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Exploratory studies towards various anion recognition chemistry by two different sized cleft shaped organic ligands

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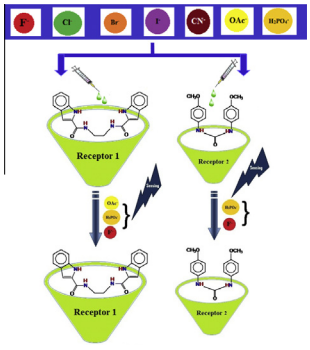
HIGHLIGHTS

- We report cost effective luminescent as well as electrochemical chemosensors.
- The sensors can be made following a simple synthetic route.
- Shape and size selectivity of chemosensors are modelled for biologically important anions (F^-, OAc^- and $H_2PO_4^-$).
- The sensing interactions are well explained by convenient spectrophotometric and electrochemical techniques.
- The receptors have improved binding abilities.

GRAPHICAL ABSTRACT

Exploratory studies towards various anion recognition chemistry by two different sized cleft shaped organic ligands



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ABSTRACT

Indole and urea based two organic receptors have been synthesized by an easy synthetic process. These two receptors have strong sensitivity and selectivity for several bio-relevant anions. Receptor **1** and **2** were synthesized from indole-2-carboxylic acid and *p*-anisidine respectively, which are low cost starting materials. Receptor **1** can selectively sense anions like F^-, OAc^- and $H_2PO_4^-$, while receptor **2** can only sense F^- and $H_2PO_4^-$. Both receptors are silent toward anions like Cl^-, Br^-, I^- and NO_3^-. It is the difference in their shape and size which are responsible for different anion sensing. The nature of these host–guest type interactions was analyzed by convenient spectrophotometric techniques like UV–Vis, fluorescence, ^{1}H NMR, FT-IR studies and also confirmed by electrochemical techniques like cyclic voltammetry studies of the two ligand receptors with convenient anions. Between receptor **1** and **2**, receptor **2** was crystallographically characterized also.

Introduction

Designed synthesis of artificial molecular receptors as sensors for anions is nowadays a growing and demanding area of interest concerning their enormous role in a wide range of applications starting from environmental, industrial as well as in biological systems [1–4]. Therefore sensing of anions has become a popular field

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of research in modern age. Of several bio relevant anions fluoride is one of the most important one and has received much attention due to its unique properties. It is well established in the scientific community because of its usefulness in dental care and also in the clinical treatment of osteoporosis [5–7]. Similar to fluoride, acetate ion detection is also crucial keeping in mind that it is an integral part of acetyl coenzyme-A [8]. Several groups of scientists and researchers are working worldwide towards systematic development of suitable organic receptors with several functional groups especially of the kind; $-NH/-SH/-CONH_2$ for sensing bio-relevant anions through H-bonding and in presence of several other weak van der Waal's interactions. In the last few years urea, amide and pyrrole based receptors have gained much attention [9–13]. The use of indoles and urea as a component for constructing neutral receptor for selective anion recognition has been presented herein [14–17]. A receptor system generally consists of two parts. One part is considered as the anion binding unit and the other being the fluorophore part which converts the chemical process related to binding phenomenon into optical or electrochemical signals [18]. Herein we are disclosing two cost effective and easy to synthesize neutral anion binding receptors e.g.; N,N′-(ethane-1,2-diyl)bis(1H-indole-2-carboxamide) receptor **1** and 1,3-bis(4-methoxyphenyl)urea receptor **2** (*vide* Chart 1) both of which have shown quite interesting binding properties with bio benign anions like fluoride, acetate and dihydrogen phosphate effectively and selectively.

Experimental

Materials

All starting materials (chemical reagents, solvents) were commercially available and were of analytical grade. Solvents like dichloromethane, acetonitrile were distilled and dried prior to use. All tetrabutyl ammonium salt of anions like fluoride (hydrate), chloride, nitrate, acetate and phosphate monobasic were purchased from Sigma Aldrich chemical company and used as it was received. Tetrabutyl ammonium bromide and iodide were procured from Alfa Aesar chemical company. Solvents like Methanol, DMSO, water were of spectroscopic grade and purchased from Merck India Pvt. Ltd. and used without doing any further purification.

Apparatus

The infrared spectra were recorded in a Perkin Elmer FT-IR Spectrum 100 spectrophotometer. The mass spectra obtained in Advion's CMS Expression serial number: 3013-0140 compact mass spectrometer. ^{1}H NMR was recorded in a Bruker AV-400 spectrometer. UV–Vis spectra were taken in SEC2000, ALS spectrophotometer. Fluorescence was done in Perkin Elmer LS-45 spectrophotometer. Cyclic voltammetric experiments were executed in Biologic's SP-150 series instrument.

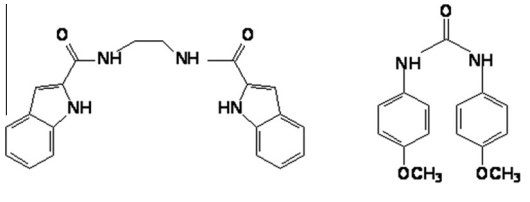

Chart 1.

Preparation of receptor **1**; N,N′-(ethane-1,2-diyl)bis(1H-indole-2-carboxamide)

A solution of indole-2-carboxylic acid (0.32 g, 2 mM) and carbonyldiimidazole (CDI) (0.41 g, 2.55 mM) were taken in a solution of acetonitrile (20 ml) and refluxed for 2 h. Ethylenediamine (1 mM, 0.060 g) was added dropwise and the solution was refluxed for 6 h at 353 K. A curdy white precipitate was appeared which was filtered after cooling. The filtrate was washed repeatedly with 60 ml ether (3 × 20 ml fractions). The white powder of receptor **1** was finally collected after drying (Scheme 1).

Yield: (0.69 g, 80%) mp 220 °C.

(ESI-MS) *m*/*z* Calcd: for $C_{20}H_{18}O_2N_4$: 346 ($M+H^+$), Found: 345 (Fig. S1); Anal. Calcd. for $C_{20}H_{18}O_2N_4$: C = 69.36, H = 5.20, N = 16.18; found: C = 69.41, H = 5.29, N = 16.23; Proton (^{1}H) NMR (δ in ppm)(400 MHz; DMSO-d_6; Me_4Si) 11.57(s, 2H, —NH indole), 8.651(s, 2H, —NH urea), 7.605(d, 2H, Ar—H), 7.424((d, 2H, Ar—H), 7.16(t, 2H, Ar—H), 7.109(s, 2H, Ar—H), 7.027(s, 2H, Ar—H), 3.489(t, 4H, CH_2): IR (cm^{-1}) KBr: 3596 cm^{-1}, 3464 cm^{-1}, 3418 cm^{-1}, 1615 cm^{-1}, 1541 cm^{-1}, 1398 cm^{-1}, 789 cm^{-1}.

Preparation of receptor **2**; 1,3-bis(4-methoxyphenyl)urea

To a solution of *p*-anisidine(0.123 g,1 mM) in dichloromethane solid triphosgene(0.296 g,1 mM) was added under N_2. Immediately a saturated aqueous solution of $NaHCO_3$ (7 ml) was added dropwise. Effervescence of carbon dioxide was observed which gradually diminished. Stirring was continued for 12 h under nitrogen atmosphere. The crude material thus obtained was collected and placed in a separating funnel and washed with water several times to remove the excess $NaHCO_3$ (Scheme 2). The pink colored dichloromethane solution was collected after washing with water and excess water was removed by passing over anhydrous Na_2SO_4. White crystals of receptor2 were obtained by slow evaporation of the DCM-Hexane solution (Scheme 2).

Yield: (0.248 g, 85%) mp 292 °C: (ESI-MS) *m*/*z* Calcd: 272 for $C_{15}H_{16}O_3N_2$, Found: 273 (Fig. S2); Anal. Calcd. for $C_{15}H_{16}O_3N_2$: C = 66.17, H = 5.88, N = 10.29; found: C = 66.12, H = 5.90, N = 10.32. Proton (^{1}H) NMR (δ in ppm) (400 MHz; DMSO-d_6; Me_4Si) 8.352(s, 2H, —NH), 7.33(d, 4H, Ar—H), 6.85(d, 4H, Ar—H), 3.709(s, 6H, —OCH_3); IR (cm^{-1}): 3294 cm^{-1}, 1633 cm^{-1}, 1607 cm^{-1}, 1565 cm^{-1}, 1506 cm^{-1}, 1169 cm^{-1}, 1030 cm^{-1}, 827 cm^{-1}.

Results and discussion

Receptor **1** was synthesized in good yield (~80%) by simple coupling of commercially available indole-2-carboxylic acid with ethylenediamine using carbonyl diimidazole (CDI) as an amide-coupling reagent. Receptor **2** was synthesized, by reaction of *para*-anisidine with triphosgene in a mixture of dichloromethane and saturated aqueous $NaHCO_3$ solution under dry nitrogen atmosphere. Receptor **1**, was giving white colored crystalline material and it was fully characterized by ^{1}H NMR, UV–Vis, ESI-MS and CHN analysis. X-ray quality single crystals of receptor **2** were obtained from DCM-HXN (slow evaporation). The ORTEP and atom numbering scheme of receptor **2** was shown in Fig. S3(a) which authenticates its structure. The intermolecular H-bonding for the receptor **2** was shown in Fig. S3(b).

X-ray structure determination

[1,3-bis(4-methoxyphenyl)urea], receptor **2** was recrystallized from DCM (dicholoromethane). X-ray quality single crystal of receptor **2** was obtained from slow evaporation of dichloromethane–hexane (2:1) solution mixture of receptor **2**. ORTEP and atom numbering