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Effect of side chain substituents on the electron injection abilities of unsymmetrical perylene diimide dyes

Haluk Dinçalp^{a,*}, Zuhal Aşkar^a, Ceylan Zafer^b, Sıddık İçli^b

^a Department of Chemistry, Faculty of Art and Science, Celal Bayar University, Muradiye, 45030 Manisa, Turkey
^b Solar Energy Institute, Ege University, Bornova, 35100 Izmir, Turkey

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ABSTRACT

Three near-infrared (NIR) absorbing unsymmetrical perylene diimide D–A–D type dyes containing 6-undecanoxy as donor group were utilized in dye-sensitized nanocrystalline TiO₂ solar cells. Structure of the acceptor side of the molecules were improved by adding 4-[2-methyl-5-(cyanoacrylic acid)-3-thienyl]-phenyl (**V**), 3-carboxy-2-pyridil (**VI**) and 3-carboxy-2-pyrazyl (**VII**) moieties attached to one of the N-side of the dye. The relationship between the molecular structure of the acceptor sites of the dyes and the photovoltaic performances were discussed. Electrochemical measurements indicated that band gaps of the dyes were energetically favorable for electron injection from the excited state of the dyes to the conduction band of TiO₂ nanoparticles. However, three dyes gave lower conversion efficiency on DSSC applications. Strong electron-withdrawing nature of perylene core might not permit to transfer the photo-generated electrons to the carboxyl groups anchoring to TiO₂ surface, and then solar-to-electricity conversion efficiencies of the dyes were reduced.

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PIĞMĔNTS

1. Introduction

Electron transporting capacity of organic materials is significant property in the discussion of photovoltaic mechanisms for achieving the high charge separation and efficient photovoltaic properties. Suitable electron transfer from donor site to the acceptor side of the molecule enhances the intramolecular charge-transfer process and increases photo-generated electrons responsible for displaying the high solar-to-electricity conversion efficiency in DSSCs [1].

Much more efforts have been put into design and synthesis of special molecular systems which can imitate the photoinduced charge transfer and electron injection reactions in natural photosynthetic systems. Several groups have reported different sensitizers which initiate electron transfer when absorbs a photon in DSSCs such as triphenylamine- [2], pyrrole- [3], carbazole- [4], phenothiazine- [5], indole- [6], indolin- [7], coumarin- [8,9], phthalocyanine- [10] and tetrahydroquinoline-based [11] dyes. During the last few years, several groups have devoted significant performance on perylene diimide (PDI) dyes, which exhibit high electron mobilities [12], specific carrier injection-tuning properties [13], large molar absorption coefficients at wavelength between 480

and 550 nm [14], good electron transporting properties [15] and excellent photo [16] and thermal stabilities [17]. PDI dyes tune easily their optical and physical properties by introducing an appropriate ligand in bay positions, which is crucial in DSSC applications [18]. Systematic tuning of HOMO and LUMO level of PDI dyes improve both light harvesting properties and electron injection capabilities to TiO₂ conducting band for obtaining the high efficiency.

Another strategy for enhancing power conversion is to incorporate donor–linker–acceptor $(D-\pi-A)$ into the framework. Introducing $D-\pi-A$ groups increase intramolecular charge transfer from donor to acceptor side of the molecule by π linker, which results a strong electron transfer from excited state of dye molecule to the conduction band of TiO₂ nanoparticles. Various dyes of $D-\pi-A$ [19], D-A-D [20] and A-D-A [21] structures have been synthesized to increase power conversion efficiency. Electron-donating perylene tetracarboxylic acids give high power conversion efficiencies in DSSCs [22]. However, A-D-A type PDI dyes do not always show better photovoltaic performances than their counterparts, because electronic structure of perylene acceptor inhibits the correct direction of transferring the photo-generated electrons in these systems [23].

The present study has employed unsymmetrical PDI dyes based on 6-undecanoxy group in the 1- and 7-positions of the perylene ring as donor substituent, and the effects of the electron acceptor units attached to the one of the N-side of the ring on electron



^{*} Corresponding author. Tel.: +90 236 2412151/2543; fax: +90 236 2412158. *E-mail addresses*: haluk.dincalp@bayar.edu.tr, hdincalp@hotmail.com (H. Dinçalp).

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Scheme 1. Synthesis of compounds T1-4: i) NBS, benzoyl peroxide, AcOH, 70 °C, 7 h, 70%; ii) cyanoacetic acid, piperidine, Me–CN, reflux, 10 h, 90%; iii) bis(pinacolato)diboron, Pd₂(dba)₃, P(*t*-Bu)₃, triethylamine, anhydrous THF, 40 °C, 6 h, 75%; iv) 4-iodoaniline, Pd₂(dba)₃, [HP(*t*-Bu)₃]BF₄, NaF, K₂CO₃, anhydrous THF, RT, 2 h, 50%.

injection efficiency have been studied. The report herein is based on photochemical and photophysical properties of synthesized novel dyes **V**, **VI** and **VII** and their precursors (Schemes 1 and 2) in common solvents of different polarities. The absorption, emission and electrochemical properties of the dyes have been extensively studied.

2. Experimental section

2.1. General procedures

Materials were characterized by means of ¹H NMR and ¹³C NMR (Bruker spectrometer), FT-IR (Perkin Elmer-Spectrum BX spectrophotometer), UV–vis (Analytic Jena Speedcord S-600 diode-array spectrophotometer) spectroscopy. Mass spectra were recorded with a MALDI-TOF MS Bruker Reflex III. Fluorescence spectra were obtained using a PTI QM1 fluorescence spectrophotometer. The fluorescence quantum yields of dyes **III–VII** were determined at 298 K against the perylene-3,4,9,10-tetracarboxylic-bis-N,N'-dodecyl diimide ($\Phi_{\rm F} = 1.0$ in chloroform, $\lambda_{\rm exc} = 485$ nm) standart in solutions [24]. Fluorescence lifetimes were measured using a sub-

nanosecond pulsed LEDs which properties were explained in details previously [25]. Solutions of the samples were contained in 1 cm path-length quartz cells at the optical density below 0.1 for fluorescence studies.

CV measurements were conducted in a 100 mM [TBA][PF6] solution in Me–CN solution using a CH instruments (Electrochemical Workstation) at a scan rate of 200 mV/s at room temperature. A glassy carbon, a Pt wire, and Ag/Ag⁺ were used as the working electrode, counter electrode, and reference electrode, respectively. The reference electrode was calibrated using ferrocene–ferrocenium (Fe/Fe⁺) couple which was exhibited at about +0.47 V. Fe/Fe⁺ couple was used as internal reference for the calculation of E_{red}^{onset} values. Redox potentials of dyes **III–VII** were calculated from reversible waves with the formula $[E_{p(ox)} + E_{p(red)}]/2$.

Theoretical calculations using Hyperchem Package Version 8.0 computational software were carried out to characterize the three dimensional geometry and energy densities of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) surfaces of ground states for dye **V** and **VI** followed by MM+ force field and ZINDO/S (Single Point/CI) methods.



Scheme 2. Synthesis of dyes **I–VI**: i) I₂, Br₂, H₂SO₄, 85 °C, 10 h, 84%; ii) 2,6-diisopropyl aniline, propionic acid, 130 °C, 26 h, 60%; iii) 6-undecanol, K₂CO₃, DMF, 80 °C, 4 h, 50%; iv) KOH, *t*-BuOH, 80 °C, 2 h, 55%; v) **T4**, imidazole, 130 °C, 2 h, 45%; vi) 2-aminonicotinic acid, 130 °C, 2 h, 50%; vii) 3-aminopyrazine-2-carboxylic acid, 130 °C, 2 h, 55%.

1,7-Dibromo-perylene-3,4,9,10-tetracarboxylic dianhydride (I) and N,N'-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10tetracarboxylic diimide (II) were synthesized according to literature [26]. N-bromosuccinimide (NBS), benzoyl peroxide, piperidine, NaBH₄, triethylamine, propionic acid, DMF, t-BuOH, I₂ and NH₄Br were obtained from Merck Company. Bis(pinacolato)diboron, P(t-Bu)₃, tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃], K₂CO₃, 5methyl-2-thiophenecarboxaldehyde, 6-undecanone and 2,6-diisopropyl aniline were purchased from Aldrich. 4-iodoaniline, imidazole, perylene-3,4,9,10-tetracarboxylic acid dianhydride were purchased from Acros Organics. Cyanoacetic acid (from Alfa Aesar), bromine (Carlo Erba) and 2-aminonicotinic acid (from ABCR GmbH) were used as received. Other chemical reagents and organic solvents were analytical grade and used without further purification.

Solvent dependent kinetics and photophysical properties of dyes **III–VII** were investigated in four different solvents of increasing polarities including toluene ($\varepsilon = 2.4$), chloroform ($\varepsilon = 4.8$), ethanol ($\varepsilon = 24.6$) and benzonitrile ($\varepsilon = 26.0$) [27].

2.2. Synthesis

2.2.1. Preparation of [(t-Bu)₃PH]BF₄

Title compound was prepared according to a literature procedure [28]. HBF₄ [(48% aqueous solution), 185 µL, 1.40 mmol] was poured into a solution of P(*t*-Bu)₃ [(0.4 M in toluene), 0.5 mL, 0.20 mmol] in 5 mL of methylene chloride at room temperature. The resulting mixture was stirred vigorously for 5 min. Then, organic layer was dried over magnesium sulfate, and concentrated under vacuum. The white product was obtained. C₁₂H₂₈BF₄P, Yield: 95%, FT-IR (KBr pellet, cm⁻¹): 2957 (aliphatic ν_{C-H}), 2873 (aliphatic ν_{C-H}), 2300 (ν_{P-H}), 1476, 1395, 1370, 1247, 1104 (ν_{B-F}), 1020 (ν_{B-F}), 942, 811, 674, 640 cm⁻¹.

2.2.2. Preparation of 6-undecanol

50 mL of 1.2 N NaBH₄ (60 mmol) solution in ethanol was slowly added to a solution containing 6-undecanone (2.4 mL, 11.7 mmol) in 100 mL of ethanol at room temperature. The solution was stirred for 1 h. Then, the 50 mL of saturated NH₄Br solution was poured into the reaction mixture. The resulting solution was stirred for 1 h, and then extracted with ethyl acetate. White powder was obtained after concentration of the solution under vacuum. C₁₁H₂₄O, Yield: 90%, FT-IR (KBr pellet, cm⁻¹): 3334 (O–H stretching), 2957 (aliphatic ν_{C-H}), 2930 (aliphatic ν_{C-H}), 2859 (aliphatic ν_{C-H}), 1468, 1423, 1395, 1329 (O–H bending), 1134 (ν_{C-O}), 1075, 909 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 4.08 (1H, s), 3.59 (1H, s), 1.29 (16H, m), 0.87 (6H, t, *J* = 7.0 Hz) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.0 ppm (3 peaks)]: 72.1, 37.6, 32.1, 25.5, 22.8, 14.2 ppm.

2.2.3. Synthesis of 4-bromo-5-methyl-2-thiophenecarboxaldehyde (**T1**)

Following the published procedure [29], N-bromosuccinimide (1.19 g, 6.69 mmol) and benzoyl peroxide (16.2 µg, 66.9 µmol) were dissolved in 5 mL of acetic acid, and 5-methyl-2-thiophenecarbox-aldehyde (0.7 mL, 6.5 mmol) was added slowly. The solution was stirred at 70 °C for 7 h and extracted with dichloromethane. The combined organic layers were extracted with 1 M NaOH solution, washed with brine, dried over magnesium sulfate, and concentrated under vacuum. The reaction mixture was purified by column chromatography by using *n*-hexane:ethyl acetate (40:10). C₆H₅BrOS, Yield: 70%, FT-IR (KBr pellet, cm⁻¹): 2920, 2855, 1673 ($\nu_{C=0}$), 1520 (aromatic $\nu_{C=C}$), 1450, 1384, 1307, 1223, 1133, 838, 798, 684, 485 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.26 ppm): δ = 9.77 (1H, s), 7.58 (1H, s), 2.49 (3H, s) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.0 ppm (3 peaks)]: 181.7 (C=O), 145.9, 140.3, 138.8, 111.4, 16.0 ppm.

2.2.4. Synthesis of 3-(4-bromo-5-methyl-thien-2-yl)-2-

cyanoacrylic acid (**T2**)

Following the published procedure [30], a mixture of compound **T1** (0.1 g, 0.49 mmol), cyanoacetic acid (54 mg, 0.63 mmol), piperidine (10 µL, 0.1 mmol), and Me–CN (10 mL) was refluxed for 10 h. The crude product was crystallized from the solvent. The product was obtained as yellowish crystals. C₉H₆BrNO₂S, Yield: 90%, FT-IR (NaCl disc, cm⁻¹): 3431 (carboxylic acid O–H stretching), 2949 (aliphatic ν_{C-H}), 2808 (aliphatic ν_{C-H}), 2215 ($\nu_{C=N}$), 1742 ($\nu_{C=0}$), 1599 ($\nu_{C=C}$), 1514 (aromatic $\nu_{C=C}$), 1458, 1342, 1240 (ν_{C-O}), 1150, 999, 830, 775 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.26 ppm): δ = 8.74 (1H, s), 8.05 (1H, s), 7.34 (1H, s), 2.44 (3H, s) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.0 ppm (3 peaks)]: 173.1 (C=O), 140.4, 130.0, 108.7, 101.8, 88.7, 87.5, 84.5, 15.8 ppm.

2.2.5. Synthesis of 3-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-methyl-thien-2-yl]-2-cyanoacrylic acid (**T3**)

Following the published procedure [31], compound T2 (50 mg, 0.18 mmol), triethylamine (25 µL, 0.18 mmol), Bis(pinacolato)diboron (53 mg, 0.21 mmol), tris(dibenzylideneacetone) dipalladium(0) [Pd₂(dba)₃] [(21.8 mM in toluene), 211 µL, 4.6 μmol], P(*t*-Bu)₃ [(0.4 M in toluene), 11.5 μL, 4.6 μmol], and 2 mL of anhydrous THF were placed in a Schlenk tube. The solution was stirred at 40 °C under argon atmosphere for 6 h. The reaction progress was controlled by TLC. The reaction mixture was then cooled to room temperature and diluted with methylene chloride. Black particles were removed by filtration. The organic solvent was removed at reduced pressure. Pure sample was obtained by column chromatography on silica gel using chloroform:methanol (35:15) as eluent. C₁₅H₁₈BNO₄S, Yield: 75%, FT-IR (NaCl disc, cm⁻¹): 3444 (carboxylic acid O–H stretching), 2923 (aliphatic v_{C-H}), 2852 (aliphatic v_{C-H}), 2252 $(\nu_{C=N})$, 1714 $(\nu_{C=O})$, 1609 $(\nu_{C=C})$, 1565 (aromatic $\nu_{C=C})$, 1418, 1384 (ν_{B-O}), 1151 (ν_{C-O}), 1093, 888, 704 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 8.19 (1H, s), 7.65 (1H, s), 2.52 (3H, s), 1.25 (12H, s) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.0 ppm (3 peaks)]: 173.2 (C=O), 147.3, 137.4, 125.7, 111.5, 110.0, 107.6, 106.3, 75.3, 29.2, 25.0 ppm.

2.2.6. Synthesis of 3-[4-(4-aminophenyl)-5-methyl-thien-2-yl]-2cyanoacrylic acid (**T4**)

Following the published procedure [32], a Schlenk tube was charged, in no specific order, with compound T3 (41 mg, 0.13 mmol), sodium fluoride (16 mg, 0.38 mmol), 4-iodoaniline (28 mg, 0.13 mmol), potassium carbonate (106 mg, 0.77 mmol), Pd₂(dba)₃ [(21.8 mM in toluene), 89 µL, 1.9 µmol], [(t-Bu)₃PH]BF₄ [(23.4 mM in toluene), 186 µL, 4.4 µmol], and 1 mL of anhydrous THF. The mixture was stirred at room temperature under argon atmosphere for 3 h. The reaction progress was controlled by TLC. The reaction mixture was diluted with diethyl ether. Black particles were removed by filtration. The organic layer was evaporated to afford the crude product. The crude product was purified by column chromatography on silica gel using *n*-hexane:ethyl acetate (40:10) as eluent. C₁₅H₁₂N₂O₂S, Yield: 50%, FT-IR (NaCl disc, cm⁻¹): 3420 (carboxylic acid O–H stretching), 3215 (N–H stretching), 2924 (aliphatic v_{C-H}), 2857 (aliphatic v_{C-H}), 2218 ($\nu_{C=N}$), 1734 ($\nu_{C=O}$), 1653 (N–H bending), 1619 ($\nu_{C=C}$), 1496 (aromatic v_{C=C}), 1448, 1367, 1339, 1183 (v_{C-O}), 1096, 979, 875 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 7.76 (1H, s), 7.72 (1H, s), 7.62 (2H, d, J = 7.4 Hz, benzene H), 7.52 (2H, s), 7.40 (2H, d, J = 7.4 Hz, benzene H), 7.10 (1H, s), 3.00 (3H, s) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.0 ppm (3 peaks)]: 175.2 (C=O), 147.6, 141.9, 139.4, 138.0, 137.9, 132.8, 129.1, 126.3, 123.6, 114.5, 109.9, 12.0 ppm.

2.2.7. Synthesis of N,N'-bis(2,6-diisopropylphenyl)-1,7-bis(6undecanoxy)perylene-3,4,9,10-tetracarboxylic diimide (III)

A mixture of dye II (50 mg, 57.6 µmol), 6-undecanol (50 mg, 0.29 mmol), and potassium carbonate (80 mg, 0.58 mmol) was dissolved in 3 mL of DMF. The solution was stirred at 80 °C for 4 h. Then the reaction mixture was cooled to room temperature and poured into a 20 mL of water. The resulting precipitate was collected by suction filtration and then purified by column chromatography on silica gel using chloroform:methanol (48:02) as eluent. C₇₀H₈₆N₂O₆, Yield: 50%, FT-IR (KBr pellet, cm⁻¹): 2963 (aliphatic ν_{C-H}), 2924 (aliphatic ν_{C-H}), 2868 (aliphatic ν_{C-H}), 1706 $(\nu_{C=0})$, 1661 $(\nu_{C=0})$, 1588 (aromatic $\nu_{C=C}$), 1507, 1465, 1406, 1337 (ν_{C-N}) , 1244 (ν_{C-O}) , 839, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 9.66 (2H, d, J = 8.6 Hz, perylene H), 8.80–8.67 (4H, perylene H), 7.51 (2H, t, J = 7.8 Hz, benzene H), 7.37 (4H, d, I = 7.8 Hz, benzene H), 3.55 (2H, s), 2.75 (4H, septet, I = 6.2 Hz), 2.16 (8H, s), 1.56 (32H, aliphatic H), 1.15 (24H, d, *J* = 6.2 Hz), 0.87 (4H, m) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.5 ppm (3 peaks)]: 165.6 (C= 0), 145.9, 145.8, 139.6, 134.9, 132.3, 132.1, 130.6, 124.9, 124.5, 124.3, 124.2, 119.2, 37.6, 32.1, 29.8, 29.4 (CH(CH₃)₂), 25.5, 24.2 (CH(CH₃)₂), 22.8, 14.2 ppm.

2.2.8. Synthesis of N-(2,6-diisopropylphenyl)-1,7-bis(6undecanoxy)perylene-3,4,9,10-tetracarboxylic

3,4-anhydride 9,10-imide (IV)

Following the published procedure [33], powdery KOH (10 mg, 0.18 mmol) was added to 20 mL of *t*-BuOH and the solution was stirred at 80 °C for 1 h. Then, dve III (34 mg, 32.3 umol) was added. and the solution was stirred at same temperature for 2 h. After completion, the reaction mixture was poured into a solution of 4 mL of AcOH and 2 mL of 2 N HCl. The precipitate was washed with NaHCO₃ solution until the pH of the solution was reached to 6–7. The precipitate was purified by column chromatography on silica gel eluting with chloroform:methanol (48:02). C₅₈H₆₉NO₇, Yield: 55%, FT-IR (KBr pellet, cm⁻¹): 2964 (aliphatic ν_{C-H}), 2927 (aliphatic v_{C-H}), 2873 (aliphatic v_{C-H}), 1771 (anhydride $v_{C=0}$), 1701 (imide $v_{C=0}$) 0), 1669 (imide $v_{C=0}$), 1594 (aromatic $v_{C=C}$), 1462, 1360 (v_{C-N}), 1338, 1247 (ν_{C-0}), 1198 (anhydride ν_{C-0}), 811 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 8.79–8.70 (6H, m, perylene H), 7.51 (1H, benzene H), 7.37 (2H, benzene H), 3.52 (2H), 2.76 (2H), 2.16 (22H), 1.55 (10H), 1.25–1.19 (20H, aliphatic H), 0.88 (4H) ppm. ¹³C NMR [100 MHz, methanol-d₄, δ 47.5 ppm (7 peaks)]: 163.5 (C=O), 163.0 (C=0), 157.5, 145.9, 138.1, 134.4, 133.9, 132.1, 131.1, 130.6, 129.5, 129.1, 127.7, 127.2, 126.1, 123.9, 123.2, 122.9, 122.0, 120.5, 118.6, 117.2, 29.5, 29.3, 29.2, 29.1, 23.4, 23.3, 23.2, 23.1 ppm.

2.2.9. Synthesis of N-(2,6-diisopropylphenyl)-N'-{4-[2-methyl-5-(cyanoacrylic acid)-3-thienyl]-phenyl}-1,7-bis(6-undecanoxy) perylene-3,4,9,10-tetracarboxylic diimide (**V**)

Dye **IV** (16 mg, 17.3 µmol), compound **T4** (15 mg, 52.7 µmol), and imidazole (0.6 g, 8.8 mmol) were stirred under argon atmosphere at



Fig. 1. The normalized UV-vis absorption spectra of dye V in different solvents of increasing polarities at the concentrations of 10^{-6} M.

130 °C for 2 h. The reaction progress was monitored by TLC. After completion, the reaction mixture was poured into an excess of water and extracted with chloroform $(3 \times 15 \text{ mL})$. The organic phases were dried and evaporated. The crude solid was purified by column chromatography on silica gel eluting with chloroform:methanol (45:05). Yield: 45%, FT-IR (KBr pellet, cm⁻¹): 3422 (carboxylic acid O–H stretching), 3137 (aromatic ν_{C-H}), 2957 (aliphatic ν_{C-H}), 2929 (aliphatic ν_{C-H}), 2862 (aliphatic ν_{C-H}), 1734 (carboxylic acid $\nu_{C=0}$), 1692 (imide $\nu_{C=0}$), 1655 (imide $\nu_{C=0}$), 1625, 1586 (aromatic $\nu_{C=C}$), 1544, 1496, 1460, 1406, 1334 (*v*_{C-N}), 1239 (carboxylic acid *v*_{C-O}), 1065, 841 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 10.23 (1H, s, COOH), 8.92 (2H, perylene H), 8.58 (2H, perylene H), 8.45 (2H, pervlene H), 7.69 (1H, thiophene H), 7.60 (1H, -C=C-H), 7.39 (1H, t, *I* = 7.8 Hz, benzene H), 7.31 (2H, d, *I* = 7.8 Hz, benzene H), 7.10 (2H, benzene H), 7.02 (2H, benzene H), 4.10 (2H, s), 2.75 (2H), 1.28-0.88 (59H, aliphatic H) ppm. ¹³C NMR [100 MHz, CDCl₃, δ 77.5 ppm (3 peaks)]: 181.7 (carboxylic acid C=O), 163.5 (C=O), 163.0 (C=O), 152.4, 150.3, 145.8, 143.5, 140.4, 138.5, 134.6, 132.1, 131.5, 131.2, 130.7, 130.0, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 128.6, 127.3, 126.4, 125.7, 125.6, 124.2, 124.1, 115.5, 111.8, 109.3, 106.3, 106.1, 98.5, 32.1, 29.9, 29.5, 29.3, 28.9, 24.2, 24.1, 22.9, 14.3 ppm. MS (MALDI-TOF): m/z $[M]^+ = 1158$ (calcd for C₇₃H₇₉N₃O₈S: 1158.49).

2.2.10. Synthesis of N-(2,6-diisopropylphenyl)-N'-(3-carboxy-2-pyridil)-1,7-bis(6-undecanoxy)perylene-3,4,9,10-tetracarboxylic diimide (**VI**)

Dye **IV** (15 mg, 16.8 μ mol), 2-aminonicotinic acid (6.9 mg, 50.0 μ mol), and imidazole (0.5 g, 7.3 mmol) were stirred under argon atmosphere at 130 °C for 2 h. The reaction progress was monitored

Table 1

Long-wavelength absorption (λ /nm), emission maxima (λ_{em} /nm), Stokes shifts ($\Delta\lambda$) and fluorescence quantum yields (Φ_F) of dyes III–VII in different solvents of increasing polarities ($\lambda_{exc} = 485$ nm).

Dyes	Solven	ts														
	Toluene				Chloroform			Ethanol			Benzonitrile					
	λ	λ_{em}	Δλ	$\Phi_{ m F}$	λ	λ_{em}	Δλ	$\Phi_{ m F}$	λ	λ_{em}	Δλ	$\Phi_{ m F}$	λ	λ_{em}	Δλ	$\Phi_{\rm F}$
III	546	567	82	0.40	543	563	78	0.38	702	543	58	0.02	781	537	52	0.02
IV	546	566	81	0.43	543	563	78	0.38	704	543	58	0.02	781	538	53	0.03
V	667	561	76	0.11	528	548	63	0.15	690	554	69	0.04	772	540	55	0.34
VI	667	561	76	0.08	528	548	63	0.09	692	563	78	0.01	772	530	45	0.03
VII	667	561	76	0.20	527	548	63	0.18	693	554	69	0.07	772	530	45	0.05



Fig. 2. The normalized UV-vis absorption spectra of dyes III-V in benzonitrile at the concentrations of 10^{-6} M.

by TLC. 5 mL of ethanol was then slowly added to the resulting solution with rapid stirring. Then, the reaction mixture was poured into a solution of 5 mL of 2 N HCl and was stirred for 2 h. The resulting precipitate was chromatographed using chloroform:methanol (45:05) as eluent. Yield: 50%, FT-IR (KBr pellet, cm⁻¹): 3137 (carboxylic acid O–H stretching), 2963 (aliphatic ν_{C-H}), 2924 (aliphatic v_{C-H}), 2862 (aliphatic v_{C-H}), 1695 (imide $v_{C=0}$), 1664 (carboxylic acid $v_{C=0}$), 1653 (imide $v_{C=0}$), 1630, 1586 (aromatic $v_{C=C}$), 1538, 1465, 1404, 1331 (*v*_{C-N}), 1244, 1141 (carboxylic acid *v*_{C-O}), 1062, 844 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, δ 7.25 ppm): δ = 10.22 (1H, s, COOH), 9.57 (1H, d, *J* = 7.0 Hz, pyridine H), 8.97 (2H, s, perylene H), 8.68 (2H, m, perylene H), 8.57 (2H, d, J = 7.8 Hz, perylene H), 8.05 (1H, s, pyridine H), 7.42 (1H, t, *J* = 7.8 Hz, benzene H), 7.32 (2H, d, J = 7.8 Hz, benzene H), 7.17 (1H, s, pyridine H), 3.18 (2H, s), 2.73 (4H, septet, J = 6.2 Hz), 1.25–1.09 (50 H, aliphatic H), 0.88 (4H) ppm. ¹³C NMR [100 MHz, methanol-d₄, δ 48.0 ppm (7 peaks)]: 168.1 (C=O), 163.9 (C=0), 162.7 (C=0), 146.2, 146.0, 137.2, 135.4, 131.8, 131.3, 131.0, 130.0, 129.6, 129.5, 129.3, 129.2, 129.1, 128.7, 128.5, 128.3, 123.9, 123.8, 121.6, 119.8, 117.3, 115.6, 112.7, 111.6, 111.0, 29.5, 29.3, 29.2, 23.4, 23.3, 23.2, 22.5, 13.2 ppm, MS (MALDI-TOF): $m/z [M - 3H]^+ = 1009$ (calcd for C₆₄H₇₃N₃O₈: 1012.28).



Fig. 3. The normalized fluorescence spectra of dye V in different solvents of increasing polarities ($\lambda_{exc} = 485$ nm).



Fig. 4. Comparison of the normalized fluorescence spectrum of model dye **III** with that of dye **VII** in chloroform solution ($\lambda_{exc} = 485$ nm).

2.2.11. Synthesis of N-(2,6-diisopropylphenyl)-N'-(3-carboxy-2pyrazyl)-1,7-bis(6-undecanoxy)perylene-3,4,9,10-tetracarboxylic diimide (**VII**)

Dve IV was converted to dve VII by the same procedures as employed for dye VI. Dye IV (18 mg, 20.2 µmol), 3-aminopyrazine-2-carboxylic acid (8.4 mg, 60.4 umol), and imidazole (0.5 g, 7.3 mmol) were used. The resulting residue was chromatographed using chloroform: methanol (45:05) as eluent. Yield: 55%, FT-IR (KBr pellet, cm⁻¹): 3439 (carboxylic acid O–H stretching), 2963 (aliphatic v_{C-H}), 2929 (aliphatic v_{C-H}), 2868 (aliphatic v_{C-H}), 1695 (imide $v_{C=0}$), 1664 (carboxylic acid $v_{C=0}$), 1653 (imide $v_{C=0}$), 1637, 1586 (aromatic $\nu_{C=C}$), 1574, 1541, 1457, 1404, 1331 (ν_{C-N}), 1239, 1149 (carboxylic acid ν_{C-0}), 1060 cm⁻¹. ¹H NMR (400 MHz, methanol-d₄, δ 4.84 and δ 3.30 ppm): δ = 9.77 (1H, d, *J* = 8.5 Hz, pyrazil H), 8.61 (2H, s, pervlene H), 8.48 (2H, pervlene H), 8.24 (2H, pervlene H), 7.86 (1H, d, J = 8.5 Hz, pyrazil H), 7.38 (1H, benzene H), 7.32 (2H, benzene H), 3.63 (2H, s), 2.95 (2H), 2.00 (2H), 1.23-1.16 (50H, aliphatic H), 0.87 (4H) ppm. ¹³C NMR [100 MHz, methanol-d₄, δ 48.0 ppm (7 peaks)]: 167.8 (C=0), 164.2 (C=0), 162.7 (C=0), 146.2, 138.6, 137.5, 137.3, 135.3, 131.7, 131.3, 130.9, 130.1, 129.4, 129.3, 129.2, 128.8, 128.5, 127.5, 123.9, 123.8, 123.2, 121.9, 121.6, 119.9, 117.4, 116.2, 115.1, 29.6, 29.5, 29.3, 29.2, 23.4, 23.3, 23.2, 10.5 ppm. MS (MALDI-TOF): $m/z [M]^+ = 1013$ (calcd for $C_{63}H_{72}N_4O_8$: 1013.27).

2.3. Fabrication of nc-TiO₂ electrodes and DSSC assembly

 TiO_2 nanoparticles were synthesized by sol-gel method and growth to the 20–25 nm by Ostwald ripening in autoclave. The

Table 2

Fluorescence decay times (τ_f/ns) obtained by global analysis at 25 °C (collected emission of wavelength is 545 nm), radiative lifetimes (τ_0/ns), fluorescence rate constants ($k_f^r \times 10^8/s^{-1}$), non-radiative rate constants ($k^{nr} \times 10^8/s^{-1}$), and singlet energies ($E_s/kcal mol^{-1}$) of dyes III–VII in chloroform ($\lambda_{exc} = 485 nm$).^a

0.0			J			CAC		
Dyes	$\tau_{f(1)}$	$\tau_{\rm f(2)}$	$\tau_{f(3)}$	$\tau_{\rm f}$	τ_0	k_f^r	k ^{nr}	Es
Ш	5.0	3.2	0.3	2.8	7.5	1.3	2.2	53.4
IV	4.5	2.4	0.3	2.4	6.3	1.6	2.6	53.4
v	3.7	1.4	0.2	1.8	0.1	0.9	4.8	54.9
VI	3.4	1.2	0.2	1.6	0.2	0.6	5.7	54.9
VII	3.4	1.2	0.2	1.6	9.0	1.1	5.1	55.0

^a Photophysical parameters are calculated with the formulas: $\tau_f = \sum \tau_{f(n)}/n$, $\tau_0 = \tau_f/\Phi_F$, $k_f = 1/\tau_f = k_f^r + k^{nr}$, $k_f^r = 1/\tau_0$, $E_s = 0.0029/\lambda_{long} \times 10^{-7}$ [39,40].



Fig. 5. Cyclic voltammograms of dyes V-VII in Me–CN containing [TBA][PF6]. Scan rate = 200 mV/s.

synthesis is done by small modification of procedure reported by Gratzel et al. [34].

As a first step, compact layer of TiO₂ was coated on transparent conductive oxide coated glass electrodes (SnO₂:F, TEC15, R_{sheet}: 15 ohm/square) by spray pyrolysis technique. Spray pyrolysis was done by spraying 10% (v/v) tetraisopropyl orthotitanate:acetylacetone (1:1) (mol/mol) solution in ethanol on TCO substrate at 450 °C. After spraying the solution, samples heated additional 45 min at 450 °C. The thickness of compact TiO₂ layer is measured with Ambiostech XP1 high resolution profilometer and determined about 100 nm.

The nanocrystalline TiO₂ paste was coated on compact TiO₂ layer coated TCO substrates by screen printing technique. TiO₂ electrodes first dried at room temperature and then sintered at 450 °C for 1 h with 10 °C/min heating rate. After sintering the TiO₂ films were leaved in 0.02 M TiCl₄ solution for 30 min at 70 °C to obtain an electrical contact between the nanoparticles. Finally TiO₂ electrodes sintered again at 500 °C for 30 min with 10 °C/min heating rate. At the end of process nanocrystalline mesoporous TiO₂ film with 4 μ m thickness was obtained.

Sintered electrodes were allowed cool down slowly. While electrode temperature is around 100 °C, TiO₂ electrodes were immersed in dye solution containing 0.3 mM **Z907** dye in aceto-nitrile:*tert*-butanol (1:1) and 0.3 mM **V**, **VI** and **VII** dyes in CH₃OH:CHCl₃ (1:1) for 12 h. Sensitized TiO₂ electrodes were rinsed with acetonitrile and kept in desiccator. Counter electrode was prepared by thermal reduction of hexachloroplatinic acid to the platinum. 1% (v/v) solution in 2-propanol was used for platinization of FTO coated electrode. Drop casted electrodes annealed at 400 °C for 20 min.

The DSSCs were prepared by placing the electrodes in sandwich geometry top of each other and in the middle 50 μ m thick thermoplastic polymer frame Surlyn[®] 1702 (DuPont). The electrodes

sealed by heating around 100 °C and pressing slightly. Electrolytes consist of iodide/triiodide redox couple filed into cell via pre-drilled small hole by vacuum. The electrolyte composition was 0.6 M 1-butyl-3-methy-imidazolium iodide (BMII), 0.1 M lithium iodide (LiI), 0.05 M iodine (I₂) and 0.5 M *tert*-butyl pyridine (TBP) dissolved in 3-methoxy propyonitrile (MPN). The active areas of the prepared solar cells were adjusted to 1.0 cm² by mask.

The photovoltaic characterizations of the DSSCs were done under the dark and standard conditions by illumination of AM1.5 global radiation with 100 mW/cm² light intensity.

3. Results and discussion

3.1. Optical and fluorescence emission properties

Different unsymmetrical PDI dyes with 4-[2-methyl-5-(cyanoacrylic acid)-3-thienyl]-phenyl (V), 3-carboxy-2-pyridil (VI) and 3-carboxy-2-pyrazyl (VII) terminal groups present a broad absorption band in the NIR region and all of these compounds are highly soluble in various organic solvents such as PhMe, CHCl₃, MeOH and PhCN. Dye V exhibits an absorption band peak at 528 nm in chloroform with characteristic vibronic structure which is attributed to allowed $\pi - \pi^*$ transitions localized on the perylene core (Fig. 1). However, dye V shows unusual absorption behavior in toluene and more polar ethanol and benzonitrile solutions. The maximum and the shoulder of the absorption band of the dye in these solvents are shifted to NIR region. Also, new bands around 430 nm appear. These findings suggest reasonable photoinduced intramolecular charge transfer in these solvents. Electron deficient nature of perylene core initiates the movement of electron density from the 6-undecanoxy donors located in bay positions of the ring to the perylene core, then the polarizability of the whole molecule changes in the excited state, leading to significant shift to NIR region on their absorption spectra. These observations in high polar organic solvents are attributed to the formation of perylene diimide anion radical which was previously reported [35-38].

Comparison of the absorption and emission data of model dye **III** with unsymmetrical PDI dyes in solvents of different polarities is given in Table 1 and also illustrated in Fig. 2. In general, the absorption spectra of unsymmetrical PDI dyes **V**–**VII** give a considerable hypsochromic shift compared to the corresponding spectra of symmetrical dye **III** in studied solvents except toluene. This observation is explained by the low polarizability of the excited state of the perylene ring in the solvents. When the different electron-withdrawing substituents incorporated to the one of the N-side of the molecule are replaced by the 2,6-diisopropylphenyl group, there were less polarizability on the dihedral angle of the perylene core. Because of the different electronic nature of both the two sides of the perylene ring, new electronic transition would reallocate the electron density on the perylene core.

The steady-state emission spectra of dye V in different solvents of increasing polarities are displayed in Fig. 3. It is understood that higher the polarities of the solvents, the more increase the blue-shifted wavelength of emission maxima of unsymmetrical PDI dyes

 Table 3

 Cyclic voltammetry data and molecular orbital energies of dyes III-VII with respect to the vacuum level.^a

Dyes	$E_{red3}^{0}(V)$	$E_{red2}^{0}(V)$	$E_{red1}^{0}(V)$	$E_{ox1}^{0}(V)$	$E_{ox2}^{0}(V)$	LUMO-1 (eV)	LUMO (eV)	HOMO (eV)	HOMO-1 (eV)	E_{gap1} (eV)	$E_{gap}\left(eV ight)$
III	-1.34	-0.94	-0.62	0.90	1.47	-3.39	-3.71	-5.23	-5.80	2.41	1.50
IV	-	-0.92	-0.58	0.96	1.46	-3.41	-3.75	-5.29	-5.79	2.38	1.50
V	-	-1.13	-0.75	0.77	0.94	-3.20	-3.58	-5.10	-5.27	2.07	1.52
VI	_	-1.10	-0.72	0.73	0.88	-3.23	-3.61	-5.06	-5.21	1.98	1.45
VII	_	-1.10	-0.72	0.74	0.91	-3.23	-3.61	-5.07	-5.24	2.01	1.46

^a HOMO and LUMO energy levels of the dyes were determined by the formulas: $E_{LUMO} = -(4.8 + E_{red}^{onset})$, $E_{red}^{onset} = E_{red}^{0} - E_{ox(ferrocene)}^{0}$, $E_{HOMO} = E_{LUMO} - E_{gap}$ [44].



Fig. 6. Cyclic voltammograms of dye **V** in 0.1 M [TBA][PF6]/Me–CN at various scan rates on glassy carbon working electrode. (1) 50, (2) 100, (3) 200, (4) 400, (5) 600, (6) 800, (7) 1000 mV/s.

V–VII and perylene monoanhydride dye **IV**, excluding in ethanol solution. Hydrogen bonding ability of ethanol with the unshared electron pairs of the heteroatoms of the unsymmetrical dyes enhances charge-transfer by donating a partial positive charge into the functional group [39], leading to significant shift to long-wavelength region on their emission spectra. Introduction of 3-carboxy-2-pyrazyl group to the perylene structure gives a marked blue shift of 15 nm in emission maximum compared to the corresponding spectra of model dye **III** in chloroform (Fig. 4) and other studied solvents which do not form hydrogen bond.

As given in Table 1, fluorescence quantum yields of unsymmetrical PDI dyes **V**–**VII** are lower than that of the model dye **III** in apolar toluene and chloroform solvents. This may be explained by the formation of charge-transfer complex because of the unsymmetrical structure of PDI dyes. In high polarity solvents such as ethanol and benzonitrile, all quantum yields of the dyes are very low, because of an effective quenching between the perylene core and side chain substituents, leading to formation of charge-separated state.

Photophysical parameters of the dyes obtaining from the single photon analysis are given in Table 2. Fluorescence decays of dye



Fig. 7. The normalized UV–vis absorption spectra of dyes V-VII adsorbed on nc-TiO $_2$ surface.



Fig. 8. Current-voltage graphs of dyes IV-VII under illumination with 100 mW/cm² light intensity.

III—**VII** are analyzed as a three-exponential decay in chloroform solution. The highest decay times indicate the PDI chromophore. Fast decay components below 1 ns suggest a fast charge separation and a reaction from charge-separated state to the locally excited state. Similar process has been observed for reversible intra-molecular exciplex formation for peryleneimide chromophores [41–43]. Fluorescence rate constants of unsymmetrical PDI dyes **V**—**VII** are lower than that of the model dye **III**. This means that the HOMO level of the substituents lie above the HOMO level of PDI chromophore, leading to an efficient electron transfer process.

3.2. Electrochemical properties

Fig. 5 shows typical cyclic voltammograms of dyes **III**–**VII** and the results are listed in Table 3. While symmetrical model dye **III** exhibits three reduction waves $(E_{red1}^0 = -0.62 \text{ V}, E_{red2}^0 = -0.94 \text{ V},$ $E_{red3}^0 = -1.34 \text{ V})$ and two oxidation waves $(E_{ox1}^0 = 0.90 \text{ V},$ $E_{ox2}^0 = 1.47 \text{ V})$, reduction processes for unsymmetrical PDI dyes **V–VII** are slightly shifted to negative region. Dye **V** exhibits reduction waves at -0.75 and -0.13 V, indicating the formation of stable PDI monoanion and dianion radicals, respectively. Also, dye **V** exhibits oxidation waves at 0.77 and 0.94 V, indicating the formation of thiophene and PDI cation radical, respectively. In comparison to the dye **V**, both first and second reduction waves of dye **VI** and **VII** are shifted to positive region ($\Delta E^0 = 30 \text{ mV}$).

It is clearly seen from Table 3 that LUMO energy levels of unsymmetrical PDI dyes **V–VII** are higher than that of the model

Table 4

Photovoltaic data^a of DSSCs containing nc-TiO₂/PDI dyes **IV–VII** photoactive electrodes with respect to standart dye **Z907** under illumination with 100 mW/cm² light intensity.

Dyes	IV	v	VI	VII	Z907
Isc [mA/cm ²]	0.289	0.070	0.099	0.117	11.87
$V_{\rm oc} [{\rm mV}]$	350	320	390	410	700
FF	0.67	0.42	0.47	0.52	0.56
MPP [mW/cm ²]	0.067	0.009	0.018	0.025	4.66
$V_{\rm mp}$ [mV]	300	200	260	290	460
$I_{\rm mp}$ [mA/cm ²]	0.225	0.047	0.069	0.085	10.138
η	0.067	0.009	0.018	0.025	4.66

^a Filling factor (FF) and efficiency [%] (η) are calculated with the formulas: FF = $V_m I_m / V_{oc} I_{sc}$ $\eta = I_{sc} V_{oc} FF / P_{in} A$ [open circuit voltage (V_{oc}), short current (I_{sc}), current (I_m) and potential (V_m) maximum power point, intensity of incident light (P_{in}), cell area (A)].



Fig. 9. Ground and excited state molecular orbitals of energy densities of V and VI dyes for comparison.

dye **III**. This difference is explained by the unsymmetrical structure of dyes **V**–**VII** which have different electron-withdrawing nature of the carbonyl group at imide nitrogen. LUMO energy levels of dyes **V**–**VII** show no obvious difference due to the similar energy node at imide nitrogen. Fig. 6 shows the cyclic voltammogram of dye **V** at various scan rates. ΔE_p values [$E_{p(anodic)} - E_{p(cathodic)}$] for first reduction waves changed from 17 to 43 mV with the scan rates ranging from 50 to 1000 mV/s for dye **V**.

Thus, the LUMO levels of all the studied dyes are higher than the conduction band of TiO_2 , indicating the more efficient electron transfer process for DSSC applications. Also, LUMO level of unsymmetrical PDI dyes are higher than that of symmetrical model dye **III**, leading to stronger electron injection driving force.

3.3. Photovoltaic performance of DSSCs based on dyes V-VII

Fig. 7 exhibits the absorption behavior of PDI dyes **V**–**VII** on the surface of TiO₂ electrode. Fig. 8 shows the current density–voltage characteristics obtained with perylene dyes **IV**–**VII** and the and photovoltaic data are listed in Table 4. Under standard solar conditions, dye **V**, **VI** and **VII** sensitized solar cells gave a short current density (I_{sc}) of 0.070, 0.099 and 0.117 mA cm⁻², an open circuit voltage (V_{oc}) of 320, 390 and 410 mV, leading to efficiencies (η) of 0.009, 0.018, and 0.025, respectively. Both the I_{sc} and the V_{oc} values for DSSCs based on pyridine and pyrazole substituted dyes **VI** and **VII** are higher than those for dye **V** under these conditions. This progress may be related to the lower LUMO level of dyes **VI**–**VII** (–3.61 V) than that of dyes **V** (–3.58 V).

Lower photon to electric conversion efficiencies of unsymmetrical PDI dyes **V**–**VII** might be related to strong electron-withdrawing nature of perylene core, leading to inhibit the transfer of photo-generated electrons from the electron donor side to the acceptor and anchoring side of the molecule. Similar low values were observed for DSSCs based on benzo[e]indole substituted PDI

dyes in the literature [23]. These low efficiencies were explained by the unbeneficial transferring direction of photo-generated electrons on the perylene ring. To understand better the electron distribution of frontier orbitals on whole molecule, we studied the HOMO–LUMO energy distributions of dyes V and VI using Hyperchem models illustrated in Fig. 9. The calculations illustrate that both the HOMO and LUMO levels of dyes V and VI are delocalized over the π -delocalized system through pervlene rings between the two different imide groups. The change in electron distribution initiated by the photoexcitation does not occur in the studied molecules. For dye V, then the pervlene core became electron donor group, and LUMO + 1 level of the molecule was delocalized over the cyano-carboxylic acid group which was new electron acceptor side of the molecule. Photo-generated electrons do not directed from the pervlene core to the carboxylic acid groups anchoring on TiO₂ surface, leading to the give extremely low solar-to-electricity conversion efficiency.

Among the obtained DSSC performances based on the synthesized dyes, dye **VI** and **VII** containing pyridine and pyrazole groups, respectively, gave higher efficiency (η) than those for dye **V** under same conditions. This small improvement in η values may be related to the ability of nitrogen atoms of heteroaromatic structures to undergo protonation reaction with carboxyl groups attached to pyridine [45] or pyrazil [46] groups. This means the anionic structure of the carboxylate group is more readily anchored to TiO₂ surface and then, the dye absorption of TiO₂ electrode is improved.

4. Conclusions

In summary, we have synthesized three new unsymmetrical PDI dyes, in which the carboxylic acid groups are incorporated into the main structure to improve the interaction with nc-TiO₂ surface. The absorption spectra of these dyes cover the whole solar spectra in common organic solvents. Photophysical calculations and single

photon analyses of the dyes suggest that photoinduced intramolecular charge transfer is responsible for extra long-wavelength shift of absorption maxima of the dyes.

The LUMO energy levels of the dyes were suitable for an effective electron injection to conduction band of TiO_2 surface. However, all the dyes have poorer conversion efficiencies. Polarizability of the dyes is focused on the perylene core and photo-generated electrons may not transfer to the carboxyl groups anchoring to TiO_2 surface. Also, intramolecular proton transfer reaction in pyridine or pyrazole substituted PDI dyes give an opportunity of raising the solarto-electricity conversion efficiency.

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