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Synthesis, characterization and photophysical properties of novel thiazole substituted pyridine derivatives

Manjusha Suryawanshi[a], Varsha Gujar[b], Divya Ottoor[b] & Vivek Bobade*[a]
[a] Department of Chemistry, H.P.T Arts & R. Y. K. Science College, Nashik 422 005, India
[b] Department of Chemistry, Savitribai Phule Pune University, Pune 411 007, India
E-mail: v_bobade31@rediffmail.com

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Three series of isomeric 2-pyridyl 4-aryl thiazoles have been synthesized by reacting 2/3/4-pyridine thioamides derived from the corresponding nitriles with various 4-substituted phenacyl bromides using Hantzsch thiazole synthesis. Amongst the three isomeric series, 2-pyridyl and 4-pyridyl isomers are found to exhibit better photophysical properties than 3-pyridyl series. 4-Pyridyl isomer with methoxy substituent on phenyl ring is found to exhibit high luminescence quantum yield. The relationship between the structure and the photophysical properties have been studied using DFT calculations.

Keywords: Hantzsch synthesis, photo physical properties, quantum yield, DFT

Fluorescent dyes are widely used for detection and monitoring in the fields of chemistry, biochemistry, molecular biology, medicine and material sciences. Due to sensitive and selective detection methods and un-problematic toxicology, they have almost completely replaced radioactive tags. Widely used representatives include dansyl chloride, fluoresceins, rhodamines and boron-dipyrromethenes (BODIPYs) [1]. Molecular probes are widely used tools in chemical biology that allow tracing of bioactive metabolites and selective labelling of proteins and other bio-macro-molecules. A successful class of fluorophores used for probing in life science comprises the heterocyclic thiazoles. This structural element can be found in commercial products, such as thiazole orange, SYBR® Green I or TOTO®, which are used for DNA labelling. In these compounds the thiazole ring is part of a benzothiazole. Based on the luminescent properties of pyridyl-thiazoles, the synthesis of BPT (4-(3-azidopropoxy)-5-(4-bromophenyl)-2-(pyridin-2-yl)thiazole) with superior fluorescence properties have been reported[2].

1,3-Azoles are an important scaffold for providing fluorescent molecules due to presence of acceptor imine linkage and dative heteroatom that can be used in chemosensors[3,4]. Recently, these π-functional materials[5] are of increasing interest for the studies of organic electronics, such as organic photovoltaic's (OPVs), organic field effect transistors (OFETs) and organic light-emitting diodes (OLEDs). Symmetrical / asymmetrical thiazole based heterocyclic aromatic fluorescent compounds with high thermal stability and good solubility, where various electron donating and electron-withdrawing terminal groups have been reported[6]. Incorporation of electron-donating and withdrawing groups at appropriate positions of monocyclic hetero-aromatic compounds provides D-A molecules[7]. Increasing attention has been paid to fluorescent 1,3-imidazoles[8], oxazoles[9] and thiazoles[10].

The literature revealed that the pyridine containing thiazole derivatives showing fluorescent properties are mainly 2,5-diaryl / heteroaryl substituted, where the conjugation effect is clearly observed due to linear structure. We report herein the synthesis and characterization of 2-pyridyl, 4-aryl-thiazole, where such conjugation is partly observed due to nonlinearity in the structure and relative findings of the effect of change in position from 5 to 4 of the thiazole ring on photo physical properties.

Abbreviations: BODIPYs: Boron-dipyrromethenes; BPT: 4-(3-Azidopropoxy)-5-(4-bromophenyl)-2-(pyridin-2-yl)thiazole; ICT: Intramolecular charge transfer; OFETs: Organic Field Effect Transistors; OLEDs: Organic Light-Emitting Diodes; OPVs: Organic Photovoltaics; Q-TOF: Quadrupole Time Of Flight.

Experimental Section

General Remarks

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected.

All the reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F254 (mesh); spots were visualized with UV light. Merck silica gel (60-120 mesh) was used for column chromatography. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer in $CDCl_3$/DMSO-d_6 solution using tetramethylsilane as an internal standard. All chemical shifts were recorded in δ (ppm) and the following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet. The mass spectra were recorded on Waters, Q-TOF Micromass /ESI-MS at 70eV.

Spectrophotometric measurements

UV–Vis absorbance measurements were performed using UVPC-39 Shimadzu spectrophotometer. Fluorescence and relative fluorescence quantum yield data were obtained on JASCO FP 8300 spectrofluorometer, equipped with a xenon lamp (150 W) as the source. Scan speed of 1000 nm s^{-1} was maintained for all measurements. The slit width for both excitation and emission was kept at 5 nm. Concentrations of samples were kept constant at 2.5 × 10^{-6}M for all the experiments.

General procedure for the synthesis of isomeric pyridine thioamides 2,3,4

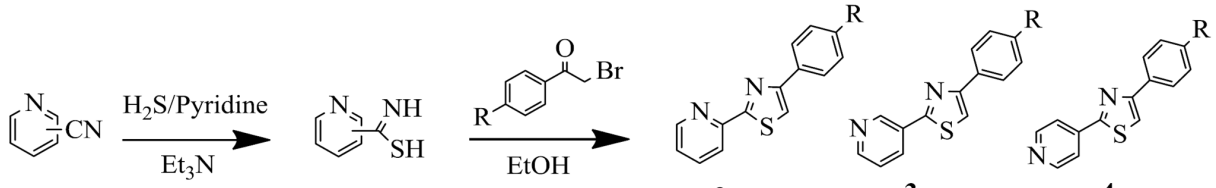
A solution of pyridine carbonitrile **1** (Scheme I) (5 g/5 mL) in pyridine (15 mL) and triethyl amine (3 mL) was stirred for 15 min. H_2S gas was then passed into the reaction mixture. The reaction was monitored on TLC. After stirring for about 2 h the solution turned into a greenish yellow solid. On completion of the reaction, the mixture was poured into crushed ice, the crude product was filtered and washed extensively with water. The product was re-crystallized from ethanol to obtain pure product. Yield: 80-90%.

General procedure for the synthesis of isomeric 4-phenylthiazol-2-pyridyl derivatives 2a-h/3a-h/4a-h

To a solution of pyridine thioamide **2/3/4** (1 g,7.2 mmol) in ethyl alcohol (4 mL), 4-substituted phenacyl bromide (7.2 mmol) was added and the reaction was refluxed for 3 h. After the completion of the reaction, as monitored on TLC, the reaction mixture was poured in cold water. The solid product obtained was filtered, washed with water, dried and purified by column chromatography using hexane: ethyl acetate as eluent.

4-Phenyl-2-(pyridin-2-yl) thiazole, 2a: Yield 87%. Yellowish green, m.p.198°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.09 (m, 1H, phenyl), 7.10-7.12 (dd, *J* = 8.0 and 7.6 Hz, 2H, phenyl), 7.33-7.34 (ddd, *J* = 7.8, 4.6 and 1.0 Hz, 1H, pyridine), 7.42 (s, 1H, thiazole), 7.76-7.79 (dt, *J* = 1.0 and 7.8 Hz, 1H, pyridine), 7.85-7.86 (dd, *J* = 8.0 and 2.3 Hz, 2H, phenyl), 8.10-8.20 (dd, *J* = 7.8 and 1.0 Hz, 1H, pyridine), 8.33-8.34 (dd, *J* = 4.6 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.80, 117.29, 117.40, 121.90, 125.60, 129.02, 129.12, 139.06, 146.36, 151.43, 157.70, 164.20.

4-(4-Fluorophenyl)-2-(pyridin-2-yl) thiazole, 2b: Yield 89%. Green, m.p.114°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.16 (dd, *J* = 10.6 and 8.0 Hz, 2H, phenyl), 7.32-7.36 (dd, *J* = 7.6, 4.8 and 1.0 Hz, 1H,



R		R		R	
H	2a	H	3a	H	4a
F	2b	F	3b	F	4b
Cl	2c	Cl	3c	Cl	4c
Br	2d	Br	3d	Br	4d
Me	2e	Me	3e	Me	4e
OMe	2f	OMe	3f	OMe	4f
CN	2g	CN	3g	CN	4g

Scheme I — Synthesis of 2-pyridyl-4-phenyl thiazoles

pyridine), 7.53 (s, 1H, thiazole), 7.80-7.85 (dt, *J* = 1.0 and 7.6 Hz, 1H, pyridine), 7.95-7.99 (dd, *J* = 8.0 and 7.4 Hz, 2H, phenyl), 8.30-8.32 (dd, *J* = 7.9 and 1.0 Hz, 1H, pyridine), 8.62-8.63 (dd, *J* = 4.8 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.86, 115.58, 115.66, 115.79, 119.86, 124.59, 128.06, 128.14, 128.35, 137.07, 149.48, 155.67, 158.12; ESI-MS: *m/z* (70 eV): 257.0612 [M+1].

4-(4-Chlorophenyl)-2-(pyridin-2-yl) thiazole, 2c: Yield 81%. Light Brown, m.p.136°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.16 (d, *J* = 7.8 Hz, 2H, phenyl), 7.42-7.45 (ddd, *J* = 7.6, 4.4 and 1.0 Hz, 1H, pyridine), 7.59 (s, 1H, thiazole), 7.86-7.87 (dt, *J* = 1.0 and 7.6 Hz, 1H, pyridine), 7.91-7.94 (d, *J* = 7.8 Hz, 2H, phenyl), 8.33-8.34 (dd, *J* = 7.6 and 1.0 Hz, 1H, pyridine), 8.65-8.66 (dd, *J* = 4.4 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.86, 117.29, 118.35, 122.29, 126.77, 130.45, 132.39, 140.87, 149.38, 152.24, 158.43, 165.16.

4-(4-Bromophenyl)-2-(pyridin-2-yl) thiazole, 2d: Yield 52%. Cream, m.p. 132°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.17 (d, *J* = 7.7 Hz, 2H, phenyl), 7.46-7.47 (ddd, *J* = 7.5, 4.2 and 1.0 Hz, 1H, pyridine), 7.60 (s, 1H, thiazole), 7.87-7.88 (dt, *J* = 1.0 and 7.5 Hz, 1H, pyridine), 7.9-7.92 (d, *J* = 7.7 Hz, 2H, phenyl), 8.34-8.35 (dd, *J* = 7.5 and 1.0 Hz, 1H, pyridine), 8.64-8.65 (dd, *J* = 4.2 and *J* = 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.72, 117.08, 118.14, 121.18, 125.60, 129.39, 131.28, 138.26, 148.23, 150.00, 157.22, 164.05.

2-(Pyridin-2-yl)-4-(p-tolyl) thiazole, 2e: Yield 73%. Yellow, m.p. 110°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98-7.0 (d, *J* = 8.4 Hz, 2H, phenyl), 7.30-7.31 (ddd, *J* = 7.0, 4.4 and 1.0 Hz, 1H, pyridine), 7.56 (s, 1H, thiazole), 7.79-7.83 (dt, *J* = 1.0 and 7.9 Hz, 1H, pyridine), 7.92-7.94 (d, *J* = 8.4 Hz, 2H, phenyl), 8.31-8.33 (dd, *J* = 7.9 and 1.0 Hz, 1H, pyridine), 8.62-8.64 (dd, *J* = 4.4 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.32 (-CH_3), 113.50, 114.20, 119.80, 124.31, 125.51, 125.61, 135.82, 148.30, 150.40, 155.39, 158.20, 166.90.

4-(4-Methoxyphenyl)-2-(pyridin-2-yl) thiazole, 2f: Yield 90%. Dark yellow, m.p. 108°C. ^{1}H NMR (400MHz, $CDCl_3$): δ 6.96-6.99 (d, *J* = 8.8 Hz, 2H, phenyl), 7.29-7.32 (ddd, *J* = 7.7, 4.8 and 1.1 Hz, 1H, pyridine), 7.45 (s, 1H, thiazole), 7.78-7.82 (dt, *J* = 1.1 and 7.7 Hz, 1H, pyridine), 7.91-7.93 (d, *J* = 8.8 Hz, 2H, phenyl), 8.30-8.32 (dd, *J* = 7.7 and 1.1 Hz, 1H, pyridine), 8.60-8.62 (dd, *J* = 4.8 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.10 (–OMe), 113.60, 114.14, 119.85, 124.43, 127.51, 127.66, 136.99, 149.44, 151.55, 156.50, 159.72, 168.61; ESI-MS: *m/z* (70 eV): 269.0817 [M+1].

4-(2-(Pyridin-2-yl) thiazol-4-yl) benzonitrile, 2g: Yield 93%. White, m.p. 168°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.22 (d, *J* = 7.9 Hz, 2H, phenyl), 7.43-7.44 (ddd, *J* = 7.2, 4.3 and 1.0 Hz, 1H, pyridine), 7.86 (s, 1H, thiazole), 7.78-7.79 (dt, *J* = 1.0 and 7.2 Hz, 1H, pyridine), 8.00-8.10 (d, *J* = 7.9 Hz, 2H, phenyl), 8.20-8.21 (dd, *J* = 7.2 and 1.0 Hz, 1H, pyridine), 8.65-8.66 (dd, *J* = 4.3 and 1.0 Hz, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.02, 114.25, 115.27, 118.70 (-CN), 124.07, 129.12, 129.24, 138.17, 146.2, 151.25, 157.06, 164.23.

4-Phenyl-2-(pyridin-3-yl) thiazole, 3a: Yield 98%. Buff white, m.p. 270°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-8.00 (m, 1H, pyridine), 8.00-8.10 (d, *J* = 8.0 Hz, 2H, phenyl), 8.00-8.40 (m, 1H, pyridine), 8.00-8.90(d, *J* = 8.0 Hz, 2H, phenyl), 8.27(s, 1H, Thiazole), 8.50-8.80 (m, 1H, phenyl), 8.97(m, 1H, pyridine), 9.51(m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.00, 122.00, 128.00, 128.00, 131.50, 132.00, 139.00, 142.10, 144.10, 155.10, 157.10, 161.10.

4-(4-Fluorophenyl)-2-(pyridin-3-yl) thiazole, 3b: Yield 82%. White, m.p. 120°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.74 (m, 1H, pyridine), 8.30-8.50 (m, *J* = 8.0 Hz, 2H, phenyl), 8.40 (m, 1H, pyridine), 8.70 (s, 1H, Thiazole), 7.90-8.00 (m, *J* = 8.0 Hz, 2H, phenyl), 8.70-8.80 (m, 1H, pyridine), 9.10 (m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.00, 120.78, 121.00, 127.10, 128.10, 130.92, 131.00, 132.10, 139.70, 140.10, 144.40, 155.10, 156.40, 162.00, 164.45.

4-(4-Chlorophenyl)-2-(pyridin-3-yl) thiazole, 3c: Yield 69%. Light yellow, m.p.244°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.50 (d, *J* = 8.0 Hz, 2H, phenyl), 8.20-8.40 (d, *J* = 8.0 Hz, 2H, phenyl), 8.30 (s, 1H, thiazole), 8.03 (m, 1H, pyridine), 8.00-8.10 (m, 1H, pyridine), 8.40-8.80 (m, 1H, pyridine), 9.30 (m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.00, 120.00, 128.00, 129.80, 131.00, 133.40, 138.10, 142.00, 143.50, 154.94, 156.10, 161.00.

4-(4-Bromophenyl)-2-(pyridin-3-yl) thiazole, 3d: Yield 48%. Light Brown, m.p. 226°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.62 (d, *J* = 8.5 Hz, 2H, phenyl), 8.00-8.05 (d, *J* = 8.5 Hz, 2H, phenyl), 8.06-8.09 (m, 1H, pyridine), 8.27(s, 1H, thiazole), 8.92-

8.94 (m, 1H, pyridine), 8.97 (m, 1H, pyridine), 9.51(m, 1H, pyridine); ^{13}C NMR (100MHz, $CDCl_3$): δ 117.20, 121.88, 127.00, 128.00, 131.51, 132.36, 139.98, 141.32, 144.50, 154.94, 156.00, 160.98; ESI-MS: *m/z* (70 eV): 316.9769 [M+1] and 318.9743 [M+2].

2-(Pyridin-3-yl)-4-(p-tolyl) thiazole, 3e: Yield 81%. Light Yellow, m.p. 280°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.15 (m, 1H, pyridine), 7.50 (s, 1H, thiazole), 7.71-7.79 (d, *J* = 8.0 Hz, 2H, phenyl), 7.90-8.00 (d, *J* = 8.0 Hz, 2H, phenyl), 8.00-8.09 (m, 1H, pyridine), 8.10-8.19 (m, 1H, pyridine), 9.20 (m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.32 (CH_3), 117.00, 124.10, 125.10, 128.01, 130.01, 134.01, 141.02, 148.40, 152.10, 155.10, 157.00, 164.90.

4-(4-Methoxyphenyl)-2-(pyridin-3-yl) thiazole, 3f: Yield 97%. Dark yellow, m.p.204°C. ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.40-7.42 (m, 1H, pyridine), 7.43-7.46 (s, 1H, thiazole), 7.72-7.92 (d, *J* = 8.3 Hz, 2H, phenyl), 7.90-8.00(d, *J* = 8.3 Hz, 2H, phenyl), 8.34-8.36 (m, 1H, pyridine), 8.71 (m, 1H, pyridine), 9.25 (m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.10 (OMe), 116.57, 122.00, 124.10, 127.00, 129.30, 132.50, 138.50, 148.00, 151.20, 153.90, 157.00, 166.00.

4-(2-(Pyridin-3-yl)thiazol-4-yl) benzonitrile, 3g: Yield 75%. White, m.p. 260°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 1H, pyridine), 7.73 (s, 1H, thiazole), 8.02-8.04 (d, *J* = 8.2 Hz, 2H, phenyl), 8.10-8.20 (d, *J* = 8.2 Hz, 2H, phenyl), 8.32-8.52 (m, 1H, pyridine), 8.50 (m, 1H, pyridine), 9.25 (m, 1H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.57, 118.10(CN), 122.87, 123.90, 127.00, 129.00, 132.50, 139.84, 147.10, 152.00, 154.00, 156.05, 166.35.

4-Phenyl-2-(pyridin-4-yl) thiazole, 4a: Yield 87%. Yellowish green, m.p.198°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.40 (m, 1H, phenyl), 7.45-7.48 (d, *J* = 8.8 Hz, 2H, phenyl), 7.60 (s, 1H, thiazole), 7.89-7.90 (d, *J* = 5.0 Hz, 2H, pyridine), 7.97-8.00 (d, *J* = 8.8 Hz, 2H, phenyl), 8.72-8.73 (d, *J* = 5.0 Hz, 2H, pyridine); ^{13}C NMR(100 MHz, $CDCl_3$): δ 110.81, 121.32, 127.13, 128.17, 129.42, 133.40, 143.75, 149.81, 152.35, 154.92.

4-(4-Fluorophenyl)-2-(pyridin-4-yl) thiazole, 4b: Yield 89%. Green, m.p. 114°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.15 (d, *J* = 8.0 Hz, 2H, phenyl), 7.52 (s, 1H, thiazole), 7.85-7.86 (d, 2H, *J* = 4.0 Hz, pyridine), 7.87-7.95 (dd, *J* = 4.0 Hz, J = 8.0 Hz, 2H, phenyl), 8.70-8.71 (d, *J* = 4.0 Hz, 2H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.85, 116.36, 116.57, 121.34, 128.67, 130.61, 130.70, 143.74, 149.83, 152.34, 154.94, 160.53, 162.98.

4-(4-Chlorophenyl)-2-(pyridin-4-yl) thiazole, 4c: Yield 81%. Light Brown, m.p. 136°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.45 (d, *J* = 8.5 Hz, 2H, phenyl), 7.58 (s, 1H, thiazole), 7.87-7.88 (d, *J* = 6.1 Hz, 2H, pyridine), 7.90-7.94 (d, *J* = 8.5 Hz, 2H, phenyl), 8.72-8.74 (d, *J* = 6.1 Hz, 2H, pyridine); ^{13}C NMR (100MHz, $CDCl_3$): δ 110.85, 121.30, 128.95, 129.37, 131.15, 134.34, 143.76, 149.86, 152.37, 154.94.

4-(4-Bromophenyl)-2-(pyridin-4-yl) thiazole, 4d: Yield 52%. Cream, m.p.132°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.58 (d, *J* = 9.0 Hz, 2H, phenyl), 7.59 (s, 1H, thiazole), 7.85-7.86 (d, *J* = 6.2 Hz, 2H, pyridine), 7.87-7.89 (d, *J* = 9.0 Hz, 2H, phenyl), 8.72-8.74 (d, *J* = 6.2 Hz, 2H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.81, 121.20, 123.15, 128.34, 132.08, 132.15, 143.74, 149.87, 152.34, 154.56.

2-(Pyridin-4-yl)4-(p-tolyl) thiazole, 4e: Yield 73%. Yellow, m.p.110°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.27 (d, *J* = 5.8 Hz, 2H, pyridine), 7.52 (s, 1H, thiazole), 7.86-7.87 (d, *J* = 8.2 Hz, 2H, phenyl), 7.87-7.88 (d, *J* = 8.2 Hz, 2H, phenyl), 8.70-8.72 (d, *J* = 6.2 Hz, 2H, pyridine); ^{13}C NMR($CDCl_3$): δ 110.86, 121.00, 123.02, 128.22, 131.08, 132.05, 143.44, 149.57, 152.44, 154.38, 21.33(-CH_3). ESI-MS: *m/z* (70 eV) 253.0790 [M+1].

4-(4-Methoxyphenyl)-2-(pyridin-4-yl) thiazole, 4f: Yield 90%. Dark yellow, m.p. 108°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.99 (d, *J* = 8.8 Hz, 2H phenyl), 7.45 (s, 1H, thiazole), 7.87-7.88 (d, *J* = 6.1 Hz, 2H, pyridine), 7.90-7.93 (d, *J* = 8.8 Hz, 2H, phenyl), 8.70-8.72 (d, *J* = 6.1 Hz, 2H, pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.37 (OMe), 112.61, 114.21, 120.34, 126.93, 127.82, 140.47, 150.64, 157.00, 159.97, 164.67; ESI-MS: *m/z* (70 eV) 269.0733 [M+1].

4-(2-(Pyridin-4yl)thiazole-4-yl) benzonitrile, 4g: Yield 93%. White, m.p.168°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.77 (d, *J* = 8.4 Hz, 2H, phenyl), 7.76 (s, 1H, thiazole), 7.88-7.90 (d, *J* = 6.1 Hz, 2H, pyridine), 8.10-8.12 (d, *J* = 8.4 Hz, 2H, phenyl), 8.75-8.76 (d, *J* = 6.1 Hz, 2H pyridine); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.11, 112.66, 118.66 (CN), 121.23, 126.05, 132.41, 137.63, 143.47, 149.58, 152.43, 154.95.

Quantum yield measurements

Naphthalene was selected as a standard for quantum yield measurements as the compounds under investigation have absorbance in the same region. In ethanol, naphthalene was found to have a quantum yield of 12% (Ref: Page no. 267, C. A. Parkar, Photoluminescence of solutions, Elsevier, Amsterdam, 1968). It shows maximum absorbance at 254 nm and maximum emission at 330 nm in ethanol. To measure the quantum yield, the samples were dissolved in ethanol and further dilutions were performed carefully to match the absorbance value close to 0.1. Further, the fluorescence spectra for all samples were taken by keeping excitation wavelength at 254 nm with a bandwidth of 5 nm. The area under the curve was calculated for all samples and using Equation.1 quantum yields of samples were calculated.

$$\phi_x = \phi_{std} \times \frac{I_x}{I_{std}} \times \frac{A_{std}}{A_x} \times \frac{\eta_x^2}{\eta_{std}^2} \quad \text{Equation (1)}$$

where ϕ denotes quantum yield, I is the integrated area under the peak, A denotes absorbance and η is the refractive index of solvent. Subscript 'x' denotes the sample and 'std' denotes naphthalene.

Results and Discussion

Synthesis and characterization

We have synthesized thiazole, attached at all the three positions of pyridine that is not only the reactive C-2 and C-4 but also the non reactive C-3, without using any metal catalyst. Three new series of 2-pyridyl-4-phenyl-thiazole were synthesized by the reaction of thioamides and 4-substituted phenacyl bromides as shown in the Scheme I. Three series resulted in the formation of 21 derivatives, **2a-g, 3a-g** and **4a-g** which were subjected to fluorescence studies to evaluate the effect of change in position of pyridine on the photo-physical properties and placing different electron donating and withdrawing groups at 4-position of the phenyl ring. The structures of the title compounds were confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy and HRMS.

The representative ^{1}H NMR of 2-pyridyl series, compound **2f** showed singlet at δ 8.71 for thiazole proton, while the aromatic protons of phenyl and pyridine ring showed multiplet between δ 7.40-9.25. The methoxy protons appeared as singlet at δ 3.85. The aromatic carbons of compound **2f** showed 12 signals between δ 113.60-168.61 while, the methoxy carbon appeared at δ 55.36 in its ^{13}C NMR spectrum. The structure was further confirmed by its ESI-MS which showed molecular ion peak at 269 (*m/z*). Similarly, the ^{1}H NMR of the representative compound **4f**, of **4-pyridyl** series showed a singlet at δ 7.45 for thiazole proton. The pyridine C-2 and C-3 protons appeared as doublet at δ 8.70-8.72 and δ 7.87-7.88 respectively, with a coupling constant of 6.12 Hz. The phenyl protons appeared as two sets of doublets at δ 7.90-7.93 and δ 6.97-6.99 with coupling constant of 8.84 Hz, while the methoxy protons resonated at δ 3.86. The ^{13}C NMR clearly showed a signal at δ 55.37 for methoxy carbon and 12 lines for the aromatic carbons between δ 112.61-164.67. The structure was further confirmed from its HRMS which showed molecular ion peak at 269.

The representative ^{1}H NMR of compound **3d,** of 3-pyridyl series, showed singlet at δ 8.27 for thiazole proton, while the other aromatic protons of phenyl and pyridine ring showed multiplet between δ 7.60-9.51. The aromatic carbons of the **3d** showed 12 signals between δ 114.86-164.12. The molecular ion peak at 316 and M+2 peak at 318 for the molecular formula $C_{14}H_9N_2SBr$ confirmed the structure. Structures of all the synthesized compounds were similarly confirmed.

Absorption and emission properties

As shown in the Table I, Table II and Table III, all the synthesized compounds showed characteristic absorption bands from 277-341nm in their electronic spectra depending on the 4-substituents of the C-4-phenyl ring and C-2-pyridyl isomer of the thiazole ring. It was noted that the some of the synthesized thiazole molecules have a very high molar absorption coefficient (≈ 80000 $M^{-1}cm^{-1}$). In general, larger stokes shifts (> 9500 cm^{-1}) was observed for compounds with strong electron donating methoxy substituent and strong electron withdrawing cyano substituent, in all three series (compounds **2f**, **2g**, **3f**, **3g**, **4f**, **4g**). 2-pyridyl and 4-pyridyl isomers showed high absorption than the corresponding 3-pyridyl isomers. Thus the isomeric change at carbon 2 of the thiazole from 3-pyridine to 2-pyridine and 4-pyridine showed bathochromic shift. Electron donating substituent at the *para* position of the 4-phenyl ring of the thiazole shifted the absorption and emission to longer wavelength bathochromic shift and on the contrary electron withdrawing substituent on the same position showed hypsochromic shift (entry **2f**, **3f, 4f** *vs* **2g**, **3g**, **4g**).

Table I — Spectral details (λ_{abs}, absorbance, ε, λ_{em} and stokes shift)of **2a-g** in various solvents

Compd	Spectral details	Hexane	Benzene	2-propanol	THF	$CHCl_3$	Ethyl acetate	Dioxane	Methanol	Ethanol	Acetonitrile	DMSO	Water
2-pyridyl													
2a	λabs(nm)	324	323	324	322	324	320	323	322	322	322	324	322
	Absorbance	(0.156)	(0.188)	(0.158)	(0.151)	(0.181)	(0.151)	(0.162)	(0.151)	(0.163)	(0.156)	(0.166)	(0.133)
	ε $M^{-1}cm^{-1}$	62280	75200	63200	60720	72560	60600	64880	60320	65480	62360	66360	53320
	λem (nm)	377	386	391	388	390	387	387	396	394	393	398	416
	Stokes shift/cm^{-1}	4338	5053	5288	5282	5223	5410	5119	5803	5675	5610	5738	7017
2b	λabs(nm)	322	322	323	322	322	323	324	322	324	322	320	324
	Absorbance	(0.144)	(0.164)	(0.160)	(0.176)	(0.246)	(0.162)	(0.157)	(0.157)	(0.190)	(0.166)	(0.199)	(0.049)
	ε $M^{-1}cm^{-1}$	57560	65760	63840	70200	98400	64920	62720	62880	76080	66320	79760	19720
	λem (nm)	385	394	400	395	398	395	396	404	402	401	407	421
	Stokes shift/cm^{-1}	5081	5675	5959	5739	5930	5643	5611	6303	5988	6118	6679	7111
2c	λabs(nm)	323	324	322	323	324	323	324	322	324	322	323	321
	Absorbance	(0.216)	(0.237)	(0.244)	(0.228)	(0.214)	(0.242)	(0.238)	(0.224)	(0.237)	(0.228)	(0.239)	(0.091)
	ε $M^{-1}cm^{-1}$	86480	94800	97560	91240	85680	96640	95200	89720	94880	91164	95600	36280
	λem (nm)	383	393	398	394	396	393	394	402	399	398	404	386
	Stokes shift/cm^{-1}	4850	5418	5930	5579	5611	5514	5483	6180	5801	5930	6207	5245
2d	λabs(nm)	323	323	323	323	323	324	324	323	324	320	324	320
	Absorbance	(0.234)	(0.231)	(0.226)	(0.238)	(0.225)	(0.245)	(0.248)	(0.239)	(0.230)	(0.246)	(0.249)	(0.124)
	ε $M^{-1}cm^{-1}$	93560	92400	90400	95160	90000	99960	99360	95600	92160	98400	99600	49760
	λem (nm)	383	392	397	394	395	392	395	402	398	399	404	394
	Stokes shift/cm^{-1}	4850	5449	5770	5579	5643	5353	5547	6084	5738	6187	6111	5869
2e	λabs(nm)	326	326	324	324	325	324	328	325	326	325	326	324
	Absorbance	(0.136)	(0.170)	(0.149)	(0.162)	(0.159)	(0.131)	(0.138)	(0.154)	(0.135)	(0.138)	(0.143)	(0.073)
	ε $M^{-1}cm^{-1}$	54480	68120	59760	64920	63520	52400	55280	61760	53800	55280	57040	29120
	λem (nm)	396	409	415	412	420	411	411	424	420	420	425	434
	Stokes shift/cm^{-1}	5422	6224	6767	6592	6959	6533	6156	7184	6865	6959	7145	7822
2f	λabs(nm)	331	333	331	335	331	335	334	331	334	333	336	331
	Absorbance	(0.106)	(0.129)	(0.103)	(0.115)	(0.123)	(0.106)	(0.110)	(0.101)	(0.111)	(0.104)	(0.1194)	(0.042)
	ε $M^{-1}cm^{-1}$	42320	51400	41360	46160	49160	42280	44120	40560	44280	41520	47760	16640
	λem (nm)	403	414	437	423	427	424	424	451	442	443	446	**483**
	Stokes shift/cm^{-1}	5397	5875	7328	6210	6792	6265	6355	8038	7315	7456	7340	9507
2g	λabs(nm)	290	291	291	277	301	290	291	292	297	296	291	293
	Absorbance	(0.052)	(0.056)	(0.058)	(0.334)	(0.053)	(0.057)	(0.057)	(0.052)	(0.053)	(0.055)	(0.058)	(0.042)
	ε $M^{-1}cm^{-1}$	20772	22432	23116	23338	21064	22828	22640	20788	21224	22052	23040	16960
	λem (nm)	375	383	384	382	382	382	384	387	385	386	391	**391**
	Stokes shift/cm^{-1}	7816	8254	8322	9923	7044	8304	8322	8406	7696	7877	8788	8554

This family of isomeric pyridyl-thiazoles are fluorescent-active from blue to yellow (400-490 nm). Bathochromic shifts have been observed in the fluorescence emission spectra of these compounds for the isomeric change at carbon 2 of thiazole from 3-pyridine to 2 and 4-pyridine and also presence of electron donating substituent at phenyl ring (**3f =** 468 nm, **2f =** 483 nm, **4f =** 490 nm). The opposite trend of hypsochromic shift for the fluorescence emission is also observed for electron withdrawing substituent (**3g =** 386 nm, **2g =** 391 nm, **4g =** 404 nm).

The thiazole derivatives containing halogens (F, Cl, Br) showed both absorbance and emission in an intermediate range between that of donating and withdrawing substituents due to-I effect with the similar trend of isomeric change of pyridine like 4-pyridine > 2-pyridine > 3-pyridine.

Solvatochromism

Most of the thiazole derivatives are colored in solution and solid state. To assess the solvatochromic behavior, the absorption and emission profile of the thiazole derivatives were determined in a series of solvents with increasing polarity, *i.e.* hexane < toluene < 2-propanol < tetrahydrofuran < chloroform < ethyl acetate < dioxane < methanol < ethanol < acetonitrile < dimethyl sulphoxide < water (Table I, Table II and Table III). The influence of the solvent on the photo physical properties of synthesized thiazoles was elucidated. The synthesized thiazole compounds did not exhibit solvatochromism in absorbance, the absorption maxima of compounds are almost same with increasing solvent polarity from hexane to water. Fluorescence emission spectra of these compounds are found to be strongly dependent

Table II — Spectral details (λ_{abs}, absorbance, ε, λ_{em} and stokes shift) of **3a-g** in various solvents

Compd	Spectral details	Hexane	Benzene	2-propanol	THF	$CHCl_3$	Ethyl acetate	Dioxane	Methanol	Ethanol	Acetonitrile	DMSO	Water
3-pyridyl													
3a	λabs(nm)	318	324	315	315	313	322	320	318	312	323	318	311
	Absorbance	(0.133)	(0.181)	(0.119)	(0.147)	(0.143)	(0.155)	(0.142)	(0.134)	(0.163)	(0.188)	(0.135)	(0.116)
	ε $M^{-1}cm^{-1}$	53080	72560	47520	58920	57200	61840	56880	53560	65120	75200	54040	46520
	λem (nm)	385	385	374	387	388	384	386	397	393	392	397	407
	Stokes shift/cm^{-1}	5472	4890	5008	5906	6175	5014	5343	6257	6605	5449	6257	7584
3b	λabs(nm)	324	323	320	315	318	313	318	322	318	318	312	311
	Absorbance	(0.156)	(0.189)	(0.142)	(0.147)	(0.120)	(0.143)	(0.135)	(0.151)	(0.133)	(0.134)	(0.163)	(0.116)
	ε $M^{-1}cm^{-1}$	62280	75200	56880	58920	48000	57200	54040	60320	53080	53560	65120	46520
	λem (nm)	396	397	390	390	395	376	393	387	399	386	387	416
	Stokes shift/cm^{-1}	5611	5770	5608	6105	6130	5353	6001	5216	6383	5539	6211	8115
3c	λabs(nm)	318	318	318	314	315	314	318	318	313	318	318	318
	Absorbance	(0.146)	(0.143)	(0.164)	(0.151)	(0.136)	(0.136)	(0.144)	(0.152)	(0.172)	(0.192)	(0.140)	(0.064)
	ε $M^{-1}cm^{-1}$	58240	57000	65400	60240	54560	54200	57520	60840	63680	76720	56080	25640
	λem (nm)	374	385	391	386	388	384	385	395	393	392	396	407
	Stokes shift/cm^{-1}	4708	5472	5871	5940	5972	5805	5472	6130	6503	5936	6194	6876
3d	λabs(nm)	317	318	318	313	318	313	316	319	319	316	315	318
	Absorbance	(0.163)	(0.234)	(0.169)	(0.187)	(0.164)	(0.176)	(0.170)	(0.197)	(0.176)	(0.161)	(0.208)	(0.038)
	ε $M^{-1}cm^{-1}$	65000	93480	67640	74800	65480	70200	68120	78800	70320	64200	83160	15240
	λem (nm)	375	385	390	385	387	384	384	396	393	392	396	416
	Stokes shift/cm^{-1}	4879	5472	5805	5974	5606	5907	5603	6095	5902	6135	6493	7408
3e	λabs(nm)	318	322	323	318	320	318	319	323	322	318	324	314
	Absorbance	(0.199)	(0.215)	(0.223)	(0.217)	(0.241)	(0.215)	(0.221)	(0.218)	(0.226)	(0.217)	(0.405)	(0.192)
	ε $M^{-1}cm^{-1}$	79600	85880	89320	86680	96400	85800	88240	87280	90360	86680	162040	76960
	λem (nm)	381	392	400	396	397	395	396	408	405	396	406	423
	Stokes shift/cm^{-1}	5199	5545	5959	6194	6061	6130	6095	6449	6364	6194	6233	8206
3f	λabs(nm)	323	329	328	325	328	324	326	324	322	328	328	316
	Absorbance	(0.090)	(0.095)	(0.108)	(0.112)	(0.114)	(0.123)	(0.111)	(0.107)	(0.11)	(0.105)	(0.116)	(0.112)
	ε $M^{-1}cm^{-1}$	36120	38080	43280	44840	45560	49080	44200	42680	44000	42160	46240	44760
	λem (nm)	393	408	432	413	418	418	412	443	**468**	435	440	439
	Stokes shift/cm^{-1}	5514	5885	7339	6556	6564	6940	6403	8290	9688	7499	7760	8866
3g	λabs(nm)	284	296	277	282	283	290	288	281	282	284	288	282
	Absorbance	(0.140)	(0.235)	(0.245)	(0.249)	(0.243)	(0.244)	(0.248)	(0.247)	(0.240)	(0.241)	(0.238)	(0.239)
	ε $M^{-1}cm^{-1}$	56040	94000	98000	99600	97200	97600	99200	98800	96000	96400	95200	95600
	λem (nm)	366	373	378	371	373	373	374	381	379	377	384	**386**
	Stokes shift/cm^{-1}	7888	6974	9646	8506	8526	7673	7984	9340	9075	8686	8680	9545

on the polarity of the solvent: the emission wavelength of compound **2f** and **4f** showed strong bathochromic shift of ≈ 80 nm; from 403 nm (hexane) to 483 nm (water) for **2f** and from 412 nm (hexane) to 490 nm (water) for **4f**. The emission wavelength of compound **3f** was found to increase from 393 nm (hexane) to 468 nm (ethanol). This fluoro-solvatochromic behavior which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds exhibiting an intramolecular charge transfer (ICT) upon excitation and has been fully documented with donor-acceptor flurophores, typically for the 2,5-diaryl / heteroaryl 1,3-azoles. This same fluoro-solvatochromic behavior is observed for the 2-pyridyl, 4-phenyl thiazole derivatives **2a-g / 3a-g** and **4a-g** as shown in Table I, Table II and Table III. The notable results are found for the electron donating methoxy containing

Table III — Spectral details (λ_{abs}, absorbance, ε, λ_{em} and stokes shift)of **4a-g** in various solvents

Compd	Spectral details	Hexane	Benzene	2-propanol	THF	$CHCl_3$	Ethyl acetate	Dioxane	Methanol	Ethanol	Acetonitrile	DMSO	Water
4-pyridyl													
4a	λabs(nm)	324	323	324	322	324	320	323	322	322	322	324	322
	Absorbance	(0.156)	(0.188)	(0.158)	(0.151)	(0.181)	(0.151)	(0.162)	(0.151)	(0.164)	(0.156)	(0.166)	(0.133)
	ε $M^{-1}cm^{-1}$	62280	75200	63200	60720	72560	60600	64880	60320	65480	62360	66360	53320
	λem (nm)	377	386	391	388	390	387	387	396	394	393	398	416
	Stokes shift/cm^{-1}	4338	5053	5288	5282	5223	5410	5119	5803	5675	5610	5738	7017
4b	λabs(nm)	320	320	324	319	322	319	323	325	318	320	320	318
	Absorbance	(0.174)	(0.203)	(0.202)	(0.188)	(0.196)	(0.211)	(0.201)	(0.215)	(0.073)	(0.195)	(0.201)	(0.078)
	ε $M^{-1}cm^{-1}$	69440	81400	80760	75040	78320	84440	80320	86040	29240	78000	80280	31120
	λem (nm)	385	400	410	403	398	397	397	415	411	410	412	432
	Stokes shift/cm^{-1}	5275	6250	6473	6534	5930	6159	5770	6672	7115	6859	6978	8298
4c	λabs(nm)	318	322	325	318	324	320	320	324	325	319	318	324
	Absorbance	(0.162)	(0.201)	(0.201)	(0.184)	(0.212)	(0.185)	(0.242)	(0.197)	(0.198)	(0.291)	(0.207)	(0.044)
	ε $M^{-1}cm^{-1}$	64760	80440	80560	73480	84840	74000	96760	78680	79320	116240	82920	17600
	λem (nm)	383	394	404	398	408	396	393	411	409	404	408	423
	Stokes shift/cm^{-1}	5336	5675	6016	6320	6354	5997	5804	6533	6319	6595	6936	7223
4d	λabs(nm)	320	320	324	321	324	321	321	324	326	320	324	328
	Absorbance	(0.244)	(0.237)	(0.248)	(0.246)	(0.241)	(0.222)	(0.249)	(0.242)	(0.239)	(0.229)	(0.225)	(0.215)
	ε $M^{-1}cm^{-1}$	97600	94800	99200	98400	96400	88800	99600	96800	95600	91600	90000	86000
	λem (nm)	381	393	403	397	399	395	396	413	409	406	410	413
	Stokes shift/cm^{-1}	5003	5804	6050	5963	5801	5836	5900	6651	6224	6619	6473	6274
4e	λabs(nm)	319	328	329	323	328	324	326	331	330	324	314	325
	Absorbance	(0.249)	(0.174)	(0.165)	(0.172)	(0.163)	(0.175)	(0.178)	(0.189)	(0.194)	(0.204)	(0.248)	(0.126)
	ε $M^{-1}cm^{-1}$	99600	69560	65960	68760	65240	69840	71040	75560	77720	81720	116220	50360
	λem (nm)	389	405	420	409	414	406	407	427	422	419	425	452
	Stokes shift/cm^{-1}	5641	5796	6585	6509	6333	6233	6104	6792	6606	6997	8317	8645
4f	λabs(nm)	335	339	339	338	337	335	335	340	341	333	341	330
	Absorbance	(0.188)	(0.197)	(0.212)	(0.193)	(0.186)	(0.190)	(0.203)	(0.226)	(0.208)	(0.236)	(0.212)	(0.1122)
	ε $M^{-1}cm^{-1}$	75000	78760	84600	77080	74360	75840	81240	90520	83160	94440	84640	44880
	λem (nm)	412	427	455	443	436	438	432	472	460	461	463	**490**
	Stokes shift/cm^{-1}	5578	6079	7520	7012	6737	7019	6702	8225	7586	8338	7727	9803
4g	λabs(nm)	288	289	290	281	292	289	291	289	291	289	294	288
	Absorbance	(0.239)	(0.248)	(0.242)	(0.248)	(0.241)	(0.246)	(0.245)	(0.244)	(0.247)	(0.243)	(0.249)	(0.239)
	ε $M^{-1}cm^{-1}$	95600	99200	96800	99200	96400	98400	98000	97600	98800	37200	99600	95600
	λem (nm)	377	383	389	385	382	384	385	394	391	390	395	**404**
	Stokes shift/cm^{-1}	8197	8492	8775	9613	8068	8560	8390	9221	8788	8961	8697	9969

Long wavelength absorption maximum, in nm; c=2.5μM; ε = molar absorption coefficient $M^{-1}cm^{-1}$; Fluorescence maximum in nm; c=2.5μ M; Stokes shift$^1cm^{-1}$

substituent in compound **2f, 3f** and **4f** as shown in Figure 1, Figure 2 and Figure 3.

Photophysical data of isomeric 2-pyridyl,4-phenyl thiazole derivatives 2a-g, 3a-g, 4a-g

Correlation of solvatochromic shifts with various solvent polarity scales

Solvent dependent spectral shifts are often interpretated in terms of the Lippert equation, which describes Stokes' shift in terms of the change in dipole moment of the fluorophore upon excitation and the dependence of energy of the dipole on the dielectric constant and refractive index of the solvent and is given as,

$$\nu_F - \nu_A = \frac{2}{hc}\left(\left(\frac{\varepsilon-1}{2\varepsilon-1} - \frac{\eta^2-1}{2\eta^2+1}\right)\frac{(\mu_E-\mu_G)^2}{a^3}\right) + \mathbf{C} \quad \text{Equation (2)}$$

where ν_A and ν_F are the wavenumbers (cm^{-1}) of the absorption and emission, h is Planck's constant, c is the speed of light, a is the radius of the cavity in which the fluorophore resides, ε is the dielectric constant of the medium, η is the refractive index of the solvent and the term $\Delta f = \left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{\eta^2-1}{2\eta^2+1}\right)$ is the orientation polarisability, the resultant effect of both the mobility of electrons in the solvent and the dipole moment of the solvent. A Lippert Mataga plot, which is a plot of Stokes' shift *versus* orientation polarisability Δf of the solvent, provides a valuable framework for the consideration of the solvent dependent spectral shifts. Figure 4 represents the Lippert

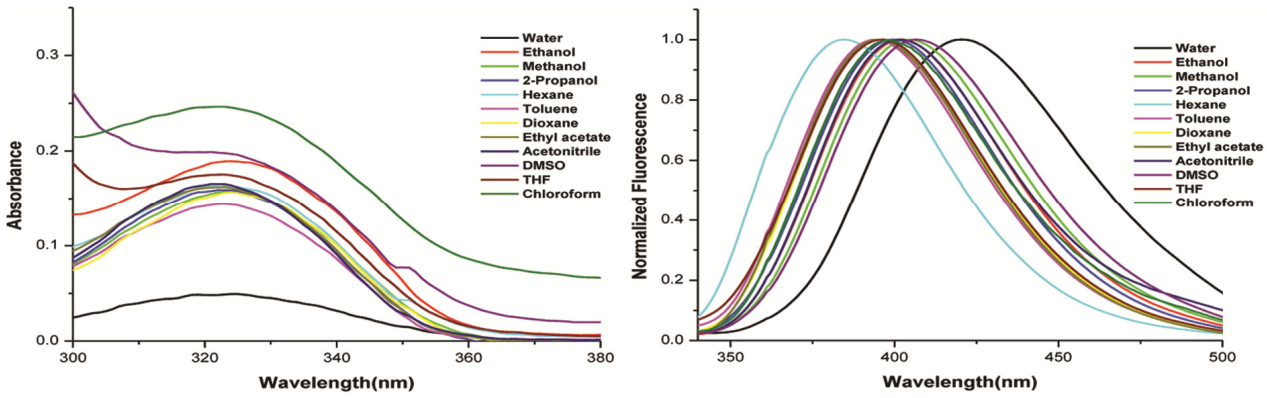


Figure 1 — Absorption and emission spectra of compound **2f** in different solvents; absorption c=2.5μ M; emission c = 2.5μ M

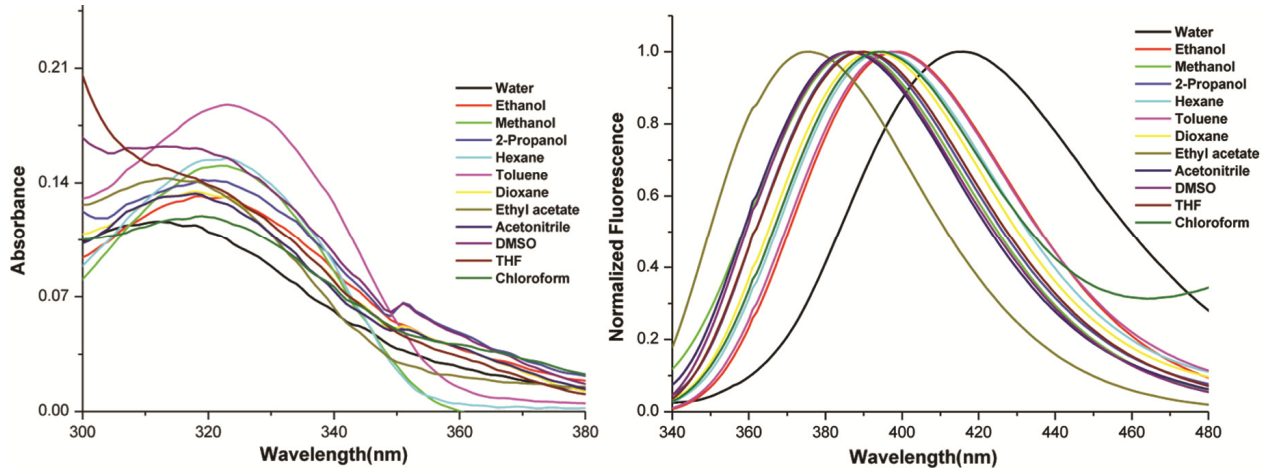


Figure 2 — Absorption and emission spectra of compound **3f** in different solvents; absorption c=2.5μ M; emission c = 2.5μ M

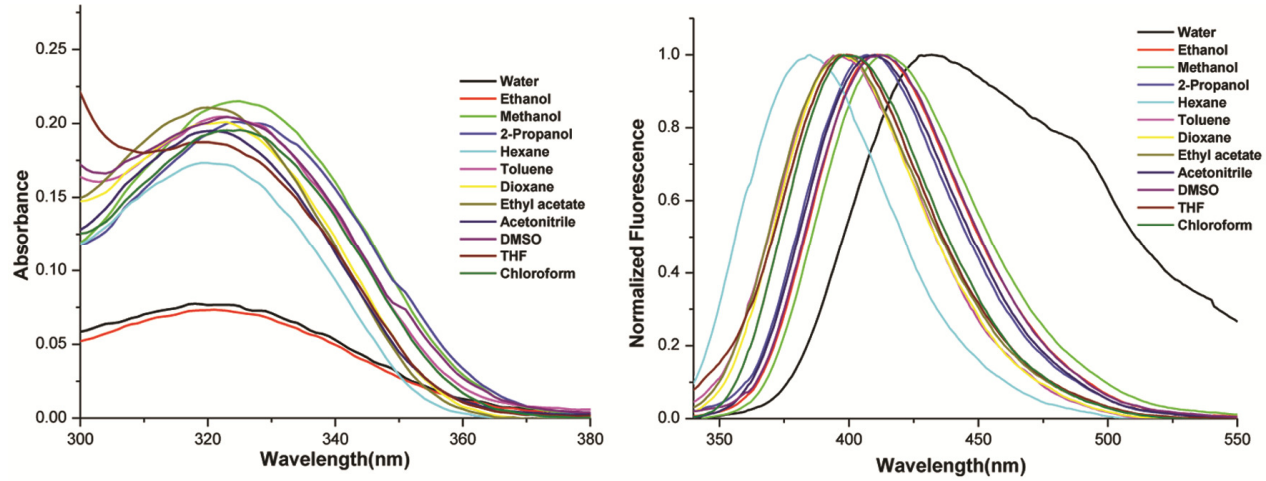


Figure 3 — Absorption and emission spectra of compound **4f** in different solvents; absorption c=2.5μ M; emission c = 2.5μ M

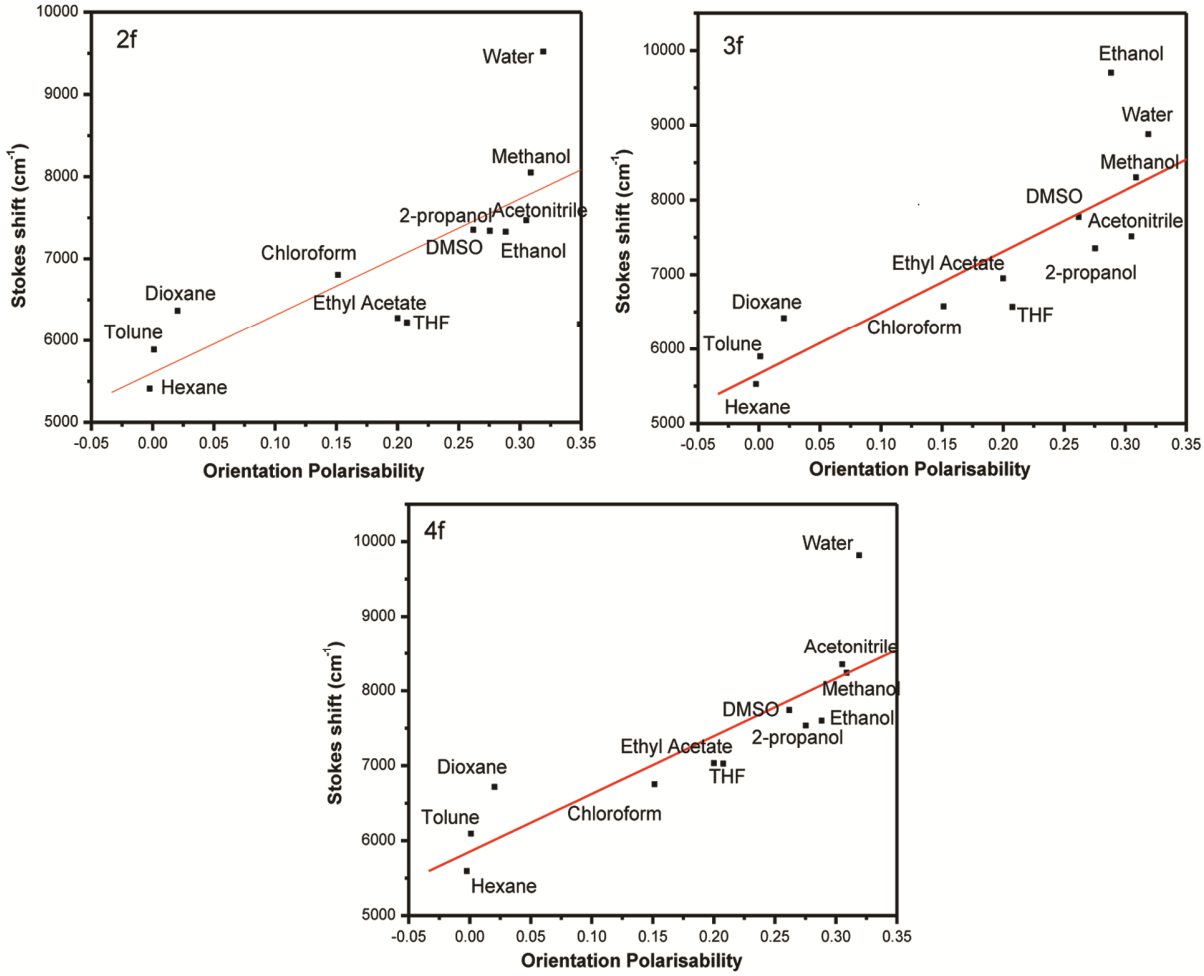


Figure 4 — Lippert-Mattaga plot for **2f**, **3f** and **4f** in different solvents showing the variation of Stokes' shift as a function of orientation polarization of the solvents

Mataga plot for methoxy containing compounds (**2f, 3f, 4f**) in different solvents. Except water, dioxane and ethanol, rest of the solvents showed almost linear correlation. As is evident from Figure 4, there is a good linear relationship of the Stokes shift *versus* Δf for the twelve solvents of Table I, Table II and Table III [for compound **2f** correlation coefficient r = 0.79, slope = 7092.04 cm-^{1}, intercept= 5602.15, for compound **3f** correlation coefficient r = 0.8292, slope = 8212.72 cm-^{1}, intercept = 5668.37, for compound **4f** correlation coefficient r = 0.8543, slope = 7702.91^{-1}, intercept = 5853.29cm].

A linear correlation was observed, which indicated a solvent effect in the excited state, although the standard deviation for **3f** was greater than those of the isomeric compound **2f** and **4f**. A large change in the dipole moment indicates a more pronounced intramolecular charge transfer for these molecules in the excited state. For fluorescent molecules that show intramolecular charge transfer, these are generally planar in the ground state and twisted in the excited state. Solvatochromism was observed for fluorescence spectra. In this regard, the relationship between solvent polarity and Stokes shifts was elucidated on the basis of Lippert–Mataga plots. The change in the dipole moments of the representative derivatives **2f, 3f** and **4f** between the ground and excited states showed that these compounds were more polarized in the excited state.

Acidochromic properties

Application of fluorescent compounds in monitoring *p*H change has attracted considerable attention. The presence of pyridine ring in the synthesized compounds prompted us to study the possibility of protonation of this compound in

ethanol. The optical properties of **4f** and **4g** in ethanol solution was studied with the electron donating methoxy and electron withdrawing cyano substituent at three different *p*H (Acidic, Neutral and Alkaline). The change in the fluoroscence emission spectra of **4f** and **4g** upon addition of acid and base is illustrated in Figure 5. Upon addition of hydrochloric acid to a solution of **4g** in ethanol at *p*H 2, showed a significant (404 nm to 470 nm) bathochromic shift (70 nm) in emission spectra which may be explained by initial protonation of the pyridine ring and CN substituent at 4-position that leads to an increased donor-acceptor interplay as shown in Scheme II. Upon addition of NaOH to a solution of **4f** in ethanol at *p*H 8, showed only small (490 nm to 500 nm) bathochromic shift (10 nm) in fluoroscence emission while at acidic *p*H 2 there is intense hypsochromic shift.

Quantum yield

Considering the significant change in the absorption and emission spectra 4-pyridyl series and fluorosolvatochromism, we calculated the quantum yields of these compounds. The results are shown in Table IV. Compound **4f** shows an extraordinarily high luminescence quantum yield (Φ) of 66.35% compared to standard naphthalene 12.00%. Positional isomeric change is also observed for the quantum yield in the order 4-pyridyl > 2-pyridyl > 3-pyridyl.

DFT calculations

We have performed the DFT calculation based on the Gaussian 03 program. The functional is B3LYP

Table IV — Fluorescence quantum yield (Φ) relative to naphthalene in ethanol

Compd	ϕ in %	Compd	ϕ in %	Compd	ϕ in %
2a	6.27	**3a**	1.35	**4a**	7.33
2b	6.091	**3b**	3.84	**4b**	10.66
2c	7.66	**3c**	5.78	**4c**	9.355
2d	8.25	**3d**	5.07	**4d**	9.874
2e	5.786	**3e**	3.34	**4e**	12.21
2f	**17.19**	**3f**	6.56	**4f**	**66.35**
2g	14.82	**3g**	6.80	**4g**	15.84

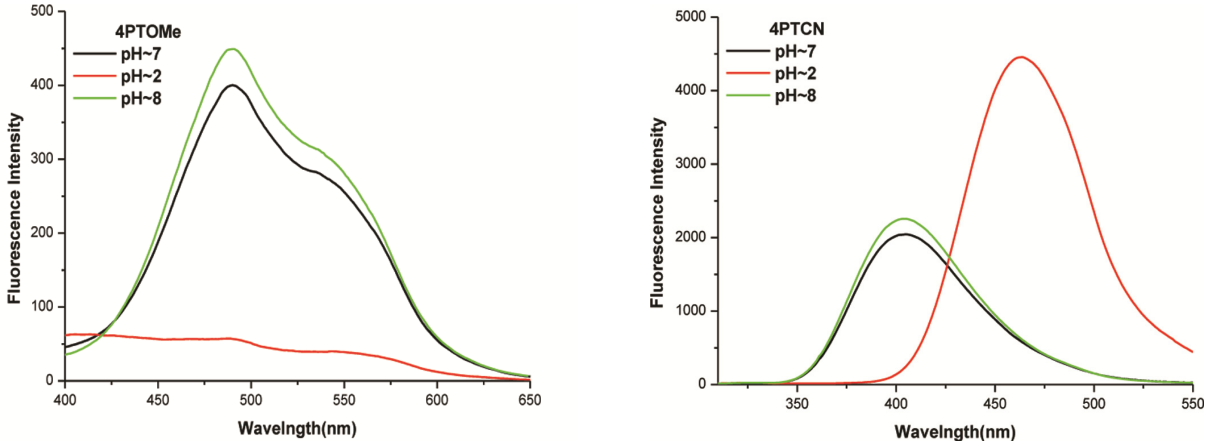
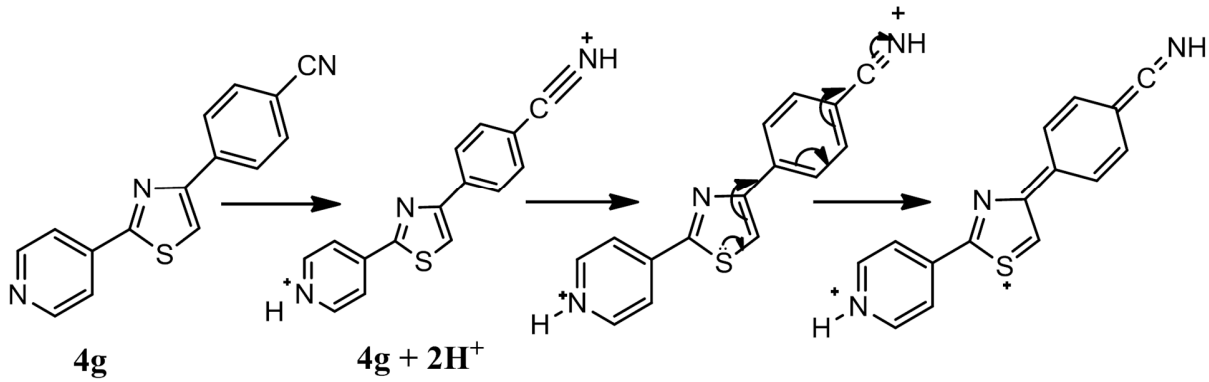


Figure 5 — Emission spectra of compound **4f** and **4g** at different *p*H and c = 2.5uM



Scheme II — Prototropic equilibria of **4g**

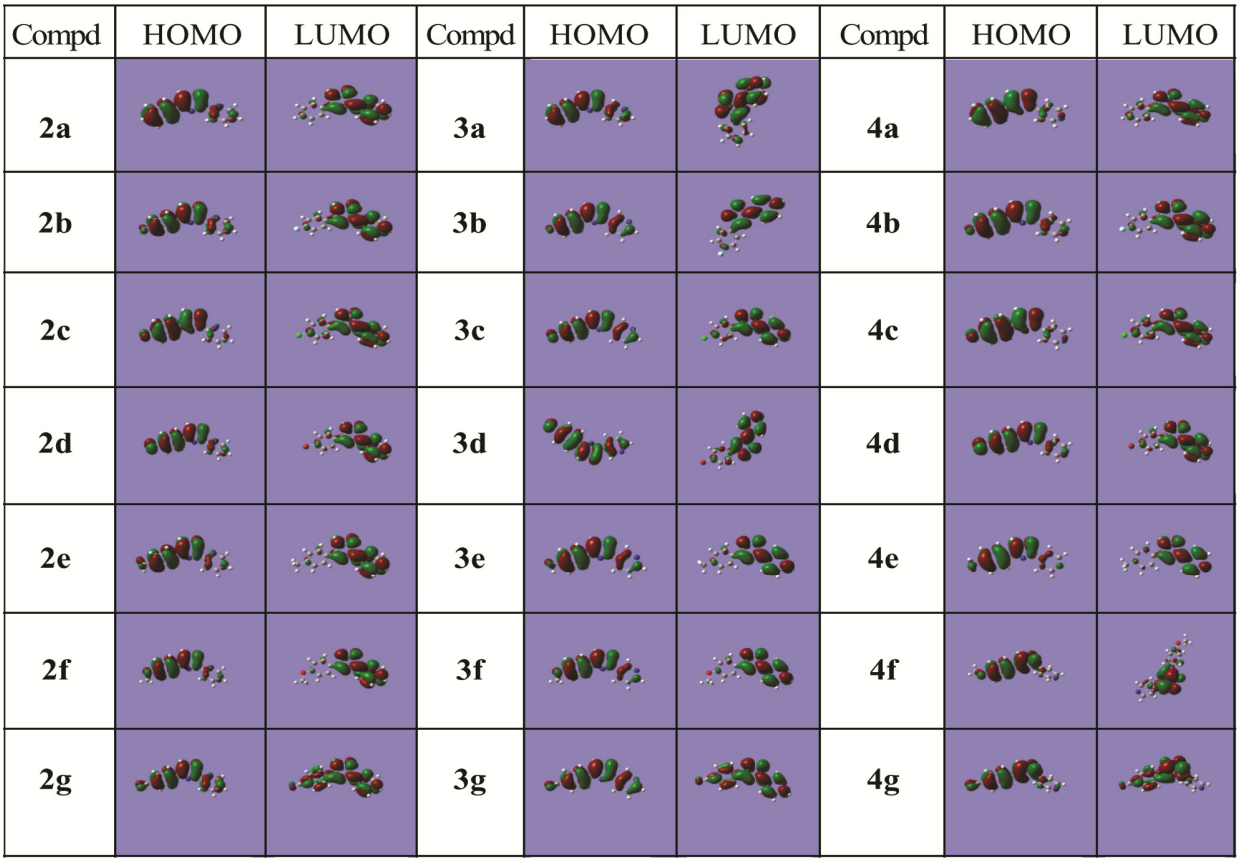


Figure 6 — Frontier orbitals HOMO and LUMO for thiazoles **2a-g / 3a-g / 4a-g**

with 6–31G basis sets. Figure 4 shows their charge density distribution of the frontier molecular orbitals. For electron donating substituents on the phenyl ring (**2f, 3f, 4f**) the energy of both HOMO and LUMO increases compared to **2a, 3a** and **4a**, while electron withdrawing substituent on phenyl ring (**2g**, **3g**, **4g**) decreases the energy of this frontier orbital's. For the isomeric change of pyridine the energy of both HOMO and LUMO decreases from 2-pyridyl to 3-pyridyl to 4-pyridyl. The energy of HOMO in **2f =-**0.29647 eV**, 3f =-**0.29848 eV and **3f =-**0.31128 eV, while the LUMO energy is **2f** = 0.0667 eV, **3f** = 0.0661 eV, **4f** = 0.0454 eV (Figure 6). This same trend is observed for the electron withdrawing substituent in **2g, 3g** and **4g** as shown in Table V.

For the reactant orbital HOMO, the electron cloud density is concentrated on all three rings pyridine, thiazole and phenyl, in 2-pyridyl and 3-pyridyl isomers but for the 4-pyridyl derivatives the electron cloud density lies on middle thiazole ring and the phenyl ring only, due to certain symmetry as shown in Figure 4. Substituent change on phenyl ring

Table V — HOMO's and LUMO's calculated with B3LYP/6-31G*

Compound		R	HOMO (eV)	LUMO (eV)	ΔE (eV)
2-Pyridyl	**2a**	H	-0.30265	0.06746	0.37011
	2b	F	-0.30725	0.06342	0.37067
	2c	Cl	-0.33343	-0.04530	0.28813
	2d	Br	-0.30593	0.06256	0.36849
	2e	Me	-0.29609	0.06897	0.36506
	2f	OMe	-0.29647	0.06676	0.36323
	2g	CN	-0.32115	0.05473	0.37588
3-Pyridyl	**3a**	H	-0.30531	0.07111	0.37642
	3b	F	-0.30897	0.06257	0.37154
	3c	Cl	-0.31206	0.06023	0.37229
	3d	Br	-0.30776	0.06163	0.36939
	3e	Me	-0.29849	0.06818	0.36667
	3f	OMe	-0.29848	0.06614	0.36462
	3g	CN	-0.32197	0.05298	0.37495
4-Pyridyl	**4a**	H	-0.33528	-0.04427	0.29101
	4b	F	-0.31281	0.05876	0.37157
	4c	Cl	-0.33782	-0.04923	0.28859
	4d	Br	-0.31102	0.05788	0.3689
	4e	Me	-0.30363	0.06545	0.36908
	4f	OMe	-0.31128	0.04549	0.35677
	4g	CN	-0.33388	0.03139	0.36527

does not show any notable change on the electron density. In LUMO of **2f** and **3f** the electron density cloud lies on the heterocyclic rings pyridine and thiazole whereas in **4f** the electron density cloud is concentrated only on middle thiazole due to two opposing effect of the methoxy substituent and pyridine ring as shown in Figure 4. Thus the isomeric change and substituent effect is notable.

Conclusion

Three series of isomeric pyridyl thiazole derivatives were successfully synthesized by simple method. Photo physical properties of the compounds were studied. The longest wavelengths in their UV−Vis spectra were within the range from 277 to 341 nm, whereas their emissions ranged from 375 to 490 nm. Amongst these three isomeric series 2-pyridyl and 4-pyridyl isomers are exhibiting better photo physical activities than 3-pyridyl series. 4-pyridyl isomer with methoxy substituent on phenyl ring was found to have high luminescence quantum yield. Bathochromic shift of the emission band was observed with increasing solvent polarity, fluoro solvatochromism was observed for all the compounds but no solvatochromism was found with respect to absorption. The absorption of **2f, 3f** and **4f** arises due to the intramolecular charge transfer (ICT) transition with high molar extinction coefficients. Lippert–Mataga analysis on the solvatochromic data implies that these molecules are more polar in the excited state, which is additional support for ICT. 4-pyridyl isomer with electron withdrawing CN as substituent at 4-position (compound **4g**) showed a strong acidochromic behavior. DFT calculations showed that electron donating substituent increases and electron withdrawing substituent decreases the energy of frontier orbitals. Position isomeric change also affected the energy of the frontier orbitals. We have succesfully synthesized, characterized and concluded that the nonplanar 2-pyridyl, 4-aryl thiazoles possess similar behavior in photophysical properties like that of planar 2,5-diaryl/heteroaryl thiazoles.

These results thus warrant the need for synthesis of similar libraries with other substituents to ascertain the trend described in this work.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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