

Solvent-dependent host–guest complexation of two homologous merocyanines by a water-soluble calix[8]arene: Spectroscopic analysis and structural calculations

Andrea Lodi ^a, Monica Caselli ^a, Alessandro Casnati ^b, Fabio Momicchioli ^a,
Francesco Sansone ^b, Davide Vanossi ^a, Glauco Ponterini ^{a,*}

^a Dipartimento di Chimica, Università di Modena e Reggio Emilia and INSTM, via Campi 183, 41100 Modena, Italy

^b Dipartimento di Chimica Organica e Industriale, Università di Parma and INSTM, V.le G. P. Usberti 17/A, 43100 Parma, Italy

Received 11 October 2006; received in revised form 28 December 2006; accepted 8 January 2007

Available online 21 January 2007

Abstract

The sulfonated calixarene I₈C₁₂ acts as a host for homologous merocyanines Mc1 and Mc2 in organic solvents, exhibiting neither selectivity towards the guest dyes nor solvent dependence of the complexation equilibria. In water, on the contrary, only the lower homologue, Mc1, is solubilized in the presence of the calixarene. A combination of UV–visible and fluorescence spectroscopic and photophysical analysis and MD structural simulation of the calixarene–dye complexes was employed to account for the observations, and suggests that a radical change in the complexation mode occurs upon moving from an organic to an aqueous environment.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Inclusion complexes; Merocyanines; Calixarenes

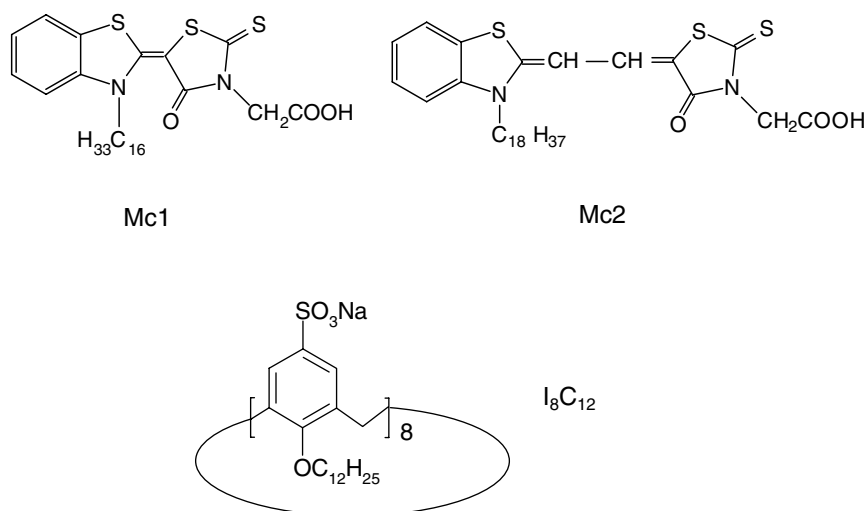
1. Introduction

In the early 1990s, after about a decade of intensive research, calixarenes were recognized to possess the properties – ability to complex both metal ions and organic molecules, selectivity, ease of large-scale preparation – to be classified as the third generation of ‘supramolecules’, following cyclodextrins and crown ethers [1]. Studies of complexation by calixarenes received strong impetus from the preparation of water-soluble hosts obtained by introducing charged or neutral hydrophilic groups in the para positions (‘upper rim’) [2]. Among these, calix[*n*]arenes carrying sulfonate groups on the ‘upper rim’ and *n*-alkyl groups on the ‘lower rim’ (phenolic –OR groups) proved particularly efficient in complexing, sometimes selectively, organic molecules in water [3–15]. This approach to solubilization and

transport of organic molecules in water takes advantage of hydrophobic interactions involving the guest and the *n*-alkyl chains of the host [6], with complex formation often characterized by an overall entropy gain [9,12].

Calixarenes have also been extensively employed to build-up mono- and multilayers with a number of potential applications [16]. *p*-Sulfonated calixarenes, being polyanions, can be alternated with polycations to make multilayers by electrostatic adsorption [17]. This technique offers advantages over other approaches for obtaining thin films, such as Langmuir–Blodgett deposition or the build-up of covalently bound self-assembled layers [18]. Obviously, neutral molecules need to be complexed by multicharged carriers in order to be included in electrostatically self-assembled multilayers (ESAMs). To the best of our knowledge, the use of *p*-sulfonated, *O*-alkylated calixarenes for including water-insoluble organic molecules into ESAMs has been reported only once [19]. We have decided to further explore the potential of these calixarenes in the build-up of ESAMs containing neutral molecules by trying to

* Corresponding author. Tel.: +39 053 2055084; fax +39 059 373543.
E-mail address: ponterini.glauco@unimore.it (G. Ponterini).



Scheme 1.

include in such films dyes of the families of merocyanines and ketocyanines. The second-order optical properties of these push–pull molecules (containing electron donating and electron accepting groups) have been the subject of extensive theoretical and experimental investigation [20–30]. So, ESAMs incorporating such dyes may be taken into consideration as nonlinear optical materials. The obvious pre-requisite for the inclusion of a water-insoluble dye in an ESAM is its complexation with a suitable multicharged carrier. In this paper, we show how moving from an organic solvent to water drastically changes the ability of calixarene I_8C_{12} to act as a host for merocyanines Mc1 and Mc2, which differ essentially in the length of the chromophoric chain (formulas are shown in Scheme 1). While both dyes are complexed by the calixarene with similar association constants in organic solvents, only the lower analogue, Mc1, is complexed, and thereby dissolved, in water. An interpretation of the spectroscopically monitored behaviour is attempted with the aid of simple MD simulations in the absence of solvent (giving qualitative information on the structures in low-polarity organic media) as well as taking into account the expected structural modifications undergone by the hydrophobic lower rim of the calixarene in an aqueous environment.

2. Experimental

Merocyanines Mc1 and Mc2 were obtained, respectively, from Imation s.p.a., Ferrania, Italy, and from Hayashibara Biochemical Laboratories, Inc., Okayama, Japan. Octasulfonato-octadodecyloxy-calix[8]arene (I_8C_{12}) was synthesized according to the procedure used for hexasulfonato-hexadodecyloxy-calix[6]arene [4] starting from octasulfonato-calix[8]arene. Pure compound I_8C_{12} was obtained by crystallization from methanol/water and then water. Elem. Anal. for $C_{152}H_{232}Na_8O_{32}S_8 \times 8H_2O$: required C, 60.96; H, 8.35; found: C, 60.82; H, 8.51. Mp

>360 °C; 1H NMR (D_2O , 300 MHz, rt) δ 7.5 (16H, ArH, br s), 3.6 (16H, ArCH₂Ar, br s), 3.44 (16H, OCH₂, t, $J = 7$ Hz), 1.64 (16H, OCH₂CH₂, m), 1.42 (144H, OCH₂CH₂(CH₂)₉CH₃, br s), 1.03 (24H, CH₃, t, $J = 7$ Hz); ^{13}C { 1H } NMR (DMSO-*d*₆, 75 MHz, rt) δ 13.5 (CH₃), 22.0 (CH₂CH₃), 25.9, 28.5, 28.9, 29.3, 29.5, 29.7, 31.3 (OCH₂(CH₂)₅CH₂, ArCH₂Ar), 72.7 (OCH₂), 125.9 (ArH_m), 132.3 (ArH_o), 142.2 (ArH_p), 155.6 (ArH_i). All solvents (dichloromethane (DCM), ethanol and dimethylsulfoxide (DMSO)) were of spectroscopic grade and were checked to have negligible emissions in the experimental conditions adopted. The same held for deionized water (Millipore, Milli-Q, resistivity of 18.2 M Ω cm). Spectra were recorded on a Varian Cary 100 spectrophotometer and a Spex Jobin-Yvon Fluoromax2 spectrofluorometer. Fluorescence quantum yields (Φ_F) were determined relative to quinine bisulfate in 1 N H₂SO₄ ($\Phi_F = 0.546$ [31]) for Mc1 and to acridine orange HCl in ethanol ($\Phi_F = 0.46$ [32]) for Mc2. All spectroscopic measurements were carried out at 18–20 °C.

3. Computational

The analysis of the structures of the host–guest calixarene–merocyanine complexes was tackled at an empirical level using a force field in the framework of classical molecular mechanics/dynamics (MM/MD). The force field adopted here to investigate the structure of I_8C_{12} –Mc1 and I_8C_{12} –Mc2 complexes was the Universal Force Field (UFF) [33,34] contained in the Cerius² simulation package. After setting up reasonable 3D model structures for the two merocyanines and the calixarene, a calculation of the atomic point charges was made at the SCF PM3 level for Mc1 and Mc2 whereas, because of the large number of atoms, the charge-equilibration method [35] was employed for I_8C_{12} . Using the UFF, the geometries of Mc1, Mc2 and I_8C_{12} were fully optimised with a standard local BFGS

Download English Version:

<https://daneshyari.com/en/article/1410704>

Download Persian Version:

<https://daneshyari.com/article/1410704>

[Daneshyari.com](https://daneshyari.com)