

# Synthesis, Characterization and Photophysical Properties of Novel Azole Derivatives

Muhammad Saleem · Ki Hwan Lee

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**Abstract** This paper concerns the design, synthesis, structural characterization, thermal stability evaluation and fluorescence properties of novel triazolothiadiazole derivatives. The target compounds 6a–e were synthesized by condensing 4-amino-3-(4-methoxybenzyl)-1*H*-1,2,4-triazole-5 (4*H*)-thione (5) with biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl carboxylic acid in the presence of phosphorous oxychloride. The structures of newly synthesized compounds were characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis. The photophysical properties of synthesized compounds were measured in a variety of organic solvents of variable polarities. Spectral properties of the compounds were highly dependent on the nature of the substituent and coupling components attached to the triazolothiadiazole skeleton as well as slightly affected by the solvent polarities. Correlation of the absorption spectra and fluorescence emission response of 6a–e with the substituent revealed that the fluorescent properties can easily be tuned by varying conjugation length of side coupled groups. The newly synthesized derivatives represent a new type of fluorescent materials with efficient visible absorption and surpassing brightness which could be a promising candidate for bioimaging, photonic applications, organic light emitting diodes and dye sensitized solar cells.

**Keywords** Fused heterocycle · Triazolothiadiazole · Photophysical properties · Solvatochromism · Thermal analysis

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M. Saleem · K. H. Lee (✉)  
Department of Chemistry, Kongju National University,  
Gongju, Chungnam 314-701, Republic of Korea  
e-mail: khlee@kongju.ac.kr

## Introduction

There is a growing interest for the design and development of efficient fluorescent heterocyclic compounds with high fluorescent quantum yield, larger Stokes shift, relatively high molar absorption coefficient and facile synthetic strategy due to their potential applications in biotechnology, textile and polymer field, dye and plastic industry, liquid crystal technology, fluorescent whitening agent, photoconducting materials, bioimaging and biosensing [1, 2]. The application of fluorescent dyes in textiles is becoming more fashionable due to their low cost and color durability [3]. Organic compounds with extended conjugation have received prodigious interest in electronic devices such as organic light emitting diodes, organic photovoltaics, organic thin film transistors, flat-panel displays, photoelectric cells, and solar batteries [4–7]. The slightly basic fluorescent dyes used as selective *in vivo* staining and visualization of acidic subcellular vesicles such as lysosomes, endosomes, and Golgi vesicles for biomolecule characterization employing various labelling techniques. [8, 9] Fluorescent dyes found applications as fluorescent probes and marker in varieties of electrophoresis techniques [10]. Fluorescent organic dyes fabricated in photoelectrochemical cells proved to be a cheaper alternative to the commercialized silicon-based solar cells in power generation attracting significant academic and commercial interest as viable energy source [11–17].

Fluorescent imaging by using fluorescent organic dyes is emerging as a very promising technique for drug discovery and development. Organic dyes have been extensively used for fluorescent labelling of biomolecules and cells in order to investigate the *in vivo* or *in vitro* mechanism in living cells and tissues due to their commercial availability and ease of use by incorporating optical properties [18, 19]. The prerequisite criteria in the selection of organic dyes include the best fluorescence response on irradiation in the visible range and less

toxicity toward the living cells and tissues. Among several heterocyclic compounds, the fused heterocyclic derivatives including triazolothiadiazole have received considerable attentions owing to their synthetic and potent pharmacological applications. Due to friendly nature toward biomolecules, the triazolothiadiazole derivatives might be frontier candidates for fluorescent imaging, fluorescent labelling of biomolecules and bioimaging assay.

The present study was aimed to design and synthesize a series of biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl bearing 3,6-disubstituted 1,2,4-triazolo [3,4-*b*] 1,3,4-thiadiazole derivatives and evaluated their photophysical properties, solvatochromism behavior and thermal stability. All the synthesized derivatives exhibited interesting photophysical properties with improved molar absorption coefficient, Stokes shift and considerable fluorescent quantum yield. The optical behavior of triazolothiadiazole derivatives can easily be tuned toward longer wavelength by incorporating extended conjugation on substituting fluorophore at position 3 and 6 of the fused triazolothiadiazole core skeleton. The target molecules showed commodious bathochromic shift by substituting the *p*-terphenyl, pyrenyl and ferrocenyl group which indicate that emission color of triazolothiadiazole can easily be tuned from blue to red by increasing conjugation length. The considerable high thermal stability of synthesized fused triazolothiadiazole molecules fulfils the thermal stability requirement for energy storage devices and these kind of materials might be used in organic light emitting diodes (OLED) and dye sensitized solar cells (DSSC). The synthesized triazolothiadiazole derivatives represent a new type of fluorescent materials which could be a promising candidate for photonic applications possessing efficient visible absorption, larger quantum yields and higher brightness. The synthetic protocol for the synthesis of target compounds was quite simple which give high product yield without involvement of complex chromatographic techniques for purification of compounds.

## Experimental

### Substrate and Reagents

The biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl carboxylic acids and phosphorous oxychloride were purchased from Aldrich. Hydrazine hydrate (80 %), TEA, CS<sub>2</sub>, KOH, sodium hydrogen carbonate were obtained from Sigma-Aldrich. Ethanol, methanol, chloroform, water, acetonitrile, dimethyl sulfoxide, petroleum ether, ethyl acetate, *n*-hexane (Samchun Chemicals, Korea), H<sub>2</sub>SO<sub>4</sub>, HCl (Jin Chemical & Pharmaceutical Co. Ltd., Korea) were used in these experiments.

### Instrumentations

The reaction progress was monitored by thin layer chromatographic (TLC) analysis and the *R<sub>f</sub>* values were determined by employing pre-coated silica gel aluminum plates, Kieselgel 60 F<sub>254</sub> from Merck (Germany). TLC was visualized under a UV lamp (VL-4 LC, France). The melting points were determined on a Fisher Scientific (USA) melting point apparatus and are uncorrected. The IR spectra were recorded in KBr pellets on a SHIMADZU FTIR-8400S spectrometer (Kyoto, Japan). Proton and carbon nuclear magnetic resonance (<sup>1</sup>H NMR & <sup>13</sup>C NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard. The chemical shifts are reported as  $\delta$  values (ppm) downfield from the internal tetramethylsilane of the indicated organic solution. Peak multiplicities are expressed as follows: s, singlet; d, doublet and m, multiplet. Abbreviations are used as follows: DMSO-*d*<sub>6</sub>, Dimethyl sulfoxide-*d*<sub>6</sub>; FT-IR spectroscopy, Fourier transform infrared spectroscopy. The schematic representation of synthetic route adopted to obtain 3,6-disubstituted-[1,2,4] triazolo [3,4-*b*] [1,3,4] thiadiazoles (6a–e) are shown in Scheme 1.

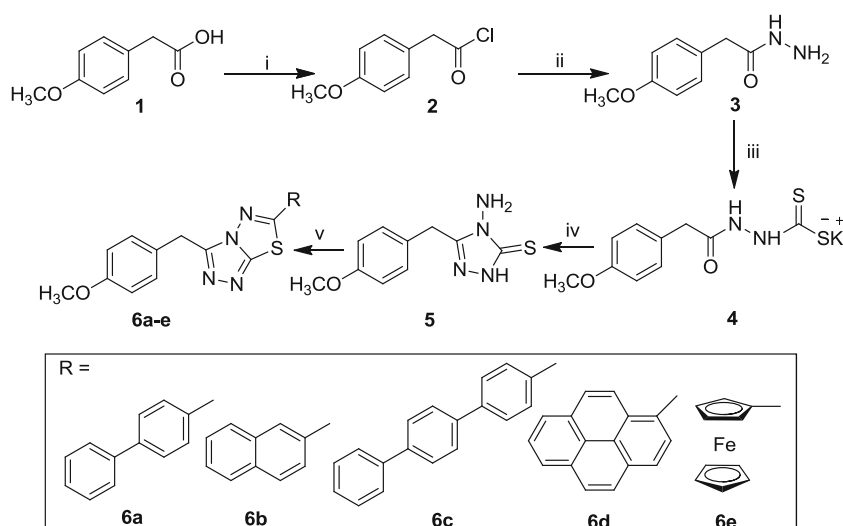
### Synthesis of 2-(4-Methoxyphenyl) Acetohydrazide (3)

2-(4-Methoxyphenyl) acetyl chloride (2) were synthesized by the reaction of 2-(4-methoxyphenyl) acetic acid 1 (1 mmol) in the presence of 1,2-dichloroethane (12 mL) solvent and phosphorous oxychloride (0.4 mL) chlorinating agent under reflux for 3 h. Then, the resulting solution was cooled to room temperature, and the solvent was removed under reduced pressure to afford 2-(4-methoxyphenyl) acetyl chloride (2), which was directly used in the next step without further purification. 2-(4-Methoxyphenyl) acetyl chloride (2) was dissolved in acetonitrile (80 mL), added drop wise to a solution containing hydrazine hydrate (1 mmol), TEA (0.5 mL), acetonitrile (20 mL) are allowed to reflux for 3 h with monitoring by TLC. After consumption of the starting material, the reaction mixture was cooled to room temperature. Evaporation of the solvent under reduced pressure yielded crude 2-(4-methoxyphenyl) acetohydrazide (3) as a white solid on cooling, which was purified by column chromatography if needed and crystallized in methanol [20].

### 2-(4-Methoxyphenyl) Acetohydrazide (3)

White solid; yield: 86 %; mp 134–136 °C; *R<sub>f</sub>*: 0.54 (*n*-hexane : ethyl acetate, 1:1); FT-IR ( $\nu$  /cm<sup>-1</sup>): 3334, 3302 (NH<sub>2</sub>), 3205 (NH) 3037 (sp<sup>2</sup> CH), 2958, 2837 (sp<sup>3</sup> CH), 1610 (C=O), 1541, 1511, 1497 (C=C of phenyl ring); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.21 (s, 1H, NH), 7.19 (aromatic, d, 2H, *J*=8.4 Hz), 6.86 (aromatic, d, 2H, *J*=8.4 Hz), 4.23 (s, 2H, broad, NH<sub>2</sub>), 3.71 (s, 3H, OCH<sub>3</sub>), 3.28 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C

**Scheme 1** Synthesis of 3,6-disubstituted-[1,2,4] triazolo [3,4-*b*] [1,3,4] thiadiazoles (6a–e): Reagents and conditions: (i)  $\text{POCl}_3$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , reflux 3 h; (ii) Hydrazine hydrate, TEA, MeCN, reflux 3 h; (iii)  $\text{CS}_2$ , KOH, methanol, stirring, 0 °C, 1 h; (iv) Hydrazine hydrate (80 %), water, reflux, 10–12 h; (v)  $\text{POCl}_3$ , carboxylic acids (biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl carboxylic acids), reflux, 4–6 h



NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  170.7, 159.6, 143.2, 129.7, 120.8, 114.6, 111.7, 55.3, 35.4.

#### Synthesis of 4-Amino-3-(4-Methoxybenzyl)-1*H*-1,2,4-Triazole-5 (4*H*)-Thione (5)

Potassium hydroxide (0.125 mol) was dissolved in dry methanol (50 mL). To the solution, 2-(4-methoxyphenyl) acetylhydrazide (3) (0.125 mol) was added and cooled the solution in ice. To this, carbon disulfide (0.125 mol) was added in small portions with constant stirring for 2–3 h. The solid product of potassium 2-[2-(4-methoxyphenyl) acetyl] hydrazinecarbodithioate (4) formed, was filtered, washed with chilled diethyl ether and dried. It was directly used for next step without purification. The potassium 2-[2-(4-methoxyphenyl) acetyl] hydrazine carbodithioate (4) was taken in deionized water (20 mL) and hydrazine hydrate (0.250 mol) was added, and followed by refluxed for 8–10 h. The reaction mixture turned to yellow green with evolution of hydrogen sulfide and finally it became homogeneous. It was then poured in crushed ice and acidified with hydrochloric acid. The white precipitates of 4-amino-3-(4-methoxybenzyl)-1*H*-1,2,4-triazole-5 (4*H*)-thione (5) was filtered, washed with cold water and crystallized from aqueous methanol [21, 22].

#### 4-Amino-3-(4-Methoxyphenyl)-1*H*-1,2,4-Triazole-5 (4*H*)-Thione (5)

White solid; yield: 75 %; mp 215–217 °C;  $R_f$ : 0.71 (pet ether : ethyl acetate, 7:3); IR ( $\nu/\text{cm}^{-1}$ ) 3294, 3130 (NH), 3350–3273 (NH<sub>2</sub>), 2937 ( $\text{sp}^2\text{CH}$ ), 1585 (C=N), 1561–1506 (C=C), 1335 (C=S); <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.81 (s, 1H, NH), 7.98–7.95 (m, 2H, Ar-H), 7.07–6.97 (m, 2H, Ar-H), 5.76 (s, 2H, NH<sub>2</sub>), 3.72 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.12, 161.31, 158.22, 132.57, 130.11, 118.61, 56.32.

#### Synthesis of 3,6-Disubstituted-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazoles (6a–e)

A mixture of 4-amino-3-(4-methoxybenzyl)-1*H*-1,2,4-triazole-5 (4*H*)-thione (5) (1 mM) and biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl carboxylic acids (1 mM) in phosphorous oxychloride (8–10 mL) were refluxed for 5–6 h. The reaction mixture was slowly poured in crushed ice with stirring and neutralizes it with sodium hydrogen carbonate. Solid material was filtered, washed with cold water and dried to furnish 3,6-disubstituted-[1,2,4] triazolo [3,4-*b*] [1,3,4] thiadiazoles (6a–e) as different color solid [23].

#### 6-[(1,1'-Biphenyl)-4-yl]-3-(4-Methoxybenzyl)-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazole (6a)

Yellow solid; yield: 77 %;  $R_f$ : 0.43 (chloroform : methanol, 9:1); IR ( $\nu/\text{cm}^{-1}$ ): 3018 ( $\text{sp}^2\text{CH}$ ), 2930, 2854 ( $\text{sp}^3\text{CH}$ ), 1577 (C=N), 1544, 1521, 1496 (C=C), 1021 (C–S); <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01–7.95 (m, 2H, Ar-H), 7.75–7.45 (m, 2H, Ar-H), 7.31–7.27 (m, 2H, Ar-H), 7.75–7.67 (m, 2H, Ar-H), 7.59–7.51 (m, 2H, Ar-H), 7.50–7.39 (m, 3H, Ar-H), 7.25–7.15 (m, 2H, Ar-H), 6.97–6.92 (m, 2H, Ar-H), 4.51 (s, 2H, CH<sub>2</sub>), 3.89 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 160.2, 159.4, 149.1, 133.4, 131.0, 128.5, 128.4, 126.4, 125.3, 122.4, 122.1, 122.0, 119.7, 118.7, 115.6, 114.5, 55.7, 28.9.

#### 3-(4-Methoxybenzyl)-6-(Naphthalen-2-yl)-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazole (6b)

Off white solid; yield: 81 %;  $R_f$ : 0.47 (chloroform : methanol, 9:1); IR ( $\nu/\text{cm}^{-1}$ ): 3021 ( $\text{sp}^2\text{CH}$ ), 2935, 2894 ( $\text{sp}^3\text{CH}$ ), 1588 (C=N), 1540, 1507, 1478 (C=C), 1017 (C–S); <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00–7.91 (m, 1H, Ar-H), 7.86–7.81 (m, 2H, Ar-H), 7.76–7.74 (m, 1H, Ar-H), 7.67–7.64 (m, 1H,

Ar-H), 7.50–7.47 (m, 2H, Ar-H), 7.27–7.18 (m, 2H, Ar-H), 6.96–6.91 (m, 2H, Ar-H), 4.49 (s, 2H, CH<sub>2</sub>), 3.87 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.7, 161.0, 158.9, 149.7, 134.2, 134.0, 130.1, 128.7, 127.1, 126.4, 123.8, 119.4, 118.9, 118.4, 115.7, 114.8, 114.5, 55.6, 28.1.

6-[(1,1':4',1''-Terphenyl)-4-yl]-3-(4-Methoxybenzyl)-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazole (6c)

Sea green solid; yield: 75 %; R<sub>f</sub>: 0.48 (chloroform : methanol, 9:1); IR (ν /cm<sup>-1</sup>): 3037 (sp<sup>2</sup> CH), 2936, 2874 (sp<sup>3</sup> CH), 1578 (C=N), 1534, 1517, 1487 (C=C), 1024 (C–S); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81–7.79 (m, 2H, Ar-H), 7.67–7.61 (m, 2H, Ar-H), 7.24–7.14 (m, 2H, Ar-H), 7.05–6.64 (m, 11H, Ar-H), 4.51 (s, 2H, CH<sub>2</sub>), 3.87 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.5, 161.1, 160.0, 149.4, 135.6, 134.1, 133.1, 130.4, 127.4, 127.3, 127.0, 125.6, 122.3, 121.8, 120.7, 118.7, 118.2, 115.6, 114.3, 55.6, 28.7.

3-(4-Methoxybenzyl)-6-(Pyren-4-yl)-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazole (6d)

Antique white solid; 77 %; R<sub>f</sub>: 0.40 (chloroform : methanol, 9:1); IR (ν /cm<sup>-1</sup>): 3022 (sp<sup>2</sup> CH), 2933, 2861 (sp<sup>3</sup> CH), 1578 (C=N), 1540, 1521, 1500 (C=C), 1023 (C–S); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90–7.56 (m, 9H, Ar-H), 7.18–7.11 (m, 2H, Ar-H), 6.96–6.87 (m, 2H, Ar-H), 4.52 (s, 2H, CH<sub>2</sub>), 3.88 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 164.0, 159.8, 149.4, 134.6, 133.2, 132.4, 130.4, 132.4, 130.2, 129.5, 127.3, 127.6, 126.3, 125.5, 124.1, 122.0, 119.5, 118.3, 114.1.

6-(4-Ferrocenyl)-3-(4-Methoxybenzyl)-[1,2,4] Triazolo [3,4-*b*] [1,3,4] Thiadiazole (6e)

Dark pink solid; yield: 86 %; R<sub>f</sub>: 0.53 (chloroform : methanol, 9:1); IR (ν /cm<sup>-1</sup>): 3018 (sp<sup>2</sup> CH), 2941, 2850 (sp<sup>3</sup> CH), 1578 (C=N), 1540, 1496 (C=C), 1024 (C–S); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18–7.14 (m, 2H, Ar-H), 6.96–6.93 (m, 2H, Ar-H), 4.51 (s, 2H, CH<sub>2</sub>), 4.08–4.12 (m, 9H, Ferrocene), 3.84 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 161.0, 160.1, 149.5, 131.2, 129.5, 117.4, 90.1, 88.2, 68.6, 68.1, 67.9, 55.9.

## Results and Discussions

### Synthesis

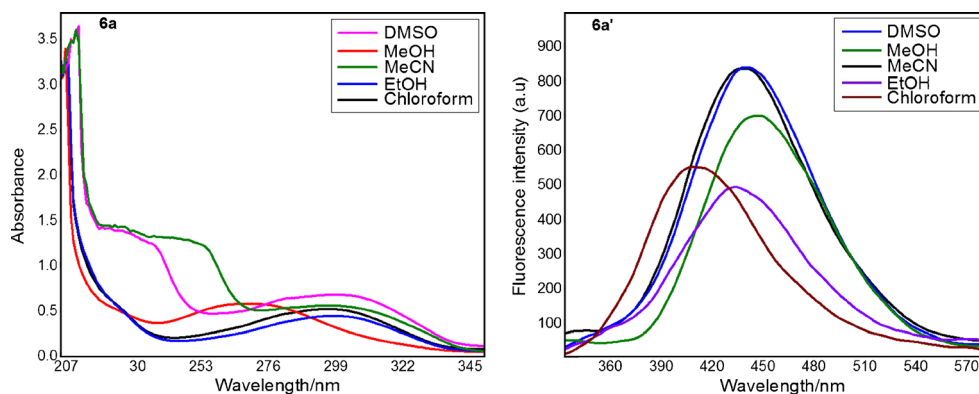
The conversion of 2-(4-methoxyphenyl) acetic acid (1) to 2-(4-methoxyphenyl) acetyl chloride (2) was indicated in the IR spectral data by the disappearance of broad signal in the range of 3400–2500 cm<sup>-1</sup> due to acid hydroxy group

stretching vibrations. The formation of 2-(4-methoxyphenyl) acetohydrazide (3) was indicated in the IR spectral data due to appearance of new signal at 3334, 3302 and 3205 due to primary and secondary amino group of acid hydrazide. Meanwhile there was slight shift in the carbonyl stretching vibration from 1733 to 1620 cm<sup>-1</sup> indicate the successful conversion of 2-(4-methoxyphenyl) acetyl chloride (2) into 2-(4-methoxyphenyl) acetohydrazide (3). The appearance of broad singlet at 9.21 as well as 4.23 ppm further confirms the 2-(4-methoxyphenyl) acetohydrazide (3) formation. The structures of 4-amino-3-(4-methoxybenzyl)-1*H*-1,2,4-triazole-5 (4*H*)-thione (5) was characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral analysis. In IR spectrum, a peak in the range of 3294, 3130 cm<sup>-1</sup> for NH stretching and a relatively strong peak with shoulder in the range of 3350–3273 cm<sup>-1</sup> for NH<sub>2</sub> stretching were observed. In the <sup>1</sup>H NMR, NH proton appear at 13.81 ppm and this proton exists as thione-thiol tautomeric form and the dominant form is thione indicated in the IR spectral data as there was no peak for SH group in IR spectrum in the range of 2500–2400 cm<sup>-1</sup>. Synthesis of 3,6-disubstituted-[1,2,4] triazolo [3,4-*b*] [1,3,4] thiadiazoles (6a–e) were confirmed by IR as well as NMR spectra by the disappearance of signals for NH and NH<sub>2</sub> group while appearance of new signal in both <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra confirm the formation of fused heterocyclic compounds 3,6-disubstituted-[1,2,4] triazolo [3,4-*b*] [1,3,4] thiadiazoles (6a–e).

### Photophysical Properties and Solvatochromism Study

The UV-visible properties, fluorescence emission characteristics and photophysical parameters of the target compounds 6a–e (1 × 10<sup>-5</sup> molL<sup>-1</sup>) are summarized in Figs. 1, 2, S1–3 (Supporting information) and Table 1. To evaluate the effect of solvent polarities on the absorption and emission characteristics of the synthesized triazolothiadiazole derivatives, all the synthesized compounds 6a–e were tested in the different solvents of variable polarities including chloroform, ethanol, acetonitrile, methanol and dimethyl sulfoxide. The solvatochromism study of the compound 6a shows that there was single absorption peak ranging from 389 to 399 nm in relatively less polar solvent including chloroform, ethanol and acetonitrile with least molar absorptivity of 19.3 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, 17.6 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> and 15 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively while there was two distinct absorption signal, one in the range of 237–253 nm and the other in the range of 301–303 nm with higher molar absorptivity values of 41.6 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, 40.6 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> for shorter wavelength signal and 23 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, 19 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> for longer wavelength range signal. The highest absorption signal was observed in methanol with molar absorptivity's of 41.6 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> and 23 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> in case of compound 6a. The compound 6a exhibit emission spectra in the range of 389–415 nm in varieties of solvent with Stokes shift of

**Fig. 1** UV-visible absorption spectra (6a) and fluorescence emission spectra (6a') of 6a ( $1 \times 10^{-5}$  molL $^{-1}$ ) in varieties of solvents



8240–11467  $\text{cm}^{-1}$  for longer wavelength signal while 15429–17803  $\text{cm}^{-1}$  for shorter wavelength signal. The compound 6a shows largest Stokes shift of 11467  $\text{cm}^{-1}$  in chloroform with hypsochromic shift of 34 nm and fluorescence quantum yield of 0.006. The relative fluorescence quantum yield of 6a varies from 0.0051 to 0.0071 in various solvents of different polarities (Fig. 1 and Table 1).

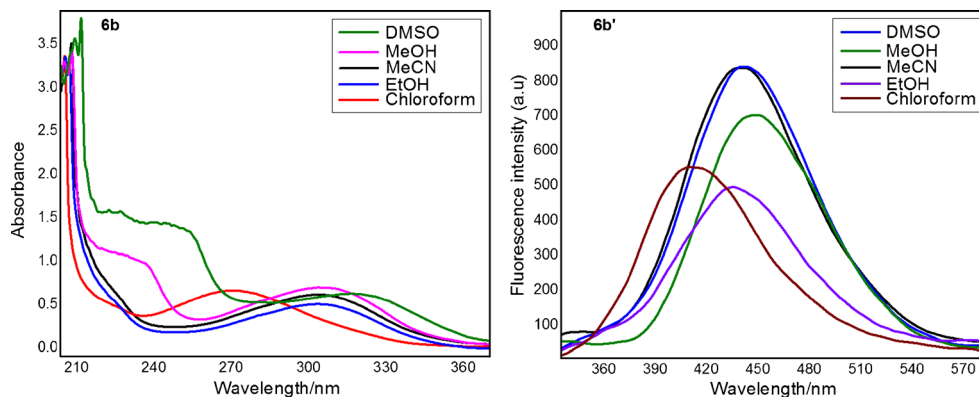
The compound 6b exhibited single absorption signal in the range of 271–306 nm in chloroform, ethanol and acetonitrile with molar absorptivity's of  $22 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $17 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $20.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. The two absorption signal was observed in methanol and DMSO at 236, 253 and 306 nm, 319 nm with molar absorptivity's of  $32.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $45.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for shorter wavelength signal and  $23.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $20.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for longer wavelength signal, respectively. The compound 6b emits in the range of 410–449 nm with Stokes shift of 9848 to 12510  $\text{cm}^{-1}$  for longer wavelength signal and 17253  $\text{cm}^{-1}$ , 19697  $\text{cm}^{-1}$  for shorter wavelength absorption signal. The largest hypsochromic shift of 48 nm was observed in chloroform with least quantum yield of 0.0032 while maximum quantum yield of 0.016 was harvested by 6b in DMSO (Fig. 2 and Table 1).

The compound 6c shows one absorption signal at 265 nm with shoulder at 252 nm, 253 nm in chloroform and acetonitrile except in DMSO where no prominent shoulder signal was

observed while 6c exhibited additional prominent isolated signal in shorter wavelength region at 236 nm, 237 nm in ethanol and methanol (Fig. S1). The maximum molar absorptivity of  $17 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was exhibited by 6c in acetonitrile at longer wavelength while at shorter wavelength the maximum molar absorptivity of  $40.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was found in methanol. The compound 6c emits in the range of 438–448 nm with Stokes shift of 16851–20001  $\text{cm}^{-1}$  for shorter wavelength signal and 14904–15701  $\text{cm}^{-1}$  for longer wavelength signal, respectively. There was shoulder peak for 6c in all solvents except DMSO in between 330 and 340 nm. The compound 6c exhibited relative fluorescence quantum yield ranging from 0.011 to 0.014. The maximum quantum yield of 0.014 was harvested in methanol and DMSO while minimum quantum yield of 0.011 was harvested in ethanol (Fig. S1 and Table 1).

The compound 6d exhibited three distinct absorption maxima at 226–239, 276–280 and 352–374 nm in all tested solvents of different polarities with the molar absorptivity's at  $37.3\text{--}44.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $25.6\text{--}36.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $21.6\text{--}25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. The maximum absorption coefficient of  $44.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $36.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was observed by 6d in acetonitrile while minimum molar absorptivity of  $37.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $25.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $21.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was exhibited by 6d in chloroform. The compound 6d emits in the range of 393–456 nm with Stokes shift of 14432–19911, 10786–13784

**Fig. 2** UV-visible absorption spectra (6b) and fluorescence emission spectra (6b') of 6b ( $1 \times 10^{-5}$  molL $^{-1}$ ) in varieties of solvents



**Table 1** Observed UV-visible absorption maxima, fluorescence emission maxima, molar absorptivity, Stokes shift and relative fluorescence quantum yield of substituted fused triazolothiadiazole derivatives 6a–e in different solvents

Comp.	Solvents	<sup>a</sup> $\lambda_{\text{abs}}$ (nm)	<sup>b</sup> $\lambda_{\text{em}}$ (nm)	<sup>c</sup> $\epsilon \times 10^4$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	<sup>d</sup> S. shift ( $\text{cm}^{-1}$ )	<sup>e</sup> $\Phi_{\text{FL}}$
6a	Chloroform	269	389	19.3	11467	0.006
	Ethanol	298	395	17.6	8240	0.0051
	Acetonitrile	300	399	15	8270	0.0067
	Methanol	237, 301	410	41.6, 23	17803, 8832	0.0071
	DMSO	253, 303	415	40.6, 19	15429, 8906	0.0067
6b	Chloroform	271	410	22	12510	0.0032
	Ethanol	304	435	17	9906	0.0053
	Acetonitrile	306	438	20.6	9848	0.0061
	Methanol	236, 306	441	32.6, 23.3	19697, 10004	0.0084
	DMSO	253, 319	449	45.3, 20.6	17253, 9076	0.016
6c	Chloroform	252, 265	438	13.6, 13.6	16851, 14904	0.0120
	Ethanol	237, 265	440	26.6, 5.3	19466, 15008	0.011
	Acetonitrile	253, 262	446	17.6, 17	17104, 15746	0.0121
	Methanol	236, 265	447	40.6, 14.3	20001, 15364	0.014
	DMSO	263	448	31.3	15701	0.014
6d	Chloroform	226, 276, 352	393	37.3, 25.6, 21.6	18802, 10786, 2963	0.0130
	Ethanol	228, 277, 363	399	39, 25.6, 22	18796, 11038, 2485	0.0129
	Acetonitrile	227, 278, 366	400	44.3, 36.3, 25	19052, 10971, 2322	0.0133
	Methanol	254, 277, 367	401	44.3, 32.6, 23	14432, 11163, 2310	0.0130
	DMSO	239, 280, 374	456	43.3, 27.3, 20	19911, 13784, 4808	0.0131
6e	Chloroform	275, 318, 431	453	48.3, 18.6, 15.6	14288, 9371, 1126	0.010
	Ethanol	275, 320, 435	438	48.3, 18.3, 16.3	13532, 8418, 157	0.009
	Acetonitrile	276, 320, 437	459	48.4, 18.3, 16.6	14445, 9463, 1096	0.011
	Methanol	278, 326, 437	464	48.4, 19.0, 17.0	14419, 9123, 1331	0.0140
	DMSO	284, 333, 471	494	48.6, 19.3, 18.3	14968, 9787, 988	0.0193

<sup>a</sup>UV-visible absorption maxima<sup>b</sup>Fluorescence emission maxima<sup>c</sup>Molar absorption coefficient<sup>d</sup>Stokes shift<sup>e</sup>Relative fluorescence quantum yield

and 2310–4808  $\text{cm}^{-1}$ , respectively. The compound 6d shows hyperchromic shift of 12, 14, 15 and 24 nm in ethanol, acetonitrile, methanol and DMSO as compare to chloroform. The highest fluorescence quantum yield of 0.0133 and 0.0131 was observed in MeCN and DMSO, respectively while minimum quantum yield of 0.0129 was observed in ethanol (Fig. S2 and Table 1).

The compound 6e exhibited three distinct absorption signals with the absorption maxima at 275–284, 318–333, 431–471 nm with molar absorptivity in the range of  $48.3\text{--}48.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $18.6\text{--}19.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $15.6\text{--}18.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. The maximum absorption coefficient was observed for DMSO while minimum molar absorptivity was shown by 6e in ethanol. The emission maxima for compound 6e were recorded in the range of 453–494 nm in variety of solvents (Fig. S3). The compound 6e exhibited hyperchromic shift of 41 nm in DMSO as compare to

chloroform with maximum quantum yield of 0.0193 while the quantum yield of 6e in various solvent are in the range of 0.009–0.0193 and quantum yield was found to reduce by decreasing solvent polarity as shown in Table 1.

The Stokes shift of triazolothiadiazole derivatives 6a–e was calculated by using Eq. 1 and molar absorption coefficient was calculated by using Beer Lambert law [24, 25].

$$(\nu_A - \nu_F) = \left( \frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (1)$$

The fluorescent quantum yield was calculated by using Eq. 2 [26]. All the compounds exhibited moderate to low fluorescent quantum yield and the experimental values are tabulated in Table 1. Quinine sulfate (0.5 M stock solution in 0.1 N sulfuric acid) was used as reference standard for

relative fluorescence quantum yield determination of triazolothiadiazole derivatives [27–29].

$$\Phi_{\text{unk}} = \Phi_{\text{std}}(I_{\text{unk}}/A_{\text{unk}})(A_{\text{std}}/I_{\text{std}})(n_{\text{unk}}/n_{\text{std}})^2 \quad (2)$$

Where  $\Phi_{\text{unk}}$  is the fluorescence quantum yield of the sample,  $\Phi_{\text{std}}$  is the quantum yield of the standard,  $I_{\text{unk}}$  and  $I_{\text{std}}$  are the integrated fluorescence intensities of the sample and the standard, respectively,  $A_{\text{unk}}$  and  $A_{\text{std}}$  are the absorbance's of sample and the standard at the absorption wavelength, respectively,  $n_{\text{unk}}$  and  $n_{\text{std}}$  are the refractive indices of corresponding solvents.

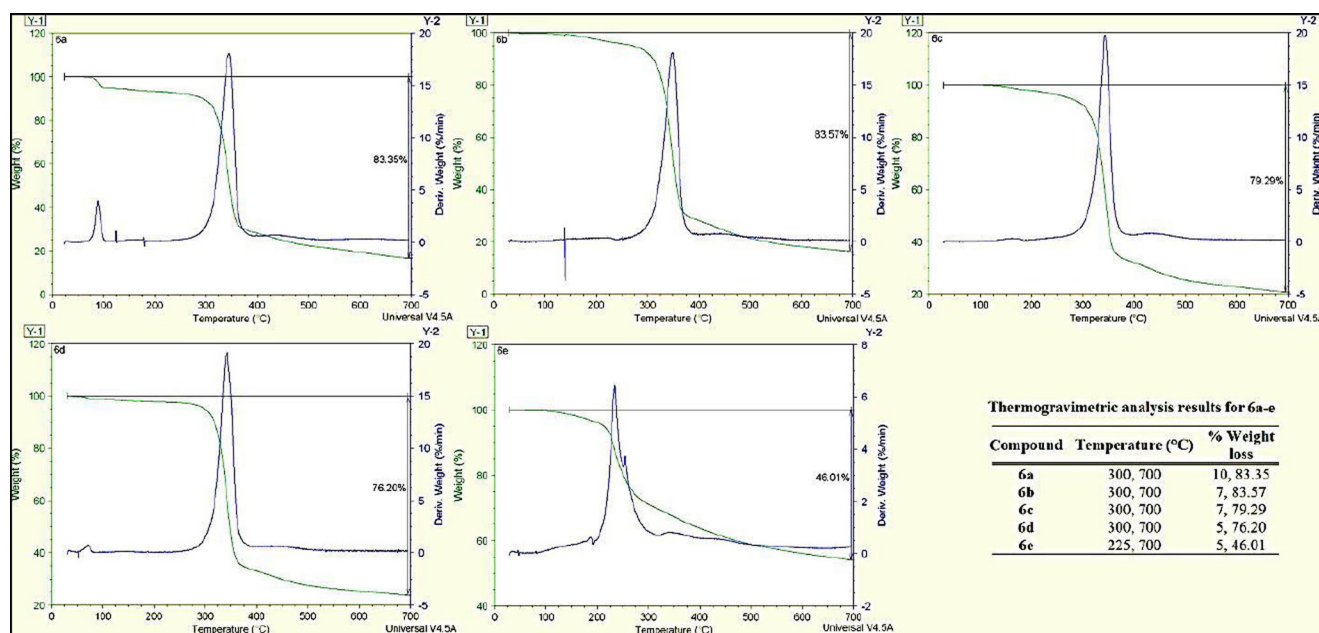
From the fluorescent quantum yield data (Table 1), the result indicates that the quantum yield of the triazolothiadiazole derivatives 6a–e were directly dependent on the substituent attached to the triazolothiadiazole skeleton. The relative fluorescence quantum yield of pyrenyl and ferrocenyl substituted triazolothiadiazole derivatives 6d and 6e were higher as compare to other derivatives 6a–c. The *p*-terphenyl substituted triazolothiadiazole derivative 6c exhibit moderate fluorescence quantum yield among the series while least fluorescence quantum yield were harvested for biphenyl and naphthyl substituted triazolothiadiazole derivatives 6a and 6b. The structure activity relationship of the synthesized compounds 6a–e revealed that on substituting more conjugated side coupled R group, there was momentous increment in the fluorescent quantum yield and the derivatives with less conjugated side coupled group displayed decline in the relative fluorescent quantum yield.

## Thermogravimetric Analysis

The thermal stability of organic materials is prerequisite for the durability, lifetime and efficiency of OLED devices. Degradation of amorphous organic layer due to high temperature may reduce the efficiency of OLED. To assess the thermal stability of newly synthesized derivatives 6a–e, thermogravimetric analysis (TGA) was performed by flowing drying nitrogen atmosphere at the heating rate of 10 °C/min using approximately 7.85 mg sample in the temperature range of 25–700 °C. All the compounds 6a–e shows very good thermal stability above 300 °C with approximately 20 % weight loss except 6e which showed 20 % weight loss at 225 °C but it exhibit very interesting thermal stability profile with only 46 % weight loss up to 700 °C. There was a sharp weight loss below 100 °C in the TGA curve of compound 6a and 6d which was probably due to loss of moisture from the compounds. None of the compounds 6a–e completely decomposed up to 700 °C (Fig. 3). This considerable high thermal stability of synthesized fused triazolothiadiazole molecules 6a–e fulfils the thermal stability requirement for energy storage devices and these kind of materials might be used in organic light emitting diodes (OLED) and dye sensitized solar cells (DSSC).

## Computational Study

In order to better understand the electronic transition occurring in the synthesized organic dyes during fluorescent emission and UV-visible spectral recording, the frontier molecular

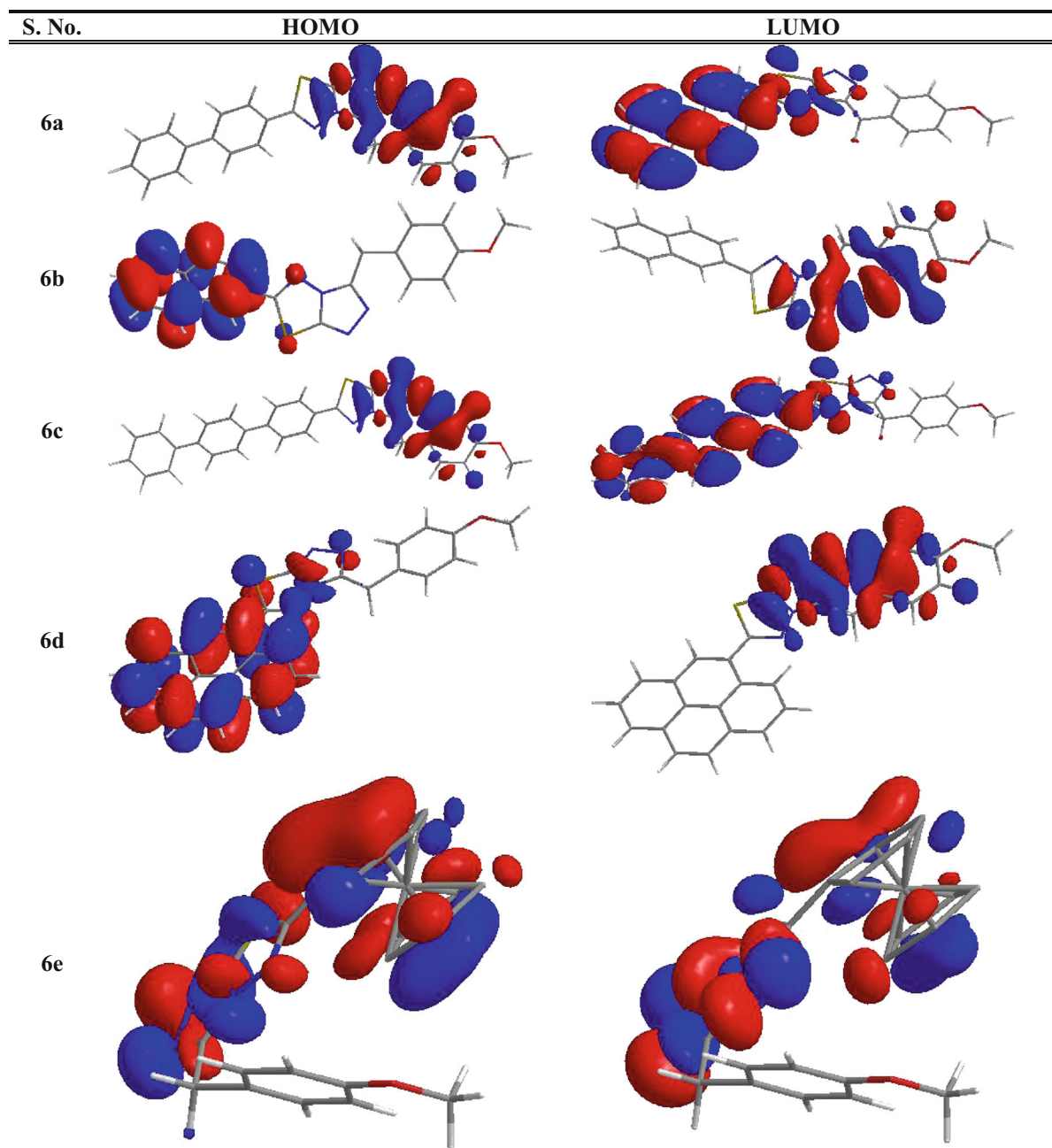


**Fig. 3** Thermogravimetric analysis results for compounds 6a–e

orbital *i. e.*, HOMO and LUMO were generated for the substituted fused triazolothiadiazole derivatives 6a–e (Table. 2). The electron density distribution pattern was not linear for HOMO and LUMO of all the compounds 6a–e. In HOMO of compounds 6a and 6c, the electron density were spread over the triazole ring and the aralkyl ring attached to the fused triazole moiety while there was no electronic cloud on the side coupled group substituted to the fused thiadiazole ring. During the time, the case was divergent in LUMO where an expansion of electronic cloud over the side coupled group substituted to the central triazolothiadiazole nucleus was

observed. Meanwhile the electron distribution was on the side coupled naphthyl as well as pyrenyl group attached to the central fused heterocyclic nucleus, respectively in HOMO of 6b and 6d inversely in LUMO, there was electronic distribution over triazole and aryl ring. However, the electron distribution pattern was quite different in case of 6e. There was expansion of electron density over central fused heterocyclic nucleus as well as side coupled ferrocenyl group in case of both HOMO and LUMO of 6e while negligible difference were observed in the electronic distribution pattern between both the selected orbitals.

**Table 2** Computer generated frontier molecular orbitals of compounds 6a–e





## Conclusion

A series of five 3,6-disubstituted 1,2,4-triazolo [3,4-*b*] 1,3,4-thiadiazole derivatives bearing biphenyl, naphthyl, *p*-terphenyl, pyrenyl and ferrocenyl group were synthesized and evaluated their photophysical properties including UV-visible absorption spectra, fluorescence emission spectra, molar absorption co-efficient, Stokes shift and the relative fluorescence quantum yield in a variety of organic solvents in order to investigate their potential as an efficient fluorescent dyes with maximum light harvesting potential. Spectral properties of the compounds were highly dependent on the nature of the substituent and coupling components attached to the triazolothiadiazole skeleton as well as slightly affected by the solvent polarities. The thermal stability of the target compounds were evaluated by thermogravimetric analysis. All the compounds 6a–e shows very good thermal stability above 300 °C with approximately 20 % weight loss except 6e with 20 % weight loss at 225 °C. However, it exhibits very interesting thermal stability profile with only 46 % weight loss up to 700 °C. The considerable high thermal stability of synthesized fused triazolothiadiazole molecules may fabricate them in organic light emitting diodes (OLED) and dye sensitized solar cells (DSSC). Due to low toxicity of triazolothiadiazole skeleton toward biomolecules, facile synthetic strategy with economic compatibility and fascinating photophysical properties may be utilized in bioimaging, fluorescent labelling of biomolecules and cells.

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