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Design of a new molecular fluorescent signalling system acting via both electron and energy transfer

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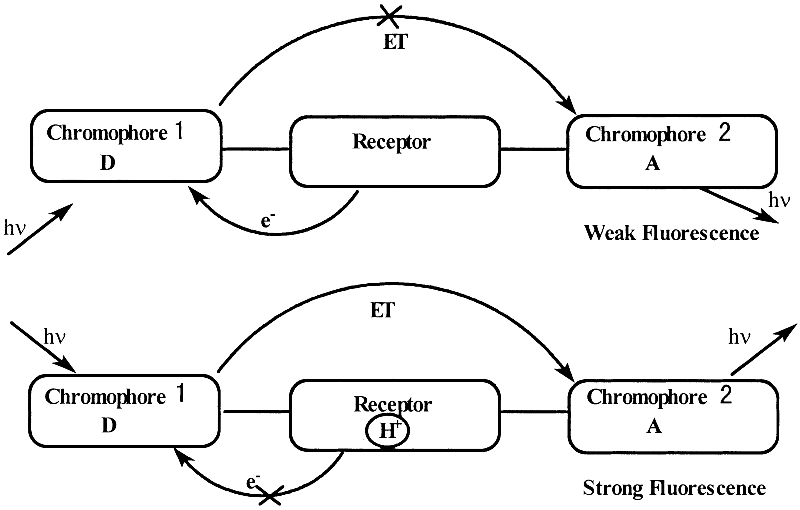
Abstract

A new molecular fluorescent signalling compound has been designed and synthesized in this work. In a molecule, there are two non-conjugated chromophores included, one of them acts as an electronic acceptor and energy transfer donor, while the other is used as an acceptor of energy transfer. The advantages of this design are as follows: first, it can lead to a long-wavelength emission upon excitation at a short wavelength after the system was protonized. The second is that this system offers a large flexibility in choosing dyes with different wavelength of absorption and emission. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fluorescence chemosensor; Electron transfer; Energy transfer

The design of fluorescent chemosensor has received much attention in recent years because of its implication in biology, medicine, environment, etc., and the possible development of chemical logics [1–3]. A few different systems have been designed based on the basic photophysical principles. For instance, de Silva et al. [4] designed a switch on–off system as an AND logical gate based on the photoinduced electron transfer (PET) process. Verhoeven et al. [5] showed that the proton-induced change system based on the 9-arylacridinium ions bearing dimethylamino group. Among these designs only one chromophore was involved. The signal comes from the change of properties of this fluorophore, for example, the suppression of charge transfer in the conjugate D–A system, the inhibition of electron transfer in PET system. Here, we demonstrate a new design of sensing system by using two non-conjugate chromophores. One chromophore contributes to the PET and acts as the donor of energy transfer and the sensing part. The



Scheme 1.

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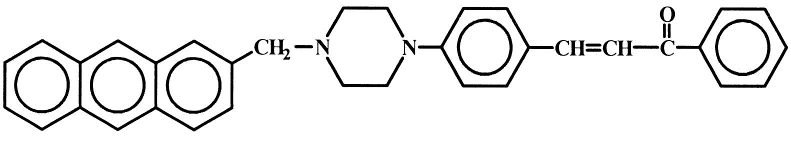
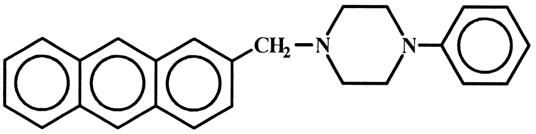
other chromophore is a luminescent compound that acts as an acceptor of energy transfer in this system. This combination constructs the D–A energy transfer system (Scheme 1). In order to turn the schematic illustration into the practical system, we chose the well-known PET system aminomethylanthrancene as the donor of the energy transfer and the receptor of proton, and used a chalcone derivative whose photophysics was investigated systematically in our group as an acceptor on the basis of consideration of the efficient energy transfer.

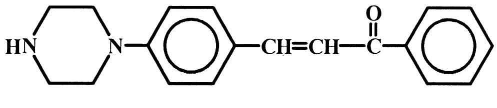
Three compounds were synthesized and characterized by ^{1}H-NMR, MS, and the detailed procedures will be reported elsewhere. The structures were shown as follows:



(1)



(2)



(3)

Fig. 1 shows the change of the absorption spectra of compound **1** in acetonitrile containing different concentrations of CF_3COOH. It can be observed that the absorbance of long wavelength (396 nm) decreases and concomitantly the absorbance at short wavelength (360 nm) increases with an increase of concentration of CF_3COOH with an isosbestic point about 380 nm. When the concentration of CF_3COOH increases further no further evolution of spectra can be observed. Compared with the change of absorption spectra of compound **2** with anthryl group (Fig. 2), the spectrum's behavior can be attributed to the protonation of nitrogen atom linked to anthryl–CH_2-group. From Fig. 3 the intensity of fluorescence around 510–520 nm attributed to chalcone moiety (see λ_{em} of compound **3** in Table 1) increases significantly with increase in the concentration of CF_3COOH and at concentration above 5 μm almost no further increase can be found. Considering the fact that the fluorescence intensity ($\Phi_f(H^+)$) of compound **3** increases only slightly (see Table 1), we can draw a conclusion that the significant enhancement of fluorescence intensity of compound **1** is due to the efficient intramolecular energy transfer from anthryl to the chalcone moiety. Table 1 gives a collection of photophysical and spectra's data.

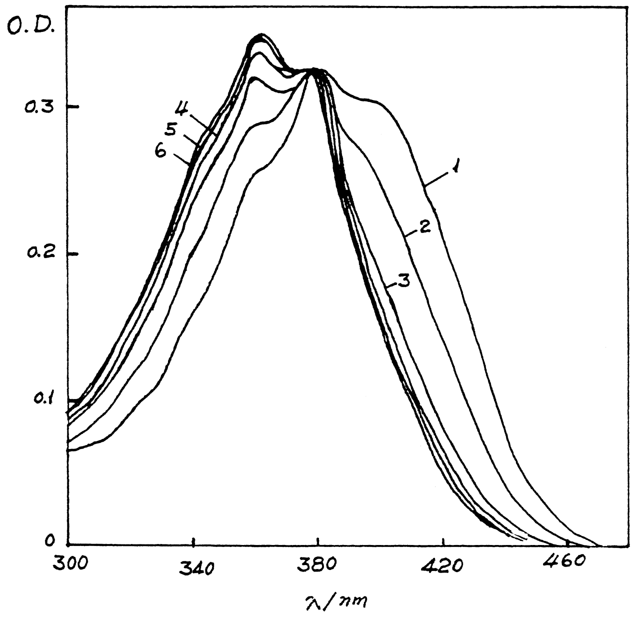


Fig. 1. Absorption spectra of compound **1** in acetonitrile at different concentrations of CF_3COOH [M]=1.0×10^{-5} mol l^{-1}, [CF_3COOH]: 1–0, 2–1, 3–1.5, 4–2.5, 5–5, and 6–10 μm.

From the Table 1, we do observe the significant increase of fluorescence quantum yield of compound **1**, indicating that this design is sensitive to the proton concentration.

The design of non-conjugate D–A system can lead to a long wavelength emission upon excitation at a short

Table 1
The spectra and photophysical data of compounds in acetonitrile in different conditions (λ_{ex}=360 nm for compound **2**, λ_{ex}=380 nm for compounds **1** and **3**)

Compounds	1	2	3
$\lambda_{abs.}$ (nm)	360, 378, 396	342, 358, 378	402
$\lambda_{abs.}$ (H^+) (nm)	360, 378	342, 358, 378	385
$\lambda_{em.}$ (nm)	530	381, 410, 432	521
$\lambda_{em.}$ (H^+) (nm)	507	381, 410, 432	508
Φ_f	0.070	0.011	0.061
$\Phi_f(H^+)$	0.48	0.56	0.066
pK_a^{obs}	602	6.10	6.14

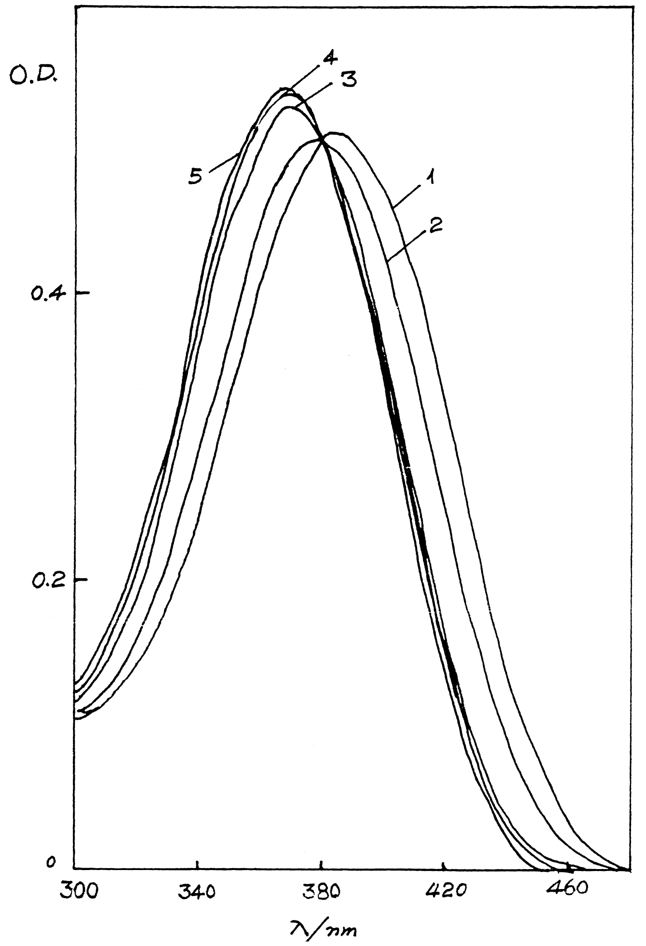


Fig. 2. Absorption spectra of compound **2** in acetonitrile at different concentrations of CF_3COOH [M]=1.0×10^{-5} mol l^{-1}, [CF_3COOH]: 1–0, 2–1, 3–3, 4–5, 5–10 μm.

wavelength (a very large Stokes shift), concomitantly a significant enhancement while the PET system only shows the increase of fluorescence intensity, and the D–A conjugate system (ICT compound) often shows only a slight wavelength shift. Another advantage of this design is that, in principle, this system offers a large flexibility in choosing different dyes with different absorption and emission wavelengths so that one can get the different D–A pairs to adapt to the diversified materials. The system can also be extended to the ion sensing system when an azacrown ether is used as an ion receptor instead of the proton receptor in the present design.

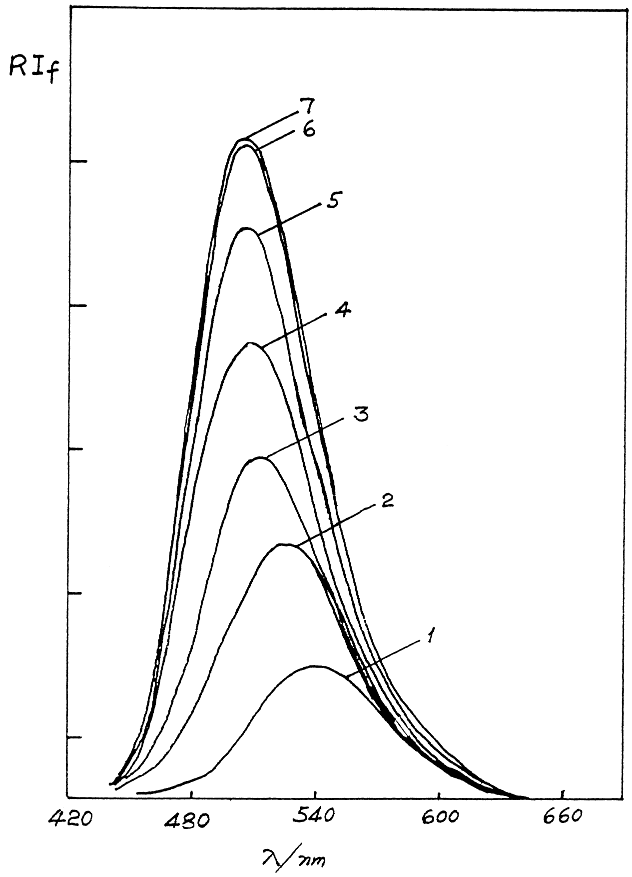


Fig. 3. Fluorescence spectra of compound **1** in acetonitrile at different concentrations of CF_3COOH [M]=1.0×10^{-5} mol l^{-1}, [CF_3COOH]: 1–0, 2–0.5, 3–1, 4–1.5, 5–2.5, 6–5, 7–10 μm.

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