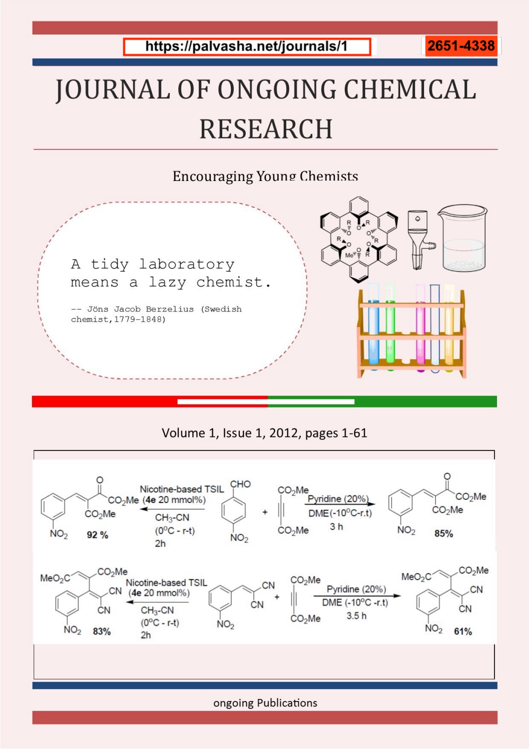
A MINI REVIEW ON THE INDIGO DERIVATIVES



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Encouraging Young Chemists

A tidy laboratory means a lazy chemist.

-- Jöns Jacob Berzelius (Swedish chemist, 1779-1848)

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A Mini Review On The Indigo Derivatives

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Abstract

The current review aims to collect short information about application field, properties of indigo dyes. Indigo dye is blue colour used as colorant for painting and dying. The structure of the indigo includes the central double bond connecting the two rings with two carbonyl groups (electron acceptor group), carbon-carbon double bonds, aromatic core and NH (electron donor groups). Indigo has a much longer wavelength of absorption maximum (λ_{max}: 600-610 nm). It is the source of the color in blue jeans. Indigo are in the field of optoelectronic devices, organic light-emitting diode, sensors, organic photonics, organic solar cells, and biodegradable organic field effect transistors displays, and integrated circuits. Indigo dye represents an interesting class of organic semiconducting materials.

Keywords: chemistry, indigo, organic semiconducting materials, solar cells materials, indigo in synthesis,

Indigo, nowadays still used color known as the earliest most popular dye, is the blue color used as a colorant for painting and dying [Rondao et al, 2012; Woodtli et al, 2018; Watanabe et al, 2016; Guo et al, 2014]. The indigo blue dye has been widely used since as early as 1600 BC. [SeixasdeMelo et al, 2004]. Until the late 19th century, indigo was obtained from natural sources. Today indigo is produced synthetically [Rebelo et al, 2014].

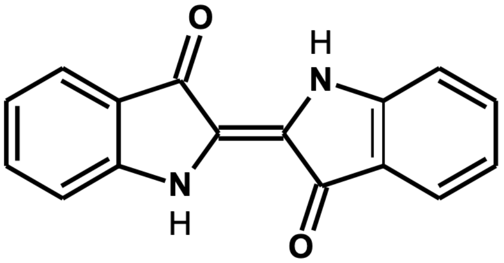

Figure 1: Molecular structure of indigo

The structure of the indigo, a dimeric 3-indolinone, includes fundamental chromophore the central double bond connecting the two rings with two carbonyl groups (electron acceptor group), carbon-carbon double bonds, aromatic core and NH (electron donor groups) [SeixasdeMelo et al, 2004; deMelo et al, 2006]. The π-electrons on the indigo skeleton are highly delocalized. So indigo has a much longer wavelength of absorption maximum (λ_{max}: 600-610 nm). The nonsubstituted indigo can form intramolecular hydrogen bonding [Furuyama et al, 2018; Guo et al, 2014]. Indigoids exist in the trans form. The trans isomer is maintained by intramolecular hydrogen bonding between the adjacent amine and ketone groups. Solubility is very low in organic solvents [Glowacki et al, 2012; Shadi et al, 2003]. Indigo dye, of all vat dyes, is largely soluble in solvents of organic origin [Ngan et al, 2007].

1 R1 = F; R2 = H (HOMO eV: -5.88, LUMO eV: -3.90, E_geV: 1.98)
2 R1 = Cl; R2 = H (HOMO eV: -5.88, LUMO eV: -3.90, E_geV: 1.98)
3 R1 = Br; R2 = H (HOMO eV: -5.88, LUMO eV: -3.90, E_geV: 1.98)
4 R1 = CF3 ; R2 = H (HOMO eV: -5.85, LUMO eV: -4.10, E_geV: 1.75)
5 R1 = CN; R2 = H (HOMO eV: -5.90, LUMO eV: -4.14, E_geV: 1.76)
6 R1 = H; R2 = F (HOMO eV: -5.77, LUMO eV: -3.97, E_geV: 1.80)
7 R1 = H; R2 = Cl (HOMO eV: -5.83, LUMO eV: -3.91, E_geV: 1.92)
8 R1 = H ; R2 = Br (HOMO eV: -5.92, LUMO eV: -3.97, E_geV: 1.93)
9 R1 = F; R2 = F (HOMO eV: -5.77, LUMO eV: -3.90, E_geV: 1.95)

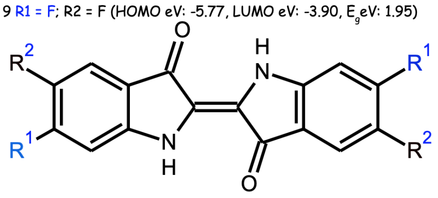

Figure 2: Structure of indigo derivatives synthesized by Troshin

While indigo was used to cotton and wool fabric for millenia, nowadays apllications of indigo are in the field of optoelectronic devices, organic light-emitting diode, sensors, organic photonics, organic solar cells, and biodegradable organic field effect transistors displays, and integrated circuits. Indigo dye represents an interesting class of organic semiconducting materials. It is the source of the color in blue jeans [Zhao et al, 2014;Bouzidi et al, 2017]. Indigo was shown to be one of the most promising biocompatible semiconductor materials, exhibiting balanced ambipolar transport in OFETs and good performance in inverter circuits. Low toxicity of indigo and its derivatives, natural occurrence of some indigoids in combination with good semiconductor characteristics and chemical stability open wide opportunities for their use in the development of sustainable electronics [Klimovich et al, 2014]. Also, indigo is useful for anticancer and antibacterial effects [Bouzidi et al, 2017].

In the present review, we summarized the information from literature about indigo derivatives in two contexts: Structure of indigo derivatives and application information of indigo derivatives. Troshin et. al reported the derivatives of indigo as shown Fig.2. Molecules are useful for indigoid-based semiconductors with advanced properties.

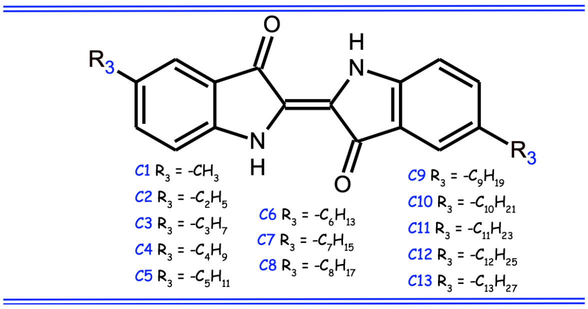

Figure 3: Structure of indigo derivatives snthesized by Watanabe

They synthesized derivatives of indigo with electron withdrawing groups such as halogen atoms, CN and CF_3. When compared to the parent indigo, it is expected to lower the LUMO energy levels of synthesized indigo derivatives bearing electron withdrawing substituents. They reported that such modification should lead to an improved stability of their anion species. All indigoids exhibit very characteristic absorption spectra. The spectral properties of indigo derivatives are dependent on the electronic nature of the substituents of molecules. The spectroscopic properties of indigo derivatives can be tuned by the substituent on the aromatic ring of indigo structure. It is obvious that the HOMO energies of indigo derivatives are effected when chlorine and bromine atoms are introduced to the indigo core while their LUMO levels remain unchanged compared to parent indigo. The electron density of the LUMO on the moity of indigo is localized mostly on the carbonyl groups. Such behavior can be explained by the fact that LUMO in indigo is localized mostly on the carbonyl groups Their results show that it is possible to lower LUMO energy of indigoids with electron deficient substituents such as CN, CF_3 and NO_2. It is important small decrease in the LUMO energy levels of the corresponding indigoids bearing two or four fluorine atoms. The LUMO and HOMO energy levels for indigo are -3.90 eV and -5.77 eV. The band gap value of indigo is 1.87 [Klimovich et al, 2014].

Watanabe et al reported synthesis of 5-5′ position alkyl chain substituent indigo as illustrated in figure 3.

Watanabe et. all reported the synthesis a series of alkylated indigos (C1- C13). Introducing to alkyl chains to indigo molecule is useful to incresing the solubility in organic solvents.

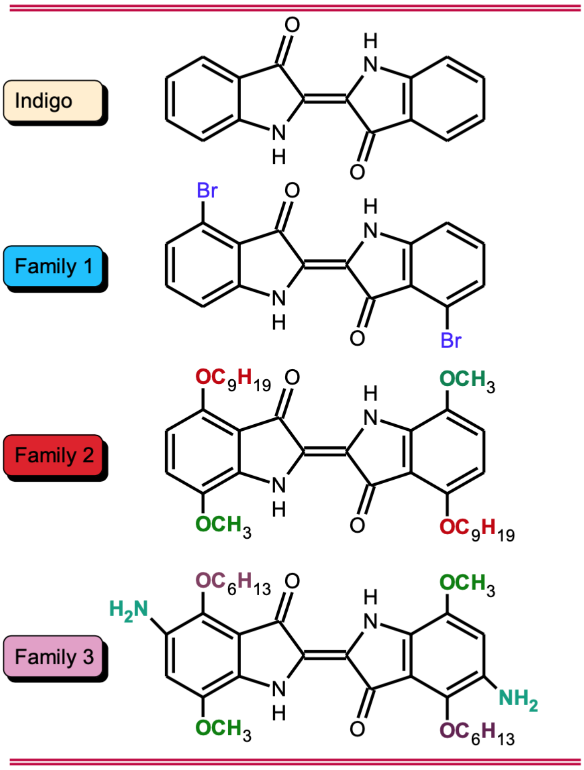

Figure 4: Structure of indigo derivatives snthesized by Melo

The absorption spectra results show that absorption peaks of molecules of indigo of C1- C13 were slightly red-shifted to 615-617 nm for alkylated indigos are of the π-π* transition type while the absorption bands at 600 nm for parent indigo. Alkyl chains, especially long alkyl chains, is increase solubility. The reduction potentials for C1- C13 varied between -0.79 to -0.85 V. The alkylation on the 5,5′ positions slightly reduces the electron accepting properties and increases the electron donating abilities. For all molecules, HOMOs and LUMOs were delocalized over the indigo skeleton. HOMO and/or LUMO energy levels are decreased by the introduction of alkyl chains according to absorption and electrochemical results [Watanabe et al, 2016].

Table 1. Spectral data including absorption in different solvents (3)

Compnd	**λ_{abs} (Dioxan)**	**λ_{abs} (Benzene)**	**λ_{abs} (DMF)**
Indigo	-	-	610
Family 1	602	605	616
Family 2	629	635	638
Family 3	732	735	748

Melo et. al discussed the donor and acceptor groups can be influenced by peripherical substitution at the indigo benzene rings. Also, they reported the effect of substitution on the spectral and photophysical properties of several indigo derivatives. Spectral data are given table 1.

Chunyue et all aim to study the influence of the different donors, different number of anchoring groups on the photophysics, electrochemical properties and photovoltaic performances by spectral, electrochemical, photovoltaic experiments. The corresponding molecular structures of the three dyes are shown in Fig. 3.

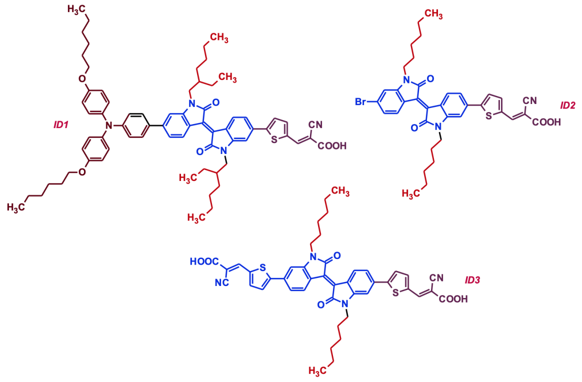

Figure 5: Molecular Structure of three ID dyes

ID1, ID2 and ID3 showed the maximum absorption at λ_{max} 351 and 450 nm, 400 nm, respectively, which were corresponding to HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) transition. The optical band gap calculated from the molecular absorption edges is 2.06 eV, 2.67 eV and 1.82 eV, respectively. Amongst these photo-sensitizers, ascribed to strong electron donating ability of triphenylamine unit, the ID1 dye with the triphenylamine electron donor presents widest absorption range and longest maximum absorption wavelength, which is an advantageous spectral property for light harvesting of the solar spectrum. The HOMO levels of dyes (ID1–ID3) are −5.16, −4.93, −5.0 eV, respectively, which shows that all the HOMOs are lower than the I/I_3- potential, suggesting that there is enough driving force for the regeneration of the dye. The LUMO level of the three dyes calculated from $E_{HOMO} - Eg$ are −3.1, −2.26 and −3.18 eV, respectively, which are higher than the TiO_2 conduction band (−3.9 eV). The ID1 shows higher conversion efficiency (η) of 3.33% (680 mV, 6.80 mA cm^{-2}, 0.72), because of its better donor capability when introduce the triphenylamine on the other side of ID2. The ID2 shows higher conversion efficiency (η) of 3.00%. The ID3 shows higher conversion efficiency (η) of 2.57% [Gang et al, 2014].

Bibliography

Bouzidi et al, 2017 Bouzidi, A; Yahia, IS; El-Sadek, MSA (2017). *Dyes and Pigments*, **146**, 66-72

Furuyama et al, 2018 Furuyama, Taniyuki; Tamura, Daichi; Maeda, Hajime; Segi, Masahito (2018). *Tetrahedron Letters*, ,

Gang et al, 2014 Gang, Wang; Haijun, Tan; Yiping, Zhang; Yingying, Wu; Zhubin, Hu; Guipeng, Yu; Chunyue, Pan (2014). *Synthetic Metals*, **187**, 17-23

Glowacki et al, 2012 Glowacki, Eric Daniel; Voss, Gundula; Leonat, Lucia; Irimia-Vladu, Mihai; Bauer, Siegfried; Sariciftci, Niyazi Serdar (2012). *Israel Journal of Chemistry*, **52**, 540-551

Guo et al, 2014 Guo, Chang; Sun, Bin; Quinn, Jesse; Yan, Zhuangqing; Li, Yuning (2014). *Journal of Materials Chemistry C*, **2**, 4289-4296

Klimovich et al, 2014 Klimovich, IRINA V; Leshanskaya, LI; Troyanov, SI; Anokhin, DV; Novikov, DV; Piryazev, AA; Ivanov, DA; Dremova, NN; Troshin, PA (2014). *Journal of Materials Chemistry C*, **2**, 7621-7631

Ngan et al, 2007 Ngan, Vu Thi; Gopakumar, G; Hue, Tran Thanh; Nguyen, Minh Tho (2007). *Chemical Physics Letters*, **449**, 11-17

Rebelo et al, 2014 Rebelo, Susana LH; Linhares, Margarida; Sim~oes, M'ario MQ; Silva, Artur MS; Neves, M Gracca PMS; Cavaleiro, Jos'e AS; Freire, Cristina (2014). *Journal of Catalysis*, **315**, 33-40

Rondao et al, 2012 Rondao, R; de Melo, J Seixas; Schaberle, FA; Voss, G (2012). *Physical Chemistry Chemical Physics*, **14**, 1778-1783

SeixasdeMelo et al, 2004 Seixas de Melo, J; Moura, AP; Melo, MJ (2004). *The Journal of Physical Chemistry A*, **108**, 6975-6981

Shadi et al, 2003 Shadi, IT; Chowdhry, BZ; Snowden, MJ; Withnall, R (2003). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **59**, 2213-2220

Watanabe et al, 2016 Watanabe, Motonori; Uemura, Naoki; Ida, Shintaro; Hagiwara, Hidehisa; Goto, Kenta; Ishihara, Tatsumi (2016). *Tetrahedron*, **72**, 4280-4287

Woodtli et al, 2018 Woodtli, Pascal; Giger, Sandro; M"uller, Patrick; S"agesser, Lucie; Zucchetto, Nicola; Reber, Michael J; Ecker, Achim; Br"uhwiler, Dominik (2018). *Dyes and Pigments*, **149**, 456-461

Zhao et al, 2014 Zhao, Na; Qiu, Li; Wang, Xiao; An, Zengjian; Wan, Xiaobo (2014). *Tetrahedron Letters*, **55**, 1040-1044

deMelo et al, 2006 de Melo, J S'ergio Seixas; Rond~ao, Raquel; Burrows, Hugh D; Melo, Maria J; Navaratnam, Suppiah; Edge, Ruth; Voss, Gundula (2006). *ChemPhysChem*, **7**, 2303-2311

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