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Spectroscopic properties of cyclophane/anthracene and cyclophane/9-fluorenone complexes in dichloromethane

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Abstract

Host/guest interactions of cyclophane/anthracene (C/A) and cyclophane/9-fluorenone (C/F) complexes in dichloromethane, where the cyclophane molecule is the host, are investigated. The stability constants, log K_a, for the C/A and C/F complexes are determined by absorption and fluorescence spectroscopy. For the C/A system, log K_a is 4.2±0.2 as determined from absorption (at 325 nm) and emission (at 382, 403 and 427 nm) spectroscopic data. The analogous measurements yield 3.6±0.2 from absorption (at 309 nm) and emission (at 505 nm) spectroscopic data for the C/F system. Heats of formation of these complexes were determined by measuring the complex association constants at 25, 29 and 32 °C. These results reveal that binding of the anthracene guest by this cyclophane molecule is thermodynamically favored over that for a 9-fluorenone guest. Excited state lifetimes of these systems are also determined.

Keywords: Host/guest complexation; Titration; Association constant; Cyclophane; Aromatic compounds

1. Introduction

Molecular recognition by supramolecular receptors has been subject of numerous experimental [1–10] and theoretical [11–15] investigations over the past two decades. The synthesis and design of new cyclophanes that exhibit neutral molecular binding ability is a rapidly emerging branch of supramolecular chemistry. These molecules are important because of their potential for application in biological, medicinal and chemical fields. Moreover, there has been an increasing interest in using cyclophanes to separate certain neutral molecules, such as polyaromatic hydrocarbons (PAHs), from environmental systems. Hence, the development of sensors for neutral molecules is essential. A new class of cyclophane molecules (referred to as "corrals" by their founders) [2–4] that have high selectivity for one aromatic compound over similar aromatic molecules has been synthesized.

In this paper, we report the 1:1 interactions of corral **2** with anthracene and with 9-fluorenone (Fig. 1) in dichloromethane (DCM). A crystal structure of the complex of corral **2** with anthracene demonstrating intracavity complexation in the solid phase has been reported [2]. We shall refer to this cyclophane host molecule from now on as corral **2** in compliance with the original nomenclature [2,3]. Other corrals in this series have different cavity sizes achieved by varying the number of carbons in the multi-methylene spacers from four to six, as shown in Fig. 1. Alternatively, addition of four or eight methyl groups to the end aromatic units (e.g., in **4**–**6**) also changes the size of the cavity and its properties.

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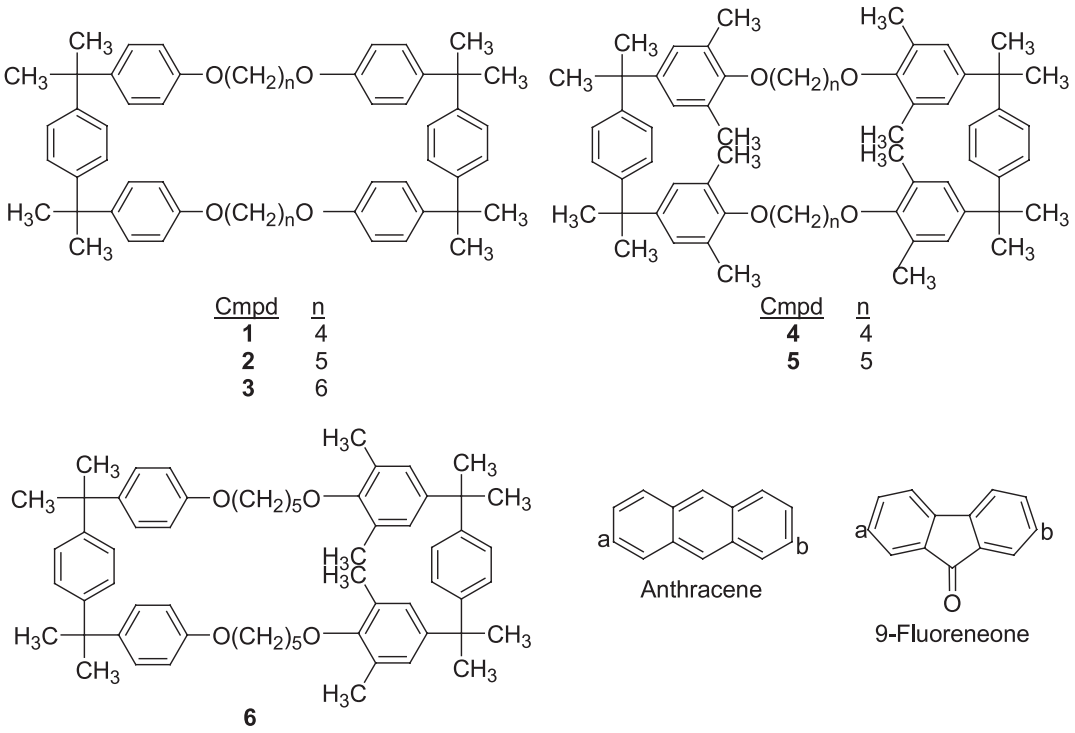

Fig. 1. Structures of cyclophanes (or corrals) **1**–**6**, anthracene and 9-fluorenone.

Selective binding of a molecule (guest) by a molecular receptor (host) to form a complex is governed by the nature of the interacting species. Size, medium and temperature play vital roles in the binding capabilities of supramolecular receptors. If the cavity of the host is too large, it results in ineffective guest binding. Binding constants generally increase as the host covers more of the surface of the guest thereby strengthening intermolecular forces.

Primarily van der Waals interactions, such as π–π stacking, edge-to-face aromatic–aromatic interaction (T stacking) and hydrogen bonding, are found in these systems. However, intracavity complexation lowers the degrees of host conformational freedom.

In this study, we have investigated complexation to form C/A and C/F in solution using absorption and fluorescence spectroscopy. Our studies reveal that corral **2** forms a stable 1:1 complex in DCM with both anthracene and 9-fluorenone. However, the stability constant is larger for formation of the anthracene complex. Excited state lifetimes of these systems have also been determined.

2. Experimental procedures

The following chemicals were purchased from Aldrich and used as received: anthracene, 9-fluorenone and spectrophotometric grade DCM. Corral **2** was synthesized by the reported method [2]. Stock solutions in DCM were prepared: 1×10^{-5} to 1×10^{-3} M for corral **2** and 5×10^{-5} M for anthracene and 9-fluorenone. The absorbances of the prepared stock solutions were measured using a Shimadzu UV–VIS spectrophotometer (model UV-2101 PC). Beer's law was used to determine the molar extinction coefficients and these parameters are tabulated in Table 1. The stock solutions of corral **2** were combined (1:1, by volume, that is 5+5 mL in a 10-mL volumetric flask) with a constant concentration of anthracene or 9-fluorenone solution. The absorption spectrum was collected a few minutes following each addition. Variation of guest absorption intensity was monitored as a function of the host concentration in DCM at 25 °C. For thermodynamic studies, absorption spectra of these systems were measured also at 29 and 32 °C.

The same solutions prepared for absorption measurements were used for fluorescence measurements. Fluorescence spectra were measured with a Shimadzu RF-5301 PC spectrofluorometer. All solutions were equilibrated in a water bath at 25 °C. However, these samples were not deoxygenated due to the low boiling point of dichloromethane (39–40 °C). For excited state lifetime measurements, samples in a 1-cm quartz cuvette were bubbled with

Table 1
Molar absorptivities (ε_λ at absorption maximum) in DCM at 25 °C

Substance	ε_λ (M^{-1} cm^{-1})
Corral **2**	$\varepsilon_{278\ nm}$=8400
	$\varepsilon_{285\ nm}$=6800
Anthracene	$\varepsilon_{325\ nm}$=2800
	$\varepsilon_{358\ nm}$=7500
9-Fluorenone	$\varepsilon_{294\ nm}$=4000