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Different Methods in the Synthesis of Polyheterocyclic Cyanine Dyes: A Review

H. A. Shindy ^{a, *}

^a Department of Chemistry, Faculty of Science, Aswan University, Aswan 81528, Egypt

Abstract

In this paper review different methods in the synthesis of polyheterocyclic cyanine dyes have been reviewed. In this paper review detailed synthesis steps for the synthesis of some polyheterocyclic cyanine dyes were represented via equations. The synthesis covers polyheterocyclic monomethine cyanine dyes (simple cyanine dyes), dimethine cyanine dyes, trimethine cyanine dyes (carbocyanine dyes), tetramethine cyanine dyes, pentamethine cyanine dyes (dicarbocyanine dyes), aza-methine cyanine dyes, hemicyanine dyes (styryl cyanine dyes), merocyanine dyes (acyclic merocyanine dyes and cyclic merocyanine dyes). Besides, in the introduction section of this paper review some light is focused on the some recent applications of cyanine dyes. This review paper is very readable, informative, and useful for synthetic dye chemists, researchers and students who looks for the different methods in the synthesis and preparation of various classes of polyheterocyclic cyanine dyes. In addition, this paper review can be used and/or will be most valuable as a thesis and/or as a note book for student lectures, particularly for the post graduate students and researchers in the field of heterocyclic and/or cyanine dyes chemistry. This specific type of collective review in the different methods in the synthesis of only polyheterocyclic cyanine dyes has been paid little attention and is lacking in the chemistry literature.

Keywords: Cyanine dyes, synthesis, polyheterocyclic cyanine dyes, different classes of cyanine dyes, uses of cyanine dyes, applications of cyanine dyes, properties of cyanine dyes.

1. Introduction

Many and many attention and have been paid to the chemistry of cyanine dyes (Shindy, 2016; Shindy, 2017; Shindy, 2018; Shindy, 2018a; Shindy, 2012; Shindy et al., 2018; Shindy, 2019; Shindy et al., 2019; Shindy et al., 2019a; Shindy et al., 2017; Komljenovic et al., 2016; Zhang et al., 2016; Solomon et al., 2014; Keisar et al., 2014; Yi et al., 2014; Hyun et al., 2015; Njiojob et al., 2015; Wada et al., 2015; Sun et al., 2013; Zhao et al., 2013). This is strong evidence and/or a certificate for the great importance of these large class of heterocyclic dyes in the modern science and advanced technology. Cyanine dyes have been used in photography for more than 100 years to sensitize silver halide efficiently upon the absorption of light (Hamer, 1964). So, cyanine dyes can be used to sensitize nanocrystalline TiO₂ in solar cells. The high extinction coefficients of cyanine dyes can make them absorb enough light and the absorption spectra of cyanine dyes can be tuned easily in the whole spectrum by tailoring their structures. Therefore it is of great interest to study their sensitization for nanocrystalline TiO₂ (or other semiconductors) solar cells. In addition, extensive synthetic procedures for generating cyanine dyes of diverse molecular structure were developed so far (Mishra et al., 2000; Wang et al., 2003; Wang et al., 2003a) This is because cyanine dyes (polymethine dyes) have found various applications as photographic sensitizers for both color and non-color (black and white) films and as textile dyes. They are also useful as

* Corresponding author

E-mail addresses: hashindy2@hotmail.com (H.A. Shindy)

photosensitizers in blue green light and as analytical reagent over a wide pH medium. In addition cyanine dyes (hemicyanine dyes) can be used as fluorescence probes in biochemistry and biophysical area (Ephardt, Fromhers, 1989). They are also commonly applied to lasers (Zhao et al., 1996), electronics (Gromov et al., 1992) and non-linear optics (He et al., 1995).

2. Results

Different Methods in the Synthesis of Polyheterocyclic Cyanine Dyes

Phenoxazine bis dimethine cyanine dye were synthesized via reaction of bis oxazole dimethine cyanine dye containing a free aldehyde group with 2-methyl-5-acetyloxazolo[4,5-b]phenoxazine-3-methiodide (Osman et al., 1978), Scheme 1.

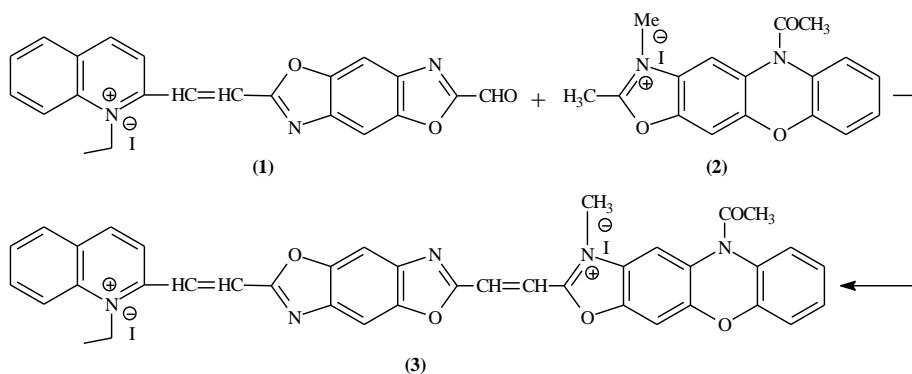


Fig. 1. Scheme 1

A number of aza-cyanine dyes by the use of N-bridgehead heterocyclic indolizinium ylide were prepared (Koraïem et al., 2006), Scheme 2.

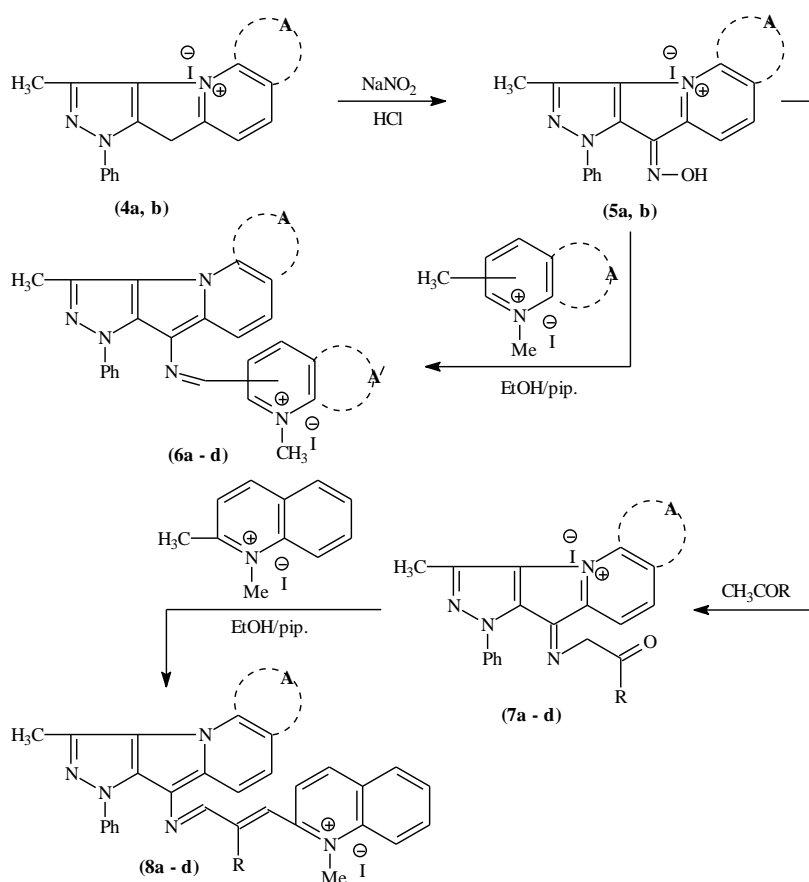


Fig. 2. Scheme 2

Substituents in Scheme 2:

(4a, b); (5a, b): A = indolizinium iodide (a); benzoindolizinium iodide (b).

(6a – d): A = indolizinium iodide, A' = 1-methylpyridine-2-ium (a);

A = indolizinium iodide, A' = 1-methyl quinoline-2-ium (b);

A = indolizinium iodide, A' = 1-methyl-pyridine-4-ium (c);

A = benzoindolizinium iodide, A' = 1-methyl-quinoline-2-ium (d).

(7a – d): A = indolizinium iodide, R = H (a);

A = indolizinium iodide, R = CH₃ (b);

A = indolizinium iodide, R = C₆H₅ (c);

A = benzoindolizinium iodide, R C₆H₅ (d).

(8a – d): A = indolizine, R = H (a); A = indolizine, R = CH₃ (b);

A = indolizine, R = C₆H₅ (c); A = benzoindolizine, R = C₆H₅ (d).

A series of monomethine cyanine dyes were synthesized (Abd El-Aal, Younis, 2004), Scheme 3.

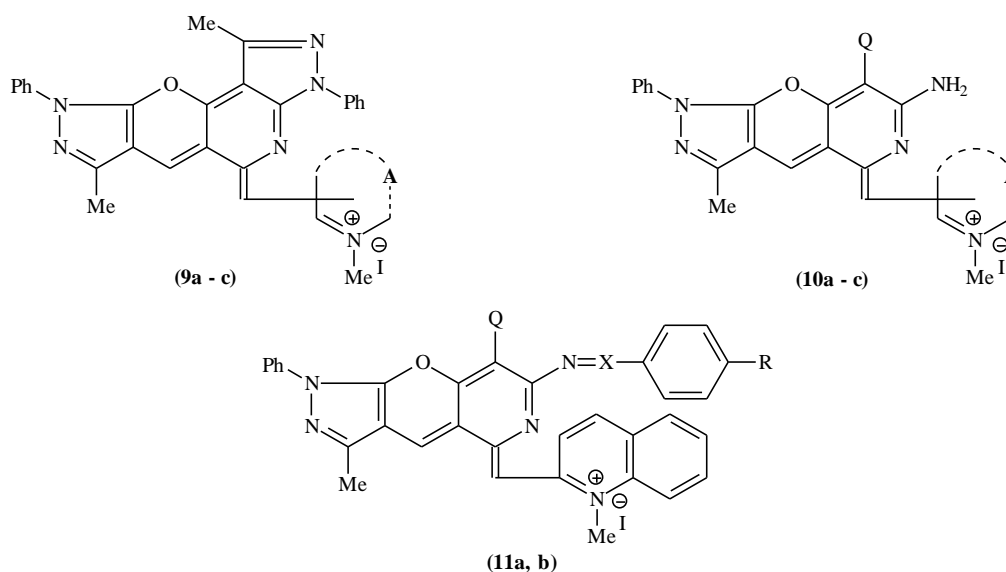


Fig. 3. Scheme 3

Substituents in Scheme 3:

(9a – c): A = 1-methyl-pyridinium-2-yl salt (a);

1-methyl-quinolinium-2-yl salt (b);

1-methyl-pyridinium-4-yl salt (c).

(10a – c): Q = imidazolyl, A = 1-methyl-pyridinium-2-yl salt (a);

Q = imidazolyl, A = 1-methyl-quinolinium-2-yl salt (b);

Q = imidazolyl, A = 1-methyl-pyridinium-4-yl salt (c).

(11a, b): X = N, R = OH (a); X = CH, R = OH (b).

Unsymmetrical 2[2(4)]-monomethine cyanine dyes derived from thiazolo-bis-[2,3-b; 5,4-d] pyrimidine were synthesized (Abd El-Motaleb, 2002), Scheme 4.

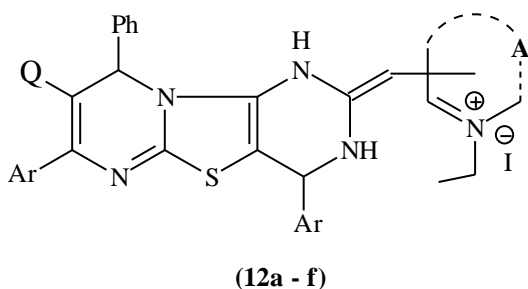


Fig. 4. Scheme 4

A number of hemicyanine dyes with multi-carboxyl group in the acceptor part and used them to sensitize TiO₂ electrode (Meng et al., 2003), Scheme 7.

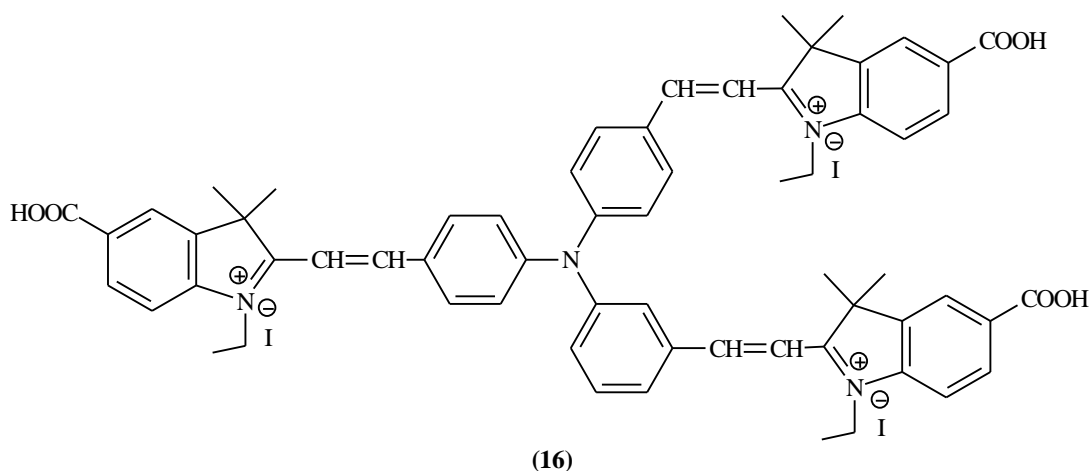


Fig. 7. Scheme 7

Dyes with two or three positive charged in the chromophore were synthesized by condensation of 4-chloroquinolinium salts with benzothiazolium salts and additional quaternization with ω -bromoalkyl substituents (Deligeogiev et al., 1989; Gadjev et al., 1999), Scheme 8.

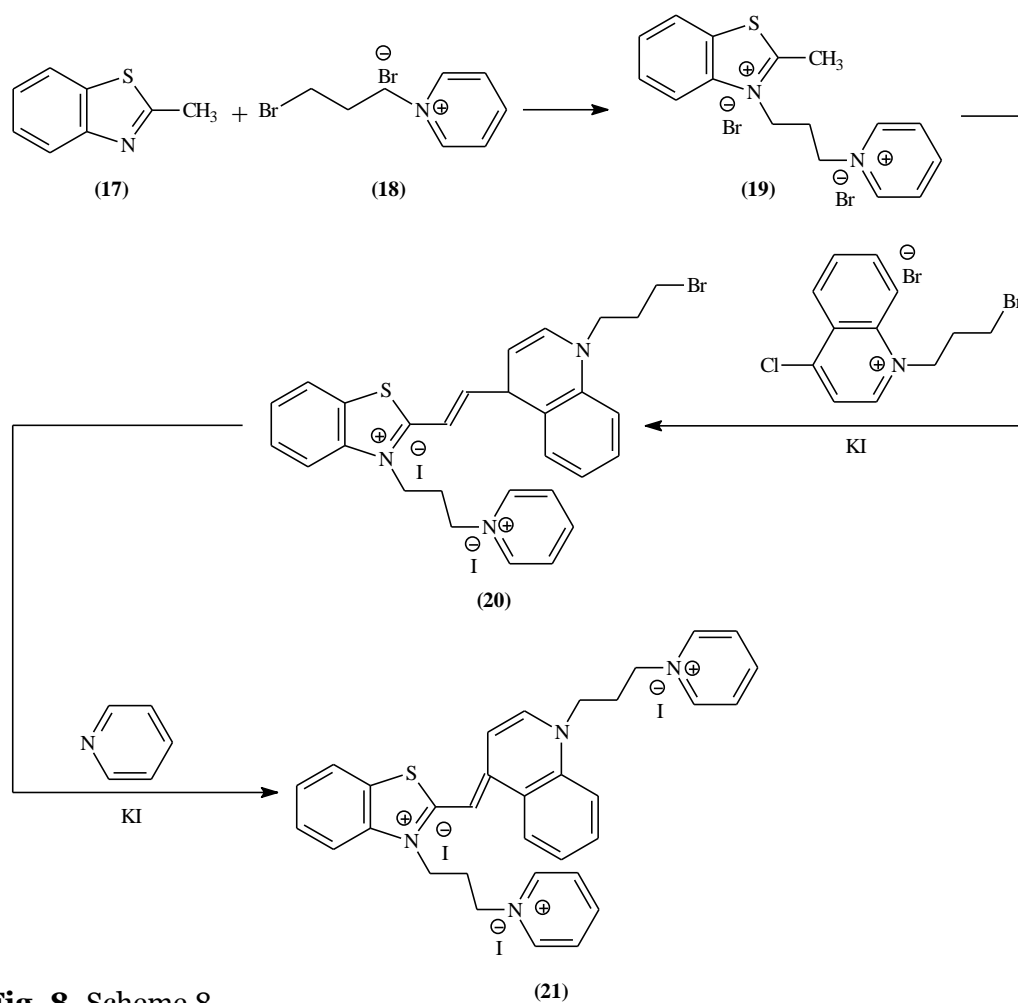


Fig. 8. Scheme 8

A number of monomethine cyanine dyes having three positive charges were prepared (Vasilev et al., 2005), Scheme 9.

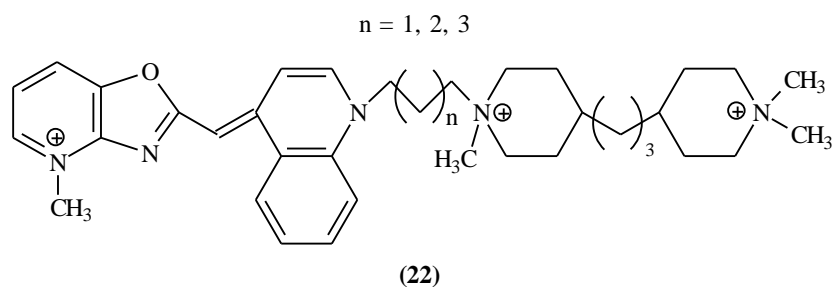


Fig. 9. Scheme 9

Trimethine cyanine dye (24) was synthesized through reaction of the quaternary salt (23) with sodium formate, ethylorthoformate or diphenylformamidine in the presence of acetic anhydride (Osman, Khalil, 1975), Scheme 10.

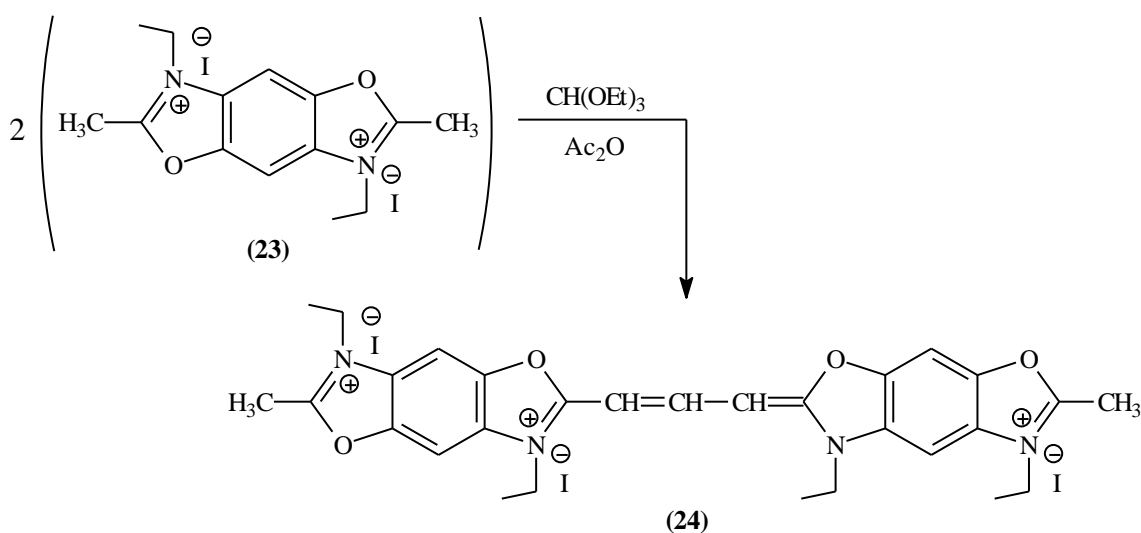


Fig. 10. Scheme 10

A series of monomethine meso-substituted pentamethine mixed cyanine dyes were prepared (Abd El-Aal, Koraiem, 2002), Scheme 11.

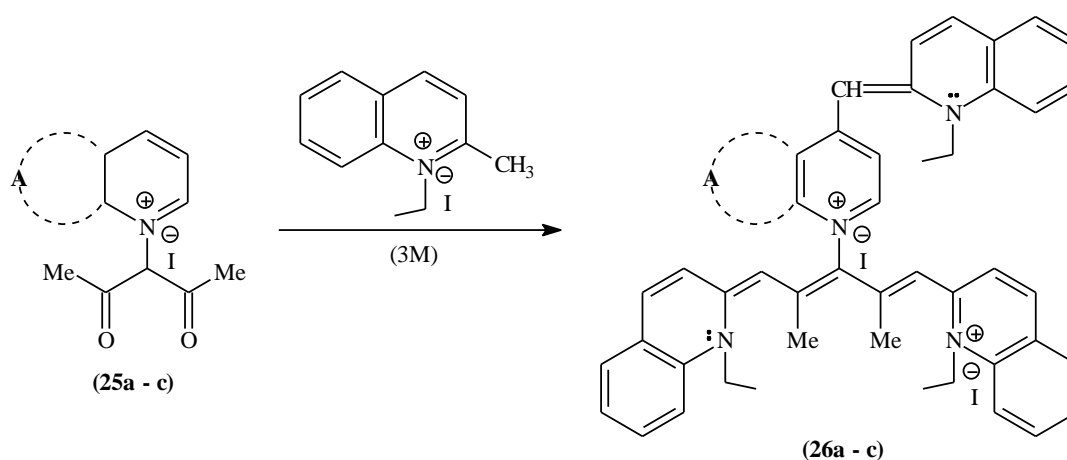


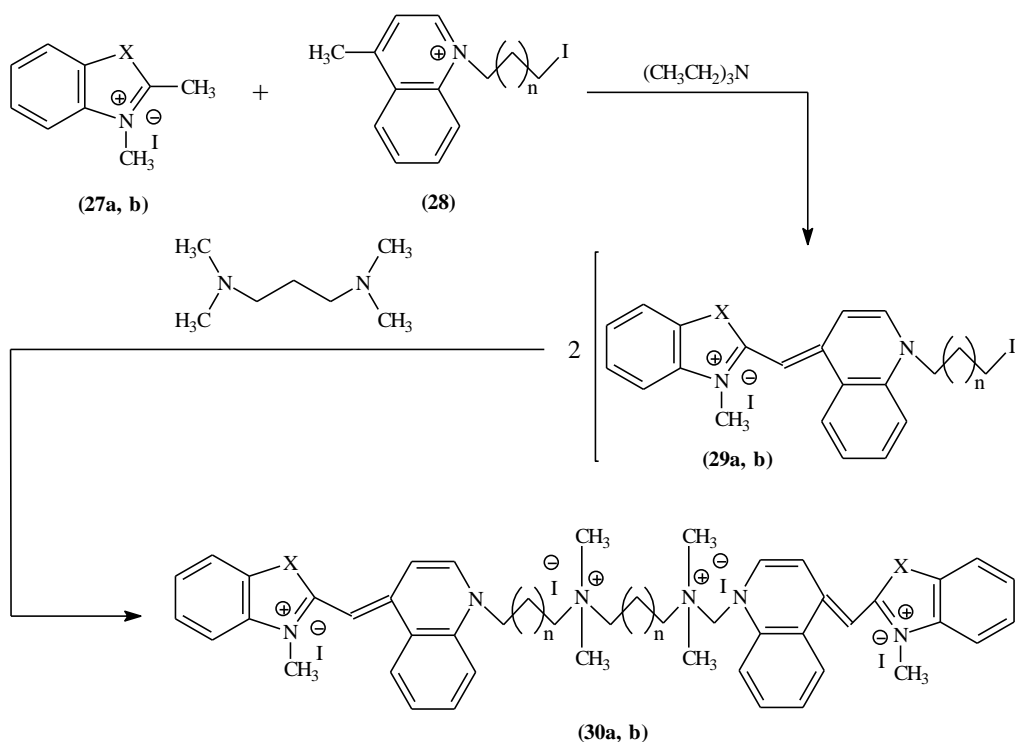
Fig. 11. Scheme 11

Substituents in Scheme 11:

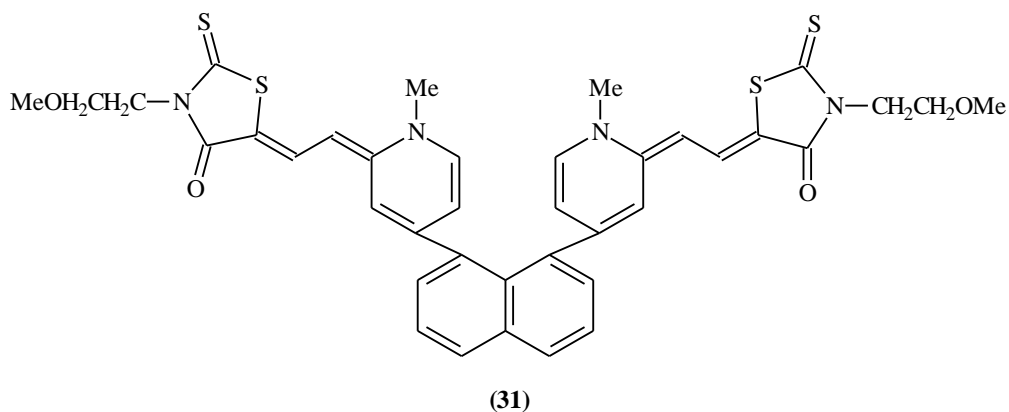
(25a – c), (26a – c): A = N-pyridinium (a); N-quinolinium (b);

N-isoquinolinium (c).

A number of monomethine cyanine dyes containing thiozole and/or oxazole nucleus were synthesized (Deligeorgiev et al., 2000), Scheme 12.

**Fig. 12.** Scheme 12**Substituents in Scheme 12:**(27a, b); (29a, b); (30a, b): $n = 1$, X = S (a); O (b).

Bis cyclic merocyanine dye linked by a 1,8-Naphthalene Skeleton were synthesized (Takashi et al., 1998), Scheme 13.

**Fig. 13.** Scheme 13

A number of hemicyanine dyes and bis hemicyanine dyes with a benzo[2,3-b; 2',3'-b']bis-furo[3,2-d]pyrazolium nucleus were prepared (Shindy, koraiem, 2008), Scheme 14.

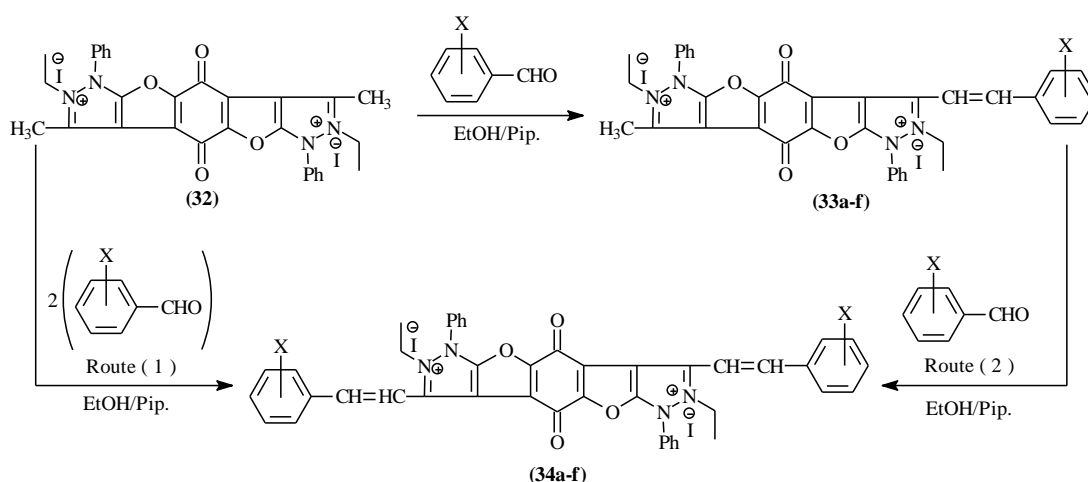


Fig. 14. Scheme 14

Substituents in Scheme 14:

(33a-f); (34a-f): X = H (a); *p*-OH (b); *p*-OCH₃ (c); *p*-N(CH₃)₂ (d);
p-NO₂ (e); *p*-Cl (f).

A series of tetramethine cyanine dyes and bis tetramethine cyanine dyes derived from benzo[2,3-*b*; 2',3'-*b'*]bispyrazolo[4,5-*b*]-1,4-(oxa, thia, and pyra)-zine-6,12-dione nucleus were synthesized (Shindy et al., 2009), Scheme 15.

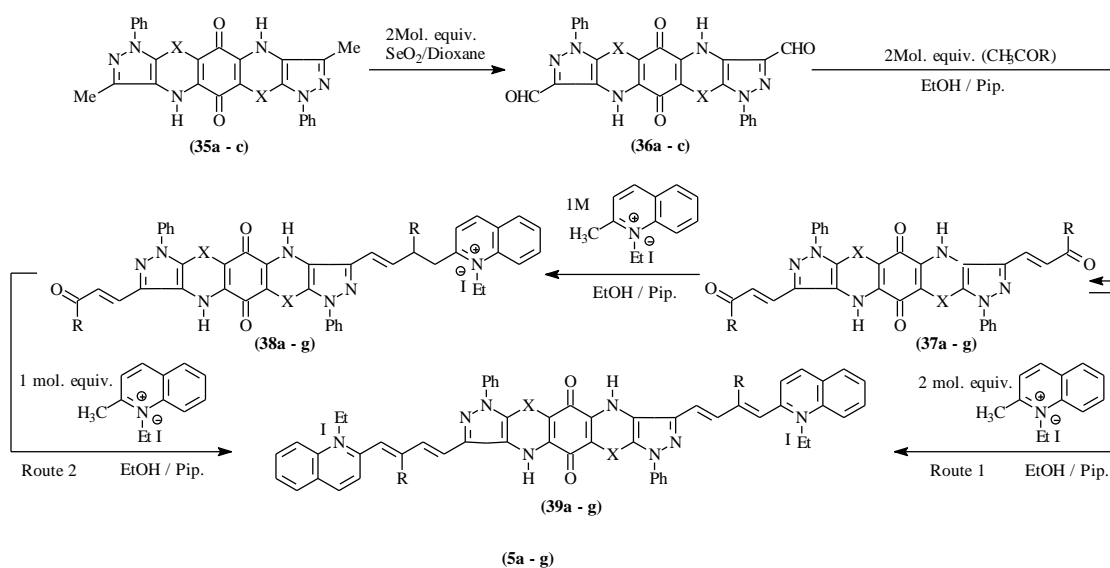
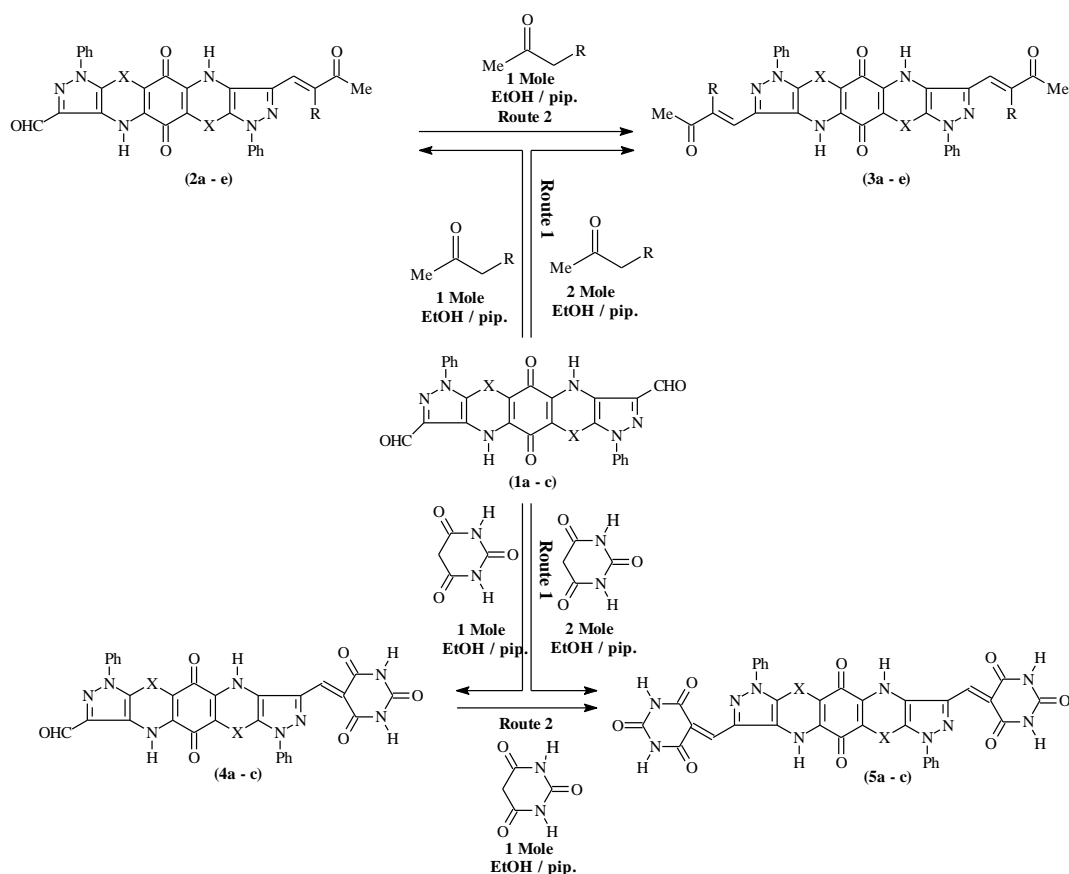


Fig. 15. Scheme 15

Substituents in Scheme 15

(37a-g); (38a-g) & (39a-g): X = O, R = H (a); X = O, R = CH₃ (b);
X = O, R = C₆H₅ (c); X = O, R = C₆H₄-*p*.OCH₃ (d);
X = O, R = C₆H₄-*p*.NO₂ (e); X = S, R = H (f);
X = NH, R = H (g).

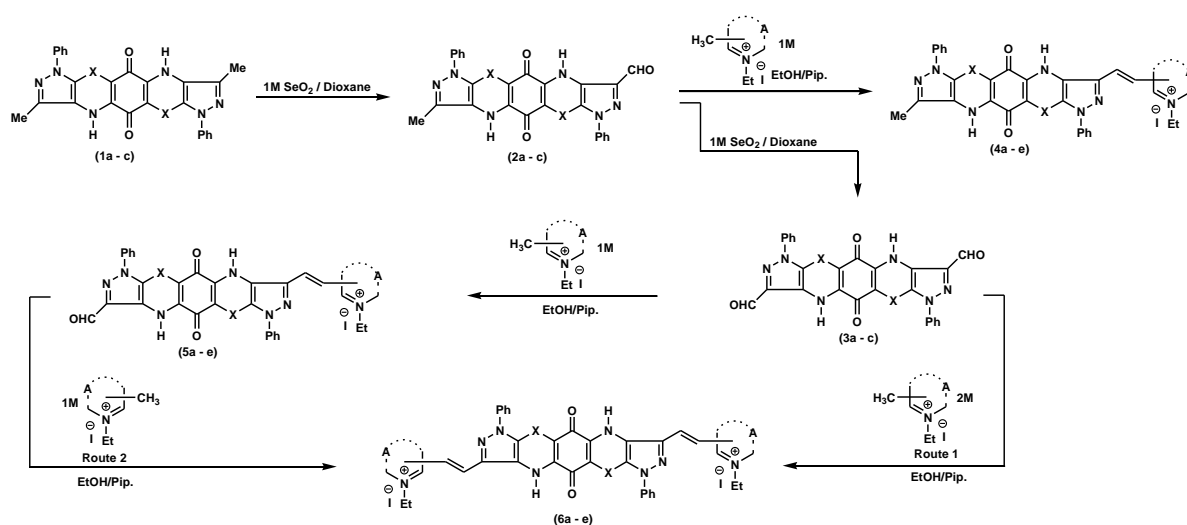
A number of merocyanine dyes including a cyclic merocyanine dyes and cyclic merocyanine dyes incorporating benzo[2,3-*b*; 2',3'-*b'*]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia- and pyra)-zine-6,12-dione were prepared (Shindy et al., 2012), Scheme 16.



1a-c, 4a-c, 5a-c: a, X = O
b, X = S
c, X = NH

2a-e; 3a-e: a, X = O, R = H
b, X = O, R = COCH₃
c, X = O, R = COOEt
d, X = S, R = H
e, X = NH, R = H

Fig. 16. Scheme 16. A series of dimethine and bis-dimethine, cyanine dyes derived from benzo[2,3-b; 2',3'-b']bis-pyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)zine-6,12-dione were synthesized (Shindy et al., 2014), Scheme 17.



(1a-c); (2a-c); (3a-c): (a), X = O; (b), X = S; (c), X = NH. (4a-e); (5a-e) & (6a-e): (a) X = O, A = 1-ethyl pyridinium-2-yl salt; (b) X = O, A = 1-ethyl quinolinium-2-yl salt; (c) X = O, A = 1-ethyl pyridinium-4-yl salt; (d) X = S, A = 1-ethyl quinolinium-2-yl salt; (e) X = NH, A = 1-ethyl quinolinium-2-yl salt

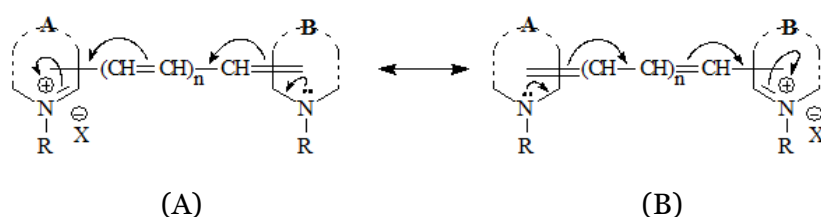
Fig. 17. Scheme 17

3. Conclusion

1. The structure of cyanine dyes consists of two heterocycles containing nitrogen linked together by a number of methine groups. If one methine unit, the cyanine named monomethine cyanine dyes, if two methine units, the cyanine called dimethine cyanine dyes, if three methine units, the cyanine termed trimethine cyanine dyes, and so on. The two heterocycles one acts as electron donor (the basic center of the dye) and the other acts as electron acceptor (the acidic center of the dye) and vice versa, creating and/or generating an push-pull system throughout the conjugated structure system of the cyanine dyes molecules, Scheme (18).

2. The intensity of the colour of the cyanine dyes is illustrated according to suggested two mesomeric electronic transitions structures (two resonance forms) (A) and (B) producing a delocalized positive charges over the conjugated chromophoric group system of the dyes structures, Scheme 18.

3. Cyanine dyes are electronic charge transfer pathways dyes. These charge transfer pathways is due to transfer of lone pair of electrons from the N •• -B-hetero nitrogen atom of the dyes (the electron donor and/or the basic center of the dyes) to the quaternary +N-A- hetero nitrogen atom of the dyes (the electron acceptor and/or the acidic center of the dyes), and vice versa, Scheme 18.



(n = 0, 1, 2, 3, etc.); R=CH₃, CH₃CH₂;

X=I; Br, ClO₄; A = Heterocyclic nucleus; B = Heterocyclic nucleus

General structure, colour intensity and electronic charge transfer pathways illustration of cyanine dyes.

Fig. 18. Scheme 18

4. Cyanine dyes are solid state organic solar cell dyes (Kim, 2006). The appropriate electrochemical properties of cyanine make it possible to be used both as donor and acceptor in thin film heterojunction solar cells. Another property of cyanine is that it can be spin coated from solution to form good film, which is of great interest for large area photovoltaic production. The effect of counter ion on the properties of solid state solar cells have been discussed before. The covalently linked cyanine-fullerene dyad is also a promising material for photovoltaic devices due to the photo induced intramolecular electron transfer from cyanine to fullerene.

5. Cyanine dyes are pH sensitive dyes, and so, their ethanolic solutions give changeable colours in acid and base media being yellow or colourless on acidification, and getting back (restore) their permanent intense colour on basification, Scheme 19.

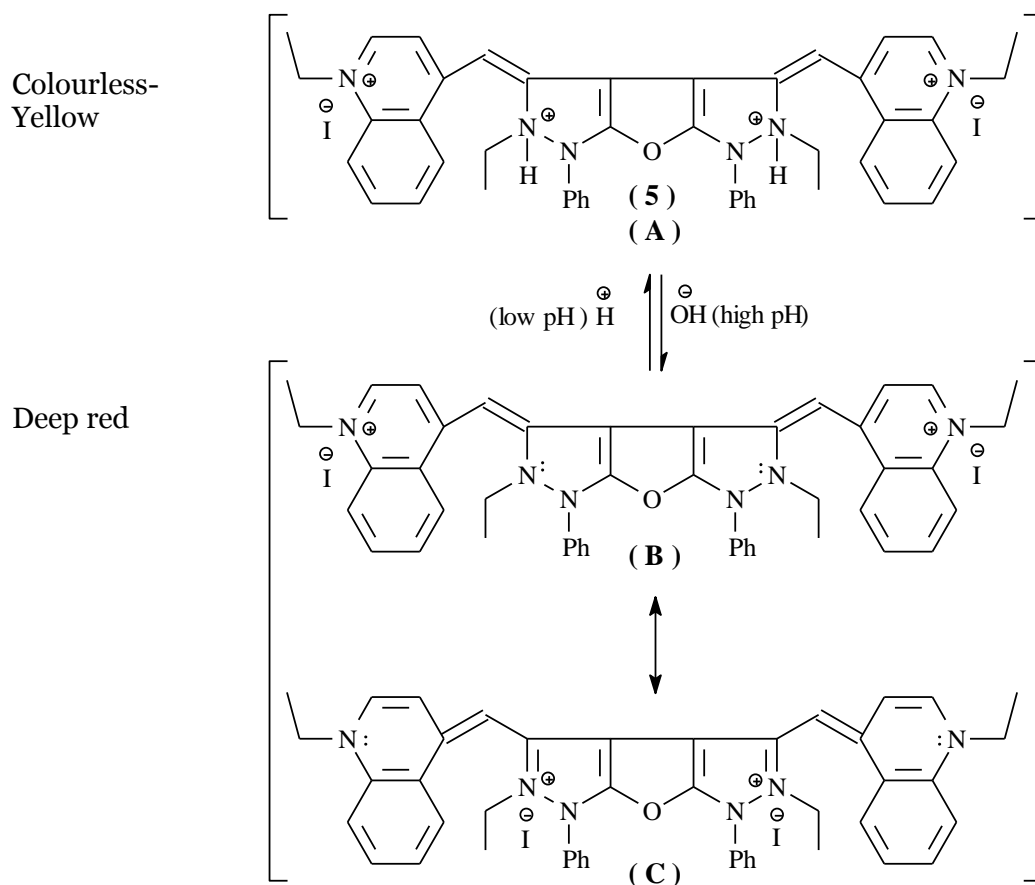


Fig. 19. Scheme 19. Decolourization (protonation) and colourization (deprotonation) of the bis mnomethine cyanine dye (5) in acid and base media, respectively (acido-basic equilibrium)

6. This review paper is recommended for chemists and researchers in the field of heterocyclic and/or cyanine dyes chemistry.

7. This paper review is recommended to all who are keen to have and know different methods in the synthesis of various classes of polyheterocyclic cyanine dyes and/or to get some basic applications, properties and characterization in the chemistry of cyanine dyes.

8. Because cyanine dyes have multi purposes uses and applications in various fields and different research area, this review paper is recommended not only for heterocyclic and/or cyanine dyes chemists but also for other scientists in other fields like biology, biotechnology, biochemistry, physics, engineering, pharmacology and medicine.

9. This review paper is recommended for all whom interested in the light absorbing systems in their research, labeling of biomolecules and/or in the synthesis and characterization of complex organic compounds.

10. This paper review is recommended to anyone interested in the subject, to chemistry libraries and also for the personal bookshelves of every organic heterocyclic and cyanine dyes chemist.

Current future development

The current and the future research developments aim to provide novel synthetic methods for the preparation of different classes of highly antimicrobial (antibacterial and anti-fungi) active, anti-tumor, anti-cancer, p-H sensitive, highly photographic sensitizers, non-toxic, high stability, light fastness, near IR (Infrared), fluorescent, anti-corrosion, strong labeled DNA and extra conjugated cyanine dyes. Such as oxadiazine cyanine dyes, thiazole cyanine dyes, metal stabilized cyanine dyes, pentamethine cyanine dyes, heptamethine cyanine dyes, nonamethine cyanine dyes, undecamethine cyanine dyes and tridecamethine cyanine dyes.

Also, the current and/or the future research developments aimed to provide new, novel and/or patent review papers in the field of color, dyes and pigments chemistry. The aimed review papers will covers and/or includes topics like the origin of color, the relation between color and constitutions, synthesis of dyes, properties of dyes, classification of dyes, uses and/or applications of dyes. Also, additional important topics for the current and/or the future research developments for the aimed review papers will includes methine cyanine dyes, hemicyanine dyes (styryl cyanine dyes), merocyanine dyes, apocyanine dyes, monoheterocyclic cyanine dyes, biheterocyclic cyanine dyes, polyheterocyclic cyanine dyes, six membered heterocyclic cyanine dyes, five/six membered heterocyclic cyanine dyes, five membered heterocyclic cyanine dyes and benz(naphth)/five membered heterocyclic cyanine dyes.

A very bright future for cyanine dyes chemistry can be expected through joint efforts (collaboration) of a large heterogenous community groups composed of synthetic cyanine dyes chemists, molecular biologists, physicists, biotechnologists, pharmacologists, technological engineerists and medical scientists.

4. Conflict of interest

There is no conflict of interest.

5. Acknowledgements

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