

A FLUORESCENT CHEMOSENSOR WITH SELECTIVITY FOR Hg(II)

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Abstract: Geometric immobilization of polyamine ligands is expected to change their binding properties toward practical ion discrimination. Chemosensor 5 senses only two transition metal ions in water- Hg(II) (K, 14 pM) and Cu(II) (K 56 pM)- which can be compared with bindings of a non-immobilized reference compound (9-(trpnmethyl)-anthracene; 3) with Hg(II) (K, 14 pM) and **Cu(II) (K, 39 pM)**. A related bridged cyclen derivative (7) showed no effect on fluorescence by any metal ion examined. These results suggest that the rigid immobilization of polyamine ligands onto a fluorophore framework may be employed successfully in the creation of selective chemosensors.

1. Introduction

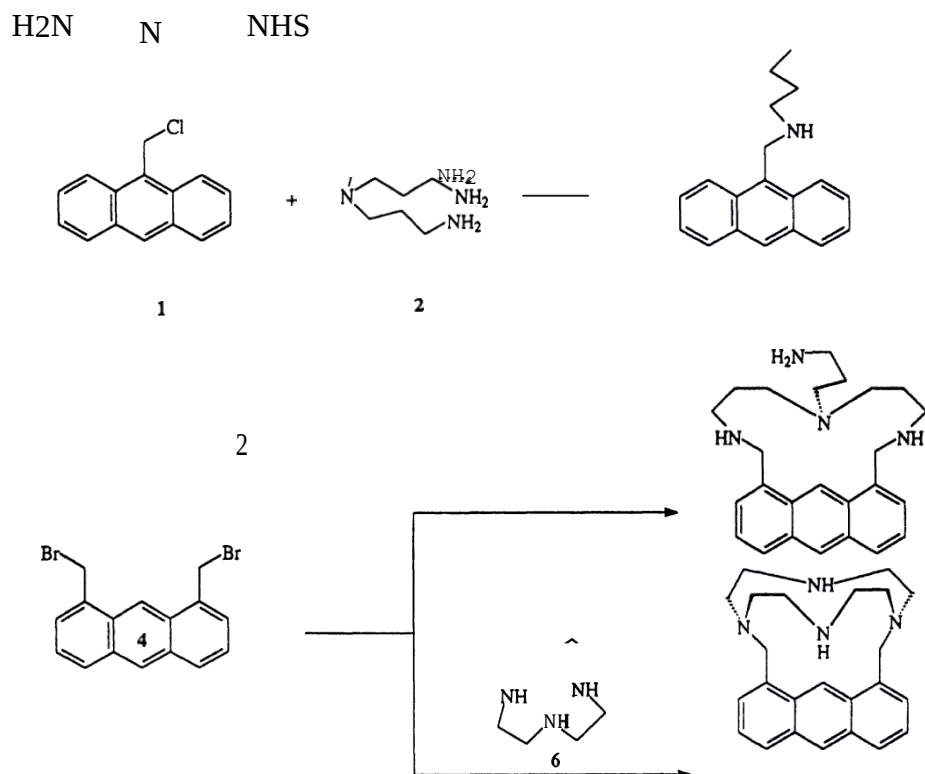
While the analytical determination of trace species in solution demands high sensitivity, real-time sensing applications typically do not. Instead, sensing demands the availability of reporter molecules with analyte affinity engineered to that of a median background analyte concentration. Chemosensors are abiotic molecules that signal interactions with analytes reversibly and in real-time [1]. Of the many signal types available, fluorescence signaling has the potential to afford high sensitivity and direct application to fiber optic- based remote sensing schemes [2]. The generally high affinity of polyamine ligands for transition metal ions has provided for the formulation of metal ion chemosensors that function in water. However, the same high affinity makes ion discrimination based on complexation affinities problematical. Thus, there are as yet no fluorescent chemosensors reported for any transition metal ion that combine real-time reversibility with sufficient selectivity for the monitoring of complex ionic mixtures. Engineering such selectivity based on ligand engineering is a primary goal of chemosensor research. We now report a novel approach to the attainment of binding discrimination in

chemosensors, based upon the rigid immobilization of polyamine ligands onto a fluorophore framework. This approach has yielded a fluorescent chemosensor for the Hg(II) ion [3].

2. Results

Our synthesis began with 1,8-bis(bromomethyl)anthracene (4), available using the procedures of Nakagawa [4]. Compound 5 was synthesized by addition of 4 to a warm (50-60°C) mixture of trpn (2; 1 eq.), CO₃ and CHCl₃ (Scheme I). After complete 190 addition, the solution was Washed with 50 mM pH 7.5 phosphate (2 x 200 mL). The aqueous washes were adjusted to pH>11 with NaOH and extracted with CHCl₃, to give S, and the HCl salt was precipitated from EtOH in 19 % overall yield. Microanalysis, in conjunction with ¹H NMR, ¹³C NMR, and exact mass EI mass spectroscopy, provided confirmation of structure. Bridged cyclen 7 was synthesized by the reaction of 4 with cyclen (6) at room temperature. Compound 7 could be purified by silica gel column chromatography using 30% MeOH/CHCl₃. Anthrylpolyamine 3 was made using the literature procedure [5].

Scheme 1



The perchlorate salts of **Al(III)**, **Ca(II)**, **Cd(II)**, **Co(II)**, **Cr(III)**, **Cu(II)**, **Eu(III)**, **Fe(III)**, **Ga(III)**, **Gd(III)**, **Hg(II)**, **In(III)**, **Mg(II)**, **Mn(II)**, **Ni(II)**, **Pb(II)**, **Rb(I)**, **Sr(II)**, **Yb(III)**, and **Zn(II)** were used to evaluate metal ion binding. All titration studies were conducted at pH 7 (0.1 M HEPES) and using a 4 pM concentration of chemosensor. Using these metal ions (100 pM), compound 5 displayed chelation-enhanced quenching (CHEQ).