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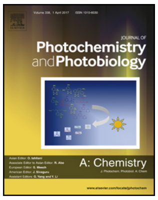

Invited paper

Hydrogen-bonded self-assembly, spectral properties and structure of supramolecular complexes of thiamonomethine cyanines with cucurbit[5,7]urils

Marina V. Fomina[a], Alexander S. Nikiforov[a], Vitaly G. Avakyan[a], Artem I. Vedernikov[a], Nikolai A. Kurchavov[a], Lyudmila G. Kuz'mina[b], Yuri A. Strelenko[c], Judith A.K. Howard[d], Sergey P. Gromov[a,e,*]

[a] Photochemistry Center, Russian Academy of Sciences, Novatorov str. 7A-1, Moscow 119421, Russian Federation
[b] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 31, Moscow 119991, Russian Federation
[c] N. D. Zelinskiy Institute of Organic Chemistry, Russian Academy of Sciences, Leninskiy prosp. 47, Moscow 119991, Russian Federation
[d] Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham DH1 3LE, England, United Kingdom
[e] Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russian Federation

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ABSTRACT

The complex formation of thiamonomethine cyanine dyes bearing two *N*-ammoniohexyl or two *N*-ethyl substituents with cucurbit[5,7]urils (CB[5,7]) in aqueous solutions was studied by electronic and ^{1}H NMR spectroscopy, including spectrophotometric, fluorescence, and ^{1}H NMR titration methods. It was found that CB[5] forms external complexes with the dyes, while CB[7] forms internal (inclusion) complexes of 1:1 and 1(dye):2(CB[5,7]) composition. The complexation with CB[5,7] changes the absorption spectra of cyanine dyes and induces a considerable fluorescence enhancement. The stability constants of the complexes were determined ($\log K_{1:1}$ varies in the range from 3.53 to more than 6, and $\log K_{1:2}$ varies in the range from 3.5 to 4.32). The dye with ammoniohexyl substituents forms more stable complexes owing to hydrogen bond formation between the NH_3^+ groups and the carbonyl groups of the CB[5,7] portals. The structure of supramolecular complexes was confirmed by quantum chemical calculations.

1. Introduction

Cucurbit[*n*]urils (CB[*n*], *n* = 5–10) represent a promising class of macromolecular receptors in supramolecular chemistry. These cavitand molecules are macroheterocycles with a rigid hydrophobic intramolecular cavity and two identical polar portals formed by the carbonyl oxygen atoms. Owing to the specific structural features, CB[*n*] can form stable inclusion complexes of the host–guest type with both neutral molecules and positively charged species such as metal or organic cations [1–8]. The inclusion of an organic dye into the cavitand (host) cavity changes the photochemical properties of the guest molecule: the fluorescence intensity, lifetime, and quantum yield increase, the photostability and disaggregation increase, and so on [9–15]. These photoactive supramolecular systems can be used as fluorescent probes and sensors, for stabilization of laser dyes, for optical information recording systems and so on [16–22].

Previously, we have studied the complex formation of CB[7,8] with 1,2-di(hetaryl)ethylene derivatives [23,24] and cyanine [25,26] and styryl dyes [27–34]. The complex formation has been found to considerably affect the spectral and photochemical properties of the dyes. Indeed, the insertion of a diquinolylethylene derivative into the CB[8] cavity stabilizes its *cis*-isomer [23], while the formation of 2:1 complexes between styryl dyes and CB[8] promotes stereospecific [2 + 2]-photocycloaddition reactions [27,30]. The formation of pseudorotaxane complexes of 4-pyridine-based styryl dyes with CB[7] leads to pronounced enhancement of fluorescence [28–34]. Fluorescence intensity also increases upon the addition of CB[7] to aqueous solutions of trimethine cyanine dyes [25,26].

The presence of ammonioalkyl groups in the dye molecule provides additional options for the dye self-assembly to supramolecular complexes *via* hydrogen bonding with the carbonyl oxygen atoms of the CB[*n*] portals. Indeed, dihetarylethylene derivatives containing two ammonioalkyl groups at nitrogen atoms form

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[*] Corresponding author at: Photochemistry Center, Russian Academy of Sciences, Novatorov str. 7A-1, Moscow 119421, Russian Federation.
E-mail address: spgromov@mail.ru (S.P. Gromov).

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stable inclusion complexes with CB[8] in aqueous solutions (log$K$ >5), an important role in these complexes being played by hydrogen bonds between the guest ammonium groups and the oxygen atoms of the CB[8] portals [23]. Meanwhile, the complexation between CB[*n*] and cyanine dyes with terminal ammonium groups in *N*-substituents of heterocyclic residues has not been studied. One can expect a considerable stability increase for these complexes and a noticeable change in the photochemical characteristics of the cyanine dyes.

In this communication, we present the results of electronic and ^{1}H NMR-spectroscopic studies of the self-assembly of complexes formed by CB[5,7] with monomethine cyanine dye **1** containing two *N*-ammoniohexyl groups in the benzothiazole residues and with model compounds, monomethine cyanine dye **2** containing two *N*-ethyl groups and 1,6-hexanediammonium diperchlorate (**3**). The effects of the guest structure and solvent nature on the composition, spatial structure, and stability of the supramolecular complexes with CB[5,7] were elucidated. The structures of the compounds are shown in Fig. 1.

In the series of CB[*n*], the cavity and portal sizes gradually increase on going from CB[5] to CB[10] at a constant height of 0.91 nm [3]. The structural similarity with different sizes of inner cavities and portals provides selective binding of CB[*n*] to guest molecules [3,22,35,36]. It is known from the literature that CB[*n*] form inclusion complexes with alkylammonium and 1,ω-alkanediammonium ions [37–39]. In the series of alkanediammonium ions, which can be considered as structural analogues of the *N*-ammonioalkyl group of type **1** dyes, the dication of compound **3** forms inclusion complexes with CB[6] and larger cucurbiturils [37,38], but the portal width and the cavity volume of CB[5] are insufficient for encapsulation of this cation. In the crystal, CB[5] binds to 1,6-hexanediammonium ions only at the ammonium groups *via* hydrogen bonding with the carbonyl oxygen atoms of the portals of neighboring cavitand molecules, thus forming supramolecular polymers [37,40]. Using X-ray diffraction data for cucurbiturils [3], the 1,6-hexanediammonium dichloride complex with CB[5] [37], and dye **2** (the X-ray diffraction data are described below), it is possible to evaluate in advance their geometric matching for the formation of inclusion complexes (Fig. 1).

Probably, *N*-ammoniohexyl substituents of dye **1** are able to penetrate through CB[7] portals into the cavity, whereas the heterocyclic residue can be only slightly (by the benzene moiety) embedded into CB[7]. Small sizes of CB[5] portals and cavity allow the formation of only “external” complexes with **1**.

2. Experimental

2.1. Materials

3-(6-Ammoniohexyl)-2-{(*Z*)-[3-(6-ammoniohexyl)-1,3-benzothiazol-2(3*H*)-ylidene]methyl}-1,3-benzothiazol-3-ium triperchlorate (**1**), 1,6-hexanediammonium diperchlorate (**3**), 3-ethyl-2-methyl-1,3-benzothiazol-3-ium iodide (**4**), and 3-ethyl-2-(ethylsulfanyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**5**)

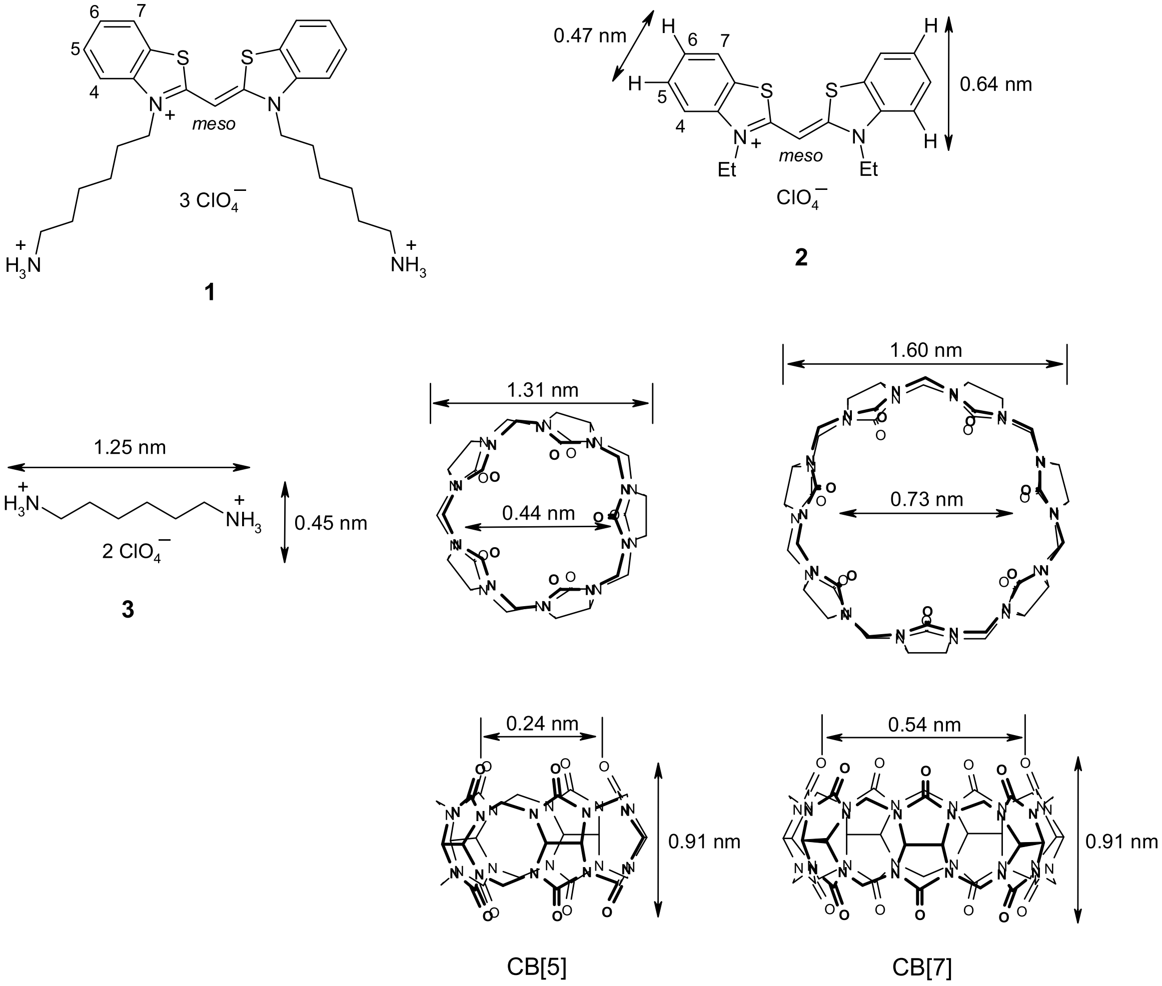

Fig. 1. Structures of the studied guest molecules **1**–**3** and host molecules CB[5] and CB[7].