

Alkylensulfanyl-Bridged Bithienyl Cores for Simultaneous Tuning of Electronic, Filming, and Thermal Properties of Oligothiophenes

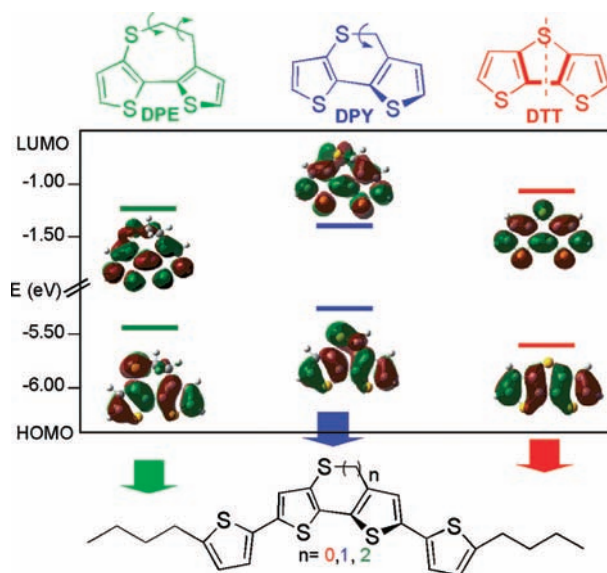
Maria Luisa Navacchia,[†] Manuela Melucci,^{*,†} Laura Favaretto,[†] Alberto Zanelli,[†] Massimo Gazzano,[†] Alessandro Bongini,[‡] and Giovanna Barbarella[†]

Consiglio Nazionale delle Ricerche (CNR), Istituto per la Sintesi Organica e la Fotoreattività (ISOF), via Gobetti, 101, I-40129, Bologna, Italy, and Dipartimento di Chimica 'G. Ciamician', Università di Bologna, via Selmi 2, I-40126 Bologna, Italy

mmelucci@isof.cnr.it

Received June 4, 2008

ABSTRACT



DPY and DPE alkylensulfanyl-bridged bithienyls were prepared by a highly effective ring-closing reaction via arylalkylsulfonium intermediate and used as inner cores in oligothiophenes. HOMO–LUMO energy levels, conformational flexibility, and intrinsic asymmetry of the cores are reflected in the electronic, film-forming, and thermal properties of the corresponding oligomers.

Thiophene-based compounds have found remarkable applications as electroactive and light-emitting materials in a variety of (opto)-electronic devices, as optical transducers in biosensors and as fluorescent markers for biopolymers.¹ The search for design strategies to tune the electronic

properties, maintaining both solubility and desired self-assembly features for low-cost processing, is actively being pursued.^{1a} Thienyl ring chemical modifications,² shape engineering,³ and supramolecular organization through spe-

[†] Istituto per la Sintesi Organica e la Fotoreattività (ISOF).

[‡] Università di Bologna.

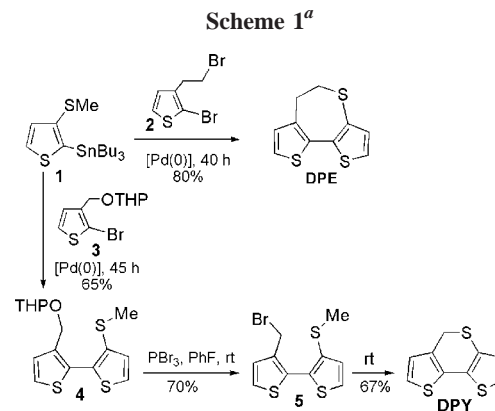
(1) (a) *Chem. Rev.* **2007**, *104*, 4. Theme issue on organic electronics and optoelectronics. (b) Barbarella, G.; Melucci, M.; Sotgiu, G. *Adv. Mater.* **2005**, *17*, 1581–1593.

cific noncovalent interactions⁴ are among the most investigated approaches. Introduction of planar electron-rich or electron-deficient fused heterocycles into the oligothiophene backbone influences the frontier orbitals energies and the self-assembly capability.⁵ Moreover, the inner planar core combined with alkyl ends promotes liquid crystallinity (LC).⁶ Less attention has been devoted to the effects of the insertion of alkyl-bridged heterocycles.⁷ Methylene- or alkoxyalkyl-bridged bithienyl cores induce conformational changes that strongly affect the extent of π - π delocalization and thus the spectral features.^{7e,f}

Here, we introduce nonsymmetric and conformationally flexible β,β' -alkylenesulfanyl-bridged bithienyls (DPE and DPY) as inner cores for alkyl-ended oligothiophenes. An unprecedented and direct synthetic approach to DPE and DPY, based on an intramolecular C-S bond formation, is presented. Subsequent chemical manipulation through Pd-catalyzed cross-couplings furnished new asymmetric oligothiophenes. We demonstrate that in this way a fine tuning of electronic, self-organization, and thermal behavior of the final oligomer can be simultaneously achieved.

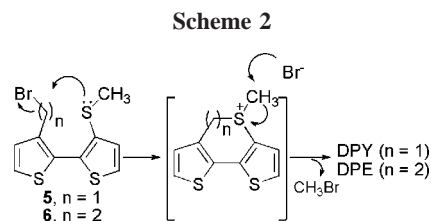
The synthesis of 5,6-dihydrodithieno[3,2-*b*:2',3'-*d*]thiopyne (DPE) was efficiently achieved by one-pot [Pd(PPh₃)₄]-catalyzed Stille coupling reaction between the stannyl derivative **1**⁸ and bromoderivative **2** (toluene, 112 °C, 40 h, 80% yield, Scheme 1). Reaction of **1** with 2-bromo-3-(bromomethyl)thiophene led to a complex mixture of unidentified products. Therefore, the synthesis of 5*H*-dithieno[3,2-*b*:2',3'-*d*]thiopyrane DPY relied on the key intermediate bithiophene **4**, which was prepared via Stille coupling between compounds **1** and **3** (45 h, 65% yield). The

deprotection/bromination was obtained in one pot by treating **4** with PBr₃ at room temperature in fluorobenzene (70% yield). Ring closure of **5** occurred spontaneously on standing at room temperature (67% yield, Scheme 1).



^a[Pd(0)] = [Pd(PPh₃)₄]; THP = tetrahydro-4*H*-pyranyl.

From a mechanistic point of view, the formation of DPE and DPY can be explained in terms of intramolecular S_N2 reaction with formation of a sulfonium salt, followed by bromide-assisted demethylation (Scheme 2).⁹ This hypothesis



was confirmed by the isolation of bromo-derivatives **5** and **6**, which spontaneously convert to DPY and DPE.

DPY and DPE were then used to build the asymmetric oligothiophenes **10** and **11** through a procedure based on Stille coupling. To this purpose, bistannanes **7** and **8** were coupled to 2-bromo-5-*n*-butyl-thiophene **9** under standard conditions (Scheme 3). Noteworthy, despite the relatively poor reaction yield, our approach is more convenient than the ring-by-ring growth required to synthesize asymmetric nonidentical alkyl-ended oligothiophenes, since no tedious purifications to remove "symmetrical" side products are required.¹⁰ To evaluate the role of conformational flexibility and molecular asymmetry in oligomers **10** and **11**, the symmetric and planar derivative **14**¹¹ was prepared by using dithienothiophene, DTT¹² as inner core. For the synthesis of this oligomer, dibromination of DTT followed by Stille

(2) (a) Murphy, A. R.; Fréchet, J. M. *J. Chem. Rev.* **2007**, *107*, 1066–1096. (b) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: New York, 1998. (c) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205.

(3) (a) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273–276. (b) Bilge, A.; Zen, A.; Forster, F.; Li, H.; Galbrecht, F.; Nehls, B. S.; Farrell, T.; Neher, D.; Scherf, U. *J. Mater. Chem.* **2006**, *16*, 3177–3182. (c) Yu, K.; Chernichenko, Sumerin, V. V.; Shpanchenko, R. V.; Balenkova, E. S.; Nenajdenko, V. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7367–7370.

(4) (a) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. *J. Chem. Rev.* **2005**, *105*, 1491–1546. (b) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38–68.

(5) Kim, H.-S.; Kim, Y.-H.; Kim, T.-H.; Noh, Y.-Y.; Pyo, S.; Yi, M. H.; Kim, D.-Y.; Kwon, S.-K. *Chem. Mater.* **2007**, *19*, 3561–3567. (6) Tian, H.; Wang, J.; Shi, J.; Yan, D.; Wang, L.; Geng, Y.; Wang, F. *J. Mater. Chem.* **2005**, *15*, 3026–3033. (c) Ando, S.; Murakami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996–14997.

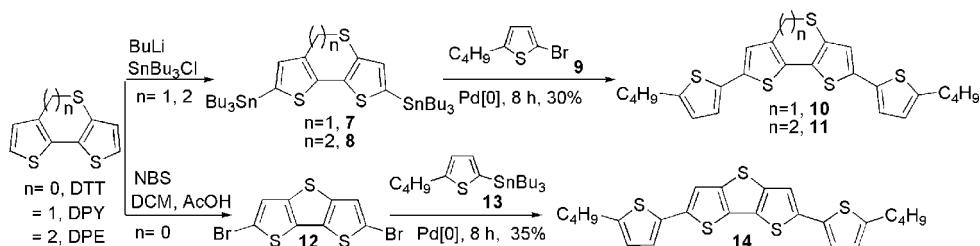
(6) Melucci, M.; Favaretto, L.; Bettini, C.; Gazzano, M.; Camaioni, N.; Maccagnani, P.; Ostojia, P.; Monari, M.; Barbarella, G. *Chem. Eur. J.* **2007**, *13*, 10046–10054.

(7) For fluorene-thiophene co-oligomers, see: (a) Surin, M.; Sonar, P.; Grimdale, A. C.; Müllen, K.; De Feyter, S.; Habuchi, S.; Sarzi, S.; Van der Auweraer, M.; De Schryver, F. C.; Cavallini, M.; Moulin, J.-F.; Biscarini, F.; Femioni, C.; Lazzaroni, R.; Leclère, P. *J. Mat. Chem.* **2007**, *17*, 728–735. (b) Tian, H.; Wang, J.; Shi, J.; Yan, D.; Wang, L.; Geng, Y.; Wang, F. *J. Mater. Chem.* **2005**, *15*, 3026–3033. For all-thiophene-based systems, see: (c) Jousselme, B.; Blanchard, P.; Levillain, E.; Delaunay, J.; Allain, M.; Richomme, P.; Rondeau, G.; Gallego-Planas, N.; Roncali, R. *J. Am. Chem. Soc.* **2003**, *125*, 1363–1370. (d) Pasini, M.; Destri, S.; Botta, C.; Porzio, W. *Tetrahedron* **1999**, *55*, 14985–14994. (e) Benincori, T.; Bongiovanni, G.; Botta, C.; Cerullo, G.; Lanzani, G.; Mura, A.; Rossi, L.; Sannicolò, F.; Tubino, R. *J. Phys. Rev. B* **1998**, *58*, 9082–9086. (f) Zerbi, G.; Radaelli, G.; Veronelli, M.; Brenna, E.; Sannicolò, F.; Zotti, G. *J. Chem. Phys.* **1993**, *98*, 4531–4541.

(8) Barbarella, G.; Zambianchi, M. *Tetrahedron* **1994**, *50*, 11249–11256.

(9) (a) Shevchenko, N. E.; Nenajdenko, V. G.; Balenkova, E. S. *Synthesis* **2003**, 1191–1200. (b) Koval', I. V. *Russ. J. Org. Chem.* **2007**, *43*, 319–346.

Scheme 3



coupling with 2-tributylstannyl-5-*n*-buthyl- thiophene **13** was found to be the most efficient pathway (Scheme 3).

The optical properties of isolated cores and oligomers, calculated and experimental HOMO–LUMO energy values are listed in Table 1. A marked red shift of the maximum

Table 1. Summary of Electronic Properties of Isolated Cores and Corresponding Oligomers

item	λ_{\max} (nm) ^a	λ_{PL} (nm) ^a	E_{g}^b	E_{ox} (V) ^c	E_{red} (V) ^c	E_{HOMO} (eV)	E_{LUMO} (eV)
DPY	356	406	3.06			-5.29 ^d	-1.38 ^d
DPE	327	398	3.26			-5.44 ^d	-1.23 ^d
DTT	291	343	3.88			-5.60 ^d	-1.09 ^d
10	440	500, 527, 580	2.46	0.74	-1.86	-5.48 ^e	-2.88 ^e
11	417	486, 511, 570	2.58	0.82	-2.0	-5.52 ^e	-2.7 ^e
14	397	445, 468, 520	2.75	0.81	-2.2	-5.55 ^e	-2.5 ^e

^a In CH_2Cl_2 , for PL $\lambda_{\text{excitation}} = 325$ nm. ^b $E_{\text{g}} = 1240/\lambda_{\text{onset}}$. ^c Versus SCE; $E^{\circ}_{\text{ferrocene}} = 0.41$ V versus SCE. ^d DFT calculated values. ^e Estimated from the peak potentials of the CVs as $E_{\text{HOMO}} = -4.50 + e(E_{\text{sce}} + E_{\text{pa1}})$; $E_{\text{LUMO}} = -4.50 + e(E_{\text{sce}} + E_{\text{pc1}})$.¹⁸

absorption wavelength (λ_{\max}) was found for DPY and DPE (356 and 327 nm, respectively) compared to the fully conjugated DTT (291 nm). Although somewhat unexpected, this result was confirmed by DFT B3LYP/6-31G* calculations on frontier energy orbitals¹³ (energy gaps 3.91, 4.21, and 4.51 eV, respectively).¹⁴ It is worth noting that a similar trend was observed for simple¹⁵ and condensed^{7f,16} five-, six-, and seven-membered cyclic systems and ascribed to the strong angular tension of the five-membered ring. In agreement with this, our calculations showed that DTT is

(10) (a) Casado, J. M.; Ruiz Delgado, C.; Rey Merchán, M. C.; Hernández, V.; López Navarrete, J. T.; Pappenfus, T. M.; Williams, N.; Stegner, W. J.; Johnson, J. C.; Edlund, A. B.; Janzen, D. E.; Mann, R. K.; Orduna, J.; Villacampa, B. *Chem. Eur. J.* **2006**, *12*, 5458–5470. (b) Funahashi, M.; Hanna, J. I. *Adv. Mater.* **2005**, *17*, 594–598.

(11) Single-crystal X-ray analysis on a dihexyl-ended analogue showed an almost planar conformation. See ref 6.

(12) San Miguel, L.; Porter, W. W., III; Matzger, A. J. *Org. Lett.* **2007**, *6*, 1005–1008. (b) Frey, J.; Proemmel, S.; Armitage, M. A.; Holmes, A. B. *Org. Synth.* **2006**, *83*, 209–216.

(13) Cartesian coordinates of all the optimized structures are reported as Supporting Information, and energy and shape of the orbitals are shown in the graphical abstract.

(14) Calculated as $E_{\text{LUMO}} - E_{\text{HOMO}}$ from values in Table 1.

(15) Scott, A. I. *Interpretation of the Ultraviolet Spectra of Natural Products*; Pergamon Press: Oxford, 1964; pp 48–51.

(16) Coppo, P.; Turner, M. J. *Mater. Chem.* **2005**, *15*, 1123–1133.

characterized by highly rigid and fully planar conformation and strong angular tension. On the contrary, high conformation flexibility was found for DPE, characterized by two isomeric forms with two thienyl rings tilted by 24° and 38°, respectively. The calculated energy barrier to interconversion is 3.7 Kcal/mol, with the first isomer being more stable by 0.8 Kcal/mol. DPY resulted to be a more rigid system than DPE, with a preferred conformation characterized by a nearly coplanar arrangement of the two thienyl rings forming a dihedral angle of about 17°.

UV and PL spectra of oligomers **10**, **11**, and **14** (Figures SI_8–SI_16, Supporting Information) show a trend parallel to that observed for the isolated cores, indicating that the properties of the inner core are reflected in the electronic properties of the final oligomer. As shown in Table 1, a red shift of both absorption and emission wavelengths was observed for **10** and **11** with respect to **14**. Noteworthy, a marked red shift was observed also with respect to conventional alkyl-ended quaterthiophenes (about 50 nm).^{4a,17}

In agreement with the trend of λ_{\max} , the electrochemical HOMO–LUMO energy gap (E_{g})¹⁴ of **10** and **11** (Figure

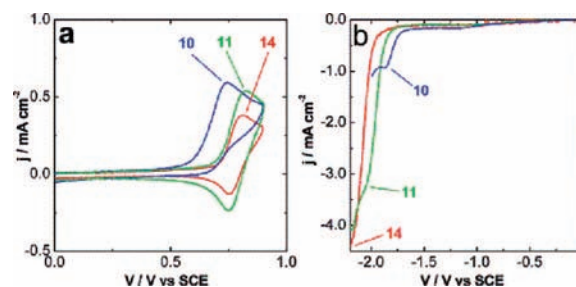


Figure 1. (a) CVs and (b) LSVs at 0.2 V s⁻¹ of **10**, **11**, and **14** (~1 mmol L⁻¹) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1) with 0.1 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$.

1) was lower than that of **14** (2.60 and 2.8 vs 3.0 eV).¹⁹ The CVs of **11** and **14** display oxidation waves with the maximum at 0.82 V ($E^{\circ} = 0.78$ V, quasi-reversible) and 0.81 V ($E^{\circ} = 0.78$ V, reversible), respectively. On the

(17) Melucci, M.; Zambianchi, M.; Zanelli, A.; Camaioni, N.; Gazzano, M.; Bongini, A.; Barbarella, G. *Chem. Phys. Chem.* **2007**, *8*, 2621–2626.

(18) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: Hoboken, 2001; pp 54–63. (b) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955–966.

contrary, the CV of **10** displays an irreversible oxidation wave with the maximum at 0.74 V ($E_{1/2} = 0.69$ V). In the region of the negative potentials, the linear sweep voltammograms (LSVs, Figure 1b) show the reduction wave of **10** with the maximum at -1.86 V ($E_{1/2} = -1.80$ V) but allowed only an indicative assignment of reduction potentials for **11** and **14** because the processes occur below -1.9 V.²⁰ Taking into account that the peak potentials shift only about 0.05 V changing the scan rate from 0.2 to 0.02 V s⁻¹, the data unambiguously show that the reduction wave of **10** occurs at a potential less negative than **11** (about 0.14 V), which in turn is reduced at a potential less negative than **14** (about 0.2 V). Remarkably, the lowering of the LUMO level obtained by DPY respect to DTT insertion is comparable to that observed upon introduction of perfluoroalkyl chains in quaterthiophene, a functionalization leading to high n-type FET charge mobility.²¹

Polarized optical microscopy (POM) on cast films of **14** exhibited the deposition of micrometer sized birefringent fibrils (see Supporting Information). In the case of **10**, the growth of birefringent rods was observed only after 48 h from the deposition (Figure 2a). On the contrary, compound

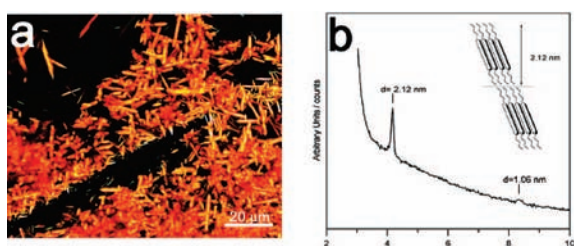


Figure 2. Cast film of **10** from CH₂Cl₂: (a) optical micrograph with crossed polars showing birefringent rods, (b) X-ray profile after melt-quenching and proposed molecular organization.

11 showed an amorphous morphology independent of the solvent and casting conditions employed. Clearly, the self-organization capability of asymmetric **10** and **11** in solution-cast films is lower than that of **14** but higher than that of conventional alkyl-ended oligothiophenes.^{2a} This suggests that the π -core of **10**, **11**, and **14** promotes aggregation and that the more planar the core, the higher is the π -stacking tendency. However, as indicated by the slow rate of

aggregation of **10**, molecular asymmetry affects the aggregation kinetics.

In agreement with the observed thin film morphologies, the melting points of **10** and **11** were markedly lower than that of **14** (61, 38, and 130 °C, respectively, determined by the Koffler method). Differential scanning calorimetry (DSC) and hot-stage POM revealed LC behavior for compound **14**, with a Schlieren textures converting to nematic droplets above 150 °C (Figure SI_4, Supporting Information). No multiple transitions were found for **10** and **11** in the DSC traces independently of scan rates. However, on cooling of the melt, hot-stage POM analysis on **10** revealed a shimmering birefringent texture at about 40 °C that persisted at room temperature upon cooling (Figure SI_5, Supporting Information). Interestingly, a similar behavior was observed for hexynyl-hexyl end-substituted asymmetric quaterthiophene.^{10b} The X-ray diffraction pattern of melt-quenched films of **10** (Figure 2b) suggests that the molecules are arranged in parallel layers spaced by 2.12 nm. The molecular length in the extended all-*trans* configuration being about 2.5 nm, the molecules must be somewhat tilted with respect to the substrate (as in smectic C phase). Such orientation is favorable to charge transport encouraging investigations in melt-processed films of **10** as the active elements in FET devices.²²

In conclusion, we have presented an unprecedented ring bridging strategy for the tuning of HOMO–LUMO energies in oligothiophenes. Alkylsulfanyl bridging could be efficiently achieved by a simple one-pot cyclization reaction, starting from 3-alkylbromo,3'-methylene-sulfanyl bithienyl units. Introduction of alkylsulfanyl-bridged cores into oligothiophenes led to an increase in electron affinity comparable to that obtained employing electron-withdrawing substituents. Furthermore, a simultaneous tuning of filming and thermal properties could also be achieved. Such results may aid in the design of innovative self-assembling, multifunctional oligothiophenes, as modifications of the alkylsulfanyl bridge (length, insertion of stereocenters) and of the aromatic backbone (size, end-substitution, shape) can be envisaged.

Acknowledgment. This work was partially supported by project FIRB RBNE03S7XZ_005 (SYNERGY). Thanks are due to Cristian Bettini (Mediteknology SRL) for helpful assistance.

Supporting Information Available: Experimental procedures and full characterization for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL801261R

(19) Electrochemical E_g was 0.2–0.3 eV wider than the optical one because it is estimated from peak potential instead of redox potentials.

(20) Under these conditions, the reduction processes appeared irreversible.

(21) (a) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480–13501.

(22) Maunoury, J. C.; Howse, J. R.; Turner, M. L. *Adv. Mater.* **2007**, *19*, 805–809.