Synthesis and Characterization of Bis-Thienyl-9,10-anthracenes Containing Electron Withdrawing 2-Cyanoacrylic Acid or 2-Methylenemalononitrile Group[†]

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A series of new bis-thienylanthracene derivatives **D1 ~ D5** containing 9,10-antharcene moiety in the center and 2-methylenemalonotitrile or 2-cyanoacrylic acid functional group on the terminal thiophenes were synthesized and characterized by ^{1}H-NMR and high-resolution mass spectroscopy. Their optical, electrochemical, and thermal properties were measured. They have absorption λ_{max} in the range of 437 ~ 480 nm and ε_{max} of 7.4 $\times$ $10^3 \sim 2.0 \times 10^4 \, M^{-1} cm^{-1}$. The substitution of 2-cyanoacrylic acid group allows greater value of ε_{max} than that of 2-methylenemalonotitrile. TGA curves showed that **D4** and **D5** which have 2-cyanoacrylic acid functional group on the terminal thiophene(s) exhibit good thermal stability and **D4** was thermally stable up to 400 °C. Their optical properties and LUMO energy levels measured suggest that they can serve as potential candidates for electron donor materials of organic photovoltaic cells (OPVs) or **D4** and **D5** which contain 2-cyanoacrylic acid group can be used as organic dyes of dye-sensitized solar cells (DSSCs).

Key Words : Bis-thienylanthracene derivatives, 2-Malononitrile, 2-Cyanoacrylic acid, OPVs, DSSCs.

Introduction

Thiophene-based conjugated materials are an important and prospect class of organic materials for their use in organic photovoltaic cells (OPVs),[1] dye-sensitized solar cells (DSSCs),[2-6] organic light-emitting diodes (OLEDs),[7] and organic thin film transistors (OTFTs).[8] Thiophene containing oligomers have been explored as active materials for organic semiconductors due to facile chemical modification of their structures which allow fine-tuning of their optical and electrical properties. Furthermore, these materials are attractive due to their low density, flexibility, and processibility over large coverage areas.[9] Thiophene-based poly(3-hexylthiophene) (P3HT) has been extensively applied and studied as electron donor in bulk heterojunction (BHJ).[10-11] Recently, Bader *et al.* have shown that oligothiophenes with tricyanovinyl (TCV) substitution which exhibit oxidations of more anodic potentials due to the electron-withdrawing nature of the tricyanovinyl group.[12-13] It is also reported that thiophene oligomers with α,ω-disubstitution and additional rings ($\geq$ 3) result in stable materials towards both oxidations and reductions.[12-13] For many cases, internal charge transfer (ICT) character occurring from an electron-rich unit to an electron-deficient unit has been used to obtain low band gap conjugation materials.[14-16] Recently, models have been proposed to estimate the material performance in BHJ solar cells.[17-19] The material must be air-stable and thus the HOMO energy level needs to be below the air oxidation threshold (*ca.* −5.27 eV or 0.57 V *vs* SCE).[20] The LUMO

energy level of the material must be positioned above that of the acceptor (i.e., [6,6]-phenyl C61 butyric acid methyl ester (PCBM)) by at least 0.2 ~ 0.3 eV to ensure efficient electron transfer from the material to the acceptor.[21] Therefore, the ideal donor HOMO energy level is recommended to range −5.2 ~ −5.8 eV and LUMO energy level to be −3.7 ~ −4.0 eV.

Dye-sensitized solar cells (DSSCs) have emerged as an important class of photovoltaic devices and are under intensive studies.[2,3] In most studied and efficient DSSCs, sensitizing dyes bound *via* carboxylate group to photoanode TiO_2 nanoparticles act as light-harvesting intermediates, absorbing visible and near-infrared radiation, injecting the resulting excited-state electrons into conduction band of the photoanode TiO_2, and being converted to their dye cations. To complete a photocurrent circuit the dye cations which are generated in the electron injection processes accept electrons from hole transport materials (HTM) regenerating dye molecules for continuous sensitizing.

As one of the crucial parts in DSSCs research, there have been many efforts to develop new pure organic dyes of donor-acceptor π-conjugate systems along with dyes of transition metal complex including ruthenium metal.[4] Organic dyes have many advantages over the dyes of metal complexes, such as lower cost, higher absorption coefficient and easy control of LUMO and HOMO redox potential levels. Successful dyes used in DSSCs should fulfill some essential characteristics. The dye is desired to cover the whole visible region of absorption spectrum and to have anchoring groups (-COOH, $-H_2PO_3$, $-H_2SO_3$, etc.) for a strong binding on to TiO_2 surface. The LUMO energy level of dye should be higher than the conduction band edge of TiO_2 (−4.4 eV) for a rapid and efficient electron transfer

process between the excited dye and conduction band of TiO$_2$. In contrast, the HOMO energy level of dye should be lower than that of HTM (−4.9 eV or 0.4 V *vs* NHE for I$^-$/I$^-_3$ of common DSSCs).

Anthracene is a good candidate for semiconductors because anthracene single crystals have good hole mobilities measured by time-of-flight photocurrent technique and have high chemical stabilities.[22] In our recent researches,[23-24] we synthesized new series of α,ω-dihexyl and -disilyl end-capped thienylanthracene oligomers containing 9,10-anthracene moiety in the center as our efforts to develop new semiconducting materials.
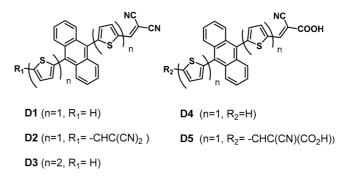
In this investigation, we designed and synthesized a series of new bis-thienylanthracene derivatives which contain 9,10-antracene moiety in the center and 2-methylenemalonotitrile or 2-cyanoacrylic acid functional group on the terminal thiophenes as electron-withdrawing groups (Scheme 1) aiming at a possible development of new electron donor materials for OPVs and (or) dyes for DSSCs. Herein we report the synthesis of the target bis-thienylanthracene derivatives and their optical, electrochemical and thermal properties.
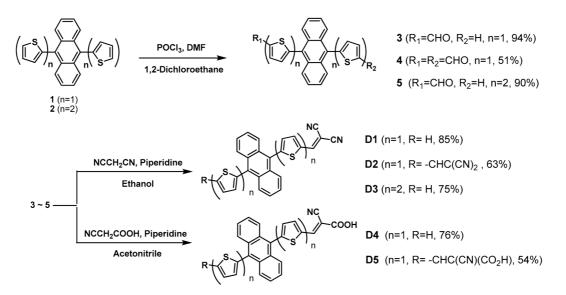
Results and Discussion

Synthesis. We designed and synthesized 9,10-bis(2-thienyl)anthracene derivatives **D1** ~ **D5** containing an anthracene unit in the center of molecules and electron withdrawing 2-methylenemalononitrile or 2-cyanoacrylic acid group on 2'-position of the terminal thiophene(s) to develop low band gap conjugate materials of donor-π-acceptor (D-π-A) type which might be used as a new electron donor for OPVs or dye for DSSCs (Scheme 1). The syntheses of the target molecules were achieved through three step synthetic route summarized in Scheme 2 starting from 9,10-bis(2-thienyl)anthracene (**1**) and 9,10-bis(2,2'-bithiophene-5-yl) anthracene (**2**) which were prepared by following reported

literature method.[23] Hydroformyl aldehyde groups could be introduced on 2'-position of the terminal thiophenes of **1** and **2** in a symmetric or asymmetric manner by using Vilsmeier-Haak reaction in moderate and very good yields (51 ~ 94%) to produce hydroformyl substituted bis-thienylanthracenes **3** ~ **5**. Knoevenagel reactions of hydroformyl bis-thienylanthra-cene **3** ~ **5** and malononitrile (or cyanoacetic acid) could lead to the production of the target molecules, the mono- or di-2-methylenemalononitrile (or 2-cyanoacrylic acid) containing thienylanthracene molecules **D1** ~ **D5** in moderate and good yields (54 ~ 85%). The synthesized materials **D1** ~ **D5** are soluble in organic solvent like chloroform and chloroform-methanol and could be purified by silica-gel column chromatography. Structures of the synthesized material **D1** ~ **D5** were characterized based on spectroscopic data including ^{1}H-NMR and high-resolution mass spectroscopy (HRMS).

Data obtained from ^{1}H-NMR spectra of bis-thienylan-thracene derivatives **D1** ~ **D5** have led to the full assignment of the structures along with high resolution mass spectral data. Fig. 1 shows ^{1}H-NMR spectra of 2-methylenema-lononitrile substituted bis-thienylanthracene **D1**, **D2** and **D3**. ^{1}H-NMR spectrum of bis-thienylanthracene **D1** which contains one 2-methylenemalononitrile group on the 2'-position of

D1 (n=1, R$_1$= H)   **D4** (n=1, R$_2$=H)

D2 (n=1, R$_1$= -CHC(CN)$_2$)   **D5** (n=1, R$_2$= -CHC(CN)(CO$_2$H))

D3 (n=2, R$_1$= H)

Scheme 1. Structure of bis-thienylanthracene derivatives **D1** ~ **D5**.

3 (R$_1$=CHO, R$_2$=H, n=1, 94%)

4 (R$_1$=R$_2$=CHO, n=1, 51%)

5 (R$_1$=CHO, R$_2$=H, n=2, 90%)

D1 (n=1, R= H, 85%)

D2 (n=1, R= -CHC(CN)$_2$, 63%)

D3 (n=2, R= H, 75%)

D4 (n=1, R=H, 76%)

D5 (n=1, R= -CHC(CN)(CO$_2$H), 54%)

Scheme 2. Synthesis of symmetric or unsymmetric bis-thienylanthracene derivatives **D1** ~ **D5**.
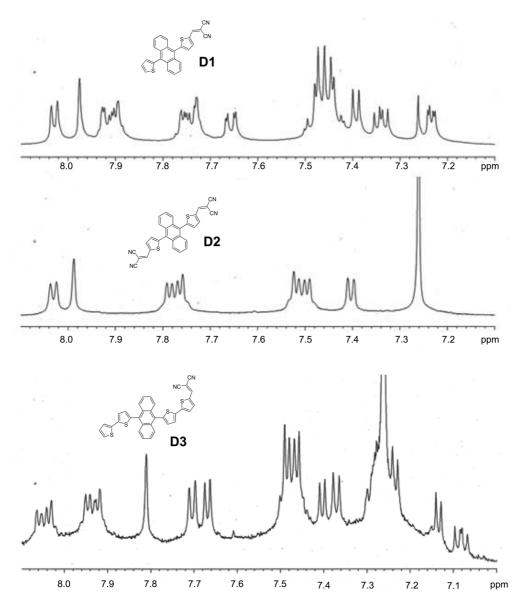
Figure 1. ^{1}H-NMR spectra of **D1**, **D2** and **D3**.

thiophene in one side of the molecule unsymmetrically shows a singlet at 7.97 ppm for 2-methylenemalonotitrile vinyl hydrogen and two doublets at 7.39 and 8.02 ppm (J = 3.9Hz) for two β-hydrogens of α-methylenemalonotitrile group substituted thiophene. Peaks for three hydrogens of monosubstituted thiophene of **D1** appear at 7.23 (dd, J = 3.5Hz, 1.2Hz), 7.34 (dd, J = 5.0Hz, 3.5Hz), and 7.65 ppm (dd, J = 5.0Hz, 1.2Hz) respectively. Peaks for total eight hydrogens of unsymmetrically subsitiuted anthracene of **D1** appear at 7.42-7.49 (m, 4H), 7.72-7.76 (m, 2H), and 7.89-7.92 ppm (m, 2H). Similarly ^{1}H-NMR spectrum of **D3** shows a singlet peak at 7.81 ppm for the 2-methylene-malonotitrile vinyl hydrogen and two doublets at 7.37 and 7.70 ppm (J = 3.9Hz) for two β-hydrogens of α-methylene-malonotitrile group substituted terminal thiophene. The peaks for three hydrogens of mono-substituted terminal thiophene of **D3** appear at 7.08 (dd, 1H, J = 5.0Hz, 3.5Hz)

and 7.29-7.27 ppm (m, 2H). Four doublets appear at 7.13, 7.24, 7.40, and 7.67 ppm (J = 3.6Hz) for four hydrogens of two internal disubstituted thiophene. Peaks for eight hydrogens of anthracene appear at 7.44-7.50 (m, 4H), 7.91-7.95 (m, 2H), and 8.03-8.06 ppm (m, 2H).

In contrast to the case of **D1** and **D3**, symmetrically substituted bis-thienylanthracene **D2** with two 2-methylene-malononitrile groups shows more simplified feature as expected in its ^{1}H-NMR spectrum which shows only two doublets for total four hydrogens of the thiophene at 7.40 and 8.03 ppm (J = 3.9Hz). Peaks for two 2-methylene-malonotitrile vinyl hydrogens appear at 7.98 ppm as singlet. Peaks for eight arene hydrogens of the symmetrically substituted anthracene appear at 7.49-7.52 (m, 4H) and 7.75-7.79 ppm (m, 4H).

Spectral data of ^{1}H-NMR spectra of **D4** and **D5** which have 2-cyanoacrylic acid group on 2'-position of the
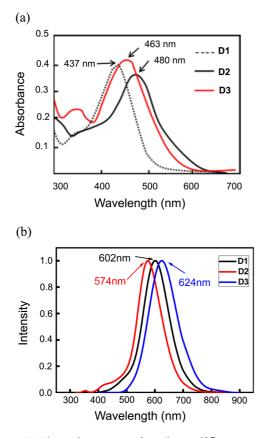
(a)

(b)

(a)

(b)

Figure 2. (a) Absorption spectra of **D1** (λ_{max} = 437 nm, ε_{max} = 7.8 × 10^3 $M^{-1}cm^{-1}$), **D2** (λ_{max} = 480 nm, ε_{max} = 8.4 × 10^3 $M^{-1}cm^{-1}$), and **D3** (λ_{max} = 463 nm, ε_{max} = 7.4 × 10^3 $M^{-1}cm^{-1}$) in CHCl₃ solution (5 × 10^{-4} M) and (b) normalized emission spectra in CHCl₃ solution (1 × 10^{-4} M) of **D1** ~ **D3**.

Figure 3. (a) Absorption spectra of **D4** (λ_{max} = 441 nm, ε_{max} = 2.0 × 10^4 $M^{-1}cm^{-1}$) and **D5** (λ_{max} = 441 nm, ε_{max} = 1.9 × 10^4 $M^{-1}cm^{-1}$) in CHCl₃ solution (5 × 10^{-4} M) and (b) normalized emission spectra of **D4** and **D5** in CHCl₃ solution (5 × 10^{-4} M).

terminal thiophene(s) also led to full assignments of their structures as in the cases of **D1**, **D2**, and **D3**.

¹H-NMR spectrum of bis-thienylanthracene **D4** which contains one 2-cyanoacrylic acid group on the 2'-position of thiophene shows a singlet at 7.94 ppm for 2-cyanoacrylic vinyl hydrogen and two doublets at 7.44 and 7.99 ppm (*J* = 3.9Hz) for two β-hydrogens of 2-cyanoacrylic acid group substituted thiophene. Peaks for three hydrogens of monosubstituted thiophene of **D4** appear at 7.33 (dd, *J* = 3.6Hz, 1.2Hz), 7.41 (dd, *J* = 5.1Hz, 3.6Hz), and 7.94 ppm (dd, *J* = 5.1Hz, 1.2Hz) respectively. Peaks for total eight hydrogens of unsymmetrically substitiuted anthracene of **D4** appear at 7.51-7.58 (m, 4H) and 7.76-7.81 (m, 2H). Symmetrically substituted bis-thienylanthracene **D5** with two 2-cyanoacrylic acid groups shows more simplified feature as in the case of **D2** in its ¹H-NMR spectrum which shows only two doublets for total four hydrogens of the thiophene at 7.35 and 7.98 ppm (*J* = 3.9Hz). Peaks for two 2-cyanoacrylic acid vinyl hydrogens appear at 7.90 ppm as singlet. Peaks for eight arene hydrogens of the symmetrically substituted anthracene appear at 7.50-7.53 (m, 4H) and 7.85-7.86 ppm (m, 4H).

Absorption and emission properties. The absorption and emission spectra of synthesized materials (**D1** ~ **D5**) are measured in 1.0×10^{-4} ~ 5.0×10^{-4} M in chloroform solution.
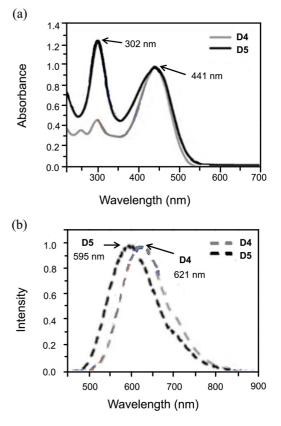
As expected, the absorption and emission properties vary as function of electron-withdrawing property and conjugation length. The long wavelength absorption maxima of synthesized **D1** ~ **D3** appear at 437, 480, and 463 nm respectively (Fig. 2. (a)). Symmetrically substituted bis-thienylanthracene **D2** with two 2-methylenemalononitrile groups **D2** which has an additional 2-methylenemalononitrile group exhibits 43 nm red-shifted absorption λ_{max} comparing with that of **D1** whcich contains only one 2-methylenemalononitrile group on one terminal thiophene moiety. Moreover **D2** has broader absorption region due to increase the number of 2-methylenemalononitrile groups in molecule than that of **D1**. As compared with the absorption maxima of **D1** and **D3**, increase of number of thienyl group by one from mono- to bi-thienyl-9,10-anthracenes (**D1** to **D3**) is observed to lead 27 nm bathochromic shift of absorption which is much larger in shift than those (3 ~ 4 nm bathochromic shift) observed in our previous studies with hexyl- and silyl end-capped bis-bithienyl-9,10-anthracene and bis-terthienyl-9,10-anthracene derivatives.[23,24] The emission maxima of **D1** ~ **D3** appear at 602, 574, and 624 nm respectively (Fig. 2. (b)). Bis-bithienylanthracene derivative **D3** has 16 nm red-shifted emission λ_{max} than that of bis-monothienyl-lanthracene **D1** according to the extension of conjugation length with one more of thiophene ring. The extent of

Table 1. Optical, electrochemical and thermal properties of the synthesized **D1** ~ **D5**

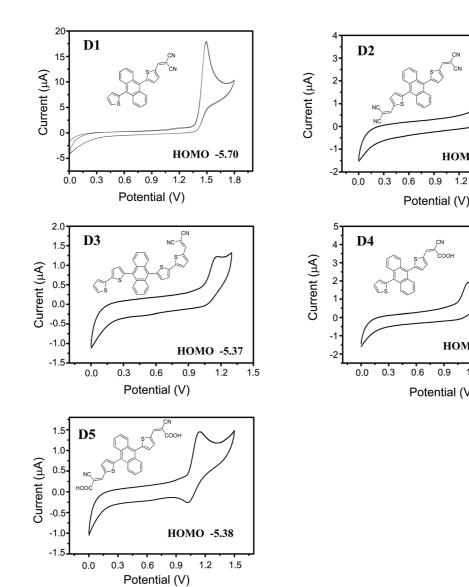| Dye	Abs $_{max}$ (nm)	ε_{max} (M^{-1}cm^{-1})	PL $_{max}$ (nm)	E_g^{op}	E_{HOMO} (eV)	E_{LOMO} (eV)	TGA (5% weight loss, °C)
D1	437	7.8×10^3	602	2.48	−5.70	−3.22	297
D2	480	8.4×10^3	574	2.18	−5.83	−3.65	−
D3	463	7.4×10^3	624	1.96	−5.37	−3.41	−
D4	441	2.0×10^4	621	2.33	−5.44	−3.11	453
D5	441	1.9×10^4	595	2.35	−5.38	−3.05	393

Figure 4. Cyclic voltammogram of synthesized bis-thienylanthracenes, **D1** ~ **D5**.

observed red-shifted emision 16 nm in **D3** is comparing with the red-shift (16 ~ 20 nm) observed in our previous studies with hexyl- and silyl end-capped bis-bithienyl-9,10-anthracene and bis-terthienyl-9,10-anthracene derivatives.[23,24] Derivatives **D1** ~ **D3** which contain 2-methylenemalono-nitrile groups exhibit very large molar extinction coefficient (ε_{max}) 7.4×10^3 ~ 8.4×10^3 M^{-1}cm^{-1}.

Bis-thienylanthracene derivatives **D4** and **D5** are designed to contain 2-cyanoacrylic acid which has –COOH anchoring group to make a strong binding the molecule to semiconductor TiO$_2$ nanoparticles surface instead of 2-methylenemalononitrile. The optical properties of **D4** and **D5** including their absorption and emission show different behaviors from those of **D1** ~ **D3** which contain 2-methylenemalononitrile groups. Whereas an additional 2-methylenemalononitrile group in **D2** comparing to **D1** has

led to a large bathochromic shift of absorption maxima (43 nm), **D5** with an additional 2-cyanoacrylic acid group has resulted in almost no bathochromic shift comparing with **D4** and both of **D4** and **D5** exhibit similar absorption shape and λ_{max} at 441 nm though there is hyperchromic change at 302 nm in the absorption of **D5** (Fig. 3. (a)). Bis-thienylanthracene derivatives **D4** and **D5** containing 2-cyanoacrylic acid have larger molar extinction coefficient (ε_{max}) 1.9×10^4 ~ 2.0×10^4 $M^{-1}cm^{-1}$ than those of **D1** ~ **D3** with 2-methylenemalononitrile group. The emission of **D5** shows unexpectedly emission maxima at shorter wavelength than that of **D4**. The emission maxima of **D4** and **D5** appear at 621 and 595 nm respectively (Fig. 3. (b)). The absorption and emission properties of synthesized materials are summarized in Table 1.

Electrochemical Properties. The electrochemical behaviors of the synthesized bis-thienylanthracenes **D1** ~ **D5** were investigated by using cyclic voltammetry. A three electrode cell used to make measurment on substrates in 0.1 M of TBAP in CH_2Cl_2 at a scan rate of 100 $mV·s^{-1}$. For this purpose, Ag/AgCl was employed as the reference electrode, a platinum electrode as working electrode, and a Pt wire as counter electrode (Fig. 4). The band gap energies between HOMO-LUMO levels of the **D1** ~ **D5** could be estimated to be 2.48, 2.18, 1.96, 2.33, and 2.33 eV respectively from the absorption end-edge 499, 568, 632, 531, and 531nm of their UV-vis absorption spectra. The HOMO energy level of the **D1** ~ **D5** were determined to be −5.70, −5.83, −5.37, −5.44, and −5.38 eV respectively by assuming that the energy of Fc/Fc$^+$ is −4.8 eV. Their LUMO energy levels were calculated to be −3.22, −3.65, −3.41, −3.11, and −3.05 eV from their HOMO energy levels and the optical band gap energies obtained from their absorption end-edge in UV-vis absorption spectra.

The oxidation potential data indicate that the synthesized materials (**D1** ~ **D5**) have good air stability, the HOMO energy level being below the air oxidation threshold (ca. −5.27

eV or 0.57 V *vs* SCE). The LUMO energy levels of the materials are positioned above the LUMO energy level of the best known acceptor ([6,6]-phenyl C61 butyric acid methyl ester (PCBM)) by 0.65 ~ 1.25 eV to ensure efficient electron transfer from the material to the acceptor in BHJ solar cells. All they fit well on the ideal HOMO-LUMO energy level range of electron donor materials towards electron acceptor PCBM for OPVs (Fig. 5). The estimated LUMO energy levels (−3.11 and −3.05 eV) of synthesized bis-thienylanthracene **D4** and **D5** are higher than energy level of conduction band (−4.4 eV) and their HOMO energy levels (−5.44 and −5.38 eV) are lower than the oxidation potential of a common HTM material (I^-/I^-_3, −4.9 eV or 0.4 V *vs* NHE) of DSSCs strongly support that they can be a possible candidate for organic dyes of DSSCs.

Thermal Properties. The thermal stability of synthesized materials is an important parameter for their device application. Thermal stabilities of synthesized bis-thienylanthracenes **D1**, **D4**, and **D5** were measured by thermogravimetric analysis (TGA). TGA curves showed that **D4** and **D5** exhibit better thermal stability than **D1** (Fig. 6) indicating that substitution of 2-cyanoacrylic acid (**D4**) gives better thermal stability than that of 2-methylenemalononitrile substitution (**D1**). The TGA thermograms of bis-thienylanthracene **D1**, **D4**, and **D5** revealed that 5% weight loss occurs on heating at about 297 °C, 453 °C, and 393 °C respectively. Bis-thienylanthracene **D4** which has one 2-cyanoacrylic acid group on a terminal thiophene moiety in an unsymmetric manner is observed to be thermally stable up to 400 which support that **D5** can be applied as a stable organic material of OPVs or DSSCs. **D4** loses 21% weight at 522 °C which corresponds to the loss of gem-cyanocarboxymethylidene (molecular weight = 83) and **D5** loses 34% weight at 530 °C which indicates loss of two gem-cyanocarboxymethylidene parts (molecular weight = 169) in the molecule. Bis-thienylanthracene **D1** loses about 58% weight on heating up to 350 °C which corresponds to the
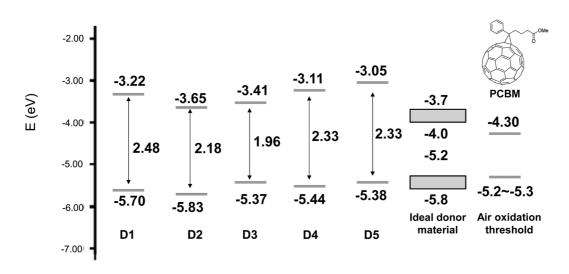

Figure 5. Energy levels of synthesized bis-thienylanthracenes, **D1** ~ **D5**, fit well on the ideal range of HOMO-LUMO energy levels of electron donor towards acceptor PCBM.
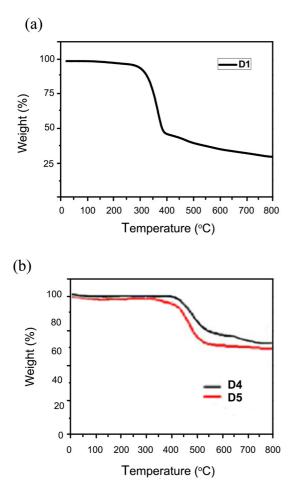
(a)

(b)

Figure 6. Thermogravimetric analysis (TGA) curves of synthesized bis-thienylanthracenes (a) **D1**, (b) **D4**, and **D5**.

loss of thiophene units along with 2-methylenemalonitrile group from the molecule leaving the central anthracene unit.

Experimental Section

Chemicals and Instruments. Chemical reagents were purchased from Aldrich Chemical Co. and were used without further purification. Tetrahydrofuran (THF) was distilled over sodium in the presence of benzophenone. ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Mercury 300 MHz spectrometer. The absorption and photoluminescence (PL) spectra were measured using a Jasco V-570 UV-vis spectrometer and a Hitach F-4500 fluorescence spectrometer in chloroform respectively at room temperature. The thermal gravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA 851 and 822 analyzer under N_2 atmosphere at a rate of 10 °C/min. The electrochemical experiments were performed using a CHI600C and the electrochemical cell was consisted of the platinum electrode (2 mm diameter), a Pt wire counter electrode, and a Ag/AgCl reference electrode. The electrochemical properties were evaluated at room temperature by cyclic voltammetry, using tetrabutylammonium perchlorate (Bu_4NClO_4, TBAP)

and dichloromethane (Aldrich, HPLC grade) as supporting electrolyte.

5-(10-(Thiophen-2-yl)anthracene-9-yl)thiophene-2-carbaldehyde (3): Phosphorous oxychloride (0.12 mL, 1.4 mmol) was added to a solution of 9,10-bis-(2-thienyl) anthracene[23] (1 g, 0.5 mmol) and DMF (0.11 ml, 1.4 mmol) in 1,2-dichloroethane (12 mL) cooled in an ice bath. The solution was then warmed up to room temperature and heated to reflux. Upon refluxing overnight the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (50 mL) and stirred for several hours to complete the hydrolysis. The yellow suspension formed was extracted with dichloromethane (3 × 300 mL). The organic layer was combined and washed with water (1 × 100 mL), dried over Na_2SO_4, and concentrated *in vacuo.* Column chromatography of the residue over silica gel (100% chloroform) yielded **3** as yellow crystals (0.23 g, 94% yield). $R_f = 0.5$

^{1}H-NMR (CDCl$_3$) δ 7.23 (dd, 1H, $J = 3.6$Hz, 1.2Hz), 7.35-7.32 (m, 2H, thiophene-H), 7.47-7.41 (m, 4H, Ar-H), 7.65 (dd, 1H, $J = 5.2$ Hz, 1.2Hz, thiophene-H), 7.807-7.772 (m, 2H, Ar-H), 7.92-7.88 (m, 2H, Ar-H), 8.01 (d, 1H, $J = 3.6$Hz, thiophene-H), 10.07 (s, 1H, -C<u>H</u>O)

5,5'-(Anthracene-9,10-diyl)dithiophene-2,2'-dicarbalde-hyde (4): Phosphorous oxychloride (0.24 mL, 2.8 mmol) was added to a solution of 9,10-bis(2-thienyl)anthracene[23] (1 g, 0.5 mmol) and DMF (0.22 ml, 2.8 mmol) in 1,2-dichloroethane (20 mL) cooled in an ice bath. The solution was then warmed up to room temperature and heated to reflux. Upon refluxing overnight the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (50 mL) and stirred for several hours to complete the hydrolysis. The yellow suspension formed was extracted with dichloromethane (3 × 300 mL). The organic layer was combined and washed with water (1 × 100 mL), dried over Na_2SO_4, and concentrated *in vacuo.* Column chromatography of the residue over silica gel (100% chloroform) yielded **4** as yellow crystals (0.13 g, 51% yield). $R_f = 0.25$

^{1}H-NMR (CDCl$_3$) δ 7.34 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.48-7.44 (m, 4H, Ar-H), 7.81-7.78 (m, 4H, Ar-H), 8.01 (d, 1H, $J = 3.6$Hz, thiophene-H), 10.07 (s, 2H, -C<u>H</u>O)

5'-(10-(2,2'-Bithiophen-5-yl)anthracen-9-yl)-2,2'-bithio-phene-5-carbaldehyde (5): Phosphorous oxychloride (0.12 mL, 1.4 mmol) was added to a solution of 9,10-bis(2,2'-bithiophene-5-yl)anthracene[23] (1 g, 0.5 mmol) and DMF (0.11 ml, 1.4 mmol) in 1,2-dichloroethane (20 mL) cooled in an ice bath. The solution was then warmed up to room temperature and heated to reflux. Upon refluxing overnight the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (50 mL) and stirred for several hours to complete the hydrolysis. The yellow suspension formed was extracted with dichloro-methane (3 × 300 mL). The organic layer was combined and washed with water (1 × 100 mL), dried over Na_2SO_4, and concentrated *in vacuo.* Column chromatography of the residue over silica gel (100% chloroform) yielded **5** as

yellow crystals (0.2 g, 90% yield). $R_f = 0.6$

^{1}H-NMR (CDCl$_3$) δ 7.07 (dd, 1H, $J = 5.2$Hz, 3.6Hz, thiphene-H), 7.13 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.20 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.29 (m, 2H, thiophene-H), 7.40 (d, 1H, $J = 3.6$Hz), 7.46 (m, 4H, ArH), 7.59 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.73 (d, 1H, $J = 4.2$Hz, thiophene-H), 7.95 (m, 2H, ArH), 8.03 (m, 2H, ArH), 9.91 (s, 1H,-C$\underline{H}$O), ^{13}C-NMR (CDCl$_3$) δ 123.8, 123.9, 124.6, 125.9, 126.2, 126.3, 126.8, 127.9, 128.9, 130.4, 130.9, 131.3, 131.4, 137.1, 137.5, 137.6, 139.1, 141.1, 141.9, 146.9, 182.5

2-((5-(10-(Thiophen-2-yl)anthracen-9-yl)thiophen-2-yl) methylene)malononitrile (D1): The thiophene carbaldehyde compound **3** (0.26 g, 0.62 mmol), malononitrile (0.07 g, 0.96 mmol), ethanol (20 mL), and piperidine (0.2 ml) were mixed together and heated at boiling temperature for 6 h. The clear red solution formed was cooled to room temperature to yield a dark colored precipitate. It was washed with chloroform (20 ml) and then with water (20 ml). Column chromatography of the residue over silica gel (100% chloroform) yielded **D1** as yellow crystals (0.22 g, 85% yield). ^{1}H-NMR (CDCl$_3$) δ 7.23 (dd, 1H, $J = 3.5$Hz, 1.2Hz, thiophene-H), 7.34 (dd, 1H, $J = 5.0$Hz, 3.5Hz, thiophene-H), 7.39 (d, 1H, $J = 3.9$Hz, thiophene-H), 7.42-7.49 (m, 4H, ArH), 7.65 (dd, 1H, $J = 5.0$Hz, 1.2Hz, thiophene-H), 7.72-7.76 (m, 2H, ArH), 77.89-7.92 (m, 2H, ArH), 7.97(s, 1H, -C$\underline{H}$C(CN)$_2$), 8.02 (d, 1H, $J = 3.9$Hz, thiophene-H), HRMS (M$^+$ 418.0603, Calcd. 418.0598).

2,2'-(5,5'-(Anthracene-9,10-diyl)bis(thiophene-5,2-diyl)) bis(methan-1-yl-1-ylidene)dimalononitrile (D2): Thiophene dicarbaldehyde compound **4** (0.30 g, 0.62 mmol), malononitrile (0.16 g, 1.56 mmol), ethanol (30 mL), and piperidine (0.3 ml) were mixed together and heated at boiling temperature for 6 h. The clear red solution formed was cooled to room temperature to yield a dark colored precipitate. It was washed with chloroform (20 ml) and then with water (20 ml). Column chromatography of the residue over silica gel (methanol:chloroform = 1:4) yielded **D2** as yellow crystals (0.19 g , 63% yield). ^{1}H-NMR (CDCl$_3$) δ 7.40 (d, 2H, $J = 3.9$Hz, thiophene-H), 7.49-7.52 (m, 4H, ArH), 7.75-7.79 (m, 4H, ArH), 7.98 (s, 2H, -C$\underline{H}$C(CN)$_2$), 8.03 (d, 2H, $J = 3.9$Hz, thiophene-H), HRMS (M$^+$ 494.0664, Calcd. 494.0660).

2-((5'-(10-(2,2'-Bithiophen-5-yl)anthracen-9-yl)-2,2'-bithiophen-5-yl)methylene)malononitrile (D3): The bithiophene carbaldehyde compound **5** (0.33 g, 0.62 mmol), malononitrile (0.07 g, 0.96 mmol), ethanol (20 mL), and piperidine (0.2 ml) were mixed together and heated at boiling temperature for 6 h. The clear red solution formed was cooled to room temperature to yield a dark colored precipitate. It was washed with chloroform (20 ml) and then with water (20 ml). Column chromatography of the residue over silica gel (chloroform) yielded **D3** (0.27 g, 75% yield). ^{1}H-NMR (CDCl$_3$) δ 7.08 (dd, 1H, $J = 4.8$ Hz, 3.6Hz, thiophene-H), 7.13 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.24 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.29-7.27 (m, 2H, thiophene-H), 7.37 (d, 1H, $J = 3.9$Hz, thiophene-H), 7.40 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.44-7.50 (m, 4H, Ar-H), 7.67 (d, 1H, $J = 3.6$Hz, thiophene-H), 7.70(d, 1H, $J = 3.9$Hz, thiophene-

H), 7.81 (s, 1H, -C$\underline{H}$C(CN)$_2$), 7.91-7.95 (m, 2H, Ar-H), 8.03-8.06 (m, 2H, Ar-H), HRMS (M$^+$ 582.0350, Calcd. 582.0353).

2-Cyano-3-(5-(10-(thiophen-2-yl)anthracen-9-yl)thiophen-2-yl)acrylic acid (D4): Thiophene carbaldehyde compound **3** (0.26 g, 0.62 mmol), cyanoacetic acid (0.10 g, 0.96 mmol), ethanol (30 mL), and piperidine (0.3 ml) were mixed together and heated at boiling temperature for 6 h. The clear red solution formed was cooled to room temperature to yield a dark colored precipitate. It was washed with chloroform (20 ml) and then with water (20 ml). Column chromatography of the residue over silica gel (methanol: chloroform 1:4) yielded **D4** (0.21 g, 76% yield).

^{1}H-NMR (DMSO-d_6) δ 7.33 (dd, 1H, $J = 3.6$Hz,1.2 Hz, thiophene-H), 7.41 (dd, 1H, $J = 5.1$Hz,3.6 Hz, thiophene-H), 7.44 (d, 1H, $J = 3.9$ Hz, thiophene-H), 7.51-7.58 (m, 4H, Ar-H), 7.76-7.81 (m, 4H, Ar-H), 7.94 (dd, 1H, $J = 5.1$Hz,1.2 Hz, thiophene-H), 7.94 (s, 1H, -C$\underline{H}$(CN)(COOH)), 7.99 (d, $J = 3.9$ Hz, thiophene-H), 8.28 (s, 1H, -COO$\underline{H}$), HRMS (M$^+$ 437.0549, Calcd. 437.0544).

3,3'-(5,5'-(Anthracene-9,10-diyl)bis(thiophene-5,2-diyl)) bis(2-cyanoacrylic acid) (D5): The compound **4** (0.30 g, 0.62 mmol), cyanoacetic acid (0.15 g, 1.56 mmol), ethanol (30 mL), and piperidine (0.3 ml) were mixed together and heated at boiling temperature for 6 hours. The clear red solution formed was cooled to room temperature to yield a dark colored precipitate. It was washed with chloroform (20 ml) and then with water (20 ml). Column chromatography of the residue over silica gel (methanol : chloroform / 1:4) yielded **D5** (0.18 g , 54% yield).

^{1}H-NMR (CD$_3$OD) δ 7.35 (d, 2H, $J = 3.9$Hz, thiophene-H), 7.50-7.53 (m, 4H, Ar-H), 7.85-7.86 (m, 4H, Ar-H), 7.90 (s, 2H, -C$\underline{H}$(CN)(COOH)), 7.98 (d, 2H, $J = 3.9$Hz, thiophene-H), 8.34 (s, 2H, -COO$\underline{H}$), HRMS (M$^+$ 532.0560, Calcd. 532.0551).

Conclusion

We successfully synthesized and characterized a series of new bis-thienylanthracene derivatives **D1** ~ **D5**, containing 9,10-anthracene moiety in the center and 2-methylenemalonotitrile or 2-cyanoacrylic acid on the terminal thiophenes as electron-withdrawing groups. The target molecules were obtained by Stille- and Suzuki-coupling reaction, Vilsmeier-Haak reaction, and Knoevenagel reactions as key step reactions. The synthesized materials were characterized by ^{1}H-NMR and high-resolution mass spectroscopy (HRMS). Their optical, electrochemical, and thermal properties were measured. They have absorption λ_{max} range at 437 ~ 480nm and ε_{max} 7.4 × 10^3 ~ 2.0 × 10^4 M^{-1}cm^{-1}. The substitution of 2-cyanoacrylic acid group has greater value of ε_{max} than that of 2-methylenemalonotitrile substitution. The synthesized materials (**D1** ~ **D5**) show good air stability, the HOMO energy level being below the air oxidation threshold (ca. −5.27 eV or 0.57 V *vs* SCE) and the LUMO energy levels are positioned above the LUMO energy level of the acceptor (PCBM) by 0.65 ~ 1.25 eV. Their HOMO-LUMO energy

levels belong to the HOMO-LUMO range of ideal donor materials for OPVs. TGA curves showed that **D4** and **D5** exhibited good thermal stability and the weight loss of **D4** and **D5** were less than 5% on heating to about 453 °C and 393 °C. **D4** was thermally stable up to 400 °C and its thermal stability leads **D4** to be applicable to device as a stable organic material. **D4** loses 21% weight at 522 °C and **D5** loses 34% weight at 530 °C which correspond to the loss of the unit of gemcyanocarboxymethylidene(s). Their optical properties and LUMO energy levels measured suggest that they can serve as potential candidates for electron donor materials of organic photovoltaic cells (OPVs) or **D4** and **D5** which contain 2-cyanoacrylic acid group can be used as organic dyes of dye-sensitized solar cells (DSSCs).

References

1. (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474. (b) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (c) Kang, M. S.; Oh, J. B.; Roh, S. G.; Kim, M.-R.; Lee, J. K.; Jin, S.-H.; Kim, H. K. *Bull. Korean Chem. Soc.* **2007**, *28*, 33.
2. Robertson, N. *Angew. Chem. Int. Ed.* **2006**, *45*, 2338.
3. Hamann, T. W.; Jensen, R. A.; Martinson, A. B. F.; Van Ryswyk, H.; Hupp, J. T. *Energy Environ. Sci.* **2008**, *6*, 66.
4. Chen, Z.; Li, F.; Huang, C. *Curr. Org. Chem.* **2007**, *11*, 1241.
5. Kalaignan, G. P.; Y. S. Kang, Y. S. *J. Photochem. Photobiol. C.*

6. Gratzel, M. *MRS Bulletin* **2005**, *30*, 23.
7. (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Lee, W. L.; An, J.-G.; Yoon, H.-K.; Jang, H.; Kim, N. G.; Do, Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 1569.
8. (a) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365. (b) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478.
9. Rogers, J. A.; Bao, Z. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 3327.
10. Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* **2005**, *87*, 083506.
11. Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.
12. Bader, M. M.; Custelcean, R.; Ward, M. D. *Chem. Mater.* **2003**, *15*, 616.
13. Fraxedas, J. *Adv. Mater.* **2002**, *14*, 1603.
14. Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355.
15. Mullekom, H. A. M. v.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R.* **2001**, *32*, 1.
16. Ajayaghosh, A. *Chem. Soc. Rev.* **2003**, *32*, 181.
17. Scharber, M. C.; Muhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.
18. Thompson, B. C.; Kim, Y. G.; Reynolds, J. R. *Macromolecules* **2005**, *38*, 5359.
19. Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. *Appl. Phys. Lett.* **2006**, *88*, 093511.
20. de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einhard, R. E. F. *Synth. Met.* **1997**, *87*, 53-59.
21. Choulis, S. A.; Nelson, J.; Kim, Y.; Poplavskyy, D.; Kreouzis, T.; Durrant, J. R.; Bradley, D. D. C. *Appl. Phys. Lett.* **2003**, *83*, 3812.
22. Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
23. Choi, J. H.; Cho, D. W.; Jin, S. H.; U. C. Yoon, *Bull. Korean Chem. Soc.* **2007**, *28*(7), 1175
24. Choi, J. H.; Cho, D. W.; Sung, N. K.; Jin, S. H.; U. C. Yoon, *Bull. Korean Chem. Soc.* **2007**, *28*(11), 1931.
25. J. T. Pinhey, E. G. Roche, *J. Chem. Soc. Perkin Trans.* **1988**, *1*, 2415.