



**Photoinduced Electron Transfer Based
Fluorescent Sensors
For
Metal Ion Detection**

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Abstract

This thesis describes the synthesis and complexation characteristics of a series of fluorescent sensors of the photoinduced electron transfer (PET) based Fluorophore-Spacer-Receptor design. The ligands synthesised consist of a 9,10-disubstituted anthracene, an alkyl spacer (methyl, ethyl or propyl) and a receptor (morpholine and analogues or monoaza-15-crown-5). Upon metal ion complexation (or protonation) the fluorescence emission of the synthesised ligands is significantly increased (up to 30-fold) due to the suppression of the fluorescence quenching PET process.

The acid dissociation constants were determined in 1,4-dioxane-water (40:60; v/v) solution ($I = 0.05 \text{ mol dm}^{-3}$) for the soluble ligands, although no metal ion complexation was observed. The protonation of only one (of the two) nitrogen amines in close proximity to the anthracene was found not to restore the fluorescence emission in 1,4-dioxane-water. In addition, it was necessary to use buffered solutions to prevent protons liberated from metal ion hydrolysis causing increased fluorescence.

The alkali and alkaline earth metal ion complexation characteristics of the ligands were studied in anhydrous acetonitrile and a series of spectrofluorimetric titrations were performed to determine the stability constants (K_1 and K_2) of the complexes that formed. Minimal changes in the absorption spectra were observed. Increasing the spacer length (methyl to propyl) increased the quantum yield of the unbound ligand and the stability of the complexes formed (350-fold increase for Mg^{2+}). Little cooperative binding between the two receptors was observed and K_1 was always larger than K_2 . The general stability series observed for the six-membered ring receptors was $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} \leq \text{Ba}^{2+}$.

Utilising the larger azacrown receptor, the stability constants in acetonitrile could not accurately be determined for the alkaline earths as K_1 and $K_2 \geq 10^7 \text{ dm}^3 \text{ mol}^{-1}$. Biphasic binding curves were observed due to the low fluorescence of the (metal)•(ligand) complex and high fluorescence of the (metal)₂•(ligand) complex. This receptor also displayed increased fluorescence emission with alkali metal ions, although of lower stability. The magnitude of the stability constants and quantum yield changes was chiefly controlled by the charge density of the bound metal ion.

This work furthers understanding of the requirements for PET based fluorescent sensors to detect metal ions.