Electropolymerization of triphenylamine–dithiafulvene hybrid extended pi-conjugated systems†

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Extended hybrid conjugated systems based on a triphenylamine core with 1, 2 and 3 peripheral dithiafulvenyl units have been studied by cyclic voltammetry and UV-Vis absorption spectroscopy. The substitution pattern of the triphenylamine core determines two different electrochemical coupling mechanisms leading to two types of electrogenerated extended conjugated electroactive systems. The structure and properties of polymeric species are also presented.

Introduction

Triphenylamine (TPA)-based compounds have been widely used as hole injection layers or as active materials in light-emitting diodes.[1] Recently, hybrid star-shaped systems involving a TPA core derivatized with linear short-chain conjugated systems have been reported, as well as their use as active materials in organic field-effect transistors (OFET) and organic solar cells.[1–4] Thus, hole mobilities of up to 1×10^{-2} cm^2 V^{-1} s^{-1} have been obtained on OFET based on TPA derivatized with oligothiophenes.[2] Furthermore, it has been shown that the creation of an internal charge transfer by fixation of electron-withdrawing groups on TPA-based conjugated systems leads to organic solar cells presenting extended photoresponse and improved open-circuit voltage efficiency and stability.[3,4]

On the other hand, recent years have witnessed a strong renewal of interest for tetrathiafulvalene (TTF) derivatives as active materials for OFET, and high hole mobility values have been reported.[5] In this context, we have recently undertaken the development of a new series of extended conjugated systems associating the TPA and TTF building blocks in view of reaching new materials combining the isotropic charge transport of TPA materials and the well known propensity of TTF derivatives to develop strong intermolecular interactions.[6]

As such compounds may undergo polymerization upon oxidation, their use as precursors for electrode material or for electrochromics is also envisaged. Therefore, in the continuation of our current interest in hybrid systems associating TPA and TTF moieties, we report here on the synthesis and properties of four TPA derivatives **1–4** grafted with one to three dithiolylidene groups (Scheme 1). Upon oxidation, these derivatives undergo a polymerization that may imply two different electrochemical coupling mechanisms.

Electrochemical and spectroscopic experiments on compounds and corresponding polymers as well as theoretical calculations provide a coherent picture of the behavior of these derivatives upon oxidation.

Results and discussion

The synthesis of compounds **3** and **4** is described elsewhere.[6] Compounds **1** and **2** have been synthesized by condensation of corresponding 2-thioxo-1,3-dithioles onto the mono- and dialdehyde of the TPA in the presence of triethylphosphite (Scheme 1).[7]

The electrochemical and optical data of compounds **1–4** are gathered in Table 1. All compounds present a large π–π* absorbance band with a λ_{max} that depends both on the number of dithiafulvene groups and on the nature of the substituents grafted on the dithiole cycle. The introduction of one, two and three dithiafulvenyl moieties in the structure induces a bathochromic shift of λ_{max} from 378 to 408 nm. On the other hand, the data for the fully substituted compounds **3** and **4** show that the position of λ_{max} also depends on the electron-donating ability of the dithiafulvenyl group, the stronger donor alkylsulfanyl substituent in **3** leading to a slight red shift compared to the benzo-substituted compound **4**.

The cyclic voltammogram of all compounds exhibits two oxidation processes with anodic peak potentials $E_{pa}{}^1$ and $E_{pa}{}^2$ around 0.5–0.6 and 1.1–1.2 V (Table 1). In contrast with optical data, comparison of the data for compounds **1a**, **2** and **3** shows that $E_{pa}{}^1$ depends only slightly on the number of dithiafulvenyl groups. Thus derivatives **1a**, **2** and **3** present very close oxidation potentials. On the other hand, comparison of the data for compounds **1a** and **1b** or **3** and **4** shows that the nature of the substituents grafted on the dithiafulvenyl group significantly affects $E_{pa}{}^1$; the electron-withdrawing cyanoethyl or benzo groups leading to positive shifts. These results suggest that the first oxidation process essentially involves the dithiafulvenyl units.

This assumption is corroborated by *ab initio* quantum calculations performed on compound **1a** with the Gaussian 03 package[8] of programs at a hybrid density functional theory (DFT) level. Calculations have been carried out using the

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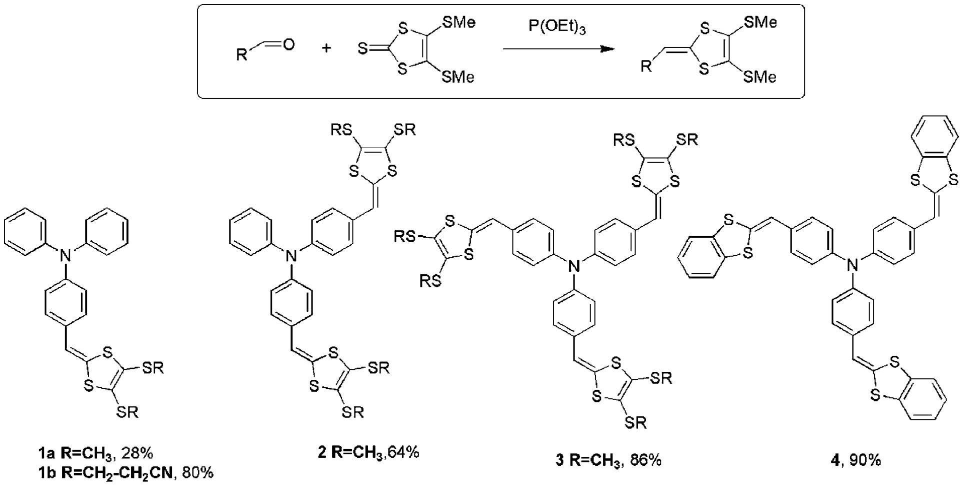
† Electronic supplementary information (ESI) available: UV-vis spectra of **1**, **2** and **3**; CV of derivative **4** and CV trace of poly(**4**). See DOI: 10.1039/b819675c



Scheme 1

Table 1 Optical and electrochemical properties of compounds **1–4** and of corresponding polymers

	λ_{max}[a]	E_{pa}^{1}[b]	E_{pa}^{2}[b]	λ_{max}[c] Poly	λ_{max}[c] Poly^{ox}	E_{ox}^{1}[c] Poly	E_{ox}^{2}[c] Poly
1a	378	0.53	1.12	—	—	—	—
1b	377	0.59	1.09	—	—	—	—
2	399	0.53	1.18	376	353–644	0.44	1.00
3	408	0.51	1.18	386	345–640	0.44	1.17
4	398	0.63	1.01	401	360–489	0.52	1.20

[a] 10^{-5} M in CH_2Cl_2. [b] Oxidation peak *vs.* SCE measured from cyclic voltammetry, $<10^{-3}$ M of compounds with 0.1 M Bu_4NPF_6 as supporting electrolyte, v = 100 mV s^{-1}. [c] Deposited on Pt electrode with 0.1 M Bu_4NPF_6 as supporting electrolyte.

U-B3LYP/6-31G* level for the cation radical states. The SOMO of the radical cation is at −7.80 eV. In the radical cation, the phenyl and dithiol rings are coplanar and the SOMO is essentially located on the arm bearing the dithiafulvene moiety. Coefficients are negligible on the terminal position of phenyl rings while high coefficients are observed on the carbons of the vinyl linkage (Fig. 1).

The CV of compound **1a** presents two successive one-electron oxidation processes (Fig. 2). The first process is irreversible and a blue coloration appears in solution around the electrode during oxidation. Such a behavior may be attributed to an electrochemical coupling. As **1b** suffers from complex adsorption phenomena during its oxidation the interpretation of its CV curve appears difficult.

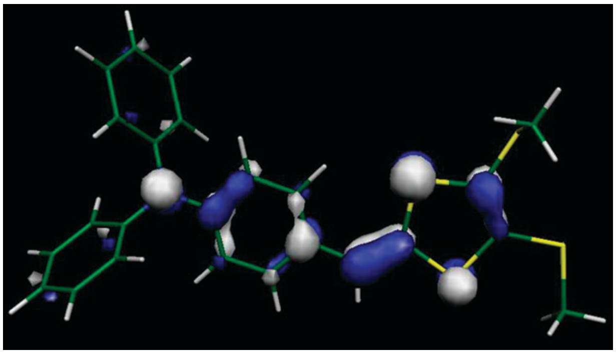


Fig. 1 Calculated SOMO of $\mathbf{1}^{+\bullet}$.

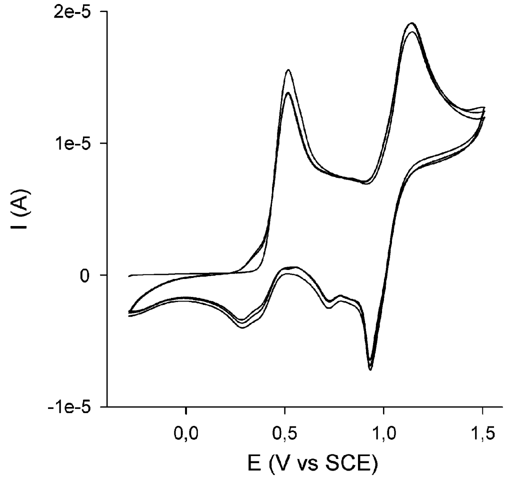
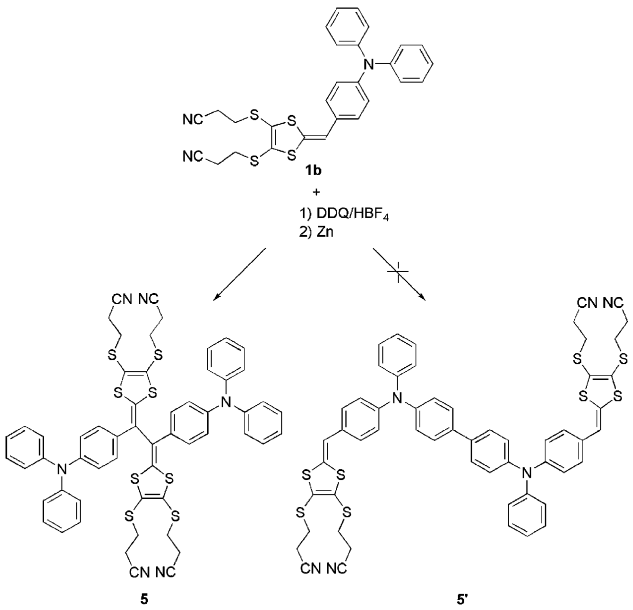


Fig. 2 CV of compound **1a** in 0.10 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}.

This observation, in addition to calculation results, brings further support to the hypothesis of an intermolecular coupling of $\mathbf{1}^{+\bullet}$ at the vinyl linkage between phenyl and dithiole rings position.[9–11]

This supposition is confirmed by chemical experiments: compound **1b** has been chemically oxidized using DDQ and HBF_4.[12,5b] After reduction with zinc, compound **5**, which results from a coupling at the vinylic linkage was isolated in 60% yield together with a large amount of starting material (Scheme 2). Note that derivatives **1b** and **5**, which both possess cyanoethylsulfanyl groups, could be functionalized for further applications.[13] We can then assume that, upon oxidation of derivatives **1**, the vinyl linkage is favored compared to the phenyl linkage.[9–11]

The CV of compound **5** exhibits two two-electron oxidation steps with E_{pa}^{1} and E_{pa}^{2} at 0.61 and 1.14 V (Fig. 3), very close to that of **1b**. Indeed, dimerization on encombered dithiafulvene moiety is known to lead to sterically constrained extended TTF analogs with oxidation potentials rather similar to that of



Scheme 2

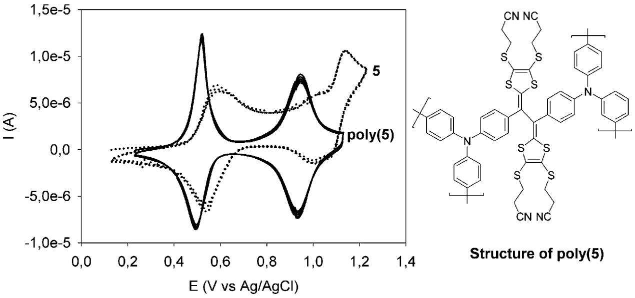


Fig. 3 CV of compound **5** in 0.1 M Bu_4NPF_6–CH_2Cl_2 (dotted line) and CV of the electrodeposited material on Pt in 0.1 M Bu_4NPF_6–CH_3CN, scan rate 100 mV s^{-1}.

the starting material.[10,11] As the first oxidation process is reversible, application of repetitive scans with a positive limit set at $E_{pa}{}^2$ results in the deposition of an electroactive material onto the electrode surface.

The CV of the resulting electrodeposited material exhibits two reversible oxidation processes with $E_{pa}{}^1$ and $E_{pa}{}^2$ at 0.52 and 0.94 V, respectively (Fig. 3). These anodic peaks are shifted toward negative potentials by 90 and 200 mV compared to the starting compound **5**, which is consistent with an extension of the conjugated system resulting from coupling on the terminal position of the phenyl rings.[9] These results can thus doubtless be interpreted by the electrodeposition of a polymeric system resulting from the coupling on terminal positions of phenyl rings.[14]

The CV of compound **2** exhibits a first reversible two-electron oxidation wave peaking at 0.50 V, leading to a stable dication followed by an irreversible wave at 1.20 V. Repetitive cycling up to the first oxidation wave leaves the CV unchanged, whereas cycling up and over the second wave leads to the development of growing redox system typical of an electrodeposition process (Fig. 4). For compounds **3** and **4**, the CV shows a first non-reversible three-electron oxidation wave followed by a non-reversible one-electron oxidation process. For these two compounds **3** and **4**, a quite different behavior is observed when compared to that of **2**. Indeed, cycling up to the first oxidation step already triggers the electrodeposition process (Fig. 4).

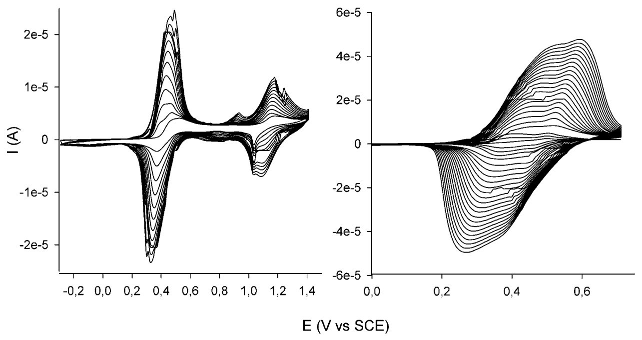


Fig. 4 Potentiodynamic electropolymerization of **2** (left) and **3** (right) in 0.10 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}.

These results suggest that electrooxidation of compound **2** leads to a stable dicationic species and that it is therefore necessary to form the trication radical at the second oxidation to produce a reactive species able to electropolymerize. In contrast, in the case of compounds **3** and **4**, the reactive tris-cation radical is directly generated at the first three-electron oxidation step.

Electrooxidation of compound **2** can lead to two different reactions pathways yielding two different coupling products linked either at the *para*-position of the phenyl ring or at the dithiafulvenyl linkage similarly to compound **1b** and to related compounds previously investigated.[10,14] In contrast, for compounds **3** and **4**, only the second reaction pathway is possible.

Fig. 5 shows the CVs of the materials electrodeposited by electrooxidation of compounds **2–4**. These three CVs are very similar and exhibit a first intense redox system with $E_{pa}{}^1$ at *ca.* 0.45 V and a less intense wave with $E_{pa}{}^2$ in the 1.00–1.15 V region. The two redox processes present relative intensities of 2 : 1 for poly(**2**) and 3 : 1 for poly(**3**) and poly(**4**), respectively, which corresponds to the relative quantities of dithiafulvenyl and TPA moieties in the compounds. For the three polymers, $E_{pa}{}^2$ is observed at a higher potential than for poly(**5**), which is consistent with a shorter effective conjugation due to the absence of phenyl–phenyl coupling. The less positive values of $E_{pa}{}^1$ and $E_{pa}{}^2$ for poly(**3**) compared to poly(**4**) can be attributed to the more electron-releasing effect of the methylsulfanyl groups compared to the fused phenyl rings.

The high similarity of the three CVs, their difference with that of poly(**5**) and the impossibility for compounds **3** and **4** to undergo phenyl–phenyl coupling strongly support the conclusion that electrooxidation of the three compound **2**, **3** and **4** leads to a unique type of electrochemical coupling involving the vinyl linkage of the dithiafulvenyl unit, as already demonstrated for compound **1b** and extended TTF derivatives.[10]

Films of compounds **2**, **3** and **4** have been electropolymerized on ITO-coated glass electrodes. The difficult polymerization of **5** did not allow its electrodeposition on ITO. All electrodeposited materials exhibit a stable CV with no evidence of

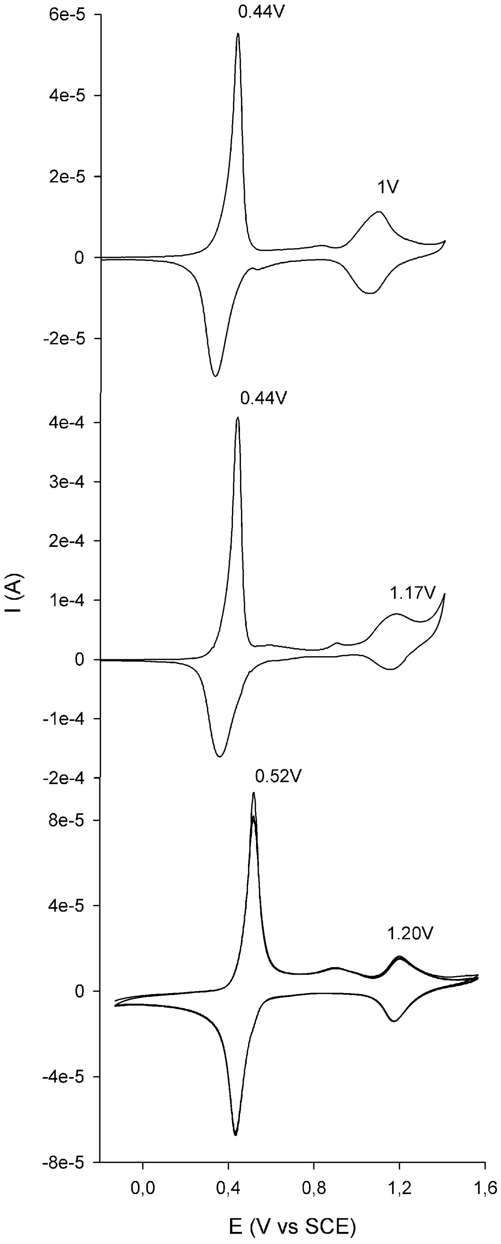


Fig. 5 CV of poly(**2**) (top), poly(**3**) (middle) and poly(**4**) (bottom) in 0.10 M Bu_4NPF_6–CH_3CN, scan rate 100 mV s^{-1}.

degradation after repetitive cycling on the first redox process for several hundred cycles or after prolonged storage in air in neutral or oxidized state. However, electrooxidation up to the second oxidation process leads to a steady decrease of the film electroactivity.

As shown in Table 1, the neutral polymer films show absorption maxima at slightly shorter wavelengths than their precursor molecules, suggesting that the effective conjugation in the polymers is limited by distortions caused by steric interactions.

The three compounds lead to homogeneous polymer films that are yellow in their neutral state and present electrochromic properties.[15] Poly(**2**) and poly(**3**), in which the terminal dithiole rings are substituted with electron-donating methylsulfanyl groups, present two maxima around 350 and 640 nm in their oxidized form and appear blue (Fig. 6). The oxidized form of poly(**4**) presents a maximum at 489 nm, this blue shift compared to the two other polymers can be attributed to its lower donor ability.

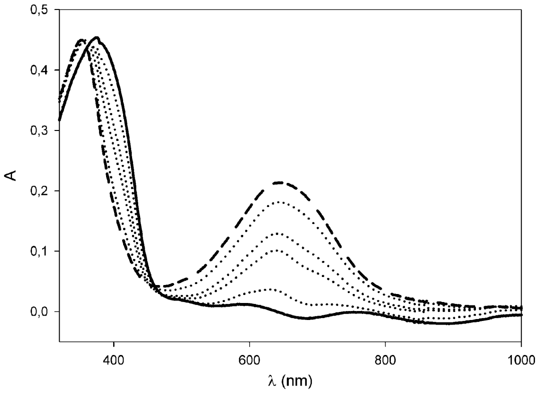


Fig. 6 Spectroelectrochemistry of a film of poly(**3**) on ITO electrode in 0.10 M Bu_4NPF_6–CH_3CN at various applied potentials. Solid line (neutral state at 0 V); short dash (fully oxidized state at 0.8 V); dotted lines (intermediate states).

Conclusions

Four new hybrid conjugated systems combining a triphenylamine core and one to three dithiafulvenyl branches have been synthesized. Electrooxidation of these compounds leads to dimerization or polymerization products. Electrochemical results together with theoretical calculations provide consistent results indicating that electrochemical coupling occurs at the vinylic linkage. Polymeric films of **2–4** present well defined redox processes and electrochromic properties.

Experimental

General

Solvents were purified and dried using standard protocols. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker Biflex-III, equipped with a N2 laser (337 nm). For the matrix, dithranol in CH_2Cl_2 was used. High resolution mass spectra were recorded under FAB mode on a Jeol JMS 700 spectrometer. UV-visible optical data were recorded with a Perkin-Elmer lambda 19 spectrophotometer. Thermal analyses were performed using a DSC 2010 CE (TA Instruments). For cyclic voltammetry (scan rate 100 mV cm^{-1}), the electrochemical apparatus consisted of a potentiostat EG&G PAR 273A and a standard three-electrode cell. As the working and counter electrodes, a platinum foil and a platinum wire were used, respectively, while as a reference a Ag/AgCl electrode served as reference. Electrochemical experiments were carried out in methylene chloride or acetonitrile (spectroscopic grade) containing 0.10 M tetrabutylammonium hexafluorophosphate (Fluka puriss, used as received). Spectroelectrochemical experiments were carried out with a home-made cell on polymers grown on ITO.

Note that experimental procedures for **3** and **4** have been published elsewhere.[6] Due to low solubility in organic solvents and to low stability in acidic media, ^{13}C NMR of compounds appeared difficult and was not undertaken.

Syntheses

4-[((4,5-Bis(methylthio)-1,3-dithiol-2-ylidene)methyl) phenyl]-diphenylamine 1a. 178 mg (0.64 mmol) of 4-(diphenylamino)-benzaldehyde and 248 mg (2 eq.) of 4,5-(dimethylthio)-2-thioxo-1,3-dithiole are dissolved in 2 mL of boiling toluene, then 2 mL of triethylphosphite are added. The mixture is refluxed for 5 h under a nitrogen atmosphere. After cooling and addition of methylenechloride, the mixture is washed with brine and dried on magnesium sulfate. The residue is then chromatographed twice (EP–CH_2Cl_2 5 : 1 and then EP–CH_2Cl_2 1 : 1) leading to a yellow oily solid (80 mg, 28%). Decomp. ≈ 45 °C. $R_f = 0.81$ (EP–CH_2Cl_2 1 : 1). NMR ^{1}H ($CDCl_3$): 7.27 (m, 4H), 7.10 (m, 6H), 7.04 (m, 4H), 6.42 (s, 1H), 2.44 (s, 3H, SCH_3), 2.41(s, 3H, SCH_3). MS (Malditof) $C_{24}H_{21}NS_4$: ms M^+: 451.1, theor.: 451.1. HRMS M^+ (calcd) (451.0557) 451.0538.

4-[((4,5-Bis(cyanoethylthio)-1,3-dithiol-2-ylidene)methyl) phenyl]-diphenylamine 1b. 50 mg (0.18 mmol) of 4-(diphenylamino)-benzaldehyde and **2** eq. of 4,5-(dicyanoethylthio)-2-thioxo-1,3-dithiole are dissolved in 10 mL of boiling toluene, then 2 mL of triethylphosphite are added. The mixture is refluxed for 3 h under a nitrogen atmosphere. After cooling and evaporation of the toluene, the mixture is triturated in petroleum ether and a yellow oil appears in the flask. This procedure is done three times, which allows the elimination of triethylphosphite. Pure **1b** is isolated as a yellow oil after column chromatography (methylene chloride) in 80% yield. $R_f = 0.6$ (CH_2Cl_2). NMR ^{1}H ($CDCl_3$): 7.26 (m, 4H), 7.10 (m, 4H), 7.05 (m, 6H), 6.46 (s, 1H), 3.08 (2 × t, 4H), 2.75 (2 × t, 4H). MS (MALDI-TOF) $C_{28}H_{23}N_3S_4$: ms M^+: 529.1, theor.: 529.1.

Bis[4-((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)phenyl]-phenylamine 2. 300 mg (1 mmol) of bis[4-formylphenyl]phenyl-amine and 900 mg (4 eq.) of 4,5-bis(methylthio)-2-thioxo-1,3-dithiole are dissolved in 3 mL of boiling toluene, then 2 mL of dry triethylphosphite are added. The mixture is refluxed for 4 h under a nitrogen atmosphere. After cooling and addition of methylene chloride, the mixture is washed with brine and dried over magnesium sulfate. After evaporation of solvent and dissolution of the residue in the minimum of methylene chloride, the addition of petroleum ether affords the formation of a pure orange solid (220 mg, 64% yield). m.p. = 145 °C. $R_f = 0.6$ (EP–CH_2Cl_2 1 : 1). NMR ^{1}H ($CDCl_3$): 7.25 (m, 1H), 7.07 (m, 12H), 6.42 (s, 2H), 2.43 (s, 6H), 2.41 (s, 6H). MS (MALDI-TOF) $C_{30}H_{27}NS_8$: ms M^+: 656.9, theor.: 657.0. HRMS M^+ (calcd) (656.9909) 656.9890.

Compound 5. 50 mg of **1b** (0.1 mmol) are dissolved in 10 mL of dry diethyl ether. Then 30 mg of DDQ, 0.4 mL of HBF_4, H_2O and two drops of concentrated hydrochloric acid are added. The yellow solution turns deep green and is stirred for 1 h at room temperature. The solution is then filtered and a magnificent purple powder is isolated. Note that the filtrate contains a large amount of unreacted **1b**. The precipitate is dissolved in acetonitrile, leading to a blue solution, 1 mL of acetic acid, an excess of zinc is added and the mixture is stirred for 45 minutes at room temperature. After filtration of zinc and evaporation of the solvent, pure derivative **5** (30 mg, 60% yield) is isolated as a yellow glassy solid. NMR ^{1}H ($CDCl_3$): 7.25 (t, 8H, J = 7.5Hz), 7.2 (d, 4H, ^3J = 8.5Hz), 7.10 (d, 8H, J = 8Hz), 7.04 (t, 4H, J = 7.5Hz), 6.97 (d, 4H, ^3J = 8.5Hz), 3.06 (8H, q, ^3J = 7 Hz), 2.76 (4H + 4H, 2 × q, ^3J = 7Hz). HRMS: M^+ (calcd) for $C_{56}H_{44}N_6NaS_8$: (1079.1291), 1079.1885.

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