



Colorimetric macrocyclic anion probes bearing nitrophenylurea and nitrophenylthiourea binding groups



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ABSTRACT

Two novel molecular probes bearing two urea (sensor **1**) or thiourea (sensor **2**) groups (as anion recognition site) coupled with a nitrophenyl group (chromogenic unit) were synthesized and evaluated according to the binding site-signaling subunit approach.

The behavior of these different compounds toward metal ions (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+}) and anions (F^- , Cl^- , Br^- , I^- , ClO_4^- , NO_3^- , CN^- , OH^- , CH_3COO^- , and H_2PO_4^-) was investigated by UV–vis spectroscopy in DMSO.

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1. Introduction

The study of new ligands, hosts, or receptors for cations and anions has been an area of considerable interest in the field of supramolecular chemistry.¹ Historically, cation complexation has received greater attention, but during recent years, the study of receptors for anions, such as halides and acid anions has become an area of vigorous research effort.²

The slower development of anion sensors, compared to cation sensors, is due in part to the fact that detecting small inorganic anions is often more difficult than detecting cations.³ Furthermore, while cations are often monatomic and spherical, polyatomic inorganic anions exhibit a range of geometries with charges that are delocalized over a number of atoms. The variety of anions makes each receptor less general and requires it to incorporate individual design elements.⁴

In recent years, considerable attention has been paid to the development of colorimetric and fluorescent chemosensors for sensing anionic species.^{5–7} Commonly, such sensors offer many advantages, such as high sensitivity and simplicity, especially for real-time and on-line analysis of analytes.⁸

The design and synthesis of colorimetric neutral chemosensors for anions^{9,10} usually involves the covalent linking of a chromogenic fragment to a neutral receptor capable of establishing selective interactions with the envisaged anion.^{11,12} Although various supramolecular interactions have proven to be significant, the most frequent binding motif is arguably hydrogen bonding.^{13,14}

It is well-known that urea/thiourea with a nitrophenyl group as a signaling unit showed an enhancement in both the hydrogen-bond donor tendency and acidity.¹⁵

Selectivity of receptors containing one or more urea and thiourea subunits is related to the energy of the receptor–anion interaction; in this sense, strong H-bond interactions are established with anions containing the most electronegative atoms as fluoride¹⁶ or inorganic oxoanions.^{17,18} Solvent cannot be water or any other hydrogen bond-forming medium (e.g., alcohols) since they

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would compete successfully with the receptor for the anion. Thus, aprotic solvents of varying polarity are currently employed in anion recognition studies based on H-bonds (e.g., CHCl₃, MeCN, and DMSO) in order to preclude the competition of the solvent as a hydrogen-bond donor.¹⁹

In recent years, polyazamacrocycle-based receptors have been well-studied for anions,²⁰ and some of them have been proven as effective systems showing high selectivity and affinity for simple inorganic²¹ to biological anions.²² Compared to acyclic anion sensors, reports on cyclic anion sensors are quite limited, which often require complicated synthetic pathways.²³

With this idea in mind and continuing our efforts in producing new macrocyclic receptors²⁴ we set out to synthesize two novel colorimetric anion sensors that comprise two urea (sensor **1**) and thiourea (sensor **2**) groups (anion binding site) coupled with a nitrophenyl group (chromogenic unit) (Fig. 1). The behavior of these different compounds toward anions (F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, CN⁻, OH⁻, CH₃COO⁻, and H₂PO₄⁻) and also toward metal ions (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and Cd²⁺) was investigated by UV–vis spectroscopy in DMSO.

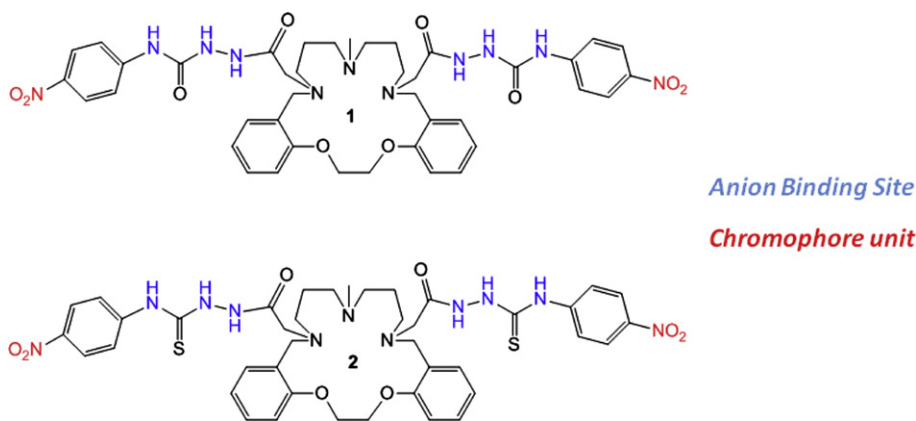
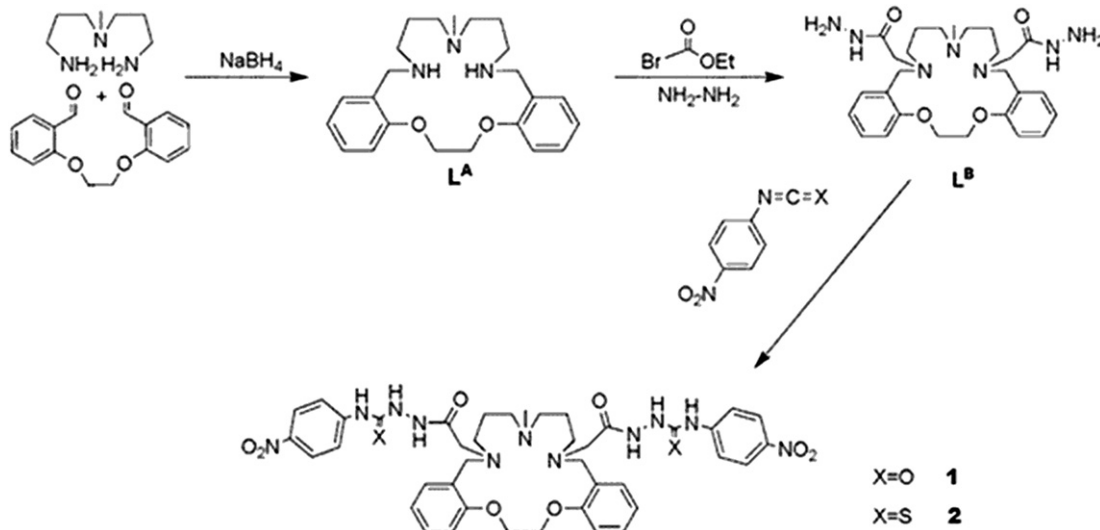


Fig. 1. Schematic representation of chemosensors **1** and **2**.

2. Results and discussion

2.1. Synthesis and characterization of L^B

Ligand L^B was isolated as an air-stable yellow oil in 72% yield by using a two-step procedure involving the alkylation of L^A



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

(Scheme 1) with ethyl bromoacetate and subsequent reaction of the intermediate ester with hydrazine hydrate.²⁵ The infrared spectrum (KBr disc) of L^B shows bands at 769 and 3316 cm⁻¹ assigned to the out-of-plane bending and stretching vibrations of the hydrazone groups, respectively, together with a band at 1675 cm⁻¹ associated with the ν (C=O) vibration of the carbonyl groups. The ESI mass spectrum presents an intense peak at 528 amu corresponding to the molecular ion [L^B+H]⁺. The ¹H NMR spectrum shows signals corresponding to the NH groups (8.9, 8.5 ppm). In the ¹³C NMR spectrum the signal at 170.3 ppm corresponds to a carbonyl group.

2.2. Synthesis and characterization of the colorimetric probes **1** and **2**

Therefore, we propose the synthesis of two new potential anion receptors **1** and **2** containing nitrophenylurea and nitrophenylthiourea moieties, respectively, outlined in Scheme 1.

In the first step, a solution of 4-nitrophenylisocyanate or 4-nitrophenylisothiocyanate in dry dichloromethane was added

dropwise to a refluxing solution of the precursor L^B in the same solvent.^{24a,26} 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 layers were dried over anhydrous Na₂SO₄, and the final solutions were evaporated to dryness yielding solids, characterized as the

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