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Effect of a pi-bridging unit in triphenylamine-benzothiadiazole based donor acceptor chromophores for dye-sensitized solar cells

Mesude Zeliha Yigit[a], Hakan Bilgili[b], Emre Sefer[c], Serafettin Demic[a], Ceylan Zafer[b], Mustafa Can[d,*], Sermet Koyuncu[e,**]

[a] Department of Material Sciences and Engineering,Faculty of Engineering and Architecture, Izmir Katip Celebi University, Cigli, 35620 Izmir, Turkey
[b] Ege University, Solar Energy Institute, 35040 Bornova, Izmir, Turkey
[c] Department of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University 17020 Çanakkale/TURKEY
[d] Department of Engineering Sciences, Faculty of Engineering, Izmir Katip Celebi University, Cigli, 35620 Izmir, Turkey
[e] Department Chemical Engineering, Faculty of Engineering, Çanakkale Onsekiz Mart University, 17100Çanakkale, Turkey

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ABSTRACT

Two new metal free sensitizers based on triphenylamine-benzothiadiazole were synthesized and used in dye sensitized solar cells (DSSCs). Electrochemical and optical properties of the dyes were studied by cyclic voltammetry, UV-vis absorption and fluorescence spectroscopy. A red shift was observed by the attachment of a thiophene (**MZ-259**) instead of a phenylene (**MZ-255**) bridge. The reverse effect was observed in the electrochemical properties because of the more electron-donating thiophene incorporated into the cyanoacrylic acid as an anchoring-acceptor unit in this system resulted in a higher LUMO level. The charge distribution of the dyes was also proved by DFT calculations using the Spartan10 program with the parameters of B3LYP and 6-31G** basis set. Finally the photovoltaic performances were investigated under standard AM 1.5 illumination with a power of 100 mW/cm^2 using an ionic liquid based electrolyte. The power conversion efficiencies, η, were increased from 3.16% to 3.81% by using thiophene instead of phenylene as a π-bridge unit.

1. Introduction

Since the first cell was discovered by Gratzel et al. in 1991, dye sensitized solar cells (DSSCs) have proven to be a promising alternative for photovoltaic technology, because of their easy fabrication, high efficiency and low cost.[1,2]First, ruthenium (II) polypyridyl complexes have tremendous interest for this technology. Nowadays, the photoelectric conversion efficiency of DSSCs used by ruthenium polypyridyl sensitizer has achieved maximum power conversion efficiency greater than 11% [3–5]. Recently, metal free organic dyes have been studied heavily as an alternative choice to ruthenium polypyridyl complexes owing to advantages of flexibility in their structure tunability, high molar extinction coefficients, compliance with environmental issues and low cost preparation processes [6]. Up to now, hundreds of metal free organic dyes have been studied to act as sensitizers for DSSCs and have gained impressive efficiencies [7]. Recently, 11% percent conversion efficiency has been achieved with indoline type dyes by Gratzel et al. by using cobalt based electrolyte [8].

There is increased focus and effort devoted to the development of novel metal free organic dyes. In particular, donor-π-acceptor (D-π-A) dyes,[9] with both electron-donating (D) and electron-accepting (A) groups linked by a π-conjugated bridge exhibiting broad and intense absorption spectra, have been proposed as being one of the most promising organic dye sensitizers [10–15]. A variety of organic donor compounds such as coumarine[16], carbazole,[4,17–19] phenothiazine,[20] triphenylamine[21–23] have been examined for DSSCs and they all exhibit good performances. On the other hand, many researchers have devoted themselves to optimize chemical structures for obtaining improvements in performance. In 2011, Zhu et al. reported the 8.7% and 6.6% efficiencies from the indoline-benzothidiazole based donor acceptor dyes by using solvent based liquid and ionic liquid based electrolyte, respectively [24]. Furthermore, Tian et al. reported a series of novel donor-acceptor-π bridge-acceptor (D-A-π-A) organic dyes incorporating an additional acceptor such as benzothiadiazole, benzotriazole and quinoxaline into a traditional D-π-A framework in 2012 [25–27]. The inclusion of an additional

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[*] Corresponding author. Fax: +90-232-3293999; Tel: +90-232-3293535.
[**] Corresponding author. Fax: +90-286-2180541; Tel: +90-286-2180540.
E-mail addresses: mustafa.can@ikc.edu.tr (M. Can), skoyuncu@comu.edu.tr (S. Koyuncu).

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acceptor chromophore to the so-called backbone structure of the dye is expected to facilitate electron transfer from the light absorbing donor side to the anchoring acceptor side, and have a diverse effect on the photovoltaic performance in the D-A-π-A system.

Herein, we report two new D-A-π-A metal free dyes containing a hexyloxy triarylamine group as the strong electron donor (D) moiety, benzothiadiazole as the acceptor linker (A), thiophene or phenylene as a π-bridge (π), and cyanoacrylic acid both as electron acceptor unit and anchoring group as well (Scheme 1) (). The optical band gap of the thiophene attached dye was found to be less than that of the dye containing phenylene as a result of the more effective π-bridging capability of thiophene. On the other hand, when MZ-259, strongly reduced on comparison to MZ-255 due to the more electron-rich thiophene unit, is attached to the cyanoacrylic acid as acceptor and anchoring group, it determines the LUMO position of the MZ dyes. Because of this effect, the electrochemical band gap of **MZ-259** is lower than that of **MZ-255** although it contains a more electron rich thiophene π-bridge unit in the system. Finally, the photovoltaic performances were investigated under standard AM 1.5 illumination with a power of 100 mW/cm^2. It was found that there is a large increase from 3.16% to 3.81% in the power conversion efficiency of a DSSC device fabricated from thiophene containing a dye instead of phenylene group, when an ionic liquid electrolyte (0.5 M LiI (99,9%) and 0.05 M I2 (99,9%) in 3- methoxypropionitrile) was used in this system.

2. Experimental Section

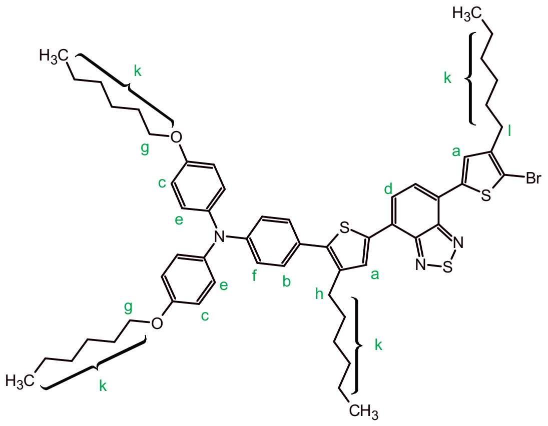
All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Copper(I) iodide, 1-bromohexane were purchased from Fluka. Acetone, dichloromethane, toluene, 18-crown-6, phenantroline, n-buthyllithium, 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), trimethyl borate,[1,1′-bi(diphenylphospino) ferrocene]dichloropalladium(II) were purchased from Sigma-Aldrich. 4-Iodophenol and 4-bromoaniline were purchased from Alfa Aesar. Potassium carbonate and potassium hydroxide were purchased from Riedel de Haen. On the other hand, 4-[bis[4-(hexyloxy) phenyl]amino]phenyl]-boronic acid,[17,28] 4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole[29] were prepared from previously published procedures.

2.1. Synthesis

2.1.1. 4-{5-[7-(5-Bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazol-4-yl]-3-hexyl-2-thienyl}phenyl) bis[4-(hexyloxy) phenyl]amine (1)

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (190 mg, 0.3 mmol), (4-{bis[4-(hexyloxy) phenyl]amino}phenyl) boronic acid (97.9 mg, 0.2 mmol) and Pd(dppf)Cl$_2$ (20.4 mg,0.025 mmol) were added to a Schlenk flask, then K$_2$CO$_3$ (2 mL, 1.5 mmol) and 18 mL DME was added under an argon atmosphere and reaction mixture was heated to 90°C. The reaction was stirred overnight. CHCl$_3$ was added and the mixture was washed with water. The organic solvent was evaporated. The crude product was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/n-hexane, 1:2) to afford the product as a red powder (90 mg, %45 yield).

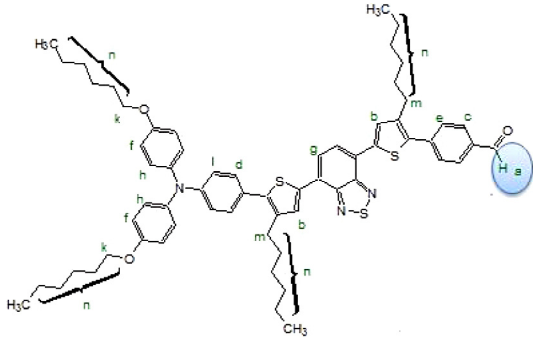
^{1}H NMR (400 MHz CDCl$_3$): δ 8.00(s, 2H, Ar-H$_a$), 7.77 (m, 1H, Ar-H$_d$), 7.12(d, 2H, Ar-H$_c$), 6.90(d, 2H,Ar-H$_f$), 6.84(d, 4H, Ar-H$_e$), 3.94(t, 4H, OCH$_2$), 2.72(t, 2H, CH$_2$), 2.63(t, 2H, CH$_2$), 1.78(m, 5H, CH$_2$), 1.34 (m, 27H, CH$_2$), 0.91(m, 12H, CH$_3$). ^{13}C NMR (400 MHz CDCl$_3$): δ 155.94, 152.74, 152.63, 148.57, 143.18, 140.63, 139.33, 139.92, 136.26, 130.88, 129.85, 127.95, 127.12, 126.52, 126.05, 125.31, 125.02, 124.80, 199.88, 115.57, 115.52, 111.39, 68.29, 31.83, 29.56, 25.98, 22.83, 14.24



2.1.2. 4-(5-{7-[5-(4-{Bis[4-(hexyloxy) phenyl]amino}phenyl)-4-hexyl-2-thienyl]-2,1,3-benzothiadiazol-4-yl}-3-hexyl-2-thienyl) benzaldehyde

4-(Formylphenyl) boronic acid (16.4 mg, 0.11 mmol), **1** (90 mg, 0.09 mmol) and Pd(dppf)Cl$_2$ (7.35 mg, 0.009 mmol) was added to a Schlenk flask, then K$_2$CO$_3$ (1 ml, 0.6 mmol) and 10 mL DME was added under an argon atmosphere and the reaction was heated to 90 °C. The reaction was stirred overnight. CH$_2$Cl$_2$ was added and the mixture was washed with water. The solvent was evaporated. The crude product was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/n-hexane 1:2) to afford the product as a dark red powder (50 mg, 55%).

^{1}H NMR (400 MHz CDCl$_3$): δ 10.03(s,1H, Ar-H$_a$), 7.98(s, 2H, Ar-H$_b$), 7.92(d, 2H, Ar-H$_c$), 7.77(d, 2H, Ar-H$_d$), 7.67(d, 2H,Ar-H$_e$), 7.30(d, 2H, Ar-H$_g$), 7.09(d, 4H, Ar-H$_f$), 6.95(d, 2H, H$_i$), 6.84(d, 4H, H$_h$), 3.93(t, 4H, OCH$_2$), 2.74(m, 4H, thiophene-CH$_2$), 1.78(m, 4H, CH$_2$), 1.70(m, 4H, CH$_2$), 1.34(m, 12H, CH$_2$), 1.30(m, 12H, CH$_2$), 0.92(m,12H, CH$_3$). ^{13}C NMR (400 MHz CDCl$_3$): δ 191.69, 155.95, 152.63, 148.39, 141.47, 140.62, 139.31, 137.76, 136.28, 135.22, 130.19, 129.61, 127.13, 124.96, 119.89, 115.58, 68.51, 31.85, 29.58, 26.01, 22.85, 14.35.



2.1.3. 3-[4-(5-{7-[5-(4-{Bis[4-(hexyloxy)phenyl]amino}phenyl)-4-hexyl-2-thienyl]-2,1,3-benzothiadiazol-4-yl}-3-hexyl-2-thienyl) phenyl]-2-cyanoacrylic acid (MZ255)

4-(5-{7-[5-(4-{Bis[4-(hexyloxy)phenyl]amino}phenyl)-4-hexyl-2-thienyl]-2,1,3-benzothiadiazol-4-yl}-3-hexyl-2-thienyl)benzaldehyde (50mg, 0.05mmol) and cyanoacetic acid (12.8mg, 0.15mmol) were added to a flask under an argon atmosphere, then 15mL dry CHCl$_3$ and piperidine (0.05mL, 0.55mmol) were added. The solution was refluxed overnight. After the solution was cooled, CH$_2$Cl$_2$ was added and the mixture was washed with water. The solvent was evaporated.Then the crudeproduct was purified by column chromatography (CH$_2$CH$_2$/MeOH: 9:1) to afford the product as a dark purplish-red powder (37mg, %68.5 yield).