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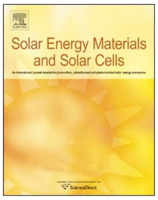

Synthesis of thiophenyl-substituted unsymmetrical anthracene derivatives and investigation of their electrochemical and electrooptical properties

Arif Kivrak[a,*], Hatice Çalış[a], Yasemin Topal[c], Hilal Kivrak[b], Mahmut Kuş[c]

[a] *Yüzüncü Yıl University, Department of Chemistry, Faculty of Sciences, 65080 Van, Turkey*
[b] *Yüzüncü Yıl University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 65080 Van, Turkey*
[c] *Selçuk University, Faculty of Engineering and Architecture, Department of Chemical Engineering, Konya, Turkey*

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ABSTRACT

Novel thiophenyl-substituted anthracene derivatives (D-A) bearing a variety of electron-withdrawing groups were designed and synthesized for organic solar cells (OSCs). Their electrochemical and electro-optical properties were examined with strong donor-acceptor interaction. The electrochemical properties were examined by cyclic voltammetry (CV) measurements. These estimated values from CV measurements are in good agreement with the optical band gaps. HOMO, LUMO, and Eg values of designed organic materials were estimated. Furthermore, these new generation organic materials were fabricated to find their solar cell performances.

1. Introduction

Small conjugated organic compounds have a significance due to their different and crucial properties [1]. They have been used in solar cells [2], transistor [3], LEDs [4], biosensors [5], sensors [6], and electrochromic devices [7–10]. The design and synthesis of efficient electron-transporting materials appear to be more attractive. Thus, a considerable research effort has been focused on developing efficient small-molecule materials for improved device performance [11–13]. Many different structural design strategies have been developed for OSCs. However, the donor-acceptor- (D-A) materials are the most popular and efficient method due to its advantages such as; light weight, quite thin (as thin as a paper), flexible, low cost, robust, electrochemically stable [14,15]. Recently, anthracene-based solar cells [16,17], dye sensitized solar cells [18], organic light emitting devices (OLEDs) [19], and organic thin film transistors were reported to have impressive charge carrier mobility and high energy conversion efficiency [20–24]. These properties could depend on the crystalline, conjugated, and planar structure of anhtracene structure [25,26]. In literature, it was reported that different kind of anhtracene-based organic compounds were synthesized by using different methodologies and groups. On the other hand the application of these anhtracene-based organic compounds have not been studied extensively. In literature, there are such a few studies including their applications [22-28]. Wang and coworkers prepared symmetrical and unsymmetrical anthracene based small organic molecules, good candidate for many applications due to their electrochemical and electro-optical properties [29]. However, one could note that there is not any information about OSC applications of these symmetrical and unsymmetrical anthracene based small organic molecule.

Herein, the design, synthesis, and photovoltaic characteristics of new D-A type anthracene derivatives containing strong electron withdrawing groups were investigated. Furthermore, electrochemical and electro-optical properties were investigated. Finally, all synthesized compounds were fabricated and tested for OSCs.

2. Experimental

The design, synthesis, and photovoltaic characteristics of new D-A type anthracene derivatives containing strong electron withdrawing groups were studied. Synthesized molecules were determined by ^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent NMR (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from an internal TMS (trimethylsilane) reference. Coupling constants (J) are reported in hertz (Hz). In addition, spin multiplicities are presented by the following symbols: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). DEPT ^{13}C NMR information is given in parentheses as C, CH, CH_2, and CH_3. Flash chromatography was performed using thick-walled glass columns and 'flash grade' silica (Merck 230–400 mesh). Thin layer chromatography (TLC) was performed by using commercially prepared 0.25 mm silica gel plates and visualization was effected

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[*] Corresponding author.
E-mail address: akivrak@yyu.edu.tr (A. Kivrak).

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with short wavelength UV lamp. The relative proportions of solvents in chromatography solvent mixtures refer to the volume to volume ratio. Absorption spectra was measured on a Thermo Scientific Multiskan Go UV–VIS spectrophotometer. All commercially available reagents were used directly without purification unless otherwise stated. All the solvents used in reaction experiments were distilled for purity. The inert atmosphere was created by slight positive pressure (ca. 0.1 psi) of argon. All glassware was dried in an oven prior to use. The electrochemical properties were estimated by cyclic voltammetry (CV) measurements. These estimated values from CV measurements were compared with the ones obtained from UV–vis measurements.

2.1. *Synthesis of compounds*

2.1.1. *Synthesis of 9,10-di(thiophen-2-yl)anthracene (DTA)*

To a stirred solution of 9,10-dibromoanhtracene (9 mmol, 3 g) and 2-(tributylstannyl)thiophene (22.5 mmol, 7.08 mL) in Toluene (25 mL) was added tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (0.356 mmol, 396 mg). Furthermore, the solution was allowed to stir at 110 °C under Argon atmosphere overnight. After the reaction was completed, solvent was removed under vacuum. The crude mixture was then extracted with CH_2Cl_2 (3×10 mL). The organic layer was collected and dried over anhydrous $MgSO_4$. After the filtration, the solvent was removed on a rotary evaporator. Then, residue was purified by flash chromatography over silica gel eluting with Hexane/Ethyl acetate (9:1, v/v) to give a 9,10-di(thiophen-2-yl) anthracene (**DTA**) (2.78 g, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (m, 4H), 7.65 (dt, *J*=5.1; 1.2 Hz, 2H), 7.43 (m, 4H), 7.34 (m, 2H), 7.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 131.7, 130.5, 129.8, 127.4, 127.0, 126.9, 125.9. The spectral data are in agreement with those reported previously for this compound [26].

2.1.2. *Synthesis of 5-(10-(thiophen-2-yl)anthracen-9-yl)thiophene-2-carbaldehyde (TATC)*

Vilsmeier Haack reagent was prepared by adding phosphorous oxychloride (8.76 mmole, 8.1 mL) in DMF (8.76 mmole, 6.7 mL) at 0 °C. Then, 9,10-di(thiophen-2-yl)anthracene (DTA) (2.92 mmole, 1 g) was added to the reagent at 0 °C. The reaction mass was stirred at room temperature for an hour then refluxed for 4 h. The reaction mixture was cooled at room temperature. After cooling, it was poured into cold aq. sodium carbonate solution (20 mL, 10%) and stirred at room temperature for 2 h more. After the reaction completed, the crude mixture was extracted with CH_2Cl_2 (3×10 mL). Then, the organic layer was collected and dried over anhydrous $MgSO_4$. After the filtration, the solvent was removed on a rotary evaporator. Following this, the residue was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (4:1, v/v) to give 5-(10-(thiophen-2-yl)anthracen-9-yl)thiophene-2-carbaldehyde **(TATC)** (830 mg, 76%).^1H NMR (400 MHz, $CDCl_3$) 10.07 (s, 1H), 8.00 (m, 1H), 7.90 (m, 2H), 7.79 (m, 2H), 7.65 (m, 1H), 7.44(m, 4H), 7.33 (m, 2H), 7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 183.2, 150.2, 145.3, 138.7, 136.9, 131.7, 131.6, 131.3, 130.9, 129.9, 128.4, 127.5, 127.2, 127.2, 126.5, 126.1, 126.0.

2.1.3. *Synthesis of 1,1'-(anthracene-9,10-diylbis(thiophene-5,2-diyl)) bis(ethan-1-one) (DTAA) and 1-(5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)ethan-1-one (TATA)*

9,10-Di(thiophen-2-yl)anthracene (**DTA**) 1.540 g, 4.5 mmol) was dissolved in dry DCM (24 mL) by constant stirring under argon. Then, acetyl chloride (1 mL, 13.5 mmol) was added to the resultant solution. The flask was immersed in a 0–5 °C ice-water bath. Anhydrous aluminium chloride (2.39 g, 18 mmol) was slowly added into small portions to the reaction flask. The reaction mixture was stirred at room temperature for 5 h. Then, it was recooled to 0–5 °C by a fresh ice-water bath. By the slow addition of cold water (4×0.5 mL), the reaction mixture was hydrolyzed. Then, a further 3 mL of cold water was added more rapidly. The hydrolyzed reaction mixture was extracted with DCM and collected organic extracts were washed with 5% NaOH solution followed by brine solution. The organic phase was dried over anhydrous $MgSO_4$ and filtered off. After the filtration, the solvent was removed on a rotary evaporator. The residue was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (9:1, v/v) to give as 1,1'-(anthracene-9,10-diylbis(thiophene-5,2-diyl))bis(ethan-1-one) **(DTAA)** (708 mg, 55%) and 1-(5-(10-(thiophen-2-yl) anthracen-9-yl)thiophen-2-yl)ethan-1-one **(TATA)** (413 mg, 36%). **DTAA:**^1H NMR (400 MHz, $CDCl_3$) 7.95 (d, J=3.7 Hz, 2H), 7.85 (m, 4H), 7.47 (m, 4H), 7.28 (d, *J*=4.1 Hz, 2H), 2.72 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) 190.9, 148.0, 145.9, 132.9, 131.2, 130.9, 129.7, 126.5, 126.5, 27.2. **TATA:**^1H NMR (400 MHz, $CDCl_3$) 7.92 (m, 3H), 7.84 (m, 2H), 7.64 (dd, *J*=1.28, 0.8 Hz; 1H), 7.44 (m, 4H), 7.34 (m, 1H), 7.23 (m, 2H), 2.70 (s,3H). 13C NMR (100 MHz, $CDCl_3$) 190.9, 148.4, 145.7, 138.6, 132.9, 131.5, 131.3, 131.1, 130.9, 129.8, 128.8, 127.4, 127.1, 127.0, 126.3, 126.2, 126.0, 27.1.

2.1.4. *Synthesis of 2-((5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)methylene) malononitrile (Mono-ThAnt-E1A)*

TATC (200 mg, 0.54 mmol), malononitrile (143 mg, 2.15 mmol) in toluene (25 mL), and Aluminium oxide (Al_2O_3) (5.92 mmole, 605 mg) were placed in a dry flask and kept under argon atmosphere. The mixture was heated at 110 °C for 24 h. After reaction was done, solvents were removed under vacuum and the residue was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (4:1, v/v) to give as 2-((5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl) methylene)malononitrile (**Mono-ThAnt-E1A**) (223 mg, 99%). ^1H NMR (400 MHz, $CDCl_3$) 7.94 (m, 4H), 7.73 (m, 2H), 7.62 (m, 1H), 7.45 (m, 4H), 7.34 (m, 2H), 7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 152.5, 150.9, 138.8, 138.4, 137.0, 132.3, 132.0, 131.5, 130.91, 129.9, 127.5, 127.3, 127.3, 127.1, 126.9, 126.1, 125.8, 114.4, 113.3. IR (KBr) 3433.3, 2225.8 (CN), 1573.9, 1099.4.

2.1.5. *Synthesis of (Z)-2-(3-oxo-2-((5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)methylene)-2,3-dihydro-1H-inden-1-ylidene) malononitrile (Mono-ThAnt-E2A)*

TATC (96 mg, 0.26 mmol) and malononitrile (100 mg, 0.52 mmol) were placed in a microwave reactor tube (30 mL). Dichloromethane (15 mL) was added to this mixture followed by pyridine (80 mg, 0.26 mmol) under argon atmosphere. This mixture was heated at 75 °C for 3 h in a microwave reactor (Anton Paar MW-300). After reaction was done, solvents were removed under vacuum and the residue was purified by flash chromatography over silica gel eluting with chloroform to give (Z)-2-(3-oxo-2-((5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)methylene)-2,3-dihydro-1H-inden-1-ylidene) malononitrile **(Mono-ThAnt-E2A)** (26 mg, 17%). ^1H NMR(400 MHz, $CDCl_3$) 9.39 (d, *J*=3.88 Hz, 1H), 8.44 (dt, *J*=7.52; 0.9 Hz, 1H), 7.98 (m, 2H), 7.88 (m, 2H), 7.81 (m, 1H), 7.72 (m, 1H), 7.64 (m, 1H), 7.58 (m, 1H), 7.53 (m, 1H), 7.42 (m, 4H), 7.33 (m,2H), 7.23 (dd, *J*=1.0; 3.36 Hz,1H). ^{13}C NMR (100 MHz, $CDCl_3$) 188.15, 167.77, 160.99, 159.87, 151.38, 146.0, 145.07, 138.73, 138.21, 135.64, 134.09, 133.56, 132.32, 131.67, 131.38, 130.95, 130.90, 130.54, 129.86, 129.54, 128.79, 127.21, 126.71, 126.59, 125.88, 125.75, 123.83, 123.39, 113.79. IR (ATR) 2933.6, 2208.6 (CN), 1698.3 (C=O), 1559.2, 1518.7, 1207.7, 1006.7.

2.1.6. *Synthesis of 2-(1-(5-(10-(thiophen-2-yl)anthracen-9-yl) thiophen-2-yl)ethylidene)malononitrile (Mono-ThAnt-E1B)*

TATA (200 mg, 0.52 mmol) and malononitrile (172 mg, 2.6 mmol) in toluene (25 mL) were placed in a dry flask. Furthermore, Aluminium oxide (Al_2O_3) (5.72 mmole, 577 mg) was added this flask. This flask was kept under argon atmosphere. The mixture was heated at 110 °C for 24 h. After reaction was done, solvents were removed under vacuum and the residue was purified by flash chromatography over silica gel eluting with hexane/ethyl acetate (4:1, v/v) to give as 2-((5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)methylene)malono-