

Photoinduced intramolecular electron transfer in an anthraquinone–fluorescein–carbazole model

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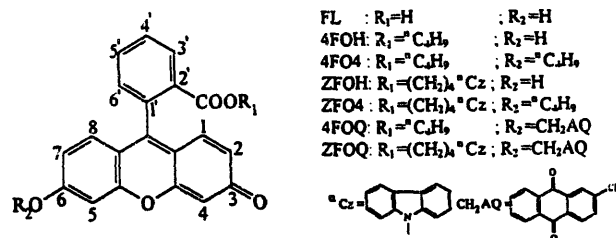
Abstract

A triad molecule consisting of fluorescein covalently linked to carbazole at site 2' and anthraquinone at site 6 was synthesized and investigated by comparison of its photophysical properties with those of the model dyads. The absorption and emission spectra and fluorescence quenching results indicate that the intramolecular ground state interaction between donor and acceptor is negligible and photoinduced intramolecular electron transfer is mainly a dynamic process. In the triad molecule, there is competing electron transfer between the fluorescein–carbazole and anthraquinone–fluorescein pairs. The electron transfer between fluorescein and carbazole dominates the initiated process with $\Phi_{et} = 0.94$ and $K_{ET} = 1.8 \times 10^9 \text{ s}^{-1}$, which are in good agreement with other work. We have also estimated the free energy change of the other electron transfer and the back reaction in our triad molecule.

Keywords: Anthraquinone; Carbazole; Fluorescein; Photoinduced intramolecular electron transfer; Triad molecule

1. Introduction

Over the past decade, significant emphasis has been placed on the development of an understanding of photoinduced charge separation reactions as a means of capturing and storing solar energy [1]. Covalently linked multicomponent models have been reported, in which the dependence of the electron transfer rate constant on the donor–acceptor distance, orientation, free energy of reaction and electronic coupling has been studied [1]. The key step of the conversion of light to chemical potential energy includes not only the photodriv- en charge separation, but also the prevention of the back reaction, which has proved difficult to control. This may be accomplished by rapidly moving the electron or hole, or both, away from the site of excitation to a more stable environment. Fluorescein (Scheme 1) is an important xanthen e dye with a large variety of technical applications due to its high fluorescence quantum yield [2]. It contains two active groups, the hydroxyl group (site 6) and the carboxyl group (site 2'), which can link donors or acceptors to form multicomponent compounds [3]. In order to improve our understanding of intramolecular electron transfer in polyads, the synthesis and properties of a series of dyads and a triad with flexible spacers (fluorescein as sensitizer, carbazole as donor and anthraqui- none as acceptor) are described.



Scheme 1. Structural formula of model compound and polyads.

2. Experimental section

2.1. Physical measurements

Solvents for all spectroscopic experiments were dried and re-distilled. Proton nuclear magnetic resonance (NMR) spectra were obtained on a 400 MHz Varian XL-400 spectrometer. UV–visible absorption spectra were recorded on an HP-8451 or Hitachi-557 spectrophotometer. Fluorescence spectra were obtained using a Perkin–Elmer LS-5 fluorometer interfaced to a 3600 data station. Samples (10^{-6} M) for fluorescence measurements were contained in 1 cm cuvettes. The emission was measured 90° to the excitation beam. Fluorescence quantum yields were determined by integrating the digitized emission spectra from 480 to 800 nm and referenc- ing to fluorescein ($\Phi_0 = 0.93$). The redox potentials of the model compounds were measured by cyclic voltammetry

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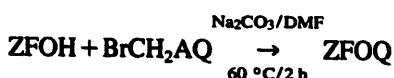
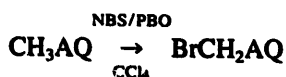
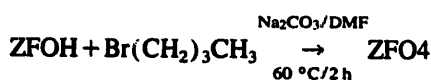
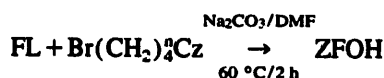
with pyrolytic graphite as the working electrode, platinum bridged by saturated KCl solution as the counter-electrode and Ag/AgCl (saturated KCl) as reference electrode. LiCl (0.1 M) was employed as the electrolyte for a solution of 10^{-4} M in MeOH. The singlet energy was determined from the overlap between the normalized absorption and emission spectra. Fluorescence lifetimes were determined using a HORIBA NAES-1100 single-photon counting apparatus.

2.2. Syntheses

The *N*-substituted carbazole derivatives were prepared according to the procedures described in the literature [4,5] and recrystallized from cyclohexane.

Compound 4FO4 was prepared as follows. A mixture of fluorescein (2 g, 6 mmol), bromobutane (1.5 ml, 15 mmol), potassium carbonate (1 g) and *N,N*-dimethylformamide (DMF) (20 ml) was stirred at 60 °C for 2 h. The solution was cooled and added to 5 ml of ether. The organic solution was stripped on a rotary evaporator leaving a yellow residue, which was quickly chromatographed on 254 silica gel with chloroform. The yellow fraction was combined and stripped on a rotary evaporator to give a yield of 85%. $^1\text{H NMR}$ (deuterated dimethyl sulphoxide ($^d\text{DMSO}$)) δ : 0.66 (3H, t), 0.85 (3H, t), 1–2 (8H, m), 3.89 (2H, t), 4.15 (2H, t), 6.23 (1H, s), 6.40 (1H, d), 6.78–6.93 (3H, m), 7.23 (1H, s), 7.49 (1H, d), 7.77 (1H, t), 7.83 (1H, t), 8.18 (1H, d). Mass spectrometry (MS): $M^+ = 444$. UV–visible (methanol) λ_{max} (nm): 454, 482. IR (KBr) (cm^{-1}): 3052, 1714, 1637, 1592.

The polyads were synthesized as shown below



where FL is fluorescein, AQ is anthraquinone and Cz is carbazole.

Table 1
Singlet state energies and redox potentials of model compounds

Compound	E_s (kcal mol $^{-1}$)	$E_O(D^+/D)$ (eV)	$E_R(A^-/A)$ (eV)
CzCH $_3$	83.2	1.1	
FL	55.8	0.9	-1.2
MAQ	66.5		-0.96

The spectral results are as follows. Compound ZFO4. $^1\text{H NMR}$ ($^d\text{DMSO}$) δ : 0.92 (3H, t), 1–2 (8H, m), 3.9 (2H, t), 4.08 (2H, t), 4.25 (2H, t), 6.24 (1H, s), 6.4 (1H, d), 6.8 (3H, m), 7.14 (1H, s), 7.18 (2H, t), 7.42 (2H, t), 7.45 (2H, d), 7.49 (1H, d), 7.74 (1H, t), 7.84 (1H, t), 8.13 (3H, m). MS: $M^+ = 610$. UV–visible (methanol) λ_{max} (nm): 454, 482. IR (KBr) (cm^{-1}): 1709, 1637, 1592. Compound 4FOQ. $^1\text{H NMR}$ ($^d\text{DMSO}$) δ : 0.66 (3H, t), 1–2 (4H, m), 3.9 (2H, t), 5.51 (2H, s), 6.26 (1H, s), 6.41 (1H, d), 6.80–6.90 (2H, m), 7.06 (1H, d), 7.38 (1H, s), 7.51 (1H, d), 7.79 (1H, t), 7.87 (1H, t), 7.92–7.98 (2H, m), 8.01 (1H, d), 8.18 (1H, d), 8.22–8.26 (2H, m), 8.29 (1H, d), 8.30 (1H, s). MS: $M^+ = 610$. UV–visible (methanol) λ_{max} (nm): 454, 482. IR (KBr) (cm^{-1}): 1707, 1668, 1636, 1591, 1513. Compound ZFOQ. $^1\text{H NMR}$ ($^d\text{DMSO}$) δ : 1–2 (4H, m), 3.88 (2H, t), 4.15 (2H, t), 5.52 (2H, s), 6.24 (1H, s), 6.38 (1H, d), 6.79–6.98 (3H, m), 7.14 (2H, t), 7.33 (1H, s), 7.44–7.47 (4H, m), 7.49 (1H, d), 7.76 (1H, t), 7.87 (1H, t), 7.88–7.98 (3H, m), 8.06 (2H, d), 8.09–8.13 (3H, m), 8.22 (1H, d), 8.29 (1H, s). MS: $M^+ = 775$. UV–visible (methanol) λ_{max} (nm): 456, 482. IR (KBr) (cm^{-1}): 1704, 1668, 1635, 1592, 1541, 1514.

3. Results and discussion

3.1. Energetics

The singlet state energy of the sensitizer and the redox potentials of the butyl ester of fluorescein, *N*-butyl-carbazole and 2-methyl-anthraquinone are given in Table 1.

We can calculate the free energy changes (ΔG) of electron transfer reactions using the Rehm–Weller equation [6]

$$\Delta G = E_O(D) - E_R(A) - E_{0,0} - C$$

where $E_O(D)$ is the oxidation potential of the donor, $E_R(A)$ is the reduction potential of the acceptor, $E_{0,0}$ is the singlet state energy of the sensitizer and C is the solubilizing energy of D^+A^- (can usually be regarded as 0.06 eV or 1.4 kcal mol $^{-1}$ in polar solvents) [7].

Table 2 shows the calculated results of the singlet energy difference (δE_s) and the free energy changes of electron transfer between the donors and acceptors (FL, fluorescein; Cz, carbazole; AQ, anthraquinone; S, sensitizer; A, acceptor; D, donor; ΔG^f and ΔG^r , free energy changes of forward and

Table 2
Calculated results of the energy difference (δE_s) and the free energy changes of electron transfer between donors and acceptors

Compound	δE_s (kcal mol $^{-1}$)	ΔG^f (eV)	ΔG^r (eV)
FL S A D Cz D	-27.3	-0.19	-2.30
FL S D AQ A	-10.7 [8]	-0.63	-1.86
FL $^{\cdot-}$ D AQ A		-0.24	0.24
FL $^{\cdot+}$ A D Cz D		0.20	-0.20

back electron transfer respectively). ΔG^f can be calculated using equation $\Delta G^f = E_R(A) - E_O(D)$ [9].

Table 2 shows that the singlet state energy of fluorescein is less than that of carbazole ($\Delta E < 0$) so that, when fluorescein is excited, there will be no energy transfer between fluorescein and carbazole. However, the free energy change of forward electron transfer between fluorescein and carbazole is -0.19 eV, indicating that electron transfer between the lowest excited state of fluorescein and the attached carbazole is feasible. For fluorescein and anthraquinone, the results are similar: $\Delta E < 0$, which rules out energy transfer, and $\Delta G^f = -0.63 < 0$, which favours electron transfer from excited fluorescein to ground state anthraquinone. The free energy changes of the back reaction (ΔG^r) for these two pairs are -2.30 eV (for fluorescein–carbazole) and -1.86 eV (for fluorescein–anthraquinone). Both are in the Marcus inverted region. In the triad molecule, if the initial photoinduced electron transfer proceeds between carbazole and fluorescein ($AQ-FL-Cz \rightarrow AQ-FL^{\cdot-}-Cz^{\cdot+}$), the next step in the formation of the final charge-separated state will be the electron transfer process $AQ-FL^{\cdot-}-Cz^{\cdot+} \rightarrow AQ^{\cdot-}-FL-Cz^{\cdot+}$ which competes with the recombination reaction $AQ-FL^{\cdot-}-Cz^{\cdot+} \rightarrow AQ-FL-Cz$. Table 2 shows that the electron transfer step $AQ-FL^{\cdot-}-Cz^{\cdot+} \rightarrow AQ^{\cdot-}-FL-Cz^{\cdot+}$ is exergonic by -0.24 eV and ΔG^r of the recombination reaction ($AQ-FL^{\cdot-}-Cz^{\cdot+} \rightarrow AQ-FL-Cz$) is in the Marcus inverted region (-2.30 eV); this implies that the electron transfer from $FL^{\cdot-}$ to AQ is the predominant process. If the initial photoinduced electron transfer proceeds between anthraquinone and fluorescein (not carbazole) ($AQ-FL-Cz \rightarrow AQ^{\cdot-}-FL^{\cdot+}-Cz$), the subsequent step will involve electron transfer from the cation radical of fluorescein to carbazole ($AQ^{\cdot-}-FL^{\cdot+}-Cz \rightarrow AQ^{\cdot-}-FL-Cz^{\cdot+}$), which will be thermodynamically inhibited ($\Delta G^f = 0.20$ eV).

3.2. Absorption and fluorescence spectra

The absorption spectra of the dyads and triads are nearly identical to the sum of the spectra of the unlinked chromophores. There is no broadening or red shifting of the fluorescein absorption or emission bands. These observations

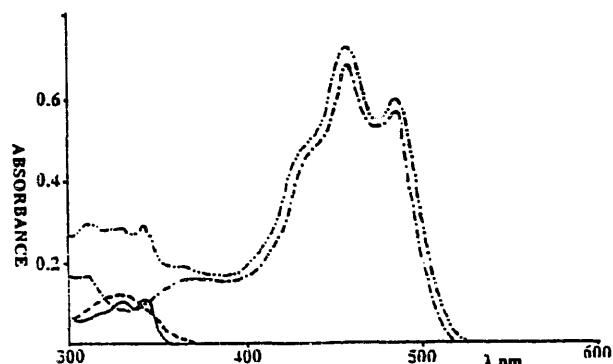


Fig. 1. Absorption spectra of triad and model compounds: \cdots , 4FO4; —, CzC4; ---, MAQ; $-\cdot-, ZFOQ.$

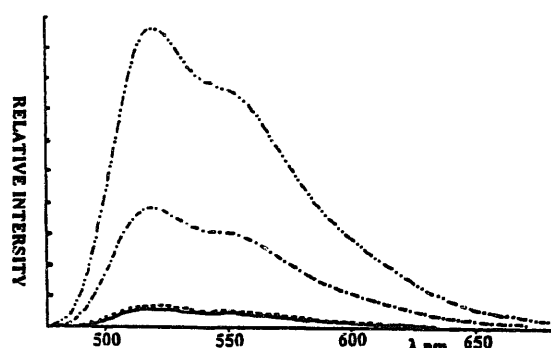


Fig. 2. Fluorescence spectra of model compound and polyads: \cdots , 4FO4; ---, ZFO4; $-\cdot-, 4FOQ; —, ZFOQ.$

provide good evidence for the absence of ground state interactions between the xanthene ring and its attached carbazole or anthraquinone (Fig. 1 and Fig. 2).

3.3. Rate constant and efficiency of electron transfer reactions

We take 4FO4 as the model compound, which shows a single-exponential fluorescence decay. According to other studies, we assume that the photophysical properties, such as K_f , K_{ic} and K_{isc} , of fluorescein in polyads do not change significantly when electron transfer takes place. Comparing the photophysical properties of polyads with those of the model compound, it can be seen that the fluorescence quantum yields and fluorescence lifetimes are strongly decreased in the polyads. It is thus reasonable to assume that singlet-initiated intramolecular electron transfer occurs. The values of the rate constants and efficiencies can be obtained from the following equations:

1. efficiency of singlet-initiated intramolecular electron transfer, $\Phi_{ET} = 1 - \Phi_f / \Phi_f^0$;
2. rate constant of singlet-initiated intramolecular electron transfer, $K_{ET} = (\Phi_f^0 / \Phi_f - 1) / \tau$;
3. efficiency of dynamic electron transfer, $\Phi_{ET-D} = 1 - \tau / \tau^0$;
4. rate constant of dynamic electron transfer, $K_{ET-D} = 1 / \tau - 1 / \tau^0$;
5. efficiency of static electron transfer, $\Phi_{ET-S} = \Phi_{ET} - \Phi_{ET-D}$;
6. rate constant of static electron transfer, $K_{ET-S} = K_{ET} - K_{ET-D}$.

Φ_f^0 and τ^0 represent the fluorescence quantum yield and fluorescence lifetime of the model compound, whereas Φ_f and τ represent the fluorescence quantum yield and fluorescence lifetime of the polyads. The values of these rate constants and efficiencies were obtained as described above from the measured fluorescence lifetimes τ of the model compound and the polyads.

Table 3 shows that the intramolecular electron transfer is mainly a dynamic process in our polyads, and there are no obvious ground state interactions. The fluorescence lifetimes of the dyads and triad exhibit a double-exponential decay.

Table 3
Photoproperties of model compounds and polyads

Compound	Φ_f	τ (ns)	$Q\tau$	Φ_{ET}	Φ_{ET-D}	Φ_{ET-S}	$K_{ET} \times 10^{-9}$	$K_{ET-D} \times 10^{-9}$	$K_{ET-S} \times 10^{-9}$
4FO4	0.35	2.63	1.0						
ZFO4	0.025	0.304	0.92	0.93	0.88	0.05	3.05	2.9	0.16
		2.35	0.08						
4FOQ	0.14	1.41	0.72	0.59	0.46	0.13	0.42	0.33	0.092
		2.26	0.28						
ZFOQ	0.022	0.518	0.98	0.94	0.80	0.14	1.8	1.6	0.27
		1.29	0.02						

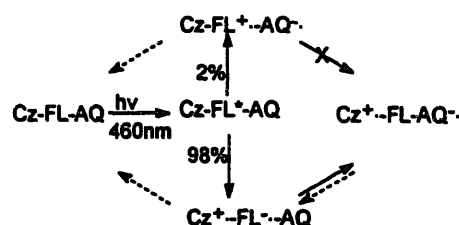
4FO4 is the model compound; $Q\tau$ represents the fractional percentage of the double-exponential component; the solvent is methanol.

The longer lived components of the dyads have lifetimes of 2.35 and 2.26 ns and approach that of model 4FO4 which has a lifetime of 2.63 ns. These lifetimes can probably be ascribed to the fluorescence of residual amounts of the incorrect orientation of the two moieties, which arises from the rotary movement of the flexible spacer $-(CH_2)_4-$ between the donor and acceptor. However, this represents only 8% for ZFO4 and 28% for 4FOQ. The triad ZFOQ also exhibits double-exponential behaviour. The shorter lived component has a lifetime of 0.518 ns, which is very similar to that (0.304 ns) of ZFO4; the longer lived component has a lifetime of 1.29 ns, which is close to that (1.41 ns) of 4FOQ. The shorter lived fraction represents 98%, whereas the longer lived fraction represents only 2% in the triad. Thus it is obvious that competing electron transfer reactions exist in the triad: when the orientation of fluorescein and carbazole is appropriate for electron transfer, an electron will be transferred from carbazole to fluorescein; when their orientation is not appropriate for electron transfer, but the orientation of fluorescein and anthraquinone favours electron transfer, an electron will be transferred from fluorescein to anthraquinone. The results of fluorescence lifetime quenching in the triad molecule suggest that the electron transfer reaction between fluorescein and carbazole is the predominant photoinitiated process.

According to former work [10], it is reasonable to assume that the orientation of fluorescein and carbazole in the triad is nearly face-to-face, whereas the orientation of fluorescein and anthraquinone is partially shoulder-to-shoulder. The face-to-face orientation is preferred for the electron transfer process rather than the shoulder-to-shoulder orientation. Therefore the results of this work are in good agreement with our former conclusions.

Based on thermodynamic analysis (Section 3.1), the secondary electron transfer from the anion radical of fluorescein to anthraquinone, following the initiated one-electron photoreduction of fluorescein, will be the predominant process to form the final charge-separated state ($AQ^{\cdot-}-FL-Cz^{\cdot+}$). Unfortunately, due to the limitation of the experimental conditions, we could not detect the final charge-separated state or the transient intermediate or obtain the rate constants of electron recombination, secondary electron transfer, etc. However, according to the discussion above, it is reasonable

to assume that a stable charge-separated state ($AQ^{\cdot-}-FL-Cz^{\cdot+}$) exists in our triad molecule, which has a relatively large distance between the positive and negative charges and will slow down charge recombination. The multistep electron transfer in our triad molecule probably occurs as follows



4. Conclusions

The ground state interaction in our polyads is negligible. The photoinduced intramolecular electron transfer is mainly a dynamic process. Competing electron transfer reactions exist between the fluorescein-carbazole and anthraquinone-fluorescein pairs in the triad ZFOQ. The electron transfer from carbazole to fluorescein dominates the initial process. The secondary electron transfer reaction between $FL^{\cdot-}$ and AQ is favoured from a thermodynamic point of view. This implies the possible formation of a stable charge-separated state.

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