ELSEVIER
Dyes and Pigments 51 (2001) 127–136
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis and fluorescence properties of triad compounds with aromatic sulfur bridges

Yan Wang[a], Chen-Pin Chang[b], Yongzhong Wu[a], He Tian[a,]*

[a]*Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China*
[b]*Department of Chemistry, Fu Jen Catholic University, Shin Chuang, Taiwan*

Received 25 May 2001; received in revised form 26 July 2001; accepted 6 September 2001

Abstract

Several novel triad compounds with fluorescence were synthesized, in which aromatic sulfur components (such as disulfide, 9H-thioxanthen-9-one and thianthrene) were used as "bridges". The fluorescence lifetimes of these compounds in various solvents have been measured by the single-photon counting technique. The characteristic longer wavelength emission of these compounds was observed, which may result from the formation of intramolecular exciplex or ICT excited state. The photoinduced electron transfer (PET) phenomenon was observed for the disulfide series compounds. When PET occurs, the fluorescence of compound is quenched. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Triad compounds; Synthesis; Photoinduced electron transfer; Fluorescence spectra; Fluorescence lifetime

---

1. Introduction

The preparation and study of molecules for potential use as switches in optoelectronic devices or future computer's fundamental unit are areas of active research [1]. The related studies are focused on *cis-trans*-isomer, reversible photochromism (spiropyrans, fulgides, etc.), photon-transfer isomer, the changing of molecular chirality and so on [2,3]. An important criterion for a molecular switch is the ability to rapidly control the "states" of the switch. The optical switching sensitivity of photochromic molecular switches is definitely restricted within a limit by absorption sensitivity. However, all the materials based on the photochromism involve changes of chemical bonds such as *cis–trans* isomerizations or heterolytic bond cleavage. These processes can be a limiting factor to realize a rapid response and the isomerizations can be accompanied by unwanted side reactions. In order to realize molecular switching function, Walz [4] used photochromic fulgides as the spacer for intramolecular energy transfer in molecular fluorescent system. When the compounds were irradiated by ultraviolet light, the fulgide section would have a closure ring and a conjugated polyenic chain system and would then turn on an "energy trap" that prevented the IET process from donor to acceptor (switch off). On the other hand, the compound was irradiated by visible light, the ring would open and the IET process would progress again (switch

---

* Corresponding author. Fax: +86-21-6425-2288.
E-mail address: tianhe@ecust.edu.cn (H. Tian).

PII: S0143-7208(01)00063-8

on). The fluorescence they used for switching function has an obvious advantage with high sensitivity. However, the process based on photochromic fulgides mentioned above did not realize rapid response.

In order to find novel rapid photoinduced molecular switch system, we developed some triad compounds with sulfur aryl bridge [5]. Aromatic sulfur molecules have been reported to produce sulfur radicals upon flash photolysis [6–8], and the chemical and physical properties of these radicals have been investigated [9,10]. In the study, a longer wavelength emission for those triads with sulfur aryl bridge was observed [5], which was considered to result from an excited state with cross configuration due to the flexible bridge.

In this paper, the phenomena of molecular fluorescence and Intramolecular Charge Transfer (ICT) are combined in one molecule. A series of donor–bridge–acceptor triads are synthesized and shown in Fig. 1, in which aromatic sulfur components (such as disulfide, 9H-thioxanthen-9-one and thianthrene) are used as "bridge". For the compounds with disulfide bridges, a cross configuration would obviously exist due to a more flexible bridge. Besides the architectural role, disulfide, specially vicinal disulfide bridges in the neurotoxins are critical for insecticidal activity and play key functional role [11]. In fact, except high sensitivity, the advantages of molecular fluorescence or luminescence for sensing and switching include feasibility of human-molecule communication, and sub-nanometer spatial resolution with sub-micron visualization. There exist considerable opportunities for modulating structural features, which control fluorescence efficiency via effects including double-bond torsion, low energy $n\pi^*$ levels, heavy atoms, weak bonds, and opportunities for photoinduced electron transfer or electronic energy transfer, by means of chemical or physical methods at the molecular level [10].

2. Experimental

IR spectra (KBr) were recorded on a Nicolet Magna-IR 550 spectrometer and ^{1}H NMR were recorded on a Brucker AM 500 spectrometer using TMS as the standard. Mass spectra and MALDI-TOF mass spectra were obtained on at 70eV on a VG 12-250 (VG Mass lab) and Mariner API TOF spectrometers (time of flight, TIS ion source, PE Corp.). Fluorescence spectra were recorded on a Hitachi 850 spectrometer. The fluorescence lifetime study was performed by an Edinburgh FL 900 photon counting system with a hydrogen-filled flash lamp/ or a nitrogen lamp as the excitation source. Data were analyzed using a nonlinear least-squares fitting program with deconvolution method. The temporal resolution after deconvolution of the exciting pulse is ~200 ps. Compounds **1–5** were synthesized as literature [5]. 2-nitro-7-bromo-thioxanthen-9-one was prepared according to the literature [12,13], m.p. 282–284 °C (literature 282–285 °C), MS (m/z): 335 (M^+) 85.14%; 291, 30.34%; 182, 100%. 2,7-dinitrothianthrene was synthesized according to the literature [13], m.p.: 264-266 °C (literature, 263–264 °C), MS (m/z): 305 (M^+)100%; 260, 40.08%;, 214, 63.55%. 4,4′-diaminophenyl disulfide was synthesized according to the literature [14], m.p.: 75–76 °C (literature, 75–76 °C). 1,8-Naphthalic anhydride and 4-nitro-1,8-naphthalic anhydride were obtained from Aldrich, 4-bromo-benzenesulfonyl chloride, carbazole and 2-chloro-5-nitroaniline were obtained from Acros. All the compounds mentioned above were used without purification. 4-bromo-1,8-naphthalic anhydride was recrystallized with ethanol. The structures of compounds are shown in Fig. 1. The synthesis of the compounds (**8–13**) for comparison has been published in detail [15]. 4-Piperidino-1,8-naphthalic anhydride and 4-*N*-dimethyl-1,8-naphthalic anhydride was synthesized according to reference [16,17].

4-Amino-4′-(4-bromo-1,8-naphthalimido)-diphenyl disulfide (**6**): 4,4′-diaminodiphenyl disulfide (2.80 g, 11 mmol) and 4-bromo-1,8-naphthalic anhydride (2.77 g, 0.01 mol) were added to anhydrous ethanol (60 ml) under nitrogen. The reaction mixture was drastically stirred and slowly heated to reflux. When refluxing, the solid reduced slowly at first, then increased gradually and the color turned from pale yellow to yellow. After refluxing for 48 h, the precipitate was filtered when hot and washed with anhydrous ethanol for several times

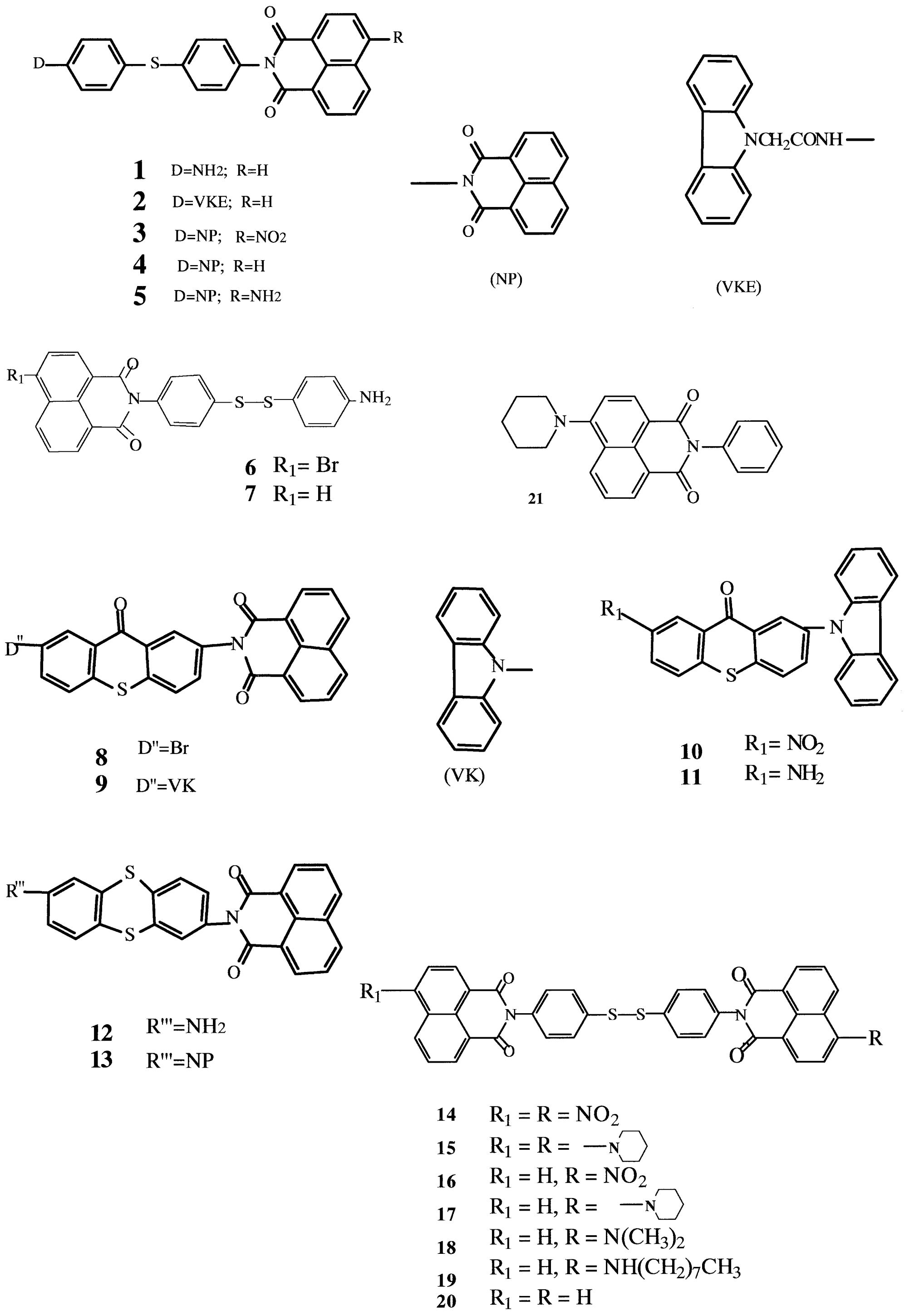

Fig. 1. Chemical structures of triad compounds synthesized.

to yield orange powder (4.52 g, 89.2%), m.p. 200–202 °C. IR (KBr): NH_2: 3480, 3370 cm^{-1}; MS (*m*/*z*): 124 (100%), 506 (0.696%), 508 (0.716%) (M^+, two bromine isotopes); ^1H NMR (DMSO-d_6): δ 5.56 (s, 2H) 6.53 (d, 2H, $J=8.5$ Hz), 7.25 (d, 2H, $J=8.5$ Hz), 7.40 (d, 2H, $J=8.5$ Hz), 7.66 (d, 2H, $J=8.5$ Hz), 8.02 (t, 1H), 8.25 (d, 1H, $J=7.8$ Hz), 8.33(d, 1H, $J=7.8$ Hz), 8.59 (m, 2H).

4-Amino-4′-(1,8-naphthalimido)-diphenyl disulfide (**7**): yellow powder (yield 79.5%). IR (KBr): NH_2: 3480, 3370 cm^{-1}; MALDI-TOF-MS: Calc. for $C_{24}H_{16}N_2O_2S_2$: 428.0653, found: 429.0734 (M + 1); ^1H NMR (DMSO-d_6): δ 6.54 (d, 2H, $J=8.6$ Hz), 7.26 (d, 2H, $J=8.6$ Hz), 7.41 (d, 2H, $J=8.5$ Hz), 7.65 (d, 2H, $J=8.5$ Hz), 7.91 (t, 2H), 8.51 (ortho-coupled doublets, 4H).

Table 1
The absorption maximum (λ^{ab}_{max} (nm)), coefficient (ε(10^4 M^{-1} cm^{-1})) and fluorescence maximum (λ^{fl}_{max}(nm)) data of the compounds in different solvents[a]

	Dioxane		THF		MeOH	
	λ^{ab}_{max} (ε)	λ^{fl}_{max}	λ^{ab}_{max} (ε)	λ^{fl}_{max}	λ^{ab}_{max} (ε)	λ^{fl}_{max}
1	330 (1.84) 345 (1.55)	366				
2	292 (3.33) 330 (2.05) 410 (0.39)	362 510				
3	332 (2.67) 346 (2.64)	485				
4	331 (3.18) 345 (2.74)	370 520				
7	330 (2.08)	417	328 (4.7) 344 (4.2)	355 370	333 (0.88)	390
15	398 (2.27)	506				
16	346 (2.77) 332 (2.79)	410				
17	397 (0.99) 346 (1.82) 331 (2.05)	505				
18	405 (0.78) 347 (1.03) 331 (1.16)	498				
19	424 (1.19) 345 (1.1) 330 (1.31)	496				
20	331 (3.51) 346 (2.99)	370 503	330 (3.0) 345 (2.7)	354 373	335	382
21	396 (1.21) 341 (0.32) 322 (0.25)	505				

[a] The fluorescence data were measured by excitation at 330 nm for **1**; 292 nm for **2**; 332 nm for **3**; 331nm for **4** (data of compounds **1–4** taken from Ref. [5]); 330 nm for **7** in dioxane, 320 nm for **7** in THF (data of compound **7** taken from Ref. [19]); 398 nm for **15**; 346 nm for **16**; 295, 330, 397 nm for **17**; 295, 330, 405 nm for **18**; 295, 330, 424 nm for **19**; 330 nm for **20**; 295, 330, 396 nm for **21**, respectively.

4,4′-Di(4-nitro-1,8-naphthalimido)-diphenyl disulfide (**14**): 4,4′-diaminodiphenyl disulfide (0.992 g, 4 mmol) and 4-nitro-1,8-naphthalic anhydride (1.994 g, 8 mmol) were added to acetic acid (20 ml) under nitrogen. The reaction mixture was drastically stirred and slowly heated to reflux. After refluxing for 3 h, the precipitate was filtered after cooling and washed with 30% Na_2CO_3 and water to neutral, then with anhydrous ethanol for several times. The product was recrystalized with chlorobenzene to give yellow solid (1.9 g, yield 68.0%), m.p.$>$320. IR (KBr): NO_2: 1530, 1350 cm^{-1}; ^1H NMR (DMSO-*d*$_6$): δ 7.49 (d, 4H, *J*= 8.4 Hz), 7.76 (d, 4H, *J*= 8.4 Hz), 8.13 (t, 2H), 8.60 (m, 4H), 8.64 (d, 2H, *J*= 7.3 Hz), 8.76 (d, 2H, *J*= 7.3 Hz).

4,4′-Di(4-piperidino-1,8-naphthalimido)-diphenyl disulfide (**15**): 4,4′-diaminodiphenyl disulfide (0.248 g, 1 mmol) and 4-piperidino-1,8-naphthalic anhydride (0.62 g, 2.2 mmol) were added to 2-methoxyethanol (20 ml) with little piperidine under nitrogen. The reaction mixture was drastically stirred and slowly heated to reflux. After refluxing for 20 h, the solid began to appear and after another 30 h, the precipitate was filtered after standing cool overnight and washed with anhydrous ethanol several times. The product was recrystallized with chlorobenzene to give a yellow solid (0.48 g, yield 62.0%), m.p.$>$320 °C. IR (KBr): CON: 3450 (b), 1670 cm^{-1} (s); MALDI-TOF-MS: Calc. for $C_{46}H_{38}N_4O_4S_2$: 774.2335, found: 775. 2595 (M + 1); ^1H NMR (DMSO-d$_6$): δ 1.67 (m, 4H), 1.84 (m, 8H), 3.23 (m, 8H), 7.36 (d, 2H, *J*= 8.2 Hz), 7.43 (d, 4H, *J*= 8.5 Hz), 7.72 (d, 4H, *J*= 8.5 Hz), 7.85 (t, 2H), 8.40 (d, 2H, *J*= 8.2 Hz), 8.48 (m, 4H).

4-(1,8-Naphthalimido)-4′-(4-nitro-1,8-naphthalimido)-diphenyl disulfide (**16**): brown solid (yield 61.2%), m.p. $>$320 °C. IR (KBr): NO_2: 1530, 1350 cm^{-1}; MALDI-TOF-MS: Calc. for $C_{36}H_{19}N_3O_6S_2$: 653.0715, found: 654.2 (M + 1); ^1H NMR (DMSO-*d*$_6$): δ 7.49 (m, 4H), 7.76 (m, 4H), 7.92 (t, 2H), 8.14 (t, 1H), 8.52 (t, 4H), 8.61 (m, 2H), 8.66 (d, 1H, *J*= 8.7 Hz), 8.77 (d, 1H, *J*= 8.7 Hz).

4-(1,8-Naphthalimido)-4′-(4-piperidino-1,8-naphthalimido)-diphenyl disulfide (**17**): yellowish brown powder (yield 43%), m.p. $>$320 °C. IR (KBr): CON: 3450 (b), 1670 cm^{-1} (s); MALDI-TOF-MS: Calc. for $C_{41}H_{29}N_3O_4S_2$: 691.1599, found: 692.1491 (M + 1); ^1H NMR (DMSO-*d*$_6$): δ 1.68 (m, 2H), 1.84 (m, 4H), 3.23 (m, 4H), 7.35 (d, 1H, *J* = 8.2 Hz), 7.43 (d, 2H, *J* = 8.4 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 7.75 (t, 4H), 7.84(t, 1H), 7.91 (t, 2H), 8.40 (d, 1H, *J* = 8.2 Hz), 8.47 (m, 2H), 8.52 (m, 4H).

4-(1,8-Naphthalimido)-4′-(4-N,N-dimethylamino-1,8-naphthalimido)-diphenyl disulfide (**18**): yellow solid. m.p. $>$320 °C. IR (KBr): CON: 3450 cm^{-1} (b), 1670cm^{-1} (s); MALDI-TOF-MS: Calc. for $C_{38}H_{25}N_3O_4S_2$: 651.1287, found: 652.1652 (M + 1); ^1H NMR (DMSO-*d*$_6$): δ 3.19 (s, 6H), 7.33 (d, 1H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.6 Hz), 7.54 (d, 2H, *J* = 8.6 Hz), 7.82 (m, 4H), 7.86 (t, 1H), 7.98 (t, 2H), 8.42 (d, 1H, *J* = 8.3 Hz), 8.54 (d, 1H, *J* = 8.4 Hz), 8.57 (m, 4H), 8.64 (d, 1H, *J* = 8.4 Hz).

4-(1,8-Naphthalimido)-4′-(4-octylamino-1,8-naphthalimido)-diphenyl disulfide (**19**): yellow solid. m.p.$>$320 °C. IR (KBr): CON: 3450 (b), 1670 cm^{-1} (s); MALDI-TOF-MS: Calc. for $C_{44}H_{37}N_3O_4S_2$: 735.2226, found: 736.2305 (M + 1); ^1H NMR (DMSO-*d*$_6$): δ 0.86 (m, 5H), 1.32–1.40 (m, 10H), 1.70 (m, 2H), 6.82 (d, 1H, *J* = 8.6 Hz), 6.99 (m, 2H), 7.48 (m, 2H), 7.72 (m, 5H), 7.91 (t, 2H), 8.27 (d, 1H, *J*= 8.6 Hz), 8.44 (d, 1H, *J*= 8.2 Hz), 8.52 (m, 4H), 8.76 (d, 1H, *J* = 8.2 Hz).

3. Results and discussion

The absorption and fluorescence spectra data of these triad compounds are listed in Table 1 and 2. Besides fluorescence emissions in the shorter wavelength region, compounds **2** and **4** have longer wavelength emissions, respectively at 510 and 520 nm with the Stokes shift 218 and 189 nm. In order to compare the fluorescence spectra of two corresponding mixture systems: **1** and 9-carbazolylacetic acid (molar ratio 1:1) as well as **1** and

Table 2
Relative fluorescence integrated ratio of compounds **15** and **17** in different solvents[a]

Solvents	Dioxane	THF	CH_2Cl_2
15/**21**	1.38	1.40	1.37
17/**21**	0.92	0.87	0.73

[a] The values are ratio of fluorescence area integrated from 450 to 650 nm relative to compound 21 at the same absorbance excited at 397 nm.

1,8-naphthalic anhydride (molar ratio 1:1) were measured. When excited at 292 nm, which is the maximum absorption of carbazole unit, the system (1 and 9-carbazolylacetic acid) shows emission at 362 nm. When excited at 331 nm, which is the maximum absorption of 1,8-naphthalic anhydride unit, the system (**1** and 1,8-naphthalic anhydride) shows emission at 370 nm. There is no emission in the longer wavelength region and the fluorescence emission in the short wavelength region is very similar. The emission in short wavelength region was due to the the characteristics of compound **1** in the mixture systems. These results indicate that the phenomena that compounds **2** and **4** have longer wavelength emissions may result from the existence of excimer or exciplex [18]. Compared with the intramolecular charge transfer, the efficiency of intermolecular charge transfer was relative small. For compounds **2** and **4**, there may be intramolecular charge transfer through chemical bonds or intermolecular charge transfer through molecule stacking (partially overlap the configuration between donor and acceptor). The photoinduced charge transfer results in the exciplex, which leads to the remarkable red-shift of the fluorescence emission wavelength. Not only through chemical bonds do intramolecular electron transfer processes exist, but also through molecular stacking between donor and acceptor there exist intermolecular electron transfer processes. These processes would induce the formation of exciplex or ICT excited state, which emits at a longer wavelength.

For compound **3**, the intrinsic fluorescence emission of one naphthalimide unit substituted with nitro-group was quenched by nitro-substitution. Consequently, the fluorescence emission resulting from the exciplex was also quenched obviously by nitro-substitution, despite the fact that intramolecular charge transfer in the compound enhances with nitro-substitution.

The concentration $[(M{-}M)^*]$ of the exciplex existing in compounds **2** and **4** decays with time (t) according to the relationship of biexponential function [18], which is shown in Eq. (1):

$$[(M-M)^*] = \frac{k_{\mathrm{ET}}C}{k_1 - k_2 - k_{\mathrm{ET}}} \left\{\exp[-(k_{\mathrm{ET}} + k_2)t] - \exp(-k_{1t})\right\} \quad (1)$$

where k_1 is the rate constant of the formation process of the exciplex; k_2 is the rate constant of the decay process of the exciplex; k_{ET} is the rate constant of the electron transfer process between two chromophores in the exciplex; C is a constant. The fluorescence decay kinetic analysis shows that the fluorescence of these compounds (such as **2** and **4**) has two lifetimes in longer wavelength region, listed in Table 3. When compound **2** excited at the wavelengths of maximum absorption of carbazole unit (293 nm) and the naphthalimide unit (320 nm), the fluorescence emissions of **2** (THF as the solvent) are both at 540 nm. This shows the longer wavelength fluorescence emission results from the intramolecular interaction between the excited states of carbazole unit and the naphthalimide unit. This kind of interaction would produce intramolecular exciplex. Meanwhile, due to the solvent effect, it can be seen from Table 2 that the different solvents influence the detection results. Compounds **2** and **4** also have two fluorescence lifetimes at 540 nm in THF, which is consistent with the postulation that the fluorescence emission in the longer wavelength results from the forming of exciplex and which is also consistent with the fluorescence decay kinetic equation mentioned earlier.

Compounds **2** and **4** have fluorescence emissions both in the short wavelength region and in long wavelength region, the decay of fluorescence has two lifetimes and the emission in long wavelength region results from the exciplex induced by intramolecular charge transfer. This phenomenon makes it possible for these molecules to have the potential application for rapid response fluorescence molecular switch. The exciplex would be formed by the process of intramolecular charge transfer through chemical bonds (the aromatic sulfur bridge recovering) or by the intermolecular charge transfer through the molecules stacking (the overlap configuration between donor and acceptor). The fluorescence emission in the long wavelength region would appear, and the system would be “on” state. This process illustrates that the system may alternate the “on” state and “off” state rapidly by the detection of the fluorescent signal in the long wavelength region, because the sulfur radicals can form and recombine rapidly

Table 3
Fluorescence lifetimes (τ (ns)) of compounds in different solvents

	THF	Cyclohexane	MeOH
	λ^{EX}(nm); λ^{EM}(nm)	λ^{EX}(nm); λ^{EM}(nm)	λ^{EX}(nm); λ^{EM}(nm)
	τ_1(ns) (%)[a] τ_2(ns) (%)	τ_1(ns) (%) τ_2(ns) (%)	τ(ns)
1	1.19 (320; 400)	1.92 (300; 400)	1.33 (320; 400)
2	1.57 (48); 5.89 (52) (320; 540) 1.1 (39); 4.8 (61) (293; 540)	79 (83); 5.09 (17) (340; 470) 0.66 (40); 7.58 (60) (293; 350)	4.87 (320; 520)
4	0.43 (91); 5.33 (9) (320; 540) 1.23 (76); 6.62 (24) (320; 410)		
20	1.19 (350; 400)	1.03 (320; 400)	0.28 (320; 400)
7	1.32 (330; 400)	0.29 (320; 360)	1.53 (320; 400)
15	6.4±0.04 Ex: 290; 330; 400 λ^{EM}: 520	0.88(56); 8.42(44) (420; 540) in DMSO	8.69 (420; 540) in CH_2Cl_2
17	6.1±0.06 Ex: 290; 330; 400 λ^{EM}: 520	9.06(53); 0.44(47) (420; 540) in DMSO	8.77 (420; 540) in CH_2Cl_2

[a] The percentage is the weight distribution of that lifetime.

(faster than 10^{-9} s scale) [6]. The properties of molecular switch used by these compounds are being measured.

The absorption and fluorescence spectra of compounds **21**, **15** and **17** were shown in Figs. 2–4. As seen in the figures, the fluorescence maximum of **15** and **17** were the characteristics of 21. However, compared with **21**, **17** showed relative low emission and **15** shows relative high intensity. Due to the symmetric configuration of **15**, the dipole moment between the two naphthalimides in excited state is demolished. Hence, the intramolecular electric field between the two naphthalimides disappears and the photoinduced electron transfer (PET) output path is switched off [20,21]. That is to say, in compound **15**, there is no electron transfer between disulfide, which links the two identical naphthalimides (**21**). In compound **17**,

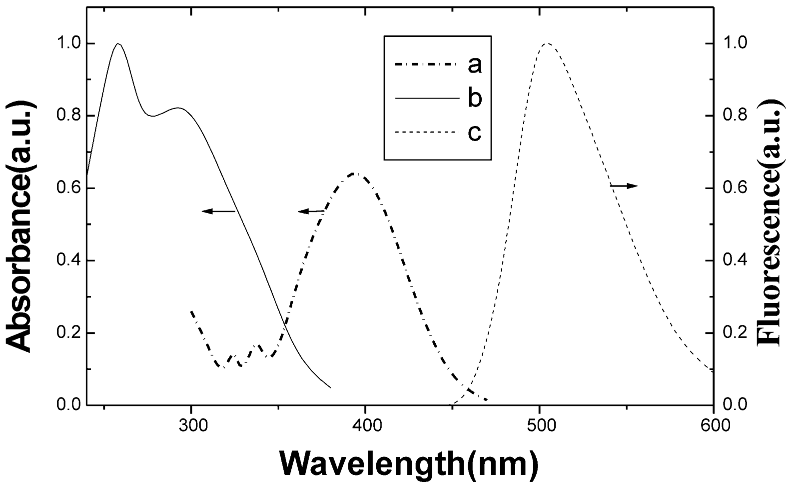

Fig. 2. The absorption of **21** (curve a) and 4,4′-diamino-biphenyl-disulfide (curve b) and fluorescence of **21** in dioxane (curve c).

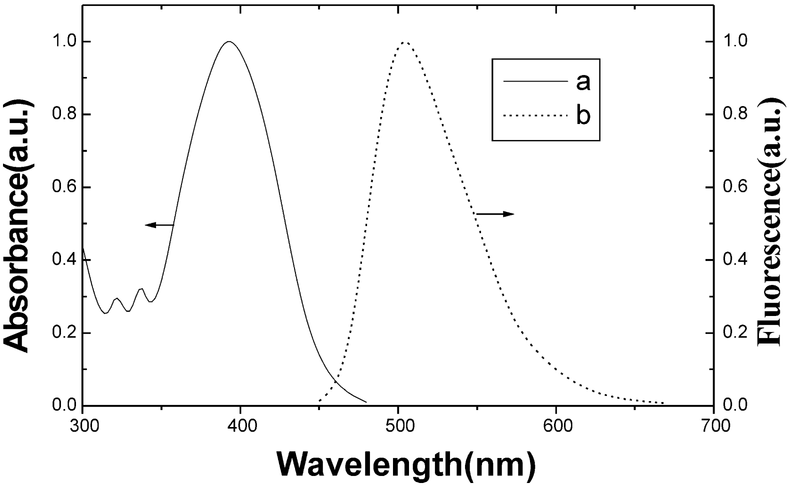

Fig. 3. The absorption and fluorescence (excited at 397 nm) spectra of **17** in dioxane.

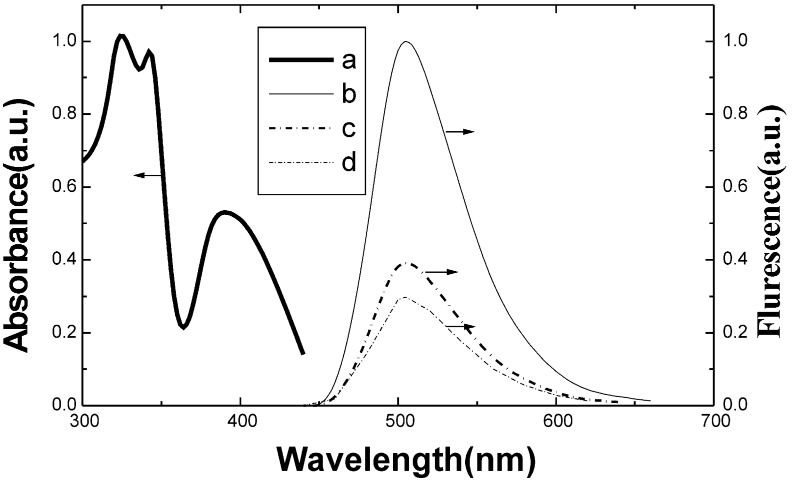

Fig. 4. The absorption and fluorescence (curve b: excited at 397 nm; curve c: excited at 346 nm; curve d: excited at 331 nm) spectra of **15** in dioxane.

PET still occurs from the fluorophore i.e. 4-piperidino-1,8-naphthalimide (which acts as a donor at this time) to electron acceptor i.e. the non-substituted 1,8-naphthalimide, and causes the fluorescence to be quenched. As seen in Table 2, the relative fluorescence integrated area of 17 was less than that of the reference compound **21**. In conclusion, the fluorescence of 4-piperidino-1,8-naphthalimide fluorophore recovers or enhances only if the output PET path is switched off.

For compound **17**, the free energy ΔG_{CS} for charge separation from the excited singlet state of 4-piperidino-1,8-naphthalimide to the non-substituted 1,8-naphthalimide acceptor can be calculated using the following equation: [22]

$$\Delta G_{\mathrm{CS}} = E_{\mathrm{Ox}} - E_{\mathrm{Red}} - \frac{e_0^2}{\varepsilon_{\mathrm{s}} r_{12}} - E_{\mathrm{s}} \qquad (2)$$

where E_{Ox} is the oxidation potential energy of the donor, E_{Red} is the reduction potential energy of the acceptor, E_{s} is the potential energy of first excited singlet state of the donor, e_0 is the charge of an electron, ε_{s} is the static dielectric constant of solvent, and r_{12} is the center-to-center distance between the donor and acceptor. E_{Ox} of 4-piperidino-1,8-naphthalimide is around 1.1eV vs SCE [22,23], E_{Red} of the non-substituted 1,8-naphthalimide is -1.23eV vs SCE [24], ε_s of is 2.24 for toluene [25]. The sufficient negative value of ΔG_{CS} shows that for compound **17**, the PET process between the piperidino-substituted naphthalimide and the non-substituted naphthalimide is thermodynamically feasible. The fluorescence lifetime τ of **17** is measured to be 6.1 ns, longer than that of **21** (1.19 ns). The prolongation of excited state in **17** may be ascribed to the additional PET process from 4-piperidino-1,8-naphthalimide to the non-substituted 1,8-naphthalimide, which otherwise does not occur in compound **20**. PET can occur between the two different naphthalimides via a disulfide bridge exactly. On the other hand, PET process is largely influenced by the polarity of solvents, because PET is considerably accelerated in polar media for 4-piperidino-1,8-naphthalimide and fluorescence will be diminished in the solvent with high polarity [26]. In Table 2, Fluorescence Integrated Ratio of the compounds **17** is much poorer in highly polar solvent CH_2Cl_2 than that measured in low polar solvent dioxane, due to the occurrence of PET in the compound. But comparably, the Fluorescence Integrated Ratio of the compounds **15** remains steady versus the solvent polarity, since the output electron path is switched off in as we have discussed before.

4. Conclusions

Several “donor-bridge-acceptor” triad compounds were synthesized, in which aromatic sulfur components (such as disulfide, 9H-thioxanthen-9-one and thianthrene) were used as “bridge”. The fluorescence lifetimes of these compounds in various solvents have been measured by single-photon counting technique. The characteristic longer wavelength emission of these compounds was observed, which may be due to the formation of intramolecular exciplex. The photoinduced electron transfer (PET) phenomenon was observed for the disulfide series compounds. When PET occurs, the fluorescence of compound would be quenched. The PET process between the piperidino-substituted naphthalimide and the non-substituted naphthalimide is thermodynamically feasible. PET can occur between the two different naphthalimides via a disulfide bridge exactly.

Acknowledgements

This work was financially supported by NSFC/China.

References

[1] Waldeck DH, Beratan DN. Science 1993;261:576.

[2] Schneider HJ, Durr H. Fronties in supermolecular organic chemistry and photochemistry. New York: VCH, 1991.

[3] de Silva AP, Gunaratne HQN. J Am Chem Soc 1997; 119:7891.

[4] Walz J, Ulrich K, Wolf HC. Chem Phys Lett 1993; 213:321.

[5] Tian H, Yang K, Luo X. J Photochem Photobiol A: Chem 1997;110:253.

[6] Thyrion FC. J Phys Chem 1973;77:1478.

[7] de Silva AP, Gunaratne HQN. Chemical Review 1997; 97:1515.

[8] Hirata Y, Niga Y, Okada T. Chem Phys Lett 1994; 221:283.

[9] Ito O, Matsuda M. J Am Chem Soc 1982;104:1701.

[10] Kim K, Hull VJ, Shine HJ. J Org Chem 1974;39:2534.

[11] Wang X-H, Connor M, Smith R, Maciejewski MW, Howden MEH, Nicholson GM, Christie MJ, King GF. Nature Structural Biology 2000;7:505.

[12] Protiva M, Sindelar K, Holubek J. Collect Czech Chem Commun 1981;46:1788.

[13] Ian WJ, Sayeed VA. Synthesis Commun 1983;13:1181.

[14] (special issue). Organic Synthesis Collection 1955;3:86.

[15] Wang Y, Wu Y, Tian H. Dyes and Pigments 2000;44:93.

[16] Peters AT, Bide MJ. Dyes and Pigments 1985;6:349.

[17] Plakidin VL. Zh Org Fhim 1981;17(5)1118; 1988;24(3):625.

[18] Turro NJ, Kavarnos GJ. Chemical Review 1986;86:401.

[19] Wu Y, Zhang Z, Tian H. Ganguang Kexue Yu Guang Huaxue (in Chinese) 1999;17(2):172; Chem Abstract 1999; 391143.

[20] de Silva AP, Gunaratne HQN, Lynch PLM, Patty AJ, Spence GL. J Chem Soc Perkin Trans 1993;2:1611.

[21] Meyer YH, Bourson J, Valeur B. Chem Phys Lett 1993; 202:425.

[22] de Silva AP, Gunaratne HQN, Habib-Jiwan J, McCoy CP, Rice TE, Soumillion J. Angew Chem Int Ed Engl 1995;34:1728.

[23] Tian H, Tao X, Zhao Y, Chen K. J Chem Soc Perkin Trans 1999;2:545.

[24] West RC. Handbook of chemistry and physics. 70th ed. Cleveland: Chemical Rubber Co. Press, 1990.

[25] Wiederrecht GP, Yoon BA, Svec WA, Wasielewski MR. J Am Chem Soc 1997;119:3358.

[26] Alexiou MS, Tychopoulos V, Ghorbanian S, Tyman JHP, Brown RG, Brittain PI. J Chem Soc Perkin Trans 1990; 2:837.