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Synthesis and luminescence properties of triad compounds with a disulfide bridge

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Abstract

Several novel triad compounds with fluorescence were synthesized, in which aromatic disulfide was used as a “bridge”. The fluorescence lifetimes of these compounds in various solvents have been measured by a single-photon counting technique. The photoinduced electron transfer (PET) phenomenon was observed for the disulfide series compounds. When PET occurs, the fluorescence of the compound would be quenched. The aromatic disulfide compound was preliminary explored acting as the hole transporting material for organic electroluminescent device. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Triad compounds; Fluorescence spectra; Fluorescence lifetime; Electroluminescence

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 (spiro-pyrans, 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 photo-

chromism 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 conjugated polyenic chain system and 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 on). The fluorescence they used for the switching function has an obvious advantage

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with high sensitivity. However, the process based on photochromic fulgides mentioned above can not realize rapid response.

In order to find a novel rapid photoinduced molecular switch system, we developed some triad compounds with a 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 a 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 disulfide was used as a “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 a key role with biological function [11]. In fact, except high sensitivity, the advantages of molecular fluorescence or luminescence for sensing and switching

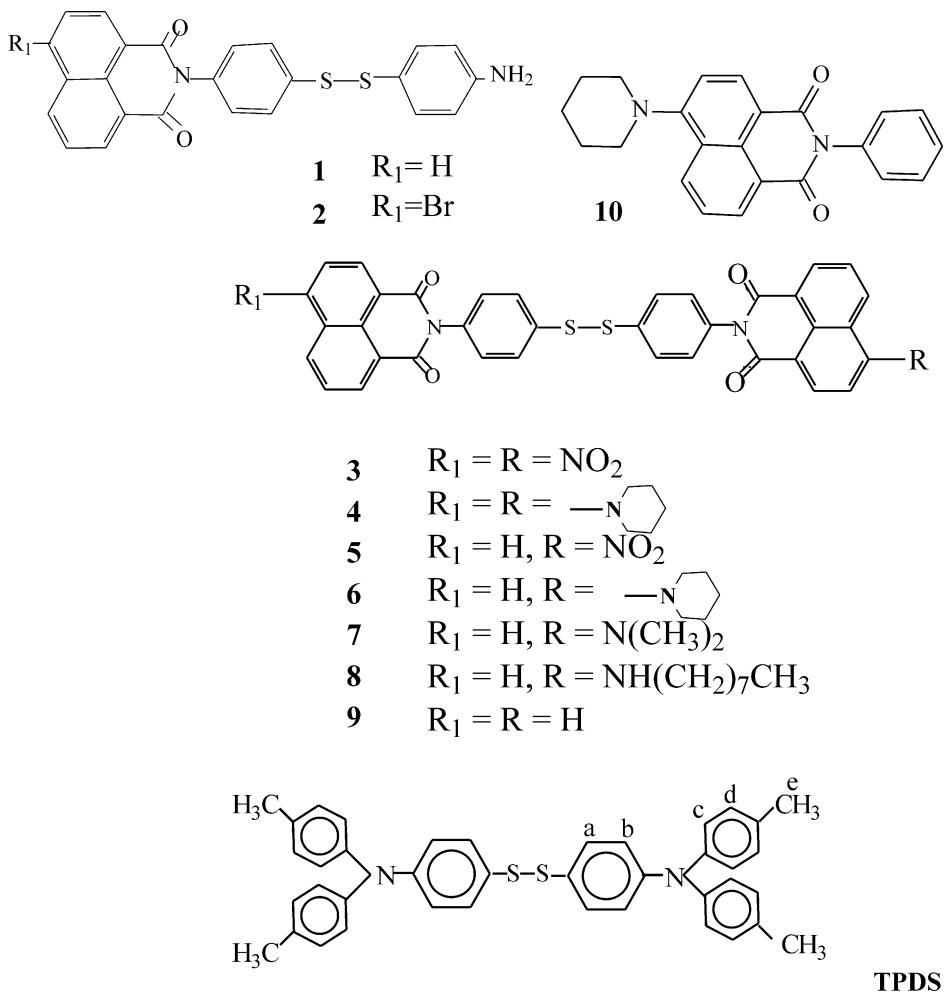


Fig. 1. Chemical structures of triad compounds synthesized.

include feasibility of human-molecule communication, subnanometer spatial resolution with submicron visualization. There exist considerable opportunities for modulating structural features, which control fluorescence efficiency via the effects including double-bond torsion, low energy np^* 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 ^1H NMR were recorded on a Brucker AM 500 spectrometer using TMS as the standard. Mass spectra and MALDI-TOF mass spectra were obtained at 70 eV 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 a deconvolution method. The temporal resolution after deconvolution of the exciting pulse is ~ 200 ps. Compounds TPDS were synthesized based on the method in the literature [12]: 0.496 g (2 mmol) 4,4'-diaminodiphenyl disulfide, 2.18 g (0.01 mol) 4-iodotoluene, K_2CO_3 2.2 g (0.016 mol), copper powder 0.512 g (8 mmol) and 2.46 g poly (ethylene glycol) 600 were added and dissolved in 10 ml 1, 2-dichlorobenzene, and the reaction mixture was heated to reflux under the nitrogen gas for 5 h, then filtered to remove the solvent by reducing pressure. The rude product was purified by the silicon column (elute: petroleum ether) to give a white solid 0.22 g, yield 36.2%. ^1H NMR (d_6 -DMSO): δ 2.26 (s, 12H, H-e), 6.83 (d, 4H, $J_{\text{ba}}=8.7$ Hz, H-b), 6.94 (d, 8H, $J_{\text{cd}}=10.8$ Hz, H-c), 7.13 (d, 8H, $J_{\text{dc}}=10.8$ Hz, H-d), 7.21 (d, 4H, $J_{\text{ab}}=8.7$ Hz, H-a). 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-Piperidino-1,8-naphthalic anhydride and 4-N-dimethyl-1,8-naphthalic anhydride was synthesized according to reference [13].

2.1. 4-Amino-4'-(4-bromo-1,8-naphthalimido)-diphenyl disulfide (2)

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 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): 506 (0.69%), 508 (0.716%) (M^+ , two bromine isotopes); ^1H NMR (d_6 -DMSO): 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).

2.2. 4-Amino-4'-(1,8-naphthalimido)-diphenyl disulfide (1)

Yellow powder (yield 79.5%). IR (KBr): NH_2 : 3480, 3370 cm^{-1} ; MALDI-TOF-MS: calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$: 428.0653, found: 429.0734 ($\text{M}+1$); ^1H NMR (d_6 -DMSO): 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).

2.3. 4,4'-Di(4-nitro-1,8-naphthalimido)-diphenyl disulfide (3)

Yellow solid (yield 68.0%), m.p. > 320 °C. IR (KBr): NO_2 : 1530, 1350 cm^{-1} ; ^1H NMR (d_6 -DMSO): 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).

2.4. 4,4'-Di(4-piperidino-1,8-naphthalimido)-diphenyl disulfide (4)

Brown solid (yield 62%), m.p. > 320 °C. IR (KBr): -CON-: 3450 (b), 1670 cm⁻¹ (s); MALDI-TOF-MS: Calcd. for C₄₆H₃₈N₄O₄S₂: 774.2335, found: 775.2595 (M + 1); ¹H NMR (d₆-DMSO): 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).

2.5. 4-(1,8-Naphthalimido)-4'-(4-nitro-1,8-naphthalimido)-diphenyl disulfide (5)

Brown solid (yield 61.2%), m.p. > 320 °C. IR (KBr): NO₂: 1530, 1350 cm⁻¹; MALDI-TOF-MS: calcd. for C₃₆H₁₉N₃O₆S₂: 653.1, found: 654.2 (M + 1); ¹H NMR (d₆-DMSO): 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).

2.6. 4-(1,8-Naphthalimido)-4'-(4-piperidino-1,8-naphthalimido)-diphenyl disulfide (6)

Yellowish brown powder (yield 43%), m.p. > 320 °C. IR (KBr): -CON-: 3450 (b), 1670 cm⁻¹ (s); MALDI-TOF-MS: calcd. for C₄₁H₂₉N₃O₄S₂: 691.1599, found: 692.1491 (M + 1); ¹H NMR (d₆-DMSO): 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).

2.7. 4-(1,8-naphthalimido)-4'-(4-N,N-dimethylamino-1,8-naphthalimido)-diphenyl disulfide (7)

Yellow solid. m.p. > 320 °C. IR (KBr): -CON-: 3450 cm⁻¹ (b), 1670 cm⁻¹ (s); MALDI-TOF-MS: calcd. for C₃₈H₂₅N₃O₄S₂: 651.1287, found: 652.1652 (M + 1); ¹H NMR (d₆-DMSO): 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).

2.8. 4-(1,8-Naphthalimido)-4'-(4-octylamino-1,8-naphthalimido)-diphenyl disulfide (8)

Yellow solid. m.p. > 320 °C. IR (KBr) -CON-: 3450 (b), 1670 cm⁻¹ (s); MALDI-TOF-MS: calcd. for C₄₄H₃₇N₃O₄S₂: 735.2226, found: 736.2305 (M + 1); ¹H NMR (d₆-DMSO): 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 Tables 1 and 2. Before the discussion of spectral properties of the triad compounds with a flexible bridge herein (disulfide), the fluorescence spectra of the triad compounds **11** and **12** with a rigid bridge (9H-thioxanthan-9-one or thianthrene) have been investigated, as seen in Fig. 2. The synthesis of the triad compounds **11** and **12** has been published in detail previously [14] and their chemical structures were shown in Fig. 3.

Compounds **11** and **12** have characteristic fluorescence in long wavelength region (respectively 495 and 598 nm, Stokes shift is correspondingly 173 and 265 nm, shown in Fig. 2). Compound **11** also has short wavelength fluorescence emission (370 nm, Stokes shift is 48 nm). In order to discuss the fluorescence spectra of compound **11**, the fluorescence of a corresponding mixture systems: *N*-(1,8-naphthalimido)-7'-amino-thioxanthan-9'-one and 9-carbazolylacetic acid (molar ratio 1:1) was measured. When excited at 292 nm, which is the maximum absorption of carbazole unit, the mixture system shows emission at 362 nm. When excited at 331 nm, which is the maximum absorption of 1,8-naphthalimide unit, this mixture system shows emission at 370 nm, which is the characteristic emission of 1,8-naphthalimide unit. There is no longer wavelength emission band for the corresponding mixture system under the same condition of measurements for compound **11**. And the fluorescence emission in short wavelength

Table 1

The absorption maximum ($\lambda_{\max}^{\text{ab}}$) and coefficient ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and fluorescence maximum ($\lambda_{\max}^{\text{fl}}$) data of compounds in different solvents

Compound	1	4	5	6	7	8	9	10
($\lambda_{\max}^{\text{ab}}/\text{nm}$) (ϵ) in dioxane			346 (2.77)	397 (0.99)	405 (0.78)	424 (1.19)	331 (3.51)	396 (1.21)
	330 (2.08)	398 (2.27)	332 (2.79)	346 (1.82)	347 (1.03)	345 (1.1)	346 (2.99)	341 (0.32)
				331 (2.05)	331 (1.16)	330 (1.31)		322 (0.25)
($\lambda_{\max}^{\text{ab}}/\text{nm}$) (ϵ) in THF	328 (4.7)						330 (3.0)	
	344 (4.2)						345 (2.7)	
($\lambda_{\max}^{\text{ab}}/\text{nm}$) (ϵ) in MeOH	333 (0.88)						335	
($\lambda_{\max}^{\text{fl}}/\text{nm}$) ^a in dioxane	417	506	410	505	498	496	370 ; 503	505
($\lambda_{\max}^{\text{fl}}/\text{nm}$) ^a in THF	355; 370						354; 373	
($\lambda_{\max}^{\text{fl}}/\text{nm}$) ^a in MeOH	390						382	

^a The data were measured by excitation at 330 nm for **1** in dioxane, 320 nm for **1** in THF; 398 nm for **4**; 346 nm for **5**; 295, 330, 397 nm for **6**; 295, 330, 405 nm for **7**; 295, 330, 424 nm for **8**; 330 nm for **9**; 295, 330, 396 nm for **10**; respectively.

Table 2

Relative fluorescence integrated ratio of compounds **4** and **6** in different solvents

Solvents	Dioxane	THF	CH_2Cl_2
4/10	1.38	1.40	1.37
6/10	0.92	0.87	0.73

The values are ratio of fluorescence area integrated from 450 to 650 nm relative to compound **10** at the same absorbance excited at 397 nm.

region, however, is also 370 nm and is very similar to that observed in compound **11**. These results indicate that the phenomena that the longer wavelength emission of compound **11** may result from the existence of excimer or exciplex [15].

The structure of compound **12** is very special, in which thianthrene is used as the bridge. Thianthrene was assumed a folded C_2V conformation with a dihedral angle at $\theta=131^\circ$. In the crystal, each of the phenylene groups and the two sulfur atoms are coplanar, and the two planes intersect along the S–S bond axis [6]. It can be believed that the two naphthalimides in compound **12** were not in one plane and they have interaction each other. This may easily result in the exciplex. The longer wavelength fluorescence emission of compound **12** could be explained by its molecular configuration. These interactions including the formation of intramolecular exciplex and non-planar configuration would result in long wavelength fluorescence emission.

Compared with the intramolecular charge transfer, the efficiency of intermolecular charge

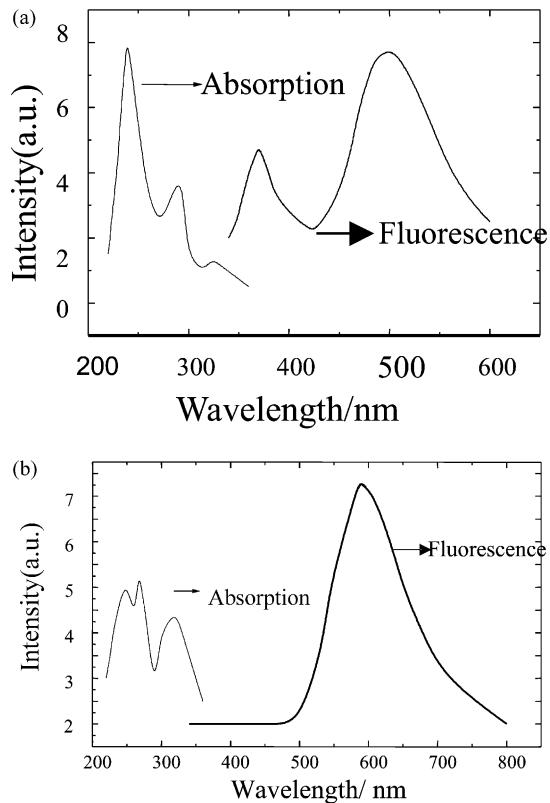


Fig. 2. The absorption and fluorescence spectra of **11** (a) and **12** (b) in THF.

transfer was relative small. For compounds **11** and **12**, there may be intramolecular charge transfer through chemical bonds or intermolecular charge transfer through molecule stacking (partially overlap configuration between donor and acceptor).

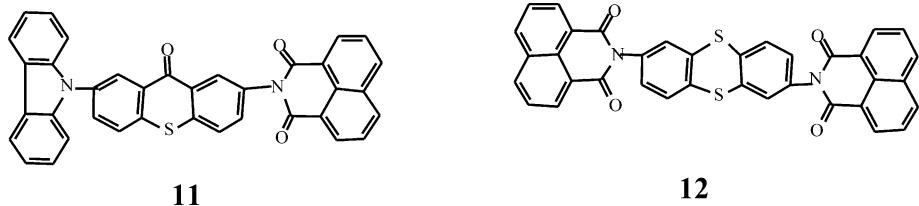


Fig. 3. The chemical structures of triad compounds with a rigid bridge reported previously [14].

The photoinduced charge transfer results in the exciplex, which leads to the remarkably red-shift of the fluorescence emission wavelength. Not only through chemical bonds there exist intramolecular electron transfer processes, 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 longer wavelength.

The absorption and fluorescence spectra of compounds **10**, **4** and **6** were shown in Figs. 4–6. As seen in the figures, the fluorescence maximum of **4** and **6** were the characteristics of **10**. However, comparing with **10**, **6** showed relative low emission and **4** showed relative high intensity of the emission. Due to the symmetric configuration of **4**, 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 [16, 17].

That is to say, in compound **4**, there is no electron transfer between disulfide, which links the two identical naphthalimides (**10**). In compound **6**, 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 quenched. As seen in Table 2, the relative fluorescence integrated area of **6** was less than that of the reference compound **10**. 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 **6**, 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 [18]:

$$\Delta G_{\text{CS}} = E_{\text{Ox}} - E_{\text{Red}} - \frac{e_0^2}{\varepsilon_s r_{12}} - E_s \quad (1)$$

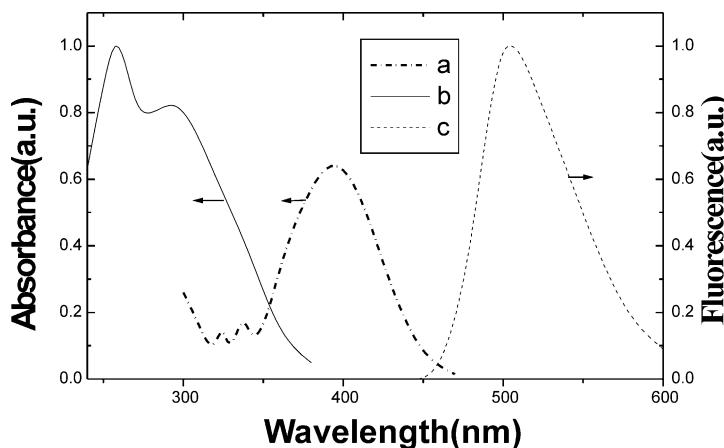


Fig. 4. The absorption of **10** (curve a) and 4, 4'-diamino-biphenyl-disulfide (curve b) and fluorescence of **10** in dioxane (curve c).

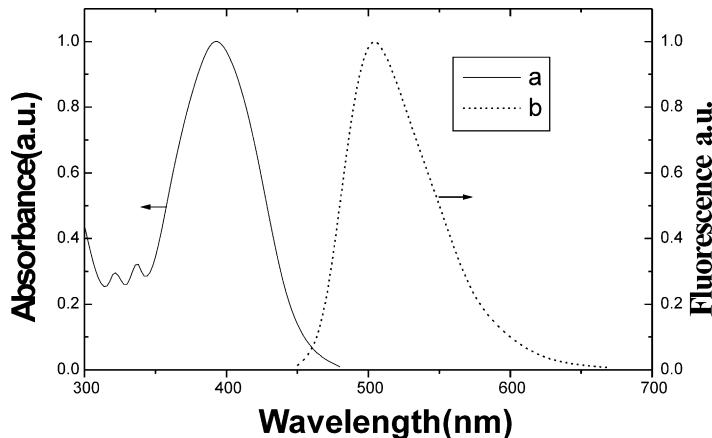


Fig. 5. The absorption and fluorescence (excited at 397 nm) spectra of **6** in dioxane.

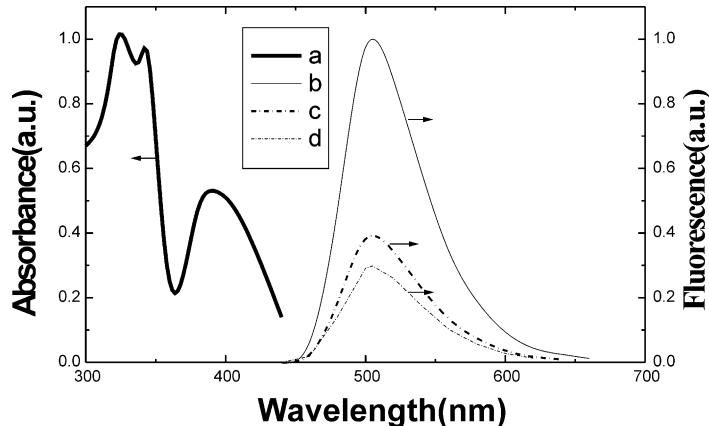


Fig. 6. The absorption and fluorescence (curve b: excited at 397 nm; curve c: excited at 346 nm; curve d: excited at 331 nm) spectra of **4** in dioxane.

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 1.1 eV vs SCE [19,20], E_{Red} of the non-substituted 1,8-naphthalimide is -1.23 eV vs SCE [21], ε_s is 2.24 for toluene [22]. The enough negative value of ΔG_{CS} shows that for compound **6**, the PET process between the piperidino-substituted naphthalimide and the non-substituted naphthalimide is thermodynamically feasible. The fluorescence lifetime τ of **6** is

measured to be 6.1 ns, longer than that of **9** (1.2 ns, shown in Table 3). The prolongation of excited state in **6** 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 **9**. 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 [23]. In Table 2, the fluorescence integrated ratio of the compounds **6** is much poorer in highly polar solvent CH_2Cl_2 than that measured in low polar

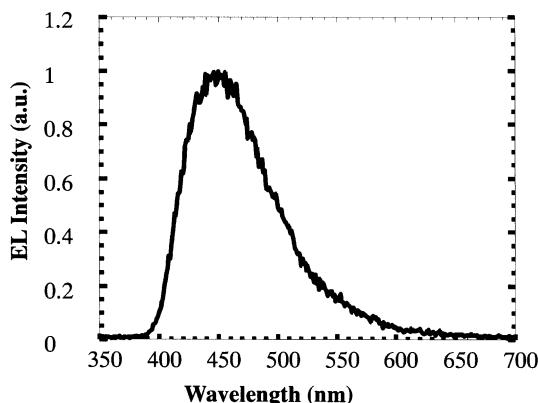


Fig. 7. The EL spectra of the device: ITO/TPDS (100 nm)/BePP₂ (40 nm)/LiF (0.7 nm)/AlLi.

solvent dioxane, due to the occurrence of PET in the compound. But comparably, the fluorescence integrated ratio of the compounds 4 remains steady versus the solvent polarity, since the output electron path is switched off in as we have discussed before [19].

The recent development of organic light emitting diodes (OLEDs) has revealed that organic semiconductors have high potential for use as display devices because of their high emission efficiency and various emission colors [24,25]. Improving the durability of OLEDs under continuous operation, however, is still a significant issue for practical device applications, although various efforts reported in previous studies have improved the durability of the devices. In these efforts, Adachi and Kafafi et al. [26] have developed highly durable OLEDs by the doping of a hole transport materials containing sulphide amine. In this study, we used *N,N,N',N'*-tetraltolyl-1,1'-diphenyldisulfide-4,4'-diamine (TPDS, shown in Fig. 1) as the hole transport layer (HTL) and expect enhancement of the OLED device duration.

A blue EL device using bis[2-(2-hydroxyphenyl) pyridinato] beryllium (BePP₂) and TPDS was fabricated showing a luminance of ~ 50 cd/m² and current density of ~ 100 mA/cm² at 15 V. The EL spectra, shown in Fig. 7, recorded with a PTI QM1 spectrometer. The thickness of samples was measured by a profilometer (Tenco Alpha-Step Model 500). The sheet resistance of the ITO anode

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

	THF $\lambda^{\text{EX}}/\text{nm}$; $\lambda^{\text{EM}}/\text{nm}$		Cyclohexane $\lambda^{\text{EX}}/\text{nm}$; $\lambda^{\text{EM}}/\text{nm}$		MeOH $\lambda^{\text{EX}}/\text{nm}$; $\lambda^{\text{EM}}/\text{nm}$
	τ_1 (%)	τ_2 (%)	τ_1 (%)	τ_2 (%)	τ
1	1.32 (330; 400)		0.29 (320; 360)		1.53 (320; 400)
4	6.4 ± 0.04		0.88 (56); 8.42 (44)		8.69
	Ex: 290; 330; 400		(420; 540)		(420; 540)
	λ^{EM} : 520		in DMSO		in CH_2Cl_2
6	6.1 ± 0.06		9.06 (53); 0.44 (47)		8.77
	Ex: 290; 330; 400		(420; 540)		(420; 540)
	λ^{EM} : 520		in DMSO		in CH_2Cl_2
9	1.19		1.03		0.28
	(350; 400)		(320; 400)		(320; 400)

is ~ 20 Ω/square . The metal cathode of the EL device was prepared by vacuum deposition at 1×10^{-7} Torr. The organic layer (100 nm) for hole transport was made by vacuum evaporation of TPDS. Then 40 nm thick the electron-transporting emitter BePP₂ was deposited. The cathode of the fabricated devices were made of 0.7 nm thick LiF and 200 nm Al. The insert 0.7 nm-thick alkaline metal compounds between a cathode and an electron transport layer (ETL) would reduce electron injection barrier. The reduction of the injection barrier improved device durability as well as decrease of the driving voltage [27,28]. The EL peak at around 460 nm should be due to BePP₂, as seen in Fig. 6, because that the PL peak of BePP₂ thin film on quartz substrate is at 460 nm [29,30]. The EL spectrum consisted completely of BePP₂'s fluorescence, thus holes and electrons were trapped by BePP₂ molecules. The EL peak is exactly corresponding to the transition between the LUMO state of BePP₂ and HOMO state of TPDS. The electrons are injected into the LUMO state of BePP₂ from the metal electrode, and holes to HOMO of TPDS from the positively biased contact (ITO). Holes and electrons are transported through *p*-type TPD and *n*-type BePP₂, respectively, and confined at the TPDS/BePP₂ heterojunction. Part of holes tunneling across the barrier and transferring to the HOMO state of BePP₂ allow electron-hole capture and excitonic electroluminescence in the BePP₂ layer peaking at 460 nm.

Fluorescent properties of a metal-chelate complex are strongly dependent upon the ligand structure if there exists no intramolecular energy transfer to the coordinating ions. A careful selection of the ligand structure will increase the energy gap and therefore blue-shift the emitting color of the material. For example, as compared with bis(10-hydroxybenzoquinolinto) beryllium (BeBq_2) which is known as one of metal complexes superior than Alq_3 [31], the ligand of bis[2-(2-hydroxyphenyl)pyridinato] beryllium (BePP_2) has a reduced conjugation. As a result, BePP_2 shows a luminescent peak at 450 nm in comparison to that of BeBq_2 at 515 nm [29]. The ionization energy measured by cyclic voltammetry is 5.7 eV; the electron affinity energy was obtained to be 2.6 eV by subtracting the energy band gap (3.2 eV from absorption spectrum) from the ionization energy [29,30]. BePP_2 can form uniform thin film by vacuum evaporation. Under UV illumination this material does not show strong fluorescence, which suggest it does not have a high PL efficiency. The limited fluorescent efficiency of BePP_2 may result in a relative low EL brightness of the device in the study.

Compared with the device reported in the reference [26] using N,N,N',N' -tetra-tolyl-1,1'-diphenylsulfide-4,4'-diamine as HTM, the EL device duration in the study here was poor. Because that the difference in chemical structure between two HTMs (N,N,N',N' -tetra-tolyl-1,1'-diphenylsulfide-4,4'-diamine and N,N,N',N' -tetra-tolyl-1,1'-diphenyldisulfide-4,4'-diamine) is that between disulfide and sulfide, it seems probable that such dependencies of hole transport materials (HTMs) are closely related to the stability of HTM's excited states. It can be expected that when the radical species are stable in carrier transport process, both hole and electron transport, and it will contributes to the enhancement of the device stability. Work is in the progress to reveal the real reason of this complication.

4. Conclusions

Several “donor–bridge–acceptor” triad compounds were synthesized, in which aromatic disulfide components was used as a “bridge”. The

fluorescence emission spectra and the lifetimes of these compounds in various solvents have been measured by a fluorescence spectrometer and single-photon counting technique. 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. One of triad disulfide compound, N,N,N',N' -tetra-tolyl-1,1'-diphenyldisulfide-4,4'-diamine (TPDS) was used as the hole transport layer (HTL) of the OLED device. The possible mechanism to influence on the durability by HTM has been discussed.

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