Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
ELSEVIER
Tetrahedron 63 (2007) 11386–11390

Synthesis and optoelectronic properties of a red emitting branched polymer containing V-shaped oligothiophene-*S*,*S*-dioxides as repeating units

Manuela Melucci,[a,*] Laura Favaretto,[a] Giovanna Barbarella,[a] Alberto Zanelli,[a]
Nadia Camaioni,[a] Marco Mazzeo[b,c] and Giuseppe Gigli[b,c]

[a]*Consiglio Nazionale Ricerche (ISOF), Via Gobetti 101, 40129 Bologna, Italy*
[b]*National Nanotechnology Laboratory (NNL) of INFM-CNR, Distretto tecnologico ISUFI, via Arnesano, 73100 Lecce, Italy*
[c]*Dipartimento di Ingegneria, Università degli Studi di Lecce, via Monteroni, 73100 Lecce, Italy*

Received 26 April 2007; revised 3 August 2007; accepted 23 August 2007
Available online 30 August 2007

Abstract—The synthesis, optical characterization and redox potentials of a branched polythiophene (**V-PT**), obtained by the Stille polycondensation of V-shaped 2,3-dibromo-benzo[*b*]thiophene-1,1-dioxide and 3,3-dimethyl-5,5′-tributylstannyl-2,2′-bithiophene, are reported. The branched shape favours the suppression of aggregation effects and the presence of the benzo[*b*]thiophene-1,1-dioxide moiety leads to a marked increase in electron affinity. A single layer light-emitting diode having **V-PT** as the active material showed a luminance of 948 cd m^{-2}.

1. Introduction

The development of organic materials with pre-defined enhanced functionalities requires the search for novel efficient design strategies. Tuning the optoelectronic properties of conjugated materials by modifying the molecular structure is a current challenging topic.[1]

Thiophene-based materials are a nice example of compounds with tuneable functional properties by proper molecular engineering.[2] For instance, conventional thiophene oligomers are not suitable for application in light-emitting devices,[3] since they are characterized by low electron affinities[4] and low solid-state photoluminescence efficiencies.[5–7a] However, the transformation of oligothiophenes into the corresponding oligothiophene-*S*,*S*-dioxides has been demonstrated to be a useful strategy for increasing both thin film photoluminescence efficiencies and molecular energy levels.[6,7]

An even greater improvement in electroluminescence (EL) properties was obtained by replacing linear oligothiophene-*S*,*S*-dioxides with V-shaped ones, where the V-shape was conferred by the presence of the benzo[*b*]thiophene rigid core. V-shaped oligothiophenes form more amorphous films with respect to their linear analogues with consequently better performances both in light emitting and in photovoltaic applications.[8,9] Huang et al. have developed V-shaped diarylamine derivatives of dibenzothiophene-*S*,*S*-dioxide displaying ambipolar carrier transport properties that have been successfully employed in the fabrication of single-layered LED.[10]

The preparation of polymers incorporating V-shaped emitting oligothiophenes as repeating units is highly desirable, as better mechanical properties and easier preparation procedures are expected for the resulting polymeric materials. Moreover, the branched structure is known to suppress aggregation in the solid state, this being of crucial importance for enhanced photoluminescence.[5d] Recently, 3,4-diphenylmaleimide has been used as a V-shaped spacer in thiophene–fluorene copolymers, which have yielded bright orange-red EL.[11,12] However, no examples of branched polymeric materials based on the benzo[*b*]thiophene-*S*,*S*-dioxide unit have been reported so far.

Herein, we report the synthesis and characterization of the first polymer (**V-PT**) containing the V-shaped benzo[*b*]-thiophene-*S*,*S*-dioxide and 2,2′-bithiophene components, alternated in the way depicted in Figure 1 (for comparison, the sketch of a polymer with linearly alternating thienyl-*S*,*S*-dioxide and 2,2′-bithienyl units is also shown).

2. Results and discussion

The synthesis of polymer **V-PT** was accomplished by the Stille polycondensation of equimolar amounts of 2,3-dibromo-benzo[*b*]thiophene-1,1-dioxide (**1**) and 3,3′-

---

* Corresponding author. E-mail: m.melucci@isof.cnr.it

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.08.084

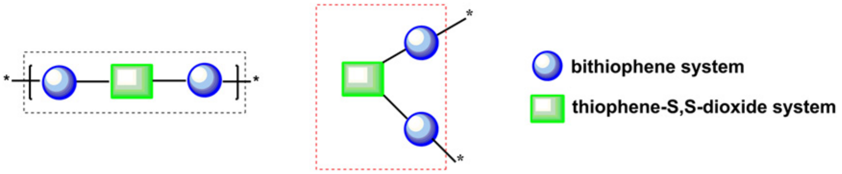


Figure 1. Structure of polymers containing a linear (left) and a V-shaped (right) oligothiophene *S*,*S*-dioxide as the repeating unit.

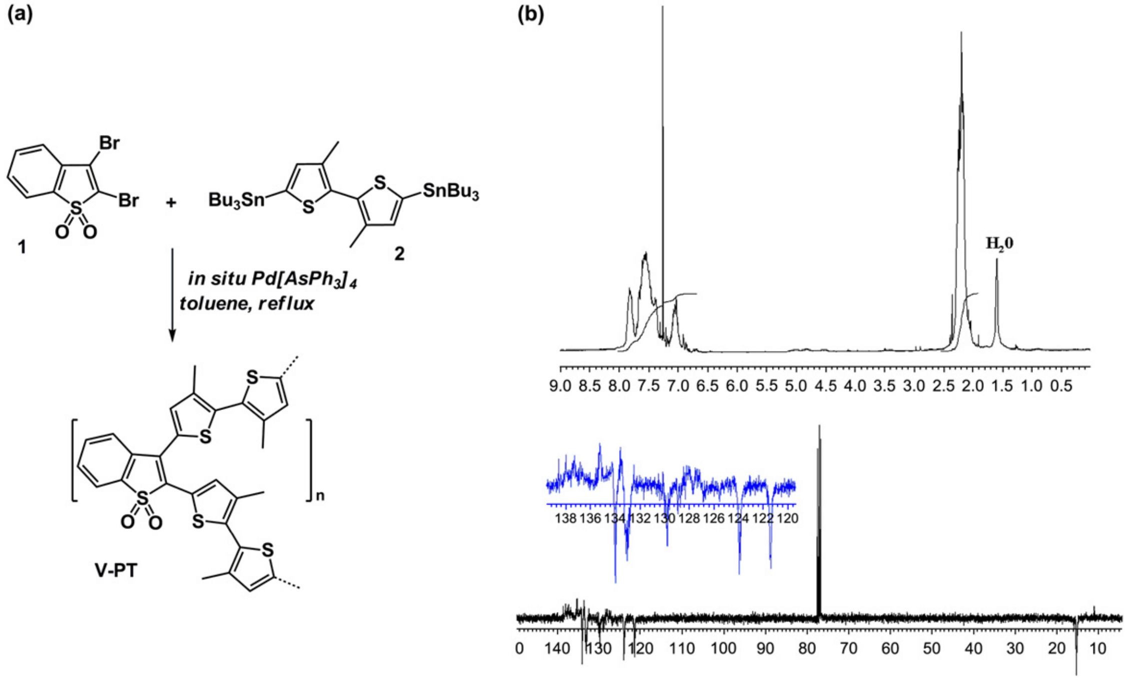
dimethyl-5,5′-bis-tributylstannanyl-2,2′-bithiophene (**2**), as reported in Scheme 1a. As palladium catalyst, in situ generated Pd[$(AsPh)_3$]$_4$ was employed, which was proven to be highly effective in the synthesis of thiophene-based oligomers under Stille cross-coupling conditions.[13]

To remove possible unreacted bromine end groups, 5-tributylstannyl-3,3′-dimethyl-2,2′-bithiophene was added after 16 h. The synthesis was repeated several times with reproducible NMR, GPC (Gel Permeation Chromatography) and optical responses.

V-PT was isolated as a red powder, soluble in different organic solvents, e.g., toluene, xylene, THF, chloroform, etc. Upon flash chromatography using $CH_2Cl_2 \rightarrow$ AcOEt as the eluent, the short fractions as well as the self-coupling by-products were separated and identified by ^{1}H NMR and mass spectrometries. GPC analysis of **V-PT**, using polystyrene as the standard, gave a number-average molecular weight of M_n=1130 and a weight-average molecular weight of M_w=1575, with a polydispersity index of M_w/M_n=1.39. These data suggest the formation of a polymer made by the repetition of about four benzo[*b*]thiophene-*S*,*S*-dioxide and four bithiophene subsystems. However, owing to the structural dissimilarity between **V-PT** and polystyrene used as standard, these data are only indicative.

Differential Scanning Calorimetry (DSC) thermograms of **V-PT** (heating run from 50–300 °C at 15 °C min^{-1} and subsequent cooling run) showed a second-order glass transition (T_g) at 227 °C and no evidence of first-order phase transition such as melting or crystallization. The ^{1}H NMR spectrum of **V-PT** (Scheme 1b) appeared very simple and showed a nearly 1:1 ratio between the aliphatic and the aromatic protons, in agreement with a regular alternation of benzo[*b*]thiophene-*S*,*S*-dioxide and 3,3′-dimethyl-2,2′-bithiophene components. The ^{1}H and ^{13}C NMR spectra were very similar, both in peak shape and chemical shifts to the spectra of the V-shaped oligomers already reported.[14] Moreover, the absence of fine structure in the range 0.9–1.7 ppm (^{1}H NMR) and of signals in the range 110–119 ppm (^{13}C NMR) indicates that tributyltin groups and bromine atoms directly linked to terminal thiophenes were absent. It is worth noting that the linkage of compound **2** to the benzo[*b*]thiophene-*S*,*S*-dioxide unit **1** can occur at either the α or β positions. Therefore, although the α-position is much more reactive than the β one, we cannot exclude the presence of more than one single regioisomer.

The cyclic voltammetry (CVs) of **V-PT** film reported in Figure 2 shows a trend similar to that of V-shaped *S*,*S*-dioxide oligothiophenes.[15] The maximum of the **V-PT** oxidation wave occurred at 1.42 V versus SCE while the reverse wave showed a maximum at 1.13 V versus SCE with reverse-reduction/oxidation charge ratio ($\eta = Q_{red}/Q_{ox}$) of about 40%. The reduction wave appeared to be completely irreversible with two maxima at −0.95 and −1.25 V. The charge involved in the reduction process is (Q_{red}) comparable



Scheme 1. (a) Synthetic route to the preparation of polymer **V-PT**. (b) ^{1}H NMR and ^{13}C NMR (APT) of **V-PT**.

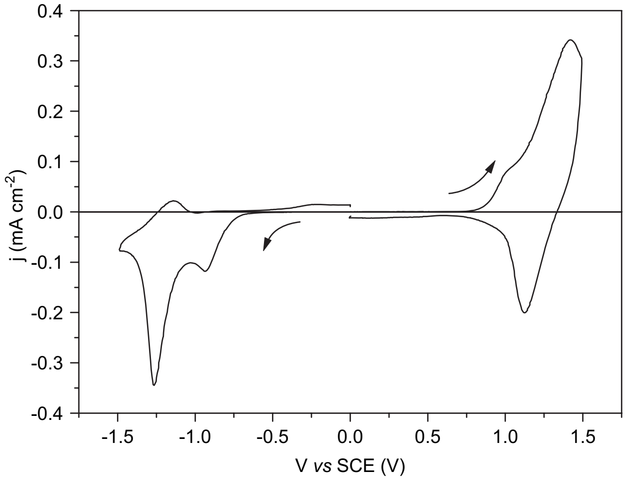


Figure 2. Cyclic voltammetry at 100 mV s^{-1} of a **V-PT** solid film onto ITO-coated glass plates in 0.2 $CH_3CN–N(C_4H_9)_4ClO_4$ Q_{ox}=1.3 mC cm^{-2}, η=41%, Q_{red}=−1.0 mC cm^{-2}.

to that of the oxidation one. A value of 3.89 eV for the lowest unoccupied molecular orbital (LUMO) level of **V-PT** was estimated by converting the first reduction potential to the value relative to the vacuum level.[15]

The absorption and photoluminescence (PL) spectra of **V-PT** in dichloromethane and in a spin-coated film (from chloroform) are reported in Figure 3. The absorption spectrum in solution displayed similar features in various solvents (dichloromethane, toluene, methanol, DMSO and the very viscous decalin), showing a maximum at λ_{max}=420 nm. The photoluminescence maximum in methylene chloride (λ_{PL}= 610 nm) indicates a large Stokes shift between the absorption and emission signals. Moreover, on passing from dichloromethane to decalin, the PL signal undergoes a blue shift of 13 nm.

Oligothiophene-*S*,*S*-dioxides are usually characterized by very low photoluminescence efficiencies in solution (less than 0.1%).[16] This behaviour was attributed to the energy relaxation mechanism from the excited state that is dominated by the internal conversion process.[17]

The photoluminescence quantum yield measured for **V-PT** in dichloromethane was ≈2% relative to Rhodamine b (ethanol solution) as the standard. This value, although small, is roughly one order of magnitude higher than that measured for linear or V-shaped oligothiophene-*S*,*S*-dioxides[16] and can be likely ascribed to the greater rigidity of the present system. Passing from dichloromethane to the much more viscous decalin, the PL wavelength shifts to 597 nm and the photoluminescence intensity increases by a factor of nearly three, in agreement with what has been observed for linear oligothiophene-*S*,*S*-dioxides.[18]

The absolute photoluminescence quantum yield of **V-PT** in thin film, measured using an integrated sphere, was found to be 1–2%, i.e., in the range of the lowest values measured for V-shaped oligothiophene-*S*,*S*-dioxides.[8]

The electroluminescence spectrum of **V-PT** is reported in Figure 4 (top). It can be seen that the spectrum perfectly

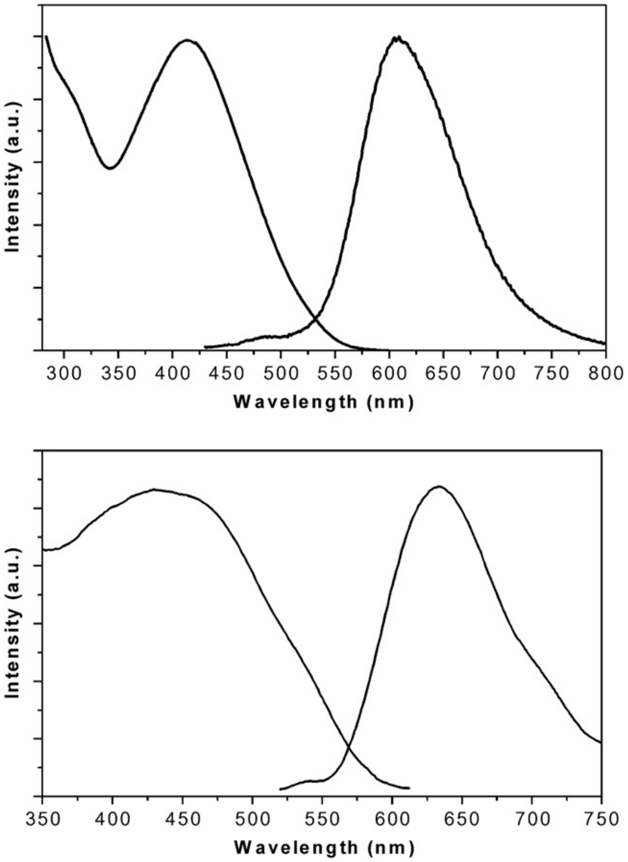


Figure 3. Absorption and photoluminescence spectra of **V-PT** in CH_2Cl_2 (top) and in spin-coated film from $CHCl_3$ (bottom).

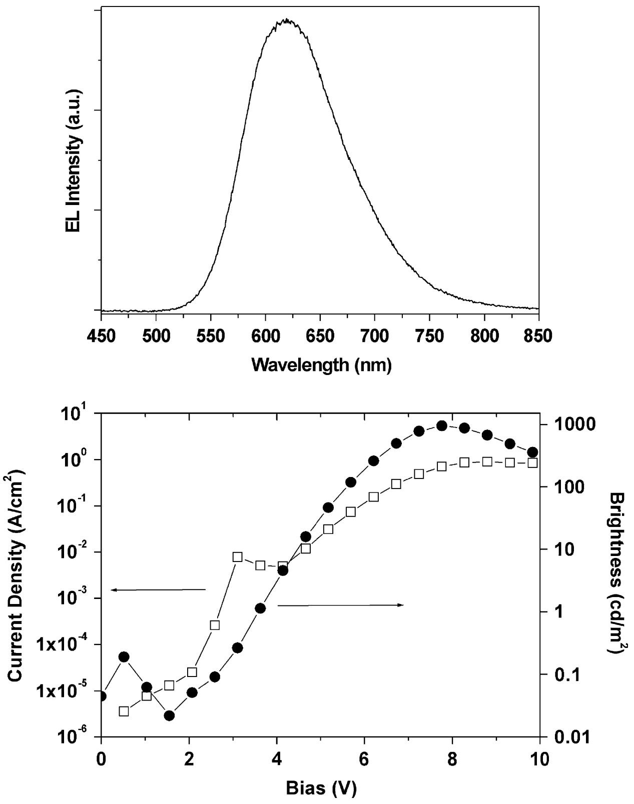


Figure 4. Top: electroluminescence spectrum of **V-PT**. Bottom: luminance versus applied voltage of the same device.

overlaps the PL spectrum, indicating that the EL signal arises from the same states involved in PL emission. Moreover, the similar broadening of the EL spectrum with the PL spectrum in solution is an indication that no aggregation or formation of excimer states takes place under device operation. Figure 4 (bottom) shows the current density and brightness versus the applied bias. The low working voltages between 3 and 8 V are due to the presence of the thienyl-*S*,*S*-dioxide units, which provide a better match to the work function of the cathode.[7b] The maximum luminance of 948 cd m^{-2}, obtained at 8 V, is the best performance obtained so far with polymers bearing thienyl-*S*,*S*-dioxide units.[7b,12] This is probably due to the branched shape of **V-PT**, which leads to amorphous thin films, as revealed by optical microscopy (not reported here), reducing the possible formation of aggregates and consequently non-radiative interchain molecular decay.[8]

3. Conclusions

In summary, we have demonstrated that the V-shaped benzo[*b*]thiophene-*S*,*S*-dioxide unit can be inserted in branched polymeric structures maintaining its high electron affinity and luminescence properties but affording better processability. Although **V-PT** is characterized by poor thin film photoluminescence efficiency, the single layer LED prepared with this polymer displayed the highest luminance (948 cd m^{-2}) measured so far for polymers containing thienyl-*S*,*S*-dioxide units. This improved performance was ascribed to the amorphous nature of the polymer, conferred by its branched shape.

We are currently working on structural modifications of **V-PT** that would allow us to combine the high electron affinity with the amorphous nature of the polymer in order to achieve improved optoelectronic performance.

4. Experimental section

4.1. Synthesis

General information: tris(dibenzylidene acetone) dipalladium(0) chloroform adduct and triphenylarsine were commercially available. Flash chromatography was carried out using silica gel 60 (230–400 mesh ASTM). 5-Tributylstannyl-3,3′-dimethyl-2,2′-bithiophene used as capping agent, 5,5′-tributylstannyl-3,3′-dimethyl-2,2′-bithiophene and 2,3-dibromo-benzo[*b*]thiophene-1,1-dioxide **1**, have already been described.[14,19] NMR spectra were recorded on a Varian Mercury 400 spectrometer at 400 MHz. The UV–vis spectrum in solution was recorded on a Perkin–Elmer lambda 20 spectrometer. PL-emission spectrum in solution was recorded on a Spex Fluorolog II spectrofluorimeter (continuous 150 W Xe lamp) equipped with a Hamamatsu R-928 photomultiplier tube.

4.1.1. Synthesis of polymer V-PT. Pd catalyst was prepared in situ by refluxing under nitrogen atmosphere a toluene solution (30 ml) of $Pd_2(dba)_3$ (0.026 g, 0.025 mmol) and $AsPh_3$ (0.061 g, 0.2 mmol). When the solution turned black, **1** (200 mg, 0.62 mmol), dissolved in dry toluene (10 ml), and **2** (480 mg, 0.62 mmol), dissolved in dry toluene (5 ml), were added.

After 16 h refluxing, 5-tributylstannyl-3,3′-dimethyl-2,2′-bithiophene (50 mg, 0.10 mmol) was added in order to remove possible bromine end groups. The reaction was quenched after an additional 5 h. The mixture was filtered off to remove the precipitated catalyst black residues and then the solvent was evaporated. The crude material so obtained was passed through a plug of silica. Elution with CH_2Cl_2 allowed the separation of shorter oligomers and by-products such as 3,4′,3″,4‴-dimethyl-2,2′:5′,2″:5″,2‴ quaterthiophene, which were isolated and characterized by ^1H NMR and mass spectrometries. Afterwards, the use of AcOEt as the eluent allowed the isolation of polymer **V-PT** that was further purified by reprecipitation in an excess of MeOH to furnish 150 mg of a deep red powder soluble in the most common organic solvents.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 (br s), 7.62 (m), 7.01 (m), 2.2 (br s); ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 15.1 (CH_3), 121.8 (CH), 123.9 (CH), 130.2 (CH), 133.2 (CH), 133.8 (C), 135.2 (C), 134.1 (CH), 137.3 (C), 138.0 (C), 138.4 (C). UV (CH_2Cl_2) 420 nm; PL (CH_2Cl_2) 610 nm; GPC (toluene, PS) M_w=1575, M_n=1130, M_w/M_n=1.39.

4.2. Electrochemical measurements

V-PT films were spin-coated from chloroform solution (20 g L^{-1}) onto Indium Tin Oxide (ITO)-coated glass substrates (Balzers, 35 ×15 mm, 20 Ω square^{-1}) to a thickness ranging between 75 and 100 nm. Cyclic voltammetries were performed at room temperature in a three compartment glass electrochemical cell under Ar pressure by using a potensiostat/galvanostat AMEL model 5000. Support electrolyte was 0.2 M $N(C_4H_9)_4ClO_4$ (Fluka crystallized from CH_2Cl_2 and vacuum dried) in CH_3CN (Merck, Uvasol over molecular sieves 3 Å), reference electrode was Saturated Calomel Electrode (SCE) and auxiliary electrode was Pt.

4.3. Photo and electroluminescence measurements

Photoluminescence measurements were carried out using thin films cast from $CHCl_3$ solution, by exciting the sample at 420 nm with a He–Cd laser in an integrating sphere and detecting the homogeneous signal by a CCD spectrograph. The OLEDs were realised by spin coating onto preliminary O_2-plasma treated ITO-coated glass substrates, a hole-transporting layer, namely poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS). Afterwards, the active material was spin-cast and finally a 50 nm layer of Ca followed by 100 nm of aluminium was deposited as cathode by thermal evaporation (10^{-6} mbar). The device characterization was performed at room temperature in air atmosphere.

Acknowledgements

This work was partially supported by project FIRB RBNE03S7XZ_005 (SYNERGY).

References and notes

1. *Chem. Rev.* **2007**, *107*. Issue on Organic electronics and Optoelectronics.
2. (a) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581–1593; (b) Lukevics, E.; Arsenyan, P.; Pudova, O. *Heterocycles* **2003**, *60*, 663–687.
3. (a) Perepichka, D. F.; Perepichka, I. F.; Meng, H.; Wudl, F. *Organic Light-Emitting Materials and Devices*; Li, Z., Meng, H., Eds.; CRC: Boca Raton, FL, 2006; pp 45–293; (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471–1507; (c) Kraft, A.; Grimsdale, A. M.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428.
4. Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839–1854.
5. (a) Oelkrug, D.; Egelhaaf, H. J.; Gierschner, J.; Tompert, A. *Synth. Met.* **1996**, *76*, 249–253; (b) Fichou, D. *Handbook of Oligo and Polythiophenes*; Wiley-VCH: New York, NY, 1999; (c) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: New York, NY, 1998; (d) Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers*; J. Wiley and Sons: Chichester, UK, 1997.
6. Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Bongini, A.; Arbizzani, C.; Mastragostino, M.; Anni, M.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **2000**, *122*, 11971–11978.
7. (a) Gigli, G.; Inganäs, O.; Anni, M.; De Vittorio, M.; Cingolani, R.; Barbarella, G.; Favaretto, L. *Appl. Phys. Lett.* **2001**, *11*, 1493–1495; (b) Pasini, M.; Destri, S.; Porzio, W.; Botta, C.; Giovanella, U. *J. Mater. Chem.* **2003**, *13*, 807–809; (c) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281–2305.
8. Mazzeo, M.; Vitale, V.; Della Sala, F.; Pisignano, D.; Anni, M.; Barbarella, G.; Favaretto, L.; Zanelli, A.; Cingolani, R.; Gigli, G. *Adv. Mater.* **2003**, *15*, 2060–2063.
9. (a) Camaioni, N.; Ridolfi, G.; Fattori, V.; Favaretto, L.; Barbarella, G. *J. Mater. Chem.* **2005**, *15*, 2220–2225; (b) Leclerc, N.; Michau, A.; Sirois, K.; Morin, J. F.; Leclerc, M. *Adv. Funct. Mater.* **2006**, *16*, 1694–1704.
10. Huang, T.-H.; Lin, J.-T.; Chen, L.-Y.; Lin, Y.-T.; Wu, C.-C. *Adv. Mater.* **2006**, *18*, 602–606.
11. Chan, L.-H.; Lee, Y.-D.; Chen, C.-T. *Macromolecules* **2006**, *39*, 3262–3269.
12. (a) Berlin, A.; Zotti, G.; Zecchin, S.; Schiavon, G.; Cocchi, M.; Virgili, D.; Sabatini, C. *J. Mater. Chem.* **2003**, *13*, 27–33; (b) Beaupré, S.; Leclerc, M. *Adv. Funct. Mater.* **2002**, *12*, 192–196; (d) Drolet, N.; Beaupré, S.; Morin, J. F.; Tao, Y.; Leclerc, M. *J. Opt. A: Pure Appl. Opt.* **2002**, *4*, S252–S257; (e) Charas, A.; Morgado, J.; Martinho, J. M. G.; Alcàcer, L.; Cacialli, F. *Chem. Commun.* **2001**, 1216–1217; (f) Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Palsson, L.-O. *Chem. Commun.* **2005**, 3397–3399.
13. Barbarella, G.; Sotgiu, G.; Zambianchi, M.; Favaretto, L.; Bongini, A. *Tetrahedron* **1997**, *53*, 9401–9406.
14. Barbarella, G.; Favaretto, L.; Zanelli, A.; Gigli, G.; Mazzeo, M.; Anni, M.; Bongini, A. *Adv. Funct. Mater* **2005**, *15*, 664–670.
15. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley-VCH: New York, NY, 1980.
16. Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Fattori, V.; Cocchi, M.; Cacialli, F.; Gigli, G.; Cingolani, R. *Adv. Mater.* **1999**, *11*, 1375–1379.
17. Lanzani, G.; Cerullo, G.; de Silvestri, S.; Barbarella, G.; Sotgiu, G. *J. Chem. Phys.* **2001**, *115*, 1623–1625.
18. Bongini, A.; Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M. *Tetrahedron* **2002**, *58*, 10151–10158.
19. Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Botta, C. *Tetrahedron* **2002**, *58*, 2245–2251.