

Photophysical, electrochemical and photovoltaic properties of thiophene-containing arylene-ethynylene/arylene-vinylene polymers

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Abstract

This work reports the properties of two types of thiophene-containing poly(arylene-ethynylene)-*alt*-poly(arylene-vinylene)s polymers, whose repeating units $(-\text{Ph}-\text{C}\equiv\text{C}-\text{Th}-\text{CH}=\text{CH}-\text{Ph}-\text{CH}=\text{CH}-)_n$, **1**, and $(-\text{Th}-\text{C}\equiv\text{C}-\text{Ph}-\text{C}\equiv\text{C}-\text{Th}-\text{CH}=\text{CH}-\text{Ph}-\text{CH}=\text{CH}-)_n$, **2**, consist respectively of a 1:2 and a 2:2 ratio of $-\text{C}\equiv\text{C}-/-\text{CH}=\text{CH}-$ moieties. Although similar electrochemical data (HOMO: -5.43 eV, LUMO: ~ -3.15 eV, $E_g^{\text{sc}}=2.28$ eV) as well as identical thin film absorption behaviour ($\lambda_a=501$ nm, $E_g^{\text{opt}}=2.10$ eV) were obtained for both types of materials, significant differences in their thin film photoluminescence behaviour and photovoltaic properties were observed. While polymer **1** shows a fluorescence maximum at $\lambda_e=568$ nm (with a fluorescence quantum yield of $\Phi_f=7\%$), a total fluorescence quenching was observed in **2**. Solar cells (set up: ITO/PEDOT:PSS/active layer/LiF/Al; active layer consisting of **1** or **2** as donor and PCBM as acceptor in a 1:3 ratio by weight) designed from **1** (best cell: $V_{\text{OC}}=900$ mV, $I_{\text{SC}}=2.51$ mA·cm⁻², FF=53.7%, $\eta_{\text{AM1.5}}=1.21\%$) show far better photovoltaic performance than those from **2** (best cell: $V_{\text{OC}}=500$ mV, $I_{\text{SC}}=1.44$ mA·cm⁻², FF=37.1%, $\eta_{\text{AM1.5}}=0.27\%$).

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1. Introduction

The organic photovoltaic devices can be seen as part of the worldwide effort towards renewable energy sources.[1,2] Their easy processability into flexible, lightweight and efficient solar cell devices make them a potential alternative to conventional inorganic photovoltaic devices. The first report of ultrafast photoinduced femtosecond charge transfer from a poly(*p*-phenylene-vinylene) derivative to the Buckminsterfullerene by Sariciftci et al. in 1992 resulted in worldwide efforts to use this phenomenon in organic photovoltaic devices [3].

Polythiophenes, e.g. poly(3-hexylthiophene), have been proven to be efficient donor materials for photovoltaic devices in conjunction with fullerenes, delivering relatively high short circuit currents (I_{SC}) of up to 10 mA/cm², attributed to high

degree of intermolecular ordering leading to high charge carrier mobility [4–6]. Power conversion efficiencies of up to 3.5% have been reported [5]. The open circuit voltage, V_{OC} , of such devices generally does not exceed 650 mV [5]. Whereas poly(arylene-ethynylene)-*alt*-poly(arylene-vinylene) (PAE-PAV) based solar cell devices have shown higher V_{OC} 's [7–9]. The combination of both types of structures within a conjugated polymeric backbone may offer a path to new class of polymers for high performance photovoltaic devices. This contribution presents two types of thiophene-containing arylene-ethynylene/arylene-vinylene alternating copolymers **1** and **2**, whose backbone consist respectively of 1:2 and 2:2 ratio of *triple bond*/*double bond* units (Fig. 1). Comparison of their photophysical, electrochemical and photovoltaic properties has been carried out.

2. Experimental

All starting materials were purchased from commercial suppliers (Fluka, Merck and Aldrich).

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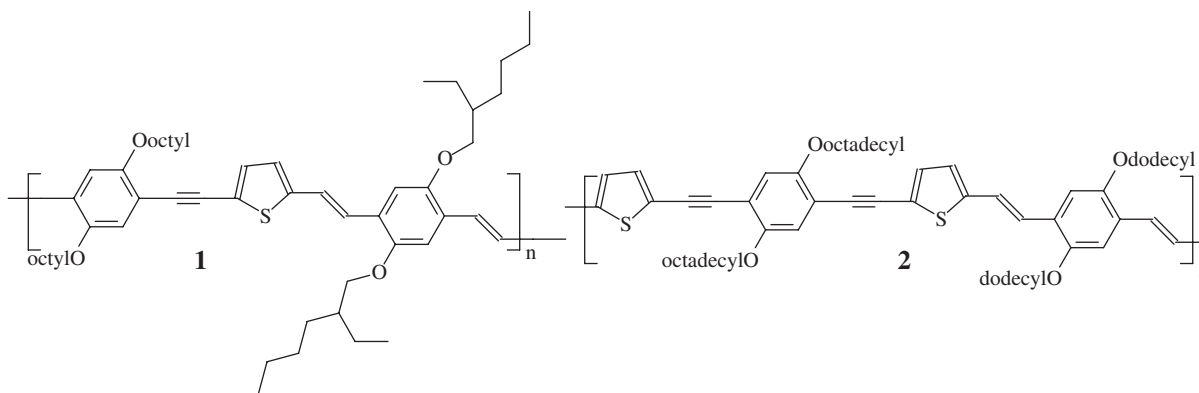
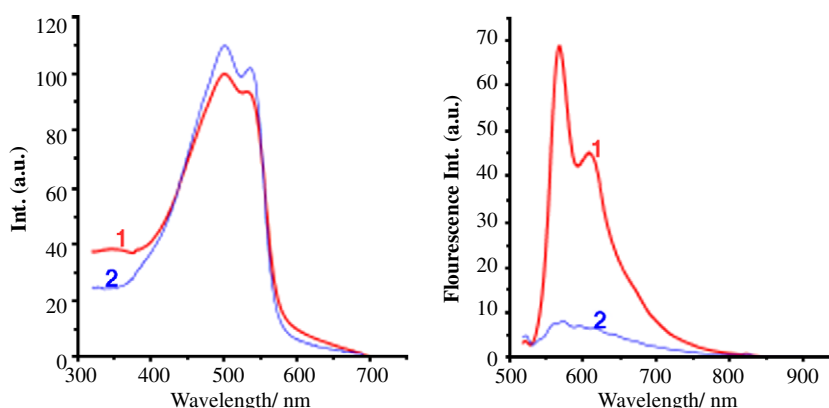


Fig. 1. Chemical structure of the polymers.

Fig. 2. Normalized absorption spectra (left) and emission spectra (right) of polymers **1** and **2** in thin film.

The instrumentations for structural analysis together with experimental details for electrochemical and photovoltaic studies have been described elsewhere [7,8].

Poly{1,4-(2,5-dioctyl)phenylene-ethynylene-thiophene-2,5-ylene-vinylene-1,4-[2,5-bis-(2'-ethyl)hexyloxy]phenylene-vinylene}(**1**) [10]: $M_w=74,000$ g/mol, $M_n=28,000$ g/mol, PDI=2.68. Anal. Calcd for $(C_{80}H_{124}O_4S_2)_n$ (1214.00) $_n$: C, 79.15; H, 10.30; S, 5.28. Found: C, 77.24; H, 10.97; S, 4.88.

Poly[2,5-thiopheneethynylene-1,4-(2,5-dioctadecyloxyphenylene)ethynylene-2,5-thiophene-vinylene-1,4-(2,5-dioctadecyloxyphenylene)vinylene] (**2**) [10,11]: $M_w=20,000$ g/mol, $M_n=9000$ g/mol, $M_z=40,000$ g/mol PDI=2.22. Anal. Calcd for $(C_{88}H_{140}O_4S_2)_n$ (1326.22) $_n$: C, 79.70; H, 10.64; S, 4.84. Found: C, 78.11; H, 12.03; S, 4.53.

3. Results and discussion

3.1. Photophysical studies

The dilute $CHCl_3$ solution absorption and emission spectra of polymer **1** ($\lambda_a=486$ nm, $\lambda_e=542$ nm) are red shifted relative to those of polymers **2** ($\lambda_a=475$ nm, $\lambda_e=535$ nm). Their well structured emission spectra consist additionally of a 0–1 transition band at $\lambda_e=583$ nm for **1** and $\lambda_e=576$ nm for **2**. Solution fluorescence quantum yield around 50% were obtained for both types of materials.

Contrary to the solution, both **1** and **2** show identical absorptive behaviour in thin film (Fig. 2 left). Their solid state absorption spectra consist of two maxima centered around 501 and 531 nm. Optical band gap energies of ca. 2.10 eV were obtained. In contrast, a great disparity is observed in their solid state emissive behaviour (Fig. 2 right). While polymer **1** has a thin film fluorescence spectrum, which is similar in shape to that in solution, but red shifted, and consisting of a 0–0

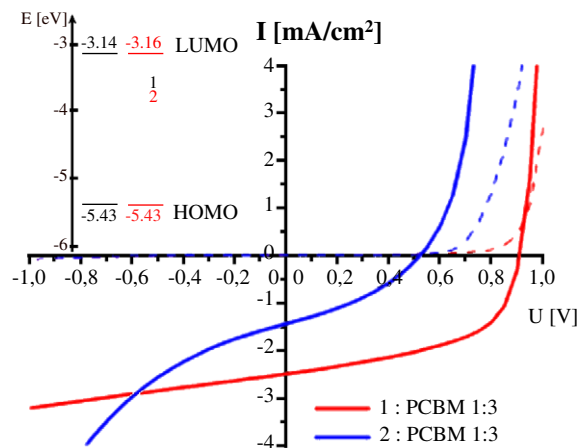


Fig. 3. Current–voltage ($I-V$) curves of **1** and **2** solar cells in dark (dash) and under illumination (solid line) with white light at an irradiation intensity of 100 mW/cm 2 . Inset presents the HOMO and LUMO energy levels as determined from CV and EVS.

Table 1
Photovoltaic parameters from devices of configuration: ITO/PEDOT:PSS/
polymer: PCBM(1:3)/LiF/Al

Code	Active area [mm ²]	Pin [mW·cm ⁻²]	V_{OC} [mV]	I_{SC} [mA·cm ⁻²]	FF [%]	η [%]
1	10.2	100	900	2.51	53.7	1.21
1	15.3	100	900	2.44	50.6	1.11
1	11.6	100	800	3.21	46.3	1.19
2	10.8	100	500	1.46	35.8	0.26
2	16.2	100	500	1.44	37.1	0.27
2	10.2	100	600	1.15	36.8	0.25

transition at $\lambda_e=568$ nm and a 0–1 transition at $\lambda_e=608$ nm ($\Phi_f=7\%$), **2** exhibits a structureless fluorescence spectrum of extremely low intensity ($\Phi_f \sim 0\%$). This might be ascribed to the higher number of triple bond units (enabling very strong $\pi-\pi$ interchain interactions) and thiophene moieties (heavy atom effects) [10] in **2** and other radiationless deactivation pathways.

3.2. Electrochemical studies

Identical HOMO (-5.43 eV) as well as LUMO (~ -3.15 eV) were obtained for both types of polymers by using the combination of cyclic voltammetry (CV) and electrochemical voltage spectroscopy (EVS). [7] An E_g^{ec} value of ca. 2.28 eV was obtained. Energy diagram is shown as inset in Fig. 3.

3.3. Photovoltaic studies

photovoltaic devices of configuration ITO/PEDOT:PSS/active layer/LiF/Al were studied under AM1.5 conditions. The active layer consisted of either polymer **1** or **2** as donor component and the C₆₀-derivative 1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C₆₁ (PCBM) as acceptor, mixed together in a 1:3 weight ratio. Fig. 3 depicts the $J-V$ curves of the best cells from both polymers. The PV parameters of three cells from each polymer are summarized in Table 1.

It is obvious from the obtained data that devices designed from polymer **1** show far better characteristics than those from polymer **7b**. They exhibit open circuit voltages, V_{OC} , as high as 900 mV and filling factors, FF, around 50%; but low short circuit currents, I_{SC} , around 2.5 mA·cm⁻² were obtained leading to power conversion efficiencies between 1% and 1.2%. Actions to optimize the device parameters, especially to increase the I_{SC} , are currently on the way and the results will be reported elsewhere. The best cell from **2** has following characteristics: $V_{OC}=500$ mV, $I_{SC}=1.44$ mA·cm⁻², FF=37.1% and $\eta_{AM1.5}=0.27\%$. The main limiting factors in this case are,

apart from the comparatively (to **1**) lower molecular-weight [12], (1) the higher number of $-C\equiv C-$ units within the backbone of **2** [7,9] together with (2) the longer octadecyl and dodecyl side chains [13]. The analysis of the data showed that morphology of the polymer film and length of the chain influence the operation voltage of the devices. The higher number of triple bonds, not only slow the mobility of the photogenerated charges [7], but also might enable strong $\pi-\pi$ interactions among the donor molecules, thereby limiting the contact area between donor and acceptor molecules. The longer side chains in **2** moreover might reinforce the limitation of interfacial areas between the donor and acceptor conjugated cores [13]. They also might favour an easy recombination of the photogenerated charges by elongating their percolating path to the electrodes [13].

4. Conclusion

It is evident from the comparison of the properties of polymers **1** and **2** that reducing the number of $-C\equiv C-$ units in combination with the grafting of shorter side chains [13] and higher molecular-weight [12] improves the photovoltaic performance.

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