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# Indoline and benzothiazole-based squaraine dye-sensitized solar cells containing bis-pendent sulfonate groups: Synthesis, characterization and solar cell performance

Sultan A. Al-horaibi<sup>a,b</sup>, Abdullah M. asiri<sup>c,d</sup>, Reda M. El-Shishtawy<sup>c,e</sup>, Suresh T. Gaikwad<sup>a</sup>, Anjali S. Rajbhoj<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra 431001, India <sup>b</sup>Department of Chemistry, Al-Baydha University, Yemen.

<sup>c</sup>Department of Chemistry, King Abdulaziz University, P.O BOX 80203, Jeddah, Saudi Arabia.

<sup>e</sup>Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Center, Dokki, Cairo, 12622, Egypt.

\* Corresponding author e-mail address: anjali.rajbhoj@hotmail.com

Abstract: Two new symmetric squaraine sensitizers (SQTHZ and SQIND) carrying benzothiazole and indoline moieties as strong electron donating groups to inject the electron into the TiO<sub>2</sub> nanoparticles were tested as DSSC. The theoretical calculations and absorption results show that the electron density of LUMO of SQTHZ is delocalized in the whole chromophore, leading to strong electronic coupling between SQTHZ sensitizer and the conduction band of TiO<sub>2</sub>. Furthermore, the presence of long alkyl chain with pendent bis-SO<sub>3</sub><sup>-</sup> groups would inhibit recombination and decrease the dye aggregation. Interestingly, SQTHZ displayed UV-Vis and NIR absorption at a longer wavelength compared to SQIND. This structure feature, as well as optical properties, would lead to improved efficiency of dye-sensitized solar cell with overall better photovoltaic performance ( $\eta$  of 3.31 %, Jsc of 7.65 mA/ cm<sup>2</sup>, Voc of 0.59, ff of 0.71 and IPCE of 47 % at 674 nm) compared to SQIND.

**Keywords:** Dye-sensitized solar cell, Symmetric squaraine dyes, Photoelectrochemical properties, DFT.

# **1** Introduction

For the last four decades, conventional silicon solar cells have witnessed development rapidly, with energy current-conversion efficiencies of more than 23%, by addressing the optical effects of impurities, by incorporation of alloys and superlattices, and silicon-based tandem cells [1, 2]. Dye-sensitized solar cells (DSSC) are one of the most important sources of renewable energy[3, 4]. It has seen tremendous growth and a great deal of interest from scientists and economic researchers because

<sup>&</sup>lt;sup>d</sup>Center of Excellence for Advanced Materials Research.

of their low cost, eco-friendly and ease of fabrication compared to conventional silicon cells based. Several organic dyes for example, coumarin [5], indoline[6], triphenylamine[7], hemicyanine[8, 9], squaraine dyes [10], phthalocyanine [9, 11], and perylene [12], have been developed and used in DSSC. In addition, the squaraine dyes (SQ) are particularly important in research as they are ecofriendly, low-cost and give high-performance, this is resulting from photovoltaic and electrochemical stability as well as high molar extinction coefficients in the visible region [13, 14]. A perusal revision to photoconversion by potential dye-sensitizer used in dye-sensitized solar cells confirms that photoreceptor efficiency can be achieved to 12% even with the photon harvest mainly in the visible absorption area of 400-700 nm of the solar spectrum [15, 9]. This indicates an urgent need to improve photovoltaic efficiency by developing high-capacity sensitizer's dyes to harvest photons in NIR-IR wavelength region [16]. Among the various organic dyes, squaraine dyes are considered the best candidates for use in applications of dye-sensitized solar cells. They are low cost and have higher molar extinction coefficients  $\approx 3 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>, also squaraine dyes absorb the photons in the range 400 to 800 nm [17, 18]. Our previous studies indicated that the absorption bands of squaraine dyes could be easily tuned to get into NIR region by structural modification, which closely matches the spectral response of sunlight. In addition, theoretical calculations on squaraine dyes revealed their suitability for DSCC, as their LUMO energy lie above the LUMO energy of TiO<sub>2</sub> conduction band and thus ease electron injection from the dye to  $TiO_2$  [19-23].

The purpose of the present work is to fabricate and develop an efficient photovoltaic system capable of absorption at long wavelength of the spectrum through the application of two types of benzothiazole and indoline based symmetric squaraine sensitizers containing bis-sulfonate groups which act as anchors for DSSC.

We have synthesized, characterized and studied photovoltaic properties of two new squaraine sensitizers. The SQTHZ and SQIND were calculated by Gaussian 09 packages to have a detailed understanding of the ground, excited state electron density distribution and band gap [19, 24, 25]. These two types of SQTHZ and SQIND sensitizers exhibited a panchromatic response from the visible region to the NIR region. The presence of long alkyl chain in SQTHZ with pendent bis-SO<sub>3</sub><sup>-</sup> groups would inhibit recombination and decrease the dye aggregation and thus resulting in improved dye-sensitized solar cell efficiency.

### 2. Materials, Instruments and Methods

### 2.1 Materials

All chemicals, 4-Bromophenyl hydrazine hydrochloride (98%), Phenyl hydrazine (97%),

Squaric acid (98%), Isopropyl methyl ketone (98%), 1,4-butan sultone, 1,3-propane sultone, n-Butanol, Toluene, Acetonitrile (98%), Methanol, Ethanol (99.9%), petroleum ether 60/80 and silica gel 60-120 mesh for column chromatography (Vetec) were from Sigma-Aldrich. Synthesis processes of SQTHZ and SQIND are showed in Scheme 1.

### 2.2 Instrumental analysis

All HNMR spectra were recorded on Bruker AVANCE III WM 400 spectrometers (Karlsruhe, Germany) and <sup>13</sup>C NMR at 150 MHz using DMSO-d<sub>6</sub> and CDCl<sub>3</sub>. UV-vis spectra were recorded on a Perkin Elmer UV-1800 in dimethyl sulfoxide. The oxidation/ reduction properties of the SQTHZ and SQIND were examined by cyclic voltammetry (CV) on a Metrohm Autolab PGSTAT 128N in dried dimethyl sulfoxide with three electrode systems consists of a saturated Ag/AgCl reference electrode, a platinum wire auxiliary electrode and Pt electrode as working electrode. The scan rate was 100 mV/ s. The optimization geometries for SQTHZ and SQIND were calculated at B3LYP/3-21G (d, p) level of calculations using Gaussian 09 program package. Fluorescence spectra were conducted on a RF-6000 spectrofluorometer and LabSolutions RF software using methanol solution (0.5  $\mu$ M) for both dyes and were corrected for wavelength-dependent instrument sensitivity. The dye solution was filled in a 1-cm standard transparent quartz cell, and the sample was purged with argon for 15 min prior measurements. Emission maxima were determined with an accuracy of ±1.0 nm.

## 2.3 Synthesis and characterizations

### 2.3.1 Synthesis of 2-methylbenzo[d]thiazole (1)

A mixture of 2-aminothiophenol (14.92 g, 0.1 mol) in acetic anhydride (40 ml) was refluxed for 4 h at temperature 150 °C. It was then cooled to room temperature. The solvent was removed under reduced pressure. Water was added to the product in addition to aqueous NaOH until pH=8. It was then extracted with ethyl acetate (3-4×50 ml) to give compound (1) as an oil in 98.3% yield. The FT-IR spectrum showed an absorption bands at  $\gamma$ (cm<sup>-1</sup>) 3062(st C-H), 1713(N=C), 1594(C=C), 1240(C-N). <sup>1</sup>HNMR (400MHz-CDCl<sub>3</sub>) spectrum recorded at  $\delta$ (ppm ) 2.74(s, 3H, CH<sub>3</sub>), 7.28(t,1H, J=5.6 Hz, Ar-H), 7.39(t, 1H, J= 9.2 Hz, Ar-H), 7.72(d, 1H, J=8.04Hz, Ar-H), 7.94(d, 1H, J=8.16 Hz, Ar-H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 19.74 (CH<sub>3</sub>), 121.08, 122.04, 124.38, 125.60(carbon phenyl aromatic), 148.53, 153(C<sub>7</sub>, C<sub>8</sub> respectively), 166.62(C<sub>2</sub>).

### 2.3.2 Synthesis of 5-bromo 2, 3, 3-trimethyl -3H -indolenine (2)

In a round bottom flask p-bromophenylhydrazine hydrochloride (7.55 g, 33.85 mmol), isopropyl methyl ketone (5.85 g, 67.5 mmol) and acetic acid (60 ml) were refluxed under  $N_2$ 

atmosphere for 7 h and stirred at RT for 19 h. The solvent was removed and the residue was dissolved in Et<sub>2</sub>O/H<sub>2</sub>O (3×5 ml). The combined organic phases were washed with aqueous KOH/H<sub>2</sub>O solution (3×100 ml) and dried over MgSO<sub>4</sub> for 1h with stirred, then filtered and washed with diethyl ether to give compound (2) as brownish oil in 97% yield. <sup>1</sup>HNMR (400MHz-DMSO-d<sub>6</sub>) spectrum recorded at  $\delta$ (ppm ) 1.21(s, 3H, CH<sub>3</sub>), 1.9(s, 6H, 2CH<sub>3</sub>), 7.45(d,1H, J=8.2 Hz ,Ar-H), 7.69(d, 1H, J= 8.6 8Hz, Ar-H),7.74(s, 1H, Ar-H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) 21.68, 21.76 (CH<sub>3</sub>, 2CH<sub>3</sub>), 54.52 (C<sub>3</sub>), 118.70, 119.43, 125.6, 139.90(carbon phenyl aromatic), 146.17, 153.26(C<sub>8</sub>, C<sub>9</sub> respectively), 178.98 (C<sub>2</sub>).

# 2.3.3 Synthesis of 4-(2-methylbenzo[d] thiazol-3- ium -3 -yl) butane-1-sulfonate (3)

A mixture of 2-methylbenzothiazole (3 g, 0.02 mmol), 1, 4-butane sultone (2.74 g, 0.02 mmol) and 1, 2 dichlorobenzene (20 ml, anhydrous) were heated at 110 °C for 18 h. After cooling to room temperature, the mixture was diluted with diethyl ether (350 ml). The product was collected by vacuum filtration, washed with ether (3×100 ml) and then dried in vacuum to give compound (3) as light orange solid in yield 64%. <sup>1</sup>HNMR (400 MHz-DMSO-d<sub>6</sub>) spectrum recorded at  $\delta$ (ppm) 1.77(pent, 2H, CH<sub>2</sub>-SO<sub>3</sub>), 2.07 (pent, 2H, CH<sub>2</sub>-SO<sub>3</sub>), 3.22(s,3H, CH<sub>3</sub>), 3.30(t, 2H, J=6.12Hz, N-CH<sub>2</sub>),4.47(t, 2H, J= 5.4Hz, CH<sub>2</sub>-SO<sub>3</sub>), 7.79(t, 1H, J=7.12Hz, Ar-H), 7.88(t, 1H, J=7.08 Hz, Ar-H), 8.42 (overlapping doublets, 2H, J=8.36 Hz, Ar-H).

# 2.3.4 Synthesis of 3-(5-bromo-2, 3, 3-trimethyl- 3H- indol-1-ium-1-yl) propane-1-sulfonate (4)

A mixture of 5-bromo-2,3,3-trimethyl-3H-indole (2.5 g, 0.0105 mmol) and 1, 3-propane sultone (2.5 g, 0.005 mmol) was refluxed for 6 h under N<sub>2</sub> atmosphere in nitromethane (20 ml) and cooled to room temperature, then diethyl ether was added and left for 1h. It was then filtered and washed with diethyl ether to give compound (4) as light brown colour in 77% yield. <sup>1</sup>HNMR (400MHz-DMSO-d<sub>6</sub>) spectrum was recorded at  $\delta$ (ppm) 1.45(s,6H, 2CH<sub>2</sub>), 1.89(pent, 2H, CH<sub>2</sub>), 2.26 (t, 2H, CH<sub>2</sub>-SO<sub>3</sub>), 4.47(t, 2H, CH<sub>2</sub>-N<sup>+</sup>), 7.78( d, 1H, J=6.84Hz, Ar-H), 7.87(d, 1H, J=8.56 Hz, Ar-H), 8.04(s, 1H, Ar -H).<sup>13</sup>C-NMR(DMSO-d<sub>6</sub>) 21.83, 23.78, 25.27, 26.83, 33.17, 47.74(C<sub>3</sub>), 54.32(CH<sub>2</sub>-N<sup>+</sup>), 117.14, 123.11, 126.59, 131.94 (carbon phenyl aromatic), 139.97, 143.74 (C<sub>8</sub>, C<sub>9</sub> respectively), 174.54(CO), 196.67 (C<sub>2</sub>).

# 2.3.5 Synthesis of SQIND

A mixture of 3-(5-bromo-2, 3, 3-trimethyl- 3H- indolium-1-yl) propane-1-sulfonate (3 g, 0.0069 mmol) and squaric acid (0.395 g, 0.00346 mmol) was taken 40 ml of dry BuOH/toluene 1:1 (v/v) was added and reaction mixture was refluxed for 8 h using Dean–Stark trap for azeotropic removal of water. The product was purified by silica gel 60-120 mesh column chromatography with hexane and methanol (9:1, 9:2, 9:3, 9:4 and 9:5 v/v) to give SQIND as blue dye in 78% yield. <sup>1</sup>HNMR

(400MHz-DMSO-d<sub>6</sub>) spectrum recorded at  $\delta$ (ppm) 1.55 (s, 6H, 2CH<sub>3</sub>), 1.68(s, 6H, 2CH<sub>3</sub>), 1.98 (pent, 2H, CH<sub>2</sub>), 2.13(pent, 2H, CH<sub>2</sub>), 2.6-2.67(t t, 4H, CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>), 4.2(t, 2H, CH<sub>2</sub>-N), 4.6 (t, 2H, CH<sub>2</sub>-N<sup>+</sup>), 5.83(s, 1H, CH=C), 7.4(d, 1H, J=8.56Hz, Ar-H), 7.54(d, s, 2H, J=6.52Hz, Ar-H), 7.88(s, 1H, Ar-H), 8.0(d, 1H, Ar-H), 8.16(d, 1H, Ar- H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) 13.73, 19.15, 24.61, 26.61, 26.50, 26.71, 27.06, 30.66, 34.00(C<sub>3</sub>), 43.65 (N-CH<sub>2</sub>), 49.39(N<sup>+</sup>-CH<sub>2</sub>), 64.31(C<sub>3</sub>), 87.15(C=CH), 110.68, 116.74, 125(carbon phen -yl aromatic), 130.76, 141.45(C<sub>8</sub>, C<sub>9</sub> respectively), 169.55(C<sub>2</sub>), 173.43 (CO).

# 2.3.6 Synthesis of SQTHZ

A mixture of 4-(2-methylbenzo[d]thiazol-3-ium-3-yl) butane-1-sulfonate (3 g, 0.011 mmol) with squaric acid (0.559 g, 0.0052 mmol) was taken and 40 ml of dry BuOH/toluene1:1 (v/v) was added and reaction mixture was refluxed for 8 h using Dean–Stark trap for azeotropic removal of water. Reaction mixture was cooled to room temperature, solvent was evaporated. The product was purified by silica gel 60-120 mesh column chromatography with ethyl acetate and methanol (9:1, 9:2, 9:3, 9:4 and 9:5 (v/v)) to give SQTHZ as blue dye solid in 47% yield. <sup>1</sup>HNMR (400MHz-DMSO-d<sub>6</sub>) spectrum was recorded at  $\delta$ (1.5 pent, 4H, 2CH<sub>2</sub>), 1.7(t, 4H, 2CH<sub>2</sub>), 3(t, pent, 4H, CH<sub>2</sub>-N), 7.5(t, t, 2H, J=7.68 Hz, Ar-H), 7.7(tt, 2H, J=7.4Hz, Ar-H), 8(2dd, 4H, J=3.8Hz, Ar-H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) spectrum was recorded at 16.69, 22.10, 26.53, 48.92, 50.11, 117.03, 124.50, 128.05, 128.05, 129.02, 129.33, 140.88, and 177.07. Mass spectral (*m*/*z*): [M<sup>+</sup>] calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub><sup>2-</sup> = 618.03: found: 618.41.



### 2.4 Preparation, Fabrication and measurements of DSSC

A mixture of TiO<sub>2</sub> powder  $\leq 25$  nm (3 g), nitric acid aqueous solution 0.5 ml in dimethyl sulfoxide 3 ml, and deionized water 2 ml was taken and reagent of Triton X-100 (2 ml) was added. The TiO<sub>2</sub> paste was stirred by a rod glass for 10 min and then left it for 5 min and stored in a closed bottle for later use. The conducting glasses substrate indium tin oxide glass slide were cleaned in a detergent solution for 10 min by sonication and with acetone for 10 min, then with deionized water for 10 min and finally with ethanol for 10 min. The conducting glass was dried by air and then in oven. The glass square ( $\sim 8\Omega$ ) was measured by a multi-meter set to examine the conductive side, then strips of Scotch Magic tape on were put on the edges of the glass square by the doctor blade technique. The  $TiO_2$  paste was deposited in the middle of the glass square. The conducting glass  $TiO_2$  porous film was left in the air for 5 min, and then placed on hotplate for 30 min at 70 °C. In the final step it was placed in furnace for 1 h at 450 °C and immersed in squaraine dyes solution (SQTHZ and SQIND) for 25 h in the dark in ethanol with chenodeoxycholic acid (CDCA) (0.001 M). Counter electrode was prepared as follows: A mixture of polyvinylpyrrolidone (PVP) 1 g, H<sub>2</sub>PtCl<sub>6</sub> 0.3 g was dissolved in deionized water (2 ml) under stirring and NaBH<sub>4</sub> solution was added to the mixture. The color of the mixture was changed from orange to black, finally the counter electrode PVP-coated was placed in furnace at 450 °C for 1 h. The solution iodide/tri-iodide ( $I/I_3$ ) electrolyte was prepared as follows: A mixture of iodine (0.03 M), lithium iodide (0.02 M), 1-butyl-3-methylimidazolium iodide (0.015 M), and 4-tertbutylpyridine (0.5 M) were taken in CH<sub>3</sub>CN.

The photovoltaic performance of the fabricated SQTHZ & SQIND based DSSC were measured under sunlight (AM 1.5, 100 mW/  $cm^2$ ) solar simulator (Dayton, Instruments, USA) with a source meter (Keithley, 2400) at 25 °C.

### **3 Results and Discussion**

# 3.1 Synthesis and spectro-electrochemical properties of the SQTHZ and SQIND dyes

The synthesis details of squaraine sensitizers (SQTHZ and SQIND) are showed in Scheme1. SQTHZ and SQIND based benzothiazole and indoline have two sulfonate groups in each dye to facilitate electron injection to the conduction band of nanocrystalline TiO<sub>2</sub>.

**Fig.1** shows the normalized UV-Vis absorption spectra on  $TiO_2$  along with the fluorescence emission for SQTHZ and SQIND dissolved in methanol solution are summarized in Table1. The bands maxima of SQTHZ and SQIND are observed at 655 and 669 nm, respectively, and their

corresponding high molar extinction coefficient values  $2.36 \times 10^5$  and  $2.84 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup> are in agreement with  $\pi$ - $\pi$ \* transitions.



Fig 1. The UV-vis absorption spectrum of SQTHZ and SQIND.



Fig 2. The UV-vis absorption spectrum of SQTHZ and SQIND on TiO<sub>2</sub>.

In **Fig. 2** the absorption spectrum of the SQTHZ on TiO<sub>2</sub> shift towards a longer wavelength compared to the SQIND. The absorption spectra of SQTHZ and SQIND sensitizers on TiO<sub>2</sub> semiconductor electrode are broad which strongly refer to the increased interaction between sulfonate groups for SQTHZ and SQIND and nanopourus TiO<sub>2</sub>. The SQTHZ and SQIND showed fluorescence emission at 685 and 676 nm, respectively in MeOH. The  $\lambda_{max}$  of SQTHZ shifts from 669 to 689 nm ( $\Delta\lambda_{shift}$ , SQTHZ=20 nm), while the  $\lambda_{max}$  of SQIND shifts from 655 to 674 nm ( $\Delta\lambda_{shift}$ , SQIND=19 nm). The  $\Delta\lambda_{shift}$ , SQTHZ is one nm higher than  $\Delta\lambda_{shift}$ , SQIND (see Fig .3). This refers to that SQTHZ sensitizer shows interaction electronic coupling with the TiO<sub>2</sub> better than SQIND. SQTHZ sensitizer has long alkyl chain with bis-sulfonate groups,

which inhibit recombination and decrease the dye aggregation and thus resulting in an improved dyesensitized solar cell efficiency compared with SQIND and dye1 & dye 2. The  $E_{0-0}$  (band gap) energy was estimated from the intersection of the absorption and emission spectra in the MeOH solution for SQTHZ and SQIND to be 1.85 and 1.88 eV, respectively.



Fig 3. Fluorescence intensity spectrum of SQTHZ and SQIND.

To investigate the electrochemical property of dye, cyclic voltammetry (CV) measurement was performed on a Metrohm Autolab PGSTAT 128N with three electrode systems consists of a saturated Ag/AgCl reference electrode, a platinum wire auxiliary electrode and Pt electrode as working electrode. Cyclic voltammetry measurement was performed in DMSO using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte and 0.001 M of **SQTHZ** and **SQIND** at room temperature. The potential scan was taken from -1.5 to 1.0 V at scan rate 25 mV/s (see **Fig.4**).



Fig 4. Cyclic voltammograms of SQTHZ and SQIND.

We have also estimated the energies of frontier orbitals (HOMOs-LUMOs) in SQTHZ and SQIND sensitizers in order to justify its candidatures as sensitizers in DSSC.

In Table 1, the photophysical and electrochemical properties of SQTHZ & SQIND. The  $E_{\text{oxd}}$  of SQTHZ and SQIND was 0.63 and 0.61 V, respectively which estimated from the oxidation potential of dyes molecules in CV graph using question (1). The values of SQTHZ and SQIND were converted on an absolute scale of -5.06 and -5.04 eV, respectively. The HOMO energy levels

$$E_{\text{HOMO}} = -(E_{ox}^{onset} - E_{Fc/Fc^+}^{onset}) - 4.8(\text{eV}) \dots (1)$$
 were calculated using the

equation (1) [25].

where  $E_{ox}^{onset}$  and  $E_{Fc/Fc^+}^{onset}$  are the onset oxidation potentials for the squaraine sample and ferrocene against the Ag/AgCl reference electrode, while the value -4.8 eV is the HOMO energy level of ferrocene against vacuum [25].

While LUMO energies were estimated by using following equation (2).

The values of band gap ( $E_{0-0}$ ) for SQTHZ and SQIND were obtained based on the intersection (685 nm for SQTHZ and 676 nm for SQIND) of the normalized absorption and fluorescence spectra, respectively. The oxidation level of  $E_{ox}$  (HOMO) for SQTHZ and SQIND are more positive than the redox potential of the iodide/triiodide couple used as an electrolyte. The energy reduction level of  $E_{red}$  (LUMO) for SQTHZ and SQIND is sufficiently

negative to inject electrons into the conduction band of TiO<sub>2</sub>.

In Table 1, the data of experimental reveal that the benzohiazole-indoline based squaraine sensitizers (SQTHZ and SQIND) have superior absorption wavelengths ( $\lambda_{max}$ ), fluorescence emission spectrum ( $\lambda_{em}$ ) and bands gap ( $E_g$ ) compared to dye 1 & dye 2. The  $\lambda_{max}$  of SQTHZ and SQIND, are red shifted by 31, 40 nm and 16, 25 nm compared to dye 1 & dye 2 respectively. SQTHZ and SQIND are red shifted more than dye1 & dye 2.

**Table1**.The comparative study of photophysical and electrochemical properties of SQTHZ and SQIND

Dye	λ <sub>max</sub> (nm)	$\frac{\mathcal{E}_{\max}}{(M^{-1} \text{ cm}^{-1})}$	$\lambda_{\max}$ on TiO <sub>2</sub> (nm)	λ <sub>em</sub> (nm)	$E_{0-0}^{a}$ (eV)	<i>E</i> <sub>oxd</sub> <sup>b</sup> (V vs.NHE)	HOMO (eV)	LUMO (eV)	Ref. No
SQTHZ	669	236000	674	685	1.85	0.63	-5.06	-3.21	
SQIND	654	284000	671	676	1.88	0.61	-5.04	-3.19	
Dye 1	638	155000	-	648	2.02	0.91	-5	-2.98	[26]
Dye 2	629	287000	-	643	2.18	0.72	-4.98	-2.80	

<sup>a</sup> The  $E_{0.0}$  was determined from the intersection of the absorption and emission spectra. <sup>b</sup>The  $E_{ox}$  was measured on 0.1 M TBAPF<sub>6</sub> in DMSO (counter electrode (Pt), reference electrode (Ag/AgCl), working electrode (Pt)) and calibrated with ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>).

### 3.2 Frontier molecular orbitals calculations

In the charge density distribution patterns of the ground state highest occupied molecular orbitals (HOMOs and HOMOs-1), lowest unoccupied molecular orbitals (LUMOs and LUMOs+1) of (SQTHZ and SQIND) benzothiazole and indole-based squaraine dyes are illustrated in Fig. 5.



**Fig 5.** The charge density distribution of the frontier molecular orbitals (0.02 contour value) of SQTHZ and SQIND based squaraine sensitizers at B3LYP/3- 21G (d, p) level of theory.

The HOMO-1 is distributed on center of squaric acid and on right is indoline moiety in SQTHZ while it is distributed on center of squaric acid in SQIND. The charge density of HOMO is distributed on center of squaric acid and only on right indoline moiety in SQTHZ as compared SQIND. The charge densities of HOMOs are localized on squaraine moieties. The computed energies of HOMO ( $E_{\text{HOMOs}}$ ), LUMO ( $E_{\text{LUMOs}}$ ), and LUMOs +1 ( $E_{\text{LUMOs+1}}$ ) and energy gaps ( $E_{\text{g}}$ ) of SQTHZ and SQIND benzothiazole-indoline based squaraine dyes at B3LYP/3-21G (d, p) level of theory.

In Fig. 5, the charge density distribution on LUMO is expected on SQTHZ to be more stable after anchoring with the  $TiO_2$  surface. Furthermore, bis-SO<sub>3</sub><sup>-</sup> groups would be a favorable site to transfer electrons from dyes to the  $TiO_2$  surface [26]. The electron distributions for HOMO-1, HOMO-LUMO and LUMO+1 are shown in Fig. 5.

## 3.3 Photovoltaic characterized of the SQTHZ and SQIND

The photocurrent short-circuit density-Photovoltage (*J*-*V*) characteristics were tested for SQTHZ and SQIND of DSSC having  $\Gamma/I_3^-$  as redox electrolyte under illumination with AM 1.5G solar showed in Fig. 6 and summarized in Table 2.

In Table 2, lists the *J-V* characteristics of DSSC fabricated based benzothiazole-indoline squaraine sensitizers (SQTHZ and SQIND) on TiO<sub>2</sub> film with redox electrolyte  $\Gamma/I_3$ . The SQTHZ showed better photovoltaic performance than SQIND. The SQTHZ sensitizer exhibits a  $J_{SC}$  at 7.65 mA/cm<sup>2</sup>,  $V_{OC}$  at 0.59 V, *FF* at 0.73 and  $\eta$  at 3.31 %, while SQIND sensitizer gives a  $J_{SC}$  at 10.24 mA /cm<sup>2</sup>,  $V_{OC}$  at 0.53 V, *FF* at 0.53, and  $\eta$  at 2.94. Table 2 shows the values of  $J_{sc}$ =7.65 mA/ cm<sup>2</sup>,  $V_{oc}$ =0.59V, *FF*=0.73,  $\eta$ = 3.31 % and  $J_{sc}$  =10.24 mA/ cm<sup>2</sup>,  $V_{oc}$ =0.53V, *FF* =0.53,  $\eta$  =2.94 % respectively, for squaraine sensitizers (SQTHZ and SQIND) which are superior to squarylium dyes (dye1 & dye2),  $J_{sc}$ =0.62 mA/ cm<sup>2</sup>,  $V_{oc}$ =0.27 V, *FF*=0.47,  $\eta$ =1.03% and  $J_{sc}$  = 0.03 mA/ cm<sup>2</sup>,  $V_{oc}$ =0.03V, *FF* =0.10,  $\eta$ =0.008 % respectively, revealing that the SQTHZ and SQIND sensitizers study of in the present article would be efficient materials for DSSC and improved electron injection to TiO<sub>2</sub> [26].

The Eq. (3) was used to measure the incident photon to current conversion efficiencies (*IPCE*) from the measurements.

$$IPCE(\%) = \frac{1240 \times Jsc\left(\frac{\mu A}{cm^2}\right)}{Wavelength(nm) \times P_{in}\left(\frac{watt}{m^2}\right)}.....(3)$$

So, the IPCE of SQTHZ and SQIND base DSSC were 47% and 41% respectively.

Table 2. The comparative	ve study	of Photo-	electro	chemical	charact	eristics for DSSC based	
benzothiazole-indoline	DSSC	$J_{ m sc}$	$V_{ m oc}$	FF	η	squaraine dyes under the $mW/am^2$ with dye 1 on	
dye 2 as a standard.		$(mA/cm^2)$	(V)	(%)	(%)	mw/cm ) white dye 1 and	
	SQ-5	7.65	0.59	0.73	3.31		
	SQ-6	10.24	0.53	0.53	2.94		
	<sup>a</sup> Dye 1	0.62	0.27	0.47	1.03		
	<sup>a</sup> Dye 2	0.03	0.03	0.10	0.008		

<sup>a</sup>Details can be found in reference [26].

The low-conversion efficiency in DSSC refer to charge  $\pi$ -aggregates on squaraine sensitizers, causing charge recombination on TiO<sub>2</sub> electrode leading to reduced cell efficiency. So, the addition certain amount of CDCA enhances the dye sensitized solar cell reducing the  $\pi$ -aggregates of the squaraine sensitizers, thus increasing the process of electron injection to nanoporus titanium dioxide and increasing cell efficiency [27, 28, 25].

In Fig.7, shows the incident photon-to-current conversion efficiency (*IPCE*) spectrum of DSSC based on SQTHZ and SQIND. The *IPCE* spectrum for SQTHZ exhibited better performance than SQIND. The SQTHZ and SQIND sensitizer's photoanodes without CDCA showed a poor photocurrent because of the large amount of charge losses caused by charge recombination on the  $\pi$ -aggregated squaraine dyes. The additions of CDCA act to enhance the photocurrent generation significantly in DSSC based on SQTHZ and SQIND. In this regard, the DSSC based SQTHZ sensitized solar cell generate larger photocurrents than SQIND sensitized ones though the whole visible wavelength [29-31].

In SQTHZ sensitizer, the enhancement was due to the high charge transfer rate in the interfacial region which is verified by *J-V* characterization and electrochemical impedance spectral (EIS) [32-34]. It can be concluded that the strong electronic coupling between SQTHZ, SQIND and TiO<sub>2</sub> leads to a marked improvement in photovoltaic performance under solar radiation.



Fig 6. Photocurrent density-voltage (J-V) characteristics for SQTHZ and SQIND.



Fig.7 The IPCE spectrum for DSSC based on SQTHZ and SQIND.

**Fig. 8** Depicts Nyquist plots of DSSC based on SQTHZ and SQIND measured under AM 1.5G illuminations (100 mW/cm<sup>2</sup>). The SQTHZ showed that the major semicircle in the electrochemical impedance spectral (EIS) Nyquist plot corresponds to the resistance of electron transport at the TiO<sub>2</sub>/dye/ electrolyte interface [30, 25]. It is clear from the Nyquist plot that SQTHZ showed a lesser

recombination resistance because of the lower driving force from the electron injection. The smaller semicircle diameters on the right are attributed to the diffusion of electrolytes which do not differ significantly between SQTHZ and SQIND. The radius larger semicircle on the left contain R1 from the charge transfer at the electrode and R2 from the electron transfer in the  $TiO_2/dye/$  electrolyte interface, decreased in the order of dye1, dye2 > SQIND > SQTHZ. This result indicates that electron generation and transport in DSSC based SQ-sensitizers (SQTHZ and SQIND) are similar but batter than the dye1 and dye 2.



Fig 8. Nyquist plots for SQTHZ and SQIND based DSSC.

### **4** Conclusions

Synthesis, characterization, and photovoltaic properties of two new symmetric benzothiazole and indoline based squaraine dyes (SQTHZ and SQIND) were tested in DSSC with nanoporous  $TiO_2$ . The theoretical calculations and absorption results showed that the electron density of LUMO of benzothiazole-based squaraine dye (SQTHZ) is delocalized in the whole chromophore, leading to strong electronic coupling between SQTHZ sensitizer and the conduction band of  $TiO_2$ . Additionally, it has a long alkyl chain with pendent bis-SO<sub>3</sub><sup>-</sup> groups that would inhibit recombination and decrease the dye aggregation and thus resulting in improved dye-sensitized solar cell efficiency. Therefore, the SQTHZ sensitizer exhibits better photovoltaic performance.

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# Highlight

• Two new symmetric Benzothiazole and Indoline based squaraine dyes (SQTHZ and SQIND) were tested in DSSC with nanoporous TiO<sub>2</sub>.

• The theoretical calculations and absorption results showed that the electron density of LUMO of SQTHZ dye is delocalized in the whole chromophore, leading to strong electronic coupling between SQTHZ sensitizer and the conduction band of  $TiO_2$ .

• The SQTHZ sensitizer exhibits better photovoltaic performance.