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Syntheses and Photophysical Properties of Amphiphilic Dyads of Fluorescein and Carbazole Linked with a Flexible or Semi-rigid Bridge

Aimin Song, Tao Wu, Shen Chen, Manhua Zhang* & Tao Shen

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, 100101, People's Republic of China

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ABSTRACT

Four amphiphilic dyads consisting of a fluorescein moiety covalently linked to a carbazole moiety at the 2′ or the 6-position with a flexible ($-(CH_2)_4-$*) or semi-rigid (*$-CH_2phCH_2-$*) bridge were synthesized and investigated by comparison of photophysical properties with those of model compounds. Absorption and emission spectra and fluorescence quenching results indicate that the ground state interaction between fluorescein and carbazole is negligible. When fluorescein was excited, photoinduced electron transfer from carbazole to fluorescein occurred (*$K_{EIT} = 1.2 \times 10\,-^{10}\ s^{-1}\ mol^{-1}\ l$ *in the intermolecular case,* $\Phi_{EIT} = 0.92$ *and* $K_{EIT} = 1.47 \times 10^9\ s^{-1}$ *in the dyad linked with a flexible bridge at site 2′). The face-to-face conformation and a polar solvent were favourable for the photoinduced intramolecular electron transfer. When carbazole was excited, its singlet energy could easily transfer to fluorescein in the intermolecular (*$K_{EnT} = 2.4 \times 10^{13}\ s^{-1}\ mol^{-1} l$*) or intramolecular (*$\Phi_{EnT} \approx 1$*) case; in addition, intramolecular electron transfer could also take place, especially in polar solvents.*

Keywords: amphiphilic dyad, fluorescein, carbazole, photoinduced electron transfer, energy transfer, polarity of solvents.

INTRODUCTION

Over the past years, significant emphasis has been put on the development and understanding of photoinduced electron transfer reactions as a method

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*Corresponding author.

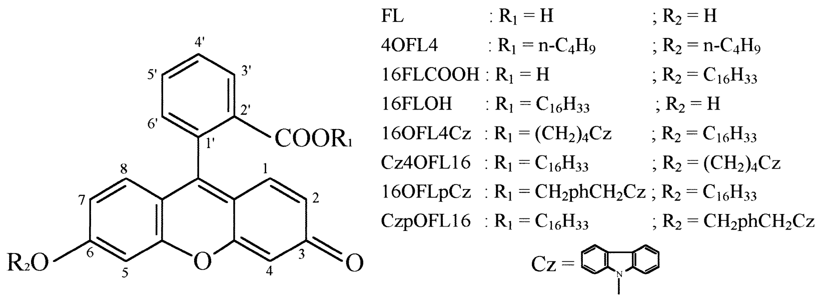
of converting and storing solar energy [1]. Covalently linked multicomponent models have been reported, in which the dependence of the electron transfer rate constant on the donor-acceptor distance, orientation, free energy of reaction and electronic coupling has been studied [1, 2]. Moreover, amphiphilic multicomponent compounds, which can be made into a highly ordered monolayer on a conductive substrate for constructing models of molecular photoelectronic devices, have been studied [3–5].

Fluorescein (FL) (Scheme 1) is an important xanthene dye with a large variety of technical applications due to its high quantum yield of fluorescence, large absorption in the visible range and its redox potentials [6]. Fluorescein contains two active groups, viz, the carboxyl group (site 2′) and the hydroxyl group (site 6), which can link donors or acceptors to form multicomponent compounds [7, 8]. In the present study, four amphiphilic dyads of fluorescein and carbozole, linked covalently with a semi-rigid or flexible bridge at site 2′ or site 6, and in which there are a hydrophilic xanthene ring and a lipophilic long alkyl chain, were synthesized. The processes of intramolecular electron transfer and energy transfer were studied by selectively exciting each of the two moieties of the heterodimers, respectively. The relationships between the intramolecular electron transfer efficiency, with mutual orientation of the two chromophores in the dyads, and of the polarity of the solvent, were also investigated.

RESULTS AND DISCUSSION

Energetics

We selected dibutyl fluorescein (4OFL4) and 9-butylcarbazole (Cz4) as model compounds of the chromophores of fluorescein and carbazole in the dyads. The singlet state energy and the redox potentials of dibutyl fluorescein



FL : $R_1 = H$; $R_2 = H$
4OFL4 : $R_1 = n\text{-}C_4H_9$; $R_2 = n\text{-}C_4H_9$
16FLCOOH : $R_1 = H$; $R_2 = C_{16}H_{33}$
16FLOH : $R_1 = C_{16}H_{33}$; $R_2 = H$
16OFL4Cz : $R_1 = (CH_2)_4Cz$; $R_2 = C_{16}H_{33}$
Cz4OFL16 : $R_1 = C_{16}H_{33}$; $R_2 = (CH_2)_4Cz$
16OFLpCz : $R_1 = CH_2phCH_2Cz$; $R_2 = C_{16}H_{33}$
CzpOFL16 : $R_1 = C_{16}H_{33}$; $R_2 = CH_2phCH_2Cz$

Scheme 1. Structure of the model compounds and polyads.

and 9-butylcarbazole are shown in Table 1. In polar solvents, the free energy changes () of electron transfer reactions can be calculated by the Rehm–Weller equation [9]:

$$= E_O(D) - E_D(A) - E_S - C$$

where $E_O(D)$ is the oxidation potential of the donor, $E_D(A)$ is the reduction potential of the acceptor, E_S is the singlet state energy of the sensitizer and C is the solubilizing energy of $D^{\cdot +}A^{\cdot -}$, which can usually be regarded as 0.06 eV or 1.4 kcal·mol^{-1} in polar solvents [10].

When fluorescein is excited, the free energy change of the 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. When carbazole is excited, the result is similar: = −0.37 eV, which favours the electron transfer from excited carbazole to ground state fluorescein.

Table 1 shows that the singlet state energy of carbazole is higher than that of fluorescein, so the singlet energy transfer from carbazole to fluorescein is thermodynamically permitted when carbazole is excited, while the energy transfer in the converse direction is endothermic, and can thus be ruled out when fluorescein is excited. The fluorescence spectrum of Cz4 and the absorption spectrum of 4OFL4 are shown in Fig. 1. There is a complete overlap between the fluorescence spectrum of Cz4 and the absorption spectrum of 4OFL4, indicating that the singlet energy transfer from carbazole to fluorescein should be very efficient.

Photoinduced interaction between models

When Cz4 was excited, its fluorescence was easily quenched by 4OFL4; at the same time, we observed the fluorescence of 4OFL4 at longer wavelengths. According to the quenching results, the rate constant of energy transfer was $2.4 \times 10^{13}\,\mathrm{s^{-1}\,mol^{-1}\,l}$, i.e. much higher than that controlled by diffusion, indicating the singlet energy transfer was a long-range interaction.

When 4OFL4 was excited, its fluorescence was also quenched by Cz4, and the results conformed with the Stern–Volmer equation [10, 11]:

TABLE 1
Singlet State Energy and Redox Potentials of Model Compounds

Compound	E_S/eV	$E_O(D^{\cdot+}/D)/eV$	$E_R(A^{\cdot-}/A)/eV$
Cz4	3.60	1.1	
4OFL4	2.42	0.9	−1.2

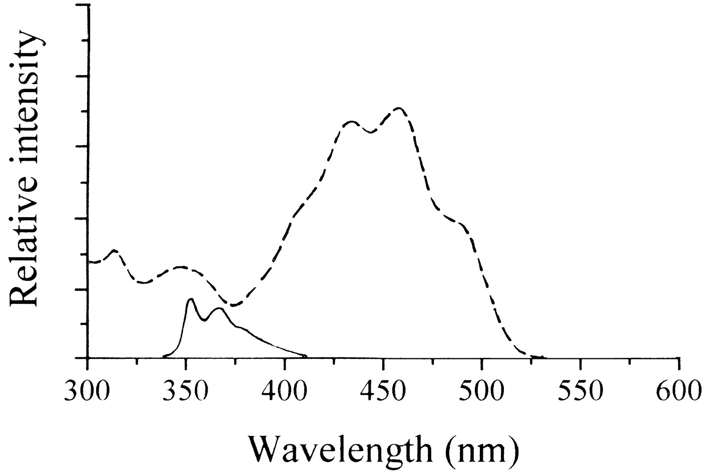


Fig. 1. Fluorescence spectrum of Cz4 (——) and absorption spectrum of 4OFL4 (- - -) in toluene.

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

where $\Phi_{f,0}$ and $\tau_{f,0}$ are the fluorescence quantum yield and the fluorescence lifetime of 4OFL4 in the absence of quencher, Φ_f is the fluorescence quantum yield of 4OFL4 in the presence of quencher, $[Q]$ is the concentration of the quencher, k_q is the quenching rate constant.

The quenching rate constant was $1.2\times10^{10}\,\mathrm{s}^{-1}\,\mathrm{mol}^{-1}\,\mathrm{l}$, and $\tau_{f,0}/\tau_f = \Phi_{f,0}/\Phi_f$ (τ_f is the fluorescence lifetime of 4OFL4 in the presence of quencher), which indicated that the process of intermolecular electron transfer was controlled dynamically by diffusion.

Photoinduced intramolecular electron transfer in dyads

The absorption spectra of the model compounds Cz4 and 4OFL4, and of the dyad 16OFL4Cz are shown in Fig. 2. The absorption spectra of the dyads Cz4OFL16, 16OFLpCz and CzpOFL16 are very similar to that of 16OFL4Cz (spectra are omitted). The absorption spectra of the dyads are almost identical to the sum of the spectra of the unlinked chromophores. This observation provides good evidence for the absence of ground state interactions between the xanthene ring and its attached carbazole moiety.

Figure 3 shows the fluorescence spectra of fluorescein in the dyads, and those of the model compound 4OFL4 in methanol, when excited at 460 nm. From this figure, we can see that the fluorescence of the fluorescein moieties is strongly quenched by carbazole moieties.

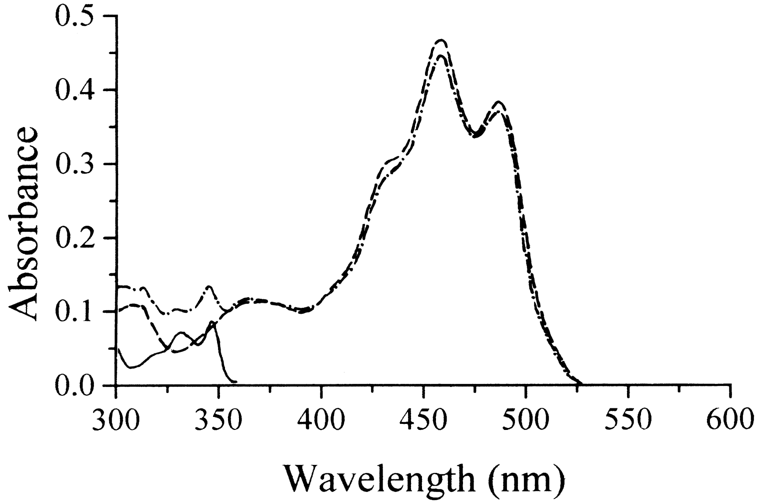


Fig. 2. Absorption spectra of Cz4 (——), 4OFL4 (- - -) and 16OFL4Cz (-·-·-) in methanol.

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

1. efficiency of singlet-initiated intramolecular electron transfer, $\Phi_{EIT} = 1 - \Phi_f/\Phi_{f,0}$;
2. rate constant of singlet-initiated intramolecular electron transfer, $K_{EIT} = \Phi_{EIT}/\tau$;
3. efficiency of dynamic electron transfer, $\Phi_{EIT-D} = 1 - \tau/\tau_0$;
4. rate constant of dynamic electron transfer, $K_{EIT-D} = 1/\tau - 1/\tau_0$;
5. efficiency of static electron transfer, $\Phi_{EIT-S} = \Phi_{EIT} - \Phi_{EIT-D}$;
6. rate constant of static electron transfer, $K_{EIT-S}K_{EIT} - K_{EIT-D}$.

In which $\Phi_{f,0}$ 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 dyads, The values of these rate constants and efficiency were obtained as described above from the measured fluorescence lifetimes of the model compound and the dyads.

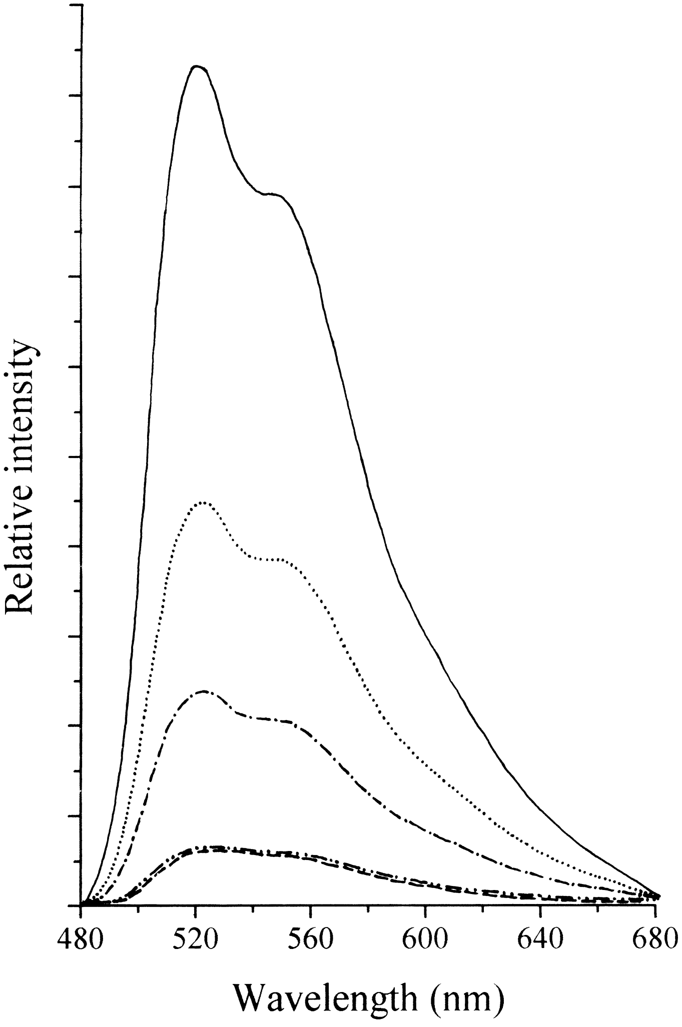


Fig. 3. Fluorescence spectra of dyads and model compound in methanol: ——, 4OFL4; - - -; 16OFL4Cz; -·-·-, Cz4OFL16; -·-·-·-, 16OFLpCz; ······, CzpOFL16.

Table 2 shows that the intramolecular electron transfer is mainly a dynamic process in the dyads investigated, and that there are no obvious ground state interactions.

Effect of molecular conformation upon electron transfer reaction

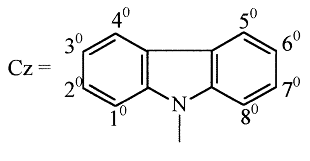
From the data listed in Table 2, we know that the rate constants and efficiency of photoinduced electron transfer in 16OFL4Cz or 16OFLpCz are higher than those in Cz4OFL16 or CzpOFL16. To resolve this, we analyzed

TABLE 2
Photophysical Properties of Model Compounds and Dyads in Methanol

Compound	Φ_f	τ(ns)	Φ_{EIT}	Φ_{EIT-D}	Φ_{EIT-S}	$K_{EIT} \times 10^{-9}$ (s^{-1})	$K_{EIT-D} \times 10^{-9}$ (s^{-1})	$K_{EIT-s} \times 10^{-9}$ (s^{-1})
4OFL4	0.35	2.74						
16OFL4Cz	0.029	0.625	0.92	0.77	0.15	1.47	1.24	0.23
Cz4OFL16	0.10	0.819	0.71	0.71	0	0.86	0.86	0
16OFLpCz	0.033	0.795	0.91	0.71	0.20	1.14	0.89	0.25
CzpOFL16	0.19	1.48	0.46	0.46	0	0.31	0.31	0

the conformations of 16OFL4Cz and Cz4OFL16 in solution based on the ^{1}H NMR results. The chemical shifts of the carbazole hydrogens of the dyads and of the model compound (Scheme 2) in a polar solvent (^{d}DMSO) are shown in Table 3.

From Table 3, for 16OFL4Cz, the hydrogens of carbazole shift to up-field relative to those in Cz4, especially for hydrogens 1^0 and 8^0. For Cz4, they are at 7.57, while for 16OFL4Cz they are at 7.45. Thus, in 16OFL4Cz, the hydrogens of carbazole are in the shielding field of the xanthene ring, and therefore the mutual orientation of the xanthene ring and the carbazole moiety in the dyads linked at site $2'$ is face-to-face to sonic degree. For Cz4OFL16. the hydrogens of carbazole shift to down-field gradually, in the order from 1^0 to 2^0 to 3^0, relative to those of Cz4, especially for hydrogens 1^0 and 8^0. For Cz4, they are at 7.57, while for Cz4OFL16 they are at 7.63. Thus, in Cz4OFL16, the hydrogens of carbazole are in the deshielding field of the xanthene ring. Therefore, the mutual orientation of the xanthene ring and carbazole system in the dyas linked at site 6 is shoulder-to-shoulder to



Scheme 2. Structural formula of carbazole.

TABLE 3
Chemical Shifts of Carbazole Hydrogens (^{d}DMSO) (Ppm)

Compound	$\delta(1^0, 8^0)$	$\delta(2^0, 7^0)$	$\delta(3^0, 6^0)$	$\delta(4^0, 5^0)$
Cz4	7.57	7.43	7.18	8.13
16OFL4Cz	7.45	7.42	7.18	8.13
Cz4OFL16	7.63	7.45	7.19	8.15

some degree. The face-to-face orientation, as compared with the shoulder-to-shoulder orientation, is the more favourable orientation between the two π–ring systems for photoinduced electron transfer. The rate constants and efficiency of photoinduced electron transfer of 16OFL4Cz and 16OFLpCz are therefore superior to Cz4OFL16 and CzpOFL16.

Table 2 also shows that the rate constants and efficiency of the photoinduced electron transfer in the dyads linked with a flexible chain (16OFL4Cz and Cz4OFL16) are higher than those in dyads linked with a semi-rigid chain (16OFLpCz and CzpOFL16). This is because the flexible chain between the two chromophores can not only rotate, but also bend, so it is easier for 16OFL4Cz and Cz4OFL16 to take a proper mutual orientation for intramolecular electron transfer than for 16OFLpCz and CzpOFL16, in which the semi-rigid chain can only rotate but not bend.

Relationship of electron transfer efficiency with polarity of solvent

The fluorescence quantum yields of 16OFL4Cz, Cz4OFL16 and model compound 4OFL4, and the electron transfer efficiency in 16OFL4Cz and Cz4OFL16 in solvents with different polarity are listed in Table 4. The intramolecular electron transfer efficiency in the dyad decreased with decrease in the polarity of the solvent. It is evident that a weaker polar or nonpolar solvent is not beneficial to electron transfer, while a polar solvent is favourable to this process.

Photoinduced energy transfer in dyads

We selected toluene as an appropriate solvent to study intramolecular energy transfer reactions to prevent the effect of electron transfer reactions. When excited at 320 nm, the fluorescence spectra of the model compounds Cz4, 4OFL4 and of the dyad 16OFL4Cz are shown in Fig. 4. The fluorescence spectra of the dyads Cz4OFL16, 16OFLpCz and CzpOFL16 are very similar to those of 16OFL4Cz (spectra are omitted). In Fig. 4, the fluorescence of the

TABLE 4
Fluorescence Quantum Yields (Φ_f) of 4OFL4, 16OFL4Cz and Cz4OFL16 and Efficiency of Intramolecular Electron Transfer ($\Phi_{E/T}$) in the Solvents with Different Polarity

Compound		*Methanol*	*Chloroform*	*Toluene*	*Cyclohexane*
4OFL4	Φ_f	0.35	0.15	0.0038	0.00073
16OFL4Cz	Φ_f	0.029	0.086	0.0038	0.00072
	$\Phi_{E/T}$	0.92	0.43	≈ 0	≈ 0
Cz4OFL16	Φ_f	0.10	0.094	0.0037	0.00072
	$\Phi_{E/T}$	0.71	0.37	≈ 0	≈ 0

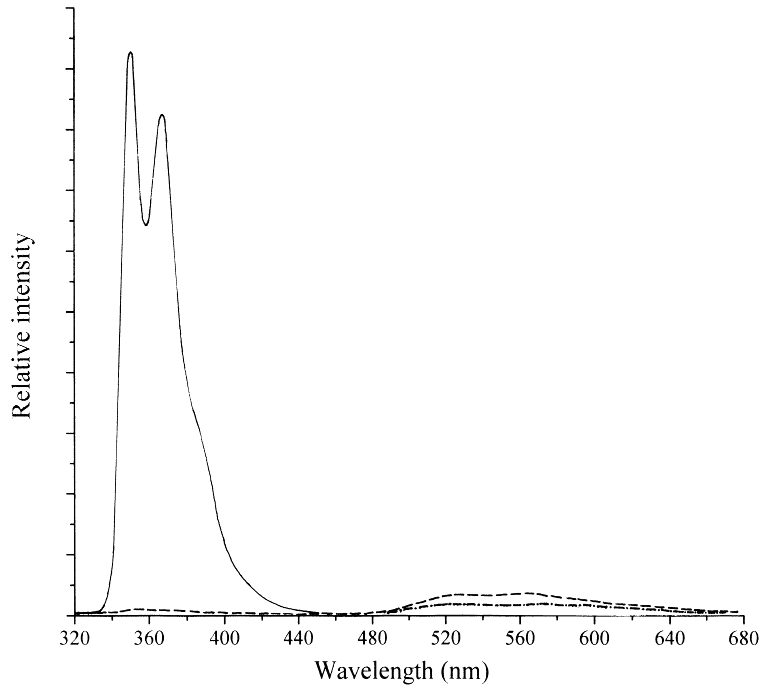


Fig. 4. Fluorescence spectra of Cz4 (——), 4OFL4 (-·-·-) and 16OFL4Cz (- - -) in toluene.

carbazole moieties is seen to be nearly completely quenched by fluorescein moieties, and, simultaneously, the fluorescence of fluorescein at longer wavelengths obviously increases. The energy transfer efficiency (Φ_{EnT}) in the different dyads are almost equal ($\Phi_{EnT} \approx 1$). There is no observable difference of energy transfer efficiency in the different dyads, indicating that the energy transfer is independent of the molecular conformation and that, it is a long-range interaction, similar to intermolecular energy transfer. In the polar solvent methanol, when excited at 320 nm, the fluorescence of the carbazole moieties is also strongly quenched by fluorescein moieties in the dyads, but increase in the fluorescence of fluorescein moieties is not observed. This implies that in polar solvents, the interaction between fluorescein moieties and carbazole moieties in dyads is mainly an electron transfer process.

EXPERIMENTAL SECTION

Physical measurements

Solvents for all spectroscope experiments were dried and re-distilled before used. ^{1}H NMR spectra were obtained on a 400 MHz Varian XL-400 spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were obtained on a Hitatch MPF 4F spectrofluorimeter. Samples 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 330 to 800 nm, and referring to fluorescein in methanol ($\Phi_f = 0.93$) [6]. The redox potentials of the model compounds were measured by cyclic voltammetry with pyrolytic graphite as the works electrode, platinum bridged saturated KC1 solution as the counter-electrode and Ag/AgC1 (saturated KC1) as the electrolyte for a solution of 10^{-4} M in methanol. The singlet energy was determined from the overlap between the normalized absorption and emission spectra [7]. Fluorescence lifetimes were determined using an HORIBA NAES-1100 single-photon counting apparatus.

Preparation of model compounds and intermediate materials

9-Butyl carbazole (Cz4) and 9-(4-bromo)-butyl carbazole (Cz4Br), the hexadecyl ester of fluorescein (16FLOH) and the hexadecyl ether of fluorescein (16FLCOOH), and dibutyl fluorescein (4OFL4) were prepared according to the procedures previously described [12–14].

The preparation of 9-(p4-chloromethyl)-benzylcarbazole has been previously noted [12]. ^{1}H NMR (deuterated chloroform ($CDCl_3$)) δ: 4.55 (2H, s), 5.54 (2H,S), 7.15 (2H,d), 7.29 (2H,t), 7.32 (2H,d), 7.38 (2H,d), 7.46 (2H,t), 8.18 (2H, d). MS (FAB): $M^+ = 305$. UV-Vis (methanol) $\lambda_{\max}$ (nm): 345, 330. IR (KBr) (cm^{-1}): 3053, 2941, 1625, 1594.

Syntheses of dyads

Compound 16OFL4Cz was synthesized as follows:

A mixture of 16FLCOOH (1 g, 1.8 mmol), Cz4Br (0.8 g, 2.7 mmol), anhydrous potassium fluoride (0.3 g, 5.2 mmol) and *N*,*N*-dimethylformamide (DMF) (20 ml) was stirred at 60°C for 15 h. The solution was stripped on a rotary evaporator leaving a red residue, which was washed with water, dried under vacuum, and chromatographed on silica gel F_{254} with a mixture of ethyl acetate and cyclohexane (3:2 V/V). After recrystallization from ethyl acetate, orange crystals were obtained in a yield of 80%.

^{1}H NMR ($CDCl_3$) δ: 0.90 (3H,t), 1.2–1.5 (28H,m), 1.69 (2H,m), 1.73 (2H,m), 3.96 (2H,t), 4.01 (2H, t), 4.21 (2H,t), 6.52 (1H,s), 6.60 (1H,d), 6.69 (1H, d), 6.84 (1H,d), 6.86 (1H,d), 6.90 (1H, s), 7.24 (1H, d), 7.29 (2H,t), 7.32 (2H, d), 7.46 (2H, t), 7.68 (1H, t), 7.76 (1H,t), 8.10 (2H, d), 8.21 (1H, d). MS (FAB): $(M+H)^+ = 778$. UV-Vis (methanol) $\lambda_{\max}$ (nm): 458, 487, 345. IR

(KBr) (cm^{-1}): 3056, 2924, 2853, 1721, 1643, 1599, 1519. Elemental analysis: Calc. (%), $C_{52}H_{59}O_5N$, C, 80.27; H, 7.64; N, 1.78; Found (%), $C_{52}H_{59}O_5N$, 80.28; H, 7.80; N, 1.52.

Compounds Cz4OFL16, 16OFLpCz and CzpOFL16 were obtained by procedures similar to that for compound 16OFL4Cz. Spectra data are as follows:

Compound Cz4OFL16
^{1}H NMR (CDCl$_3$) δ: 0.90 (3H, t), 1.0–1.5 (26H, m), 1.70 (2H, m), 1.91 (2H, m), 2.14 (2H, m), 3.97 (2H,t), 4.02 (2H,t) 4.43(2H,t), 6.46 (1H,s), 6.57 (1H,d), 6.69 (1H, d), 6.86 (2H,m), 6.89 (1H, s), 7.24 (1H, d), 7.30 (2H, t), 7.44 (2H,d), 7.47 (2H,t), 7.68 (1H, t), 7.74 (1H, t), 8.12 (2H,d), 8.27 (1H,d). MS (FAB): $(M+H)^+=778$. UV-Vis (methanol) λ_{max} (nm): 458, 487, 345. IR (KBr) (cm^{-1}): 3056, 2924, 2853, 1720, 1643, 1599, 1519. Elemental analysis: Calc. (%), $C_{52}H_{59}O_5N$, C, 80.27; H, 7.64; N, 1.78; Found (%), $C_{52}H_{59}O_5N$, C, 80.27; H, 7.82; N, 1.49.

Compound 16OFLpCz
^{1}H NMR (CDCl$_3$) *d*: 0.90 (3H,t), 1.2–1.6 (26H, m), 1.69 (2H, m), 3.42 (1H, m), 3.66 (1H, m), 4.77 (1H, d), 4.93 (1H, d), 5.56 (2H, s), 6.23 (1H, s), 6.38 (1H, s), 6.54 (1H, d), 6.61 (1H, d), 6.71 (2H, d), 6.77 (1H, d), 6.81 (1H,d), 6.95 (2H, d), 7.23 (1H, d), 7.31 (2H, t), 7.48–7.58 (4H, m), 7.67 (1H, t), 7.72 (1H, t), 8.17 (2H, d), 8.29 (1H, d). MS (FAB): $(M+H)^+=826$. UV-Vis (methanol) λ_{max} (nm): 458, 487, 345. IR (KBr) (cm^{-1}): 3056, 2925, 2853, 1719, 1638, 1599, 1516. Elemental analysis: Calc. (%), $C_{56}H_{59}O_5N$, C, 81.42; H, 7.20; N, 1.70; Found (%), $C_{56}H_{59}O_5N$, C, 81.24; H, 7.20; N, 1.69.

Compound CzpOFL16
^{1}H NMR (CDCl$_3$) δ: 0.92 (3H,t), 1.0–1.5 (28H, m), 3.99(2H, t), 5.07 (2H, s), 5.51 (2H, s), 6.48(1H, s), 6.58 (1H, d), 6.79 (1H, d), 6.89 (1H, d), 6.92(1H, d), 6.98 (1H, s), 7.18 (2H, d), 7.24 (1H, d), 7.29 (2H, t), 7.34 (2H, d), 7.37 (2H, d), 7.44 (2H,t), 7.68 (1H, t), 7.72 (1H, t), 8.15 (2H, d), 8.28(1H, d). MS (FAB): $(M+H)^+=826$. UV-Vis (methanol) λ_{max} (nm): 458, 487, 345. IR (KBr) (cm^{-1}): 3056, 2925, 2853, 1722, 1642, 1599, 1521. Elemental analysis: Calc. (%), $C_{56}H_{59}O_5N$, C, 81.42; H, 7.20; N, 1.70; Found (%), $C_{56}H_{59}O_5N$, C, 81.16; H, 7.34; N, 1.48.

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