

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

O.P. Kolesnikova^{1,2}, D.A. Ivanov², I.V. Kryukov², N.Kh. Petrov^{1,2}¹ Moscow Center for Advanced Studies, Kulakova Str, 2, Moscow, Russia²Photochemistry Center of the Russian Academy of Sciences, Federal Scientific Research Centre "Crystallography and Photonics" RAS, 119421, Moscow, str. Novatorov, 7A-1

INTRODUCTION & AIM

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 Fig. 1) was studied by the methods of optical spectroscopy. Cucurbit[n]urils are cavitands composed of n glycoluril units linked by methylene bridges [1]. Due to their negatively charged portals, cucurbiturils can form complexes with cationic styryl dyes of suitable size. This complexation alters the dye photophysical properties, such as fluorescence in the case of 1:1 complexes (binding constant $\log K_1 = 5.5$) [2].

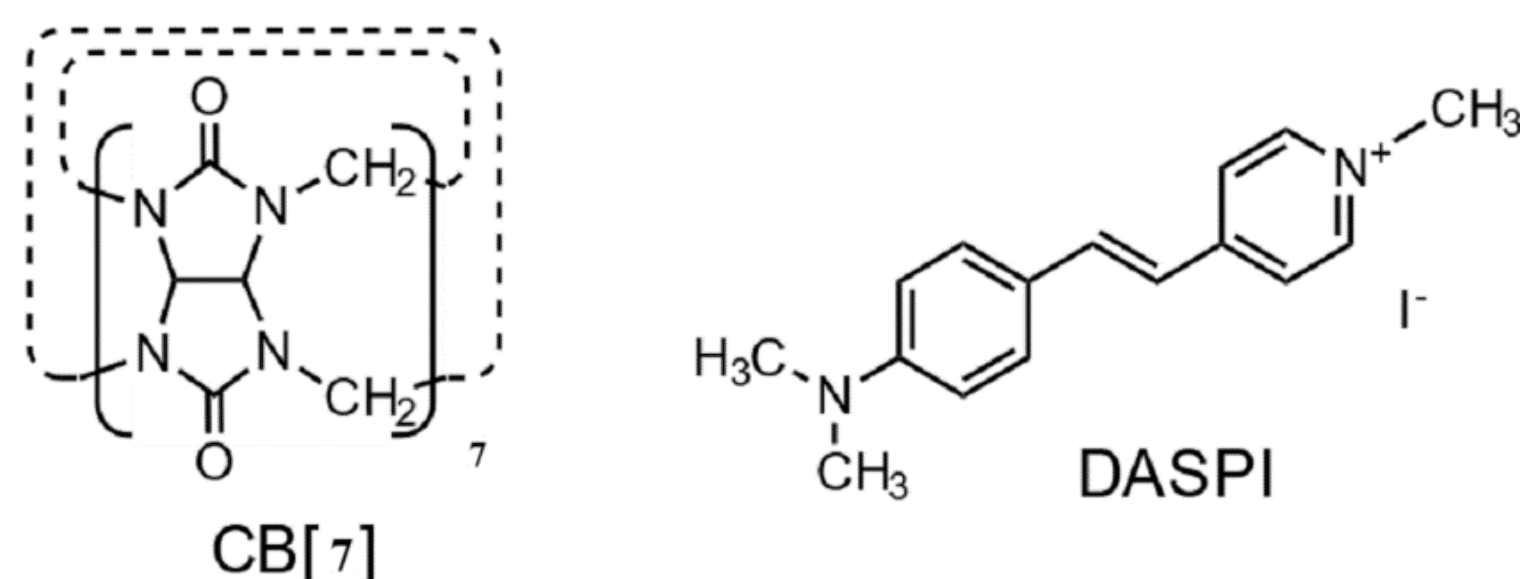


Figure 1. Structural formulas of cucurbit[7]uril and DASPI dye.

METHOD

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 cuvettes 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 (Fig. 2): the spectra of pure 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).

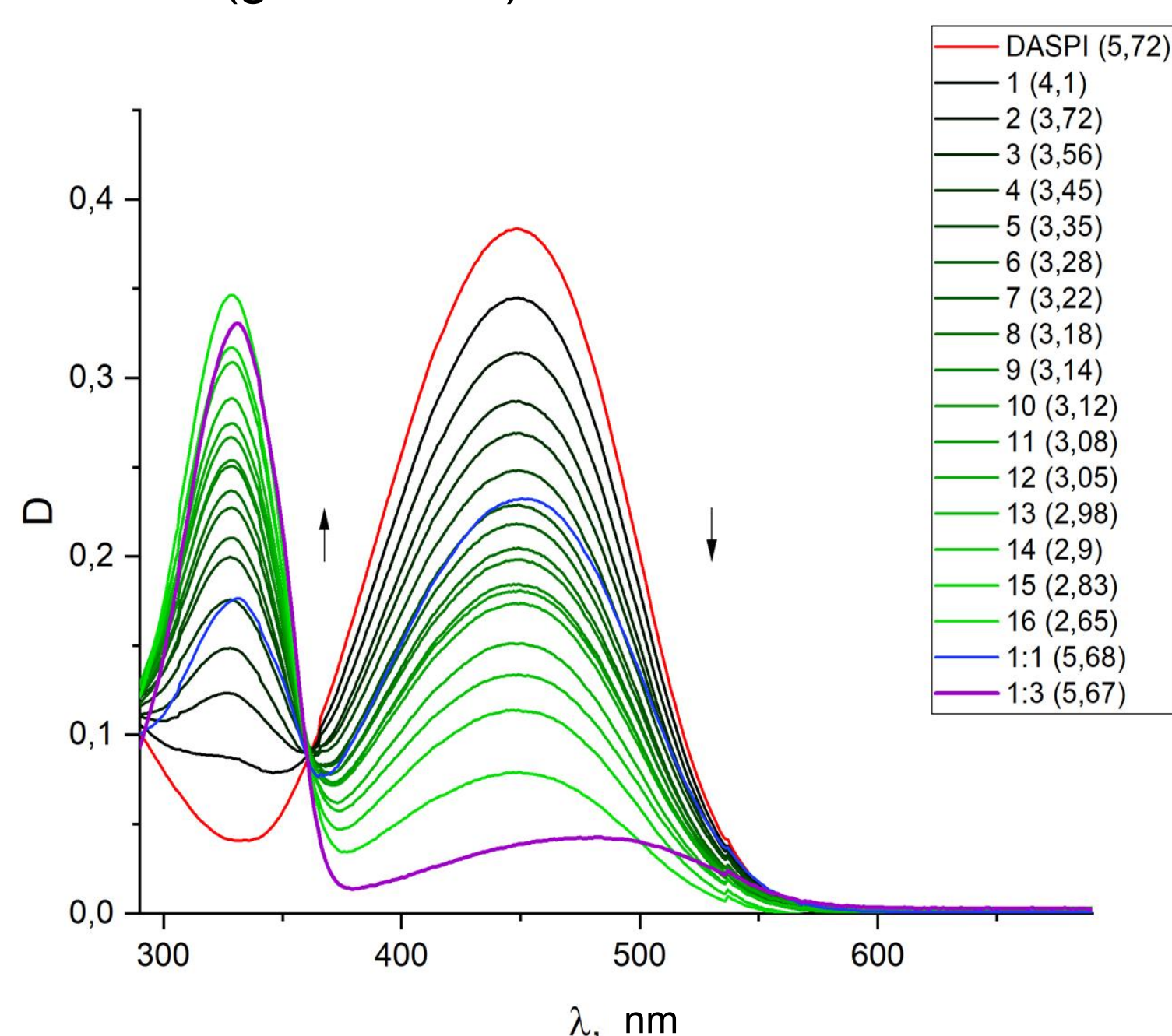


Figure 2. Absorption spectra.

RESULTS & DISCUSSION

It was previously found that the formation of 1:2 inclusion complexes leads to a blue shift in the absorption band to around 330 nm and the appearance of an additional fluorescence band at 450 nm (binding constant $\log K_2 = 5.1$) [2]. Such changes were previously attributed to protonation of the dye [3].

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 ($\text{pH} = 5.67$), so that the observed effects cannot be attributed to dye protonation. Indeed, it can be shown [2] that the molar fraction of the protonated dye $x = [\text{DH}^+]/[\text{D}]_0 \approx 1$ only when $\text{pK}_a > \text{pH}$. The experimentally determined value of $\text{pK}_a = 3.23$ for DASPI at 23 °C [2] indicates that significant protonation of the dye occurs only when $\text{pH} \lesssim 3.5$. 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 $\text{pH} \approx 2.65$ (see Fig. 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 (see Fig. 3) on the conjugated π -electron system of the dye.

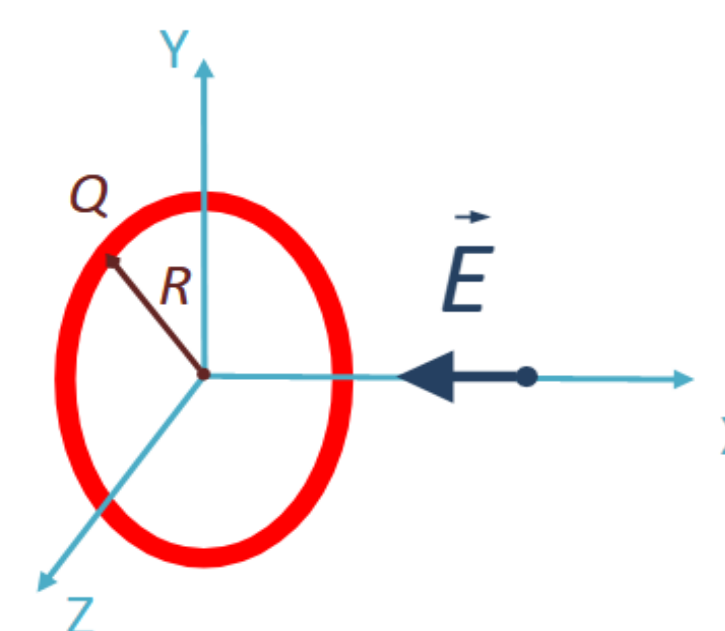


Figure 3. Schematic view of the cucurbit[7]uril portal.

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 [4]. 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).

CONCLUSION

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.

FUTURE WORK / REFERENCES

- [1] Kim K., Murray J., Selvapalam N., Ho Ko Y., Hwang J. // Cucurbiturils: chemistry, supramolecular chemistry and applications. New Jersey, World Scientific, 2018
- [2] Ivanov D. A., Kolesnikova O. P., Kryukov I. V., & Petrov N. K. (2025). Features of complexation of a styryl dye dimethylamino derivative with Cucurbit[7]uril. High Energy Chemistry, 59(3), 222–226. <https://doi.org/10.1134/s0018143925700031>
- [3] Shiguo Sun, Ye Yuan, Zhiyong Li, Si Zhang, Hongyan Zhanga, Xiaojun Peng // Interaction of a hemicyanine dye and its derivative with DNA and cucurbit[7]uril. New J. Chem., 38, 3600–3605, 2014
- [4] Autschbach, J. (2007). Why the particle-in-a-box model works well for cyanine dyes but not for conjugated polyenes. Journal of Chemical Education, 84(11), 1840