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Anion sensing properties of new colorimetric chemosensors based on macrocyclic ligands bearing three nitrophenylurea groups

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ABSTRACT

Two new colorimetric ligands (**1**–**2**) based on macrocyclic structures linked to three nitrophenylurea groups were synthesized in good yields, and their responses toward anions were studied. Anions with different shape, such as of fluoride, chloride, bromide, iodide, hydroxide, nitrate, perclhorate, cyanide, or dihydrogen phosphate in DMSO solution were added and only fluoride, hydroxide, cyanide, and dihydrogen phosphate enhances π delocalization and shifts the π–π* transition in both ligands, leading to the generation of a pleasant orange color.

The result is a balance between the acidity of the nitrophenylurea-NH donors modulated by the basic character of the anions. Stability constants for both receptors and the anions fluoride, hydroxide, cyanide, and dihydrogen phosphate were determined spectrophotometrically using the program HYSPEC. ^{1}H NMR titrations experiments with fluoride were carried out.

1. Introduction

Anion receptor chemistry continues to be a very vigorous area of research,[1] mainly due to the important roles of anions in biological systems, but because the toxic and deleterious effects, for example, as environment pollutants. Efforts are currently being directed toward the use of anion receptors as membrane transport agents for halide in biological systems, as ion-pair receptors, as sensors for the detection of biologically important anionic species and in a variety of other applications.[1a]

Anionic molecules are challenging targets for recognition studies principally because they are present in a wide range of sizes and shapes.[2] Binding directly to charged anionic groups, which are highly solvated in aqueous solution, is essential in the recognition of inorganic or small organic anions. Summarizing this supramolecular approach comprises two important premises: firstly a selective detection of the analyte by the coordination site and secondly a transduction of this event throughout modulation the spectroscopic or electrochemical properties.

To achieve selective recognition of these anions with synthetic receptors, we can learn a great deal from how nature addresses the problem and can apply the design principles of natural receptors to synthetic ones. Anion binding hosts may also be divided on the basis of their flexibility or degree of pre-organisation. If the host does not undergo a significant conformational change upon guest binding it is said to be pre-organised. Host pre-organisation is a key concept because it represents a major contribution to the overall free energy of guest complexation. During the binding process the host undergoes conformational readjustment in order to arrange its binding sites in the fashion most complementary to the guest and at the same time minimising unfavorable interactions between one binding site and another on the host.

Rigidly pre-organised hosts, such as anion binding cryptands[3] may quite often have high complexation activation energy and tend to exhibit slower guest binding kinetics. In contrast, conformationally mobile hosts are able to adjust rapidly to changing conditions and both complexation and decomplexation are usually rapid. Although generally having less intrinsic affinity for their guest than conformationally rigid molecules, flexible hosts are potentially more useful receptors in sensing applications because of their fast response times, reversible binding, and the possibility of detecting binding by means of the altered conformation.[1d,4]

We will particularly highlight the synthetic macrocyclic receptors that present a reduced conformational flexibility as compared with acyclic molecules.[5] These kind of host structures that possess a rigid scaffold and urea[6] or thiourea[7] functional groups as side-arms have been reported to be very effective in the binding of anions.

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These urea systems can donate two hydrogen bonds using the N–H fragment(s) integrated into the chromogenic subunit. The negative charge brought about by the anion modifies the dipole of the chromophore leading to a modification of the UV–vis spectrum and to a color change. Thanks to their synthetic accessibility they have been included in a wide variety of anion receptors and a great deal of effort is still being made to synthesize and study these effective receptors.[8] Fabbrizzi and co-workers have conducted a huge number of studies into the anion triggered deprotonation of ureas and thioureas.[9] In organic solution, basic anions, such as fluoride and acetate have been shown to deprotonate a variety of neutral hydrogen bond donor receptor systems. Deprotonation processes are often driven by the formation of a particularly stable species, such as HF_2^-.[10]

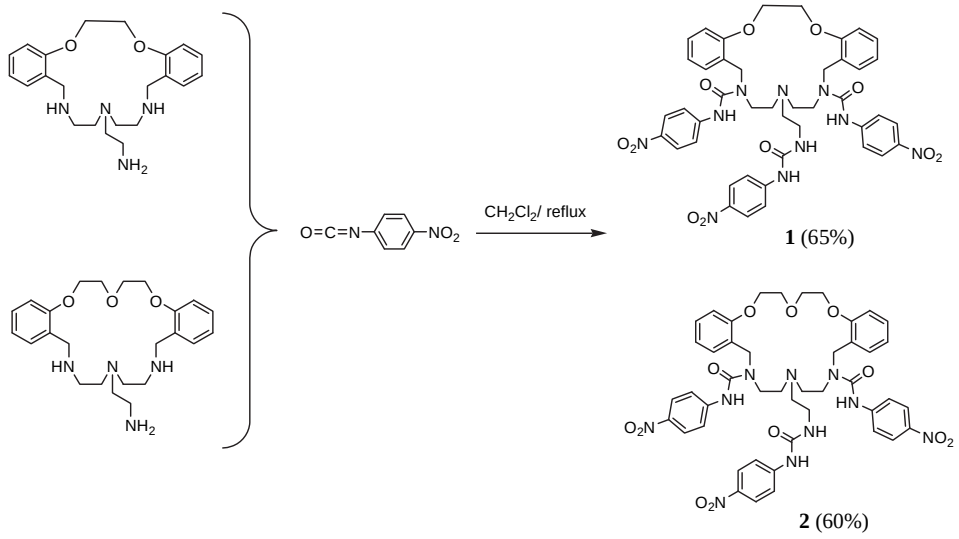
Recently, some of us have reported several acyclic and macrocyclic systems for optical applications as colorimetric and/or fluorimetric chemosensors.[11]

Taking these results in mind, we now report the synthesis, characterization, and anion sensing properties of two new poly-oxa aza macrocyclic ligands bearing three nitrophenylurea pendant-arms as binding anion sites. These two new systems have more places to interact with the anions, increasing the sensor capacity, and introduce the possibility to use them too as ditopic receptors, recognition of metal ions, and anions.

2. Results and discussion

2.1. Synthesis

Until now the reported anion receptors are mainly based on acyclic ligands.[12] Therefore, we propose the synthesis of new macrocyclic chemosensors **1** and **2** containing three nitrophenylurea moieties, outlined in Scheme 1 as potential anion receptors.



Scheme 1. Synthesis of chemosensors **1** and **2**.

Macrocyclic precursors **a** and **b** were carried out using methods described in the literature.[13] In the first step, a solution of 4-nitrophenylisocyanate in dry dichloromethane was added dropwise to a refluxing solution of the precursors **a** and **b** in the same solvent. The resulting solutions were gently refluxed with magnetic stirring for ca. 24 h and then evaporated to dryness. The residues were extracted with water/chloroform. The organic layer was dried over anhydrous Na_2SO_4. Both compounds were purified by column chromatography. The final solution was evaporated to dryness, yielding yellow solids, characterized as the pure chemosensors **1** and **2**, in good yields (60–65%). Compounds **1** and **2** were fully characterized by elemental analyses, ^1H and ^{13}C NMR, IR and UV–vis spectroscopy, X-ray diffraction, and MS spectrometry.

2.2. X-ray crystallography

Crystals of sensors **1** and **2** suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of both compounds responding to the formulas (**1**)·0.125H_2O·0.5CH_3CN and (H**2**)(NO_3)·2CH_3CN, respectively. Crystal data and structure refinement are given in Table 1. The molecular structure and the crystal packing are given in Figs. 1 and 2.

In both cases, the pendant groups radiate out away from the ligand hole, located two of them to the same side, and the third to the opposite side.

Intramolecular face-to-face π,π-stacking interactions were observed in the crystal structure of **1** between the aromatic rings of adjacent pendant groups. The phenyl rings are parallel to each other, with a distance between the planes containing the aromatic rings of 3.309 Å, and distance between centroids of 3.542 Å (see Fig. 2a).

In the crystal structure of **2**, intermolecular face-to-face π,π-stacking interactions were observed between the aromatic rings of adjacent pendant groups, but intramolecular interactions were not presented. The phenyl rings are parallel to each other, with a distance between the planes containing the aromatic rings of 3.314 Å, and distance between centroids of 3.850 Å (see Fig. 3). C–H···π intermolecular interactions were also observed, with a distance of 2.640 Å (see Fig. 2b).

In the crystal structure of sensor **2** the pendant groups are involved in several hydrogen-bonding interactions. The H atoms of the –NH groups from the pendant fragments are involved in intermolecular hydrogen-bonding interactions with the nitrate oxygen atoms. Relevant hydrogen-bonding interactions observed in compound **2** are listed in Table 2.

2.3. Visual sensing of anions

Interaction of **1** and **2** with the anions (OH^-, CN^-, $H_2PO_4^-$, NO_3^-, ClO_4^-, F^-, Cl^-, Br^-, I^-) was investigated by spectrophotometric and spectrofluorimetric titrations, by adding a standard solution of the

Table 1
Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{44}\ H_{45.75}\ N_{10.50}\ O_{11.13}$	$C_{49}\ H_{55}\ N_{13}\ O_{15}$
Formula weight	899.66	1066.06
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	C2/*c*	*P*−1
Unit cell dimensions	*a*=25.3790(12) Å α=90°	*a*=10.9979(13) Å α=91.024(4)°
	b=15.8639(8) Å β=108.193(3)°	*b*=14.296(2) Å β=99.332(4)°
	c=24.0814(11) Å γ=90°	*c*=16.930(2) Å γ=107.066(4)°
Volume	9210.7(8) Å^3	2504.9(6) Å^3
Z	8	2
Density (calculated)	1.298 g/cm^3	1.413 g/cm^3
Absorption coefficient	0.096 mm^{-1}	0.107 mm^{-1}
F(000)	3778	1120
Crystal size	0.26×0.20×0.08 mm^3	0.22×0.13×0.07 mm^3
Theta range for data collection	1.54–21.96°	1.22–23.26°
Index ranges	−26≤*h*≤25, 0≤*k*≤16, 0≤*l*≤25	−12≤*h*≤11, −15≤*k*≤15, 0≤*l*≤18
Reflections collected	53432	7147
Independent reflections	5628 [*R*(int)=0.0829]	7143 [*R*(int)=0.1138]
Completeness to theta	100.0% (21.96°)	100.0% (23.26°)
Absorption correction	Empirical (Sadabs)	Empirical (Sadabs)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on *F*^{2}
Data/restraints/parameters	5628/7/631	7143/0/709
Goodness-of-fit on F^2	1.104	1.049
Final *R* indices [*I*>2sigma(*I*)]	R_1=0.0789, wR_2=0.2278	R_1=0.0634, wR_2=0.1305
R indices (all data)	R_1=0.1226, wR_2=0.2548	R_1=0.1626, wR_2=0.724
Largest diff. peak and hole	0.774 and −0.304 eÅ^{-3}	0.348 and −0.452 eÅ^{-3}

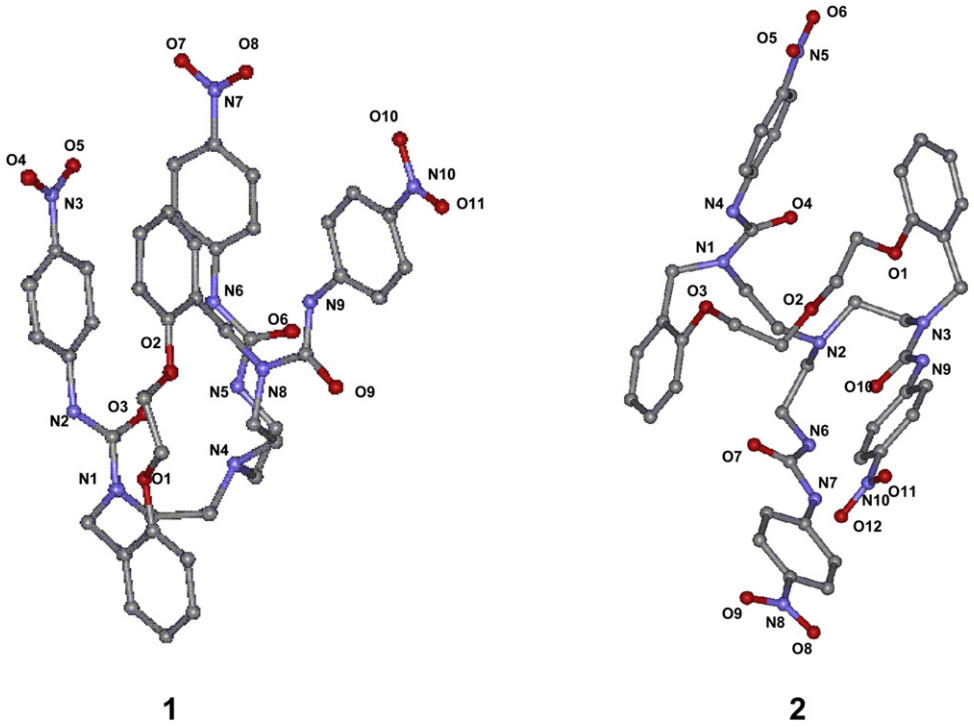


Fig. 1. Crystal structure of compounds **1** and **2**.

corresponding tetrabutylammonium salts in DMSO to a solution of compounds **1** and **2** at room temperature in the same solvent. However, both ligands show very low emissive properties in our conditions, both nitrophenylurea-based receptors allow naked-eye detection of OH^-, CN^-, $H_2PO_4^-$, and F^- anions, showing more intense colors in the case of compound **2**.

The interaction of the urea hydrogen atoms with the substrates enhances π delocalization and red shifts the π−π* transition with the formation of a charge transfer band (CT) in the visible region, resulting in the generation of an orange (F^-, CN^-) or intense yellow (OH^-) color. No change occurred upon interaction with NO_3^-, ClO_4^-, Cl^-, Br^-, and I^- anions. In the case of the receptor **2**, for $H_2PO_4^-$ a pale yellow color was observed.

2.4. UV−vis Spectral responses of sensors 1 and 2

Chemosensors **1** and **2** shows very low solubility in water; and in water/DMSO solutions (50:50, v/v) those ligands precipitated. For

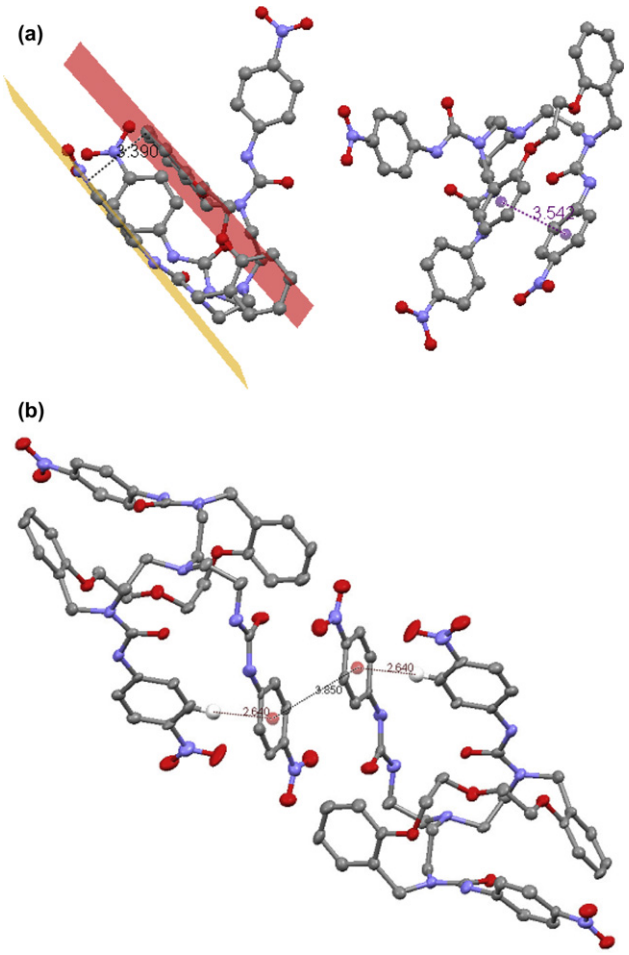


Fig. 2. (a) Crystal packing of sensor **1** showing π,π-stacking interactions. (b) Crystal packing of sensor **2** showing π,π-stacking and C–H···π interactions.

Table 2
Hydrogen-bonding interactions observed in the X-ray crystal structure of sensor **2**

D–H	A	d (D–H)/Å	d (H···A)/Å	d (*D*···A)/Å	a (DHA)
N7–H7N	O3N #1	0.772	2.232	2.961	157.81
N7–H7N	O1N′ #1	0.772	2.316	3.004	148.93
N7–H7N	O1N #1	0.772	2.595	3.267	146.55
N6–H6N	O1N #1	0.888	2.300	3.109	151.26
N6–H6N	O1N′ #1	0.888	2.350	3.102	142.39
N6–H6N	O2N′ #2	0.888	2.471	3.055	123.73
N4–H4N	O3	0.826	2.228	2.929	142.79
N2–H2N	O10	0.858	1.811	2.645	163.61
N9–H9N	O1N′ #3	0.825	2.209	3.024	169.76
N9-H9N	O1N #3	0.825	2.250	3.051	163.96

#1: [$-x+2$, $-y+1$, $-z+1$]; #2: [$x+1$, $y-1$, z]; #3: [x, $y-1$, z].

the aforementioned reasons all the spectroscopic studies have been done in a non-protic solvent, DMSO.

The spectrophotometric characterization of receptors **1** and **2** in DMSO are reported in Fig. 4. In both cases a UV band centered at 348 nm was observed. This band was coincident with the excitation spectrum in both cases. This band is attributable to the π–π* transitions in the ligand.[9] Even both systems show a very low fluorescence emission property, the spectra of **1** and **2** show a band centered at 451 nm.

The spectroscopy characterization of both receptors after anion addition is summarized in Table 3.

Among various receptors, hydrogen-bond donor urea, and thiourea functionalities have been widely used for selective binding of anions (A^-) like (OH^-, CN^-, $H_2PO_4^-$, NO_3^-, ClO_4^-, F^-, Cl^-, Br^-, I^-) through H-bonded adduct formation.[14] The strength of this H bonding also depends on the relative acidity of the H atom ($HN_{urea/thiourea}$) of the urea and thiourea functionalities.[15] Urea-based receptors, functionalized with electron-withdrawing groups, behave as a Brönsted acid in the presence of an excess of certain anions.[12g,m,16] The high thermodynamic stability of HA_2^- is believed to govern this equilibrium process.[17]

There are many reports describing the anion recognition phenomena and their possible implication in different applications but precise relationships between the acidity of the H-bond donor

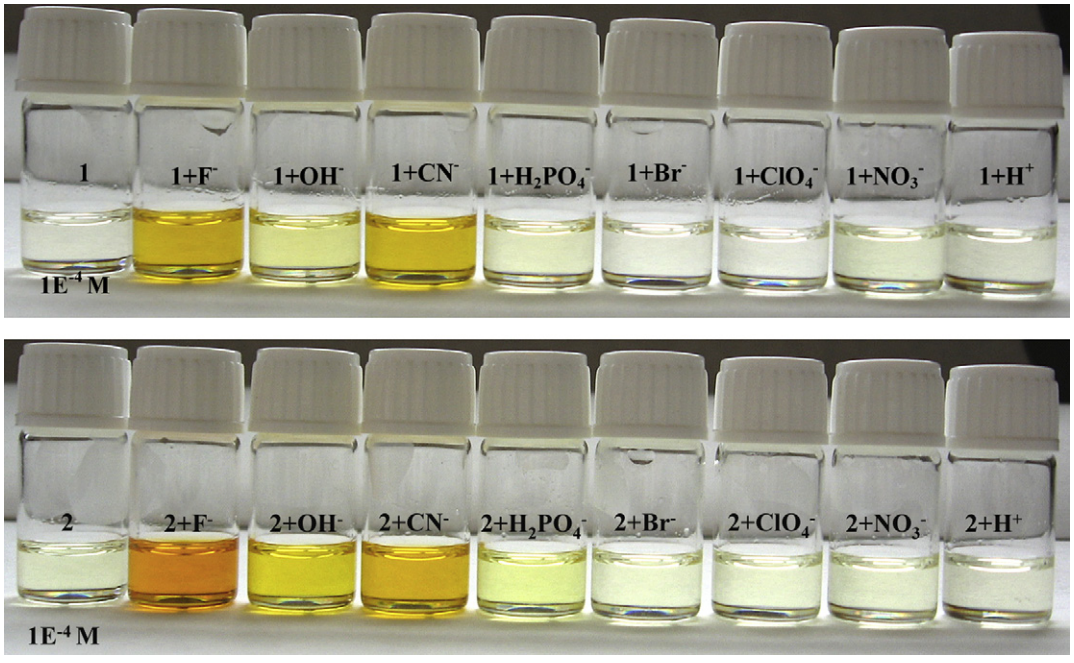


Fig. 3. Colorimetric effect in systems **1** and **2** after interaction with different ions in DMSO.

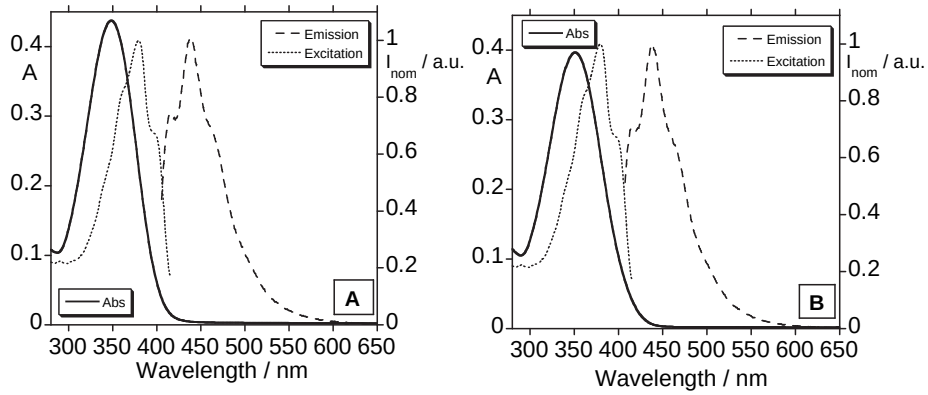


Fig. 4. Absorption (full line), emission (broke line) and excitation (dotted line) spectra of compounds **1** (A) and **2** (B) (λ_{exc}=347 nm; λ_{em}=451 nm, [1]=[2]=1.00×10^{-5} M) in DMSO at room temperature.

Table 3
Spectroscopic data for sensor **1** and **2**

Receptor **1**				Receptor **2**		
Anion	$\lambda_{ab1(protonated)}$ (nm)	$\lambda_{ab1(deprotonated)}$ (nm)	log ε	$\lambda_{ab1(protonated)}$ (nm)	$\lambda_{ab1(deprotonated)}$ (nm)	log ε
OH^-	348	355, 474	3.73	348	335, 480	4.85
$H_2PO_4^-$	348	355, 471	2.95	348	360, 475	3.15
CN^-	348	353, 471	3.60	348	355, 479	3.43
F^-	348	354, 480	3.77	348	336, 484	4.82

fragment and the relative affinity of a receptor toward different analytes are not addressed in detail.[18]

Addition of fluoride anions produced a marked red shift in the absorption due to the deprotonation of the NH to N^- in the nitrophenylurea groups, and the UV–vis absorption band was shifted to a lower wavelength. The deprotonation lowers the steric hindrance between the nitrophenyl units and the NH group and enables the formation of a more extended π-conjugated system.

Titration of chemosensors **1** and **2** with tetrabutylammonium fluoride in DMSO solution at 298 K (Fig. 5), can be followed by the formation of a new band centered at ca. 480 nm, in both cases, and a decrease in the band assigned to the π–π* transition of the chromophore centered at 348 nm in the case of chemosensor **2**.

anions, this new band was assigned to a charge transfer (CT) process. For receptor **2**, well-defined isosbestic points were observed at 315 and 408 nm. This behavior suggests that presence of two species in solution, the protonated and deprotonated compound.

After the addition of 100 equiv of CN^- to **1** or **2**, the yellow color changed to pale orange and a small new visible band centered at 471 and 479 nm appeared in both cases, respectively. Similar results were obtained with the addition of 100 equiv $H_2PO_4^-$ (but with less intensity color). See Fig. 7.

Fig. 8 shows a comparison chart of the absorption of receptor **2** at 485 nm after addition of F^-, OH^-, CN^-, and $H_2PO_4^-$. A stronger increase in the molar coefficient absorption was observed for F^- and OH^-; In the case of perchlorate, nitrate, chloride, bromide, and

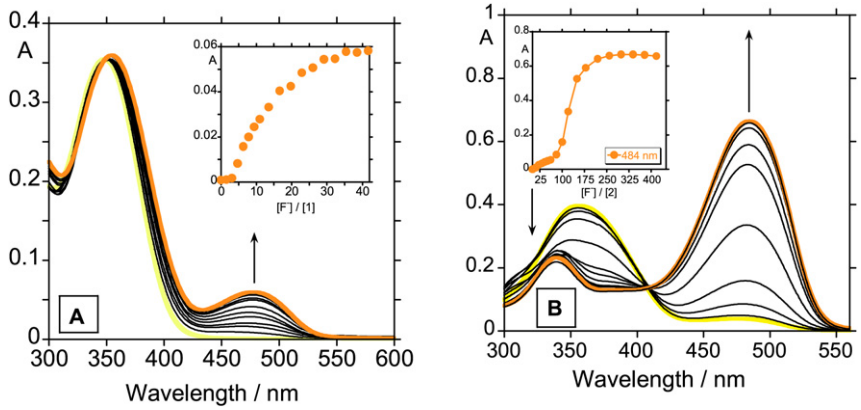


Fig. 5. Changes in UV–vis spectra for compound **1** (A) and **2** (B) (1.00×10^{-5} M) in DMSO with the addition of DMSO solution of $[(Bu)_4N]F$. Absorptions read at 484 nm.

On the other hand, addition of increasing amounts of tetrabutylammonium hydroxide to an DMSO solution of sensors **1** and **2** (Fig. 6), at 298 K, led to a decrease in the band assigned to the π–π* transition of the chromophore centered at 348 nm and a new band centered at 474 and 480 nm, appeared, respectively. For both iodide ions, no change was observed upon addition of up to 100 M equiv.

The stability constants for the interaction of receptors **1** and **2** in the presence of the fluoride, hydroxy, cyanide, and dihydrogen phosphate ions are summarized in Table 4.[19]

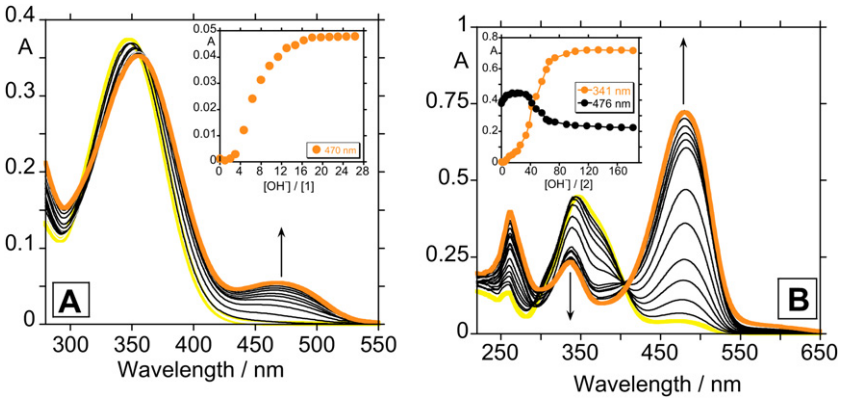


Fig. 6. Changes in UV–vis spectra for compound **1** (A) and **2** (B) (1.00×10^{-5} M) in DMSO with addition of $[(Bu)_4N]OH$. Absorptions read at 470 and 476 nm, respectively.

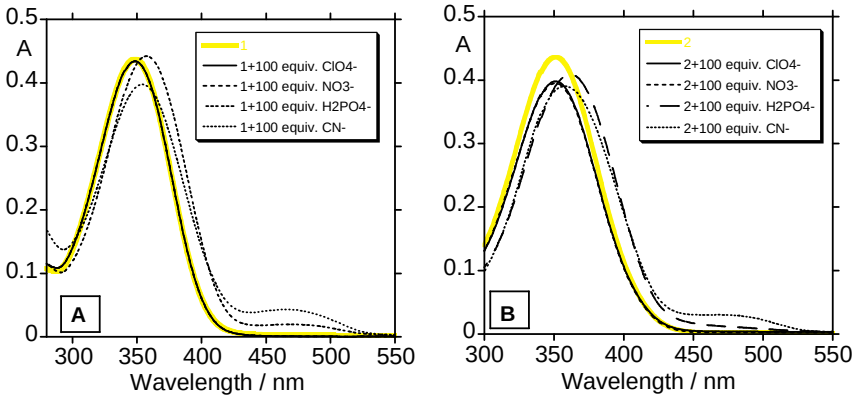


Fig. 7. Spectral changes of **1** (A) and **2** (B) in DMSO (1.00×10^{-5} M) with the addition of nitrate, perchlorate, dihydrogen phosphate, and cyanide anions.

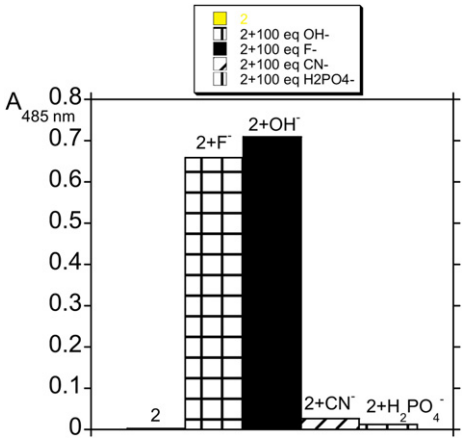


Fig. 8. Comparison chart of the absorption of sensor **2** at 485 nm after addition of F^-, OH^-, CN^-, and $H_2PO_4^-$.

Table 4
Stability constants for ligands **1** and **2** in the presence of some anions in DMSO

Receptor	Interaction	log β
1	F^- (1:1)	$5.08\pm3.67\times10^{-3}$
1	OH^- (1:1)	$3.92\pm2.80\times10^{-3}$
1	CN^- (1:1)	$4.06\pm2.34\times10^{-3}$
1	$H_2PO_4^-$ (1:1)	$3.22\pm3.84\times10^{-3}$
2	F^- (1:1)	$5.55\pm1.51\times10^{-2}$
2	OH^-(1:1)	$5.41\pm5.27\times10^{-2}$
2	CN^- (1:1)	$4.95\pm2.51\times10^{-2}$
2	$H_2PO_4^-$ (1:1)	$4.84\pm9.02\times10^{-3}$

Taking into account these data the strongest interaction is expected for chemosensor **2**, with bigger cavity and more flexibility. The observed sequence, in decreasing order was F^->OH^-> CN^->$H_2PO_4^-$. In the case of the small compound **1**, the sequence obtained was similar. These results can rely on to the cavity size of both macrocyclic ligands and the structure flexibility.

2.5. NMR responses of sensors 1 and 2

In order to understand the effect of the fluoride anion on the NH protons[20] of receptors **1** and **2**, the ^1H NMR spectra were registered in DMSO-d_6—0.5% water solution; the amide NH signals appear in compound **1** at 9.28, 9.24, and 6.37 ppm (Fig. 9) and at 9.34, 9.19, and 6.33 ppm in compound **2**. Addition of 1 equiv of tetrabutylammonium fluoride to the solutions of receptors **1** and **2** in DMSO-d_6—0.5% water was enough to promote the complete deprotonation process.[21] Even due to the presence of three nitrophenylurea groups, one fluoride anion is enough to stabilize the spectra.

The deprotonation of the urea subunits in receptors **1** and **2** can induce two distinct effects on the aromatic substituents: (i) it increases the electron density on the phenyl rings with a through-bond propagation, which generates a shielding effect and should produce an upfield shift of C–H protons; (ii) it induces the polarisation of the C–H bonds via a through-space effect, where the partial positive charge created onto the proton causes a deshielding effect and produces a downfield shift. It is seen in Fig. 9 that the electrostatic effect predominates for protons H_2 and H_3, as indicated by the slight downfield shift. Protons H_4, H_5, and H_6 are too far away from the N–H protons to be subjected to any electrostatic effect.

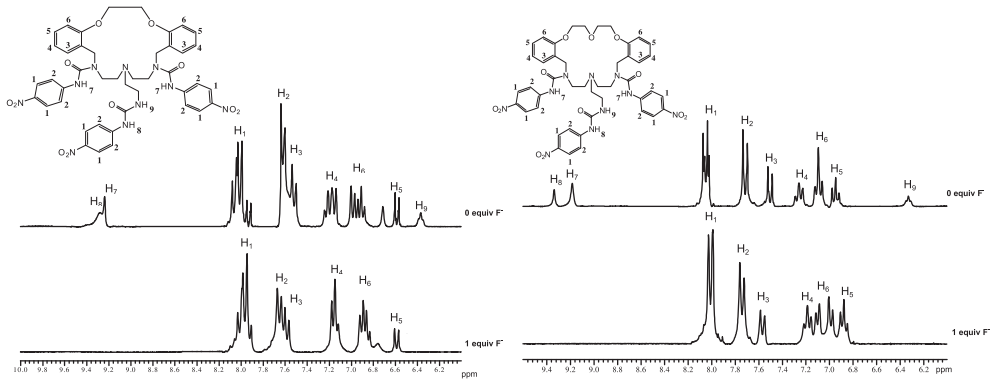


Fig. 9. ^{1}H NMR spectra taken in the course of the titration of a DMSO-d_6 solution 1.00×10^{-3} M in receptors **1** (left) and **2** (right) with a standard solution of [Bu_4N]F. Key: no [Bu_4N]F addition (top); addition of 1 equiv of [Bu_4N]F (bottom).

3. Conclusions

Two novel macrocyclic chemosensors **1** and **2** containing three nitrophenylurea moieties were sythesized and fully characterized. Receptors **1** and **2** proved to be a colorimetric anion sensor, which shows a selective coloration for F^-, OH^-, CN^-, and $H_2PO_4^-$ in DMSO solutions. No effect for perchlorate, nitrate, chloride, bromide, and iodide ions was observed. Taking into account the values of the stability constants for the interaction of chemosensors **1** and **2** in the presence of the fluoride, hydroxy, cyanide, and dihydrogen phosphate the sequence, in decreasing order is $F^->OH^->CN^->H_2PO_4^-$, for both receptors. These results can rely on to the cavity size of both macrocyclic ligand and the flexibility of the pendant arms in the macrocyclic skeleton.

4. Experimental section

4.1. Measurements

Elemental analyses were performed on a Fisons Instruments EA1108 microanalyser by the Universidade de Santiago de Compostela. Infra-red spectra were recorded as KBr discs on a BIORAD FTS 175-C spectrometer. FAB and ESI mass spectra were recorded using a KRATOS MS50TC spectrometer with 3-nitrobenzyl alcohol as the matrix. ^{1}H and ^{13}C NMR spectra were recorded in CD_3CN solutions on a Bruker 500 MHz spectrometer. ^{1}H NMR spectra titrations were recorded in DMSO solutions on a Bruker 500 MHz spectrometer. Assignments were based in part on COSY, DEPT, and HMQC experiments.

UV–vis absorption spectra (200–800 nm) were performed using a JASCO-650 UV-visible spectrophotometer and fluorescence spectra on a HORIBA JOVIN-IBON Spectramax 4. All spectrophotometric titrations were performed as follows: stock solutions of compounds **1** and **2** (ca. 10^{-3} M) were prepared with DMSO UVA-solv and used in the preparation of titration solutions by appropriate dilution. Titration of the compounds **1** and **2** was carried out by addition of microliter amounts of standard solutions of the ions (anions) in DMSO. All anions (F^-, Cl^-, Br^-, I^-, ClO_4^-, NO_3^-, CN^-, and $H_2PO_4^-$) were used as their tetrabutylammonium salts. The acidity of the dimethylsulfoxide solutions was adjusted by the addition of methanesulphonic acid and tetrabutylamonium hydroxide.

The stability constants for the interaction of receptors **1** and **2** in the presence of the fluoride, hydroxy, cyanide, and dihydrogen phosphate ions were calculated using the spectrophotometric data and the HypSpec software. For all of these cases very good mathematical fits were obtained.

4.2. X-ray crystal structure of 1 and 2

Crystals suitable for X-ray diffraction were obtained for (**1**)·$0.125H_2O\cdot0.5CH_3CN$ and (H**2**)(NO_3)·$2CH_3CN$. The details of the X-ray crystal data, and the structure solution and refinement are given in Table 1. Measurements were made on a Bruker X8 kappaAPEXII diffractometer. Graphite monochromated Mo Kα was used. All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for all the crystal structures obtained.[22] Complex scattering factors were taken from the program package SHELXTL.[23] The structures were solved by direct methods using SHELX-97,[24] which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using WebLab ViewerPro.

4.3. Synthesis of sensors 1 and 2

A solution of 4-nitrophenylisocyanate (0.5 g, 3 mmol) in dry dichloromethane (25 mL) was added dropwise to a refluxing solution of the precursor ligand **a** (0.38 g, 1 mmol) and **b** (0.4 g, 1 mmol) in the same solvent (25 mL), respectively. The resulting solutions were gently refluxed with magnetic stirring for ca. 24 h at room temperature and then evaporated to dryness. The residues were extracted with water/chloroform. The organic phase was dried ($MgSO_4$), filtered, and solvent removal gave yellow solids characterized as the compounds **1** and **2**, respectively.

*4.3.1. Receptor **1**.* Yellow solid (65%); ^{1}H NMR (400 MHz, CD_3CN) δ 2.45 (t, 4H), 2.55 (t, 2H), 3.26 (c, 2H), 3.49 (t, 4H), 4.46 (s, 4H), 4.65 (s, 4H), 6.81–8.13 (m, 20H); ^{13}C NMR (100 MHz, CD_3CN) δ 37.21, 46.09, 46.11, 53.56, 53.88, 67.29, 112.26–154.87, 156.7, 155.3; FAB/MS, $[\mathbf{1}+H]^+$=877; IR (KBr, cm^{-1}) 1672, 1544, 1302, 1329, 1112. Anal. Calcd for $C_{43}H_{48}N_{10}O_{13}$: C, 56.6; H, 5.3; N, 15.3. Found: C, 56.4; H, 5.5; N, 15.3.

*4.3.2. Receptor **2**.* Yellow solid (60%); ^{1}H NMR (400 MHz, CD_3CN): δ 2.74–2.76 (m, 8H), 3,51 (t, 4H), 3.79–3.82 (m, 4H), 4.18–4.20 (m, 4H), 4.68 (s, 4H), 6.69–8.03 (m, 20H); ^{13}C NMR (100 MHz, CD_3CN): 39.7, 39.9, 52.3, 54.4, 56.1, 67.9, 69.2, 112.4–154.8, 155.7, 156.3; FAB/MS, $[\mathbf{2}+H]^+$=921; IR (KBr, cm^{-1}) 1670, 1559, 1303, 1329, 1111. Anal. Calcd for $C_{45}H_{54}N_{10}O_{15}$: C, 55.4; H, 5.8; N, 14.4. Found: C, 55.4; H, 5.6; N, 14.5.

5. Supplementary data

CCDC 785406 and 785407 contain the supplementary crystallographic data for (**1**)·$0.125H_2O\cdot0.5CH_3CN$ and (H**2**)(NO_3)·$2CH_3CN$,

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.09.054.

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