The Unusual Fluorescence Strengthened by Steric Hindrance

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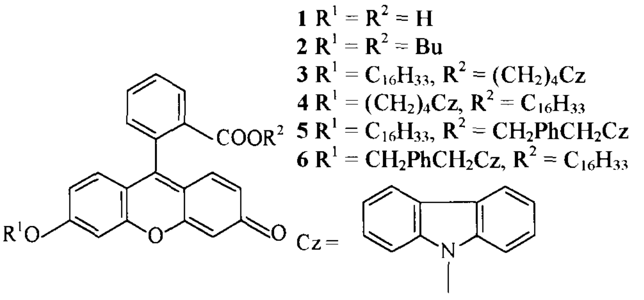
In four dyads of fluorescein and carbazole, photoinduced intramolecular electron transfer occurred in polar solvents and was negligible in nonpolar solvents. However, unprecedented fluorescence strengthening in the dyad linked with a semi-rigid bridge (-CH_2-Ph-CH_2-) at the carboxyl of fluorescein (as 3.2 and 10 times as the model dibutyl derivative of fluorescein in toluene and cyclohexane, respectively) was observed. Experimental data showed it could result from steric hindrance.

Over the past years, significant emphasis has been put on the development and understanding of photoinduced electron transfer reactions as a method of converting and storing solar energy.[1] Covalently linked multicomponent models have been reported.[1] Fluorescein **1** (Scheme 1) is an important xanthene dye with a large variety of technical application due to its high quantum yield of fluorescence, large absorption in visible range and proper redox potentials.[2] Fluorescein contains two active group, the carboxyl and hydroxyl, which can link donors or acceptors,[3,4] so is a good photosensitizer for constructing multicomponent compounds. On the other hand, carbazole is one of excellent electron donors.[5] To observe the photoinduced intramolecular electron transfer from carbazole to fluorescein in solutions and on LB films when fluorescein was excited, we synthesized the model compound dibutyl derivative of fluorescein **2** and four amphiphilic dyads **3-6** containing fluorescein as photosensitizer and electron acceptor, carbazole as electron donor, linked by flexible (-$(CH_2)_4$-) and semi-rigid (-CH_2-Ph-CH_2-) bridges, respectively (Scheme 1).[6]



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = Bu$
3 $R^1 = C_{16}H_{33}$, $R^2 = (CH_2)_4Cz$
4 $R^1 = (CH_2)_4Cz$, $R^2 = C_{16}H_{33}$
5 $R^1 = C_{16}H_{33}$, $R^2 = CH_2PhCH_2Cz$
6 $R^1 = CH_2PhCH_2Cz$, $R^2 = C_{16}H_{33}$

Scheme 1. Structural formula of dyads and model compounds.

In dyads **3** and **4**, the carbazole can be both rotated and bent, relative to the fluorescein due to the flexibility of butylene spacer. However, in dyads **5** and **6**, relative to the fluorescein, carbazole may rotate, but can not bend freely because of the semi-rigidity of the p-xylylene bridge, -CH_2-Ph-CH_2-.

The absorption spectra of all dyads are similar to one another, like the sum of 9-butyl-carbazole and dibutyl derivative of fluorescein **2** in the same proportion, indicating the absence of ground state interactions. There is no any signs of aggregation.[7]

Their fluorescence quantum yields, fluorescence lifetimes and fluorescence quenching efficiencies were also determined when fluorescein therein was excited at 460 nm, where carbazole has no absorption. The results are listed in Table 1.

Table 1. Photophysical properties of dyads and the model in different solvents

Solvents		Model **2**	Dyad **3**	Dyad **4**	Dyad **5**	Dyad **6**
Methanol	Φ_F	0.35	0.029	0.10	0.033	0.19
	τ_F (ns)	2.74	0.625	0.819	0.795	1.48
	Φ_Q		0.92	0.71	0.91	0.46
Chloroform	Φ_F	0.15	0.086	0.094	0.087	0.12
	Φ_Q		0.43	0.37	0.42	0.18
Toluene	Φ_F	0.0038	0.0038	0.0037	0.012	0.0037
	Φ_Q		≈ 0	≈ 0	—	≈ 0
Cyclohexane	Φ_F	0.00073	0.00072	0.00072	0.0073	0.00072
	Φ_Q		≈ 0	≈ 0	—	≈ 0

In the table, Φ_F is the fluorescence quantum yield, τ_F the fluorescence lifetime, Φ_Q the fluorescence quenching efficiency.

Table 2. Singlet state energy and redox potentials of model compounds

Compound	E_S (eV)	$E_O(D^{+}/D)$ (eV)	$E_R(A^{-}/A)$ (eV)
9-Butyl carbazole	3.60	1.10	
Model **2**	2.42	0.90	−1.20

E_S, E_O and E_R repsent the singlet state energy, oxidation potentials and reduction potentials of compounds, respectively.

The singlet state energy and the redox potentials of the models are shown in Table 2. When fluorescein was excited, the singlet energy transfer in the dyads is ruled out. However, in

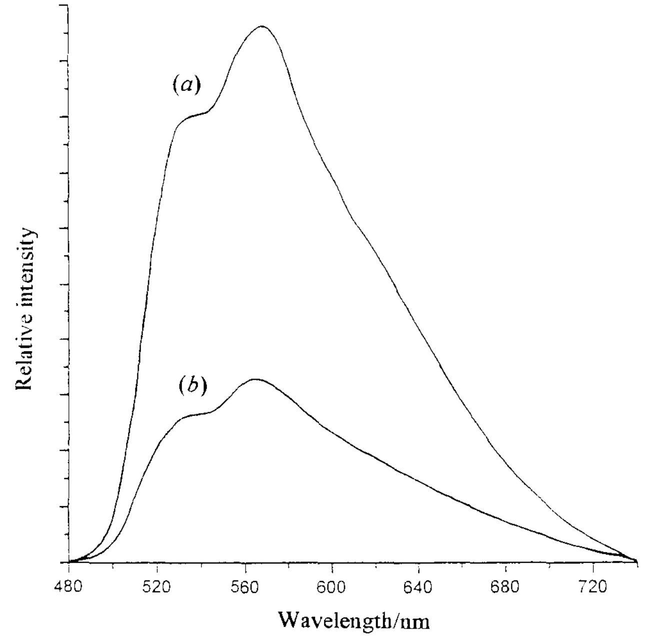


Figure 1. Fluorescence spectra of model compound and dyads (*a*) dyad **5**, (*b*) model **2**, dyads **3**, **4**, and **6** in toluene when fluorescein was excited at 460 nm.

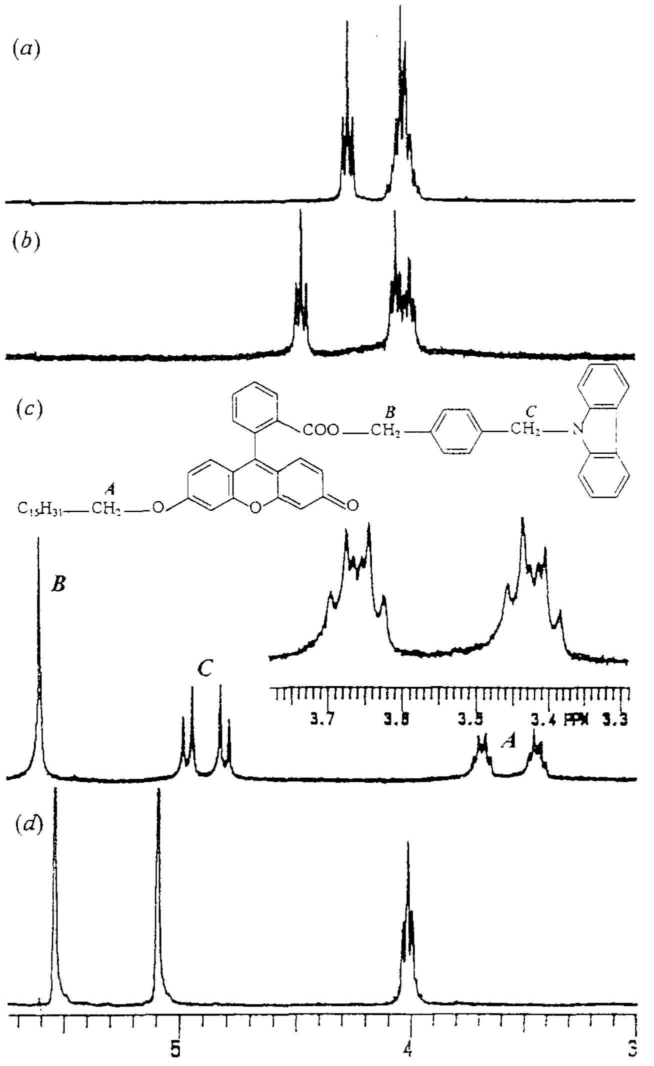


Figure 2. 300 MHz ^{1}H NMR spectra of dyads (*a*) 3, (*b*) 4, (*c*) 5 and (*d*) 6 in $CDCl_3$; the other protons are not shown.

polar solvents (methanol (E_T^N = 0.762), chloroform (E_T^N = 0.259))[8], compared with that of model **2**, the fluorescence of fluorescein in dyads **3-6** is indeed quenched by carbazole due to the electron transfer from carbazole to the singlet excited fluorescein (according to the Rehm-Weller equation,[9] the free energy change is −0.19 eV).

Previously,[10,11] we have found that in polar solvents the mutual orientation of the two chromophores in dyads linked at the carboxyl of fluorescein is face-to-face to some degree, while that in dyads linked at the hydroxyl of fluorescein is shoulder-to-shoulder to some degree. The face-to-face orientation, as compared with the shoulder-to-shoulder orientation, is the more favorable orientation between the two π-ring systems for intramolecular electron transfer, thus the electron transfer efficiencies in dyads **3** and **5** are higher than those in dyads **4** and **6**, respectively.

The fluorescence quenching efficiencies in the dyads decrease quickly with the decreasing of the polarity of solvents (Table 1). In non-polar solvents (toluene (E_T^N = 0.099), cyclohexane (E_T^N = 0.006))[8], the photoinduced electron transfer is negligible. The fluorescence of fluorescein in dyads should be the same as in the model. The dyads **3**, **4**, and **6** behaved so, but dyad **5** did not. In dyad **5**, observed was the unprecedented fluorescence strengthening, the fluorescence of fluorescein therein is much stronger than the model's (Figure 1). The fluorescence quantum yield of fluorescein in dyad **5** is as 3.2 and 10 times as that of the model **2** in toluene and cyclohexane, respectively.

Why? Comparing the ^{1}H NMR spectra of these dyads (Figure 2), it is found that in dyad **5**, totally different than in others, two hydrogens between carbazole and benzene ring are split into doublet located around 4.77 and 4.93 ppm, respectively. On the other side, two hydrogens of the cetyl near to chromophore are also split into sextet around 3.42 and 3.66 ppm. Furthermore, all the corresponding hydrogens in dyad **5** are shifted to upfield to some extent. It means that these hydrogens can not freely change their relative orientation, and they are located in the shielding region of fluorescein and carbazole in the dyad, respectively.

In the molecule of fluorescein, the phenyl of fluorescein is almost perpendicular to the chromophoric plane.[12] The carbazole linked with a semi-rigid bridge at the carboxyl of fluorescein is restricted to a comparatively fixed position, face-to-face to some extent, relative to the xanthene ring. Such steric hindrance made the hydrogens between carbazole and benzene ring chemically nonequivalent. Just because of this bulky obstacle, the rotation of the cetyl linked at the hydroxyl is also restricted, resulting in that the hydrogens near to the chromophore situated in different chemical environments, too.

Usually, radiationless decay of excited state involves large-amplitude nuclear motions.[13] So it is reasonable to assume that for fluorescein, the torsional motion of the phenyl group may be coupled to the radiationless transition from the excited state to the ground state. This is well known for triphenyl methane derivatives such as malachite green.[14] When the torsional motion of phenyl group was restricted by steric hindrance, the rate of radiationless transition was reduced, resulting in the fluorescence enhancement.

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