ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 97 (1996) 53–56

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photoinduced singlet interactions between esters of xanthene dyes and anthroic acid

Qiang Yu, Jian-jun He, Tao Shen *

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Received 7 July 1995; accepted 20 January 1996

Abstract

Four dyads from 9-anthroic acid and different xanthene dyes linked with the same flexible bridge were synthesized and characterized. Their photoinduced singlet electron transfer and energy transfer, intermolecularly and intramolecularly, were studied by static and dynamic fluorescence quenching and the comparison of excitation spectra and absorption spectra. The results were discussed from the viewpoint of structural factors, especially conformation of the dyads.

Keywords: Photoinduced singlet interactions; Xanthene dyes; Anthroic acid

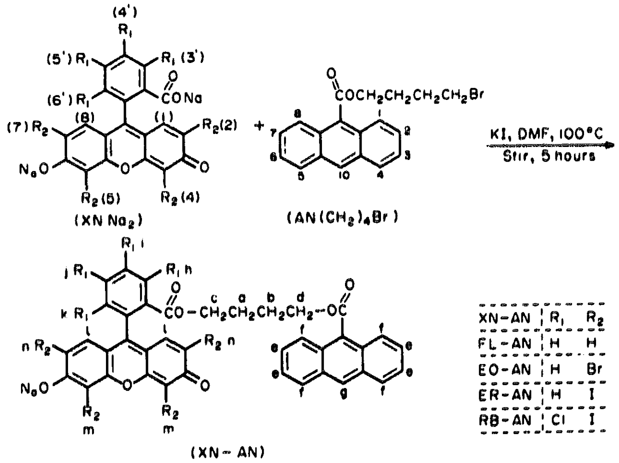
1. Introduction

As models of the photochemical reaction centre in the imitation of photosynthesis, many dyads and even polyads have been synthesized and studied [1]. We have also done some of this kind of work using xanthene (XN) dyes as photosensitizers [2–12]. To reveal step by steep the relationship of photoinduced electron transfer (ElT) and energy transfer (EnT) efficiencies to various structural factors, this time we synthesized four dyads composed of anthroic acid and different XN dyes with the same flexible butylene bridge. Their absorption spectra, excitation spectra, fluorescence spectra, fluorescence lifetimes, and static and dynamic fluorescence quenching were determined. Their intermolecular and intramolecular photoinduced singlet electron transfer and energy transfer were studied. Their differences in efficiencies are discussed.

2. Experimental details

2.1. Synthesis and structure assignment

Synthesis of 9-anthroic acid ethyl ester (ANEt), ethyl ester of fluorescein (FLEt), ethyl ester of eosin (EOEt), ethyl ester of erythrosin (ERE t), ethyl ester of rose bengal (RBEt) and *n*-bromobutyl ester of anthroic acid was described in Refs. [11,13]. The synthetic procedure for the dyads is shown in following scheme.



XN–AN	R₁	R₂
FL–AN	H	H
EO–AN	H	Br
ER–AN	H	I
RB–AN	Cl	I

Let us take EO–AN for an example. 690 mg of $EONa_2$ (eosin disodium, 1.0 mmol) and 350 mg of $AN(CH_2)_4Br$ (*n*-bromobutyl ester of anthroic acid, 0.97 mmol) were dissolved in 30 ml dimethylformamide (DMF) solvent, a little KI (potassium iodide) was added and the mixture was stirred at 100 °C for 5 h; the DMF solvent was evaporated under reduced pressure, the residue was separated in a silica gel column and, after washing with ethyl acetate and MeOH (methanol) (5:1, by volume), the red part was collected. The separation was repeated until the compound was purified. The chemical shifts were measured and are assigned according to the fine splitting in Table 1.

---

* Corresponding author.

PII S1010-6030(96)04325-0

Table 1
The chemical shifts of EO–AN in MeOH

Protons	Chemical shift (ppm)	Peak shape	Number
a, b	1.52–1.63	m	4
c, d	4.04–4.48	m	4
e	7.53–7.61	m	4
f	8.14–8.17	m	4
g	8.77	s	1
h	7.92–7.94	d	1
i	7.84–7.86	t	1
j	7.74–7.78	t	1
k	7.50–7.52	d	1
l	6.97	s	2

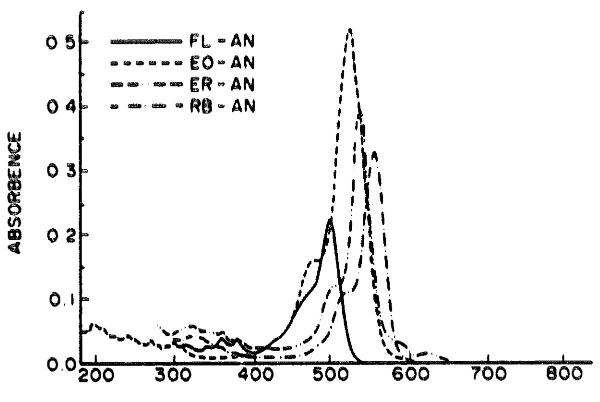


Fig. 1. Absorption spectra of XN–AN in MeOH.

A similar synthetic method was applied for FL–AN, ER–AN, and RB–AN. All the synthesized compounds were characterized by UV–visible, IR, and nuclear magnetic resonance (NMR) spectroscopy. The absorption spectra of the synthesized dyads are shown in Fig. 1 (concentrations were about 10^{-5} mol l^{-1}).

2.2. Photophysical measurements and calculations

In experiments, the solvent MeOH (AR grade) was redistilled; the concentration was in the range from 10^{-5} M to 10^{-6} M. Absorption spectra were measured with a Hitachi 557 UV–visible spectrophotometer and IR spectra were obtained with a Perkin-Elmer 983 G grating spectrophotometer using KBr pellets. H NMR spectra were obtained from a Varian XL 400 MHz spectrometer and fluorescence and excitation spectra were recorded with a Perkin-Elmer LS-5 luminescence photometer with a 3600 data station. Fluorescence lifetimes were automatically fitted with a Hiroba WAES 1100 single photon counting instrument. The redox potentials were also measured by means of cyclic voltammetry [10].

The quantum yield ϕ_f of fluorescence was calculated from following equation [4]:

$$\phi_f = (F^*A_0/F_0^*A)\phi_{f,0}$$

where A and F represent absorbance and fluorescence strength respectively. 0 denotes the reference compound. Anthracene (AN) and ethyl fluorescein were used as references: $\phi_f(\mathrm{AN}) = 0.27$ [14], $\phi_f(\mathrm{FLEt}) = 0.50$. The static and dynamic fluorescence quenchings were carried out and calculated by the same procedure described in Ref. [10]. Singlet state energy E_S was calculated from the absorption spectra and fluorescence spectra data [4].

3. Results and discussion

3.1. Intermolecular photoinduced singlet interactions

3.1.1. Energy transfer between models

The ANEt and the ethyl ester of XN dyes (XNEt) may serve as models of the corresponding moieties in dyads. E_S of the models is listed in Table 2.

Singlet energy transfer from ANEt to XNEt should be efficient on account of the good overlap between the fluorescence of the ANEt and the absorption spectra of the XNEt (significant Förster J integral). Energy transfer in the reverse direction is endothermic and can be ruled out.

In fact, when ANEt was excited, its fluorescence was easily quenched by XNEt; at the same time, we observed the XNEt's fluorescence at longer wavelengths. According the quenching results, k_{EnT} is more than of the order of 10^{13} s^{-1} mol^{-1} dm^3, much higher than that controlled by diffusion. This is because the singlet EnT is a long-range interactions. No contact between the donor and the dye esters is necessary.

3.1.2. Electron transfer between models

When XNEt was excited, its singlet state energy is lower than that of ANEt, so EnT was impossible. In this case, the decrease in dyes' fluorescence quantum yield in the same region can be caused by intramolecular ElT between models, because, for the excited dyes, other decay paths should basically be the same as those without ANEt.

In polar solvents, the free energy change ΔG of one ElT can be estimated by Rehm-Weller equation [2,15]:

$$\Delta G = E_O(\mathrm{D}) - E_R(\mathrm{A}) - E_S - C$$

where $E_O(\mathrm{D})$ and $E_R(\mathrm{A})$ are donor's oxidation potential and acceptor's reduction potential respectively, E_S is the singlet energy, and C is the stability constant of ions in polar solvent; here, in MeOH, we take $C = 0.06$ eV [2]. The redox potentials of model compounds were measured and are listed in Table 3.

Table 2
Singlet state energies of model compounds

Compound	ANEt	FLEt	EOEt	EREt	RBEt
E_S (kcal mol^{-1})	74.0	56.0	53.0	52.8	50.0
E_S (eV)	3.21	2.43	2.30	2.29	2.17

Table 3
Redox potentials of model compounds (vs. Ag/AgCl) (saturated KCl))

Compound	ANEt	FLEt	EOEt	EREt	RBEt
E_O (V)	0.95	0.90	0.80	0.79	0.88
E_R (V)	−1.74	−1.20	−1.04	−1.09	−0.95

If XNEt is considered to be an electron acceptors and ANEt an electron donor, ΔG is −0.32 eV (FLEt), −0.38 eV (EOEt), −0.32 eV (EREt) and −0.34 eV (RBEt). So, photoinduced EIT reactions from ANEt to XNEt were thermally permitted. Conversely, if XNEt served as an electron donor and ANEt as an acceptor, the corresponding ΔG values are 0.17 eV, 0.17 eV, 0.18 eV and 0.39 eV respectively. It seems to be impossible for electrons to transfer from XNEt to ANEt.

Our experiments showed that the fluorescence of FLEt, EOEt, EREt and RBEt was quenched by ANEt, and the results conformed with the Stern–Volmer equation [2,16], if there is no ground complex formation:

$$\phi_{f,0}/\phi_f = 1 + k_q\tau_{f,0}[Q]$$

where $\tau_{f,0}$ is the lifetime of XNEt without any quenchers.

Quenching data were processed with linear regression and the results are listed in Table 4.

A ground state complex was not observed in absorption spectra. From the k_q values listed in Table 4, we knew that the process of intermolecular EIT was controlled dynamically by diffusion, showing that the EIT reaction occurs only in the case of collision.

3.2. The conformation of dyads in solution

A dyad in a definite solvent should have a definite conformation statistically [17]. Let us also see it first from the NMR data in Table 5.

In dyads, moieties are linked by a flexible butylene bridge. On the basis of the above data, according to the analysis in Ref. [11], in FL–AN the conformation in which two chromophoric moieties are near to vertical with respect to each other should be dominant, while for EO–AN, ER–AN and RB–AN the conformation in which two chromophoric moieties are nearly parallel to one another seems preferred. We do not know why there is this difference in the conformation, but we do know that the latter three dyads contain heavy halogen atoms, whereas FL–AN does not.

Table 4
Quenching data of XNEts fluorescence by ANEt

XNEt	λ_{Ex} (nm)	λ_{Em} (nm)	τ_f (ns)	r	$k_q \times 10^{-9}$ (s^{-1} m^{-1})
FLEt	480	540	5.26	1.00	3.90
EOEt	510	570	3.20	0.99	3.54
EREt	530	590	0.55	0.99	3.45
RBEt	540	600	0.60	0.98	3.29

Table 5
Chemical shifts of hydrogens

	δ (ppm) in models	δ (ppm) in dyads	$\Delta\delta$ (ppm)
ANEt$_{10}$	8.49		
FLEt$_{1,8}$	6.60		
EOEt$_{1,8}$	7.15		
EREt$_{1,8}$	7.30		
RBEt$_{1,8}$	7.74		
FL–AN$_{10}$		8.40	−0.09
EO–AN$_{10}$		8.77	0.28
ER–AN$_{10}$		8.77	0.28
RB–AN$_{10}$		8.79	0.30
FL$_{1,8}$–AN		6.90	0.30
EO$_{1,8}$–AN		6.97	−0.18
ER$_{1,8}$–AN		7.10	−0.20
RB$_{1,8}$–AN		7.50	−0.24

$\Delta\delta$, difference between chemical shift of dyads and that of models.

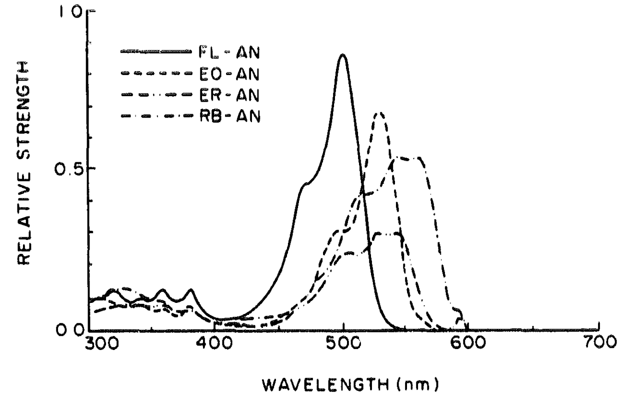


Fig. 2. Fluorescence excitation spectra of XN–AN in MeOH: λ_{Em}(FL–AN) = 540 nm; λ_{Em}(EO–AN) = 570 nm; λ_{Em}(ER–AN) = 590 nm; λ_{Em}(RB–AN) = 600 nm.

3.3. Intramolecular photoinduced singlet interactions

3.3.1. Energy transfer in dyads

When ANEt in the dyads was excited, its singlet energy can also transfer to the dyes' ester. The intramolecular EnT efficiency η_{EnT} was measured and calculated from [11]

$$\eta_{EnT} = (A_1/A_2)/(E_1/E_2)$$

where A is the area of absorption spectra and E represents the area of excitation spectra; 1 denotes the anthroic ester and 2 the dyes' ester.

The excitation spectra of the dyads are shown in Fig. 2 (concentration were about 10^{-5} mol l^{-1}). Compared with

Table 6
Intramolecular energy transfer efficiency in dyads

Dyad	FL–AN	EO–AN	ER–AN	RB–AN
η_{EnT}	0.88	0.85	0.86	0.85

The excitation wavelength is 360 nm and the fluorescence-detecting wave-

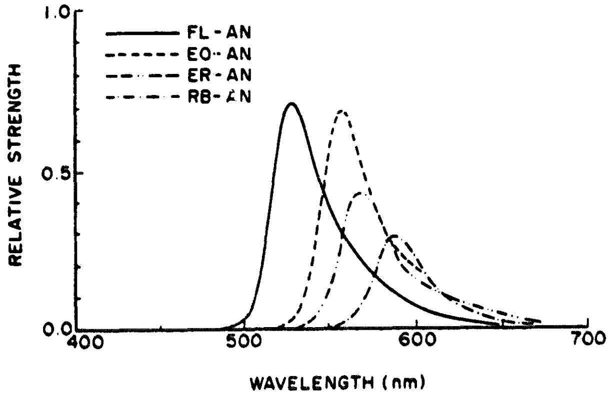


Fig. 3. Fluorescence emission spectra of XN–AN in MeOH: $\lambda_{Ex} = 360$ nm.

their absorption spectra in Fig. 1, one can see a remarkable difference because of the EnT from ANEt to XNEts.

Results are listed in Table 6.

Data in Table 6 showed that, when ANEt in dyads we excited, most of its singlet energy transferred to XN dyes' ester. The fluorescence spectra of the dyads are shown in Fig. 3.

According to the Förster equation [18], the EnT here is related to the overlap integral J and orientation factor κ^2. In our series, FL's maximum absorption is at 495 nm, where it has a much better overlap with the fluorescence spectrum of ANEt than EO, ER and RB, whose absorptions range from 525 to 550 nm. On the contrary, the latter three dyads are favourable in conformation for EnT. Combination of these two factors makes their EnT rates comparable. Anyway, the distances between donors and acceptors are limited in dyads compared with intermolecular cases; their EnT efficiency is still quite high. Because of the high efficiency of EnT, the fluorescence of ANEt itself is hardly observed.

3.3.2. Electron transfer in dyads

When XNEt in dyads is excited, its singlet energy cannot transfer to ANEt. The total decrease in fluorescence quantum yield may be caused by either the excited complex between XNEt and ANEt which does not emit or EIT expressed by the decrease in XNEt's fluorescence lifetime. So, the efficiency η_{EIT} of EIT is equal to $\eta_{q,D}$, the dynamic quenching efficiency expressed by the change in fluorescence lifetime, and the efficiency η_C of formation of a complex which does not emit at excited state, given by $\eta_C = \eta_q - \eta_{q,D}$ where $\eta_q = 1 - \phi_f/\phi_{f,0}$ and $\eta_{q,D} = 1 - \tau_f/\tau_{f,0}$.

Table 7
The quantum yield ϕ and lifetimes τ of the fluorescence (f), and the efficiency η of the fluorescence quenching (q), the electron transfer and the complex (C) formation

	ϕ_f	τ_f (ns)	η_q	η_{EIT}	η_C
FLEt	0.50	5.26			
EOEt	0.39	3.20			
EREt	0.053	0.55			
RBEt	0.044	0.60			
FL–AN	0.38	5.10	0.24	0.03	0.21
EO–AN	0.20	2.43	0.49	0.24	0.25
ER–AN	0.033	0.43	0.38	0.22	0.15
RB–AN	0.029	0.48	0.34	0.20	0.14

The quantum yield and lifetime of fluorescence in MeOH were measured. The related data were calculated and are listed in Table 7.

In the comparable data, one can see that the photoinduced intramolecular EIT efficiency of FL–AN is obviously lower than that of others. On the basis of the analysis above, it may be related to that conformation in which the two chromophores are not mainly arranged face to face.

4. Conclusion

When ANEt is excited, its singlet energy can easily transfer to XNEt, no matter what happens in the intermolecular or intramolecular case. However, when XNEt was excited, photoinduced EIT from ANEt to XNEt occurred. The intermolecular reaction rate is controlled by diffusion. The intramolecular EIT efficiency is related to the conformation of the moieties in the dyads. It seems to us that the face-to-face conformation is favourable for photoinduced EIT in our series.

Acknowledgment

This project was supported by the National Science Foundation of China.

References

[1] J.S. Connolly and J.R. Bolton, in M.A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Part D, Elsevier, Amsterdam, 1988, pp. 303–393.
[2] T. Shen et al., *Kexue Tongbao (Science, Beijing)*, *16* (1986) 1241.
[3] T. Shen, *Dyes Pigments*, *8* (5) (1987) 375–380.
[4] T. Shen, Z.G. Zhao, Q. Yu and H.J. Xu, *J. Photochem. Photobiol. A*, *47* (1989) 203–212.
[5] Z.G. Zhao, T. Shen and H.J. Xu, *Spectrochim. Acta A*, *45* (1989) 1113–1116.
[6] Q.F. Zhou, S.Y. Shen, Z.L. Yuan, Y.L. Zhou and T. Shen, *J. Photochem. Photobiol. A*, *51* (1990) 229–235.
[7] Z.G. Zhao, T. Shen and H.J. Xu, *J. Photochem. Photobiol. A*, *52* (1990) 47–53.
[8] Z.G. Zhao and T. Shen, Chin. Chem. Lett., 1 (1990) 19–20.
[9] Z.G. Zhao, H.J. Xu, T. Shen and D.W. Shen, *J. Photochem. Photobiol. A*, *56* (1991) 73–80.
[10] T. Shen, Z.G. Zhao and H.J. Xu, *Sci. China, Ser. B*, *35* (2) (1992) 137–145.
[11] I.J. He and T. Shen, *Acta Chim. Sin.*, *50* (1992) 708.
[12] F. Yuan, T. Shen and H.J. Xu, *Sci. China, Ser. B*, *38* (7) (1995) 778–783.
[13] J. Quick and R. Oetsor, *Tetrahedron Lett.*, (1977) 599.
[14] S.T. Murov, *Handbook of Photochemistry*, Dekker, New York 1973, p. 3.
[15] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, *73* (1969) 834.
[16] N.J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, New York, 1978, p. 247.
[17] A.L. Moore, G. Dirks, D. Gust and T.A. Moore, *Photochem. Photobiol.*, *32* (1980) 691–695.
[18] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum, New York, 1983, Chapt. 10, pp. 303–309.