Photophysics of xanthione and 4*H*-1-benzopyran-4-thione in β-cyclodextrin complexes

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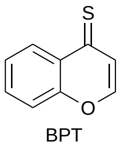
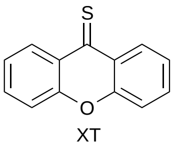
The phosphorescence decays of β-cyclodextrin (β-CD) complexes of xanthione (XT) and 4*H*-1-benzopyran-4-thione (BPT) show that self-quenching and oxygen quenching are not important in such complexes, and that the existence of bimodal inclusion in solid complexes can be identified using the width of the distribution parameter of the Gaussian distribution of the logarithm of the observed rate constants for decay.

Aromatic thioketones show interesting photochemical behaviour including fluorescence from the second excited singlet state, S_2, room temperature phosphorescence from the first excited triplet state, T_1, thermally activated delayed fluorescence from the first excited singlet state, S_1, and photochemistry arising from the T_1 state as well as from the S_2 state.[1] In addition, the S_2 and T_1 states of thiones are quenched at or near diffusion limited rates by a wide variety of substances including ground state thione (self-quenching) and oxygen. Moreover, studies of S_2 are complicated by the fact that thione non-radiative decay rates are extremely sensitive to the nature of the solvent since quenching by many common solvents occurs at diffusion-limited rates.[1] Attempts to overcome the self-quenching problem in solution have involved the incorporation of thiones in micelles.[2] In these organised media a decrease in the contribution of the self-quenching process to the decay of T_1 states of thioketones was achieved as a consequence of the compartmentalisation process.[2]

Recently, the formation of β-CD inclusion complexes of xanthione (XT) and 4*H*-1-benzopyran-4-thione (BPT) in aqueous solution have been reported.[3] Cyclodextrins (CDs) are cyclic oligosacharides of six to eight α-d-glucose units (α-CD, six; β-CD, seven; γ-CD, eight) that posses internal hydrophobic cavities able to include a great variety of guest molecules in aqueous solutions.[4] These complexes have been used for studying the photophysics and photochemistry of the guest molecules in an organised environment.[5] Here we report a preliminary account on the photophysics of XT and BPT β-CD complexes in water and in the solid state.†



BPT



XT

The absorption spectrum of BPT in water shows a maximum at 376 nm ($S_0 \rightarrow S_2$ band). Upon addition of 0.011 m β-CD, a small blue shift is observed (λ_{max} = 373 nm). The absorption spectrum of XT in water could not be recorded by us in 1 cm pathlength cells due to the low solubility ($S = 2.5 \times 10^{-7}$ m, $\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[2b] The solubility of XT increases upon addition of β-CD and the absorption spectrum was recorded ($S_0 \rightarrow S_2$ band, λ_{max} = 406 nm).

Steady-state emission spectra of XT and BPT in air-equilibrated aqueous solution show dramatic changes in the emission intensity upon addition of β-CD to the solution. The positions of the wavelength maxima are collected in Table 1. These changes are depicted in Fig. 1(*a*) for XT. In the case of BPT there is a substantial increase in the $S_2 \rightarrow S_0$ fluorescence and in the $T_1 \rightarrow S_0$ phosphorescence, and a blue shift of the phosphorescence band (not shown). In the case of XT we were able to observe very little emission, if any, without β-CD. However, in the presence of β-CD, $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence appear. These results confirm earlier reports[3] about the formation of β-CD inclusion complexes of XT and BPT in aqueous solution and show the protection offered by the β-CD cavity from oxygen quenching of thione molecules in such inclusion complexes. A similar conclusion was reached for other guest molecules in CD inclusion complexes in aqueous media[6] and also for solid state complexes.[7]

Ground state diffuse reflectance absorption spectra of XT–β-CD and BPT–β-CD solid complexes do not show noticeable changes in relation to the spectra observed in aqueous solution in the presence of β-CD (see Table 1). Steady-state emission spectra of XT–β-CD [Fig. 1(*b*)] and BPT–β-CD air-equilibrated solid complexes were recorded (see Table 1). In both cases, $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence are observed. The relative intensity fluorescence/phosphorescence is very similar in both cases to that observed for the complexes in aqueous solution. For the sake of comparison fluorescence measurements were performed for XT and BPT on cellulose mechanical mixtures with similar concentrations to those employed for the β-CD solid complexes. Practically no phosphorescence was observed for these mechanical mixtures presumably because in these cases efficient oxygen quenching occurred. Moreover, no emission was observed from XT crystals.

Time resolved phosphorescence of XT–β-CD and BPT–β-CD solid complexes was studied using diffuse reflectance

Table 1 Spectral properties of XT and BPT in different media

	Absorption $\lambda_{max}(S_0 \rightarrow S_2)$/nm	Fluorescence $\lambda_{max}(S_0 \rightarrow S_2)$/nm	Phosphorescence $\lambda_{max}(S_0 \rightarrow S_2)$/nm
BPT in water	376	425	644
BPT in water + 0.011 m β-CD	373	427	628
BPT–β-CD solid complex	370	439	618
XT in water	—[a]	—	—
XT in water + 0.011 m β-CD	406	430–490	667
XT–β-CD solid complex	408	457	661

[a] Solubility too low to be measured ($S = 2.5 \times 10^{-7}$ m, $\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) [ref. 2(*b*)].

laser flash photolysis equipment.‡,[8] The phosphorescence decays were fitted according to the Albery model[9] for dispersive kinetics§ [see Fig. 1(*b*) for XT as example]. The mean rate constants for triplet state decay obtained using the Albery model in the β-CD solid complexes [$k = (2.61 \pm 0.05) \times 10^5\ \mathrm{s}^{-1}$ for BPT and $k = (2.24 \pm 0.01) \times 10^5\ \mathrm{s}^{-1}$ for XT] are comparable to the values previously reported in solution at infinite dilution for BPT[10] and XT.[11] The mean decay constant of a XT–β-CD complex sample with eight times less XT loading was practically identical [$k = (2.04 \pm 0.02) \times 10^5\ \mathrm{s}^{-1}$] to the mean decay constant of the sample with higher loading. Practically identical phosphorescence decay of a XT–β-CD complex sample was observed when the sample was degassed prior to excitation, presumably due to the protection from oxygen quenching offered by the CD in the solid state.[7] These results suggest that self-quenching and oxygen quenching do not play an important role in the photophysics of thioketones in solid β-CD inclusion complexes.

It is interesting to note the difference in the width of the distribution parameter, γ, obtained from fitting to the Albery model the phosphorescence decay of the XT–β-CD and BPT–β-CD complexes ($\gamma = 1.11 \pm 0.02$ for BPT and $\gamma = 0.62 \pm 0.01$ for XT). The higher value for the BPT complex can be attributed to the existence of two non interconverting¶ major orientations of the BPT molecules within the β-CD cavity (see Fig. 2). By contrast, XT can only be fitted within the cavity in one major orientation due to its symmetry. The existence of multimodal inclusion of the guest molecules in the CD cavity has been studied in solution by different methods: electron paramagnetic resonance (EPR),[13] electron nuclear double-resonance (ENDOR),[14] fluorescence methods[15] and theoretical methods.[16]

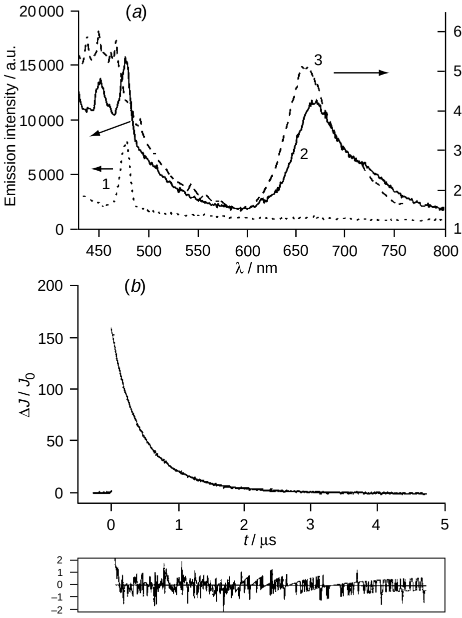


Fig. 1 (*a*) Steady-state emission spectra of XT ($\lambda_{\mathrm{exc}} = 410$ nm, non deoxygenated samples at room temperature) in water (1), in water with β-CD 0.011 m (2) and in the β-CD complex in the solid state (3). (*b*) Phosphorescence decay trace of the XT–β-CD solid complex at 660 nm and fit according to the Albery model (ref. 9) with the plot of residuals.

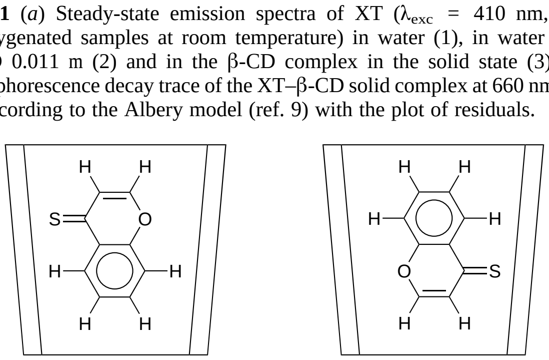


Fig. 2 Major orientations of the BPT molecules within the β-CD cavity

In summary, the results presented here show that β-CD inclusion complexes in aqueous solution and in the solid state might be a particularly useful media for studying the intramolecular photophysics of aromatic thioketones due to the fact that self-quenching and quenching by oxygen are not important in such inclusion complexes. As far as we know, this is the first reported example of bimodal inclusion in solid state cyclodextrin complexes. The methodology applied in the present work (analysis of the phosphorescence decay according to the Albery model) is a new alternative to the fluorescence method and might be a powerful tool for investigating in the microsecond domain the existence of different inclusion orientations in solid cyclodextrin complexes.‖

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Footnotes

† CD solid complexes were prepared by dissolving a certain amount of the thione in 0.011 m β-CD aqueous solutions under magnetic stirring at 70 °C for 4 h. After evaporation of water *in vacuo* with a rotary evaporator, the solid obtained was dried under vacuum at 40 °C for 4 h. Sample loading were around 0.5–2 mg of the thione per gram of β-CD.

‡ A detailed description of the laser system can be found in ref. 8. The excitation wavelength was 355 nm.

§ Complex kinetics are normally observed in heterogeneous media (*i.e.* solid surfaces, polymer matrices, biological membranes) due to the variety of solute environments, every one with its own decay mode. The Albery model (ref. 9) describes the kinetics of heterogeneous systems by a Gaussian distribution of the logarithm of the observed rate constants with two parameters: the mean rate constant, *k*, and a distribution parameter, γ, that defines the spread of the Gaussian distribution (if $\gamma = 0$, the Albery model becomes a simple first-order exponential decay equation).

¶ The diameter of the β-CD cavity (ref. 4) is 6.0–6.4 Å and the largest diameter of the BPT molecule is *ca* 6.5 Å according to standard bond lengths (ref. 12). Therefore the molecule of BPT does not have inside the solid complex the possibility of interchanging the orientations depicted in Scheme 1.

‖ A lifetime distribution study of xanthone and benzophenone triplets in cyclodextrin complexes in the solid state using an exponential series method has been reported in the literature (ref. 7).

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