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Control of the optical properties upon a reversible [2+2] cycloaddition of 3-(4-*N,N*-dibutylamino)-styryl)-3'-(dicyanovinyl)-bithiophene

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ABSTRACT

In the course of our studies of D- π -A push-pull chromophores we have envisioned the design of the novel 3-(4-*N,N*-dibutylamino)-styryl)-3'-(dicyanovinyl)-bithiophene derivative as a potential building block for optoelectronic applications. However, during the synthesis of this chromophore, a cycloadduct compound confirmed by X-ray structure was obtained by an intramolecular [2 + 2] cycloaddition reaction. The retro cycloaddition reaction carried out in thermal conditions and followed by UV-Visible absorption spectrophotometry afforded quantitatively the target chromophore. Electrochemical properties recorded are in good agreement with open and close compounds. Mechanism involves cis/trans isomerization was proposed to explain the complete conversion.

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1. Introduction

During the last two decades the design and synthesis of push-pull chromophores (D- π -A) have been widely matured due to their intrinsic properties that are useful in various optoelectronic applications [1]. At glance, D- π -A architectures are commonly used in nonlinear optics (NOs) [2], field-effect transistors (OFETs) [3], light emitting diodes (OLEDs) [4], photovoltaic cells (OPVs) [5] and dye sensitizing solar cells (DSSCs) [6]. Notwithstanding, the development and performance of such devices can be hampered by some hurdles. For instance, in the case of bulk heterojunction organic solar cells, even if during the last few years a significant increase of the photovoltaic efficiency has been achieved, spontaneous phase segregation can occur at the inner of the active layer which can turn to be detrimental for the photovoltaic performances.

To circumvent these limitations, it is of crucial of importance to invest unexplored approaches that can bring substantial improvement or outperform the previous. In that context, several

approaches have been developed for OPVs such as based on π -conjugated D/A alternation polymers or molecular D- σ -A assemblies (Chart 1a-b) [7]. Interestingly, a literature survey highlights that among the myriad of architectures developed so far, none have suggested the possibility to insert the push-pull chromophores orthogonally to the π -conjugated backbone (Chart 1c), the latter acting as the electron relay between the D and A moieties.

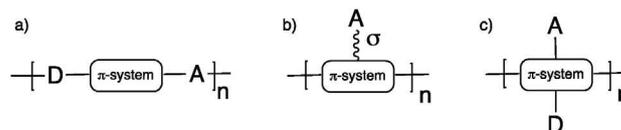


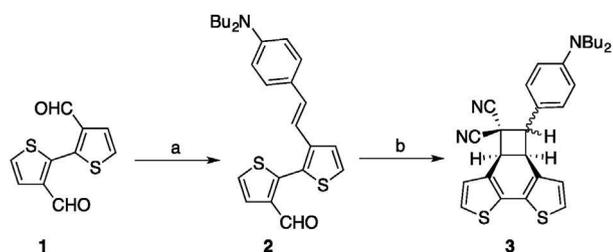
Chart 1. Molecular D- σ -A assemblies.

Thus, in the course of our studies on D/A scaffolds [8] we envisioned the synthesis of 3-(4-*N,N*-dibutylamino)-styryl)-3'-(dicyanovinyl)-bithiophene as a potential building block for such application. The synthesis of this specific chromophore appears somewhat trivial nonetheless we have evidenced that during its preparation it evolves to the formation of a cycloadduct. This behavior is well-documented in literature noticeably with electron rich alkenes and the tetracyanoethylene [9] (TCNE) but poorly with its parent compound the dicyanovinyl moiety [10]. Based on this ascertainment we have undertaken a joint experimental and

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Scheme 1. Synthetic route for the preparation of the cycloadduct **3**. (a) 4-(dibutylamino)benzyltriphenylphosphonium bromide, CH_2Cl_2 , $t\text{BuOK}$ crown ether 18C_6 , 0°C , 2 h, 35%; (b) malonodinitrile, piperidine, ethanol, rt, 18 h, 66%.

theoretical study to give us some insights on the underlying mechanisms involved in the cycloaddition reaction and also on the retro-cycloaddition process leading to the corresponding push-pull chromophore.

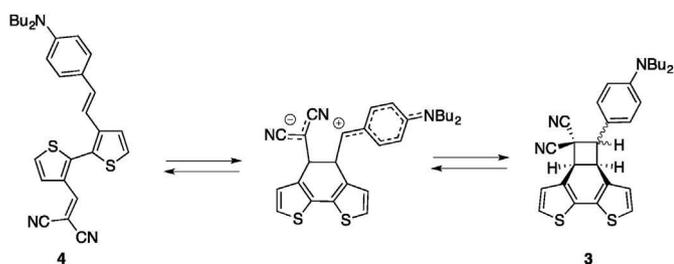
2. Results and discussion

The synthesis of the titled compound was envisioned to be carried out in two consecutive steps, ensuing a similar literature procedure [11], starting from the 2,2'-bithiophene-3,3'-dicarboxaldehyde **1** (Scheme 1) [12]. Thus, the reaction was carried out in high dilution conditions in order to favor the mono-Wittig product **2** by reacting the bisaldehyde **1** with 4-(dibutylamino)benzyltriphenylphosphonium bromide [13] in CH_2Cl_2 in presence of $t\text{BuOK}$ and crown ether 18C_6 at 0°C during 2 h. Subsequent substitution of the aldehyde **2** with malonodinitrile in ethanol, at room temperature during 18h, in presence of piperidine interestingly has afforded the unexpected cycloadduct **3** in 66% yield as a yellowish solid.

The derivative **3** was ascribed to be formed upon an intramolecular [2 + 2] cycloaddition reaction that proceeded through a dipolar intermediate which undergoes a rapid ring closure affording the cyclobutane ring (Scheme 2) [14]. The dipolar intermediate behaves like a zwitterionic specie (highly polar non-electrolyte molecule) having the lowest Coulomb potential and obtained from the reaction of the electron-rich alkene and the dicynavinyl group. Based on the Kirkwood [15], Laidler and Eyring [16] electrostatic model, the reaction is supposed to be under the control of solvent polarity.

Suitable single crystals for X-ray analysis were grown as yellow prisms from a dichloromethane solution. As shown in the ORTEP view (Fig. 1) a racemic mixture is obtained during the course of the cycloaddition process. In addition, the X-ray structure confirms the supported ^1H NMR analysis.

As we are interested in the synthesis of the derivative 3-(4-*N,N*-dibutylamino)-styryl)-3'-(dicyanovinyl)-bithiophene **4**, we have experienced the retro cycloaddition reaction from **3** to **4**. To achieve the interconversion several attempts have been performed and



Scheme 2. Ring opening and closing of cycloadduct **3** and push-pull chromophore **4**.

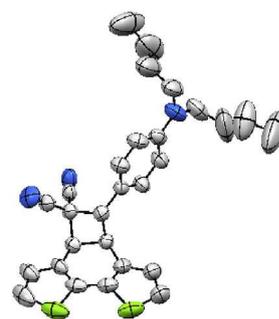


Fig. 1. ORTEP diagram (H are omitted for clarity, green: S; blue: N; black: C) for the crystal structure of the S-cis cycloadduct **3** enantiomer.

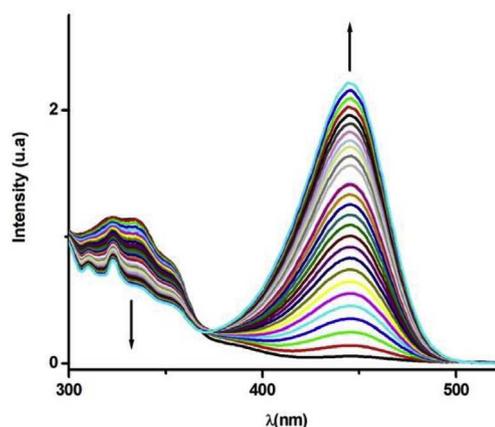


Fig. 2. Evolution of the UV/Vis spectrum of **3** upon heating in DMSO.

more particularly under thermal conditions. Hence, by heating the cycloadduct **3** in DMSO at 70°C over a period of 14 h, and following by UV/Vis spectroscopy (Fig. 2), or in CHCl_3 at 50°C during 72 h affords the open form **4** depicted in Scheme 2.

The interconversion is clearly evidenced as the open and closed forms exhibit different behaviors in UV/Visible absorption spectra. Indeed, the cycloadduct **3** shows a fine vibronic structure centered at $\lambda_{\text{max}} = 320\text{ nm}$ (in DMSO) as expected and similar to already literature reported 3,3'-bridged bithiophene [17] analogues whereas compound **4** shows a charge transfer band centered at $\lambda_{\text{max}} = 438\text{ nm}$ (in DMSO).

TDDFT calculations found the same trend between **3** and **4** (around 90 nm bathochromic effect). The observed band at 320 nm for compound **3**, is a combination of two transitions between HOMO/LUMO and HOMO⁻¹/LUMO molecular orbital whereas for **4**, the band at 438 nm presents three transitions (HOMO/LUMO, HOMO/LUMO⁺¹ and HOMO⁻¹/LUMO) (Fig. 3).

We can note that the rigidification of the thiophene moiety in **3** results in a LUMO which is located on all the thiophene backbone, compared with the LUMO of **4** localized on the cyano groups (in small combination with only one thiophene).

Thus, the process is highlighted both by a huge bathochromic shift associated with a hyperchromic effect while the retro-cycloaddition occurs and by the appearance of an unequivocal isobestic point. At the time that **4** appears an hyperchromic effect occurs gradually at 438 nm whereas a hypochromic effect takes place at 320 nm. Moreover, the comparison of the optical properties between **4** and its 5,5'-substituted bithiophene analogous ($\lambda_{\text{max}} = 550\text{ nm}$ in DMSO) [18] shows a 112 nm blue shift due to the

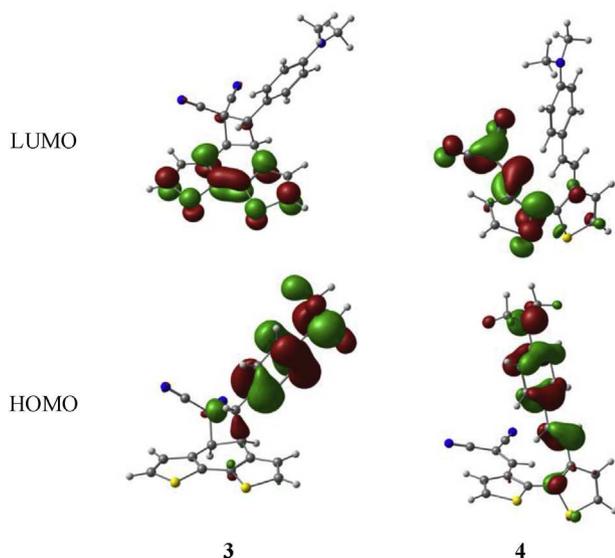


Fig. 3. HOMO/LUMO representations for compounds 3 and 4.

less conjugation between the donor and acceptor moieties where they are in the position 3 and 3'. Unfortunately, DFT calculations cannot argue on an explanation of the reversibility of this reaction considering the solvents effect. Indeed, we found - in accord with the experimental observation - an energetically easy first step corresponding to the opening of the ring but, although, in the case of the presence of ethanol, we found a higher activation energy (23.8 versus 10.3 kcal/mol taking into account ethanol and DMSO respectively using Solvation Model based on Density (SMD)), the barriers remain low and this cannot explain a difference in behaviour depending on the solvents (Fig. 4).

Theoretically, the rotation barriers around thiophenes are low (around 10 kcal/mol), on the other hand even if the presence of delocalization coupled with donor and acceptor groups should have facilitated the cis/trans isomerization reactions around the styryl group, by lowering their barriers, the latter are calculated very high (~45 kcal/mol in DMSO, consistent with the heating of the reaction mixture for several hours required for complete conversion).

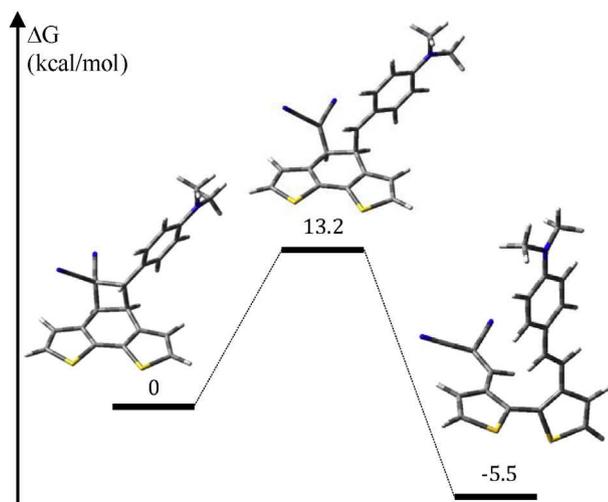


Fig. 4. First step of the opening ring reaction B3LYP/(6-31G(d,p)) in the gas phase.

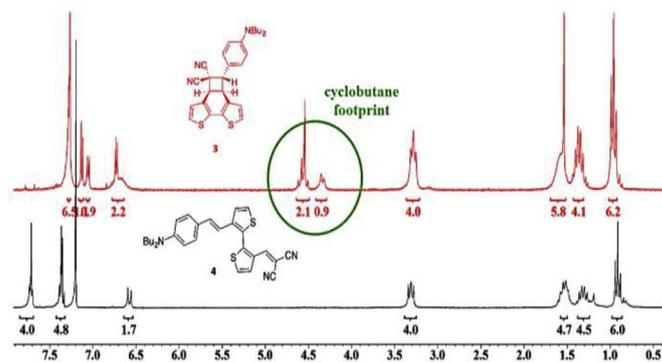


Fig. 5. Comparison of the ^1H NMR of 3 (red) and 4 (black) in CDCl_3 .

In parallel ^1H NMR analysis of the resulting yellowish powder has confirmed unequivocally a nearly quantitative cyclization by the vanishing of the peaks initially present at 6.80 and 6.99 ppm (ethylenic double bond) from compound 2 and the appearance of new peaks at 4.33 (1H) and 4.55 ppm (2H) corresponding to the cyclobutane protons footprint of compound 3. This unique signal confirmed the formation compound 3 supported by the X-ray structure as a raemic. Heating compound 3 in CDCl_3 at 50°C during 72h affords the compound 4 evidenced by the complete disappearance of the cyclobutane protons and the emerging of the ethylenic protons at 6.55–6.59 ppm (Fig. 5).

The redox properties of the resulting chromophores were studied using cyclic voltammetry in CH_2Cl_2 with $n\text{-Bu}_4\text{NPF}_6$ (0.1M) as the supporting electrolyte. The redox potentials vs the ferrocene/ferricinium couple (Fc/Fc^+) are shown in Fig. 6. Both states, i.e. open or closed, of the molecular scaffold are associated with a quasi-reversible one-electron oxidation process. The oxidation potential is clearly affected by the nature of the form with a lowered oxidation potential in favor to the closed form.

The lowest oxidation potential can be unambiguously attributed to the covalent bridge bithiophene derivative [19]. This covalent rigidification leads to a lower oxidation potential as it was already emphasized in the bithiophene chemistry. Indeed, the oxidation potential of the cycloadduct ($E_{\text{ox}} = 490\text{ mV}$) is 216 mV lower than the open form. Interestingly, we can point out in the cyclic

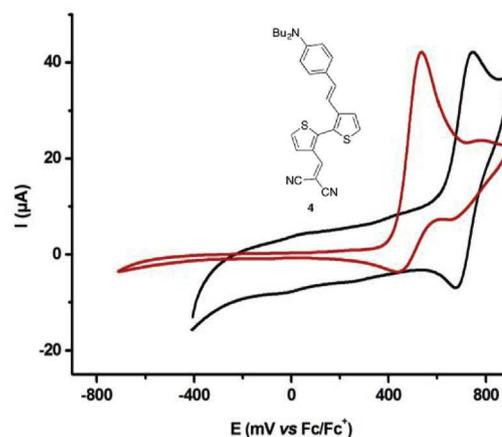


Fig. 6. Cyclic voltammetry for compounds 3 (red) and 4 (black) 10^{-3}M in CH_2Cl_2 , $n\text{-Bu}_4\text{NPF}_6$ (0.1M) scan rate 100 mV s^{-1} .

voltammogram of the cycloadduct **3** the emergence of a second oxidation corresponding to a minor conversion into the open form **4**.

3. Conclusion

We have reported herein the synthesis of a novel D- π -A push-pull chromophore having a bithiophene core substituted at the 3 and 3' positions respectively by a dibutylamino-styryl donor group and a dicyanovinyl electron withdrawing group. Interestingly, the synthesis of this compound is not trivial because a retro cycloaddition reaction from a cycloadduct intermediate is necessary to obtain the target D- π -A push-pull compound. The possibility to have interconversion between two bithiophene derivatives associated with acceptable electro-optical properties make them suitable for the foreseen applications. Further studies on the insertion of this novel building block in now ongoing.

4. Experimental section

4.1. Reagents and analysis

4-(*N,N*-dibutylbenzyl) triphenylphosphonium bromide and 2,2'-bithiophene-3,3'-dicarboxaldehyde **1** were synthesized according to reported literature procedures [12,13], *tert*-BuONa, 18-crown-6, malononitrile were purchased from Sigma Aldrich and used as received. Absolute ethanol, methylene chloride (CH₂Cl₂), dry dimethylsulfoxide (DMSO), petroleum ether were purchased from Carlo Erba. Tetrabutylammonium hexa-fluorophosphate (*n*-Bu₄NPF₆) was purchased from Fluka and was used as received.

4.2. Physico-chemical analyses

¹H NMR spectra were recorded on Bruker AC 250 at 250 MHz. 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 = 0.71073 Å) under monocrystal **3** was made with a Bruker-Nonius spectrometer (For more informations, see website of Spectropôle from Aix-Marseille University: <http://www.spectropole.u-3mrs.fr/presentation0.htm>). Yellow crystals of **3** were obtained by slow evaporation of a CH₂Cl₂ solution, with the monoclinic space group P21/c with *a* = 18.9655 (7) Å, *b* = 9.3553 (3) Å, *c* = 15.9233 (4) Å, α = 90°, β = 113.822 (1)°, γ = 90° at 293 K, with *Z*=4 and *V*= 2584.54 (14) Å³. The refinement of 6239 reflections and 307 parameters yielded *R*₁= 0.1052 for all data (2509 reflections with *I* > 2 σ (*I*)). Atomic coordinates, bond lengths, angles and thermal parameters for **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC number: 2014387). Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB21EZ, UK. Email: deposit@ccdc.cam.ac.uk.

4.3. 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 the compound in DMSO. 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 hexa-fluorophosphate served as a supporting electrolyte (0.1 M). All experiments were carried out in methylene chloride (electronic grade purity) at 20 °C. Ferrocene was used as an internal standard. Electrochemical oxidation potential values versus 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.

4.4. Computational methodology

Calculations were carried out with the Gaussian 09 program [20] at the DFT level of theory using both B3LYP [21a-c] and M06 [21d] functionals. All the different atoms (C, N, H, O, S) have been described with a 6-31G(d,p) double-z basis set [22]. Geometry optimizations were carried out without any symmetry restrictions.

Geometry optimizations were carried out without any symmetry restrictions, the nature of the *extrema* (*minima* or transition state) was verified with analytical frequency calculations. All total energies and Gibbs free energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies. The connection between the transition states and the corresponding minima was confirmed by IRC calculations [23,24].

In order to verify if an increase in the basis set provides a benefit in the quality of the modeling, we used the more extensive 6-311++G(d,p) basis set. We have observed the same trend and conclude in the same way regardless of the basis used.

4.5. Synthesis

(*E*)-3'-(4-(dibutylamino)styryl)-[2,2'-bithiophene]-3-carbaldehyde (**2**) Under an inert atmosphere, 0.188 g (1.70 mmol) of dried *tert*-BuONa was added to a solution of 0.470 g (0.84 mmol) of 4-(*N,N*-dibutylbenzyl) triphenylphosphonium bromide in 250 mL of anhydrous CH₂Cl₂. After stirring 10 min at 0 °C, 0.01 g (0.26 mmol) of 18-crown-6 and 0.186 g (0.84 mmol) of the dialdehyde **1** were added. The reaction mixture was then stirred at 0 °C for another 2 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over SiO₂ using CH₂Cl₂/Petroleum ether (1:1) to afford a reddish orange solid in 35% yield. ¹H NMR (250 MHz, CDCl₃) δ : 0.87 (t, 6H, 2CH₃); 1.18–1.30 (m, 4H, 2CH₂); 1.42–1.50 (m, 4H, 2CH₂); 3.16–3.20 (m, 4H, 2CH₂); 6.58 (d, 2H, ³*J* = 9.0 Hz, H_{phe}); 6.80 (d, 1H, ³*J* = 16.0 Hz, 1H, H_{ethy}); 6.99 (d, 1H, ³*J* = 16.0 Hz, 1H, H_{ethy}); 7.26 (d, 2H, ³*J* = 8.8 Hz, H_{phe}); 7.36 (dd, 1H, ³*J* = 5.5 Hz, ³*J* = 0.8 Hz, H_{thio}); 7.43 (s, 1H, H_{thio}); 7.44 (s, 1H, H_{thio}); 7.59 (d, 1H, ³*J* = 5.5 Hz, H_{thio}); 9.76 (s, 1H, CHO). Elemental analysis for C₂₅H₂₉NOS₂ (%): C, 70.88; H, 6.90; N, 3.31; O, 3.78; S, 15.14; Found: C, 69.66; H, 6.58; N, 2.79; S, 16.76. HRMS (ESI): calculated, *m/z*: 424.1763 [M+H]⁺; found, *m/z*: 424.1765 [M+H]⁺.

(3*bR*,5*S*,5*aR*)-5-(4-(dibutylamino)phenyl)-5,5*a*-dihydrocyclobuta [5,6]benzo[2,1-*b*:3,4-*b'*]dithiophene-4,4(3*bH*)-dicarbonitrile (**3**). Under an inert atmosphere, 0.060 g (0.14 mmol) of compound **2** was solubilized in 1.70 mL of absolute ethanol and 0.011 g (0.17 mmol) of malononitrile in solution in 3 mL of absolute ethanol was subsequently added followed by 10 μ L of piperidine. The reaction mixture was stirred at room temperature for 3 h prior further addition of 2 mg of malononitrile and left under stirring overnight. A precipitate appeared, filtered off from the solution and carefully washed with cold ethanol affording the titled compound **3** as a pale yellow solid in 66% yield. ¹H NMR (250 MHz, CDCl₃) δ : 0.95 (t, 6H, 2CH₃); 1.30–1.45 (m, 4H, 2CH₂); 1.55–1.66 (m, 4H, 2CH₂); 3.36–3.22 (m, 4H, 2CH₂); 4.33 (m, 1H, H_{cyclo}); 4.55 (m, 2H, H_{cyclo}); 6.72 (d, 1H, ³*J* = 5.0 Hz, H_{thio}); 7.05 (d, 1H, ³*J* = 4.9 Hz, H_{thio}); 7.12 (d, 1H, ³*J* = 5.1 Hz, H_{thio}); 7.26 (s_{large}, 4H, H_{phe}); 7.27 (d, 1H, ³*J* = 5.1 Hz,

H_{thio}). Elemental analysis for C₂₅H₂₉NOS₂ (%): C, 71.30; H, 6.20; N, 8.91; S, 13.60; Found: C, 71.17; H, 6.25; N, 9.02; S, 13.21. HRMS (ESI): calculated for C₂₈H₂₉N₃S₂, *m/z*: 472.1803 [M+H]⁺; found, *m/z*: 472.1876 [M+H]⁺.

(*E*)-2-((3'-(4-(dibutylamino)styryl)-[2,2'-bithiophen]-3-yl)methylene)malononitrile (**4**). In a NMR tube compound **3** was heated at 50 °C during 72h. ¹H NMR (250 MHz, CDCl₃) δ: 0.90 (t, 6H, 2CH₃); 1.27–1.35 (m, 4H, 2CH₂); 1.48–1.57 (m, 4H, 2CH₂); 3.27–3.34 (m, 4H, 2CH₂); 6.55–6.59 (2H, H_{ethy}); 7.33 (d, 2H, ³J = 5.20 Hz, H_{thio}); 7.35 (s, 1H, -CH=C(N)₂); 7.37 (d, 2H, ³J = 5.20 Hz, H_{thio}); 7.70 (m, 4H, H_{phe}). HRMS (ESI): calculated for C₂₈H₂₉N₃S₂, *m/z*: 472.1803 [M+H]⁺; found, *m/z*: 472.2000 [M+H]⁺.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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