



## Novel organic dyes based on thioindigo for dye-sensitized solar cells



Mozhgan Hosseinnzhad<sup>a</sup>, Siamak Moradian<sup>b, c</sup>, Kamaladin Gharanjig<sup>a, c, \*</sup>

<sup>a</sup> Department of Organic Colorants, Institute of Color Science and Technology, P.O. Box 16656118481, Tehran, Iran

<sup>b</sup> Faculty of Polymer and Color Engineering, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

<sup>c</sup> Center of Excellence for Color Science and Technology, Institute of Color Science and Technology, P.O. Box 16656118481, Tehran, Iran

### ARTICLE INFO

#### Article history:

Received 25 April 2015

Received in revised form

11 July 2015

Accepted 13 July 2015

Available online 18 July 2015

#### Keywords:

Thioindigo

Dye-sensitized solar cells

Sensitizers

Conversion efficiencies

Photocurrent–photovoltage curves

Light fastness

### ABSTRACT

Two novel metal free organic dyes based on thioindigo were prepared and used as sensitizers in dye-sensitized solar cells. The synthesized dyes together with their corresponding intermediates were purified and characterized by analytical techniques. Such techniques confirmed the corresponding structures of dyes and their intermediates and the yield of all the stages of dye preparation were calculated to be above 75%. Fluorometric analyses show fluorescence in the red region of the visible spectrum for both dyes. Oxidation potential measurements for both dyes ensured an energetically permissible and thermodynamically favourable charge transfer throughout the continuous cycle of photo-electric conversion. Finally, dye sensitized solar cells were fabricated in order to determine the photovoltaic behaviour and conversion efficiencies of each dye. Such evaluations demonstrate rather high conversion efficiencies of 6.10% and 6.45% for such simple structured dyes 1 and 2, respectively.

© 2015 Elsevier Ltd. All rights reserved.

### 1. Introduction

Dye-sensitized solar cells (DSSCs or Grätzel cells) have attracted a great deal of interest, as they could offer high energy conversion efficiencies at low cost [1]. Recently, more and more attention has been directed toward the application of metal-free organic dyes in dye-sensitized solar cells because such organic dyes do not contain the expensive ruthenium of limited resource, and have additionally, the advantages of relatively facile dye synthesis and capability of easy molecular tailoring [2]. Many organic dyes inclusive of coumarine [3], polyene [4], hemicyanine [5], thiophene based [6], and indoline [7] dyes exhibiting relatively high performances in dye-sensitized solar cells have so far been designed and developed. In such compounds the electron-donating (D) and the electron-accepting groups (A) are connected through a  $\pi$ -conjugated linker (a D– $\pi$ –A molecular structure). Their properties can be finely tuned by independently altering, alternating or matching different groups in such D– $\pi$ –A dyes. In search for high efficiency organic dyes for solar cells, development of new materials offering

optimized thermal and photochemical stabilities, as well as appropriate optical and electrical properties is of utmost importance [8]. Due to the ever increasing energy crisis, many research, in recent years has been focused on the synthesis of new sensitizers and/or on the study of the mechanism of energy conversion [9]. The results suggest that smartly designed metal-free organic dyes could be good potential competitive candidates as photosensitizers in DSSCs due to advantages mentioned above [2,9].

In the present investigation, two novel metal-free donor acceptor  $\pi$ -conjugated organic dyes based on thioindigo (in fact thioindoxyl) as the electron donor, a simple naphthyl residue, as part of the  $\pi$ -conjugated system and acrylic acid or cyanoacrylic acid as the electron withdrawing (acceptor) anchoring groups are proposed and investigated for the first time. Like all vat dyes thioindigo is classified by color index 10 as both a dye (i. e. C. I. vat red 41 and C. I. disperse red 364) and a pigment and solvent dye (i. e. C. I. solvent red 242). The parent molecule, indigo (a blue colorant) and its brominated form, better known as Tyrian Purple (i. e. 6,6'-dibromo indigotin), are colorants of antiquity and were originally extracted from natural plant and animal sources, respectively. Although, halogenations of indigo shifts the blue color of indigo to a reddish blue as in Tyrian Purple but a true red color is only possible when both imide (NH) residues of indigo are replaced by sulphur. Thioindigo is not found in nature and was synthesized over a hundred and ten years ago [10,11]. Thioindigo has lost its

\* Corresponding author. Department of Organic Colorants, Institute of Color Science and Technology, P.O. Box: 16656118481, Tehran, Iran. Tel.: +98 21 22969777; fax: +98 21 22947537.

E-mail addresses: [hosseinnzhad-mo@icrc.ac.ir](mailto:hosseinnzhad-mo@icrc.ac.ir) (M. Hosseinnzhad), [moradian@aut.ac.ir](mailto:moradian@aut.ac.ir) (S. Moradian), [gharanjig@icrc.ac.ir](mailto:gharanjig@icrc.ac.ir) (K. Gharanjig).

importance as a vat dye, but a series of its halogenated and/or methylated forms are considered to be very important pigments of high durability. Can thioindigo (a more than a hundred and ten year old colorant) be revived as a dye sensitizer to be utilized in the modern high technology dye sensitized solar cells? Seeking the answer to this question is the fundamental basis for the present investigation.

In fact, there are several good reasons to pursue the utilization of thioindigo in DSSCs, the most important being its red color. For a colorant to be red, it must absorb all the short (i. e. blue) and the medium (i.e. green) wavelength ranges of the visible spectrum (i.e. 2/3 of the most high energy portion of the light spectrum) leaving the low energy long waves which are collectively of a red color. The absorption of two thirds of the most energy full portion of the light spectrum must be beneficial in dye sensitized solar cells. Additionally, thioindigo and its substituted analogues are interesting cross conjugated molecules of extreme thermal, chemical and photochemical durabilities which are also considered to be very advantageous in DSSCs. However it must be noted that thioindigo itself gives very low light to electricity conversion efficiencies (i.e. a 7-carboxylic acid thioindigo tested in our laboratories gave a very low conversion efficiency of 0.03%). It is the objective of this investigation to illustrate, how by reacting thioindigo with a simple naphthyl residue as part of the  $\pi$ -conjugated system and simple acrylic acid or cyanoacrylic acid acceptor anchoring groups, the conversion efficiency values are enhanced enormously. The dyes together with their corresponding intermediates were then purified and characterized. The spectrophotometric properties of the prepared organic dyes in solution in Tetrahydrofuran (THF) and on a nano anatase TiO<sub>2</sub> substrate were examined. The absorption maxima and intensities of the resultant dyes were also obtained. Dye sensitized solar cells were then fabricated utilizing these metal-free organic dyes and their photovoltaic behaviors were determined. Schematic representation of the route for synthesis of the prepared metal-free organic dyes is given in Fig. 1.

## 2. Experimental section

### 2.1. Materials and instruments

All compounds used in this study were of analytical grade unless otherwise stated. The FTIR measurements were carried out on a Perkin Elmer instrument. NMR measurements were carried out on a 500 MHz Joel instrument. Differential scanning calorimetry (DSC) analyses were carried out on a Dupont 2000DSC instrument. UV-Visible spectrophotometry and fluorimetry were carried out on a Cecil 9200 double beam transmission spectrophotometer and Ocean Optics Usb2000flg fluorometer, respectively.

### 2.2. Synthesis of intermediates

#### 2.2.1. Component 2

8 mmol of Component **1**, 20 mmol of dimethyl malonate, 6 mmol of ammonium acetate and 9 mmol of piperidine were added to 20 mL of acetonitrile. The mixture was refluxed for 6 h. After the reaction was complete, the mixture was cooled to room temperature. The mixture was poured into methylenechloride (90 mL) and then filtered and washed with water, the organic phase was removed under reduced pressure by the aid of a rotary evaporator and subsequently purified by silica gel column chromatography (ethyl acetate:hexane = 1:5) (Yield = 75%). mp 102–106 °C, FTIR (KBr) (Cm<sup>-1</sup>): 2960: CH str. Ar, 1690: C=O str. Acid, 1533, 1460: C=C str; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 3.86 (s, 3H, OCH<sub>3</sub>), 6.79–6.82 (dd,  $J_{12} = 2.0$  Hz,  $J_{13} = 7.9$  Hz, 2H), 6.84–6.89 (d,  $J = 7.7$  Hz, 3H), 7.16 (t,  $J = 7.2$  Hz, 2H), 7.36–7.38 (d,

$J = 7.5$  Hz, 1H); Elem. Anal. Calcd. for C<sub>14</sub>H<sub>11</sub>BrO<sub>2</sub>(%): C, 57.75; H, 3.78. Found: C, 57.76; H, 3.80.

#### 2.2.2. Component 3

8 mmol of Component **1**, 16 mmol of methyl cyanoacetate and 9 mmol of piperidine were added to 20 mL of acetonitrile. The mixture was refluxed for 6 h. After the reaction was complete, the mixture was cooled to room temperature. The resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate:hexane = 1:5) (Yield = 77%). mp 122–125 °C, FTIR (KBr) (Cm<sup>-1</sup>): 3050: CH str. Ar, 1686: C=O str. Acid, 1529, 1461: C=C str; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 3.85 (s, 3H, OCH<sub>3</sub>), 6.72 (s, 1H), 7.25–7.30 (d,  $J = 7.8$  Hz, 3H), 7.37 (t,  $J = 7.5$  Hz, 2H), 7.38–7.44 (d,  $J = 8.3$  Hz, 1H); Elem. Anal. Calcd. for C<sub>15</sub>H<sub>10</sub>BrNO<sub>2</sub>: C, 56.98; H, 3.16; N, 4.43. Found: C, 56.96; H, 3.18; N, 4.46.

#### 2.2.3. Component 4

To 0.194 mmol of [Pd(PPh<sub>3</sub>)<sub>4</sub>] was added a deoxygenated solution of 1.94 mmol of **2** in DME (10 mL). This was followed by a deoxygenated solution of 2.91 mmol of 3-boromothioindoxyl in 5 mL of ethanol, and then a deoxygenated solution of 16.5 mmol of sodium carbonate in 8.2 mL of water. The resultant mixture was refluxed under nitrogen for 46 h over which time it turned red. After cooling to room temperature, the mixture was quenched with 50 mL of water. the remaining precipitate was filtered and purified by silica gel column chromatography (ethyl acetate:hexane = 1:3) (Yield = 76%). mp 136–138 °C, FTIR (KBr) (Cm<sup>-1</sup>): 3039: CH str. Ar, 1731: C=O str. Acid, 1613, 1508: C=C str; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 2.14 (s, 2H, CH<sub>2</sub>), 3.87 (s, 3H, OCH<sub>3</sub>), 6.48–6.52 (dd,  $J_{12} = 1.8$  Hz,  $J_{13} = 8.2$  Hz, 2H), 6.67–6.69 (d,  $J = 8.7$  Hz, 3H), 6.71–6.75 (d,  $J = 7.6$  Hz, 3H), 7.89 (t,  $J = 7$  Hz, 1H), 7.95 (t,  $J = 7.1$  Hz, 2H); Elem. Anal. Calcd. for C<sub>22</sub>H<sub>16</sub>SO<sub>3</sub>: C, 73.33; H, 4.44. Found: C, 73.35; H, 4.41.

#### 2.2.4. Component 5

To 0.194 mmol of [Pd(PPh<sub>3</sub>)<sub>4</sub>] was added a deoxygenated solution of 1.94 mmol of **3** in DME (10 mL). This was followed by a deoxygenated solution of 2.91 mmol of 3-boromothioindoxyl in 5 mL of ethanol, and then a deoxygenated solution of 16.5 mmol of sodium carbonate in 8.2 mL of water. The resultant mixture was refluxed under nitrogen for 46 h over which time it turned red. After cooling to room temperature, the mixture was quenched with 50 mL of water. The remaining precipitate was filtered and purified by silica gel column chromatography (ethyl acetate:hexane = 1:3) (Yield = 79%). mp 163–165 °C, FTIR (KBr) (Cm<sup>-1</sup>): 2974: CH str. Ar, 1733: C=O str. Acid, 1620, 1462: C=C str; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 2.25 (s, 2H, CH<sub>2</sub>), 3.86 (s, 3H, OCH<sub>3</sub>), 6.60 (s, 1H), 7.38–7.39 (d,  $J = 7.9$  Hz, 3H), 7.43–7.45 (d,  $J = 7.2$  Hz, 3H), 7.47 (t,  $J = 7.1$  Hz, 1H), 7.57 (t,  $J = 7.3$  Hz, 2H); Elem. Anal. Calcd. for C<sub>23</sub>H<sub>15</sub>NSO<sub>3</sub>: C, 71.68; N, 3.63; H, 3.89. Found: C, 71.65; N, 3.65; H, 3.90.

#### 2.2.5. Component 6 and Component 7

Under an inert atmosphere of argon, a solution of 9 mmol of Component **4** or Component **5** together with 5 mmol of thioindoxyl in 15 mL of methanol was vigorously stirred and to which small portions of Na<sub>2</sub>CO<sub>3</sub> was added. After 1 h of stirring at 45 °C, the dark red residue was filtered and successively and intensively washed with methanol and cold water. The resulting precipitate was filtered and purified by silica gel column chromatography (ethyl acetate:hexane = 1:2).

#### 2.2.6. Component 6

Yield = 83%, mp 186–188 °C, FTIR (KBr) (Cm<sup>-1</sup>): 2928: CH str. Ar, 1656: C=O str. Acid, 1602, 1518: C=C str; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 3.92 (s, 3H, OCH<sub>3</sub>), 6.60–6.62 (dd,  $J_{12} = 1.9$  Hz,  $J_{13} = 7.5$  Hz, 2H), 7.38–7.39 (d,  $J = 7.9$  Hz, 6H), 7.43–7.45 (d,

Download English Version:

<https://daneshyari.com/en/article/175654>

Download Persian Version:

<https://daneshyari.com/article/175654>

[Daneshyari.com](https://daneshyari.com)