

Synthesis and Spectral Characterization of Calix[4]Diazafluorenepyrrole

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1. Introduction

Calix[4]pyrroles have been around since 1886¹ when Baeyer synthesized a fully *meso*-substituted porphyrinogen. Since then there has been a lot of work to understand and improve the anion binding properties that are inherent to these molecules². Also, work has been done with substituting on the pyrrole rings and a very small amount on adjusting the *meso* carbons. In this paper a calix[4]pyrrole will be presented with the *meso* carbons contained within a heterocyclic compound able to bind metal ions (Figure 1). The synthesis and unusual spectral characteristics will be discussed.

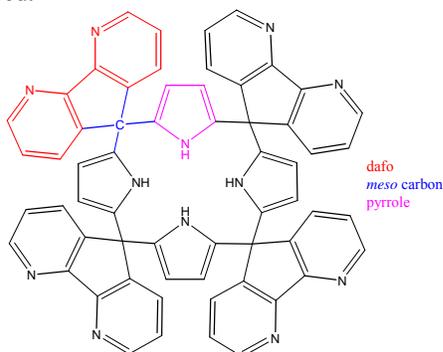


Fig. 1. Calix[4]5-(pyrrol-2-yl)-4,5-diazafluorene

2. Experimental

All chemicals were used as received. 4,5-diazafluore-9-one (dafo) was synthesized as described previously³.

Calix[4]5-(pyrrol-2-yl)-4,5-diazafluorene: 100 mg of dafo, 7 mL of glacial acetic acid, and 5 mL of nitrobenzene were brought to a reflux. 38.12 μ L of pyrrole was added and mixture was refluxed for 4 hours. The mixture was cooled and ether was added. The solid was removed by filtration and dried overnight. Yield: 86%. ¹H NMR (300 MHz, CDCl₃), δ : 7.62-7.72 (m, 8H

dafo, 4H pyrrole), 7.78-7.86 (m, 8H dafo), 8.22-8.26 (m, 8H dafo, 4H pyrrole) ppm.

Absorption Studies: Absorption spectra were obtained with a Cary-14 UV/Vis/NIR spectrophotometer.

Emission Studies: Emission spectra were obtained with the Spex Fluorolog. Slits were set at 6 mm to allow for room temperature spectra to be obtained.

Computational Studies: Calculations were effected using Gaussian '98W, version 5.4 (Rev. A9), and Gaussian '03 (Rev. B.03) for UNIX. The molecules were optimized using Becke's three-parameter hybrid functional B3LYP^{4a} with the local term of Lee, Yang, and Parr^{4b} and the nonlocal term of Vosko, Wilk, and Nassiar^{4c}. The basis set SDD was chosen for all atoms to allow for correlation with other molecules in the future. The optimizations and the simulated absorption spectrum were all run in the gas phase.

3. Results and Discussion:

Absorption Studies:

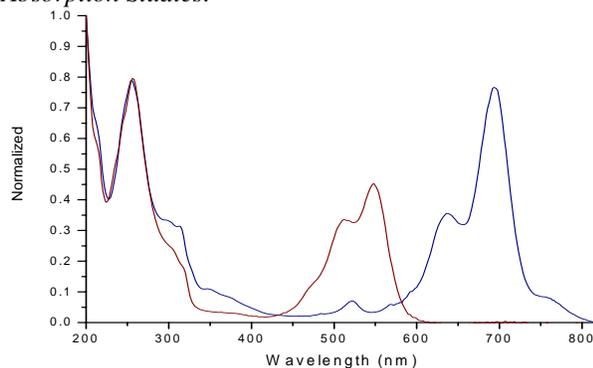


Fig. 2. Absorption spectra of the calix[4]pyrrole

Spectra were run in chloroform for solubility reasons and to avoid interaction of the solvent with the binding

of the anion in question. In Figure 2 the red spectrum was obtained from the calix[4]pyrrole without anions present and the blue spectrum was obtained after fluoride was added. The red-shift is indicative of the molecule changing shape and enveloping the fluoride ion.

Emission Studies:

Emission spectra of free (red) and fluoride bound (blue) calix (Fig. 3) were collected at 77K in 4:1 EtOH:MeOH

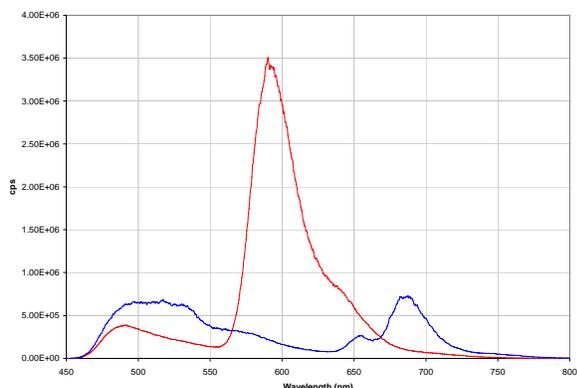


Fig. 3 Emission spectra of the calix in the unbound form (red line) and the fluoride bound form (blue line)

solvent. Both spectra were obtained by exciting at 316 nm. The unbound form is the easier spectrum to understand because the peak at 490 nm arises from the emission from the dafo part of the molecule. The peaks at 590 and 640 nm were found to originate from the absorption peak at 490 nm, not at 316 nm. The same is true for the fluoride bound calix. The emission observed at 500 nm is generated from the 316 nm excitation. The other peaks are generated from a combination of different excitation wavelength.

Computational Studies:

Conformational studies have been conducted to investigate the energy difference between the anion bound and unbound states. Figure 4 shows the conformational change the molecule undergoes when an anion, in this case fluoride, binds. Beside the structure is the calculated energy. When the fluoride binds the symmetry changes from C_s to C_{2v} , this is consistent with a

drop in the overall energy of the system. This conformational change is believed to assist in the shift seen the absorption spectra.

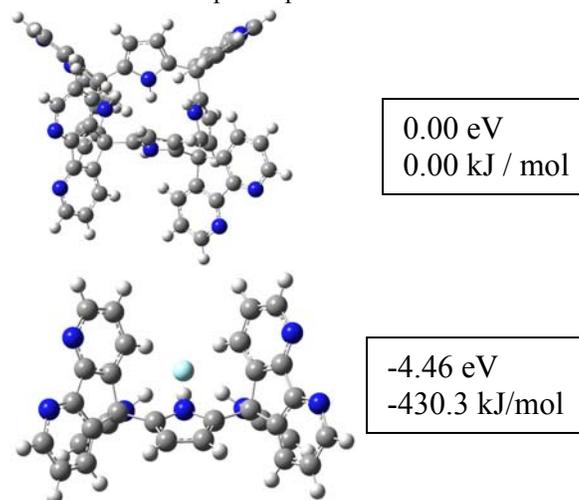


Fig.4 Calculated structural conformations along with the energy difference between them.

4. Conclusions:

The synthesized calix[4]pyrrole has exhibited unique electronic properties which are evident in the absorption spectra. The ability of the molecule to recognize anions of various sizes can be exploited and possibly catalysis could take place, such as conversion of hydroxide into oxygen. The next step is to attach metal containing groups and explore the various properties of those systems.

5. References:

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