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Detection of Photoinduced Intramolecular Electron Transfer in 4-(1-Pyrenyl)butyl 9-Anthracenecarboxylate by Transient Absorption and Resonance CARS Spectra

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Transient absorption and resonance CARS spectra of title molecule have been observed in acetonitrile solution to show the presence of cationic pyrenyl group and anionic 9-anthryl group (or 9-anthracenecarbonyloxy group). The 337 nm UV pulse was used for the excitation. The result was combined with the linear dependence of the signals on the intensity of UV pulse to prove that the ionic radicals were produced by the intramolecular electron transfer from the locally excited pyrenyl group to the 9-anthryl group (or 9-anthracenecarbonyloxy group).

As reviewed by De Schryver et al.[1)] the intramolecular exciplex formation on electron transfer, which occurs in molecules having two chromophores separated by unconjugated spacer group, have been investigated with such interests as to study the kinetics and mechanisms of intermolecular interactions under the control of separation and mutual orientation of interacting moieties,[2—6)] to design and control photochemical reactions,[7,8)] or to probe the structure of macromolecules.[9,10)] Molecules consisting of identical halves with arylic chromophores such as 1,2-di(9- and 1-anthryl)ethane[11)] or 1,3-di(1-pyrenyl)propane[4)] and those in which arylic rings and *N*,*N*-dimethylamino group, functioning as electron acceptor and donor, respectively, are separated by alkyl chains,[2,5)] have been studied extensively. The use of alkyl chains as spacer group sometimes poses problem in defining the separation and orientation of the two chromophore groups bacause of low barrier of internal rotation around the carbon–carbon single bonds of alkyl chain, and the investigation of cyclophanes[12,13)] or bridged molecules[3)] were made to avert this problem by rigidly fixing the chromophores. Vanderauwera et al. carried out an experiment[2)] in which alkyl ester groups with various chain length were used to separate dimethylamino group and 9-anthryl group. Aromatic esters are characterized by the C–O single bond where the alkyl group and carbonyl oxygen are in cis conformation and the carbonyl, *O*-alkyl bond, and aryl rings are coplanar. Combining this with the flexibility of alkyl chain, Vanderauwera et al. adjusted the separation between the chromophores by the length of alkyl chain in their investigation of the kinetics of intramolecular exciplex formation and electron transfer in the series of ω-(dimethylamino)alkyl esters of 2-anthracenecarboxylic acid.

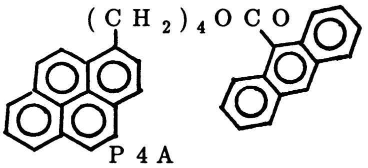
Recently, however, the present authors (M. I. and K. T.) have unveiled several unexpected features in the photochemical behavior of 1-pyrenylmethyl 9-anthracenecarboxylate;[4)] broad emission band was observed for the solution (10^{-5} M; 1 M=1 mol dm^{-3}) in polar solvent (acetonitrile) when either the pyrenyl (at 313 nm) or the anthracene (at 365 nm) moieties were excited by UV pulse, the intensity of the excitation with respect to that of fluorescence by locally excited species increased monotonically from 200 K to 293 K, and the broad emission of the solution in nonpolar isooctane was asymmetric and double-peaked.

In this paper we describe about the combined use of transient resonant CARS and transient absorption spectroscopy to the characterization of one-photonically produced ionic radical group.

It should be mentioned that the analysis of fluorescence and exciplex emission spectra has been the principal tool for the investigation of the intramolecular exciplex formation and electron transfer, and even in those papers that reported on the transient absorption spectrum of ionic species the *possibility that the ionic species can also be produced* from the two-photon processes was overlooked, thus the experimental verification of the one-photonical production of ionic species has been lacking.

Transient absorption and the transient resonance Raman spectra have been used for the study of photoinduced species. The resonance Raman effect is particularly useful because we get information of the molecular vibrations in the electronic state. The CARS (coherent anti-Stokes Raman spectroscopy) is a nonlinear Raman spectroscopy having its exclusive advantage for the observation of luminous samples because conventional resonance Raman spectroscopy is not operative in such samples. The vibrational spectrum of the various transient species produced in photoexcited pyrene has been studied by this method.[15,16)]

Present study of transient absorption and transient resonance CARS spectra was undertaken to get solid evidence for the occurrence of intramolecular electron transfer and to investigate the direction and degree of the transfer that takes place between the two chromophores in the UV excited 4-(1-pyrenyl)butyl 9-anthracenecarboxylate (**1**) that is abbreviated as P4A hereafter.



P 4 A

The absorption spectrum of P4A as well as those of other 1-pyrenylalkyl 9-anthracenecarboxylates studied so far exhibits the feature that is the 1:1 superposition of the spectra of 1-pyrenylmethanol and 9-anthracenecarboxylic acid, with just slight shifts by a few nm in peak positions, indicating the absence of any specific interaction between the chromophores in the ground state.[14]

Experimental

The preparation of purified sample has been described elsewhere.[14] The purified P4A was dissolved in acetonitrile (spectrograde) to make the sample solution of 10^{-3} M concentration.

The output beam of an N_2 laser (Molectron UV-24) with output power of 9 mJ/pulse and duration time of 10 ns was used both to excite the sample and to pump the dye lasers. No time delay was imposed between the UV and dye laser pulses. The confirmation that the observed signals originated from the transient species of P4A and not from the decomposition products was made by examining the absorption spectrum taken after the experiment. The transient absorption spectrum was obtained by alternately blocking the UV pulse that excited P4A and comparing the intensity of the transmitted dye laser with and without the irradiation by the UV pulse. The two laser beams were adjusted so that the transient absorption was maximal. The intensity I of the transmitted dye laser beam with the UV beam irradiating the cell was divided by the intensity I_0 that is the value recorded without the irradiation at various wavelengths of the dye laser. The derived values of $\log(I_0/I)$ for the deaerated solution are plotted against wavenumber in Fig. 1a for the region where the spectrum of pyrene cation radical is expected. Figure 1c shows the result of the observation in the region where the absorption by anthracene anion radical is expected. Partly owing to the lower sensitivity of the used photomultiplier and the lower intensity of the dye laser output in the longer wavelength region, the observation in the region failed to give distinct absorption peak although the presence of transient absorption was evident from the attenuation of the laser beam on the excitation by UV light.

The procedure for the transient resonance CARS experiment has been described in our previous paper.[15] Briefly, two dye lasers pumped by the N_2 laser were used when ω_1 beam (pump beam) was set resonant with the transient absorption while ω_2 beam (probe beam) was scanned over the range where the difference ω_1-ω_2 varied from 1000 to 1700 cm^{-1}.

The dependence of both the transient absorption and the resonance CARS signals on the power of excitation UV beam was measured by attenuating the UV beam. The sets of filters with 76% transmission per sheet at 337.1 nm were used.

Results and Discussion

Transient Absorption Spectrum. The transient absorption spectra observed on the photoexcitation of pyrene have been reported by several authors. Post et al. reported the observation of absorption peaks at 19500 cm^{-1} and 21200 cm^{-1} that they assigned to $S_n \leftarrow S_1$ and $S_m \leftarrow S_1$ bands, respectively.[17] The $T_n \leftarrow T_1$ absorption band at 24000 cm^{-1} was reported by the same authors and by Grellmann[18] who also reported on the absorption spectra of anion and cation radicals of pyrene at 20400 cm^{-1} and 22500 cm^{-1}, respectively. Siomos and Christophorou verified that the ion radicals are produced by two-photon ionization and gave the value of 38700 cm^{-1} as the threshold energy of the process.[19] Typical results of our observations of the transient species of pyrene are reproduced in Fig. 1b.

We find from the comparison of Figs. 1a and 1b that the transient absorption spectrum of P4A exhibits close resemblance with that of pyrene in methanol. Considering that the fluorescence lifetime of the S_1 state of pyrene is longer than 100 ns and that the related molecule P1A was found to give the emission with the quantum yield of about 1% and the emission lifetime of less than 1 ns,[14] it is expected under the present experimental condition that the sample contained such transients as the species in which the pyrenyl group was locally excited to the S_1 state, the species where the pyrenyl group was in the lowest triplet state T_1 and the ones that had undergone the intramolecular electron transfer with or without the formation of exciplexes. We thus associate the peaks at 23800 cm^{-1} and 20000 cm^{-1} in Fig. 1a with the pyrenyl-localized $T_n \leftarrow T_1$ and $S_m \leftarrow S_1$ absorption bands, respectively, and the peak at 21500 cm^{-1} is assigned as the overlap of pyrenyl-localized $S_n \leftarrow S_1$ band and the absorption band of cationic pyrenyl group. The presence of cationic pyrenyl group was confirmed by the CARS experiment as described below. The formation of the T_1 species of P4A was verified by the observation of the resonance (ω_1=23750 cm^{-1}) CARS signal at 1365 cm^{-1} that corresponds to the intense Raman band of pyrene in the T_1 state. We note that the $T_n \leftarrow T_1$ absorption of P4A shows up in both the deaerated and air-saturated solutions while the band of pyrene is observed only in the air-saturated solution. The reason for the appearance of the $T_n \leftarrow T_1$ band of pyrene in only air-saturated solutions

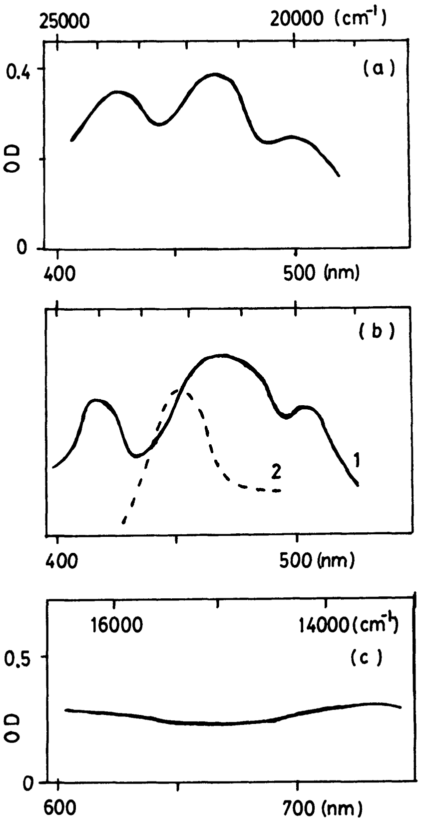


Fig. 1. Transient absorption spectra of the photoproduced transient species of P4A and pyrene. (a): the spectrum from 400 to 550 nm of the deaerated solution of P4A in acetonitrile (10^{-3} M concentration) under the irradiation of UV pulse at 337.1 nm, (b): the spectra from 400 to 550 nm of the UV produced transient species of molecular pyrene and curve 1 is the spectrum observed in air-saturated methanol solution in which the S_1 and T_1 species of pyrene are present and curve 2 is the spectrum of pyrene cation radicals that were produced in the aqueous micellar solution of hexadecyltrimethylammonium bromide, and (c): the spectrum observed from 600 to 740 nm region for the same system as described in (a). The UV pulse at 337.1 nm having the pulse duration time of 10 ns and the repetition rate of 10 pps was used throughout.

is attributed as owing to the dissolved oxygen working as the effective promoter of intersystem crossing. The present observation suggests that the production pathway of the T_1 state from the S_1 state, both localized to the pyrenyl group, of P4A is different from that of pyrene.

Anthracene anion radical has been known to have the peak of the absorption band at 13700 cm^{-1} (730 nm).[20] Actually, the question whether the ionic moiety of the present transient is either the 9-anthryl group, 9-anthracenecarbonyl group, or 9-anthracenecarbonyloxy group remains to be solved and we expect that absorption peak may be shifted outside the present observation for latter two groups. In any event, it is likely that the obvious absorption giving the change of 0.3 in the optical density under the optical pass length of 1 mm in the region of 730 nm in P4A (see Fig. 1c) originates from one of the abovementioned species.

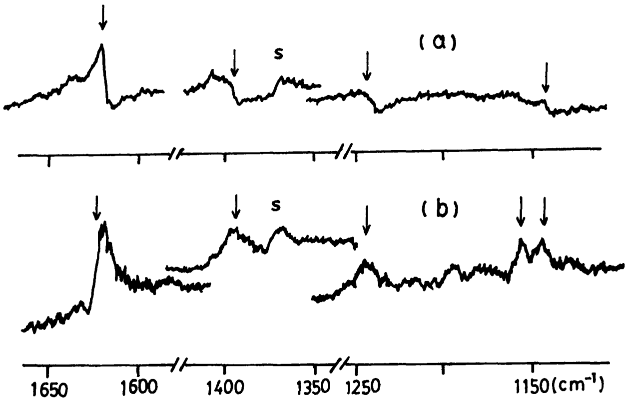


Fig. 2. Transient resonance CARS spectra of P4A in deaerated acetonitrile solution (10^{-3} M concentration) observed when the solution was irradiated by 337.1 nm pulse under the conditions (a): ω_1= 21000 cm^{-1} and (b): 21800 cm^{-1}. Arrow and s denote the Raman bands of the transient species and the solvent molecule, respectively.

Transient Resonance CARS Spectrum. The resonance CARS spectrum of P4A was observed by setting the ω_1 beam resonant with the transient absorption band at 21500 cm^{-1}. Figures 2a and 2b show the results for the settings of ω_1=21800 cm^{-1} and ω_1=21000 cm^{-1}, respectively. From Figs. 2a and 2b one notes that the Raman band at 1622 cm^{-1} shows dispersion dips on mutually opposite side of the peak. The feature shows that one-photon electronic resonance effect is at work on the totally symmetric vibrations and that of the absorption band is the 0–0 band origin located near 21500 cm^{-1}. The wavenumbers of the observed six Raman bands that showed up only when the UV light was incident are listed in the first column of Table 1. The reported values of pyrene in various states are also listed in the following columns. The present result is close to the reported values of the Raman shifts for the cation radical of pyrene that has been produced by UV-irradiation of pyrene in such systems as acetonitrile, methanol, cationic micelle, and pyrene–dicyanobenzene in acetonitrile solutions.[15] It should be noted that the Raman frequencies of the present study were obtained under electronically resonant condition and thus the participation of the pyrenyl group in the ground state can be disregarded.

The behavior of the CARS signals by the change of the intensity of UV light was examined to prove that the signals were associated with the cationic pyrenyl group and not with either the free pyrenyl cation radicals that could have resulted from two-photonic ionization or the photofragmented pyrenyl radicals.

Table 1. Observed Raman Shifts of Photo-excited P4A and Various Species Pyrene (cm^{-1})

P4A*, CARS (acetonitrile solution)[a]	S_0, Raman (solid)[b]	S_1, CARS (pentane-d_{12} solution)[c]	T_1, CARS (heptane solution)[c]	Anion, Raman (THF solution)[c]	Cation, CARS (CTAB[d] aqueous micellar solution)[c]
	1642 s ($\mathrm{b_{1g}}$)				
		1633 vw ($\mathrm{a_g}$?)			
1622	1627 vs ($\mathrm{a_g}$)				1627 m ($\mathrm{a_g}$)
			1595 s ($\mathrm{a_g}$)	1604 s ($\mathrm{a_g}$)	
	1584 s ($\mathrm{a_g}$)				
		1565 m ($\mathrm{b_{1g}}$)			
	1549 w ($\mathrm{b_{1g}}$)				
		1500 m ($\mathrm{a_g}$)			
		1445 s ($\mathrm{a_g}$)			
1396	1405 vs ($\mathrm{a_g}$)	1433 s ($\mathrm{b_{1g}}$)			1410 s ($\mathrm{a_g}$)
			1365 vs ($\mathrm{a_g}$)	1364 m ($\mathrm{a_g}$)	
	1371 m ($\mathrm{b_{1g}}$)		1345 m ($\mathrm{a_g}$)		
	1359 vw ($\mathrm{a_g}$, $\mathrm{b_{1g}}$)	1329 s ($\mathrm{a_g}$)	1340 m ($\mathrm{a_g}$)		
		1315 vw ($\mathrm{b_{1g}}$)			
1240	1236 vs ($\mathrm{a_g}$)	1246 s ($\mathrm{a_g}$)			1245 m ($\mathrm{a_g}$)
	1206 vw ($\mathrm{b_{1g}}$)			1225 m ($\mathrm{a_g}$)	
	1174 vw ($\mathrm{b_{1g}}$)		1188 w ($\mathrm{a_g}$)		
1155	1142 s ($\mathrm{a_g}$)			1123 m ($\mathrm{a_g}$)	1138 m ($\mathrm{a_g}$)
1142		1113 w ($\mathrm{b_{1g}}$)	1110 m ($\mathrm{a_g}$)		
	1107 vw ($\mathrm{b_{1g}}$)	1107 vw ($\mathrm{a_g}$?)			
	1066 s ($\mathrm{a_g}$)				
		1032 w ($\mathrm{a_g}$)			

a) Originating from transient species of P4A, present study. b) S. J. Cyvin, B. N. Cyvin, J. Brunvoll, J. C. Whitmer, K. Klaeboe, and J. E. Gustavsen, *Z. Natureforsch.*, **34a**, 876 (1979). Symmetry species of the vibrational mode based on D_{2h} symmetry are shown in parentheses. c) Ref. 15. Symmetry species of the vibrational mode based on D_{2h} symmetry are shown in parentheses. d) Hexadecyltrimethylammonium bromide.

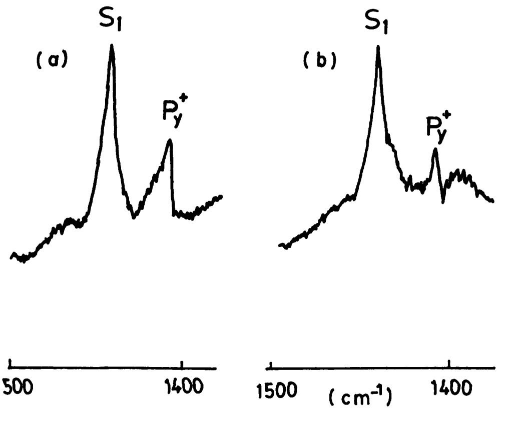


Fig. 3. The effect of UV power on the transient CARS signal of photoproduced species of pyrene under ω_1=21800 cm^{-1}; (a) without attenuation and (b) under attenuation by about 50% of UV power. The methanol solution (10^{-3} M) of pyrene were used for the measurement and the signals from the one-photon excited S_1 species and that from the two-photon ionized pyrene cation radical (marked by S_1 and P_y^{+}, respectively) are seen to exhibit distinctly different dependence on the intensity of UV pulse.

Figure 3 shows the population change in the pyrene/methanol system as observed on the resonance CARS signals of the pyrene cation radical and the S_1 state species. The frequency of ω_1 was set at 21800 cm^{-1}. The signal at 1445 cm^{-1} originates from the S_1 state of pyrene produced by one-photon excitation and the signal at 1410 cm^{-1} is from the pyrene cation radical that is produced by two-photon ionization. Figure 3 shows that the relative intensity of the two CARS signals changed by the intensity of UV excitation and the change evidently resulted from the difference in the population processes of the two species; the production of S_1 species by one-photon processes vs. the two-photon process to produce the cation radical. Figure 4 shows the decrease of CARS signal of cationic pyrenyl group in P4A at 1396 cm^{-1} (marked by arrow) and that of solvent acetonitrile (marked by s) when the UV power (at 337.1 nm) was attenuated by 0%(a), 58%(b), and 100%(c). Figures 4d—4g are the results of computer simulation. Of three components of CARS susceptibility, the Raman nonresonant background term and the term that is resonant to the Raman band of solvent molecule stay constant of the intensity of UV radiation and their relative magnitude was determined by simulating the feature of Fig. 4c to give the curve shown in Fig. 4f. The term causing the 1396 cm^{-1} band is proportional to the population of photoproducts and its relative magnitude with respect to other terms was determined for the condition that gives the trace in Fig. 4a and the trace shown in Fig. 4d was derived from the simulation. The attenuation of UV power causes the

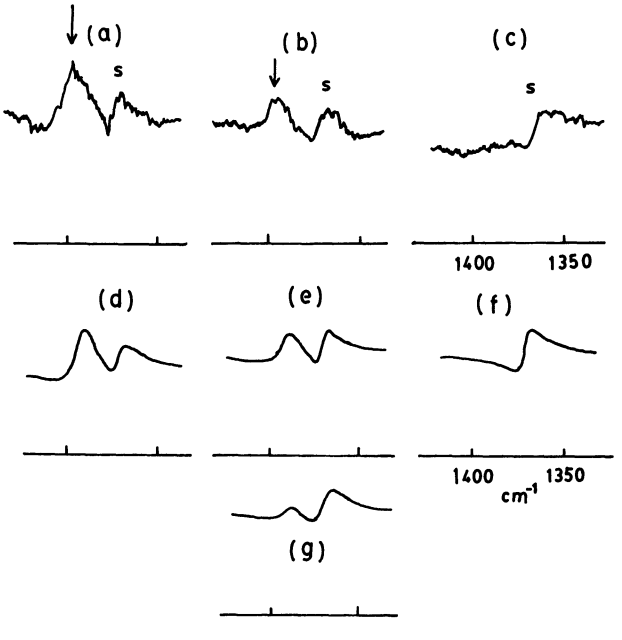


Fig. 4. The UV-power-dependent variation of the observed and simulated features of the CARS spectrum in the region where the resonance CARS signal of photoexcited P4A (marked by arrows) and the CARS signal of solvent acetonitrile are observed. The signals observed under the attenuation of UV power by 0%, 58%, and 100% are shown in (a), (b), and (c), respectively, while the simulation was made by using the traces in (a) and (c) as references giving the reference curves of (d) and (f), respectively, and the theoretical curves of (e) and (g) were obtained for the cases when the population of the transient species changes linearly (e) and quadratically (g), with intensity of UV pulse.

population of the photoproduced species to decrease leading to the change in the spectral profiles. Figures 4e and 4g are the results of the simulations for the linear and quadratic dependencies, respectively, of the population on UV power, and we note that Fig. 4e is the better reproduction of the observed feature of Fig. 4b.

The frequency (21800 cm^{-1}) of the ω_1 beam is inside the absorption band of transient cationic species and the intensity of the ω_1 beam changed by the intensity of UV beam. The intensity of the ω_1 beam at the point through the sample is plotted in Fig. 5 against the UV power used for the photoexcitation where the intensity of ω_1 beam is expressed in the unit of optical density of the sample. The linear production of the cationic pyrenyl radicals with respect to the intensity of UV beam as verified above is in clear contrast with the two-photonic production of the pyrene cation radicals.

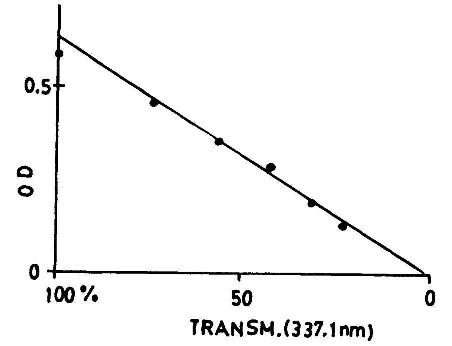


Fig. 5. Plot of the change in the intensity of transient absorption at 21800 cm^{-1} by the intensity of UV irradiation. Linear increase of the absorption with increasing UV power is derived from the plot.

The overall feature of the transient absorption spectrum of P4A in the acetonitrile solution resembles that of UV-irradiated pyrene in methanol where the signals from both the cation radical and the S_1 state of pyrene have been observed. The resonance CARS signals of only the cationic pyrenyl group were, however, observed in the present sample, suggesting the different processes of the production of cationic species in the two systems.

The present result points to the conclusion that the cationic species in P4A resulted by the internal conversion and successive intramolecular relaxation from one-photonically excited Franck–Condon state of pyrenyl group. We have also mentioned from the observation of weak yet distinct transient absorption around 730 nm region that either the anthryl group or the anthracenecarbonyloxy group in P4A acquired anionic nature following the photoexcitation of pyrenyl group. Hence the present observation is a direct indication that the pyrenyl group becomes cationic through the intramolecular electron transfer of nearly unit charge from the locally excited 1-pyrenyl group to the 9-anthryl group (or 9-anthracenecarbonyloxy group). Although the attempt to observe the transient CARS signal of negatively charged anthryl group failed owing to small electronic resonance effect and the technical difficulty in obtaining enough power of the dye lasers in the near infrared region, the present picture of intramolecular transfer of an electron from pyrenyl to anthryl group (or anthracenecarbonyloxy group) fits the model that was presented in Ref. 14, that is, through-bond electron transfer takes place before the Coulombic attraction between the two oppositely charged moieties enables the rotation around the C–O bond to let the s-trans conformation of P4A in ground state change into s-cis conformation that is necessary for the formation of stable intramolecular exciplex with two chromophores sitting in face-to-face conformation. The Coulombic attraction is needed to overcome the potential barrier of about 50 kJ mol^{-1} lying expectedly between the two conformations.

In conclusion, the occurrence of intramolecular electron transfer from the locally excited 1-pyrenyl group to the 9-anthryl group (or 9-anthracenecarbonyloxy group) in the acetonitrile solution of P4A has been confirmed from the observation of transient absorption and resonance CARS spectra. Further work is under way to solve the remaining questions such as if the species under study was identical with the species for which the broad exciplex-like emission band was observed and if the two chromophores are of elongated end-to-end conformation or of sandwitch type. The undertaken experiments on related molecules and of time-resolved spectroscopy are expected to provide further informations on the chemical and physicochemical characteristics of bichromophoric carbohydrates.

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