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Approaches to Fused Tetrathiafulvalene/Tetracyanoquinodimethane Systems

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In the search for transformations of quinone moieties into the corresponding tetracyano-*p*-quinodimethane (TCNQ) systems, Knoevenagel-type condensations of 2-thioxo-1,3-dithiole-*p*-benzoquinone systems, TTF-*p*-benzoquinone dyads and a *p*-benzoquinone-TTF-*p*-benzoquinone triad with malononitrile under different experimental conditions were investigated. In order to avoid the well-known Michael 1,4-addition onto the quinone moiety, cyclopentadiene or cyclohexadiene units were incorporated as protecting groups through [4+2] Diels–Alder cycloadditions. On the one hand, aromatization leading to fused 2-thioxo-1,3-dithiole-hydroquinones was observed in the presence of acetic acid and pyridine. With use, on the other hand, of the nucleophilic malononitrile anion, an unprecedented ring-opening process of the 1,3-dithiole moiety occurred, affording stable ketene imines. Finally, successful conversion of 1,3-dithiole-*p*-benzoquinones into the corresponding TCNQ systems was achived by treatment with malononitrile in the presence of titanium(IV) chloride and pyridine as Lehnert's reagents. All new TCNQ derivatives were unambiguously characterized. So far, the application of such experimental conditions to protected TTF-*p*-benzoquinone dyads and a *p*-benzoquinone-TTF-*p*-benzoquinone triad has been unsuccessful, maybe due to the high reactivity of the TTF moiety.

Introduction

Tetrathiafulvalene (TTF) and its derivatives were historically prepared for their applications as strong electron-donor molecules for the development of electrically conducting materials such as the famous tetrathiafulvalene/tetracyano-*p*-quinodimethane (TTF-TCNQ) intermolecular charge-transfer complex.[1] During the last few years, there has been increasing interest in the search for covalent linkage of TTFs to electron-acceptor moieties, because of the potential applications of such attractive materials in molecular electronics and optoelectronics.[2] The performances of the corresponding devices clearly depend on the energies of relevant molecular orbitals and, as a result, molecular systems presenting low HOMO–LUMO gaps are of particular importance.[3] Covalent attachment of TTF to TCNQ as an electron acceptor was initiated in a theoretical paper by Aviram and Ratner, who proposed the concept of a unimolecular rectifier represented by the TTF-σ-TCNQ system **1** (Scheme 1).[4] This rectification behaviour was observed in a molecular junction device based on a donor–acceptor (D-A) TTF-σ-trinitrofluorene dyad, which exhibits an extremely low HOMO–LUMO gap (0.3 V).[5] However, the combination of a strong donor with a high HOMO, such as TTF, and a strong acceptor with a low LUMO, such as TCNQ, still represents a real synthetic challenge because of the formation of stable and insoluble intermolecular charge-transfer complexes between the two counterparts prior to their covalent linking. Historically, the investigated synthetic method consisted of using the weaker acceptor *p*-benzoquinone and its subsequent conversion into TCNQ. This protocol was considered in many cases, but seemed to be quite challenging.[6]

An alternative strategy based on the use of covalent linking at –100 °C between highly reactive functionalities grafted onto both TTF and TCNQ moieties to obtain the first well-characterized TTF-σ-TCNQ dyad **2** has been reported.[7] Its electrochemical HOMO–LUMO gap (0.17 eV), suggested as the lowest gap known in an organic molecule, leads to spontaneous electron transfer inside this dyad. More recently, the elaboration of the TCNQ-σ-TTF-σ-TCNQ system **3**, involving a rigid saturated bridge, has been investigated and its bent structure was suggested to be responsible for a 20% through-space intramolecular charge transfer.[8] We have been interested in the synthetic challenge in obtaining the planar and fused TCNQ-TTF-TCNQ and TTF-TCNQ systems **4** and **5**, respectively, because these would be expected to exhibit low HOMO–

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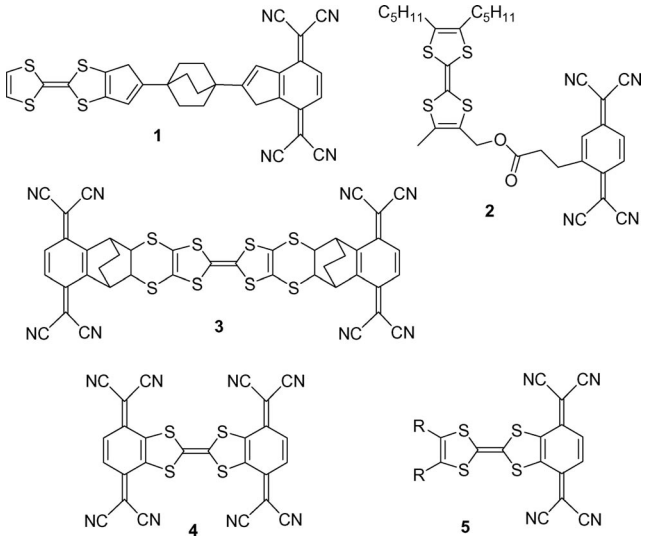
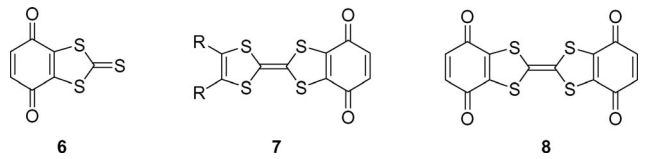


Scheme 1. TTF-TCNQ systems: the Aviram–Ratner molecular rectifier conceptual model **1**, molecules **2** and **3** described in the literature, and the fused TTF-TCNQ target molecules **4** and **5**.

LUMO gaps. Up to now, only one striking example of a fused π-conjugated molecule incorporating TTF and a TCNQ-type bithienoquinoxaline has been reported, exhibiting electrochemically amphoteric properties with a small HOMO–LUMO gap of 0.52 V.[9] Obviously, the annulation of the D and A moieties into a planar configuration facilitates photoinduced intramolecular charge-transfer (CT) processes. As confirmation of the importance of this parameter of planarity, electroactive A_2D triads incorporating one π-extended TTF unit and two tetracyano-*p*-anthraquinodimethane (TCAQ) units have been described, but negligible electronic interaction between the redox chromophores was observed, due to the distortion of the molecule out of planarity.[10]

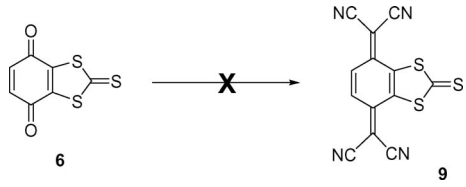
Some of us were previously interested in systems incorporating moderate acceptors such as *p*-benzoquinone, which can be used as precursors for targets **4** and **5**. Consequently, the fused 2-thioxo-1,3-dithiole-*p*-benzoquinone **6**, the TTF-*p*-benzoquinone (TTF-Q) dyads **7** and the *p*-benzoquinone-TTF-*p*-benzoquinone (Q-TTF-Q) triad **8** were chosen as starting materials (Scheme 2).[11] In this work we focus on the feasibility of transforming such quinone functionalities through Knoevenagel condensations with malononitrile under different experimental conditions.



Scheme 2. Starting materials: the 2-thioxo-1,3-dithiole-*p*-benzoquinone **6**, the TTF-*p*-benzoquinone (TTF-Q) dyads **7** and the *p*-benzoquinone-TTF-*p*-benzoquinone (Q-TTF-Q) triad **8**.

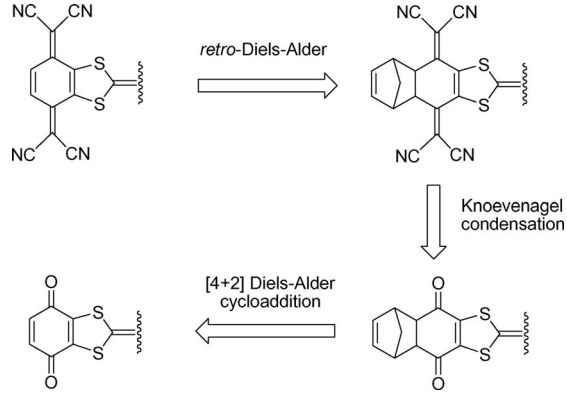
Results and Discussion

Our first investigations focused on conversion of compound **6**[11a,12] into the corresponding TCNQ derivative by treatment with malononitrile. Despite intensive efforts and modifications of the experimental conditions, no evidence for the formation of compound **9** was found in the resulting crude mixtures, consistently with previous observations of side reactions in attempted transformations of *p*-benzoquinone derivatives into their TCNQ analogues (Scheme 3).[13]



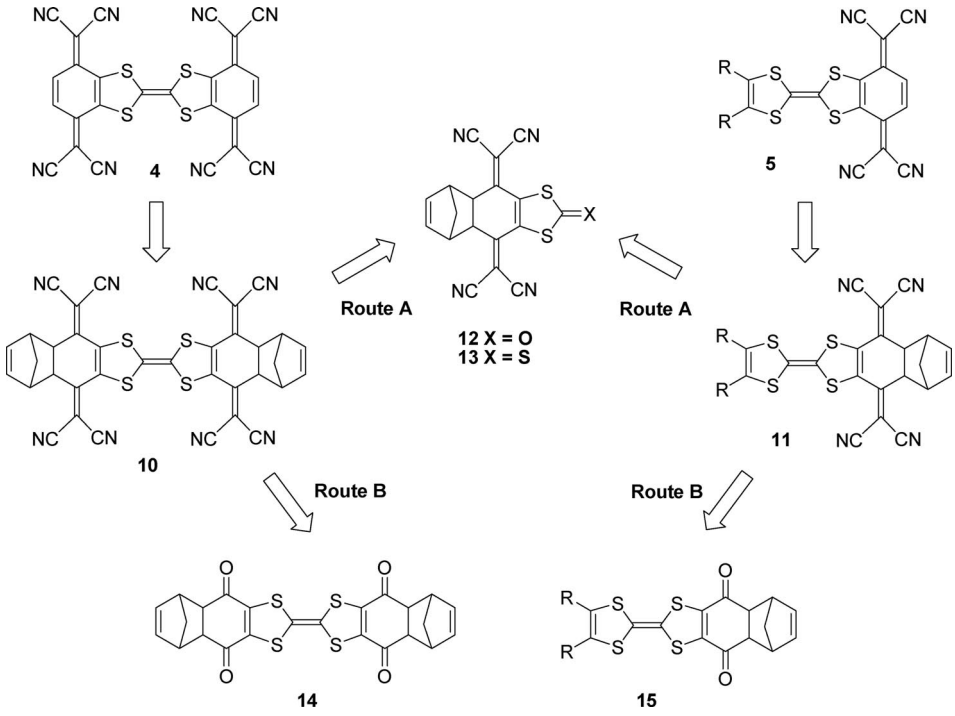
Scheme 3. Attempts to transform the 2-thioxo-1,3-dithiole-*p*-benzoquinone **6** into its TCNQ analogue.

Such reactions are known to be highly dependent on substituent effects, steric hindrance induced by bulky groups and side reactions leading to the decomposition of the quinone derivatives under strongly acidic or basic conditions. Therefore, in order to perform the synthesis of the TCNQ systems **4**, **5** and **9**, a Diels–Alder protecting group strategy was investigated. Yamashita's methodology, as shown in the retrosynthetic Scheme (Scheme 4), consists of successive Diels–Alder (with cyclopentadiene) and thermal retro-Diels–Alder reactions.[14] This strategy was successfully applied for the preparation of quinonoid π-extended TTF systems after the Horner–Wadsworth–Emmons (HWE) reaction used for the creation of the extended TTF core had been found to be subject to an unexpected electron transfer between the phosphonate anion and the quinone moiety.[11a,15] Use of an initial Diels–Alder reaction with the quinone derivatives avoids such side reactions, thanks to the weaker electron-accepting abilities of the corresponding cyclopentadiene adducts.



Scheme 4. Retrosynthetic analysis of the protection/deprotection strategy used for the quinone unit.

For this strategy, retrosynthetic analysis of intermediates **10** and **11**, precursors of targets **4** and **5**, respectively, suggests two different routes. In route A, the disconnection of

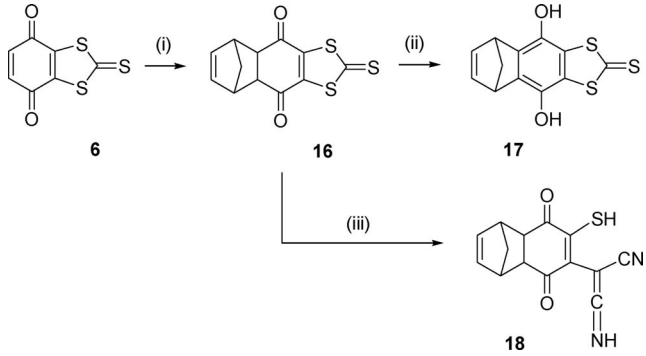


Scheme 5. Retrosynthetic analysis of the fused TTF-TCNQ assemblies **4** and **5**.

the TTF central double bond leads to the 2-(thi)oxo-1,3-dithioles **12** and **13** as starting materials and implies classical self- or cross-coupling reactions in the TTF series.[16] Route B corresponds to functionalization of the protected triad **14** and dyad **15**, originating from the Q-TTF-Q **8** and the TTF-Q **7**, respectively (Scheme 5).

Here we focus on our efforts devoted to transformations of quinone derivatives to produce the 2-(thi)oxo-1,3-dithioles **12** and **13**, with application to the TTF analogues **10** and **11**.

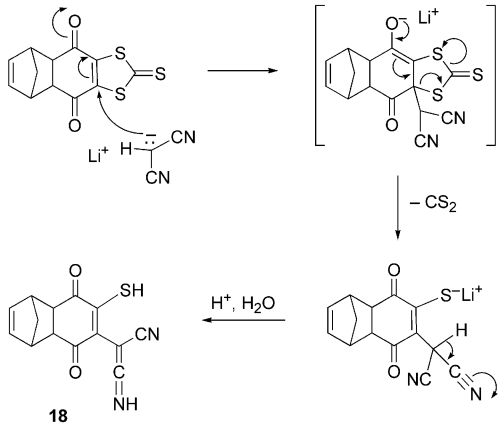
The starting material **16** (Scheme 6) is easily available from compound **6** through a [4+2] cycloaddition with freshly distilled cyclopentadiene, either in THF (94%)[11a] or in Et_2O (97%). The first attempts to transform its carbonyl groups into dicyanomethylene moieties were carried out through a typical Knoevenagel reaction procedure with malononitrile in the presence of a mixture of glacial acetic acid and pyridine. Under such conditions, however, only aromatization leading to compound **17** was observed, as has also been reported in the literature for other cyclopentadiene adducts of quinone derivatives.[17] We noted that this phenomenon was rapid in the presence of a glacial acetic acid/pyridine mixture but that the kinetics of this same reaction were slower in acetic acid medium. The synthetic strategy then evolved with the objective of generating the malononitrile anion in situ. Two equivalents of malononitrile anion, prepared by addition of LDA in THF at –78 °C, were added to compound **16**. Surprisingly, after hydrolysis and purification by column chromatography, compound **18** was isolated in 45% yield. The spectral characterization was consistent with the formation of this stable conjugated ketene imine derivative, and the EI mass spectrum (see the Supporting Information) exhibits the molecular peak at *m*/*z* = 270 and shows some characteristic fragmentation patterns. The ^1H and ^{13}C NMR spectra measured in [D_6]-DMSO suggest the presence of the ketene imine functionality rather than the malononitrile –$CH(CN)_2$ group. Firstly, the expected singlet characteristic of the –$CH(CN)_2$ group at around δ = 3.70 ppm is absent and has been replaced by a broad singlet at δ = 8.50 ppm corresponding to both SH and NH labile protons. Secondly, this structure is confirmed by the HMBC and HMQC 2D ^{13}C NMR spectra, which show three quaternary carbons at δ = 81.3, 113.7 and 170.2 ppm for the –C(CN)=C=NH group.



Scheme 6. Reagents and conditions: i) cyclopentadiene, Et_2O, room temperature, overnight, 97%; ii) $CH_2(CN)_2$, AcOH, pyridine, 70 °C; iii) $CH_2(CN)_2$, LDA, THF, –78 °C to room temperature, then H^+/H_2O, 45%.

The formation of compound **18** could be explained in terms of the mechanism presented in Scheme 7. The nucleophilic attack of the malononitrile anion should proceed

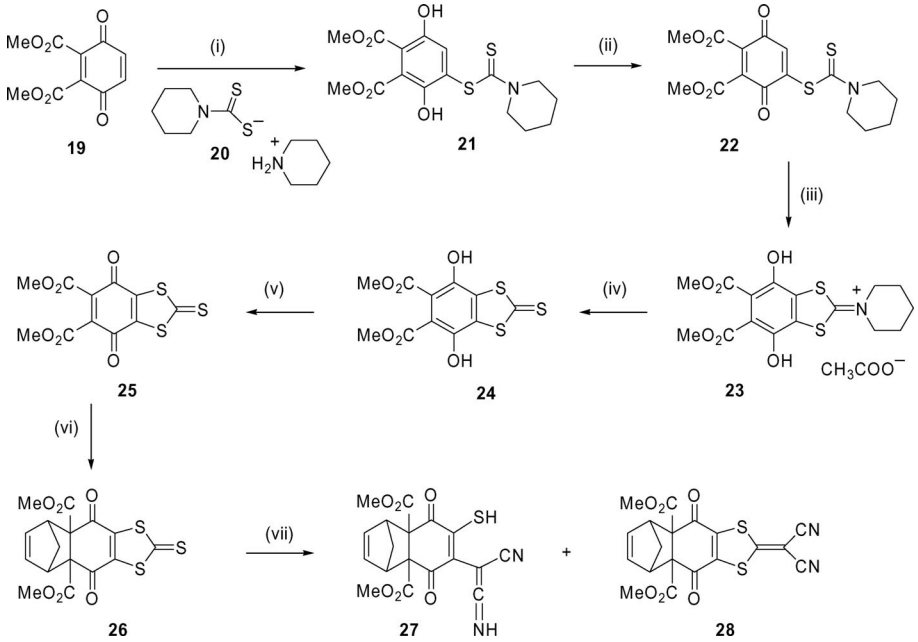
through a Michael 1,4-addition, and the lithium alkoxide could then rearrange with spontaneous elimination of CS_2 to afford the stable conjugated ketene imine after hydrolysis.



Scheme 7. Proposed mechanism for the formation of the ketene imine **18** through 1,4-addition and ring opening of the 1,3-dithiole moiety.

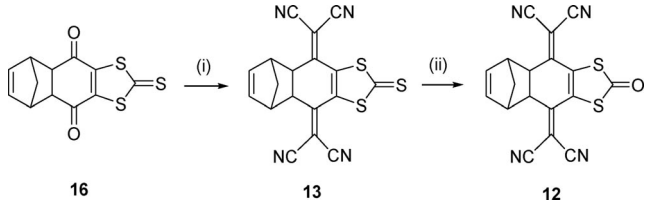
To the best of our knowledge, this reaction constitutes an unprecedented ring opening in the 1,3-dithiole series.[18] We then extended this synthesis to a quinonic electrophile in which both hydrogen atoms were replaced with methoxycarbonyl groups (Scheme 8). The synthesis of the key intermediate **25** started with the 2,3-dimethoxycarbonyl *p*-benzoquinone **19**, which was prepared from succinic anhydride as described in the literature.[19] A Michael addition of the dithiocarbamate salt **20** onto the quinone derivative **19** in the presence of glacial acetic acid afforded intermediate **21** in excellent yield. This was further oxidized to **22** with *p*-benzoquinone, and subsequent cyclisation upon treatment with glacial acetic acid led to the iminium salt **23** in 44% yield for the two steps. Transformation into the 2-thioxo-1,3-dithiole **24** with sodium sulfide was followed by oxidation with DDQ to furnish the fused 2-thioxo-1,3-dithiole-*p*-benzoquinone **25**. Diels–Alder cycloaddition could then be performed, affording the required electrophilic substrate **26** in excellent yield. Subsequent treatment with two equivalents of malononitrile anion was carried out. Consistently with the mechanism previously observed for compound **18**, ketene imine **27** was isolated in 31% yield after purification by column chromatography. It should be noted that in the case of compound **27**, the ^1H NMR spectrum measured in $CDCl_3$ exhibits two broad singlets at δ = 7.96 and 8.73 ppm, which could be ascribed to both NH and SH groups. This compound was also accompanied by the major compound **28**, obtained in 47% yield and the result of an unprecedented Knoevenagel condensation occurring on the 2-thioxo-1,3-dithiole functionality.

The experimental conditions for the Knoevenagel condensation between malononitrile and compound **16** were further modified. Finally, **16** was converted into compound **13** by treatment with titanium(IV) chloride and pyridine (Lehnert's reagents[20]). The reaction was optimized by use of a malononitrile/titanium(IV) chloride/pyridine ratio of 6:8:16 in dichloromethane at reflux and compound **13** was isolated in 67% yield after column chromatography (Scheme 9). The MALDI-MS reveals a peak at *m*/*z* = 309.95 corresponding to removal of the cyclopentadiene during this measurement. This phenomenon has been observed previously in the study of quinonoid π-extended TTF systems.[15] The IR spectrum of compound **13** shows the C≡N stretching vibration band at 2218 cm^{-1}, whereas the intense C=O stretching vibration band of starting mate-



Scheme 8. Reagents and conditions: i) salt **20**, AcOH, DMF/DMSO, 96%; ii) *p*-benzoquinone; iii) glacial AcOH, 44% from **21**; iv) $Na_2S{\cdot}9\,H_2O$, MeOH, 96%; v) DDQ, THF, 90%; vi) cyclopentadiene, THF, 95%; vii) $CH_2(CN)_2$, BuLi, THF, –78 °C to room temperature, then H^+/H_2O, 31% for **27** and 47% for **28**.

rial **16** at 1662 cm^{-1} has disappeared. The ^{13}C NMR spectrum reveals the CN groups at δ = 111 ppm and the thione at δ = 201 ppm. Compound **13** underwent transchalcogenation to afford the 2-oxo-1,3-dithiole derivative **12** in 97% yield.



Scheme 9. Reagents and conditions: i) $CH_2(CN)_2$, pyridine, $TiCl_4$, CH_2Cl_2, 0 °C, then reflux for 2 h, 67%; ii) $Hg(OAc)_2$, glacial AcOH, CH_2Cl_2, reflux, 2 h, 97%.

With the aim of extending this synthesis of fused 1,3-dithiole-TCNQ systems, we performed the same synthetic strategy but with protection with cyclohexa-1,3-diene instead of cyclopentadiene (Scheme 10). The Diels–Alder reaction between compound **6** and a slight excess of cyclohexa-1,3-diene led to the formation of the Diels–Alder adduct **29** in 76% yield. Knoevenagel condensation was carried out with use of a malononitrile/titanium(IV) chloride/pyridine ratio of 6:8:50 at room temperature in dichloromethane and compound **30** was isolated in 74% yield. The IR spectrum of compound **30** shows the C≡N stretching vibration band at 2225 cm^{-1}.

By modification of the experimental conditions, the dicyanomethylene compound **31** could be also isolated. Knoevenagel condensation carried out on adduct **29** with a malononitrile/titanium(IV) chloride/pyridine ratio of 1:8:16 led to the formation of **31** in 69% yield. Clearly, high dilution, a short reaction time and a stoichiometric amount of malononitrile favour the formation of **31**. Compound **31** was fully characterized by its MS and ^1H NMR spectra, as well as by X-ray diffraction analysis (see the Supporting Information). Its IR spectrum shows the C≡N stretching vibration band at 2224 cm^{-1} and the C=O stretching vibration band at 1676 cm^{-1}. Transchalcogenation of compounds **30** and **31** afforded the 2-oxo-1,3-dithiole derivatives **32** and **33**, respectively in 96% yields.

The structure of the 2-oxo-1,3-dithiole **32** was verified by X-ray crystallography. Single crystals were obtained by slow evaporation of a dichloromethane/acetone (1:1) solution of compound **32**. It crystallises in an orthorhombic polar space group (*Cmc* 2_1) with one molecule in the asymmetric unit. An ORTEP view of compound **32** shows the atomic labelling scheme (Figure 1). The X-ray crystallographic analysis reveals that the molecule adopts an *endo* configuration. The central quinonoid ring is in a boat conformation in order to minimize the steric strain between the cyano groups and the adjacent atoms in *peri* positions. The angle describing the molecular distortion from planarity for **32** is γ = 24.4° (tilting of the dicyanomethylene groups with respect to the C10–C10a–C2–C2a plane). The C2–C1 single bond (1.502 Å) in the quinonoid ring is significantly shorter than the C3–C2 single bond (1.573 Å) as a consequence of the steric strains of the quinonoid ring. The intramolecular

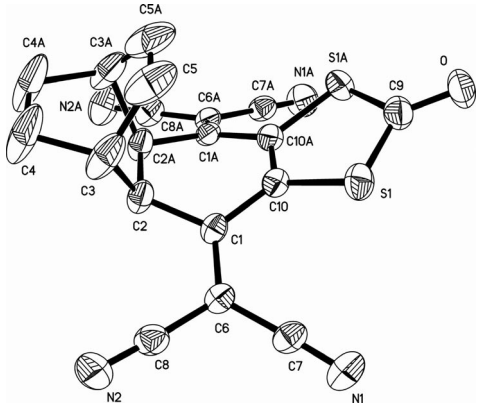
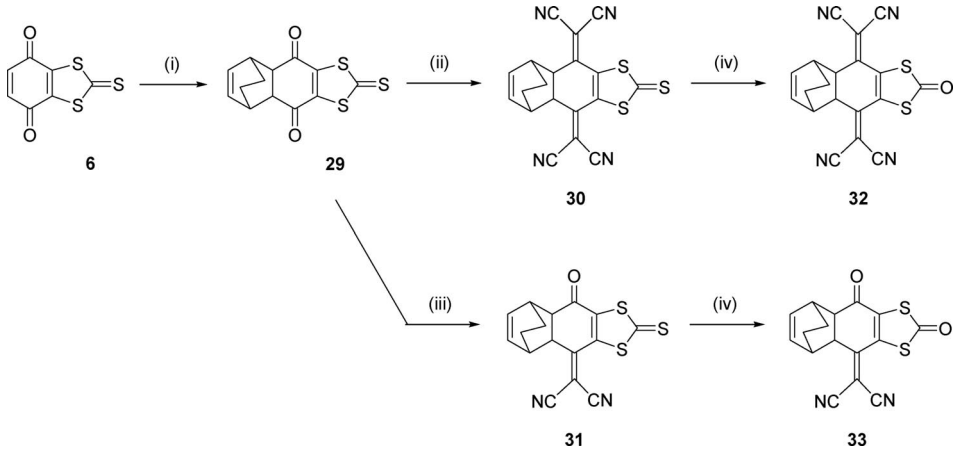


Figure 1. ORTEP representation (ellipsoids at 50% probability) of the molecular structure of compound **32**. Hydrogen atoms are omitted for clarity.



Scheme 10. Reagents and conditions: i) cyclohexa-1,3-diene, Et_2O, overnight, 76%; ii) $CH_2(CN)_2$, pyridine, $TiCl_4$, CH_2Cl_2, 0 °C, then reflux for 2 h, 74%; iii) $CH_2(CN)_2$, pyridine, $TiCl_4$, CH_2Cl_2, 0 °C, then reflux for 1 h, 69%; iv) $Hg(OAc)_2$, glacial acetic acid, CH_2Cl_2, reflux, 2 h, 96% for **32** and **33**.

S···N contacts (S1···N1 3.346 Å) are of the same order as the sum of the corresponding van der Waals radii (3.35 Å).[21]

As a result of the presence of the bulky group in the structure of **32**, no intermolecular short S···S contacts were observed in the crystal packing (Figure 2). Along the *c*-axis, the molecules are connected by short intermolecular interactions between the oxygen and the C2–C2a single bond (O···C2, O···C2a 3.204 Å). Along the *a*-axis, the molecules are connected by C–H···N hydrogen bonds (C3–H3···N2 2.575 Å).

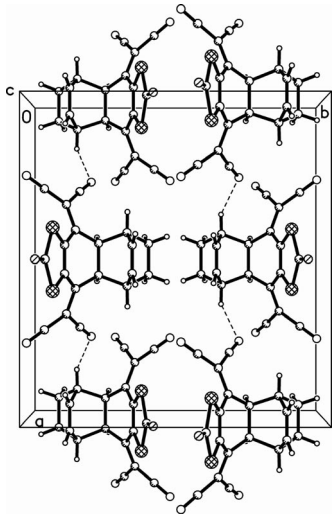


Figure 2. Crystal packing of compound **32**.

The electronic absorption spectra of compounds **6**, **16**, **25** and **26** in dichloromethane ($c = 10^{-4}$ M) are shown in Figure 3. The UV/Vis spectrum of compound **6** displays a broad absorption band in the 400–600 nm region, centred at 510 nm. This band is attributed to intramolecular charge transfer from the 1,3-dithiole-2-thione moiety to the *p*-benzoquinone core.[11c] This absorption band was blue-shifted (λ_{max} = 397 nm) for cycloadduct **16**, as a consequence of the decreased acceptor strength. It should be noted that the UV/Vis spectrum of the quinonic derivative **25** also shows this broad absorption band, now centred at λ_{max} = 547 nm. This red-shift of the absorption band relative to that of compound **6** ($\Delta\lambda$ = 37 nm) is consistent with the increase in the accepting character of the quinone moiety due to the presence of the two methoxycarbonyl groups. This phenomenon is less important for compound **26** (λ_{max} = 407 nm) than for the analogous protected compound **16** ($\Delta\lambda$ = 10 nm).

The absorption spectrum of the bis(dicyanomethylene) derivative **13** in dichloromethane shows an absorption peak at 482 nm. This band, red-shifted relative to that in compound **16**, is attributed to intramolecular charge transfer from the 1,3-dithiole-2-thione moiety to the electron-withdrawing [=C(CN)$_2$] groups (Figure 4).

The same trend was observed in the absorption spectra (in chloroform) of the bis(dicyanomethylene) and mono(dicyanomethylene) cyclohexadiene Diels–Alder adducts **30** and **31**, respectively, with an absorption band at λ_{max} = 478 nm for **30** and at λ_{max} = 449 nm for **31**, in comparison with the absorption spectrum of starting material **29** (Figure 5).

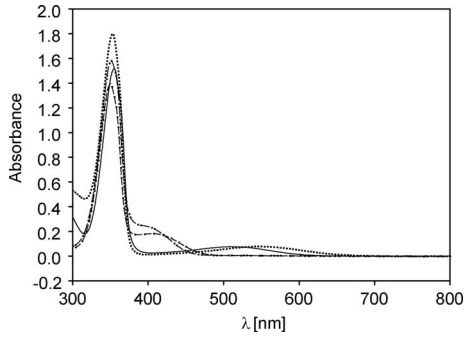


Figure 3. UV/Vis absorption spectra of compounds **6** (solid), **16** (dash-dotted), **25** (dotted) and **26** (short-dashed) in CH_2Cl_2 ($c = 10^{-4}$ M).

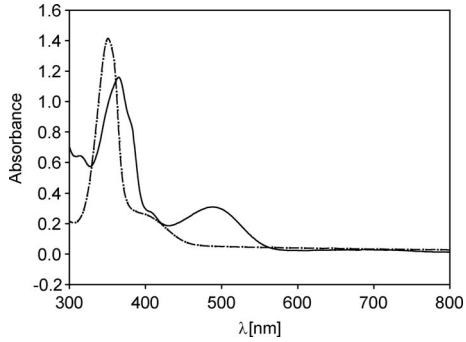


Figure 4. UV/Vis absorption spectra of compounds **13** (solid) and **16** (dash-dotted) in CH_2Cl_2 ($c = 10^{-4}$ M).

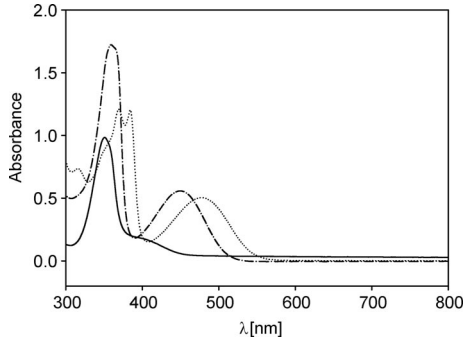
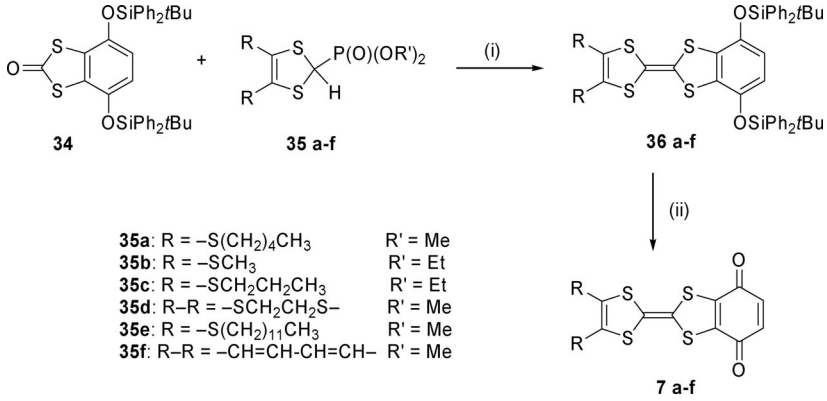


Figure 5. UV/Vis absorption spectra of compounds **29** (solid), **30** (dotted) and **31** (dash-dotted) in $CHCl_3$ ($c = 10^{-4}$ M).

As an extension to this strategy for the transformation of quinones into bis(dicyanomethylene) intermediates, the preparation of Diels–Alder adducts **15** (Scheme 12, below) from TTF-*p*-benzoquinone dyads and their subsequent Knoevenagel condensation with malononitrile were investigated. Several TTF-*p*-benzoquinone dyads **7** were prepared by a procedure that some of us had previously developed for **7a** (Scheme 11).[11c] The key step in obtaining dyads **7**



Scheme 11. Reagents and conditions: i) *n*BuLi, THF, –78 °C to room temperature, overnight, 90% for **36a**, 75% for **36b**, 83% for **36c**, 88% for **36d**, 22% for **36e**, 84% for **36f**; ii) nBu$_4$NF, THF, then *p*-benzoquinone, 75% for **7a**, 59% for **7b**, 63% for **7c**, 42% for **7d**, 63% for **7e**, 55% for **7f**.

involved HWE olefination to construct the TTF core[15a] with Akiba's phosphonate reagent.[22] The phosphonates **35a**–**f** were synthesized by a well-known and efficient procedure.[23] The phosphonate carbanions generated in situ by deprotonation (*n*-butyllithium) were treated with the 2-thioxo-1,3-dithiole derivative **34**[11c] to afford the TTF derivatives **36** in good yields. In the case of **36b**, the structure has been confirmed by X-ray crystallography (see the Supporting Information). Removal of the silyl groups of **36** and subsequent oxidation with *p*-benzoquinone afforded the TTF-*p*-benzoquinone dyads **7** in good yields.

Diels–Alder reactions with dyads **7a**–**d** in the presence of excess freshly distilled cyclopentadiene afforded the expected Diels–Alder cycloadducts **15a**–**d** in high yields (Scheme 12). It should be noted that the multi-step transformation of compound **36a** into the protected compound **15a** could be carried out in an improved overall 79% yield without isolation of the intermediate TTF-*p*-benzoquinone **7a**.

Single crystals were obtained by slow evaporation of a dichloromethane/hexane (1:3) solution of **15b**. Compound **15b** crystallises in a monoclinic cell (*C*2/c) with one molecule in the asymmetric unit (Figure 6). The X-ray crystallographic analysis reveals that **15b** adopts an *endo* configuration, this stereochemistry being consistent with the ^{1}H NMR spectroscopy results.

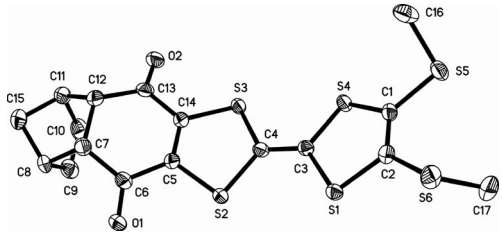
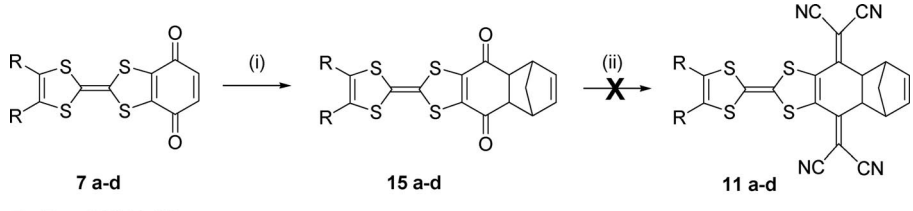


Figure 6. ORTEP representation (ellipsoids at 50% probability) of the molecular structure of **15b**. Hydrogen atoms are omitted for clarity.

The mass spectra of compounds **15a**–**d** each display the monoisotopic molecular peak with the concomitant presence of the peak resulting from the retro-Diels–Alder fragmentation at m/z – 66. The UV/Vis spectra in dichloromethane each show an intramolecular charge-transfer band around 600 nm (λ_{max} = 603 nm for **15a**, 582 nm for **15b**, 586 nm for **15d**), whereas the corresponding TTF-*p*-benzoquinone system **7a** exhibits an intramolecular charge-transfer centred at λ_{max} = 839 nm in dichloromethane (see the Supporting Information).

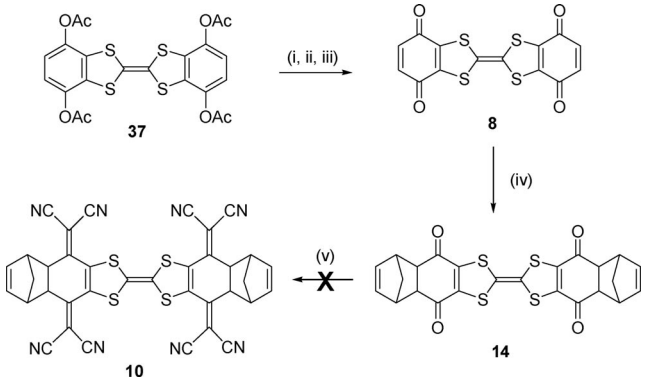
Knoevenagel condensations of **15a**–**d** with malononitrile were attempted either in the presence of glacial acetic acid and pyridine or by addition of the malononitrile anion generated by addition of LDA at –78 °C. The expected



Scheme 12. Reagents and conditions: i) cyclopentadiene, CH_2Cl_2 or THF, 93% for **15a**, 92% for **15b**, 85% for **15c**, 74% for **15d**.

bis(dicyanomethylene) compounds **11a**–**d**, however, were not detected under such experimental conditions. The condensations were then attempted with use of different malononitrile/titanium(IV) chloride/pyridine ratios in dichloromethane at room temperature or at reflux, as in the experimental procedure used for compounds **13** and **30**. Under such conditions, the solutions turned green and thin layer chromatography indicated the disappearance of the starting materials **15**. The solutions were washed with water and concentrated to afford some green powders. The MALDI MS and the ^{1}H NMR spectra, however, showed no evidence of the formation of the expected products. This could be attributed to the sensitivity of the TTF nucleus to the strong Lewis acid titanium(IV) chloride, which led to the decomposition of starting materials and therefore prevented the conversion into dicyanomethylene groups.

The *p*-benzoquinone-TTF-*p*-benzoquinone triad **8** (Scheme 13) was synthesized by a three-step, one-pot sequence. Methanolysis of compound **37** and subsequent acidic treatment afforded the bis(hydroquinone)-TTF intermediate. Subsequent addition of DDQ to the solution led to the triad **8**, which was isolated in 88% yield after chromatographic purification on neutral alumina gel. We should note that this constitutes an improvement on the previous synthesis reported by some of us.[11c] Diels–Alder reactions between triad **8** and cyclopentadiene afforded the expected bis-Diels–Alder adduct **14** in high yield (Scheme 13). The ^{1}H NMR spectrum corresponds to the superposition of two isomers in a 65:35 ratio. This could be attributed to a mixture of two stereoisomers (*endo-syn-endo* and *endo-anti-endo* adducts). These isomers could be separated by thin-layer chromatography with dichloromethane as the eluent (R_f = 0.46 and 0.55). The Knoevenagel condensation conditions used for the synthesis of compound **13** were applied with use of different malononitrile/titanium(IV) chloride/pyridine ratios in dichloromethane at room temperature or at reflux, but no evidence for the formation of the expected product **10** was found, consistently with our observations for the attempted transformations of compounds **15** to produce derivatives **11**.



Scheme 13. Reagents and conditions: i) MeONa, MeOH/THF, ii) PTSA, iii) DDQ, 88% from **37**; iv) cyclopentadiene, CH_2Cl_2, overnight, 94%.

Conclusions

It has been shown that condensations between *p*-benzoquinones and malononitrile, depending on the experimental conditions, can proceed through the expected Knoevenagel condensation in the presence of Lehnert's reagents to afford the corresponding TCNQ analogues. Surprisingly, under different conditions Michael addition can predominate together with the subsequent ring opening of the 1,3-dithiole moieties, leading to unprecedented stable ketene imines. So far, the application of Knoevenagel condensation conditions to protected TTF-*p*-benzoquinone dyads and a *p*-benzoquinone-TTF-*p*-benzoquinone triad has been unsuccessful, maybe due to the high reactivity of the TTF moiety. However, attachment of the electron-rich 2-thioxo-1,3-dithiole moiety to TCNQ electron acceptors leads to the formation of the highly conjugated compounds **12**, **13** and **30**–**33**, in which the remarkable redox properties are combined with strong photoinduced intramolecular CT transitions. Such a combination of optical and electronic properties makes these compounds promising as nonlinear optical and electro-optical materials. As a consequence, tests of the performance of these π-conjugated materials for charge transport in molecular electronic applications will be of particular interest.

Experimental Section

General Procedures: All reagents were of commercial quality and were used without purification. Tetrahydrofuran was obtained by distillation from Na/benzophenone. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel (60 F_{254}, Merck 5554) or ALUGRAM® SIL G/UV_{254} (Macherey–Nagel) and on alumina plates (0.20 or 0.25 mm, POLYGRAM® ALOX N/UV_{254}, Macherey–Nagel). Column chromatography was carried out on silica gel 60 (Merck 9385, 230–400 mesh), on neutral and basic aluminium oxide (CAMAG) or on Florisil (Acros 200–400 mesh). Melting points were determined with a Reichert hot-plate microscope or a Büchi 510 apparatus and are uncorrected. ^{1}H (300, 400, 500 MHz), and ^{13}C (75, 100, 125 MHz) NMR spectra were recorded variously with a Bruker Avance 300, a Bruker Avance II 400 or a Bruker Avance II 500 instrument, with tetramethylsilane (TMS) or the residual solvent as the internal standard. Infrared spectra were measured with a Perkin–Elmer Spectrum One FT-IR spectrometer or a Perkin–Elmer 841 spectrometer as KBr pellets. UV/Vis spectra were obtained with a Perkin–Elmer Lambda 10 or a Perkin–Elmer Lambda 19 spectrometer. Mass spectra were obtained with an AutoSpecQ or a JEOL JMS 700B/ES spectrometer for the EI ionisation mode (70 eV). MALDI MS were carried out with a FTMS 4.7T BioAPEX II spectrometer with dithranol, DHB or DCTB as matrices. MALDI-TOF MS were measured either with an Axima spectrometer from Shimadzu with a nitrogen laser (337 nm) in the linear mode or with a Brucker Biflex III spectrometer with DCTB, dithranol and DHB as matrices. Elemental analyses were either measured with a Carlo Erba EA 1110 CHNS instrument or were performed by the Central Service of Microanalysis of the CNRS (France).

Compound 7a: Bu_4NF (0.26 mL, 0.26 mmol) was added to a solution of TTF **36a** (100 mg, 0.1 mmol) in dichloromethane (10 mL).

The mixture was stirred for 30 min at room temperature and *p*-benzoquinone (11 mg, 0.1 mmol) was added. Stirring was continued for a further 5 min. Purification by column chromatography (Florisil gel, 100–200 mesh) with dichloromethane as the eluent was followed by recrystallization from dichloromethane/petroleum ether to afford compound **7a** as green crystals (38 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.1 Hz, 6 H, CH_3CH_2), 1.30–1.50 (2×m, 8 H, $CH_3CH_2CH_2$), 1.63 (q, J = 7.1 Hz, 4 H, CH_2CH_2S), 2.81 (t, J = 7.1 Hz, 4 H, CH_2S), 6.75 (s, 2 H, CH=CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 22.2, 29.5, 30.7, 36.4, 110.2, 115.4, 128.1, 143.6, 136.8, 177.9 ppm. IR (KBr): $\tilde{\nu}$ = 1648 (C=O) cm^{-1}. MS (EI): *m*/*z* (%) = 488 (100) $[M]^{+\cdot}$, 384 (13), 347 (12), 259 (10), 226 (22). $C_{20}H_{24}O_2S_6$ (488.77): calcd. C 49.15, H 4.95, S 39.36; found C 49.11, H 5.00, S 37.92.

Compound 7b: Bu_4NF (0.3 mL, 0.303 mmol) was added to a solution of TTF **36b** (100 mg, 0.116 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for 30 min and *p*-benzoquinone (18 mg, 0.166 mmol) was added. After concentration, the residue was redissolved in dichloromethane and washed with water and brine. The organic layer was dried with sodium sulfate and the solvents were evaporated. The green oil was purified by column chromatography on neutral aluminium oxide gel with dichloromethane/ethyl acetate (1:1) as a mixture of eluents to afford **7b** (26 mg, 59%) as a green powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 6 H, SCH_3), 6.76 (d, J = 7.5 Hz, 2 H, =CH) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1651 (C=O) cm^{-1}. MS (MALDI, DCTB as matrix, positive mode) calcd. for $[M + 2H]^+$ 377.900; found 377.900.

Compound 7c: Bu_4NF (0.57 mL, 0.57 mmol) was added to a solution of TTF **36c** (200 mg, 0.219 mmol) in tetrahydrofuran (15 mL). The mixture was stirred for 1 h and *p*-benzoquinone (40 mg, 0.370 mmol) was added. After concentration, the residue was redissolved in dichloromethane and washed with water and brine. The organic layer was dried with sodium sulfate and the solvents were evaporated. The black oil was purified by column chromatography on neutral aluminium oxide gel with dichloromethane as eluent to afford **7c** (58 mg, 63%) as a dark green powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 7 Hz, 6 H, CH_3), 1.69 (sextet, J = 7.2 Hz, 4 H, CH_2), 2.83 (t, J = 7 Hz, 4 H, SCH_2), 6.75 (d, J = 7.3 Hz, 2 H, =CH) ppm.

Compound 7d: Bu_4NF (0.6 mL, 0.6 mmol) was added to a solution of TTF **36d** (200 mg, 0.234 mmol) in tetrahydrofuran (15 mL). The mixture was stirred for 1 h and *p*-benzoquinone (38 mg, 0.351 mmol) was added. After concentration, the residue was redissolved in dichloromethane and washed with water and brine. The organic layer was dried with sodium sulfate and the solvents were evaporated. The green oil was purified by column chromatography on neutral aluminium oxide gel with dichloromethane/ethyl acetate (1:1) as a mixture of eluents to afford **7d** (36 mg, 42%) as a green powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.31 (s, 4 H, SCH_2CH_2S), 6.75 (d, J = 7.5 Hz, 2 H, =CH) ppm.

Compound 7e: Bu_4NF (0.44 mL, 0.44 mmol) was added to a solution of TTF **36e** (200 mg, 0.17 mmol) in dichloromethane (20 mL). The mixture was stirred for 30 min and *p*-benzoquinone (18.7 mg, 0.173 mmol) was added. After concentration, the residue was purified by column chromatography on Florisil gel with dichloromethane as the eluent to afford **7e** (74 mg, 63%) as green crystals; m.p. 72 °C (dichloromethane/petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 6 H, CH_3), 1.26–1.29 (m, 32 H, CH_2), 1.39–1.42 (m, 4 H, $SCH_2CH_2CH_2$), 1.59–1.65 (m, 4 H, SCH_2CH_2), 2.81 (t, J = 7.3 Hz, 4 H, SCH_2), 6.76 (s, 2 H, =C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.5, 29.1, 29.3, 29.5, 29.6, 29.65, 29.7, 29.8, 31.9, 36.4, 105.2, 115.4, 128.1, 136.8, 143.6, 177.9 ppm. IR (KBr): $\tilde{\nu}$ = 1648 (C=O) cm^{-1}. MS (MALDI, dithranol as matrix, positive mode): calcd. for $[M + 2H]^+$ 686.24; found 686.07.

Compound 7f: Bu_4NF (2.6 mL, 2.6 mmol) was added to a solution of TTF **36f** (840 mg, 1.03 mmol) in dichloromethane (80 mL). The mixture was stirred for 30 min and *p*-benzoquinone (112 mg, 1.03 mmol) was added. After concentration, the residue was purified by column chromatography on Florisil gel with dichloromethane/ethyl acetate (9:1) as a mixture of eluents to afford **7f** (190 mg, 55%) as a green powder. Compound **7f** was insoluble in solvents commonly used for NMR spectroscopy. IR (KBr): $\tilde{\nu}$ = 1631 (C=O) cm^{-1}. MS (EI): *m*/*z* (%) = 334 (100) $[M]^{+\cdot}$, 304 (12), 196 (40), 152 (20), 120 (8), 108 (18). $C_{14}H_{16}O_2S_4$ (333.93): calcd. C 50.28, H 1.81, S 38.35; found C 50.16, H 1.86, S 38.15.

Compound 8: Freshly prepared sodium methoxide (2.5 mL, 1.86 mmol) was added to a solution of compound **37** (100 mg, 0.186 mmol) in tetrahydrofuran (12 mL). The mixture was stirred at 60 °C for 1 h, followed by the addition of *p*-toluenesulfonic acid (354 mg, 1.86 mmol). The resulting solution was allowed to cool to room temperature and DDQ (106 mg, 0.466 mmol) was added. The mixture was stirred for 2 h. After evaporation of the solvent, the residue was redissolved in dichloromethane and washed with water and brine. The organic layer was dried with sodium sulfate and the solvents were evaporated. The crude product was purified by chromatography on neutral alumina gel with dichloromethane as eluent to afford triad **8** (60 mg, 88%) as a blue-black powder. Spectroscopic characterizations are in agreement with those reported previously.[11c]

Compound 12: A mixture of compound **13** (380 mg, 1 mmol), mercury(II) acetate (636 mg, 2 mmol) in dichloromethane (80 mL) and glacial acetic acid (40 mL) was heated at reflux for 2 h. The resulting orange solution was extracted several times with dichloromethane. The combined organic layers were washed with water and brine and dried with sodium sulfate, and the solvents were evaporated. The orange residue was chromatographed on silica gel with elution with dichloromethane/hexane (5:1) to afford compound **12** (349 mg, 97%) as red-orange microcrystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (br. s, 2 H, CH_2), 3.64–3.65 (m, 2 H, CH), 3.90–3.91 (m, 2 H, CH), 5.98–5.99 (m, 2 H, =CH) ppm.

Compound 13: Titanium(IV) chloride (0.875 mL, 8 mmol) was added dropwise at 0 °C to a solution of compound **16** (280 mg, 1 mmol) in dichloromethane (40 mL). The reaction mixture was stirred for 15 min, followed by the successive addition of malononitrile (396 mg, 6 mmol) in dichloromethane (10 mL) and pyridine (1.3 mL, 16 mmol) in dichloromethane (15 mL) over 15 min. The mixture was heated at reflux for 2 h. The resulting black residue was poured into ice/water and extracted with dichloromethane. The combined organic layers were washed with water and brine and dried with sodium sulfate, and the solvents were evaporated. The black residue was purified by chromatography on silica gel with dichloromethane/hexane (2:1, v/v) as a mixture of eluents to afford compound **13** (252 mg, 67%) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74–1.76 (m, 2 H, CH_2), 3.65–3.66 (m, 2 H, CH), 3.89–3.91 (m, 2 H, CH), 6.05 (s, 2 H, =CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.0, 50.3, 53.0, 85.9, 111.6, 111.9, 135.5, 144.3, 159.0, 201.1 ppm. IR (KBr): $\tilde{\nu}$ = 2218 (CN), 1087 (C=S) cm^{-1}.

Compound 14: Freshly distilled cyclopentadiene (0.05 mL, 0.61 mmol) was added dropwise to a solution of triad **8** (20 mg, 59.4 μmol) in dichloromethane (3 mL). The green mixture was stirred overnight. The solvent was evaporated under high vacuum to afford, after chromatography on neutral aluminium oxide with

dichloromethane as eluent, compound **14** (27.7 mg, 94%) as a blue powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (35%) and 1.49 (65%) (m, 2 H), 1.57 (65%) and 1.61 (35%) (t, J = 1.8 Hz, 2 H, CH_2), 3.34 (dd, J = 1.2 and 2.3 Hz, 4 H, CH–CO), 3.56 (m, 4 H, –*CH*–CH_2), 6.12 (65%) and 6.13 (35%) (2 × t, J = 1.9 Hz, 4 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.1, 49.2, 50.1, 135.2, 150.8, 189.2 ppm (some quaternary carbons are missing). IR (KBr): $\tilde{\nu}$ = 1656 (C=O) cm^{-1}. MS (EI): *m*/*z* (%) = 496 (2) $[M]^{+\cdot}$, 430 (12), 364 (100), 226 (36), 66 (53). MS (FAB$^+$ *m*NBA): *m*/*z* (%) = 496 (75) $[M]^{+\cdot}$, 430 (42), 419 (45), 364 (78), 307 (100). MS (MALDI, DHB as matrix, positive mode) calcd. for $C_{24}H_{16}O_4S_4$ 495.993; found 495.990.

Compound 15a: Freshly distilled cyclopentadiene (0.02 mL, 0.25 mmol) was added dropwise to a solution of dyad **7a** (25 mg, 51 μmol) in tetrahydrofuran (10 mL). The mixture was stirred for 30 min at room temperature and the solvent was evaporated under high vacuum. The residue was purified by chromatography on silica gel with dichloromethane/petroleum ether (1:1, v/v) as a mixture of eluents to afford compound **15a** (26 mg, 93%) as a blue powder; m.p. 66 °C (dichloromethane/petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 6 H, C*H*$_3$CH$_2$), 1.29–1.39 (m, 9 H, CH$_3$C*H*$_2$C*H*$_2$ and 1 H from CH_2 group), 1.47 (d, J = 8.7 Hz, 1 H, 1 H from CH_2 group), 1.62 (q, J = 7 Hz, 4 H, C*H*$_2$CH$_2$S), 2.79 (t, J = 7 Hz, 4 H, CH_2S), 3.33 (dd, J = 1.2, 2.3 Hz, 2 H, CH–CO), 3.55 (br. s, 2 H, C*H*–CH_2), 6.12 (br. s, 2 H, CH=CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 22.2, 29.4, 30.6, 36.4, 49.1, 49.2, 50.1, 106.2, 115.4, 127.9, 135.2, 151.0, 189.3 ppm. IR (KBr): $\tilde{\nu}$ = 1662 (C=O) cm^{-1}. MS (EI): *m*/*z* (%) = 554 (65) $[M]^{+\cdot}$, 488 (100), 384 (10), 350 (10), 199 (15), 137 (12). $C_{25}H_{30}O_2S_6$ (554.06): calcd. C 54.11, H 5.45, S 34.67; found C 53.70, H 5.62, S 33.92.

Compound 15b: Freshly distilled cyclopentadiene (0.03 mL, 0.37 mmol) was added dropwise to a solution of dyad **7b** (20 mg, 53.1 μmol) in dichloromethane (3 mL). The mixture was stirred overnight. The solvent was evaporated under high vacuum to afford, after chromatography on neutral aluminium oxide with dichloromethane as eluent, compound **15b** (21.6 mg, 92%) as a blue green powder; m.p. 154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 1.57 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 2.41 (s, 6 H, SCH_3), 3.32 (br. dd, J = 1.5 and J = 2.2 Hz, 2 H, CH), 3.54 (s, 2 H, CH–CO), 6.11 (br. s, 2 H, =CH) ppm. IR (KBr): $\tilde{\nu}$ = 1658 (C=O) cm^{-1}. MS (MALDI, DCTB as matrix, positive mode) calcd. for $C_{17}H_{14}O_2S_6$ 441.931; found 441.932. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/hexane (1:3) solution of compound **15b**.

Compound 15c: Freshly distilled cyclopentadiene (0.2 mL, 2.45 mmol) was added dropwise to a solution of dyad **7c** (193 mg, 446 μmol) in dichloromethane (15 mL). The mixture was stirred for 2 h at room temperature. The solvent was evaporated under high vacuum. The residue was purified by chromatography on neutral aluminium oxide with dichloromethane/hexane (1:1) as a mixture of eluents to afford compound **15c** (189 mg, 85%) as a blue powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.2 Hz, 6 H, CH_3), 1.46 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 1.55 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 1.63 (sextet, J = 7.3 Hz, 4 H, CH_2), 2.77 (t, J = 7.2 Hz, 4 H, SCH_2), 3.31 (br. dd, J = 1.5 Hz and J = 2.2 Hz, 2 H, CH), 3.54 (s, 2 H, CH–CO), 6.11 (br. t, J = 1.7 Hz, 2 H, =CH) ppm.

Compound 15d: Freshly distilled cyclopentadiene (0.03 mL, 0.37 mmol) was added dropwise to a solution of dyad **7d** (22.5 mg, 60.1 μmol) in dichloromethane (3 mL). The mixture was stirred overnight at room temperature and the solvent was evaporated under high vacuum. The residue was purified by chromatography on neutral aluminium oxide with dichloromethane as eluent to afford compound **15d** (19 mg, 74%) as a blue-green powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 1.55 (br. d, J = 7.9 Hz, 1 H from CH_2 group), 3.34 (br. dd, J = 1.5, 2.2 Hz, 2 H, CH), 3.29 (s, 4 H, SCH_2CH_2S), 6.09 (br. s, 2 H, CH), 3.54 (s, 2 H, =CH) ppm.

Compound 17: A solution of compound **16** (270 mg, 0.96 mmol) and malononitrile (145 mg, 2.2 mmol) in glacial acetic acid (5 mL) and pyridine (5 mL) was heated at 70 °C for 1 h. After addition of dichloromethane (100 mL), the organic layer was washed with water (2 × 15 mL), an aqueous $NaHCO_3$ saturated solution (2 × 15 mL) and water (15 mL) and dried with magnesium sulfate, and the solvents were evaporated. The residue was purified by chromatography on silica gel with dichloromethane/ethyl acetate (9:1) as a mixture of eluents to afford compound **17** as white crystals (221 mg, 82%); m.p. 234 °C (dec.). ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 2.08 (dd, J = 7.3, 9.2 Hz, 2 H, CH_2), 4.27 (t, J = 7.3 Hz, 2 H, CH_2–C*H*), 6.77 (s, 2 H, HC=CH), 9.81 (s, 2 H, OH) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 47.8, 69.0, 127.2, 138.5, 139.1, 143.1, 214.9 ppm. IR (KBr): $\tilde{\nu}$ = 3387 (OH), 1071 (C=S) cm^{-1}. MS (EI): *m*/*z* (%) = 280 (72) $[M]^{+\cdot}$, 203 (33), 171 (13), 118 (10), 20 (100).

Compound 18: LDA (2 M solution in hexane, 0.62 mL, 1.24 mmol) was added under nitrogen at –78 °C to a solution of malononitrile (74.4 mg, 1.13 mmol) in anhydrous tetrahydrofuran (10 mL). After the system had been stirred at –78 °C for 10 min, a solution of compound **16** (158 mg, 0.56 mmol) in tetrahydrofuran (15 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 1 h 30, and was then allowed to stand at room temperature. After hydrolysis with an aqueous saturated ammonium chloride solution and extraction with ethyl acetate, the organic layer was dried with magnesium sulfate and the solvent was concentrated under vacuum. The residue was purified by chromatography on silica gel with dichloromethane/ethyl acetate (4:1) as a mixture of eluents to afford compound **18** as a yellow powder (68 mg, 45%); m.p. 258 °C (dichloromethane/ethyl acetate). ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 1.43 (d, J = 8.4 Hz, 1 H, 1 H from CH_2 group), 1.53 (d, J = 8.4 Hz, 1 H from CH_2 group), 3.34 (m, 2 H, CH–C*H*–CO), 3.38 (d, J = 5.4 Hz, 2 H, C*H*–CH–CO), 6.05 (d, J = 7.2 Hz, 2 H, HC=CH), 8.47 (br. s, 2 H, NH + SH) ppm. ^{13}C NMR (100 MHz, CD_3SOCD_3): δ = 47.6, 47.9, 48.4, 49.0, 50.0 (CH and CH_2), 81.3 [–*C*(CN)=C=NH], 113.7 (CN), 131.6 (=C–SH), 134.9 (2 × =CH), 143.8 [=*C*–C(CN)=], 170.3 [–C(CN)=*C*=NH], 189.6 (C=O), 191.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3422, 3324, 3209, 2216 (CN), 1671, 1643, 1627, 1540, 1508, 1442 cm^{-1}. MS (EI, positive mode): *m*/*z* (%) = 270 (46) $[M]^{+\cdot}$, 242 (10), 204 (86), 176 (29), 148 (16), 121 (7), 66 (100). $C_{14}H_{10}N_2O_2S$ (270.05): calcd. C 62.21, H 3.73, N 10.36, S 11.86; found C 62.06, H 3.84, N 10.32, S 11.98.

Compound 21: A solution of compound **19** (4.63 g, 1 mmol) in glacial acetic acid (10 mL) and DMF (10 mL) was added at 0 °C to a solution of the dithiocarbamate salt **20** (4.63 g, 0.019 mol) in a mixture of DMF (10 mL) and DMSO (6 mL). The solution was stirred for 3 h at room temperature. After addition of water, the precipitate was filtered to afford compound **21** as yellow crystals (6.43 g, 96%); m.p. 166 °C (ethyl acetate). Compound **21** was insoluble in solvents commonly used for NMR spectroscopy.

Compound 23: *p*-Benzoquinone (1.95 g, 0.018 mol) was added to a suspension of compound **21** (6.43 g, 0.018 mol) in methanol (120 mL). A bordeaux precipitate appeared and the mixture was stirred for an additional 30 min and then filtered. The precipitate

was washed with methanol. After its dissolution in the minimum possible amount of glacial acetic acid, the solution was heated for 10 min at 90 °C. After concentration under vacuum and precipitation with ethyl acetate, compound **23** was isolated as yellow crystals (3.55 g, 44%) that were used without further purification. Compound **23** was insoluble in solvents commonly used for NMR spectroscopy. IR (KBr): $\tilde{\nu}$ = 2962 (OH), 1716 (C=O ester), 1558 (C=O) cm^{-1}. MS (MALDI, dithranol as matrix, positive mode): *m/z* (%) = 384 $[M - OAc]^+$. $C_{18}H_{21}NO_8S_2$ (443.07): calcd. C 48.75, H 4.77, N 3.16; found C 48.82, H 4.68, N 3.36.

Compound 24: Sodium sulfide nonahydrate (3.96 g, 16.5 mmol) was added to a solution of the iminium salt **23** (1.86 g, 4.2 mmol) in methanol (20 mL). After stirring at room temperature for 5 h, the solution was poured into a mixture of glacial acetic acid (10 mL) and water (150 mL). The precipitate was filtered, washed with water and dried under vacuum. Compound **24** was isolated as yellow crystals (1.32 g, 96%); m.p. 244 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.93 (s, 6 H, CH_3), 9.50 (br. s, 2 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.2, 110.4, 135.1, 145.7, 168.9, 211.2 ppm. IR (KBr): $\tilde{\nu}$ = 1752 (C=O), 1082 (C=S) cm^{-1}. MS (EI): *m/z* (%) = 332 (70) $[M]^{+\cdot}$, 300 (100), 268 (73), 240 (13).

Compound 25: A solution of DDQ (350 mg, 1.54 mmol) in anhydrous tetrahydrofuran (5 mL) was added at –78 °C to a solution of compound **24** (450 mg, 1.35 mmol) in anhydrous tetrahydrofuran (10 mL). The reaction mixture was allowed to stand at room temperature for 1 h. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel with dichloromethane as eluent to afford compound **25** as orange crystals (400 mg, 90%); m.p. 152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.93 (s, 6 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.7, 137.2, 146.7, 161.3, 172.7, 205.1 ppm. IR (KBr): $\tilde{\nu}$ = 1736 (C=O ester), 1673 (C=O), 1074 (C=S) cm^{-1}. MS (EI): *m/z* (%) = 330 (100) $[M]^{+\cdot}$, 299 (17), 271 (11).

Compound 26: Freshly distilled cyclopentadiene (0.25 mL, 3 mmol) was added to a solution of compound **25** (200 mg, 61 mmol) in anhydrous tetrahydrofuran (5 mL). The mixture was stirred for 1 h at room temperature and the solvent was evaporated under vacuum. The residue was dissolved in dichloromethane (2 mL) and methanol was added until precipitation of compound **26**. After filtration, compound **26** was isolated (227 mg, 95%) as orange crystals; m.p. 204 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.77 (m, 1 H, 1 H from CH_2 group), 2.58 (m, 1 H, 1 H from CH_2 group), 3.73 (m, 8 H, CH_3 and CH), 6.24 (s, 2 H, =CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 47.5, 52.5, 53.6, 69.5, 138.8, 152.5, 169.3, 183.9, 207.4 ppm. IR (KBr): $\tilde{\nu}$ = 1739 (C=O ester), 1666 (C=O quinone), 1082 (C=S) cm^{-1}. MS (EI): *m/z* (%) = 396 (78) $[M]^{+\cdot}$, 364 (36), 337 (25), 305 (62), 299 (61), 66 (100). $C_{16}H_{12}O_6S_3$ (395.98): calcd. C 48.47, H 3.05, S 24.26; found C 48.26, H 3.11, S 24.66.

Compounds 27 and 28: *n*-Butyllithium (0.31 mL, 0.55 mmol, 1.6 M in hexane) was added at –78 °C to a solution of malononitrile (33.3 mg, 0.50 mmol) in anhydrous tetrahydrofuran (5 mL). After the system had been stirred for 10 min at –78 °C, a solution of compound **26** (100 mg, 0.25 mmol) in tetrahydrofuran (10 mL) was added. The reaction mixture was allowed to stand at room temperature. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel with dichloromethane as eluent, affording compound **28** as yellow crystals (50 mg, 47%) in a first fraction, and compound **27** as yellow crystals (30 mg, 31%) in a second fraction.

Compound 27: M.p. 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 9.5 Hz, 1 H, 1 H from CH_2 group), 2.51 (d, *J* = 9.5 Hz, 1 H, 1 H from CH_2 group), 3.58 (s, 2 H, C*H*–C–CO_2Me), 3.64 (s, 3 H, CH_3), 3.67 (s, 3 H, CH_3), 6.15 (s, 2 H, H–C=C–H), 7.96 (s, 1 H, NH), 8.73 (br. s, 1 H, SH) ppm. IR (KBr): $\tilde{\nu}$ = 2213 (CN), 1752 (C=O ester), 1657 (C=O quinone) cm^{-1}. MS (EI): *m/z* (%) = 386 (14) $[M]^{+\cdot}$, 355 (15), 327 (25), 322 (25), 320 (26), 295 (48), 289 (60), 174 (31), 109 (25), 66 (100). $C_{18}H_{14}N_2O_6S$ (386.06): calcd. C 55.95, H 3.65, N 7.25, S 8.30; found C 55.72, H 3.91, N 7.13, S 8.11.

Compound 28: Yellow crystals (50 mg, 47%); m.p. 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.80 (m, 1 H, 1 H from CH_2 group), 2.59 (m, 1 H, 1 H from CH_2 group), 3.73 (s, 6 H, CH_3), 3.75 (m, 2 H, C*H*–C–CO_2Me), 6.22 (s, 2 H, H–C=C–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 47.7, 52.5, 53.8, 70.2, 111.4, 138.8, 148.9, 168.8, 184,4 ppm. IR (KBr): $\tilde{\nu}$ = 2213 (CN), 1761 (C=O ester), 1669 (C=O quinone) cm^{-1}. MS (EI): *m/z* (%) = 428 (17) $[M]^{+\cdot}$, 368 (12), 363 (25), 351 (15), 336 (34), 331 (72), 299 (48), 244 (14), 108 (19), 66 (100). $C_{19}H_{12}N_2O_6S_2$ (428.01): calcd. C 53.27, H 2.82, N 6.54, S 14.97; found C 53.41, H 3.08, N 6.97, S 14.24.

Compound 29: Freshly distilled cyclohexa-1,3-diene (0.133 mL, 1.4 mmol) was added dropwise to a solution of compound **6**[11a] (214 mg, 1 mmol) in diethyl ether (30 mL). The solution was stirred overnight, and after concentration compound **29** (223 mg, 76%) was isolated as a yellow powder; m.p. 162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39–1.42 (m, 2 H, CH_2) 1.73–1.75 (m, 2 H, CH_2), 3.14 (s, 2 H, CH), 3.27–3.29 (m, 2 H, CH–CO), 6.28 (dd, *J* = 3, 4.6 Hz, 2 H, =CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 36.3, 50.9, 134.0, 154.4, 189.1, 208.6 ppm. IR (KBr): $\tilde{\nu}$ = 1664 (C=O), 1076 (C=S) cm^{-1}. MS (EI): *m/z* (%) = 294 (74) $[M]^+$, 266 (100).

Compound 30: Titanium(IV) chloride (0.57 mL, 5.16 mmol) was added dropwise at 0 °C to a solution of compound **29** (190 mg, 0.64 mmol) in dichloromethane (30 mL). The mixture was stirred for 5 min, followed by the successive addition of malononitrile (255 mg, 3.87 mmol) in dichloromethane (10 mL) and pyridine (0.83 mL, 32 mmol) in dichloromethane (10 mL) over 10 min. The solution was kept at room temperature and stirred overnight. The resulting dark red solution was poured into ice/water and extracted with dichloromethane. The combined organic layers were washed with water and brine and dried with sodium sulfate, and the solvents were evaporated. The red residue was purified by chromatography on silica gel with dichloromethane/hexane (2:1, v/v) as the mixture of eluents to afford compound **30** (186 mg, 74%) as a red-brown powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47–1.49 (m, 2 H, CH_2), 1.94–1.97 (m, 2 H, CH_2), 2.95 (br. s, 2 H, CH), 3.70 (s, 2 H, CH–C=), 6.23 (dd, *J* = 3.2, 4.5 Hz, 2 H, =CH) ppm. IR (KBr): $\tilde{\nu}$ = 2225 (C≡N), 1078 (C=S) cm^{-1}. MS (EI): *m/z* (%) = 390 (32) $[M]^+$, 337 (12), 310 (4). MS (MALDI, DCTB as matrix, negative mode) calcd. for $C_{19}H_{10}N_4S_3$ 390.006; found 390.01.

Compound 31: Titanium(IV) chloride (0.85 mL, 8 mmol) was added dropwise at 0 °C to a solution of compound **29** (294 mg, 1 mmol) in dichloromethane (100 mL). The reaction mixture was stirred for 15 min, followed by the successive addition of malononitrile (66 mg, 1 mmol) in dichloromethane (15 mL) and pyridine (1.28 mL, 16 mmol) in dichloromethane (15 mL) over 15 min. The mixture was heated at reflux for 1 h. The resulting blue-black solution was poured into ice/water and extracted with dichloromethane. The combined organic layers were washed with water and dried with sodium sulfate, and the solvents were evaporated. The black residue was purified by chromatography on silica gel with dichloromethane/hexane (2:1) as a mixture of eluents to afford compound **31** (235 mg, 69%) as an orange-brown powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43–1.48 (m, 2 H, CH_2), 1.74–1.82 (m, 1 H, 1 H from CH_2 group), 1.93–2.01 (m, 1 H, 1 H from CH_2 group), 2.94–2.96 (m, 1 H, CH), 3.08 (dd, *J* = 3.4, 8.3 Hz, 1 H, CH), 3.26–

3.28 (m, 1 H, CH–C=O), 3.76 [dd, J = 3.1, 9.9 Hz, 1 H, CH–C=C(CN)$_2$], 6.25 (td, J = J = 1.3 and 8.3 Hz, 1 H, =CH), 6.33 (td, J = 1.3, 8.3 Hz, 1 H, =CH) ppm. IR (KBr): $\tilde{\nu}$ = 2224 (C≡N), 1676 (C=O), 1078 (C=S) cm^{-1}. MS (EI): m/z (%) = 342 (46) [M]$^+$, 314 (82), 270 (19). MS (MALDI, DCTB as matrix, negative mode) calcd. for $C_{16}H_{10}N_2OS_3$ 341.995; found 341.99. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/hexane (10:1) solution of compound **31**.

Compound 32: A mixture of compound **30** (50 mg, 0.13 mmol), mercury(II) acetate (81 mg, 0.25 mmol) in dichloromethane (40 mL) and glacial acetic acid (20 mL) was heated at reflux for 2 h and then filtered through sodium sulfate. The resulting orange solution was extracted several times with dichloromethane. The combined organic layers were washed with water and brine and dried with sodium sulfate, and the solvents were evaporated. The orange residue was chromatographed on silica gel with elution with dichloromethane/hexane (3:1) to afford compound **32** (47 mg, 96%) as an orange powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (br. d, J = 8.4 Hz, 2 H, CH_2), 1.96 (br. d, J = 8.4 Hz, 2 H, CH_2), 2.94 (br. s, 2 H, CH), 3.71 (s, 2 H, CH–C=), 6.17 (dd, J = 3.1, 4.5 Hz, 2 H, =CH) ppm. MS (EI): m/z (%) = 374 (14) [M]$^+$, 346 (8), 296 (13), 270 (9). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/acetone (1:1) solution of compound **32**.

Compound 33: A mixture of compound **31** (18 mg, 52.5 μmol), mercury(II) acetate (33 mg, 105 μmol) in dichloromethane (10 mL) and glacial acetic acid (5 mL) was heated at reflux for 2 h and then filtered through sodium sulfate. The resulting orange solution was extracted several times with dichloromethane. The combined organic layers were washed with water and brine and dried with sodium sulfate, and the solvents were evaporated. Compound **33** was isolated as a yellow-orange powder in 96% yield after recrystallization from tetrahydrofuran/hexane (1:6). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.42 (br. m, 2 H, CH_2), 1.76–1.81 (m, 1 H, 1 H from CH_2 group), 1.94–2.01 (m, 1 H, 1 H from CH_2 group), 2.93–2.95 (m, 1 H, CH), 3.09 (dd, J = 3.2, 8.3 Hz, 1 H, CH), 3.25–3.27 (m, 1 H, CH–C=O), 3.76 [dd, J = 3.2, 9.9 Hz, 1 H, CH–C=C-(CN)$_2$], 6.22 (td, J = 1.3, 8.3 Hz, 1 H, =CH), 6.28 (td, J = 1.3, 8.3 Hz, 1 H, =CH) ppm. IR (KBr): $\tilde{\nu}$ = 2223 (C≡N), 1716 (C=O), 1658 (C=O) cm^{-1}. MS (EI): m/z (%) = 326 (16) [M]$^+$, 298 (18).

Compound 36b: A solution of *n*-butyllithium (2.7 M in heptane, 0.7 mL, 1.8 mmol) was added dropwise at –78 °C to a solution of phosphonate **35b** (565 mg, 1.7 mmol) in tetrahydrofuran (15 mL). The solution was stirred for 10 min and a solution of compound **34** (0.507 g, 0.75 mmol) in tetrahydrofuran (15 mL) was then added dropwise over 15 min. The solution was kept at room temperature and stirred for 3 h. After all solvents had been removed under vacuum, the crude oil was purified by chromatography on silica gel with dichloromethane/hexane (1:3) as a mixture of eluents to afford compound **36b** (482 mg, 75%) as a yellow orange powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 18 H, *t*Bu), 2.47 (s, 6 H, SCH_3), 5.73 (s, 2 H, =CH), 7.30 (tt, J = 1.5, 7.5 Hz, 8 H, H_{para}), 7.38 (tt, J = 1.5, 7.5 Hz, 4 H, H_{meta}),7.60 (dt, J = 1.5, 6.5 Hz, 8 H, H_{ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8, 26.9, 30.7, 116.3, 128.2, 130.4, 132.5, 135.8, 144.4 (some carbon signals are missing due to the insolubility of **36b**) ppm. MS (EI): m/z (%) = 854 (100) [M]$^+$. MS (MALDI, dithranol as matrix, positive mode) calcd. for $C_{44}H_{46}O_2S_6Si_2$ 854.136; found 854.135. $C_{44}H_{46}O_2S_6Si_2$ (855.38): calcd. C 61.81, H 5.42; found C 62.31, H 5.58. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a tetrahydrofuran/petroleum ether (1:7) solution of **36b**.

Compound 36c: A solution of *n*-butyllithium (2.7 M in heptane, 0.77 mL, 2.1 mmol) was added dropwise at –78 °C to a solution of phosphonate **35c** (777 mg, 2 mmol) in tetrahydrofuran (20 mL). The solution was stirred for 15 min and a solution of compound **34** (0.677 g, 1 mmol) in tetrahydrofuran (20 mL) was then added dropwise over 15 min. The solution was kept at room temperature and stirred overnight. After all solvents had been removed under vacuum, the crude oil was purified by chromatography on silica gel with dichloromethane/hexane (1:3) as a mixture of eluents. Further recrystallization from dichloromethane/petroleum ether afforded compound **36c** (763 mg, 83.7%) as a yellow powder; m.p. 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.0 Hz, 6 H, CH_3), 1.06 (s, 18 H, *t*Bu), 1.69 (sextet, J = 7.2 Hz, 4 H, CH_2), 2.85 (t, J = 7.0 Hz, 4 H, SCH_2), 5.72 (s, 2 H, =CH), 7.31 (tt, J = 1.5, 7.4 Hz, 8 H, H_{meta}), 7.35 (tt, J = 1.5 and 7.4 Hz, 4 H, H_{para}), 7.60 (dt, J = 1.5, 6.5 Hz, 8 H, H_{ortho}) ppm. MS (EI): m/z (%) = 910 (100) [M$^+$]. MS (MALDI, DCTB as matrix, positive mode) calcd. for $C_{48}H_{54}O_2S_6Si_2$ 910.198; found 910.204.

Compound 36d: A solution of *n*-butyllithium (1.25 mL, 2.17 mmol, 1.6 M in hexane) was added dropwise at –78 °C to a solution of phosphonate **35d**[23] (596 mg, 1.97 mmol) in tetrahydrofuran (20 mL). The solution was stirred for 15 min and a solution of 4,7-bis(*tert*-butyldiphenylsilyloxy)-1,3-benzodithiole-2-one (**34**, 1.02 g, 1.51 mmol) in tetrahydrofuran was then added dropwise. The solution was kept at room temperature and stirred overnight. After addition of methanol, the precipitate was filtered and washed with methanol to afford compound **36d** (1.13 g, 88%) as a yellow powder; m.p. 206 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 18 H, *t*Bu), 3.31 (s, 4 H, CH_2), 5.73 (s, 2 H, =CH), 7.31 (tt, J = 1.5, 7.4 Hz, 8 H, H_{meta}), 7.37 (tt, J = 1.5, 7.4 Hz, 4 H, H_{para}),7.60 (dt, J = 1.5, 6.6 Hz, 8 H, H_{ortho}) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 19.4, 26.5, 30.3, 107.0, 114.1, 115.9, 116.6, 127.8, 128.0, 130.0, 132.2, 135.4, 143.6 ppm. MS (EI): m/z = 852 [M]$^{+\cdot}$. $C_{44}H_{44}O_2S_6Si_2$ (852.12): calcd. C 61.93, H 5.20; found C 61.81, H 5.26.

Compound 36e: A solution of *n*-butyllithium (1.6 M in hexane, 0.73 mL, 1.15 mmol) was added dropwise at –78 °C to a solution of phosphonate **35e** (640 mg, 1.04 mmol) in tetrahydrofuran (15 mL). The solution was stirred for 10 min and a solution of compound **34** (800 mg, 1.04 mmol) in tetrahydrofuran (15 mL) was then added dropwise. The solution was kept at room temperature and stirred overnight. After all solvents had been removed under vacuum, the crude oil was purified by chromatography on silica gel with dichloromethane/petroleum ether (1:9) as a mixture of eluents to afford compound **36e** (300 mg, 22%) as yellow crystals; m.p. 179 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.8 Hz, 6 H, CH_3), 1.08 (s, 18 H, *t*Bu), 1.20–1.50 (m, 36 H, CH_2), 1.68 (q, J = 7.2 Hz, 4 H, CH_2), 2.87 (t, J = 7.2 Hz, 4 H, CH_2S), 5.75 (s, 2 H, =CH), 7.34 (t, J = 7.2 Hz, 8 H, H_{meta}), 7.39 (t, J = 7.2 Hz, 4 H, H_{para}), 7.62 (t, J = 7.2 Hz, 8 H, H_{ortho}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 19.4, 22.7, 26.5, 29.1, 29.3, 29.4, 29.5, 29.6, 29.65, 29.7, 29.8, 31.9, 36.4, 109.3, 112.3, 115.8, 127.3, 127.8, 128.1, 129.9 132.2, 135.4, 143.6 ppm. $C_{66}H_{90}O_2S_6Si_2$ (1162.48): calcd. C 68.10, H 7.79; found C 68.36, H 7.87.

Compound 36f: A solution of *n*-butyllithium (1.6 M in hexane, 2.6 mL, 4.2 mmol) was added dropwise at –78 °C to a solution of phosphonate **35f** (1 g, 3.82 mmol) in tetrahydrofuran (15 mL). The solution was stirred for 10 min and a solution of compound **34** (1.29 g, 1.91 mmol) in tetrahydrofuran (15 mL) was then added dropwise. The solution was kept at room temperature and stirred overnight. After all solvents had been removed under vacuum, the residue was dissolved in dichloromethane. The organic layer was washed with water and dried with magnesium sulfate, and the solvents were evaporated. Crystallization with dichloromethane/petro-

leum ether afforded compound **36f** (1.3 g, 84%) as yellow crystals; m.p. 171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 18 H, *t*Bu), 5.97 (s, 2 H, =CH), 7.30–7.48 (m, 16 H), 7.63–7.68 (m, 8 H) ppm. $C_{46}H_{44}O_2S_4Si_2$ (812.18): calcd. C 67.93, H 5.45; found C 67.66, H 5.69.

X-ray Crystallographic Study: Diffraction data for single crystals of **32** and **15b** were collected with a Stoe Mark II Imaging Plate Diffractometer System (Stoe & Cie, 2002) fitted with a two-circle goniometer and a graphite-monochromator and with a Stoe Imaging Plate Diffractometer System fitted with a one-circle goniometer and a graphite-monochromator, respectively, at –100 °C with use of Mo-K_α X-radiation (λ = 0.71073 Å). Crystal data for **32**: $C_{19}H_{10}N_4OS_2$, M_r = 374.03, T = 173(2) K, crystal dimensions 0.450 × 0.383 × 0.300 mm, orthorhombic, *cmc*2$_1$, a = 15.8506(11) Å, b = 14.7266(8) Å, c = 7.3784(4) Å, $\alpha = \beta = \gamma$ = 90°, V = 1722.31(18) Å^3, Z = 4, $\rho_{calcd.}$ = 1.444 g cm^{-3}, F(000) = 768, μ = 0.325 mm^{-1}, $2\theta_{max}$ = 29.26°, 16279 measured reflections, 2394 independent reflections (R_{int} = 0.0421), 2174 strong reflections [$I_0 > 2\sigma(I_0)$], 121 refined parameters, R_1 = 0.0284 (strong data) and 0.0320 (all data), wR_2 = 0.0780 (strong data) and 0.0792 (all data), *GOF* = 1.053, 0.237 and –0.275 e Å^{-3} max. and min. residual electron density. A semiempirical absorption correction was applied with the aid of MULABS (PLATON,[24] T_{min} = 0.775, T_{max} = 0.903). The structure was solved by direct methods with the aid of the SHELXS-97[25] program and refined by full-matrix least-squares on F^2 with SHELXL-97.[26] All hydrogen atoms were placed on calculated positions derived from ideal geometries. All non-hydrogen atoms were refined anisotropically. The highest remaining electron density of 0.24 electrons/Å^3 is located next to atom C10. The molecule lies on a crystallographic mirror plane. The carbon atoms C3, C4 and C5 of the bicyclooctene moiety show strongly anisotropical adps.

Crystal Data for 15b: $C_{17}H_{14}O_2S_6$, M_r = 442.64, T = 173(2) K, crystal dimensions 0.45 × 0.30 × 0.20 mm, monoclinic, *C*2/*c*, a = 25.743(2) Å, b = 6.5857(4) Å, c = 22.842(2) Å, β = 108.529(9)°, V = 3671.8(5) Å^3, Z = 8, $\rho_{calcd.}$ = 1.601 g cm^{-3}, F(000) = 1824, μ = 0.754 mm^{-1}, $2\theta_{max}$ = 26.06°, 14044 measured reflections, 3604 independent reflections (R_{int} = 0.0408), 2618 strong reflections [$I_0 > 2\sigma(I_0)$], 228 refined parameters, R_1 = 0.0278 (strong data) and 0.0439 (all data), wR_2 = 0.0623 (strong data) and 0.0655 (all data), *GOF* = 0.891, 0.255 and –0.345 e/Å^3 max. and min. residual electron density. The structure was solved by direct methods with the aid of the SHELXS-97[25] program and refined by full-matrix least-squares on F^2 with SHELXL-97.[26] The hydrogen atoms were included in calculated positions and treated as riding atoms by use of the SHELXL-97 default parameters. No absorption correction was applied.

CCDC-735636 (for **15b**), -735637 (for **31**), -735638 (for **32**) and -735639 (for **36b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): MS and NMR spectra of ketene imine **18**, cyclic voltammograms of compounds **6**, **15b**, **29** and **30**, UV/Vis spectra of **7a** and **15a** and single-crystal structures of compounds **31** and **36b**.

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