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# The improvement of photovoltaic performance of quinoline-based dye-sensitized solar cells by modification of the auxiliary acceptors

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# ABSTRACT

Three new dyes containing diphenylamine as electron donor, benzene (**BIM1**), benzothiadiazole (BTD) (**BIM2**) and *N*-ethylhexylbenzotriazole (BTZ) (**BIM3**) as auxiliary electron acceptors, quinoline as  $\pi$ -bridge and cyanoacrylic acid as anchoring group were synthesized in D-A- $\pi$ -A structure for use in dye-sensitized solar cells (DSSCs). The optical, electrochemical, theoretical and photovoltaic methods were performed to understand the auxiliary acceptor influence on the performance of these dyes. Compared to the other dyes, the DSSC with dye **BIM3** slightly increases the open circuit voltage ( $V_{oc}$ ) owing to the retardation of charge recombination by BTZ. However, replacement of benzene or BTZ by BTD unit causes a large red shift of the absorption spectra, leading **BIM2** cell to produce the highest short circuit current density ( $J_{sc}$ ). Thus, among the three D-A- $\pi$ -A dyes, **BIM2** is determined to be the most efficient dye, which reached a  $V_{oc}$  of 0.627 V and  $J_{sc}$  of 11.53 mA cm<sup>-2</sup>, corresponding to an overall power conversion efficiency of 5.21 % in the presence of chenodeoxycholic acid (CDCA) as the coadsorbent. These results suggest that the insertion of benzothiadiazole as auxiliary acceptor into quinoline-based D-A- $\pi$ -A dyes can effectively improve photovoltaic performance of DSSCs.

#### 1. Introduction

Metal-free organic dye sensitized solar cells (DSSCs) have low cost, ease of production, environmental friendliness, a high molar absorptivity, easily adjustable power conversion efficiency (PCE). Thanks to these advantages, it has attracted attention as one of the most important methods of converting solar radiation into electrical energy as an alternative to silicon solar cells [1-6]. The molecular structure of dves used as sensitizers is one of the main factors that depend on the photovoltaic performance of DSSCs [7]. A traditional organic dye is in the form of a donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) and the induced electron is transported from the donor to the acceptor by intra-molecular charge transfer (ICT) [8]. The main component of sensitizers is aromatic  $\pi$ -bridge which affects absorption capacity of the molecule and ICT process the most [9]. It has been found that  $\pi$ -bridges with fused conjugated systems increase photovoltaic performance by wide absorption in the visible radiation region. The planar structure of these systems may also promote charge transfer between D and A units [10]. Many

compounds containing various  $\pi$ -bridges such as dibenzonaphthyridine [10], phenothiazine [11,12], anthracene [13], N-annulated perylene [14], phenanthrocarbazole [15], phenylene [16], furan [17], thiophene derivatives [9,18] and quinoline [19] were synthesized and used in DSSCs. In most D- $\pi$ -A dyes, triphenylamine, carbazole, dialkylamine or diphenylamine electron-rich groups are used as electron donating groups and carboxylic acid or cyanoacrylic acid electron-withdrawing groups are used as acceptor/anchoring groups. The strong ester bond formed between carboxyl groups and TiO<sub>2</sub> surface improves electron conduction [20]. To achive higher short-circuit photocurrent density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ), and thus superior PCE, various new type structure such as D-A- $\pi$ -A, D-D- $\pi$ -A, double D- $\pi$ -A and multi-anchoring dyes have been developed in recent years [6,21–23].

Zhu et al. developed an efficient and stable new type of organic sensitizers in the D-A- $\pi$ -A structure by adding an electron-withdrawing group to act as an auxiliary acceptor into the  $\pi$ -bridge of the D- $\pi$ -A structure [24]. In recent years, low-bandgap electron-withdrawing moieties such as benzothiadiazole, benzotriazole, quinoxaline,

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Fig. 1. Molecular structures of dyes BIM1-3.

phthalimide and diketopyrrolopyrrole have been added between the  $\pi$ -bridge and electron donor, and D-A- $\pi$ -A dyes have been obtained [25, 26]. It was confirmed that the D-A- $\pi$ -A system not only increased the energy conversion efficiency and photostability of the dye but also suppressed electron recombination and reduced aggregation [27].

In addition to medical applications, quinolines can also be used in polymer chemistry, electronics, high efficiency electron transport materials (ETMs) and corrosion prevention [1]. They have superior thermal and oxidative stability. Thanks to its exciting optoelectronic features, it has been used in OLEDs [28–34]. Due to the unsaturated nitrogen atom which increases electron affinity, these fused planar species are promising as light sensitizers in DSSCs [35]. There aren't many notification on the practice of quinoline derivatives for DSSCs [36]. Recently, our group have been reported quinoline or pyridocarbazole-based D- $\pi$ -A dyes for coadsorbent free DSSCs [19].

In this work, we synthesized three dyes (Fig. 1) containing diphenylamine as donors, benzene, benzothiadiazole or *N*-ethylhexylbenzotriazole as auxiliary acceptor, quinoline as  $\pi$ -bridge and cyanoacrylic acid as anchoring group. We report synthesis steps, photophysical characteristics, density functional theory studies and photovoltaic performances of compounds **BIM1**, **BIM2** and **BIM3** in structure D-A- $\pi$ -A. We compare power conversion efficiencies when benzene, benzothiadiazole and *N*-ethylhexylbenzotriazole auxiliary acceptor is added to the structure of the dyes.

# 2. Experimental

The used materials and instruments, preparation and characterization of DSSCs, theoretical calculations, synthesis of compounds **1-15**, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, fluorescence and FT-IR spectra were supplied as electronic supplementary information (ESI).

# 2.1. Synthesis

# 2.1.1. Synthesis of 2-cyano-3-(6-(4-(diphenylamino)phenyl)-2-methoxyquinolin-3-yl)acrylic acid. **BIM1**

Compound **13** (0.11 g, 0.25 mmol), 2-cyanoacetic acid (0.106 g, 1.25 mmol), 0.1 mL of piperidine were dissolved in 10 mL of chloroform and 10 mL of acetonitrile in a 50 mL flask. This mixture was refluxed for 12 h. After the reaction was complete, the solvent was removed. The residue was extracted using ethyl acetate-water mixture. Organic layers were combined, dried over anhydrous calcium chloride and the solvent was evaporated off. The crude product was purified from silica gel column (methanol:dichloromethane (1:10)) to give the desired product as

dark yellow solid. 0.106 g, 85 % yield. Mp; 170–171 °C. <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  8.82 (s, 1 H), 8.23 (s, 1 H), 8.21 (d, J =1.7 Hz, 1 H), 8.05 (dd, J = 8.7, 2.1 Hz, 1 H), 7.85 (d, J =8.7 Hz, 1 H), 7.76 (d, J =8.7 Hz, 2 H), 7.40–7.27 (m, 4 H), 7.20–6.98 (m, 8 H), 4.08 (s, 3 H). <sup>13</sup>C NMR (150 MHz, DMSO) 163.24, 159.43, 147.39, 147.33, 145.86, 142.79, 138.26, 136.34, 133.22, 130.28, 130.06, 128.22, 127.47, 125.48, 124.98, 124.67, 124.54, 123.78, 123.58, 118.95, 118.53, 54.36. IR (cm<sup>-1</sup>): 3035, 2948, 2223, 1711, 1587, 1490, 1352, 1268. HRMS-ESI (+) m/z: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>24</sub>N<sub>3</sub>O<sup>+</sup><sub>3</sub>, 498.1818; found, 498.1837.

# 2.1.2. Synthesis of 2-cyano-3-(6-(7-(diphenylamino)benzo[c][1,2,5] thiadiazol-4-yl)-2-methoxyquinolin-3-yl)acrylic acid. **BIM2**

Compound BIM2 was synthesized using compound 14 (0.122 g, of 6-(4-(diphenylamino) 0.25 mmol). instead phenvl)-2methoxyquinoline-3-carbaldehyde by the identical method used for compound BIM1. The crude product was purified from silica gel column (methanol:dichloromethane (1:10)) to give the desired product as red solid. 0.111 g, 80 % yield. Mp; 226–227 °C. <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  8.82 (s, 1 H), 8.53 (s, 1 H), 8.33 (dd, J = 8.7, 2.0 Hz, 1 H), 8.17 (s, 1 H), 7.93 (dd, J = 13.6, 8.3 Hz, 2 H), 7.34–7.22 (m, 5 H), 7.09–6.96 (m, 6 H), 4.08 (s, 3 H).  $^{13}\mathrm{C}$  NMR (75 MHz, DMSO)  $\delta$  163.00, 160.17, 154.96, 151.79, 147.87, 146.38, 141.27, 139.37, 138.28, 134.02, 132.52, 130.08(x2), 128.98, 128.17, 127.31, 125.02, 124.72, 124.34, 124.04, 119.75, 119.44, 118.29, 54.65. IR (cm<sup>-1</sup>): 3042, 2954, 2214, 1643, 1543, 1490, 1350, 1268. HRMS-ESI(+) m/z: [M+H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>22</sub>N<sub>5</sub>O<sub>3</sub>S<sup>+</sup>, 556.1443; found, 556.1458.

# 2.1.3. Synthesis of 2-cyano-3-(6-(7-(diphenylamino)-2-(2-ethylhexyl)-2Hbenzo[d][1,2,3]triazol-4-yl)-2-methoxyquinolin-3-yl)acrylic acid. **BIM3**

Compound **BIM3** was synthesized using compound **15** (0.146 g, 0.25 mmol), instead of 6-(4-(diphenylamino)phenyl)-2-methoxyquinoline-3-carbaldehyde by the identical method used for compound **BIM1**. The crude product was purified from silica gel column (methanol: dichloromethane (1:10)) to give the desired product as orange solid. 0.135 g, 83 % yield. Mp; 229–230 °C. <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  8.75 (s, 1 H), 8.57 (s, 1 H), 8.38 (d, *J* =8.0 Hz, 1 H), 8.17 (s, 1 H), 7.85 (d, *J* =8.8 Hz, 1 H), 7.74 (d, *J* =8.0 Hz, 1 H), 7.26 (t, *J* =7.7 Hz, 4 H), 7.08–6.94 (m, 7 H), 4.52 (d, *J* =5.9 Hz, 2 H), 4.07 (s, 3 H), 1.91–1.81 (m, 1 H), 1.23–1.04 (m, 8 H), 0.81–0.71 (m, 6 H). <sup>13</sup>C NMR (150 MHz, DMSO)  $\delta$  162.96, 159.68, 147.42, 145.95, 143.86, 141.53, 140.47, 137.95, 137.08, 133.53, 131.33, 129.66, 127.49, 127.08, 125.72, 124.77, 124.15, 124.07, 123.64, 120.32, 119.24, 119.01, 117.30, 58.95, 54.38, 30.37, 28.38, 23.81, 22.71, 14.34, 10.84. IR (cm<sup>-1</sup>): 3035, 2926, 2217, 1624, 1587, 1493, 1337, 1262. HRMS-ESI(+) *m/z*: [M+H]<sup>+</sup> calcd



# Scheme 1. Synthetic pathway for BIM1, BIM2 and BIM3.

(a):DCM, Na<sub>2</sub>CO<sub>3</sub>, 0°C, Ac<sub>2</sub>O, rt, 3 h, (b):DMF, 0°C, POCl<sub>3</sub>, 80 °C, 16 h, (c):KOH, MeOH, 3 h, reflux, (d):B<sub>2</sub>pin<sub>2</sub>, Pd(dppf)Cl<sub>2</sub>, KOAc, 1,4-dioxane, 18 h, reflux, (e): DMF, NBS, 0 °C, 5 h, (f): DCM, TEA, SOCl<sub>2</sub>, 5 h, reflux, (g):NBS, H<sub>2</sub>SO<sub>4</sub>, 60 °C, 3 h, (h):Diphenylamine, Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, t-BuONa, toluene, reflux, 18 h, (i):NaBH<sub>4</sub>, CoCl<sub>2</sub>.6H<sub>2</sub>O, EtOH, reflux, 4 h, (j):AcOH, NaNO<sub>2</sub>, H<sub>2</sub>O, rt, 30 min, (k):K<sub>2</sub>CO<sub>3</sub>, DMF, 2-ethylhexyl bromide, 70 °C, 2 h, (l):Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene:THF (1:1), 2 M K<sub>2</sub>CO<sub>3</sub>, reflux, 24 h, (m): cyanoacetic acid, piperidine, chloroform:acetonitrile (1:1), reflux, 12 h.



Fig. 2. Absorption spectra of BIM1–3 (a) in DMSO  $(1\times 10^{-5}$  M) and (b) on the TiO\_2.

#### Table 1

Optical properties of the dyes BIM1-3.

Dye	$\lambda_{max} \ [nm]^{a} (\epsilon \ [x \ 10^{4} M^{-1} \ cm^{-1}]^{a})$	λ <sub>onset</sub> [nm] <sup>a</sup>	λ <sub>max</sub> (TiO <sub>2</sub> ) [nm] <sup>b</sup>	$E_{0-0}$ (opt) [eV] <sup>c</sup>
BIM1 BIM2	272 (6.72), 342 (5.86) 300 (9.78), 476 (1.56)	386 552	390 484	3.21 2.25
BIM3	294 (6.74), 400 (4.18)	456	426	2.72

<sup>a</sup>  $\lambda_{max}$ : absorption maximum wavelength;  $\epsilon$ : molar extinction coefficient;  $\lambda_{onset}$ : absorption onset wavelength.

<sup>b</sup>  $\lambda_{max}$ (TiO<sub>2</sub>): absorption maximum wavelength on the TiO<sub>2</sub> film.

<sup>c</sup>  $E_{0-0}$  (opt): optical band gap, estimated using the equation  $E_{0-0} = 1240/\lambda_{onset}$ .

for C<sub>40</sub>H<sub>39</sub>N<sub>6</sub>O<sup>+</sup><sub>3</sub>, 651.3084; found, 651.3087.

#### 3. Results and discussion

#### 3.1. Synthesis of dyes

The total synthesis of dyes **BIM1**, **BIM2** and **BIM3** is shown in Scheme 1. Acetylation of commercially available 4-bromoaniline followed by Vilsmeier reaction and the nucleophilic substitution reaction gave compound **3** to form the  $\pi$ -bridge of the dyes [37–39]. This compound was converted to the boronic acid ester for use in coupling reactions to give compound **4** [40]. For coupling reactions, firstly, bromine-containing compounds **5**, **8**, and **12** were synthesized [41–46]. Subsequently, by Suzuki-Miyaura coupling reaction of compound **4** with compounds **5**, **8** and **12**, compounds **13**, **14** and **15** were obtained, respectively [40]. Finally, dyes **BIM1**, **BIM2** and **BIM3** were

obtained by Knoevenagel condensation [47].

#### 3.2. Optical characteristics

UV-Vis absorption spectra of **BIM1-3** in DMSO  $(10^{-5} \text{ M})$  and on the  $TiO_2$  film are depicted in Fig. 2 and the corresponding parameters presented in Table 1. It can be seen from Fig. 2a, the absorption band below 300 nm is attributed to the  $\pi - \pi^*$  transition, while the band between 300-600 nm is the intramolecular charge transfer (ICT) from the diphenylamine donor to the cyanoacrylic acid acceptor through the quinoline  $\pi$ -bridge.  $\lambda_{max}$  for dyes **BIM1**-3 are 342, 476 and 400 nm for the ICT band, respectively. Compared to the reference dye BIM1, significant red-shifts (58-134 nm) are observed for dyes BIM2 and BIM3. This can be attributed to the presence of stronger electron-withdrawing BTD and BTZ units on the dyes, which can efficiently improve electron delocalization and broaden the spectral response range [48]. Similarly, the  $\lambda_{max}$  for dye **BIM2** bearing BTD is clearly more red-shifted than that of BTZ-based dye BIM3 since the stronger electron-withdrawing ability of the sulfur than the nitrogen, which reduces the band gap [49,50]. However, the  $\varepsilon$  for the ICT band of **BIM2** is lower than those of **BIM1** and **BIM3**. This could be ascribed to the low oscillator strength (f) of the charge-transfer transition due to reduced electronic coupling (Table S1) [51]. The emission maximum for BIM2 was observed at longer wavelength than those of BIM1 and BIM3 (Fig. S45), this put forward that the BTD group in the dye likewise influences both light absorption and fluorescence. To determine the effect of benzothiadiazole group on absorbance, BIM2 was compared with a compound containing quinoline unit coded as BPA-Q in the literature [52]. The solution absorbance bands are 466 nm for BPA-Q and 476 nm for BIM2 whereas the absorbance bands on the TiO2 surface are 460 nm for BPA-Q and 484 nm for BIM2. This means both of the solution and solid absorbance bands of BIM2 are more red shifted due to strong electron withdrawing ability of benzothiadiazole moiety. Since BIM2 absorbs a wider wavelength of light, the DSSC based on this dye has a higher power conversion efficiency.

The normalized absorption spectra of the dyes adsorbed onto the  $TiO_2$  are shown in Fig. 2b. It can be seen that the absorption spectra are broadened and red-shifted when compared with the solution spectra, indicating existence of J-aggregation of dye molecules and the interactions between the anchoring groups and titanium ions [53]. In order to explain the binding of dyes **BIM1–3** on  $TiO_2$ , FT-IR spectra of pure powders and their adsorbed forms on  $TiO_2$  film were measured (Fig. S46). Considering the FT-IR spectra of the dye adsorbed films, two characteristic streching vibrations are observed at ~1592 and ~1355 cm<sup>-1</sup>, respectively, which relate to the asymmetric and symmetric streching of the carboxylate groups bonded to the titanium atoms. In addition, the stretching vibrations of the free carboxylic acid groups observed in the FT-IR spectra of the dye powders were completely disappear when they were adsorbed onto the  $TiO_2$  surface [54].

#### 3.3. Electronic absorptions spectra, FMOs and band gap analyses

The experimental UV – Vis absorption maximum peaks of **BIM1–3** assigned as the  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$  transitions were appeared at the range of 272–476 nm in DMSO solvent. It is seen from Table S1 that the electronic absorption bands were calculated at the range from 616.4–305.7 for dye **BIM1**, from 539.1–317.8 for dye **BIM2** and from 652.8–323.2 for dye **BIM3** by using TD–B3LYP/6–311 G(d,p) level in gas phase.

The important FMOs contributes belonging to electronic transitions associated with  $\lambda_{abs}$  were determined via using Q-CHEM//Chemissian programs (see Table S1). Among dye compounds **BIM1–3**, it is clear that the similar  $\pi$ -system, electron-donor and -acceptor groups, as well as different auxiliary acceptor moiety affect remarkable on the theoretical  $\lambda_{abs}$  results. The largest  $\lambda_{abs}$  obtained at 616.4, 539.1 and 652.8 nm in gas phase were assigned as the electronic contributions of H $\rightarrow$ L(99.3 %)



Fig. 3. The HOMO and LUMO being the most active in electronic transition for dyes BIM1-3 at B3LYP/6-311 G(d,p) in gas phase.

 $[D(67 \%)+AA(24 \%)+\pi$ -sys $(9\%) \rightarrow A(53 \%)+AA(3\%)+\pi$ -sys(43 %)] for **BIM1**,  $H \rightarrow L(94.5 \%)$   $[D(61 \%)+AA(30 \%)+\pi$ -sys $(9\%) \rightarrow A(52 \%)+AA(5\%)+\pi$ -sys(42 %)] for **BIM2** and  $H \rightarrow L(99.0 \%)$   $[D(58 \%)+AA(32 \%)+\pi$ -sys $(10 \%) \rightarrow A(54 \%)+AA(4\%)+\pi$ -sys(43 %)] for **BIM3**. It could be stated that the minor differences in these contributions demonstrate the strength of the different auxiliary acceptor moiety in dyes **BIM1–3**.

The other remarkable peaks for dyes BIM1-3 emerged at 272, 300 and 294 nm in DMSO solvent were obtained at 305.7, 317.8 and 323.3 nm with different FMOs contributions, respectively. These FMOs contributions for dye **BIM1** were assigned as H-6 $\rightarrow$ L(44.2 %) [D(73)+ AA(26 %)+ $\pi$ -sys(1%) $\rightarrow$ A(53 %)+AA(3%)+ $\pi$ -sys(43 %)] and H-5 $\rightarrow$ L (36.1%) [D(65%)+AA(33%)+ $\pi$ -svs(1%) $\rightarrow$ A(53%)+AA(3%)+ $\pi$ -svs(43 %)]. As for dyes **BIM2** and **BIM3**, the FMOs contributions with  $H-8\rightarrow L$ (95.0 %) and  $H-1\rightarrow L+1(87.0 \%)$  appeared at depending on between different percent and group transition of A(12 %)+ $\pi$ -sys(87 %) $\rightarrow$ D (6%)+AA(85 %)+π-sys(8%) and D(30 %)+AA(24 %)+π-sys(45 %)→D (10 %)+AA(65 %)+ $\pi$ -sys(24 %), respectively. As can be seen in Table S1, the variations of the effect of  $\pi$ -system and auxiliary group in dyes BIM2 and BIM3 are observed while the influence of the electron-acceptor and -donor groups in dye BIM1 draw the attention. Furthermore, Fig. 3 depicts the occupied and unoccupied molecular orbitals for dyes BIM1-3 being the most active in electronic transitions estimated at B3LYP/6-311 G(d,p) level. It is clearly concluded from Fig. 3 that the noteworthy electronic transitions for dyes BIM1-3 depending on among the impact of the electron-accepting (cyano group) and -donating (diphenylamine) strengths and the different auxiliary groups (benzene for BIM1, benzothiadiazole for BIM2 and N-ethylhexylbenzotriazole for BIM3)

The energy gap is a critical parameter and characterized by the molecular stability and spectroscopic properties of the molecular systems between the HOMO and LUMO energies. It is also used to determine molecular electrical transport properties because of providing measurement of electron conductivity. Furthermore, the chemical hardness ( $\eta$ ) owing to the depending the energy band gap parameter is a good indicator of the chemical stability. The smaller energy gap

describes chemically soft molecule which can be easily polarizable since they need small energy to excite one electron from ground state to excited state.  $\chi$  parameter demonstrates that electron will be partially transferred from the one of low  $\chi$  to that of high  $\chi$  for any two compounds contrary to the electrons flow from high chemical potential to low chemical potential [19,55]. In this context, the investigation of the relationship between FMOs and energy band gap for BIM1-3 were fulfilled at B3LYP/6-311 G(d,p) level by using FMO energies and related parameters (the electronegativity ( $\chi$ ), chemical hardness ( $\eta$ ) and softness (S) parameters). The  $\chi$ ,  $\eta$  and S values were computed by using  $\chi =$ (IP + EA)/2,  $\eta = (IP - EA)/2$  and  $S = 1/\eta$  equations [55,56]. Theoretical energy band gaps of dyes BIM1-3 were obtained at 2.31, 2.45 and 2.23 eV, and the corresponding optical values were found to be 3.21, 2.25 and 2.72 eV, respectively. The band gap obtained from DFT calculation nicely corresponds with optical band gap for compounds BIM2 and BIM3. However, the optical band gap for BIM1 differs from the theoretical one. It can be attributed to the interaction of dyes with solvent molecules [57]. The  $\chi$ ,  $\eta$  and S values of BIM1–3 were found at the range of 4.12-4.19 eV, 1.12-1.22 eV and 0.408-0.448 eV<sup>-1</sup>, respectively. The theoretically obtained small  $\eta$  values display that the charge transfer will be occurred in BIM1-3. Considering  $\eta$  and S values, the dyes BIM1-3 could be depicted as the soft molecules. Since dipole moment is a quantitative measure of the polarization tendency of a bond, the large dipole moment characterizes polar compounds. Although it depends on the presence of the strength of electron donor and acceptor groups between the compounds, it is clear that the electronic structure difference plays a leading role in the change of this parameter. Moreover, to understand the variation of the dipole moment in BIM1-3 structures, the ground, excited and transition electric dipole moments ( $\mu_g$ ,  $\mu_e$ ,  $\mu_{eg}$ , in Debye) of **BIM1–3** were investigated by using the same level. The  $\mu_g$  and  $\mu_e$  dipole moments for **BIM1-3** were obtained at the range from 2.40 to 5.49 and from 31.54 to 34.82. The differences between ground and excited dipole moment for BIM1-3 range from 28.25 to 31.29 D. The values of  $\mu_{eg}$  dipole moment for BIM1-3 were calculated at the range of 1.28 and 2.82 D. All parameters display dyes



Fig. 4. CV and DPV of dyes BIM1–3 in DMSO including 0.1 M TBABF<sub>4</sub> at a scan rate of 0.050 V s<sup>-1</sup>.

**BIM1–3** are polar compounds owing to the high difference between ground and excited dipole moments, and the low transition dipole moment values. It could be said that these differences attribute to the depending on the strength of the different auxiliary acceptor moiety (benzene for **BIM1**, benzothiadiazole for **BIM2** and *N*-ethylhexylbenzotriazole for **BIM3**). By considering electronic parameters, it could be concluded that dyes **BIM1–3** exhibit the ICT and the polarizations depending on the strength of the different auxiliary acceptor moiety.

#### 3.4. Electrochemical properties

The electrochemical properties of BIM1-3 in DMSO solution were

explored by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Fig. 4) and the numerical data are listed in Table 2. The ionization potential (IP) and electron affinitiy (EA) values, correspond to the HOMO and LUMO energy levels vs. vacuum, were estimated using the oxidation ( $E_{\text{ox onset}}$ ) and reduction onset potentials ( $E_{\text{red onset}}$ ) [21,58]. CVs show that all of the three dyes undergo irreversible oxidation and reduction processes (Fig. 4). The band gaps obtained by the CV data are in good agreement with the DPV data. Moreover, the trend of the electrochemical band gaps nicely compares with the optical band gaps (**BIM2** < **BIM3** < **BIM1**). On the other hand, the band gaps as well as the HOMO and LUMO energy levels estimated from the CV results are significantly different from the theoretical ones. This difference may be due to the fact that theoretical analysis uses the molecular orbitals, while CV corresponds to the ionization energy [59].

The ground state oxidation potentials  $(E_{ox})$  of the dyes are almost the same (1.01 V for BIM1; 0.98 V for BIM2; 0.99 V for BIM3) due to the same electron donor unit in these dyes [40]. The  $E_{ox}$  values match well that of the previously reported quinoline-based BPA-Q dye which contained a butoxy modified diphenylamine as the donor chromophore [52]. These values are also more positive than the potential of  $I^{-}/I_{3}^{-}$ redox couple (0.4 V vs NHE), ensuring the dye regeneration [41]. The excited state oxidation potentials  $(E_{ox}^*)$  for BIM1-3 are located at -1.35, -0.94 and -1.10 V vs NHE, respectively. The  $E_{0x}^*$  values decrease with increasing the electron withdrawing ability of the auxiliary acceptors [60]. The decreasing trend is also in accordance with the red shift of their ICT band due to a decrease in the band gap [61]. The  $E_{ox}^*$  values for BIM2 and BIM3 are down-shifted compared to the similar dye BPA-Q [52], which is attributed to the presence of electron with drawing BTD and BTZ groups in former dyes. The  $E_{ox}^*$  values of the sensitizers are also above the conduction band of  $TiO_2$  (-0.5 V vs NHE), indicating enough driving force for electron injection [49].

#### 3.5. Photovoltaic properties of DSSCs

To study the influence of the auxiliary acceptors on the photovoltaic performance, DSSCs were constructed using dyes BIM1-3 and their performance was measured under AM 1.5 illumination. The current density-voltage (J-V) curves of DSSCs based on the three quinoline sensitizers are presented in Fig. 5a and the detailed photovoltaic parameters of short-circuit current density (Jsc), open-circuit voltage (Voc), fill factor (FF), power conversion efficiency (PCE) and dye loading amount are all summarized in Table 3. As expected, the dye loading amounts for BIM2 and BIM3 with larger size are lower than that of BIM1. The PCEs of DSSCs increase in the trend of BIM1 (1.78%) < BIM3 (3.26 %) < BIM2 (4.08 %), which is in accordance with their J<sub>sc</sub> values. The best PCE based on these DSSCs reaches about 61 % of the cell with N719 (6.58 %) under the same condition. This is mainly due to their narrow absorption profiles compared to N719 [62]. However, the PCE for both BIM2 and BIM3 is high when compared to the similar dye BPA-Q may be due to the presence of electron withdrawing groups in former dyes [46]. Similarly, despite the lower dye loading amounts, the Jsc of the DSSCs based on BIM2 and BIM3 are much higher than that of BIM1 due to their wider absorption spectrum which arises from the incorporation of BTD and BTZ auxiliary acceptors on the dyes [46]. The  $V_{oc}$  value of BIM3 (0.632 V) was slightly higher than those of BIM1 (0.602 V) and BIM2 (0.619 V). It suggests that the branched alkyl chain at the nitrogen atom of the triazole unit (BTZ) can effectively suppress the unwanted electron recombination between the TiO<sub>2</sub> and the electrolyte [60].

CDCA has been broady utilized as a coadsorbent that not only suppresses the dye aggregation but also protects the semiconductor metal oxide from the redox electrolyte, leading to enhanced  $J_{sc}$  and  $V_{oc}$  after DSSC fabrication [63]. In the presence of CDCA, the  $J_{sc}$ ,  $V_{oc}$  and FF of devices based on dyes **BIM1-3** are in the range of 5.38–11.53 mA cm<sup>-2</sup>, 0.611–0.634 V and 0.70–0.74, respectively, corresponding to an overall PCE of 2.30–5.21 % (Fig. 5b, Table 3). The DSSC based on **BIM2** has the

#### Table 2

Electrochemical properties of the dyes <b>BIM1</b> –3	3
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Dye	$E_{\rm ox onset}/E_{\rm red onset}$ (CV) [V] <sup>a</sup>	$E_{0-0}$ (CV) [eV] <sup>b</sup>	$E_{\rm ox}/E_{\rm ox}^*({\rm CV}) [V]^c$	$E_{\rm HOMO}/E_{\rm LUMO}$ (CV) [eV] <sup>d</sup>	$E_{\text{ox onset}}/E_{\text{red onset}}$ (DPV) [V] <sup>e</sup>	$E_{0-0}$ (DPV) [eV] <sup>f</sup>
BIM1	0.38/- 1.98	2.36	1.01/- 1.35	- 5.48/- 3.12	0.29/- 1.94	2.23
BIM2	0.35/- 1.57	1.92	0.98/- 0.94	- 5.45/- 3.53	0.21/- 1.49	1.70
BIM3	0.36/- 1.79	2.15	0.99/- 1.10	- 5.46/- 3.31	0.23/- 1.71	1.94

<sup>a</sup> E<sub>ox onset</sub>/E<sub>red onset</sub> (CV): oxidation and reduction onset potentials in the CVs, referred to the external Fc/Fc<sup>+</sup> standard (0.34 V vs. Pt disk).

<sup>b</sup>  $E_{0-0}$  (CV): electrochemical band gap, estimated using the equation  $E_{0-0} = E_{\text{ox onset}}$  (CV) –  $E_{\text{red onset}}$  (CV).

<sup>c</sup>  $E_{ox}/E_{ox}^*$ : ground and excited state oxidation potentials vs NHE.  $E_{ox}$  was obtained by addition of  $E_{Fc/Fc^+}^0 = 0.63$  V vs NHE to the  $E_{ox}$  onset.  $E_{ox}^*$  was calculated from the  $E_{ox}^* = E_{ox} - E_{0-0}$  (CV).

<sup>d</sup>  $E_{\text{HOMO}}/E_{\text{LUMO}}$ : HOMO and LUMO energy levels vs vacuum were estimated by  $E_{\text{HOMO}} = -5.1 - E_{\text{ox onset}}$  (CV) and  $E_{\text{LUMO}} = -5.1 - E_{\text{red onset}}$  (CV) [21].

<sup>e</sup>  $E_{\text{ox onset}}/E_{\text{red onset}}$  (DPV): oxidation and reduction onset potentials vs Fc/Fc<sup>+</sup> in the DPVs.

<sup>f</sup>  $E_{0-0}$  (DPV): electrochemical band gap, obtained from the equation  $E_{0-0} = E_{0x \text{ onset}}$  (DPV) -  $E_{\text{red onset}}$  (DPV).



Fig. 5. J-V curves of dyes BIM1-3 based DSSCs (a) without and (b) with CDCA.

 Table 3

 Photovoltaic parameters of the DSSCs with dves BIM1–3.

best PCE (5.21 %) among all, reaching 66 % of the device with N719-based DSSC fabricated in the presence of CDCA having 7.92 % PCE. Compared with our previous quinoline or pyridocarbazole-based D- $\pi$ -A dyes [19], using the BTD as the auxiliary acceptor unit proved to promote the  $J_{sc}$  resulting from the broad spectral response of **BIM2**. The PCEs of DSSCs with **BIM1** and **BIM2** represent over 28 % of enhancement with respect to the cell without the coadsorbent, implying that the insertion of CDCA to the dye bath decreases the unfavorable dye aggregation on the TiO<sub>2</sub> surface [64]. However, the DSSC based on **BIM3** with CDCA only obtains 12 % enhancement with respect to the DSSC without the coadsorbent, which demonstrates that the BTZ unit retards the aggregation due to its branched alkyl chain structure [49].

To further confirm the difference among the  $J_{sc}$  values of the three dyes, the IPCE curves are plotted in Fig. 6a and the corresponding data are summarized in Table 3. In accordance with their spectral responses on the  $TiO_2$  film [19], the thresholds of the IPCE responses of these dyes-based DSSCs are 530 nm (BIM1), 660 nm (BIM2) and 600 nm (BIM3), respectively. The IPCE values of dyes BIM1-3 are over 64 % from 375 to 450 nm (maximum IPCE value of 69.7 % at 400 nm), from 425 to 590 nm (maximum IPCE value of 77.4 % at 490 nm) and from 400 to 525 nm (maximum IPCE value of 73.9 % at 440 nm), respectively. The  $J_{sc}^{IPCE}$  values integrated from the IPCE spectra are in good consistence with the  $J_{sc}$  values measured in the J-V tests. Consequently, the cell with dye BIM2 gives highest and broadest IPCE spectrum, confirming its highest  $J_{sc}$  [65]. In the presence of CDCA, the  $J_{sc}^{IPCE}$  values of the DSSCs based on dyes BIM1-3 with enhanced by 12 %, 11 % and 4 %, respectively, with respect to the DSSCs without CDCA (Fig. 6b). The improved IPCE responses are consistent with the improved  $J_{sc}$  [66].

To understand the  $V_{oc}$  difference among the DSSCs without CDCA, electrochemical impedance spectroscopy (EIS) experiments were recorded in the dark. The larger semicircles in the Nyquist plots are related to the charge recombination resistance ( $R_{rec}$ ) between the TiO<sub>2</sub> and the electrolyte (Fig. 7a). Obviously, the  $R_{rec}$  values increased in the order **BIM1** (65  $\Omega$ ) < **BIM 2** (71  $\Omega$ ) < **BIM3** (80  $\Omega$ ), this tendency is in agreement with the  $V_{oc}$  order of the DSSCs. In the Bode plots, the electron lifetime ( $\tau_e$ ) calculated by the equation  $\tau_e = 1/2\pi f(f \text{ signify the peak}$ frequency in the left side of the Bode plots) are 5.87, 9.03 and 13.90 ms

Dye	$J_{sc}^{IPCE}$ (mA cm <sup>-2</sup> ) <sup>a</sup>	IPCE (%) <sup>b</sup>	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF	PCE (%)	Dye loading amount (mol cm <sup>-2</sup> )
BIM1 BIM1 + CDCA	4.79 5.36	69.7 71.4	4.77 5.38	0.602	0.62	1.78 2 30	$3.37 \times 10^{-7}$ 2.69 × 10^{-7}
BIM2	10.43	77.4	10.46	0.619	0.63	4.08	$3.09 \times 10^{-7}$
BIM2 + CDCA BIM3	11.52 7.62	80.6 73.9	11.53 7.69	0.627 0.632	0.72 0.67	5.21 3.26	$2.53  imes 10^{-7}$ $2.81  imes 10^{-7}$
BIM3 + CDCA	7.89	74.7	7.77	0.634	0.74	3.65	$2.62\times 10^{-7}$
N719 N719 + CDCA	-	-	14.03	0.721	0.65	6.58 7.92	-

<sup>a</sup>  $J_{sc}^{IPCE}$  values were integrated from the IPCE spectra.

<sup>b</sup> IPCE values were obtained  $\lambda_{max}$  from the IPCE spectra.



Fig. 6. IPCE spectra of the dyes-based cells (a) without and (b) with CDCA.

for **BIM1–3**, respectively (Fig. 7b). Therefore, longest  $\tau_e$  and largest  $R_{rec}$  for **BIM3** revealed that the BTZ unit can effectively restrain the charge recombination, leading to the higher  $V_{oc}$  [67].

# 4. Conclusions

In summary, three new quinoline  $\pi$ -bridge based D-A- $\pi$ -A dyes bearing benzene, benzothiadiazole (BTD) or N-ethylhexylbenzotriazole (BTZ) as auxiliary electron acceptor, respectively, were synthesized for DSSCs. As compared to BIM1 and BIM3, BIM2 shows 166 and 96 nm red shift of the absorption onset wavelength, which is due to the stronger electron-withdrawing ability of the BTD unit on the latter dye. Upon coadsorption with CDCA as the anti-aggregation agent, the DSSC based on dye BIM2 exhibited the PCE of 5.21 %, which is better than those of 2.30 % and 3.65 % for BIM1 and BIM3, respectively. PCEs of the DSSCs based on dyes BIM1-3 with coadsorbent improved by 29%, 28% and 12 %, respectively, compared to the DSSCs without coadsorbent. It implies BTZ moiety on dye BIM3 not only suppresses the intermolecular aggregation but also retard charge recombination to a certain degree. Based on the above findings, the incorporation of a suitable auxiliary acceptor between the donor and  $\pi$ -spacer is an effective way to increase the photovoltaic performance of the DSSCs.

#### CRediT authorship contribution statement

Barış Seçkin Arslan: Methodology, Validation, Writing - original draft. Burcu Arkan: Investigation, Resources. Merve Gezgin: Investigation. Yavuz Derin: Methodology, Data curation. Davut Avcı:



Fig. 7. (a) Nyquist plots and (b) Bode plots of the DSSCs in the absence of CDCA.

Software, Formal analysis. Ahmet Tutar: Visualization. Mehmet Nebioğlu: Supervision, Conceptualization. İlkay Şişman: Supervision, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors reported no declarations of interest.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 112936.

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