Long-lived phosphorescence of arenes in complexes with cyclodextrins

2.* Room-temperature phosphorescence of ternary complexes of naphthalene and phenanthrene with β-cyclodextrin and adamantane derivatives in the presence of oxygen

V. B. Nazarov,[a] V. G. Avakyan,[b]* E. I. Bagrii,[c] T. G. Vershinnikova,[a] and M. V. Alfimov[b]

[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 515 3588. E-mail: vnazarov@icp.ac.ru
[b]*Photochemistry Center, Russian Academy of Sciences,*
7A ul. Novatorov, 119421 Moscow, Russian Federation.
Fax: +7 (495) 936 1255. E-mail: avak@photonics.ru
[c]*A. V. Topchiev Institute of Petrochemical Syntheses of Russian Academy of Sciences,*
29 Leninsky prosp., 119991 Moscow, Russian Federation.
E-mail: bagrii@ips.ac.ru

Long-lived room-temperature phosphorescence (RTP) of arene—β-cyclodextrin (β-CD)—cage hydrocarbon complexes in the presence of oxygen was studied. Naphthalene-d_8, phenanthrene, and fluorene were used as arenes and adamantane, 1,3-dimethyladamantane, diamantane, and diadamantyl were used as the cage hydrocarbons (according to PM3 quantum chemical calculations, the use of these compounds might cause the appearance of long-lived RTP). The RTP lifetime of the naphthalene-d_8—β-CD—diadamantyl complex is 11.9 s at 20 °C.

Key words: room-temperature phosphorescence, phosphorescence lifetime, ternary complexes cyclodextrin—arene—cage hydrocarbons, naphthalene, phenanthrene, adamantane, diamantane, diadamantyl, quantum chemical calculations.

Studies of supramolecular systems are of considerable interest for basic research and practice because their components often possess new, unusual properties. For instance, in our previous study[1] we first showed that in a molecularly organized system based on aggregated ternary complex naphthalene-d_8—β-cyclodextrin (β-CD)—adamantane (Ad) the probe molecule of naphthalene-d_8 exhibits long-lived room-temperature phosphorescence (RTP) with a lifetime, τ, of 10.3 s in the presence of molecular oxygen (major quencher of phosphorescence under normal conditions). Removal of oxygen from the sample results in an increase in τ to 15.5 s. This means that in the aggregates formed the naphthalene-d_8 molecule is reliably isolated from oxygen and intra-aggregate oxygen diffusion is essentially hindered. The results obtained suggested that other cage hydrocarbons used as the third components could also act as good/reliable "steric shields" and that in the complexes based on them the probe arene molecule will phosphoresce in the presence of oxygen.

Room-temperature phosphorescence of inclusion complexes of arenes with cyclodextrin in the presence of oxygen with RTP lifetimes of the order of a few milliseconds was reported in studies of complexes containing heavy atoms.[2—4] Under such conditions, the quenching action of oxygen is about three orders of magnitude weaker than in the samples characterized by the RTP lifetimes of the order of a few or tens of seconds. It is these complexes that were studied in this work. Naphthalene-d_8 was mainly used as arene; the lifetime of phosphorescence of this compound in a frozen EtOH—isopentane—Et_2O (2 : 5 : 5) solution is 18.3 s at 77 K.[5]

Taking into account the available conclusions and recommendations,[1] it was of interest to examine the possibility of observing long-lived RTP of β-CD complexes with other arenes and cage hydrocarbons in the presence of oxygen. Essential conclusions drawn earlier are as follows. Long-lived RTP appears only if poorly water-soluble hydrocarbons are used as the third components of complexes (this favors aggregation of the ternary complexes). The third-component molecule must be sufficiently large to be strongly bound to the arene—β-CD complex and to ensure efficient protection of naphthalene from collisions with oxygen molecules in the wide part of the β-CD cavity. These requirements are met by Ad and its derivatives. Therefore the set of the third components of the com-

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plexes also included dimethyladamantane (DMAD), diamantane (DA), and diadamantyl (DAD). The probe molecules in the ternary complexes with β-CD were naphthalene-d_8, phenanthrene, and fluorene.

The structures of the molecules and complexes and the complexation energies were calculated by the PM3 quantum chemical method,[1] which was successfully employed in earlier studies of related systems. Thus, the aim of this work was to examine, both experimentally and theoretically, the possibility of observing long-lived RTP in the presence of oxygen of ternary complexes prepared with a larger number of arenes and cage hydrocarbons.

Experimental

1,3-Dimethyladamantane (DMAD) was obtained by heating perhydroacenaphthene in the presence of an aluminum halide-based complex following a known procedure.[6] The reaction mixture was poured on ice, the organic layer was separated, dried over calcium chloride, filtered, and distilled on a column. The fraction containing at least 99% of the target product (GLC monitoring) was collected.

Diamantane (DA) was synthesized using a known procedure[7] involving hydrogenation of the (4+4)-dimer of norbornadiene (binor-S) followed by isomerization pentacyclic hydrocarbons that formed.

1,1-Diadamantyl (DAD) was obtained from 1-bromoadamantane formed by refluxing adamantane in liquid bromine following a known procedure.[8] The characteristics of the compounds synthesized were consistent with the published data.

Complexes with β-CD were prepared as prescribed earlier,[1] except for DAD added to the binary complex as a weighed sample. Phenanthrene and fluorene were purified by recrystallization monitored by the absorption and luminescence spectra. Naphthalene-d_8 (Isotope, Russia), Ad, DA, and DAD were purified by sublimation *in vacuo*. Compounds β-CD (Cyclolab, Hungary) and hydroxypropyl-β-CD (Aldrich) were used without purification. Bidistilled water was used as solvent.

The absorption and fluorescence spectra were measured with a Specord M-40 spectrophotometer and Elumin-2M spectrofluorimeter. Both instruments were connected to personal computers for recording and primary processing of spectral data. The phosphorescence lifetimes were measured on a setup reported elsewhere.[1]

Quantum chemical calculations. Semiempirical quantum chemical calculations of substrate molecules (naphthalene-d_8, phenanthrene, fluorene, Ad, DMAD, DA and DAD) and their 1 : 1 and ternary inclusion complexes with β-CD were carried out by the MNDO/PM3 (from this point on, PM3) method with standard parametrization[9] using the PC GAMESS 99 program package.[10] A structure obtained in earlier calculations[11] was used as the starting structure of the β-CD molecule. This fully optimized structure is similar to that corresponding to the global minimum, has a C_7 symmetry, a heat of formation (ΔH_f) of −1468.4 kcal mol^{-1},[11] and is stablilized by intramolecular hydrogen bonds, O(2)—H···O(3´), between the secondary OH groups of the wide part of the cavity (2-OH groups of a glucose unit act as proton donors and oxygen atoms of 3-OH groups of the adjacent glucose unit act as proton acceptors). The heats of formation of isolated molecules and complexes and the complexation energies calculated by the PM3 method are listed in Table 1.

Table 1. Heats of formation (ΔH_f) and complexation energies (ΔE) of complexes and isolated molecules obtained from PM3 calculations

Compounds and complexes	$-\Delta H_f$	$-\Delta E_{tot}$[a]	$-\Delta E$[b]
	kcal mol^{-1}		
β-CD	1468.4	—	
2β-CD	2949.1	12.6[c]	—
Naphthalene-d_8	40.7	—	—
Ad	35.0	—	—
DA	39.0	—	—
DAD	59.9	—	—
β-CD—naphthalene-d_8	1440.1	12.4	—
β-CD—Ad	1522.0	18.6	—
β-CD—DA	1526.7	19.3	—
β-CD—DAD	1549.7	21.4	—
β-CD—naphthalene-d_8—Ad	1500.7	38.0	25.6
β-CD—naphthalene-d_8—DA	1481.8	15.1	2.7
β-CD—naphthalene-d_8—DAD	1503.2	15.6	3.2
2β-CD—2(naphthalene-d_8)	2894.7	14.5[c]	—

[a] Total energy of complexation.

[b] Inclusion energy of cage hydrocarbon.

[c] Dimerization energy of β-CD.

Results and Discussion

Spectral data. Inclusion complexes naphthalene-d_8—β-CD formed in aqueous solution of naphthalene-d_8 ($C = 1 \cdot 10^{-4}$ mol L^{-1}) in the presence of β-CD ($C = 5 \cdot 10^{-3}$ mol L^{-1}) exhibit fluorescence typical of naphthalene-d_8. At these concentrations of the components, the 2(naphthalene-d_8)—2β-CD complexes exhibiting excimer fluorescence (EF)[12] are also formed, undergoing partial aggregation and precipitation.[13] The addition of a hydrocarbon (hexane, cyclohexane, Ad, *etc.*) to this solution is followed by disappearance of EF immediately after preparation of the sample and it is possible to observe RTP. Here, with Ad as the third component, there is no need of removing oxygen from the solution. However, the addition of DMAD to the complex naphthalene-d_8—β-CD is followed by retention of EF and the absence of RTP in the presence of oxygen. Once oxygen is chemically bound with sodium sulfite, one can simultaneously observe three types of luminescence from the same sample, namely, fluorescence of single molecules of naphthalene-d_8, EF of the complexes 2(naphthalene-d_8)—2β-CD, and RTP (Fig. 1). Storage of the sample at room temperature for 5—7 days results in disappearance of EF and appearance of RTP in the presence of oxygen in the luminescence spectrum, which is nine times less intense than RTP from the sample with Ad. This

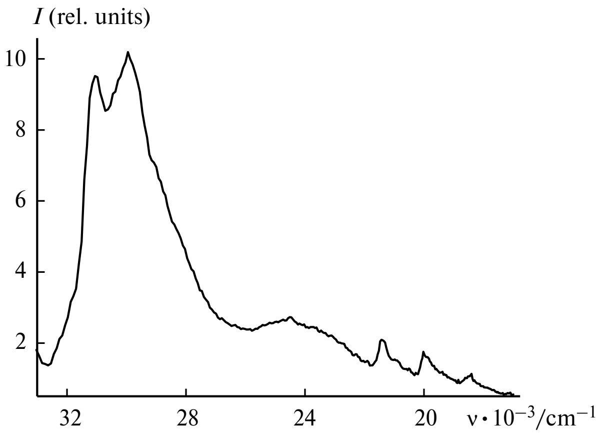

Fig. 1. Room-temperature luminescence spectrum of complex naphthalene-d_8—β-CD—DMAD after chemical binding of oxygen.

means that breakdown of the 2(naphthalene-d_8)—2β-CD complex and formation of aggregates, which preclude quenching of phosphorescence, takes a longer time on adding DMAD than Ad.

Earlier,[1] we showed that the presence of aggregated complexes is the key condition for their ability to exhibit long-lived RTP. Here, the use of solid (at room temperature) hydrocarbons is preferred. In contrast to Ad, DMAD is a liquid at room temperature, which seems to preclude the formation of aggregates exhibiting RTP in the presence of oxygen. This conclusion is based on the following. The solubility of solids and liquids are different. The probability for compounds to escape from the complex to the aqueous phase and thus break down the complex is higher for liquids (under normal conditions). For instance, aggregates of ternary complexes with liquid hydrocarbons as the third components break down as the sample temperature increases to 50 °C, which is detected by disappearance of light scattering in suspension in water. The use of urotropin (solid, under normal conditions, and well-soluble in water compound with a cage structure similar to that of Ad) as the third component causes no aggregation and appearance of RTP at all.[1] In contrast to this, with Ad as the third component of the complex both aggregates and light scattering are retained in the sample at 50 °C. Therefore, preferred use of solid (at room temperature) hydrocarbons becomes understandable. Indeed, passage to DA or DAD (both are solids at room temperature) led to quite different results.

At first, the addition of DA to the 2(naphthalene-d_8)—2β-CD complex caused no changes in the luminescence spectrum, namely, EF was observed while RTP was not. Storage of the sample under normal conditions for 7 days led to disappearance of EF similarly to the complex with DMAD and simultaneous appearance of a weak signal of RTP in the presence of oxygen, which is twice as intense as that from the DMAD-containing sample. Such a slow evolution of the spectra is probably due to larger size of the DA molecules, which is responsible for slowing down complexation and formation of aggregates exhibiting RTP.

The addition of DAD to the 2(naphthalene-d_8)—2β-CD complex in the presence of oxygen immediately results in the appearance of a luminescence spectrum similar to that shown in Fig. 1. After passage of a few days RTP became somewhat more intense, whereas EF initially remained unchanged and disappeared only after the sample was kept at room temperature for 7 days. Simultaneously, RTP became as intense as that observed from the sample with Ad.

As the third component of the complex, DAD behaves in significantly different fashion compared to Ad (adding the latter results in immediate disappearance of EF). The reason may be the difference between the complexation constants of the cage hydrocarbons with β-CD and with the naphthalene-d_8—β-CD and 2(naphthalene-d_8)—2β-CD complexes. It is noteworthy that the concentration of the cage hydrocarbons in solution exceeds those of β-CD and arene by a factor of two and by two orders of magnitude, respectively. Therefore, if three components are present in the solution, the cage hydrocarbon—β-CD binary complexes predominate and the formation of these species competes with that of the 2(naphthalene-d_8)—2β-CD complexes responsible for EF.

Not only the rigid matrix but also the absence of phosphorescence quenchers (first of all, molecular oxygen) near the arene molecule are necessary for long-lived arene phosphorescence with τ of the order of a few seconds. Usually, these conditions hold in frozen solutions where rigidity is provided by the crystal structure of the solvent and oxygen diffusion is suppressed. At room temperature, this was first achieved by using a molecularly organized system based on arene—β-CD—cage hydrocarbon ternary complexes aggregated in water into solid microparticles. This system is characterized by two levels of arene protection from oxygen. These are (i) a ternary inclusion complex arene—β-CD—cage hydrocarbon, which ensures rigidity of the matrix, and (ii) a "cloud" surrounding this complex. The cloud is comprised of binary complexes (cage hydrocarbon—β-CD) that preclude oxygen diffusion toward arene and are responsible for the formation of solid microparticles. Therefore, the choice of the cage hydrocarbon plays the key role in this case.

The RTP lifetimes of the naphthalene-d_8—β-CD complexes with different cage hydrocarbons in the presence (in the numerator) and in the absence of oxygen in the sample (in the denominator) at 20 °C are given below. For DAD, we present the values measured at the day the sample was prepared and 24 h after preparation of the sample (figures in parentheses). For comparison, we present the data obtained earlier[1] using Ad.

Hydrocarbon	DAD	DA	Ad
τ/s	10.5±0.3 (11.9±0.3)	9.4±0.3	10.3[1]
	13.6±0.4	14.5±0.4	15.5[1]

The quenching constants can be estimated from the relationship[1] $k_q \cong (1/\tau_1 - 1/\tau_2)/[O_2]$, where k_q is the rate constant for quenching of phosphorescence by oxygen; τ_1 and τ_2 are the RTP lifetimes in the presence of unbound and bound oxygen, respectively; and $[O_2] = 2.9 \cdot 10^{-4}$ mol L^{-1}.[5] For the complexes with DAD and DA we get $k_q \cong 36$ and 129 L mol^{-1} s^{-1}, respectively. Comparison of the values with a value of 112 L mol^{-1} s^{-1} obtained for the complex with Ad shows that in the ternary complex DAD provides a much better protection of naphthalene-d$_8$ from oxygen than Ad, whereas DA is less efficient. The rate of nonradiative processes that shorten the lifetime of RTP in the absence of oxygen decreases in the series DAD, DA, Ad, as indicated by τ values increasing in the same order.

The RTP spectra of ternary complexes with different cage hydrocarbons, measured under identical conditions in the presence of oxygen, are shown in Fig. 2. With DAD, the RTP intensity is much higher than with DA.

The results of calculations are as follows. (1) The energy of dimerization of the naphthalene-d$_8$—β-CD complexes into 2(naphthalene-d$_8$)—2β-CD is sufficiently high to shift the equilibrium toward the latter complex, characterized by a constant of formation of $4 \cdot 10^3$ L mol^{-1} s^{-1}, in the absence of cage hydrocarbon. In the 2(naphthalene-d$_8$)—2β-CD complex two naphthalene-d$_8$ molecules are parallel to each other, which results in the appearance of EF of naphthalene in the luminescence spectrum. (2) The energies of formation of the β-CD—cage hydrocarbon complexes (see Table 1) are higher than that of the complex 2(naphthalene-d$_8$)—2β-CD. Therefore, the appearance of a cage hydrocarbon in solution can lead to breakdown of the latter and formation of β-CD—cage hydrocarbon complexes. (3) Only with Ad as the cage hydrocarbon the inclusion energy of the cage hydrocarbon is much higher than the energy of formation of the 2(naphthalene-d$_8$)—2β-CD complex. Therefore, the addition of Ad to the solution immediately results in the formation of aggregates of ternary complexes that exhibit RTP. Since the ΔE values for other cage hydrocarbons are much smaller than the energy of dimerization of the naphthalene-d$_8$—β-CD complexes into 2(naphthalene-d$_8$)—2β-CD, the quenching of excimers and formation of ternary complexes is hindered and takes a rather long time. However, this process is energetically favorable (all ΔE values are negative) and results in ternary complexes and emission of RTP.

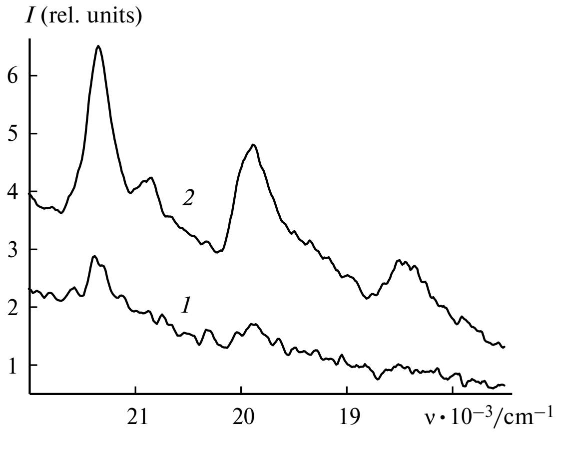

Fig. 2. RTP spectra at 20 °C of naphthalene-d$_8$—β-CD complex in water in the presence of oxygen, obtained after adding DA (*1*) and DAD (*2*).

The structures of the ternary complexes (Fig. 3) show that all cage hydrocarbons can protect naphthalene-d$_8$ from oxygen, because they shield the entrance to the CD cavity from the wide part of the "basket". However, the actual structure of the aggregate is still unclear.

Complexes of other arenes with CD. The phenanthrene—β-CD complex in aqueous solution exhibits only fluorescence of isolated phenanthrene molecules (no EF). The addition of Ad to this complex also results in the appearance of long-lived RTP in the presence of oxygen

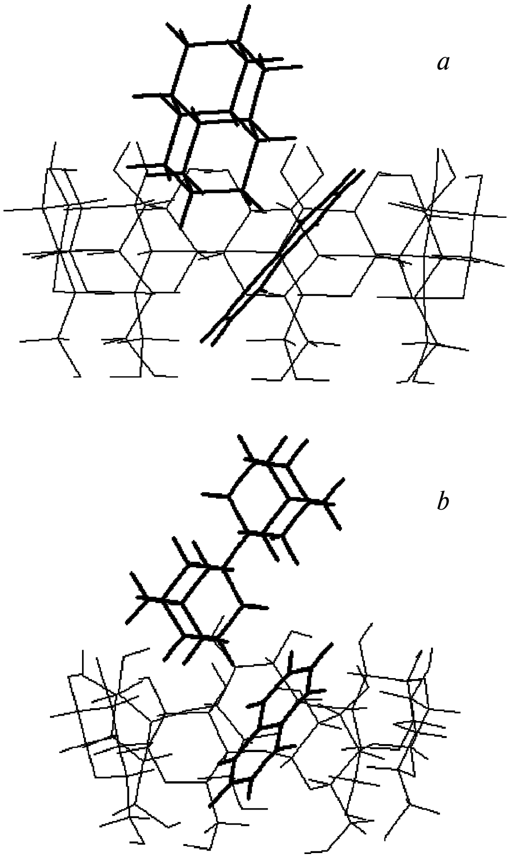

Fig. 3. Structures of ternary complexes naphthalene-d$_8$—β-CD—DA (*a*) and naphthalene-d$_8$—β-CD—DAD (*b*).

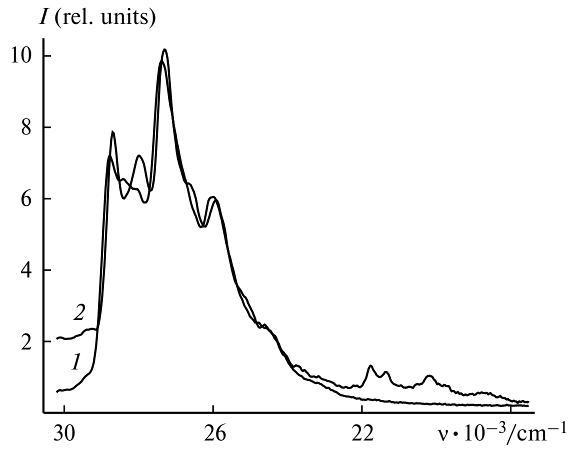

Fig. 4. Luminescence spectrum of phenanthrene—β-CD complex in the absence of (*1*) and after adding adamantane (*2*).

(Fig. 4), characterized by τ = 2±0.3 s at 292 K. Once oxygen is chemically bound with sodium sulfite, the RTP lifetime increases to 3.2 s, which is very similar to that obtained[5] for frozen solution (3.4 s).

The RTP intensity of the Ad—fluorene—β-CD complex is an order of magnitude lower than that of the Ad—phenanthrene—β-CD complex; the RTP lifetime increases from 2.2±0.3 to 4.1 s after chemical binding of oxygen (*cf.* Ref. 5: τ = 5 s for frozen solution). From here it follows that in the ternary complex the bulkier phenanthrene molecule is more efficiently protected from oxygen than fluorene.

Complexes of naphthalene-d$_8$ with hydroxypropyl-β-CD. We also studied complexes of naphthalene-d$_8$ with hydroxypropyl-β-CD (the solubility of the latter compound in water is an order of magnitude higher compared to β-CD). However, we failed to observe both EF and RTP even in the absence of oxygen in solutions using different hydrocarbons as the third component. This is due to the fact that no aggregation occurs with hydroxypropyl-β-CD, *i.e.*, the necessary condition for emission of EF and RTP in these molecularly organized systems[1,13] is not met.

Thus, to initiate long-lived RTP of arene—β-CD—cage hydrocarbon complexes in the presence of oxygen, all components of the complexes should be poorly soluble in water. Regarding cage hydrocarbons, not only Ad already studied[1] but also certain derivatives of this compound satisfy these requirements. Bulk molecules of these cage hydrocarbons plug the wide part of the β-CD cavity containing the arene molecule, providing for isolation of the latter from oxygen and emission of long-lived RTP in the presence of oxygen.

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