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LETTERS

Effects of Protic Solvents upon Intramolecular Interaction of Polymethylene Bis-*p*-phenylenediacrylates

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Abstract

Measurements of fluorescence spectra of a series of polymethylene bis(*p*-(2-ethoxycarbonylvinyl)cinnamates) [$(CH_2)_n(p\text{-PDAmC}_2)_2$ (n=2–12)] in various solvents indicate that alcoholic solvents induce intramolecular association of the diacrylate chromophores, exhibiting excited pair emission, of which the intensity is dependent upon the methylene chain length.

Keywords: Aggregation; Esters; Fluorescence; Solvents & solvent effects

1. Introduction

Photochemical behavior of *p*-phenylenediacrylate and cinnamate derivatives has been extensively studied in film and solid states [1–3]; however, few reports on simple polymethylene bis(*p*-phenylenediacrylates) and dicinnamates have appeared [4]. Recent work on the effect of polar solvents on a bispyrenyl alcohol [5] prompted us to report our own results on the effect of alcoholic solvents inducing intramolecular association of the *p*-phenylenediacrylate (*p*-PDAmC$_2$) moieties, as studied by their emission spectra.

2. Preparation and absorption spectra

A series of bichromophoric systems, polymethylene bis(*p*-(2-ethoxycarbonylvinyl)cinnamates) [$(CH_2)_n(p\text{-PDAmC}_2)_2$: C$n$ (n=2–12)], were prepared from reactions of ethyl hydrogen *p*-phenylenediacrylate with 1,*n*-dibromoalkanes in *N,N*-dimethylacetamide in the presence of potassium carbonate. The prepared Cn exhibited an absorption band in the range of 250–350 nm with a maximum around 320 nm and a shoulder around 335 nm, as shown in Figure 1. The observed spectra are quite similar to that of diethyl *p*-phenylenediacrylate (*p*-PDAdC$_2$) and have a nearly twice of absorptivity of *p*-PDAdC$_2$ (for example, ε_{max} 75000 cm^2 mmol^{-1} for C8 vs. ε_{max} 40000 cm^2 mmol^{-1} for *p*-PDAdC$_2$ in benzene). In polar solvents the band was slightly shifted to the lower wavelengths (Figure 1).

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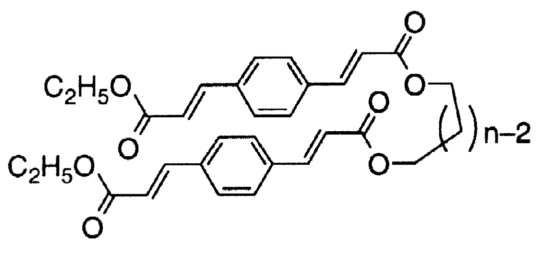

$(CH_2)_n(p\text{-}PDAmC_2)_2$: C*n* (*n* = 2–12)

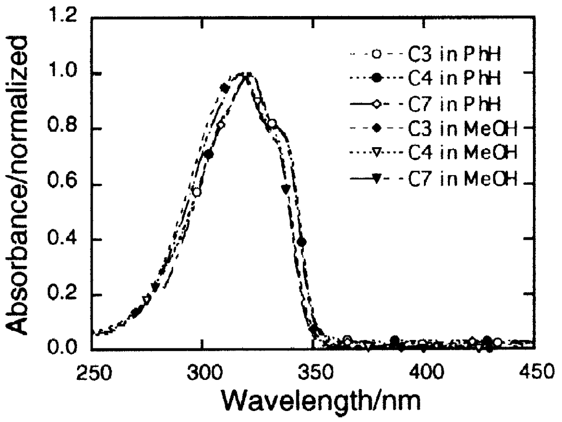

Figure 1. Absorption spectra of C3, C4, and C7 in a concentration of 1×10^{-4} mol dm^{-3} in benzene and methanol. The spectra are normalized at the absorption maximum.

3. Fluorescence spectra

3.1. Effects of solvent and excitation wavelength

Fluorescence spectra of a series of C*n* were measured at ambient temperature by exciting their sample solutions of 10^{-5} to 10^{-4} mol dm^{-3} at 320 nm in various solvents (Figure 2 for C4). In benzene, as an example, some C*n* showed a very weak broad band in the long wavelength region of the strong monomer emission band (λ_{max} 371 nm). In methanol, however, the broad band was significantly intensified for C4, C5, C7, and C9 (λ_{max} ca 450 nm, Figure 3). The long wavelength bands can be ascribed to the emission from intramolecular excimers. *p*-PDAdC2 was reported to show intermolecular dimer emission in the identical wavelength region in its higher concentrations than 0.1 mol dm^{-3} [6]. In the present concentration range lower than 10^{-4} mol dm^{-3}, the intermolecular interactions in the excited state could be neglected. In fact, C2 showed no long wavelength emission band on excitation with 320 nm-light in our concentration range. Among the solvents employed, ethanol and 2-pro-

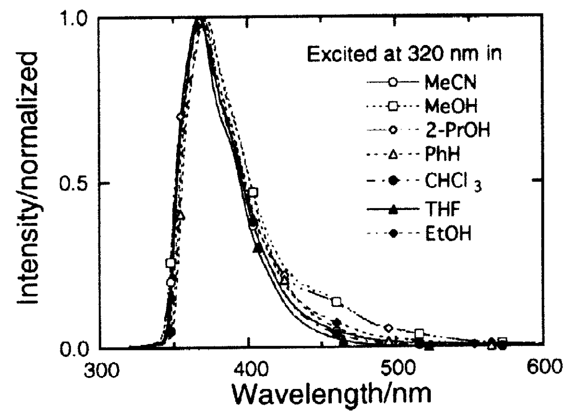

Figure 2. Fluorescence spectra observed on excitation of C4 (1×10^{-4} mol dm^{-3}) at 320 nm in different solvents. The spectra are normalized at the emission maximum.

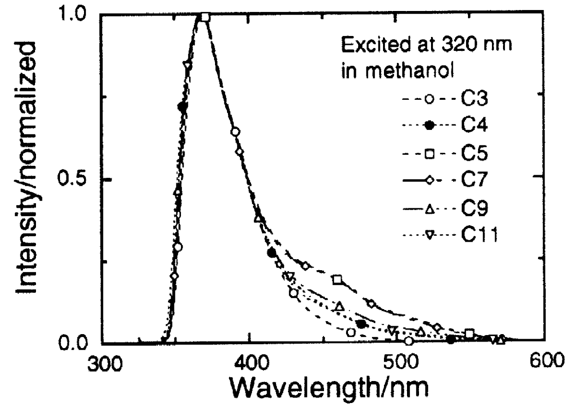

Figure 3. Fluorescence spectra observed on excitation of C*n* (1×10^{-4} mol dm^{-3}) at 320 nm in methanol. The spectra are normalized at the emission maximum.

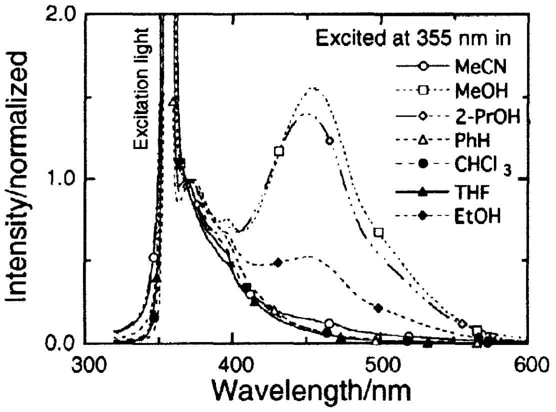

Figure 4. Fluorescence spectra observed on excitation of C4 (1×10^{-4} mol dm^{-3}) at 355 nm in different solvents. The spectra are normalized at the monomer emission maximum.

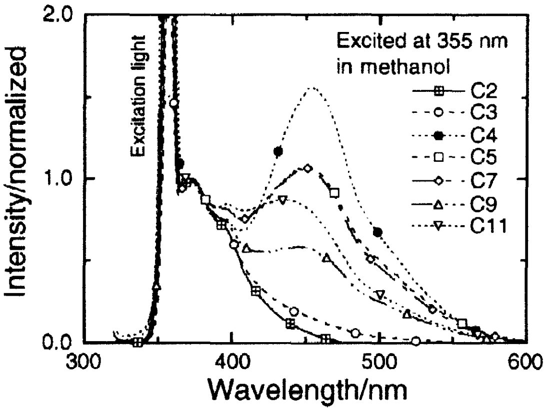

Figure 5. Fluorescence spectra observed on excitation of C*n* (1×10^{-4} mol dm^{-3}) at 355 nm in methanol. The spectra are normalized at the monomer emission maximum.

panol showed an effect similar to that of methanol, but chloroform, THF, and acetonitrile were ineffective for excimer emission.

The effect of alcohols as solvent was much more remarkable on excitation of the sample solutions with 355-nm light irradiating at the longer wavelength edge of the absorption band (Figure 4 for C4). Some of the bichromophores (C4, C5, C7, C9, and C11) showed a marked emission band (λ_{max} 450 nm) in methanol in the same wavelength region as that of the intramolecular excimer emission which was detected on 320 nm excitation (Figure 5), while such an effect was not observed in benzene. The intensity of 450-nm band of C4, as an example, was linearly increased with increasing the concentration up to 10^{-4} mol dm^{-3} in methanol. Fluorescence excitation spectra of C4, as monitored at 375 and 450 nm, were almost identical with its absorption spectrum; however, the excitation spectrum monitored at 450 nm was extended to longer wavelengths (>350 nm) than that monitored at 375 nm. These observations indicate that intramolecularly associated species play an important role in absorption of 355-nm light and emission in the long wavelength region. Intermolecular interaction is assumed to play no role in the long wavelength emission, since no long wavelength emission band was detected for C2 under similar conditions.

The effect of alcohols could be ascribed to their hydrophilic property, which might facilitate association of the hydrophobic *p*-PDAmC$_2$ chromophores in the ground state. Previously *p*-PDAmC$_2$ groups were shown to form ground-state pairs when introduced in poly(vinyl alcohol) as side chains; this was ascribed to repulsive interaction between the hydrophobic side chains and the hydrophilic main PVA polymer chain [7].

3.2. Effects of methylene chain length

It has been reported that the so-called n=3 rule [8] does not hold for the emission of dimeric species on excitation of a pair of chromophores interacting in the ground state; as examples, for a series of dinucleotide analogs having a stacked structure, only the emissions from their excited-state complexes were observed [9]. In the present work, we have found that the 450-nm emission intensity on 355-nm excitation in methanol was dependent upon the methylene chain length; C2 exhibited no long wavelength emission as described above, and

C3, C6, C8, C10, and C12 showed only a weak emission band, though the latter three had no enough solubility in methanol. On the contrary, C4, C5, C7, C9, and C11 exhibited a strong emission due to the excited pairs and its intensity increased in the order of C9, C11, C7, C5, and C4. In particular, C4 displayed in methanol the most intense long wavelength band among the C*n* employed, while it exhibited no long wavelength tail in benzene. Esters in general strongly prefer a conformation for the C-O single bond in which the alkyl group and carbonyl group are cis, and the carbonyl and *O*-alkyl bonds are coplanar [10,11]. Such a conformational constraint in the chromophores might be related to the feature that the odd numbers of methylenes gave stronger emissions and the even numbers exerted weaker ones except n=3 and 4. This feature is quite different from that observed for bichromophoric systems [12] obeying the n=3 rule and showing "difficulty in medium-sized ring formation" in intramolecular interactions [13], such as α,ω-dipyrenylalkanes in methylcyclohexane [14] and polymethylene di-2-anthracenecarboxylates in dichloromethane [15]

The facts that the intra- and inter-molecularly associated pairs of C*n* and *p*-PDAdC$_2$ [6], respectively, exhibited identical emission maxima indicates that the excited pairs involved have similar energies and, probably, similar structures. For exciplexes arising from molecules with no ground-state interaction, their energies (emission maxima) are rather insensitive to their structure [16,17]. However, the ground-state interactions may require some particular geometries such as a stacked structure [2,6]. The more flexible nature of the *p*-PDA chromophore, compared with the rigid pyrene moiety, might contribute to the aggregate formation; the odd numbers of methylenes might be more favorable than the even numbers for the stacked conformation in alcoholic solvents, though the structures of the aggregates have not been clarified. Further studies are in progress on the methylene chain length effects on emission from the C*n* solutions and crystals.

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