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Synthesis of "donor–bridge–acceptor" triad compounds containing the aromatic sulfur bridges

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Abstract

Novel donor–bridge–acceptor triad compounds, in which diphenyl disulfide, thioxanthone and thianthrene are used as a bridge, have been synthesized. With the introduction of amino groups in aromatic sulfur compounds, triads containing 1,8-naphthalic anhydride were synthesized via the condensation of the amino groups with the anhydride. A carbazole moiety was introduced by a solid-phase Ullmann reaction, using copper powder as the catalyst. Spectroscopic properties of the synthesized compounds are reported. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Triad compounds; Synthesis; Molecular switch

1. Introduction

There are numerous studies involving aryl sulfides and heterocyclic sulfur compounds. For instance, antitubercular activity has been reported for compounds containing thioxanthone and diphenylsulphide groups [1]. Aromatic sulfur molecules have been reported to produce sulfur radicals upon flash photolysis [2,3], and the chemical and physical properties of these radicals have been investigated [4,5]. Polyimides that contain thianthrene and 4,4′-diaminodiphenyl sulfide were investigated for their thermal stability [6]. Transient absorption bands were observed in the long wavelength region for aryl sulfides, diphenyl disulfides, and sulfur-containing polycyclic molecules (such as thionaphthene, dibenzothiophene, thioxanthene, and thianthrene). Since these absorptions correspond to the triplet state, triad molecules containing aromatic sulfur components are potential substrates for the development of optical molecular switches.

Photoinduced intramolecular energy transfer (IET) is a fast process that can be measured by highly sensitive molecular fluorescence. Walz et al. [7] used photochromic fulgides as spacers for intramolecular energy transfer in a molecular fluorescent system, but the IET process based on such molecules does not provide a rapid response. Thyrion [8] reported the photolysis of aromatic sulfur molecules. After flash photolysis, the sulfur radicals obtained served as an "energy trap", preventing the IET process. After ending flash photolysis, the sulfur radicals recombined and the IET process recovered to give rapid photoinduced IET switching behavior. Based on this observation we developed some triad compounds containing a sulfur aryl bridge (Fig. 1). Specifically, a series of

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donor–bridge–acceptor (D–B–A) triads have been synthesized, in which aromatic sulfur components such as disulfide, 9H-thioxanthen-9-one and thianthrene are used as the "bridge". As a result, molecular fluorescence and intramolecular charge transfer (ICT) properties are built into the same molecule.

2. Result and discussion

2.1. Synthesis

Triad I was made by in the route shown in Scheme 1. The key intermediate bis-(4-aminophenyl) disulfide (**2**) was synthesized by the reaction of 4-chloronitrobenzene (**1**) and sodium sulfide.

The initial step in this sequence was influenced significantly by temperature. Below 50°C, the reaction between **1** and Na_2S tended to form the sodium salt of 4-nitrothiophenol (**3**). By increasing the reaction temperature, the nitro group was easily reduced to amino group (cf.**6**). When Na_2S was added below 50°C, if the mol proportion of 4-chloronitrobenzene (**1**) to Na_2S was 2:1, a high yield of pure bis(4-nitrophenyl) sulfide (**4**) was obtained. If the quantity of Na_2S employed was three times that of 4-chloronitrobenzene, compound **5** was obtained, making the formation of bis(p-aminophenyl) disulfide (**2**) possible. This chemistry is outlined in Scheme 2.

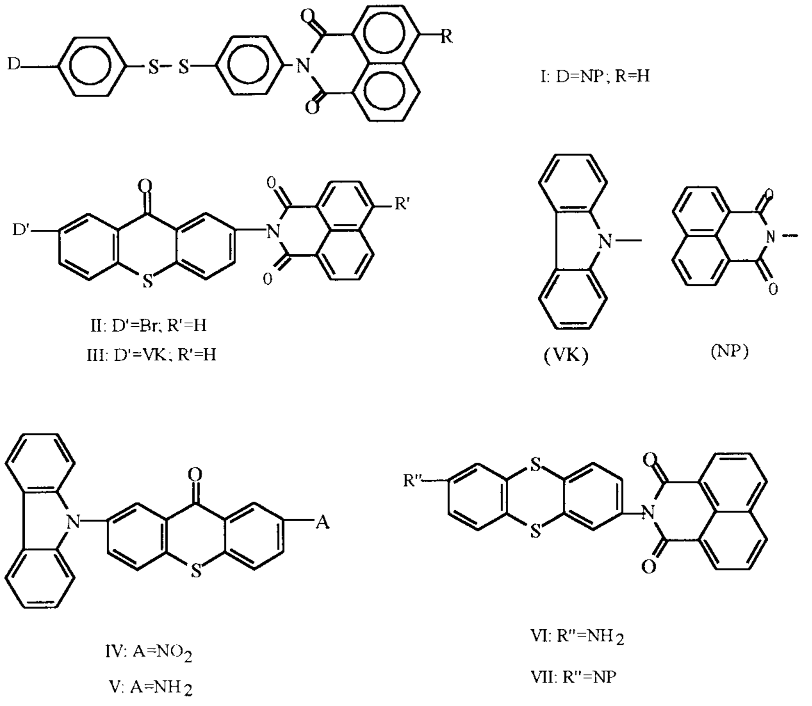
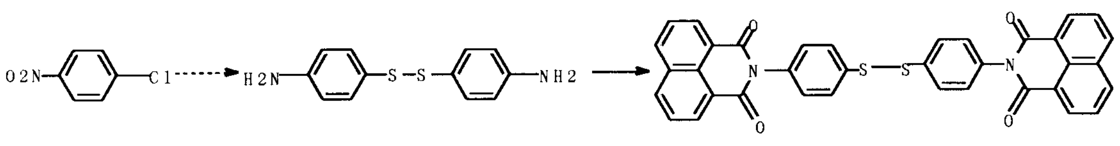


Fig. 1. Chemical structures of triad compounds synthesized in this investigation.

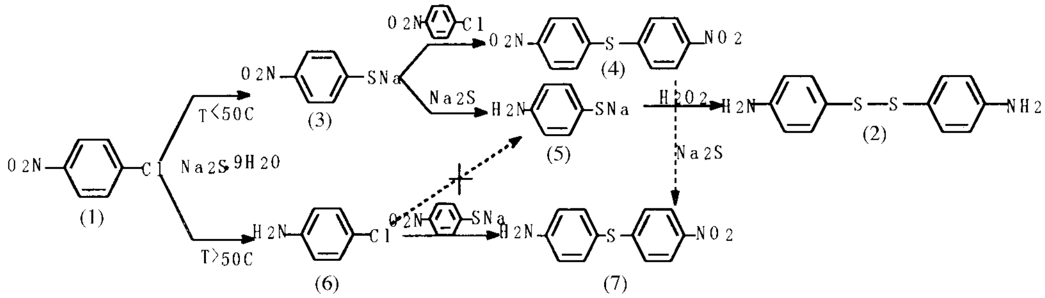


(1) (2) (I)

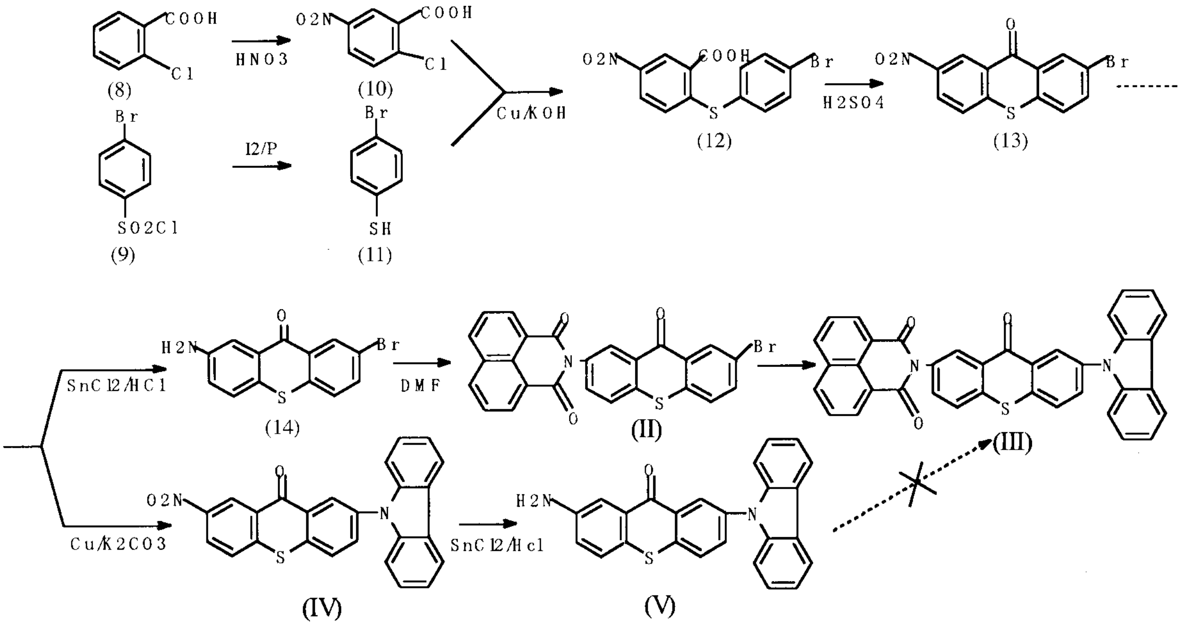
Scheme 1. Synthesis of Triad **I**.

As is shown in Scheme 3, 2-nitro-7-bromothioxanthen-9-one (**13**) was prepared by cyclodehydration of 5-nitro-2-(4-bromothiophenoxy)-benzoic acid (**12**) in concentrated sulfuric acid [10]. The starting thioether was made from 2-chloro-5-nitrobenzoic acid (**10**) and 4-bromothiophenol (**11**). Formation of **13** was followed by reduction of the nitro group, condensation with 1,8-naphthalic anhydride, to give compound **II**, and Ullmann reaction with carbazole [10] to give compound **III**. Purification by column chromatography afforded pure triad **III**. Another approach to synthesizing compound **III** involved a solid phase Ullmann reaction between **13** and carbazole to give **IV**, followed by reduction and reaction of **V** with 1,8-naphthalic anhydride. The last step failed, although several solvents were used, including DMF, pyridine and dioxane.

In order to produce target compound **VII**, one strategy employed a thianthrene heterocycle. The thianthrene was acetylated by a Friedel–Crafts reaction [3] and a Gutterman reaction on 2,7-diacetylthianthrene produced the corresponding ketoxime. A Beckman rearrangement of the ketoxime was carried in PPA, and hydrolysis of the 2,7-diacetamidothianthrene gave diaminothianthrene. In this paper, we adopted an improved method involving



Scheme 2. The influence of temperature on the formation of compound **2**.



Scheme 3. Synthesis of compound **III**.

base-catalyzed cyclodehydrochlorination [12] of 2-chloro-5-nitrobenzenethiol (**17**), as shown in Scheme 4. The conditions used in the subsequent step had a great influence on the reduction of 2,7-dinitrothianthrene (**18**). While iron was an effective reagent for the reduction of the nitro group, the product could not be purified completely. When stannous chloride was employed, the diamine could be used in the condensation without further purification. In this case, excess sodium hydroxide was used to release the amino groups from the metal complex.

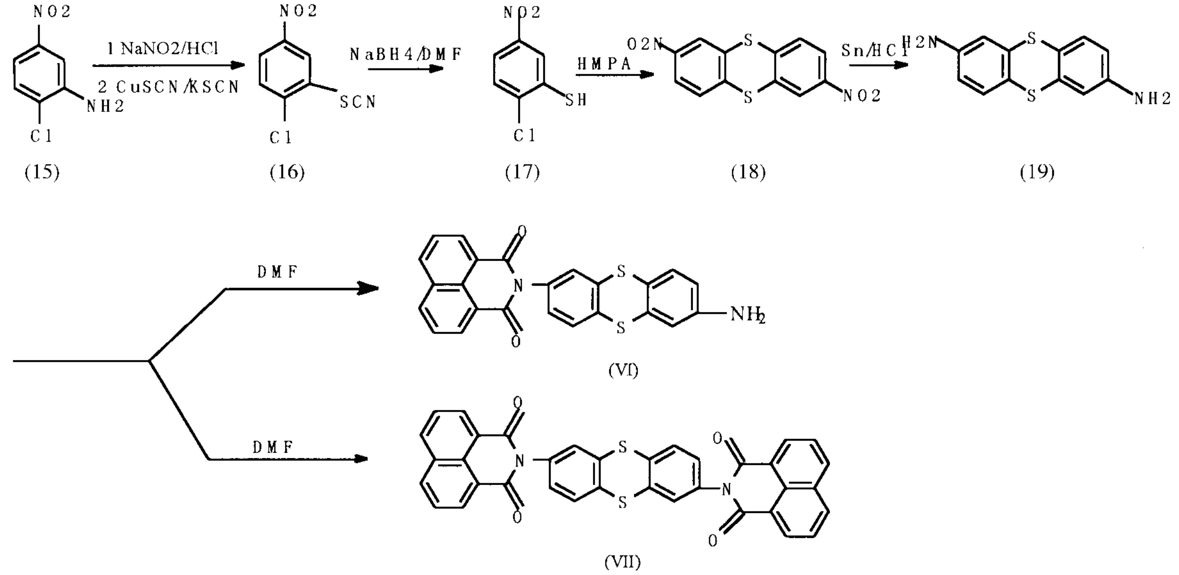
3. Properties

With the introduction of amino groups in aromatic sulfur-containing compounds, triads based on 1,8-naphalic anhydride were synthesized. For the compounds with disulfide bridges, a through space interaction between the end groups would obviously exist due to the flexible bridge. On the other hand, two end components connected with 9H-thioxanthen-9-one and thianthrene would form definite configurations according to stertic conformation of the bridges. For instance, in compound **VII** the two side benzo groups of the thianthrene are not in the same plane. They form a dihedral angle of 131° with the two sulfurs as the axis. Consequently, the two ends (naphthalimides) of compound **VII** have through space interactions with each other. When such molecules are excited, an intramolecular exciplex is produced [9]. The formation of this species leads to a characteristic longer wavelength emission at 598nm.

From Table 1, it is clear that the absorption maximum of compound **III** produces a peak fluorescence maximum of 495 nm and still has fluorescence emission at a shorter wavelength. We belive this makes **III** an ideal D–B–A compound. Although the donor and the acceptor in compound VII are the same, this compound provides a useful basis for compoaring other D–B–A combinations. Studies involving fluorescence lifetime, and flash photolysis of triads containing a thioxanthone or thianthrene bridge are underway, the results of which will be reported in due course.

4. Experimental

IR spectra (KBr) were recorded on a Nicolet Magna-IR 550 spectrometer and ^{1}H NMR were



Scheme 4. Synthesis of compounds **VI** and **VII**.

Table 1
The absorption and fluorescence spectral data for **II–VII** in THF

Compound	**II**	**III**	**IV**	**V**	**VI**	**VII**
$\lambda_{\max}^{ab}$ (nm)	269, 311, 334	237, 292, 322	236, 291, 322	291, 325, 362	250, 268, 321	240, 291, 333
$\lambda_{\max}^{fl}$ (nm)[a]	370	370, 495	362	363	374	598

[a] Excited at 321 nm.

recorded on a Brucker AM 300 spectrometer, and mass spectra (EI, 70 V) was obtained on a VG 12-250 spectrometer. 1,8-Naphthalic anhydride and 4-nitro-1,8-naphthalic anhydride were obtained from Aldrich Chemical Co., 2-chlorbenzoic acid was purchased from Fluka, and 4-bromobenzenesulfonyl chloride, carbazole and 2-chloro-5-nitroaniline were obtained from Acros. All of the compounds mentioned above were used without purification.

4.1. *Bis(4-aminophenyl) disulfide*(**2**)

4-Chloronitrobenzene (23.6 g, 0.15 mol) and $Na_2S{\cdot}9H_2O$ (96 g, 0.40 mol) were stirred vigorously in water (250 ml) at room temperature. When the solution was heated slowly to reflux, the color of the solution became reddish-brown. The solution was stirred under reflux for 20 h, then cooled and filtered. The filtrate was concentrated to 150 ml and H_2O_2 (30%, 23 ml) was added dropwise over 1.5 h, at 65–70°C. The reaction mixture was cooled and filtered. The solid was dissolved in anhydrous alcohol (100 ml), filtered hot, then diluted with water (80 ml). The precipitate was recrystallized from alcohol:water (1:1) to give colorless needles (8.2 g, yield 44%), m.p. 74–76°C (literature [11]: 75–76°C).

4.2. *Bis[4-(1,8-naphthalimido)phenyl] disulfide* (**I**)

Bis(*p*-aminophenyl) disulfide (0.62 g, 2.5 mmol) and 1,8-naphthalic anhydride (0.99 g, 5 mmol) were added to DMF (15 ml) under nitrogen. The reaction mixture was stirred vigorously and slowly heated to reflux. After refluxing for 20 h, the mixture was cooled and the yellow solid was recrystallized from DMF, yielding light orange needles **I** (0.8 g, 53%), m.p. 307–309°C. EIMS (*m*/*z*): 608 (M^+, 1.0%); 576 (1.39%); 305 (91.92%); 272 (14.57%); 180 (100%); ^{1}H NMR (d_6-DMSO): δ 7.47–7.49 (m, 4H); δ 7.74 (d, 4H); δ 7.91 (t, 4H); δ 8.51 (m, 8H).

4.3. *2-Chloro-5-nitrobenzoic acid* (**10**)

Nitric acid (65–68%, 14 ml, 0.313 mol) and conc. H_2SO_4 (22 ml) were added dropwise a mixture of 2-chlorobenzoic acid (32 g, 0.204 mol) and conc. H_2SO_4 (87 ml) below 0°C, over 1 h. The reaction mixture was continued to stirred for 16 h at room temperature, then at 60°C for 10 min. After cooling, the mixture was poured to 600 g ice with stirring. The precipitate was filtered and washed with 20% NaOH, to give 30 g (72.8%) **10**, white crystals, m.p. 166–168°C.

4.4. *4-bromothiophenol* (**11**)

A solution of 4-bromobenzenesulfonyl chloride (25 g, 0.098 mol) in glacial HOAc (40 ml) was added dropwise to a stirring and refluxing mixture of glacial HOAc (50 ml), red phosphorus (11 g) and iodine (0.6 g). The mixture was refluxed for 3 h. After standing overnight, water (12 ml) was slowly added, followed by refluxing for 1 h and steam distillation. After cooling the distillate, the precipitated product was filtered and dried in vacuum over $CaCl_2$, yielding 15.4 g, (86.5%) **11**, m.p. 68–70°C. EIMS (*m*/*z*): 190 (14.35%); 189 (M^+, 52.92%); 188 (15.46%); 187 (51.39%); 110 (31.02%); 109 (100%).

4.5. *5-Nitro-2-(p-bromothiophenoxy)benzoic acid* (**12**)

A mixture of 4-bromothiophenol (5.1 g, 0.027 mol), 2-chloro-5-nitrobenzoic acid (4.8 g, 0.024 mol), KOH (3.6 g, 0.063 mol) and a trace of copper powder in 95% alcohol (250 ml) was refluxed for

22 h under Argon gas. After about two-thirds of the solvent had been removed by distillation, water (250 ml) was added to the residue, and the resultant mixture was acidified to congo red (pH3) using HCl. The yellow precipitate was recrystallized from alcohol to give a yellow crystalline powder (6.0 g, 81.2%), m.p. 226–228°C (literature [10], 224–226°C).

4.6. 2-Nitro-7-bromothioxanthen-9-one (**13**)

5-Nitro-2-(4-bromothiophenoxy)benzoic acid (6.0 g, 0.0194 mol) was dissolved in concentrated H_2SO_4 (90 ml) at 100°C. The solution was maintained at this temperature for 2 h. After cooling to room temperature, the solution was poured onto crushed ice (800 g). The resultant precipitate was washed, dried, and recrystallized in acetic anhydride to give yellow-greenish microcrystalline powder (3.0 g, 50%), m.p. 285–288°C (literature [10], 282–285°C). EIMS (*m*/*z*): 335 (M^+, 85.13%); 291 (30.33%); 182 (100%).

4.7. 2-Amino-7-bromothioxanthen-9-one (**14**)

2-Nitro-7-bromothioxanthen-9-one (1.0 g, 3 mmol) was added to glacial HOAc (6 ml), a suspension of $SnCl_2{\cdot}2H_2O$ (2.54 g) and conc. HCl (2.54 ml) was added. The mixture was refluxed at 80–85°C for 5 h. After cooling, the precipitate was filtered and treated with cold 20% NaOH, washed thoroughly with water, and dried at 100°C. The crude product was reduced again to give a slightly yellow powder (0.8 g, yield 87.8%), m.p. 208–210°C. IR (KBr): $-NH_2$ 3430 cm^{-1}, 3350 cm^{-1}; EIMS *m*/*z*: 308 (15.68%); 307 (99.32%); 306 (15.01%); 305 (M^+, 100%); 273 (14.38%); 199 (19.67%).

4.8. 2-(1,8-Naphthalimido)-7-bromothioxanthen-9-one (**II**)

Anhydrous DMF (50 ml) was added to a mixture of 2-amino-7-bromothioxanthen-9-one (0.5 g, 1.634 mmol) and 1,8-naphthalic anhydride (0.4 g, 2.02 mmol) with stirring. Upon refluxing, a yellow-brownish solution formed. After 6 h, the mixture was cooled overnight, and poured into water (200 ml). The solid was collected, washed with dichloromethane, 20% aqueous sodium hydroxide, and water, and dried at 100°C to yield **II** (0.2 g, 25.1%), yellow powder, m.p. > 260°C. IR (KBr): -CON- 3350 cm^{-1}, 1700 cm^{-1}; -CO- 1670 cm^{-1}, 1630 cm^{-1}. EIMS *m*/*z*: 487 (97.75%); 486 (42.28%); 485 (M^+, 92.13%); 180 (100%). ^1H NMR (d_6-DMSO): δ 7.36 (m, 2H); δ 7.78 (t, 1H); δ 7.88–7.96 (m, 3H); δ 8.56–8.92 (d, 6H).

4.9. 2-(1,8-Naphthalimido)-7-(9-carbazole)-thioxanthen-9-one (**III**)

To a mixture of **II** (0.23 g, 0.472 mmol), carbazole (0.1g,0.599 mmol) and K_2CO_3 (0.1 g, 1.01 mmol) catalyst grade copper was added. The mixture was slowly heated to 250°C during which the sublimate (carbazole) was readded to the reaction mixture. The reaction was maintained at 250°C for 11 h and cooled overnight. Dichloromethane (100 ml) was added and the brown mixture was filtered. The solvent was removed under reduced pressure. Flash chromatography of the crude product using dichloromethane as eluent gave **III** (0.05 g, 18.5%), as a yellowish-brown solid, m.p. > 300°C. EIMS *m*/*z*: 572 (M^+, 5.23%); 498 (23.55%); 485 (10.95%); 333 (100%); 180 (28.83%); 167 (50.38%). ^1H NMR ($CDCl_3$): δ 7.25–7.48 (d, 10H); δ 7.76–7.94 (m, 3H); δ 8.20–8.30 (m, 3H); δ 8.68 (m, 1H); δ 8.84 (t, 1H).

4.10. 2-Nitro-7-(9-carbazole)-thioxanthen-9-one (**IV**)

To a mixture of 2-nitro-7-bromo-thioxanthen-9-one (0.4 g, 1.19 mmol), carbazole (0.25 g, 1.50 mmol) and potassium carbonate (0.2 g, 2.02 mmol), catalyst grade copper powder was added. The mixture was slowly heated to 230°C, during which the sublimed carbazole was readded to the reaction mixture. Dichloromethane (200 ml) was added and the greenish-brown solution was filtered. The solvent was then removed under reduced pressure, and the crude product was purified by using dichloromethane as eluent. This gave **IV** (0.2 g, 39.8%), yellowish-green solid, m.p. 256–258°C. IR (KBr): -CON- 3410 cm^{-1}; $-NO_2$ 1340 cm^{-1}, 1520 cm^{-1}.. EIMS *m*/*z*: 422 (M^+, 100%); 423 (31.28%); 377 (19.10%); 347 (24.32%); 332 (11.85%); 166 (12.28%). ^1H NMR ($CDCl_3$): δ 7.36 (m, 3H); δ

7.75–7.80 (m, 2H); δ 7.86–7.92 (m, 2H); δ 8.18–8.22 (m, 2H); yield 8.26–8.31 (m, 2H); δ 8.48 (t, 1H); δ 8.86 (t, 1H); δ 9.48 (m, 1H).

4.11. 2-Amino-7-(9-carbazole)-thioxanthen-9-one (V)

IV (0.2 g, 0.474 mmol) was added to HOAc (15 ml), then a suspension of $SnCl_2{\cdot}2H_2O$ (0.5 g) and conc. HCl (3 ml) was added. The mixture refluxed at 80–85°C for 6 h, then filtered immediately. The precipitate was treated with cold 20% NaOH, thoroughly washed with water and dichloromethane, dried to give green powder (0.1 g, 53.8%), m.p. 240–244°C. IR (KBr): $-NH_2$ 3410 cm^{-1}, 3380 cm^{-1}. EIMS *m/z*: 392 (29.66%); 391(M^+ δ, 100%); 360 (8.44%); 196 (9.64%).

4.12. 2-Chloro-5-nitrophenyl thiocyanate (16)

To a mixture of stirred 2-chloro-5-nitroaniline (20 g, 116 mmol), conc. HCl (60 ml) and water (140 ml) at 0°C, $NaNO_2$ (9.0 g, 130 mmol) in water (20 ml) was added, over a period of 2 h under Argon gas, keeping the temperature at 0–3°C. The resultant mixture was added dropwise to a solution of KSCN (16 g, 164 mmol) and CuSCN (14 g, 116 mmol) in water (40 ml) at room temperature over 2 h. The black foamy mixture was stirred overnight at room temperature, filtered and the precipitate was washed with water until neutral. The solid was extracted with dichloromethane (3×100 ml), an the orange solution and washed with water, and dried with anhydrous $MgSO_4$. The solvent was removed under vacuum, and the obtain crude product was recrystallized from alcohol to give light yellow crystals of 2-chloro-5-nitrophenyl thiocyanate (10.4 g, 54%), m.p. 96–98°C (literature [10], 102°C). IR: 2190 cm^{-1} (-CN); 1535 cm^{-1}, 1350 cm^{-1} ($-NO_2$).

4.13. 2-Chloro-5-nitrobenzenethiol (17)

To a stirred solution of 2-chloro-5-nitrophenyl thiocyanate (2 g, 9.5 mmol) in DMF (30 ml) at 20°C, $NaBH_4$ (0.5 g, 13.5 mmol) was added in one portion under Argon gas. The mixture was stirred for 10 min and poured over crushed ice (100 g). The mixture was acidified with conc. HCl (37%, 5 ml), and the yellow precipitate was filtered, washed until neutral and extracted with dichloromethane (100 ml). The organic layer was further washed with water, dried over $MgSO_4$, and evaporated to give light brown crystals of 2-chloro-5-nitrobenzenethiol (1.2 g, 69%), m.p. 58–61°C. EIMS (*m/z*): 192 (38%); 191 (16%); 190 (M^+ δ, 100%); 143 (18%); 131 (32%).

4.14. 2,7-Dinitrothianthrene (18)

To a solution of 2-chloro-5-nitrobenzenethiol (1.4 g, 7.5 mmol) in dry acetone (250 ml), hexamethylphosphoramide (1 ml) and triethylamine (1.3 ml) were added. The mixture was stirred under Argon gas for 24 h, during which time a color change from dark red–brown to light yellow occurred and a solid formed. The mixture was evaporated to 50 ml, and conc. HCl was added. The yellow precipitate obtained which was washed with water and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and evaporated to give yellow crystals of 2,7-dinitrothianthrene (0.7 g, 58%). The solid was recrystallysed from HOAc to give, m.p. 264–266°C (literature [11], 263–264°C). IR: 1520, 1340 cm^{-1} (NO_2); EIMS (*m/z*): 305 (M^+) (100%); 306 (18%); 260 (40%); 214 (63%); 170 (37%).

4.15. 2,7-Diaminothianthrene (19)

To 2,7-dinitrothianthrene (0.4 g, 1.307 mmol) in HOAc (10 ml), a suspension of $SnCl_2{\cdot}2H_2O$ (1.2 g) and conc. HCl (8 ml) was added. The mixture was stirred under reflux for 12 h, then cooled and filtered. The precipitate was treated with cold 20% NaOH, thoroughly washed with water and dried at 110°C. The crude product was reduced again to give dark brown solid (0.1 g, 31.1%), m.p. 221–224°C. IR (KBr): $-NH_2$ 3480 cm^{-1}. EIMS *m/z*: 246 (M^+, 100%); 247 (19.37%); 214 (21.21%); 186 (13.29%). ^1H NMR (d_6-DMSO): δ 3.46 (s, 4H); δ 6.93 (m, 2H); δ 7.15 (m, 2H); δ 7.42 (m, 2H).

4.16. 2-Amino-7-(1,8-naphthalimido) thianthrene (VI)

Pyridine (10 ml) was added to the mixture of 2,7-diaminothianthrene (0.2 g, 0.813 mmol) and 1,8-

naphthalic anhydride (0.2 g, 1.01 mmol) with stirring, and when heated to reflux. The redish-brown solution was stirred under reflux for 8 h, and the precipitate was filtered, washed with 20% NaOH, washed with water, and dried at 100°C, giving **VI** (0.05 g, 14.4%), gray solid, m.p. >260°C. IR (KBr): -NH_2 3470 cm^{-1}; EIMS *m/z*: 426 (M^+, 13.452%); 412 (6.658%); 393 (7.026%); 378 (15.925%); 276 (70.709%). ^1H NMR (d_6-DMSO): δ 5.5 (s, 2H); δ 6.58 (m, 2H); δ 6.76 (m, 2H); δ 7.45 (m, 2H); δ 7.78 (m, 1H); δ 7.86 (m, 1H); δ 8.20 (m, 1H); δ 8.27 (m, 1H); δ 8.60 (m, 2H).

4.17. 2,7-Di(1,8-naphthalimido)thianthrene (**VII**)

A stirred mixture of anhydrous pyridine (20 ml), 2,7-diaminothianthrene (0.2 g, 0.813 mmol) and 1,8-naphthalic anhydride (0.35 g, 1.768 mmol) was heated to reflux. The reddish-brown solution was stirred under reflux for 12 h, and cooled overnight. The solution was poured into water (250 ml) with stirring and the mixture was filtered. The collected solid was treated with 20% NaOH, washed well with water, and dried at 100°C. The crude product was purified by column chromatography (CH_2Cl_2, silica gel), to give **VII** (0.05 g, 12.5%), reddish-brown solid, m.p. >260°C. IR (KBr): -CON- 3350 cm^{-1}, 1720 cm^{-1}. EIMS *m/z*: 605 (M^+, 12.09%); 475 (25.53%); 426 (20.98%); 186 (12.73%); 126 (100%). ^1H NMR ($CDCl_3$): δ 7.62–7.68 (m, 6H); δ 8.18–8.24 (m, 6H); δ 8.30–8.33 (m, 6H).

Acknowledgements

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