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Microwave-assisted solvent-free synthesis and fluorescence spectral characteristics of some monomethine cyanine dyes

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ABSTRACT

A series of mono- and dicationic monomethine cyanine dyes belonging to the thiazole orange family have been prepared via an improved synthetic procedure, by the condensation of benzothiazolium salts with quaternary salt of quinolines having reactive methyl group in the presence of triethylamine under solvent-free microwave irradiation. The effects of microwave power and irradiation time on yield were examined. The products were identified using elemental analysis, ^{1}H-NMR, ^{13}C-NMR, FTIR, FAB-MS, UV-vis spectra. The electronic absorption and steady state fluorescence spectra of prepared dyes have been investigated. Fluorescence properties indicate significance in singlet oxygen sensitization and makes the present compounds as potential candidates in the area of photodynamic therapy (PDT).

Keywords*: monomethine cyanine dyes, lepidinium salts, homodimeric cyanine dyes, benzothiazolium salts,*
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INTRODUCTION

Methine cyanine dyes are among the most important organic functional dyes They have found use in a large number of diverse fields .and are used extensively in biological, medical and drug development areas [1-3]. They are extensively used as fluorescent labels and probes [4-11] in detection of proteins [12, 13], flow cytometry [14, 15], DNA sequencing [16-18], quantification of nucleic acids in capillary and gel electrophoresis [19-22]. Besides, they are commonly applied to photographic sensitizers [23-26], optical recording media in laser disks [27], laser dyes [28], electronics [29], nonlinear optics [30], CD recording materials [31-33], and solar cells [34].

The classical synthesis of hemicyanine dyes with quinoline nucleus is often carried out by refluxing the mixture of benzothiazolium salts with quaternary salt of quinoline having reactive methyl group and catalyst in an organic medium [35-38]. This preparation has substantial drawbacks, such as relatively strenuous reaction condition namely refluxing reactants for several hours in organic solvents not friendly to environment, and complexity of isolation of products.

Microwave irradiation presents a powerful tool toward organic reactions [39, 40]. Solvent-free microwave irradiation is well known as environmentally benign method, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures [41]. In this communication, microwave–assisted synthesis of some lepidinium, monomethine and cyanine dyes without solvents are described.

EXPERIMENTAL SECTION

2.1. Measurements.

Melting points were taken on a XT-4 micromelting apparatus and are uncorrected. IR spectra were recorded with PERKIN ELMER MODEL 1720 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured with a Varian EM 390 and Bruker AC-250 spectrometers respectively. The chemical shifts in ppm are expressed in the δ scale using tetramethylsilane (Me$_4$Si) as internal standard. Coupling constants are given in Hz. Fast Atom Bombardment Mass Spectra [FAB-MS] were recorded in a Micromass Autospec M, operating at 70 eV, using a matrix of 3-nitrobenzyl alcohol. UV-Vis absorption spectra were recorded on a Shemadzu UV-1700 UV-Vis spectrometer. Fluorescence spectra were recorded on Hitachi F-4500 Spectrofluorimeter. TLC was performed on Merck silica gel 60-F 254 precoated plastic plates.

2.2. Synthetic procedure:

Quaternary benzothiazolium salts were prepared by the conventional methods [scheme 1], according to the literatures [36, 37]

All microwave reactions **[Schemes 2- 4]** were conducted using Start S Milestone S/N 129802 microwave apparatus.
2.2.1. General procedure for synthesis of benzothiazoles 2, 3$_{a, b}$.

A mixture of **1$_{a,b}$** (5 mmol) and the corresponding alkylating agent (15 ml) was heated at 100 $^{\circ}$C for 6h. After cooling, the residue was washed with diethylether and air-dried.

1,4-Dimethylenephenyl-[3,3̀-bis(3H-benzothiazol-2-thione)] (2)

Yield: 55%, m.p.: > 320 $^{\circ}$C; FAB = 434; ^{1}HNMR (DMSO-d$_6$): δ = 5.70 (s, 4H, 2CH$_2$), 7.27 (s, 4H, Ar-H), 7.30-7.80 (m, 8H, Ar-H); C$_{22}$H$_{16}$N$_2$S$_4$ (434); C, 59.29; H, 3.85; N, 6.29; found: C, 59.67; H, 3.62, N, 6.07.

4-(4-Chloromethyl-benzyl)-3H-benzothiazole-2-thione (3$_a$)

Yield 58%, m.p.: 162-164 $^{\circ}$C; FAB = 306; ^{1}HNMR (DMSO-d$_6$): δ = 4.70 (s, 2H, CH$_2$), 5.76 (s, 2H, CH$_2$), 7.31-7.80 (m, 8H, Ar-H); ^{13}CNMR: δ = 45.6 (CH$_2$), 48.1 (CH$_2$), 113.5, 121.9, 125.0, 126.4, 127.2, 128.9, 129.1, 134.8, 137.0, 140.9 (Ar-C), 189.0 (C=S); C$_{15}$H$_{12}$Cl N S$_2$ (305.5); C, 58.91; H, 3.95, N, 4.58; found: C, 58.80; H, 4.00, N, 4.71.

3-Benzyl-3H-benzothiazole-2-thione (3$_b$)

Yield 59%, m.p.: 150-152 $^{\circ}$C; ^{1}HNMR (DMSO-d$_6$): δ = 5.75 (s, 2H, CH$_2$), 7.28-7.81 (m, 9H, Ar-H); ^{13}CNMR: δ = 48.4 (CH$_2$), 113.6, 121.9, 125.0, 126.4, 126.9, 127.2, 127.6, 128.6, 134.7, 141.0 (Ar-C), 189.0 (C=S); C$_{14}$H$_{11}$N S$_2$ (257.4); C, 64.21; H, 4.43, N, 5.35; found: C, 64.19; H, 4.23, N, 5.24.

2.2.2. General procedure for preparation of benzothiazolium salts 4$_{a-d}$

A solution of triethyloxonium tetrafluoroborate (2 mmol) in 5 ml CH$_2$Cl$_2$ was added to a solution of benzothiazole derivative (2 mmol) in 15 ml CH$_2$Cl$_2$ at -20 $^{\circ}$C. The reaction mixture temperature was raised to room temp. in the course of 30 min. and stirring was continued for 1h. Dropwise addition of diethylether afforded fine crystals.

2-Benzylsulfanyl-3-ethylbenzothiazol-3-ium tetrafluoroborate (4$_a$)

Yield 68%, m.p.: 160-161°C; FAB = 286(373-87); ^{1}HNMR (DMSO-d$_6$): δ = 1.44 (t, *j=7.2 Hz*, 3H, CH$_3$), 4.68 (q, *j=7.3 Hz* 2H, CH$_2$), 5.00 (s, 2H, CH$_2$), 7.30-7.97 (m, 7H, Ar-H), 8.26 (d, *j=7.3 Hz*, 1H, CH), 8.38 (d, *j=7.3 Hz*, 1H); ^{13}CNMR: δ = 12.1 (CH$_3$), 36.6 (CH$_2$), 45.6 (CH$_2$), 115.6, 124.2, 127.3, 128.5, 128.6, 128.9, 129.3, 129.4, 133.0, 140.8 (Ar-C), 177.8 (NCS); C$_{16}$H$_{16}$N S$_2$ BF$_4$ (373.3); C, 51.49; H, 4.32, N, 3.74; found: C, 51.41; H, 4.34, N, 3.81.

3-Ethyl- 2-methylsulfanyl-benzothiazol-3-ium tetrafluoroborate (4$_b$)

Yield 75%, m.p.: 209-211°C; ^{1}HNMR (DMSO-d$_6$): δ = 1.45 (t, *j=7.2 Hz*, 3H, CH$_3$), 4.67 (q, *j=7.2 Hz*, 2H, CH$_2$), 3.14 (s, 3H, SCH$_3$), 7.73 (t, *j=6.3 Hz*, 1H), 7.84 (t, *j=6.3 Hz*, 1H), 8.21 (t, *j=8.4 Hz*, 1H), 8.38 (d, *j=8.1 Hz*, 1H), ^{13}CNMR: δ = 12.0 (CH$_3$), 18.0 (SCH$_3$), 45.4 (NCH$_2$), 115.4, 121.7, 124.1, 127.1, 129.3, 141.4 (Ar-C), 180.8 (NCS).

3-(4-Chloromethyl-benzyl)-2-ethylsulfanyl-benzothiazol-3-ium tetrafluoroborate (4$_c$)

Yield 70%, m.p.: 182-184°C; FAB = 334(421-87); ^{1}HNMR (DMSO-d$_6$): δ = 1.56 (t, *j=7.0 Hz*, 3H, CH$_3$), 3.66 (q, *j=7.3 Hz*, 2H, CH$_2$), 4.75 (s, 2H, CH$_2$) 5.95 (s, 2H, NCH$_2$), 7.33 (d, *j=8.1 Hz*, 2H), 7.47 (d, *j=8.2 Hz*, 2H, CH$_2$), 7.80 (m, 2H, Ar-H), 8.20 (d, *j=8.0 Hz*, 1H), 8.44 (d, *j=9.1 Hz*, 1H); ^{13}CNMR: δ = 13.0 (CH$_3$), 31.1 (CH$_2$), 45.4 (CH$_2$), 52.3 (CH$_2$), 115.7, 124.2, 127.3, 127.5, 127.8, 128.6, 129.5, 132.1, 138.1, 141.8 (Ar-C), 181.0 (NCS); C$_{17}$H$_{17}$Cl N S$_2$ BF$_4$ (421.7); C, 48.42; H, 4.06, N, 3.32; found: C, 48.68; H, 4.01, N, 3.33.

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3-Benzyl-2-ethylsulfanyl-benzothiazol-3-ium tetrafluoroborate (4$_d$)

Yield 74%, m.p.: 165-168°C; FAB = 286(373-87); ^{1}HNMR (DMSO-d$_6$): δ = 1.56 (t, *j=7.3 Hz,* 3H, CH$_3$), 3.67 (q, *j=7.3 Hz,* 2H, CH$_2$), 5.95 (s, 2H, CH$_2$), 7.32-7.46 (m, 5H, Ar-H), 7.72-7.86 (m, 2H, Ar-H), 8.21 (d, *j=8.0 Hz,* 1H), 8.43 (d, *j=8.0 Hz,* 1H); ^{13}CNMR: δ = 115.8, 124.2, 127.2, 127.3, 128.6, 129.1, 129.5, 132.0, 141.8 (Ar-C), 180.9 (NCS); C$_{16}$H$_{16}$NS$_2$BF$_4$ (373.3); C, 51.49; H, 4.32, N, 3.74; found: C, 51.65; H, 4.09, N, 3.81.

3-methyl-2-methylsulfanyl-benzothiazol-3-ium tetrafluoroborate (5)

A mixture of 2-methylthiobenzothiazole **1$_b$** (5 mmol) and methyltosylate (10 mmol) in 15 ml dioxane was boiled under reflux for 8h. Evaporation of the solvent and washing the residue with diethylether afforded pale yellow solid. (yield 70%). m.p.: 109-111 °C; ^{1}HNMR (DMSO-d$_6$): δ = 2.27 (s, 3H, CH$_3$), 3.08 (s, 3H, SCH$_3$), 4.07 (s, 3H, NCH$_3$) 7.11 (d, *j=7.9 Hz,* 2H), 7.51 (d, *j=7.9 Hz,* 2H), 7.69 (t, *j=7.4 Hz,* 1H), 7.80 (t, *j=7.4 Hz,* 1H), 8.15 (d, *j=8.3 Hz,* 1H), 8.36 (d, *j=8.0 Hz,* 1H); ^{13}CNMR: δ = 18.0 (CH$_3$), 20.8 (SCH$_3$), 36.4 (NCH$_3$), 15.7, 123.9, 125.5, 126.9, 128.2, 128.3, 129.1, 138.0, 142.4, 145.1 (Ar-C), 181.3 (NCS).

5,6,7,8-tetrahydro-benzo[d]thiazolo[2,3-b]thiazol-4-ylium tosylate (6)

A mixture of 2-methylthiobenzothiazole (**1$_b$**) and 2-chloroethyl tosylate (10 mmol) was heated with stirring at 90 °C for 6h. After cooling, 20 ml of diethylether was added, where colorless fine crystala was precipited. (yield, 45%). m.p.: 218-221°C; FAB = 194(365-171); ^{1}HNMR (DMSO-d$_6$): δ = 2.28 (s, 3H, CH$_3$), 4.24 (t, *j=7.0 Hz,* 2H, CH$_2$) 4.96 (t, *j=7.0 Hz,* 2H, CH$_2$), 7.11 (d, *j=8.2 Hz,* 2H) Cl), 7.46 (d, *j=8.1 Hz,* 2H), 7.64 (t, *j=7.2 Hz,* 1H), 7.75 (t, *j=7.1 Hz,* 1H), 7.95 (d, *j=8.1 Hz,* 2H), 8.27 (d, *j=8.2 Hz,* 2H); C$_{16}$H$_{15}$NO$_3$S$_3$ (365.5); C, 51.32; H, 4.31, N, 3.74; found: C, 51.10; H, 4.24, N, 3.59.

2.2.3. General procedure for preparation of quinolinium iodide salts (7$_{a-c}$ & 8$_{a-c}$)

A mixture of lepidine (10 mmol) and diiodoalkane (50 mmol) was subjected to microwave irradiation for proper time and temperature as given in **[Table 1]**. Filtration and washing with ether afforded yellow precipitate of two compounds. Extraction with hot acetone afforded pure dark yellow precipitate of monomer **7$_{a-c}$**, and the residue of yellow dimmer **8$_{a-c}$**.in the ratio of 1 : 4 continuously.

1-(3-Iodo-propyl)-4-methylquinolinium iodide (7$_a$)

Yellow crystals, m.p.: 175-177°C; ^{1}HNMR (DMSO-d$_6$): δ = 2.52 (m, 2H, CH$_2$), 3.02 (s, 3H, CH$_3$), 3.38 (t, *j=7.2 Hz,* 2H, CH$_2$), 5.06 (t, *j=7.4 Hz,* 2H, CH$_2$), 8.04-8.64 (m, 5H, Ar-H), 9.42 (d, *j=6.1 Hz,* 1H, Ar-H).

1-(4-Iodo-butyl)-4-methylquinolinium iodide (7$_b$)

Yellow crystals, m.p.: 158-160 °C; ^{1}HNMR (DMSO-d$_6$): δ = 1.92 (m, 2H, NCH$_2$), 2.09 (m, 2H, CH$_2$), 3.02 (s, 3H, CH$_3$), 3.34 (t, *j=6.6 Hz* 2H, CH$_2$), 5.08 (t, *j=7.3 Hz* 2H, CH$_2$), 8.04-8.66 (m, 5H, Ar-H), 9.44 (d, *j=6.0 Hz,* 1H, Ar-H); ^{13}CNMR: δ = 7.2 (CH$_2$), 19.7 (CH$_2$), 29.6 (CH$_2$), 30.4 (CH$_3$), 55.7 (CH$_2$), 119.2, 122.6, 127.1, 128.9, 129.5, 135.0, 136.6, 148.2 (Ar-C), 158.6 (C=N$^+$)

1-(5-Iodo-pentyl)-4-methylquinolinium iodide (7$_c$)

Yellow crystals, m.p.: 118-120 °C; ^{1}HNMR (DMSO-d$_6$): δ = 1.52 (m, 2H, CH$_2$), 1.83 (m, 2H, CH$_2$), 2.01 (m, 2H, CH$_2$), 3.03 (s, 3H, CH$_3$), 3.31 (m, 2H, CH$_2$), 5.02 (m, 2H, CH$_2$), 8.04-8.5 (m, 6H, Ar-H); ^{13}CNMR: δ = 8.3, 19.6, 26.5, 28.1, 56.5, (5CH$_2$), 32.0 (CH$_3$), 119.2, 122.5, 127.0, 128.8, 129.4, 135.0, 136.6, 148.1 (Ar-C).

Propane-1,3-bis[4-methylquinolinieeum]diiodide (8$_a$)

Dark yellow crystals, m.p.: 288-291°C; ^{1}HNMR (DMSO-d$_6$): δ = 2.52 (m, 2H, CH$_2$), 3.02 (s, 6H, 2CH$_3$), 5.06 (t, *j=7.1 Hz,* 4H, 2CH$_2$), 8.02-8.66 (m, 5H, Ar-H), 9.48 (d, *j=6.1 Hz,* 2H, Ar-H).

Butane-1,4-bis[4-methylquinolinium]diiodide (8$_b$)

Dark yellow crystals, m.p.: 258-260°C; ^{1}HNMR (DMSO-d$_6$): δ = 2.10 (bm, 4H, 2CH$_2$), 3.01 (s, 6H, 2CH$_3$), 5.08 (bm, 4H, 2CH$_2$), 8.05-8.67 (m, 10H, Ar-H), 9.41 (d, 2H, *j=6.0 Hz,* 2H, Ar-H); ^{13}CNMR: δ = 19.7 (2CH$_3$), 26.2 (2CH$_2$), 56.2 (2NCH$_2$), 119.3, 122.6, 127.1, 128.9, 129.5, 135.1, 136.6, 148.3, (Ar-C), 158.6 (C=N$^+$).

pentane-1,5-bis[4-methylquinolinium]diiodide (8$_c$)

Dark yellow crystals, m.p.: 226-228°C; ^{1}HNMR (DMSO-d$_6$): δ = 1.57 (m, 2H, CH$_2$), 2.06 (m, 4H, 2CH$_2$), 3.04 (s, 6H, 2CH$_3$), 5.05 (t, *j=7.3 Hz,* 4H, 2CH$_2$), 8.04-8.64 (m, 5H, Ar-H), 9.48 (d, *j=6.0 Hz,* 2H, Ar-H); ^{13}CNMR: δ = 19.7 (2CH$_2$), 22.6 (CH$_2$), 28.7 (2CH$_3$), 56.5 (2CH$_2$), 119.3, 122.5, 127.0, 128.8, 129.5, 135.0, 136.6, 148.2, 158.4 (Ar-C).

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1,4-Dimethylenephenyl[1,1̀-bis(4-methylquinolinium)]dibromide (9)
A mixture of lepidine (20 mmol), 4-(bromomethyl) benzylbromide (10 mmol) and few drops of triethyl amine was subjected to microwave irradiation for proper time and temperature as given in **[Table 1]**, the residue was washed with diethylether afforded dark yellow crystals. m.p.: 285-288°C; FAB = 469(550-80), 390 (469-80); ^{1}HNMR (DMSO-d_6): δ = 2.77 (s, 6H, 2CH$_3$), 6.16 (s, 4H, 2CH$_2$), 7.31 (s, 4H, Ar-H), 7.50-8.17 (m, 10H, Ar-H), 9.23 (d, *j=6.0 Hz* 2H, Ar-H); ^{13}CNMR: δ = 20.4 (2CH$_3$), 60.9 (2CH$_2$), 119.7, 123.6, 127.6, 128.9, 129.1, 130.4, 130.5, 135.2, 136.2, 148.8, 161.5 (Ar-C); C$_{28}$H$_{26}$Br$_2$N$_2$ (550.4); C, 58.25; H, 5.06, N, 4.85; found: C, 58.57; H, 4.85, N, 4.76.

1, 4-Dimethyl-quinolinium iodide (10$_a$)
A mixture of lepidine (5 mmol) and methyl iodide (10 mmol) was subjected to microwave irradiation for proper time and temperature as given in **(Table 1).** Filtration and washing with ether afforded yellow fine crystals, m.p.: 185-186°C; ^{1}HNMR (DMSO-d_6): δ = 3.02 (s, 3H, CH$_3$), 4.61 (s, 3H, CH$_3$), 8.04-8.56 (m, 5H, Ar-H), 9.40 (d, 1H, *j=6.1Hz*); ^{13}CNMR: δ = 19.5 (CH$_3$), 45.0 (CH$_3$), 119.4, 122.3, 126.7, 128.3, 129.5, 134.8, 137.5, 148.8 (Ar-C), 158.0 (C=N$^+$).

1-[(4-chloromethyl)benzyl-4-methylquinolinium chloride (10$_b$)
A mixture of lepidine (10 mmol) and 4-(chloromethyl) benzylchloride (30 mmol) was was subjected to microwave irradiation for proper time and temperature as given in [**Table 1**], the residue was washed with diethylether and air-dried. m.p.: 222-223°C; FAB = 282(318-36; ^{1}HNMR (DMSO-d_6): δ = 3.05 (s, 3H, CH$_3$), 4.73 (s, 2H, CH$_2$), 6.45 (s, 2H, CH$_2$), 7.42 (s, 4H, Ar-H), 9.87 (d, *j=5.4 Hz* 1H, Ar-H); ^{13}CNMR: δ = 19.8 (CH$_3$), 45.4 (CH$_2$), 58.0 (CH$_2$), 119.7, 123.0, 127.3, 127.4, 127.8, 129.1, 129.4, 129.6, 134.3, 134.7, 135.2, 136.7, 138.1, 149.3, (Ar-C), 159.6 (C=$^+$N); C$_{18}$H$_{17}$Cl$_2$N (282); C, 67.93, H, 5.38, N, 4.40; found: C, 67.86.03, H, 5.54, N, 4.38.

2.2.4. *General procedure for preparation of monocyanine dyes (11$_{a-j}$)*
Benzothiazolium salt (2 mmol), 4-methylquinolinium salt (2mmol) and few drops of triethylamine were mixed in glass conical flask. The mixture was subjected to microwave irradiation for a proper time and power. After cooling and washing with diethyl ether orange to yellowish orange precipitate (18$_{a-j}$) was obtained. The details of reaction conditions and yield are provided in **[Table 2]** and the optimizing process for experimental conditions of dye **(18$_a$)** is listed in **[Table 3]**.

1-(3-Iodopropyl)-4-[(3-methyl-3H-benzothiazol2-ylidene)methyl]] quinolinium iodide (11$_a$)
Orange crystals, m.p.: 233-235 °C; IR(KBr): ν = 1469 (SH), 1500, 1608 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d_6): δ = 2.36 (m, 2H, CH$_2$), 3.39 (t, *j=7.0 Hz*, 2H, CH$_2$), 3.97 (s, 3H, CH$_3$), 4.56 (t, *j=7.3 Hz*, 2H, CH$_2$), 6.76 (s, 1H, =CH), 7.15-8.72 (m, 10H, Ar-H); ^{13}CNMR: δ = 2.3 (CH$_2$), 32.4 (CH$_2$), 33.9 (CH$_3$), 54.3 (CH$_2$), 88.5 (=CH), 107.5, 112.7, 117.4, 122.6, 123.7, 123.8, 124.2, 125.6, 126.5, 127.8, 133.0, 136.6, 140.0, 143.9, 148.0 (Ar-C), 159.7 (NCS).

1-(3-Iodobutyl)-4-[(3-methyl-3H-benzothiazol-2-ylidene)methyl]]quinolinium iodide (11$_b$)
Orange crystals, m.p.: 206-209°C; FAB = 473(600-127); IR(KBr): ν = 1473 (SH), 1516, 1612 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d_6): δ = 1.91 (bm, 4H, 2CH$_2$), 3.56 (t, 2H, ICH$_2$), 4.00 (s, 3H, NCH$_3$), 4.62 (t, 2H, N$^+$CH$_2$), 6.88 (s, 1H, =CH); 7.09-8.79 (m, 10H, Ar-H) ^{13}CNMR: δ = 7.5 (ICH$_2$), 29.8 (2CH$_2$), 33.8 (NCH$_3$), 67.9 (NCH$_2$), 88.0 (=CH), 107.6, 112.8, 117.8, 122.7, 123.7, 124.3, 125.4, 125.7, 126.6, 127.9, 133.0, 136.7, 137.4, 140.1, 143.9 (Ar-C), 148.2, 159.8 (NCS, C=N).

1-(3-Iodopropyl)-4-[(3-benzyl-3H-benzothiazol-2-ylidene)methyl]] quinolinium tetrafluoroborate (11$_c$)
Orange fine crystals, m.p.: 236-238 °C; FAB = 535(622-87); IR(KBr): ν = 1465 (SH), 1492, 1612 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d_6): δ = 2.38 (m, 2H, CH$_2$), 3.34 (t, 2H, ICH$_2$), 4.64 (t, 2H, NCH$_2$), 5.96 (s, 2H, NCH$_2$), 6.98 (s, 1H, =CH), 7.30-8.64 (m, 15H, Ar-H); C$_{27}$H$_{24}$N$_2$IS (535.5); C, 51.37; H, 3.99, N, 4.44; found: C, 51.56; H, 3.91, N, 4.44.

1-(3-Iodopentyl)-4-[(3-methyl-3H-benzothiazol-2-ylidene)methyl]] quinolinium iodide (11$_d$)
Yellowish orange crystals, m.p.: 206-208 °C; FAB = 487(614-127); IR(KBr): ν = 1469 (SH), 1504, 1608 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d_6): δ = 1.46 (t, *j=6.7 Hz*, 2H, CH$_2$), 1.83 (m, 4H, 2CH$_2$), 3.28 (m, 2H, CH$_2$), 3.99 (s, 3H, CH$_3$), 4.58 (m, 2H, CH$_2$), 6.85 (s, 1H, =CH), 7.27-8.77 (m, 10H, Ar-H); ^{13}CNMR: δ = 8.5 (CH$_2$), 26.7, 27.6, 32.1, 53.7 (4CH$_2$), 33.8 (CH$_3$), 87.9 (=CH), 107.6, 112.8, 17.9, 122.7, 123.7, 124.0, 124.3, 125.7, 126.6, 127.9, 133.1, 136.8, 140.2, 144.1, 148.2 (Ar-C), 159.8 (NCS); [C$_{23}$H$_{24}$N$_2$SI$_2$] (614.3); C, 44.97; H, 3.94, N, 4.56; found: C, 44.72; H, 4.01, N, 4.51.

1-(3-Iodobutyl)-4-[(3-ethyl-3H-benzothiazol-2-ylidene)methyl)]quinolinium tetrafluoroborate (11$_e$)
Orange fine crystals, m.p.: 220-221°C; FAB = 487(574-87); IR(KBr): ν = 1473 (SH), 1512, 1612 cm^{-1} (C=C, C=N);; ^{1}HNMR (DMSO-d$_6$): δ = 1.40 (t, 3H, CH$_3$), 1.92 (m, 4H, 2CH$_2$), 3.33 (t, 3H, ICH$_2$), 4.66 (m, 4H, 2NCH$_2$), 6.93 (s, 1H, =CH); 7.37-8.81 (m, 10H, Ar-H) C$_{23}$H$_{24}$N$_2$S I (487.4); C, 46.65; H, 4.43, N, 4.73; found: C, 46.48; H, 4.04, N, 4.64.

1-(3-Iodopropyl)-4-[(3-ethyl-3H-benzothiazol-2-ylidene)methyl)]quinolinium tetrafluoroborate (11$_f$)
Orange fine crystals, m.p.: 249-251°C; FAB = 473 (560-87); IR(KBr): ν = 1465 (SH), 1512, 1612 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 1.40 (t, 3H, CH$_3$), 2.40 (m, 2H, CH$_2$), 3.33 (t, 2H, ICH$_2$), 4.67 (m, 4H, 2NCH$_2$), 6.95 (s, 1H, =CH); 7.37-8.81 (m, 10H, Ar-H); C$_{22}$H$_{22}$N$_2$I S (473.4); C, 46.42; H, 4.07, N, 4.92; found: C, 46.65; H, 3.91, N, 4.89.

1-methyl-4-[(3-ethyl-3H-benzothiazol-2-ylidene)methyl)]quinolinium tetrafluoroborate (11$_g$)
Yellowish orange crystals, m.p.: 272-273 °C; FAB = 319 (406-87); IR(KBr): ν = 1465 (SH), 1519, 1616 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 1.39 (t, *j=7.0 Hz*, 3H, CH$_3$), 4.15 (s, 3H, CH$_3$), 4.62 (q, *j=6.8 Hz*, 2H, CH$_2$), 6.89 (s, 1H, =CH), 7.32-8.76 (m, 10H, Ar-H); ^{13}CNMR: δ = 12.2 (CH$_3$), 40.9 (CH$_2$), 42.3 (CH$_3$), 87.1 (=CH), 107.8, 112.6, 118.1, 122.8, 123.9, 124.4, 125.4, 126.9, 128.2, 133.1, 137.9, 139.4, 144.8, 148.6 (Ar-C), 158.8, (NCS).

1-methyl-4-[(3-methyl-3H-benzothiazol-2-ylidene)methyl)]quinolinium iodide (11$_h$)
Orange fine crystals, m.p.: 285-286°C; FAB = 305(432-127); ν = 1481 (SH), 1523, 1612 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 3.91 (s, 3H, CH$_3$), 4.10 (s, 3H, CH$_3$), 6.75 (s, 1H, =CH), 7.14-8.71 (m, 10H, Ar-H); ^{13}CNMR: δ = 33.7 (CH$_3$), 42.2 (CH$_3$), 87.6 (=CH), 107.4, 112.6, 117.9, 122.5, 123.5, 123.6, 124.1, 125.3, 126.7, 127.8, 132.9, 137.6, 140.0, 144.6, 148.0, (Ar-C), 159.3 (NCS); C$_{19}$H$_{17}$I N$_2$S (429); C, 51.71, H, 4.11, N, 6.35; found: C, 51.21, H, 3.87, N, 6.15.

1-methyl-4-[(3-benzyl-3H-benzothiazol-2-ylidene)methyl)]quinolinium tetrafluoroborate (11$_i$)
Orange crystals, m.p.: 295-296°C; IR(KBr): ν = 1469 (SH), 1504, 1616 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 6.17 (s, 3H, CH$_3$), 5.93 (s, 2H, CH$_2$), 6.95 (s, 1H, =CH$_2$), 7.30-8.64 (m, 15H, Ar-H); ^{13}CNMR: δ = 42.4 (CH$_3$), 48.5 (CH$_2$), 88.0 (=CH), 108.3, 112.8, 118.3, 122.9, 123.7, 124.0, 124.5, 125.0, 126.6, 127.0, 127.8, 128.2, 128.9, 133.2, 135.1, 137.9, 140.2, 145.1, 148.7, (Ar-C), 159.2 (NCS). [C$_{25}$H$_{21}$N$_2$S B F$_4$] (486.3); C, 61.74; H, 4.77, N, 5.76; found: C, 61.42; H, 4.11, N, 5.66.

1-methyl-4-[3-(4-chloromethyl)benzyl-3H-benzothiazol-2-ylidene)methyl)] quinolinium iodide (11$_j$)
Reddish orange crystals, m.p.: 209-211°C; FAB = 429 (556-127); ^{1}HNMR (DMSO-d$_6$): δ = 4.17 (s, 3H, NCH$_3$), 4.70 (s, 2H, CH$_2$Cl), 5.91 (s, 2H, NCH$_2$), 6.92 (s, 1H, =CH), 7.34-8.60 (m, 14H, Ar-H); ^{13}CNMR: δ = 42.6 (CH$_2$Cl), 45.7 (NCH$_2$), 48.6 (NCH$_3$), 88.2 (=CH), 108.7, 113.0, 118.4, 123.1, 124.0, 124.3, 124.8, 125.2, 127.2, 127.3, 128.5, 129.7, 133.5, 135.5, 137.7, 138.2, 140.5, 145.4 (Ar-C), 149.1, 159.5 (SCN, C=N).

1-(4-(chloromethyl)benzyl) -4-[(3-methyl-3H-benzothiazol-2-ylidene)methyl)] quinolinium tosylate (11$_k$)
Orange crystals, m.p.: 225-227°C; FAB = 429(601-171); IR(KBr): ν = 1504, 1612 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 2.27 (s, 3H, CH$_3$), 4.05 (s, 3H, NCH$_3$), 4.73 (s, 2H, ClCH$_2$), 5.88 (s, 2H, NCH$_2$), 6.96 (s, 1H, =CH), 7.07-8.82 (m, 14H, Ar-H); ^{13}CNMR: δ = 20.7 (CH$_3$), 33.9 (NCH$_3$), 45.5 (ClCH$_2$), 59.1 (NCH$_2$), 88.6 (=CH), 107.6, 113.1, 118.3, 122.8, 124.0, 124.6, 124.9, 125.4, 125.7, 126.6, 126.9, 127.1, 127.9, 128.1, 129.3, 133.0, 136.5, 137.0, 137.4, 137.5, 140.3, 144.7 (Ar-C), 148.5, 160.5 (NSC, C=N); C$_{33}$H$_{29}$N$_2$Cl S$_2$O$_3$ (610.2); C, 64.96; H, 4.96, N, 4.59; found: C, 64.67; H, 4.94, N, 4.63.

2.2.5. General procedure for preparation of cyanine dyes dimer 12$_{a-e}$
Benzothiazolium salt (4 mmol), lepidinium dimmer (2mmol) and 5 ml of triethylamine were mixed in glass conical flask. The mixture was subjected to microwave irradiation for a proper time and power. Cooling and addition of diethyl ether afforded reddish orange crystals. The details of reaction conditions and yield are provided in **[Table 4]**

1,3-bis[4-(3-methyl-3H-benzothiazol-2-ylidene)methyl]quinolinyl-propane iodide tosylate (12$_a$)

Reddish orange crystals, m.p.: 219-220°C; FAB = 749(876-127); IR(KBr): ν = 1473 (SH), 1512, 1608 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 2.28 (s, 2H, CH$_2$), 3.92 (s, 6H, 2NCH$_3$), 4.81 (s, 4H, 2NCH$_2$), 6.80 (s, 2H, 2=CH), 7.10-8.71 (m, 20H, Ar-H); C$_{39}$H$_{34}$I$_2$N$_4$S$_2$ (876.7); C, 53.43; H, 3.91, N, 6.39; found: C, 53.49; H, 3.94, N, 6.30.

1,5-bis[4-(3-methyl-3H-benzothiazol-2-ylidene)methyl]quinolinyl-pentane diiodide (12$_b$)
Reddish orange, m.p.: 216-2218°C; FAB = 777 (904-127), 650 (777-127); ^{1}HNMR (DMSO-d$_6$): δ = 1.45 (bm, 2H, CH$_2$), 1.93 (bm, 4H, 2CH$_2$), 3.94 (s, 6H, 2NCH$_3$), 4.59 (bm, 4H, 2CH$_2$), 6.84 (s, 2H, 2=CH), (s, 2H, 2=CH), 7.08-8.78 (m, 20H, Ar-H); ^{13}CNMR: δ = 22.6 (CH$_2$), 28.1 (2CH$_2$), 33.8 (2CH$_3$), 53.6 (2CH$_2$), 88.0 (2=CH), 107.5, 112.8,

117.9, 122.7, 123.6, 125.7, 126.6, 127.9, 128.0, 133.1, 136.8, 140.2, 144.1, 148.3 (Ar-C), 159.5 (NCS); $[C_{41} H_{38} I_2 N_4 S_2]$ (904.7); C, 52.85; H, 4.44, N, 6.01; found: C, 53.01; H, 4.58, N, 5.57. The details of reaction conditions and yield are provided in Table (5)

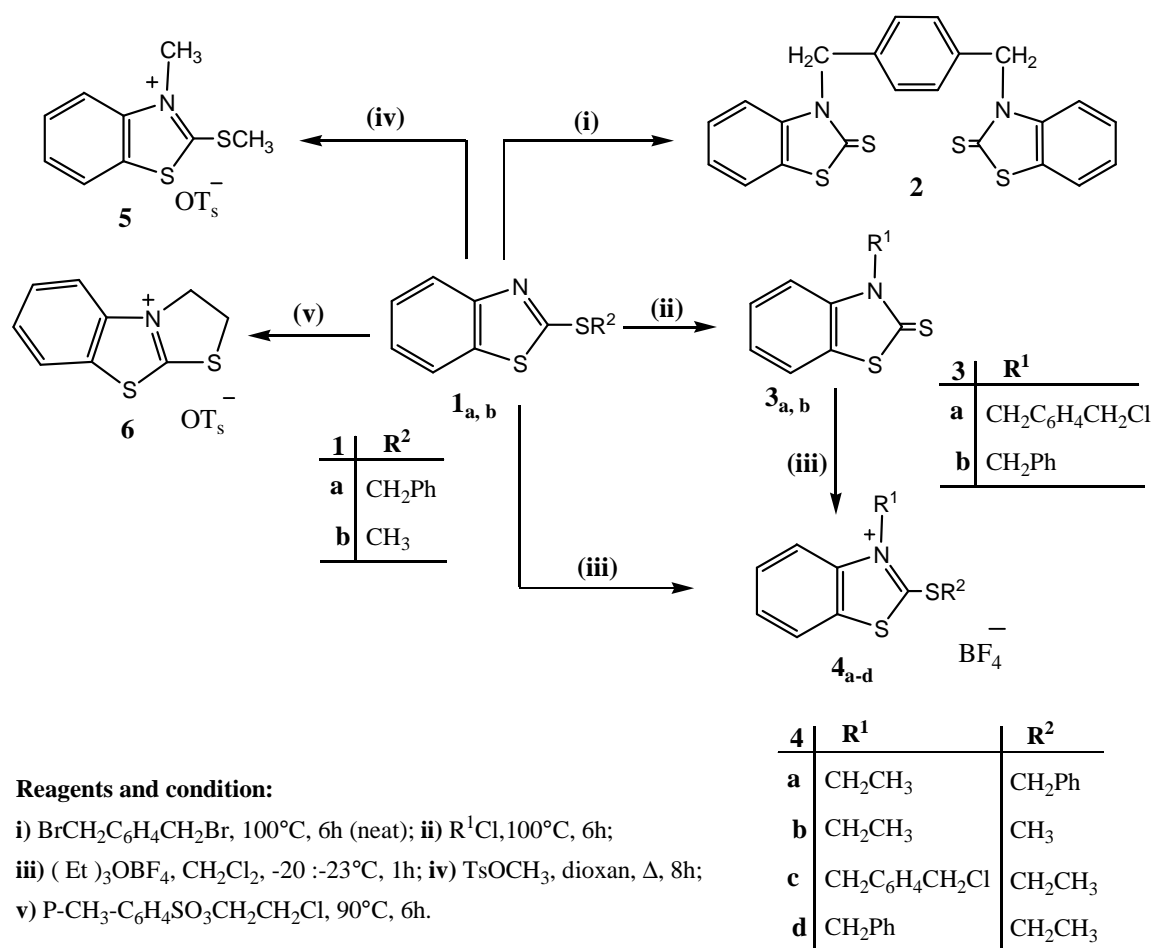### *1,4-bis[4-(3-methyl-3H-benzothiazol-2-ylidene)methyl]quinolinyl-butane iodide tosylate (12$_c$)*

Dark red crystals, m.p.: 209-211°C; FAB = 429(556-127); IR(KBr): ν = 1477 (SH), 1512, 1608 cm^{-1} (C=C, C=N); ^{1}HNMR (DMSO-d$_6$): δ = 2.00 (s, 4H, 2CH$_2$), 2.26 (s, 3H, CH$_3$), 4.01 (s, 6H, 2NCH$_3$), 4.64 (s, 4H, 2NCH$_2$), 6.90 (s, 2H, 2=CH), 7.07-8.78 (m, 24H, Ar-H).

1,4-bis[4-(3-ethyl-3H-benzothiazol-2-ylidene)methyl]quinolinyl-butane di-tetrafluroborate (12$_d$)

Reddish orange crystals, m.p.: 325-328 °C; FAB = 751 (838-87), 664 (751-87); ^{1}HNMR (DMSO-d$_6$): δ = 1.41 (bt, 6H, 2CH$_3$), 2.21 (bm, 4H, 2CH$_2$), 4.55 (bm, 4H, 2CH$_2$), 4.65 (bm, 4H, 2CH$_2$), 6.92 (s, 2H, 2=CH), 7.35-8.77 (m, 20H, Ar-H); ^{13}CNMR: δ = 12.2 (2CH$_3$), 25.7 (2CH$_2$), 41.4 (2CH$_2$), 53.5 (2CH$_2$), 87.4 (2=CH), 107.8, 112.8, 118.0, 122.9, 124.0, 124.1, 124.5, 125.8, 126.8, 128.2, 133.1, 136.9, 139.5, 144.1, 148.7 (Ar-C), 159.1, (NCS); $[C_{42} H_{40} N_4 S_2 B_2 F_8]$ (838.6); C, 57.68; H, 5.07, N, 6.41; found: C, 57.92; H, 4.65, N, 6.16.

1,3-bis[4-(3-ethyl-3H-benzothiazol-2-ylidene)methyl]quinolinyl-propane diiodide (12$_e$)

Orange crystals, m.p.: 239-241°C; FAB = 777 (904-127), 650 (777-127); ^{1}HNMR (DMSO-d$_6$): δ = 1.32 (t, 6H, *j=7.2 Hz*, 2CH$_3$), 2.55 (bm, 2H, CH$_2$), 4.61 (bq, 4H, 2CH$_2$), 4.75 (bt, 4H, 2CH$_2$), 6.88 (s, 2H, 2=CH), 7.30-8.73 (m, 20H, Ar-H); ^{13}CNMR: δ = 12.1 (2CH$_3$), 27.8 (CH$_2$), 41.0 (2CH$_2$), 51.6 (2CH$_2$), 87.5 (2=CH), 108.0, 112.7, 117.8, 122.8, 123.9, 124.0, 124.5, 125.7, 126.7, 128.2, 133.0, 136.8, 139.3, 144.0, 148.5 (Ar-C), 159.2, (NCS); $[C_{41} H_{38} I_2 N_2 S_2]$ (904.7); C, 54.43; H, 4.23, N, 6.19; found: C, 54.35; H, 4.40, N, 6.00.

Reagents and condition:

i) BrCH$_2$C$_6$H$_4$CH$_2$Br, 100°C, 6h (neat); **ii)** R^{1}Cl,100°C, 6h;

iii) (Et)$_3$OBF$_4$, CH$_2$Cl$_2$, -20 :-23°C, 1h; **iv)** TsOCH$_3$, dioxan, Δ, 8h;

v) P-CH$_3$-C$_6$H$_4$SO$_3$CH$_2$CH$_2$Cl, 90°C, 6h.

1	R^2
a	CH$_2$Ph
b	CH$_3$

3	R^1
a	CH$_2$C$_6$H$_4$CH$_2$Cl
b	CH$_2$Ph

| 4	R^1	R^2
a	CH$_2$CH$_3$	CH$_2$Ph
b	CH$_2$CH$_3$	CH$_3$
c	CH$_2$C$_6$H$_4$CH$_2$Cl	CH$_2$CH$_3$
d	CH$_2$Ph	CH$_2$CH$_3$

Scheme 1. Synthesis of benzothiazolium salts

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RESULTS AND DISCUSSION

3.1. *Synthesis*

Quaternary benzothiazolium salts (**2 - 6**) were prepared by the conventional methods **[Scheme 1]**, according to the literatures [36, 37]. The structure proposal of the prepared compounds was derived from the analytical data (^{1}H NMR, ^{13}C NMR, IR) and satisfactory elemental analyses.
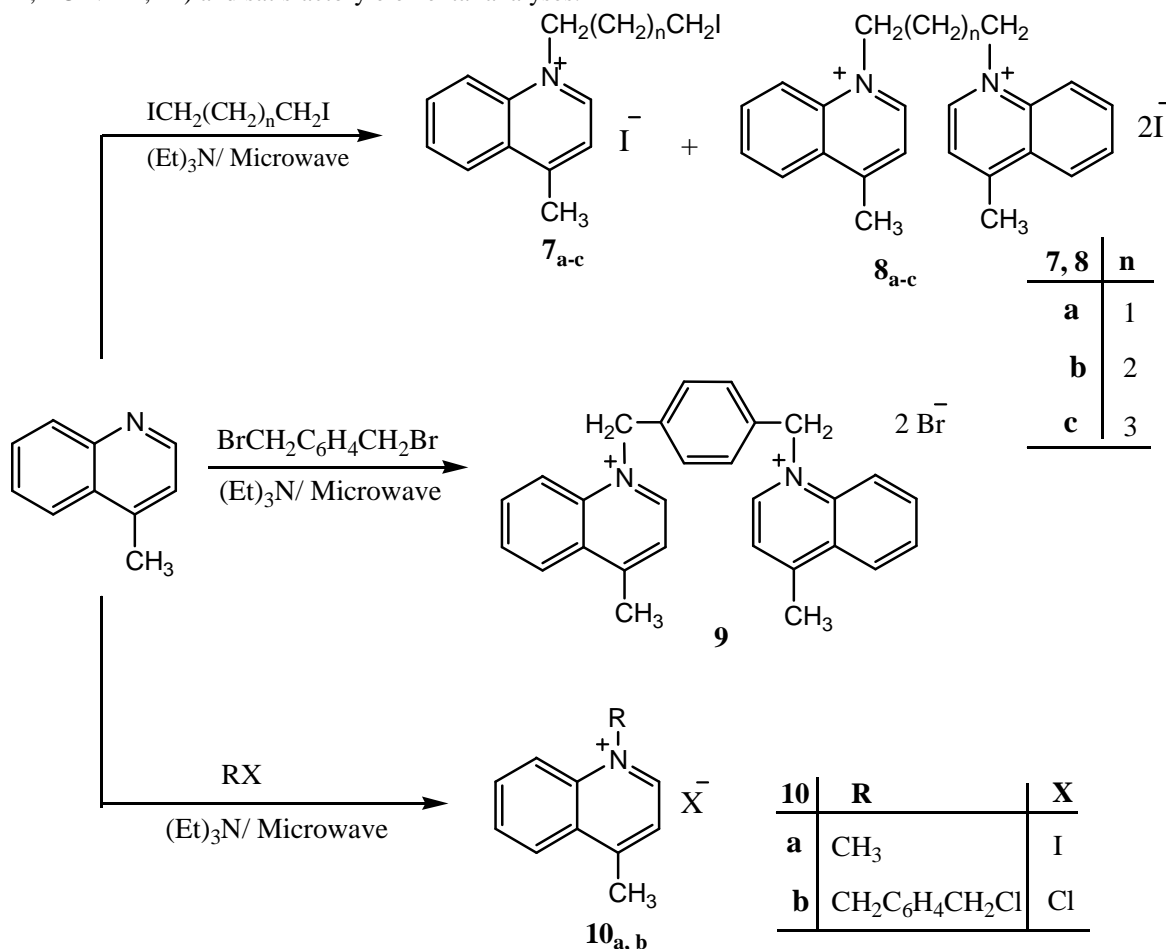
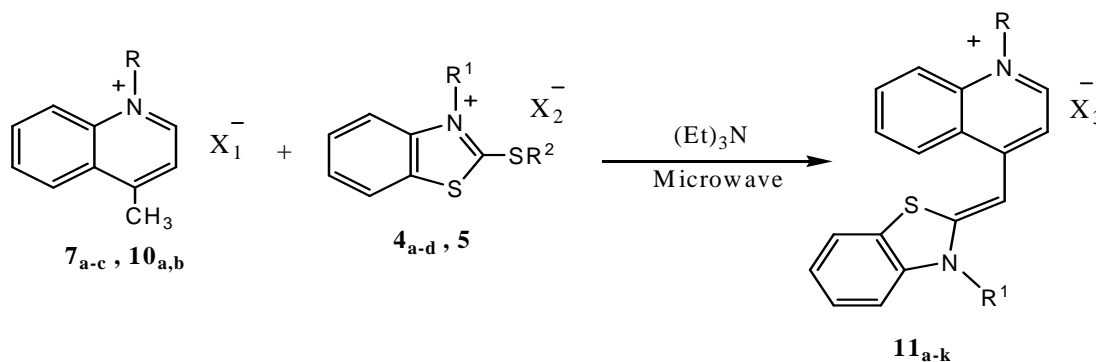**Scheme 2**. Microwave Synthesis of Quinolinium Salts

Table 1.

The reaction conditions and yields for quinolinium iodide salts

Compounds	Temp ($^\circ$C)	Time (min)	Yield (%)
$7_a, 8_a$	120	2	85
$7_b, 8_b$	120	1	90
$7_c, 8_c$	120	1	83
9	130	3	86
10_a	120	2	92
10_b	130	4	87

A series of quinolinium salts **(7 - 10)** were synthesized by the reaction of lepidine and listed alkyl halide **[Scheme 2]**. The mixture was subjected to microwave irradiation for proper time and temperature. The details of reaction conditions and yields are provided in **[Table 1]**. The reactions proceeded well even when both the starting reactants were solids and the reaction temperature was maintained below the melting points of both components.

Mono methinecyanine dyes **(11$_{a-k}$)** were synthesized by the reaction of benzothiazolium salts with 4-methylquinolinium salts in the presence of triethylamine. The mixture was subjected to microwave irradiation for a proper time and power **[Scheme 2]**. The details of reaction conditions and yield are provided in **[Table 2]**, the optimizing process for experimental conditions of dye **(11$_a$)** is listed in **[Table 3]**. It is necessary to emphasize that some of listed dyes were previously synthesized by classical methods e.g. monomethine cyanine dyes (11$_a$, 11$_b$, 11$_c$, 11$_d$ and 11$_f$) were prepared according to literatures [36, 37] and used for other purposes.

Dye 11	R	R^1	R^2	X$_1$	X$_2$	X$_3$
a	(CH$_2$)$_3$I	CH$_3$	CH$_3$	I	OT$_s$	I
b	(CH$_2$)$_4$I	CH$_3$	CH$_3$	I	OT$_s$	I
c	(CH$_2$)$_3$I	CH$_2$Ph	CH$_3$CH$_2$	I	BF$_4$	BF$_4$
d	(CH$_2$)$_5$I	CH$_3$	CH$_3$	I	OT$_s$	I
e	(CH$_2$)$_4$I	CH$_3$CH$_2$	CH$_3$	I	BF$_4$	BF$_4$
f	(CH$_2$)$_3$I	CH$_3$CH$_2$	CH$_3$	I	BF$_4$	BF$_4$
g	CH$_3$	CH$_3$CH$_2$	CH$_3$	I	BF$_4$	BF$_4$
h	CH$_3$	CH$_3$	CH$_3$	I	OT$_s$	I
i	CH$_3$	CH$_2$Ph	CH$_3$CH$_2$	I	BF$_4$	BF$_4$
j	CH$_3$	ClCH$_2$C$_6$H$_4$CH$_2$	CH$_3$CH$_2$	I	BF$_4$	I
k	ClCH$_2$C$_6$H$_4$CH$_2$	CH$_3$	CH$_3$	Cl	OT$_s$	OT$_s$

Scheme 3. Microwave Synthesis of Monomethine Cyanine Dyes.

Table 2.

The reaction conditions and yields for cyanine dyes (11_{a-j}).

Dyes	Power (W)	Time (min)	Yield (%)
11_a	320	8	90
11_b	252	6	85
11_c	280	5	93
11_d	320	8	77
11_e	280	6	87
11_f	260	7	82
11_g	260	5	87
11_h	320	5	80
11_i	280	6	80
11_j	280	7	75
11_K	320	7	85

Table 3.

The effect of microwave power and irradiation time on dye (11_a).

Power (W)	Time (min)	Yield (%)
180	2	33
180	3	37
180	5	39
180	6	35
280	3	43
280	5	45
280	7	50
280	8	53
280	9	61
280	10	59
320	4	66
320	5	79
320	7	83
320	8	90
320	9	87

Finally a series of cyanine dyes dimmer (12_{a-e}) were prepared by the reaction of Benzothiazolium, lepidinium dimmer and triethylamine **[Scheme 3]** The mixture was subjected to microwave irradiation for a proper time and power. The details of reaction conditions and yield are provided in **[Table 4]**. The optimized reaction conditions of (12_b) dye are presented in **[Table 5]**.

Dye 12	n	R^1	X	X^1	X^2
a	1	CH_3	OT_s	I	OT_s
b	3	CH_3	OT_s	I	I
c	2	CH_3	OT_s	I	OT_s
d	2	CH_2CH_3	BF_4	BF_4	BF_4
e	1	CH_2CH_3	BF_4	I	I
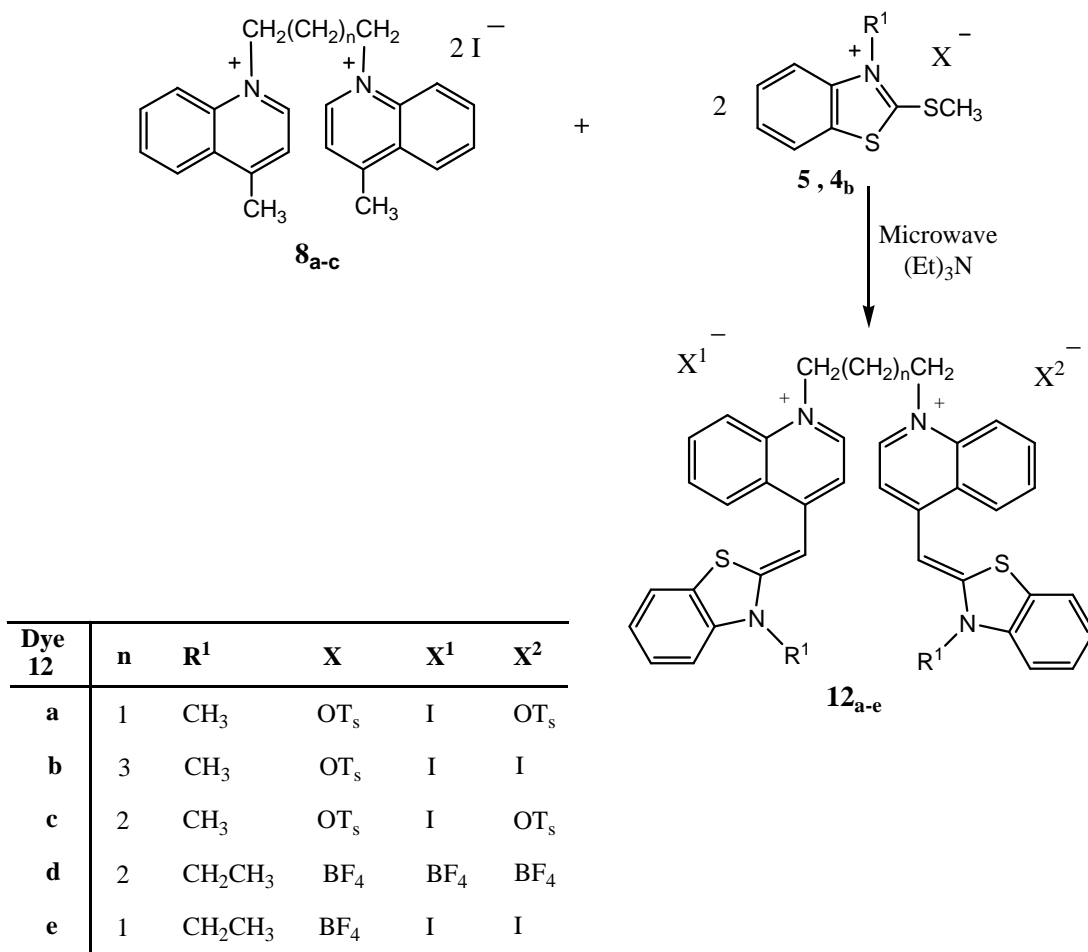
Scheme 4. Microwave Synthesis of Cyanine Dyes Dimmer

Table 4. The reaction conditions and yields for cyanine dye dimmers (12_{a-e})

Dyes	Power (W)	Time (min)	Yield (%)
12_a	200	10	88
12_b	240	10	90
12_c	220	10	87
12_d	240	12	79
12_e	200	10	81

Compared with the solvent refluxing method, the microwave radiation technique has a better yield and a shorter reaction time. It could be found that the yield increased obviously with prolonging irradiation time within a certain power until achieving optimized reaction time. It could also be found that the reaction yield decreases under lower power and the reaction time becomes shorter with the increase of microwave power. This indicates that the greater the microwave radiation power, the faster the reaction rate as shown in tables **[3** and **5]** which explain the effect of microwave power and irradiation time on dyes (**11a**) and (**12b**) respectively.

During the last decades, most asymmetric monomethine cyanine dyes have been prepared by the conventional method involving the reaction of 2-methylmercaptobenzothiazolium salts with 1-alkyl-4-methylquinolinium salts [24, 42]. This encounters a substantial drawback related to the evolution of methyl mercaptan as a pollutant that possesses unpleasant odor. Another drawback is that alkyl groups at sulphur and nitrogen in the quaternized

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alkylmercapto starting materials may exchange their positions leading to unexpected reaction byproducts [43, 44]. By using microwave radiation, we avoid all these aforementioned disadvantages.

3.2. *Spectroscopic study*
The constitution of the prepared compounds was secured by their elemental analysis, UV.-Vis absorption spectra, IR, H^1 NMR, ^{13}C NMR; FAB-MS data (see experimental part).

3.3. **Fluorescence spectral study for some synthesized dyes.**
The electronic absorption spectra of the studied cyanine dyes are shown in Figures (**1-9**). The dyes are generally characterized by very small values of Stoke's shifts between absorption and emission spectral bands indicating that the absorption and emission photons exhibit close frequencies. Other emission broad bands in the near IR spectral range are also obtained that are attributed to phosphorescence and are good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization and makes the present compounds as potential candidates in the area of photodynamic therapy (PDT) [45 - 47].

At higher energies, a second excited electronic state absorption occurs at around 290 nm. This second electronic state gives its characteristic fluorescence at around 390 nm**.** This is yet a peculiar behavior of these compounds since fluorescence dominates the internal conversion (ic) photo physical process.

The electronic absorption spectra of some compounds show two- split absorption peaks which are assigned to the first singlet state absorption of monomeric and J-aggregates of the dye which is a common phenomenon of many cyanine dyes [48, 49].

3.3.1. *Compound [11$_a$]*
The electronic absorption spectrum of compound 11$_a$ shows single absorption peak at 510 nm. This singlet state absorption gives fluorescence peak of emission maximum at 546 nm. The spectral pattern does not alter upon excitation at 480 nm or 510 nm. Like other cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence (**Fig.1**). This becomes of great significance in singlet oxygen sensitization by this compound.
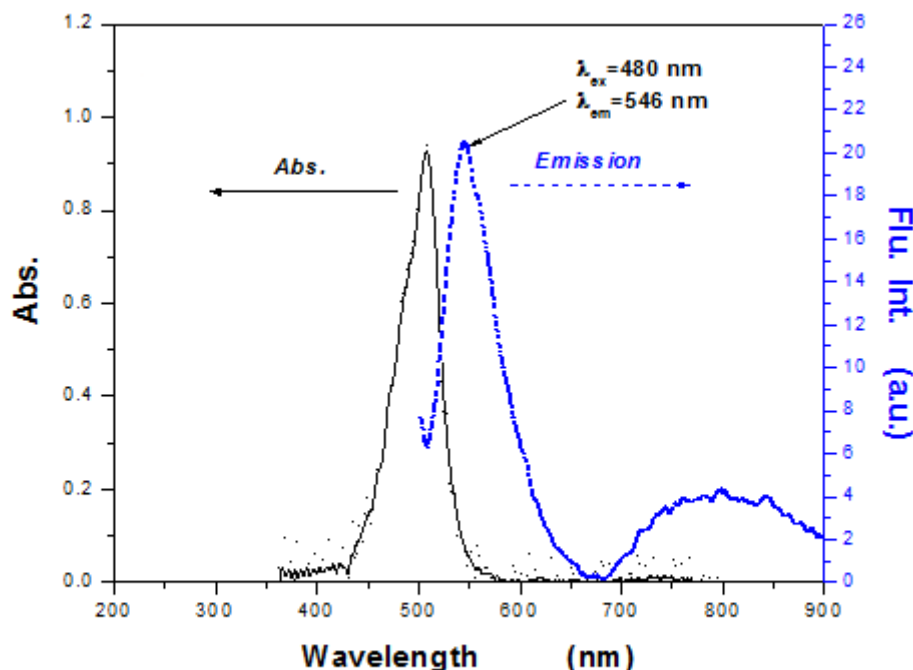
Fig. 1. Absorption and emission spectra of dye 11$_a$

3.3.2. *Compound [11$_e$]*
The electronic absorption spectrum of compound 11$_e$ shows absorption peak at 505 nm. This singlet state absorption gives a symmetrical fluorescence peak of emission maximum at 544 nm upon excitation using 480 nm. light. The compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit

close frequencies. Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

At higher energies, a second excited electronic state absorption occurs at 288 nm. This second electronic state gives its characteristic fluorescence at 388 nm **(Fig.2).** This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
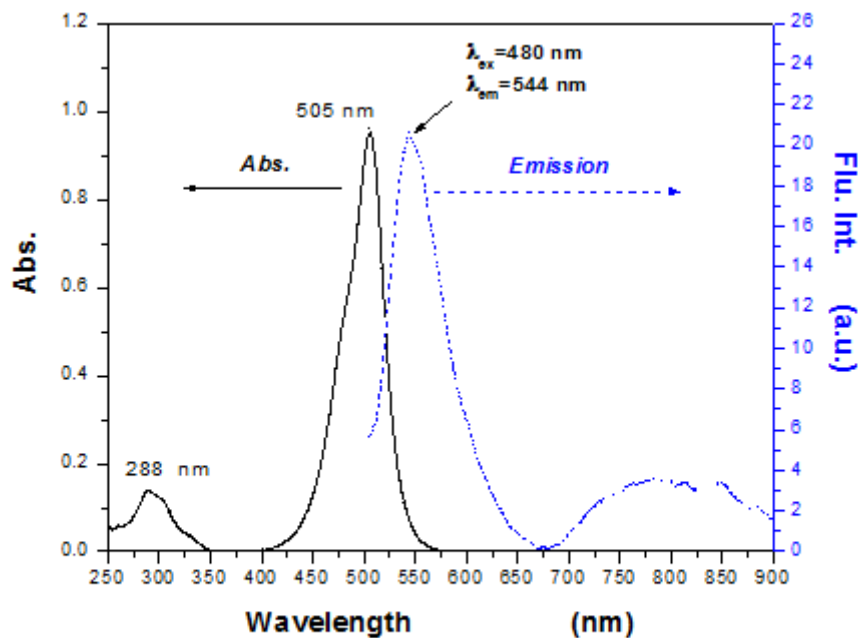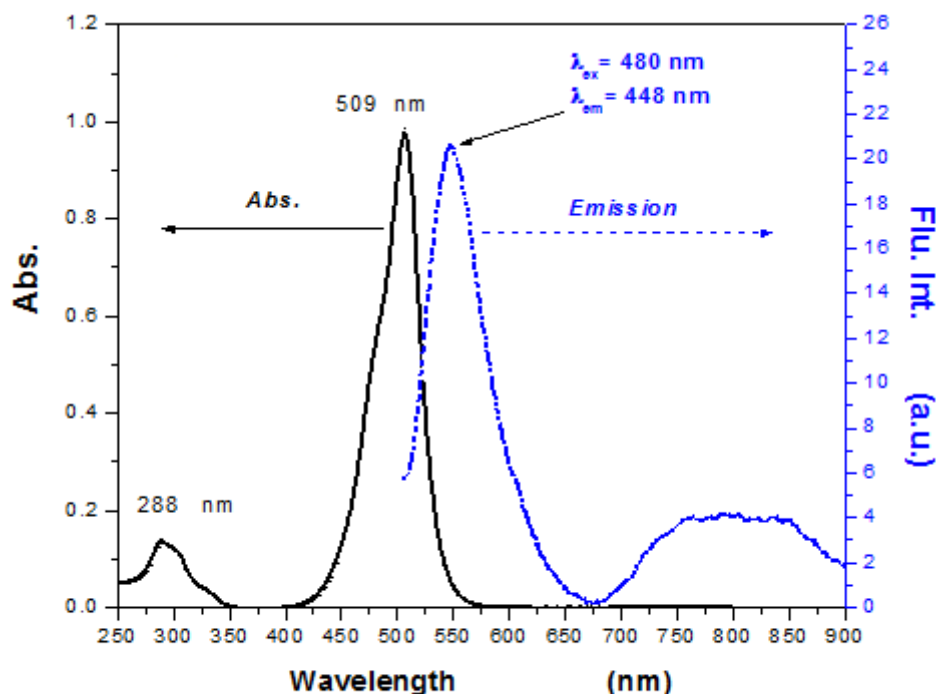

Fig. 2. Absorption and emission spectra of dye 11$_e$

Fig. 3. Absorption and emission spectra of dye 11$_f$

3.3.3. *Compound [11$_f$]*
The electronic absorption spectrum of compound 11$_f$ shows absorption peak at 509 nm, this singlet state absorption gives a symmetrical fluorescence peak of emission maximum at 488 nm upon excitation wavelength 480 nm.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization. At higher energies, a second excited electronic state absorption occurs at 288 nm. This second electronic state gives its characteristic fluorescence at 385 nm **(fig.3).** This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.

3.3.4. Compound [11$_g$]

The electronic absorption spectrum of compound 11$_g$ shows absorption peak at 505 nm, this singlet state absorption gives a symmetrical fluorescence peak of emission maximum at 549 nm. The spectral pattern does not alter upon excitation at 480 nm or 505 nm.

Another emission broad band in the spectral range 700-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization. Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 288 nm. This second electronic state gives its characteristic fluorescence at 385 nm **(fig.4).** This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
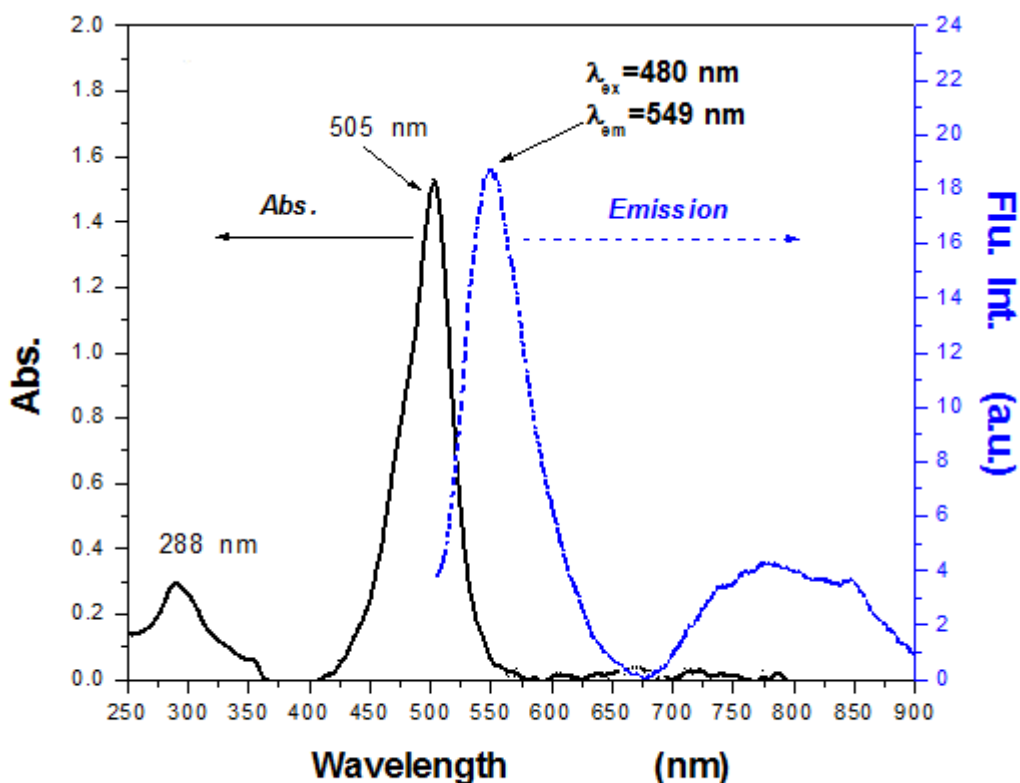

Fig. 4. Absorption and emission spectra of dye 11$_g$

3.3.5. Compound [11$_h$]

The electronic absorption spectrum of compound 11$_h$ shows absorption peak at 500 nm, a first excited electronic state absorption occurs at 480 nm. This first electronic state gives its characteristic fluorescence peak of emission maximum at 552 nm. Another emission broad band in the spectral range 675-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

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At higher energies, a second excited electronic state absorption occurs at 288 nm. This second electronic state gives its characteristic fluorescence at 386 nm **(fig.5)**. This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
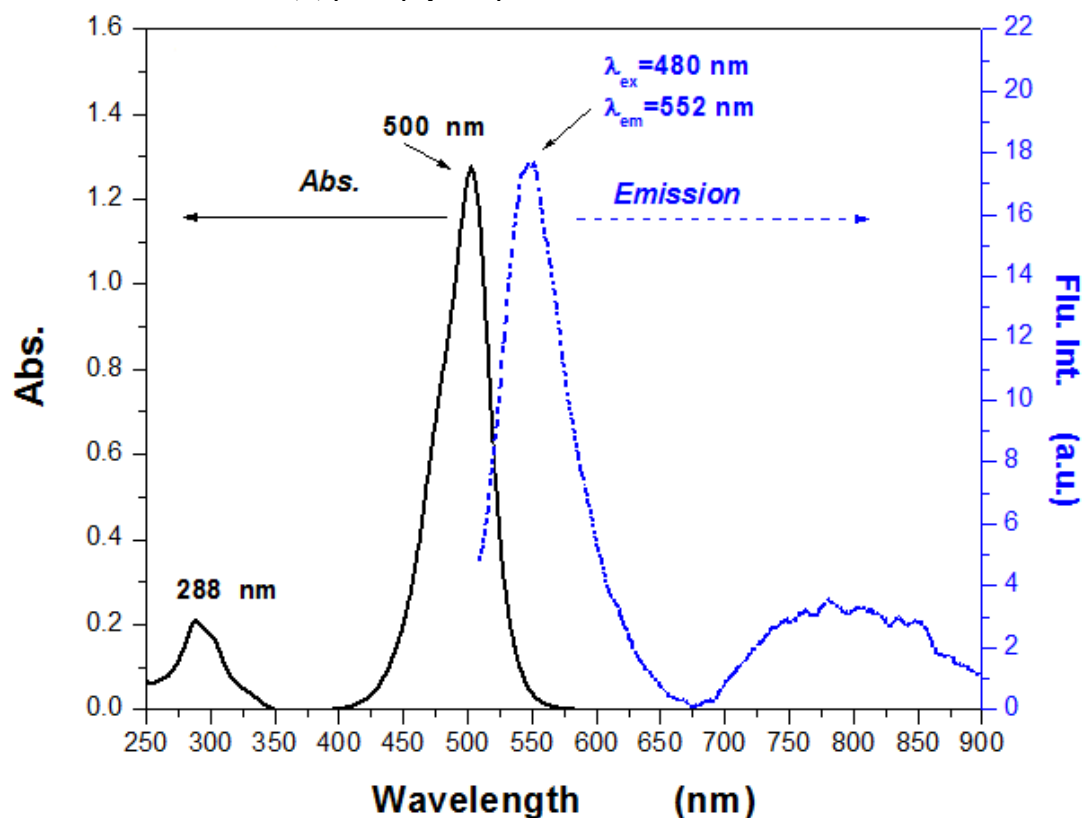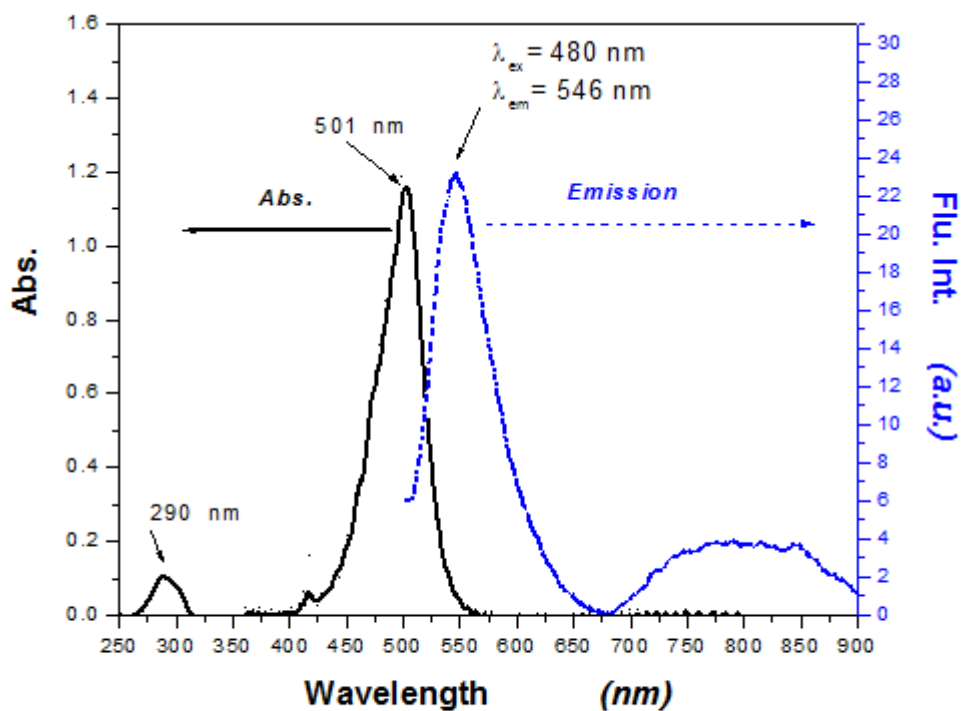

Fig. 5. Absorption and emission spectra of dye 11$_h$

Fig. 6. Absorption and emission spectra of dye 11$_i$

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3.3.6. *Compound [11ᵢ]*

The electronic absorption spectrum of compound 11_i shows single absorption peak   at 503 nm, this singlet state absorption gives a symmetrical fluorescence peak of emission maximum at 546 nm. The spectral pattern does not alter upon excitation at 480 nm or 546 nm. Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 290 nm. This second electronic state gives its characteristic fluorescence at 390 nm **(fig.6)**. This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.

3.3.7. *Compound [11ⱼ]*

The electronic absorption spectrum of compound 11_j shows absorption peak at 500 nm, a first excited electronic state absorption occurs at 480 nm. This first electronic state gives its characteristic fluorescence peak of emission maximum at 542 nm., another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 290 nm. This second electronic state gives its characteristic fluorescence at 386 nm. **(fig.7).** This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
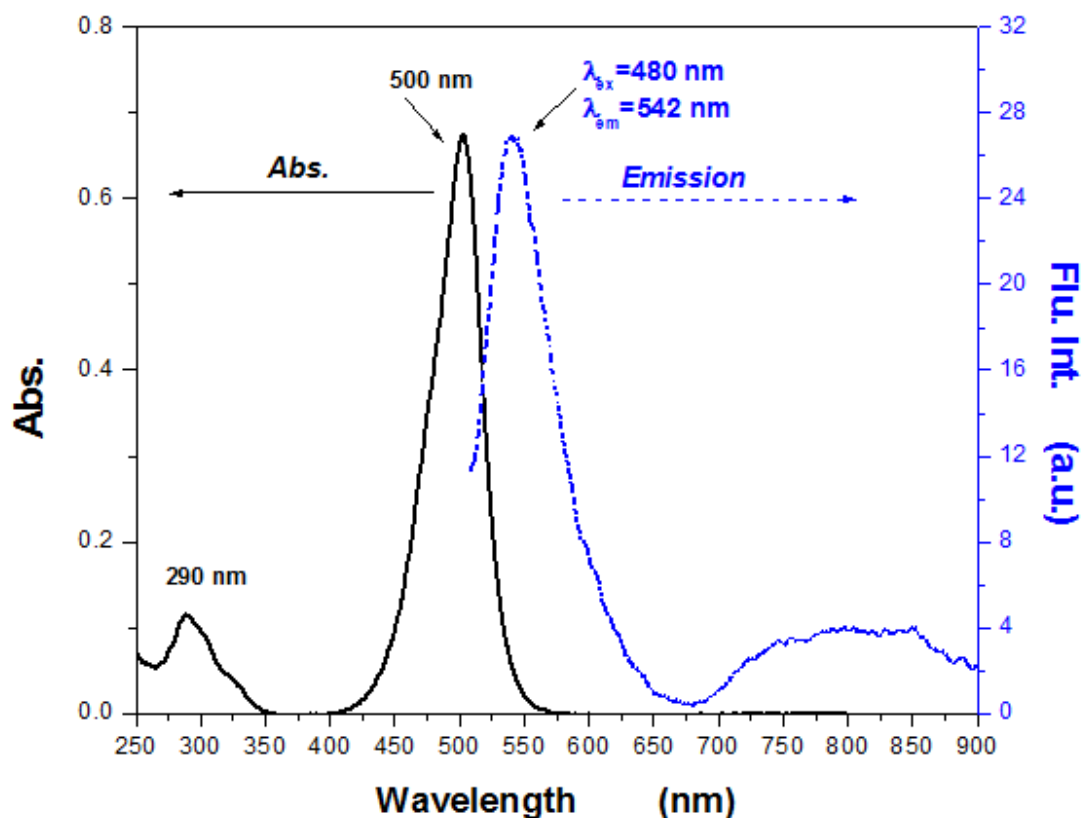

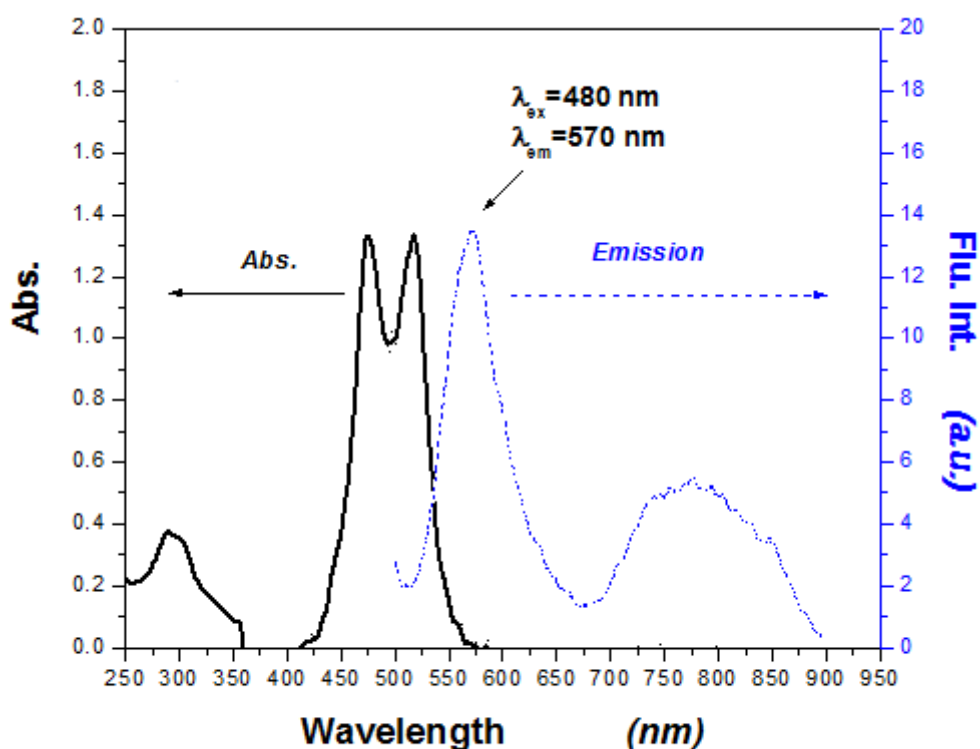**Fig. 7.** Absorption and emission spectra of dye 11_j

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3.3.8. *Compound [12ₐ]*

The electronic absorption spectrum of compound 12_a shows two- split absorption peaks at 477 and 516 nm which are assigned to the first singlet state absorption of monomeric and J-aggregates of the dye [48, 49]. These lower energy J- aggregates give a symmetrical fluorescence peak of emission maximum at 570 nm. The symmetry of this peak together with the fact the its spectral pattern does not alter upon excitation at 477 nm (absorption of monomeric species) or 516 nm (absorption of J-aggregates) indicates an energy transfer from higher energy monomeric species to lower energy aggregates during excited state lifetime. Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 290 nm. This second electronic state gives its characteristic fluorescence at 388 nm. **(fig.8)** this is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
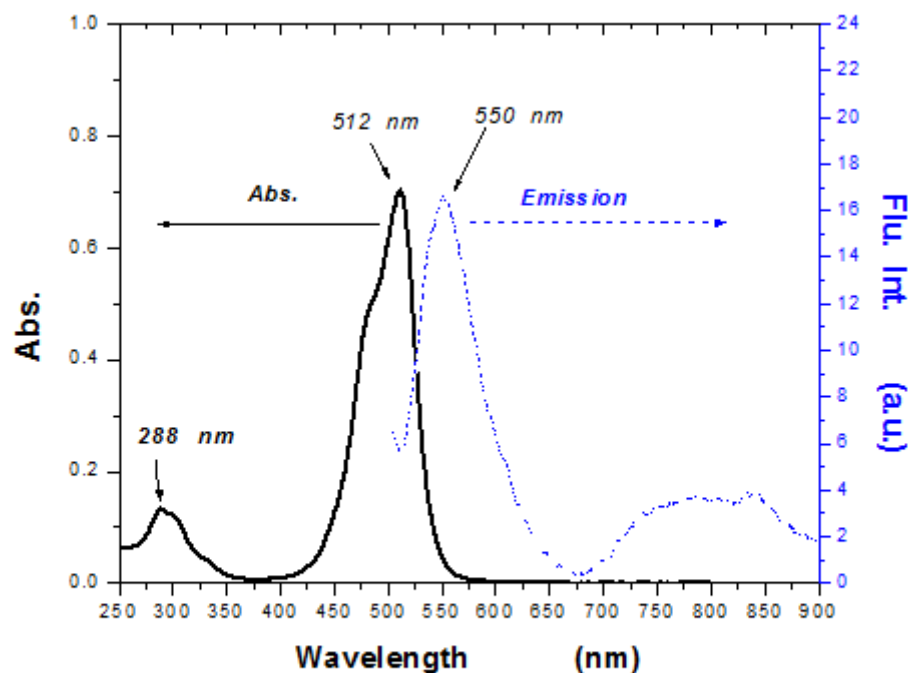

Fig. 8. Absorption and emission spectra of dye 12_a

3.3.9. *Compound [12c]*

The electronic absorption spectrum of compound **12c** shows absorption peak at 512 nm, this singlet state absorption gives a symmetrical fluorescence peak of emission maximum at 550 nm. The spectral pattern does not alter upon excitation at 480 nm or 515 nm. Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization.

Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 288 nm. This second electronic state gives its characteristic fluorescence at 386 nm. **(fig.9)**. This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.
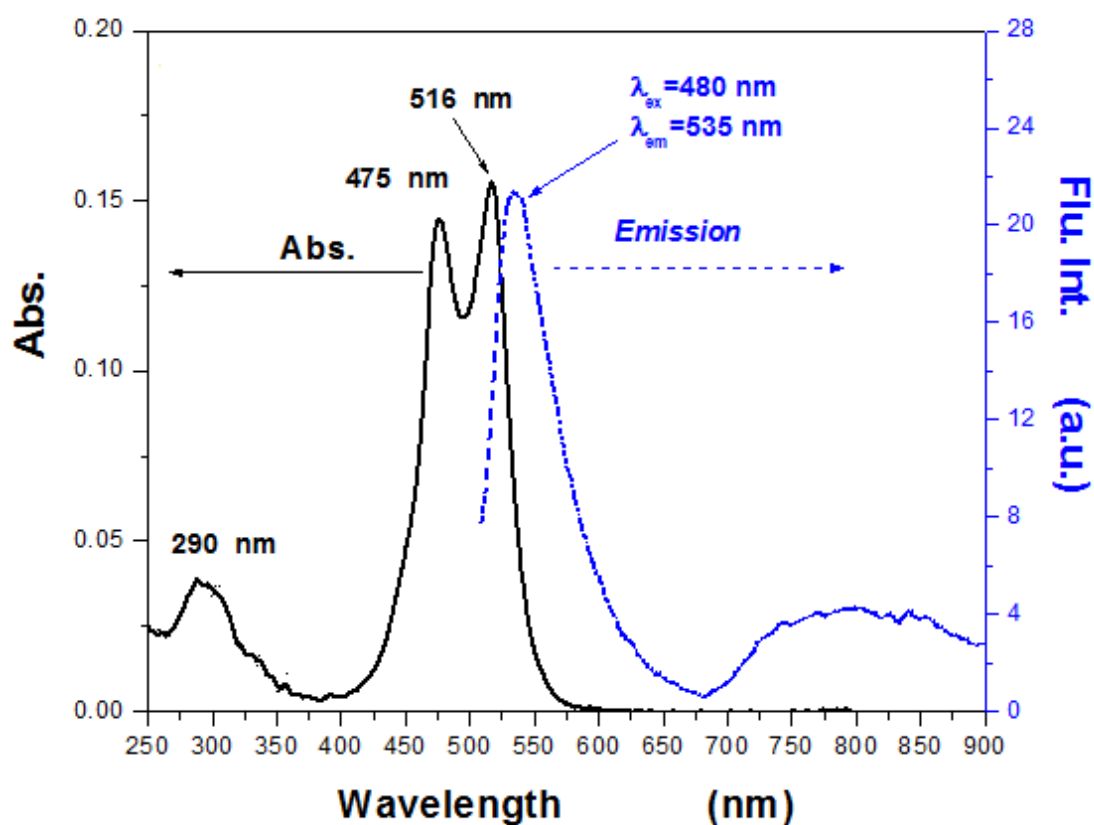
Fig. 9. Absorption and emission spectra of dye **12ₑ**

Fig. 10. Absorption and emission spectra of dye **12ₑ**

3.3.10. *Compound [12ₑ]*

The electronic absorption spectrum of compound **12ₑ** shows two- split absorption peaks at 475 and 516 nm which are assigned to the first singlet state absorption of monomeric and J-aggregates of the dye[48, 49]. These lower energy

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J- aggregates give a symmetrical fluorescence peak of emission maximum at 535 nm. The symmetry of this peak together with the fact the its spectral pattern does not alter upon excitation at 475 nm (absorption of monomeric species) or 516 nm (absorption of J-aggregates) indicates an energy transfer from higher energy monomeric species to lower energy aggregates during excited state lifetime.

Another emission broad band in the spectral range 680-900 nm is also obtained that is attributed to phosphorescence and is a good indication of triplet state formation. This becomes of great significance in singlet oxygen sensitization. Like cyanine dyes, the compound is characterized by very small values of Stoke's shifts where absorption and emission photons exhibit close frequencies.

At higher energies, a second excited electronic state absorption occurs at 290 nm. This second electronic state gives its characteristic fluorescence at 388 nm. **(fig.10)**. This is yet a peculiar behavior of this compound since fluorescence dominates the internal conversion (ic) photo physical process.

CONCLUSION

We have described rapid and highly efficient method for the synthesis of monomethine cyanine dyes with quinoline nucleus under solvent- free microwave irradiation. The electronic absorption and steady state fluorescence spectra of prepared dyes have been investigated revealing a potential use of these dyes as singlet oxygen sensitizers. The prepared dyes absorb in the region 500-618 nm and their fluorescence emissions are located at 448-570 nm.

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