



## Methylene blue–calixarenesulfonate supramolecular complexes and aggregates in aqueous solutions

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### ABSTRACT

The complexation of methylene blue (**MB**) by calix[*n*]arenesulfonates (**SCAn**, *n*=4, 6, 8) was studied in aqueous solutions with various ionic strengths, using absorption and fluorescence spectroscopy and laser flash photolysis. The simultaneous reactions **MB**+**SCAn** ↔ **MB**·**SCAn** (1) and **MB**·**SCAn**+**MB** ↔ **MB**<sub>2</sub>·**SCAn** (2) were observed. The equilibrium constants *K*(1) and *K*(2) are high (10<sup>5</sup>–10<sup>7</sup>), their dependence on the ionic strength can be described by the extended Debye–Hückel law. *K*(2) > *K*(1) for all the three systems, in accord with the strongly aggregating nature of **MB**. In **MB**–**SCA8** mixtures complexes with more than two **MB** units were also detected. The fluorescence of the dye is partially or completely quenched in the complexes, the formation of triplet state complexed **MB** cations is negligible. At low **SCAn** concentrations and ionic strengths the formation of colloidal aggregates was detected by resonance Rayleigh scattering.

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### 1. Introduction

The thiazine dye methylene blue (**MB** in Fig. 1) has many applications. It is a commonly used cellular stain, a textile dye in industry and a redox indicator. Besides, **MB** is frequently employed as a spectroscopic probe. In particular, its adsorption on minerals [1] and its binding to RNA [2], DNA [3] and proteins [4,5] attract considerable research interest. **MB** also has important medical applications: it is used as sensitizer in photodynamic therapy of cancer [6], and as sensitizer for photodynamic antimicrobial chemotherapy [7,8]. An important feature of **MB** is the formation of aggregates in water even at relatively low concentrations, which has to be taken into account in the above applications.

The effects of the local environment on the aggregation and/or on the redox properties of **MB** were studied in cyclodextrin [9,10] and in cucurbituril [11] supramolecular complexes as model systems. In our present work the interaction of **MB** with calix[*n*]arenesulfonates (**SCAn** in Fig. 1, *n*=4, 6, 8) has been investigated. Whereas in cyclodextrin and cucurbituril complexes the dye cation guest is partly embedded in a hydrophobic cavity, calixarenesulfonates represent environments with high negative charge density. The optical spectroscopic features of calixarenes

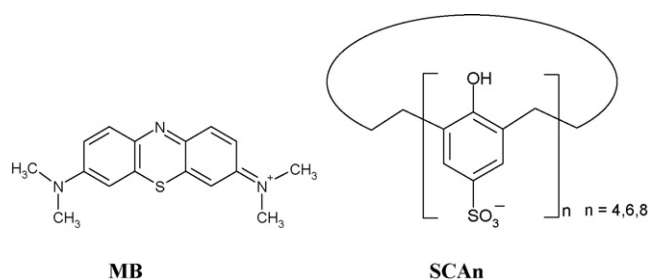
and their complexes, involving various calixarene–dye complexes are summarized in a recent review by Mohammed-Ziegler and Billes [12].

In our previous study we found that oxazine 1 (**OX**), a cationic dye with low dimerization affinity forms a 1:1 and a 2:1 complex with **SCA8** (**OX:SCA8**) [13]. In the present work our goal has been to describe the changes in the photophysical properties of a chemically similar, but easily aggregating dye, **MB**, induced by the supramolecular interaction with the multiply charged **SCAn** hosts. We applied stationary absorption and fluorescence spectroscopy and – with respect to the significance of triplet states in the medical applications – laser flash photolysis as experimental methods. A qualitative analysis of the visible absorption spectra of **MB**–**SCAn** (*n*=4, 6) supramolecular systems indicated the occurrence of a 1:1 complex and of **MB** dimer in aqueous solutions [14]. The absorption spectra of these systems in methanol–water mixtures suggested the presence of complexes with 1:1 and 1:2 stoichiometry (**MB:SCAn**, *n*=4, 6, 8) [15].

We performed a detailed quantitative analysis of the spectral data yielding the spectra of the **MB**–**SCAn** complexes and the equilibrium constants characterizing their stability. These results might have some practical importance, since many supramolecular systems consisting of a macrocyclic host and a fluorescent dye guest can be applied in competitive fluorescent techniques [16–18]. The principle of these techniques is that the analyte, which is a non-fluorescent compound, or has a fluorescence spectrum not sensitive to complexation, expels the fluorescent host from the complex.

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**Fig. 1.** Structures of methylene blue cation (**MB**) and calixarenesulfonate anions (**SCAn**).

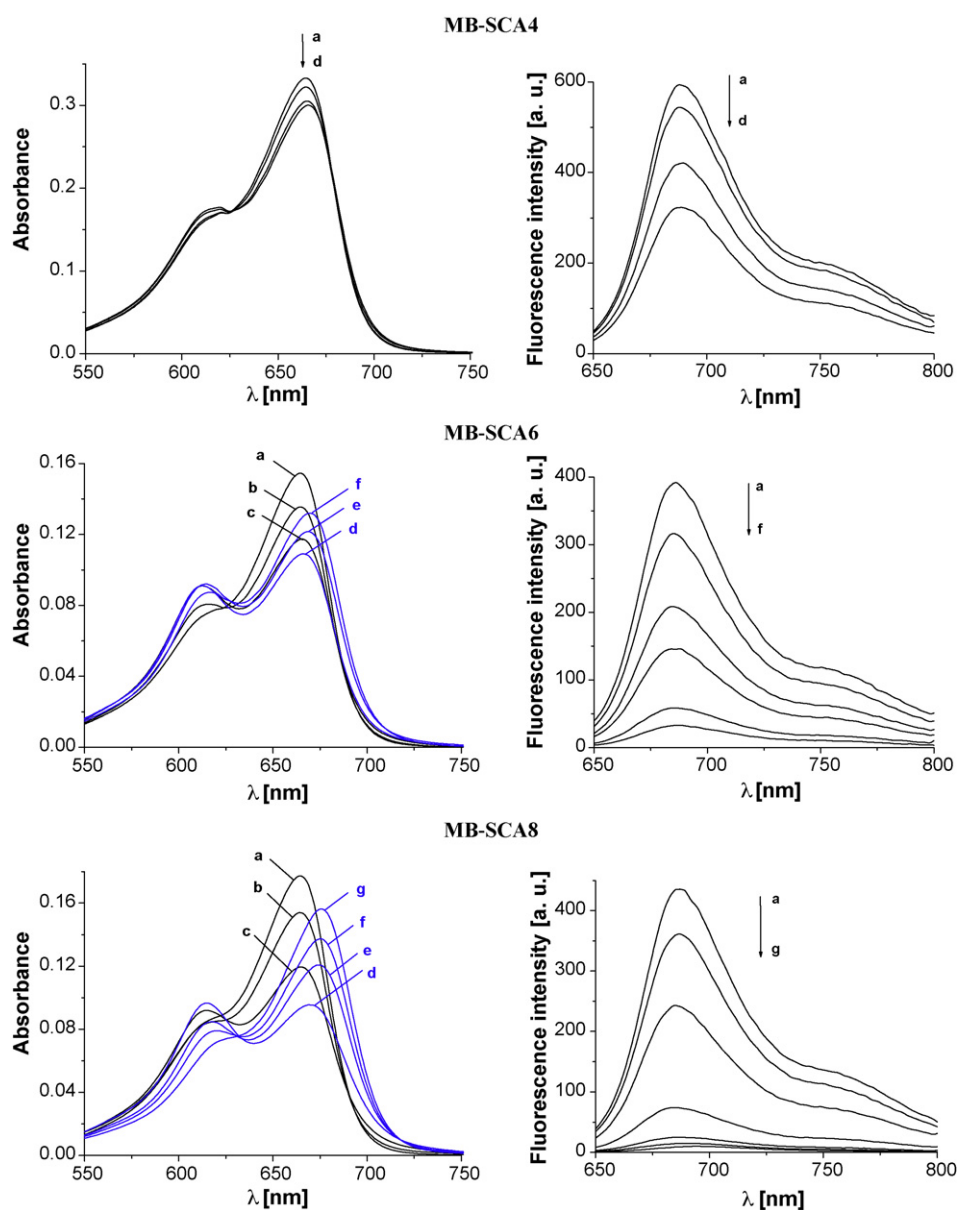
## 2. Materials and methods

**MB** (chloride salt) was purchased from Fluka. The syntheses of the three calixarenesulfonate sodium salts was described in our

previous work [13]. Their purity was checked by electrospray ionization mass spectrometry and no impurity was detected. (Before the mass spectrometric measurements the  $\text{Na}^+$  ions were removed from the samples by consecutive ion exchange steps.)

The initial concentration of **MB** in the samples used for the absorption and fluorescence spectroscopic measurements was  $4 \times 10^{-6}$  and  $2 \times 10^{-6}$  M, respectively, that of the sulfocalixarenes was varied from 0 to  $10^{-4}$  M. The measurements were carried out in phosphate buffer medium (to avoid the uncertainties arising from the presence of different metal ions, the buffer was made of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ ). The ionic strengths of the solutions was set by the addition of  $\text{NaCl}$ . Since **MB** strongly adsorbs on glass/water interface [19], the stock solutions and the **MB-SCAn** mixtures were prepared in polypropylene vessels. The mixtures were kept for 1 day before measuring the spectra.

All the spectroscopic measurements were carried out at 25 °C. UV-vis absorption spectra were recorded on an Agilent 8453 spectrophotometer. Fluorescence spectra were taken by using a



**Fig. 2.** Absorption and fluorescence spectra of **MB-SCAn** mixtures. Concentrations: **MB-SCA4** (pH 5.3,  $I = 1.6 \times 10^{-2}$  M)  $[\text{MB}]_0 = 4 \times 10^{-6}$  M,  $[\text{SCA4}]_0 =$  (a) 0 M, (b)  $2.2 \times 10^{-6}$  M, (c)  $1 \times 10^{-5}$  M, (d)  $2.2 \times 10^{-5}$  M; **MB-SCA6** (pH 7.4,  $I = 8.2 \times 10^{-3}$  M)  $[\text{MB}]_0 = 2 \times 10^{-6}$  M,  $[\text{SCA6}]_0 =$  (a) 0 M, (b)  $1 \times 10^{-6}$  M, (c)  $4.6 \times 10^{-6}$  M, (d)  $1 \times 10^{-5}$  M, (e)  $4.6 \times 10^{-5}$  M, (f)  $1 \times 10^{-4}$  M; **MB-SCA8** (pH 6.5,  $I = 8.2 \times 10^{-3}$  M)  $[\text{MB}]_0 = 2 \times 10^{-6}$  M,  $[\text{SCA8}]_0 =$  (a) 0 M, (b)  $1 \times 10^{-7}$  M, (c)  $4.6 \times 10^{-7}$  M, (d)  $2.2 \times 10^{-6}$  M, (e)  $1 \times 10^{-5}$  M, (f)  $2.2 \times 10^{-5}$  M, (g)  $1 \times 10^{-4}$  M.

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