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DOI: 10.1016/j.tet.2016.01.038

Reference: TET 27445

To appear in: Tetrahedron

Received Date: 24 October 2015

Revised Date: 17 January 2016

Accepted Date: 19 January 2016

Please cite this article as: Aboubakr H, Praveen C, Malytskyi V, Sawadogo R, Sotiropoulos J-M, Belec L, Brisset H, Raimundo J-M, D/A cruciform bithiophene chromophores as potential molecular scaffolds for optoelectronics applications, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.01.038.

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Tetrahedron journal homepage: www.elsevier.com



D/A cruciform bithiophene chromophores as potential molecular scaffolds for optoelectronics applications.

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ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Thiophene Push-pull chromophore Optoelectronics

ABSTRACT

Thiophene-based molecular semiconductors are of high interest in the development of optoelectronics devices and are extensively used. So far, structural variations have been widely performed on linear molecular push-pull in order to optimize their photophysical properties while 2D systems are quite limited. We report herein the synthesis of four new chromophores based on bithiophene core end-capped with dibutylaminostyryl groups and functionalized on the 3,3' position with different electron withdrawing groups. Optical and electrochemical characterizations have been performed as well as theoretical calculations that corroborate the experimental data.

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1. Introduction

The design and synthesis of organic materials that can be used as an alternative to silicon based optoelectronic devices has tremendously increased over the last two decades.¹ Indeed, organic materials offer the advantage to be produced through out low-cost solution technologies such as spin coating, inkjet printing or roll-to-roll processes associated with lower environmental impact.² For the main foreseen applications, namely light-emitting diodes (OLEDs),³ field-effect transistors (OFETs)^{4,5} and photovoltaics (OPVs),^{6,7,8} reproducible effective organic semiconductors are desired. Therefore, design of innovative and optimized target-specific semiconductors is strongly recommended in order to optimize their performance and lifetime. To achieve this goal, organic semiconductors need to fulfill peculiar structural and molecular criteria that depend on the focused applications.^{9,10,11} For instance, molecular packing, charge carrier mobility and transport, energy gap and levels, solution-processability, molar extinction coefficients are some of the important parameters that plays key role on the mentioned devices performances.

Until recently, most of the efforts have been concentrated almost on polymers with respect to their better film quality compared to small molecules. However, small molecules have gained increased interests to overcome some drawbacks of polymer technology *i.e.* their difficulties of purification, low reproducibility in synthesis and weakness in determining structure-properties relationships. Additionally, small molecules have also the benefits both to be chemically and specifically modified to fine tune their optoelectronic properties. For example, judicious choice of appropriate conjugated units (such as heteroaromatic cores) and incorporation of electron-donating or electron withdrawing and side chains in the molecules serve to adjust the HOMO/LUMO energy levels and control the HOMO– LUMO bandgap.¹²

Our longstanding interest in controlling the electronic properties and continuing efforts on synthesis of new organic semiconductors for optoelectronic applications have led us to use a novel interesting scaffold, as spacer, based on the 2,2'bithiophene core.^{13,14,15,16,17} The new functionalized spacer permits an iterative functionalization selectively on the 3,3' and 5,5' positions allowing us the possibility to synthetize asymmetric compounds with donors and acceptors groups (Chart 1). This will be very helpful to gain further insights into the structure-properties relationships for the above applications.



Chart 1. Structure of new D/A cruciform bithiophene chromophores 1-4.

2. Results and discussion

Synthesis

The core skeleton has been prepared from commercially available thiophene-3-carboxaldehyde in 3 steps. First, reacting thiophene-3-carboxaldehyde with 1,2-ethandiol in presence of

PPTS resulted in the successful protection of aldehyde group and subsequent dimerization led to the protected dimer 7 in 43% yield as reported in literature.¹⁸ Formylation of **7** was achieved by treating with 2 equiv of n-BuLi, followed by the addition of DMF and subsequent hydrolysis afforded 3,3'-(1,3-dioxolane)-5,5'diformyl-2,2'-bithiophene 6 in 68% as yellow powder (Scheme Then, Wittig olefination of 6 with 4-(N,N-1)1). dibutylbenzyl)triphenylphosphonium iodide¹⁹ led to compound 5 which in turn was treated with PPTS in acetone to afford the bisaldehyde 4 in 93% yield. The target compounds 1 and 2 were obtained in 53 and 52% yield by Knoevenagel condensation of 4 with malonodinitrile and diethylthiobarbituric acid, respectively. Compound 3 was prepared by through Wittig olefination of 4 with the *p*-nitrobenzyltriphenylphosphonium bromide salt. All chromophores were obtained as dark or dark-blue/green powders and have been thoroughly characterized by ¹H NMR, ¹³C NMR, mass spectrometry, and elemental analysis.



Scheme 1. Synthetic pathway of chromophores 1-4.

Crystallographic structure

Unexpectedly, the crystallographic structure of single crystal of **4** (C 2/c space group) exhibits a *syn* conformation, with a dihedral angle of 41.55° between the two thiophenediaminostyryl moieties that are coplanar (Figure **1**). In the crystal lattice, each molecule shows eight interactions with four other neighboring molecules. Thus, a half molecule presents both two C-C interactions with a neighboring compound and two O-H interactions A with E another. Examination of the C-C (3.327Å) and O-H (2.517Å) distances shows that these distances are significantly shorter than the sum of the Van der Waals radii, which evidences the occurrence of strong intramolecular interactions. Respectively a C-C interaction was found between the C of the aromatic ring bearing the dibutylamino group and the C of the carbonyl group of another molecule and inversely. In addition, O-H interactions are formed between the nearest ethylenic H beside the thiophene and the O of the carbonyl group from a neighboring molecule and vice versa. All these interactions can be found in number and length on the second half part of the molecule **4**.



Figure 1. ORTEP view of compound 4 (black: C; blue: N; green: S and red: O, for clarity H are omitted).

Optical properties of the chromophores 1-4 have been investigated by UV-Visible spectroscopy in CHCl₃. It was anticipated that replacing the CHO group by a stronger acceptor could contribute to a hypso/bathochromic shift of the corresponding chromophores. Thus as expected, malonodinitrile substitution in 2 leads to a 147 nm bathochromic shift of the maximum of absorption compared to the parent compound 4. Nevertheless, changing the malonodinitrile to 4vinylnitrobenzene 3 or 1,3-diethylthiobarbituric 1 acceptors induces a more or less pronounced hypsochromic shift of the maximum of absorption (Table 1 and Figure 2).



Figure 2. UV-Vis spectra of chromophores 1-4 in in $CHCl_3$ (C = 10^{-5} M).

Table 1. Absorption maximum (λ_{abs} nm) and molar extinction coefficient (log ϵ L.mol⁻¹.cm⁻¹) of compounds 1-4.

1		2		3		4	
λ_{abs}	logε	λ_{abs}	logε	λ_{abs}	logε	λ_{abs}	logε
302	4.43	348	4.59	327	4.54	256	4.83
381	4.15	399	4.34	414	4.81	374	5.03
425	4.08			600	4.09	453	4.90

These observations suggest that the π -conjugated system, for compounds 1 and 3, undergoes a twist compared to the more planar chromophore 4 because of the steric hindrance induced by

the use of more bulky acceptors (Figure 2). The deviation from the planarization of the π -conjugated system contributes to a diminution of the effective conjugation leading to a hypsochromic shift of the maximum of absorption. Furthermore, the observed blue shift might be ascribed to the *syn-* or *trans*conformation of the bithiophene core, as shown in the ORTEP view of 4 (Figure 1).

Molecular structure and electronic properties of the molecules 1-4 were obtained thanks to DFT calculations using B3LYP and M06 with the 6-31G (d,p) basis set (Table 2) in order to determine the most favorable conformation. For all compounds two minima are found on the potential energy surface closed in energies (B3LYP: from 0.5 to 1 kcal/mol and M06: from 0.5 to 5 kcal/mol). The anti conformers of the compounds 2 and 3 are slightly privileged (~0.8 and 0.5 kcal/mol respectively) with the M06 functional but only the 2-anti with B3LYP (0.9 kcal/mol). For 1 and 4, both functional calculations found the syn conformations slightly more stable than the anti ones (B3LYP: 0.73 and 0.46 kcal/mol; M06: 4.98 and 1.59 kcal/mol respectively). We can note that considering solvent effect using the continuum solvation model with B3LYP, the relative stabilities of syn and anti isomers 1 and 4 remain the same but are reversed for 2 and 3.

All these results show the importance of crystal effect on the structure found experimentally. Nevertheless, It is noteworthy, that if we consider the compound **4**, theoretical structural calculations in the gas phase are in good agreement with experimental results (*vide supra*). In fact, we calculated for the *syn* conformer a dihedral angle around 45°. Both functionals show that all HOMO levels are located along the π -conjugated system where as the LUMO levels are mainly centralized on the bithiophene core and lateral acceptor groups (Table **2**). The energy values of these frontier orbitals can be correlated with the cyclic voltammetry experiments.

Table 2. DFT structure for compound 4 and corresponding frontier Kohn Sham molecular orbitals. HOMO/LUMO calculated values in eV for 1-4 compounds (B3LYP/6-31G(d,p))



	<mark>Syn conj</mark>	ormation	Anti conjormation		
	HOMO	LUMO	HOMO	LUMO	
<mark>1</mark>	<mark>-4.788</mark>	<mark>-2.833</mark>	<mark>-4.785</mark>	<mark>-2.995</mark>	
<mark>2</mark>	<mark>-5.026</mark>	<mark>-2.941</mark>	<mark>-4.995</mark>	<mark>-3.073</mark>	
<mark>3</mark>	<mark>-4.730</mark>	<mark>-2.518</mark>	<mark>-4.563</mark>	<mark>-2.523</mark>	
<mark>4</mark>	<mark>-4.756</mark>	<mark>-2.113</mark>	<mark>-4.749</mark>	<mark>-2.120</mark>	

Cyclic voltammograms (CV) of chromophores 2-4 are characterized by one reversible one-electron oxidation redox system corresponding to the formation of the radical cation while the CV of the compound 1 exhibits a second oxidation redox system ascribed to a more constrained π -conjugated system (Figure 3 - Table 3). All compounds display similar value for $E_{1/2}(ox_1)$, except the compound **3** which shows a lowest oxidation potential, attributed to an extended π -system, and correlates with the DFT calculations (Table 2). Compound 2 has a reduction potential shifted to more positive value attributed to a stronger acceptor character of the dicyanomethylene (DCN) groups compared to the aldehyde groups of the derivative 4. However, replacement of the DCN groups by a stronger acceptor such as 1,3-diethylthiobarbituric acid (1) doesn't lead to a lowered reduction potential. These observations suggest that both geometric and/or steric parameters as well as the nature of the acceptors contribute to these strong changes. Nevertheless a roughly good correlation is found, for the reduction potentials, between experimental values and LUMO position calculated by DFT (B3LYP); (E_{1/2}(red1)/E_{LUMO} calculated): 4 (-1.79/-2.11), 1 (-1.60/-2.83), 3 (-1.53/-2.52), 2 (-1.18/-3.07) assuming the most stable syn or anti conformations for each compounds. Moreover, the comparison between the calculated and the electrochemcial bandgap are in good agreement with the same tendency.



Figure 3. Cyclic voltammetry of compounds 1-4 at 10^{-3} M in odichlorobenzene, *n*-Bu₄NPF₆ (0.1M) scan rate 100 mV.s⁻¹.

The four compounds are degraded around 500°C with the same amount of residual char. However a great dispersion in terms of thermal stability is observed between the four compounds (Figure 4). As shown in Figure 4, the weight loss starts from 156°C for compound 1, whereas it only starts around 320°C for compound 4. The following decreasing thermal stability is observed: compound 4 > compound 2 > compound 3 > compound 1. The degradation mode is also very different. No marked steps can be clearly detected for compound 1, whereas two steps degradation are visible for compounds 2 and 4 and three steps can be detected for compound **3**. The differences at low temperatures can be attributed to the lateral groups nature and/or to impurities resulting from synthesis. Concerning compounds **2** and **4**, the high degradation temperatures are rather consistent with the first hypothesis, the difference being attributed to bond energies in lateral groups. Indeed, compound **2** lateral group involves C-C bonds (C=C(CN)₂) which are not present in compound **4** (C=O). Above 300°C, the degradation steps for compound **1** and **3** are almost twice of those compounds **2** and **4**. At these temperatures, chemical bonds such as C-N and C-C bonds can be broken, releasing lateral groups of compound **1**. NO₂ groups and lateral cycles of compound **3** are probably released in the same temperature range.



Figure 4. TGA curves of compounds 1 to 4 in nitrogen with a heating rate of 20 °C/min.

3. Conclusion

We have reported the synthesis of four novel DAAD chromophores having a bithiophene core end-capped with dibutylaminostyryl as a donor group and functionalized with four different acceptors on the 3,3' positions of the bithiophene core. Interestingly, in contrast to what it was expected, two chromophores from the studied series have shown a *syn* conformation supported by the theoretical calculations as well as by the XRD analysis of the crystal structure of compound **4**. Their acceptable electro-optical properties associated to high thermal stabilities make them suitable for the foreseen applications.

4. Experimental Section

Reagents and analysis. Tetrahydrofuran (THF), dimethylformamide (DMF), chloroform (CHCl₃), ethanol. methylene chloride (CH₂Cl₂), cyclohexane (C₆H₁₂), anhydrous acetone, diethylether, o-dichlorobenzene were purchased from CarloErba. Tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) was purchased from Fluka and was used as received. Potassium tert-butoxide (t-BuOK), crown ether 18C6, nbutyllithium 2.5 M in hexane (n-BuLi), 4-(N,N-dibutylbenzyl)triphenylphosphonium bromide, $4 - (p - 1)^{-1}$ nitrobenzyl)triphenylphosphonium bromide, malonodinitrile. pyridinium-p-toluenesulfonate (PPTS), ethylenediammonium diacetate (EDDA), 1,3-diethylthiobarbituric acid were purchased from Sigma-Aldrich and used as received.

Physico-chemical analyses. Melting points were obtained from an Electrothermal 9100 apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AC 250 at 250 MHz and 62.5 MHz, respectively. High resolution mass spectrometry (HRMS) was made with a Qstar Elite spectrometer (Applied Biosystems SCIEX) by electrospray ionization (ESI) method. Elemental analysis was recorded with an EA 1112 series from ThermoFinnigan. XR-diffraction (λ MoK α = 0.71073Å) under monocrystal **4** was made with a Bruker-Nonius spectrometer.²⁰

Physico-chemical measurements in solution. UV-visible absorption spectra were obtained on a Varian Cary 1E spectrophotometer. The electronic absorption maxima (λ_{max}) were directly extracted from absorption spectra of compound as chloroform solution. Cyclic voltammetry (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system based on a platinum (Pt) working electrode (diameter 1.6 mm), a Pt counter electrode and an Ag/AgCl (with 3 M NaCl filling solution) reference electrode was used. Tetrabutylammonium hexafluorophosphate served as a supporting electrolyte (0.1 M). All experiments were carried out in o-dichlorobenzene (electronic grade purity) at 20 °C. Ferrocene was used as an internal standard. Electrochemical reduction/oxidation potential values vs Fc/Fc⁺ were determined from the cyclic voltammogram at a concentration of 1.10⁻³ M with a scan rate of 100 mV.s⁻¹. Thermal properties of the compounds were explored by thermogravimetric analysis (TGA) on a Q600 from TA instruments. The thermal stability of the compounds was studied under 100 mL/min nitrogen flow with a heating rate of 20 °C/min from room temperature to 800 °C. A purge nitrogen flow of 400 mL/min was applied over a period of 20 min inside the oven before starting the experiment to remove all oxygen from the oven.

Computational Methodology: Calculations were carried out with the Gaussian 09 program²¹ at the DFT level of theory using both B3LYP^{22a-c} and M06^{22d} functionals. All the different atoms (C, N, H, O, S) have been described with a 6-31G(d,p) double- ζ basis set.²³ Geometry optimizations were carried out without any symmetry restrictions. The nature of the *minima* was verified with analytical frequency calculations, by the absence of negative eigenvalue.

3,3'-di(1,3-dioxolan-2-yl)-[2,2'-bithiophene]-5,5'-dicarbaldehyde (6). At 0 °C, under argon 13.82 mL of n-BuLi (34.55 mmol; 2.5 M in hexane) was added dropwise to a solution of 4.32 g (13.94 mmol) of 3,3'-(1,3-dioxolane)-2,2'-bithiophene 7 in 50 mL of anhydrous THF. After 15 min of addition, 2.72 mL (34.82 mmol) of anhydrous DMF was added. After 7 h of agitation at room temperature, 100 mL of water was added and extracted thrice with 50 mL of chloroform. After dried over anh. MgSO4, filtration and evaporation of the solvent under vacuum, the crude product was purified by crystallization in ethanol to afford 3.50 g (68%) of title compound as yellow solid. Mp = 146-148 °C. 1 H NMR (250 MHz, CDCl₃) δ: 3.98-4.00 (m, 4H, 2 x O-CH₂-CH₂-O-); 4.10-4.14 (m, 4H, 2 x O-CH2-CH2-O-); 5.73 (s, 2H 2 x -CH-O-); 7.91 (s, 2H, 2 x H_{thio}); 9.91 (s, 2H, 2 x -CHO). ¹³C NMR (67.5 MHz, CDCl₃) δ: 65.5 (CH₂); 98.0 (CH); 135.5 (C_{thio}); 139.4 (C); 140.4 (C); 144.5 (C); 181.6 (CHO); 182.7 (CHO). HRMS (ESI⁺) m/z: 367 [M+H]⁺; 398 [M+Na]⁺; 405 [M+K]⁺. Elemental analysis for C16H16O6S2 (%), calculated: C, 52.45; H, 3.85; O, 26.20; S, 17.50 - Found: C, 53.35; H, 4.09; O, 25.19; S, 17.22.

4,4'-((1E,1'E)-(3,3'-di(1,3-dioxolan-2-yl)-[2,2'-bithiophene]-5,5'diyl)bis(ethene-2,1-diyl)bis(N,N-dibutylaniline) (**5**). Under an inert atmosphere, 0.26 g (2.32 mmol) of dry *t*-BuOK was added to a solution of 1.26 g (2.26 mmol) of 4-(N,N-dibutylbenzyl)triphenylphosphonium iodide in 10 mL of CH₂Cl₂. After 10 min of stirring at 0 °C, 10 mg (0.26 mmol) of 18-crown-6 and 0.15 g (0.42 mmol) of compound 6 were added. The mixture was stirred for 24 h at room temperature and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column using CH_2Cl_2 to give 0.31 g (96%) of title compound as orange oil. ¹H NMR (250 MHz, CDCl₃) δ : 0.93-0.97 (t, 12H, ${}^{3}J = 7.3$ Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 1.31-1.37 (m, 8H, 4 x -CH2-CH2-CH2-CH3); 1.56-1.62 (m, 8H, 4 x - $CH_2-CH_2-CH_2-CH_3$; 3.26-3.31 (t, 8H, ${}^{3}J = 7.6$ Hz, 4 x $-CH_2$ -CH₂-CH₂-CH₃); 3.94-4.00 (m, 4H, 2 x O-CH₂-CH₂-O-); 4.11-4.17 (m, 4H, 2 x O-CH₂-CH₂-O-); 5,76 (s, 2H, 2 x -CH-O); 6.61 $(d, 4H, {}^{3}J = 8.5 \text{ Hz}, 4 \text{ x H}_{\text{benz}}); 6.87 (s, 2H, 2 \text{ x H}_{\text{thio}}); 7.11 (d, 2H,$ ${}^{3}J = 13.3$ Hz, 4 x H_{eth}); 7.22 (d, 2H, ${}^{3}J = 13.3$ Hz, 4 x H_{eth}); 7.31 (d, 4H, ${}^{3}J = 8.5$ Hz, 4 x H_{benz}). ${}^{13}C$ NMR (62.5 MHz, CDCl₃) δ : 14.0 (CH₃); 20.4 (CH₂); 29.5 (CH₂); 50.8 (CH₂); 65.3 (CH₂); 98.9 (CH); 111.7 (C_{benz}); 116.3 (C_{benz}); 123.4 (C_{thio}); 123.8 (C_{thio}); 127.8 (C_{thio}); 129.8 (C_{eth}); 129.9 (C_{eth}); 138.2 (C_{benz}); 145.3 (C_{thio}); 148.0 (C_{benz}). HRMS (ESI⁺) m/z: 769.4068 $[M+H]^+$ (calculated: 769.4067). Elemental analysis for $C_{46}H_{60}O_4S_2N_2$ (%), calculated: C, 71.84; H, 7.86; S, 8.34; N, 3.64 - Found: C, 68.85; H, 7.82; S, 7.42; N, 3.57.

5,5'-bis((E)-4-(dibutylamino)styryl)-[2,2'-bithiophene]-3,3'-

dicarbaldehyde (4). Under an inert atmosphere, 1.50 g (1.95 mmol) of 5 and 1.96 g (7.8 mmol) of pyridinium ptoluenesulfonate (PPTS) were dissolved in 100 mL of anhydrous acetone. The reaction mixture was refluxed for 72 h. After removal of the solvent under reduced pressure the crude product was dissolved in CH₂Cl₂ and successively washed with NaHCO₃ (1M) and brine. Organic phases were dried over anh. MgSO₄ and the solvent was removed under reduced pressure to afford 1.23 g (93%) of title compound as a red solid. Mp = 172-174 °C. ¹H NMR (250 MHz, CDCl₃) δ : 0.95-1.00 (t, 12H, ³J = 7.3 Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 1.33-1.42 (m, 8H, 4 x -CH₂ CH₃); 1.54-1.65 (m, 8H, 4 x -CH₂-CH₂-CH₂); 3.28-3.34 (t, 8H, ${}^{3}J = 7.7$ Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 6.62 (d, 4H, ${}^{3}J = 8.7$ Hz, 4 x H_{benz}); 6.92 (m, 4H, 2 x H_{eth} and 2 x H_{thio}); 7.35 (d, 4H, ${}^{3}J$ $= 8.7 \text{ Hz}, 4 \text{ x H}_{\text{benz}}$; 7.42 (d, 2H, ³J = 14.1 Hz, 2 x H_{eth}); 9.87 (s, 2H, 2 x CHO). ¹³C NMR (62.5 MHz, CDCl₃) δ: 13.0 (CH₃); 19.3 (CH₂); 28.5 (CH₂); 49.7 (CH₂); 110.6 (C_{benz}); 113.7 (C_{benz}); 121.8 (C_{thio}); 121.9 (C_{thio}); 127.2 (C_{thio}); 131.5 (C_{eth}); 137.3 (C_{eth}); 139.6 (C_{benz}); 145.6 (C_{thio}); 147.5 (C_{benz}); 183.4 (CHO). HRMS (ESI⁺) m/z: 681.3559 $[M+H]^+$ (calculated: 681.3543). Elemental analysis for C₄₂H₅₂O₂S₂N₂ (%), calculated: C, 74.07; H, 7.70; S, 9.42; N, 4.11 - Found: C, 74.04; H, 7.83; S, 9.32; N, 3.97.

4,4'-((1E,1'E)-(3,3'-bis(4-nitrophenyl)-[2,2'-bithiophene]-5,5'-

diyl)bis(ethene-2,1-diyl))bis(N,N-dibutylaniline) (3). Under an inert atmosphere, 0.05 g (0.49 mmol) of an oven dried t-BuOK was added to a solution of 0.23 g (0.47 mmol) of 4-(pnitrobenzyl)triphenylphosphonium bromide in 10 mL of anhydrous CH2Cl2. After 10 min of stirring at 0 °C, 0.01 g (0.26 mmol) of 18-crown-6 and 0.07 g (0.10 mmol) of 4 were added. The reaction mixture was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure the crude product, thus obtained was purified over silica gel column using CH_2Cl_2/C_6H_{12} (1:1) to afford 0.03 g (28%) of the title compound as a redish orange solid. Mp = 236-238 °C. ¹H NMR (250 MHz, CDCl₃) δ : 0.94-1.00 (t, 12H, ³J = 7.3 Hz, x-CH₂-CH₂-CH₂-CH₃); 1.33-1.39 (m, 8H, x-CH₂-CH₂-CH₂-CH₃); 1.60-1.63 (m, 8H, x- $CH_2-CH_2-CH_2-CH_3$; 3.28-3.34 (t, 8H, ³J = 7.1 Hz, x-CH₂-CH₂-CH₂-CH₃); 6.63 (d, 4H, ${}^{3}J = 8.7$ Hz, 4xH_{benz}); 6.90 (d, 2H, ${}^{3}J$ =15.6 Hz, 2 x H_{eth}); 6.99 (d, 2H, ${}^{3}J$ = 15.6 Hz, 2xH_{eth}); 7.00 (d, 2H, ${}^{3}J = 16.6$ Hz, 2 x H_{eth}); 7.23 (d, 4H, ${}^{3}J = 16.6$ Hz, 2xH_{eth}); 7.32 (s, 2H, 2xH_{thio}); 7.35 (d, 4H, ${}^{3}J = 8.7$ Hz, 4xH_{benz}); 7.45 (d, 4H, ${}^{3}J = 8.6$ Hz, 4xH_{benz}); 8.07 (d, 4H, ${}^{3}J = 8.6$ Hz, 4 x H_{benz}).

HRMS (ESI⁺) m/z: 918.4207 M⁺⁻ (calculated: 918.4207). $M \land N$

Elemental analysis for C₅₆H₆₂N₄S₂O₄(%): C, 73.17; H, 6.80; S, 6.98; N, 6.09 - Found: C, 71.30; H, 7.25; S, 6.17; N, 5.30. 2,2'-((5,5'-bis((E)-4-(dibutylamino)styryl)-[2,2'-bithiophene]-*3,3'-diyl)bis(methanylylidene))dimalonodinitrile* (2). То а solution of 0.05 g (0.074 mmol) of compound 4 and 0.01 g (0.154 mmol) of malonodinitrile in 4 mL of anhydrous CH₂Cl₂ were added 30 mol% of ethylenediammonium diacetate (EDDA). The mixture was stirred at room temperature for 1 h. After addition of water and extraction with CH₂Cl₂, the organic phase was washed with NaHCO₃ (1M) and brine before drying on anh. MgSO₄. After filtration the solvent was removed under reduce pressure and the crude product was purified by crystallization in diethyl ether to give 0.03 g (52%) of title compound as dark green solid. Mp = 212-214 °C. ¹H NMR (250 MHz, CDCl₃) δ : 0.94-1.00 (t, 12H, ${}^{3}J = 7.3$ Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 1.33-1.42 (m, 8H, 4 x -CH₂-CH₂-CH₂-CH₃); 1.54-1.66 (m, 8H, 4 x - $CH_2-CH_2-CH_2-CH_3$; 3.28-3.34 (t, 8H, ³J = 7.7 Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 6.63 (d, 4H, ${}^{3}J = 8.7$ Hz, 4 x H_{benz}); 6.96 (s, 4H, 4 x H_{eth}); 7.37 (d, 4H, ${}^{3}J = 8.7$ Hz, 4 x H_{benz}); 7.50 (s, 2H, 2 x H_{thio}); 7.89 (s, 2H, 2 x H_{eth}). HRMS (ESI⁺) m/z: 799.4 [M+Na]⁺. Elemental analysis for $C_{48}H_{52}N_2S_2$ (%): C, 74.19; H, 6.74; S, 8.25; N, 10.81 - Found: C, 74.14; H, 6.86; S, 8.34; N, 10.63.

5,5'-((5,5'-bis((E)-4-(dibutylamino)styryl)-[2,2'-bithiophene]-3,3'-diyl)bis(methanylylidene))bis(1,3-diethyl-2-

thioxodihydropyrimidine-4,6(1H,5H)-dione) (1). To a solution of 0.05 g (0.073 mmol) of compound 4 and 0.03 g (0.154 mmol) of 1,3-diethylthiobarbituric acid in 4 mL of anhydrous CH₂Cl₂ were added 30 mol% of ethylenediammonium diacetate (EDDA). The mixture was stirred at room temperature for 30 min. After addition of water and extraction with CH₂Cl₂, the organic phase was washed with NaHCO₃ (1M) followed by brine and dried over anh. MgSO₄. The solvent was removed under reduce pressure and the crude product was purified by crystallization in diethyl ether to give 0.04 g (53%) of title compound as a dark green solid. Mp = 264-266 °C. ¹H NMR (250 MHz, CDCl₃) δ : 0.94-1.00 (t, 12H, ${}^{3}J = 7.3$ Hz, 4 x -CH₂-CH₂-CH₂-CH₃); 1.33-1.42 (m, 8H, 4 x -CH₂-CH₂-CH₂-CH₃); 1.54-1.66 (m, 8H, 4 x - $CH_2-CH_2-CH_2-CH_3$; 3.28-3.34 (t, 8H, ³J = 7.7 Hz, 4 x -CH₂- CH_2 - CH_2 - CH_3), 6.63 (d, 4H, ${}^{3}J = 8.7$ Hz, 4 x H_{benz}); 6.96 (s, 4H, 4 x H_{eth}); 7.37 (d, 4H, ${}^{3}J = 8.7$ Hz, 4 x H_{benz}); 7.50 (s, 2H, 2 x H_{thio}); 7.89 (s, 2H, 2 x H_{eth}). HRMS (ESI⁺) m/z: 1044.5 M⁺ (calculated: 1044.5). Elemental analysis for C₅₈H₇₂N₆S₄O₄ (%): C, 66.63; H, 6.94; S, 12.27; N, 8.04 - Found: C, 65.75; H, 8.46; S, 6.83; N, 4.76.

Acknowledgement

This work was supported by the Centre National de la Recherche Scientifique (CNRS) and the Ministère de l'Enseignement Supérieur et de la Recherche. Financial support from ANR program (SAGe III-V project ANR-11-BS10-012) and "Solutions Communicantes Sécurisées" (SCS) competitive cluster are also acknowledged. We also thank M. Giorgi (Spectropole, Marseille) for the crystal structure determinations. H.A. also thanks the Ministère de l'Enseignement Supérieur et de la Recherche for his doctoral Financial support. MCIA (Mesocentre de Calcul Intensif Aquitain) is gratefully acknowledged for calculation facilities.

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