# Properties of molecular switch triad compounds for photoinduced intramolecular energy transfer

He Tian *, Kongsheng Yang, Xuehong Luo

*Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, People's Republic of China*

Accepted 17 June 1997

## Abstract

This paper reports the synthesis and transient absorption decay kinetics of several triad compounds, in which a sulfur aryl section is used as the spacer for intramolecular energy transfer (IET). After flash photolysis the producing sulfur radicals will provide an 'energy trap' to stop the IET process, after stopping flash photolysis the sulfur radicals reversibly recombine and the IET process recovers, and then a rapid photoinduced IET switchable function is realized.   © 1997 Elsevier Science S.A.

*Keywords:* Energy transfer; Synthesis; Molecular switch; Triad compounds; Fluorescence properties

## 1. Introduction

Special functional supramolecular compounds that are constructed by different independent subunits with different bonding methods and their photophysical and photochemical properties have been actively studied in recent years [1]. The supramolecular compounds are used as molecular switches to realize the storage, data processing and transfer of information at the molecular level [2]. Photoinduced intramolecular energy transfer (IET) is a fast process, which can be measured by highly sensitive molecular fluorescence. The energy can be transferred by spacer from an energy donor to an energy acceptor. This process results in the quenching of the fluorescence of the donor. Recently, molecular switches based on the IET process have become an active study field [3]. But there are many challenging problems: for instance, how to improve the reversible response time of switch devices. In order to realize the molecular switchable function, Walz et al. [4] used photochromic fulgides as the spacer for intramolecular energy transfer in a 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 occurring 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 process based on photochromic fulgides mentioned above

cannot realize a rapid response, so it is necessary to find a novel rapid photoinduced switchable system.

Thyrion [5] has reported the transient absorption spectra of a series of aryl sulfur radical compounds after flash photolysis. After flash photolysis, the transient absorption spectra of many aryl sulfur compounds turned on an irregular redshift due to the produced sulfur radical. Based on these, we can design and synthesize the triad compounds, in which a sulfur aryl section is used as the spacer for intramolecular energy transfer. After flash photolysis, the produced sulfur radicals will provide an 'energy trap' to stop the IET process, after stopping flash photolysis, the sulfur radicals reversibly recombine and the IET process recovers, and then a rapid photoinduced IET switchable function is realized. This paper reports the synthesis and fluorescence properties as well as transient absorption decay kinetics of these triad compounds.

## 2. Experimental

IR spectra were recorded on a Nicolet 5SxC and ¹H NMR spectra were recorded on a Brucker AM300 spectrometer at 300 MHz, using TMS as the standard and deuteriodimethyl-sulfoxide (DMSO-$d_6$) as the solvent. Mass spectra (electron impact) were obtained at 70 eV on a VG 12-250 (VG Mass lab) spectrometer. Fluorescent spectra were recorded on a Hitachi 650 spectrometer. Bis(*p*-aminophenyl)sulfide was prepared according to the literature [6], m.p. 105~107°C (literature, 108°C); 9-carbazolylacetic acid was synthesized according to the literature [7], m.p. 192~194°C (literature,

* Corresponding author.

192 ~ 196°C); 4-nitro-1,8-naphthalic anhydride was obtained from Aldrich and used without purification. The time resolved absorption decay kinetics were measured by laser flash kinetic spectrophotometry. The solutions (in 2 cm × 2 cm quartz cells) were excited at 337 nm (nitrogen gas laser with a 6–7 ns pulse wide, Radiant Dyes Laser, Acce, GmbH), and transient optical density ($\Delta$OD) at 488 nm (Ar ion laser, 5500 AWC, Ion Laser Technology) can be detected by a fast response diode (DET2-Si, Thorlabs Inc.) and displayed on a digital storage oscilloscope (Tektronix TDS 420). In the measurements, 'O$_2$ aerated' means that the solutions were saturated by bubbling with oxygen gas for 20 min. All measurements were performed at room temperature. For structures of compounds see Fig. 1.

*Synthesis of compound S1* [8]. 1.08 g (5 mmol) bis-(p-aminobenzenyl) thionyl and 0.99 g (5 mmol) 1,8 naphthalic anhydride were added to 20 ml water under nitrogen. The reaction mixture was drastically stirred and slowly heated to reflux. When refluxing, the solid became red–brownish oil-like. After refluxing for 6 h, the orange solid came out, was cooled, the precipitate was filtrated and washed with acetone, and the filtrate was recrystallized in acetone to yield 1.54 g(78%) orange particle crystals, S1, m.p. 239–241°C. IR(KBr): NH$_2$ 3460 cm$^{-1}$, 3380 cm$^{-1}$; MS $m/z$: 396 (M$^+$, 100%); 180(53.44%); $^1$H NMR: 5.60 (s, 2H, –NH$_2$); 6.68 (m, 2H, $J$=8.4 Hz); 7.12 (m, 2H, $J$=8.4 Hz); 7.24–7.27 (m,4H); 7.85 (t,2H); 8.50 (m,4H).

*Synthesis of compound S2*. 0.26 g (1.16 mmol) 9-carbazolylacetic acid and 0.1 g sodium hydroxide were added to 20 ml nitrobenzene, stirring and heating to 120–130°C for 0.5 h, the reaction mixture was pale yellow–greenish, then cooled to 60–70°C, 0.46 g compound S1 was added, 0.5 ml PCl$_3$ (redistillation) was slowly dropped with stirring, then heated to 135°C for 2 h, filtrated while hot, the filtrate cooled, then ethyl ether was added and the solid was precipitated, the crude product was recrystallized in DMF, yield 0.2 g(29%), pale gray solid, S2, m.p.>300°C. IR(KBr): –CONH– 3300 cm$^{-1}$, 3200 cm$^{-1}$; MS $m/z$: 603 (M$^+$, 19.72%); 180 (100%); $^1$H NMR: 5.25(s, 2H, –CH$_2$CO–); 7.15–7.25 (m, 4H); 7.32 (m, 2H, $J$=8.47 Hz); 7.44 (t, 2H); 7.51 (d, 2H, $J$=8.44 Hz); 7.57 (d, 2H, $J$=8.21 Hz); 7.72 (d, 2H, $J$=8.53 Hz); 7.88 (m, 2H); 8.15 (d, 2H); 8.45 ~ 8.55 (m, 4H).

*Synthesis of compound S3*. 0.3 g (0.76 mmol) compound S1 and 0.18 g (0.76 mmol) 4-nitro-1,8-naphthalic anhydride were mixed. 10 ml anhydrous pyridine was added to the mixture, stirring, the mixture was slowly heated to reflux, the reaction mixture became a pale yellow–brownish solution, after refluxing for 5 h, and then cooled overnight. The resulting material was poured into a lot of water, filtrated, the resulting solid washed with acetone, the crude product recrystallized in DMF twice, yield 0.20 g(42%), red–brownish solid, S3, m.p.>300°C. IR(KBr): –NO$_2$ 1350 cm$^{-1}$(s), 1530 cm$^{-1}$(m); MS $m/z$: 621 (M$^+$, 16.66%); 591 (15.05%); 180 (57.94%); $^1$H NMR: 7.43(m, 4H); 7.77(m, 4H); 7.89 (m, 2H, $J$=7.7 Hz); 8.15 (t, 1H); 8.52 (m, 4H,

S1:    D = NH$_2$;    R = H
S2:    D = CZ;    R = H
S3:    D = NP;    R = NO$_2$
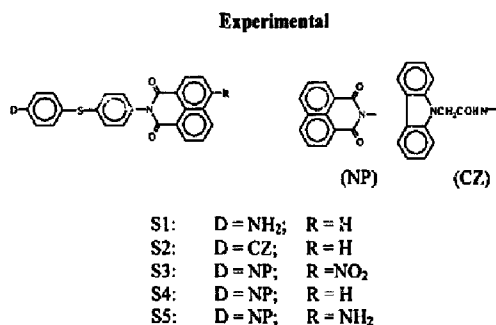S4:    D = NP;    R = H
S5:    D = NP;    R = NH$_2$

Fig. 1. Chemical structures of the compounds in the study.

$J$ = 7.8 Hz); 8.61 (m, 1H, $J$ = 8.0 Hz); 8.66(m, 1H, $J$ = 8.10 Hz); 8.68 (m, 1H); 8.79 (m, 1H).

*Synthesis of compound S4*. 0.99 g (5 mmol) 1,8-naphthalic anhydride and 0.58 g (2.7 mmol) bis-(p-aminobenzenyl) thionyl mixed with 15 ml DMF under nitrogen, the reaction mixture was stirred and heated slowly to reflux, when refluxing solvent was orange–yellow, refluxed for 24 h, cooled, then the resulting material was poured into a lot of water, filtrated, the solid was recrystallized in DMF twice, yield 0.78 g (54%), pale yellow crystals, S4, m.p. >300°C. IR(KBr): –CON– 3450 cm$^{-1}$(b), 1710 cm$^{-1}$(s); MS $m/z$: 576(M$^+$, 100%); 180 (94.78%); $^1$H NMR: 7.40(d, 4H, $J$= 8.3 Hz); 7.52 (d, 4H, $J$=8.5 Hz); 7.87–7.99(t, 4H); 8.48–8.62 (d, 8H).

*Compound S5*. $^1$H NMR: 6.85 (d, 1H, $J$=8.4 Hz); 7.43 ~ 7.63 (m, 8H); 7.84 ~ 7.96 (t, 3H); 8.20 (d, 1H); 8.50 ~ 8.70 (m, 6H). MS $m/z$: 591 (M$^+$, 98.48%).

The synthesis of compound S1 was involved in the reaction selectivity, because the two amino groups could react with 1,8-naphthalic anhydride. In order to synthesize the terminal product with one amino substituent, we should control the ratio of the reactants (1,8-naphthalic anhydride could not be in excess); on the other hand, suitable solvents should be selected. When using DMF as the solvent, although the amino compound was in excess, the byproduct (2:1, two substituents) would be produced; if we used water as the solvent, although the ratio of the reaction mixture was 1:1, we could also obtained the terminal product (1:1) with high yield. On the contrary, to obtain compound S4, we used water as the solvent, although 1,8-naphthalic anhydride was in excess, but we could not obtain the terminal product (2:1); we used DMF as the solvent, although the mixture reacted in the ratio of 2:1, so we could also obtain compound S4 with high yield.

## 3. Results and discussion

The absorption and fluorescence spectra data of these triad compounds are listed in Table 1. There exists the characteristic absorption of carbazole in the absorption of triad compound S1, as seen as in Table 1. The absorption of these new triad compounds was the exact sum of that of the constituent

Table 1
The absorption and fluorescence data of the compounds in dioxane

| Compounds | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|
| $\lambda_{max}^{ab}$ (nm) | 330 (1.84) | 292 (3.33) | 332 (2.67) | 331 (3.18) | 330 (2.07) |
| $\epsilon$ ($10^4$ l mol$^{-1}$cm$^{-1}$) | 345 (1.55) | 330 (2.05) | 346.4 (2.64) | 345.4 (2.74) | 345 (1.86) |
| | | 410 (0.39) | | | 406 (0.78) |
| $\lambda_{max}^{fl}$ (nm) [a] | 366.5 | 362; 510 | 485 | 370; 520 | 399; 412; 492 |

[a] The emission was measured by excitation at 330 nm for S1; 292 nm for S2; 332 nm for S3; 331 nm for S4; 329 nm for S5, respectively.

Table 2
The fluorescence intensity ratio between the triad compounds and the corresponding mixture at the same fluorescence wavelengths ($\lambda_{max}^{fl}$)

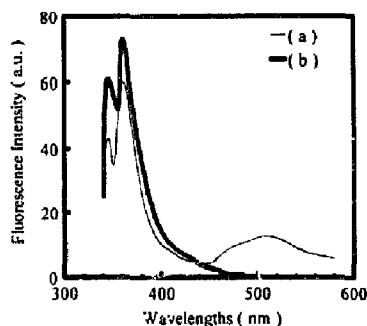| Systems | S2 | S4 |
|---|---|---|
| | S1 + 9-carbazolylacetic acid (1:1) | S1 + 1,8-naphthalic anhydride (1:1) |
| Ratio (%) ($\lambda_{max}^{fl}$) | 1.7 (362 nm, Ex: 292 nm) | 2.6 (370 nm, Ex: 331 nm) |



Fig. 2. Fluorescence spectra of S2 (curve a) and the mixture (curve b) of 9-carbazolylacetic acid and S1 (1:1) excited at 330 nm in dioxane.

chromophores. This indicates that there is little or no interaction between chromophores, so their individual characteristics should be maintained in the triad compounds. However, when excited at 292 nm, which is a maximum absorption of carbazole chromophore, the emission at 362 nm for triad compound S2 was quenched, as seen as in Table 2, which means there exists an intramolecular energy transfer from the carbazole moiety to naphthalimide in the triad compound [9]. Meanwhile, at longer wavelength regions, a new emission was observed compared with that of the corresponding mixture, as shown in Fig. 2. This new emission might result from the large conjugated system of phenyl sulfide and naphthalimide.

On comparing with the corresponding mixtures, as shown in Figs. 2 and 3, the new triad compounds synthesized in this paper have a new emission in a longer wavelength region. This new emission could be explained as a result of the large conjugated system of phenyl sulfide and naphthalimide. When these triad compounds were dissociated by photolysis

to form a thionyl-radical (cited the fact that aromatic disulfide was dissociated by a photon from a XeCl-excimer laser at 308 nm to form two thionyl-radicals [10]), the constituents of the split chromophores are similar to those of the corresponding mixture (9-carbazolylacetic acid and S1 for S2; 1,8-naphthalic anhydride and S1 for S4, respectively). At this time the longer wavelength emission would disappear, this means that the intramolecular energy transfer through the sulfide bridge between two chromophores will be inhibited due to the breaking of the sulfide bridge. At this longer wavelength, fluorescence emission disappears and the system then turns on an 'energy trap' that prevents the intramolecular energy transfer process from donor to acceptor (i.e. switch-off state). Since the formation and recombination of thionyl-radicals are fast processes, it is possible that the triad compounds synthesized in this paper may be used as novel rapid photoinduced switchable systems.

The transient absorption for these triad compounds at 488 nm are listed in Table 3. The aerated dioxane solutions of these compounds gave no transient absorption at 632.8 nm
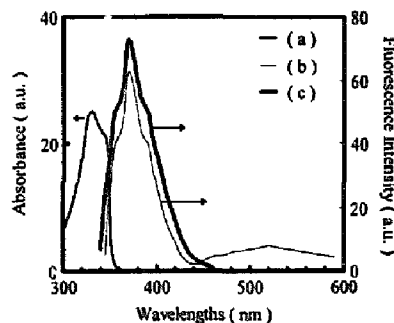


Fig. 3. The absorption (curve a) and fluorescence spectra (curve b, excited at 331 nm) of S4 and the fluorescence spectrum (curve c, excited at 328 nm) of the mixture of 1,8-naphthalic anhydride and S1 (1:1) in dioxane.

Table 3
The kinetic data of transient ΔOD at 488 nm for the triad compounds in dioxane

| Compounds | S1 | S2 | S3 | S4 |
|---|---|---|---|---|
| $\tau$ ($\pm 0.1$ μs) aerated | No signal | 5.0 | 2.5 | 3.0 |
| $\tau$ ($\pm 0.1$ μs) O$_2$-saturated | | 2.0 | 1.2 | 1.7 |

(He–Ne laser as monitoring light, at least within the sensitivity of our measurement system). However, for aerated dioxane solutions of the triad compounds, the transient absorptions at 488 nm are observed. The transient absorption at 488 nm with oxygen-saturated conditions are also observed for some compounds (Table 3). This means that the transient absorption at 488 nm results from the triplet absorption or charge transfer state absorption of these compounds, since oxygen is a particularly effective quencher of triplet states and charge transfer (CT) states. Based on the view of the CT processes, the transient absorption decay lifetimes of these triad compounds should vary and have some correlation with the CT ability of them. However, the results shown in Table 3 indicate that there is no relationship between the lifetimes and the CT ability of the compounds. This implies that the transient absorption at 488 nm results from the triplet state.

## Acknowledgements

## References

[1] H.J. Schneider, H. Durr (Eds.), Fronties in Supermolecular Organic Chemistry and Photochemistry, VCH, New York, 1991.

[2] J.M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.

[3] G. Blessing, N. Holl, H. Port, H.C. Wolf, F. Effenberger, T. Kesmarszky, Mol. Cryst. Liquid Cryst. 183 (1990) 21.

[4] J. Walz, K. Ulrich, H.C. Wolf, J. Wonner, F. Effenberger, Chem. Phys. Lett. 213 (1993) 321.

[5] F.C. Thyrion, J. Phys. Chem. 77 (1973) 1478.

[6] R.C. Fuson, S. Melamed, J. Org. Chem. (1948) 692.

[7] M.H. Litt, J. Kim, J. Polym. Sci. Polym. Chem. Ed. 23 (1985) 1307.

[8] S. Kumar, M. Seth, A.P. Bhaduri, J. Med. Chem. 27 (1984) 1083.

[9] H. Tian, J. Photochem. Photobio. A: Chem. 91 (1995) 125.

[10] N.P. Ernsting, Chem. Phys. Lett. 166 (1990) 221.