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Photochemistry of N, Ń-ditridecyl-3,4:9,10-perylenetetracarboxylic diimide in chloromethane solvents

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Abstract

The spectral behaviour, lifetime and fluorescence quantum yield of N,N-ditridecyl-3,4:9,10-perylenetetracarboxylic diimide (DTPD) have been measured in chloromethane solvents, such as methylene chloride, chloroform and carbon tetrachloride. The excitation energy transfer to DTPD has been studied to improve the laser emission of DTPD. The value of energy transfer rate constant (K_{ET}) and critical transfer distance (R_0) indicate a Förster type energy transfer mechanism. The photodecomposition of DTPD in chloromethane solvents has been also studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: N,Ń-ditridecyl-3,4:9,10-perylenetetracarboxylic diimide; Re-absorption; Energy transfer; Photodecomposition

1. Introduction

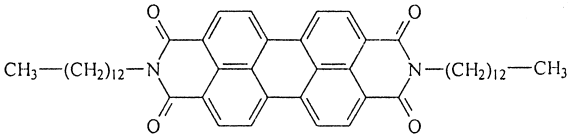
The dyes derived from 3,4:9,10-perylenetetracarboxylic dianhydride have high molar absorptivity, high fluorescence quantum yield and excellent stability to heat and light. These properties render such perylene dyes attractive as potential laser dyes [1], photosensitizers in energy and electron transfer reactions [2–4], in site-selective spectroscopy experiments with biological systems [5] and photon counters in solar cells [6]. Also, Perylene derivatives were found to include some promising microcrystalline photoconductors for electrophotography and have been incorporated in prototype photovolatic cells [6].

In our previous papers [7–11], the photophysical and photochemical behaviour of N,Ń-bis (2,5-di-*tert*-butylphenyl)-3,4:9,10-perylene bis (dicarboximide) and N,Ń-bis (2,6-dimethylphenyl)-3,4:9,10-perylene tetracarboxylic diimide have been studied. In this paper, we report on the spectral behaviour, fluorescence lifetime, energy transfer and photodecomposition of N,Ń-ditridecyl-3,4:9,10-perylenetetracarboxylic diimide (DTPD) in chloromethane solvents.

2. Experimental

N,Ń-ditridecyl-3,4:9,10-perylenetetracarboxylic diimide (DTPD) and 7-dimethylamino-4-methyl coumarin (DMC), (Aldrich) were used without further purification. The solvents used in this work were of spectroscopic grade.

Steady state emission spectra were measured with a Shimadzu RF 510 spectrofluorometer, connected to an ultra-thermostate (Julabo F 10) with temperature precision ±0.1°C, using a rectangular quartz cell of dimensions 0.2 × 1 cm to minimize the re-absorption. The emission was monitored at right angle. The UV–Vis absorption spectra were measured using a Shimadzu UV-2100 S spectrophotometer. The fluorescence decay curves were measured in a conventional 1 cm cuvette using a time correlated single photon counting technique (TCSPC). The decay curves were analyzed using iterative non-linear least squares method. The experimental details of fluorescence decay measurements and analysis of the data have been described elsewhere [12]. Fluorescence quantum yields were measured by using optically diluted solutions, relative to rhodamine 6G as a standard in air saturated ($\phi_f = 0.96$) [13]. Quantum yields for DTPD were averaged from values obtained at three excitation wavelengths in the range of 450–520 nm. The light intensity was measured by using ferrioxalate actinometry [14].



(DTPD)

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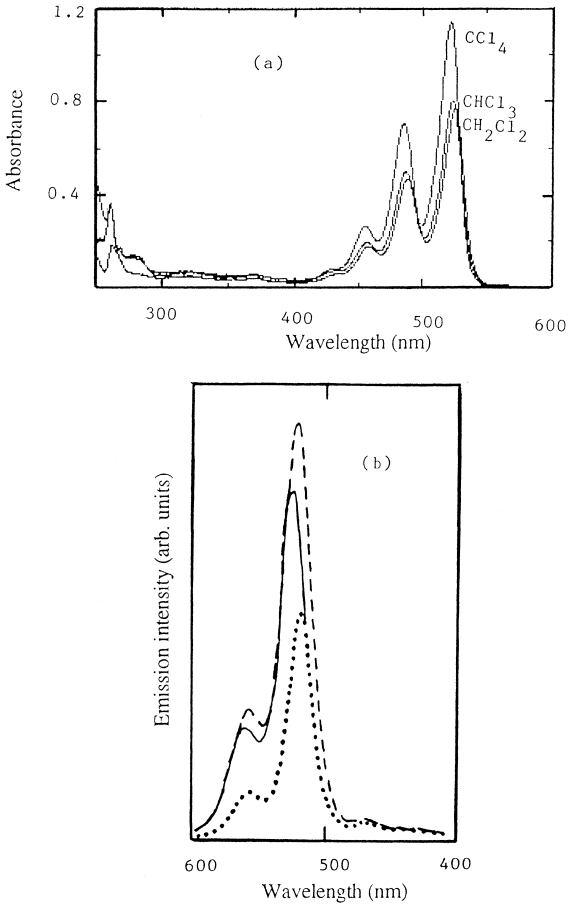

Fig. 1. (a) Electronic absorption spectra of 1×10^{-5} mol dm^{-3} DTPD in CCl_4, $CHCl_3$ and CH_2Cl_2. (b) Corresponding emission spectra in: (...) CCl_4; (—) $CHCl_3$ and (----) CH_2C1_2.

3. Results and discussion

3.1. Spectral behaviour of DTPD

The electronic absorption and emission spectra of DTPD were measured in methylene chloride, chloroform and carbon tetrachloride. As shown in Fig. 1, the energy of $0 \rightarrow 0$ transitions in the absorption spectra are identical with those of $0 \leftarrow 0$ transitions of the emission spectra (Franck–Condon transition) which indicates no change in the geometry of DTPD molecules upon excitation. The peak position and relative intensities of electronic transitions as well as the molar extinction coefficient (ε) of $0 \rightarrow 0$ band are listed in Table 1. The fluorescence quantum

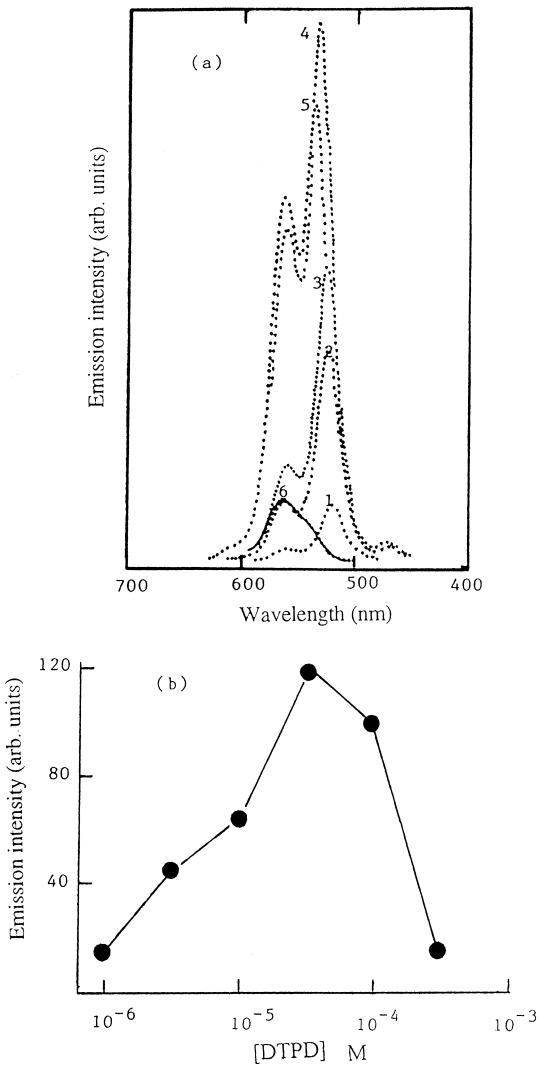

Fig. 2. (a) Emission spectra of different concentrations of DTPD in $CHCl_3$: (1) 1×10^{-6}; (2) 5×10^{-6}; (3) 1×10^{-5}; (4) 5×10^{-5}; (5) 1×10^{-4} and (6) 5×10^{-4} mol dm^{-3} ($\lambda_{ex} = 450$ nm). (b) Plot of [DTPD] versus fluorescence intensity measured at 510 nm.

yields (ϕ_f) of DTPD in chloromethane solvents are also given in Table 1. DTPD is highly fluorescent in these solvents with ϕ_f close to unity. DTPD is free from molecular aggregation and excimer like effects since no red shifted emission band is observed as the concentration is raised up to 5×10^{-4} mol dm^{-3} in $CHCl_3$. However, the emission intensity decreases with increasing the concentration in the range from 5×10^{-5} to 5×10^{-4} mol dm^{-3} (Fig. 2). This

Table 1
Absorption and fluorescence data of DTPD in chloromethane solvents[a]

Solvent	Absorption peak (nm)			$\varepsilon \times 10^4$ (M^{-1} cm^{-1})	Fluorescence peak (nm)[a]		ϕ_f
	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$		$0 \leftarrow 0$	$1 \leftarrow 0$	
CH_2Cl_2	525 (1)	489 (0.6)	458 (0.22)	6.8	525 (1)	560 (0.31)	0.96
$CHCl_3$	524 (1)	487 (0.6)	456 (0.22)	7.1	524 (1)	558 (0.32)	0.95
CCl_4	522 (1)	486 (0.6)	455 (0.22)	9.1	522 (1)	556 (0.20)	0.94

[a] Values in parentheses are the relative intensities.

Table 2
Fluorescence lifetime (τ, ± 0.07 ns), probability of re-absorption (a) and the average number of re-absorption cycle $\langle n \rangle$ at different DTPD concentrations in $CHCl_3$ ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 510$ nm)

[DTPD] (M)	τ (ns)	$\langle n \rangle$	a
1×10^{-6}	4.04	1.00	0.0
5×10^{-6}	4.65	1.15	0.137
1×10^{-5}	5.48	1.36	0.274
5×10^{-5}	5.80	1.43	0.316
1×10^{-4}	6.45	1.59	0.389
5×10^{-4}	7.43	1.84	0.475

decrease in the emission intensity of DTPD is due to the strong overlap between its absorption and emission spectra, which leads to re-absorption of the emitted photons by ground state DTPD molecules. The overlap integral (J), which express the degree of spectral overlap between the absorption and emission spectra, was calculated by using the following equation [15]:

$$J = \int \frac{F(\bar{v})\varepsilon(\bar{v})}{\bar{v}^4} \mathrm{d}\bar{v} \quad (1)$$

where $F(\bar{v})$ is the emission intensity normalized to unity and $\varepsilon(\bar{v})$ is the molar absorptivity of DTPD. For DTPD $J = 14.3 \times 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{cm}^3$ in chloroform. Re-absorption was confirmed by measuring the fluorescence lifetime at different concentrations of DTPD in $CHCl_3$. As shown in Table 2, the fluorescence lifetime increases from 4.04 to 7.43 ns on raising the concentration from 1×10^{-6} to 5×10^{-4} mol dm^{-3}, respectively. Furthermore, the decay of DTPD fluorescence remains single exponential over the whole concentration range examined as shown in Fig. 3, indicating the absence of excimer formation.

The apparent fluorescence lifetime (τ) can be related to the true molecular fluorescence lifetime (τ_M) (i.e. as measured at infinite dilution), by the average number of re-absorption cycle $\langle n \rangle$ [12,16,17] such that:

$$\tau = \langle n \rangle \tau_M \quad (2)$$

Also, the probability of self re-absorption (a) was calculated from Eq. (3) [15], where

$$\tau = \frac{\tau_M}{1 - a\phi_f} \quad (3)$$

where ϕ_f is the fluorescence quantum yield. The probability of self re-absorption depends on the overlap between the emission and absorption spectra as well as the path length of fluorescence through the sample. Table 2 summarizes the fluorescence lifetime, number of reabsorption cycle and probability of re-absorption at each concentration of DTPD in $CHCl_3$. A similar study has been reported earlier for R6G [17] and N,Ń-bis (2,5-di-*tert*-butylphenyl)-3,4:9,10-perylene bis (dicarboximide) [10].

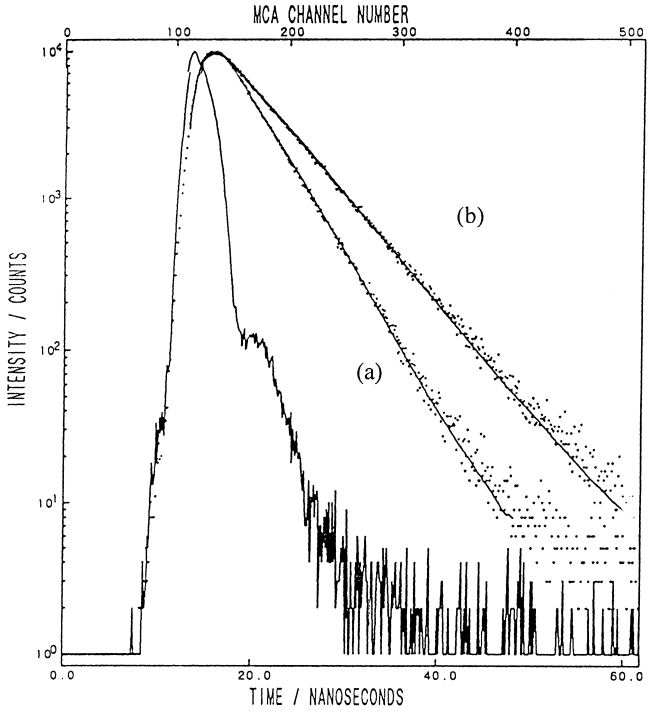

Fig. 3. Fluorescence decay curves of (a) 1×10^{-6} and (b) 1×10^{-4} mol dm^{-3} DTPD in $CHCl_3$ ($\lambda_{ex} = 450$ nm and $\lambda_{em} = 510$ nm).

3.2. Excitation energy transfer

A 5×10^{-4} mol dm^{-3} solution of DTPD in $CHCl_3$ gives weak laser emission in the lasing range 530–580 nm with emission maximum at 560 nm. The weak laser emission of DTPD can be attributed to the strong overlap between its emission and electronic absorption spectra, low solubility in $CHCl_3$ and low molar absorptivity at pumping wavelength (337.1 nm). The excitation energy transfer from DMC ($\lambda_{ex} = 337.1$ nm) as a donor to DTPD as an acceptor has been studied to improve the laser emission of DTPD when excited by nitrogen laser. The DMC/DTPD pair represents an efficient energy transfer laser system achieving better harvesting of light photons at 337.1 nm. Fig. 4a shows the increase in the output energy of laser emission from DTPD at 560 nm as the concentration of donor (DMC) increases. At relatively higher DMC concentrations ($> 12 \times 10^{-4}$ mol dm^{-3}), the maximum output energy of laser decreases due to self-absorption which is responsible for screening of the laser emission.

The rate of energy transfer (K_{ET}) in DMC/DTPD pair has been calculated by studying the fluorescence quenching of DMC using DTPD as a quencher. Fig. 4b shows the corresponding Stern–Volmer plot. The Stern–Volmer relation is in the form [18]:

$$\frac{I_0}{I} = 1 + K_{ET}\tau_0[Q] \quad (4)$$

where I_0 and I are the fluorescence intensities of DMC in the absence and presence of quencher, respectively. [Q] is

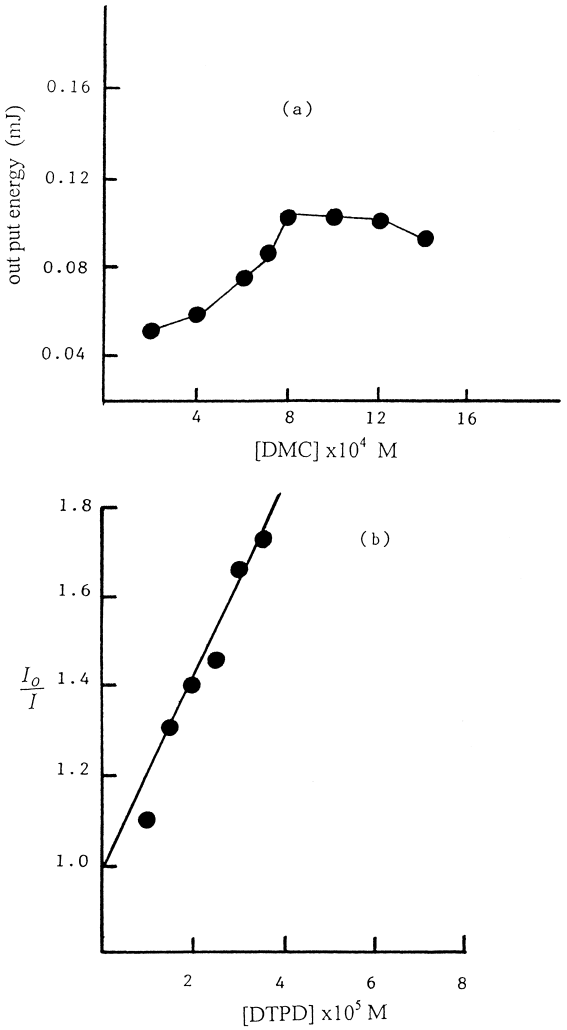

Fig. 4. (a) Output energy of DTPD laser emission as a function of DMC concentration in $CHCl_3$. (b) Stern–Volmer plot for the quenching of DMC fluorescence by DTPD in $CHCl_3$.

the quencher concentration, K_{ET} is the rate constant of energy transfer and τ_0 is the fluorescence lifetime of donor in the absence of quencher ($\tau_0 = 3.6$ nm for DMC in $CHC1_3$). From the slope of the plot, K_{ET} was found to be $5.8 \times 10^{12}\,M^{-1}\,s^{-1}$. This value is much higher than the diffusion rate constant in chloroform ($K_{diff} = 17 \times 10^9\,M^{-1}\,s^{-1}$) at room temperature indicating a diffusionless energy transfer mechanism. From the spectral data there is a significant overlap between the absorption spectrum of DTPD and the emission spectrum of DMC. The critical transfer distance (R_0) has been calculated for the DMC/DTPD pair by applying the Forster equation [19]:

$$R_0^6 = \frac{9000 \ln(10) k^2 \phi_D}{128\pi^5 n^4 N_A} \int_0^\infty \frac{F_D(\bar{\nu})\varepsilon(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu} \quad (5)$$

where ϕ_D is the emission quantum yield of donor in the absence of acceptor, K is the orientation factor ($K^2 = 0.67$ for randomly distributed molecules), N_A is the Avogadro's number and n is the solvent refractive index. The integral is the overlap integral for the fluorescence spectrum of donor normalized to unity (F_D) and the absorption spectrum of the acceptor (ε_A). R_0 was calculated as 34 Å in $CHCl_3$. This value is much greater than those characterizing collisional energy transfer for which $R_0 \leqslant 10$ Å [19]. This indicates that the underlying mechanism of energy transfer is that of resonance energy transfer due to long-range dipole–dipole interaction between excited donor and ground state acceptor.

3.3. Photodecomposition of DTPD

DTPD dye displays photodecomposition in CH_2Cl_2, $CHCl_3$ and CCl_4 upon irradiation at 254 nm ($I_0 = 5 \times 10^{-6}$ Einsten min^{-1}). As seen from Figs. 5 and 6, both absorption and emission of DTPD decrease with increasing the irradiation time. However, the emission around 440 nm increases with irradiation time. The emission at 440 nm may be due to a photo-degradation product.

The rate constant of photodecomposition of DTPD was calculated by applying the simple first-order rate equation

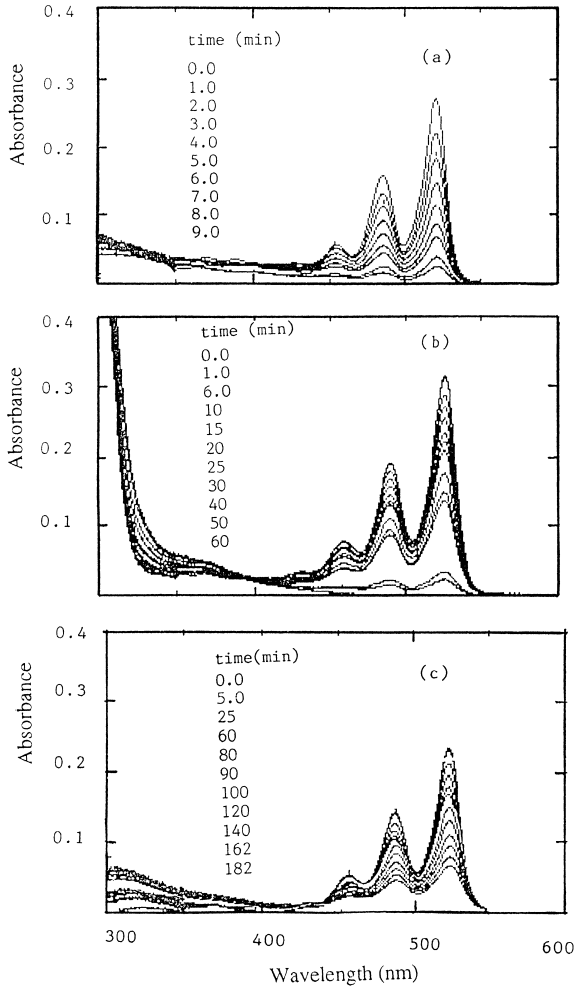

Fig. 5. Effect of irradiation at 254 nm on the electronic absorption spectra of DTPD in (a) CCl_4; (b) $CHCl_3$ and (c) CH_2Cl_2. Irradiation times (min) are indicated in the figure.

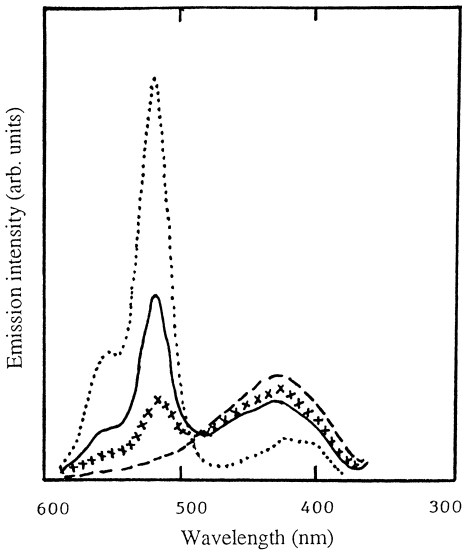

Fig. 6. Effect of irradiation at 254 nm on the emission spectra of DTPD in CCl_4. Irradiation times at decreasing emission intensity at 522 nm are 0.0, 3.0, 5.0 and 7.0 min.

as follows:

$$\ln\frac{A_0 - A_\infty}{A_t - A_\infty} = kt \quad (6)$$

where A_0, A_t and A_∞ are the initial absorbance, absorbance at time (t) and infinity, respectively. k is the rate constant. The rate constants were found to be 0.007, 0.014 and 0.23 min^{-1} in CH_2Cl_2, $CHCl_3$ and CCl_4, respectively. It was observed that the rate constant of photodecomposition of DTPD increases with the electron affinity of chloromethane solvents (E_A = 1.36, 1.75 and 2.12 eV for CH_2Cl_2, $CHCl_3$ and CCl_4, respectively). This indicates that an electron transfer from excited DTPD* molecules to chloromethanes is taking place. The following Scheme can be proposed to account for the photodecomposition of DTPD dye in chloromethane solvents;

$$DTPD \xrightarrow{254\,nm} {}^2(DTPD)^* \text{ absorption of light} \quad (7)$$

$${}^2(DTPD)^* \xrightarrow{ic} {}^1(DTPD)^* \text{ internal conversion} \quad (8)$$

$${}^1(DTPD)^* \rightarrow DTPD + h\nu \text{ fluorescence} \quad (9)$$

$${}^1(DTPD)^* + CH_nCl_{4-n} \rightarrow {}^1[DTPD^{+\delta} \ldots {}^{-\delta}CH_nCl_{4-n}]^* \text{exciplex} \quad (10)$$

$${}^1[DTPD^{+\delta} \ldots {}^{-\delta}CH_nCl_{4-n}]^* \rightarrow h\nu \text{ (Fluorescence) exciplex} \quad (11)$$

$${}^1[DTPD^{+\delta} \ldots {}^{-\delta}CH_nCl_{4-n}]^* \rightarrow [DTPD^{+\bullet} \ldots {}^{-}{}^{\bullet}CH_nCl_{4-n}] \text{ electron transfer} \quad (12)$$

$$[DTPD^{+\bullet} \ldots {}^{-}{}^{\bullet}CH_nCl_{4-n}] \rightarrow [DTPD^{+\bullet} \ldots {}^{\bullet}Cl \ldots {}^{\bullet}CH_nCl_{3-n}] \quad (13)$$

$$[DTPD^{+\bullet} \ldots {}^{-}Cl \ldots {}^{\bullet}CH_nCl_{3-n}] \rightarrow \text{photoproducts formed in the solvent cage} \quad (14)$$

We propose an initial electron transfer from excited singlet DTPD to CH_nCl_{4-n} leading to formation of a transient exciplex, step (4). This is followed by formation of intermolecular ion pair, step (7), which gives ($DTPD^{+\bullet} \ldots Cl^{-\bullet} \ldots CH_nCl_{3-n}$) via the well known reaction; $CH_nCl_{4-n} + e \rightarrow^{+} CH_nCl_{3-n} +^{-} Cl$ and the formation of contact ion pair between DTPD radicat cation and chloride ion, step (8). The photodecomposition of several electron donors has been reported earlier [20–24]. Also, the photoionization of some aromatic and aliphatic amines in halomethane solvents has been reported [25].

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