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Proceeding Paper

Influence of the Cucurbit[7]uril on Photophysical Properties of the Encapsulated Styryl Dye †

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Abstract

The interaction between the styryl dye 4-{(E)-2-[4-(dimethylamino)phenyl]vinyl}-1-methylpyridinium iodide (DASPI) and cucurbit[7]uril (CB[7]) in aqueous solution was studied by optical spectroscopy methods. Due to negatively charged portals, cucurbit[7]urils can form complexes with cationic styryl dye. This complexation alters the dye photophysical properties, such as absorption and fluorescence. It was previously found that the formation of 1:2 inclusion complexes leads to a shift in the absorption band. Such changes were previously attributed to protonation of the dye. To explain the effect, we hypothesize that the effect arises from the influence of the electrostatic field generated by the negatively charged portals of cucurbit[7]uril on the conjugated π-electron system of the dye.

Keywords: styryl dyes; cucurbit[7]uril; inclusion complexes; fluorescence; electrostatic interactions

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1. Introduction

Supramolecular chemistry provides versatile tools for the design of host–guest systems with tunable properties. Among the wide variety of synthetic cavitands, cucurbit[n]urils (CB[n]) have attracted considerable attention due to their unique rigid structure, high binding affinities, and selectivity towards cationic guests [1–3]. Their applications range from drug delivery [4] and molecular recognition to photochemical transformations [5]. Compared to other macrocyclic hosts such as cyclodextrins and calixarenes, cucurbiturils exhibit stronger electrostatic interactions at their carbonyl-fringed portals, which makes them particularly efficient for encapsulating positively charged dyes [6]. Understanding the influence of CB[n] complexation on the photophysical properties of styryl dyes is therefore essential both for fundamental insights and for the development of new functional materials.

In this work, we studied the interaction between the styryl dye 4-{(E)-2-[4-(dimethylamino)phenyl]vinyl}-1-methylpyridinium iodide (DASPI) and cucurbit[7]uril (CB[7]) in aqueous solution (see Figure 1) by means of optical spectroscopy. Due to their negatively charged portals, CB[7] can form complexes with cationic DASPI, which significantly alters the dye's absorption and fluorescence behavior (binding constant $\log K_1 = 5.5$) [7].

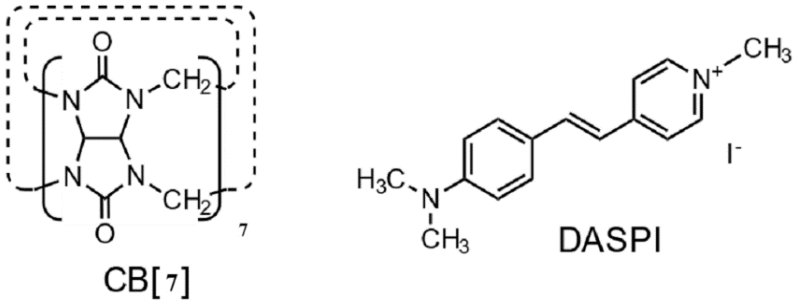

Figure 1. Structural formulas of cucurbit[7]uril and DASPI dye.

2. Materials and Methods

Cucurbit[7]uril and styryl dye DASPI from Sigma-Aldrich were used without further purification. Millipore Simplicity distilled water was used to prepare the solutions, and the dye concentration was maintained at 1×10^{-5} M.

The absorption spectra were recorded using a Shimadzu UVmini 1240 spectrophotometer. Absorption spectra were measured in plastic cuvets with an optical path length of 1 cm, which ensured reproducibility and comparability of the data in different series of experiments. In addition, absorption spectra were recorded under different pH conditions (see Figure 2): the spectra of unbound DASPI (red line), in the presence of 1 and 3 equivalents of CB[7] (blue and violet lines), as well as at varying pH values adjusted with hydrochloric acid (green lines). The pH values were measured using a Smart Sensor Ph Meter PH818.

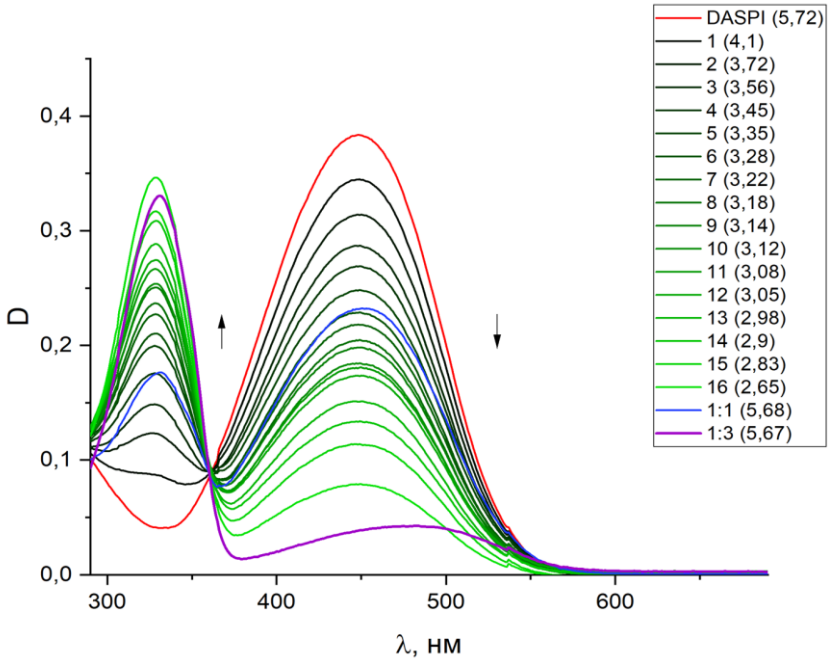

Figure 2. The absorption spectra of water solutions of DASPI 1×10^{-5} M: unbound (red line), in the presence of 1 and 3 equivalents of CB[7] (blue and violet lines), at varying pH values (green lines).

3. Results

It was previously found that the formation of 1:2 inclusion complexes leads to a hypsochromic shift in the absorption band to around 330 nm and the appearance of an

additional fluorescence band at 450 nm (binding constant $\log K_2 = 5.1$) [7]. Such changes were previously attributed to protonation of the dye [8].

However, the direct measurements of pH show that dissolving 10^{-5} M CB[7] in water does not significantly change the acidity of the solution (pH = 5.67), so that the observed effects cannot be attributed to dye protonation. Indeed, it can be shown [7] that the molar fraction of the protonated dye $x = [DH^+]/[D]_0 \approx 1$ only when pKa > pH. The experimentally determined value of pKa = 3.23 for DASPI at 23 °C [7] indicates that significant protonation of the dye occurs only when pH $\lesssim$ 3.5. Therefore, at the working pH of 5.67, protonation can be neglected. Moreover, absorption spectra in the presence of CB[7] were recorded at pH 5.72, yet the spectral changes observed are even more pronounced than those induced by acidification down to pH ≈ 2.65 (see Figure 2).

To explain this effect, we hypothesize that it arises from the influence of the electrostatic field generated by the negatively charged portals of cucurbit[7]uril (which can be considered as charged rings with charge Q and radius R (see Figure 3)) on the conjugated π-electron system of the dye.

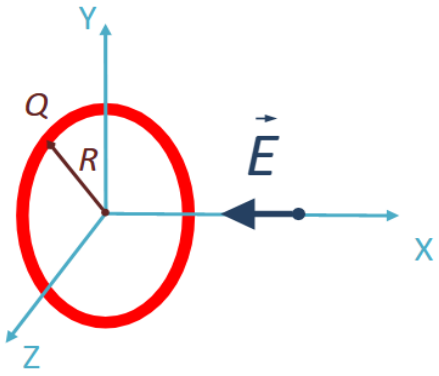

Figure 3. Schematic view of the cucurbit[7]uril portal.

From the standpoint of the quantum mechanical "particle in a box" model, the energy gap between the HOMO and LUMO levels directly depends on the effective length of the coupled π-system [9]. Exposure to the electrostatic field of CB[7] portals disrupts conjugation and effectively reduces the extent of π-delocalization. This, in turn, increases the HOMO–LUMO gap and causes the shift of the absorption bands observed experimentally (emergence of a band at 330 nm and attenuation at 450 nm).

4. Conclusions

The study demonstrated that the observed changes in the absorption spectra of the styryl dye DASPI upon complexation with cucurbit[7]uril cannot be explained by protonation effects, since the working pH excludes significant protonation. Instead, the data indicate that the spectral shifts arise from the influence of the electrostatic field generated by the negatively charged portals of cucurbit[7]uril, which perturbs the conjugated π-system of the dye and modifies the HOMO–LUMO gap. These findings highlight the crucial role of host guest electrostatic interactions in determining the photophysical behavior of encapsulated styryl dyes.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DASPI	the styryl dye 4-{(E)-2-[4-(dimethylamino)phenyl]vinyl}-1-methylpyridinium iodide
CB[7]	Cucurbit[7]uril

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