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Dual excimer emission of *p*-terphenyl induced by γ -cyclodextrin in aqueous solutions

G. Pistolis *

Molecular Electronic Spectroscopy Laboratory, Institute of Physical Chemistry, N.R.C.P.S. "Demokritos", GR-153 10 Aghia Paraskevi, Athens, Greece

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Abstract

Steady-state and time-resolved fluorescence spectroscopy of *p*-terphenyl (*p*-T) in an aqueous solution of γ -cyclodextrin (γ -CD) has revealed the presence of three emitting species, namely the locally-excited *p*-terphenyl, a low-energy excimer emitting at $\lambda_{\max} = 408$ nm and a higher-energy excimer at $\lambda_{\max} = 390$ nm. In the presence of β -cyclodextrin (β -CD), only the locally-excited state is observed. The identity and the kinetics of the emitting species are discussed. This Letter reports on the detection of excimer fluorescence for *p*-terphenyl. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

An attractive field of molecular recognition in chemistry and biology is that of host–guest phenomena, which concern inclusion complexes formed through noncovalently controlled interactions between the reactants (host and guest) [1,2]. Such phenomena can be signalled qualitatively and quantitatively with fluorescence sensors and switches owing to the substantial alteration of the photophysical properties of the latter, induced by environmental stimuli [3]. Of special interest, moreover, are the multiple inclusion capabilities of the host. In such cases, the resulting superstructures can usually be easily recognized, since preassociated fluorophores give rise to the formation of excimer state(s) [3]. Cyclodextrins [4], in particular γ -CD, have been

used as a host suitable for multiple inclusion of numerous probes, i.e. pyrene and its derivatives [5–7], α -terthiophene [8], thioflavin T [9], *trans*-stilbene [10], oxazole and oxadiazole derivatives [11–13]. Most of these inclusion complexes are of 2:2 or 2:1 (guest:host) stoichiometry. The appearance of excimer fluorescence in these systems is a manifestation of the spatial restrictions induced by the geometrical characteristics of the γ -CD cavity, in which guest molecules are obligated to adopt totally or partially overlapping configurations.

p-Terphenyl (*p*-T) is among the most commonly used luminophors for plastic scintillators [14]. However, little is known regarding the effect of microenvironments on its electronic states [15]. To the best of our knowledge, *p*-terphenyl neither produces excimer emission in fluid solutions [16], nor dimerizes in the crystalline state [17]. We have observed dual excimer emission probably induced from two different 2:2 (host:guest) populations in an aqueous solu-

* Fax: +30-1-651-1766; e-mail: pistol@mail.demokritos.gr

tion of γ -CD, as demonstrated by steady-state and time-resolved fluorescence spectroscopy and we report the results in this Letter.

2. Experimental section

p-Terphenyl was purchased from Riedel-De Haën Co. and was of scintillation grade. β -CD and γ -CD were a high-purity product of Cyclolab and were used as received. All the *p*-T aqueous solutions in the presence of dissolved cyclodextrin, were prepared by stirring the solvent overnight in contact with the solute, which had previously been deposited as a thin film on the walls of an Erlenmeyer flask.

Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer, while for steady-state fluorescence spectra both the Perkin-Elmer Model LS-50B and the Edinburgh Instruments Model FS-900 spectrofluorometers were used. The spectra were corrected for the wavelength dependence of the sensitivity of the system. Time-resolved fluorescence measurements were carried out using an Edinburgh Instruments FL-900 fluorescence lifetime spectrometer based on the single correlated photon counting technique. The full-width at half-maximum of the overall excitation pulse was 780 ps. The temperature was kept constant at $23 \pm 0.1^\circ\text{C}$ using a Julabo F-18 temperature bath.

3. Results and discussion

Fig. 1 shows the absorption and normalized fluorescence spectra of $0.58 \mu\text{M}$ *p*-T, in ethanol, in an aqueous 10 mM β -CD solution, whereas for the corresponding γ -CD solutions two concentrations of *p*-T are employed, namely 0.58 and $0.78 \mu\text{M}$. As can be seen, there is a significant red-shift and broadening of the *p*-T absorption spectrum, its maximum being shifted from 277 to 298 nm when γ -CD is added as compared to those obtained in ethanolic and aqueous β -CD solution. The emission spectrum, on the other hand, in the presence of γ -CD shows an interesting, new, structureless excimer-like emission band centered at $\sim 400 \text{ nm}$, which grows with increasing *p*-T concentration. The excitation spectrum also, monitored at the low-energy band of the emission spectrum, shows a notable broadening with respect to that in the high energy, increasing its FWHM by 350 cm^{-1} (not shown). In contrast to the excimer-like emission observed in γ -CD aqueous solution, β -cyclodextrin does not produce a similar band, as manifested by its absorption and fluorescence spectra.

One would maintain that the new, structureless band observed in aqueous γ -CD solution is probably due to a suspension of *p*-T microcrystals. Such a possibility, however, must be excluded since it is known that the absorption spectrum of microcrystals

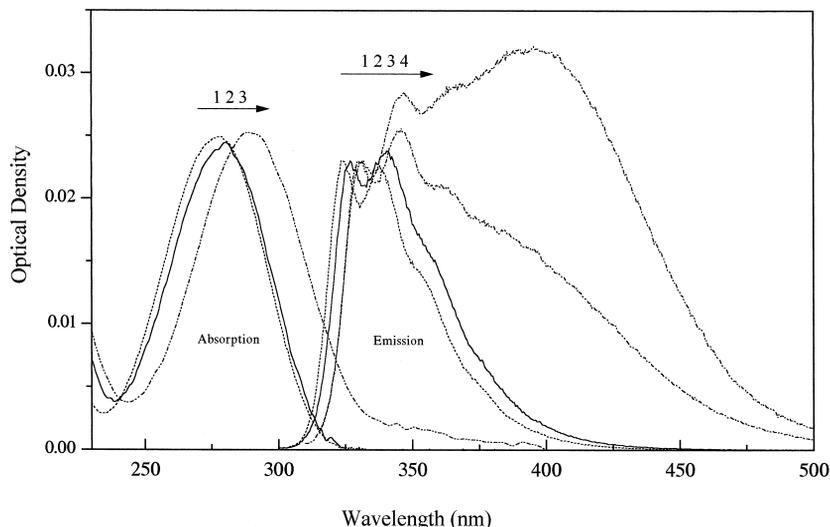


Fig. 1. Absorption (left) and normalized emission spectra (right) of $0.58 \mu\text{M}$ *p*-T in: (1) ethanol; (2) aqueous solution of 10 mM β -CD; and (3) aqueous solution of 10 mM γ -CD. (4) Emission spectrum of $0.78 \mu\text{M}$ *p*-T in aqueous solution of 10 mM γ -CD.

reveals the existence of a low-lying 1L_b state around 334 nm [15,18]. This is not manifested in our absorption and excitation spectra, where only the strong conjugation band 1L_a was detected. Furthermore, such microcrystals should also form in the presence of β -CD under identical concentrations and preparation procedure.

The observed red-shift and broadening of the absorption spectrum of p -T in the presence of γ -CD strongly support the formation of interacting couples of p -T molecules in the ground state [3]. A similar behaviour of the absorption spectra of various fluorophores which form excimers within the framework of γ -CD has been observed [8,10,11,19]. It is believed that the toroidally-shaped truncated cone of γ -CD constrains two guest molecules into adopting more or less overlapping configurations suitable for excited dimer formation. However, the nature of the guest–guest interactions does not manifest itself as being a pre-formed excimer-like dimer in a single γ -CD cavity (2:1 guest:host) or in a barrel-type configuration (2:2 guest:host). One cannot eliminate the possibility that both inclusion complexes, namely the 2:1 and 2:2 between p -T and γ -CD, coexist in aqueous solution. If such complexes were to occur, one might expect that when the pH of an aqueous p -T: γ -CD solution increases beyond ~ 12 ($pK_a = 12.1$ for γ -CD [20,21]), only barrel-type complexes (2:2 guest:host) would break down because of the repulsion between negatively charged oxygen atoms of secondary hydroxyl groups of the head-to-head facing cyclodextrins. Our findings¹ strongly support 2:2 aggregates existing in the ground state, since at pH = 13.4, not only does the broad structureless emission band totally disappear, but the resulting emission and absorption spectra are also blue-shifted and coincide with those observed for the locally-excited state.

¹ Since p -T is practically insoluble in water, a mixture of MeOH/H₂O, 20:80 by volume, has been used as solvent, in which identical observations as in pure water have been made with regard to excimer appearance. This medium, though, can accommodate at least 0.78 μ M of p -T in the absence as well as in the presence of γ -CD at pH = 13.4. This is in contrast to the pure water/ γ -CD system, in which some of the p -T molecules, at high pH, tend to precipitate in the bulk water phase, thus forming microcrystals which cause confusion in the recorded spectra.

Furthermore, by adding an excess of γ -CD to an aqueous solution already containing the reactants (0.78 μ M p -T and 10 mM γ -CD), the structureless excimer-like emission band drops notably and the emission profile changes towards the normal one of the locally-excited state of p -T. A new complex is formed, whose population grows at the expense of the 2:2 dimers. This new species should possess a different stoichiometry than those of 2:2 and their precursor 1:1 complexes. It is believed that this is a 1:2 (guest:host) complex. Support of this view was obtained from a recent report [22], where it was shown, using computer simulations, that these complexes (1:2) are favored at high cyclodextrin concentration, and act as an inhibitory factor to the formation of 2:2 or higher aggregation adducts between cyclodextrins and α,ω -diphenylpolyenes. Identical conclusions regarding the dependence of excimer profile on both the pH and the cyclodextrin concentration for pyrene [6] and α -terthiophene [8] in the presence of γ -CD, have been reached in the literature.

On the basis of steady-state spectra alone, one cannot absolutely rule out the existence of more than one excimer state. Time-resolved fluorescence studies, however, have clarified this point. The gated time-resolved fluorescence spectra recorded for an aqueous solution of p -T (0.78 μ M) containing 10 mM of γ -CD are shown in Fig. 2. The early gated spectrum, which corresponds to fluorescence emitted during the first 1.5–3.1 ns (Fig. 2A), consists principally of the locally-excited state emission (singly occupied complexes). At longer times following pulse excitation ($6.3 \text{ ns} \leq \Delta t \leq 6.9 \text{ ns}$, Fig. 2B) and ($7.8 \text{ ns} \leq \Delta t \leq 9.5 \text{ ns}$, Fig. 2C), both the locally-excited state as well as a broad emission centered at 390 nm contribute to the total emission spectrum, the latter being predominant as time elapses. In the late-gated spectrum ($\Delta t \geq 35 \text{ ns}$, Fig. 2D) the above emitting species almost disappear and a new, structureless band with a maximum at 408 nm is observed. The identification and kinetics of all emitting species is further studied by analyzing fluorescence decay traces at various emission wavelengths (Fig. 3). The fitting parameters and goodness of fits are given in Table 1.

The decay curves monitored at 450 and 420 nm are analyzed as triple-exponential decays consisting of a major component ($\tau_4 = 27.0 \text{ ns}$) and two minors

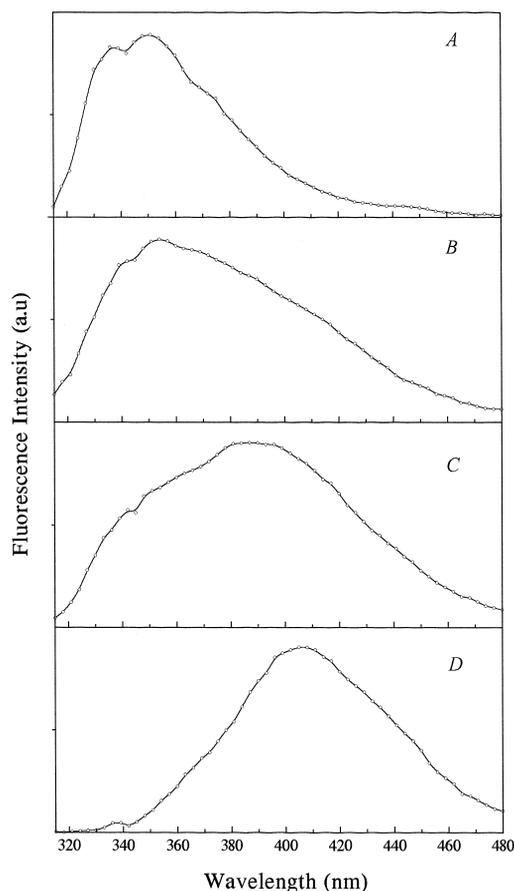


Fig. 2. Gated time-resolved fluorescence spectra of 0.78 μM *p*-T in an aqueous 10 mM γ -CD solution. The gate times of spectra A, B, C, and D are 1.5–3.1, 6.3–6.9, 7.8–9.5, and 35 ns, respectively.

components ($\tau_3 = 7.6$ ns and $\tau_2 \cong 1.4$ ns). At intermediate wavelengths of the spectral region (390 and 360 nm, respectively), an additional fast component ($\tau_1 \approx 360$ ps) contributes to the fluorescence decay, which becomes predominant at the shorter wavelength. Finally, at the high-energy band of the spectrum (330 nm), both the fast ($\tau_1 \approx 360$ ps) and 'normal' ($\tau_2 \approx 1.2$ ns) decaying components represent the total decay trace, with only a minor (5%) contribution of the ($\tau_3 = 7.6$ ns) species. In conformity with the time-resolved spectra, the formation of two types of excimers is demonstrated by analyzing the decay traces. One is a long-living excimer D_2 ($\tau_4 = 27.0$ ns, $\lambda_{\text{max}} \approx 408$ nm) observed at the late-

gated spectrum ($\Delta t \geq 35$ ns) of the time-resolved spectra (see Fig. 2D). The other is a shorter-living excimer D_1 ($\tau_3 = 7.6$ ns, $\lambda_{\text{max}} \approx 390$ nm) which has a major contribution at intermediate times (6.3 ns $\leq \Delta t \leq 9.5$ ns) after pulse excitation. It should be noted that the singlet state of *p*-T decays with a fluorescence lifetime of ~ 1 ns [23–25]. Also, the fluorescence decay in the system β -CD/*p*-T is strictly a single exponential over the whole spectral region studied ($\tau_F = 1.2 \pm 0.1$ ns, $\chi_v^2 = 1.05$), a fact which strongly suggests singly occupied complexes. In view of these observations, we assign the 'normal' decaying component ($\tau_2 \approx 1.2$ ns) in γ -CD/*p*-T system as the locally-excited state of *p*-T, arising from singly occupied complexes, which are 1:1 and 1:2 (*p*-T: γ -CD) inclusion complexes. Due to the multiexponential behaviour of the fluorescence decays, there has been uncertainty in directly detecting a fast 'growing-in' component into the long-wavelength spectral region. If such dimers are present in the ground state, one would expect this to be a fast process (< 500 ps), since this should be consistent with the rapid trapping of the initially formed singlet exciton at pre-formed excimer-like dimer configurations [3]. Nevertheless, in contrast to the γ -CD/*p*-T system, this fast component ($\tau_1 \approx 360$ ps) which contributes to the fluorescence decay in the spectrum region, where the locally excited state emits, is totally absent in the β -CD/*p*-T system. This means that it plays a major role when excimer emission is dominant. We believe that this fast component reflects the lifetime for excimer formation, in other words, during 0–360 ps the photoexcited dimer is changed into the excimer state [26,27].

The dual excimer emission of various fluorophores has been frequently observed not only in organized media in dilute solutions, [3,27,28], but also in the crystalline state [29,30]. Without exceptions, the low-energy component has been assigned to a 'normal' excimer with a sandwich-type arrangement of aromatic moieties, whereas the higher-energy component has been attributed to a partially overlapped pair of fluorophores. The former excimer is commonly observed in concentrated solutions. Since no available data exist concerning the identification of the normal excimer for *p*-T, it seems reasonable to adopt somewhat similar structural conformations for the D_2 and D_1 excimers observed in the present

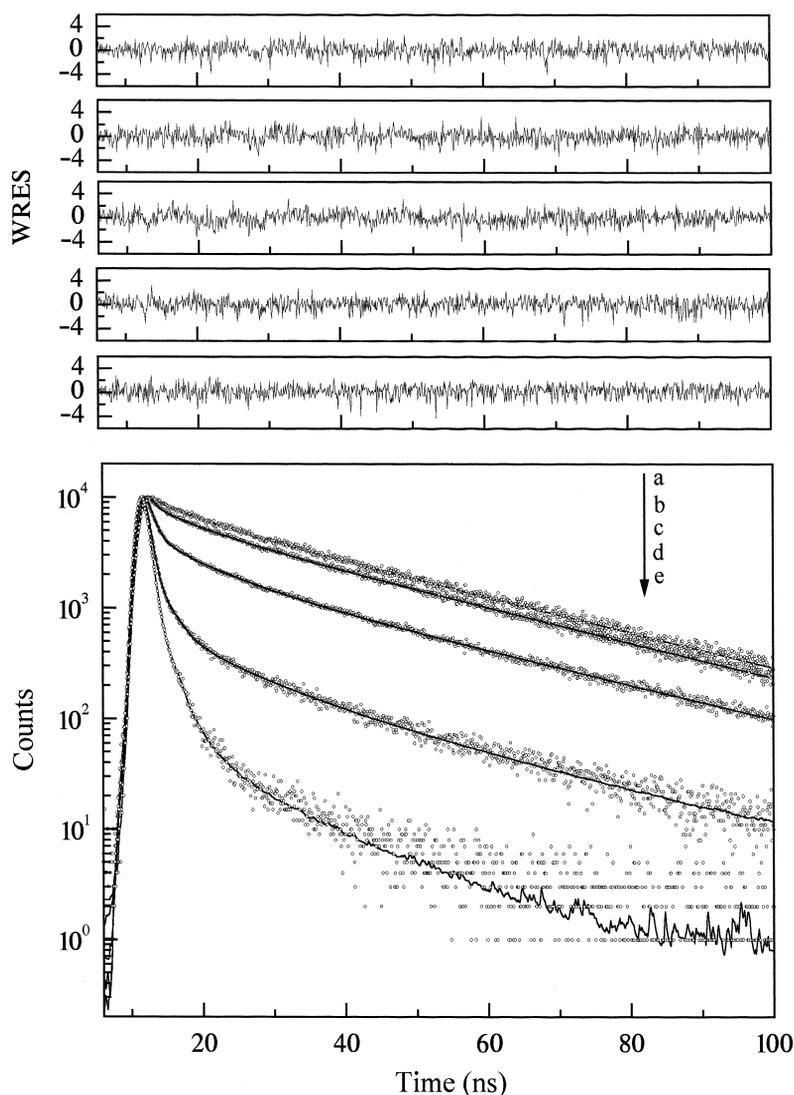


Fig. 3. Fluorescence decay traces and best-fitting curves of $0.78 \mu\text{M}$ $p\text{-T}$ in an aqueous 10 mM $\gamma\text{-CD}$ solution at various wavelengths; from (a) to (e): 450, 420, 390, 360, and 330 nm, respectively. The excitation was at 300 nm. The corresponding weighted residuals (WRES) are shown on top in the same order. Estimated fitting parameters and goodness of the fits are given in Table 1.

work. In the above structures, the motion of $p\text{-T}$ molecules should be highly restricted. Therefore, D_1 presumably is unable to undergo the necessary conformational changes required for producing the more stable 'normal' excimer D_2 . This means that the excimers D_1 and D_2 are not subsequent states of the excited monomer M but may be considered to be directly excited following a pulse excitation. As a consequence, each excimer will be deactivated by

itself. Support of this view is obtained from our time-resolved studies. If such a kinetic scheme were to occur ($M^* \rightarrow D_1^* \rightarrow D_2^*$), a delay in the rise time of the D_2 fluorescence identical with the fluorescence decay time ($\tau_3 = 7.6 \text{ ns}$) of its precursor D_1 would be observed [31]. Such a case, however, was not manifested. Additional support is given in Fig. 4 where time-integrated (1) and time-resolved emission spectra (2, 3 and 4) constructed from a family of

Table 1

Recovered decay times τ (ns) and percentages (% τ) of the emitting species in an aqueous 10 mM γ -CD solution containing 0.78 μ M p -T at various wavelengths (nm)

Emission wavelength	τ_1	τ_2	τ_3	τ_4	% τ_1	% τ_2	% τ_3	% τ_4	χ_v^2
450	–	1.6 ± 0.8	7.6 ± 2.5	27.0 ± 1.4	–	2	9	89	0.996
420	–	1.2 ± 0.4	7.8 ± 2.3	27.1 ± 1.4	–	4	12	84	1.06
390	0.38 ± 0.07	1.3 ± 0.4	7.6 ± 2.2	27.0 ± 1.0	12	6	16	66	1.00
360	0.35 ± 0.06	1.2 ± 0.3	7.6 ± 2.2	27.1 ± 1.1	33	28	15	24	1.05
330	0.36 ± 0.06	1.1 ± 0.3	7.9 ± 2.4	–	56	39	5	–	1.00

The analysis of the fluorescence decay traces was made by using exponential curve fitting of three or four exponential terms. The statistical parameter χ_v^2 is given in the last column.

deconvolved decay functions [32], of an aqueous 10 mM γ -CD solution containing 0.58 μ M (a) and 0.78 μ M (b) of p -T, respectively, are shown. The spec-

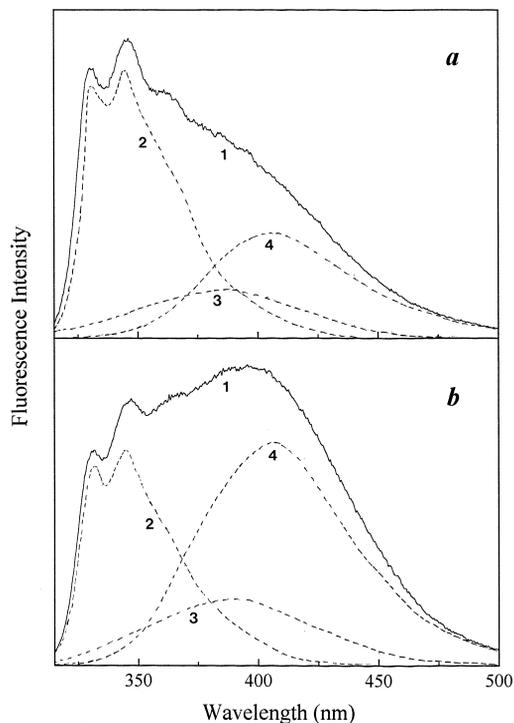


Fig. 4. Emission spectra of an aqueous solution of 10 mM γ -CD containing: (a) 0.58 μ M p -T and (b) 0.78 μ M p -T [(1) time-integrated emission; (2)–(4) time-resolved emission spectra]. The spectrum analysis into components was made according to their relative fractions in the decay functions by assuming three components, one monomer (2) and two excimers D_1 (3) and D_2 (4). The delay times (Δt) and gate widths (δt) respectively were: (2) 1.0 and 0.9 ns; (3) 6.3 and 0.85 ns; (4) 35 and 18 ns.

trum analysis into components was made by assuming three components, one monomer (2) and two excimers D_1 (3) and D_2 (4). Although decay times for each component were essentially invariant at both concentrations, their relative proportions varied considerably, D_2 being notably favored in the concentrated p -T solution. Such a concentration dependence of the D_1 and D_2 relative fractions further corroborates a non-successive kinetic scheme for the aforementioned excimers. It is suggested, therefore, that D_1 and D_2 species exist independently in solution, and probably represent two distinct populations of 2:2 inclusion complexes. Amongst these, the one containing p -T molecules in a nearly sandwich-type arrangement (D_2) seems to possess a greater stability with respect to the other which consists of partially overlapped conformations of p -T (D_1).

In summary, complexation of p -T in an aqueous solution of γ -CD leads to a multiple equilibrium scheme consisting of 1:1, 1:2, and presumably of two distinct populations of 2:2 inclusion complexes between p -T and γ -CD, respectively. The topology of the 2:2 adducts is such that p -T molecules are held in a suitable proximity, resulting, upon excitation, in the observation of two excimer states. It is noted that excimer emission for p -T chromophore was observed for the first time in this work.

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