

Cyclodextrin-Enhanced Room-Temperature Phosphorescence

Abstract

Cyclodextrin-enhanced room-temperature phosphorescence (CD-RTP) is an analytical technique that offers well-resolved spectra and subpicogram detection limits. When polynuclear aromatic hydrocarbons (PAHs) are included in cyclodextrin molecules in the presence of a heavy-atom moiety such as 1,2-dibromoethane, they exhibit intense, well-defined phosphorescence emissions, often with distinct vibrational structure. Moreover, the cyclodextrin moiety inhibits quenching of PAH phosphorescence by O_2 present in the bulk solution.

Introduction

Cyclodextrins (CDs) are made up of glucose monomers coupled to form a rigid, conical structure with an interior hydrophobic cavity. The most common cyclodextrins, α , β , and γ , are composed, respectively, of six, seven, and eight monomers. Initially, each cyclodextrin contains one or more water molecules, produced during the monomer coupling. Because these included water molecules are easily displaced by hydrophobic species that fit into the cyclodextrin interior, cyclodextrins have a unique ability to form stable inclusion complexes with a variety of molecules.

This inclusion capability has led to an important use of cyclodextrins in luminescence spectroscopy. Cyclodextrins have been found to enhance fluorescent and phosphorescent emissions from molecules present in the CD cav-

ity.^{1,2,3,4,5} Of particular interest is the phenomenon of CD-RTP, which suggests a highly selective analytical technique based on the molecular geometry of the lumiphor.

Chromophores such as PAHs exhibit virtually no phosphorescence in conventional fluid media. Scypinski and Cline Love report, however, that intense room-temperature phosphorescence occurs when these carcinogens are present, with an external heavy atom, in the cavity of cyclodextrin.⁴ Fig. 1 depicts the inclusion of a phenanthrene molecule within the cavity of a β -cyclodextrin. Scypinski and Cline Love also have observed CD-RTP in nitrogen heterocycles and bridged biphenyls.⁵

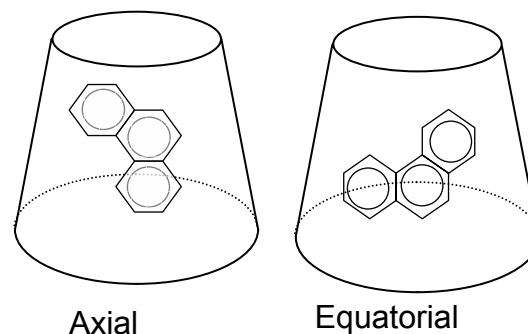


Fig. 1. Axial and equatorial inclusions of phenanthrene within β -cyclodextrin.


¹ Hoshino, M.; Imamura, M.; Ikehara, K.; Hama, Y. *J. Phys. Chem.* **1981**, 85, 1820.

² Turro, N.J.; Bolt, J.D.; Duroda, Y.; Tabushi, I. *Photochem. Photobiol.* **1982**, 35, 69.

³ Turro, N.J.; Cox, G.S.; Li, X. *Photochem. Photobiol.* **1983**, 37, 149.

⁴ Scypinski, S.; Cline Love, L.J. *Anal. Chem.* **1984**, 56, 322.

⁵ Scypinski, S.; Cline Love, L.J. *Anal. Chem.* **1984**, 56, 331.



A description of the experiments with PAHs illustrates CD-RTP, and helps to assess its advantages.

Experimental method

Each PAH analyte was dissolved in either methanol or acetone, after which the solvent was gently evaporated. Addition of a 0.1–0.5-mL aliquot of 1,2-dibromoethane was followed by dilution with 0.01-M aqueous cyclodextrin solution. Upon vigorous shaking, the complex formed. The resulting cloudy solution was then deoxygenated for fifteen minutes with nitrogen gas prepurified in an Alltech Oxy-Trap™.

All spectra were taken on a modular Fluorolog® spectrophotometer with double excitation and emission monochromators. A 450-W xenon CW lamp was used as the excitation source, and a cooled R928 photomultiplier (PMT) tube as the detector. Slits were 14.4 nm (excitation) and 3.6 nm (emission). Scan rate = 1 nm s⁻¹. All emission spectra were corrected for fluctuations in lamp intensity and PMT responses.

Results and discussion

The investigation showed the CD-RTP technique to be extremely sensitive, producing intense, well-structured phosphorescence signals at nanomolar concentrations. Detection limits of two typical phosphors, phenanthrene and acenaphthene, were estimated at 5×10^{-13} M and 1×10^{-11} M, respectively. Although the excited triplet state is known to be susceptible to oxygen quenchers, inclusion of the lumiphor inside the cyclodextrin cavity was observed to offer some protection against quenching by oxygen molecules in the bulk solution. In these experiments, 10%

to 40% of the RTP remained after aeration of the sample—a signal still strong enough for analysis.

The success of CD-RTP with PAHs depends on the formation of a proposed three-component complex of cyclodextrin, lumiphor, and external heavy atom. The internal cavity of the cyclodextrin must be large enough to accommodate both the lumiphor, which must fit at least partially inside, and the heavy atom.

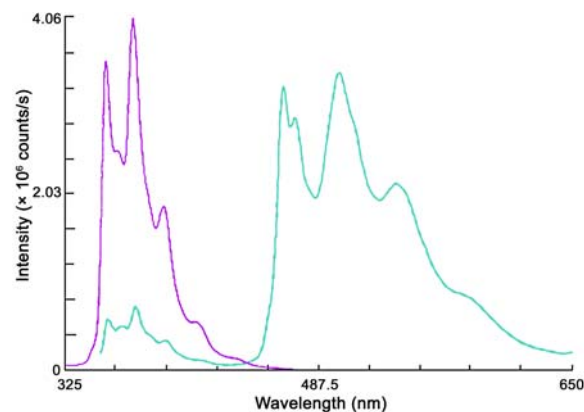


Fig. 2. Corrected emission spectra ($\lambda_{exc} = 300$ nm) of 5×10^{-5} -M phenanthrene in 0.01-M β -cyclodextrin alone (purple) and with 0.58-M dibromoethane (blue-green).

Fig. 2 shows the luminescence spectra for phenanthrene included in β -cyclodextrin, with and without the addition of the “heavy-atom” dibromoethane. Because the heavy-atom moiety enhances spin-orbit coupling and the rate of intersystem crossings, addition of dibromoethane quenches much of the fluorescence while intensifying the phosphorescence.

The physical dimensions of the cyclodextrin cavities, relative to the geometry of the individual PAH, determined the most effective cyclodextrin-form for each analyte. For example, although the phenanthrene molecule fits

inside the cavity of the α -cyclodextrin, which has an inner diameter of 0.6 nm, there is apparently not enough room remaining to accommodate the dibromoethane molecule. Both phenanthrene and dibromoethane molecules, however, can be included in the larger β -cyclodextrin cavity, with an inner diameter = 0.78 nm. Fig. 3 compares the luminescence spectra for the same solution of phenanthrene and dibromoethane in α - and β -cyclodextrin. Anthracene, larger than phenanthrene, phosphoresced only weakly in β -cyclodextrin, but γ -cyclodextrin, with an inner diameter = 1.0 nm, induced stronger emissions.

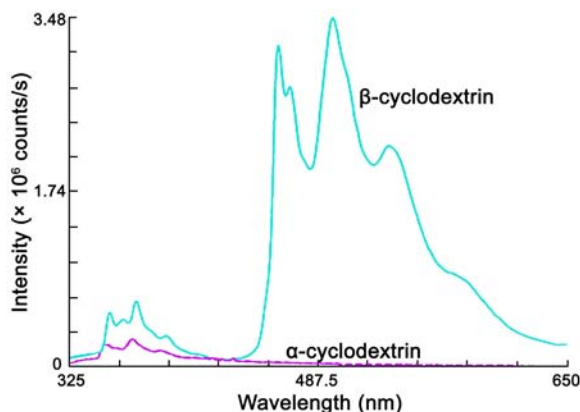


Fig. 3. Corrected emission spectra ($\lambda_{\text{exc}} = 300$ nm) of 5×10^{-5} -M phenanthrene in 0.01-M β -cyclodextrin (blue-green) and in 0.01-M α -cyclodextrin (purple). [dibromoethane] = 0.58 M.

The geometrical limitations imposed by CD-RTP may be exploited as a selective means of analysis based on molecular size and shape. For example, it is possible to discriminate between naphthalene, which can phosphoresce in β -cyclodextrin, and its bulkier derivative 1-phenyl-naphthalene, which only fluoresces under the same conditions.

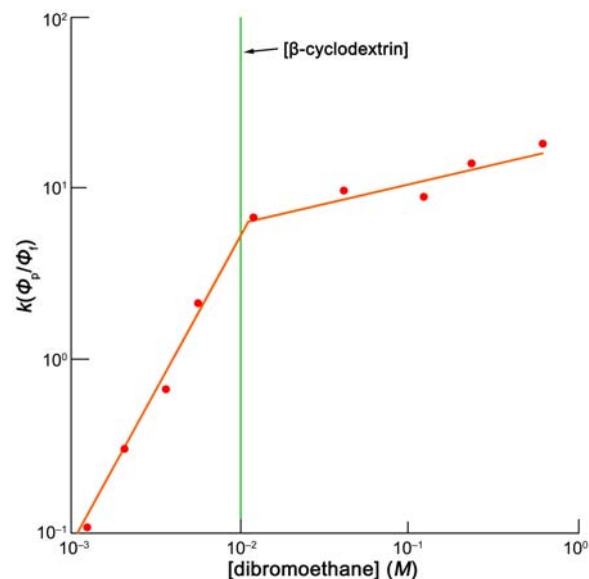


Fig. 4. Dependence of the relative phosphorescence intensity of 5×10^{-5} -M phenanthrene on the concentration of dibromoethane in 0.01-M β -cyclodextrin. $k(\Phi_p/\Phi_f)$ is the ratio of the integrated intensities of the corrected phosphorescence to corrected fluorescence spectral profiles. $\lambda_{\text{exc}} = 300$ nm.

In these experiments, the phosphorescence intensity of the included PAH was found to depend on the concentration of the heavy-atom moiety and on the concentration of cyclodextrin. Fig. 4 illustrates the relationship of the phosphorescence intensity of phenanthrene to the concentration of dibromoethane. As long as the dibromoethane concentration is low compared to cyclodextrin, dibromoethane molecules added into the solution are incorporated in the trimolecular inclusion complex, causing a sharp increase in phosphorescence intensity. When the dibromoethane concentration reaches that of the cyclodextrin, so that complexation is nearly complete, further addition of dibromoethane enhances the phosphorescence only slightly.

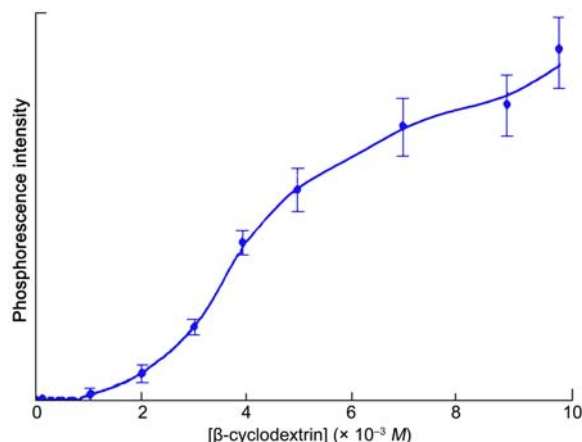


Fig. 5. Dependence of phosphorescence intensity (number of photons) of 5×10^{-5} -M phenanthrene on the concentration of β -cyclodextrin with 0.58-M dibromoethane present. $\lambda_{\text{exc}} = 300$ nm, (error bars are $\pm 10\%$ RSD); $\lambda_{\text{em}} = 501$ nm.

Fig. 5 demonstrates the dependence of phosphorescence intensity on the cyclodextrin concentration. The S-shaped curve traces the phosphorescence intensity of the phenanthrene-dibromoethane solution as β -cyclodextrin is added. The initial steep slope is attributed to the sharply-increasing probability that a phenanthrene molecule exiting the cavity of a cyclodextrin-dibromoethane molecule will find another cyclodextrin-dibromoethane molecule nearby.⁴

Conclusion

Cyclodextrin-enhanced room-temperature phosphorescence (CD-RTP) shows promise as a sensitive analytical technique. Sample preparation is simple, data-acquisition and processing are easily automated with a Fluorolog[®] spectrometer, and the result is an intense, well-structured RTP signal. CD-RTP offers the advantages of increased selectivity based on molecular geometry, and partial immunity to quenching by dissolved O_2 molecules.

Acknowledgement

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