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Current state of the art in cyclodextrin-induced room temperature phosphorescence in the presence of oxygen

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Abstract

Cyclodextrin-induced room temperature phosphorescence was reviewed in detail in the presence of oxygen. The mechanism aspects involve in the space-regulation, core-shell complex, covering effect and the formation of the microcrystals. The third and fourth components, include halide alkanes and alcohols, alkanes without heavy atom, alcohols, aliphatic amines and surfactants.

Keywords: Room temperature phosphorescence; Cyclodextrin; Non-deoxygenation

1. Introduction

Phosphorescence of organic molecules can be defined as the radiative transtion originating from the lowest excited triplet state, T_1, to the singlet ground state, S_0. In contrast to fluorescence, singlet S_1 to singlet S_0, phosphorescence is a spin-forbidden process and phosphorescence quantum yield is usually lower, which can be expressed as Eq. (1) [1]:

$$\phi_{\mathrm{p}} = \vartheta_{\mathrm{ISC}}\vartheta_{\mathrm{P}} = \frac{k_{\mathrm{ISC}}}{k_{\mathrm{ISC}} + k_{\mathrm{f}} + k_{\mathrm{nf}} + \sum k_{\mathrm{q,f}}[Q]} \frac{k_{\mathrm{p}}}{k_{\mathrm{p}} + k_{\mathrm{np}} + \sum k_{\mathrm{q,p}}[Q]} \quad (1)$$

where ϑ_{ISC}, ϑ_{P} are the quantum efficiency of intersystem crossing and phosphorescence processes, respectively. k_{ISC} is the intersystem crossing rate constant, k_{f} and k_{p} are the rate constants of fluorescence and phosphorescence, respectively, k_{nf} and k_{np} are the rate constants of non-radiative decay, and $\sum k_{\mathrm{q,f}}[Q]$ and $\sum k_{\mathrm{q,p}}[Q]$ are the sums of all effective (unimolecular) quenching rate constants of fluorescence and phosphorescence, respectively. From Eq. (1), it can be seen that phosphorescence quantum yield can be improved by means of two ways. One is to increase k_{ISC} by internal or external spin-orbit coupling, named heavy atomic effect, which mixes pure singlet and triplet states to produce states with a mixed character in spin multiplicity. This way is exclusive in the review. Another is to reduce non-radiative rate constants, (k_{np}, $\sum k_{\mathrm{q,p}}[Q]$) and (k_{nf}, $\sum k_{\mathrm{q,f}}[Q]$). In vitreous body at low temperature, the non-radiative processes can be inhibited largely, and high-analytical sensitivity of phosphorimetry and well-defined fine structures of phosphorescence spectra can obtained thereby. However, the additional devices for getting cryogenic conditions were required and the selection of solvents was restricted because of the crack of the vitreous body that affected the analytical characteristics of phosphorimetry. Therefore, the room temperature phosphorescence has been of the interesting topics in analytical chemistry for a long time. Up to date, to minimize the nonradiative and quenching processes for high ϕ_{P} at room temperature, various phosphorescence procedures in methodologies, for example, solid substrate-RTP (SS-RTP), based on immobilizing phosphores on solid supports or matrix, liquid-RTP, such as, micelle-stabilized room temperature (MS-RTP), cyclodextrin-induced room phosphorescence (CD-RTP) etc., based on protecting phosphor from quenching in the presence of media and so on have been established. Specially for liquid-RTP, the following three factors have been considered

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conventionally as necessary conditions for getting RTP [2]: (a) heavy atom perturbation for enhancing intersystem crossing rate, further enhancing the population of triplet state; (b) organization medium for protecting the triplet state from quenching of oxygen or other quenchers; and (c) complete removal of dissolved oxygen in sample solution. However, in the recent years more and more investigation showed that it is not indispensable to have three conditions at the same time. In fact, the analytically useful RTP signal could be obtained under combination of any two of the above conditions, namely: (a) complete removal of dissolved oxygen from the solution in the presence of heavy atom perturbers without any organization medium, resulting in non-protected fluid RTP [3–6]; (b) rigid microenviroment, even without any heavy atom compound, which was able to confine the motion of phosphors and keep phosphor and quencher out of the collision distance, avoiding efficient quenching of phosphorescence, resulting in the anti-oxygen-quenching RTP or non-deoxygenated RTP [7,8]. Up to date, four kinds of liquid RTP methodologies without deoxygenation have been reported. The first one is the CD system based on the inclusion of CD with guest molecule/s, including phosphor and other small organic molecule as a space-regulator in matching dimension and on the formation of microcrystals [9–18]. The second is sodium deoxycholate system reported recently [7]. It is believed that the deoxycholate molecules aggregate exist as dimmers under certain conditions and the analyte is sandwiched in the rigid, hydrophobic, and probably also oxyphobic region between two back to back molecules in the dimmer [7,8,19,20].The third is the colloidal microcrystal system proposed by Cline Love [21–23] and developed by Liang et al. [24]. Additionally, if bromonaphthalene is embedded in the inorganic sol–gel vitreous particles formed by hydrolysis of tetramethoxysilane, strong phosphorescence would be produced even in the presence of oxygen under excitation, which was successfully applied to sensing heavy metal ion and pH in the aqueous FIA system [25–27]. The review specifically focuses on the current state of the art in the non-deoxygenated CD-RTP involving in the effects of the third or the fourth component on CD-RTP and the enhancement mechanism.

2. Mechanism aspects of non-deoxygenated CD-RTP

Non-deoxygenated room temperature phophorescence can be obtained mainly by interaction of cyclodxtrin–phosphor inclusion complex with the third or with both third and fourth components. The third and fourth component is defined here as the substance that can interact with cyclodextrin–phosphor inclusion complex and affect the photophysical, thermodynamic and kinetic properties of the complex remarkably. The mechanism of the interaction of the third or fourth component with the cyclodextrin–phosphor inclusion complex has been put forward as follows.

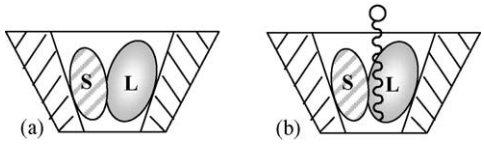


Fig. 1. Ternary and quarternary inclusion complex model (S is space-regulator or the third component and L is phosphor). a, Ternary complex; b, quarternary inclusion complex.

2.1. Space-regulating

The third or the third and the fourth component together with the phosphor enter spontaneously the cavity of CD, and the motion of the phosphor in the cavity is largely confined. On the other hand, there is no enough void space to contain the oxygen molecule, which restricts the contact of the excited triplet phosphor with the ground triplet oxygen molecule. As a result, the non-radiation decay of the triplet state of the phosphor is inhibited. Obviously, both the volume and the space matching degree of the third or the fourth component with the void space of inclusion complex has the important influence on non-deoxygenated RTP. The equilibrium of the inclusion complexes can be shown in Eqs. (2)–(4).

$$\mathrm{CD/L} + \mathrm{T} \rightleftharpoons \mathrm{CD/L/T} \quad (2)$$

$$\mathrm{CD/L} + \mathrm{T} + \mathrm{F} \rightleftharpoons \mathrm{CD/L/T/F} \quad (3)$$

$$\mathrm{CD/L/T} + \mathrm{F} \rightleftharpoons \mathrm{CD/L/T/F} \quad (4)$$

where L is phosphor, T is the third component, F is the fourth component. The space regulation can be depicted in Fig. 1 as the cartoon models [28,29].

2.2. Core-shell complex

The phosphor or the phosphor with the third even the fourth component is longitudinally encapsulated between the CD molecules, the secondary cyclodextrin hydroxylic rims face each other. The cartoon model of the inclusion form is drawn in Fig. 2, and what phosphor to cyclodextrins is close similar to what core to shell of nut. (S is cyclopentanol in Fig. 2b [30]).

Hamai [31,32] observed the RTP of 6-bromo-2-naphthol (BN) in aerated aqueous solution from 2:1 α-CD/BN inclusion complex, whereas a 1:1 α-CD/BN inclusion complex did not phosphoresce at room temperature. ^{1}H·NMR signals of BN indicated that the first α-CD molecule accommodated

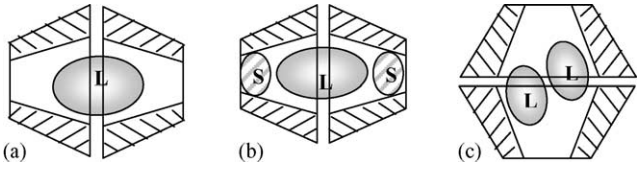
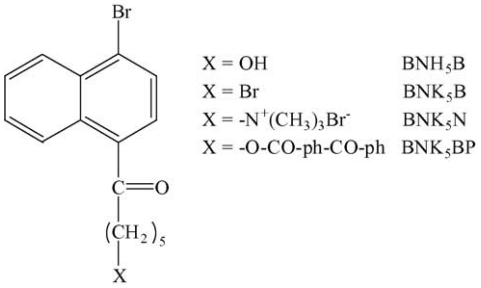


Fig. 2. Cartoon models of core-shell complex (S is space-regulator or the third component and L is phosphor). a, α-CD_2/L; b, β-CD/L/S_2; c, β-CD_2/L_2.



Scheme 1. Structure of phosphorescence probes. BNK_5BP: *p*-benzoyl [5-(4-bromo-1-naphthoyl)-1-pentyl]benzoate; BNK_5A: 5-(4-bromo-1-naphthoyl)-1-pentanol; BNK_5B: 1-bromo-5-(4-bromo-1-naphthoyl)pentane.

an end substituting a Br atom on a naphthalene ring in BN and then the second α-CD molecule encapsulated the other end substituting a hydroxyl group on the same naphthalene ring to form the 2:1 α-CD/BN inclusion complex. The hydrophobic Br end of BN interacted with the first α-CD by entering its hydrophobic cavity, and the hydroxyl end of BN gains stability and maximum protection from the solvent by entering, at least part way, the core of the second α-CD [33].

Grabner et al. [34] reported that models for 2:2 complexes of naphthalene with β-CD, which showed the important contribution of intramolecular hydrogen bonding between the secondary hydroxylic groups to the stabilization of the cavity consisting of two hosts.

Turro et al. [35] investigated the photophysical behaviors of several synthesized phosphorescence probes, BNK_5B, BNK_5A, BNK_5BP as shown in Scheme 1, in γ-CD aqueous solution. They found that the probe molecules displayed two decay behaviors: the fast decay and the slow decay in the solution containing γ-CD, and the results of the lifetime measurements were listed in Table 1. It could be found that the oxygen could completely quench the fast decay component, while the lifetime of the slow decay was not obviously influenced in the presence of or absence of oxygen. So it was inferred that the fast decay component exist as the 1:1 complex of the phosphor and the γ-CD, while the slow component exist as the 1:2 complex of the phosphor and the γ-CD.

Brewster et al. [36] constructed a temperature sensing system consisting of ternary 1:2 complex of 6-bromo-2-naphthol and α-CD for 1.6–59.7 °C based on the lifetime measurements of the complex. The largest value reported for an optical thermometer, and the small standard deviations associated with the values of τ revealed that temperature differences smaller than 0.1 °C could be measured. The relationship associated with τ and temperature was expressed as:

$$\log \frac{1}{\tau} = C + \frac{E_a}{2.303R}\frac{1}{T} \quad (5)$$

Table 1
Lifetime of the probe molecules in the γ-CD solution

Probe	Lifetime, τ (ms)		
	Fast decay	Slow decay/N_2	Slow decay/O_2
BNK_5BP	0.506	3.9	3.8
BNK_5A	0.645	3.3	2.5
BNK_5B	Small	3.4	2.8

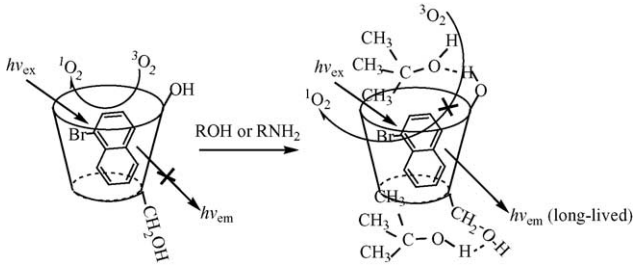


Fig. 3. Covering effect of alcohol.

2.3. Covering effect

The probability of forming H-bonding between the third or the fourth component, such as alcohol and amine molecules and primary or secondary hydroxyls of CD rims has been speculated by a number of authors [14,37,38]. Chain part of the third or the fourth component cover the entrance of the CD cavity as H-bonding forms, as shown in Fig. 3, which prevents the quenchers, especially, oxygen molecule from entering the CD cavity. However, it is a pity that the model of H-bonding form is still a speculation that lacks direct evident experiment data by far. The further work should focus on it.

The microcrystals at nano/micro scale could be formed in the presence of the excessive third or fourth component, especially, alkane with/without heavy atom group, because of the decrease of CD solubility. The microcrystals consist of CD and its various inclusion complexes, and make the rigidity of miroenvironment in which phosphor dwells enhanced further, inducing the stronger phosphorescence. In 1994, Jin et al. [12] found that the strong RTP signal of some polyaromatic hydrocarbons and nitrogen heterocycles could be observed in the CD solution in the presence of cyclohexane without any component containing heavy atom even without deoxygenation. The observation was attributed to the microcrystals suspended in solution, as shown in Fig. 4. Escandar

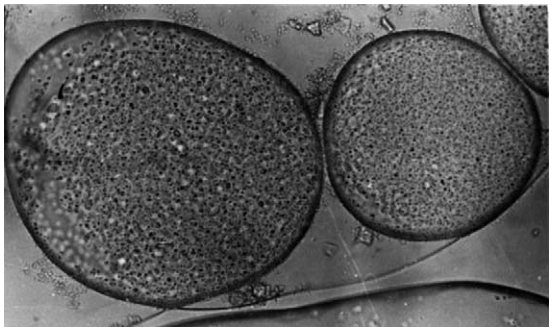


Fig. 4. Microscope photograph of cloudy suspension microcrystals (Magnification, 300×, taken in author's laboratory and unpublished ever, the conditions are same to that in Ref. [12]).

and Boldrini [39] also found that the formation of microcrystals was very important to strengthen the intensity of the RTP of the system.

3. Detail aspects of the third and fourth components in non-deoxygenated CD-RTP

Alkanes, alcohols and their halides, amines, surfactants are frequently used in the non-deoxygenated RTP. They may act as one or more of the following roles: (1) heavy atom perturber, (2) space regulator, (3) covering reagents on CD rims, (4) microcrystal inducer.

3.1. Halide alkanes and alcohols

Halide alkanes are most widely used for inducing the non-deoxygenated CD-RTP. They act not only as heavy atom perturber, which could enhance the intersystem crossing rate and the quantum yield, but also as space regulator entering the CD cavity. Muñoz de la Peña [40] investigated the CD-RTP of α-naphthylacetic acid in the presence of 1,3-dibromopropane. They thought that the formation of microcrystals was necessary for getting RTP signal.

Besides chain halide alkanes, halide cycloalkane is also a good heavy atom perturber. Wei et al. [41] found that strong RTP signal could be observed from the system of β-CD/7-methylquinoline even without deoxygenation when 1-bromocyclohexane was used as heavy atom perturber. They thought that 1-bromocyclohexane had the effect of both heavy atom and space filling. Because 1-bromocyclohexane had the structure and conformation similar to glucopyranose units in CD molecule, it could well fit with CD cavity and displace oxygen and high energy water molecules from the cavity. Consequently, ternary complex may become tight and oxygen molecule could hardly enter the cavity to quench RTP of the phosphor. Zhu et al. [42] showed that the RTP of ternary complex of β-CD/bromocyclohexane/4-iodo-4′-ethyl-biphenyl increased dramatically when the fourth component butanol was added.

Halide alcohols can also act as the third component, and the solution is transparent. Hamai [43] firstly used 2-bromoethanol as well as 2,3-dibromopropannol as the heavy atom perturber and determinated the formation constant of the ternary complex β-CD/brominated alcohol/acenaphthene. In the literature [44,45], RTP of acenaphthene are more intensive when 2,3-dibromopropanol or 2-bromoethanol acted as the third components.

3.2. Alkanes without heavy atom

For the phosphor bearing heavy atom group, the third component without heavy atom, such as chain- or cycloalkanes and chain- or cycloalcohols and amines, etc., also work well in inducing non-deoxygenation CD-RTP. Typically, cyclohexane is one of the most widely used

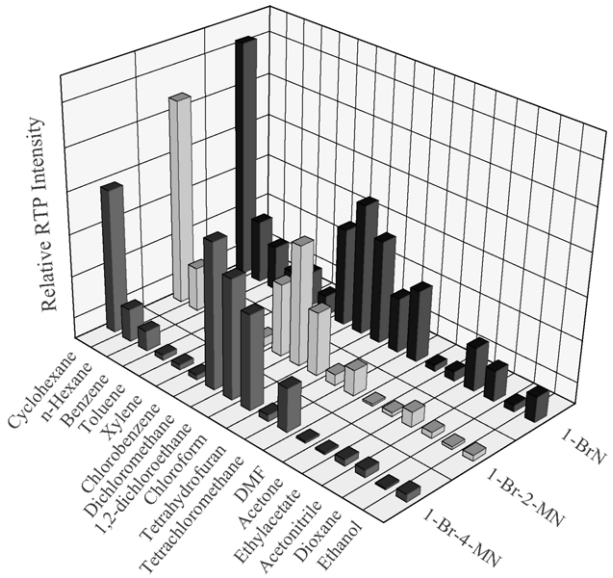


Fig. 5. The histogram of enhancement of organic solvents to CD-RTP without deoxygenation. Organic solvent, 1%; [phosphor] = 1×10^{-5} mol/L; [β-CD] = 8×10^{-3} mol/L.

compounds among them and is almost the same in function as bromocyclohexane mentioned above except for heavy atom effect. The phosphorescence lifetime and polarization of β-CD/cyclohexane/bromonaphthalene ternary complex realized that the three-dimensional conformation of cyclohexane benefited the formation and the stability of the ternary complex. As a result, strong RTP intensity was obtained without deoxygenation [16]. Zhang et al. [9] proposed the on–off effect of six-membered carbocyclic compounds on non-deoxygenation CD-RTP and cyclohexane was the best third component among the compounds investigated. The enhancement order of RTP was as the follows: cyclohexane > bromocyclohexane > cyclohexanol.

Mu et al. [2] investigated the effect of generally used organic solvent on RTP of 1-bromonaphthalene, 1-bromo-2-methynaphthalene, 1-bromo-4-methylnaphthalene and potassium 6-bromo-2-naphthylsulfate in β-CD aqueous solution in the presence of dissolved oxygen. The enhancement of the different solvent could be divided into the following three groups as order: cyclohexane > dichloromethane ∼ 1,2-dichloroethane ∼ chloroform > tetrahydrofuran ∼ ethylacetate ∼ acetonitrile, as shown in Fig. 5. The enhancement effect of tetrahydrofuran to all probes used and the enhancement effect of ethylacetate and acetonitrile to 1-bromonaphthalene was unexpected.

As voluminal effect in space-regulation, the adamantane should be better than cyclohexane, which was first used as the third component in CD-RTP by Nazarov et al. [15]. The difference between them was that admantane more tightly than cyclohexane closes the upper part of the cavity due to the higher binding energy. In addition, admantane jumps out above the upper cut of the cavity to a greater extent than cyclohexane. By monitoring the effect of

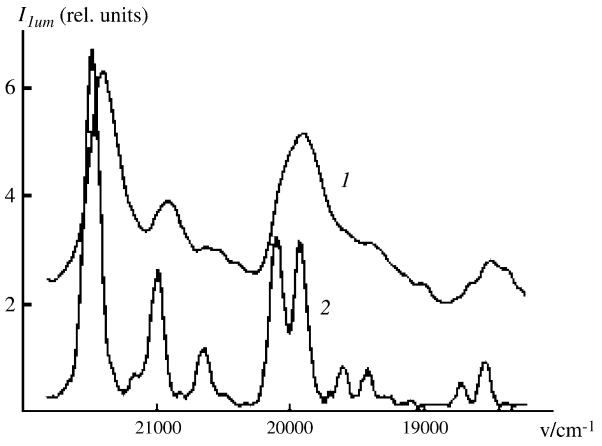


Fig. 6. Phosphorescence of the naphthalene-d_8/cyclodextrin-damantane complex (1.29 and 2.77 K).

adamantane on the RTP intensity and lifetime of cyclodextrin/naphthalene and cyclodextrin/naphthalene-d_8, they observed that the rigidity of the systems increased greatly in the presence of adamantane, and the lifetime of the system of cyclodextrin/naphthalene-d_8/adamantane reached 10.3 s! The phosphorescence spectra was shown in Fig. 6.

Peng et al. [46] compared five cyclic third components, cyclohexane, methylcyclohexane, perfluorocyclohexane, perfluoromethylcyclohexane and adamantane, in inducing strong CD-RTP of 1-bromonaphthalene without deoxygenation. It was found that the enhancement order of five compounds was as follows: cyclohexane > adamantane > methylcyclohexane > perfluorocyclohexane > perfluoromethylcyclohexane.

3.3. Alcohols

The effect of alcohols on CD-RTP is a very interesting topic. The volume and the spatial conformation of alcohols are very important to the formation of the stable ternary complex which were focused on early by fluorescence measurement using pyrene as the model compound [30,47–50]. Hamai [47] noticed that alcohol affects the absorption spectrum of a pyrene aqueous solution containing β-CD. The absorption changes indicated the formation of a 1:1:1 inclusion complex among pyrene/β-CD/alcohol. Primary alcohols as well as cyclic alcohols exhibited similar absorption changes when they formed the ternary complex and the formation constant of 1-propanol/β-CD/pyrene was the largest. Nelson et al. [48] concluded by fluorescence lifetime that the addition of alcohol fairly well protected pyrene in the CD cavity, indicating that there was a special relationship between the alcohol and γ-CD. The larger volume of the alcohol was, the longer the lifetime of the phosphor was, and the better the volume of the alcohol molecule matched the void space of β-CD/pyrene, the more stable the complex was [30]. The formation constant of *n*-butanol/β-CD/pyrene was the largest one among all the straight chain alcohols. Cyclopentanol matched β-CD best among all the branched and cyclic and aromatic alcohols studied. Another work indicated that the effect of the conformation and the volume of the alcohol on the ternary complex was less notable in the γ-CD system than in the β-CD system [49]. Because the interior space of γ-CD is larger than that of the other CD molecules, alcohol could enter or exit the γ-CD more easily [50].

In 1993, Ponce et al. [51] showed that intense phosphorescence was observed when alcohols were introduced to a glucosyl-modified cyclodextin (Gβ-CD) aqueous solution, including 1-bromonaphthalene (1-BrNp). The association of 1-BrNp to Gβ-CD was increased in the presence of the alcohols ($K = 800\ \text{mol}^{-1}$ L in the absence of ROH and $K = 1900$–$3400\ \text{mol}^{-1}$ L in the presence of ROH with the exception of cyclohexanol where $K = 760\ \text{mol}^{-1}$ L). The phosphorescence enhancement induced by alcohol was related to its effectiveness in shieding photoexcited 1-BrNp from oxygen. The rate constants for oxygen quenching decreased generally as the bulkiness of the alcohol increased. Accordingly, tert-butyl alcohol and cyclohexanol gave rise to the smallest oxygen quenching rate constants and the highest emission quantum yields among the systems they studied. For example, the quantum yield of the system containing tert-butyl alcohol was 0.034, about 170 times higher than the system containing 1-butanol. The phosphorescence lifetime was 4.6 ms, about 10 times larger than the system containing 1-butanol. The oxygen quenching rate of the system containing tert-butyl alcohol was only about 4% ($8.87 \times 10^5\ \text{mol}^{-1}\ \text{s}^{-1}$) of that ($231 \times 10^5\ \text{mol}^{-1}\ \text{s}^{-1}$) of the system containing 1-butanol.

Zhang and Johnson [52,53] established smartly a technique by measuring over-saturated dissolved oxygen concentrations from 0 to 10.9 mM (870% saturation). This is one of the best examples of the application of non-deoxygenation CD-RTP.

3.4. Amines

The effect of aliphatic or aromatic amines on the β-CD/pyrene complex was studied by fluorescence enhancement or fluorescence quenching [54,55]. Kano et al. [54] proposed that pyrene binds to the primary hydroxyl rim of the cavity, forming a pyrene-capped CD complex with trimethylamine or dimethylamine occupying the residual void space inside the CD cavity. Will et al. [55] reported a 2:1 complex β-CD/pyrene in the presence of either tert-butlyamine (TBA) or *n*-propylamine (PA). At lower amine concentration, the role of the amine was to shield pyrene from the bulk aqueous phase. However, at higher TBA concentration, there exist a competitive equilibrium between the amine and pyrene for the β-CD cavity. The formation constants for the various complexes in the presence of either amine were estimated to be of comparable order of magnitude. Hamai [56] reported that a 1:1:1 ternary inclusion complex was formed among 1-pyrenesulfonate(PS)/β-CD(CD_x)/aniline(A) when concentration of aniline was lower. However, the more complicated inclusion complex, such as PAC AC or PAC C formed

at high concentration of aniline, which might involve in the charge transfer interaction. Chen et al. [57] investigated the effect of different amines on α-BrNp/β-CD RTP emitting system. The RTP intensity was increased with the increase of the length of the straight alkyl chain and the amount of the branch chain. When the concentration of amine was just twice of that of β-CD, the enhancement effect of RTP was the largest.

The effect of the amines on non-deoxygenation CD-RTP is similar to that of the alcohols. However, the difference between them is that the nitrogen in amine molecules, especially, aromatic amine ones, will probably quench the RTP or fluorescence.

3.5. Surfactants

Surfactants are amphiphilic compounds. Their hydrophobic part tends to enter β-CD cavity, as a result the microenviroment of β-CD cavity will be changed. It was found [58] that the fluorescence of pyrene could be enhanced in the solution of non-ionic surfactant Triton X-100 and β-CD. When the concentration of Triton X-100 is below CMC, a β-CD/pyrene /Triton X-100 ternary complex was formed, which expressed in Eq. (6). On the other hand, when the concentration is above CMC, pyrene transferred from the cavity of CD to the microenvironment of micellar solution. The *p*-substituted phenyl group in Triton X-100 and OPE-10 molecules displayed fluorescence from monomer itself below CMC or in CD inclusion complex, while displayed broad, structureless fluorescence from aggregated species that occur when micelles are formed above CMC. So the character of both surfactant as an intrinsic probe with phosphorescence signal together can be used to monitor the synergetic effect on inclusion complex formation.

$$\mathrm{M} \times \mathrm{L} + \mathrm{CD} \overset{>\mathrm{CMC}}{\longleftarrow} \mathrm{S} + \mathrm{CD} \times \mathrm{L} \overset{<\mathrm{CMC}}{\longrightarrow} \mathrm{S} \times \mathrm{CD} \times \mathrm{L} \qquad (6)$$

where M is micelle, L is luminophor and S is surfactant monomer.

Du et al. [10,59] reported that cationic surfactants could induce bright phosphorescence of 1-BrN in the β-CD solution in the format of β-CD/sodium dodecylbenzene sulfonate (SDBS)/1-BrN 1:1:1 ternary complex. The phenyl ring of SDBS was encapsulated in the cavity of β-CD and a part of the hydrophobic hydrocarbon tail and the polar head group of SDBS located outside the cavity. This form provided a effective protection for the phosphor in the β-CD cavity [60–62].

Wu et al. [63] investigated the synergetic effect of β-CD/1-bromo-4-(bromoacetyl)-naphthalene (BBAN)/Brij30 ternary complex on inducing non-deoxygenation RTP by HNMR and solvatochromic probe. Chemical shift changes in H-5 of β-CD were larger than those in H-3, which indicated that the phosphor was included in the hydrophobic cavity at the narrower end. H-6 also witnessed relatively large changes in its chemical shifts. So the outside-exposed part of BBAN might be “locked” by the seven groups of methylol in the short section of the truncated cone molecule. NMR spectra also indicated that the alkyl chain of Brij30 was partially inserted into the β-CD cavity so as to enhance the rigidity of the cavity that BBAN dwelled in, whereas the polar moiety laid outside of the cyclodextrin molecule at the narrower end. Additionally, ROESY spectra validated the reciprocity between Brij30 and β-CD. To further elucidate the so-called “synergetic effect”, fluorescence measurements of solvatochromic probe 4-(dicyanomethylene)-2-methyl-6-[4-(dimethylamino)stryryl]-4H-pyram(DCM) were also conducted in the same microenviroment as that of BBAN, and the evident shifts to shorter wavelength of emission spectra implied that the BBAN resides in a more rigid environment with lower dielectric constant in the presence of both β-CD and Brij30 that exist when β-CD and Brij30 were present individually.

4. Halogen substituted CD-RTP

Heavy atom compound acts as perturber in CD-RTP system to enhance intersystem crossing rate, further enhance the population of triplet state. There are two ways to introduce heavy atom to CD-RTP system: one is that heavy atom perturber used as the third or the fourth component is added into the system that has been mentioned above. The other is that the halogenated CD acts as both host and a heavy atom perturber towards non-halogenated guests. Several literatures have been reported about this. Femia and Cline Love [64] synthesized heptakis(6-bromo-β-cyclodextrin) by replace β-CD’s primary hydroxyls with bromine which could form inclusion complex with several aromatic hydrocarbons in the solution mixed *N*,*N*-dimethylformmide with water, and this system induced strong RTP. However, the aromatic hydrocarbon outside the cavity of CD could not phosphoresce. Hamai et al. [65,66] investigated RTP of iodine substituted CD inclusion complex. Compared with parent β-CD, 6-iodo-6-deoxy-β-CD as a heavy atom perturber was more than 1.2 times as effective in enhancing the RTP of 2-chloronaphthalene [65]. However, 6-deoxy-6-iodo-α-CD which could form 2:1 inclusion complex with 6-bromo-2-naphthol could reduce the RTP intensity by 18% relative to that for the 2:1 inclusion complex composed of parent α-CD [66].

5. Conclusions

Compared with fluorescence measurement in liquid system, generally RTP looks like more unconvenient because the dissolved oxygen has to be removed. Moreover, when the inert gas is purged to deoxygenation, the reagents with low boiling point will be evaporated more quickly, which will increase the analytical unaccuracy. The non-deoxygated CD-RTP has been established to overcome these shortcomings in the recent years. Compared with the common CD-RTP, the non-deoxygenated CD-RTP has the following advantages:

(1) it is more convenient and comparable with fluorescence measurement in procedures; (2) it can be expected to be applied to those system in which deoxygenation procedures strongly affect the detection, for example, pH monitor or temperature sensor in waters or some biological samples [36]; (3) the use of the third or fourth components introduces the additional selective or recognition factor for analytical propose. In near future, non-deoxygenated CD-RTP may be developed further in the following aspects: (1) the more suitable third or fourth component will be found for improving the accuracy, sensitivity and selectivity; (2) the other new hosts which has the structure similar to cyclodextrins will be found to act as a protective medium of non-deoxygenation RTP, for example, cucurbit[n]uril or its analogues [67,68] might open a new horizon for the new generation host of RTP; (3) the inclusion complex of CD is formed not only in solution but also in solid soft film [69], which may provide a new point of view in microextraction-phosphorescence analysis similar to the single-use phosphorescence sensor [70]; (4) the mechanisms of CD-RTP in the presence of dissolved oxygen will be investigated more deeply.

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