Anthracene- and Thiophene-Containing Poly(*p*-arylene-ethynylene)/poly(*p*-arylene-vinylene)s: Towards Optimized Structures for Photovoltaic Applications

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Summary: Anthracene- and thiophene-containing PPE-PPV systems, bearing asymmetric alkoxy side chains, which are presumed to ensure optimal interfacial contact with PCBM([6,6]-phenyl C_{61} butyric acid methyl ester) in bulk heterojunction solar cells, have been synthesized and characterized. The polymers exhibit high molecular weights with polydispersity indices around 2. The effect of the position of the aromatic rings on their photophysical properties was found to be very pronounced in the case of the anthracene-containing polymers, but less significant in the case of the thiophene-containing counterparts.

Keywords: anthracene; photophysics; PPE-PPV systems; thiophene

Introduction

Introducing acetylene units within the PPV backbone opened way to new types of conjugated systems, denoted PPE-PPVs, showing outstanding optoelectronic properties.[1,2] This class of compounds has successfully been used either as donor or acceptor components in solar cell devices. Open-circuit voltages, V_{OC}, as high as 950 mV and 1.50 V, have been obtained from polymer-PCBM heterojunction cells[3–5] and from polymer-polymer bilayer cells,[6,7] respectively. The short circuit currents, I_{SC}, and the filling factors, *FF*, were found to be greatly dependent on the *triple bond/double bond* ratio as well as the nature and size of the solubilizing alkoxy side groups.[8]

The knowledge gained so far enables us in the present work to design anthracene- as well as thiophene-containing PPE-PPVs for solar cell applications, whereby the grafted alkoxy side chains are presumed to guarantee an optimal interfacial contact with either $PC_{61}BM$ or $PC_{71}BM$ in bulk heterojunction solar cell devices. Furthermore, the new polymers offer the possibility to study the effect of the position of the aromatic rings (anthracene or thiophene) within the polymeric backbone on the photophysical and photovoltaic properties.

Results and Discussion

A general synthetic route to the polymers is depicted in Scheme 1. The four polymers **MEH-PPE-PAnV** and **MEH-PPE-PThV** as well as **MEH-PAnE-PPV** and **MEH-PThE-PPV** are products from the Horner-Wadsworth-Emmons (HWE) olefination reaction of luminophoric dialdehydes **1** or **3** with bisphosphonate esters **2** or **4**. Extraction of the crude products using diethyl ether in combination with preparative gel permeation chromatography

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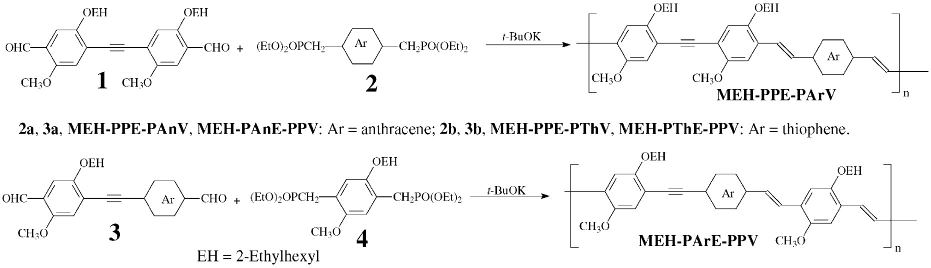

Scheme 1.
General synthetic route to the polymers.

Table 1.
GPC data (polystyrene standards, THF as eluent) and yields of the polymers.

Polymer	M_n	PDI	P_n	Yield [%]
MEH-PPE-PThV	16 600	1.9	26	28
MEH-PThE-PPV	32 500	2.3	52	54
MEH-PPE-PAnV	33 000	2.4	46	94
MEH-PAnE-PPV	31 000	2.5	43	59

resulted in high molecular weight polymers, showing Gauss-like molecular-weight distribution and Flory-like polydispersity indexes, M_w/M_n, around 2, as expected from ideal polycondensation reactions. Data from GPC (polystyrene standards, THF as eluent) are given in Table 1. The real molecular weights are approximately half of the present values due to overestimation by using polystyrene standards.The chemical structures of the new compounds were confirmed by NMR, elemental analysis and IR. The ^{1}H NMR spectra revealed more than 98% *trans*-configuration of the double bonds in all cases, as expected in HWE olefination reactions. The photophysical properties were investigated in dilute chloroform solution, in thin film and in bulk. Table 2 summarizes the photophysical data, namely, the absorption maximum, λ_a, molar absorption coefficient, ε, optical band gap energy, E_g^{opt}, emission maximum, λ_f, Stokes shift, $\Delta\nu_{af}$, relative fluorescence quantum yield, Φ_f^{rel}, as well as absolute fluorescence quantum yield, Φ_f^{abs}.

Irrespective of the position of the thiophene ring, similar absorptive and emissive behaviours were observed for **MEH-PPE-PThV** and **MEH-PThE-PPV**. This is attributed to the fact that thiophene induces planarity in polymer backbones, which is related to a very small torsion angle that it forms with its neighbors.[9] However, placing thiophene adjacent to the triple bond (–C≡C–) in **MEH-PThE-PPV**

Table 2.
Photophysical data of the polymers in dilute solution and in solid state.

Polymer	λ_a [nm]	ε [$M^{-1}\cdot cm^{-1}$]	E_g^{opt} a) [eV]	λ_f [nm]	$\Delta\nu_{af}$ b) [cm^{-1}]	Φ_f ^{rel} [%]	Φ_f ^{abs} [%]
MEH-PPE-PThV c)	491	38200	2.26	546	2050	37	33
MEH-PPE-PThV d)	508	–	2.11	572	2200	5	2 (1)
MEH-PThE-PPV c)	491	68200	2.28	542	1900	60	46
MEH-PThE-PPV d)	499	–	2.11	567	2400	8	3 (2)
MEH-PPE-PAnV c)	454	46300	2.39	583	4900	3	3
MEH-PPE-PAnV d)	453	–	2.22	607	5600	11	13 (5)
MEH-PAnE-PPV c)	498	52400	2.22	590	3100	1	1
MEH-PAnE-PPV d)	506	–	2.05	621	3700	1	1

a) $E_g^{opt} = hc/\lambda_{0,1\ max}$;
b) $\Delta\nu_{af} = 1/\lambda_a - 1/\lambda_f$;
c) in dilute chloroform solution;
d) solid state: Φ_f ^{abs}vaues in brackets were obtained from the bulk materials.

resulted in higher fluorescence quantum yield than when placed between two double bonds as in **MEH-PPE-PThV**.

Placing anthracene between two double bonds causes a significant twist of the conjugated backbone due to steric hindrance.[10] This explains the approximately 50 nm blue shift of the absorption maximum of **MEH-PPE-PAnV** compared with **MEH-PAnE-PPV**. In contrast to the other three polymers, which exhibit a bathochromic shift of λ_a going from the solution to solid state as a result of chromophore-chromophore interactions, no shift was observed in the case of **MEH-PPE-PAnV**, thus further confirming the pronounced twist of its conjugated backbone. This correlates well with the observed *CN-PPV-effect*[6] characterized by lower Φ_f in solution (3%) and higher in thin film (13%).

Conclusion

Two anthracene- (**MEH-PPE-PAnV** and **MEH-PAnE-PPV**) and two thiophene- (**MEH-PPE-PThV** and **MEH-PThE-PPV**) containing PPE-PPV copolymers designed for solar cell applications have been synthesized. The study of their photophysical properties revealed a strong *CN-PPV-effect* for **MEH-PPE-PAnV** ascribed to the positioning of anthracene between two double bonds. The electrochemical and photovoltaic properties of the new materials are currently under study and will be the subject of our forthcoming report.

[1] D. A. M. Egbe, C. Ulbricht, T. Orgis, B. Carbonnier, T. Kietzke, M. Peip, M. Metzner, M. Gericke, E. Birckner, T. Pakula, D. Neher, U.-W. Grummt, *Chem. Mater.* **2005**, *17*, 6022.
[2] E. Tekin, H. Wiljaars, E. Holder, D. A. M. Egbe, U. S. Schubert, *J. Mater. Chem.* **2006**, *16*, 4294.
[3] H. Hoppe, D. A. M. Egbe, D. Mühlbacher, N. S. Sariciftci, *J. Mater. Chem.* **2004**, *14*, 3462.
[4] M. Al-Ibrahim, A. Konkin, H.-K. Roth, D. A. M. Egbe, E. Klemm, U. Zhokhavets, G. Gobsch, S. Sensfuss, *Thin Solid Films* **2005**, *474*, 201.
[5] D. A. M. Egbe, L. H. Nguyen, B. Carbonnier, D. Mühlbacher, N. S. Sariciftci, *Polymer* **2005**, *46*, 9585.
[6] D. A. M. Egbe, T. Kietzke, B. Carbonnier, D. Mühlbacher, H.-H. Hörhold, D. Neher, T. Pakula, *Macromolecules* **2004**, *37*, 8863.
[7] T. Kietzke, D. A. M. Egbe, H.-H. Hörhold, D. Neher, *Macromolecules* **2006**, *39*, 4018.
[8] D. A. M. Egbe, L. H. Nguyen, K. Schmidtke, A. Wild, C. Sieber, S. Guenes, N. S. Sariciftci, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1631.
[9] N. Drolet, J.-F. Morin, N. Leclerc, S. Wakim, Y. Tao, M. Leclerc, *Adv. Funct. Mater.* **2005**, *15*, 1671.
[10] R. O. Garay, H. Naarmann, K. Müllen, *Macromolecules* **1994**, *27*, 1922.