

# Synthesis, Spectroscopic Properties and Antioxidant Activity of Bis-Hydrazones and Schiff's bases Derived from Terephthalic Dihydrazide

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**Abstract** A series of novel Schiff base containing bis-1,2,4-triazole and bis-hydrazone derived from terephthalic dihydrazide was synthesized. All the newly synthesized compounds were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, mass spectra, FTIR and elemental analysis. UV–vis spectra and fluorescent spectra of the compounds were recorded. The effect of substituent such as electron withdrawing and electron donating groups on the fluorescent spectra was studied. Also, the comparative discussion on fluorescent spectra of Schiff's base and hydrazones has been described. The antioxidant activity of the compounds revealed that compound 5c and 5f are the most potent compounds in this series.

**Keywords** Bis-hydrazone · Schiff's base · 1,2,4-triazole · Fluorescent spectra · Antioxidant activity

## Introduction

Schiff bases have diverse application in different areas such as catalysis, metallic deactivators, separation processes, electrochemistry, bioinorganic and environmental chemistry. Schiff's bases are also known to form stable complexes with both transition metals and rare-earth metal ions [1–5]. Hydrazones are special group of compounds in the Schiff's base which are

characterized by the presence of >C=N-N < group. Hydrazone possess an additional donor sites which make them more versatile to form complexes with metal ions with variable oxidation state [6].

1,2,4-Triazole and their derivatives represent an interesting class of heterocyclic compounds possessing wide spectrum of biological activities such as antibacterial [7], antifungal [8], antiviral [9], anti-inflammatory [10], analgesic [11], antidepressant [12], hypoglycemic [13] etc. Several potent drugs possessing triazole nucleus like Estazolam, Terconazole, Ribavirin, Vorozole, Rizatriptan and Nefazodone are in the market [14].

So in the present work a series of Schiff base containing bis-1,2,4-triazole and bis-hydrazones derived from terephthalic dihydrazide were synthesized, characterized and their fluorescent property was determined. The effect of substituent on the fluorescent spectra has been studied. These newly synthesized compounds were also tested for their antioxidant property.

## Experiments

The IR spectra (in KBr pellets) were recorded on a Shimadzu FT-IR 157 spectrophotometer. The <sup>1</sup>H NMR spectra were recorded on a Bruker Avance-II (400 MHz) NMR spectrometer using Tetra methylsilane (TMS) as internal standard. All the chemical shift values were expressed in δ scale down field from TMS and proton signals were indicated as *s* = singlet, *d* = doublet, *m* = multiplet. Mass spectra (MS) of the compounds were recorded on a Water-Micromass Q-ToF Micro LC mass spectrometer. Elemental analysis was carried out on Vario-El Elementar-III model analyzer. Elemental analysis was carried out on Vario-El Elementar-III model analyser. The melting points of the newly synthesized compounds were

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determined using the instrument DSC-SDT Q 600. The homogeneity of the compounds was checked by thin layer chromatography (TLC) using silica gel plates (obtained from Merck) using hexane: ethyl acetate (9:1) as mobile phase. The UV–vis spectra of all the compounds were recorded using Shimadzu UV-1800 Spectrophotometer in a wavelength range of 200–800 nm. The fluorescence spectra of the synthesized compounds were recorded with a JASCO FP-6200 spectrofluorometer in right angle detection mode. The photophysical studies were performed on  $10^{-6}$  M solution of the compounds in DMSO. The basic photophysical characteristics such as the absorption maxima ( $\lambda_{\text{abs}}$ ), molar absorptivity ( $\epsilon$ ), fluorescence maxima ( $\lambda_{\text{em}}$ ), Stokes shift ( $\gamma_{\text{abs}} - \gamma_{\text{em}}$ ) and fluorescence quantum yield ( $\Phi_F$ ) of the derivatives were determined and are summarized in Table 2.

### General Procedure for the Preparation of *N,N*-bis-[substituted methylidene]benzene-1,4-dicarbohydrazone (2a–g)

Equimolar quantities of terephthalic dihydrazide (1 mmol) and suitable aromatic aldehydes (2 mmol) was refluxed in DMF (15 mL) for 5 h in presence catalytic amount of glacial acetic acid. The solid separated on cooling the reaction mixture to room temperature was collected under vacuum. The crude solid was recrystallized in DMF-ethanol mixture to give the pure products.

*N,N*-bis[furan-2-ylmethylidene]benzene-1,4-dicarbohydrazone (**2a**). Brown crystalline solid, yield 58 %. MS ( $m/z$ ,  $M^+ + 1$ ): 351.1.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 6.6(dd, 2H,  $J=3.6$ , 3.2Hz, furan H-4), 6.9(d, 2H,  $J=3.2$ Hz, furan H-3), 7.8(d, 2H,  $J=3.2$ Hz, furan H-5), 8.0(s, 4H, Ar-H), 8.3(s, 2H, N=CH), 11.9(s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.60, 162.16, 149.29, 145.32, 138.12, 137.39, 132.17, 129.22, 127.95. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3313.3 (N-H), 2944.01 (C-H), 1655.5 (amide C=O), 1572.3 (C=N). Anal. Calc.: C, 61.71; H, 4.03; N, 15.99. Found: C, 61.69; H, 3.98; N, 15.92.

*N,N*-bis[thiophen-2-ylmethylidene]benzene-1,4-dicarbohydrazone (**2b**). White crystalline solid, yield 66 %. MS ( $m/z$ ,  $M^+ + 1$ ): 383.1.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.1(dd, 2H,  $J=3.6$ , 3.3Hz, furan H-4), 7.4(d, 2H,  $J=4.8$ Hz, furan H-3), 7.6(d, 2H,  $J=3.6$ Hz, furan H-5), 8.0 (s, 4H, Ar-H), 8.6(s, 2H, N=CH), 11.9 (s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.08, 162.06, 143.49, 138.88, 137.36, 132.41, 131.16, 129.14, 127.90. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3412.5 (N-H), 3033.01 (C-H), 1720.5 (amide C=O), 1571.7 (C=N). Anal. Calc.: C, 56.53; H, 3.69; N, 14.65. Found: C, 56.50; H, 3.62; N, 14.61.

*N,N*-bis[(5-methylfuran-2-yl)methylidene]benzene-1,4-dicarbohydrazone (**2c**). White crystalline solid, yield 66 %. MS ( $m/z$ ,  $M^+ + 1$ ): 379.2.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 2.3 (s, 6H,  $\text{CH}_3$ ), 6.2 (d, 2H,  $J=2.4$ Hz, furan H-3), 6.8 (d, 2H,  $J=3.2$ Hz,

furan H-4), 8.0(s, 4H, Ar-H), 8.2(s, 2H, N=CH), 11.8 (s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 162.10, 154.71, 147.77, 137.84, 136.00, 127.64, 124.62, 115.63, 108.58, 13.45. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3318.1 (N-H), 2949.1 (C-H), 1711.5 (amide C=O), 1578.3 (C=N). Anal. Calc.: C, 63.48; H, 4.79; N, 14.81. Found: C, 63.41; H, 4.75; N, 14.81.

*N,N*-bis[*p*-fluorophenylmethylidene]benzene-1,4-dicarbohydrazone (**2d**). Pale yellow solid, yield 67 %. MS ( $m/z$ ,  $M^+ + 1$ ): 407.6.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.4 (d, 4H,  $J=7.8$ Hz, meta protons of *p*-fluorophenyl), 7.5 (d, 4H,  $J=7.4$ Hz, ortho protons of *p*-fluorophenyl), 8.0(s, 4H, Ar-H), 8.2(s, 2H, N=CH), 11.8 (s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 162.10, 154.71, 147.77, 137.84, 136.00, 127.64, 115.63, 108.58, 103.45. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3298.1 (N-H), 2936.1 (C-H), 1721.5 (amide C=O), 1558.4 (C=N). Anal. Calc.: C, 65.02; H, 3.97; N, 13.79. Found: C, 64.96; H, 3.91; N, 13.88.

*N,N*-bis[*p*-methoxyphenylmethylidene]benzene-1,4-dicarbohydrazone (**2e**). White solid, yield 79 %. MS ( $m/z$ ,  $M^+ + 1$ ): 431.2.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 3.2 (s, 6H,  $\text{OCH}_3$ ), 7.4 (d, 4H,  $J=7.9$ Hz, meta protons of *p*-methoxyphenyl), 7.5 (d, 4H,  $J=7.5$ Hz, ortho protons of *p*-methoxyphenyl), 8.0(s, 4H, Ar-H), 8.1(s, 2H, N=CH), 11.5 (s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 163.10, 154.31, 146.77, 139.84, 136.88, 127.64, 125.78, 115.63, 108.58, 16.45. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3308.1 (N-H), 2956.1 (C-H), 1722.5 (amide C=O), 1538.4 (C=N). Anal. Calc.: C, 66.97; H, 5.15; N, 13.02. Found: C, 66.95; H, 5.13; N, 13.00.

*N,N*-bis[*p*-nitrophenylmethylidene]benzene-1,4-dicarbohydrazone (**2f**). Pale yellow solid, yield 62 %. MS ( $m/z$ ,  $M^+$ ): 460.5.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.2 (d, 4H,  $J=7.9$ Hz, meta protons of *p*-nitrophenyl), 7.5 (d, 4H,  $J=7.4$ Hz, ortho protons of *p*-nitrophenyl), 8.0(s, 4H, Ar-H), 8.3(s, 2H, N=CH), 11.6 (s, 2H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.30, 157.71, 147.71, 139.84, 135.20, 127.64, 125.63, 118.58, 102.45. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 3298.1 (N-H), 2963.1 (C-H), 1702.5 (amide C=O), 1558.4 (C=N). Anal. Calc.: C, 57.39; H, 3.50; N, 18.25. Found: C, 57.36; H, 3.46; N, 18.20.

### General Procedure for the Preparation of 5,5'-benzene-1,4-bis(4-{substituted methylidene}amino)-4*H*-1,2,4-triazole-3-thiol

A mixture of bis-4-amino-5-phenyl-3-mercapto-1,2,4-triazole(3) (1 mmol), substituted aromatic aldehydes (2 mmol) and 2–3 drops of concentrated sulphuric acid in 10 mL dimethyl formamide (DMF) medium was heated to reflux for 4 h. Progress of the reaction was monitored by TLC. The resulting solution was allowed to cool. The solid obtained was filtered under suction, washed with ethanol and recrystallized from DMF-ethanol mixture.

5,5'-benzene-1,4-bis(4-{{furan-2-ylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5a**). Brown solid, yield 79 %. MS (*m/z*,  $M^+$ ): 463.1.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.1 (dd, 2H,  $J=3.6, 3.5\text{Hz}$ , furan H-4), 7.4 (d, 2H,  $J=3.2\text{Hz}$ , furan H-3), 7.6 (d, 2H,  $J=4.8\text{Hz}$ , furan H-5), 8.01 (s, 4H, Ar-H), 8.6 (s, 2H, N=CH), 11.9 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 162.17, 143.38, 138.94, 136.02, 131.11, 129.10, 127.85, 127.66, 125.33. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1564.5(C=N), 2860.8 (C-H), 3426.12 (N-H). Anal. Calc.: C, 51.94; H, 3.05; N, 24.23. Found: C, 51.91; H, 3.01; N, 24.20.

5,5'-benzene-1,4-bis(4-{{thiophene-2-ylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5b**). White solid, yield 83 %. MS (*m/z*,  $M^+$ ): 495.2.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.1 (dd, 2H,  $J=3.6, 3.5\text{Hz}$ , furan H-4), 7.4 (d, 2H,  $J=3.2\text{Hz}$ , furan H-3), 7.6 (d, 2H,  $J=4.8\text{Hz}$ , furan H-5), 7.9 (s, 4H, Ar-H), 8.6 (s, 2H, N=CH), 11.8 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 162.19, 143.40, 138.96, 136.02, 133.72, 131.11, 129.11, 128.23, 127.86, 126.72. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1563.5 (C=N), 2864.0 (C-H), 3252.7 (N-H). Anal. Calc.: C, 48.56; H, 2.85; N, 22.65. Found: C, 48.53; H, 2.81; N, 22.62.

5,5'-benzene-1,4-bis(4-{{4-fluorophenylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5c**). yellow solid, yield 79 %. MS (*m/z*,  $M^+$ ): 519.5.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.3 (d, 4H,  $J=$  Hz, ortho protons of *p*-fluorophenyl), 7.8 (d, 4H,  $J=$  Hz, meta protons of *p*-fluorophenyl), 8.04 (s, 4H, Ar-H), 8.4 (s, 2H, N=CH), 11.9 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.09, 164.38, 162.61, 161.92, 160.31, 147.14, 136.04, 130.80, 129.34, 127.72. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1511.6 (C=N), 3034.3 (C-H), 3215.3(N-H). Anal. Calc.: C, 55.59; H, 3.11; N, 21.61. Found: C, 55.55; H, 3.07; N, 21.58.

5,5'-benzene-1,4-bis(4-{{4-chlorophenylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5d**). Pale Yellow solid, yield 72 %. MS (*m/z*,  $M^+$ ): 552.5.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.7 (d, 4H,  $J=8.4\text{Hz}$ , ortho proton of *p*-chlorophenyl), 7.9 (d, 4H,  $J=8.4\text{Hz}$ , meta proton of *p*-chlorophenyl), 8.02 (s, 4H, Ar-H), 8.47 (s, 2H, N=CH), 12.0 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 166.09, 165.38, 162.32, 161.92, 160.11, 147.14, 136.04, 132.80, 129.34, 127.72. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1549.7 (C=N), 3064.5 (C-H), 3222.3(N-H). Anal. Calc.: C, 52.27; H, 2.92; N, 20.32. Found: C, 52.22; H, 2.88; N, 20.30.

5,5'-benzene-1,4-bis(4-{{4-methoxyphenylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5e**). white solid, yield 84 %. MS (*m/z*,  $M^+$ ): 542.3.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 3.8 (s, 6H, OMe), 7.0 (d, 4H,  $J=7.3\text{Hz}$ , ortho proton of *p*-chlorophenyl), 7.7 (d, 4H,  $J=7.8\text{Hz}$ , meta proton of *p*-chlorophenyl), 8.03 (s, 4H, Ar-H), 8.6 (s, 2H, N=CH), 11.8 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.09, 164.38, 162.61, 161.92, 160.31, 147.14, 136.04, 130.80, 129.34, 127.72, 18.65. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1594.8 (C=N), 2838.2 (C-H), 3260.4(N-H). Anal. Calc.: C, 57.55; H, 4.09; N, 20.65. Found: C, 57.52; H, 4.02; N, 20.63.

5,5'-benzene-1,4-bis(4-{{4-nitrophenylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5f**).

Yellow solid, yield 76 %. MS (*m/z*,  $M^+$ ): 573.6.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.2 (d, 4H,  $J=7.3\text{Hz}$ , ortho proton of *p*-nitrophenyl), 7.7 (d, 4H,  $J=7.8\text{Hz}$ , meta proton of *p*-nitrophenyl), 8.03 (s, 4H, Ar-H), 8.5 (s, 2H, N=CH), 11.7 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 165.79, 164.31, 162.51, 161.93, 160.21, 147.14, 137.04, 135.80, 129.34, 127.72. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1594.8 (C=N), 2838.2 (C-H), 3260.4(N-H). Anal. Calc.: C, 50.34; H, 2.82; N, 24.46. Found: C, 50.30; H, 2.78; N, 24.40.

5,5'-benzene-1,4-bis(4-{{4-methylphenylmethylidene}amino}-4*H*-1,2,4-triazole-3-thiol) (**5g**).

White solid, yield 76 %. MS (*m/z*,  $M^+$ ): 511.2.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 1.9 (s, 6H, Me), 7.1 (d, 4H,  $J=7.3\text{Hz}$ , ortho proton of *p*-nitrophenyl), 7.4 (d, 4H,  $J=7.8\text{Hz}$ , meta proton of *p*-nitrophenyl), 8.01 (s, 4H, Ar-H), 8.6 (s, 2H, N=CH), 11.7 (s, 2H, SH/NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  in ppm: 167.79, 165.31, 162.21, 161.93, 160.21, 146.14, 135.04, 134.80, 129.34, 127.72, 13.66. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$ : 1593.8 (C=N), 2848.2 (C-H), 3263.4(N-H). Anal. Calc.: C, 61.15; H, 4.34; N, 21.94. Found: C, 61.11; H, 4.34; N, 21.89.

## Result and Discussion

### Synthesis

Bis-(4-amino-5-phenyl-3-mercapto-1,2,4-triazole) was obtained as per the synthetic route described in Fig. 1. Diethyl terephthalate on hydrazinolysis with hydrazine hydrate gave the corresponding hydrazide (1). The required bis-dithiocarbazine (3) was synthesized by reacting terephthalic dihydrazide with carbon disulfide and potassium hydroxide in absolute alcohol. This potassium salt underwent ring closure with hydrazine hydrate to give (4). The bis-1,2,4-triazole so synthesized was then condensed with substituted aromatic aldehydes in presence of conc. sulphuric acid (few drops) as catalyst to yield Schiff's base.

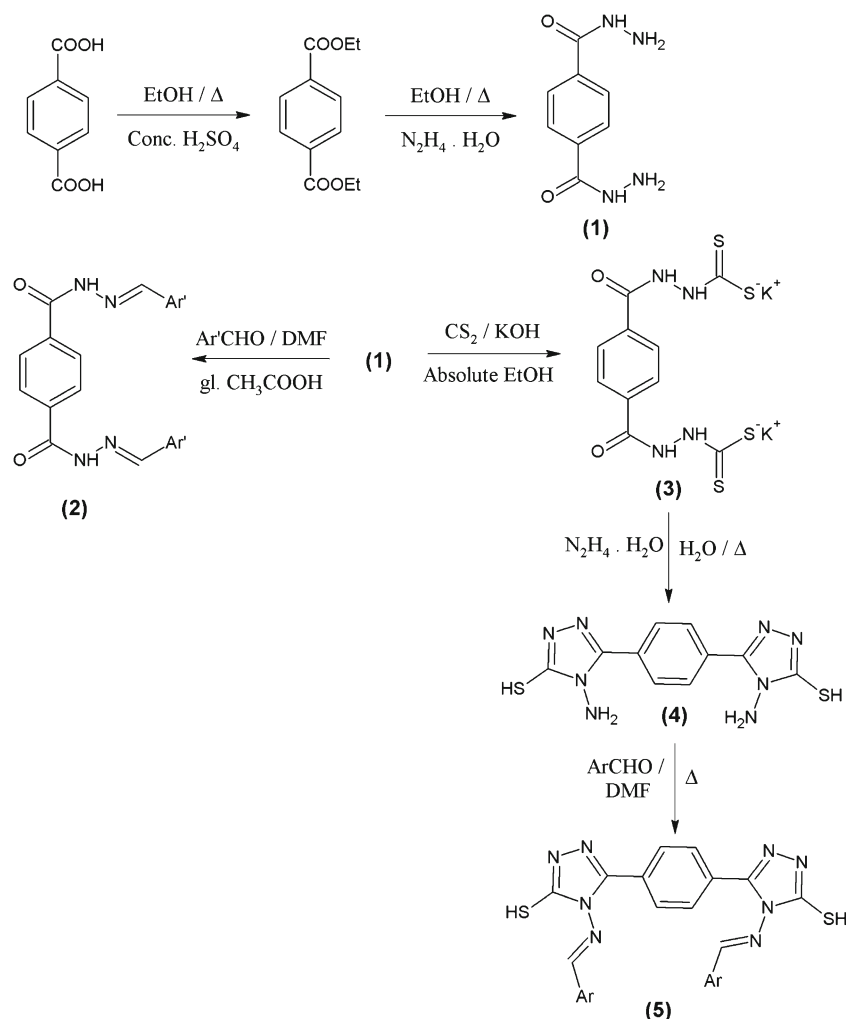
Terephthalic dihydrazide and substituted aromatic aldehydes were employed in the preparation of hydrazones. Hydrazones (2) were obtained from condensation of compound (1) with aromatic aldehyde in presence of few drops of glacial acetic acid.

The structure of synthetic compounds has been elucidated by mass spectrometry (MS), proton nuclear magnetic resonance ( $^1\text{H}$  NMR), carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR), infrared spectra (IR) and elemental analysis. The characterization data of all the synthesized compounds is summarized in Table 1.

### UV-vis Spectrum

The UV-vis spectra of the synthesized compounds were measured in DMSO and are shown in Figs. 2 and 3. The

**Fig. 1** The schematic route for the synthesis of target compound



UV–vis spectrum of all the compounds exhibited  $\lambda_{\text{max}}$  at 300–360 nm which attributed to  $\pi$  to  $\pi^*$  transition. The introduction of alkyl groups like  $\text{CH}_3$  or  $\text{OCH}_3$  shifted the absorption peak towards longer wavelength region (red shift effect). Similarly, the introduction of substituent like F, Cl and  $\text{NO}_2$  also shifted the absorption maxima towards longer wavelength region.

The molar extinction coefficients ( $\epsilon$ ) of all the derivatives are in the range  $4.1 \times 10^4$ – $30.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The molar extinction coefficients values indicate that the absorption spectrum is a charge transfer band through the  $\pi$  to  $\pi^*$  transition. The molar extinction coefficients of the derivatives with electron donating group like methyl, methoxy is high.

### Fluorescence Spectrum

The fluorescence spectra of the compounds are shown in Figs. 4 and 5. The maximum emission wavelength for each compound is summarized in Table 2. The fluorescence spectra of all the compounds exhibited maximum

emission wavelength at 330–440 nm. When compared to electron withdrawing groups like F, Cl the presence of  $\text{NO}_2$  group shifts the emission wavelength to longer wavelength region ( $\sim 30$ – $85 \text{ nm}$ ) i.e., causes red-shift. It is also observed that there is also increase in the fluorescence intensity (hyperchromic shift). This trend of red-shift and increase in fluorescence intensity is observed both in the hydrazones and Schiff's base when F and Cl are replaced by  $\text{NO}_2$  group. The electron donating groups also caused slight red shift with increase in the fluorescence intensity.

### Comparison of Fluorescent Spectra of Schiff's Base and Hydrazone

The fluorescence spectra of Schiff's base exhibited more red-shift and slight changes in the intensity than that of hydrazones. The reason for the extensive red shift in Schiff's base may be attributed to lessening of energy gap between the

**Table 1** Characterization data for compounds 2a–f and 5a–g

Compd no	Ar	Ar'	Mol. formula (M.Wt)	mp (°C)	Yield (%)
2a	–	Furyl	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> 350.3	198–201	62
2b	–	Thienyl	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub> S <sub>2</sub> 382.4	214	70
2c	–	5-methyl furyl	C <sub>20</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> 378.3	309	63
2d	–	p-fluoro phenyl	C <sub>22</sub> H <sub>16</sub> F <sub>2</sub> N <sub>4</sub> O <sub>2</sub> 406.3	331	55
2e	–	p-methoxy phenyl	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> 430.4	183–185	71
2f	–	p-nitro phenyl	C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub> 460.3	326	55
5a	Furyl	–	C <sub>20</sub> H <sub>14</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> 462.5	347	63
5b	Thienyl	–	C <sub>20</sub> H <sub>14</sub> N <sub>8</sub> S <sub>4</sub> 494.6	343	45
5c	p-fluoro phenyl	–	C <sub>24</sub> H <sub>16</sub> F <sub>2</sub> N <sub>8</sub> S <sub>2</sub> 518.5	181	42
5d	p-chloro phenyl	–	C <sub>24</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>8</sub> S <sub>2</sub> 551.4	498	43
5e	p-methoxy phenyl	–	C <sub>26</sub> H <sub>22</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub> 542.6	166	49
5f	p-nitro phenyl	–	C <sub>24</sub> H <sub>16</sub> N <sub>10</sub> O <sub>4</sub> S <sub>2</sub> 572.5	425	53
5g	p-methyl phenyl	–	C <sub>26</sub> H <sub>22</sub> N <sub>8</sub> S <sub>2</sub> 510.6	371	39

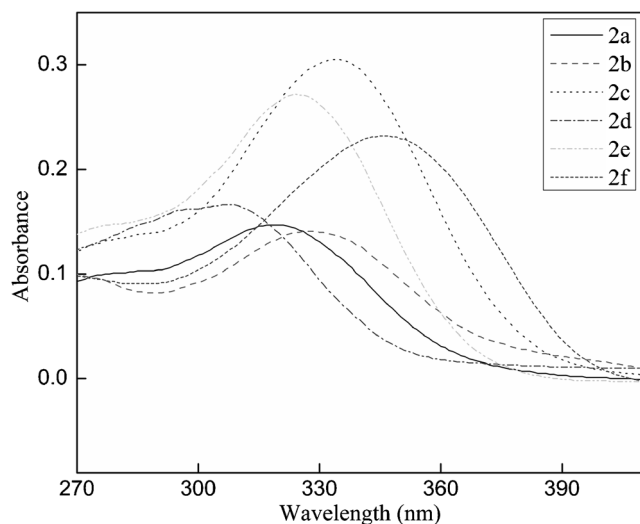
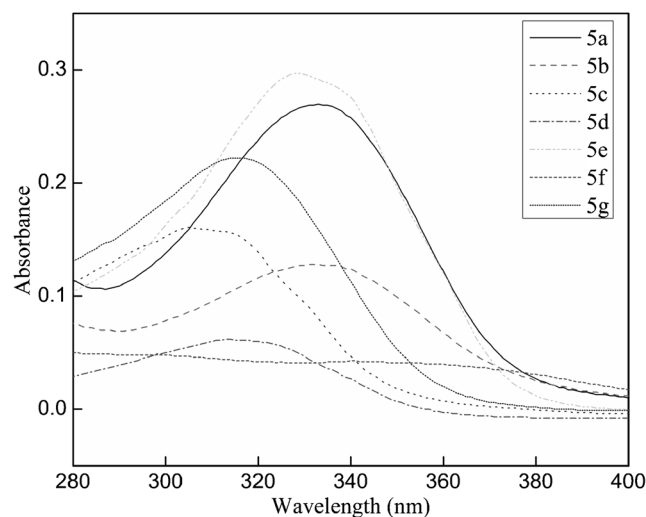
ground and excited states due to the presence of heteroatoms like N, S.

Stokes shift is the difference between positions of band maxima of the absorption and emission spectra. Stokes shift also indicates the difference in the structure and properties of the fluorescent compounds between the ground and the excited states [15]. The Stokes' shifts

(cm<sup>-1</sup>) were determined by Eq. (1).

$$(\gamma_{abs} - \gamma_{em}) = \left( \frac{1}{\lambda_{abs}} - \frac{1}{\lambda_{em}} \right) \times 10^7 \quad (1)$$

The Stokes shift of the synthesized compounds are high and are in the range 3656–6064 cm<sup>-1</sup>. High Stokes shift values indicates that there is no reabsorption of the emitted radiation.

**Fig. 2** The UV-vis spectra for the compounds 2a–f**Fig. 3** The UV-vis spectra for the compounds 5a–g



**Table 2** The observed UV-Visible absorption maxima, fluorescence emission maxima, molar absorptivity, Stokes shift and fluorescence quantum yield of compounds 2a–f and 5a–g

Compd. No	<sup>a</sup> $\lambda_{\text{abs}}$ (nm)	<sup>b</sup> $\lambda_{\text{em}}$ (nm)	<sup>c</sup> $\epsilon \cdot 10^4$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	<sup>d</sup> $\gamma_{\text{abs}} - \gamma_{\text{em}}$ ( $\text{cm}^{-1}$ )	<sup>e</sup> $\Phi_F$
2a	321	385	14.7	5178	0.0298
2b	329	411	14.1	6064	0.0365
2c	336.5	396	30.5	4465	0.0322
2d	308	349	16.6	3814	0.0245
2e	327	389	27	4874	0.0354
2f	348	414	23.2	4581	0.0325
5a	334	394	27	4559	0.0324
5b	334	399	12.8	4877	0.0324
5c	309.5	349	15.9	3656	0.0268
5d	315.5	377	6.2	5170	0.0345
5e	329	393	29.7	4949	0.0315
5f	355.5	432	4.1	4981	0.0317
5g	317.5	380	22.2	5180	0.0330

<sup>a</sup> UV-Vis absorption maxima

<sup>b</sup> Fluorescence emission maxima

<sup>c</sup> Molar absorptivity

<sup>d</sup> Stokes shift

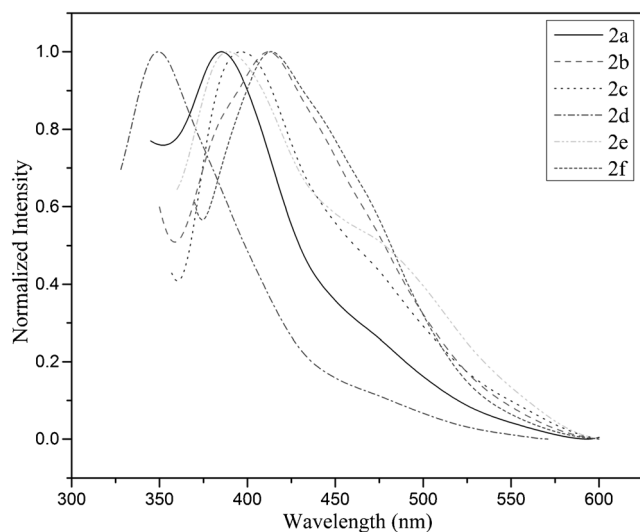
<sup>e</sup> Fluorescence quantum yield

The fluorescence quantum yield is the ratio of number of photons emitted to the number of photons absorbed. It is also an important parameter for the quantitative characterization of fluorophores. The fluorescence quantum yield was calculated according to Eq. (2), where  $S_{\text{ref}}$ ,  $A_{\text{ref}}$ ,  $n_{\text{ref}}$  and  $S_{\text{sample}}$ ,  $A_{\text{sample}}$ ,  $n_{\text{sample}}$  represents the integrated emission band area, the absorbance at the excited wavelength and refractive index of the solvent, respectively for the standard reference and the sample. The 9,10-diphenylanthracene ( $\Phi_{\text{ref}}=0.90$ ) in cyclohexane was used as standard reference [16–18]. The quantum yields of the derivatives are in the range 0.0245–0.0365.

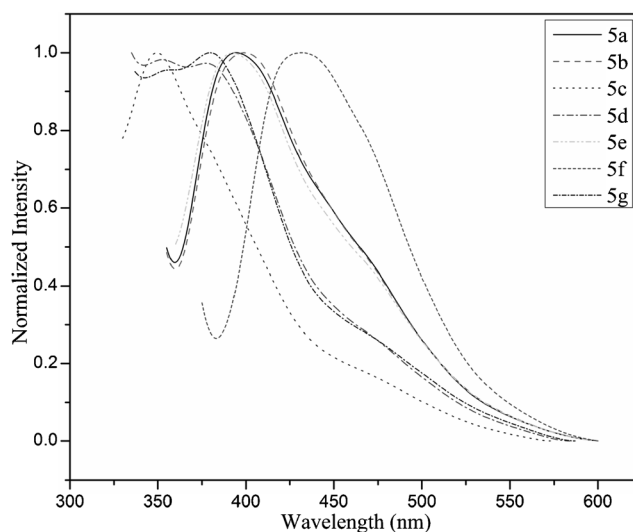
$$\Phi_F = \Phi_{\text{ref}} \left( \frac{S_{\text{sample}}}{S_{\text{ref}}} \right) \left( \frac{A_{\text{ref}}}{A_{\text{sample}}} \right) \left( \frac{n_{\text{sample}}^2}{n_{\text{ref}}^2} \right) \quad (2)$$

## Antioxidant Activity

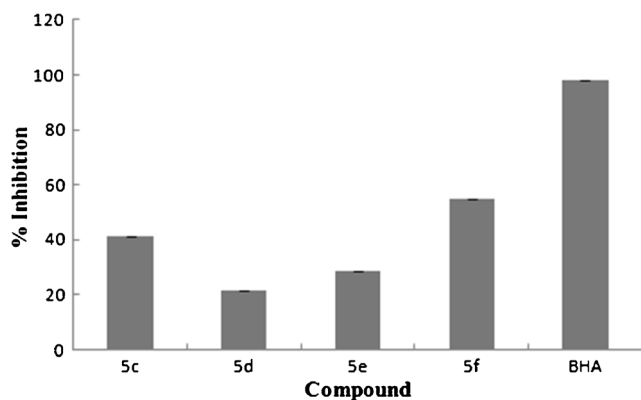
2, 2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity was determined following the method of Mensor et al. [19] and percentage radical scavenging activity was determined using the following equation where ethanol with DPPH was used as control



**Fig. 4** The fluorescence emission spectra for compound 2a–f



**Fig. 5** The fluorescence emission spectra for compound 5a–g



**Fig. 6** The DPPH radical scavenging activity of target compound

Percent radical scavenging activity

$$= \left( \frac{A_c - A_s}{A_c} \right) \times 100$$

Where  $A_c$  is the absorbance of control and  $A_s$  is the absorbance of the sample. All the experiments were performed in triplicate; the results were expressed as mean  $\pm$  standard deviation ( $SD$ ).

All synthesized compounds were screened for radical scavenging ability against DPPH radical. The pre-screening of the synthesized compounds was carried out as preliminary evaluation. The compounds were dissolved in DMSO to obtain a solution of  $0.001 \text{ mg mL}^{-1}$  concentration. From this stock solution,  $0.2 \text{ mL}$  was pipetted out and diluted to  $2.5 \text{ mL}$  with ethanol. To this solution, added the ethanolic DPPH solution ( $1 \text{ mL}$ ,  $0.3 \text{ mM}$ ). The solution was incubated at room temperature for  $30 \text{ min}$ . The absorbance of these compounds was recorded at  $518 \text{ nm}$ . Butylated hydroxyl anisole (BHA) has been used as the standard for the antioxidant activity screening. The compounds **5c** and **5f** showed moderate activity compared with standard. The percentage radical scavenging activity of the synthesized compounds has been described in the Fig. 6.

## Conclusion

A series of Schiff's base of bis-1,2,4-triazole and bis-hydrazone derived from terephthalic dihydrazide was synthesized. All the synthesized compounds were characterized by MS,  $^1\text{H NMR}$ ,  $^{13}\text{C NMR}$ , FT-IR and elemental analysis. The UV-vis spectra and fluorescent spectra of the compounds were recorded and the effect of substituent on the intensity, wavelength shifts was studied. The experimental results revealed that the presence of auxochrome such as F, Cl, and  $\text{NO}_2$  causes red shift and there are changes in the intensity. The fluorescence quantum yield was calculated and it was also observed that the derivatives exhibited high Stokes shift. The

compounds **5c** and **5f** showed moderate radical scavenging activity against standard BHA.

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