

## Peculiarities of phosphorescence of complexes between aromatic molecules and $\beta$ -cyclodextrin at room temperature

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Luminescence of complexes between  $\beta$ -cyclodextrin and phenanthrene, fluorene, or naphthalene- $d_8$  in aqueous solutions was studied at room temperature. It is found that the addition of acetone, in the absence of heavy atoms, results in the phosphorescence of these complexes at 293 K due to triplet-triplet energy transfer. The conclusion is drawn that a heavy atom is necessary for population of a triplet level, because the intersystem crossing of an aromatic molecule in the cyclodextrin cavity is suppressed due to restriction of vibration-relaxation interactions with a medium. The phosphorescence multiply increases when light-scattering polycomplexes between an aromatic molecule and cyclodextrin in the presence of a heavy atom and a sensitizer are formed.

**Key word:** sensibilization, phosphorescence,  $\beta$ -cyclodextrin, complex, intersystem crossing, lifetime.

Phosphorescence of aromatic molecules (AM) has been studied in many works at room temperature in the presence of cyclodextrins (CD),<sup>1–3</sup> in micelles,<sup>4</sup> on silica gel,<sup>5</sup> on filter paper,<sup>6</sup> etc. In this work, complexes between AM and CD are considered. Cyclodextrins are cyclic compounds<sup>7</sup> whose molecules have the form of a truncated cone and consist of glucose units linked by oxygen bridges.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD contain 6, 7, and 8 glucose units, respectively, with diameters of the cavities of 5.7, 7.8, and 9.5 Å. The hydrophobic cavity and hydrophilic outer surface determine the ability of these compounds to form stable inclusion complexes with nonpolar molecules in an aqueous medium. AM in the cavity of CD gain new properties, including the ability to phosphoresce at room temperature (RTP),<sup>1–3</sup> due to specific interactions. This property is widely used for detecting nanogram amounts of AM.<sup>8</sup>

RTP is pronounced in complexes between AM and a mixture of  $\alpha$ - or  $\beta$ -CD and NaCl.<sup>8,9</sup> Phosphorescence spectra of the complex between benzo[*f*]quinoline and  $\beta$ -CD are as resolved as those at 77 K, and the lifetime of RTP in such a matrix is only half lower than in frozen solutions.<sup>10</sup>

The addition of  $\alpha$ -,  $\beta$ -, or  $\gamma$ -CD to filter paper results in an increase in the phosphorescence intensity of several aromatic compounds that is explained by complex formation.<sup>11</sup> In all these examples, solid nontransparent matrices were used in which studying both structures of complexes formed and mechanisms of photoprocesses was difficult. It is customary to study the mechanisms of photoreactions in solutions.

There are only a few works<sup>12–14</sup> devoted to studying RTP-complexes between AM and CD in aqueous solutions. The authors of these studies<sup>12–14</sup> suggested that triple complexes containing a third molecule in addition to CD and AM are formed. It is of importance that efficient RTP in these complexes appears only in the presence of a heavy atom, which can be external<sup>12</sup> or can enter the composition of an aromatic molecule.<sup>13</sup> The role of a heavy atom remains ambiguous.

We attempted to elucidate the effect of a heavy atom and other effects on RTP in liquid solutions.

### Experimental

Absorption spectra were recorded on a Specord UV-VIS spectrophotometer, luminescence spectra were measured on an Elyumin-2M spectrofluorimeter, and lifetimes of lower triplet states were measured on an setup with a pulse lamp (time resolution <1 ms). The results of measurements were processed on a computer according to developed programs.

The purities of the AM used, phenanthrene, fluorene, and octadeuteronaphthalene, was controlled by absorption<sup>15</sup> and fluorescence spectra in ethanol. 1,2-Dibromoethane was distilled; acetone (high purity grade),  $\beta$ -CD (Aldrich), sodium sulfite (analytical grade), and argon (high purity grade, O<sub>2</sub> content lower than 10<sup>–3</sup> %) were used without additional purification.

All substances studied, except acetone, are poor soluble in water. Therefore, the systems studied comprised water-dispersed solid and liquid particles. The specified amount of CD (10<sup>–3</sup>–10<sup>–2</sup> mol L<sup>–1</sup>) added to a solution are completely dissolved in water (the solubility at room temperature is

$1.5 \cdot 10^{-2} \text{ mol L}^{-1}$ ).<sup>16</sup> The concentration of AM was 10–100 times lower than that of CD, but in all cases it did not exceed  $10^{-4} \text{ mol L}^{-1}$ . To form triple complexes, such an amount of 1,2-dibromoethane or acetone was added to a solution of AM or CD that 10–100 molecules of the additive were accounted for CD molecule.

Oxygen, which quenches phosphorescence, should be removed from samples obtained to observe their phosphorescence. Several methods for removing  $\text{O}_2$  were used: passing argon through a solution for 20 min or adding  $\sim 2 \text{ mg mL}^{-1}$  of  $\text{Na}_2\text{SO}_3$  and shaking the solution for 20 min (see Ref. 17). The second method is more convenient but is inefficient when acetone is added to a solution, due likely to the reaction between sulfite and the carbonyl group of acetone. In addition, sulfite introduces ions that could affect the state of solutions, although we did not observe this effect. Passing argon through a solution is a more versatile method, but it results in removing aromatic molecules and additives from solutions that should be controlled and taken into account.

Cells that could be evacuated were used, and oxygen was removed by careful evacuation of solutions cooled to  $0^\circ \text{C}$  (water–ice mixture) but unfrozen. No vigorous boiling or destroying a cell with ice occurred.

## Results and Discussion

When studying complexes between AM and CD, an external or internal heavy atom was commonly used to obtain efficient RTP. The authors of one of the works<sup>11</sup> believe that they succeeded in observing phosphorescence of complexes containing NaCl, CD, and AM without a heavy atom. However, chlorine also plays the role of a heavy atom, although to a lesser extent than bromine or iodine. The effect of chlorine as a heavy atom is observed in an increase in the quantum yield of triplet states to 0.95 and a decrease in their lifetimes to 0.3 s from 0.82 s for 1-chloronaphthalene (see Ref. 19) and 2.3 s for naphthalene (see Ref. 20). Only fluorescence is observed in an aqueous solution of the phenanthrene–CD complex without a heavy atom. The addition of dibromoethane results in suppression of fluorescence and appearance of RTP.<sup>12</sup> The heavy atom increases the rate of the intersystem crossing of the  $S_1$ – $T_1$  transition and the radiative rate constant from the lower triplet state. Both of the processes can favor RTP: the S–T intersystem crossing increases the occupation of the lower triplet state, while an increase in the radiative rate constant increases the quantum yield of the phosphorescence from this level. It remains unclear which of these processes is predominant for the appearance of RTP.

The quantum yield of triplet states of phenanthrene in solution is greater than 0.8 (see Ref. 20). This explains, in particular, the fact that the intensity of phosphorescence of phenanthrene in an ethanol solution at room temperature is 1000 times lower than that in a solution frozen to 77 K,<sup>21</sup> where quantum yields of phosphorescence and fluorescence are approximately equal.<sup>22</sup> Hence it follows that in the frozen solution occupation of the triplet level is quite efficient without a

heavy atom. Taking into account the similarity of the frozen solution and the complex with CD, one could assume the same quantum yield of triplet states for the complex as well. Then the role of the heavy atom for the complex between AM and CD implies to increase the radiative constant.<sup>12</sup>

We reproduced the results of the previously published work<sup>12</sup> and carried out several additional experiments. Acetone, which did not contain a heavy atom, was added instead of dibromoethane to a solution containing phenanthrene and  $\beta$ -CD, and luminescence was measured after preparing the complex and removing oxygen by passing argon through the solution.

The spectrum of luminescence of the phenanthrene– $\beta$ -CD–acetone complex is shown in Fig. 1. The spectrum consists of two components: the fluorescence and phosphorescence of phenanthrene. The RTP spectrum of the phenanthrene– $\beta$ -CD–dibromoethane complex, which revealed only phosphorescence under the same conditions, is shown in Fig. 1 for comparison. We assume that the fluorescence of the complex with acetone is caused by direct excitation of phenanthrene, while the phosphorescence of phenanthrene is the result of triplet–triplet energy transfer to it from acetone.

Acetone is a sensitizer not best matched to phenanthrene, because absorption spectra of these two substances are much overlapped, and, therefore, the pure sensitized phosphorescence cannot be obtained. In order to show that the sensitized fluorescence is observed, we used fluorene, which absorbs in a shorter wave region, instead of phenanthrene.

The spectra of luminescence of fluorene in the complex with  $\beta$ -CD in the presence of acetone are presented in Fig. 2. The spectra were excited both in the absorption range of fluorene and in a longer wave region where only acetone absorbs. In the first case, the fluorescence

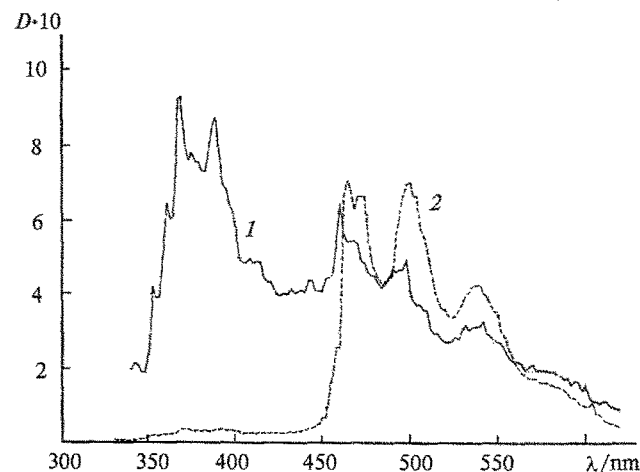


Fig. 1. Luminescence spectra (uncorrected) of the complex between phenanthrene ( $10^{-4} \text{ mol L}^{-1}$ ) and  $\beta$ -CD ( $10^{-2} \text{ mol L}^{-1}$ ) in the presence of acetone ( $0.4 \text{ mol L}^{-1}$ ) (1) or 1,2-dibromoethane ( $0.1 \text{ mol L}^{-1}$ ) (2) in water. Excitation at 300 nm; spectral gaps for excitation and observation are 15 and 4 nm, respectively.

and phosphorescence make contributions to luminescence, while in the second case, only phosphorescence is observed. This means that we observe the acetone-sensitized phosphorescence of fluorene, which appears after occupying the lower triplet level of fluorene due to triplet-triplet energy transfer from acetone. This transfer is possible, because the energies of triplet levels of acetone, fluorene, and phenanthrene are 28000, 23580, and 21600  $\text{cm}^{-1}$ , respectively (see Refs. 23 and 24). Therefore, the rate constant of the nonradiative transition from the triplet level of AM is not very high, and the radiative transition should not be facilitated by a heavy atom to increase the efficiency of RTP. This is also observed by measuring lifetimes of the acetone-sensitized RTP of the complexes between AM and  $\beta$ -CD in an aqueous solution at 293 K and the low-temperature phosphorescence in EPA<sup>19</sup> at 77 K:

	293 K	77 K
Phenanthrene	1.7	3.3
Fluorene	1.9	4.03
Octadeuteronaphthalene	8.2	22.0

The concentrations of acetone, AM, and CD were  $0.4$ ,  $0.8 \cdot 10^{-4}$ , and  $4 \cdot 10^{-3}$  mol  $\text{L}^{-1}$ , respectively.

These lifetimes change about twofold on going from 77 K to room temperature, which qualitatively coincides with the data for the AM—CD—NaCl system (see Ref. 10), but this could be merely coincidental.

Thus, in the complex between AM and  $\beta$ -CD the intersystem crossing is suppressed, and a heavy atom is required for the efficient occupation of the lower triplet level. This is the basic difference of such complexes from frozen solutions.

It is reasonable that the question about the reason for the absence of the intersystem crossing for such a microorganization of the system arises. We assume that vibrational interactions between an aromatic molecule

and a medium, which are necessary for the efficient intersystem crossing, are suppressed in the cyclodextrin cavity. For individual aromatic molecules in a gas phase, the yield of triplet molecules is also very low and the fluorescence dominates.<sup>25</sup> It is likely that the behavior of an AM in the complex with CD is similar to its behavior in a gas phase. Like the addition of an inert gas to AM in the gas phase, the addition of a heavy atom to the complex with CD results in the similar results: a decrease in fluorescence and an increase in phosphorescence of these molecules.<sup>26</sup>

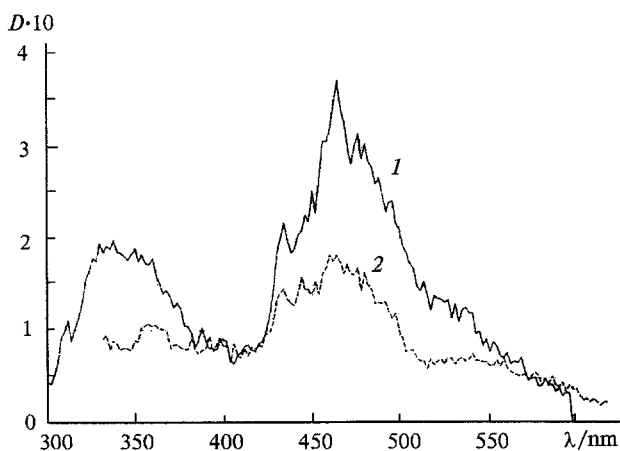
The suppression of the intersystem crossing of AM upon formation of the complex with CD in an aqueous solution should manifest itself as an increase in the fluorescence intensity and its lifetime. It is difficult to experimentally observe this phenomenon, because AM fluoresce both in the complex and without it, and it is unknown what portion of AM exists in the complex. Nevertheless, the addition of  $\beta$ -CD to an aqueous solution of 4-aminophthalimide results in an increase in the fluorescence lifetime.<sup>27</sup> An increase in the fluorescence intensity was observed for several AM after adding  $\beta$ -CD to an aqueous solution (see Ref. 28).

Unfortunately, the data presented only indirectly prove the hypothesis suggested. The addition of dibromoethane or acetone to the complexes between AM and CD used for obtaining RTP results in the appearance of light scattering of the solution, related to the formation of macrostructures (polycomplexes). Our attempts to go over to the real solution by decreasing the concentration of CD or heating to 353 K always resulted in a sharp decrease in the phosphorescence intensity. Therefore, polycomplexes that give rise to light scattering in solution are inherent in efficient RTP. The literature data also confirm this assumption. The maximum signal of RTP of *p*-aminobenzoic acid is observed when the concentration of  $\beta$ -CD is three orders of magnitude greater than the concentration of the aromatic molecule. It is difficult to explain the necessity of such an excess, if the formation of a AM— $\beta$ -CD complex of 1 : 1 composition is assumed (see Ref. 8). A long lifetime of the phosphorescence and its insensitivity to quenching by oxygen even at 1 atm are explained by the formation of a 1 : 2 complex between AM and  $\gamma$ -CD.<sup>14</sup>

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**Fig. 2.** Luminescence spectra (uncorrected) of the complex between fluorene ( $10^{-4}$  mol  $\text{L}^{-1}$ ),  $\beta$ -CD ( $2 \cdot 10^{-2}$  mol  $\text{L}^{-1}$ ), and acetone ( $0.4$  mol  $\text{L}^{-1}$ ) in water with excitation at 300 (1) and 315 nm (2). Spectral gaps for excitation and observation are 15 and 4 nm, respectively.

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