

Anthracene-Based Amido–Amine Cage Receptor for Anion Recognition under Neutral Aqueous Conditions

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Dedicated to Jean-Marie Lehn for his 80th birthday and great inspiration to develop the supramolecular chemistry

A new amido–amine cage receptor, which combines 1,8-anthracene diacboxamide subunit and a polyammonium azamacrocyclic, is reported. Bearing both the hydrogen bond donor and the acceptor binding sites, the receptor is able to bind phosphate selectively under neutral (pH 7.2) aqueous conditions. The recognition events for phosphate and dicarboxylates are accomplished by a fluorescence enhancement in the anthracene emission. As revealed by experimental and theoretical studies, phosphate and oxalate show different recognition modes. Phosphate demonstrates hydrogen bond acceptor properties, while the coordination of oxalate favours the protonation of the receptor.

Recognition and sensing of anions in an aqueous solution is an important challenge in supramolecular chemistry.^[1] The fact that anions play important roles in living systems and in the environment inspires researchers to design highly selective synthetic receptors and probes. Considerable progress has been made in the area of anion recognition during the last decade.^[2]

However, receptors that selectively bind and detect anions in a buffered aqueous solution remain rare.^[2c,3]

One of the most strongly binding receptors for anions in water are azacryptands pioneered by Simmons, Park and Lehn.^[4] This class of synthetic hosts has grown in a broad variety of rigid and flexible, high affinity binding receptors during the last two decades.^[3b,c,5]

In a search of a strategy to improve the selectivity of synthetic hosts for certain anions, various modifications in their structures have been explored including the introduction of rigid fragments, methylation^[6] and addition of straps into the receptor structure.^[7]

Combining hydrogen bond donor and acceptor groups has been proven to be a beneficial strategy to generate high selectivity for certain series of anions.^[8] This strategy could be especially advantageous for achieving a selectivity for anions carrying protons in an aqueous solution such as phosphates, carboxylates and complex organic anions.^[9] Phosphate is present in water under neutral conditions as a mixture of anions H_2PO_4^- and HPO_4^{2-} . Therefore, it is important to have both hydrogen bond acceptor and hydrogen bond donor binding sites in the structure of a host.^[10] Recent examples of such type of receptors for phosphates working in water include a macrocyclic amido–amine receptors^[11] imine cages^[12] and azacryptands bearing pyridine or pyrrole rings.^[13] Analysis of the literature shows that amide group can function as both donor and acceptor of hydrogen bonds. In this regard, 1,8-anthracene diacboxamide fragment can be a promising building block for anion recognition. Moreover, the anthracene dye can provide fluorescence properties for a synthetic receptor. There have been only a few reports published on the use of derivatives of 1,8-anthracene dicarboxylic acids in synthetic receptors, such as recognition of dicarboxylic acids^[14] and cations^[15]

Herein, we report the design and synthesis of a new amido–amine cage receptor, which combines in its structure 1,8-anthracene diacboxamide subunit and a polyammonium azamacrocyclic. The anthracene part serves not only as a source of hydrogen bond donor NH-groups and acceptor CO-groups, but also as a fluorescent dye for anion detection. The receptor shows a good binding selectivity towards phosphate over other mono- and di-negative anions in a buffered aqueous solution at pH 7.2 (50 mM TRIS buffer). Phosphate and oxalate demonstrate the strongest fluorescence enhancement among other anions studied.

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