Indian Journal of Chemistry
Vol. 45B, May 2006, pp. 1197-1203

New photosensitizer cyanine dyes: Synthesis and properties

H A Shindy*, M A El-Maghraby & F M Eissa
Department of Chemistry, Aswan Faculty of Science, Aswan, Egypt
E mail: hashindy@hotmail.com

Received 19 Nov 2003; accepted (revised) 9 Nov 2004

New photosensitizers, dimethine, bis dimethine and tetramethine cyanine dyes containing furo, thieno and pyrrolo [2,3-*b*] pyrazole nucleus are prepared. Spectral characterization of the prepared cyanine dyes are examined in 95% ethanol solution. Structural determination is carried out via elemental analysis, IR and ^{1}H NMR spectra.

Keywords: Photosensitizer, cyanine dyes, dimethine, bis dimethine, tetramethine, pyrazole

IPC: **Int.Cl.^{8} C 07 D**

Cyanine dyes are important as photographic sensitizing materials[1], model locking and lasing media for lasers[2]. Cyanines are employed extensively as spectral sensitizers for inorganic large band-gab semiconductor materials[3–8], in optical disks as recording media[9–11], in industrial paints, for trapping of solar energy[12], in light harvesting systems of photosynthesis[13–15], as photorefractive materials[16], as antitumor agents[17], and as probes for biological systems[18–22].

Results and Discussion

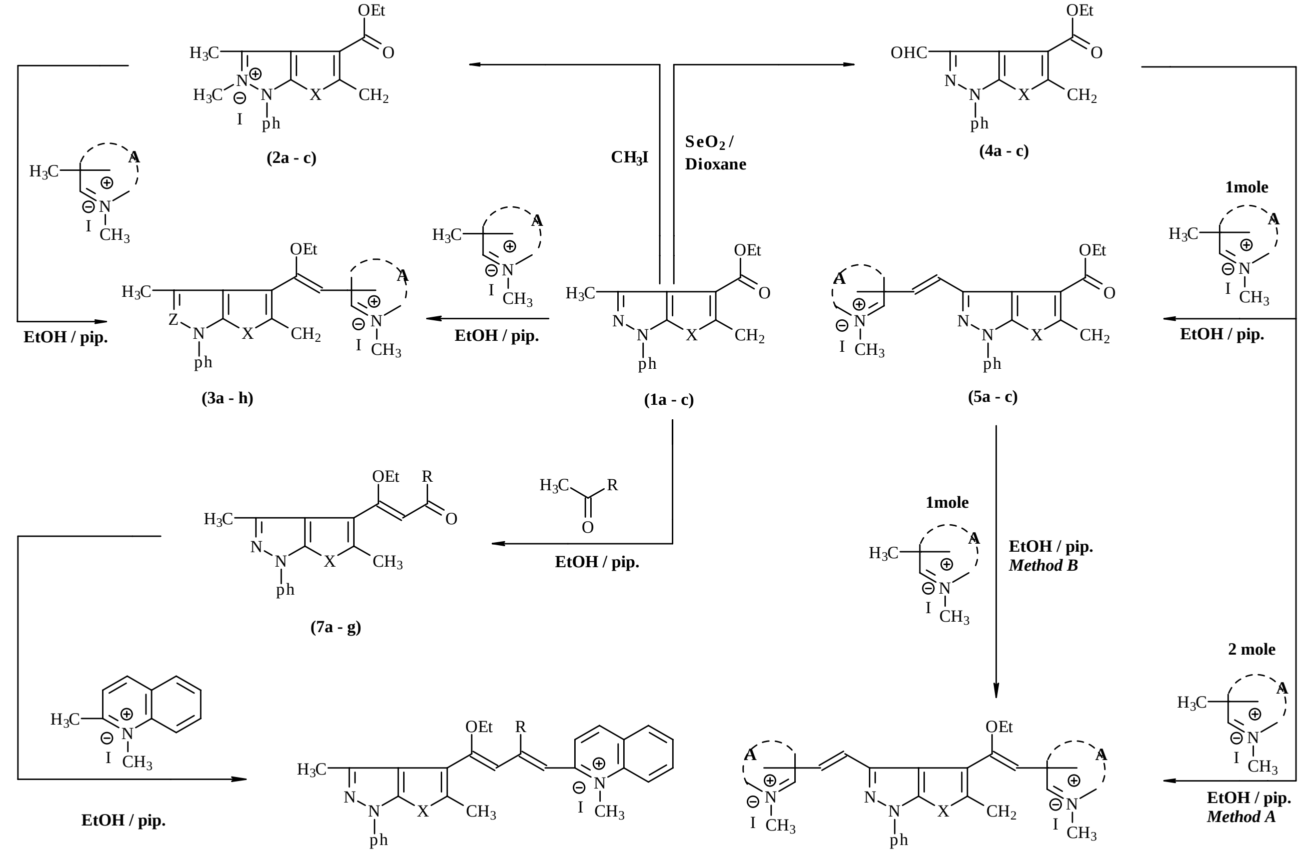
Extended to our previous publications in the field of cyanine dyes[23,24], 4-ethoxycarbonyl-3,5-dimethyl-1-phenyl-furo, thieno and pyrrolo [2,3-*b*] pyrazole **1a-c** and their 2-methyl iodide quaternary salts **2a–c** were reacted with 1,2-dimethyl pyridinium iodide salt, 1,2-dimethyl quinolinium iodide salt and 1,4-dimethyl pyridinium iodide salt in equimolar ratios and in ethanol containing piperidine and resulted in the 4[2(4)] cationic and bis cationic dimethine cyanine dyes **3a-h (Scheme I**, **Table I)**.

Selenium dioxide oxidation of **1a-c** in dioxane solution led to their carbaldehyde compounds **4a-c** which subsequently reacted with equimolar (bimolar) ratios of *N*-methyl (α-picolinium, quinaldinium, γ-picolinium) iodide salts in ethanol catalysed by piperidine to give the 3[2(4)] dimethine cyanines **5a-e** and 3,4[2(4)]-bis dimethine cyanines **6a-e (Scheme I**, **Table II)**. Chemical confirmation of **6a-e** was further supported by interacting of equimolar ratios of **5a-e** and iodomethane quaternary salts of α-picoline, quinaldine, γ-picoline in ethanolic solution under similar reaction condition giving the same compounds **6a-e**, characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data (**Scheme I**, **Table II**).

Furthermore, reaction of **1a-c** with acyl and substituted acyl compounds in ethanol and presence of few drops of piperidine led to the formation of **7a-g** as intermediate compounds. Ethanolic solution catalysed by piperidine of the intermediate **7a-g** reacted with the *N*-methyl iodide quaternary salt of 2-methyl quinoline to give the 4 (2) tetramethine cyanine dyes **8a-g (Scheme I**, **Table III)**.

The structures of the new prepared compounds were characterized by elemental analysis, IR[25] and ^{1}H NMR[26] spectra (**Tables I-III**).

The new prepared cyanine dyes are highly coloured compounds, they are partially soluble in non polar organic solvents but easily soluble in polar organic solvents exhibiting coloured solutions, accompanied by pale to intense fluorescence. The intensity and colour of the fluorescence depend upon the type of dye and solvent used. They exhibit general solute–solvent interaction depending on the dielectric constant of the solvent used, as well as specific solute–solvent interaction, this includes hydrogen bonding and molecular complex. They are soluble in concentrated H_2SO_4 liberating iodine vapour on warming. They are *p*H sensitive dyes, so their ethanolic solutions gave changeable colour on



Scheme I

Table I – Characterization of compounds **3a-h**

Compd	Nature of product	Yield (%)	m.p. °C	Mol. formula (Mol. wt.)	Calcd % (found)			UV (95% ethanol)	
					C	H	N	λ_{max} (nm)	ε_{max} (mole^{-1}cm^{2})
3a	Reddish brown crystals	35	162	$C_{23}H_{24}O_2N_3I$ (501)	—	—	—		
3b	Brown crystals	31	170	$C_{27}H_{26}O_2N_3I$ (551)	58.8 (58.7	4.7 4.9	7.6 7.4)	507, 388	12280, 15530
3c	Reddish brown crystals	36	163	$C_{23}H_{24}O_2N_3I$ (501)	55.1 (55.3	4.8 4.5	8.4 8.5)	499	11950
3d	Dark brown crystals	54	174	$C_{27}H_{26}ON_3IS$ (567)	57.1 (57.0	4.6 4.7	7.4 7.6)	508, 402	12100, 16700
3e	Dark brown crystals	43	171	$C_{27}H_{27}ON_4I$ (550)	58.9 (58.7	4.9 4.9	10.2 10.4)	511, 398	10690, 9490
3f	Brown crystals	61	169	$C_{28}H_{29}O_2N_3I_2$ (693)	48.5 (48.5	4.2 4.2	6.1 6.0)	516, 411	11150, 16280
3g	Dark brown crystals	54	191	$C_{28}H_{29}ON_3I_2S$ (709)	47.4 (47.3	4.1 4.0	5.9 6.1)	518, 411	12570, 12660
3h	Dark brown crystals	51	181	$C_{28}H_{30}ON_4I_2$ (692)	48.6 (48.3	4.3 4.2	8.1 8.3)	523, 407	11060, 13170

^{1}H NMR (DMSO): **3b**; 1.28-1.38 (t, 3H, CH_3 of ethoxy), 3.97-4.18 (q, 2H, CH_2 of ethoxy), 3.4-3.65 (m, 9H, $3CH_3$ of C_3, C_5 and *N*-quinoline), 6.94-7.95 (m, 12H, aromatic, heterocyclic and - CH=).

acid/base media giving yellow or colourless on acidification and restored their permanent colour on basification. Their intense colour is due to the two suggested mesomeric structures A[B($\bar{B}$)] producing delocalized positively charged over the conjugate system (**Scheme II**).

Spectral properties of the new prepared cyanine dyes were determined by studying their electronic visible absorption spectra in 95% ethanol solution.

Table II – Characterization of compounds **4a-c**; **5a-e** and **6a-e**

Compd	Nature of product	Yield (%)	m.p. °C	Mol. formula (Mol. wt.)	Calcd % (found)			UV (95% ethanol)	
					C	H	N	λ_{max}(nm)	ε_{max} (mole^{-1}cm^2)
4a	Reddish crystals	62	155	$C_{16}H_{14}O_4N_2$ (298)	64.4 (64.1	4.7 5.0	9.4 9.2)	—-	—-
4b	Dark red crystals	46	149	$C_{16}H_{14}O_3N_2S$ (314)	61.1 (61.0	4.5 4.3	8.9 9.1)	—-	—-
4c	Yellowish red crystals	67	152	$C_{16}H_{15}O_3N_3$ (297)	64.6 (64.4	5.1 5.3	14.1 14.2)	—-	—-
5a	Brown crystals	48	179	$C_{23}H_{22}O_3N_3I$ (515)	53.6 (53.8	4.3 4.0	8.2 8.3)	491	11980
5b	Violet crystals	46	181	$C_{27}H_{24}O_3N_3I$ (565)	57.3 (57.2	4.2 4.5	7.4 7.1)	506, 377	12020, 8380
5c	Brown crystals	40	180	$C_{23}H_{22}O_3N_3I$ (515)	53.6 (53.3	4.3 4.5	8.2 8.3)	493	9970
5d	Dark violet crystals	52	195	$C_{27}H_{24}O_2N_3IS$ (581)	55.8 (55.6	4.1 4.5	7.2 7.0)	509	13170
5e	Violet crystals	48	175	$C_{27}H_{25}O_2N_4I$ (564)	57.4 (57.8	4.4 4.1	9.9 9.7)	512	13800
6a	Deep brown crystals	31	176	$C_{30}H_{30}O_2N_4I_2$ (732)	49.2 (49.6	4.1 3.9	7.7 7.9)	499	11980
6b	Deep violet crystals	37	181	$C_{38}H_{34}O_2N_4I_2$ (832)	54.8 (54.0	4.1 4.5	6.7 6.5)	513, 397	14690, 11890
6c	Deep brown crystals	36	177	$C_{30}H_{30}O_2N_4I_2$ (732)	49.2 (49.0	4.1 4.5	7.7 7.5)	501	12010
6d	Deep violet crystals	62	195	$C_{38}H_{34}ON_4I_2S$ (848)	53.8 (53.9	4.0 4.1	6.6 6.4)	516	15690
6e	Pale violet crystals	53	183	$C_{38}H_{35}ON_5I_2$ (831)	54.9 (55.0	4.2 4.0	8.4 8.6)	518	13100

^{1}H NMR (DMSO): **4a**: 1.08-1.31(t, 3H, CH_3 of ethoxy), 3.83-4.22(q, 2H, CH_2 of ethoxy), 3.6(s, 3H, CH_3 of C_5), 6.96-7.50(m, 5H, aromatic), 9.15(s, 1H, CHO); **5b**: 1.03-1.15(t, 3H, CH_3 of ethoxy), 3.82-4.02(q, 2H, CH_2 of ethoxy), 3.30-3.67(m, 6H, $2CH_3$ of C_5 and *N*-quinoline), 6.79-7.65(m, 13H, aromatic, heterocyclic and - CH=); **6b**: 1.28-1.41(t, 3H, CH_3 of ethoxy), 3.77-4.10(q, 2H, CH_2 of ethoxy), 3.00-3.40(m, 9H, $3CH_3$ of C_5 and *N*-quinolinium), 6.51-7.62(m, 20H, aromatic, heterocyclic and = CH-).

Table III – Characterization of compounds **7a-g** and **8a-g**

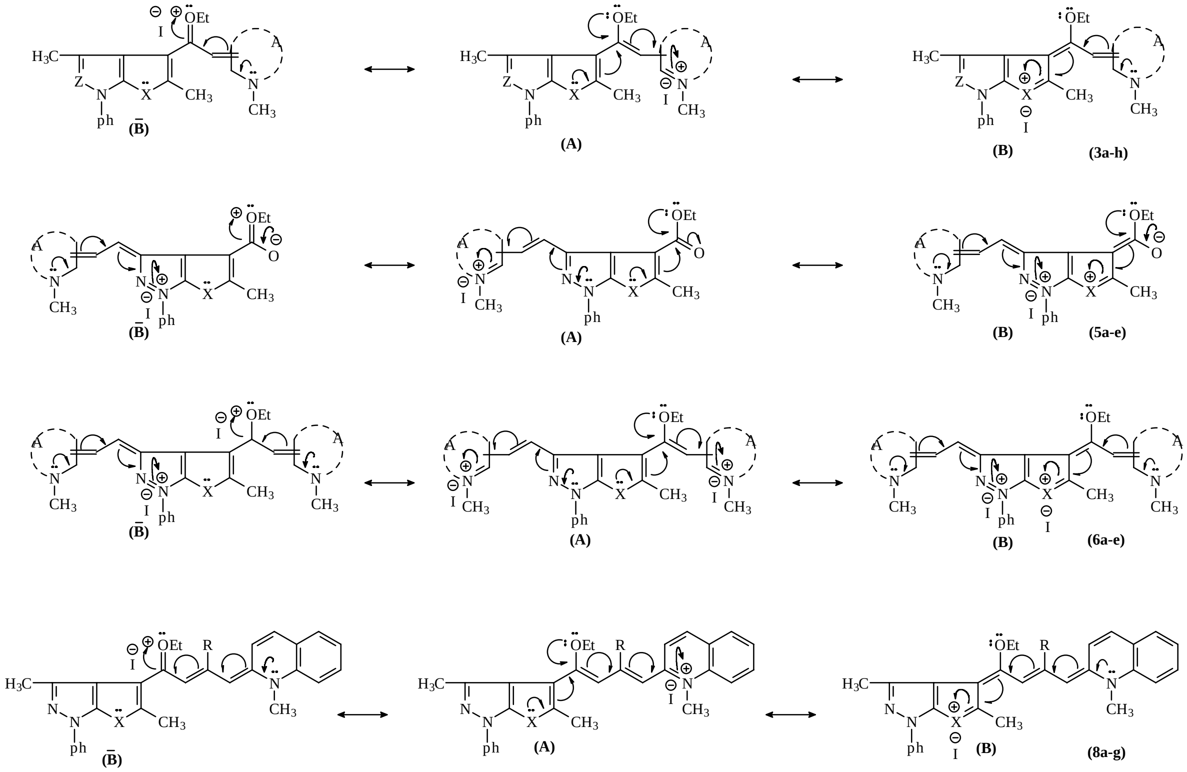
Compd	Nature of product	Yield (%)	m.p. °C	Mol. formula (Mol. wt.)	Calcd % (found)			UV (95% ethanol)	
					C	H	N	λ_{max} (nm)	ε_{max} (mole^{-1}cm^2)
7a	Brown crystals	65	180	$C_{18}H_{18}O_3N_2$ (310)	69.7 (69.4	5.8 5.7	9.0 9.3)	____	____
7b	Brown crystals	60	160	$C_{19}H_{20}O_3N_2$ (324)	70.4 (70.5	6.2 60	8.6 8.5)	____	____
7c	Pale brown crystals	52	151	$C_{24}H_{22}O_3N_2$ (386)	74.6 (74.2	5.7 6.1	7.3 7.4)	____	____
7d	Deep brown crystals	57	161	$C_{25}H_{24}O_4N_2$ (416)	72.1 (72.3	5.8 5.6	6.7 6.8)	____	____
7e	Reddish brown crystals	67	152	$C_{24}H_{21}O_5N_3$ (431)	66.8 (66.9	4.9 4.7	9.7 9.6)	____	____
7f	Deep brown crystals	59	173	$C_{19}H_{20}O_2N_2S$ (340)	67.1 (67.3	5.9 5.7	8.2 8.5)	____	____
7g	Brown crystals	61	165	$C_{19}H_{21}O_2N_3$ (323)	70.6 (70.4	6.5 6.8	13.0 13.4)	____	____
8a	Reddish violet Crystals	50	197	$C_{29}H_{28}O_2N_3I$ (577)	60.3 (60.1	4.9 5.0	7.3 7.4)	499	15250
8b	Deep violet crystals	51	191	$C_{30}H_{30}O_2N_3I$ (591)	60.9 (60.8	5.1 5.2	7.1 7.2)	508, 405	16800, 12600

—*Contd*

Table III — Characterization of compounds **7a-g** and **8a-g** — *Contd*

Compd	Nature of product	Yield (%)	m.p. °C	Mol. formula (Mol. wt.)	Calcd % (found)			UV (95% ethanol)	
					C	H	N	λ_{max} (nm)	ε_{max} (mole^{-1}cm^2)
8c	Reddish violet crystals	62	178	$C_{35}H_{32}O_2N_3I$	64.3	4.9	6.4	518, 407	17880, 15420
				(653)	(64.1	4.8	6.6)		
8d	Bluish violet crystals	51	175	$C_{36}H_{34}O_3N_3I$	63.3	5.0	6.1	528, 403	15080, 16060
				(683)	(63.5	4.8	6.4)		
8e	Brown crystals	47	201	$C_{35}H_{31}O_4N_4I$	60.2	4.4	8.0	506, 411	13990, 15151
				(698)	(60.4	4.6	8.1)		
8f	Intense violet crystals	69	187	$C_{30}H_{30}ON_3SI$	59.3	4.9	6.9	510, 401	19090, 17630
				(607)	(59.1	5.1	6.9)		
8g	Reddish violet crystals	55	195	$C_{30}H_{31}ON_4I$	61.0	5.3	9.5	512, 424	15200, 13980
				(590)	(61.3	5.1	9.4)		

^{1}H NMR (DMSO): **7b**: 1.15-1.32(t, 3H, CH_3 of ethoxy), 4.03-4.23(q, 2H, CH_2 of ethoxy), 3.41-3.72(m, 9H, 3CH_3 of C_3, C_5 and acyl), 6.80-7.34(m, 6H, aromatic and - CH=); **8b**: 1.29-1.42(t, 3H, CH_3 of ethoxy), 3.95-4.13(q, 2H, CH_2 of ethoxy), 3.28-3.8(m, 12H, 4CH_3 of C_3, C_5, *N*-quinolinium and diene CH_3), 6.73-7.72(m, 13H, aromatic, heterocyclic and - CH=).



Scheme II

The electronic absorption spectra of the dimethine cyanine dyes **3a-h**, **5a-e** and bis-dimethine cyanine dyes **6a-e** in 95% ethanol showed absorption spectra bands, which their positions and molar extinction coefficients are influenced by the nature of the heterocyclic quaternary residue, their linkage position, kind of hetero atoms in the biheterocyclic ring and the extra quaternization in pyrazole ring. The dyes **3a**, **5a**, **6a**, X = O, A = 1-methyl pyridinium-2-yl salts disclose hypsochromically shifted bands by 11 nm, 15 nm, 14 nm, if compared with the dyes **3b**, **5b**, **6b**, X = O, A = 1-methyl-quinolinium-2-yl salt accompanied by decreasing number and intensity of the bands. This is due to the increasing π-delocallization to the heterocyclic quaternary residue in the latter dyes, **(Scheme I, Tables I** and **II)**. Changing the linkage position from 2-yl salt to 4-yl salt transferring from dyes **3a**, **5a**, **6a** to dyes **3c**, **5c**, **6c** make bathochromic shift and intensification for the absorption bands **(Scheme I**, **Tables I**, **II)**. This is due to the extended conjugation present in the latter dyes. Also the dyes **3b**, **5b**, **6b** which contain the furan ring shown to give hypsochromically shifted bands if compared with their analogous dyes **3d**, **3e**, **5d**, **5e**, **6d**, **6e** which contain thiophene and pyrrole rings, and consequently the dyes **3d**, **5d**, **6d** which contain the thiophene ring disclose hypsochromically shifted bands if compared with their analogous dyes **3e**, **5e**, **6e** which contain pyrrole ring (**Scheme I, Tables I**, **II)**. This is due to that the furan ring in dyes **3b**, **5b**, **6b** has electron attracting character more than thiophene and pyrrole rings in dyes **3d**, **3e**, **5d**, **5e**, **6d**, **6e** and the thiophene ring in dyes **3d**, **5d**, **6d** is more electron attracting than pyrrole ring in dyes **3e**, **5e**, **6e**, respectively. It is also interesting to note that the dyes **3b**, **3d**, **3e** have absorption spectra bands, seem to display hypsochromically shifted if compared to their analogous dyes **3f**, **3g**, **3h (Scheme I**, **Table II)**. This is due to extra quaternization in the latter dyes. Moreover, by comparison of the absorption spectral bands of the mono cationic dimethine cyanine dyes **5a-e** with the dicationic bis dimethine cyanine dyes **6a-e**, latter dyes have bathochromically shifted bands due to the presence of two conjugated charge transfer pathways in the dyes structure from $\ddot{N}-$pyrazole to the $\overset{\oplus}{N}-$heterocyclic quaternary salt (left side of the dye molecule) and from either $\underset{\cdot\cdot}{\ddot{O}}-$furan, $\underset{\cdot\cdot}{\ddot{S}}-$thiophene, $\ddot{N}$H-pyrrole to the $\overset{\oplus}{N}-$heterocyclic quaternary salt (right side of the dye molecule), **(Schemes I**, **II, Table III)**.

The electronic absorption spectra of the tetramethine cyanine dyes **8a-g** in 95% ethanol showed bands underwent bathochromic and hypsochromic shifts depending on the substituted side chain (*R*) and the type of biheterocyclic rings. So, substituting R = H in dye **8a** by R= CH_3, phenyl to give dyes **8b**, **8c** causes bathochromic shift with increasing number and intensity of the absorption bands. This is due to the hyperconjugative electron donating character of CH_3 group in dye **8b**, and increasing π-delocallization conjugation in dye **8c** due to the presence of phenyl ring **(Scheme I**, **Table III)**. Additionally, the spectra of the dye **8c** showed to give hypsochromic and bathochromic shifted bands if compared with the dyes **8d**, **8e** respectively, **(Scheme I**, **Table III)**. This can be attributed to the electron releasing character of OCH_3 group in dye **8d** and electron attracting character of NO_2 group in dye **8e**. Furthermore, the spectra of dye **8b**, disclose blue shifted bands if compared with the spectra of the dyes **8f** and **8g**, respectively. Also the spectra of the dye **8f** disclose blue shifted bands if compared with the spectra of the dye **8g**. This confirms the same reasons mentioned before in the spectra of the former dyes **(Scheme I**, **Table III)**.

Conclusion

Based on these studies, it can be concluded that the photosensitization of the cyanine dyes are very markedly dependent on the nature of the dyes structures. Photosensitization of the dyes increases by increasing conjugation in the dye molecule and decreases by decreasing conjugation in the dye molecule. Otherwise, the photosensitization of the dyes increases by decreasing the electronegativity of the hetero atom in the biheterocyclic ring of the dye and decreases by the increasing the electronegativity of the hetero atom in the biheterocyclic ring of the dye. Electron donating groups increase the photosensitization of the dyes while electron accepting groups decrease the photosensitization. Increasing number of methine group gives more photosensitizers dyes, and dyes which have two conjugated charge transfer pathways inside the dye molecule are better photosensitizers than their analogues which have only one conjugated charge transfer pathway.

Experimental Section

All melting points are uncorrected. Elemental analyses were carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Heraeus). IR (KBr pellets) spectra were determined on a Perkin-Elmer Infrared 127 spectrophotometer (Cairo University), and the ^1H NMR spectra were obtained using 400 and 300 MHz NMR Spectrophotometer (Assiut and Cairo Universitis). Electronic visible absorption spectra were carried out on a Shimadzu UV-Visible recording spectrophotometer (South Valley University, Faculty of Science, Aswan).

Synthesis of 4-ethoxycarbonyl-3,5-dimethyl-1-phenyl-furo, thieno and pyrrolo [2,3-*b*]pyrazole 1a-c and their 2-methyl iodide quaternary salts 2a–c. These compounds were prepared by earlier literature methods[24].

Synthesis of 3,5-dimethyl (2,3,5-trimethyl)-1-phenyl-furo, thieno and pyrrolo [2,3-*b*]pyrazole

(pyrazolium iodide)-4[2(4)]-cationic (bis cationic) dimethine cyanine dyes 3a-h. Equimolar ratios (0.01 mole) of **1a-c, 2a-c** and 1-methyl (α-picolinium, quinaldinium, γ-picolinium) iodide salts were refluxed in ethanol (30 mL) in presence of piperidine (3-5 drops) for 8-10 hr. The reaction mixture changed from yellowish–brown to deep brown–violet at the end of refluxing. It was filtered while it was hot, concentrated to half of its volume, cooled and neutralized with acetic acid. The precipitated products which appeared on dilution with water were collected, washed several times with water, dried and crystallized from ethanol (**Table I**).

Synthesis of 4-ethoxycarbonyl-3-formyl-5-methyl-1-phenyl-furo, thieno and pyrrolo [2,3-*b*]pyrazole 4a-c. Selenium dioxide and **1a-c** were refluxed in equimolar ratios (0.01 mole) in dioxane (30 mL) for 16-20 hr. The reaction mixture attained a reddish brown colour at the end of refluxing. It was filtered while it was hot to remove selenium metal, concentrated and cooled. The precipitates were crystallized from ethanol (**Table II**).

Synthesis of 4-ethoxycarbonyl-5-methyl-1-phenyl-furo, thieno and pyrrolo [2,3-*b*]pyrazole-3[2(4)]-dimethine cyanine dyes 5a-e. A mixture of equimolar ratios (0.01 mole) of **4a-c** and methyl iodide quaternary salts of 2-picoline, quinaldine, 4-picoline were dissolved in ethanol (30 mL), then piperidine (3-5 drops) was added. The reaction mixture colour changed from brown to dark brown-violet after refluxing for 8-10 hr. It was filtered while it was hot, cooled, neutralized with acetic acid and precipitated by dilution with water. The precipitated products were collected, washed with water several times and crystallized from ethanol (**Table II**).

Synthesis of 5-methyl-1-phenyl-furo, thieno and pyrrolo [2,3-*b*]pyrazole 3,4[2(4)]-bis dimethine cyanine dyes 6a-e. Two different methods are used to prepare such cyanines:

Method A: Unimolar ratios of **4a-c** (0.01 mole) and bimolar ratios of *N*-methyl (α-picolinium, quinaldinium, γ-picolinium) iodide salts (0.02 mole) were heated at reflux for 8-10 hr in ethanol (50 mL) containing piperidine (3-5 drops). The reaction mixture which changed from reddish-brown to dark brown-violet at the end of refluxing, was filtered while it was hot, concentrated and neutralized with glacial acetic acid. The precipitated products which appeared on dilution with the addition of water were filtered, washed several times with water and crystallized from ethanol (**Table II**).

Method B: Dimethine cyanines **5a-e** and equimolar ratios (0.01 mole) of *N*-methyl iodide, quaternary salts of α-picoline, quinaldine, γ-picoline were heated at reflux for 3-5 hr in ethanol (50 mL) and presence of few drops (3-5) of piperidine. The reaction mixture was filtered while it was hot, concentrated to half of its volume, cooled and neutralized with acetic acid. The precipitated products which appear on dilution with water were collected, washed with water, dried and crystallized from ethanol to give the same compounds **6a-e** obtained by *Method A*, characterized by melting points, mixed melting points, identical IR and ^{1}H NMR spectra (**Tables II**).

Synthesis of 3,5-dimethyl-1-phenyl-4-[3-*R*-1-ethoxy-1-propene-3-one]-furo, thieno and pyrrolo [2,3-*b*] pyrazole 7a-g as intermediate compounds. An ethanolic solution (30 mL) of **1a-c** (0.01 mole) and acetaldehyde, acetone, acetophenone, *ρ*-methoxy acetophenone, *ρ*-nitro acetophenone (0.01 mole) were refluxed for 7-9 hr in the presence of piperidine (3-5) drops. The colour of the reaction mixture changed from reddish brown to dark brown at the end of refluxing. It was filtered while it was hot, concentrated, cooled, neutralized with acetic acid and precipitated by addition of ice-water. The precipitate was collected and crystallized from ethanol (**Table II**).

Synthesis of 3,5-dimethyl-1-phenyl -furo, thieno and pyrrolo[2, 3 - *b*]pyrazole - 4 (2) - tetramethine cyanine dyes 8a-g. A mixture of equimolar ratios (0.01 mole) of **7a-g** and 1,2-dimethyl quinolinium iodide salt were dissolved in ethanol (30 mL), to which piperidine (3-5 drops) was added. The reaction mixture was heated under reflux for about 8 hr. It is changed gradually from dark brown to dark violet at the end of refluxing. It is filtered while hot, concentrated to half of its volume and neutralized by acetic acid. The products **8a-g** which precipitated by water were collected, washed several times with water, dried and crystallized from aqueous ethanol (**Table III**).

Absorption Spectroscopy: The electronic visible absorption spectral behaviour of the prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1 cm cells on a Shimadzu UV-Visible recording spectrophotometer. A stock solution (10^{-3}M) of the dyes was diluted to a suitable volume in order to obtain the required concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

References

1 Sturmer D M & Heseltine D W, *The Theory of Photographic Process*, edited by James T H, 4th edn, (Macmillan, New York), **1977**.

2 Dexhage K H, Dye Lasers, edited by Schafer F P, 2nd edn, (Springer, Berlin), **1977**; M Maeda, Rev Laser Engineering (Osaka), 8, **1980**, 694.

3 West W, Gilman P B, *In the theory of the photographic process*; edited by James T J, 4th edn, (Macmillan, New York), **1977**, 277.

4 Sturmer D P, *In Kirk Othmer Encyclopedia of Chemical Technology*, 3rd edn; (Interscience, New York), **1979**, 393.

5 Hosoi Y, *Chemical Abstract*, 128, **1998**, 95286w.

6 Kashiwagi K & Takiguchi H, *Chemical Abstract*, 124, **1996**, 246343h.

7 Tang X & Gan F, *Proc SPIE-Int Soc Opt Eng*, 3136, **1997**, 210; *Chemical Abstract*, 128, **1998**, 8708u.

8 Chen P & Zhao J, Zheng D S, Okasaki T & Hayami M J, Inf Rec, 23, **1997**, 585; *Chemical Abstract*, 128, **1998**, 8204z.

9 Kletzmann R, Ehret A, Spitier M & Willig F, *J Am Chem Soc*, 115, **1993**, 1930.

10 Trösken B, Willig F, Schwarzburg K, Ehret A & Spitler M, *J Phys Chem*, 99, **1995**, 562.

11 Spitler M T, Ehret A, Kietzmann R & Willig F, *J Phys Chem*, 101, **1997**, 2552.

12 Saito K & Yokoyama H, *Thin Solid Films*, 234, **1994**, 526.

13 Vannikov A V & Grishina A D, *Usp. Nauchn Fotogr*, 25, **1989**, 74.

14 Wurthner F, Wortmann R, Matschiner R, Lukaszuk K, Meerholz K, Denardin Y, Bittmer R, Brauchle C & Sens R, *Angew Chem*, *Int Edn Eng*, 37, **1998**, 2765.

15 Emmelium M, Pawlowski G & Vollman H W, *Angew Chem*, *Int Edn Eng*, 28, **1989**, 1445.

16 Tocho J O, Duchowicz R, Scaffardi L, Blimes G M, Dipaolo R & Murphy M, *Trends Phys Chem*, 3, **1992**, 31.

17 Kawakami M, Koya K, Ukai T, Tatsuta N, Ikegawa A, Ogawa K, Shishidi T & Chen L B, *J Med Chem*, 41, **1998**, 130.

18 Hossain M Z, Ernst L A & Nagy J L, *Neurosci Lett*, 184, **1996**, 183.

19 Soper S A & Mattingly Q L, *J Am Chem Soc*, 116, **1994**, 3744.

20 Strekowski L, Lipowska M & Patonany G, *J Org Chem*, 57, **1992**, 4578.

21 Das S, Thomas K G, Thomas K J, Kamat P V & George M V, *J Phys Chem*, 98, **1994**, 9291.

22 Terpetschnig E, Szmacinski H, Ozinskas A & Lakowicz, J R, *Anal Biochem*, 217, **1994,** 197.

23 Shindy H A, El-Maghraby M A & Eissa F M, *Dyes and Pigments*, 52, **2002,** 79.

24 Shindy H A, El-Maghraby M A & Eissa F M, *Journal of the Chinese Chemical Society*, 49, **2002**, 1061.

25 Bellamy L J, *The Infrared spectra of complex molecules* (Methuen, London), **1962,** 249.

26 Schimann F, *Nuclear magnetic resonance of complex molecules* (Vieweg und Sohn Gmbh, Braunschweig), 1, **1970,** 41.