1,3-Alternate Calix[4]arene Bifunctional Fluorescent Receptor Containing Urea and Crown Ether Moieties

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Calix[4]arenes are important building blocks in supramolecular chemistry.1,2 The calixarene framework provides a unique possibility to organize several binding sites in an array complementary to a potential guest. A variety of calixarene-based receptors for cations,3 anions4 and neutral molecules5 have been synthesized in the past decade. Though anion recognition6 appears to be a relatively new area of research, both positively charged and neutral receptors for anionic species have been prepared in the last few years.7

As fluorogenic units, pyrenes are one of the most useful because of their relatively efficient excimer formation and emission.8 Since the intensity ratio of the excimer to the monomer emission (Ie/Im) is sensitive to conformational changes of the pyrene-appended receptors, changes in Ie/Im upon metal ion complexation can be an informative parameter in various sensing systems.9,10 The simultaneous binding of cationic and anionic guest species by ditopic receptors is a rapidly developing field for ion pair recognition of environment and biological importance. By taking advantage of calixarene framework, a few neutral bifunctional receptors11-13 were developed and showed the simultaneous complexation properties of hydrophilic anions and cations in organic media. Those receptors are, however, only focused on the cone conformers of calix[4]arene. It has been known14 that 1,3-alternate conformation of calix[4]arene could provide the two excellent binding sites for guest molecules when the proper functionalization could be achieved. We have previously reported ‘bifunctional calix[4]arene receptors’ containing two urea groups and crown ether moieties at the calix[4]arene fixed in the 1,3-alternate conformation. It was shown the simultaneous binding properties of cation and anion guests with enhanced binding affinity of halide anions in the presence of potassium ion.15

Here we report a new bifunctional receptor 1 based on 1,3-alternate conformation of calix[4]arene, which contains urea linking pyrene fluorophores instead of phenylurea and crown ether moieties at the opposite side of lower rim of calix[4]arene fixed in the 1,3-alternate conformation. Also, we studied binding affinity of various anions in the present of potassium ion.

Results and Discussion

Reaction of 216 with 1-pyrenemethylisocyanate in dioxane gave the bifunctional receptor 1 in 70% yield as shown in Scheme 1.

The 1H NMR spectrum of 1 shows the characteristics17 of 1,3-alternate conformation such as a narrow range chemical shift of aromatic protons at δ 6.7 - 7.3 and a singlet like peak at δ 3.74 for bridge methylene protons. A large singlet containing two very small outer peaks were observed instead of a pair of doublets. Four urea N-H protons appear as a broad singlet at δ 5.50 and 5.08 as expected. The 13C NMR spectra of 1 also confirmed the 1,3-alternate conformation, which showed one peak at δ 38.0 for the bridge methylene carbons as an indication of all anti oriented phenolic rings. We probed the anion binding abilities of 1 based on fluorescence changes of their DMSO solutions produced by addition of salts of the anions tetrabutylammonium CH3COO-, H2PO4-, C6H5COO-. In the free ligand, the two pyrene units in 1 exhibit weak monomer (λem = 375 nm) and strong excimer (λem = 475 nm) bands, Which could be attributed to two facing pyrene units in an intramolecular π-π stacked arrangement. Anion titration of 1 show an almost no changes in the fluorescence emission intensities of the monomer and excimer bands.

But, upon addition of K+ ion which is suitable for calix[4] crown-5 of 1, the excimer emission of pyrene unit decreases and monomer emission of pyrene unit increases because the K+ ion complexation induces the conformational change of the two pyrene ureas to quenching the π-π interaction in Figure 2. It is northworthy that the H-bonding based anions complexation are enhanced not only by an allosteriacal conformational change induced by K+ ion complexation in the crown-5 loop but also by more efficient ion-pairing electrostatic interaction.
DMSO- suggesting that receptor-K⁺ forms a 1:1 stoichiometry complexes of ligand upon binding potassium ion was not clear based on 1H NMR spectrum, indicating that electrostatic effect could be the major force for enhancing anion binding. In conclusion, 1,3-alternate calix[4]arene pyrene urea derivative 1 have been synthesized by the 2 and their corresponding 1-pyrenemethyliso- cyanate. Bifunctional receptor 1 can bind potassium cation and acetate and benzoate anions simultaneously with positive cooperation.

Experimental

25,27-Bis[(N-pyrenemethylureido)ethyloxy]calix[4]arene-crown-5, (1). To a 0.2 g (0.3 mmol) of 2 in 20 mL of 1,4-dioxane, 0.1 mL of pyrenylisocyanate was added and the mixture was stirred for 3 h under the nitrogen atmosphere. After removing the solvent, the residue was triturated with MeOH, filtered and dried to give 0.19 g (61%) of 1. 1H NMR (CDCl₃) δ 7.76-7.33 (m, 4H, ArH), 7.10 and 6.87 (d, 4H, ArH, J = 6.8 Hz), 6.73 and 6.53 (t, 4H, ArH, J = 6.2 Hz), 5.51 and 5.14 (broad s, 4H, -NH), 3.95 (s, 4H, -CH₂Py), 3.71 (s, 8H, ArCH₂Ar), 3.58 (m, 4H, -OCH₂-), 2.77 (br s, 4H, -OCH₂-); 13C NMR (CDCl₃) δ 156.4, 156.1, 155.8, 139.1, 134.9, 134.1, 129.8, 129.5, 129.1, 123.1, 122.9, and 120.1 (Ar), 73.1, 70.9, 70.0, 69.5, and 68.3 (-OCH₂-), 40.7 (-CH₂N-), 38.0 (ArCH₂Ar).

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