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Amide-nitrophenyl based colorimetric receptors for selective sensing of fluoride ions

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Abstract—New chromogenic receptors containing 2-nitrophenyl or 3,5-dinitrophenyl groups appended to the amide or in secondary amine positions have been synthesized and characterized. Upon addition of fluoride to two of the receptors in acetonitrile, the solution acquired a yellow colour. The third receptor showed an intense purple colour with fluoride in acetonitrile and the appearance of the purple colour can be detected by the naked eye at parts per million level. The addition of chloride, bromide and iodide to the receptors did not induce any colour. Thus the receptors can act as fluoride ion sensors even in the presence of other halide ions.

The design and synthesis of sensitive chemosensors for anions is of growing interest, because the anions play an important role in a wide range of environmental and chemical processes.[1] The development of chromogenic receptors for anion sensing is a relatively new area of research.[2] Indeed, colorimetric anion sensing is particularly challenging since visual detection can give immediate qualitative information.[3] Colorimetric sensors have considerable advantages over other molecular sensors because they do not require the use of costly equipment such as spectrophotometers or cyclic voltameters.[4] Among the inorganic anions, fluoride ions have received significant interest due to their beneficial effects (e.g., prevention of dental caries) and detrimental (e.g., fluorosis) roles.[5] Chromogenic receptor systems generally consist of two parts. One is the anion binding part employing various combinations of pyrroles,[6] guanidiniums,[7] Lewis acids,[8] amides[9] and urea or thioureas.[10] The other is the chromophore part, which converts binding induced changes or recognition phenomena to optical signals. Previously we have reported a ferrocene-functionalized redox-active receptor that can sense only fluoride anions among halides.[11] In this letter, we report the synthesis, characterization and colorimetric sensing nature of the receptors **R1**, **R2** and **R3** containing nitroaromatic moieties. The receptor **R1** possesses amide and amine groups that serve as interaction sites whilst the receptors **R2** and **R3** contain only amide groups.

The receptor *N*,*N*′-bis{3-(2-nitrobenzyl)aminopropyl}-oxamide **R1** was obtained in one step from the condensation of 2-nitrobenzaldehyde in methanol with a solution of $oxpnH_2$ (*N*,*N*′-bis(3-aminopropyl)oxamide)[12] in methanol (20 ml) with subsequent reduction with excess $NaBH_4$. After basic work-up, the product was purified by column chromatography on neutral alumina ($CHCl_3$–CH_3OH, 99:1 v/v). The receptor **R1** was obtained as a crystalline powder (Scheme 1). Crystals of receptor **R1** were obtained from methanol:acetonitrile (1:1) mixture. The receptors **R2** (*N*,*N*′-bis{3-(2-nitrobenzoyl)aminopropyl}oxamide) and **R3** (*N*,*N*′-bis{3-(3,5-dinitrobenzoyl)aminopropyl}oxamide) were synthesized[13] by the reaction of either 2-nitro- or 3,5-dinitrobenzoic acid with $oxpnH_2$ in THF in the presence of *N*,*N*′-dicyclohexylcarbodiimide. The reaction mixture was stirred at room temperature for 4 h, and the resulting insoluble precipitate was removed by filtration. The solvent was evaporated and the resulting compound was dissolved in ethyl acetate (10 ml). Addition of hexane (25 ml) afforded the receptors **R2** and **R3** (Scheme 2),

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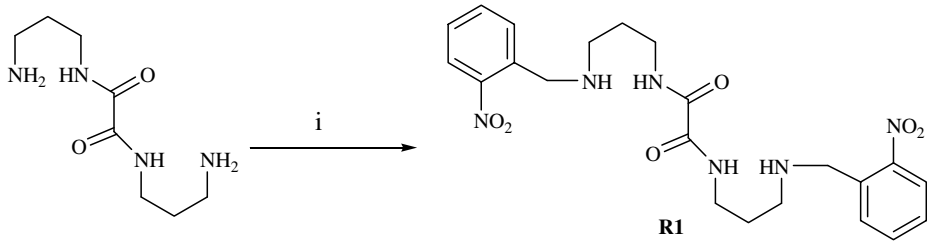
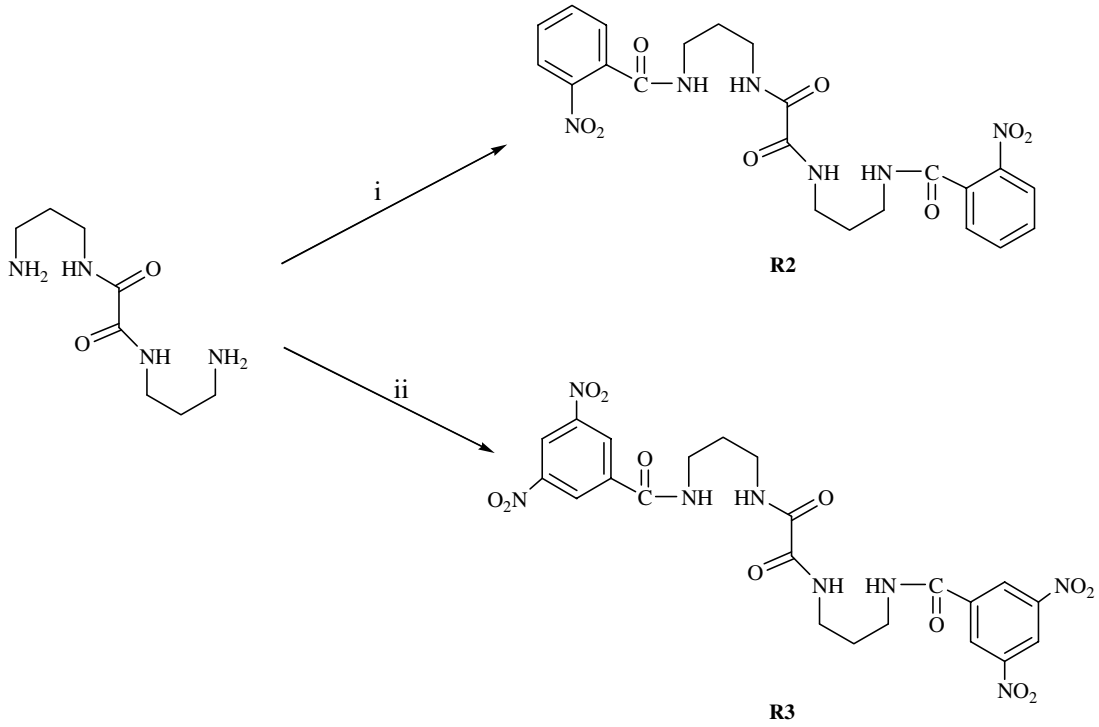


Scheme 1. Reagents and conditions: (i) 2-nitrobenzaldehyde, methanol, reflux, 6 h, then $NaBH_4$, rt, 1 h, 72%.



Scheme 2. Reagents and conditions: (i) 2-nitrobenzoic acid, *N*,*N*′-dicyclohexylcarbodiimide, THF, rt, 4 h, 68%; (ii) 3,5-dinitrobenzoic acid, *N*,*N*′-dicyclohexylcarbodiimide, THF, rt, 4 h, 70%.

which were purified by recrystallization from chloroform. Elemental and spectroscopic analysis were consistent with the proposed formulations of **R1**, **R2** and **R3**.[14] The receptor **R1** was characterized by XRD[15] and the ORTEP plot is shown in Figure 1.

The colorimetric sensing ability of the receptors **R1**–**R3** with anions (F^-, Cl^-, Br^- and I^-) in acetonitrile was monitored by UV–visible absorption and by 'naked eye' observations. The anions were added as tetrabutylammonium salts to the acetonitrile solutions (5×10^{-5}) of the receptors **R1**–**R3**.

The absorption spectra of the receptors **R1** and **R2** were characterized by the presence of single absorption maxima at 264 nm. Upon addition of fluoride, the intensity of the peak at 264 nm decreased while a new peak appeared at 427 nm along with an isosbestic point at

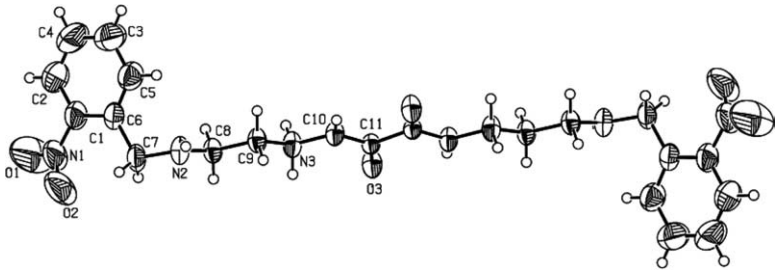


Figure 1. ORTEP plot of the crystal structure of **R1**.