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Outside rules inside: the Role of Electron-active Substituents in Thiophene-based Heterophenoquinones

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The biradicaloid vs quinoidal character of the ground state of thiophene-based heterophenoquinones bearing donor or acceptor groups is investigated. Keeping fixed the conjugation length, namely the 5,5’-bis(4-oxo-2,5-cyclohexadiene-1-ylidene)-2,2’-dihydroxy bithiophene backbone, an opposite effect occurs depending on the donating or withdrawing nature of the substituents. The character at the ground state depends not only on the electronic nature of the substituent but also on their position onto the molecular skeleton: donor groups on the 3,3’-positions of the bithiophene central core stabilize the quinoidal ground state whereas a biradicaloid electronic structure results from the introduction of the same donor groups on the lateral phenones. Withdrawing groups behave similarly to donors, but in the opposite direction.

Introduction

Due to their peculiar electronic properties, conjugated quinoidal species are appealing components in molecular electronics and optoelectronic devices for a wide range of applications. For instance, due to their good transport properties, quinone-based semiconductor channels are used in field effect transistors [1]. Although quinoidal species have emerged as promising n-channel actuators, some thiophene-based derivatives show ambipolar behaviour, which meets the key requirement for complementary circuits. For longer homologues, the effective π-conjugation along the planar molecular skeleton leads to low energy gap values with absorption in the red or near-infrared region. In this regard, 5,5’-bis(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,2’-dihydroxy bithiophene (**QBT**, Fig. 1) has been used as hole donor in an organic photodetector [2] for polymer optical fibers, which work at 650 nm [2]. In organic photovoltaic cells, the addition of a small quantity of QBT to bulk heterojunctions of P3HT:PCBM (poly-3-hexylthiophene:fullerene) resulted in the 47% increase of EQE with respect to the corresponding cells based on the P3HT:PCBM binary blend only [3]. In fact, the quinoidal species improve the non-optimal microstructure of the active layer by affecting the crystallinity of the polymer as well as the morphology of the blend.

In some conjugated quinones, the occurrence of unexpected electronic structures has been known for a long time. Thiele's [4] and Chichibabin's [5] hydrocarbons are the first examples of systems characterized by a biradicaloid ground state, as proven by both spectroscopic analysis and theoretical modeling.[6] Several further series of Chichibabin-type compounds with dicianomethylene [7], oxocyclohexadienylidene [8][9] or imidazol-ylidene [10] end groups have then been synthesized. It has been observed that molecules with a rather short sequence of conjugated units feature a quinoidal structure, whereas a diradical contribution occurs when increasing the conjugation length. Kozaki et al. reported no diradical character for **1** [11] and a diradical participation in the *cis-trans* isomerisation for **2** [10] (see Fig. 1).

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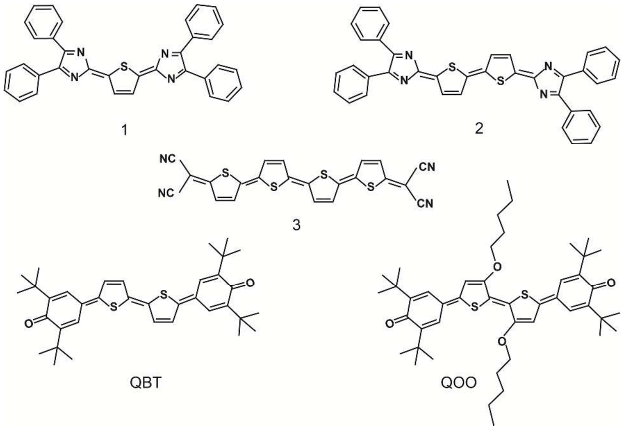


Fig. 1 Thiele's and Chichibabin's hydrocarbon analogues and heterophenoquinones.

Using Raman spectroscopy and Quantum Chemical modelling, Navarrete *et al.* demonstrated the occurrence of a diradical structure in dicyanomethylene-end-capped quinoidal oligomers when the number of thiophene rings is equal to or larger than four (**3**, Fig. 1). Further Raman spectroscopy and computational studies have clearly highlighted the peculiar ground state structure of **QBT** [12]. In the same work, Fazzi *et al.* have identified the spectroscopic signature, i.e. the frequency position of a Raman marker band, of the biradical structure for these thiophene-based heterophenoquinone homologues.

More recently, it has been found that electron-donating alkoxy groups onto the thienylene core of the 5,5’-di(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ilidene)-3,3’-H,H’-2,2’-dihydroxy bithiophene (**QOO**) provide a strong contribution to the stabilization of the quinoidal ground state structure of these species.[13] This allows for the tuning of the electronic character without significantly affecting the HOMO-LUMO energy gap.

In the present study we provide evidence of the possibility to modulate quinoid *vs.* biradicaloid structure within thiophene-based heteroquaterphenoquinones bearing electron-active substituents either on the phenoquinone or on the central core.

We take **QBT** as reference molecule as it is the shortest molecule showing the transition from quinoidal to biradicaloid electronic ground state among thiophene-based heterophenoquinones [12]. We demonstrate that the stabilisation of a given electronic structure depends on the nature and the strength of the electron-active substituents and that donor and acceptor groups provide an opposite effect. Interestingly, the quinoidal *vs.* biradicaloid character is also affected by the position of the substituents.

Results and Discussion

Materials

In oligoarylenes, as in other conjugated species, the introduction of electron-donating or electron-withdrawing substituents is known to affect the position of the frontiers energy levels and their energy gap. To highlight the role of functional groups on unsaturated phenoquinones, we have introduced different substituents on the backbone of the 5,5’-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,2’-dihydroxy bithiophene (**QBT**). The sites that we have taken into consideration for the introduction of electron-donor and electron-withdrawing groups are:

- the 3,3’-positions of the central bithienylene core (Substituted Cores, see Fig. 2 on the right). We have avoided functionalization of the 4,4’-positions since it can hamper the coupling of the core with the lateral phenols due to steric hindrance;
- the lateral 4-oxo-2,5-cyclohexadiene-1-ylidene on 3,5-positions, substituting the t-butyl groups (Substituted Wings, see Fig. 2 on the left). Again, substitution in this position is preferred to 2,6-positions in order to avoid steric hindrance during the Suzuki coupling.

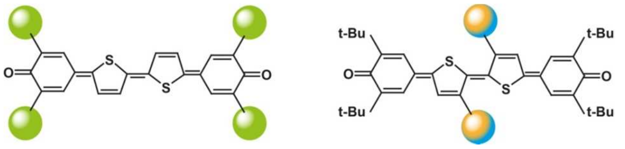


Fig. 2 General structure for the two classes of molecules: “Substituted wings”(on the left), “Substituted Core”(on the right). The spheres correspond to the donating or withdrawing groups introduced on the pristine backbone.

All the quinoidal molecules were obtained by oxidation of the corresponding aromatic precursors. Throughout this paper, molecules are labelled with acronyms where the first letter indicates aromatic (A) or quinoidal (Q) species. The remaining letters refer to the substituents.

The general scheme to produce the "Substituted core" class (Fig. 3) follows the procedure used for **QBT** consisting in a Suzuki coupling between the 5,5'-dibromo-2,2'-bithiophene and a boron-derivative of the substituted phenol. [12]

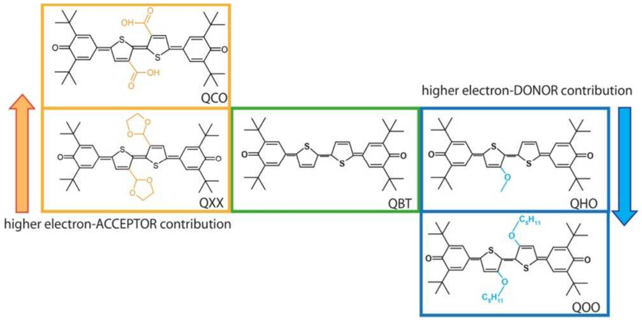
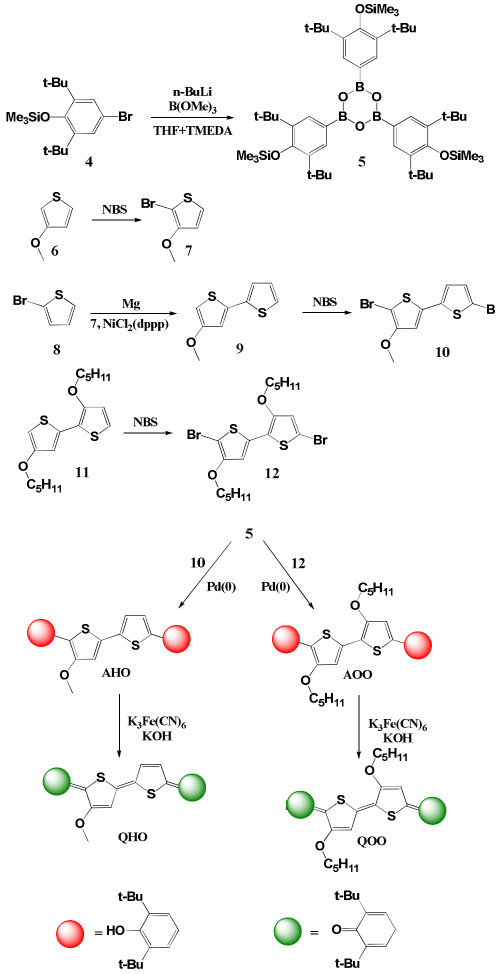


Fig. 3 ”Substituted core” class of quinoidal molecules starting from **QBT**: **QCO**, **QXX**, **QHO**, **QOO**.

3,3’-Dipentoxy-2,2’-bithiophene (**11**) was synthesized according to [14] and further brominated with NBS in DMF. For 3-methoxy-2,2’-bithiophene, a Kumada coupling between

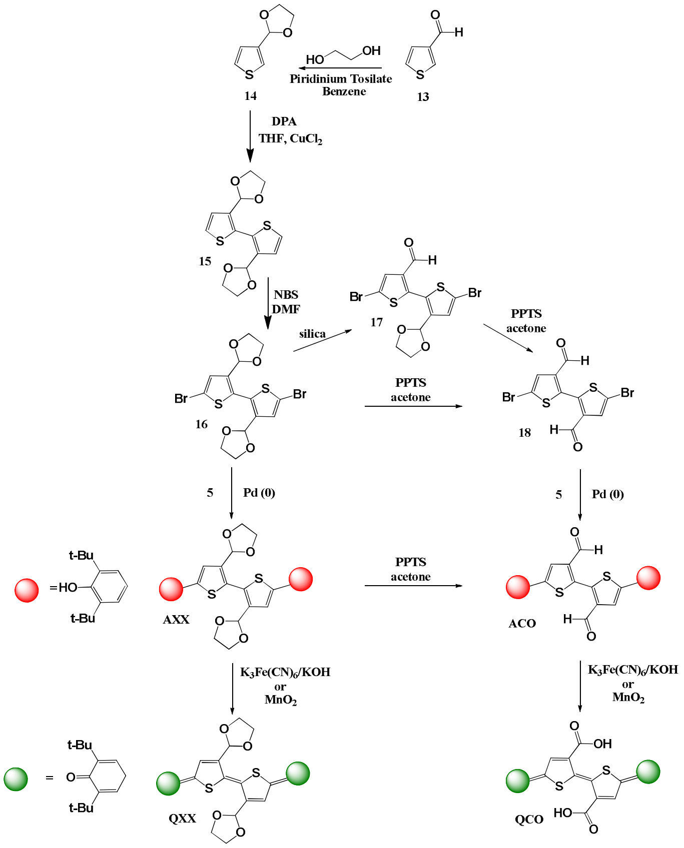
2-bromo-3-methoxythiophene with NBS, and the Grignard reagent of 2-bromothiophene was carried out (Scheme 1).



Scheme 1. Synthetic route of the quinones belonging to the "Substituted core" class, bearing donor groups.

The Suzuki coupling between the dibrominated cores and the boronic derivative **5** gave the aromatic compounds, which were subsequently oxidized with potassium ferricyanide to provide **QOO** and **QHO** in quantitative yields. As the symmetrically substituted bithiophene **AOO** tends to oxidize spontaneously upon air exposure, both the aromatic and the quinoidal products were obtained from the workup of the reaction.

As for the electron-poor QBT-derivatives, two electron-withdrawing groups have been considered, namely the 1,3-dioxolane (**QXX**) and the carboxylic acid (**QCO**). The two species were obtained in succession from the same synthetic route. In the latter case, the carboxylic group is obtained in the last oxidation step, starting from the aldehyde groups in the 3,3'-positions. The synthetic route is reported in Scheme 2.
The two dibrominated bithienylene cores (**16** and **18**) were synthesized following almost entirely the published procedure [15]. According to the original route, the 5,5'-dibromo-3,3'-diformylacetal-2,2'-bithiophene (**16**) was not isolated, but it was directly deprotected. Here, the cleavage of **40** was not carried out in a one-pot reaction.



Scheme 2. Synthetic route of the quinones belonging to the "Substituted core" class, bearing withdrawing groups.

Accordingly, compound **16** was isolated before proceeding to the next deprotection step. Incidentally, it was found that bromination of **39** did not provide only **16**, which is white coloured, but also a yellow product, which resulted to be the 5`-dibromo-3'-(1,3-dioxolan-2-yl)-[2,2'-bithiophene]-3-carbaldehyde (**17**), due to the partial deprotection of **16** on silica. The Suzuki coupling between the dibrominated cores (**16** or **18**) and the boronic derivative (**5**) gave the aromatic compounds **AXX** and **ACO**. 5,5'-Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-[2,2'-bithiophene]-3,3'-dicarbaldehyde (**ACO**) was also obtained through the deprotection of the diformylacetal groups of **AXX** with pyridinium tosylate (PPTS) in acetone (Scheme 2).
It is well known that the introduction of electron-acceptor groups induces an increase of oxidation potential in π-conjugated systems, and hence hampers the chemical and electrochemical oxidative reaction. Therefore, unlike in the case of **AOO**, where the oxidation step proceeds spontaneously, the oxidation of the aromatic precursors substituted with acceptor groups has shown to be more difficult. In addition to potassium ferricyanide, MnO_2 has also been tested as oxidizing agent. The

latter has allowed the recovery of the desired products in quantitative yields.

The set of "Substituted wings" compounds is obtained from the replacement of the t-butyl in α,α`-positions on phenol of the **QBT** structure with electron-active groups, leaving the central bithienylene core unchanged (Fig. 4).

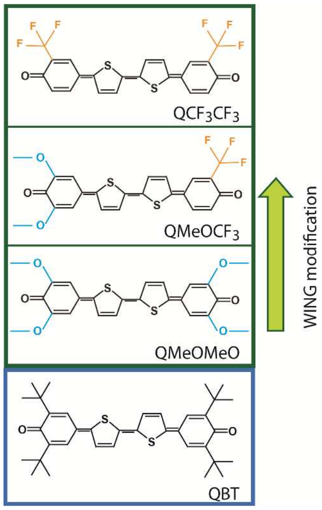
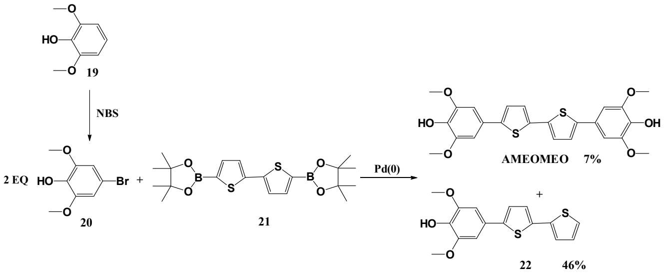


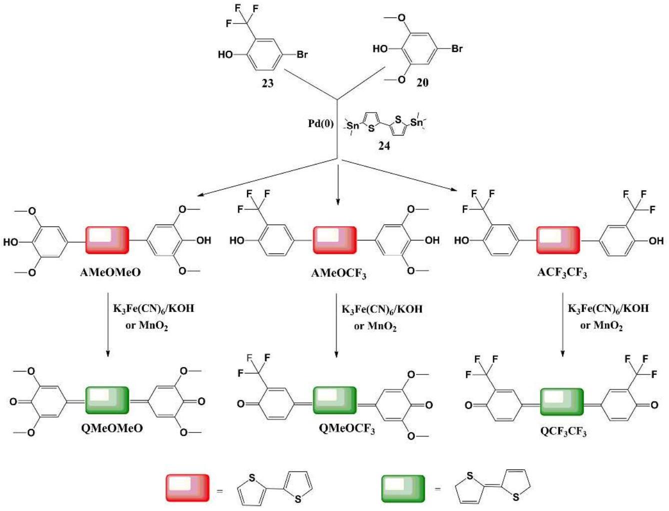
Fig. 4 "Substituted wings" class of quinoidal molecules starting from **QBT**: **QMeOMeO**, **QMeOCF$_3$**, **QCF$_3$CF$_3$**.

Two different synthetic strategies were followed. The first one employed Suzuki coupling, starting from the lateral *p*-brominated phenol and the diboronated bithienylene core. This route was applied with the phenol substituted with electron-donating groups, 4-bromo-2,6-dimethoxyphenol (**20**), and the pinacol ester of the 2,2'-bithiophene (**21**) (Scheme 3).



Scheme 3. Suzuki coupling for the synthesis of **AMeOMeO**.

This reaction gave the desired product in very low yields, with the monosubstituted (**22**) compound as the main product. Since Stille coupling between 5,5'-trimethylstannyl-2,2'-bithiophene (**24**) and **20** (Scheme 4) provided higher yields than the Suzuki reaction, the same route was applied to the synthesis of all the other molecules bearing substituted wings (i.e. **ACF$_3$CF$_3$** and **AMeOCF$_3$**). Runs were also repeated under microwave irradiations, but no significant advantage was observed.



Scheme 4. Synthetic route to yield "Substituted wings" quinoidal molecules.

The asymmetrical **AMeOCF$_3$**, which shows both a donor-substituted wing at one end and an acceptor-substituted wing at the other end, required optimization of the experimental conditions to avoid or limit the formation of the symmetrically substituted molecules as main products (i.e. **AMeOMeO** and **ACF$_3$CF$_3$**). It was found that with the simultaneous introduction of the two different phenols (Run 3 in Table 1), the asymmetrical molecule **AMeOCF$_3$** is recovered as the main product (34%), whereas the symmetrical species are formed in lower yields (4% and 9,5% for **AMeOMeO** and **ACF$_3$CF$_3$**, respectively).

Table 1 Runs aimed at determining the correct timing of introduction of the two different wings to obtain **AMeOCF$_3$**

Run	Addition Time [a]		Yields		
	20[b]	23[b]	AMeOMeO	AMeOCF$_3$	ACF$_3$CF$_3$
1	after 45	0	0%	0%	43%
2	0	after 25	34%	0%	0%
3	0	0	4%	34%	9,5%

[a] in minutes. [b] phenol derivatives used as reactants

All the aromatic compounds were oxidized to the corresponding quinones using either MnO$_2$ or potassium ferricyanide, the latter facilitating the following purification step. This oxidant is in fact soluble in the reaction medium while the desired products precipitate, thus allowing for their easy separation by filtration.

Absorption and Fluorescence spectroscopies of aryls (A) and quinones (Q)

UV-vis spectroscopy is a convenient method to highlight the strong change in π-delocalisation when passing from the aromatic to the quinoidal structure. The peculiar absorption of quinoidal species at low energy is due to the almost double inter-ring bond that forces the skeleton in a more planar conformation, leading to a loss of aromatic character and a more extended π-delocalisation.

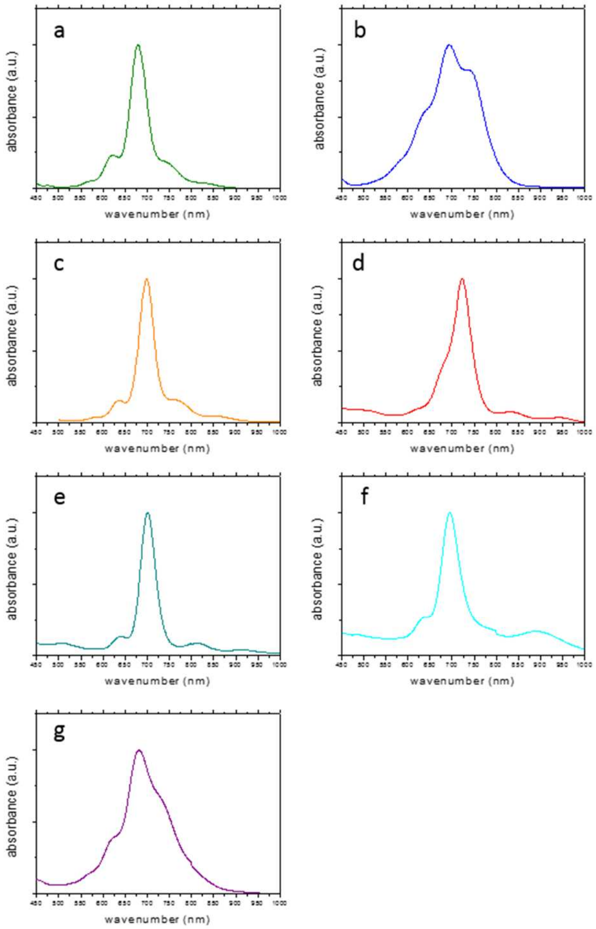


Fig. 5 Normalized absorption spectra of "Substituted core" and "Substituted wings" species in chloroform: (a) **QBT**, (b) **QOO**, (c) **QXX**, (d) **QCO**, (e) **QMeOMeO**, (f) **QMeOCF$_3$**, (g) **QCF$_3$CF$_3$**.

Except for **QOO** and **QCF$_3$CF$_3$**, the UV-vis spectra of these quinoidal species show the same features as with the reference **QBT (Fig. 5)**. Indeed, the functionalized quinones show a sharp most intense band assigned to the strongest dipole allowed transition, with a defined vibronic structure at higher energy and a weaker transition, which has been previously assigned to a dark double electron excitation at lower energy.[16]

The change in π-conjugation in going from the aromatic precursors to the corresponding quinones can be highlighted by the strong red-shift of the absorption bands (see Δ red shift in Table 2). The shift is maximum for **XX**, which was characterized by a distorted backbone in the aromatic form (**AXX**). Indeed, the presence of bulky substituents on the 3,3'-positions of the bithiophene drives a deviation from planarity through a rotation around the quasi-single thiophene-thiophene inter-ring bond: relatively to the unsubstituted **ABT**, a remarkable blue-shift of the π-π* transition is observed when acceptor groups are introduced on bithiophene (**AXX**, **ACO**). In **ACO**, together with the main absorption band at 270 nm, a weaker band at 405 nm is present, which is ascribed to the n-π* transition (see Supporting Information), in analogy with other aromatic structures containing carbonyl groups

Table 2 Absorption maxima of Aromatic (**A**- molec) and Quinoidal (**Q**-molec) compounds in chloroform solution. The extinction coefficient values ε ($M^{-1}cm^{-1}$) are reported in brackets. The red-shift going from the aromatic to the quindoidal species is also highlighted.

Compound	A-molec λ_{max} (nm)	Q-molec λ_{max} (nm)	Δ red shift (nm)
BT	382 (37000)	680 (205000)	299
OO	406 (26000)	696 (100000)	290
XX	329 (21000)	699 (96000)	370
CO	279-406 (25000-9460)	722 (111000)	316
MeOMeO	385 (19000)	702 (91000)	317
MeOCF$_3$	379 (20000)	695 (89000)	316
CF$_3$CF$_3$	372 (18000)	680 (85000)	308

Conversely, the smallest shift of the main absorption band going from the aromatic precursor to the corresponding quinone is given by the "Substituted Core" species bearing the alkoxy group (Δ red shift = 290 nm): the introduction of this substituent on the core of the molecule gives a relevant donor contribution to the aromatic backbone through a resonant effect without providing significant distortion. [17] This effect plays a significant role also in the case of aromatic compounds as shown by the red shift of the absorption maximum of **AOO** (at 406 nm) with respect to **ABT** (382 nm). Planarization both for **AOO** and **QOO** is likely related also to a stabilizing oxygen-sulphur interaction which adds up to the contribution of the resonance forms, which are expected to counterbalance any sterically-induced distortion effect.[18]

Indication about the degrees of planarity of the molecular skeleton for the aromatic species is also given by the Stokes shift values: the photoluminescence spectra of **ABT**, **AOO** are characterized by a well-defined vibronic structure with energy separation of about 0.15 eV (spectra are reported in the Supporting Information). The evidence of the vibronic structure in the emission can be ascribed to the planarization of the molecular skeleton triggered by the excitation.[19] The Stokes shift values are in the typical range of linear conjugated oligomer [20] and decrease while increasing planarization along the conjugated skeleton, as in the case of **AOO** (0.38 eV, see Supporting Information). Conversely, the photoluminescence spectrum of **ACO** is characterized by a roughly defined vibronic structure shifted at longer wavelength, whereas **AXX** does not show any vibronic shoulder and has a large Stokes shift (1.00 eV), which is ascribed to the large variation in equilibrium geometry between the ground and the excited states.

According to all the reported data, for the "Substituted Core" species the planarization of the skeleton in the quinoidal structure undoes the hindrance effect of the side groups, which is instead relevant in the aromatic precursors.

As a result of the electronic effect of the substituents, the absorption maxima of **QOO**, **QXX** and **QCO** are red-shifted with respect to **QBT**. Comparison between the three different "Substituted wings" species (i.e. **QMeOMeO**, **$QMeOCF_3$**, **QCF_3CF_3**) highlights the strongest effect of the methoxy-substituted quinones and the weakest one for the molecule with the -CF_3 acceptor groups. The shift of absorption bands when going from the aromatic to the quinoidal species (Δ red shift, Table 2) is similar for all three compounds and indicates that the introduction of donating and withdrawing groups on the lateral phenol does not cause any significant distortion of the backbone. This is also confirmed by the relatively low Stokes shift values (between 0.46 and 0.50 eV, see Supporting Information), which are comparable to that one of **ABT**. These evidences indicate that not only the conjugated backbone is not distorted by the introduction of substituents, but also their electronic effect is negligible.

Surprisingly, the donor-acceptor quinone (**$QMeOCF_3$**) has an intermediate effect with respect to the symmetrically substituted **QMeOMeO** and **QCF_3CF_3**. This behaviour suggests that no cross-talk occurs between the electron-active groups and therefore no push-pull species is actually formed. None of quinones described here show any fluorescence.

The role of functional groups in changing the electronic character: quinoidal *vs.* biradicaloid ground state

Despite controversial views regarding the correct description of the ground state electronic structure of conjugated quinones, previous works have highlighted the strict relationship between diradicals and the π-conjugation along the backbone in the homologous series of thiophene-based heterophenoquinones.[12] In this respect, Raman active modes are a powerful tool to discriminate different π-conjugated compounds on the basis of their characteristic fingerprints. In particular, the so called Я-mode, which corresponds to the oscillation of the Bond Length Alternation (BLA) parameter relative to the CC sequence along the conjugated structure [21][2], gives strong, diagnostic marker bands. As reported in our previous work [12], the Raman frequency of the Я-mode of **QBT** at 1304 cm^{-1}, is unusually low with respect to the Я frequency commonly shown by aromatic oligothiophenes and by short thienoquinoid oligomers, which is observed at about 1440 cm^{-1}. This feature is a clear signature of the biradicaloid structure of **QBT**. Indeed, the remarkable downward shift of the Я-mode can be rationalized only considering an almost "equalized" CC bonds sequence in the bithiophene moiety, as predicted by Density Functional Theory calculations adopting Broken Symmetry (BS) wave-function.[12] Conversely, not only does the most common Closed Shell (CS) approach predict a quinoidal equilibrium structure for **QBT**, but it provides a computed Raman spectrum showing the usual Я-mode band at about 1400 cm^{-1}, in total disagreement with the experimental observation.

According to these previous studies [12,13], we expect that the fine tuning of the ground state electron charge distribution by the introduction of electroactive substituents in the **QBT** skeleton results in a remarkable modulation of the Raman features. Being specifically used as a diagnostic tool to determine a possible diradical contribution to the ground state of conjugated quinones, Raman spectroscopy was carried out only for the **Q**-molecules here studied and not for the **A**-species which do not exhibit this peculiar electronic character. The direct comparison of the experimental Raman fingerprints allows to classify these quinones, without any support by theoretical modelling of the spectra, as the conjugated skeleton is the same for all the substituted species here discussed.

As previously reported the Raman spectrum of **QOO** is markedly different from that of the unsubstituted **QBT**, showing the strongest band, which is assigned to Я-mode, at 1430 cm^{-1}, up-shifted by more than 100 cm^{-1} with respect to the Я-mode transition of the biradicaloid species (Fig. 6). [13] The presence of a strong line assigned to the Я-mode at higher energy proves that the dialkoxy-substituted phenoquinone is described by a quinoidal ground state. Given this first result, the next step was to investigate whether the effect of functional groups in the 3,3'-positions of the bithienylene core (Substituted Corse) is univocal in stabilizing the quinoidal ground state or depends on their specific electronic character (i.e. donor or acceptor).

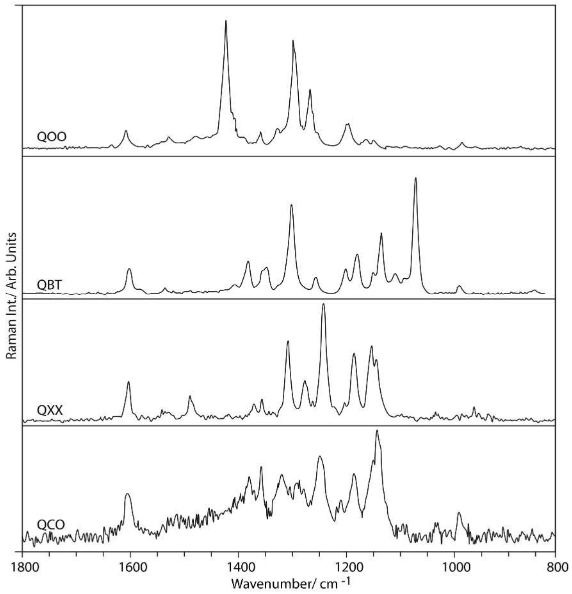


Fig. 6 Raman spectra on powder samples of (see labels on the left): **QOO** (FT-Raman) and **QBT**, **QXX**, **QCO** (excitation line: 632 nm).

QXX and **QCO** show several spectral features comparable to those of **QBT** (Fig. 6). For **QXX** and **QCO** the strongest bands are at 1230 cm^{-1} and 1130 cm^{-1} respectively, down shifted by ~200-300 cm^{-1} with respect to the Я-mode transition characteristic of the quinoidal species discussed above (**QOO**).

Since the position of the Я-mode is directly related to the molecular structure and it is red-shifted in presence of a biradicaloid character, it is possible to assign a biradicaloid geometry to the **QXX** and **QCO**.

It turns out that the modification of the electronic distribution in thiophene-based quaterphenoquinone by means of electroactive substituents onto the conjugated core turns into a stabilization of the quinoidal ground state only when donor groups are introduced. Acceptor groups likely provide the opposite effect.

QBT and **QMeOMeO** present similar Raman spectra: considering the spectral region 1800-900 cm^{-1}, the most intense peak is located at ~1300 cm^{-1} (Fig. 7). As demonstrated before for **QBT** [12], the anomalous low frequency of the Я-mode can be justified only taking into account a biradicaloid ground-state character. The similarity in the main Raman features between **QBT** and **QMeOMeO** spectra further validates the fact that **QMeOMeO** has a ground state with a biradicaloid nature.

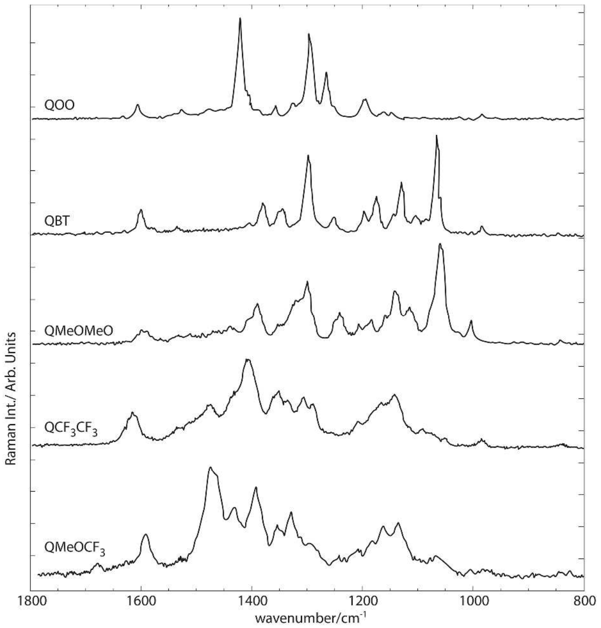


Fig. 7 Raman spectra on powder samples of (see labels on the left): **QOO** (FT-Raman) and **QBT**, **QMeOMeO**, **QCF$_3$CF$_3$**, **QMeOCF$_3$** (excitation line: 632 nm).

Conversely, **QCF$_3$CF$_3$**, which is characterized by withdrawing substituents on the phenones, strongly differs from **QBT**, while being more similar to **QOO**: its Raman spectrum shows the strongest band, assigned to the Я-mode, at ~1430 cm^{-1}, which indicates for this molecule a quinoidal ground state (Fig. 7).

This evidence leads to the conclusion that the introduction of electron active substituents on the lateral phenones has the opposite effect on the electronic behaviour of these materials, compared to the introduction of the electron donor/withdrawing groups on the central core. In other words, it has been demonstrated that the electronic character of functionalized QBTs at the ground state depends not only on the nature of electron active substituents bound, but also on their position in the main backbone. This is likely related to the diradicals delocalization over the molecular structure.

QMeOCF$_3$ shows the strongest band delocalized at higher wavelength, ~1470 cm^{-1}, suggesting a higher stability in quinoidal configuration. The donor-acceptor strategy, which has generally a relevant role in modifying the electronic distribution in aromatic oligomers, thus giving low band gap materials, is not effective in the case of conjugated phenoquinones. As a consequence, since the π-conjugation does not increase, the biradicaloid ground state is not obtained.

Crystal structure

Among all the quinones presented here, it was possible to collect a full X-ray diffraction data set only for **QOO**. This class of thiophene-based heterophenoquinones does not usually provide single crystals of sufficient quality, for X-ray data collection and to date only crystal structure of the 2,5-bis-(3,5-di-tertbutyl-oxo-2,5-cyclohexadiene-ylidene)-1,5-dihydrothiophene has been reported. [22] However, for conjugated quinones, an X-ray structure investigation may also provide a further validation for the results obtained with the Raman analysis. From XRD data of **QOO** the occurrence of a mainly quinoidal molecular structure, showing alternated shorter and longer CC bonds according to the pattern established by the pheno-quinone ends, is expected.

Small dark green needles were grown by slow evaporation from a toluene solution of **QOO** at 4°C. A summary of the major crystallographic data is reported in the Supporting Information. Data collection was done at room temperature. Despite the thin plate-like morphology of the crystals, a complete X-ray diffraction data set could be collected and the structure unambiguously determined and fully refined anisotropically. No clear diffraction was observed beyond the 2θ value at which the structure is reported. Further attempts to improve the three-dimensional size and the quality of the crystals were unsuccessful, most likely owing to the intrinsic structural features of the molecule. Overall, the structure confirms the high degree of planarity of the molecule (Fig. 8).

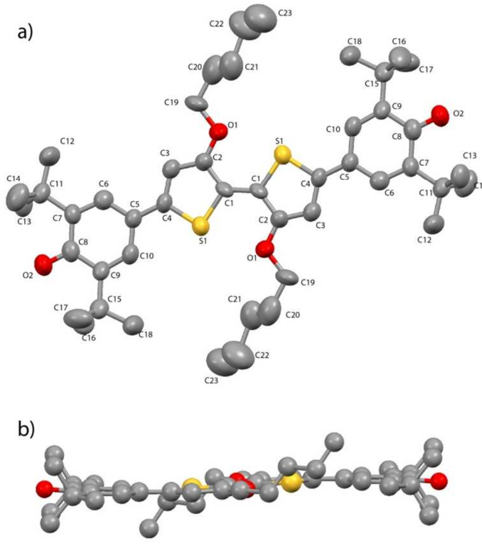


Fig. 8 Molecular structure of **QOO**, a) Top view and b) Side view.

Only half a molecule is present in the asymmetric unit, the other half being generated through an inversion centre. The two phenyl rings are essentially coplanar with the core, the C(3)-C(4)-C(5)-C(10) torsional angle being 2.6°. Further contributions to the planarity of the system are the interaction between the oxygen and sulphur atoms within the central moiety of the molecule. Indeed, the distance between the sulphur atom and the oxygen of the pentoxy group is 2.8 Å. The two pentoxy groups are slightly rising above and below the plane of the molecule (see Fig. 8b). As expected, the outmost C-atoms in the pentoxy groups show a large vibrational motion, suggesting a low degree of packing constraint.

Table 3 Bond lengths and angles in **QOO.**

BOND DISTANCE (Å)	
O(2) - C(8)	1.247 (9)
C(8) - C(7)	1.482 (11)
C(9) - C(8)	1.472 (11)
C(7) - C(6)	1.376 (10)
C(9) - C(10)	1.350 (10)
C(5) - C(6)	1.426 (10)
C(10) - C(5)	1.432 (10)
C(5) - C(4)	1.408 (10)
C(4) - C(3)	1.414 (10)
C(2) - C(3)	1.364 (10)
C(1) - C(1)	1.409 (14)
C(1) - C(2)	1.420 (10)
ANGLE	
C(4) C(5) C(6)	121.4 (8)
C(3) C(4) C(5)	128.5 (7)
TORSION ANGLE	
C(3) C(4) C(5) C(10)	177.6 (8)
C(6) C(5) C(4) S(1)	(-) 178.8 (6)

A close check of the bond distance distribution in the molecule (Table 3) shows clear differences within the phenone moiety that confirm the dearomatization process that occurs in going from the aromatic precursors to the quinoidal species. Moreover, the bond length distribution along the skeleton clearly suggests a quinoidal electronic character, as expected. Interestingly, the formal inter-ring double bonds C(1)-C(1) and C(4)-C(5) are longer than the intra-ring double bonds, namely C(2)-C(3), C(6)-C(7) and C(9)-C(10).

No π-π stacking interaction is observed in the crystal (Fig. 9).

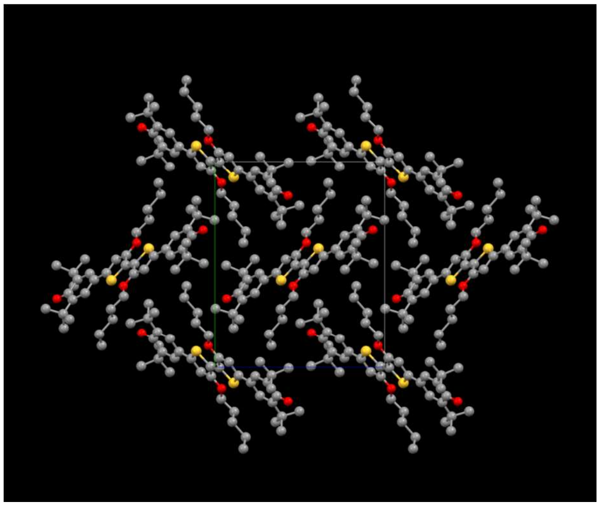


Fig. 9 Crystal structure of **QOO** viewed along a-axis.

Short intermolecular contacts of 3.6 Å between t-butyl moieties belonging to next neighbouring molecule stabilize the molecular packing arrangement in the crystal. Further C-H…π stabilizing contacts between the t-butyls and the centroids of the thiophene rings are also observed. These interactions can contribute to the stabilization of the observed crystal packing arrangement, which is characterized by the presence of large cavities.

Conclusion

New thiophene-based quaterphenoquinones with a separate control over the band gap and the quinoid vs biradicaloid structure have been investigated, by introducing electron-active substituents both onto the lateral phenoquinone or the central core.

The theoretical prediction of the Raman spectra allowed a clear identification and rationalization of the spectroscopic markers that can be taken as the signature of the transition from a quinoidal to a biradicaloid structure as a result of of suitable chemical modifications. Specifically, it was demonstrated that the presence of donor or acceptor groups onto the central moiety produced an opposite effect on the stabilization of the electronic character of the structure at the ground state. The opposite occurs when substituents are placed onto the lateral phenones, suggesting that donor groups on the 3,3'-positions of the bithiophene central core stabilize the quinoidal ground state whereas a biradicaloid electronic structure results from the introduction of the same donor groups on the lateral wings.

Finally, the simultaneous presence of donor and acceptor groups at the opposite ends of the molecule does not reduce the energy gap and therefore does not significantly affect the π-conjugation. The strength of the withdrawing trifluoromethyl group prevails over the donation of electronic charge from the alkoxy group, thus resulting in a quinoidal ground state.

Experimental Section

Synthesis

Unless otherwise specified, all reagents, catalysts, spectroscopic grade and reagent grade solvents were commercial (Sigma Aldrich). All reactions of air- water-sensitive reagents and intermediates were carried out in dried glassware and argon atmosphere. Solvents were previously dried by conventional methods and stored under argon. Air- and water-sensitive solutions were transferred with hypodermic syringes or via cannula.

3-Thiophenecarboxyaldehyde acetal (14)

A solution of 3-thiophenecarboxyaldehyde (**13**) (10.0 g, 89.17 mmol) in benzene (100 ml) was added with 1,2-ethanediol (20 ml) and pyridinium p-toluensulfonate (4.1 g); the resulting mixture was refluxed with water separation by a Dean-Stark trap until the starting aldehyde was completely reacted (ca. 6 h). Solvent was removed under reduced pressure, diethylether was added and the crude was washed with a sodium hydrogen carbonate solution and saturated sodium chloride solution. The organic phase was dried with sodium sulfate, the solvent was removed under reduced pressure and the residue was distilled ($3\bullet10^{-1}$ mbar, 55°C) to give 10.5 g of the desired product in 75% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.42 (dd, J(H,H) = 3.15 Hz,^{4}J(H,H) = 0.92 Hz,1 H; Th-H_2), 7.32 (dd, J(H,H) = 3.15 Hz,^{4}J(H,H) = 5.08 Hz,1 H; Th-H_5), 7.18 (dd, J(H,H) = 3.15 Hz, J(H,H) = 5.08 Hz,1 H; Th-H_4), 5.91 (s, 1H; O-CH-O), 4.08 ppm (dm; CH_2-CH_2).

3,3’-Diformylacetal-2,2’-bithiophene (15)

n-Butyllithium (12 ml, 30 mmol, 2.5 M in hexane) was added dropwise to a stirred solution of diisopropylamine (2.90 g, 28.7 mmol) in 25 ml of dry THF, at -78°C under argon atmosphere. After 120 minutes, 3-thiophencarboxyaldehyde-acetal (**14**) (4.50 g, 28.7 mmol) in 35 ml of dry THF was added dropwise; the resulting mixture was stirred at low temperature for further 30 minutes. Then 4.50 g of anhydrous $CuCl_2$ was added in one portion, the reaction bath was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phase was washed, dried over $MgSO_4$ and evaporated under reduced pressure. The raw product was purified by flash chromatography (silica gel, 8:2 petroleum ether: ethyl acetate) and recrystallized from petroleum ether/CH_2Cl_2 (8:2), to afford 1.99 g (45 %) of the title product as white crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$,): δ= 7.36 (d, ^{3}J(H,H) = 5.44 Hz, 2H; Th-H_5,H_5’), 7.21 (d, ^{3}J(H,H) = 5.44 Hz, 2H; Th-H_4,H_4’), 5.72 (s, 2H; O-CH-O), 4.11 (m, 4H; acetal) 3.93 ppm (m, 4H; acetal).

5,5’-Dibromo-3,3’-diformylacetal-2,2’-bithiophene (16)

NBS (3.57 g, 20.0 mmol) was added portion wise to a stirred solution of 3,3’-diformylacetal-2,2’-bithiophene (3.11 g, 10.0 mmol) in freshly distilled DMF (15 ml) at room temperature in the dark. The suspension was stirred for 5 hours, until the reaction got complete, poured onto ice and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The raw product was purified using flash chromatography (silica gel, 8:2 petroleum ether: ethyl acetate) to afford 2.30 g (48% yield) of the desired product as a pale yellow crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.16 (s, 2H; Th-H_4,H_4’), 5.66 (s, 2H; O-CH-O), 4.089 (m, 4H; acetal) 3.94 ppm (m, 4H; acetal).

1.50 g of a yellow powder were also obtained, which corresponds to the asymmetrical deprotected product, 5,5`-dibromo-3’-(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-3-carbaldehyde (**17**). ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 9.70 (s, 1H; CHO), 7.49 (s, 1H; Th-H), 7.23 (s, 1H; Th-H) 5.61 (s, 1H; O-CH-O), 4.06 (m, 2H; acetal) 3.94 ppm (m, 2H; acetal).

5,5’-Dibromo-3,3’-diformyl-2,2’-bithiophene (18)

METHOD A: A solution of 5,5’-dibromo-3,3’-diformylacetal-2,2’-bithiophene (2.25 g, 4.8 mmol) in 120 ml of acetone containing pyridinium tosylate (PPTS) (1.05 g) was refluxed until the reaction was complete (usually 2 days, thin layer test). The solvent was then removed under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with a sodium hydrogen carbonate solution and a saturated sodium chloride solution. The organic phase was dried and evaporated to give the title product in quantitative yield.

METHOD B: A solution of 5,5`-dibromo-3’-(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-3-carbaldehyde (2.00 g, 4.72 mmol) in 100 ml of acetone containing pyridinium tosylate (PPTS) (600 mg) was refluxed until the reaction was complete (usually 2 days thin layer test). The solvent was then removed under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with a sodium hydrogen carbonate solution and a saturated sodium chloride solution. The organic phase was dried and evaporated to give the title product in quantitative yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 9.75 (s, 2H; CHO), 7.58 ppm (s, 2H; Th-H_4,H_4’).

4,4’(3,3’-Di(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-5,5’-diyl)-bis(2,6-di-tert-butylphenol) (AXX)

To a solution of 5,5’-dibromo-3,3’-diformylacetal-2,2’-bithiophene (650 mg, 1.38 mmol) and $Pd(PPh_3)_4$ (160 mg, 0.14 mmol) in previously degassed DME (2:1 with respect to water), tris[3,5-di-tert-butylphenol-4-(trimethylsilyloxy)phenyl]boroxyne (**5**) (1.27 mg, 1.38 mmol) and Na_2CO_3 (1.31 g, 12.4 mmol) aq solution (1 M) were rapidly added. The resulting mixture was refluxed 19 hours. Then, it was allowed to cool to room temperature, poured into water and extracted with diethyl ether. The organic layers were combined, dried over Na_2SO_4 and filtered. After solvent removal a yellow powder was obtained. The crude was firstly washed with hot ethanol and then with ethyl acetate to yield 956 mg (96% yield) of the desired product as a bright yellow powder.

^{1}H-NMR (400 MHz, $CDCl_3$,): δ= 7.40 (s, 4H; Ph-H), 7.25 (s, 2H; Th-H_4,H_4’), 5.77 (s, 2H; O-CH-O), 5.29 (s, 2H; -OH), 4.16 (m, 4H; acetal) 3.96 (m, 4H; acetal), 1.48 ppm (s, 36H; t-Bu); HRMS (ESI): m/z calcd for $C_{42}H_{54}O_6S_2+H^+$: 741 [M+ Na^+], found: 741.3 (M+Na^+).

4,4`-(3,3`-di(1,3-dioxolan-2-yl)-5H,5`H-[2,2`-bithiophenylidene]-5,5`-diylidene)bis(2,6-di-tert-butylcyclohexa-2,5-dienone) (QXX)

METHOD A: To a solution of 4,4’(3,3’-di(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-5,5’-diyl)bis(2,6-di-tert-butylphenol) (**AXX**) (70 mg, 0.097 mmol) in CH_2Cl_2 (24 mL), $K_3Fe(CN)_6$ (320 mg, 0.97 mmol) and a 0.4 M aq. solution of KOH (546 mg, 9.74 mmol) were added. The resulting mixture was stirred until the starting material was completely reacted (≈ 2 hours). The reaction mixture was extracted with methylene chloride and washed with water and the organic solvent was removed under reduced pressure. The raw product was washed with toluene to afford 61 mg (87 % yield) of **QXX** as iridescent green solid.

METHOD B: To a solution of 4,4’(3,3’-di(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-5,5’-diyl)bis(2,6-di-tert-butylphenol) (**AXX**) (20 mg, 0.028 mmol) in CH_2Cl_2 (8 mL), MnO_2 (17 mg, 0.190 mmol) was added. The resulting mixture was stirred until the starting material was completely reacted (≈ 2 hours and 40 minutes). The reaction mixture was filtered and the organic solvent was removed under reduced pressure. The desire product was collected as iridescent green solid in quantitative yield.

^{1}H NMR (400 MHz; $CDCl_3$): δ= 7.41 (br. s; Ph-H) 7.31 (br. s; Th-H_4,H_4’), 5.72 (s, 2H; O-CH-O), 4.25 (m, 4H; acetal),4.15 (m, 4H; acetal), 1.42 ppm (s, 36H; t-Bu);

HRMS (ESI): m/z calcd for $C_{42}H_{52}O_6S_2+H^+$: 717 [M+H^+], found: 717.3 (M^+).

5,5’-Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-[2,2’-bithiophene]-3,3’-dicarbaldehyde (ACO)

METHOD A: To a solution of 5,5’-dibromo-3,3’-diformyl-2,2’-bithiophene (**18**) (500 mg, 1.32 mmol) and $Pd(PPh_3)_4$ (151 mg, 0.13 mmol) in previously degassed DME (2:1 with respect to water),tris[3,5-di-tert-butylphenol-4-(trimethylsilyloxy)phenyl] boroxine (**5**) (1.2 mg, 1.32 mmol) and Na_2CO_3 (1.25 g, 11.8 mmol) aq solution (1 M) were rapidly mixed. The resulting mixture was refluxed 18 hours. After cooling to room temperature, it was poured into water and extracted with diethyl ether. The organic layers were combined, dried over Na_2SO_4 and filtered. By solvent removal, a dark yellow powder was obtained. The crude was washed with hexane and then with ethanol to yield 549 mg (87% yield) of the desired product as a light yellow powder.

METHOD B: A solution of 4,4’(3,3’-di(1,3-dioxolan-2-yl)-[2,2’-bithiophene]-5,5’-diyl)-bis(2,6-di-tert-butylphenol) (**AXX**) (150 mg, 0.208 mmol) in 10 ml of acetone containing pyridinium tosylate (PPTS) (133 mg) was refluxed for 16 hours. The solvent was then removed under reduced pressure and the residue was dissolved in DCM and washed with a sodium hydrogen carbonate solution and a saturated sodium chloride solution. The organic phase was dried and solvent evaporated to give the title product in quantitative yield as a light yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 9.93 (s, 2H; CHO), 7.66 (s, 2H; Th-H_4,H_4’), 7.44 (s, 4H; Ph-H), 5.77 (s, 2H; O-CH-O), 5.43 (s, 2H; -OH), 1.49 ppm (s, 36H; t-Bu); HRMS (ESI): m/z calcd for $C_{38}H_{46}O_4S_2+H^+$: 631 [M+H^+], found: 629.4 (M^+);

5,5`-bis(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5H,5`H-[2,2`-bithiophenylidene]-3,3`-dicarboxylic acid (QCO)

METHOD A: To a solution of 5,5’-bis(3,5-di-tert-butyl-4-hydroxyphenyl)-[2,2’-bithiophene]-3,3’-dicarbaldehyde (**ACO**) (30 mg, 0.052 mmol) in CH_2Cl_2 (24 mL), $K_3Fe(CN)_6$ (172 mg, 0.52 mmol) and a 0.4 M aq. solution of KOH (293 mg, 5.23 mmol) were added. The resulting mixture was stirred until the starting material was completely reacted (≈ 2 hours). The reaction mixture was extracted with methylene chloride and washed with water and the organic solvent was removed under reduced pressure. The raw product was washed with toluene to afford 26 mg (84 % yield) of **QCO** as an iridescent dark green/red solid.

METHOD B: To a solution of 5,5’-bis(3,5-di-tert-butyl-4-hydroxyphenyl)-[2,2’-bithiophene]-3,3’-dicarbaldehyde (**ACO**) (30 mg, 0.0475 mmol) in CH_2Cl_2 (10 mL), MnO_2 (30 mg) was added. The resulting mixture was stirred until the starting material was completely reacted (≈ 2 hours and 30 minutes). The reaction mixture was filtered and the organic solvent was removed under reduced pressure. The desired product was collected as iridescent dark green/red solid in quantitative yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 9.2-9.4 (br. s), 1.48 ppm (s; t-Bu).

HRMS (ESI): m/z calcd for $C_{38}H_{44}O_6S_2+H^+$: 661 [M+H^+], found: 661.7 (M^+)

4-Bromo-2,6-dimethoxyphenol (20)

2,6-Dimethoxyphenol (1.0 g, 6.5 mmol) was dissolved in $CHCl_3$ (10 mL). EtOH (0.08 mL) and 50% NaH aq. Solution (3 mg, 0.13 mmol) were added and the mixture was cooled to -78°C. NBS (1.15 g, 6.48 mmol) was added portion wise and stirred at this temperature for 1 hour. Then, the cooling bath was removed and stirred at room temperature for 30 min and at 65 °C for 5 min. The reaction mixture was allowed to cool to room temperature and solvent was removed under reduced pressure. The yellowish residue obtained was dissolved in diethylether and filtered. The solvent was evaporated to obtain a yellow solid which was stirred in heptane (12 mL) at 85 °C for 15 min. The yellowish-brown oil was filtered through celite pad. The filtrate was allowed to recrystallize to give 1.0 g of the desired product as a white solid (66% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 6.73 (s, 2H; Ph-H), 5.41 (s, 1H; -OH), 3.88 ppm (s, 6H; -OCH_3).

4,4’-([2,2’-Bithiophene]-5,5’-di-yl)bis(2,6-dimethoxyphenol) (AMeOMeO)

METHOD A: A solution of 4-bromo-2,6-dimethoxyphenol (**20**) (52 mg, 0.224 mmol) and 5,5’-bis(trimethylstannyl)2,2’-bithiophene (50 mg, 0.102 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01

mmol) in anhydrous toluene, were thoroughly mixed in a process vial. The vial was capped, the mixture was heated under microwave irradiation conditions at 150°C and 150 W for 53 minutes, and then the process vial was allowed to cool to room temperature. The reaction mixture was extracted with ethyl acetate, the organic fractions were combined, dried over Na_2SO_4 and filtered. After solvent removal the raw product was purified using flash chromatography (silica gel, 7:3 hexane: ethyl acetate) to afford 15 mg (32% yield) of **AMeOMeO** as yellow solid.

METHOD B: A solution of 4-bromo-2,6-Dimethoxyphenol (325 mg, 1.40 mmol), $Pd(PPh_3)_4$ (70 mg, 0.061 mmol) and 5,5’-bis(trimethylstannyl)2,2’-bithiophene (300 mg, 0.61 mmol) in anhydrous toluene (52 mL) was refluxed for 5 hours. Then, it was allowed to cool to room temperature, poured into water and extracted with ethyl acetate. The organic fractions were combined together, dried over Na_2SO_4, filtered, and then the solvent was removed under reduced pressure. The raw product was purified using flash chromatography (silica gel, 1:1 hexane: ethyl acetate) to afford 88 mg (30% yield) of **AMeOMeO** as a dark yellow solid.

METHOD C: A solution of 4-bromo-2,6-dimethoxyphenol (**20**) (50 mg, 0.215 mmol) and 5,5’-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2’-bithiophene (41 mg, 0.09 mmol), Na_2CO_3 (86 mg, 0.81 mmol) aq solution (1 M) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) in previously degassed DME (2:1 with respect to water) were thoroughly mixed in a process vial. The vial was capped, the mixture was heated under microwave irradiation conditions at 130°C and 150 W for 42 min, and then the process vial was allowed to cool to room temperature. The reaction mixture was extracted with ethyl acetate, the organic fractions were combined, dried over Na_2SO_4 and filtered. After solvent removal the raw product was purified using flash chromatography (silica gel, 7:3 hexane: ethyl acetate) to afford 3 mg (7% yield) of **AMeOMeO** as yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.13 (d, ^{3}J(H,H)=3.71 Hz, 2H; thiophene), 7.12 (d, ^{3}J(H,H)= 3.71 Hz, 2H; thiophene), 6.82 (s, 4H; Phenyl-H), 5.55 (s, 2H; -OH), 3.96 ppm (s, 12H; $-OCH_3$);

HRMS (ESI): m/z calcd for $C_{24}H_{22}O_6S_2$+ Na^+: 493 [M+ Na^+], found: 493.4 (M+Na^+).

The monosubstituted product, 4-([2,2’-bithiophen]-5-yl)-2,6-dimethoxy phenol (**22**), was obtained as main product in METHOD C (yield 46%), while as a by product in METHOD A and B:

^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.61 (br. d, 2H; Th-H), 7.39 (br. m, 2H; Th-H), 7.14 (br. m, 3H; Th-H) 6.83 (s, 2H; Ph-H), 5.55 (s, 1H; -OH), 3.96 ppm (s, 6H; $-OCH_3$).

5,5'-Bis(3,5-di-methoxy-4-oxo-2,5-cycloexadien-1-ylidene)-5,5'-dihydro-2,2'-bithiophene (QMeOMeO)

To a solution of **AMeOMeO** (5 mg, 0.012 mmol) in benzene (22 mL), $K_3Fe(CN)_6$ (40 mg, 0.11 mmol) and a 0.1 M aq. solution of KOH (67mg, 1.1 mmol) were added. The resulting mixture was stirred until the starting material was completely reacted (≈ 45 minutes). The reaction mixture was filtered and the solid was washed with toluene. The desired product was collected as a dark blue solid in quantitative yield.

HRMS (ESI): m/z calcd for $C_{24}H_{20}O_6S_2$+H+: 469 [M+H+], found: 469.4 (M+);

4,4`-([2,2`-bithiophene]-5,5`-diyl)bis(2-(trifluoromethyl)phenol) (ACF_3CF_3)

To a solution of 4-bromo-2-(trifluoromethyl)phenol (**20**) (338 mg, 1.403 mmol) in anhydrous toluene (50 mL), $Pd(PPh_3)_4$ (80 mg, 0.0609 mmol) and 5,5’-bis(trimethylstannyl)2,2’-bithiophene (**24**) (300 mg, 0.6099 mmol) were rapidly mixed. The resulting mixture was refluxed 14 hours. Then, it was allowed to cool to room temperature, poured into water and extracted with ethyl acetate. The organic fractions were combined together, dried over Na_2SO_4, filtered, and then the solvent was removed under reduced pressure. The raw product was purified using flash chromatography (silica gel, 1:1 hexane: dichloromethane) to afford 160 mg (54% yield) of **ACF_3CF_3** as a dark yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$):δ 7.72 (d, ^{4}J(H,H)= 1.76, Hz 2H; phenyl-H), 7.63 (dd, ^{3}J(H,H)= 8.59 Hz, ^{4}J(H,H)= 1.76 Hz, 1H; phenyl-H), 7.15 (s, 4H; thiophene), 7.00 (d, ^{3}J(H,H)= 8.39 Hz, 1H; phenyl-H), 6.82 (s, 2H; phenyl-H), 5.55 (s, 1H; -OH), 5.52 (s, 1H; -OH), 3.96 ppm (s, 6H; $-OCH_3$);

HRMS (ESI): m/z calcd for$C_{22}H_{12}F_6O_2S_2$- H^+: 485 [M - H^+], found: 485.3 (M-H^+).

5,5'-Bis(3-trifluoromethyl-4-oxo-2,5-cycloexadien-1-ylidene)-5,5'-dihydro-2,2'-bithiophene (QCF_3CF_3)

To a solution of **ACF_3CF_3** (4 mg, 0.0082 mmol) in benzene (4.1 mL), $K_3Fe(CN)_6$ (27 mg, 0.082 mmol) and a 0.4 M aq. solution of KOH (46 mg, 0.82 mmol) were added. The resulting mixture was stirred until the starting material was completely reacted (≈ 1 hour). The reaction mixture was filtered and the solid was washed with toluene. The desired product was collected as a dark green solid in quantitative yield.

HRMS (ESI): m/z calcd for $C_{22}H_{10}F_6O_2S_2$+H^+: 485 [M+H^+], found: 485.3 (M^+).

4-(5`-(4-hydroxy-3-(trifluoromethyl)phenyl)-[2,2`-bithiophen]-5-yl)-2,6-dimethoxyphenol ($AMeOCF_3$)

A solution of 4-bromo-2-(trifluoromethyl)phenol (**23**) (252 mg, 1.05 mmol), 4-bromo-2,6-Dimethoxyphenol (**20**) (244 mg, 1.05mmol), $Pd(PPh_3)_4$ (97 mg, 0.105 mmol) and 5,5’-bis(trimethylstannyl)2,2’-bithiophene (**24**) (415 mg, 0.844 mmol) in anhydrous toluene (60 mL) was refluxed for 5 hours. Then, it was allowed to cool to room temperature, poured into water and extracted with ethyl acetate. The organic fractions were combined together, dried over Na_2SO_4, filtered, and then the solvent was removed under reduced pressure. The raw product was purified using flash chromatography (silica gel, 1:1 hexane: ethyl acetate) to afford 140 mg (34% yield) of **$AMeOCF_3$** as dark yellow solid. 4,4`-([2,2`-bithiophene]-5,5`-diyl)bis(2-(trifluoromethyl)phenol) (ACF_3CF_3) and 4,4’-([2,2’-bithiophene]-5,5’-diyl)bis(2,6-methoxyphenol) (AMeOMeO)

were obtained as byproducts respectively in 10% (39 mg) and 4% (16 mg) yields.
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, ^{4}J(H,H) = 1.37 Hz, 1H; Ph-H), 7.64 (dd, ^{3}J(H,H) = 8.59 Hz, ^{4}J(H,H) = 1.95 Hz, 1H; Ph-H), 7.14 (m, 4H; Th-H), 7.00 (d, ^{3}J(H,H) = 8.59 Hz, 1H; Ph-H), 6.82 (s, 2H; Ph-H), 5.55 (s, 1H; -OH), 5.52 (s, 1H; -OH), 3.96 ppm (s, 6H; $-OCH_3$);
HRMS (ESI): m/z calcd for $C_{23}H_{17}F_3O_4S_2$- H^+: 477 [M - H^+], found: 477.4 (M - H^+).

2,6-dimethoxy-4-((2,5`)-5`-(4-oxo-3-(trifluoromethyl)cyclohexa-2,5-dien-1-ylidene)-5,5`-[2,2`-bithiophenyllidene]-5-ylidene)cyclohexa-2,5-dienone (QMeOCF$_3$)

To a solution of **AMeOCF$_3$** (5 mg, 0.0105 mmol) in benzene (21 mL), $K_3Fe(CN)_6$ (35 mg, 0.105 mmol) and a 0.1 M aq. solution of KOH (59 mg, 1.05 mmol) were added. The resulting mixture was stirred until the starting material was completely reacted (≈ 1 hour and 30 minutes). The reaction mixture was filtered and the solid was washed with toluene. The desired product was collected as a dark green solid in quantitative yield.
HRMS (ESI): m/z calcd for $C_{23}H_{15}F_3O_4S_2+H^+$: 477 [M+$H^+$], found: 477.3 ($M^+$).

Measurements and characterization

^{1}H-NMR spectra were collected using a Bruker ARX 400 NMR spectrometer. Mass spectroscopy was carried out with a Bruker Esquire 3000 plus mass spectrometer. UV-vis absorption spectra were recorded with a Cary 5000 spectrophotometer (Varian). Raman spectra were recorded with a Nicolet FT-Raman Nexus NXR 9650 that employs Nd/YAG laser with excitation at λ=1064 nm and a Horiba Jobin Ivon Labram HR800 with an excitation light at 632 nm. The X-ray data were collected on a Bruker X8 Prospector APEX-II/CCD diffractometer, using CuKα radiation (λ=1.54050). The structure was solved by direct methods and refined using the SHELX-97 package. [23]

X-ray crystallographic analysis

CCDC-1029034 contains 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%5Frequest/cif.

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