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Synthesis and Optical Properties of Near-Infrared (NIR) Absorbing Azo Dyes

Sharad Rohidas Patil and Amol S. Chaudhary

Abstract

This chapter provides a general overview and information on near-infrared (NIR) absorbing azo dyes. In this work, we have developed an efficient and simple protocol for the synthesis of novel A- π -D- π -A NIR azo dyes. The near-infrared absorbing azo dyes were synthesized by using 2-hydroxy-1,4 naphthoquinone (Lawsone) and different substituted aromatic primary amines. Furthermore, author developed push-pull chromophores of A- π -D- π -A type containing an electron-withdrawing azo core, phenazine moieties, and a hydroxyl group as electron donor. The benzo[a]quinoxalino[2,3-i]phenazin-5-ol moiety was introduced to make the system planer as well as to increase the π -conjugation. The optical properties of these dyes were studied in *N,N*-dimethylformamide (DMF).

Keywords: NIR absorbing azo dyes, 2-hydroxy-1,4-naphthoquinone, Lawsone, optical properties, phenazine core

1. Introduction

In 1856, William Henry Perkin accidentally discovered the world's first commercially successful synthetic dye. Dyes are defined as colored organic or inorganic compounds, mixtures, complexes, or substances that once applied to the fibers/substrate, it imparts a permanent color to the fibers/substrate. This is able to resist fading upon exposure to sweat, light, water, and many chemicals, including oxidizing agents and microbial attack. Over 10,000 synthetic dyes were developed and used in manufacturing by the end of the nineteenth century. Azo dyes are a class of compounds containing a $N=N$ double bond and, due to their ability to absorb visible to near-infrared (NIR) light and ease of synthesis, they have been extensively used in the textile, fiber, leather, paint, and printing industries for more than a century. The azo group is substituted with benzene or naphthalene groups, which can contain many different substituents, such as chloro ($-Cl$), methyl ($-CH_3$), nitro ($-NO_2$), amino ($-NH_2$), and hydroxyl ($-OH$), carboxyl ($-COOH$), which give different types of azo dyes. Azo dyes account for the majority (more than 3000 different varieties) of all textile dyestuffs produced because of the ease and cost-effectiveness of their synthesis, their stability, and the variety of colors available compared to natural dyes. They are extensively used in the textile, paper, food, leather, cosmetics, and pharmaceutical industries [1–3].

Azo colorant represents the greatest production volume in dyestuff chemistry due to simplicity of coupling reaction, adaption to the needs of most diverse applications such as textile dyeing, coloring of plastics and polymer, in liquid crystal displays (LCD), optical data storage, nonlinear optics, biological and medical field, and advanced application in organic synthesis [4–6]. Azo chromophores have versatile applicability ranging from textile dyeing [7], leather dyeing [8], coloring of plastics, and polymer [9] to advanced applications such as liquid crystal displays [10], biological and medical studies, and advanced application in the organic synthesis [11]. Also, they contribute greatest production volume of the dyestuff industry due to simplistic mode of their synthesis with high yield.

The infrared wavelength ranges of the electromagnetic spectrum cover the area between the visible region and the microwave region. The infrared radiation spectrum is generally accepted and can be subclassified into the near-, medium-, and far-infrared regions. An important challenge in creating molecules with desired optical properties lies in achieving a well-defined architecture while maintaining adequate electron density throughout the whole molecule [12]. Organic materials with intense absorptions in the near-IR region (i.e., 750–1300 nm) are particularly important in number of applications including thermal imaging, optical data storage, automatic identification, etc. NIR absorbing dyes have been attracting increasing interest due to the rapid progress achieved in their high technology applications.

In this region, infrared radiation provides sufficient energy to the NIR dyes, which impart a $\pi \rightarrow \pi^*$ transition of electrons within dye chromophore molecules. Despite the enormous synthetic versatility of azo dyes, which accounts for representing 50–70% of all commercially available dyes, little effort has been devoted to bring their absorption into the long wavelength region, and only a few examples of NIR absorbing azo dyes have till now been disclosed [13, 14]. Near-infrared absorbing dyes have attracted significant interest for their uses in the development of functional materials for high-technology end uses. Considerable interest is evinced in recent years in the design of near-infrared absorbing organic azo dyes. They find manifold applications in the high technology areas such as dye sensitized solar cells (DSSCs) [15], laser optical storage systems [16], clear coatings [17], organic

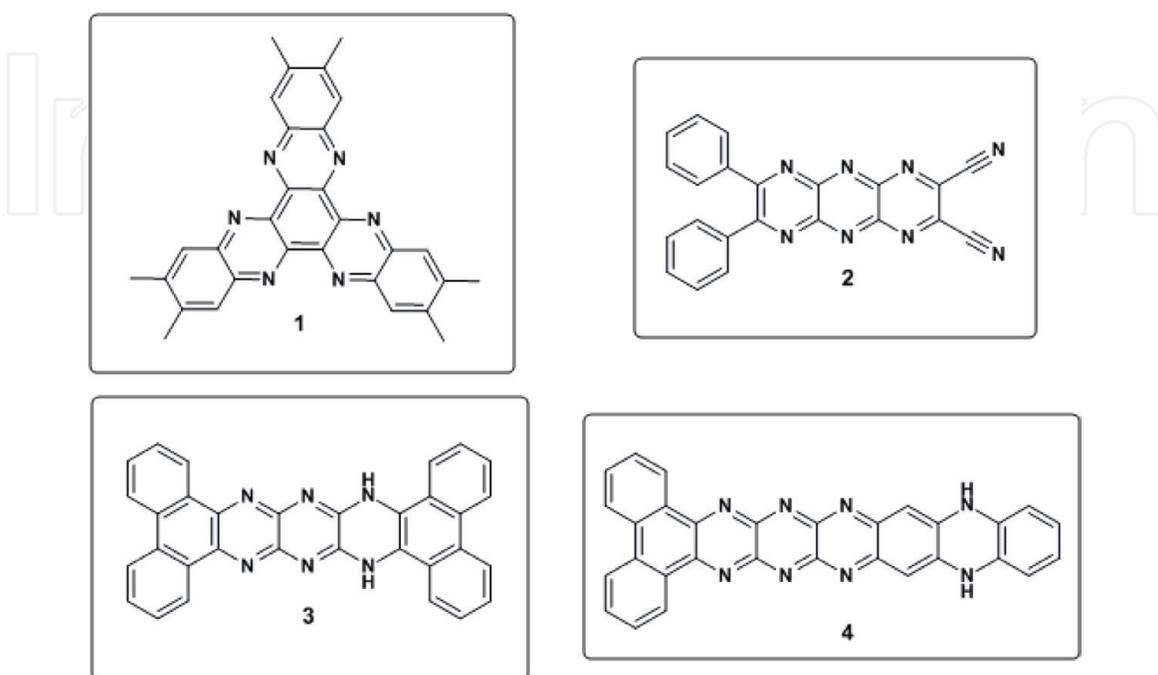


Figure 1.
Chemical structure of pyrazinacenes for organic thin film transistors.

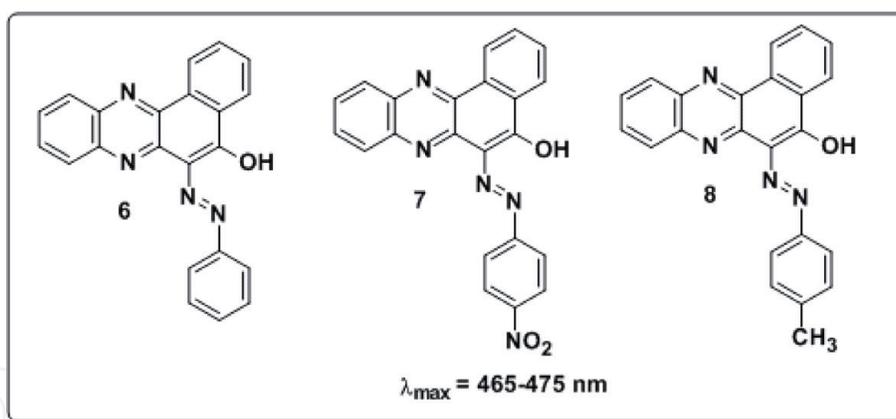


Figure 2.
Reported azo derivatives of lawsone (6–8).

photovoltaics [18], greenhouse claddings [19], molecular switches [20], NIR-active materials [21], colorimetric sensors [22], mesomorphic [23], solvatochromic [24–26], and electrochemical materials [27] and surface relief grating (SRG)-forming azo polymer films [28], laser-printing systems, laser filters, photography, photonics, and in telecommunication devices operating at wavelengths in the NIR region [29].

The planar structure of phenazine with a heterocyclic pyrazine nucleus and a fully conjugated aromatic π -system imparts to that special optical and redox properties. The optical properties give it functional for applications in molecular imaging as fluorescent tracers and stains for subcellular components and biological events. Highly electron-rich and redox-active molecules like phenazines might be functional for preparation of organic materials that includes donor- π -acceptor design. Pyrazine compounds are electron-deficient species. Hence, they are used in the design of n-type organic semiconductors; examples

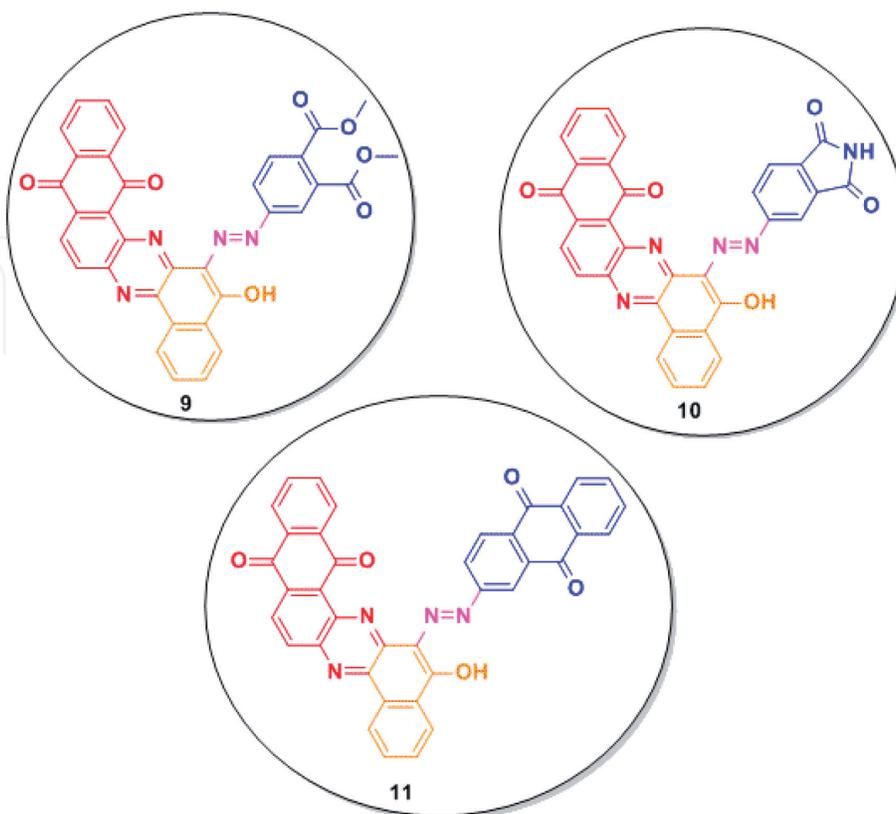


Figure 3.
Structures of the dyes 9–11.

are pyrazinoquinoxaline derivatives, hexaazatriphenylenes, diquinoxalino, phenazine, and quinoxalinophenanthro phenazine [30]. Richards et al. have shown that pyrazinacenes are good candidates as materials for organic thin film transistors as shown in the **Figure 1** [31]. The existence of a donor- π -acceptor (D- π -A) alternating structure has been proved to be an efficient way to reduce band gap energies of conjugated molecules. The phenazine core consists of the electron-withdrawing pyrazine ring which might be an excellent charge acceptor.

Romanyuk et al. has reported azo derivatives of 2-hydroxy-1,4 naphthoquinones **5** as shown in **Figure 2** [32].

There are no further reports in the use of 2-hydroxy-1,4-naphthoquinone in the synthesis of azo colorants. It is known that the molecule with a quinoid fragment shows keto-enol tautomerism when a hydroxyl group is presenting adjacent to one of the quinoid carbonyl groups: the p-quinoid structure can transform into an o-quinoid or dihydro structure.

The reactions of 2-hydroxy-1,4-naphthoquinone in the synthesis of azo colorants for NIR-absorbing dyes have been explored in our previous work. Three different kinds of near-infrared (NIR) absorbing pull-push acceptor- π -donor- π -acceptor (A- π -D- π -A) V-shaped chromophoric dyes have been synthesized. These dyes are architect by doing substitution with 5-hydroxy and 6-aryazonium on the benzo[a] naphtho[2,3-h] phenazine dione core. Phenazine and anthraquinone moieties were envisaged in a single molecule with a view to enhance the photophysical properties in NIR region as shown in **Figure 3** [33].

This work is aimed at synthesizing novel molecules containing both phenazine and azo cores that were envisaged in a single molecule with a view to enhance the photophysical properties in the NIR region. In this study, we have extended our contribution to synthesis NIR absorbing dyes (**12–14**) as shown in **Figure 4**.

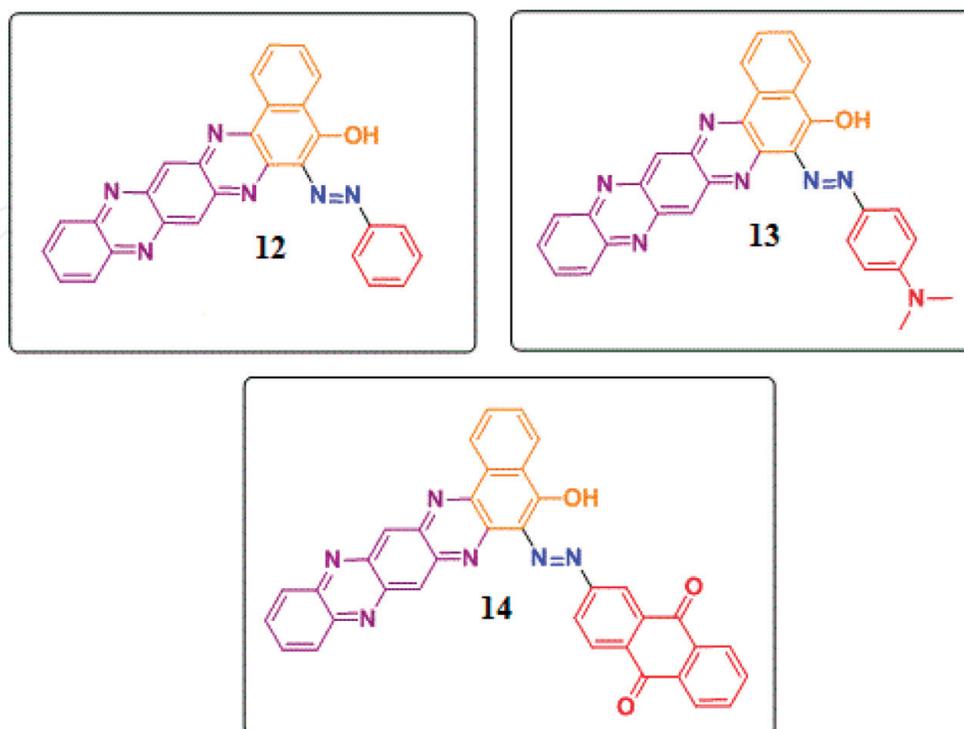


Figure 4.
Structures of the near-IR absorbing dyes (**12–14**).

2. Result and discussion

2.1 Synthesis strategy

In the present study, the use of 2-hydroxy-1,4-naphthoquinone (Lawsone) **5** coupling components and diazo components in the synthesis of azo disperse dyes followed by condensation with *o*-phenylenediamine OPDA to obtain the desired NIR absorbing azo dyes (**12–14**).

In this context, authors have extended our contribution to synthesis of three different kinds of near infrared (NIR) absorbing pull-push acceptor- π -donor- π acceptor (A- π -D- π -A) chromophoric dyes. The NIR absorbing dyes (**12–14**) were synthesized from derivatives of 2-hydroxy-3-(phenyldiazenyl)naphthalene-1,4-dione (**18–20**) and 2,3-diaminophenazine core (**21**) (**Figure 5**).

The scaffold of phenazine, *N,N*-dimethylaniline, and anthraquinone moieties was envisaged in a single molecule with a view to enhance the photophysical properties in NIR region. The UV-Vis absorption spectra of synthesized azo-azine dyes have been studied. The intermolecular interaction occurring in solvents of differing polarities as well in solution of different pH have been studied. The structures of the dyes are given in **Figure 4**. Synthetic route for the dyes **44–46** and their intermediates are depicted in **Figure 5**.

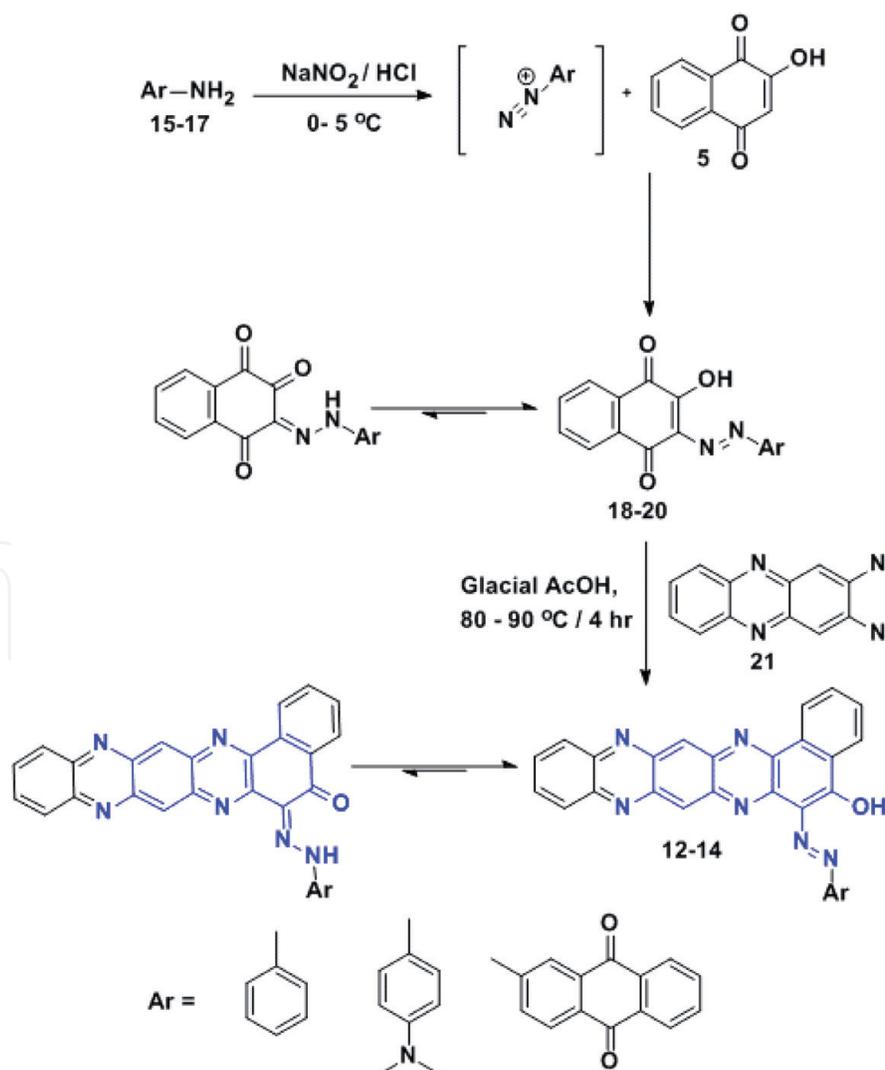


Figure 5.
Schematic representation of NIR azo dyes (**12–14**).

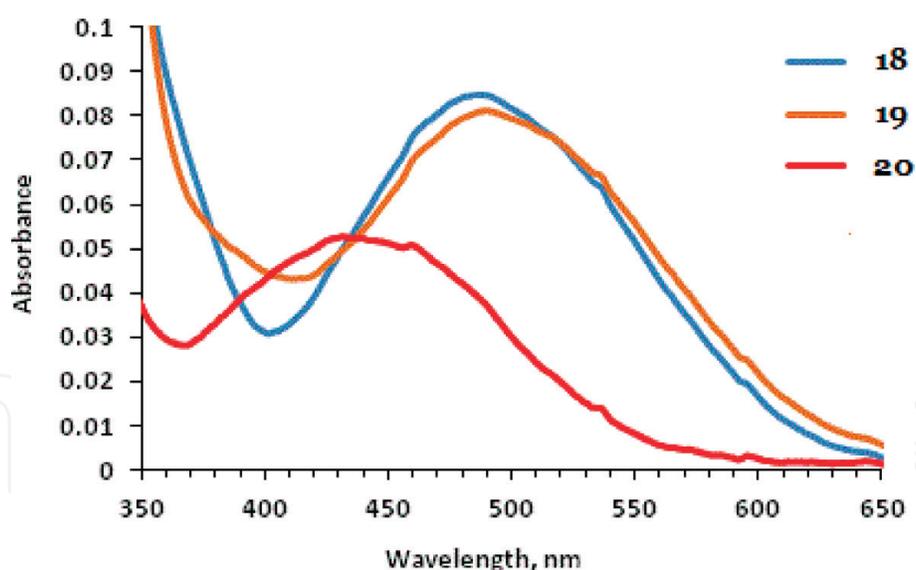


Figure 6.
Visible absorption of the dyes (18–20) in DMF solvent.

Dye	λ_{\max} (nm)	(log ϵ)	ϵ_{\max} (dm ³ mol ⁻¹ cm ⁻¹)
18	487	4.93	84,830
19	490	4.91	81,275
20	439	4.72	52,260
12	620	4.60	40,000
13	710	4.63	43,000
14	680	4.69	49,000

Table 1.
Visible absorption of the dyes (18–20 and 12–14) in DMF solvent.

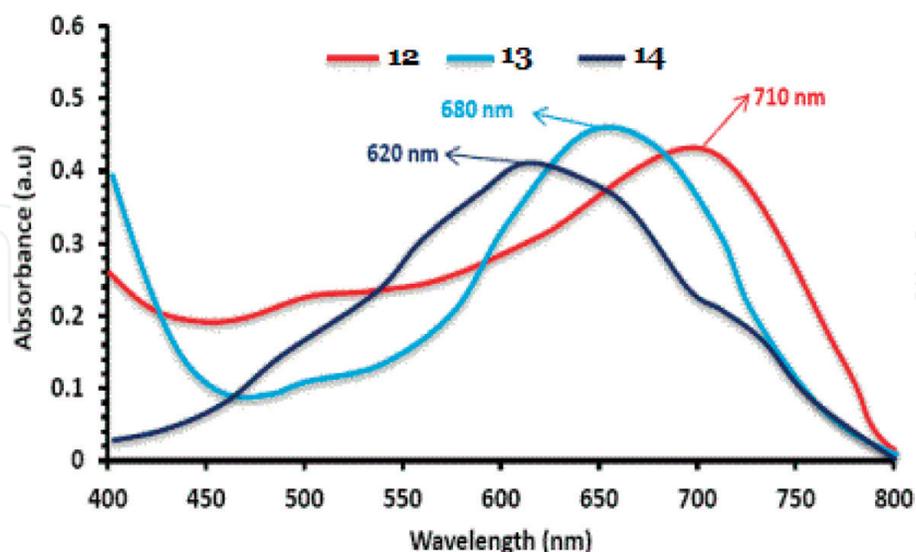


Figure 7.
Visible absorption of the dyes (12–14) in DMF solvent.

2.2 Optical properties

The UV-visible absorption spectra of the dyes (18–20 & 12–14) were measured in *N,N*-dimethylformamide (DMF). These dyes do not show solvatochromism significantly. The dyes (18–20) showed absorption at 439–490 nm (Figure 6 and Table 1).

The red-shifted absorptions owing to the π -conjugation framework are present in these dyes. The dyes (12–14) showed absorption at 620–710 nm due to the intramolecular charge transfer transition (ICT) between donor-acceptor pair (**Figure 7** and **Table 1**).

3. Experimental sections

3.1 General experimental procedure of the azo dyes (18–20)

The aromatic primary amines (5 g) was partially dissolved in conc. HCl (5 mL) in 80 mL water and cooled to 0–5°C [34]. The solution of NaNO₂ (2 g) in 5 mL water was added slowly to the reaction mixture, and the reaction temperature was kept below 5°C. The resulting aryl diazonium salt was added to the alkaline solution of Lawson (5 g) and NaOH (1.15 g) in 60 mL of water, and reaction temperature was maintained at 0–5°C. The reaction mass was stirred for 2.0–2.5 h, after which mixture was acidified with dil. HCl. The precipitate was settled down and filtered, washed with water and then with aqueous EtOH, and was dried.

3.2 General experimental procedure of the azo-phenazine dyes (12–14)

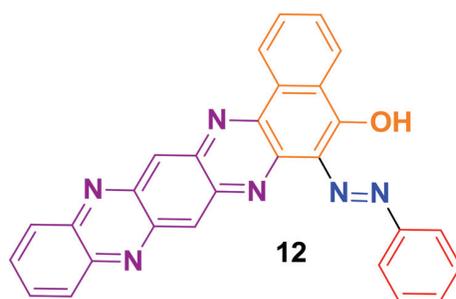
Diketo-azo derivatives (18–20) and diaminophenazine (21) were mixed together then refluxed in acetic acid for 4 h. The AcOH was removed under reduced pressure in a rotary evaporator, and water was added to the residue. The precipitate was let out and filtered, washed with water and then with aqueous ethanol, and dried.

3.3 General experimental procedure of 2,3-diaminophenazine (21)

Finally powdered *o*-phenylenediamine (54.0 g, 0.5 mol) was dissolved in conc. hydrochloric acid (83.3 ml) and distilled water (2.5 L). A filtered solution of ferric chloride (400 g) in (750 ml) water was added slowly, and the mixture was stirred mechanically. After standing overnight at room temperature, the red-brown colored crystalline product was filtered off, washed with cold dilute 0.3 N HCl until free from ferric ions, then dissolved in hot water (2.5 L), and 2,3-diaminophenazine was precipitated by the addition of a concentrated solution of potassium hydroxide. The product was filtered off, washed with water, and dried at 100–110°C. The strongly alkaline filtrate was heated and acidified (pH 4.5) with glacial acetic acid. After cooling, 2-amino-3-hydroxy phenazine was collected, washed with water, and dried at 100–110°C. The crude products were used without further purification.

3.4 Characterization

3.4.1 6-(Phenyldiazenyl)benzo[*a*]quinoxalino[2,3-*i*]phenazin-5-ol (12)

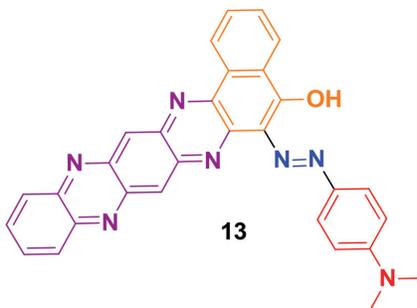


Yield 72%; melting point (measured) >300°C.

FT-IR (KBr, cm⁻¹) = 3057 (O–H), 1630 (C=N), 1589 (arom.), 1534 (arom. ring).

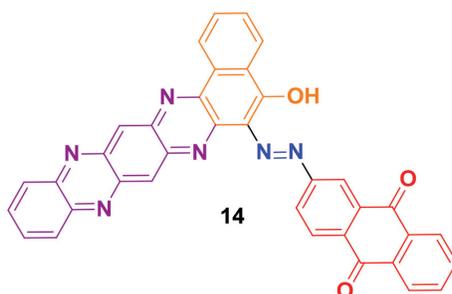
$^1\text{H-NMR}$ (DMSO, 500 MHz) = δ 8.30–8.24 (m, 4H, aromatic), 8.26–8.16 (m, 3H, aromatic), 7.92–7.76 (m, 8H, aromatic), 5.2 (1H, s, OH).

3.4.2 6-((4-(Dimethylamino)phenyl)diazenyl)benzo[a]quinoxalino[2,3-i]phenazin-5-ol (45)



Yield 80%, melting point (measured) $>300^\circ\text{C}$. FT-IR (KBr, cm^{-1}) = 3169 (O–H), 1674 (C=N), 1633 (arom.), 1514 (arom. ring). $^1\text{H-NMR}$ (DMSO, 500 MHz) = δ 8.25 (s, 2H, aromatic), 8.23–7.78 (m, 12H, aromatic), 3.86 (s, 6H, $\text{CH}_3\text{-N-CH}_3$), 6.18 (1H, s, OH).

3.4.3 2-((5-Hydroxybenzo[a]quinoxalino[2,3-i]phenazin-6-yl)diazenyl)anthracene-9,10-dione (46)



Yield 67%, melting point (measured) $>300^\circ\text{C}$. FT-IR (KBr, cm^{-1}) = 3059 (O–H), 1629 (C=N), 1590 (arom.), 1529 (arom. ring). $^1\text{H-NMR}$ (DMSO, 500 MHz) = δ 8.304 (s, 2H, aromatic), 8.292 (m, 12H, aromatic), 7.77–7.76 (m, 3H, aromatic), 5.2 (1H, s, OH).

4. Conclusions

Azo colorants represent the greatest production volume in dyestuff chemistry due to simplicity of coupling reaction, adaption to the needs of most diverse applications such as textile dyeing, coloring of plastics and polymer, in liquid crystal displays (LCD), optical data storage, nonlinear optics, biological and medical field, and advanced application in organic synthesis. In this context, authors have designed and developed push-pull chromophores of A- π -D- π -A type containing an electron-withdrawing azo core, phenazine moieties, and a hydroxyl group as electron donor. The benzo[a]quinoxalino[2,3-i]phenazin-5-ol moiety was introduced to make the system planer as well as to increase the π -conjugation. These synthesized chromophores were confirmed by FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and MS spectral analysis. The optical properties of these dyes were studied in DMF. NIR absorbing dyes have been considered in numerous recent hi-tech applications like optical device, optical recordings, laser printings, laser thermal writing displays, infrared photography, and biological/medical applications. In optoelectronic application areas, especially,

NIR absorbing dyes are being developed and new structural designs of the dye chromophore molecules are being studied. Azo dyes are the most important class of organic dyes, but many of azo dyes suspect to be carcinogenic in nature. Therefore, the research of the dyes is aimed at development of new type of chromophores. The NIR azo dyes may probably prove to be a solution to this problem.

5. Future trends

There is an excellent range of organic compounds that absorb intensively higher than 700–1300 nm owing to electronic excitation. The basic acyclic NIR chromophores (polymethine dyes) as well as the basic cyclic NIR chromophores (annulenes, porphyrines, and tetraazaporphyrins) are well recognized. Structurally, more advanced NIR dyes with some meropolymethinic, quinonoid, and/or indigoid character will eventually be found. Color structure relationships are at present better well-known and more reliably predictable for closed shell than for open shell systems.

On account of their special optical properties, there exists scope for further research into designing small molecules bearing donor and acceptor functional groups directly attached to the phenazine nucleus that could possess NIR optical spectra, which would be sensitive to presence of solution analytes such as cations/anions as well as to pollutants such as polycyclic aromatic hydrocarbons and nitroaromatics. Additionally, preparation of more examples of phenazine-based low-band gap-containing molecules will also enhance its use in the field of organic photovoltaics.

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Notes

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Author details

Sharad Rohidas Patil^{1,2*} and Amol S. Chaudhary³

1 Department of Chemistry, SPDM Arts, SBB and SHD Commerce and SMA Science College, Dhule, Maharashtra, India

2 Department of Chemistry, Uka Tarsadia University, Gopal-Vidyanagar, Maliba campus, Bardoli, Gujarat, India

3 R&D Division, Rextone Dyes Ltd, Vadodara, Gujarat, India

*Address all correspondence to: sharad.umd.patil@gmail.com

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