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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]:

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

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.

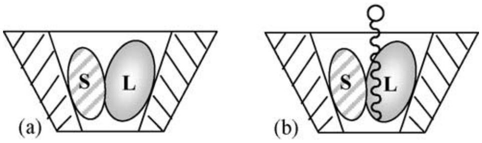

Fig. 1. Ternary and quarternary inclusion complex model (S is space-regulator or the third component and L is phosphor). a, Ternary complex; b, quarternary inclusion complex.

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).

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

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

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

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

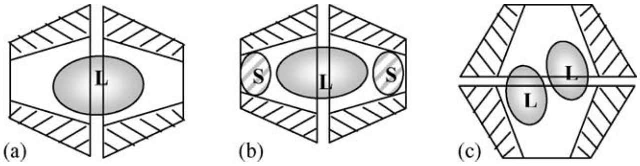

Fig. 2. Cartoon models of core-shell complex (S is space-regulator or the third component and L is phosphor). a, α-CD_2/L; b, β-CD/L/S_2; c, β-CD_2/L_2.