DOI: 10.1002/ejoc.200701005

3,3′-Disubstitued 2,2′-Bipyridines as Carboxylate Receptors: Conformational Regulation of the Bipyridine Moiety

Ana M. Costero,*[a] Salvador Gil,[a] Margarita Parra,[a] Nuria Huguet,[a] Zouhir Allouni,[a,b] Rajae Lakhmiri,[b] and Ahmed Atlamsani[b]

Keywords: Biaryls / Molecular recognition / Fluorescent probes / Receptors / Hydrogen transfer

Two bipyridine derivatives were synthesized and characterized, and their ability to act as sensors for carboxylates was evaluated by UV/Vis and fluorescence studies. The influence of the substituents of the thiourea groups on the stoichiometry of the resulting dicarboxylate complexes was established. Conformational changes in the bipyridine moiety under different conditions were evaluated.

Introduction

The construction of multicomponent molecular systems represents an important first step in the development of novel supramolecular systems for catalysis, light-to-energy conversion and chemical sensing.[1] Chemical sensing is an interesting area of research, and the application, design and synthesis of chemosensors for a wide range of substrates have become active fields in supramolecular chemistry.[2] Sensing of anionic guests has recently become an area of focus because anions play a fundamental role in many biological and chemical processes.[3] In recent years, we have been working towards the design and application of chemosensors based on the binding site–signalling unit approach. Thus, we prepared ligands derived from biphenyl, as a transducer subunit, which are able to act as fluorescent or colorimetric sensors for cations and anions.[4] The results of studies on these biphenyl derived ligands have demonstrated that conformational changes induced by modification of the dihedral angle of the biphenyl moiety have a strong influence on the fluorescent properties of the sensor.[5]

The development of new sensor systems has prompted us to synthesize new ligands. As a result of its interesting characteristics[6] and, more importantly, its analogy to the biphenyl system, bipyridine seemed an interesting target for a transducer subunit.

The bidentate ligand 2,2′-bipyridine is one of the simplest but most widely used organic linkers. In recent years, this ligand has been incorporated into a diverse range of supramolecular inorganic architectures.[7] Furthermore, chemical modification of the 2,2′-bipyridine ligand by the introduction of additional functionality at the 4-, 5- and 6-positions is well known, and the coordination chemistry of such compounds has been actively explored.

However, much fewer 3,3′-disubstituted bipyridines are available, and the coordination chemistry of only a small number of such compounds has been studied. Nevertheless, small substituents in the 3- and 3′-positions such as methyl groups,[8] carboxylic acids[9] and methyl esters[10] have all been reported. Furthermore, in the early 1980s, Rebek et al. successfully exploited the 3,3′-substitution positions for the preparation of a novel crown ether derivative that bound transition-metal ions at the bipyridine moiety or alkali-metal ions at the crown ether.[11]

We report herein the synthesis of two 2,2′-bipyridine units with thiourea groups in the 3- and 3′-positions to act as a receptor subunit. We also present the results of complexation studies with selected carboxylic acids, as well as findings on their ability to coordinate to transition-metal cations.

Results and Discussions

Synthesis

The new bipyridine-based ligands are presented in Figure 1. Compounds **1** and **2** were prepared from disubstituted bipyridyl **3** (Scheme 1). 3,3′-Diamino-2,2′-bipyridine, **3**, was prepared from 3,3′-dinitro-2,2′-bipyridine, which was obtained following the Ullman coupling procedure first described by MacBride et al.[12] However, as the reaction conditions described by MacBride proved to be problematic, we chose to follow the procedure of Kaczmarek et al.[13] This method involves the Ullman coupling of 3-ace-

[a] Departamento de Química Orgánica, Universitat de València, Dr. Moliner 50, 46100-Bujassot. Valencia, Spain
[b] Departement de Chimie, Faculté des sciences, Université Abdelmalek Essaadi, Essaadi, Morocco

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tylamino-2-chloropyridine, followed by acidic hydrolysis to afford 3,3′-amino-2,2′-bipyridine in improved yields. The reaction of **3** with the corresponding isothiocyanate afforded ligands **1** and **2**.

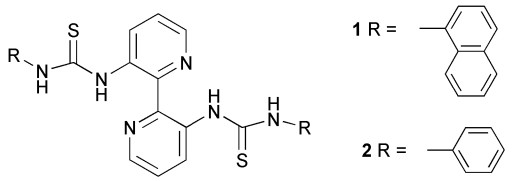
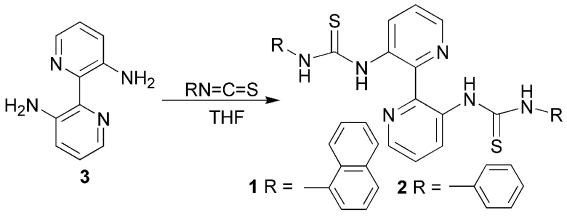


Figure 1. Bipyridine-based ligands.



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

Protonation and Complexation with Transition-Metal Cations

Ligands **1** and **2** are mainly present in solution in the s-*trans* conformation, which is stabilized through the formation of hydrogen bonds between the bipyridyl N atoms and the amide NH of the thiourea groups at the 3- and 3′-positions of the bipyridine moiety.[14] Thus, a planar bipyridine system is expected (Figure 2).

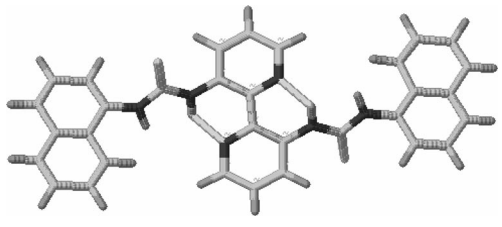


Figure 2. Conformation calculated by PcModel for ligand **1**.

The coplanarity of the pyridine groups in these ligands is in agreement with the absorption maximum in the UV spectra [λ_{max} (DMSO) = 294 nm and λ_{max} (DMSO) = 280 nm for ligands **1** and **2**, respectively].[15] In addition, ligand **1** shows absorption at 260 nm, which corresponds to the naphthalene group (Figure 3, top).

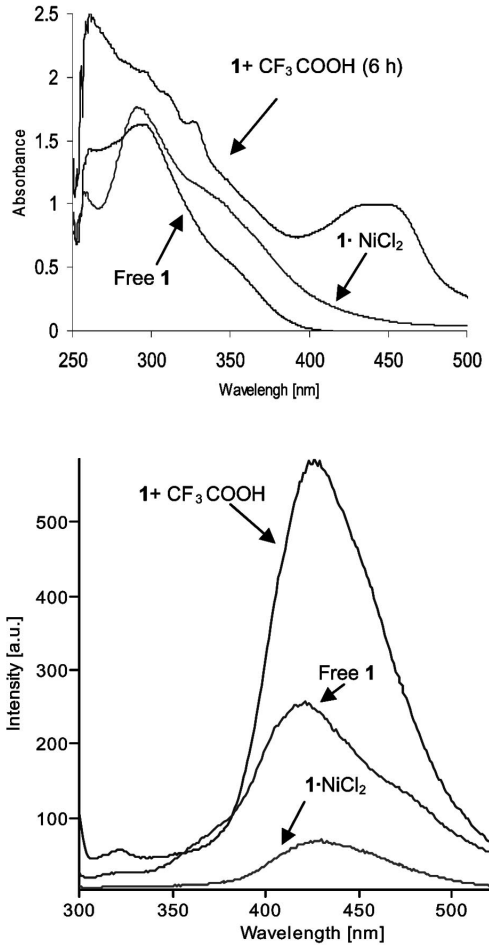
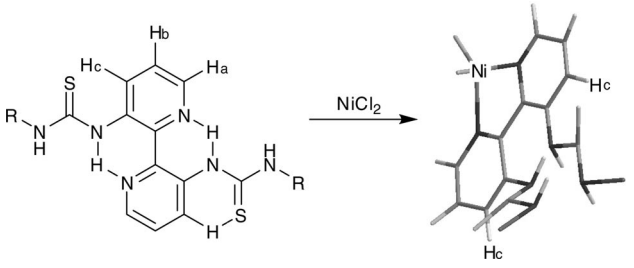


Figure 3. UV spectra of free, protonated (6 h after protonation) and Ni^{2+}-complexed ligand **1** (top); fluorescence spectra of free, protonated (immediately after protonation) and Ni^{2+}-complexed ligand **1** (bottom).

In the literature, it is established that the absorption band of bipyridine system shows a clear bathochromic shift after monoprotonation, which arises due to a conformational change between the s-*trans* and the s-*cis* forms.[15a,16] By contrast, ligands **1** and **2** showed different behaviour; in both cases, the UV spectra showed no changes upon protonation. This suggests that protonation takes place on the sulfur atom instead of on the pyridine rings, which is in agreement with the evolution of the system with time. Thus, after six hours at room temperature, a green colour attributed to the presence of a mixture of hydrolysis products was observed. As expected, the UV spectrum under these conditions showed a new band at 446 nm, which was the origin of the green colour.

The fluorescence spectra of both protonated and non-protonated systems were also studied. The emission spectrum of free ligand **1** shows an emission band at 420 nm [λ_{exc} (DMSO) = 290 nm], and the protonated system shows emission at 426 nm [λ_{exc} (DMSO) = 290 nm]. However, a large enhancement (130%) in the fluorescence was observed after protonation, probably due to an increase in the rigidity of the system (Figure 3, bottom).

Complexation experiments with $NiCl_2$ were also carried out.[17] The obtained complexes were studied by UV, fluorescence and ^1H NMR spectroscopy. The UV spectrum of **1**·$NiCl_2$ shows a shoulder at λ = 350 nm that is not present in the spectrum of free ligand **1** (Figure 3, top). This observation is in agreement with the bathochromic shift expected for the conformational change between the s-*trans* and the s-*cis* forms, which is induced by complexation (Scheme 2). This conformational change also has a strong influence on the fluorescence emission and gives rise to almost total quenching (Figure 3, bottom).



Scheme 2. Conformational change induced by complexation with $NiCl_2$.

Additionally, strong differences were observed between the ^1H NMR spectra of free ligands **1** and **2** and their corresponding Ni^{2+} complexes. Thus, the aromatic NH of the thiourea group is shifted from 11.6 to 9.9 ppm and from 12.00 to 11.00 ppm for **1** and **2**, respectively. By contrast, the second NH proton does not experience any significant shift. These observations are in agreement with conformational changes that result in cleavage of the hydrogen bonds present in the free ligand. On the other hand, interesting effects were also observed at the bipyridine moiety; thus, protons H_c are shifted from 8.88 and 8.85 ppm in the free ligand to 8.05 and 7.9 ppm in the complexes for **1** and **2**, respectively. These observations are in agreement with the proposed conformational change that places the thiourea groups out of the bipyridine plane and reduces the interaction of H_c with the sulfur atom.

Complexation Studies with Mono- and Dicarboxylates

The ability of these new ligands to act as receptors for carboxylates was studied. A series of dicarboxylates (oxalate, malonate and succinate), all as their tetrabutylammonium (TBA) salts, were used. These anions were chosen to evaluate the effect of the aliphatic chain length on the complexation constants. We also tested both acetate as a simple model and TMAOH to ensure that the observed behaviour is not due to the deprotonation of the ligand (see Supporting Information).

The carboxylates were prepared from the corresponding carboxylic acids and commercially available TBA hydroxide (2.0 equiv.) in DMSO. All studies were carried out by using UV, fluorescence and ^1H NMR spectroscopy.

The anion binding ability of receptors **1** and **2** was initially evaluated by UV/Vis titration of each receptor with the appropriate anion in DMSO solutions. UV/Vis studies reveal that **1** and **2** are able to complex dicarboxylates and acetate but the stoichiometries of the resulting complexes depend on the nature of both the ligand and the carboxylate (Figure 4). Ligand **1** gave rise to 1:2 complexes with both dicarboxylates and acetate, whereas ligand **2** formed 1:2 complexes with acetate and 1:1 complexes with dicarboxylates. These observations might be related to the different substituents on the thiourea moieties of **1** and **2**. The observed stoichiometries along with the corresponding complexation constants are summarized in Table 1.

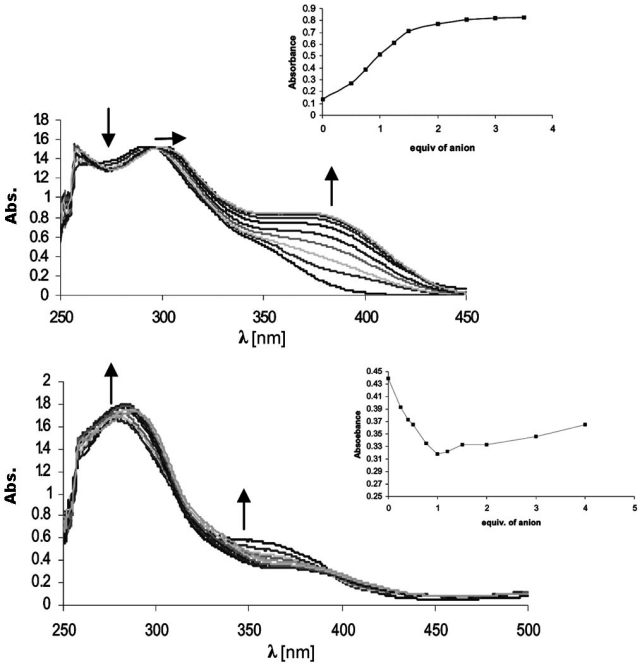


Figure 4. UV titration of ligand **1** plus TBA oxalate (top) and ligand **2** plus TBA oxalate (bottom) both in DMSO (3×10^{-4} M, increasing addition until 4 equiv. at 25 °C). For the other anions studied, see the Supporting Information.

Table 1. Stoichiometry and overall binding constant (logβ) (calculated by SpecFit software) in DMSO for **1** and **2** with various anions measured by UV/Vis spectroscopy at 25 °C.

	1		**2**	
Anion[a]	logβ	L:A	logβ	L:A
Oxalate	7.2 ± 0.2	1:2	6.0 ± 0.7	1:1
Malonate	7.7 ± 0.1	1:2	5.7 ± 0.6	1:1
Succinate	7.0 ± 0.2	1:2	6.2 ± 0.7	1:1
Acetate	7.4 ± 0.1	1:2	8.3 ± 0.1	1:2

[a] All anions were used as their TBA salts.

Titration experiments showed that the addition of increasing amounts of anion to ligand **1** gave rise to an enhancement in the fluorescence emission (for TBA oxalate, see Figure 5). These results corroborate an increase in the rigidity of the system, but not changes in the bipyridine conformation; an s-*trans* to s-*cis* conformational change should produce a strong quenching of the fluorescence (see above). Consequently, the s-*trans* conformation present in the free ligand is kept in the 1:2 complex. Similar experi-

ments carried out with ligand **2** showed a quenching of the fluorescence when increasing amounts of anion were present in the solution (Figure 5), which indicates that an s-*trans* to s-*cis* conformational change is likely. These results allow us to propose the complexation types shown in Figure 6 for the 1:1 and the 1:2 complexes.

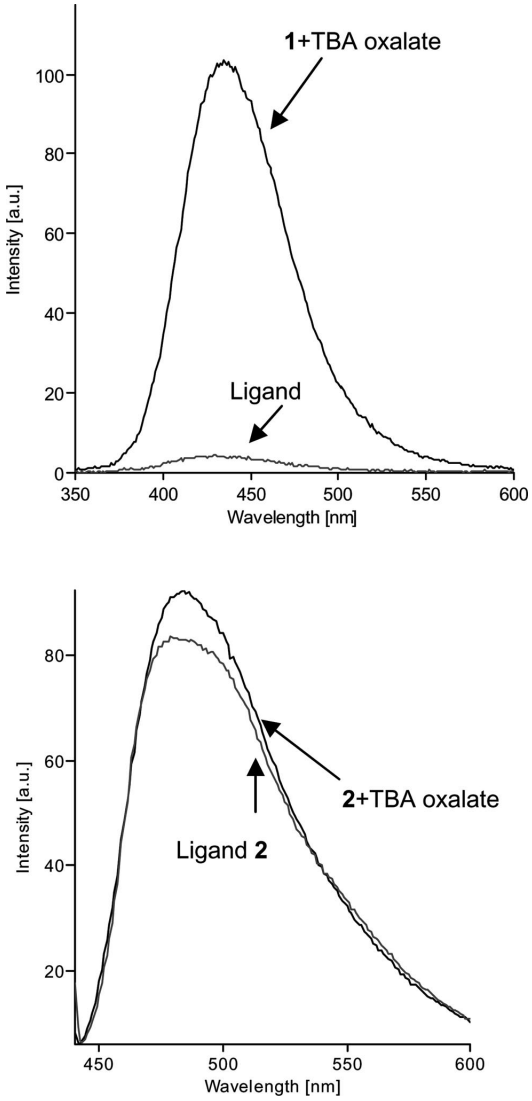


Figure 5. Titration of ligand **1** with TBA oxalate [λ_{exc} (DMSO) = 340 nm] (top) and titration of ligand **2** with TBA oxalate [λ_{exc} (DMSO) = 435 nm] (bottom).

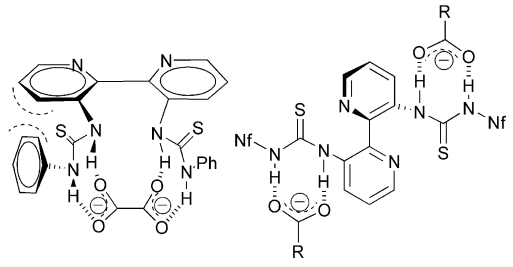


Figure 6. Complexation types of the 1:1 and 1:2 complexes.

The difference in the behaviours of the ligands should be related to the substituents on the thiourea moiety. Greater steric hindrance between the naphthyl groups in the s-*cis* conformation probably precludes the formation of 1:1 complexes of ligand **1** with dicarboxylates.

To obtain additional information about the structure of these complexes, ^{1}H NMR spectroscopic experiments were carried out. Unfortunately, broad signals were observed in the spectra; however, the signal corresponding to H_c of the ligands, which resonates at ca. 9 ppm, remained essentially unchanged after complexation of ligand **1**, but it shifted to 7.61 ppm upon complexation of ligand **2**. These observations are in agreement with the conformational change that gives rise to the 1:1 complex.

On the other hand, the bipyridine conformation in the Ni^{2+} complex places both thiourea groups close to each other, and as such, complexation with ligand **1** seems to be inhibited. Thus, UV and fluorescence studies carried out with **1** and TBA acetate demonstrated that no change was produced after the addition of increasing amounts of the anion. Therefore, this nickel complex exhibits negative allosteric cooperativity in the complexation of anions.

Conclusions

Two new bipyridine ligands were prepared. These ligands are able to complex anions through the thiourea groups or Ni^{2+} through the bipyridine moiety. They are present in DMSO solution as the s-*trans* conformer. This conformation allows two types of hydrogen bonding: (i) between the NH of the thiourea group in one ring and the pyridine nitrogen in the other ring and (ii) between H_c and the sulfur atom of the thiourea. The latter interaction is responsible for the anomalous δ value for H_c in the ^{1}H NMR spectra. Protonation experiments demonstrated that it is the sulfur atom, and not the nitrogen atom, which is bound to the proton, and under these conditions, hydrolysis takes place. By contrast, complexation with $NiCl_2$ induces a conformational change from the s-*trans* conformation to the s-*cis*.

Ligands **1** and **2** show different behaviour as anion receptors. Ligand **1** gives rise to complexes with a 1:2 stoichiometry with carboxylates, whereas the corresponding complexes of ligand **2** exist in a 1:1 stoichiometry with dicarboxylates. Finally, a clear negative allosteric cooperativity was observed for these ligands. Thus, the formation of the Ni^{2+} complex precludes coordination with the studied anions.

Experimental Section

General Procedures and Materials: Compound **3** was prepared according to a literature procedure.[14] All reagents were commercially available and used without purification. THF was distilled from Na/benzophenone under an atmosphere of argon prior to use. Water-sensitive reactions were performed under an atmosphere of argon. Column chromatography was performed with silica gel 60 (230–400 mesh, Merck) and with neutral alumina (pH = 7.0 ± 0.7) with a particle size of 0.05–0.2 nm (ref. 2210017, Sds). Silica gel upholded on a 0.2-mm thick aluminium foil DC-60 F (254) (ref.

5554, Merck) or neutral alumina on a similar support (ref. 105550, also Merck) were used for TLC. ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker Avance 300, 400 or 500 MHz spectrometer with the deuterated solvent as the lock and residual solvent as the internal reference. High-resolution mass spectra (FAB) were recorded in the positive ion mode with a Fisons VG-Autoespec. Melting points were determined with a microscope equipped with a heating slide (Cambridge Instruments). Infrared spectra were recorded with a Bruker Equinox 55 FTIR with a screen width of 4000 to 400 cm^{-1}. All spectra were recorded after 10 scans and with a step wavelength of 0.5 cm^{-1}. Samples were submitted for IR spectroscopy as KBr discs. Values correspond to the maximum absorbance for the most characteristic bands of the compounds. UV spectra were recorded at room temperature with a Shimadzu UV-2102 PC. Steady-state fluorescence measurements were carried out with a Varian Cary Eclipse Fluorimeter.

Syntheses

1: Naphthylisothiocyanate (0.35 g, 1.93 mmol) was added to a solution of 3,3′-diamino-2,2′-bipyridine (0.17 g, 0.96 mmol) in THF (5 mL). The mixture was then heated at reflux under an atmosphere of argon for 36 h. After cooling to room temperature, **1** was precipitated from dioxane as a brown-yellow solid (0.37 g, 69%). M.p. 195–197 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 11.64 (s, 2 H, NH), 10.64 (s, 2 H, NH), 8.89 (d, J = 8.5 Hz, 2 H, Ar-H), 8.06 (d, J = 8.3 Hz, 4 H, Ar-H), 7.83 (d, J = 8.3 Hz, 2 H, Ar-H), 7.67 (t, J = 7.5 Hz, 2 H, Ar-H), 7.55–7.52 (m, 10 H, Ar-H) ppm. IR (KBr) $\tilde{\nu}$ = 3124, 2922, 1593, 1567, 1524, 1397, 1193, 1072, 942, 772, 732, 635 cm^{-1}. HRMS (FAB+): calcd. for $C_{32}H_{25}N_6S_2$ [M + H]$^+$ 557.1582; found 557.1584.

2: Following the same procedure as that described for **1**, **2** was synthesized from 3,3′-diamino-2,2′-bipyridine (0.16 g, 0.86 mmol) and phenylisothiocyanate (0.20 mL, 1.72 mmol) as a white precipitate (0.36 g, 78%). M.p. 116–118 °C. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 12.21 (s, 2 H, NH), 10.78 (s, 2 H, NH), 9.02 (d, J = 7.5 Hz, 2 H, Ar-H), 7.66–7.56 (m, 14 H, Ar-H) ppm. ^{13}C NMR (100.5 MHz, [D$_6$]DMSO): δ = 179.2, 145.2, 143.0, 139.9, 136.2, 134.8, 129.6, 126.5, 125.0, 123.5 ppm. IR (KBr) $\tilde{\nu}$ = 3160, 2360, 1593, 1496, 1438, 1392, 1235, 1179, 1071, 938, 751, 691, 515 cm^{-1}. HRMS (FAB+): calcd. for $C_{24}H_{21}N_6S_2$ [M + H]$^+$ 457.1269; found 457.1265.

1·NiCl$_2$: Ligand **1** (0.12 g, 0.22 mmol) and $NiCl_2$ (0.35 g, 0.27 mmol) were suspended in EtOH (50 mL). The suspension was heated at reflux for 10 min to obtain a clear solution. The temperature was then kept around 80 °C for 2 h. After this time, the reaction was allowed to reach room temperature, and the mixture was filtered to isolate **1**·$NiCl_2$ as a yellow solid (0.12 g, 79.9%). M.p. 240 °C (dec.). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.90 (br. s, 4 H, NH), 8.05 (d, J = 8.6 Hz, 1 H), 7.97 (d, J = 8.8 Hz, 1 H), 7.86 (d, J = 7.7 Hz, 1 H), 7.71 (m, 1 H), 7.57 (m, 1 H), 7.40 (m, 1 H), 7.07 (d, J = 9.0 Hz, 1 H) ppm.

2·NiCl$_2$: Complex **2** was prepared by the same procedure as that described for **1**, and it was isolated as a brown wax (0.09 g, 73.3%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 11.00 (s, 2 H, NH), 10.21 (s, 2 H, NH), 7.93 (br. m, 2 H), 7.55 (d, J = 7.6 Hz, 2 H), 7.45 (br. s, 2 H), 7.32 (br. s, 4 H), 7.21–7.16 (m, 6 H) ppm. ^{13}C NMR (100.5 MHz, [D$_6$]DMSO): δ = 177.2, 149.6, 140.5, 130.2, 129.5, 125.5, 125.0, 124.2, 122.8, 115.3 ppm.

Binding Studies: Binding constants of ligands **1** and **2** with tetrabutylammonium dicarboxylates were evaluated by using UV/Vis titrations in DMSO. Typically, 10^{-4} M solutions of the receptors in DMSO (3 mL) were titrated by adding 2-μL aliquots of the envisaged dicarboxylates (as their TMA salts) in DMSO and recording the UV/Vis spectrum after each addition. Logβ was calculated by fitting all spectrophotometric titration curves with the SPECFIT program [SPECFIT/32 Global Analysis System v. 3.0, Spectrum Associates (Marlborough, MA, USA)].

Supporting Information (see footnote on the first page of this article): UV spectra of **1**, protonated **1**, **2** and **2**·$NiCl_2$ and their corresponding titration curves with TBA succinate, malonate, acetate and oxalate. Fluorescence spectra of **2**, protonated **2** and **2**·$NiCl_2$.

Acknowledgments

This research was supported by A.E.C.I (ref. 803/2006). We acknowledge the Universitat de Valencia (S.C.I.E.) for most of the equipment employed. We thank the Spanish Ministerio de Ciencia y Tecnología for financial support (Project CTQ2006-15456-02) and the Generalitat Valenciana for the projects ACOMP07-080 and GV/2007/061.

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Received: October 23, 2007
Published Online: January 2, 2008

