

Synthesis and Fluorescence Properties of Novel indol-3-yl-thiazolo[3,2-a][1,3,5]triazines and indole-3-carbaldehyde Schiff Bases

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Abstract Novel photoactive 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines were synthesized by the conjugate addition of ammonia to the indole-3-carbaldehyde Schiff bases followed by the condensation with 4-chlorobenzaldehyde. All the synthesized compounds were characterized by FT-IR, NMR, mass spectra and elemental analyses. Their antioxidant property, electrochemical and photophysical properties in different organic solvents were investigated. Comparative discussion on the photophysical properties of indole-3-carbaldehyde Schiff bases and 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines has been described. The fluorescence quantum yield of Schiff bases ($\Phi_f=0.66-0.70$ in DMSO) found to be interestingly higher. High fluorescence quantum yield, large molar extinction coefficient, high Stokes shift and smaller optical band gap positioning these new derivatives as an efficient metal free organic fluorescent and semiconductor material.

Keywords Indole-3-carbaldehyde Schiff bases · Indol-3-yl-thiazolo-s-triazines · Fluorescence spectroscopy · Physiochemical parameters · Antioxidant property · Cyclic voltammetry

Introduction

Over the past two decades, dye-sensitized solar cells (DSSC's) have gained much considerable interest owing to their high

efficiency of converting solar energy into electrical energy. Recent reports focused on metal-free organic dye based DSSC's because of their strong molar absorption co-efficient, intermolecular interactions, low material cost, lightweight and reduced toxicity [1]. This prompted organic chemists to design and develop photosensitizers with promising chromophores and substituents to meet the performances of DSSC's. Fluorescent materials also appear to be promising sensors for chemical sensing [2]. Thus, the interest on the fluorescent materials has steadily increased in recent years. The versatile structure, Stokes shifts, high molar extinction co-efficient and the LUMO-HUMO energy levels of metal-free organic molecules have been explored to study the performances of DSSC's [1, 3, 4]. Heterocyclic dyes such as coumarin dyes, thiophene-based dyes, indoline dyes, heteropolycyclic dyes, xanthene dyes, porphyrin dyes, merocyanine dyes, squaraine dyes, cyanine dyes and phthalocyanine dyes have been reported for DSSC's performances [5]. Also the materials with strong fluorescence, high photostability and molar extinction co-efficient have been used in industries as paints, inks and plastics [6]. In addition, materials with antioxidative property influence their photoconductance [7]. On the other hand, N-heterocycles also have been used as conducting materials, electrochemical sensors and photonics [8–12]. Their behavior has been determined by physiochemical characteristic studies such as solvatochromic, piezochromic, oscillator strength, dipole moment, fluorescent quantum yield and photostability. The photostability and polarity studies of metal free Schiff base dyes were reported by Marwani et al. [13].

Recently, the thiazolo[5,4-d]thiazoles containing both electron donor N and S atoms and electron acceptor aromatic rings have been receiving much attention in the field of electrochemistry because of their electronic, spectroscopic and dyeing properties [14]. Annulated thiazolo[3, 2-a][1, 3, 5] triazines were first synthesized by Rathke in 1887, and their

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Table 1 Reaction time, yield and melting point of 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b)

Compound	R	R'	X	Color and appearance	Reaction time (min)	Yield (%)	Melting point(°C)		GC-MS (Daltons)
							Found	Lit.	
1b	H	H	H	White solid	20	100	152	152–153 [19]	176.24
2b	Cl	H	H	White solid	22	96	162	164–165 [19]	210.13
3b	CH ₃	H	H	Golden yellow solid	20	96	132	126–127 [19]	190.19
4b	OCH ₃	H	H	White crystalline solid	20	100	204	206–207 [19]	207.17
5b	OCH ₃	OCH ₃	H	Pale yellow solid	25	72	198	–	237.24
6b	H	H	OH	Yellow crystalline solid	35	82	134	–	193.2
7b	F	H	H	Off white solid	35	95	82	102–103 [19]	194.1

bioactivities have been widely discussed. Beyond their biological properties, various substituted thiazolo[3, 2-a][1, 3, 5]triazines were found to have wide applications in industries as dye stuffs, optical bleaches, explosives, in agriculture as pesticides and also to activate the surface of the materials [15, 16]. During the past several years, synthesis, UV absorption and fluorescence studies of various substituted N-triazinyl derivatives were investigated [17]. As part our research interest to develop functional organic materials, in this paper, we have reported the three component one pot reaction of indole-3-carbaldehyde Schiff bases, ammonium acetate and p-chloro benzaldehyde to obtain hitherto unreported 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines. Spectral characterization, fluorescence, electrochemical and antioxidant studies of Schiff bases and indol-3-yl-thiazolo-s-triazines were performed. The photochemical parameters, optical band gap and fluorescence quantum yield were calculated. We found that compounds (1c–7c) have excellent antioxidant property and moderate to high photoconductivity in organic solvents.

Experimental

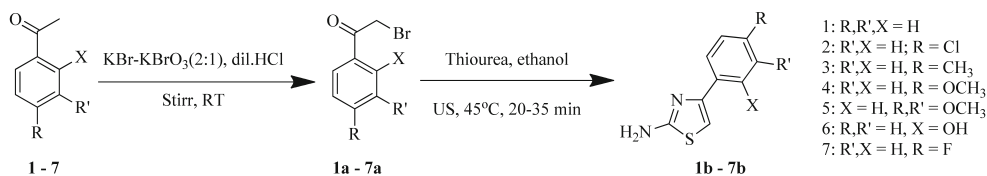
Melting points were determined in open capillary tube method and were uncorrected. Mass spectra were recorded on GC-MS spectrophotometer of GC model Clarus 680 and MS model Clarus 600(EI) using helium as a carrier gas with qualitative results. The infrared spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer using the KBr pellet technique. ¹H & ¹³C NMR was recorded on a Bruker 400 and 100 MHz FT-

NMR spectrometer. Chemical shifts in NMR spectra were reported in parts per million (ppm) from trimethylsilane (TMS) using as an internal standard and CDCl₃/DMSO-d₆ as a solvent. Splitting patterns were designated as follows: s: singlet, d: doublet, t: triplet, q: quartet and m: multiplet. The reactions were monitored by TLC on silica gel protected on aluminium sheets and the compound spots were detected by exposure to UV-lamp at 256 nm. The purification of the compounds was done by silica gel column chromatography using petroleum ether and ethyl acetate. UV-Vis electronic absorption spectra were recorded on a JASCO V-670 spectrophotometer, by using 2 mL rectangular quartz cell. Steady state fluorescence spectra were measured using Hitachi F7000 spectrophotometer using rectangular quartz cell. All absorption and fluorescence spectra were recorded after subtracting the blank in data analysis. The cyclic voltammograms were recorded in the CH electrochemical work station instrument of model CHI6003D.

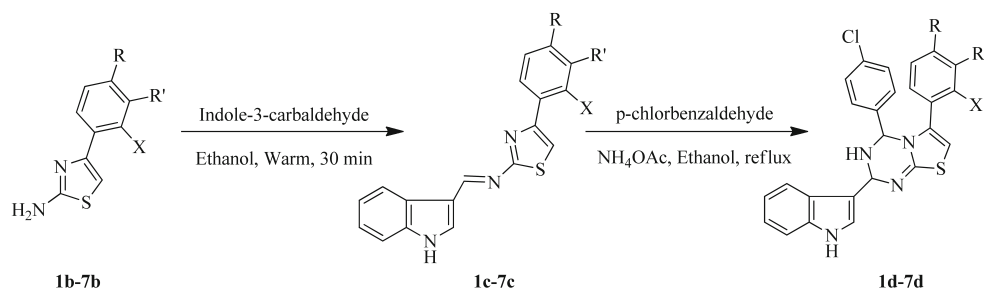
Synthesis of 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b)

α-Bromoarylethanones (deliquescent) were prepared according to the reported method [18]. The ethanolic mixture of α-bromoarylethanone (1a, 1 mmol) and thiourea in the boiling tube was ultrasonicated at 45 °C in an ultrasonic bath. The reaction was monitored by TLC at every 5 min. It was found that the heterocyclization was completed within 20 min. The same procedure was followed for the synthesis of 2-amino-4-substituted phenyl-1,3-thiazoles listed in Table 1.

Scheme 1 Preparation of α-bromoarylethanones and 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b)



Scheme 2 Preparation of thiazole Schiff bases (1c–7c) and indol-3-yl-thiazolo-s-triazines (1d–7d)



Synthesis of the indole-3-carbaldehyde Schiff base dyes (1c–7c)

An ethanolic mixture of indole-3-carbaldehyde (1 mmol) and corresponding 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b, 1 mmol) was boiled on the water bath. The reaction progress was monitored by TLC, after completion the reaction mixture was allowed to cool. On cooling, yellow solid Schiff bases separated out, which was then filtered, washed with cold ethanol and dried.

N-((1H-indol-3-yl)methylene)-4-phenylthiazol-2-amine (1c): $C_{18}H_{13}N_3S$: Yellow solid; Yield: 98 %; Melting point: 202–204 °C; FT-IR(ν in cm^{-1}): 3207.62 (N-H), 1728.22 (C=N); 1H NMR(DMSO- d_6 , 400 MHz, δ ppm): 6.838 (s, 1H, Indole C₂-H), 6.902 (s, 1H, C₅-H), 7.086–7.123 (m, 4H, Ar-H), 7.172–7.208 (t, 1H, J=7.599Hz, Ar-H), 7.284–7.302 (m, 4H, Ar-H), 7.383 (s, 1H, imino-H), 11.02 (s, 1H, -NH); ^{13}C NMR(DMSO- d_6 , 100 MHz, δ ppm): 114.58, 118.88, 121.47, 124.70, 125.99, 127.70, 127.99, 131.38, 133.53, 135.15, 138.05, 139.34, 140.42, 143.00, 145.15, 165.87; LC-MS: 305 (M+2Hpeak).

N-((1H-indol-3-yl)methylene)-4-(4-chlorophenyl)thiazol-2-amine (2c): $C_{18}H_{12}N_3S$: Yellow solid; Yield: 94 %; Melting point: 206–208 °C; FT-IR(ν in cm^{-1}): 3232.70 (N-H), 1737.86 (C=N); 1H NMR(DMSO- d_6 , 400 MHz, δ ppm): 7.206–7.287 (m, 3H, Ar-H), 7.510–7.529 (d, 1H, J=9.11Hz, Ar-H), 8.090–8.194 (m, 3H, Ar-H), 8.290–8.356 (t, 2H, J=12.01Hz, Ar-H), 9.943 (s, 1H, imino-H), 12.145 (s, 1H, N-H);

^{13}C NMR(DMSO- d_6 , 100 MHz, δ ppm): 112.38, 118.14, 120.79, 122.08, 123.42, 123.78, 124.09, 126.24, 129.53, 137.02, 138.41, 141.26, 149.90, 197.13 (C-Cl); GC-MS: 339.39 (M⁺+2 peak).

N-((1H-indol-3-yl)methylene)-4-(p-tolyl)thiazol-2-amine (3c): $C_{19}H_{15}N_3S$: Pale yellow solid; Yield: 90 %; Melting point: >200 °C; FT-IR(ν in cm^{-1}): 3213.41 (N-H), 1666.50 (C=N); 1H NMR(DMSO- d_6 , 400 MHz, δ ppm): 2.061 (s, 3H, -CH₃), 6.734–7.201 (m, 9H, C₅'-H, Ar-H), 7.597 (m, 2H, Ar-H), 8.008 (s, 1H, Indole C₂-H), 9.750 (s, 1H, imino-H), 11.043 (s, 1H, N-H); ^{13}C NMR(DMSO- d_6 , 100 MHz, δ ppm): 20.55, 111.45, 118.27, 120.90, 121.83, 123.12, 123.89, 127.67, 128.40, 128.61, 128.77, 130.19, 136.03, 136.63, 161.31; GC-MS: 318.04 (M⁺+1 peak).

N-((1H-indol-3-yl)methylene)-4-(4-methoxyphenyl)thiazol-2-amine (4c): $C_{19}H_{15}N_3OS$: Dirty white solid; Yield: 86 %; Melting point: 120–124 °C; FT-IR(ν in cm^{-1}): 2929.87 (N-H), 1672.28 (C=N); 1H NMR(DMSO- d_6 , 400 MHz, δ ppm): 3.951 (s, 3H, -OCH₃), 7.209–7.290 (m, 5H, C₅'-H, Ar-H), 7.512–7.532 (d, 2H, J=7.84Hz, Ar-H), 8.093 (s, 1H, Indole C₂-H), 8.112–8.126 (d, 2H, J=6.10Hz, Ar-H), 9.946 (s, 1H, imino-H), 12.147 (s, 1H, N-H); ^{13}C NMR(DMSO- d_6 , 100 MHz, δ ppm): 56.71 (OCH₃), 110.81, 112.24, 112.39, 118.14, 120.79, 122.09, 123.43, 124.09, 129.91, 130.91, 132.88, 137.02, 138.41, 159.05, 195.53 (Ar C-OCH₃); GC-MS: 335.04 (M+2 peak).

N-((1H-indol-3-yl)methylene)-4-(3,4-dimethoxyphenyl)thiazol-2-amine (5c): $C_{20}H_{17}N_3O_2S$: Pale

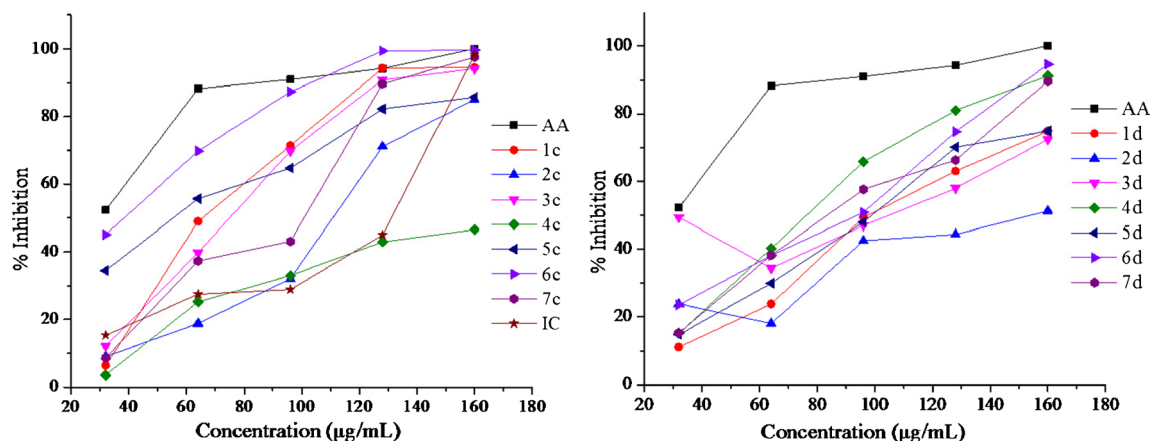


Fig. 1 Graphical representation of antioxidant results of compounds (1c–7c & 1d–7d)

Table 2 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (1c) in different solvents

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	327.5	425.9	0.3054	88.40	9000	0.00012	0.09	7054.66	0.03
Chloroform	325.9	429	0.1483	88.83	9500	0.00013	0.09	7374.24	0.07
Dichloromethane	362.2	429.1	0.2171	79.93	11,500	0.00014	0.10	4304.46	0.07
Ethylacetate	326.2	421.4	0.1996	88.75	12,000	0.00016	0.10	6925.62	0.02
Methanol	320.8	375.2	0.3085	90.25	10,500	0.00014	0.10	4519.62	0.04
DMSO	325.8	365.1	0.2634	88.86	8500	0.00011	0.09	3303.92	0.13
DMF	326	356	0.2744	88.81	6000	0.00008	0.07	2584.96	0.06

yellow solid; Yield: 90 %; Melting point: 140–142 °C; FT-IR(ν in cm⁻¹): 3367.26 (N-H), 1624.06 (C=N); ¹H NMR(DMSO-d₆, 400 MHz, δ ppm): 3.816 (s, 3H, -OCH₃), 3.844 (s, 3H, OCH₃), 7.040–7.633 (m, 8H, C5-H, Ar-H), 8.289 (s, 1H, C2-H), 8.295 (s, 1H, C2'-H), 9.947 (s, 1H, imino-H), 12.143 (s, 1H, N-H); ¹³C NMR(DMSO-d₆, 100 MHz, δ ppm): 55.44 (-OCH₃), 55.70 (-OCH₃), 110.13, 110.76, 112.39, 118.14, 120.79, 122.10, 123.08, 123.44, 124.09, 129.82, 137.02, 138.41, 148.49, 153.01, 183.81 (-OCH₃), 184.97 (-OCH₃).

2-(2-(((1H-indol-3-yl)methylene)amino)thiazol-4-yl)phenol (6c): C₁₈H₁₃N₃OS; Yellowish orange solid; Yield: 90 %; Melting point: 162–164 °C; FT-IR(ν in cm⁻¹): 3307.92 (O-H), 3167.12 (N-H), 1610.56 (C=N); ¹H NMR(DMSO-d₆, 400 MHz, δ ppm): 7.289–7.307 (m, 2H, Ar-H), 7.532–7.549 (t, 1H, J=6.83Hz, Ar-H), 7.749–7.789 (t, 1H, J=7.82Hz, Ar-H), 8.191–8.224 (m, 2H, Ar-H), 8.433–8.452 (d, 1H, J=7.81Hz, Ar-H), 8.790 (s, 1H, -OH), 9.250 (s, 1H, imino-H), 12.210 (s, 1H, -NH); ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 112.39, 112.46, 113.65, 114.22, 120.16, 122.43, 124.54, 130.36, 131.96, 135.95, 137.48, 137.96, 148.37, 149.44, 159.35, 174.67 (C-OH); LC-MS: 319.07 (M⁺ ion peak).

N-((1H-indol-3-yl)methylene)-4-(4-fluorophenyl)thiazol-2-amine (7c): C₁₈H₁₂FN₃S; Pale yellow solid; Yield: 87 %; Melting point: 98–102 °C; FT-IR(ν in cm⁻¹): 3140.11 (N-H), 1627.92 (C=N); ¹H NMR(DMSO-d₆, 400 MHz, δ ppm): 7.077–7.247 (m, 9H, Ar-H), 7.526 (s, 1H, indole C₂-H), 8.104 (s, 1H, C₅-H), 8.294 (s, 1H, Ar-H), 8.910 (s, 1H,

imino-H), 9.948 (s, 1H, N-H); ¹³C NMR(DMSO-d₆, 100 MHz, δ ppm): 112.40, 114.30, 115.03, 118.13, 120.79, 122.11, 123.45, 124.08, 125.72, 127.45, 128.90, 137.01, 138.44, 171.14 (C-F); LC-MS: 322 (M+H peak).

Synthesis of 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines (1d–7d)

To the ethanolic mixture of the appropriate Schiff bases (1c–7c, 1 mmol) and p-chlorobenzaldehyde (1 mmol), ammonium acetate (1 mmol) was added and allowed to reflux in an oil bath at 90 °C. The reaction was monitored by TLC; it was observed that the cyclization was achieved within 3 h. The reaction mixture was poured into crushed ice, filtered, washed with water and dried.

4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-phenyl-2H-thiazolo[3,2-a][1,3,5]triazine (1d): C₂₅H₁₉ClN₄S; Brown solid; Yield: 62 %; Melting point: 116–118 °C; ¹H NMR(DMSO-d₆, δ ppm): 7.258–7.556 (m, 10H, Ar-H), 7.871 (s, 1H, C₆-H), 7.991–8.009 (d, 3H, J=7.34 Hz, Ar-H), 8.319 (s, 1H, N₅-H), 8.360–8.381 (m, 2H, Ar-H), 9.237 (1H, C₄-H), 12.169 (1H, indole-NH). ¹³C MMR (DMSO-d₆, 100 MHz, δ ppm): 101.45, 111.04, 112.42, 114.23, 120.79, 121.82, 121.96, 122.11, 123.49, 124.56, 125.49, 125.84, 127.14, 127.72, 127.91, 128.42, 128.71, 134.43, 134.89, 137.46, 137.51, 138.44, 151.94, 158.82. GC-MS: 442.62 (M⁺ ion peak); Elemental analysis: Calculated: C, 68.10; H,

Table 3 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (2c) in different solvents

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	326.1	402.8	0.3054	88.78	7500	0.00010	0.08	5839.22	0.33
Chloroform	325.8	406.1	0.1483	88.86	10,500	0.00014	0.10	6069.20	0.25
Dichloromethane	325.7	422.1	0.2171	88.89	7000	0.00009	0.08	7012.03	0.20
Ethylacetate	325.9	397.5	0.1996	88.83	8500	0.00011	0.09	5527.03	0.25
Methanol	319.1	406.1	0.3085	90.73	6000	0.00008	0.07	6713.66	0.51
DMSO	329.8	383.6	0.2634	87.78	8500	0.00011	0.09	4252.59	0.72
DMF	330.1	375.5	0.2744	87.70	13,000	0.00017	0.11	3662.69	0.29

Table 4 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (4c) in different solvents

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	326.1	389.7	0.3054	88.78	7500	0.00010	0.08	5004.68	0.33
Chloroform	325.7	385.7	0.1483	88.89	8500	0.00011	0.09	4776.21	0.21
Dichloromethane	325.9	377.3	0.2171	88.83	10,000	0.00013	0.10	4180.15	0.36
Ethylacetate	325.3	379	0.1996	89.00	9000	0.00012	0.09	4355.63	0.18
Methanol	319.8	388.3	0.3085	90.53	5000	0.00007	0.07	5516.26	0.54
DMSO	329.2	381.3	0.2634	87.94	9000	0.00012	0.09	4150.60	0.70
DMF	330	377.3	0.2744	87.73	9000	0.00012	0.09	3798.92	0.33

3.89; Cl, 8.04; N, 12.71; S, 7.27; Found: C, 67.80; H, 4.32; Cl, 8.01, N, 12.65; S, 7.22.

4, 6-bis(4-chlorophenyl)-2-(1H-indol-3-yl)-2H-thiazolo[3,2-a][1,3,5]triazine (2d): C₂₅H₁₈Cl₂N₄S; Yellow solid; Yield: 59 %; Melting point: 110–112 °C; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 7.065 (s, 1H, C₄-H), 7.184–7.283 (m, 5H, Ar-H), 7.396–7.417 (d, 2H, J=8.62Hz, Ar-H), 7.487–7.513(d, 2H, J=8.73Hz, Ar-H), 7.774–7.796 (d, 2H, J=8.908Hz, Ar-H), 7.915 (s, 1H, N₅-H), 7.987–8.085 (d, 2H, J=7.508Hz, Ar-H), 8.266–8.301 (m, 2H, Ar-H), 9.918 (s, 1H, C₄-H). ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 63.53, 102.35, 112.40, 118.13, 120.79, 122.10, 123.44, 124.08, 127.21, 128.47, 131.62, 133.40, 134.39, 137.02, 138.45, 147.96, 168.42. LC-MS: 474.3 (M-2H peak); Elemental analysis: Calculated: C, 63.16; H, 3.39; Cl, 14.92; N, 11.79; S, 6.74; Found: C, 62.91; H, 3.80; Cl, 14.86; N, 11.74; S, 6.70.

4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-(p-tolyl)-2H-thiazolo[3,2-a][1,3,5]triazine (3d): C₂₆H₂₁ClN₄S; Light brown solid; Yield: 49 %; Melting point: 148–150 °C; Yield: 49 %; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 2.301 (s, 3H, -CH₃), 6.803–7.509 (m, 10H, Ar-H), 7.736 (s, N₅-H), 7.802–7.851 (m, 2H, Ar-H), 8.266–8.333 (m, 2H, Ar-H), 9.187 (s, 1H, C₄-H), 12.125 (s, 1H, indole-NH). ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 21.18, 112.08, 118.90, 121.53, 122.46, 123.75, 124.52, 128.30, 129.03, 129.24, 129.40, 130.82, 136.66, 137.26, 150.54, 161.96, 185.10. GC-MS: 458.64(M+2H peak).

4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-(4-methoxyphenyl)-2H-thiazolo[3,2-a][1,3,5]triazine (4d):

C₂₆H₁₉ClN₄OS; Off white solid; Yield: 32 %; Melting point: 96–98 °C; LC-MS: 474.87 (M+2H peak); Elemental Analysis: Calculated: C, 66.30; H, 4.07; Cl, 7.53; N, 11.90; O, 3.40; S, 6.81; Found: C, 66.04; H, 4.48; Cl, 7.50; N, 11.84; O, 3.38; S, 6.76.

4-(4-chlorophenyl)-6-(3,4-dimethoxyphenyl)-2-(1H-indol-3-yl)-2H-thiazolo[3,2-a][1,3,5]triazine (5d): C₂₇H₂₃ClN₄O₂S; semisolid; Yield: 62 %; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 3.939(s, 6H, 2-OCH₃), 6.905 (s, 1H, C₄-H), 7.254–7.601 (m, 10H, Ar-H), 7.849 (s, 2H, N₅-H & C₆-H), 8.252–8.264 (d, 2H, J=5.509Hz, Ar-H), 9.995 (s, 1H, C₄-H), 11.276 (s, 1H, indole-NH). ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 55.95, 56.04, 110.86, 112.08, 118.91, 121.52, 121.85, 122.11, 122.46, 123.02, 123.77, 124.03, 124.51, 124.73, 128.48, 129.13, 129.53, 131.15, 136.67, 137.26, 138.68, 184.94, 185.10. LC-MS: 503.0 (M+H peak).

2-(4-(4-chlorophenyl)-2-(1H-indol-3-yl)-2H-thiazolo[3,2-a][1,3,5]triazin-6-yl)phenol (6d): C₂₅H₁₉ClN₄OS; Yellow solid; Yield: 58 %; Melting point: 92 °C (decomposes); Yield: 54 %; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 6.835–7.597 (m, 14H, Ar-H & C₄-H), 7.946 (s, 1H, N₅-H), 8.225 (s, 1H, C₄-H), 10.010 (s, 1H, indole-NH). ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 99.82, 117.08, 123.46, 126.15, 127.15, 128.48, 129.24, 133.17, 133.50, 135.25, 141.97, 142.11, 149.93, 152.66, 163.35, 189.34. LC-MS: 458.5 (M⁺ ion peak).

4-(4-chlorophenyl)-6-(4-fluorophenyl)-2-(1H-indol-3-yl)-2H-thiazolo[3,2-a][1,3,5]triazine (7d): C₂₅H₁₆ClFN₄S; Light brown solid; Yield: 52 %; Melting point: 86–88 °C; ¹H NMR

Table 5 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (5c) in different solvents

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	326.5	401.9	0.3054	88.67	4000	0.00005	0.06	5746.06	I _{abs} >1
Chloroform	326.6	394.6	0.1483	88.64	2000	0.00003	0.04	5276.37	I _{abs} >1
Dichloromethane	326.8	397.9	0.2171	88.59	3000	0.00004	0.05	5467.81	I _{abs} >1
Ethylacetate	325.9	391.4	0.1996	88.83	5000	0.00007	0.07	5134.95	I _{abs} >1
Methanol	321.8	406.6	0.3085	89.97	2500	0.00003	0.05	6481.01	I _{abs} >1
DMSO	330	432.6	0.2634	87.73	5000	0.00007	0.07	7186.99	0.68
DMF	331.1	435.9	0.2744	87.44	2000	0.00003	0.04	7261.31	I _{abs} >1

Table 6 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (6c) in different solvents

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	326.7	388.3	0.3054	88.62	7000	0.00009	0.08	4855.84	0.66
Chloroform	325.7	385.4	0.1483	88.89	7000	0.00009	0.08	4756.03	0.46
Dichloromethane	326	374.7	0.2171	88.81	8000	0.00011	0.09	3986.83	$I_{ems} > 1000$
Ethylacetate	326	379	0.1996	88.81	9000	0.00012	0.09	4289.62	0.34
Methanol	321.2	391.6	0.3085	90.13	3500	0.00005	0.06	5596.99	0.36
DMSO	330.2	4226.8	0.2634	87.68	9000	0.00012	0.09	27918.82	0.66
DMF	330.2	426.1	0.2744	87.68	8500	0.00011	0.09	6816.01	0.57

(DMSO-d₆, 400 MHz, δ ppm): 7.747–8.394 (m, 15H, Ar-H), 8.730 (s, 1H, N₅-H), 10.489 (s, 1H, C₄-H), 11.946 (s, 1H, indole-NH). ¹³C NMR (DMSO-d₆, 100 MHz, δ ppm): 94.57, 106.84, 109.67, 109.88, 113.53, 116.18, 117.10, 118.25, 118.41, 119.21, 123.41, 123.96, 124.10, 124.60, 125.00, 125.58, 131.48, 131.99, 179.92. LC-MS: 460.73 (M⁺ ion peak); Elemental Analysis: Calculated: C, 65.43; H, 3.51; Cl, 7.73; F, 4.14; N, 12.21; S, 6.99; Found: C, 65.35; H, 4.03; Cl, 7.76; N, 12.26; S, 7.00.

Results and Discussion

Synthesis

Retrosynthetically, 2-amino-4-substituted phenyl-1,3-thiazoles was identified as one of the precursors to obtain novel 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines. Preparation of α -bromoarylethanones and 2-amino-4-substituted phenyl-1,3-thiazole derivatives is shown in Scheme 1. To minimize the use of the hazardous brominating agents, potassium bromide-potassium bromate mixture was used for the regioselective bromination of acetophenones [18]. And, we found that the rate of bromination of acetophenone, p-chloro, p-fluoro, p-methoxy and o-hydroxyacetophenones were faster. 2-Amino-4-substituted phenyl-1,3-thiazoles (1b–7b) were achieved by the subsequent treatment of appropriate α -bromoarylethanones (1a–7a) with thiourea in ethanol under

ultrasonic bath at 45 °C, which resulted in better yield and purity without the use of any base catalyst within 20–35 min. Their physical data are represented in Table 1.

The (1H-indol-3-yl)methylene-4-substituted phenyl-thiazol-2-amines (1c–7c) were prepared by the condensation of indole-3-carbaldehyde with corresponding 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b) in ethanol on water bath within 30 min. Indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) were synthesized by the conjugate addition of ammonium acetate with Schiff bases (1c–7c), followed by the condensation of adducts with p-chlorobenzaldehyde as shown in Scheme 2. The better yield of the compounds (35–62 %) was achieved by using an oil bath at 90–110 °C using ethanol as the solvent. Schiff bases bearing unsubstituted phenyl ring and with electron withdrawing substituents (1c, 2c and 7c) at the phenyl ring were found to be more reactive, when compared to other compounds.

The structure of the resulting compounds was confirmed by their spectral analyses. FT-IR spectra of the α -bromoarylethanones (1a–7a) exhibit absorption band at 1660–1703 cm⁻¹ for CO stretching, 2943–2951 cm⁻¹ for CH stretching of CH₂Br and 775–812 cm⁻¹ for CH wagging of CH₂Br respectively. In ¹H NMR spectra of α -bromoarylethanones (1a–7a), the singlet peak at around 4.49–4.78 ppm corresponds to CH₂Br confirmed the successful regioselective bromination of acetophenones using the non-hazardous bromide-bromate mixture. Whereas, the disappearance of the singlet peak at around 4.49–4.78 ppm and the

Table 7 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (7c) in different solvents:

Solvent	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	326	388.1	0.3054	88.81	8000	0.00011	0.09	4908.29	0.24
Chloroform	325.7	384.8	0.1483	88.89	7500	0.00010	0.08	4715.58	0.22
Dichloromethane	326	374.8	0.2171	88.81	8500	0.00011	0.09	3993.95	0.32
Ethylacetate	325.6	376.5	0.1996	88.92	20500	0.00027	0.14	4152.11	0.06
Methanol	319.2	375.1	0.3085	90.70	8000	0.00011	0.09	4668.76	0.05
DMSO	329.9	383	0.2634	87.76	8500	0.00011	0.09	4202.56	0.66
DMF	330	367.8	0.2744	87.73	6000	0.00008	0.07	3114.34	0.53

Table 8 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (1d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	234.8	352.5	0.3054	123.30	173,500	0.00319	0.41	14,220.64	0.01
Chloroform	241.8	355.2	0.1483	119.73	111,000	0.00198	0.32	13,203.34	0.01
Dichloromethane	238	340.3	0.2171	121.64	96,500	0.00175	0.30	12,630.97	0.01
Ethylacetate	256.4	333.9	0.1996	112.91	101,000	0.00170	0.30	9052.47	0.09
Methanol	243.4	352.9	0.3085	118.94	148,500	0.00264	0.37	12,748.00	0.02
DMSO	264.9	340.5	0.2634	109.29	88,000	0.00144	0.28	8381.52	0.13
DMF	267.6	336.8	0.2744	108.19	96,500	0.00156	0.30	7678.00	0.04

appearance of the singlet peak at around 6.9–7.2 ppm corresponding to C₅-H in the ¹H NMR spectra of 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b) evidenced the thiazolization under ultrasonication. In FT-IR spectra of Schiff bases (1c–7c), the absorption bands at around 1627–1666 cm⁻¹ corresponding to –C=N clearly indicates the condensation had taken place. The formation of Schiff bases (1c–7c) was also confirmed by the observation of singlet peak of imino-H at around 8.91–9.24 ppm and the imino-C peak at around 159–174 ppm in their ¹H NMR and ¹³C NMR respectively. The addition of ammonium acetate and p-chlorobenzaldehyde with corresponding Schiff bases (1c–7c) yield the final products (1d–7d) as shown in Scheme 2. The formation of thiazolo-s-triazines was highly diastereoselective in favor of the *cis* isomers [20]. The corresponding molecular ion peaks in the mass spectra, NMR and elemental analyses results of compounds (1d–7d) were confirmed the formation of indol-3-yl-thiazolo-s-triazines. The maximum absorption wavelengths at 235–265 nm of compounds (1d–7d) also stood as an additional support for the confirmation of *cis* isomers, which are of high energy.

DPPH Radical Scavenging Assay

The radical scavenging activity of synthesized compounds against 2, 2-diphenyl-2-picryl hydrazyl hydrate (DPPH) was determined by using Brand-Williams et al. 1995 method [21]. Ascorbic acid was used as a standard. The reaction mixture

contains 0.4 mL of 1 mmol freshly prepared DPPH, different volume (80, 160, 240, 320 and 400 μL) of a 1 mg/mL solution of the compounds and the required volume of ethanol to make the whole mixture to 4 mL. A blank was prepared without the addition of the samples. The reaction mixtures were kept in the dark at room temperature for 30 min. The change in color (from violet to yellow) was observed, and their absorbance was measured at 517 nm by using UV–Vis spectrophotometer. Lower the absorbance of the mixture indicates the higher radical scavenging activity. Radical scavenging activity was calculated by using the following equation:

$$\% \text{ Inhibition} = \frac{(AB-AS)}{AB} \times 100$$

Where AB – Absorbance of blank sample (t=0 min); AS – Absorbance of test samples (t=30 min).

The antioxidant property of 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b), indole-3-carbaldehyde Schiff bases (1c–7c) and indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) were carried out against DPPH radical. The results indicating that Schiff bases (1c–7c) have good antioxidant property, the thiazoles (1b–7b) and indol-3-ylthiazolo-s-triazines (1d–7d) have moderate. Out of all these, compounds (4c–6c & 4d–6d) with electron donating substituents have shown better activity. The order of reactivity of these antioxidants based on their substituents is OH>OCH₃>F>CH₃>Cl>H. The graphical representation of antioxidant results is represented in Fig. 1.

Table 9 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (2d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	234.5	360.9	0.3054	123.46	173,500	0.00320	0.40	14935.42	0.01
Chloroform	239.8	348.8	0.1483	120.73	175,500	0.00316	0.40	13031.69	0.00
Dichloromethane	235.9	340.8	0.2171	122.73	152,500	0.00279	0.37	13048.12	0.00
Ethylacetate	256.5	339.4	0.1996	112.87	100,500	0.00169	0.30	9522.60	0.09
Methanol	243.9	366	0.3085	118.70	149,500	0.00265	0.37	13678.01	0.03
DMSO	295.7	342.3	0.2634	97.91	88,500	0.00129	0.28	4603.92	0.19
DMF	297.9	338.8	0.2744	97.18	96,500	0.00140	0.30	4052.37	0.07

Table 10 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (3d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	230.5	345.3	0.3054	125.60	189,500	0.00355	0.42	14,423.62	0.00
Chloroform	258.3	335.4	0.1483	112.08	182,500	0.00305	0.41	8,899.53	0.00
Dichloromethane	254.5	335.4	0.2171	113.76	152,000	0.00258	0.37	9,477.58	0.00
Ethylacetate	258.8	327.2	0.1996	111.87	99,000	0.00165	0.30	8077.53	0.06
Methanol	268.7	345.3	0.3085	107.74	149,500	0.00240	0.37	8255.90	0.00
DMSO	293.1	338.3	0.2634	98.78	143,500	0.00212	0.36	4558.49	0.05
DMF	299.1	332.2	0.2744	96.79	72,000	0.00104	0.26	3331.29	0.04

Absorption and Emission Behavior of Compounds (1c–7c & 1d–7d) in Different Solvents

As a preliminary work, absorption and fluorescence spectra were recorded for 2-amino-4-substituted phenyl-1,3-thiazoles (1b–7b), Schiff bases (1c–7c) and indol-3-ylthiazolo[3,2-a][1,3,5]triazines (1d–7d). Among them, Schiff bases (1c–7c) and indol-3-ylthiazolo[3,2-a][1,3,5]triazines (1d–7d) were excited and studied the absorption and emission behavior of these compounds (1×10^{-5} mol/dm⁻³) in different solvents such as acetonitrile, chloroform, dichloromethane, methanol, ethyl acetate, dimethylsulfoxide (DMSO) and dimethylformamide (DMF). Maximum wavelength absorption peaks (λ_{max}) around 234–360 nm and fluorescence emission peaks (λ_{max}) around 330–435 nm were observed respectively. The conjugation in these compounds caused the bathochromic shifts in the emission spectra. Due to the strong electron-donating ability of the hydroxyl group at the *ortho* position, compound (6c) has shown high fluorescence intensity. Compound (3c) with methyl group in the phenyl ring was not shown fluorescence emission, whereas other Schiff bases (1c–7c) were shown better fluorescence emission than indol-3-ylthiazolo[3,2-a][1,3,5]triazines (1d–7d). All compounds were red shifted due to the better stabilization of the molecules in the first excited state with increasing the polarity of the solvents. The maximum emission wavelength of compounds (1c–7c) was observed in dichloromethane at 374.1–429.1 nm and compounds (1d–7d) in methanol at 354–391 nm. The calculated physiochemical parameters from the absorption and emission spectra were

tabulated in (Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14). It was found that indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) have higher molar extinction coefficients than Schiff bases (1c–7c). The spectral data indicate that the polarity of the solvent has a significant effect on absorption maxima. As the polarity of the solvent increases, the fluorescence emission of the compounds shifted to the longer wavelength (red shift) due to the intramolecular charge transfer (ICT) in the singlet excited state from electron donating groups to the electron acceptor groups in the compounds [22]. This indicates that the polarity of the compounds was raised at their singlet excited state as the polarity of the solvent increases.

The red shift of the compounds in different solvents depends upon the difference in the dipole moment between the excited singlet and the ground state of the chromophores [23]. This difference in the dipole moment can be determined using the simplified Lippert-Mataga equation [24] as follows:

$$\Delta \bar{\nu}_{st} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + \text{constant} \quad (1)$$

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

Where $\Delta \bar{\nu}_{st}$ is the Stokes shift, which increases with increasing the polarity of the solvent counted to stronger stability in the excited state in polar solvents, h is Planck's constant ($h = 6.6256 \times 10^{-27}$ ergs), c is the velocity of light in vacuum ($c = 2.9979 \times 10^8$ m/s) and a is the radius of the cavity in which the fluorophore resides. Parameters n and ϵ in (Eq. 2) denotes

Table 11 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (4d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	246.4	354.1	0.3054	117.50	178,500	0.00313	0.40	12,343.81	0.01
Chloroform	254.8	354.9	0.1483	113.62	195,000	0.00331	0.42	11,069.52	0.00
Dichloromethane	249.8	339.7	0.2171	115.90	171,000	0.00296	0.40	10,594.29	0.00
Ethylacetate	262.1	330.5	0.1996	110.46	143,500	0.00237	0.36	7896.19	0.05
Methanol	249.2	354.9	0.3085	116.18	171,000	0.00296	0.40	11,951.46	0.00
DMSO	261.1	340	0.2634	110.88	90,000	0.00149	0.29	8887.74	0.13
DMF	265.4	333.7	0.2744	109.08	108,500	0.00177	0.31	7711.94	0.05

Table 12 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (5d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	230.2	354.8	0.3054	125.76	167,500	0.00314	0.39	15,255.59	0.02
Chloroform	237.8	356.8	0.1483	121.75	171,500	0.00312	0.40	14,025.24	0.00
Dichloromethane	235.8	342.1	0.2171	122.78	154,000	0.00282	0.38	13,177.60	0.01
Ethylacetate	262	333.3	0.1996	110.50	144,500	0.00238	0.36	8164.94	0.04
Methanol	241.8	356.6	0.3085	119.73	131,500	0.00235	0.35	13,313.87	0.00
DMSO	297.6	340	0.2634	97.28	107,500	0.00156	0.31	4190.39	0.16
DMF	294	336.1	0.2744	98.47	242,000	0.00356	0.47	4260.56	0.02

the refractive index and the dielectric constant of the solvent respectively.

From the absorption and emission spectra, Stokes shift was calculated and tabulated in (Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14) using the (Eq. 3) [24].

$$\Delta \bar{\nu}_{st} = \bar{\nu}_{ex} - \bar{\nu}_{em} \tag{3}$$

where $\bar{\nu}_{ex}$ and $\bar{\nu}_{em}$ are the wavenumbers of absorption and emission maxima (cm⁻¹) respectively. The negative value (in Tables 15 and 16) of the difference in the dipole moment ($\Delta\mu$) for the compounds indicates the high polarity of the compounds in the ground state than in the singlet excited state. The oscillator strength (f) provides the absorption area of the electronic spectrum defines the effective number of dispersion electrons between ground and excited states oscillating with the corresponding frequency (ν). The oscillator strength of the compounds in different solvents was calculated using the following (Eq. 4):

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu} \tag{4}$$

where ϵ is the extinction coefficient (L Mol⁻¹cm⁻¹) and $\bar{\nu}$ represents the wavenumber in cm⁻¹. In addition, the transition dipole moment (μ in Debye) of the compounds in different solvents was calculated using the following equation [25].

$$\mu = \sqrt{\frac{f}{4.72 \times 10^{-7} \times E_{max}}} \tag{5}$$

where E_{max} is the maximum energy of absorption in cm⁻¹. It has been obviously observed the polarity of the solvent have a significant effect on the emission spectra indicating the strong polarity of the compounds in the ground state than in the singlet excited site with increasing the polarity of the solvents. The red shifts in the emission spectra increases as the polarity of the solvent increases from DCM to DMSO. The empirical Dimroth polarity value was calculated based on the below relation [26].

$$E_T = \frac{28,591}{\lambda_{max}} \tag{6}$$

where λ_{max} is the peak wavelength of the compounds in the absorption spectra. Optical band gap (E_g) was calculated from the longest absorption wavelength (λ_{onset}) of their UV absorption spectra according to the following equation [27].

$$E_g = \frac{1242}{\lambda_{onset}} \tag{7}$$

Fluorescence quantum yield (Φ_f) of the compounds (1c–7c & 1d–7d) was measured by the relative comparison procedure using quinine sulfate ($\Phi_f=0.546$, in 0.5 M H₂SO₄) as reference [28]. Relative quantum yield was determined using the equation:

$$\Phi_f = 0.546 \times \left(\frac{I_{ref}}{I_{sample}}\right) \times \left(\frac{A_{sample}}{A_{ref}}\right) \times \left(\frac{R_{sample}}{R_{ref}}\right) \tag{8}$$

Where, ref and sample corresponds to reference and sample respectively. Φ_f is the fluorescence quantum yield, I is the

Table 13 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (6d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	248.7	357.8	0.3054	116.41	185,500	0.00322	0.41	12,260.51	0.01
Chloroform	254.3	357.7	0.1483	113.85	214,500	0.00364	0.44	11,367.25	0.00
Dichloromethane	251.2	391.7	0.2171	115.25	183,000	0.00315	0.41	14,279.18	0.01
Ethylacetate	257.9	339	0.1996	112.26	130,000	0.00218	0.34	9276.19	0.05
Methanol	246	391.7	0.3085	117.69	166,000	0.00292	0.39	15,120.66	0.01
DMSO	260	341.2	0.2634	111.35	68,000	0.00113	0.25	9153.21	0.25
DMF	283.1	341.1	0.2744	102.26	121,000	0.00185	0.33	6006.29	0.11

Table 14 Physiochemical parameters and fluorescence quantum yield (Φ_f) of compound (7d) in different solvents

Solvents	λ_{ab} (nm)	λ_{em} (nm)	Δf	E_T (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	f	μ (Debye)	$\Delta \bar{\nu}$ (cm ⁻¹)	Φ_f
Acetonitrile	229.8	356.2	0.3054	125.98	184,000	0.00346	0.41	15,441.99	0.01
Chloroform	243	359.2	0.1483	119.14	158,500	0.00282	0.38	13,312.62	0.00
Dichloromethane	238.4	341.2	0.2171	121.44	177,000	0.00321	0.40	12,637.99	0.00
Ethylacetate	256.3	342	0.1996	112.96	110,000	0.00185	0.32	9777.01	0.05
Methanol	244.1	354.2	0.3085	118.60	166,500	0.00295	0.39	12,734.18	0.00
DMSO	268.2	343	0.2634	107.95	106,000	0.00171	0.31	8131.09	0.06
DMF	283.8	342.5	0.2744	102.01	185,000	0.00282	0.41	6039.00	0.01

Table 15 Change in $\Delta\mu$ of compounds (1c–7c) in different solvents

Compound	Acetonitrile	Chloroform	Dichloromethane	Ethylacetate	Methanol	DMSO	DMF	Average $\Delta\mu$
1c	-1.25	-1.50	-1.86	-1.04	-1.98	-3.44	-1.79	-1.84
2c	-4.33	-4.02	-2.92	-4.08	-3.78	-6.79	-4.23	-4.31
4c	-3.87	-3.21	-4.72	-3.63	-3.86	-6.43	-4.25	-4.28
5c	-4.28	-4.28	-4.21	-4.22	-4.31	-4.48	-4.60	-4.34
6c	-6.21	-4.95	-8.13	-5.48	-3.33	-5.83	-6.62	-5.79
7c	-3.35	-3.07	-3.81	-2.93	-2.03	-6.28	-4.21	-3.67

absorbance intensity of UV–Vis spectra, A is the area under the emission peak and R is the refractive index of the solvent. The dilute solutions of the compounds with absorbance below 1 at and above excitation wavelength of intensity below 1000 were used. Quinine sulfate in 0.1 M H₂SO₄ was used as a reference. The fluorescence quantum yield of Schiff bases (2c–7c) was comparatively higher than indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) and varied with solvents. Schiff bases (2c–7c) have shown fluorescence quantum yield of 0.20–0.36 in case of acetonitrile, chloroform and dichloromethane and 0.33–0.72 in case of DMSO and DMF. Indol-3-yl-thiazolo[3,2-a][1,3,5]triazines have shown 0.01–0.13 fluorescence quantum yield in all organic solvents. Though indol-3-yl-thiazolo[3,2-a][1,3,5]triazines have large molar extinction co-efficient, but the reason for their lower quantum yield cannot be resolved. On excitation, the strong basic (–N=) and strong acidic (p-chlorophenyl) moieties involved in

excited state intramolecular proton transfer (ESIPT) leads to small fluorescence quantum yield. On the other hand, the fluorescence quantum yield is directly proportional to the intensity of the emission spectra. It is concluded that the low fluorescence quantum yield of indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) was due to their low intense fluorescence emission peaks.

Cyclic Voltammetry

The electrochemical behavior of the Schiff bases (1c–7c) and indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) was determined by cyclic voltammetry (CV) using a standard three-electrode cell in HPLC acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The working electrode was glassy carbon, the counter electrode used a platinum wire and the

Table 16 Change in $\Delta\mu$ of compounds (1d–7d) in different solvents

Compound	Acetonitrile	Chloroform	Dichloromethane	Ethylacetate	Methanol	DMSO	DMF	Average $\Delta\mu$
1d	-0.98	-0.54	-0.71	-2.47	-1.12	-2.76	-1.69	-1.47
2d	-0.88	-0.43	-0.52	-2.48	-1.20	-3.20	-1.94	-1.52
3d	-0.52	-0.07	-0.10	-2.17	-0.34	-2.22	-1.42	-0.98
4d	-0.53	-0.07	-0.14	-1.97	-0.11	-2.72	-2.00	-1.08
5d	-1.35	-0.26	-0.72	-1.89	-0.31	-3.60	-1.82	-1.42
6d	-0.49	0.09	-0.59	-1.57	-0.64	-2.99	-2.45	-1.23
7d	-0.58	-0.17	-0.47	-1.67	-0.23	-1.87	-0.71	-0.82

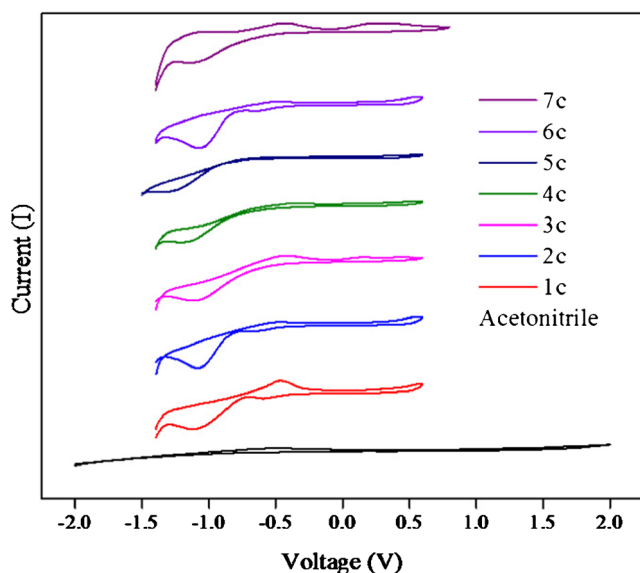


Fig. 2 Cyclic Voltammetry plots of Schiff bases (1c–7c)

reference electrode was a standard calomel electrode (SCE). The solutions were purged with nitrogen gas for 5 min before recording the electrochemical data at a scan rate of 100 mV/s.

From the cyclic voltammograms Fig. 2, irreversible wave in the reduction side was observed in the case of Schiff bases and the indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) have not shown considerable peaks. The irreversible reduction peak of Schiff bases (1c–7c) demonstrates the instability of the indolyl radical after one electron transfer, which evolves the dimerization reaction. From Fig. 2, it was found that the presence of the electron donating hydroxyl group at the *ortho* position of the phenyl ring in compound (6c) shown the strong reduction peak and the electron withdrawing chloro group at the *para* position of the phenyl ring in compound (3c) shown weak reduction peak. According to CV measurements, the Schiff bases showed cathodic peaks at around -1.08 to -1.18 V. Ferrocene was used as reference to calculate the HOMO and LUMO energy levels by measuring the redox potentials, including the ferrocene value

of -4.4 eV. The energy levels were calculated using the following equations [29].

$$E(\text{HOMO}) = -[E_{\text{ox(onset)}} + 4.4] \text{eV} \quad (9)$$

$$E(\text{LUMO}) = -[E_{\text{red(onset)}} + 4.4] \text{eV} \quad (10)$$

The onset reduction potential of the Schiff bases around -0.80 to -0.87 V gives the LUMO energies of -3.43 to -3.63 eV as summarized in the Table 17. The irreversible reduction peak suggests that the least possibility of the regeneration of the Schiff bases.

Conclusion

In summary, we have successfully achieved the synthesis of 4-(4-chlorophenyl)-2-(1H-indol-3-yl)-6-substituted phenyl-2H-thiazolo[3,2-a][1,3,5]triazines (1d–7d) starting from various substituted acetophenones (1–7) through the intermediate indole-3-carbaldehyde Schiff bases (1c–7c). Higher yields, less reaction time and the purity of the compounds were attractive in the whole synthesis. Their structures were confirmed by FT-IR, mass spectrum, NMR and elemental analyses. The compounds (1c–7c & 1d–7d) were identified as good antioxidants. The UV–Vis and fluorescence spectra were recorded for the Schiff bases (1c–7c) and indol-3-ylthiazolo[3,2-a][1,3,5]triazines (1d–7d) in seven solvents of differing polarities. Comparison on the fluorescence spectra of Schiff bases (1c–7c) and indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) revealed that Schiff bases have shown high intense fluorescence emission peaks. The physiochemical parameters and fluorescence quantum yield of compounds (1c–7c & 1d–7d) in different solvents were calculated. The indol-3-yl-thiazolo[3,2-a][1,3,5]triazines (1d–7d) possessed higher molar extinction coefficient than Schiff bases (1c–7c). The high intensity peak in the fluorescence emission spectra of Schiff bases (1c–7c) featuring for a high fluorescence quantum yield. Among all these, compound (6c) has emerged as the best

Table 17 Electrochemical properties of Schiff bases (1c–7c)

Compound	$E_{\text{red}}(\text{V})$	$E_{\text{oxd}}(\text{V})$	${}^{\text{a}}E_{\text{red onset}}(\text{V})$	${}^{\text{b}}E_{\text{oxd onset}}(\text{V})$	LUMO (eV)	HOMO (eV)	E_{g} (eV) from CV	${}^{\text{c}}E_{\text{g}}(\text{eV})$
1c	-1.11	-0.47	-1.27	-0.16	-3.13	-4.24	1.11	3.62
2c	-1.09	-0.47	-1.31	-0.14	-3.09	-4.26	1.17	3.64
3c	-1.11	-0.43	-1.29	-0.19	-3.11	-4.21	1.10	3.62
4c	-1.12	-0.34	-1.38	-0.20	-3.02	-4.20	1.18	3.63
5c	-1.30	–	-1.46	–	-2.94	–	–	3.65
6c	-1.08	-0.48	-1.30	-0.31	-3.10	-4.09	0.99	3.64
7c	-1.06	-0.44	-1.22	-0.21	-3.18	-4.19	1.01	3.65

^a Estimated from the onset reduction potential

^b Estimated from the oxidation potential

^c Estimated from UV absorption spectra

antioxidant and fluorescent material with high quantum yield (0.72). The conjugation in the Schiff bases influences their optical and electrochemical properties. The cathodic values of the reduction potential wave in the cyclic voltammetry evidences the Donor- π -Acceptor (D- π -A) systems in the Schiff bases. These results would be helpful to design a new type of donor-acceptor systems, which influences their photoconductivity towards the performances in dye-sensitized solar cells (DCSS's) and other photoelectronic applications.

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