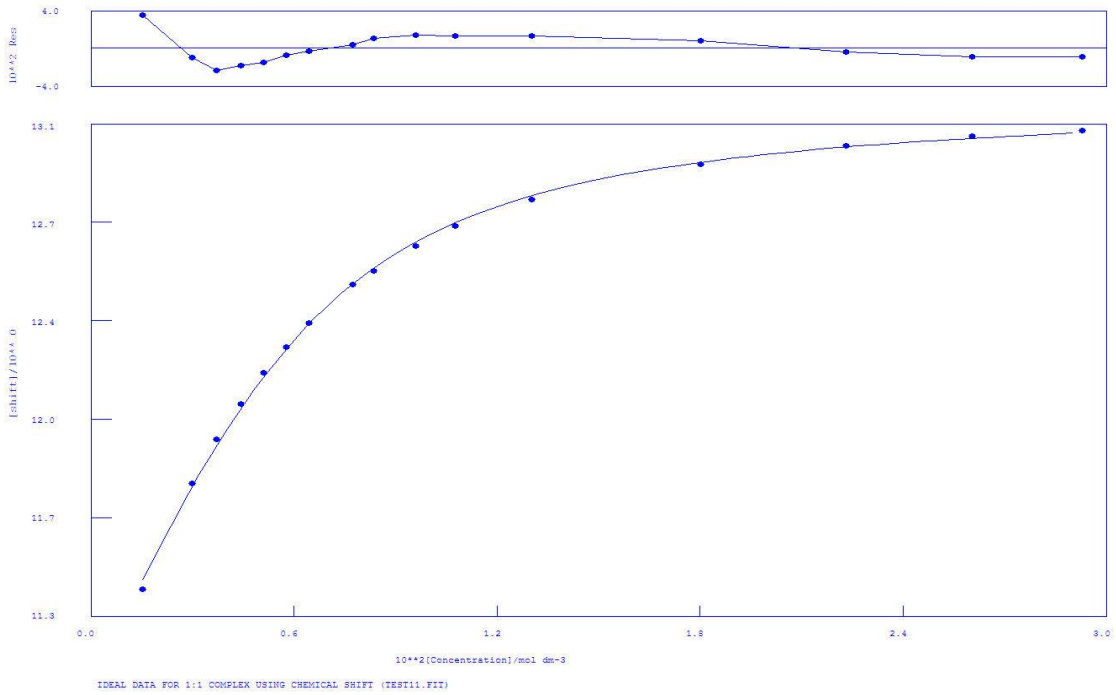
   2  1  1.01842E+01 2.000E-01 1.034E-02 2.195E+00   SHIFT M
   3  1  1.08061E+01 1.000E+00 8.433E-03 6.451E+00    SHIFT ML
```

Figure S7. ^{1}H-NMR of **L^{1}** with TBAAcO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the ureidic NH adjacent to the indole group.

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  Reaction:   M + L = ML
 FILE: TEST11.FIT
 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  6.34266E+02 2.000E-01 3.280E+01 1.035E+01    K1
   2  1  1.10338E+01 2.000E-01 1.708E-02 2.872E+00   SHIFT M
   3  1  1.32032E+01 1.000E+00 1.518E-02 6.663E+00    SHIFT ML
```
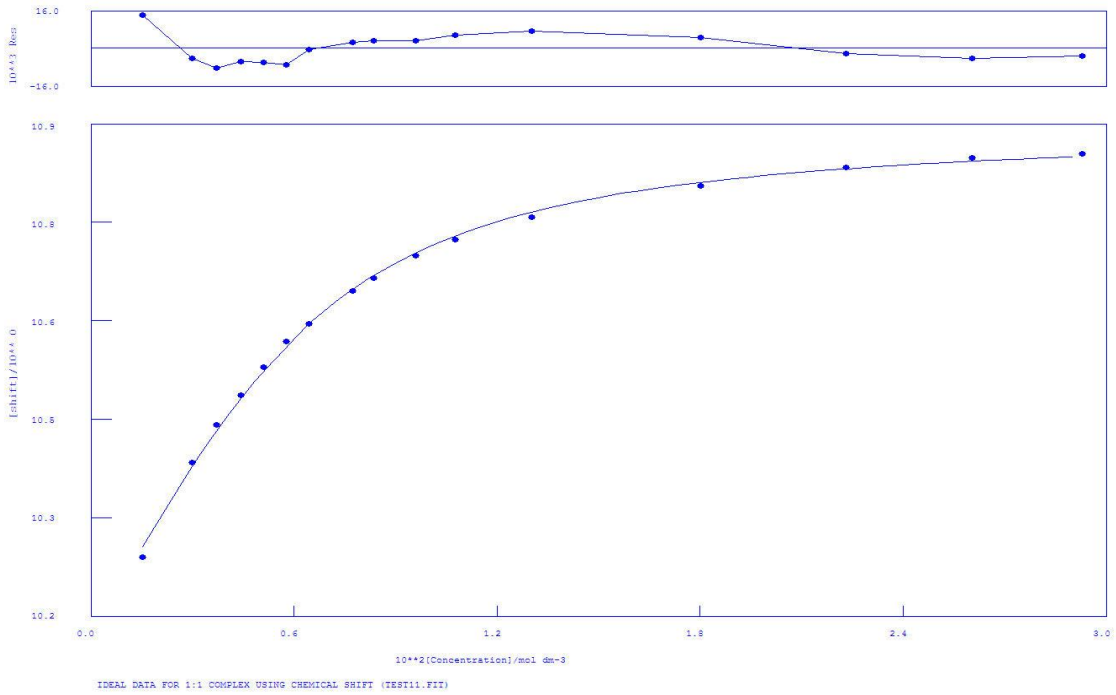

Figure S8. ^{1}H-NMR of **L^{1}** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the indolic NH.

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 FILE: TEST11.FIT
 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  6.19952E+02 2.000E-01 3.787E+01 1.048E+01    K1
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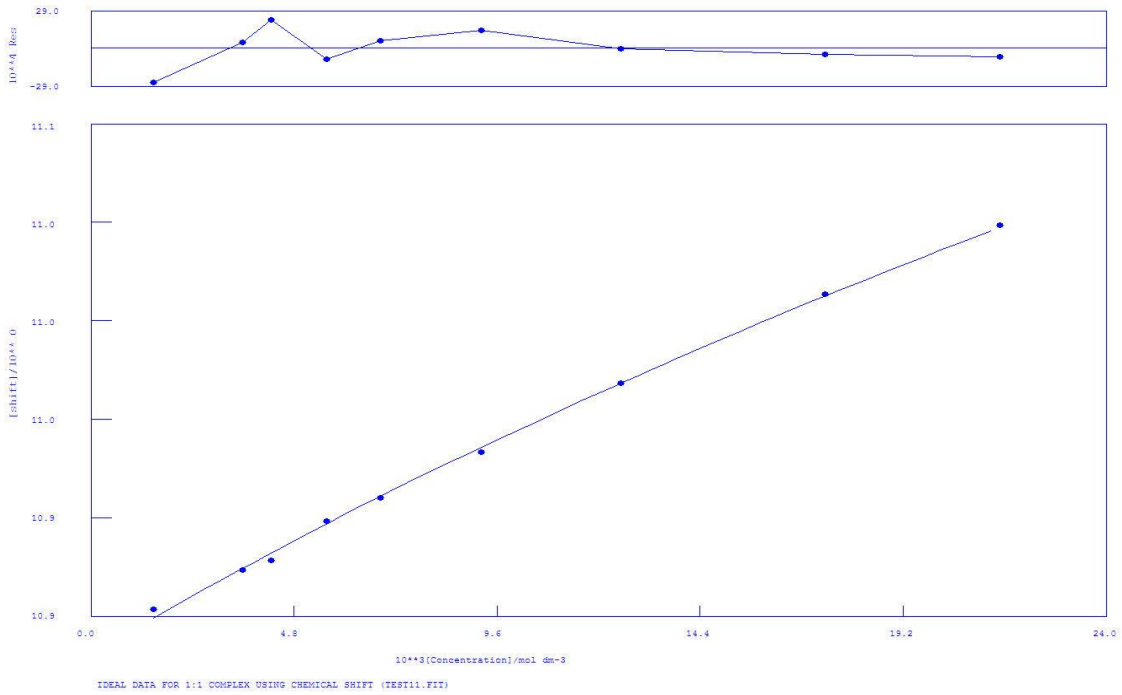
   3  1  1.09005E+01 1.000E+00 6.267E-03 6.870E+00    SHIFT ML
```

Figure S9. ^{1}H-NMR of **L^{1}** with TBABzO in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the ureidic NH adjacent to the indole group.

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 FILE: TEST11.FIT
 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0
 File prepared by M. J. Hynes, October 22 2000

NO.  A   PARAMETER    DELTA      ERROR     CONDITION   DESCRIPTION
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   2  1  1.08884E+01 2.000E-01 1.301E-03 4.901E+00   SHIFT M
   3  1  1.15419E+01 1.000E+00 1.080E-01 4.682E+02    SHIFT ML
```

Figure S10. ^{1}H-NMR of **L^{1}** with TBACl in DMSO-d_6/0.5%H_2O. The fitting has been obtained following the indolic NH.

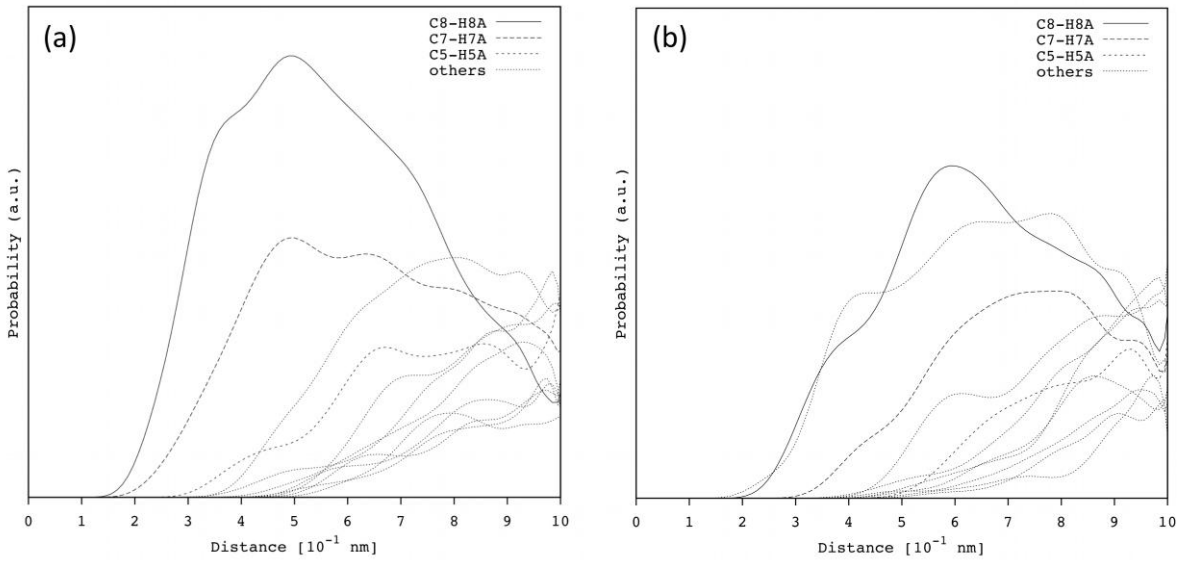

Figure S11. Radial distribution function for all the aromatic ring hydrogens for **L^{1}** in the antisymmetric (Fig. 8c) (a) and symmetric (Fig. 8b) (b) duplexes. All the distribution functions have been smoothed with a Bézier spline.

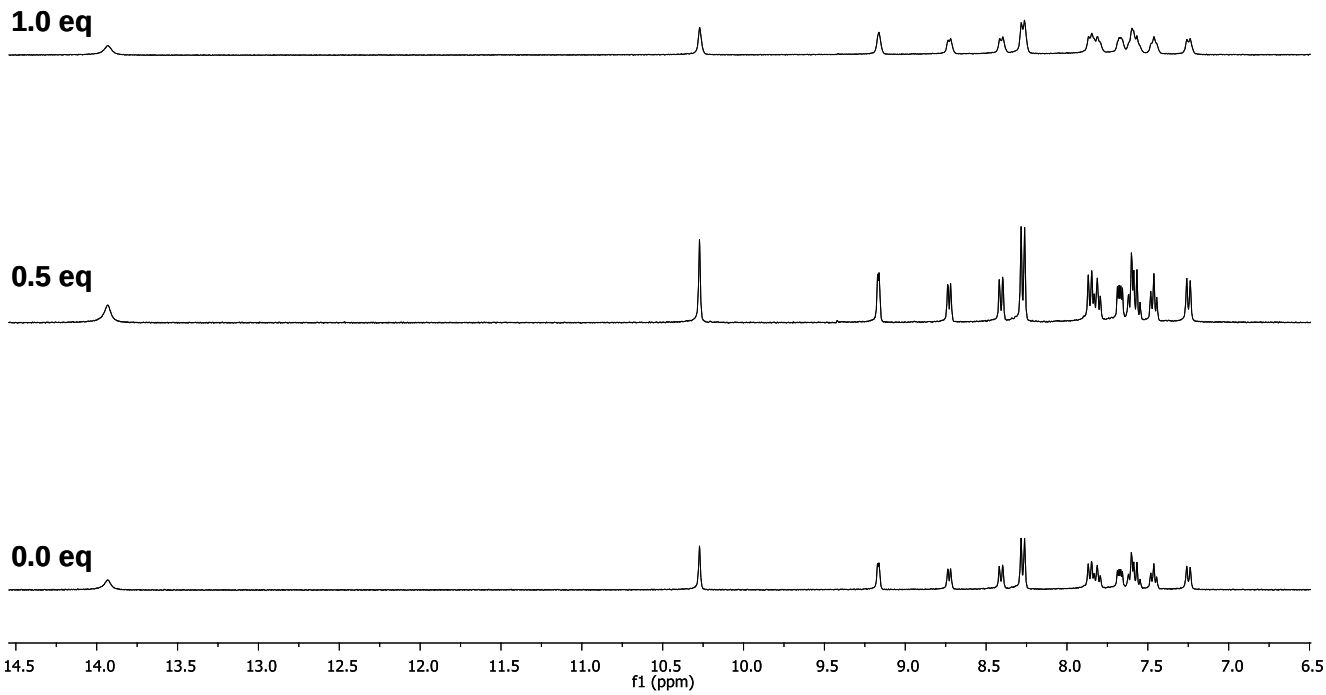

Figure S12 ^{1}H-NMR stack plot of a DMSO-d_6 solution of **L²** (0.005 M) upon addition of tetrabutylammonium acetate (0.075 M) in DMSO-d_6 at 298 K.

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