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Full Length Article

Structure and aggregation of β-cyclodextrin–pyrene–analyte supramolecular sensor: Absorption/emission spectra and simulations

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ABSTRACT

The possibility of using pyrene as a fluorescent probe in a model chemosensor composed of β-cyclodextrin–pyrene (Py–βCD) complex in aqueous solution was studied in the presence of several analytes (A) of different polarity. Absorption bands that prove the formation of the aggregated Py–βCD complex were found in the UV–VIS spectra of aqueous solution of pyrene with added βCD. The aggregate size as measured by dynamic light scattering was found to have a value of 3.2–3.6 nm. The aggregate was identified as a 1:2 complex of Py with βCD (Py@2βCD) surrounded by two empty βCD molecules. The ratio I_3/I_1 of intensity I_3 of the third vibronic band at ~26,000 cm^{-1} in the fluorescence spectrum to intensity I_1 of the 0–0 transition at ~26,800 cm^{-1} was used as an analytical characteristic of the fluorescent probe. The value of I_3/I_1 for Py@2βCD is highly sensitive to the presence of several μM of analyte in aqueous solution, and this value is markedly higher than that for pyrene in solution.

1. Introduction

Development of optical methods for reliable recognition and detection of environmentally toxic compounds is an important problem. The host–guest chemistry is a promising approach to chemical sensing and environmental monitoring. Among various hosts, cyclodextrins (CDs) are attractive for designing supramolecular recognition system because they have hydrophobic cavities of nanoscale size that enable them to adsorb various guest molecules from aqueous solution [1]. Cyclodextrin molecules, in particular, β-cyclodextrin (βCD), are known [1] to have a shape of truncated conical basket consisting of seven α-D-glucopyranose moieties bound by 1–4 glycoside bonds and a hydrophobic cavity with a hydrophilic exterior. βCD is widely known to form guest–host inclusion complexes with organic compounds in aqueous solution [1]. The stoichiometry of such complexes, βCD/substrate, as determined by absorption/emission spectroscopy, often seems to be rather simple, e.g. 1:1 [1], 2:1 [2], 2:2 [3] or 1:1:1 [4] (where the third number corresponds to molar content of the third component inserted into 1:1 or 2:2 complex).

However, such a simple notion about the structure CD complexes, when a lipophilic moiety of a hydrophobic molecule enters the hydrophobic cavity of the CD molecule, is gradually replaced by a more complicate model, according to which individual CD molecules, complexes, and complex aggregates coexist in aqueous solution [5]. Previously, the investigation on the structure and fluorescence spectra of naphthalene (Nph)–βCD inclusion complexes showed that a fluorescent excimer particle exists in submicron aggregates. The appearance of the excimer fluorescence indicated the presence of two naphthalene molecules oriented parallel to each other in such particles and, hence, the stoichiometry for this Nph–βCD complex can be expected to be 2:2, 2Nph@2βCD [3].

Although the tendency of cyclodextins, and especially βCD [6], to spontaneous aggregation was reported [7], we proposed that adding organic substrate would promote aggregation. This idea has been worked out further [8]. Light scattering measurements revealed that the size distribution of the self-assembled nanoparticles varies between 1.5 and 60–120 nm and the thermodynamic parameters of the spontaneous self-assembly of βCD in the aqueous solution were found as $\Delta_{agg}G^\circ = -16.31$ kJ mol^{-1}, $\Delta_{agg}H^\circ = -26.48$ kJ mol^{-1}, and $T\Delta_{agg}S^\circ = -10.53$ kJ mol^{-1} at 298.15 K. It has also been shown that the guest molecules act as

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glue between βCD monomers, thus stabilizing a linear βCD tube [9]. The forces controlling aggregation of the complex are relatively weak and can be easily overcome. In particular, hydrogen bonding could be an important interaction affecting the aggregation kinetics and thermodynamics [10]. In addition, the tendency of cyclodextrin molecules to form aggregates may be controlled by temperature and various additives [11]. At present, there are some reviews considering different aspects of βCD aggregation and βCD inclusion complexes [12]. However, to date there is no general rule predicting which type of aggregate will be formed by a given inclusion complex.

Various methods are being used to determine aggregate size distribution: light scattering (sometimes called photon correlation spectroscopy) [7a,11,13,14], NMR spectroscopy [15], ESR spectroscopy [16], etc. To the best of our knowledge, the first real assignment of a spectral band to the aggregate electronic absorption was made is our studies on the absorption/fluorescence spectra of pyrene (Py) solutions containing added *β*CD to form a fluorescent chemosensor [17].

In the present work, we explored the possibility of using pyrene–*β*CD (hereinafter Py@*β*CD) complex as a highly sensitive chemosensor for detection of small molecules in the environment. In contrast to a strategy using chemically modified cyclodextrins [18], we employed a self-assembly to build a chemocensor. Our previous experience implies that the luminescence spectrum of the naphthalene molecule embedded in the complex with β-cyclodextrin is sensitive to the insertion of an analyte as a third component of the complex [19]. Therefore, we studied whether the Py@βCD complex can also be used as a chemosensor for detection of small molecules. In this case, pyrene molecule plays a role of fluorescent probe in the center of the *β*CD dimer, Py@2*β*CD [2a], which, in turn, is surrounded by 'empty' CD molecules thus forming aggregates [17].

The I_3/I_1 intensity ratio of the third vibronic line (I_3) at $\sim$26,000 cm^{-1} in the fluorescence spectrum to the intensity (I_1) of the symmetry-forbidden 0–0 $S_1 \rightarrow S_0$ transition at $\sim$26,800 cm^{-1} was used as an analytical characteristic of the fluorescent pyrene probe [20]. According to the data available for 94 solvents [20c], the I_3/I_1 ratio is a characteristic of solvent and, in general, decreases with increasing dielectric constant. The nature of such sensitivity of I_3/I_1 to solvent polarity is still to be understood. The Herzberg–Teller effect [21] and diabatic intensity borrowing [22] have been mentioned as the main causes of such a behavior.

In our previous work [17] we demonstrated the capability of the designed chemosensor to absorb from aqueous solutions such simple molecules as benzene, toluene, hexane, cyclohexane, and methylcyclohexane as well as ethanol, acetone, and acetonitrile, which previously were used as solvents [20]. Here, we will call them analytes (A). Using the I_3/I_1 ratio, we showed that this chemosensor is highly sensitive to the addition of several μM of analyte to aqueous solution [17].

In this investigation, we directly use the fluorescence of pyrene, i.e. we record a change in the intensity of vibronic band in its fluorescence spectrum caused by direct contact of analyte with pyrene. A different approach was suggested in [23], where pyrene@dimethyl-*β*CD supramolecular complex immobilized on a plasticized poly(vinylchloride) membrane was used as a chemosensor. A decrease in the excimer fluorescence intensity of pyrene upon addition of analyte, bisphenol A (BPA), was attributed to the displacement of pyrene from the sensor by BPA manifested as the disappearance of the excimer fluorescence of pyrene.

In this work, we will demonstrate that: (*i*) the pyrene-based fluorescent chemosensor with the proposed structure of Py@2βCD cannot exist without additional *β*CD environment; (*ii*) Py@2*β*CD complex is indeed formed by self-assembling in aqueous solution and the water filling an empty space inside Py@2*β*CD is displaced once an analyte is added; and (*iii*) shed new light on the nature of the red shift in absorption spectra of aggregated pyrene.

2. Experimental

2.1. Materials

Reagent grade pyrene (ReaKhim) was twice recrystallized from ethanol. β-Cyclodextrin (Cyclolab, Hungary) was used without additional purification. Water was twice distilled before use. Low polar benzene, toluene, hexane, cyclohexane, and methylcyclohexane were studied as analytes. We used also ethanol, acetone, and acetonitrile as analytes with higher polarirty. Benzene (98.8%, Komponentreaktiv), toluene of HPLC grade (Fisher Scientific), and methylcyclohexane (Aldrich) were used without further purification. Cyclohexane and hexane were purified by chromatography on a silica gel column. Other solvents were purified by distillation. The purity was controlled by absorption and luminescence spectra.

2.2. Sample preparation

An aqueous solution of $5 \cdot 10^{-3}$ M βCD, at which pyrene is completely involved in the Py@2βCD complex [2], was prepared in a 10-mL test tube. A portion of pyrene solution in hexane was evaporated in another test tube, so that the calculated pyrene concentration of about several micromoles per liter was obtained by adding 10 mL of βCD aqueous solution. The test tube with pyrene and βCD was stored for several hours at 50 °C under ultrasonic treatment in a UVZ3/100MPRELTEK thermostatically controlled bath. The resulting solution was used after storing at room temperature for one day. To measure spectral characteristics of the complex, 2 mL of the solution was sampled into a fused silica cell from the test tube after intensive shaking. To obtain three-component complexes, a true aqueous solution of an analyte was prepared by the addition of 30 μL of the solvent to 500 mL of water. Only for cyclohexane the emulsion was obtained by ultrasonic treatment. Several tens of microliters of this solution (or cyclohexane emulsion) were introduced in a cell with the solution of the binary complex. Terminal concentrations of analytes added to the pyrene aqueous solution are shown in Table 1.

2.3. Spectral measurements

The absorption spectra were taken with a Specord M40 spectrophotometer at a resolution of 20 cm^{-1} (Figs. 1 and 2). The fluorescence spectra of pyrene were recorded with an Elyumin2M spectrofluorimeter at a slit width of 2 nm (both instruments with digital

Table 1
I_3/I_1 ratios in bulk solvents and in $A_n \cdot$ Py@2*β*CD complex.

Analyte	I_3/I_1[a]	I_3/I_1[b]	I_3/I_1[c]	C[d], μM
Benzene	0.88	0.95	3.12	27.7
Toluene	0.9	0.96	2.24	104
Hexane	1.65	1.72	2.5	15
Cyclohexane	1.68	1.72	2.17	40
Methylcyclohexane	1.8	1.72	2.34	26.9
Ethanol	0.91	0.85	2.5	32
Acetonitrile	0.57	0.56	1.9	66.6
Acetone	0.68	0.61	2.88	20
Water	0.63	0.53	1.55	–

[a,b] refer to bulk solvent
[a] Ref. [20b]
[b] Ref. [20c]
[c] This paper
[d] Analyte concentration