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Donor/acceptor-substituted anthradithiophene materials: synthesis, optical and electrochemical properties

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ABSTRACT

The synthesis and characterization of two new anthradithiophene (ADT) derivatives bearing electron donating (triphenylamine) or accepting (5-formylthiophen-2-yl unit) moieties have been performed to assess their potential as materials for organic photovoltaics. Optical spectroscopy was used to evaluate the effect of electron rich/poor substituents on the visible absorption spectrum and on the stability towards photo-oxidation. The results are interpreted with the assistance of quantum-chemical calculations and cyclic voltammetry experiments.

1. Introduction

Over the past 10 years, many studies have been reported in the literature on several organic semiconductors, such as acenes, oligothiophenes, and their use in various electronic devices (field-effect transistors, light-emitting diodes, photovoltaic cells and sensors).[1] Currently, fused (hetero)acenes represent one of the most studied categories of organic semiconductors. Recent publications described the functionalization of pentacene or anthradithiophene cores by several groups, such as trialkylsilylethynyl or thiophenyl groups to lead to soluble semiconductors.[2] Additionally, it has been demonstrated that the presence of such substituents enhances the stability of these derivatives towards photo-oxidation, especially in solution.[2a–c,3] With this synthetic strategy, it has been possible to reach extended fused linear (hetero) acenes.[2,4] Chemical reactions involving these compounds were also rendered feasible and were engaged in oligomerization and/or polymerization processes.[5] For example, we have recently reported the synthesis of dimers of anthrathiophene and anthradithiophene derivatives.[6] However, the stability improvements provided by these substituents still remain limited. Therefore, we investigated the influence of the substitution of the ADT skeleton by electron withdrawing or donating groups on its stability towards photo-induced degradation. We describe the synthesis and the characterization of new anthradithiophene (ADT) derivatives bearing triphenylamine as electron donor (**DADT**) and 5-formylthiophen-2-yl group as electron acceptor (**AADT**) moieties. Octyl chains were attached on positions 2 and 8 of the ADT skeleton in order to fulfil solubility requirements and to prevent side reactions, which could occur by the metallation of those positions using *n*-BuLi.[6] The spectroscopic and electrochemical properties of these semiconductors were evaluated and supported by quantum-chemical calculations.

2. Results and discussion

DADT and **AADT** were prepared as presented in Scheme 1. Synthesis of the key intermediate 2,8-dioctylanthradithiophene-5,11-dione **1** was achieved in three steps with an overall yield of 63%, starting from commercial thiophene-2,3-dicarboxaldehyde. Protection of the aldehyde functions of the latter was carried out in quantitative yield by reaction with ethylene glycol, in the presence of *p*-toluenesulfonic acid monohydrate.[4f] 5-Octylthiophene-2,3-dicarboxaldehyde (**3**) was then obtained in 75% yield by metallation of the protected compound **2** using *n*-BuLi, followed by reaction of the organolithium intermediate with 1-iodooctane and

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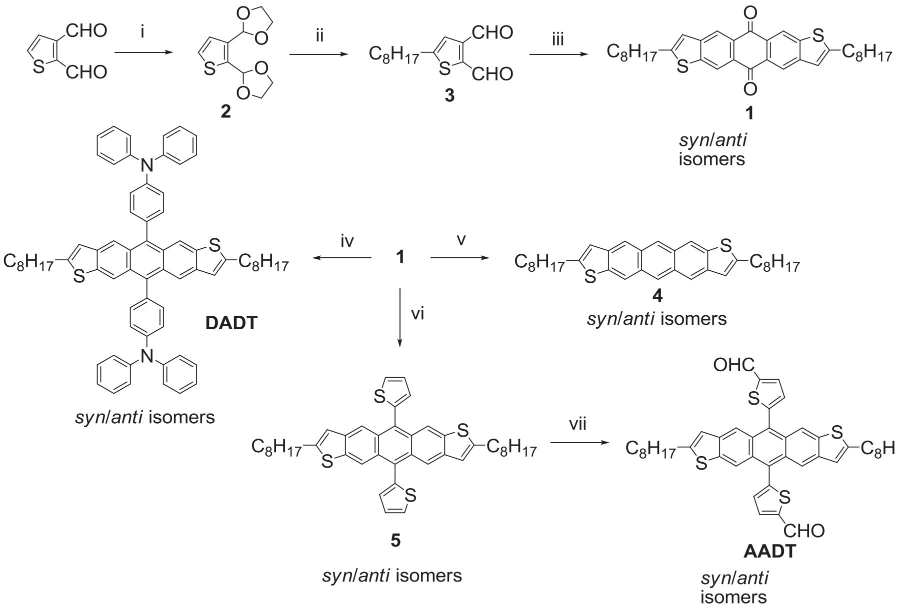

Scheme 1. Synthesis of ADT derivatives **4**, **5**, **AADT** and **DADT**. Reagents and conditions: (i) ethylene glycol/*p*-TSA/toluene/reflux/16 h/quant.; (ii) (1) *n*-BuLi/THF/−80 °C, (2) 1-iodooctane/−80 °C to rt/16 h, (3) HCl (3 M)/reflux/1 h/75%; (iii) KOH (5%)/cyclohexane-1,4-dione/ethanol/84%; (iv) (1) 4-bromo-*N*,*N*-diphenylaniline/*n*-BuLi/THF/−80 °C, (2) $SnCl_2$/HCl (6 M)/rt/80%; (v) (1) $LiAlH_4$/THF/reflux/30 min, (2) HCl (6 M)/reflux/3 h/62%; (vi) (1) thiophene/*n*-BuLi/THF/−80 °C, (2) $SnCl_2$/HCl (6 M)/rt/86%; (vii) (1) *n*-BuLi/THF/−30 °C, (2) DMF/−80 °C to rt/66%.

then by deprotection of the aldehyde functions using 3 M HCl_{aq} solution. Compound **1** was produced in 84% yield by reaction of dialdehyde **3** with cyclohexane-1,4-dione in presence of 5% KOH_{aq} solution. **DADT** and derivative **5** were achieved with yields of, respectively, 80% and 86%, by reaction of the diquinone **1** with the corresponding lithium intermediates of 4-bromo-*N*,*N*-diphenylaniline (for **DADT**) and thiophene (for **5**) followed by reduction/deoxygenation using $SnCl_2$ in 6 M HCl_{aq} solution. Metallation of the thienyl units, on positions 5,11 of the ADT **5** backbone using *n*-BuLi, followed by reaction of the corresponding dilithiated species with DMF, afforded **AADT** in good yield (66%). Finally, in order to compare the effect of electron donating or withdrawing groups on the stability towards photo-oxidation of the ADT core, the synthesis of 2,8-dioctylanthradithiophene **4** was performed. This control compound was prepared in 62% yield by reduction of the diquinone **1** using $LiAlH_4$. Note that all ADT derivatives were produced as a mixture of isomers since their synthesis were made starting from a mixture of *syn*/*anti* isomers of 2,8-dioctylanthradithiophene-5,11-dione **1**.

Except ADT **4**, other compounds possess reasonable solubilities (up to 10^{-2} M) in several common organic solvents, such as chloroform, dichloromethane, tetrahydrofuran, toluene, *o*-dichlorobenzene and nitrobenzene; and were characterized by NMR and UV/vis spectroscopies, mass spectrometry and cyclic voltammetry (See Supplementary data).

Optical measurements were carried out in chloroform solutions of the compounds and were compared to theoretical simulations. To do so, geometry optimizations have been performed at the density functional theory (DFT) level, using the B3LYP functional[7] and the 6-31G(d,p) basis set. The octyl chains in 2,8 positions of the ADT skeleton were replaced by methyl chains in the geometry optimizations to reduce the computational costs and since they do not contribute to the description of the frontier electronic levels and hence the first absorption peaks. The pendant thiophene and triphenylamine (TPA) units are found to be almost perpendicular to the conjugated core in the optimized geometry, i.e., 89° and 79° for the pendant thiophene and TPA units, respectively. The vertical transition energies to the lowest excited states of the isolated compounds were computed from the optimized geometries with the time-dependent density functional theory (TD-DFT) formalism,[8] using the same functional and basis set. Gaussian 03 package was used for all calculations.[9]

Compounds **5**, **AADT** and **DADT** present spectral profiles similar to that of the control ADT **4**, showing an intense band in the range of 300–315 nm and three additional peaks located at lower energies (Table 1, Fig. 1). Since the calculations yield a single optically-coupled excited state in this energy range, the latter are assigned to vibronic satellites (Fig. SI24). Bathochromic shifts of the absorption maxima of, respectively, 22 nm (0.11 eV) and 27 nm (0.14 eV) are observed going from **4** to **DADT** and from **4** to **5**. These observed red shifts are due to the substitution of the ADT **4** skeleton

Table 1
Experimental optical data and calculated vertical transition energies (Δ*E*vertical) to the lowest excited state as well as calculated HOMO and LUMO values of **4**, **5**, **AADT** and **DADT** in the gas phase

Product	Experimental				Theory	
	λ_{abs} [nm (eV)]	λ_{em}[a] [nm (eV)]	*Eg*[b] [eV]	Δ*E*vertical [nm (eV)]	H (eV)	L (eV)
DADT	312 (3.99) 440 (2.82) 472 (2.63) 505 (2.46)	530 (2.34)	2.40	510 (2.43)	−4.56	−1.80
AADT	310 (4.00) 455 (2.73) 483 (2.57) 516 (2.41)	577 (2.15)	2.31	524 (2.37)	−5.07	−2.38
5	310 (4.00) 446 (2.78) 475 (2.61) 510 (2.43)	528 (2.35)	2.40	517 (2.40)	−4.72	−2.02
4	304 (4.08) 424 (2.93) 452 (2.75) 483 (2.57)	493 (2.52)	2.54	490 (2.53)	−4.69	−1.86

[a] $\lambda_{excitation}=\lambda_{abs}$ of the lower energy band.

[b] Optical band gaps determined from the intersection between normalized absorption and emission spectra.

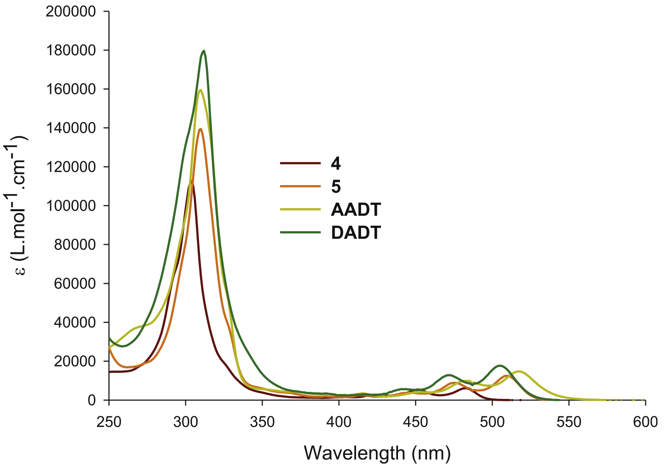

Fig. 1. UV/vis spectra of **4**, **5**, **AADT** and **DADT** in $CHCl_3$ (10^{-5} M).

on its 5,11 positions by triphenylamine (**DADT**) and thiophenyl (**5**) units. **AADT** presents also a slightly red-shifted absorption maxima of 6 nm (0.02 eV) compared to its synthetic precursor **5**. The calculated transition energies follow the same behaviour going from **4** to **5** (27 nm (0.13 eV)), from **4** to **DADT** (20 nm (0.10 eV)) and from **5** to **AADT** (7 nm (0.03 eV)). The good agreement between the experimental measurements and the calculated data points to the relevance of combining DFT and TDFT methods to characterize the optical properties of ADT derivatives since this allows: (i) explaining the relative shifts between the energy of the first excited state of each derivative and; (ii) rationalizing the nature of the low energy peaks and therefore ruling out any extrinsic effects in the experimental measurements. This also demonstrates that this methodology can prove useful to design new ADT derivatives prior to their synthesis.

All ADT derivatives show fluorescence in solution (Fig. 2). Substitution of the ADT core by thiophenyl and triphenylamine groups leads to a red shift of the emission maximum, which is in agreement with the observations made in the UV/vis spectra. Bathochromic shifts of 35 nm (0.17 eV) and of 37 nm (0.18 eV) are measured from **4** to **5** and from **4** to **DADT**, respectively. In addition, a displacement of 49 nm (0.20 eV) to the lower energies is noted from **5** to **AADT**. The optical band gaps, listed in Table 1, were estimated from the intersection of the normalized absorption and emission spectra of all ADT derivatives. The band gap value decreases from 2.54 eV for **4** to 2.40 eV for **5** and **DADT** and to 2.31 eV for **AADT**.

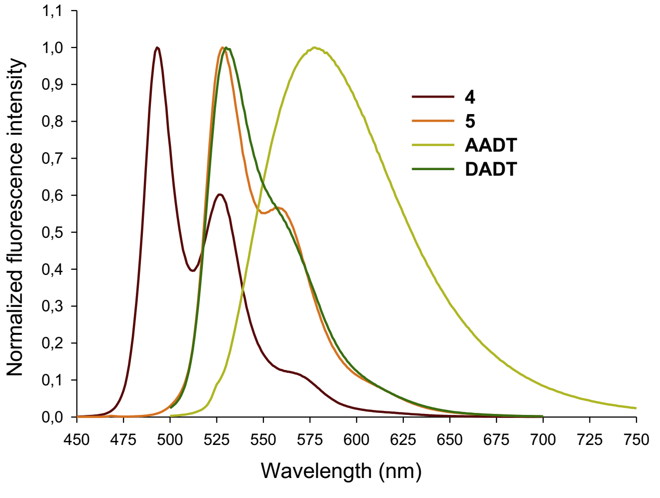

Fig. 2. Emission spectra of **4** ($\lambda_{excitation}$=483 nm), **5** ($\lambda_{excitation}$=510 nm), **AADT** ($\lambda_{excitation}$=516 nm) and **DADT** ($\lambda_{excitation}$=505 nm) in $CHCl_3$ (10^{-5} M).

The stability of **4**, **5**, **AADT** and **DADT** towards photo-oxidation was investigated by monitoring the absorbance decay of 10^{-5} M chloroform solutions stored in the dark at room temperature, under ambient atmosphere and exposed to 10 cm of 8W UV/vis lamps (λ_1=244 nm and λ_2=366 nm) (Fig. 3 and SI1–4).

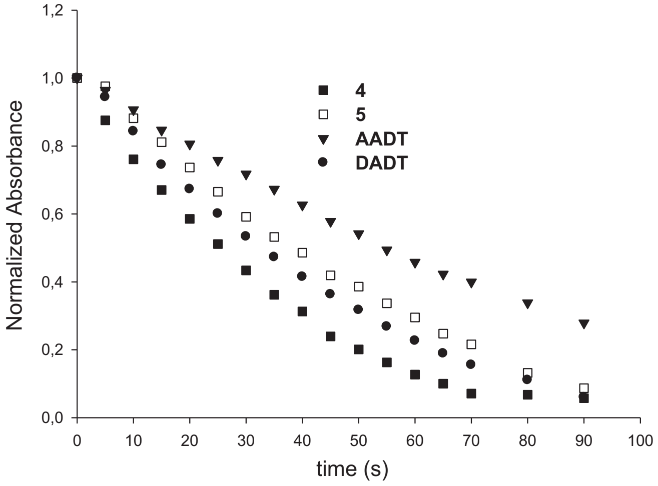

Fig. 3. Evolution of the lower energy band absorptions of **4** (483 nm), **5** (510 nm), **AADT** (516 nm) and **DADT** (505 nm) (10^{-5} M) in $CHCl_3$, under UV/vis lamps exposure (λ_1=244 nm and λ_2=366 nm) and at room temperature under ambient atmosphere.

Taking into account an absorbance decay of 50% of the lower energy bands of all ADT compounds, the stability order observed is as follows: **AADT** (58 s)>**5** (40 s)>**DADT** (35 s)>**4** (25 s). ADT derivatives substituted on the central ring of the ADT core are known to be more stable towards photo-degradation than those without any 'protecting' groups.[2a–c,3] The same tendency is observed in our case since the stability of compounds **5**, **AADT** and **DADT** is higher than that of the control ADT **4**. It can also be noticed that compounds bearing electron donating groups **DADT** and **5** possess similar stabilities (Fig. 3). Product bearing electron-withdrawing groups (**AADT**) has a higher stability than products with donor groups on their ADT backbone (**DADT** and **5**). It was previously demonstrated that the photo-induced degradation of fused linear (hetero)acenes is due to the formation of endoperoxide bridge across the most reactive central ring.[3] The reaction involved in the degradation process can be compared to a Diels–Alder cycloaddition where the diene is the central ring of the (hetero)acenes and the dienophile is the O_2 singlet formed upon UV/vis irradiation. Therefore, the reactivity of the central ring with the latter can be (i) increased with donor groups and (ii) decreased with acceptor groups on it. With this in mind, ADT bearing electron-withdrawing groups (**AADT**) is less reactive to oxygen than **5** and **DADT**, which are substituted with electron donating groups and this is likely responsible for the higher stability towards photo-oxidation of **AADT**. The higher stability of **AADT** can be rationalized from the calculated energy of the HOMO levels among the four ADT molecules (Table 1) since **AADT** possesses the deepest HOMO level (−5.07 eV). It can also be noted that **DADT** presents a higher stability than the control ADT **4**, although theoretical calculation shows that it has a less stable HOMO level (−4.56 eV) than that of compound **4** (with a deeper HOMO level at −4.69 eV). In this case, the steric hindrance afforded by the triphenylamine groups substituted on positions 5,11 of the ADT core is responsible of the higher stability of **DADT** than that of ADT **4**.

Furthermore, several isosbestic points were observed in **4**, **5**, **AADT** and **DADT** UV/vis spectra (Figs. SI1–4). This indicates the co-existence in solution of two species: the starting derivatives and their corresponding oxidized species. Throughout all these experiments, it was also found that freshly prepared solutions of all products stored in the dark remain stable for at least 24 h. As a consequence, this observation shows that the light irradiation acts as the agent responsible for the ADTs degradation.

The stability of spin-coated thin films of soluble ADT derivatives **5**, **AADT** and **DADT** towards photo-induced degradation was also assessed by following the same experimental procedure described above (Fig. 4 and SI5–8). As expected, the stability order in the thin film state is identical to the one observed in solution (**AADT**>**5**>**DADT**), however the degradation rates are different. Indeed, in solution, ADT **5** and **DADT** possess similar stabilities whereas in the solid state the first one (**5**) is much more stable. For 50% of absorbance decay of the lower energy bands of **5** and **DADT**, their stability is about 240 s and 90 s, respectively. It also can be noticed that the ADT bearing aldehyde functions (**AADT**) is extremely stable compared to products substituted with electron donating groups (**5** and **DADT**) since under irradiation for 360 s the absorbance decay of **AADT** is only about −4% (Abs_{360} of **5**=−70% and Abs_{360} of **DADT**=−80%). Moreover, after irradiation during 5 h, the absorbance of **AADT** decreases only with 25% (Fig. SI7).

The electrochemical properties of soluble ADT derivatives (**5**, **AADT** and **DADT**) were studied using cyclic voltammetry (Figs. SI25–27) and are collected in Table 2. Oxidation processes were measured in dichloromethane versus the Fc$^+$/Fc couple. All measurements were also performed under light exclusion in degassed solutions of the products to avoid the presence in solution of their photo-oxidized corresponding species. Both compounds **5** and **AADT** present single quasi-reversible oxidations at $E_{\text{ox1 } \mathbf{5}}$=0.31 V and $E_{\text{ox1 } \mathbf{AADT}}$=0.44 V, respectively. These waves are ascribed to the oxidation of **5** and **AADT** into their corresponding radical-cation species. The oxidative process of **AADT** appears positively shifted compared to that of ADT **5** due to the presence of electron-withdrawing aldehyde functions, which render **AADT** more difficult to oxidize than **5**. **DADT** exhibits multiple oxidative waves ($E_{\text{ox1 } \mathbf{DADT}}$=0.16 V, $E_{\text{ox2 } \mathbf{DADT}}$=0.44 V and $E_{\text{ox3 } \mathbf{DADT}}$=0.78 V) with the first quasi-reversible one shifted to negative potentials, which is caused by the substitution of the ADT backbone with electron rich triphenylamine groups. These electrochemical measurements also confirm the stability observed in the photo-oxidation studies since $E_{\text{ox1 } \mathbf{AADT}}>E_{\text{ox1 } \mathbf{5}}>E_{\text{ox1 } \mathbf{DADT}}$.

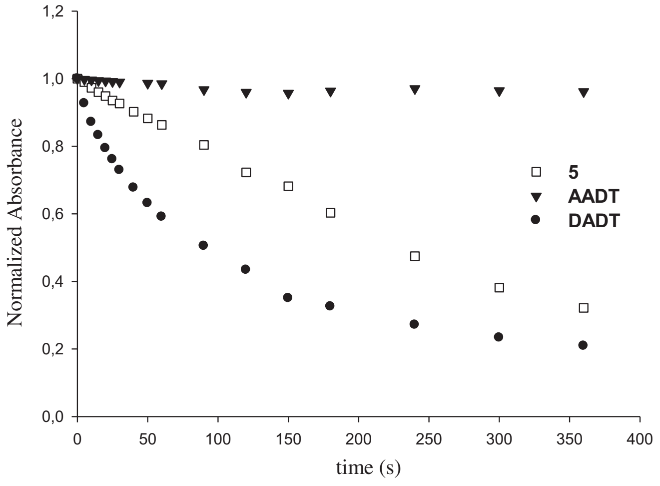

Fig. 4. Evolution of the lower energy band absorptions of **5** (516 nm), **AADT** (543 nm) and **DADT** (510 nm) thin films, under UV/vis lamps exposure (λ_1=244 nm and λ_2=366 nm) and at room temperature under ambient atmosphere.

Table 2

Oxidative potential values E=(Epc+Epa)/2 in V (vs Fc$^+$/Fc couple) of compounds **5**, **AADT** and **DADT** in CH_2Cl_2 solution containing 0.1 M of $TBAPF_6$ at scan rate of 100 mV s^{-1} and their estimated HOMO energy levels (eV)

Product	E_{ox1} (V)	HOMO[a] (eV)
DADT	0.16	−4.96
AADT	0.44	−5.24
5	0.31	−5.11

[a] HOMO energy levels are estimated from the first oxidation potential waves according to HOMO=−(4.8+E_{ox1}).[10]

3. Conclusion

Two new derivatives of 2,8-alkylated anthradithiophenes bearing electron donating (triphenylamine) and withdrawing (5-formylthiophen-2-yl) groups were prepared, isolated and characterized. These new fused heteroacene derivatives exhibit reasonable stabilities in solution without light exposure. It has also been proven by optical experiments that the ADT skeleton is much more resistant towards photo-oxidation when the latter is substituted on positions 5,11 by electron acceptor units.

4. Experimental section

4.1. Materials and methods

All chemicals and solvents were purchased from Acros, Aldrich and Alfa Aeser and were used without further purification unless otherwise stated. THF was dried by conventional method (Na/benzophenone distillation under argon) and collected with glass syringes. TLC: SiO_2 Silica gel $60F_{254}$ on aluminium sheet (Merck). Column chromatography: Silica gel 60 (particle size 0.063–0.200 mm, Merck). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on Bruker Advance 300 spectrometer. Chemical shifts are given in parts per million and coupling constants J in Hertz. The residual signal of the solvent was taken as internal reference standard. EI-HRMS and MALDI-ToF measurements were made on a Waters AutoSpec 6 and on a Waters QToF Premier apparatus, respectively. Absorption spectra were recorded in $CHCl_3$ on an Agilent 8453 spectrophotometer. Emission spectra were measured on an Aminco Bowman series 2 luminescence spectrophotometer. The thin films were prepared by spin coating 200 µL of toluene solutions of the compounds (10 mg mL^{-1}) on glass cover slides (20×20 mm) and using the following rotating sequence: 150 rpm (10 s), 750 rpm (10 s) and 1500 rpm (30 s). Melting points were observed by microscopy using a Mettler FP 82 hot stage. Cyclic Voltammetry experiments were performed with a Princeton Applied research Parstat 2273 potentiostat equipped with Electrochemistry Powersuite 2.58 software. Measurements were carried out at room temperature in a three-electrode single-compartment cell (5 mL), at a scan rate of 100 mV s^{-1}. Concentrations of 10^{-3} M in CH_2Cl_2 solutions containing $TBAPF_6$ (0.1 M) as supporting electrolyte were prepared. Before each measurement, solutions were degassed for 10 min by nitrogen bubbling. A platinum disc (Ø=1.6 mm, ALS Japan) was used as a working electrode. A platinum wire (Ø=0.5 mm, ALS Japan) was employed as counter electrode and an Ag/AgCl/NaCl(satd) electrode (ALS Japan) was used as reference. The Ag/AgCl electrode was checked against the ferrocenium/ferrocene (Fc$^+$/Fc) before and after each experiment. All potentials are reported versus Fc$^+$/Fc couple.

4.2. Synthetic procedures

*4.2.1. 2,8-Dioctylanthradithiophene-5,11-dione (syn/anti isomers) (**1**).* To a mixture of 5-octylthiophene-2,3-dicarboxaldehyde (**3**)

(3.60 g, 14.3 mmol) and 1,4-cyclohexanedione (0.80 g, 7.1 mmol), in 180 mL of absolute ethanol, was slowly added 3 mL of 5% solution of potassium hydroxide. The medium was then stirred until the total consumption of starting materials (reaction monitored by TLC (CH_2Cl_2), 30 min). The yellow precipitate formed was isolated by filtration, washed with ethanol, methanol and dried. The product was solubilized in hot toluene and purified by column chromatography to afford a pale yellow solid of *syn*/*anti* isomers mixture of 2,8-dioctylanthradithiophene-5,11-dione **1** (3.24 g, 5.95 mmol). Yield 84%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.79 (s, 2H, H^{ADT}), 8.66 (s, 2H, H^{ADT}), 7.27 (s, 2H, H^3, H^9), 3.01 (t, J=7.6 Hz, 4H, H^a), 1.80 (m, 4H, H^b), 1.38 (s, 20H, H^{c-g}), 0.93 (t, J=6.4 Hz, 6H, H^h). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 183.4, 154.0, 144.7, 144.6, 144.3, 144.2, 130.6, 130.5, 129.09, 129.07, 122.3, 121.9, 32.0, 31.3, 31.1, 29.4, 29.33, 29.29, 22.8, 14.3. R_f=0.80 (toluene). $C_{34}H_{41}O_2S_2$: MALDI-HRMS: (MH^+): calcd: 545.2548; found: 545.2550. Mp: 226–229 °C.

*4.2.2. 2,3-Bis(1,3-dioxolan-2-yl)thiophene (**2**).* It was synthesized according to procedure previously described.[4f]

*4.2.3. 5-Octylthiophene-2,3-dicarboxaldehyde (**3**).* To a solution of 2,3-bis(1,3-dioxolan-2-yl)thiophene (**2**) (4.67 g, 20.5 mmol) in 40 mL of dry THF, at −80 °C under argon, was added dropwise *n*-BuLi (2.5 M solution in hexane, 9.84 mL, 24.6 mmol) and the mixture was stirred at −80 °C for 10 min. Then 4.44 mL of 1-iodooctane (5.91 g, 24.6 mmol) was added in one portion at −80 °C and after 20 min stirring at −80 °C, the cold bath was removed and the medium was stirred for 16 h. The medium was diluted by addition of diethyl ether and washed twice with water. Organic layer was dried over $MgSO_4$, and solvents were removed under vacuum. Filtration on silica gel (petroleum ether/ethyl acetate 2/1 v/v, R_f=0.60) afforded 2,3-bis(1,3-dioxolan-2-yl)-5-octylthiophene as a pale yellow liquid, which was diluted in 40 mL of THF. HCl (40 mL, 3 M) was added and the medium was then refluxed for 1 h. After cooling to room temperature, the mixture was extracted twice with diethyl ether. The combined organic layers were washed successively with a KOH_{aq} solution (1 M), water, dried over $MgSO_4$ and the solvent was removed. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 2/1 v/v, R_f=0.86) gave 5-octylthiophene-2,3-dicarboxaldehyde (**3**) (3.89 g, 15.4 mmol) as yellow liquid. Yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 10.39 (s, 1H, CHO), 10.33 (s, 1H, CHO), 7.32 (s, 1H, H^4), 2.87 (t, J=7.6 Hz, 2H, H^a), 1.72 (m, 2H, H^b), 1.32 (m, 10H, H^{c-g}), 0.88 (t, J=6.7 Hz, 3H, H^h). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 185.0, 182.4, 156.5, 145.2, 144.1, 127.0, 31.9, 31.3, 30.7, 29.33, 29.26, 29.1, 22.8, 14.2. R_f=0.86 (petroleum ether/ethyl acetate 2/1 v/v). $C_{14}H_{20}O_2S$: EI-HRMS: ($M^{+\bullet}$): calcd: 252.1184; found: 252.1185.

*4.2.4. 2,8-Dioctylanthradithiophene (syn/anti isomers) (**4**).* Under argon, $LiAlH_4$ (0.28 g, 7.44 mmol) was slowly added to a suspension of 2,8-dioctylanthradithiophene-5,11-dione **1** (1.01 g, 1.86 mmol) in 70 mL of dry THF, at room temperature. The mixture was heated at reflux for 30 min and then was cooled to room temperature. HCl_{aq} 6 M was slowly added and the mixture was refluxed for 3 h. After cooling to room temperature, the residue was filtered and the isolated solid was washed successively with water, petroleum ether and diethyl ether. After drying, the solid residue was treated again with $LiAlH_4$ (0.28 g, 7.44 mmol) using the same procedure. 2,8-Dioctylanthradithiophene (0.60 g, 1.16 mmol) **4** was obtained as an orange solid. Yield 62%. The solubility of the compound is too low for NMR measurements. $C_{34}H_{42}S_2$: MALDI-HRMS: ($M^{+\bullet}$): calcd: 514.2728; found: 514.2737. Mp >300 °C.

*4.2.5. 2,8-Dioctyl-5,11-bis(thiophen-2-yl)anthradithiophene (syn/anti isomers) (**5**).* To a solution of thiophene (0.93 g, 0.89 mL, 11.04 mmol) in 50 mL of dry THF cooled to −80 °C under argon, was added dropwise 4.42 mL of *n*-BuLi (commercial solution 2.5 M from Acros, 11.04 mmol) and the mixture was stirred for 10–15 min. Then **1** (1.00 g, 1.84 mmol) was added in one portion. After 10 min, the cooling bath was removed and the mixture was stirred until the complete dissolution of the diquinone (∼30 min). Finally, the reaction was protected from the light and a solution of $SnCl_2$ (8. 00 g) in HCl_{aq} 6 M (20 mL) was slowly added. The reaction was stirred (still protected from the light) for additional 20 min and then the mixture was poured into 350 mL of methanol. The precipitate formed was then isolated by filtration, washed with HCl 6 M, H_2O, MeOH and dried. The desired product **5** was obtained (1.08 g, 1.59 mmol) as a red solid. Yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.21 (s, 2H, H^{ADT}), 8.09 (s, 2H, H^{ADT}), 7.70 (dd, J=5.1, 1.2 Hz, 2H, H^{thio}), 7.39 (dd, J=5.2, 3.4 Hz, 2H, H^{thio}), 7.28 (dd, J=3.4, 1.2 Hz, 2H, H^{thio}), 6.93 (s, 2H, H^3, H^9), 2.85 (t, J=7.3 Hz, 4H, H^a), 1.72 (m, 4H, H^b), 1.26 (m, 20H, H^{c-g}), 0.87 (t, J=6.7 Hz, 6H, H^h). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 150.0, 149.9, 140.14, 140.08, 139.95, 139.8, 138.9, 138.8, 129.9, 129.83, 129.75, 129.7, 129.5, 129.4, 129.0, 128.9, 128.6, 127.5, 127.48, 127.45, 127.42, 127.1, 127.03, 126.97, 119.9, 119.0, 118.9, 118.7, 118.6, 32.0, 31.53, 30.48, 29.5, 29.34, 29.25, 22.8, 14.2. R_f=0.40 (petroleum ether/dichloromethane 95/5 v/v). $C_{42}H_{46}S_4$: MALDI-HRMS: ($M^{+\bullet}$): calcd: 678.2482; found: 678.2510. Mp: 182–186 °C.

*4.2.6. 2,8-Dioctyl-5,11-bis(5-formylthiophen-2-yl)anthradithiophene (syn/anti isomers) (**AADT**).* To a solution of compound **5** (0.50 g, 0.74 mmol) in 20 mL of dry THF cooled to −30 °C under argon, was added dropwise 0.65 mL of *n*-BuLi (commercial solution 2.5 M from Acros, 1.62 mmol) and the mixture was stirred for 10–15 min. Then, the mixture was cooled to −80 °C and anhydrous DMF (0.15 g, 0.16 mL, 2.00 mmol) was added in one portion. After 10 min, the cooling bath was removed and the mixture was stirred for 10 min at room temperature. The reaction was then quenched by addition of 30 mL of water and the mixture was poured into 300 mL of methanol. The precipitate formed was then isolated by filtration, dried and purified by column chromatography on silica gel (CH_2Cl_2) to afford pure desired dialdehyde derivative **AADT** (0.36 g, 0.49 mmol) as a red solid. Yield 66%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 10.13 (s, 2H, CHO), 8.12 (s, 2H, H^{ADT}), 8.08 (d, J=3.7 Hz, 2H, H^{thio}), 8.00 (s, 2H, H^{ADT}), 7.39 (d, J=3.7 Hz, 2H, H^{thio}), 6.92 (s, 2H, H^3, H^9), 2.84 (t, J=7.3 Hz, 4H, H^a), 1.81–1.65 (m, 4H, H^b), 1.29 (m, 20H, H^{c-g}), 0.87 (t, J=6.6 Hz, 6H, H^h). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 183.1, 151.03, 150.99, 150.6, 150.4, 150.2, 145.44, 145.40, 145.35, 140.6, 139.7, 139.6, 136.9, 131.53, 131.47, 131.4, 128.6, 128.5, 128.4, 128.0, 127.9, 127.6, 126.6, 119.7, 118.3, 118.2, 118.1, 118.0, 32.0, 31.5, 30.4, 29.5, 29.33, 29.25, 22.8, 14.2. R_f=0.82 (dichloromethane). $C_{42}H_{46}O_2S_4$: MALDI-HRMS: ($M^{+\bullet}$): calcd: 734.2381; found: 734.2408. Mp: 267–273 °C.

*4.2.7. 2,8-Dioctyl-5,11-bis(4-(diphenylamino)phenyl)anthradithiophene (syn/anti isomers) (**DADT**).* To a solution of 4-bromo-*N*,*N*-diphenylaniline (2.17 g, 6.69 mmol) in 50 mL of dry THF cooled to −80 °C under argon, was added dropwise 2.68 mL of *n*-BuLi (commercial solution 2.5 M from Acros, 6.70 mmol) and the mixture was stirred for 10–15 min. Then **1** (0.91 g, 1.67 mmol) was added in one portion. After 10 min, the cooling bath was removed and the mixture was stirred until the complete dissolution of the diquinone (∼1 h). Finally, the reaction was protected from the light and a solution of $SnCl_2$ (7.00 g) in 6 M HCl_{aq} (17 mL) was slowly added. The reaction was stirred (still protected from the light) for additional 30 min and then the mixture was poured in 250 mL of methanol. The precipitate formed was then isolated by filtration, washed with HCl 6 M, H_2O, MeOH, petroleum ether and dried. The desired product **DADT** was obtained (1.34 g, 1.34 mmol) as a red solid. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.18 (s, 2H, H^{ADT}), 8.06 (s, 2H, H^{ADT}), 7.41–7.32 (m, 24H, H^{TPA}), 7.11 (m, 4H, H^{TPA}), 6.97 (s, 2H, H^3, H^9), 2.88 (t, J=7.3 Hz, 4H, H^a), 1.75 (m, 4H, H^b), 1.48–1.18 (m, 20H, H^{c-g}), 0.88 (t, J=6.4 Hz, 6H, H^h). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 149.3, 149.2, 148.0, 147.4, 147.3, 147.2, 139.6, 139.5, 138.0, 137.9, 136.5, 135.4, 133.5, 133.3, 133.1, 132.5, 129.6, 128.3, 128.1, 127.9, 127.7, 125.11, 125.05, 124.99, 123.3, 123.1, 123.03, 122.99, 120.1, 119.4, 119.3, 119.1, 119.0, 32.0, 31.6, 30.6, 29.5, 29.4, 29.3, 22.8, 14.3. $C_{70}H_{68}N_2S_2$: MALDI-HRMS: ($M^{+\bullet}$): calcd: 1000.4824; found: 1000.4852. Mp: 240–244 °C.

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Supplementary data

Cyclic voltammograms, optical studies, NMR, mass and theoritical spectra are shown in Supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.06.098.

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