J. Org. Chem. **2002,** *67,* 205−218

Design and Synthesis of Push−Pull Chromophores for Second-Order Nonlinear Optics Derived from Rigidified Thiophene-Based π-Conjugating Spacers

Jean-Manuel Raimundo,[†] Philippe Blanchard,[†] Nuria Gallego-Planas,[†] Nicolas Mercier,[†]
Isabelle Ledoux-Rak,[‡] Rolland Hierle,[‡] and Jean Roncali*,[†]

Ingénierie Moléculaire et Matériaux Organiques, CNRS UMR 6501, Université d'Angers,
2 Bd Lavoisier, 49045 Angers Cedex, and Laboratoire de Photonique Quantique et Moléculaire,
Ecole Normale Supérieure, 61 av. du Président Wilson, F-94235 Cachan

jean.roncali@univ-angers.fr

Received July 16, 2001

Two series of push−pull chromophores built around thiophene-based π-conjugating spacers rigidified either by covalent bonds or by noncovalent intramolecular interactions have been synthesized and characterized by UV−vis spectroscopy, electric field induced second harmonic generation (EFISH) and differential scanning calorimetry. Comparison of the linear and second-order nonlinear optical properties of chromophores based on a covalently bridged dithienylethylene (DTE) spacer with those of their analogues based on open chain DTE shows that the rigidification of the spacer produces a considerable bathochromic shift of the absorption maximum together with a dramatic enhancement of the molecular quadratic hyperpolarizability ($\mu\beta$) which reaches values among the highest reported so far. A second series of NLO-phores has been derived from a 2,2′-bi(3,4-ethylenedioxythiophene) (BEDOT) π-conjugating spacer. As indicated by X-ray and UV−vis data, rigidification of the spacer originates in that case, from noncovalent intramolecular interactions between sulfur and oxygen atoms. Again, comparison with the parent compounds based on an unsubstituted bithiophene spacer reveals a marked red shift of the absorption maximum and a large enhancement of $\mu\beta$. In an attempt to distinguish the contribution of the electronic and geometrical effects of the ethylenedioxy group, a third series of NLO-phores based on 3,4-ethylenedioxythiophene (EDOT) and 3,4-dihexyloxythiophene spacers has been synthesized. Comparison with compounds based on unsubstituted thiophene shows that, despite a red shift of $\lambda_{\max}$, introduction of alkoxy groups leads to a decrease of $\mu\beta$. Theoretical calculations indicate that this effect results from a decrease of the dipole moment (μ) caused by the auxiliary electron-donor alkoxy groups on the thiophene ring. In contrast, replacement of BT by BEDOT produces an increase of μ, which associated with the noncovalent rigidification of the BT system accounts for the observed enhancement of $\mu\beta$.

Introduction

Organic polymeric electrooptic materials are subject to considerable current interest because of their potential use in integrated photonic devices for telecommunications and optical information processing.[1] The active materials used in such devices involve a host polymeric matrix containing second-order nonlinear optical (NLO) chromophores incorporated either as guest molecules or by covalent attachment onto the polymer backbone. In both cases, the realization of a non-centrosymmetric active medium requires the alignment of the dipole moments of the push−pull chromophores. Dipole orientation is generally achieved by heating a polymer matrix containing the chromophore around the glass transition temperature (T_g) while maintaining an applied electric field during the cooling process. A major problem posed by such materials involves the structural relaxation of the chromophores with progressive return to an head-to-tail orientation of the dipoles resulting in a loss of NLO activity. While the use of high T_g polymers matrixes represents a possible solution, this in turn imposes stringent prerequisites regarding the chemical and thermal stability of the incorporated NLO-phores.[1]

Dipolar push−pull chromophores probably constitute the widest class of compounds investigated for their NLO properties.[2−12] Push−pull NLO-phores basically involve

---

* Corresponding author. Fax 33(0)2 41 73 54 05.

[†] Université d'Angers.

[‡] Ecole Normale Supérieure.

[1] (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (b) Zyss, J. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1993. (c) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242. (d) Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804−815. (e) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. (f) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060. (g) Shi, Y.; Zhang, C.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119−122.

[2] (a) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175−2189. (b) Wolf, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, *32*, 121−217.

[3] (a) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21−38. (b) Le Bozec, H.; Renouard, T. *Eur. J. Inorg. Chem.* **2000**, 229−239.

[4] (a) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L. T. *J. Am. Chem. Soc.* **1993**, *115*, 3006. (b) Marder, S. R.; Cheng, L. T.; Tiemann, B. G. *J. Chem. Soc., Chem. Commun.* **1992**, 672. (c) Cheng, L. T.; Tam, W.; Marder, S. R.; Steigman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10631−10643 and 10643−10652.

[5] (a) Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511. (b) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, M. S.; Wortmann, R. *Chem. Eur. J.* **1997**, *3*, 1091−1104.

10.1021/jo010713f CCC: $22.00

an electron-donor and an electron-acceptor groups interacting through a π-conjugating spacer. Structure−property relationships based on theoretical and experimental work have led to the definition of molecular engineering rules indicating that the hyperpolarizability (β), characterizing the molecular NLO efficiency, depends on the strength of the donor and acceptor groups, on the extent of the π-conjugated path and, for conjugating spacers based on aromatic systems, on the resonance stabilization energy of the aromatic system.[4]

Whereas the considerable research effort invested in the development of new donor and acceptor groups[5a,6,7] has led to major progress in the synthesis of stable and efficient NLO-phores, the relationships between the structure of the π-conjugating spacer and the molecular hyperpolarizability remain less clearly understood.

Polyenic systems represent in principle the most effective way to achieve charge redistribution between the donor and acceptor groups. Consequently, push−pull polyenes have been shown to exhibit huge nonlinearities;[5] however, the well-known limited chemical and photothermal stability of extended polyenes might represent an obstacle to the practical applications of the derived NLO-phores.

On the other extreme case, aromatic-based system such as oligophenylenes show limited efficiency due to an excessive confinement of π-electrons associated with the high aromatic stabilization energy of the benzene ring. In this context, thiophene-based π-conjugating spacers[6−10] have progressively emerged as an interesting tradeoff allowing the elaboration of stable NLO-phores with second-order hyperpolarizabilities sometimes exceeding 10000×10^{-48} esu. These good performances can be related to the moderate resonance energy of thiophene which allows a better π-electron delocalization than, for example, benzene-containing spacers.[11]

It has been shown theoretically that the static hyperpolarizability is correlated with the ground state polarization which is in turn reflected by bond length alternation (BLA) namely the difference between the average length of single and double carbon−carbon bonds along the conjugated path.[12] Optimal values of β have been predicted for BLA intermediate between those for unsubstituted polyenes (∼0.10 Å) and the cyanine limit (0.00 Å). BLA values close to the theoretical optimum have been approached by selecting appropriate combinations of donor and acceptor groups in order to tune the balance between the neutral and charge-separated limiting resonance forms.[5,12]

Optimization of the second-order molecular hyperpolarizability of NLO-phores through the control of BLA presents some similarities with the problems posed by the design of low band gap (E_g) aromatic linear π-conjugated systems with a nondegenerate ground-state such as, for example, poly(thiophene).[13] In that case, the progressive change from an aromatic to a quinoid geometry results in a narrowing of the band gap down to a minimal value which does not correspond to the cyanine limit (BLA = 0).[14]

In our longstanding interest in control of the electronic properties of thiophene-based linear π-conjugated systems,[13] we have developed various synthetic approaches for band gap engineering based on the rigidification of the π-conjugated system either by covalent bridging[15] or more recently by taking advantage of the intramolecular noncovalent interactions developed in π-conjugated oligomers and polymers containing the 3,4-ethylenedioxythiophene (EDOT) moiety.[16] In fact, recent X-ray crystallographic investigations of these later systems have revealed a planarization of the conjugated structure due to strong intramolecular interactions between the sulfur atom of thiophene and the oxygen of EDOT or other heteroatoms.

We report here an extension of this strategy of rigidification to the design of second-order NLO-phores. To this end, two novel series of push−pull chromophores derived from rigidified π-conjugating spacers have been synthesized.

Chromophores of the first series have been built around a bridged dithienylethylene (DTE) spacer[17] while compounds of the second series are derived from 2,2′-bi(3,4-ethylenedioxythiophene) (BEDOT) π-conjugating spacer.[18] Despite their markedly different chemical structures, these two systems have in common the fact that they represent rigidified versions of the parent structures

---

(6) (a) Mignani, G.; Leising, F.; Meyruex, R.; Samson, H., *Tetrahedron Lett.* **1990**, *31*, 4743−4746. (b) Jen, A. K.-Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057−2058. (c) Rao, V. P.; Cai, Y. M.; Jen, A. K.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1689−1690. (d) Jen, A. K.-Y.; Cai, Y.; Bedworth, P. V.; Marder, S. R. *Adv. Mater.* **1997**, *9*, 132.

(7) (a) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118−1120. (b) Gilmour, S.; Montgomery, R. A.; Marder, S. R.; Cheng, L.-T.; Jen, A. K.-Y.; Cai, Y.; Perry, J. W.; Dalton, L. R. *Chem. Mater.* **1994**, *6*, 1603. (c) Boldt, P.; Bourhill, G.; Bräuchle, C.; Jim, Y.; Kammler, R.; Müller, C.; Rase, J.; Wichern, J. *Chem. Commun.* **1996**, 793−795. (d) Wu, X.; Wu, J.; Liu, Y.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 472−473. (e) Wu, X.; Wu, J.; Liu, Y.; Jen, A. K.-Y. *Chem. Commun.* **1999**, 2391−2392.

(8) Sun, S.-S.; Zhang, C.; Dalton, L. R.; Garner, S. M.; Chen, A.; Steier, W. H. *Chem. Mater.* **1996**, *8*, 2539−2541.

(9) Jen, A. K.-Y.; Liu, Y.; Zheng, L.; Liu, S.; Drost, K. J.; Zhang, Y.; Dalton, L. R. *Adv. Mater.* **1999**, *11*, 452−455.

(10) (a) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron. Lett.* **1993**, *34*, 1747−1750. (b) Rao, V. P.; Wong, K. Y.; Jen, A. K.-Y.; Drost, K. J. *Chem. Mater.* **1994**, *6*, 2210−2212. (c) Gilmour, S.; Marder, S. R.; Perry, J. W.; Cheng, L. T. *Adv. Mater.* **1994**, *6*, 494−496. (d) Steybe, F.; Effenberger, F.; Gubler, U.; Bosshard, C.; Günter, P. *Tetrahedron* **1998**, *54*, 8469−8480. (e) Kim, O.-K.; Fort, A.; Barzoukas, M.; Blanchard-Desce, M.; Lehn, J.-M. *J. Mater. Chem.* **1999**, *9*, 2227−2232. (f) Cai, C.; Liakatas, I.; Wong, M.-S.; Bösch, M.; Bosshard, C.; Günter, P.; Concilio, S.; Tirelli, N.; Suter, U. W. *Org. Lett.* **1999**, *1*, 1847−1849. (g) Hutchings, M. G.; Ferguson, I.; McGeein, D. J.; Morley, J. O.; Zyss, J.; Ledoux, I. *J. Chem. Soc. Perkin Trans. 2* **1995**, 171−176.

(11) Morley, J. O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3009−3013.

(12) (a) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186−189. (b) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(13) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−205.

(14) Brédas, J.-L. *J. Chem. Phys.* **1985**, *82*, 3808.

(15) (a) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1305−1306. (b) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1765−1766. (c) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846−848. (d) Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E. H.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249−2250. (e) Brisset, H.; Blanchard, P.; Illien, B.; Riou, A.; Roncali, J. *Chem. Commun.* **1997**, 569−570. (f) Blanchard, P.; Brisset, H.; Illien, B.; Riou, A.; Roncali, J. *J. Org. Chem.* **1997**, *62*, 2401−2408. (g) Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *New J. Chem.* **1998**, 547−549. (h) Blanchard, P.; Brisset, H.; Riou, A.; Hierle, R.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 8310−8319. (i) Blanchard, P.; Riou, A.; Roncali, J. *J. Org. Chem.* **1998**, *63*, 7107−7110. (j) Jousselme, B.; Blanchard, P.; Frère, P.; Roncali, J. *Tetrahedron Lett.* **2000**, *41*, 5057−5061.

(16) (a) Turbiez, M.; Frère, P.; Blanchard, P.; Roncali, J. *Tetrahedron Lett.* **2000**, *41*, 5521−5525. (b) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, 939−940.

(17) Raimundo, J.-M.; Blanchard, P.; Ledoux-Rak, I.; Hierle, R.; Michaux, L.; Roncali, J. *Chem. Commun.* **2000**, 1597−1598.

(18) Raimundo, J.-M.; Blanchard, P.; Frère, P.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *Tetrahedron. Lett.* **2001**, *42*, 1507−1510.

namely, open chain DTE in the first case and bithiophene (BT) in the second one.

Of course, due to the electron-releasing effect of the ethylenedioxy groups, BEDOT cannot be simply considered as a rigid BT. Consequently, in an attempt to discriminate between electronic and geometrical effects, a third series of NLO-phores based on 3,4-dialkoxythiophenes has been synthesized.

The characterization of these various series of chromophores by UV−vis spectroscopy, EFISH, and differential scanning calorimetry (DSC) provides conclusive evidences showing that covalent and noncovalent rigidifications of thiophene-based systems represent powerful strategies for developing highly efficient and stable push−pull NLO-phores.

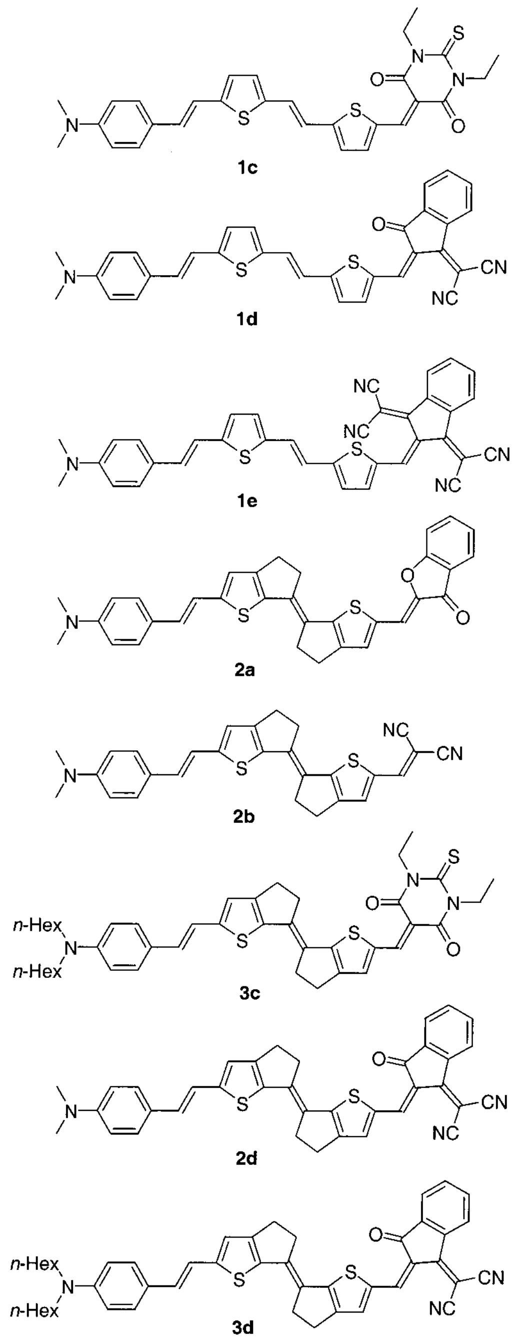
Results and Discussion

Synthesis. The structures of the three series of push−pull chromophores are shown in Charts 1−3. All these NLO-phores have been prepared according to a general synthetic methodology involving (i) monoformylation of the π-conjugated spacer by Vilsmeier reaction, (ii) introduction of the donor group by Wittig olefination of the resulting aldehyde, (iii) second monoformylation, and (iv) Knoevenagel condensation between the resulting aldehyde compound and various acceptors with active methylene groups (Scheme 1).

Except for the commercially available EDOT and BT, the various π-conjugating spacers **8f**−**13f** were prepared using known procedures. DTE **8f** of *E*-configuration was prepared by McMurry coupling of 2-thiophenecarboxaldehyde,[19] whereas the bridged analogue **9f** was obtained in four steps from 3-(3-thienyl)acrylic acid according to the already reported procedure.[15d,f] BEDOT **11f** was prepared by oxidative coupling of the lithio derivative of EDOT in the presence of $CuCl_2$.[20] 3,4-Dihexyloxythiophene **13f** was synthesized using literature procedure.[21,22]

N,*N*-Dialkylaniline was used as electron donor in all series of NLO-phores investigated. This group was introduced via a phosphonium iodide **14** or **15** (Scheme 2). Compound **14** was obtained in a one-step reaction involving treatment of freshly distilled *N*,*N*-dimethylaniline by triphenylphosphine, potassium iodide, and formaldehyde.[23] The phosphonium salt **15** was prepared using a modified literature method.[24] Alkylation of aniline with an excess of iodohexane gave *N*,*N*-dihexylaniline[24,25] which was then formylated by a Vilsmeier reaction. Reduction of the resulting aldehyde **17** with sodium borohydride gave the corresponding benzyl alcohol which was then directly converted into compound **15** using triphenylphosphonium hydrobromide[26] in refluxing chloroform.

Chart 1



All π-conjugating spacers **8f**−**13f** were subjected to a Vilsmeier reaction in the presence of $POCl_3$ and DMF in refluxing anhydrous 1,2-dichloroethane, affording selectively aldehydes **8g**−**13g** in good yield (80−94%). Subsequent Wittig olefination with phosphonium salts **14** or **15** in the presence of potassium *ter*-butylate led to compounds **8h**−**13h** and **9i** (68−97% yields) as a mixture of *E*- and *Z*-isomers. The pure *E*-isomer could be isolated by column chromatography on silica gel followed, when necessary, by a further purification by precipitation of the less soluble *E*-isomer. However, it was still possible to directly use the *E*/*Z* mixture in the subsequent Vilsmeier formylation since isomerization to the *E*-isomer occurred in the conditions of the reaction.

Formylation of **8h** was achieved by treatment of compound **8h** by 1 equiv of *n*-BuLi, followed by addition of DMF and hydrolysis. ^1H NMR analysis of all aldehyde compounds **8j**−**13j** and **9k** (36−85% yields) shows that the carbon carbon double bonds connecting the electron

---

(19) Müller, R. E.; Nord, F. F. *J. Org. Chem.* **1951**, *16*, 1380.

(20) (a) Sotzing, G. A.; Reynolds, J. R. *Adv. Mater.* **1997**, *9*, 795−798. (b) Akoudad, S.; Roncali, J. *Synth. Met.* **1998**, *93*, 111−114.

(21) Gogte, V. N.; Shah, L. G.; Tilak, B. D.; Gadekar, K. N.; Sahasrabudhe, M. B.; *Tetrahedron* **1967**, *23*, 2437−2441.

(22) Akoudad, S.; Frère, P.; Mercier, N.; Roncali, J. *J. Org. Chem.* **1999**, *64*, 4267−4272.

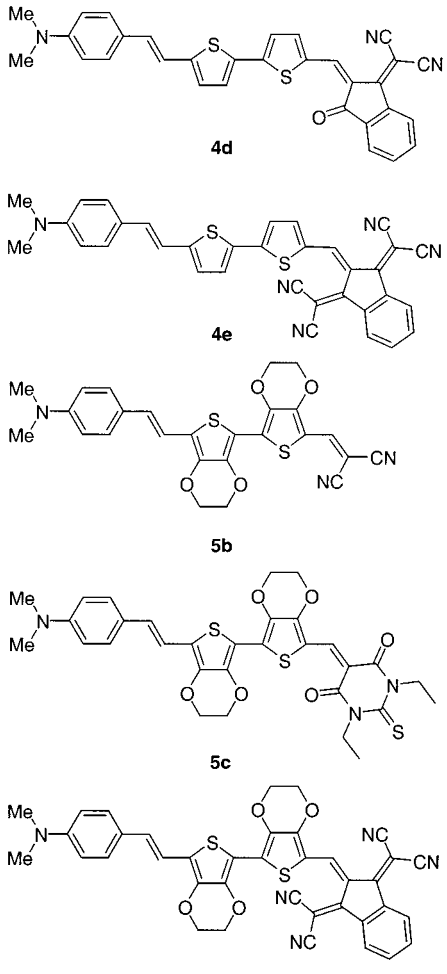
(23) Bredereck, H.; Simchen, G.; Griebenow, W. *Chem. Ber.* **1973**, *106*, 3732.

(24) Maertens, C.; Zhang, J.-X.; Dubois, P.; Jérôme, R. *J. Chem. Soc., Perkin Trans. 2* **1996**, 713−718.

(25) Willenz, J. *J. Chem. Soc.* **1955**, 1677.

(26) (a) Hercouet, A.; Le Corre, M. *Synthesis* **1988**, 157−158. (b) Arnoldi, A.; Carughi, M. *Synthesis* **1988**, 155−157.

Chart 2



4d

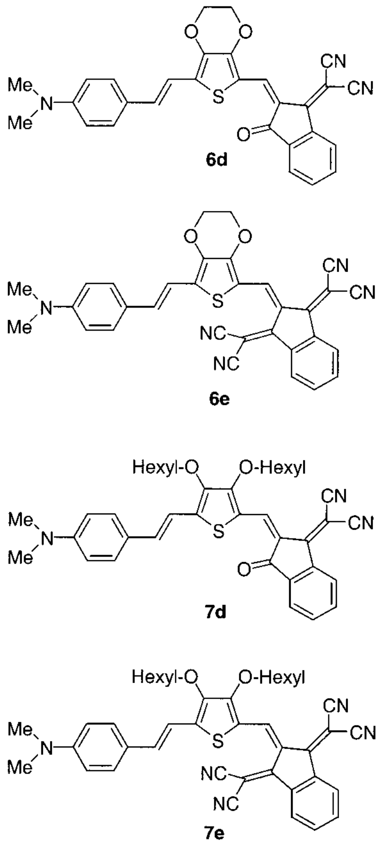
4e

5b

5c

5e

Chart 3



6d

6e

7d

7e

donor to the π-spacer are in a *E*-configuration as confirmed by a coupling constant $J \sim 16$ Hz between the two corresponding protons.

Except 3-coumaranone which has never been used as electron acceptor in push−pull chromophores, acceptors derived from malononitrile, diethylthiobarbituric acid, 3-dicyanomethylidene-1-indanone, and 1,3-bis(dicyanomethylidene)indane have already been incorporated in second-order NLO-phores.[2,6−10] The two indane derivatives were prepared from 1,3-indanedione and malononitrile.[27] The conditions used for the final Knoevenagel condensation were in each case adapted to the nature of the acceptor moiety, i.e., refluxing chloroform in the presence of triethylamine for malononitrile, stirring in chloroform at room temperature in the presence of alumina for 3-coumaranone, refluxing acetic anhydride for both thiobarbituric acid and 1,3-bis(dicyanomethylidene)indane, and refluxing ethanol for 3-dicyanomethylidene-1-indanone.

All NLO-phores were obtained as dark or dark-blue powders and have been characterized by ^{1}H and ^{13}C NMR, mass spectrometry, and elemental analysis. Note that NLO-phores based on 3-coumaranone and 3-dicyanomethylidene-1-indanone were probably obtained as mixtures of *E*- and *Z*-isomers due to the asymmetry of the electron acceptor groups. However, the two isomers which were not distinguished by ^{1}H NMR were not separated.

Push−Pull Chromophores Based on Bridged Dithienylethylene. Push−pull chromophores based on locked-polyenic spacers have been reported to exhibit improved thermal stability.[28] However the effects of this structural modification on the hyperpolarizability of the chromophores were not clearly ascertained. In the frame of our activity on the band gap engineering of oligo- and poly(thiophenes) we have synthesized various series of covalently bridged π-conjugated systems such as di-[15a] and ter-thienyl,[15c] substituted DTE,[15d−f,i] and diphenyl- and dithienylhexatrienes.[15g,h,j] Besides the planarization of the π-conjugated system which improves the overlap of p_z orbitals and hence π-electron delocalization, the covalent rigidification can also affect the electronic properties of the conjugated structure through a modification of bond length alternation. Thus experimental and theoretical work has shown that the bridging of the central double bond of DTE induces a ca. 20% decrease of BLA which results in a 0.40 eV reduction of the HOMO−LUMO gap.[15e]

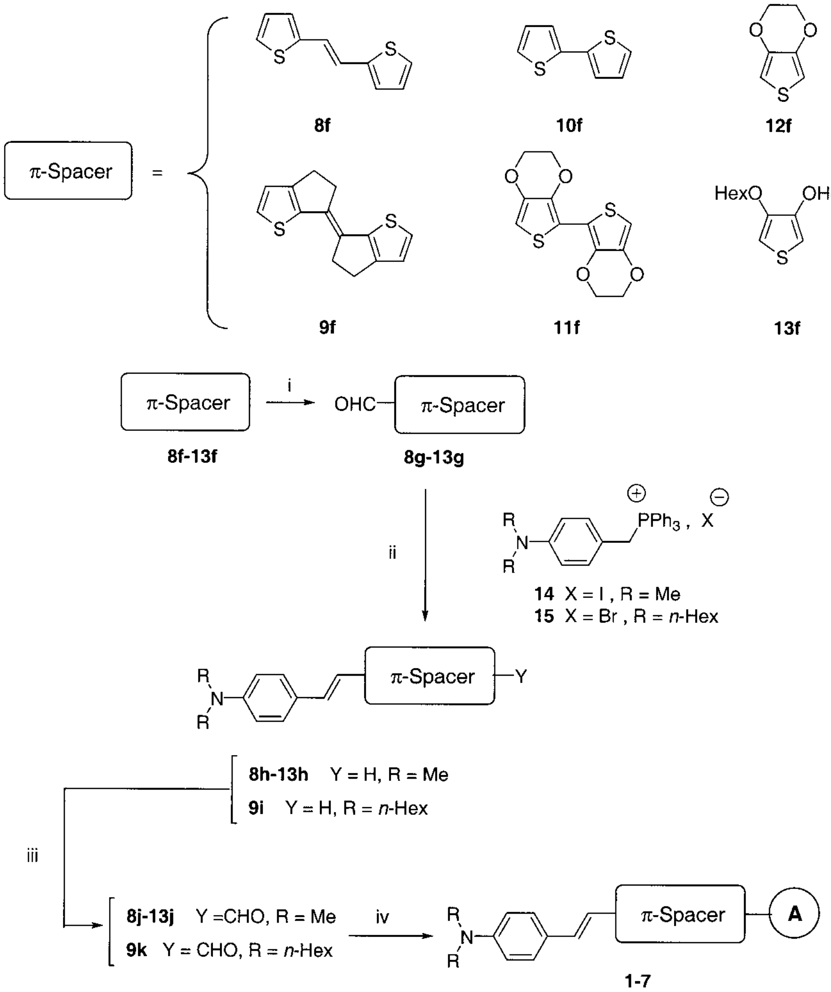
In view of the large number of efficient push−pull NLO-phores based on the open-chain DTE spacer,[6b,7a,10a,c] it was anticipated that replacing DTE by a bridged analogue with inherently reduced BLA could contribute to improving the performances and stability of the corresponding NLO-phores.

---

(27) Bello, K. A.; Cheng, L.; Griffiths, J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 815.

(28) (a) Cabrera, I.; Althoff, O.; Man, H. T.; Yoon, H. N. *Adv. Mater.* **1994**, *6*, 43−45. (b) Shu, C.-F.; Tsai, W.-J.; Jen A. K.-Y. *Tetrahedron. Lett.* **1996**, *37*, 7055−7058. (c) Shu, C.-F.; Shu, Y.-C.; Gong, Z.-H.; Peng, S.-M.; Lee, G.-H.; Jen, A. K.-Y. *Chem. Mater.* **1998**, *10*, 3284−3286. (d) Shu, Y.-C.; Gong, Z.-H.; Shu, C.-F.; Breitung, E. M.; McMahon, R. J.; Lee, G.-H.; Jen, A. K.-Y. *Chem. Mater.* **1999**, *11*, 1628−1632.

Scheme 1. General Synthetic Methodology for the Preparation of NLO-phores 1–7[a]



[a] (i) $POCl_3$/DMF; (ii) t-BuOK/MeCN-THF; (iii) $POCl_3$/DMF or n-BuLi then DMF; (iv) malononitrile, $Et_3N/CHCl_3$, reflux; 3-coumaranone, $Al_2O_3/CHCl_3$, rt; thiobarbituric acid, Ac_2O, reflux; 3-dicyanomethylidene-1-indanone, EtOH, reflux; 1,3-bis(dicyanomethylidene)indane, Ac_2O, reflux.

Scheme 2

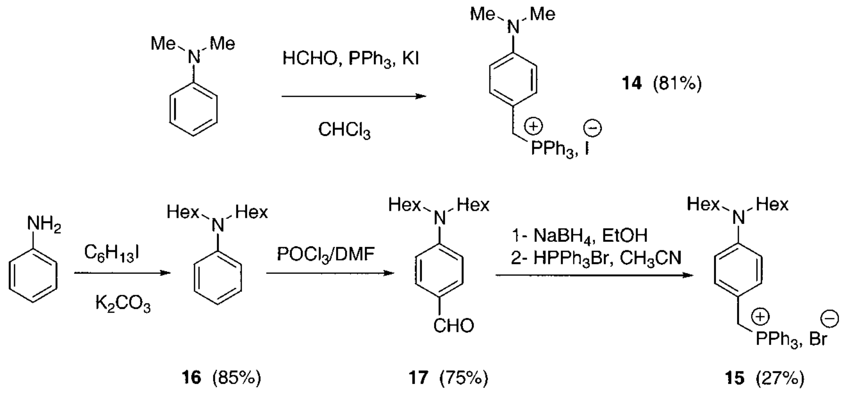


Table 1 lists the UV–vis absorption maxima (λ_{max}) and second-order nonlinear hyperpolarizabilities ($\mu\beta$) of the NLO-phores. The values of $\mu\beta$ have been determined at a wavelength of 1.907 μm on 1×10^{-3} M solutions in chloroform. Under the same experimental conditions, the zero-frequency hyperpolarizability product $\mu\beta_0$ for DR1, used as standard, was determined to be 500 10^{-48} esu. In the case of compounds **1e** and **2d** saturation of the solution occurred before complete dissolution, and hence the exact concentration of chromophore was unknown but clearly lower than to 1×10^{-3} M.

Since all compounds involve similar dialkylaniline donor groups, the progressive red shift of λ_{max} according to the sequence 3-coumaranone (**a**), malononitrile (**b**), diethylthiobarbituric acid (**c**), 3-dicyanomethylidene-1-indanone (**d**), and 1,3-bis(dicyanomethylidene)indane (**e**) is clearly related to the increase of the strength of the acceptor group.

Table 1. Absorption Maxima and Quadratic Hyperpolarizabilities of NLO-phores Based on Dithienylethylene Spacers

compound	λ_{max}/nm[a]	$\mu\beta$/10^{-48} esu[b]
1c	606	2720 (1450)
1d	656	7100 (3300)
1e	720	nd
2a	592	2500 (1500)
2b	614	3100 (1600)
3c	682	10400 (4400)
2d	756	nd
3d	768	19400 (5680)

[a] In CH_2Cl_2. [b] Measured in $CHCl_3$ at 1.9 μm by EFISH; values in parentheses represent the zero-frequency hyperpolarizability product $\mu\beta_0$

Comparison of the data for the open chain and bridged compounds containing the same donor/acceptor pairs such as **1c**/**3c** or **1d**/**2d** shows that the bridging of the spacer produces a considerable red shift of λ_{max}, (76 nm between **1c** and **3c** and 100 nm between **1d** and **2d**), indicating a correlated enhancement of π-electron delocalization.

The poor solubility of NLO-phores **1e** and **2d** in chloroform did not permit an accurate determination of $\mu\beta$ and unexpected and clearly anomalously low $\mu\beta$ values were obtained. Whereas in the case of **1e** the lack of solubility is related to the nature of the acceptor, the drop of solubility between **1d** and **2d** directly results from the bridging of the central double bond, as already observed between open chain and bridged DTE.[15d] This insolubility problem was resolved by replacing methyl by *n*-hexyl groups in the bridged compounds **3c** and **3d**. This modification produces an additional slight bathochromic shift of λ_{max} (12 nm between **2d** and **3d**) due to the stronger inductive donor effect of hexyl chains.

Comparison of the $\mu\beta$ values for open chain and bridged NLO-phores bearing the same donor and acceptor groups such as **1c**/**3c** and **1d**/**3d** clearly demonstrates that the bridging of the DTE spacer produces a huge enhancement of $\mu\beta$ which increases by a factor of 4 from 2720 to 10400 $\times 10^{-48}$ esu for the **1c**/**3c** pair, while for the **1d**/**3d** couple, $\mu\beta$ increases by a factor of 3 and reaches a value of 19400 $\times 10^{-48}$ esu. To the best of our knowledge, this value is the largest ever reported for a NLO-phore based on an heteroaromatic spacer. Thus, these results clearly demonstrate that rigidification of π-conjugating spacer by covalent bridging is an efficient strategy to optimizing the quadratic nonlinear optical susceptibility of push–pull chromophores.

Push–Pull Chromophores Derived from BEDOT. Bithiophene (BT) has already been used as π-conjugating spacer in several series of push–pull systems.[6b,10f,29] Although BT is known to be a less efficient electron relay than DTE, due to the combined effects of a less planar and more aromatic structure, it presents the advantage of an easier synthetic access. The covalent bridging of the BT system has already been investigated in the context of the synthesis of low band gap polymers.[15a] Push–pull NLO-phores based on a 3,4-[*a*,*c*]-dithienothiophene spacer were recently described.[10e] Such a spacer, which can be viewed as a particular case of sulfur-bridged BT, was claimed to lead to a significant improvement of the molecular hyperpolarizability of the derived NLO-phores compared to some of their analogues based on DTE spacers. [10e]

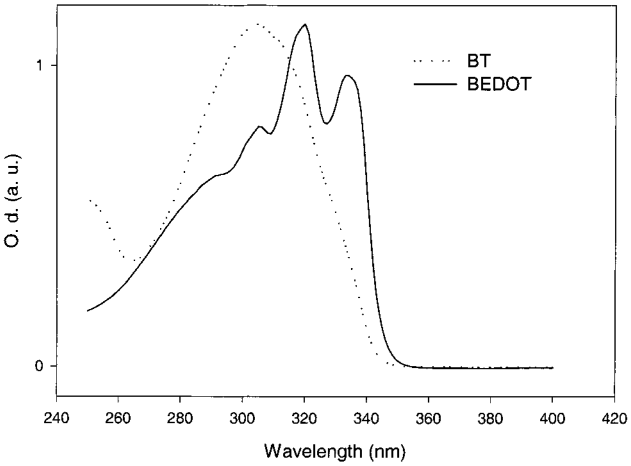


Figure 1. Electronic absorption spectra of BT and BEDOT in CH_2Cl_2.

We have already reported the synthesis and electrochemical polymerization of BEDOT.[20b] More recently the X-ray crystallographic structure of a single crystal of BEDOT was investigated.[18] The results showed that the molecule adopts a centrosymmetric structure with the S atoms in anti position. The distances between the sulfur and the oxygen atoms S(1)···O(1′) and S(1′)···O(1) (2.92 Å) are significantly shorter than the sum of the van der Waals radii of sulfur and oxygen (3.25 Å) indicating the occurrence of strong S···O intramolecular interactions.[18] As a result of these noncovalent interactions, the conjugated system of BEDOT adopts a perfectly planar geometry, unlike oligothiophenes which generally exhibit a dihedral angle of a few degrees between adjacent thiophene rings.[30] Provided it persists in solution, this planarization and rigidification of the π-conjugated system can contribute to improve the electron relay properties of BEDOT compared to BT.

The persistence of a planar and rigid structure of BEDOT in solution is supported by several electronic absorption data. Figure 1 shows the electronic absorption spectra of BT and BEDOT in dichloromethane. Whereas the spectrum of BT shows a broad unresolved absorption band, that of BEDOT exhibits a well-defined vibronic fine structure typical of a rigid conjugated system. Similar spectral features were recently reported in hybrid π-conjugated oligomers combining thiophene and EDOT.[16a] In that case, insertion of a BEDOT block in the middle of a tetrathiophene π-conjugated chain produces a strong exaltation of the vibronic fine structure and a red shift of the absorption maximum. In contrast, such spectral features were not observed in parent system in which the two EDOT groups are attached at both ends of the molecule.[16a] Finally, it is noteworthy that the occurrence of such intramolecular S···O interactions is consistent with the loss of thermochromic properties observed when

---

(29) (a) Würthner, F.; Effenberger, F.; Wortmann, R.; Krämer, P. *Chem. Phys.* **1993**, *173*, 305–314. (b) Effenberger, F.; Würthner, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 719–721. (c) Effenberger, F.; Würthner, F. Steybe, F. *J. Org. Chem.* **1995**, *60*, 2082–2091. (d) Steybe, F.; Effenberger, F.; Gubler, U.; Bosshard, C.; Günter, P. *Tetrahedron* **1998**, *54*, 8469–8480. (e) Bedworth, P. V.; Cai, Y.; Jen, A. K.-Y.; Marder, S. R. *J. Org. Chem.* **1996**, *61*, 1, 2242–2246.

(30) (a) van Bolhuis, F.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. J. *Synth. Met.* **1989**, *30*, 381. (b) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock P. B. *Acta Crystallogr., Sect. C* **1994**, *50*, 1941–1942. (c) Pelletier, M.; Brisse F. *Acta Crystallogr., Sect. C* **1994**, *50*, 1942–1945.

Table 2. Absorption Maxima and Quadratic Hyperpolarizabilities of NLO-phores Based on Bithiophenic Spacers

compound	λ_{max}/nm[a]	$\mu\beta/10^{-48}$ esu[b]
4d	650	2300 (1100)
4e	712	5000 (1900)
5b	588	2120 (1200)
5c	649	2000 (950)
5e	830	11600 (2400)

[a] In CH_2Cl_2. [b] Measured in $CHCl_3$ at 1.9 μm by EFISH; values in parentheses represent the zero-frequency hyperpolarizability product $\mu\beta_0$.

replacing BT by BEDOT in thiophene−fluorene block copolymers.[31]

Various evidence for a spontaneous rigidification of the BEDOT molecule by noncovalent interactions provides a strong inclination to use this system as a π-conjugating spacer for the synthesis of new push−pull NLO-phores.

Table 2 lists the UV−vis absorption maxima and second-order nonlinear hyperpolarizabilities of the BEDOT based NLO-phores **5b**, **5c**, and **5e** and of two BT-based compounds **4d** and **4e** synthesized for comparison.

As expected, the increase of the acceptor strength from dicyanovinyl to bis(dicyanovinyl)indane produces a large bathochromic shift of λ_{max} (from 588 to 830 nm) accompanied by an increase of $\mu\beta$. Comparison of the data for compound **5b** to those of other systems having the same donor/acceptor pair shows that the BEDOT spacer leads to an efficiency comparable to that of DTE[32] but inferior to that of bridged DTE.[17] On the other hand, comparing the data for compounds **4e** and **5e** which bear the same acceptor group shows that replacement of BT by BEDOT produces a 118 nm bathochromic shift of λ_{max} while $\mu\beta$ increases from 5000 to 11600 10^{-48} esu; however, this latter value might include a contribution due to resonance effects.

Push−Pull NLO-phores Based on 3,4-Dialkoxythiophene Spacers. While these results confirm that BEDOT is a more effective electron relay than BT and allows a significant improvement of the hyperpolarizability of the corresponding NLO-phores, the evaluation of the relative contribution of electronic and geometric effects of the ethylenedioxy groups is not straightforward.

Recently, the role of auxiliary donor and/or acceptor groups connected to the π-conjugated spacer of push−pull NLO-phores has been discussed and evaluated by theoretical methods. In particular it has been shown that the electron density of the spacer group plays a major role on the magnitude of the hyperpolarizability.[33] From this viewpoint, it is clear that besides their major role on the planarization of the BT system through intramolecular interactions, the ethylenedioxy substituents can considerably affect the electronic distribution of the push−pull system and hence its linear and nonlinear optical properties. To gain some information on these electronic effects, a series of chromophores containing a single EDOT or 3,4-dihexyloxythiophene (DHOT) group as π-conjugating spacer has been synthesized.

As observed in the previous series, replacement of 3-dicyanomethylidene-1-indanone in **6d** and **7d** by the stronger acceptor 1,3-bis(dicyanomethylidene)indane (**6e**, **7e**) produces a large bathochromic shift of λ_{max} and an increase of $\mu\beta$ from 3000 to 5000 × 10^{-48} esu for the DHOT series and from 1800 to 4600 × 10^{-48} esu for the EDOT one.

Table 3. Absorption Maxima and Quadratic Hyperpolarizabilities of NLO-phores Based on Thiophenic Spacers

compound	λ_{max}/nm[a]	$\mu\beta/10^{-48}$ esu[b]
18	690	6100
6d	673	1800 (770)
6c	768	4600 (1300)
7d	662	3000 (1350)
7e	750	5000 (1600)

[a] In CH_2Cl_2. [b] Measured in $CHCl_3$ at 1.9 μm by EFISH; values in parentheses represent the zero-frequency hyperpolarizability product $\mu\beta_0$.

For both acceptor groups, replacement of DHOT by EDOT leads to a slight bathochromic shift of λ_{max}, reflecting the higher electron-releasing properties of the ethylenedioxy group already observed for other π-conjugated systems.[22] However this red shift is accompanied by a significant decrease of $\mu\beta$, in striking contrast to the generally observed correlation between λ_{max} and $\mu\beta$. Furthermore, comparison of the data for compounds **6e** and **7e** to those reported for a parent compound based on unsubstituted thiophene (**18**)[8] suggests that despite a large red shift of $\lambda_{max,}$ ($\Delta\lambda > 60$ nm), the introduction of alkoxy substituents leads to a decrease of $\mu\beta$ from 6100 for **18**,[8] to 5000 and 4600 ×10^{-48} esu for **7e** and **6e** respectively. Thus, contrary to what is observed for chromophores based on BT and BEDOT spacers, replacement of thiophene by EDOT produces a decrease of $\mu\beta$.

To get more detailed information on these effects, the dipole moment μ of compound **6e**, its thiophene analogue (**18**), and of chromophores based on BT and BEDOT spacers **4e** and **5e** have been calculated using Gaussian 98 after optimization of the molecular geometries. For all compounds, the molecular structures were optimized by imposing a completely planar geometry and an s-trans conformation for the double bond connecting the π-conjugating spacer and the benzene ring.

As shown by the data in Chart 4, the introduction of the ethylenedioxy group on the thiophene ring produces a decrease of the dipole moment of the push−pull molecule from 9.4 to 8 D. This result suggests that the decrease of $\mu\beta$ observed between compounds **18** and **6e** is due for a large part to a decrease of the dipole moment by the ethylenedioxy group.

On the other hand, the data for the extended compounds **4e** and **5e** shows that replacement of BT and BEDOT spacer does not significantly affect the dipole moment which in contrast undergoes a slight increase from 15.9 to 17.1 D. Since such a moderate increase of μ cannot account for the more than 2-fold enhancement of $\mu\beta$ observed between compounds **4e** and **5e**, these results provide a further indirect support to the conclusion that the enhancement of $\mu\beta$ observed in BEDOT based chromophores is essentially related to the rigidification of the spacer by noncovalent interactions.

Thermal Stability. The thermal stability of the various chromophores has been investigated by DSC in ambient atmosphere (Table 4). Since many of the chro-

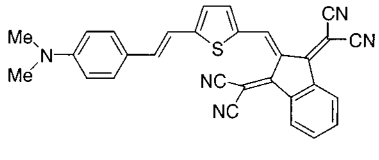
---

(31) Blondin, P.; Bouchard, J.; Beaupré, S.; Belletête, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2000**, *33*, 5874−5879.

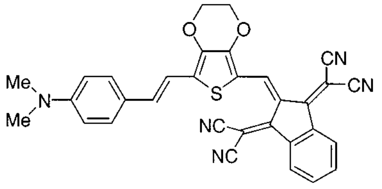
(32) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90−92.

(33) (a) Rao, V. P.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443−12448. (b) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575−6582. Breitung, E. M.; Shu, C.-F.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1154−1160.

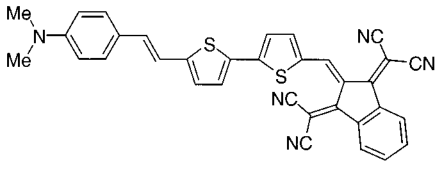
Chart 4



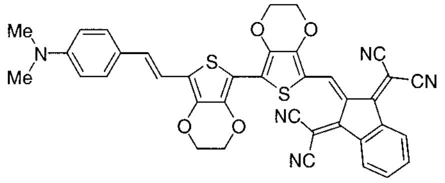
18
$\mu = 9.4$ D
$\mu\beta = 6100\ 10^{-48}$ esu



6e
$\mu = 8$ D
$\mu\beta = 4600\ 10^{-48}$ esu



4e
$\mu = 15.9$ D
$\mu\beta = 5000\ 10^{-48}$ esu



5e
$\mu = 17.1$ D
$\mu\beta = 11600\ 10^{-48}$ esu

Table 4. Decomposition Temperatures of NLO-phores 1−7 Determined by Differential Scanning Calorimetry in Ambient Atmosphere at a Rate of 10 °C min^{-1}

compound	T_d/°C
1c	235
1d	256
1e	250
2a	300
2b	308
3c	235
2d	258
3d	245
4d	251
4e	215
5b	308
5c	300
5e	206
6d	230
6e	230
7d	120
7e	145

mophores melt with decomposition, the measured decomposition temperatures (T_d) are only indicative, and they might not reflect the inherent thermal stability of the compounds. We have shown already that covalent bridging of conjugated systems leads to a significant enhancement of the thermal stability.[15g,h] Similarly, improved thermal stability has been reported for push−pull chromophores based on locked polyenes.[28,29] Except for the NLO-phores **7d** and **7e** in which the hexyloxy chains lead to a considerable decrease of the melting point, all NLO-phores exhibit T_d values above 200 °C and even 300 °C. Whereas the diversity of the acceptor groups makes it difficult to evaluate the specific effect of the spacer on the stability of the chromophores, the comparable T_d values obtained for compounds bearing the same acceptor but different spacer groups suggest that in several cases the stability of the chromophore is limited by that of the acceptor group. This is particularly apparent for compounds **1d**, **2d**, **3d**, and **4d** which, despite quite different spacer groups, exhibit similar T_d values around 250 °C.

Similarly, compounds **4e**, **5e**, and **6e** containing 1,3-bis(dicyanomethylidene)indane acceptor group show comparable T_d values (215, 206 °C and 230 °C, respectively). On the other hand, chromophores based on the bridged DTE and on BEDOT spacers associated with acceptors groups such as coumaranone, dicyanovinyl, or thiobarbituric acid, i.e., compounds **2a**, **2b**, **5b**, and **5c**, exhibit T_d values higher than 300 °C. These compounds were kept at 200 °C for 3 h and submitted to a new DCS cycle which gave unchanged T_d values. These various results thus clearly demonstrate that NLO-phores with high thermal stability can be synthesized from rigidified π-conjugating spacers.

Conclusion

New series of thiophene-based chromophores for second-order nonlinear optics built around bridged DTE and BEDOT π-conjugating spacers have been synthesized. UV−vis and EFISH data for NLO-phores derived from bridged DTE spacers have shown that covalent rigidification of DTE represents a powerful strategy for improving the electron relay efficiency of the spacer, thus allowing the synthesis of NLO-phores with $\mu\beta$ values among the highest known to date for systems based on heteroaromatic spacers.

The consequences of the rigidification of the BT spacer by intramolecular interactions in BEDOT are less evident due to a complex imbrication of the geometrical and electronic effects associated with the introduction of the ethylenedioxy groups on the thiophene ring. Nevertheless, crystallographic and electronic absorption data, results obtained on NLO-phores containing monothiophenic spacers and calculated values of the dipole moments, converge toward a coherent picture which provides strong support to the conclusion that the geometrical effects of noncovalent rigidification, i.e., the limitation of the rotational and vibrational disorder play a determining role on the enhancement of the molecular hyperpolarizability. Finally it should be noted that both strategies of rigidification allow the synthesis of thermally stable systems as long as the stability of the NLO-phores is not limited by that of the acceptor group.

Experimental Section

Theoretical calculations at the ab initio density functional level were performed using the program Gaussian98,[34] to investigate the molecular structure and the electronic properties of the molecules. Becke's three-parameter gradient corrected functional (B3lyp) with a polarized 6-31G* basis for all atoms was used to optimize the geometry of every molecule and to compute one-electron properties at this minimun energy conformation.

The geometries of compounds **4e**, **5e**, **6e**, and **18** were optimized by imposing a s-trans conformation for the carbon−carbon double bond connecting the π-spacer and the benzene ring, and the geometry for the dimethylamino group, i.e., the electron lone pair, was perpendicular to the benzene ring for optimal delocalization. For all compounds, the bis(dicyanomethylidene)indanylidene moiety is twisted out of the plane of the conjugated system due to significant steric hindrance.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz, respectively; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI or FAB mode on a VG-Autospec mass spectrometer, under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer or under positive electrospray (ESI+) on a JMS-700 JEOL mass spectrometer of reversed geometry. IR spectra were recorded on a Perkin-Elmer model 841 spectrophotometer, samples being embedded in KBr disks or thin films between NaCl plates. UV−vis absorption spectra were recorded on a lambda 2 Perkin-Elmer spectrometer. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Elemental analysis were performed by the Service Central d'Analyses du CNRS (Vernaison, France). Column chromatography purifications were carried out on Merck silica gel Si 60 (40−63 μm).

(4-Dimethylaminobenzyl)triphenylphosphonium Iodide (14). A mixture of freshly distilled *N*,*N*-dimethylaniline (24.2 g, 200 mmol), a 37 wt % aqueous solution of formaldehyde (16.2 g, 200 mmol), triphenylphosphine (52.4 g, 200 mmol), potassium iodide (33.2 g, 200 mmol), and acetic acid (40.0 g) in $CHCl_3$ (150 mL) was stirred for 10 min. Then the addition of few drops of water led to a clear reaction mixture which was left under stirring at room temperature for 3 weeks. After separation by decantation, the organic phase was dried over Na_2SO_4 and evaporated in vacuo to give a solid which was recovered by filtration and washed several times with water and Et_2O. Recrystallization from EtOH gave greenish crystals (85 g, 81% yield). Mp 240 °C. ^{1}H NMR ($CDCl_3$) δ: 7.69 (m, 3H); 7.56−7.48 (m, 12H); 6.71 (dd, 2H, $^4J_{H-P} = 2.4$, $^3J = 8.9$); 6.32 (d, 2H, $^3J = 8.7$); 4.71 (d, 2H, $^2J_{H-P} = 12.9$); 2.76 (s, 6H).

***N*,*N*-Dihexylaniline (16).** A mixture of freshly distilled aniline (2 g, 21.5 mmol), iodohexane (9.57 g, 4.51 mmol), and K_2CO_3 (6.23 g, 4.51 mmol) in EtOH (20 mL) was refluxed for 18 h. The suspension was filtered, and the resulting solid was washed with CH_2Cl_2. The filtered solution was washed with water, dried over Na_2SO_4, and concentrated in vacuo. Purification by chromatography on silca gel (eluent: CH_2Cl_2/petroleum ether 1:1) led to a colorless oil (4.8 g, 85% yield). $E_{1.7\ \mathrm{mbar}} =$ 145 °C. ^{1}H NMR ($CDCl_3$) δ: 7.26 (m, 2H); 6.68 (m, 3H); 3.30 (m, 4H); 1.63 (m, 4H, CH_2); 1.38 (m, 12H); 0.95 (s, 6H).

4-Formyl-*N*,*N*-dihexylaniline (17). To a solution of *N*,*N*-dihexylaniline **16** (4.8 g, 18.4 mmol) in anhydrous 1,2-dichloroethane (100 mL) at room temperature were successively added anhydrous DMF (1.70 mL, 18.4 mmol) and $POCl_3$ (2.05 mL, 22 mmol), and the mixture was refluxed for one night. After hydrolysis for 2 h under vigorous stirring at room temperature using an aqueous solution of sodium acetate 2M (200 mL), the product was extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporated in vacuo before a purification by chromatography on silica gel (eluent: CH_2Cl_2) to give a yellow oil (4.0 g, 75% yield). ^{1}H NMR ($CDCl_3$) δ: 9.67 (s, 1H, CHO); 7.67 (d, 2H, $^3J = 8.8$); 6.61 (d, 2H, $^3J =$ 8.8); 3.31 (t, 4H); 1.57 (m, 4H, CH_2); 1.31 (m, 12H); 0.88 (t, 6H). NMR ^{13}C ($CDCl_3$) δ: 189.7; 152.4; 132.1; 124.33; 110.51; 50.96; 31.50; 26.97; 26.56; 22.51; 13.89. IR (NaCl) ν: 1678 cm^{-1} (CO).

(4-Dihexylaminobenzyl)triphenylphosphonium Bromide (15). To a solution of aldehyde **17** (4 g, 13.8 mmol) in absolute EtOH (20 mL), an excess of $NaBH_4$ was added portionwise until consumption of the starting material as followed by TLC (CH_2Cl_2). After dilution with Et_2O, the mixture was hydrolyzed at 0 °C using a 25% aqueous solution of HCl. The organic phase was dried over Na_2SO_4 and evaporated in vacuo to give the corresponding alcohol (4.8 g) which was directly dissolved in anhydrous $CHCl_3$ (80 mL) in the presence of $HPPh_3Br$ (5.4 g, 15.7 mmol) (prepared from a solution of HBr 48% and PPh_3). The reaction mixture was refluxed for 3 h, and after cooling, the solvent was evaporated. The residue was dissolved in the minimum of $CHCl_3$, and the solution was successively washed with a saturated aqueous solution of $NaHCO_3$ and water. After evaporation of the solvent, the resulting oil was triturated in the minimum of Et_2O leading to the precipitation of a white solid which was filtered to give a white powder (2.5 g, 27% yield). Mp 179−180 °C. ^{1}H NMR ($CDCl_3$) δ: 7.75 (m, 3H); 7.65 (m, 12H); 6.81 (m, 2H); 6.34 (d, 2H, $^3J = 8.6$); 5.04 (d, 2H, $^2J_{H-P}$=12.8); 3.14 (t, 4H, $^3J = 7.6$); 1.47 (s, 4H); 1.26 (s, 12H); 0.87 (t, 6H).

(*E*)-1-(2-Formyl-5-thienyl)-2-(2-thienyl)ethene (8g). To a solution of compound **8f** (1.66 g, 8.65 mmol) and anhydrous DMF (0.85 mL, 10.9 mmol) in anhydrous 1,2-dichloroethane (20 mL) was added $POCl_3$ (1 mL, 10.9 mmol), and the mixture was refluxed for 2 h. After cooling, the mixture was poured into an aqueous solution of sodium acetate 1 M (100 mL) and stirred for 2 h. After separation of the organic phase by decantation, the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic fractions were gathered, dried over $MgSO_4$, and evaporated in vacuo. After chromatography on silica gel (eluent: CH_2Cl_2) and recrystallization from EtOH, yellow crystals were obtained (1.61 g, 85% yield). Mp 85−86 °C (lit. 88 °C[19]). ^{1}H NMR ($CDCl_3$) δ: 9.85 (s,1H, CHO); 7.95 (d, 1H, $^3J = 4.0$); 7.59 (d, 1H, $^3J = 5.0$); 7.50 (d, 1H, $^3J = 16.1$); 7.42 (d, 1H, $^3J = 4.0$); 7.35 (d, 1H, $^3J = 4.0$); 7.22 (d, 1H, $^3J =$ 16.1); 7.10 (dd, 1H, $^3J = 5.0$ and 4.0). ^{13}C NMR ($CDCl_3$) δ: 183.7; 151.1; 141.0; 140.9; 138.9; 128.7; 128.3; 128.5; 127.2; 125.7; 120.1. IR (KBr) ν cm^{-1}: 1657 (C=O); 1611 (C=C). UV (CH_2Cl_2) λ_{max}: 384 nm.

(*E*)-1-[2-(*E*)-(4-*N*,*N*-dimethylaminobenzylidenemethyl)-5-thienyl]-2-(2-thienyl)ethene (8h). Under a N_2 atmosphere, a solution of phosphonium iodide **14** (3.42 g, 6.6 mmol) in anhydrous THF (25 mL) was cooled to −50 °C, and *t*-BuOK (735 mg, 6.6 mmol) was portionwise added. The reaction mixture turned to red, and the stirring was maintained 20 min at −50 °C before dropwise addition of a solution of aldehyde **8g** (1.2 g, 5.5 mmol) in anhydrous THF (10 mL). The mixture was slowly warmed to room temperature during a period of 3 h, and the solution was concentrated under reduced pressure leading to a solid which was dissolved in CH_2Cl_2 (200 mL). The solution was washed with water (3 × 50 mL), dried over Na_2SO_4, and evaporated in vacuo. Purification by chromatography on silica gel (eluent: CH_2Cl_2) gave an orange solid (1.55 g, 84% yield). Mp 190−191 °C. ^{1}H NMR ($CDCl_3$) δ: 7.36 (d, 2H, $^3J = 8.75$); 7.17 (d, 1H, $^3J = 5.0$); 7.03−6.96 (m, 5H); 6.89−6.82 (m, 3H); 6.70 (d, 2H, $^3J = 8.75$); 2.99 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 150.1; 143.1; 142.6; 139.9; 129.0; 127.6; 127.5; 127.1; 125.8; 125.5; 125.1; 124.1; 121.7; 120.8; 117.6; 112.6; 40.3. EI MS *m*/*z* (I%): 337 ($M^{+\bullet}$, 100); 321 (5); 169 (10). HRMS calcd for $C_{20}H_{19}N_1S_2$: 337.0958; found, 337.0959. UV (CH_2Cl_2) λ_{max}: 430 nm.

(*E*)-1-[2-(*E*)-(4-*N*,*N*-dimethylaminobenzylidenemethyl)-5-thienyl]-2-(2-formyl-5-thienyl)ethene (8j). A solution of

---

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle E. S.; Pople J. A.; Gaussian 98 (Revision A.9); Gaussian; Inc.; Pittsburgh, PA.; 1998.

n-BuLi 1.6 M in hexane (2.33 mL, 3.60 mmol) was added slowly to a solution of compound **8h** (1.2 g, 3.56 mmol) in anhydrous THF (50 mL) at 0 °C under a N_2 atmosphere. The mixture was stirred for 0.5 h at 0 °C before dropwise addition of anhydrous DMF (1.37 mL, 17.8 mmol), and the reaction was left overnight under stirring at room temperature. After evaporation of the solvents, the solid was dissolved in CH_2Cl_2 (300 mL), and the solution was washed with water (3 × 100 mL), dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by chromatography on silica gel (eluent: CH_2Cl_2) affording a brown powder (850 mg, 65% yield). Mp 180−182 °C. ^{1}H NMR ($CDCl_3$) δ: 9.84 (s, 1H, CHO); 7.65 (d, 1H, ^3J = 3.9); 7.37 (d, 2H, ^3J = 8.8); 7.21 (d, 1H, ^3J = 15.7); 7.10 (d, 1H, ^3J = 3.9); 7.01 (d, 1H, ^3J = 3.9); 6.99 (d, 1H, ^3J = 16.2); 6.94 (d, 1H, ^3J = 15.7); 6.89 (d, 1H, ^3J = 3.8); 6.88 (d, 1H, ^3J = 16.0); 6.70 (d,2H, ^3J = 8.8); 3.00 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 182.4; 152.5; 150.3; 145.3; 141.1; 138.7; 137.4; 130.2; 129.6; 127.7; 126.2; 125.7; 124.8; 119.4; 117.2; 112.4; 40.4. EI MS *m*/*z* (I%): 365 ($M^{+\bullet}$, 100); 351 (10); 183 (12); 57 (15). HRMS calcd for $C_{21}H_{19}N_1O_1S_2$: 365.0908; found, 365.0914. IR (KBr) ν cm^{-1} : 1654 (C=O). UV (CH_2Cl_2) λ_{max}: 475 nm.

(*E*)-1-[2-(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidenemethyl)-5-thienyl]-2-[2-(*E*)-(4-*N*,*N*-dimethylaminobenzylidenemethyl)-5-thienyl]ethene (1c). A mixture of aldehyde **8j** (100 mg, 0.27 mmol) and *N*,*N*-diethylthiobarbituric acid (55 mg, 0.27 mmol) in acetic anhydride (2 mL) was refluxed for 1.5 h. After being cooled to room temperature, the mixture was diluted with CH_2Cl_2 (150 mL), and the solution was washed with a 5% aqueous solution of $NaHCO_3$ (30 mL), dried over $MgSO_4$, and evaporated in vacuo. The resulting solid was triturated with EtOH, collected by filtration, wash several times with hot EtOH, and dried to lead to a black powder (100 mg, 68% yield). Mp 235 °C. ^{1}H NMR ($CDCl_3$) δ: 8.60 (s, 1H); 7.77 (d, 1H, ^3J = 4.2); 7.49 (d, 1H, ^3J = 15.7); 7.38 (d, 2H, ^3J = 8.8); 7.20 (d, 1H, ^3J = 4.2); 7.07 (d, 1H, ^3J = 3.8); 6.99 (d, 1H, ^3J = 15.9); 6.97 (d, 1H, ^3J = 15.7); 6.91 (d, 1H, ^3J = 3.8); 6.90 (d, 1H, ^3J = 15.9); 6.69 (d, 2H, ^3J = 8.8); 4.64−4.56 (m, 4H); 3.00 (s, 6H); 1.37−1.30 (m, 6H). ^{13}C NMR ($CDCl_3$) δ: 178.6; 160.3; 160.0; 150.4; 148.9; 147.5; 146.6; 139.0; 136.1; 130.8; 130.7; 128.2; 127.8; 127.0; 126.0; 124.7; 119.4; 117.1; 112.3; 109.3; 43.9; 43.1; 40.3; 29.7; 12.5; 12.4. EI MS *m*/*z* (I%): 547 ($M^{+\bullet}$, 90); 365 (30); 337 (100). HRMS calcd for $C_{29}H_{29}N_3O_2S_3$: 547.1422; found, 547.1428. IR (KBr) ν cm^{-1} : 1646 (C=O); 1586 (C=S). UV (CH_2Cl_2) λ_{max}: 606 nm.

(*E*)-1-[2-(3-Dicyanomethylidene-1-indanon-2-ylidenemethyl)-5-thienyl]-2-[2-(*E*)-(4-*N*,*N*-dimethylaminobenzylidenemethyl)-5-thienyl]ethene (1d). To a solution of 3-dicyanomethylidene-1-indanone (106 mg, 0.55 mmol) in absolute EtOH (10 mL) at 60 °C under a N_2 atmosphere, compound **8j** (200 mg, 0.55 mmol) was added portionwise. The mixture was stirred 1 h at 60 °C and 1 h at room temperature. After cooling to 0 °C, the resulting precipitate was collected by filtration and washed several times with EtOH. Further purification was achieved by a Soxhlet extraction of impurities for one night using Et_2O as solvent to lead to a black powder (178 mg, 60% yield). Mp > 250 °C. ^{1}H NMR ($CDCl_3$) δ: 8.82 (s, 1H); 8.68 (d, 1H, ^3J = 7.7); 7.92 (m, 1H); 7.75 (m, 3H); 7.46 (d, 1H, ^3J = 15.4); 7.37 (d, 2H, ^3J = 8.7); 7.17 (d, 1H, ^3J = 4.0); 7.08 (d, 1H, ^3J = 4.0); 6.99 (d, 1H, ^3J = 15.8); 6.98 (d, 1H, ^3J = 15.4); 6.92 (d, 1H, ^3J = 4.35); 6.90 (d, 1H, ^3J = 15.8); 6.69 (d, 2H, ^3J = 8.7); 3.01 (s, 6H, CH_3N). EI MS *m*/*z* (I%): 541 ($M^{+\bullet}$, 100); 527 (15); 365 (10). HRMS calcd for $C_{33}H_{23}N_3O_1S_2$: 541.1282; found, 541.1289. IR (KBr) ν cm^{-1} : 2214 ($C\equiv N$); 1698 (C=O). UV (CH_2Cl_2) λ_{max}: 656 nm. Anal. Calcd for $C_{33}H_{23}N_3O_1S_2$: C, 73.17; H, 4.28; N, 7.75; found: C, 73.83; H, 4.34; N, 7.56.

(*E*)-1-{2-[1,3-Bis(dicyanomethylidene)indan-2-ylidene)methyl]-5-thienyl}-2-[2-(*E*)-(4-*N*,*N*-dimethylaminobenzylidenemethyl)-5-thienyl]ethene (1e). To a solution of aldehyde **8j** (120 mg, 0.32 mmol) in acetic anhydride (6 mL) at 60 °C under a N_2 atmosphere, 1,3-bis(dicyanomethylidene)indane (79.5 mg, 0.32 mmol) was added portionwise. The mixture was stirred 1 h at 60 °C and 2 h at room temperature. After cooling to 0 °C, the resulting precipitate was collected by filtration and washed with hot EtOH (20 mL) and several times with EtOH. After recrystallization from CH_3CN, a black powder was obtained (120 mg, 62% yield). Mp > 250 °C. ^{1}H NMR ($CDCl_3$) δ: 8.62 (s,1H); 8.57 (dd, 2H); 7.78 (dd, 2H); 7.59 (d, 1H, ^3J = 4.0); 7.38 (d, 2H, ^3J = 8.3); 7.29 (d, 1H, ^3J = 4.0); 7.11 (s, 2H); 7.04−6.86 (m, 4H); 6.70 (d, 2H, ^3J = 8.3); 3.01 (s, 6H, CH_3N). IR (KBr) ν cm^{-1} : 2220 ($C\equiv N$). UV (CH_2Cl_2) λ_{max}: 720 nm.

(*E*)-2-Formyl-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (9g). To a solution of bridged dithienylethylene **2f** (0.54 g, 2.21 mmol) and anhydrous DMF (0.20 mL, 2.46 mmol) in anhydrous 1,2-dichloroethane (70 mL) at 0 °C under N_2 atmosphere was added dropwise $POCl_3$ (0.23 mL, 2.46 mmol). The reaction mixture was refluxed for 18 h and then cooled to room temperature before addition of an aqueous solution of sodium acetate (2 M, 50 mL) and further stirring for 3 h. After extraction with CH_2Cl_2, the organic fractions were dried over Na_2SO_4 and evaporated in vacuo to give a solid which was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give a yellow-orange powder (540 mg, 83% yield). Mp 184−186 °C. ^{1}H NMR ($CDCl_3$) δ: 9.77 (s, 1H, CHO); 7.51 (s, 1H); 7.43 (d, 1H, ^3J = 4.8); 6.95 (d, 1H, ^3J = 4.8); 3.25 (m, 4H, CH_2); 3.03 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ: 182.4 (CHO); 154.1; 153.3; 150.1; 146.6; 143.3; 133.3; 131.9; 131.8; 125.1; 123.2; 35.8; 34.5; 27.4; 26.8. EI MS *m*/*z* (I%): 272 ($M^{+\bullet}$, 100). IR (KBr) ν cm^{-1} : 1642 (C=O). UV (CH_2Cl_2) λ_{max}: 433 nm.

(*E*)-2-[(*E*)-(4-*N*,*N*-Dimethylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (9h). To a suspension of aldehyde **9g** (1 g, 3.67 mmol) and phosphonium iodide **14** (3.84 g, 7.35 mmol) in a 1:1 mixture of anhydrous solvents THF/CH_3CN (100 mL) at room temperature under a N_2 atmosphere was added in one portion *t*-BuOK (0.825 g, 7.35 mmol), and the mixture was stirred for 18 h. After evaporation of the solvents under reduced pressure, the residue was dissolved in CH_2Cl_2 and the solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The resulting solid was purified by chromatography on silica gel (eluent: CH_2Cl_2), affording a brown powder (1.03 g, 72% yield) corresponding to a mixture of *E* and *Z* isomers. Trituration of an analytical sample (60 mg) of this mixture with hot MeOH and filtration gave the pure *E*-isomer (20 mg) whose analytical characteristics are described as followed: Mp 204−206 °C. ^{1}H NMR ($CDCl_3$) δ: 7.35 (d, 2H, ^3J = 8.3); 7.30 (d, 1H, ^3J = 4.5); 6.99 (d, 1H, ^3J = 16.0); 6.91 (d, 1H, ^3J = 4.5); 6.84 (d, 1H, ^3J = 16.0); 6.80 (s, 1H); 6.70 (d, 2H, ^3J = 8.3); 3.30 (m, 2H); 3.19 (m, 2H); 2.98 (m, 10H). ^{13}C NMR ($CDCl_3$) δ: 150.4; 150.1; 149.9; 148.7; 144.1; 129.2; 127.3; 127.1; 126.4; 126.0; 125.4; 123.0; 120.9; 118.5; 112.5; 40.4; 35.2; 34.5; 27.4; 27.3. EI MS *m*/*z* (I%): 389 ($M^{+\bullet}$, 100). UV (CH_2Cl_2) λ_{max}: 434 nm.

(*E*)-2-Formyl-2′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (9j). To a solution of compound **9h** as a mixture of *E* and *Z* isomers (0.80 g, 2.02 mmol) and anhydrous DMF (0.21 mL, 2.67 mmol) in anhydrous 1,2-dichloroethane (60 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (0.25 mL, 2.67 mmol) dropwise. The mixture was refluxed for 18 h and then cooled to room temperature before addition of an aqueous solution of sodium acetate (1 M, 50 mL) and further stirring for 2 h. After extraction with CH_2Cl_2, the organic fractions were dried over $MgSO_4$ and evaporated in vacuo to give a solid which was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give a red powder (0.31 g, 36% yield). Mp 258−260 °C. ^{1}H NMR ($CDCl_3$) δ: 9.77 (s, 1H, CHO); 7.51 (s, 1H); 7.36 (d, 2H, ^3J = 8.8); 6.99 (d, 1H, ^3J = 16.0); 6.89 (d, 1H, ^3J = 16.0); 6.84 (s, 1H); 6.69 (d, 2H, ^3J = 8.8); 3.31 (m, 2H, CH_2); 3.23 (m, 2H, CH_2); 3.05 (m, 2H, CH_2); 3.00 (m, 8H, $(CH_3)_2$−N, CH_2). ^{13}C NMR ($CDCl_3$) δ: 182.4; 154.6; 153.9; 151.5; 150.1; 149.9; 146.1; 140.9; 138.8; 128.6; 127.6; 125.0; 124.9; 120.9; 118.0; 112.0; 40.4; 35.2; 34.6; 27.6; 26.8. EI MS *m*/*z* (I%): 417 ($M^{+\bullet}$, 100). UV (CH_2Cl_2) λ_{max}: 500 nm.

(*E*)-2′-[(*E*)-(4-*N*,*N*-Dimethylaminobenzylidene)methyl]-2-[(3-oxo-dihydrobenzofuran-2-ylidene)methyl]-6,6′-bis-(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (2a). A mixture of aldehyde **9j** (80 mg, 0.19 mmol), 3-coumaranone (36 mg, 0.27 mmol), and neutral Al_2O_3 (0.56 g) in $CHCl_3$ (10 mL) was stirred for 2 days at room temperature. Al_2O_3 was separated by filtration and washed with EtOH. The filtered solution was evaporated in vacuo, and the residue was triturated in EtOH. The resulting precipitate was collected by filtration, washed with EtOH, and dried to give a dark blue powder (70 mg, 69% yield). A analytical sample was further purified by chromatography on silica gel (eluent: CH_2Cl_2/AcOEt 99:1) and trituration in EtOH. Mp 300 °C. ^{1}H NMR ($CDCl_3$) δ: 7.80 (d, 1H, $J = 7.5$); 7.62 (m, 1H); 7.41 (d, 2H, $^3J = 8.6$); 7.38−7.34 (m, 2H); 7.22−7.20 (m, 2H); 7.00 (d, 1H, $^3J = 15.9$); 6.89 (d, 1H, $^3J = 15.9$); 6.82 (s, 1H), 6.70 (d, 2H, $^3J = 8.6$); 3.30 (s, 4H); 3.00 (m, 10H). EI MS *m*/*z* (I%): 533 ($M^{+\bullet}$, 100); 417 (10); 266 (25). HRMS calcd for $C_{33}H_{27}N_1O_2S_2$: 533.1483; found, 533.1451. IR (KBr) ν cm^{-1} : 1692 (C═O). UV (CH_2Cl_2) λ_{max}: 592 nm.

(*E*)-2-(2,2-Dicyanoethenyl)-2′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (2b). A mixture of aldehyde **9j** (100 mg, 0.24 mmol), malononitrile (19 mg, 0.28 mmol), and one drop of Et_3N in $CHCl_3$ (10 mL) was refluxed for 18 h. At rt, the precipitate was collected by filtration, washed with EtOH, and dried to give a dark blue powder (85 mg, 76% yield). A sample for elemental analysis was further purified by chromatography on silica gel (sample adsorbed on silica gel; eluent: CH_2Cl_2/AcOEt 99.5:0.5). Mp 308 °C. ^{1}H NMR ($CDCl_3$) δ: 7.58 (s, 1H); 7.36 (d, 2H, $^3J = 8.6$); 7.29 (s, 1H); 7.00 (d, 1H, $^3J = 15.95$); 6.92 (d, 1H, $^3J = 15.95$); 6.85 (s, 1H); 6.70 (d, 2H, $^3J = 8.6$); 3.29 (m, 4H, CH_2); 3.03 (m, 10H). EI MS *m*/*z* (I%): 465 ($M^{+\bullet}$, 100); 232 (15); 266 (10). HRMS calcd for $C_{28}H_{23}N_3S_2$: 465.1333; found, 465.1344. IR (KBr) ν cm^{-1} : 2208 (C≡N). UV (CH_2Cl_2) λ_{max}: 609 nm. Anal. Calcd for $C_{28}H_{23}N_3S_2$: C, 72.23; H, 4.98; N, 9.02; S, 13.77; found: C, 72.08; H, 4.79; N, 8.88; S, 14.14.

(*E*)-2-(3-Dicyanomethylidene-1-indanon-2-ylidenemethyl)-2′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (2d). A mixture of aldehyde **9j** (0.325 g, 0.78 mmol) and 3-dicyanomethylidene-1-indanone (150 mg, 0.78 mmol) in absolute EtOH (70 mL) was refluxed for 18 h. At rt the precipitate was collected by filtration, carefully washed with EtOH until elimination of dicyanovinylindan-3-one, and dried to give a dark blue powder (305 mg, 70% yield). Further purification was achieved by a Soxhlet extraction of impurities for 2 days using EtOH as solvent. The final product was insoluble in common solvents at room temperature (EtOH, CH_2Cl_2, DMSO, CS_2, THF). Mp 258 °C. EI MS *m*/*z* (I%): 593 ($M^{+\bullet}$, 15); 389 (45); 370 (100). HRMS calcd for $C_{37}H_{27}N_3O_1S_2$: 593.1595; found, 593.1594. IR (KBr) ν cm^{-1} : 2208 (C≡N), 1682 (C═O). UV (CH_2Cl_2) λ_{max}: 756 nm.

(*E*)-2-[(*E*)-(4-*N*,*N*-Dihexylylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (9i). To a suspension of aldehyde **9g** (0.5 g, 1.83 mmol) and phosphonium iodide **15** (1.60 g, 2.57 mmol) in a 1:1 mixture of anhydrous solvents THF/CH_3CN (100 mL) at room temperature under a N_2 atmosphere was added *t*-BuOK (0.29 g, 2.57 mmol) in one portion, and the mixture was stirred for 4 h. After addition of water (40 mL) and extraction with CH_2Cl_2, the organic phase was dried over Na_2SO_4 and evaporated in vacuo. The resulting solid was purified by chromatography on silica gel (eluent: CH_2Cl_2), affording a brown powder (0.95 g, 97% yield) corresponding to a mixture of *E* and *Z* isomers. Mp 95−98 °C. ^{1}H NMR ($CDCl_3$) δ: 7.28−7.35 (m, 3H); 7.05−6.75 (m, 4H); 6.65−6.55 (m, 2H); 3.35−3.15 (m, 8H); 3.05−2.90 (m, 4H); 1.65−1.50 (m, 4H); 1.40−1.25 (m, 12H); 0.95−0.85 (m, 6H). ESI+ MS *m*/*z* (I%): 529.3 ($M^{+\bullet}$). UV (CH_2Cl_2) λ_{max}: 440 nm.

(*E*)-2-Formyl-2′-[(*E*)-(4-*N*,*N*-dihexylaminobenzylidene)methyl]-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (9k). $POCl_3$ (0.185 mL, 1.98 mmol) was added dropwise to a solution of compound **9i** (0.865 g, 1.63 mmol) and anhydrous DMF (0.152 mL, 1.93 mmol) in anhydrous 1,2-dichloroethane (80 mL) at 0 °C under a N_2 atmosphere. The reaction mixture was refluxed for 18 h and then hydrolyzed under stirring for 2 h at room temperature using an aqueous solution of sodium acetate (1 M, 30 mL). After extraction with CH_2Cl_2, the organic fractions were dried over Na_2SO_4 and evaporated in vacuo. A purification by chromatography on silica gel (eluent: CH_2Cl_2) led to a red solid (0.41 g, 45% yield). Mp 135−137 °C. ^{1}H NMR ($CDCl_3$) δ: 9.75 (s, 1H, CHO); 7.48 (s, 1H); 7.32 (d, 2H, $^3J = 8.9$); 6.95 (d, 1H, $^3J = 16.0$); 6.85 (d, 1H, $^3J = 16.0$); 6.80 (s, 1H); 6.60 (d, 2H, $^3J = 8.9$); 3.20 (m, 8H, CH_2); 3.00 (m, 4H, CH_2); 1.60 (m, 4H, CH_2); 1.32 (s, 12H, CH_2); 0.90 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 182.3 (CHO); 154.6; 153.9; 151.7; 149.9; 147.9; 146.2; 140.6; 133.0; 132.0; 128.7; 127.7; 124.7; 123.7; 120.6; 117.3; 111.5; 53.4; 51.0; 35.2; 34.6; 31.7; 27.6; 27.2; 26.8; 22.7; 14.0. EI MS *m*/*z* (I%): 557 ($M^{+\bullet}$, 100); 486 (35); 401 (20); 208 (20). HRMS calcd for $C_{35}H_{43}N_1O_1S_2$: 557.2786; found, 557.2775. IR (KBr) ν cm^{-1} : 1661 (C═O). UV (CH_2Cl_2) λ_{max}: 507 nm. Anal. Calcd for $C_{35}H_{43}N_1O_1S_2$: C, 75.36; H, 7.72; N, 2.51; S, 11.49; found: C, 74.94; H, 7.69; N, 2.50; S, 11.45.

(*E*)-2-[(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidene)methyl]-2′-[(*E*)-(4-*N*,*N*-dihexylaminobenzylidene)methyl]-2-formyl-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (3c). A mixture of aldehyde **9k** (101 mg, 0.18 mmol) and *N*,*N*-diethylthiobarbituric acid (36 mg, 0.18 mmol) in acetic anhydride (3 mL) was refluxed for 3 h under a N_2 atmosphere. After being cooled to room temperature, the mixture was diluted with EtOH (10 mL) leading to the precipitation of a solid which was collected by filtration, washed several times with EtOH, and dried to give a black powder (115 mg, 86% yield). A sample for elemental analysis was purified by chromatography on silica gel (eluent: CH_2Cl_2/AcOEt 99:1). Mp 235 °C. ^{1}H NMR ($CDCl_3$) δ: 8.51 (s, 1H); 7.60 (br s, 1H); 7.33 (d, 2H, $^3J = 8.8$); 6.96 (d, 1H, $^3J = 15.9$); 6.92 (d, 1H, $^3J = 15.9$); 6.86 (s, 1H); 6.60 (d, 2H, $^3J = 8.8$); 4.60 (m, 4H, CS−N(C*H*$_2$R)-CO); 3.43 (m, 2H); 3.29 (m, 6H); 3.09 (m, 4H, N(C*H*$_2$R)); 1.58 (m, 4H); 1.30 (m, 12H); 0.88 (m, 12H). ^{13}C NMR ($CDCl_3$) δ: 178.5; 161.6; 160.0; 157.1; 154.5; 148.2; 147.5; 145.0; 142.6; 141.0; 139.8; 130.1; 128.1; 126.1; 123.5; 120.8; 117.0; 111.6; 106.8; 92.2; 53.4; 51.0; 43.8; 42.9; 36.9; 34.8; 31.9; 31.7; 29.7; 29.3; 27.9; 27.3; 26.9; 26.8; 26.2; 22.7; 14.1; 14.0; 12.6; 12.4. EI MS *m*/*z* (I%): 739 ($M^{+\bullet}$, 50); 529 (100); 445 (75); 373 (55); 282 (60); 213 (75); 200 (85). HRMS calcd for $C_{43}H_{53}N_3O_2S_3$: 739.3300; found, 739.3293. IR (KBr) ν cm^{-1} : 1674 (C═O); 1647 (C═S). UV (CH_2Cl_2) λ_{max}: 682 nm. Anal. Calcd for $C_{43}H_{53}N_3O_2S_3$: C, 69.78; H, 7.22; N, 5.68; S, 13.00; found: C, 69.88; H, 7.15; N, 5.44; S, 12.98.

(*E*)-2-(3-Dicyanomethylidene-1-indanon-2-ylidenemethyl)-2′-[(*E*)-(4-*N*,*N*-dihexylaminobenzylidene)methyl]-2-formyl-6,6′-bis(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (3d).To a solution of aldehyde **9k** (120 mg, 0.21 mmol) in absolute EtOH (10 mL) at 60 °C was added 3-dicyanomethylidene-1-indanone (41 mg, 0.21 mmol), and the mixture was refluxed for 72 h. On cooling to room temperature, the precipitate was collected by filtration, washed several times with cold EtOH, and dried to give a black powder (120 mg, 76% yield). A sample (20 mg) for elemental analysis was purified by chromatography on silica gel (eluent: CH_2Cl_2/AcOEt 99:1). Mp 245 °C. ^{1}H NMR ($CDCl_3$) δ: 8.50 (s, 1H); 8.42 (d, 1H, $^3J = 7.7$); 7.76 (d, 1H, $^3J = 7.2$); 7.58 (t, 1H, $^3J = 7.3$); 7.52 (t, 1H, $^3J = 7.5$); 7.48 (br.s, 1H); 7.23 (d, 2H, $^3J = 8.5$); 6.76 (d, 1H, $^3J = 15.8$); 6.67 (d, 1H, $^3J = 15.8$); 6.56 (s, 1H); 6.53 (d, 2H, $^3J = 8.5$); 3.25 (m, 6H); 3.10 (m, 2H); 2.95 (m, 4H); 1.57 (m, 4H); 1.30 (m, 12H); 0.91 (m, 6H). ^{13}C NMR-($CDCl_3$) δ: 188.3; 160.2; 157.3; 155.1; 148.2; 142.7; 141.3; 140.0; 136.6; 134.0; 133.4; 130.4; 128.2; 126.3; 124.8; 123.4; 122.6; 120.6; 116.6; 115.5; 111.5; 65.8; 51.0; 36.9; 34.8; 31.7; 27.8; 27.3; 26.8; 26.1; 22.7; 14.1. EI MS *m*/*z* (I%): 733 ($M^{+\bullet}$, 5); 529 (65); 194 (100). HRMS calcd for $C_{47}H_{47}N_3O_1S_2$: 733.3160; found, 733.3141. IR (KBr) ν cm^{-1} : 2211(C≡N); 1687 (C═O). UV (CH_2Cl_2) λ_{max}: 768 nm. Anal. Calcd for $C_{43}H_{53}N_3O_2S_3$: C, 76.91; H, 6.45; N, 5.72; S, 8.74; found: C, 76.40; H, 6.14; N, 5.63; S, 9.02.

5-Formyl-2,2′-bithiophene (10g). $POCl_3$ (1.17 mL, 12.6 mmol) was added to a solution of 2,2′-bithiophene **10f** (2 g, 12 mmol) and anhydrous DMF (0.98 mL, 12.6 mmol) in anhydrous 1,2-dichloroethane (30 mL) at 0 °C under N_2 atmosphere. The solution was warmed to room temperature and then refluxed for 2 h. At rt, the mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) and stirred for 2 h to complete the hydrolysis. After separation of the organic phase by decantation, the aqueous phase was extracted with

CH_2Cl_2 (2 × 75 mL). The organic phases were gathered, dried over $MgSO_4$, and evaporated in vacuo. Purification by chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether 1:1) gave a yellow solid (2.2 g, 94% yield). Mp 57−58 °C. ^1H NMR ($CDCl_3$) δ: 9.86 (s, 1H, CHO); 7.67 (d, 1H, ^3J = 4.0); 7.36 (2d, 2H, ^3J = 4.3); 7.25 (d, 1H, ^3J = 4.0); 7.07 (t, 1H, ^3J = 4.3). ^{13}C NMR ($CDCl_3$) δ: 182.0; 147.1; 141.6; 137.3; 136.0; 128.3; 127.1; 126.1; 124.2. EI MS *m/z* (I%): 194 ($M^{+\bullet}$,100); 166 (10); 121 (45). HRMS calcd for $C_9H_6O_1S_2$: 193.9860; found, 193.9854. IR (KBr) ν cm^{-1}: 1648 (C=O). UV (CH_2Cl_2) λ_{max}: 353 nm.

5-[(*E*)-(4-*N*,*N*-Dimethylaminobenzylidene)methyl]-2,2′-bithiophene (10h). To a suspension of phosphonium iodide **14** (2.43 g, 4.6 mmol) in 25 mL of a mixture of anhydrous solvents THF/CH_3CN (1:1) at 0 °C under a N_2 atmosphere was added *t*-BuOK (0.52 g, 4.6 mmol) portionwise, and the resulting red solution was stirred at 0 °C for additional 15 min before cooling to −70 °C and subsequent dropwise addition of a solution of aldehyde **10g** (0.6 g, 3.1 mmol) in anhydrous THF (10 mL). The mixture was stirred for 1 h at −70 °C and then 2 h at room temperature. After evaporation of the solvents, CH_2Cl_2 (100 mL) was added to the residue, and the solution was washed with water (2 × 50 mL), dried over $MgSO_4$, and evaporated in vacuo. The resulting solid was purified by chromatography on silica gel (eluent: CH_2Cl_2) affording a yellow solid (896 mg, 93% yield). Mp 178 °C. ^1H NMR ($CDCl_3$) δ: 7.36 (d, 2H, ^3J = 8.75); 7.19 (dd, 1H, ^4J = 1.0, ^3J = 5.0); 7.16 (dd, 1H, ^4J = 1.0, ^3J = 3.7); 7.05 (d, 1H, ^3J = 3.7); 7.01 (dd, 1H, ^3J = 3.7 and 5.0); 6.98 (d, 1H, ^3J = 16.0); 6.87 (d, 1H, ^3J = 3.7); 6.84 (d, 1H, ^3J = 16.0); 6.70 (d, 2H, ^3J = 8.75); 2.99 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 141.4; 136.2; 133.1; 127.1; 126.2; 125.9; 124.0; 122.5; 121.7; 115.9; 110.8; 40.4. EI MS *m/z* (I%): 311 ($M^{+\bullet}$, 100); 295 (5); 155 (10). HRMS calcd for $C_{18}H_{17}N_1S_2$: 311.0802; found, 311.0816. UV (CH_2Cl_2) λ_{max}: 404 nm.

5-Formyl-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene) methyl]-2,2′-bithiophene (10j). To a solution of compound **10h** (0.5 g, 1.6 mmol) and anhydrous DMF (0.13 mL, 1.7 mmol) in anhydrous 1,2-dichloroethane (25 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (0.157 mL, 1.7 mmol) dropwise, and the mixture was refluxed for 18 h. At rt, the mixture was poured into an aqueous solution of sodium acetate (1 M, 150 mL) and stirred for 2 h. After decantation, the aqueous phase was extracted with CH_2Cl_2 (150 mL). The organic phases were gathered, dried over Na_2SO_4, and evaporated in vacuo. A purification by chromatography on silica gel (eluent: CH_2Cl_2) led to a red solid (325 mg, 60% yield). Mp 173−175 °C. ^1H NMR ($CDCl_3$) δ: 9.84 (s, 1H, CHO); 7.65 (d, 1H, ^3J = 4.0); 7.37 (d, 2H, ^3J = 8.7); 7.24 (d, 1H, ^3J = 4.0); 7.21 (d, 1H, ^3J = 4.0); 6.98 (d, 1H, ^3J = 16.0); 6.92 (d, 1H, ^3J = 4.0); 6.90 (d, 1H, ^3J = 15.5); 6.69 (d, 2H, ^3J = 8.7); 3.00 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 182.4; 150.4; 147.7; 146.3; 141.1; 137.6; 132.9; 130.5; 127.8; 126.9; 125.8; 124.6; 123.6; 116.7; 112.3; 40.4. EI MS *m/z* (I%): 339 ($M^{+\bullet}$, 100); 311 (5); 169 (12); 132 (7). HRMS calcd for $C_{19}H_{17}N_1O_1S_2$: 339.0759; found, 339.0751. IR (KBr) ν cm^{-1}: 1661 (C=O). UV (CH_2Cl_2) λ_{max}: 455 nm.

5-[3-Dicyanomethylidene-1-indanon-2-ylidenemethyl]-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-2,2′-bithiophene (4d). To a solution of 3-dicyanomethylidene-1-indanone (45 mg, 0.23 mmol) in absolute EtOH (10 mL) at 60 °C under a N_2 atmosphere was added aldehyde **10j** (80 mg, 0.23 mmol) portionwise. The stirring was maintained 1 h at 60 °C and then 1 h at room temperature. The reaction mixture was cooled to 0 °C, and the resulting precipitate was filtered, thoroughly washed with EtOH, and dried in a vacuum to give a black powder (85 mg, 70% yield). Mp 251 °C (dec). ^1H NMR ($CDCl_3$): 8.62 (s, 1H); 7.92 (m, 1H); 7.75 (m, 3H); 7.59 (d, 1H, ^3J = 4.2); 7.38 (d, 2H, ^3J = 8.8); 7.35 (d, 1H, ^3J = 3.6); 7.25 (d, 1H, ^3J = 4.2); 6.99 (s, 2H); 6.98 (d, 1H, ^3J = 3.6); 6.70 (d, 2H, ^3J = 8.8); 3.01 (s, 6H, CH_3N). EI MS *m/z* (I%): 515 ($M^{+\bullet}$, 100); 257 (12). HRMS calcd for $C_{31}H_{21}N_3O_1S_2$: 515.1126; found, 515.1112. UV(CH_2Cl_2) λ_{max}: 650 nm.

5-[1,3-Bis(dicyanomethylidene)indan-2-ylidenemethyl]-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-2,2′-bithiophene (4e). A mixture of aldehyde **10j** (80 mg, 0.23 mmol) and 1,3-bis(dicyanomethylidene)indane (57 mg, 0.23 mmol) in acetic anhydride (5 mL) was stirred at 80 °C for 1.5 h. After being cooled to room temperature, the mixture was poured into EtOH (50 mL) leading to the precipitation of a black powder which was filtered, thoroughly washed with EtOH, and dried under vacuum (105 mg, 80% yield). Mp 214 °C (dec). ^1H NMR ($CDCl_3$): 8.63 (s, 1H); 8.57 (m, 2H) ; 7.78 (m, 2H); 7.61 (d, 1H, ^3J = 4.2); 7.38 (d, 2H, ^3J = 8.8); 7.35 (d, 1H, ^3J = 3.9); 7.25 (d, 1H, ^3J = 4.2); 7.01 (d, 1H, ^3J = 15.1); 6.98 (d, 1H, ^3J = 3.9); 6.97 (d, 1H, ^3J = 15.1); 6.70 (d, 2H, ^3J = 8.8); 3.01 (s, 6H, CH_3N). EI MS *m/z* (I%): 563 ($M^{+\bullet}$, 10); 536 (25); 325 (25); 256 (100); 241 (85); 229 (55); 214 (35). HRMS calcd for $C_{34}H_{21}N_5S_2$: 563.1238; found, 563.1232. IR (KBr) ν cm^{-1}: 2200 (C≡N). UV(CH_2Cl_2) λ_{max}: 712 nm.

5-Formyl-2,2′-bi(3,4-ethylenedioxythiophene) (11g). To a solution of 2,2′-bis(3,4-ethylenedioxy)thiophene **11f** (1.5 g, 5.32 mmol) and anhydrous DMF (0.45 mL, 5.58 mmol) in anhydrous 1,2-dichloroethane (60 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (0.52 mL, 5.58 mmol) dropwise, and the mixture was refluxed for 18 h. After being cooled to room temperature, the mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) and then stirred for 2 h. The organic phase was separated by decantation and the aqueous phase was extracted with CH_2Cl_2 (2 × 150 mL). The organic phases were gathered, dried over $MgSO_4$ and evaporated in vacuo. A purification by chromatography on silica gel (eluent: CH_2Cl_2) gave a yellow solid (1.3 g, 80% yield). Mp 258 °C. ^1H NMR ($CDCl_3$) δ: 9.82 (s, 1H, CHO); 6.83 (s, 1H); 4.45−4.24 (m, 8H, CH_2O). ^{13}C NMR ($CDCl_3$) δ: 179.0; 148.5; 141.2; 140.0; 136.3; 119.9; 113.6; 107.7; 102.2; 65.5 (2C); 65.0; 64.3. EI MS *m/z* (I%): 310 ($M^{+\bullet}$, 100); 213 (30); 185 (30); 169 (20). HRMS calcd for $C_{13}H_{10}O_5S_2$: 309.9969; found, 309.9981. IR (KBr) ν cm^{-1}: 1638 (C=O); 1563 (C=C). UV (CH_2Cl_2) λ_{max}: 395 nm.

5-[(*E*)-(4-*N*,*N*-Dimethylaminobenzylidene)methyl]-2,2′-bi(3,4-ethylenedioxythiophene) (11h). To a suspension of phosphonium iodide **14** (1.57 g, 3.0 mmol) in a 1:1 mixture of anhydrous solvents THF/CH_3CN (25 mL) at 0 °C under a N_2 atmosphere was added *t*-BuOK (336 mg, 3.0 mmol) portionwise, leading to a red solution which was further stirred 15 min at 0 °C and then cooled to −70 °C before addition of a solution of aldehyde **11g** (600 mg, 1.93 mmol) in anhydrous THF (10 mL). The reaction mixture was successively stirred at −70 °C for 1 h and at room temperature for 2 h. Then the solvents were evaporated in vacuo, the residue was dissolved in CH_2Cl_2 (100 mL), and the solution was washed with water (2 × 50 mL), dried over $MgSO_4$, and evaporated in vacuo. A chromatography on silica gel (eluent: CH_2Cl_2) afforded a yellow solid (600 mg, 73% yield). Mp 217−219 °C. ^1H NMR ($CDCl_3$) δ: 7.34 (d, 2H, ^3J = 8.7); 6.97 (d, 1H, ^3J = 16.1); 6.77 (d, 1H, ^3J = 16.1); 6.68 (d, 1H, ^3J = 8.7); 6.26 (s, 1H); 4.36−4.24 (m, 8H, CH_2O); 2.97 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 141.2; 137.8; 137.2; 136.8; 127.1; 125.8; 115.9; 113.7; 112.5; 110.3; 97.5; 65.1; 65.0; 64.7; 64.6; 40.5. EI MS *m/z* (I%): 427 ($M^{+\bullet}$, 100); 326 (10); 214 (10); 190 (15); 158 (10). HRMS calcd for $C_{22}H_{21}N_1O_4S_2$: 427.0912; found, 427.0926. IR (KBr) ν cm^{-1}: 1603 (C=C); 1168 (C−O−C). UV (CH_2Cl_2) λ_{max}: 415 nm.

5-Formyl-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene) methyl]-2,2′-bi(3,4-ethylenedioxythiophene) (11j). To a solution of compound **11h** (0.43 g, 1 mmol) and anhydrous DMF (0.2 mL, 2.58 mmol) in anhydrous 1,2-dichloroethane (45 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (0.10 mL, 1.07 mmol) dropwise, and the mixture was reflux for 16 h. After being cooled to room temperature, the mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) and then stirred for 2 h. The organic phase was separated by decantation, and the aqueous phase was extracted with CH_2Cl_2 (2 × 150 mL). The organic phases were gathered, dried over Na_2SO_4, and evaporated in vacuo. A purification by chromatography on silica gel (eluent: CH_2Cl_2 and then THF) gave a red solid which was further triturated in pentane, filtered, and dried to afford the final product (385 mg, 85% yield). Mp 321 °C. ^1H NMR ($CDCl_3$) δ: 9.87 (s, 1H, CHO); 7.35 (d, 2H, ^3J = 8.8); 6.96 (d, 1H, ^3J = 16.1); 6.86 (d, 1H, ^3J = 16.1); 6.68 (d, 2H, ^3J = 8.8); 4.43−4.31 (m, 8H, CH_2O); 2.98 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 179.2; 150.0; 140.4; 137.7;

135.7; 128.0; 127.5; 125.4; 122.3; 120.5; 114.7; 113.1; 112.3; 108.7; 105.3; 65.4; 65.2; 64.8; 64.6; 40.4. EI MS *m/z* (I%): 455 ($M^{+\bullet}$, 100); 326 (30); 227 (15); 190 (25); 158 (20). HRMS calcd for $C_{23}H_{21}N_1O_5S_2$: 455.0861; found, 455.0853. IR (KBr) ν cm^{-1} : 1638 (C=O). UV (CH_2Cl_2) λ_{max}: 468 nm.

5-(2,2-Dicyanoethenyl)-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-2,2′-bis(3,4-ethylenedioxythiophene) (5b). A mixture of aldehyde **11j** (150 mg, 0.33 mmol), malononitrile (26 mg, 0.39 mmol), and one drop of triethylamine in anhydrous $CHCl_3$ (15 mL) under a N_2 atmosphere was refluxed for 18 h. After being cooled to room temperature, the solvent was evaporated in vacuo, and the residue was triturated with EtOH (10 mL). The black precipitate was filtered, washed with hot EtOH (10 mL), and several times with EtOH to eliminate unreacted malononitrile. A black solid was obtained (140 mg, 86% yield). Mp 308 °C. ^{1}H NMR ($CDCl_3$) δ: 7.75 (s, 1H); 7.36 (d, 2H, ^3J = 8.8); 6.96 (d, 1H, ^3J = 16.1); 6.91 (d, 1H, ^3J = 16.1); 6.68 (d, 2H, ^3J = 8.8); 4.45 and 4.32 (2m, 8H, CH_2O); 2.99 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 150.3; 148.3; 144.0; 141.9; 137.9; 135.5; 129.4; 127.8; 125.6; 125.0; 123.5; 116.2; 115.3; 112.9; 112.3; 110.5; 105.9; 65.8; 65.7; 64.8; 64.6; 53.4; 40.4. EI MS *m/z* (I%): 503 ($M^{+\bullet}$, 100); 326 (30); 252 (15); 190 (30); 174 (10); 158 (25). HRMS calcd for $C_{26}H_{21}N_3O_4S_2$: 503.0973; found, 503.0979. IR (KBr) ν cm^{-1}: 2222 (C≡N); 1603 (C=C); 1168 (C−O). UV (CH_2Cl_2) λ_{max}: 588 nm. Anal. Calcd for $C_{26}H_{21}N_3O_4S_2$: C, 62.01; H, 4.20; N, 8.34; O, 12.71; S, 12.73.; found: C, 61.84; H, 4.32; N, 7.94; O, 13.10; S, 12.46.

5-[(1,3-Diaza-1,3-diethyl-4,6-dioxo-2-thioxocyclohex-5-ylidene)methyl]-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-2,2′-bis(3,4-ethylenedioxythiophene) (5c). A solution of aldehyde **11j** (100 mg, 0.24 mmol) and 1,3-diethylthiobarbiturc acid (58 mg, 0.24 mmol) in acetic anhydride (2 mL) was warmed to 80 °C for 24 h. At rt, after addition of CH_2Cl_2 (50 mL), the solution was washed with a saturated aqueous solution of $NaHCO_3$ and water. The organic phase was then dried over Na_2SO_4 and evaporated in vacuo before a column chromatography on silica gel (eluent: CH_2Cl_2) to lead to a black solid (90 mg, 60% yield). Mp 300 °C (dec). ^{1}H NMR ($CDCl_3$) δ: 8.75 (s, 1H), 7.38 (d, 2H, ^3J = 8.8), 6.98 (s, 2H), 6.68 (d, 2H ^3J = 8.8), 4.62−4.53 (m, 6H), 4.49−4.45 (m, 4H), 4.37−4.36 (m, 2H); 3.00 (s, 6H), 1.35−1.30 (m, 6H). EI MS *m/z* (I%): 637 ($M^{+\bullet}$, 100); 427 (25). HRMS calcd for $C_{31}H_{31}N_3O_6S_3$: 637.1375; found, 637.1388. UV(CH_2Cl_2) λ_{max}: 649 nm.

5-[1,3-Bis(dicyanomethylidene)indan-2-ylidenemethyl]-5′-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]-2,2′-bis(3,4-ethylenedioxythiophene) (5e). A mixture of aldehyde **11j** (150 mg, 0.33 mmol) and 1,3-bis(dicyanomethylidene)indane (81 mg, 0.33 mmol) in acetic anhydride (8 mL) was refluxed for 2 h. After cooling to 0 °C, the resulting precipitate was collected by filtration, washed several times with Et_2O, and dried under vacuum to afford a black powder (130 mg, 58% yield). Mp 206 (dec). An analytical sample was further purified by chromatography on silica gel (eluent: CH_2Cl_2 and then THF) and trituration in MeOH. ^{1}H NMR (DMSO-d_6) δ: 8.53 (s, 1H), 8.34 (br s, 2H), 7.80−7.75 (m, 2H), 7.49 (br s, 2H), 7.21 (d, 1H, ^3J = 15.8), 7.09 (d, 1H, ^3J = 15.8); 6.71 (d, 2H, ^3J = 8.7); 4.65−4.48 (m, 6H); 4.45 (br s, 2H); 2.98 (s, 6H). MALDI-TOF MS calcd for $C_{38}H_{25}N_5O_4S_2$ 679.1348, found 679.1418 ($M^{+\bullet}$). IR (KBr) ν cm^{-1}: 2207 (C≡N). UV(CH_2Cl_2) λ_{max}: 830 nm. Anal. Calcd for $C_{38}H_{25}N_5O_4S_2$: C, 67.14; H, 3.71; N, 10.30; O, 9.41; S, 9.43.; found: C, 67.09; H, 3.77; N, 9.93; O, 9.01; S, 9.29.

3,4-Ethylenedioxy-2-formylthiophene (12g). To a solution of 3,4-ethylenedioxythiophene **12f** (2.0 g, 14 mmol) and anhydrous DMF (2.2 mL, 28 mmol) in anhydrous 1,2-dichloroethane (30 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (2.2 mL, 28 mmol) dropwise, and the mixture was refluxed for 2 h. After being cooled to room temperature, the reaction mixture was hydrolyzed with an aqueous solution of sodium acetate (1 M, 250 mL). After extraction with CH_2Cl_2, the organic phases were washed with water, dried over Na_2SO_4, and evaporated in vacuo. A column chromatography on silica gel (eluent: CH_2Cl_2) gave a yellow solid (2.02 g, 84% yield). Mp 146 °C (dec). ^{1}H NMR ($CDCl_3$) δ: 9.86 (s, 1H, CHO); 6.79 (s, 1H); 4.35 (m, 2H, CH_2O); 4.25 (m, 2H, CH_2O). ^{13}C NMR ($CDCl_3$) δ: 180.2; 148.6; 141.8; 118.5; 110.8; 65.3; 64.4. EI MS *m/z* (I%): 170 ($M^{+\bullet}$, 100). IR (KBr) ν cm^{-1} : 1647 (C=O).

2-[(*Z*,*E*)-(4-*N*,*N*-Dimethylaminobenzylidene)methyl]-3,4-ethylenedioxythiophene (12h). To a suspension of phosphonium iodide **14** (4.6 g, 8.85 mmol) in 50 mL of a mixture of anhydrous CH_3CN/THF (1:1) at −60 °C under a N_2 atmosphere was added *t*-BuOK (0.99 g, 8.85 mmol) portionwise, leading to a red solution which was further stirred at −60 °C for 15 min before the dropwise addition of a solution of compound **12g** (1 g, 5.88 mmol) in anhydrous THF (20 mL). The color of the solution turned rapidly to yellow-orange, and the mixture was warmed to room temperature. After extraction with CH_2Cl_2, the organic phases were washed with water, dried over Na_2SO_4, and evaporated in vacuo. A purification by chromatography on silica gel (eluent: CH_2Cl_2) led to a brown solid (1.14 g, 68% yield) corresponding to a ca.. 6:4 mixture of *E* and *Z* isomers, respectively. ^{1}H NMR ($CDCl_3$) ***E* isomer** δ: 7.36 (d, 2H, ^3J = 8.8); 6.96 (d, 1H, ^3J = 16.2); 6.81 (d, 1H, ^3J = 16.2); 6.69 (d, 2H, ^3J = 8.8); 6.15 (s, 1H); 4.30−4.12 (m, 4H); 2.98 (s, 6H). ^{1}H NMR ($CDCl_3$) ***Z* isomer** δ: 7.29 (d, 2H, ^3J = 8.8); 6.69 (d, 2H, ^3J = 8.8); 6.49 (d, 1H, ^3J = 11.9); 6.44 (d, 1H, ^3J = 11.9); 6.11 (s,1H); 4.30−4.12 (m, 4H); 2.98 (s, 6H). ^{13}C NMR ($CDCl_3$) ***E*+*Z*** isomers δ: 149.8; 148.5; 141.9; 141.8; 141.1; 139.5; 138.0; 129.8; 128.1; 127.2; 126.6; 125.8; 118.5; 118.0; 116.4; 115.1; 114.0; 112.5; 111.9; 110.8; 98.0; 96.2; 65.3; 64.8; 64.7; 64.6; 64.4; 40.5; 40.4. IR (KBr) ν cm^{-1} : 1168 (C−O−C). UV (CH_2Cl_2) λ_{max} : 368 nm.

2-Formyl-3,4-ethylenedioxy-5-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]thiophene (12j). To a solution of compound **12h** [*E*/*Z*] (0.5 g, 1.75 mmol) and anhydrous DMF (0.15 mL, 1.94 mmol) in anhydrous 1,2-dichloroethane (20 mL) at 0 °C under a N_2 atmosphere was added $POCl_3$ (0.17 mL, 1.82 mmol) dropwise, and the mixture was then refluxed for 2 h. At rt, the mixture was hydrolyzed with an aqueous solution of sodium acetate (1 M, 50 mL) under vigorous stirring for 2 h. After extraction with CH_2Cl_2, the organic phases were washed with water, dried over Na_2SO_4, and concentrated in vacuo before chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether 1:1), affording a red solid (0.37 g, 68% yield). Mp 201−202 °C. ^{1}H NMR ($CDCl_3$) δ: 9.86 (s, 1H, CHO); 7.38 (d, 2H, ^3J = 8.8); 7.07 (d, 1H, ^3J = 16.1); 6.93 (d, 1H, ^3J = 16.1); 6.67 (d, 2H, ^3J = 8.8); 4.37 (m, 2H, CH_2O); 4.33 (m, 2H, CH_2O); 2.99 (s, 6H, CH_3N). ^{13}C NMR ($CDCl_3$) δ: 179.0 (CHO); 150.6; 148.8; 137.4; 133.6; 132.3; 130.1; 129.8; 128.2; 124.2; 112.6; 112.1; 65.3; 64.4; 40.2. IR (KBr) ν cm^{-1}: 1680 (C=O); 1168 (C−O). UV (CH_2Cl_2) λ_{max}: 439 nm.

2-(3-Dicyanomethylidene-1-indanon-2-ylidenemethyl)-3,4-ethylenedioxy-5-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]thiophene (6d). 3-Dicyanomethylidene-1-indanone (60 mg, 3.10 mmol) was added portionwise to a solution of aldehyde **12j** (100 mg, 3.32 mmol) in absolute EtOH at 60−70 °C. The stirring was maintained for 0.5 h at this temperature. After being cooled to room temperature, the resulting black precipitate was collected by filtration, washed with warmed EtOH, and dried in a vacuum to give a black powder (117 mg, 71% yield). Mp > 230 °C. ^{1}H NMR ($CDCl_3$) δ: 9.00 (s, 1H); 8.63 (d, 1H, ^3J = 7.3); 7.85 (m, 1H); 7.67 (m, 2H); 7.46 (d, 2H, ^3J = 8.7); 7.41 (d, 1H, ^3J = 16.0); 7.06 (d, 1H, ^3J = 15.8); 6.70 (d, 2H, ^3J = 8.7); 4.52 (m, 2H, CH_2O); 4.38 (m, 2H, CH_2O); 3.05 (s, 6H, CH_3N). EI MS *m/z* (I%): 491 ($M^{+\bullet}$, 100); 190 (35); 158 (30). HRMS calcd for $C_{29}H_{21}N_3O_3S_1$, 491.1304; found, 491.1313. IR (KBr) ν cm^{-1}: 2215 (C≡N); 1696 (C=O); 1168 (C−O−C). UV (CH_2Cl_2) λ_{max}: 673 nm.

2-[1,3-Bis(dicyanomethylidene)indan-2-ylidenemethyl]-3,4-ethylenedioxy-5-[(*E*)-(4-*N*,*N*-dimethylaminobenzylidene)methyl]thiophene (6e). To a solution of aldehyde **12j** (100 mg, 3.32 mmol) in acetic anhydride (5 mL) warmed at 60−70 °C was added 1,3-bis(dicyanomethylidene)indane (82 mg, 3.38 mmol) portionwise. The mixture was further stirred 1 h at this temperature, and after cooling to room temperature, it was poured into a saturated aqueous solution of $NaHCO_3$. After extraction with CH_2Cl_2, the organic phases were washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was triturated in EtOH (50 mL), filtered, washed with hot EtOH, and dried under vacuum to give a black solid (100 mg, 55% yield). Mp > 230 °C. ^{1}H NMR ($CDCl_3$) δ: 8.85 (br s, 1H); 8.52 (m, 2H); 7.65 (m, 2H); 7.47 (d, 2H, $^3J = 9.0$); 7.31 (d, 1H, $^3J = 16.0$); 7.01 (d, 1H, $^3J = 15.8$); 6.68 (d, 2H, $^3J = 9.0$); 4.52 (br s, 2H); 4.39 (br s, 2H); 3.07 (s, 6H). EI MS *m*/*z* (I%): 539 ($M^{+\bullet}$, 100); 254 (40); 190 (40); 158 (24). HRMS calcd for $C_{32}H_{21}N_5O_2S_1$: 539.1416; found, 539.1413. IR (KBr) ν cm^{-1} : 2210 ($C\equiv N$); 1168 (C−O−C). UV (CH_2Cl_2) λ_{max}: 768 nm.

2-Formyl-3,4-dihexyloxythiophene (13g). To a mixture of 3,4-dihexyloxythiophene **13f** (9.0 g, 31.7 mmol) and anhydrous DMF (4.90 mL, 63.3 mmol) in anhydrous 1,2-dichloroethane at 0 °C under a N_2 atmosphere was added a solution of $POCl_3$ (4.45 mL, 47.5 mmol) dropwise, and the mixture was warmed to room temperature before refluxing for 2 h. After being cooled to room temperature, the mixture was hydrolyzed with an aqueous solution of sodium acetate (1 M, 250 mL) for a period of 1 h. After decantation, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were gathered, dried over $MgSO_4$, and evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether 1:1) to give a yellow oil (9.5 g, 92% yield). ^{1}H NMR ($CDCl_3$) δ: 10.00 (s, 1H, CHO); 7.11 (s, 1H); 4.25−3.96 (2t, 4H, CH_2O); 1.96−0.70 (m, 22H). EI MS *m*/*z* (I%): 312 ($M^{+\bullet}$, 100%).

3,4-Dihexyloxy-2-[(*Z,E*)-(4-*N,N*-dimethylaminobenzylidene)methyl]thiophene (13h). To a suspension of phosphonium iodide **14** (1.0 g, 1.91 mmol) in anhydrous THF (20 mL) at room temperature under a N_2 atmosphere was added *t*-BuOK (0.215 g, 1.92 mmol), and the solution turned red. After cooling to 0 °C, a solution of compound **13g** (0.5 g, 1.79 mmol) in anhydrous THF (10 mL) was added dropwise, and the reaction mixture was further stirred at room temperature for 1.5 h. After dilution with CH_2Cl_2 (50 mL), the solution was washed with water (2 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo to afford a residue which was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give a yellow oil (613 mg, 80% yield) corresponding to a 1:1 mixture of *E* and *Z* isomers. ^{1}H NMR ($CDCl_3$) ***E* isomer** δ: 7.39 (d, 2H, $^3J = 8.8$); 7.12 (d, 1H, $^3J = 16.2$); 6.81 (d, 1H, $^3J = 16.2$); 6.71 (d, 2H, $^3J = 8.8$); 5.97 (s, 1H); 4.10 (t, 2H, $^3J = 6.6$); 3.97 (t, 2H, $^3J = 6.6$); 3.00 (s, 6H, CH_3N); 1.84−1.80 (m, 4H); 1.50−1.49 (m, 4H); 1.41−1.36 (m, 8H); 0.97−0.94 (m, 6H, CH_3). ^{1}H NMR ($CDCl_3$) ***Z* isomer** δ: 7.32 (d, 2H, $^3J = 8.7$); 6.73 (d, 2H, $^3J = 8.7$); 6.62 (d, 1H, $^3J = 11.9$); 6.49 (d, 1H, $^3J = 11.9$); 5.94 (s, 1H); 4.08 (t, 2H, $^3J = 6.6$); 3.93 (t, 2H, $^3J = 6.6$); 2.99 (s, 6H, CH_3N); 1.84−1.80 (m, 4H); 1.50−1.49 (m, 4H); 1.41−1.36 (m, 8H); 0.97−0.94 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$) ***E*+*Z*** isomers δ: 150.4; 149.8; 149.7; 149.4; 144.7; 143.0; 129.9; 128.8; 127.2; 126.6; 126.0; 125.6; 125.0; 122.5; 117.7; 114.7; 112.3; 111.8; 94.7; 92.7; 73.5; 73.3; 39.7; 40.4; 40.3; 31.5; 31.4; 29.9; 29.0; 25.7; 25.6 (2); 25.5; 22.6; 22.55; 22.5; 14.0; 13.9. EI MS *m*/*z* (I%): 429 ($M^{+\bullet}$, 100); 344 (70); 260 (25); 190 (20). IR (Nujol) ν cm^{-1} : 1606 (C=C); 1167 (C−O−C). UV (CH_2Cl_2) λ_{max} : 356 nm.

2-Formyl-3,4-dihexyloxy-5-[(*E*)-(4-*N,N*-dimethylaminobenzylidene)methyl]thiophene (13j). To a solution of compound **13h** [E/Z] (1.8 g, 4.17 mmol), anhydrous DMF (0.65 mL, 8.39 mmol) in anhydrous 1,2-dichloroethane (100 mL) at 0 °C under N_2 atmosphere was added a solution of $POCl_3$ (0.47 mL, 5.04 mmol) dropwise, and the mixture was refluxed for 2 h. After being cooled to room temperature, the mixture was poured into an aqueous solution of sodium acetate (1 M, 250 mL) and extracted with CH_2Cl_2. The organic phases were dried over Na_2SO_4 and evaporated in vacuo to give an oil which was purified by chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether 1:1) to afford a brown solid (1.40 g, 73% yield). Mp 46 °C. ^{1}H NMR ($CDCl_3$) δ: 9.93 (s, 1H, CHO); 7.39 (d, 2H, $^3J = 8.9$); 7.03 (s, 2H); 6.69 (d, 2H, $^3J = 8.9$); 4.29 (t, 2H, $^3J = 6.6$); 4.00 (t, 2H, $^3J = 6.6$); 3.01 (s, 6H); 1.85−1.70 (m, 4H); 1.27−1.58 (m, 12H); 0.97−0.86 (m, 6H). ^{13}C NMR ($CDCl_3$) δ: 180.4; 157.2; 150.7; 144.8; 138.7; 132.0; 129.9; 128.2; 124.1; 120.2; 113.1; 112.1; 111.9; 74.5; 74.4; 40.2; 31.5; 31.4; 29.9; 29.8; 25.7; 25.5; 25.4; 22.6; 22.5; 14.0. EI MS *m*/*z* (I%): 457 ($M^{+\bullet}$, 100); 372 (60); 288 (15); 190 (20). IR (KBr) ν cm^{-1} : 1681 (C=O). UV (CH_2Cl_2) λ_{max} : 437 nm.

2-(3-Dicyanomethylidene-1-indanon-2-ylidenemethyl)-3,4-dihexyloxy-5-[(*E*)-(4-*N,N*-dimethylaminobenzylidene)methyl]thiophene (7d). To a solution of aldehyde **13j** (0.25 g, 0.547 mmol) in absolute EtOH (6 mL) warmed at 60 °C was added 3-dicyanomethylidene-1-indanone (106 mg, 0.547 mmol), and the mixture was stirred at 60 °C for 0.5 h. After cooling to 0 °C, the resulting precipitate was collected by filtration and washed with cooled EtOH (0−5 °C) to afford, after drying, a black solid (297 mg, 86% yield). Mp 120 °C (dec). ^{1}H NMR ($CDCl_3$) δ: 9.06 (s, 1H); 8.63 (d, 1H, $^3J = 6.9$); 7.85 (m, 1H); 7.68 (m, 2H); 7.44 (d, 2H, $^3J = 8.8$); 7.38 (d, 1H, $^3J = 16.1$); 7.11 (d, 1H, $^3J = 16.1$); 6.69 (d, 2H, $^3J = 8.8$); 4.37 (t, 2H, $^3J = 7.0$, CH_2O); 4.01 (t, 2H, $^3J = 6.6$, CH_2O); 3.05 (s, 6H, CH_3N); 1.89 (m, 2H, CH_2CH_2O); 1.79 (m, 2H, CH_2CH_2O); 1.55−1.33 (m, 12H); 0.91 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 188.7; 161.1; 160.7; 151.2; 147.1; 145.1; 140.2; 136.7; 135.4; 134.4; 133.7; 133.0; 129.1; 124.9; 124.0; 123.2; 119.2; 118.7; 115.6; 115.1; 113.0; 112.1; 74.8; 74.7; 66.8; 40.2; 31.6; 31.5; 30.0; 29.8; 25.7; 25.5; 22.7; 22.6; 14.0. EI MS *m*/*z* (I%): 633 ($M^{+\bullet}$, 100); 548 (25); 190 (35); 134 (25). IR (KBr) ν cm^{-1} : 2213 ($C\equiv N$); 1692 (C=O). UV (CH_2Cl_2) λ_{max} : 662 nm. Anal. Calcd for $C_{39}H_{43}N_3O_3S_1$: C, 73.90; H, 6.83; N, 6.63; O, 7.57; S, 5.05; found: C, 73.83; H, 6.83; N, 6.56; O, 7.41; S, 5.04.

2-[1,3-Bis(dicyanomethylidene)indan-2-ylidenemethyl]-3,4-dihexyloxy-5-[(*E*)-(4-*N,N*-dimethylaminobenzylidene)methyl]thiophene (7e). To a solution of compound **13j** (0.25 g, 0.55 mmol) in acetic anhydride (5 mL) at 60−70 °C under N_2 atmosphere was added 1,3-bis(dicyanomethylidene)indane (132 mg, 0.55 mmol) portionwise, and the mixture was stirred further at 60−70 °C for 1 h. At rt, after addition of water (20 mL), the mixture was extracted with Et_2O. The organic phases were washed with a saturated aqueous solution of $NaHCO_3$, dried over Na_2SO_4, and evaporated in vacuo to give a residue which was purified by chromatography on silica gel (eluent: CH_2Cl_2) to afford a black powder (250 mg, 68% yield). Mp 145 °C (dec). ^{1}H NMR ($CDCl_3$) δ: 8.88 (br s, 1H); 8.53 (m, 2H); 7.67 (m, 2H); 7.46 (d, 2H, $^3J = 8.9$); 7.16 (d, 1H, $^3J = 15.9$); 7.07 (d, 1H, $^3J = 15.9$); 6.69 (d, 2H, $^3J = 8.9$); 4.45 (br s, 2H, CH_2O); 4.03 (t, 2H, $^3J = 6.6$, CH_2O); 3.07 (s, 6H, CH_3N); 1.86 (br s, 2H, CH_2CH_2O); 1.80 (m, 2H, CH_2CH_2O); 1.56−1.35 (m, 12H); 0.93−0.89 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 160.5; 146.5; 137.5; 133.5; 129.8; 124.9; 123.6; 114.7; 112.4; 112.1; 75.2; 40.2; 31.6; 31.4; 30.0; 29.9; 25.7; 25.4; 22.6; 22.5; 14.07; 14.06. EI MS *m*/*z* (I%): 681 ($M^{+\bullet}$, 75); 596 (20); 532 (20); 254 (100); 134 (40). IR (KBr) ν cm^{-1} : 2210 ($C\equiv N$). UV (CH_2Cl_2) λ_{max}: 750 nm. Anal. Calcd for $C_{42}H_{43}N_5O_2S_1$: C, 73.97; H, 6.35; N, 10.27; O, 4.69; S, 4.70.; found: C, 73.57; H, 6.72; N, 9.89; O, 4.74; S, 4.81.

Acknowledgment. The authors thank France-Telecom for financial support.

Supporting Information Available: Computational results in the form of Cartesian coordinates with the computed total energies for compounds **4e**, **5e**, **6e**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010713F