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A Photophysical Study on Anthraquinone–Fluorescein–Anthracene

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ABSTRACT

An anthraquinone–fluorescein–anthracene (AQ–FL–AN) triad was synthesized and its absorption and fluorescence spectra were studied. In flash photolysis, the product of charge separation was observed in μs order. © 1997 Elsevier Science Ltd

Keywords: triad, anthraquinone–fluorescein–anthracene, photophysic properties.

INTRODUCTION

Great progress has been made in the artificial mimicry of the photochemical reaction centre in natural photosynthesis by a group at Arizona State University, headed by Gust and Moore. They have linked porphyrins (P) with carotenoid polyenes (C) and quinones (Q) to form triads, C–P–Q [1–10], tetrads, C–P–Q1–Q2 [11] and C–P1–P2–Q [12], and even pentads, and have been quite successful. We have now synthesized another kind of triad, viz. anthraquinone(AQ, electron acceptor like Q)–fluorescein(FL, sensitizer like P in C–P–Q)–anthracene(AN, electron donor like C). Studies of the triad have shown it to have similar properties in some aspects to the C–P–Q system. Compared with C–P–Q, this triad is easy to synthesize and more stable and may therefore be more practical.

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EXPERIMENTAL

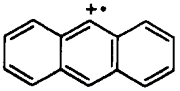
Synthesis

The synthesis, purification and identification of a diad model, 9-anthracenemethyl ester of FL (FL–AN) have been described previously [13]. The other diad model, 2-athraquinonemethyl ester of FL (FL–AQ) was similarly synthesized from FL and 2-bromomethyl anthraquinone, the latter being obtained from 2-methyl anthraquinone (MQ) and *N*-bromosuccinimide according to a previous report [14].

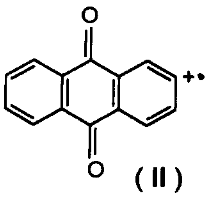
The synthesis of the triad AQ–FL–AN is shown in Scheme 1. Solutions of 3.0 g (10 mmol) of 2-bromomethyl AQ in 30 ml MeOH and 5.3 g (10 mmol) of FL–AN in 30 ml $CHCl_3$ were mixed with 1.7 g KI and refluxed overnight. After cooling, solvents were removed under vacuum and the resulting solid was washed with $CHCl_3$ and MeOH. The crude product was dissolved in MeOH, then separated and purified several times by TLC. The developing solution consisted of 10 parts of $CHCl_3$ and 0.5 parts of MeOH. The product purity was also examined by TLC, on which it showed only one spot in various developing solutions.

The UV–Vis absorption spectra were compared with those of the models: FL, MQ and 9-methyl AN (MA) in Fig. 1. ^{1}H-NMR (Varian XL-400, $CDCl_3$, δ) are shown in Fig. 2. The chemical shifts of the methylene protons were 5.9 (5.4 in 9-chloromethyl AN) and 5.7 (4.8 in 2-bromomethyl AQ). The relation of the conformation with UV–visible and NMR spectra is the following section.

FAB-MS (ZAB-HS): 743(M+1). **The fragments include 178(I+1), 208(II+1).**



(I)



(II)

Spectroscopy

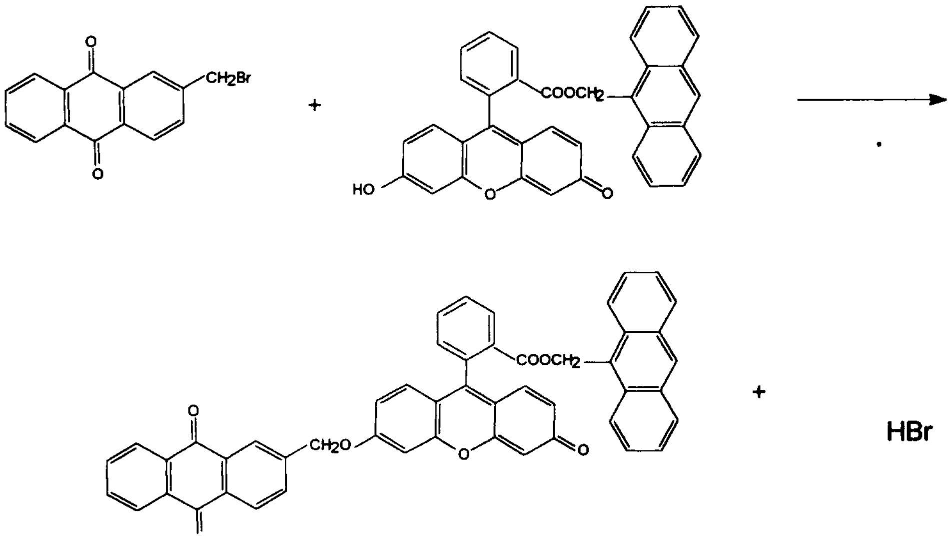
Absorption spectra were measured on a Hitachi 340 spectrophotometer and fluorescence spectra were treated on a Perkin-Elmer LS-5 luminescence spectrometer with a 3600 data station. The transient absorption spectra were determined on a flash photolysis apparatus which consisted of a DCR 2(30)A laser (Quanty Ray), a pulse xenon lamp, a multi-channel analyser, etc. interfaced with a mini-computer. The solvent was MeOH at a concentration of about 10^{-5} M.

RESULTS AND DISCUSSION

Conformation of the triad in solution

As shown in Fig. 1, the spectra of the triad are, in general, the sum of its moieties. However, in the triad the absorption maximum of FL is located at a longer wavelength than that of FL alone, while AN absorbs at shorter wavelengths than those of MA. Based on the excitation theory [15,16], it is predicted that the parallel (H-type) aggregates absorb at shorter wavelengths, but the head-to-tail (J-type) aggregates absorb at longer wavelengths. Thus, it is not difficult to interpret the spectra of the triad. The AN is linked to the phenyl carboxy, which is almost perpendicular the chromophoric plane of FL. Obviously, the AN has the opportunity to parallel to the chromophore showing an H-type absorption, whereas the FL in the triad can only be linked to AQ in the head-to-tail arrangement, thus being able to absorb at longer wavelengths.

It is also apparent (Fig. 2) that compared with those of AQ and AN, the chemical shifts of some aromatic hydrogens are moved upfield and others are shifted downfield. This shows that some aromatic hydrogens are located in the shielding zone of the chromophoric plane of FL and some are in the deshielding zone. From the CPK molecular model of the triad, only AN is able to enter the shielding zone of FL showing upfield shifts, whereas AQ can only be arranged in the deshielding zone, showing downfield movements.



(AQ-FL-AN) $C_{50}H_{30}O_7$=742

Scheme 1 Synthesis of triad AQ–FL–AN.

Energy transfer and fluorescence quenching

Data pertinent to energy transfer is listed in Table 1. It can see from this data that the singlet energy of MA is much higher than that of FL, while its triplet energy is even lower than that of the latter. In principle, their energy relation can meet the need of the mimicry of photosynthesis. In the diad model, FL–AN, the quantum efficiency of energy transfer from AN to FL is 0.38 [13]. In the triad one can also find this kind of energy transfer, as is shown in Fig. 3.

As regards the triplet energy, intermolecular energy transfer from FL to MA [17] have been found, as outlined in the scheme below.

$$\mathrm{FL} \rightarrow \mathrm{Vis}\ {}^1\mathrm{FL} \rightarrow \mathrm{ISC}\ {}^3\mathrm{FL}$$

$${}^3\mathrm{FL} + \mathrm{MA} \rightarrow \mathrm{FL} +{}^3\mathrm{MA}$$

$${}^3\mathrm{MA} +{}^3\mathrm{MA} \rightarrow{}^1\mathrm{MA} + \mathrm{MA} \qquad \text{triplet annihilation}$$

$${}^1\mathrm{MA} \rightarrow \mathrm{MA} + h\nu \qquad \text{delayed fluorescence}$$

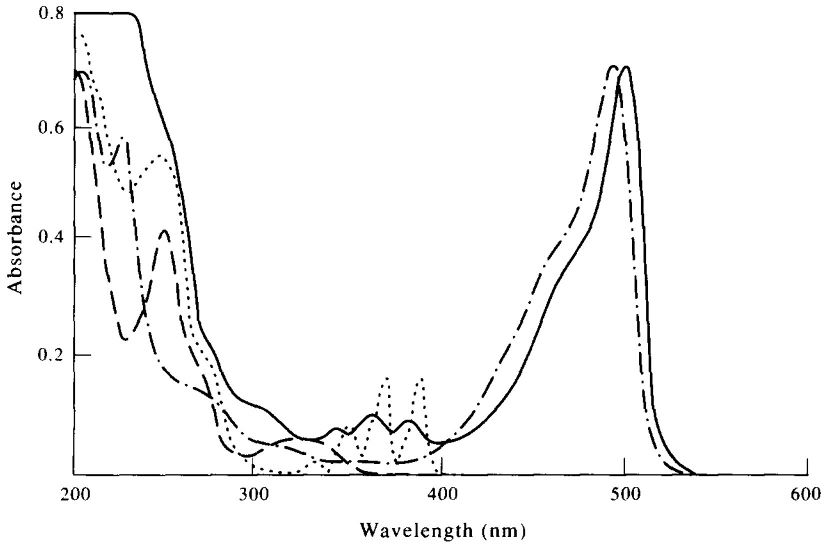


Fig. 1. Absorption spectra of AQ–FL–AN and its models. Connecting: AQ–FL–AN; dashed: MQ; dots: MA; dashdots: FL.

Using this process, we measured the intersystem crossing quantum yield of FL as 0.03 [17]. Thus, it is possible that a donor such as AN plays the roles of both antenna and protection for the dye simultaneously.

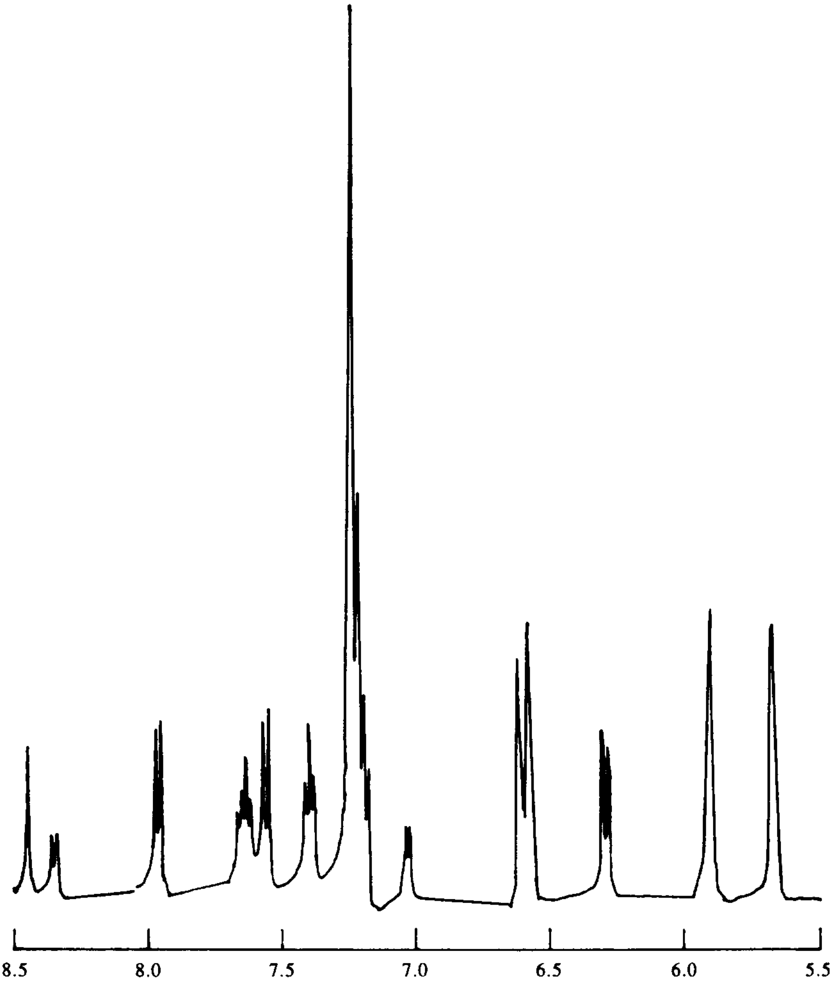


Fig. 2. ^{1}HNMR spectra of AQ–FL–AN in $CDCl_3$.

TABLE 1
Data Pertinent to Energy Transfer

	ES (kcal/mol)	*ET (kcal/mol)*
FL	55.9	44.7[17]
MA	76.3	42.7[13]

A comparison between the fluorescence of AQ–FL–AN with that of FL–AN is shown in Fig. 3 where AN was excited at 355 nm. It is apparent that, compared with the fluorescence of AN in AN–FL ($^{\Phi}F = 0.24$) [13], the fluorescence of AN in the triad is extremely decreased. There must therefore exist a remarkable extra dissipation process for the singlet excited state of the AN in the triad; the most possible dissipation path here should be the electron transfer from AN to AQ.

Flash photolysis study

To observe the photosensitized electron transfer directly, flash photolysis was carried out (ns order) many times. shows the transient difference

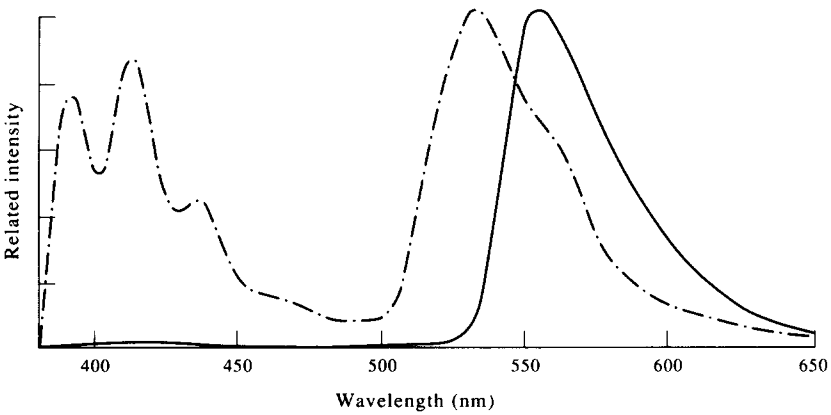


Fig. 3. Fluorescence spectra of AQ–FL–AN and FL–AN (Ex 355 nm). Connecting: AQ–FL–AN; dashdots: FL–AN.

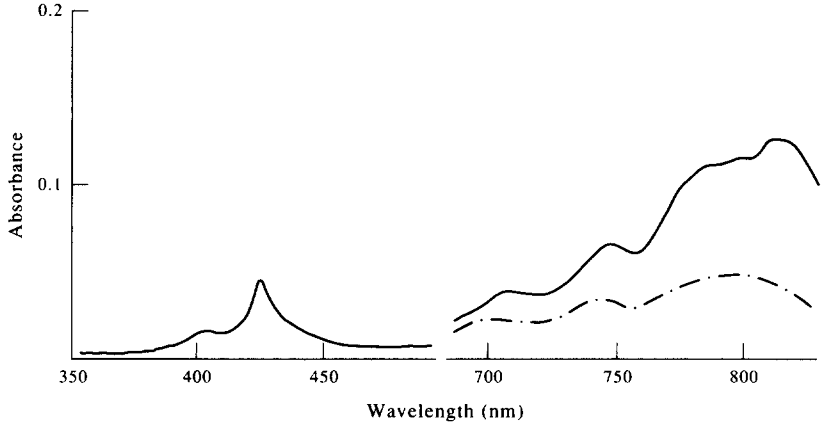


Fig. 4. Transient absorption of AQ–FL–AN. Connecting. 0 ns from flash; dashdots: 11.3 μs after flash.

TABLE 2
Controlled Experiments of Flash Photolysish

Experimental system	*Excitation wavelength (nm)*	*Absorptions round 425 nm*	*Absorptions beyond 600 nm*
FL + MA	355	+	+
	532	+	+
FL + MQ	532	–	+
FL–AN	355	–	–
	532	–	–
FL–AQ	532	–	–
AQ–FL–AN	355	+	+
	532	+	+

absorption of the triad at 532 nm excitation. Two absorptions were observed, one around 425 nm and the other above 600 nm. The former is similar to the T-T absorption of AN in some aspects, but has no rising time (an experiment under similar conditions showed that the T-T absorption of AN has a peak at 420 nm, with a rising time of about 2 μs and a lifetime of about 5 μs). To further determine what species show the absorptions in the triad, we carried out a series of controlled experiments. The results are listed in Table 2.

Based on the results shown in Table 2, and with consideration of related references, the absorption round 425 nm can be assigned to AN^+ [18],[19] while the absorption above 600 nm may be assigned to AN^+ and AQ^- [20]. The absorption at longer wavelengths is much stronger than that at shorter wavelengths. 11.3 μs from the flash starting, it remained at about 1/3, hence, it can be readily concluded that the photoinduced charge separate product has a lifetime of μs order.

ACKNOWLEDGEMENT

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