Synthesis and Characterization of Conjugated Mono- and Dithiol Oligomers and Characterization of Their Self-Assembled Monolayers

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The characterization of self-assembled monolayer molecular arrays, which serve as active layers in electronic devices, is an important step toward understanding molecular-scale electronics. To correlate the properties of self-assembled monolayers with their molecular structures, a series of conjugated mono- and dithiols and aromatic dithiols with an oxygen or sulfur atom between two aromatic units have been designed and synthesized. Their optical properties were determined by UV−vis spectroscopy. Their self-assembled monolayer films on gold surfaces were characterized by cyclic voltammetry, grazing incidence Fourier transform infrared spectroscopy (GI-FTIR), and contact angle and ellipsometry measurements. Increasing the chain length from two to four phenyl rings showed a more than linear increase of the intensity of the aromatic C−C ring stretch modes in GI-FTIR, indicating that the longer p-phenylene system is oriented toward the surface normal. Similar to oligothiophenes, when the number of repeat units for oligophenylene is increased, a more than linear increase of the intensity of the C−H bend modes implies that the longest oligothiophenenedithiol molecule is oriented close to the surface normal. Ellipsometry showed a smaller deviation from the calculated monolayer thickness with increasing number of thiophene or phenylerynerings, corroborating the GI-FTIR data. We conclude that the conjugated phenylene- and thiophene-based dithiols demonstrate a less tilted molecular orientation with respect to the surface normal with increasing chain length.

Introduction
With the advent of research activities in nanoscale molecular electronic devices,1−8 organic thiol compounds have received a great deal of attention in recent years.9,10 Because of their intrinsic semiconductor11−16 or insulator17−21 properties, conjugated thiol-capped compounds such as oligo(1,4-phenylene ethynylene) and oligo(2,5-thiophene ethynylene) have been widely studied as molecular wires.22−29 The broad applications of these materials are attributed to their potential to be used in semiconducting and conducting electronic and optoelectronic devices, some of which include field-effect transistors,22−25 light-emitting diodes,26−29 exciton diffusion in Langmuir−Blodgett films,30 and molecular rectifiers.22,26 All these applications are realized through the self-assembly of conjugated thiol-capped molecules on a substrate surface. These conjugated molecules self-assemble into ordered monolayers, which allow electronic and electrical transport across the conjugated molecules through the monolayer.10,18−21,31 Therefore, the design of conjugated molecules with functional properties is essential for the preparation of conjugated molecules for use in these applications.10,18−21,31 The self-assembly of conjugated thiol-capped molecules into ordered monolayers on metal surfaces provides a fundamental understanding of the importance of the molecular structure−monolayer−substrate interaction on the properties of conjugated solids on metal surfaces, as well as the control of molecular self-assembly of conjugated thiol-capped molecules at surfaces.10,18−21,31

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The synthesis and characterization of SAMs of conjugated thiol compounds is limited. These rigid conjugated thiols with tunable electronic properties are attractive candidates for molecular electronic devices. In this paper, we report the synthesis of various conjugated mono- and dithiol oligomers in order to understand the effect of molecular structure on self-assembled monolayer formation. Four types of synthetic strategies were used, depending on the target molecules. The optical band gap of the molecules was determined by UV–vis spectroscopy. The self-assembled monolayers were characterized by grazing incidence Fourier transform infrared spectroscopy (GI-FTIR), contact angle measurements, ellipsometry, and cyclic voltammetry. The detailed results of this characterization, together with the synthetic strategies, are presented in this paper.

**Results and Discussion**

**Synthesis.** A wide variety of aromatic and heteroaromatic thiols were synthesized to understand the structure–property relationships. Since aromatic dithiol compounds are usually easily oxidized and likely to polymerize through disulfide formation and, therefore, are difficult to handle, we used acetyl protection for the thiol functional groups similar to those described by Tour et al. The synthesis and characterization of SAMs of conjugated thiols is limited. These rigid conjugated thiols with tunable electronic properties are attractive candidates for molecular electronic devices. In this paper, we report the synthesis of various conjugated mono- and dithiol oligomers in order to understand the effect of molecular structure on self-assembled monolayer formation. Four types of synthetic strategies were used, depending on the target molecules. The optical band gap of the molecules was determined by UV–vis spectroscopy. The self-assembled monolayers were characterized by grazing incidence Fourier transform infrared spectroscopy (GI-FTIR), contact angle measurements, ellipsometry, and cyclic voltammetry. The detailed results of this characterization, together with the synthetic strategies, are presented in this paper.

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Sulfonyl chloride in this case has been performed with the biphenyl moiety (8a affects the conjugation, a planar fluorene homologue which was therefore synthesized (Scheme 1). Reduction of the dithiol derivatives of the above reaction (Scheme 2) afforded an analogous monothiol derivative of 1,4-dithiencyclohexane (23a).

Different coupling reactions were employed to synthesize longer oligomeric aromatic cores (Schemes 3–5). In this case, the thiol group has to be protected to avoid side reactions. Acetyl-protected thiols are found to work well for the coupling reactions between phenylacetylene and aryl halides. This method has been used by Tour's group to synthesize molecular wires as long as 128 Å. Accordingly, diphenylacetylene was prepared in a one-step cross-coupling reaction (Scheme 3) to study the influence of the acetylene linker.

For other types of coupling reactions, methyl-protected thiols were found to give higher yields of the products that can be deprotected almost quantitatively using the recently reported method of Gingras and co-workers. Thus, Suzuki coupling of 4-(methylthio)phenylboronic acid with different dibromophenyl and dibromophenyl homologues gave phenylene-thiophene and oligophenylenethiophene derivatives, respectively. They were demethylated with sodium tert-butylthiolate and subsequently protected with acetyl groups to give the target dithioacetyl derivatives (Scheme 4).

Diphenylacetylene derivatives were synthesized as an electron acceptor analogue of 1,5-naphthalenediethiol (12a).

Aromatic Grignard reagents and lithium compounds can react with sulfur, followed by acetylation, to give aromatic thioacetyl derivatives (Scheme 2). This method is most useful for thiophene-containing oligomers (such as compounds 15 and 17) and aromatic halides (such as compounds 13 and 19). However, an excess of organometallic compound with respect to sulfur is essential to prevent the formation of disulfides. Octafluoro derivative 20 was synthesized as an electron acceptor analogue of biphenyl dithiol (Scheme 2). Controlling the stoichiometry of the above reaction (Scheme 2) afforded an analogous monothiol derivative of 1,4-dithiencyclohexane (23a).

Incorporation of heteroatoms (N, O, S, Se) in phenyl-based systems has been shown to transmit electronic effects efficiently. Therefore, the dithiol derivatives of phenyl ether 5a and phenylthioether 6a were synthesized (Scheme 1). Arylsulfonyl chlorides 3 and 4, prepared by direct chlorosulfonation of phenyl (thio)ether, were reduced with zinc dust amalgam to give dithiols 5a and 6a, respectively, which were protected by acylation. Since the biphenyl moiety (8a) is twisted in solution, which affects the conjugation, a planar fluorene homologue 11a was therefore synthesized (Scheme 1). Reduction of the sulfonyl chloride in this case has been performed with stannous chloride in HCl-saturated acetic acid. This method was found to be particularly useful for those less soluble aryl dithiols with higher melting points (such as 1,5-naphthalenediethiols 12a).

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A Cu(I)-catalyzed coupling reaction of 5-methylthio-
2,2′-bithiophene-5-lithium followed by the above-men-
tioned demethylation—acylation sequence yielded com-
pound 38 with a quaterthiophene aromatic core (Scheme 5).

**Self-Assembled Monolayer Formation.** The self-
assembly of alkanethiols is usually carried out under
relatively high concentrations (1–10 mM). However, the self-
assembly of conjugated mono- or dithiols has to be per-
formed in much more dilute solutions (<1 mM) to avoid
multilayer formation (see below) and precipitation due to
poor solubility of some conjugated thiols. In addition,
conjugated thiols can easily dimerize due to oxidative
disulfide formation. Therefore, in situ deprotection of
thioacetyl groups by addition of NH4OH was used to
generate free thiols in nearly quantitative yield. 23 Acetyl-
protected monothiols completely suppress dimerization
and form good-quality SAMs. For dithiols, however, Tour
protected monothiols completely suppress dimerization
generate free thiols in nearly quantitative yield. 23 Acetyl-
tected ter- and quaterthiophenes
respectively) were observed as a result of oxidation of the highly
air-sensitive oligothiophene dithiols (the intensity of this

**Absorption Spectra.** The UV–vis spectra of the mono-
and dithiol oligomers were recorded in tetrahydrofuran
(THF) solution using 10 × 10 mm quartz cells and a
spectral range of 200–700 nm. The lowest energy UV–vis
absorption peaks (λ_{max}) of the studied aromatic acetyl-
protected thiols are listed in Table 1. The absorption bands
were practically unchanged after deprotection. For depro-
tected ter- and quaterthiophenes 16 and 38, however,
additional lower energy bands (459 and 490 nm, respec-
tively) were observed as a result of oxidation of the highly
air-sensitive oligothiophene dithiols (the intensity of this

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**Cyclic Voltammetry.** The electrochemistry of redox
active SAMs has attracted broad attention for the past
decade. 67–69 Besides being an invaluable tool in studying
SAMs, it was used in SAM-based sensing devices 69b,c as
well as for chemical modification of self-assembled mol-
ecules. 67 The electrochemical behavior of the studied
aromatic thioacetyl derivatives in solution is represented
by a multielectron irreversible or partially quasi-reversible
oxidation wave (Table 1), which splits into two unresolved
waves in some cases. As expected, the oxidation potential
depends strongly on the nature of the conjugated core:
icorporation of electron-rich thiophene units facilitates
the oxidation process; the lowest oxidation potential was
found for quaterthiophene 38a. Extension of the π-conju-
gation by introducing p-phenylene units also substanc-
tially decreases the E_{\text{ox}} values (cf. 18 or 32 vs 14), but in
the case of the pure oligophenylene backbone (8 → 33
→ 34) this tendency is not so pronounced, as a result of poor
conjugation in oligophenylene due to significant twisting
of benzene rings. Figure 1 shows the cyclic voltammetric
behavior of terthiophene 16 (in solution) and SAM 16a.
In both cases, scanning into positive potentials resulted in
a partially reversible oxidation wave whose position is
sensitive to the scan rate. The chemical reversibility (i.e.,
cathodic to anodic peak current ratio) increased at higher
scan rates, indicating that a slow irreversible chemical
reaction follows the oxidation. Multiple scanning of the
SAM between 0 and 1.35 V resulted in disappearance of
the oxidation wave. The irreversibility of radical cation
formation is a common feature of short oligothiophenes,
even though some derivatives (e.g., 39) can give a very
stable radical cation. 53 In the case of 39, oxidation occurs as
two single electron waves at E_{\text{ox}}^{0} = 0.86 and 1.02 V
versus saturated calomel electrode (SCE), respectively (ca.

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surface normal, that is, perpendicular to the gold surface.\(^7\)^2 A nonzero component of the transition moment along the direction of the transition dipole moment onto the surface normal. This implies that one can only probe IR modes that have a transition dipole moment oriented along the molecular axis,\(^7\)^2 Therefore, the measured infrared band intensity of a molecule depends on the projection of its transition dipole moment in the plane of the molecule and perpendicular to it.\(^6\) The detailed study of the electrochemistry of SAMs of this and other oligothiophene derivatives is under way.

**Grazing Incidence FTIR and Ellipsometry.** Ever since the discovery of SAMs of alkanethiolates absorbed on metal surfaces,\(^3\)^1 GI-FTIR has been used as a powerful technique to determine the orientation of aliphatic molecules tethered to the surface.\(^7\)^2 With GI-FTIR on metal substrates (or any near-perfect conductor at IR frequencies), the component of the external electric field (IR light) parallel to the surface plane is almost completely screened by the electronic polarization of the metal. Therefore, the measured infrared band intensity of a vibrational mode directly depends on the projection of its transition dipole moment onto the surface normal. This implies that one can only probe IR modes that have a nonzero component of the transition moment along the surface normal, that is, perpendicular to the gold surface.\(^7\)^2 With the increasing interest in self-assembled monolayers of conjugated (or semiconducting) thiols on gold substrates for molecular electronics, a detailed picture of the orientation of conjugated thiols with respect to the gold surface is required. The combination of GI-FTIR and ellipsometry can provide information on the intrinsic structure of the SAMs and provide a better understanding of those monolayers and eventually of device performance. We found that the SAM film thicknesses measured by ellipsometry are in good agreement with the calculated molecular lengths. This, together with the GI-FTIR results discussed below, is a good indication that only one monolayer of mono- or dithiol molecules was deposited with the long molecular axis pointing along the gold surface normal (edge-on on the gold surface) (Table 3). The average film thickness, measured at different spots of the same film (as large as 10 cm\(^2\)), differs only by a few angstroms. The difference between the measured and calculated thicknesses might be a result of a small tilt with respect to the surface normal of the molecules in the monolayer or the average value used for the refractive index of the SAM in calculating the layer thickness from the measured psi (\(\psi\)) and delta (\(\delta\)) values (1.55 and 1.45 for all the conjugated thiols\(^3\)^3 and hexadecanethiol,\(^3\)^5 respectively).

All the vibrational bands observed in the GI-FTIR spectra of oligothiophene SAMs are assigned according to ref 74. For the SAMs of compounds 18a, 23a, 31a, and 32a on gold, a combination of vibrational modes found in oligophenylenes (8a, 33a, and 34a) and oligothiophenes (14a and 16a) is invoked, as described below. In all the spectra taken on compounds containing thiophene rings, broad peaks are present at 1170–1180 cm\(^{-1}\) and around 1330 cm\(^{-1}\) and are assigned to an oxidized sulfur species, probably a sulfone. The intensity of the ~1175 cm\(^{-1}\) peak increases upon exposure to air. A similar broad peak has also been reported for phenyleneethynylene-based thiols and was assigned to the S=O stretching of sulfone.\(^2\)^3 Furthermore, one can infer from the GI-FTIR spectra that the deprotection of the thioacetyl moiety is not quantitative for most phenyl-based compounds. Indeed, a relatively small amount of grafted molecules still possess a thioacetyl group, as evidenced by a band just above 1700 cm\(^{-1}\) that is assigned to a strong C=O stretching mode of the thioacetyl group.

Figure 2 illustrates the dependence of the component of the transition dipole moment along the surface normal on the orientation of the rigid conjugated thiol. The transition dipole moments are expressed with respect to the molecular coordinate system with \(L\) denoting a transition dipole moment oriented along the molecular axis, \(M\) a transition dipole moment in the plane of the molecule and perpendicular to \(L\), and \(N\) a transition dipole moment perpendicular to the molecular plane. In Figure 2A–C, different orientations of the rigid molecule are depicted with the out-of-plane mode \(N\) parallel to the gold surface (not IR active). Figure 2D illustrates a general dependence of the normal components of \(L\), \(M\), and \(N\) on the tilt angle (\(\alpha\)) and the rotation angle (\(\beta\)). Figure 2E,F illustrates the special cases where the molecule axis is parallel (\(\alpha = 90^\circ\)) to the gold surface (\(L = 0\)) and \(\beta = 0^\circ\) (Figure 2F, \(N = 1\) and \(90^\circ\) (Figure 2C, \(M = 1\)).

In GI-FTIR, one can clearly distinguish components of the stretching and bending modes that are perpendicular to the gold surface (Table 2). Spectra of SAMs of phenylene-based (Figure 3) and thiophene-based dithiols on gold (Figure 4) are given as typical examples. The spectra from phenylene-based dithiols (Figure 3) exhibit strong absorption signals due to the aromatic C=C ring stretch mode (~1475 cm\(^{-1}\), mostly oriented along \(L\), with a smaller component along \(M\) and the aromatic C–H stretch modes of phenyl rings (~3030 cm\(^{-1}\), components in \(M\) and \(L\)).

(70) Exhaustive electrolysis (at the potential of the anodic peak) of 16 consumes four to six electrons per molecule (depending on the electrolysis conditions), suggesting that not only the thiophene core but also the side thiol groups are subject to oxidation. However, this value is not in direct connection with the kinetically controlled CV experiment, due to the irreversible nature of the process.

(71) Integration of the anodic peak area gives (ref 31) the estimated surface coverage of ~2 × 10\(^{-9}\) mol cm\(^{-2}\), which corresponds to a molecular area of ca. 35 Å\(^2\), calculating for the two-electron process.

as also proposed for SAMs of terphenylenes, and other oligophenylenes favor π-π stacking, the average value of \( \beta \) may vary from system to system. Leung and co-workers showed that two different phases coexist for 4-methyl-4′-mercaptobiphenyl on gold: the striped phase with a tilt angle at least 15° from the surface normal and the hexagonal phase purely consisting of \((\sqrt{3} \times \sqrt{3})R30°\) structure. Very likely, this is also true for our 4,4′-dimercaptobiphenyl SAM on gold.

Research previously conducted on terphenylenethiol SAMs revealed that the observed phases depend on the solvent used. Furthermore, it was proposed that phenyl-, biphenyl- (35a), and terphenylenethiol (36a) can adopt two different orientations on a gold surface, namely, sp and sp\(^3\), where sp implies a straight bond Au-S-C (180°) and sp\(^3\) refers to an angle of \( \sim 120° \) for Au-S-C. The orientation dearly depends on the solvent used, suggesting that the solvent–molecule–substrate interactions and the decrease in entropy have to compete with π-π stacking interactions and the decrease in surface tension due to the sulfur–gold bond. The competition between two orientations results in a less ordered monolayer for terphenylenethiol. Our measurements show that biphenylenethiol (35a) and terphenylenethiol (36a) assemble with their out-of-plane C–H bend modes (oriented along N) parallel to the surface as witnessed by the complete disappearance of the out-of-plane C–H bend mode located at \( \sim 815 \text{ cm}^{-1} \), consistent with previous data from terphenylenethiol. This does not imply that the monothiols are oriented along the surface normal since relatively strong C–H vibration modes are still observed for 35a and 36a. The strong C–H vibration modes (along molecular coordinates M and L) and the disappearance of the out-of-plane C–H bend mode (along N) can only be explained by taking into account a small tilt angle (\( \alpha \)) and a rotation angle (\( \beta \)) of 90° (Figure 2B). Though the monothiols described above have a substantial dipole moment along the asymmetric phenyl chain, which can influence the packing when grafted on the gold surface, the class of dithiols used here are initially symmetric and thus have a very small dipole once grafted on the gold surface. Consequently, the more favorable interchain interaction will influence the packing on the gold surface similar to biphenyl systems with a small molecular dipole moment. The GI-FTIR data combined with the data obtained from ellipsometry (Table 3) suggest that increasing the number of phenyl rings forces the molecules to align vertically on the surface as observed previously in similar systems.

Both the symmetric and asymmetric C–H stretch modes of the CH2 bridge (\( \sim 2930 \text{ cm}^{-1} \)) of the fluorenedithiol (11a) SAM are not observed by GI-FTIR, implying that the CH2 planes are oriented parallel to the gold surface. Ellipsometry measurements also suggest that the fluorenedithiol layer thickness corresponds to the fully extended fluorene molecule oriented nearly along the surface normal. The other thiols that are also seen in 8a are dearly identified (Table 2).

Figure 2. Schematic illustration of various vibrational transition dipole moments (L, M, and N) and the dependence of their component along the surface normal (determining their IR activity) on molecular orientation. L, M, and N denote modes oriented along the chain axis and in-plane and out-of-plane modes oriented normal to the chain axis, respectively.

which implies that the phenylene-based compounds are oriented away from the gold surface (excluding the orientations in Figures 2C, E, F). The nonlinear increase of the intensity of the C–C aromatic ring stretch mode with the number of phenyl rings (8a at 1475 cm\(^{-1}\), 33a at 1479 cm\(^{-1}\), and 34a at 1479 cm\(^{-1}\)) shows that the tilt angle (\( \alpha \)) decreases in the same order. Furthermore, a shift of this peak (\( \sim 1475 \text{ cm}^{-1} \)) toward lower frequency would be expected for phenylenes with the long axis oriented away from the gold surface (excluding the \( \sim 1479 \text{ cm}^{-1} \)). Since some \( \alpha \) depends on the tilt angle at least 15° from the surface normal and the hexagonal phase purely consisting of \((\sqrt{3} \times \sqrt{3})R30°\) structure. Very likely, this is also true for our 4,4′-dimercaptobiphenyl SAM on gold.

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4,4′-Dimercaptooctafluorobiphenyl (20a) displays C–C ring stretch modes that are similar, although shifted and less intense, to those of its hydrogenated analogue (4,4′-dimercaptobiphenyl (8a)) and features in addition quite strong C–F stretch modes. Ellipsometry measurements demonstrate that its layer thickness is much lower than that of the hydrogenated analogue.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C–H wag</th>
<th>ring stretch + bend</th>
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<th>C–H bend</th>
<th>C–O(S)–C stretch</th>
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<td>814 (o)</td>
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<td>1603, 1670</td>
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<tr>
<td>12a</td>
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behavior for this series than for the phenylene-based dithiols. First, the GI-FTIR spectrum of a SAM of terthiophenedithiol shows "antiabsorption" or negative bands that are assigned to C–S stretch modes (735, 786, and 979 cm\(^{-1}\)) and C–H out-of-plane (799, 899, and 1046 cm\(^{-1}\)) modes. For monolayers on metal substrates, such unusual (Fano) bands have so far only been observed in a few cases of atomic and diatomic adsorbates.\(^{84,85}\) They are due to nonadiabatic interactions between an adsorbate vibrational mode and the surface electronic states or conduction electrons in the metal substrate, giving rise to narrow, highly asymmetric or negative features in the surface infrared absorption spectrum.\(^{94,85}\) In the present case, C–S antiabsorption bands might therefore indicate a specific chemical interaction of one or more thiophene rings of terthiophenedithiol with the Au substrate, most likely through a Au–S bond. If this infrared absorption mechanism applies, the antiabsorption bands should be accompanied by an increase in the broadband infrared absorption spanning the entire wavenumber regime probed. Such small broadband reflectivity changes, however, are not easy to quantify experimentally due to baseline fluctuations. To clarify the exact nature of these observed antiabsorption bands, more research will be conducted.

Second, the C=O mode at 1750 cm\(^{-1}\) has disappeared, confirming the complete deprotection of the thioacetyl end group. Third, a broad band appeared around 1165 cm\(^{-1}\), which is assigned to an oxidized species (probably a sulfone) as mentioned above. Finally, similarly to the oligo(phenylene) series, the intensity of the C–C and C–H modes increased more than linearly with increasing chain length, implying that the longer terthiophenedithiol and quaterthiophenedithiol have a smaller tilt angle \(\alpha\) than bithiophenedithiol. The increased intensity of the C–H out-of-plane mode (~800 cm\(^{-1}\)) is attributed to a difference of the rotation angle \(\beta\). As mentioned above, a small but nonzero tilt angle \(\alpha\) can yield quite strong out-of-plane C–H modes, especially if the rotation angle \(\beta\) is close to 0° (Figure 2D). Therefore, it is proposed that the tilt angle decreases with increasing number of thiophene units and that the rotation angle is close to zero for the thiophene-based dithiols. Ellipsometry measurements confirm this proposal, as the measured layer thickness of 14a is much smaller than the calculated length of the molecule, whereas the measured layer thickness of 38a is almost equal to the molecular length, and terthiophene 16a represents the intermediate scenario.

Contact Angle Measurement. Contact angle measurement is a simple and useful technique to determine the macroscopic surface properties of thin films.\(^{9,10,51,81}\) An increase in the contact angle of water for different lengths of oligophenylene adsorbates was used to prove an "edge-on" orientation of densely packed SAMs. Table 3 summarizes the advancing, receding, and static contact angles of water and hexadecane on the SAM-modified surfaces. Compared with the alkanethiols, aromatic thiols are more hydrophilic as indicated by the lower contact angles in Table 3. The conjugated thiols are almost fully wetted by hexadecane.\(^{81}\) Increasing the chain length of conjugated thiols reduces the dipole moment formed on the surface, which, in turn, results in a more hydrophobic character of the longer ring system. This is demonstrated by the increase in the advancing, receding, and static angles with the length of the self-assembled molecule

A series of aromatic and heteroaromatic acetyl-protected mono- and dithiol compounds with varied lengths and different aromatic backbones have been synthesized and characterized. UV–vis spectroscopy showed a red-shifted absorption maximum with increasing chain length, especially when thiophene rings were introduced in the conjugated molecule. Obviously, the optical band gap was also lowered when the aromatic system was extended. The redox behavior of the conjugated SAMs was investigated, and data on thienothioetherdithiol were discussed in more detail. The electrochemical behavior in solution exhibits a partially reversible oxidation wave. The formation of self-assembled monolayers of these conjugated mono- and dithiol compounds on gold was achieved by in situ deprotection of the corresponding acetylated derivatives. The resulting SAMs were studied by grazing incidence FTIR, contact angle, and ellipsometry measurements, confirming the formation of edge-on monolayer structures. On the basis of the combined data from GI-FTIR, ellipsometry, and contact angle measurements, we conclude that increasing the chain length of conjugated dithiol molecules results in a less tilted molecular orientation with respect to the surface normal. GI-FTIR showed a more than linear increase of the aromatic C–C stretch modes when the chain length increased from two to four phenyl rings, indicating that the longer p-phenylenes system is oriented along the surface normal. Similarly, increasing the length of the thiophene oligomers from two to four rings resulted in a more than linear increase of the intensity of the C–H bend modes, again implying that the longest oligothienedithiol molecules are aligned very close to the surface normal, which is also corroborated by ellipsometry measurements.

### Conclusions

A series of aromatic and heteroaromatic acetyl-protected mono- and dithiol compounds with varied lengths and different aromatic backbones have been synthesized and characterized. UV–vis spectroscopy showed a red-shifted absorption maximum with increasing chain length, especially when thiophene rings were introduced in the conjugated molecule. Obviously, the optical band gap was also lowered when the aromatic system was extended. The redox behavior of the conjugated SAMs was investigated, and data on thienothioetherdithiol were discussed in more detail. The electrochemical behavior in solution of the aromatic thioacetyl derivatives studied was represented by a multielectron reversible or partially quasi-reversible oxidation wave, and the potentials are strongly dependent on the \( \pi \)-conjugated length of the molecule. The electrochemistry of terthienedithiol in a SAM and in solution exhibits a partially reversible oxidation wave. The formation of self-assembled monolayers of these conjugated mono- and dithiol compounds on gold was achieved by in situ deprotection of the corresponding acetylated derivatives. The resulting SAMs were studied by grazing incidence FTIR, contact angle, and ellipsometry measurements, confirming the formation of edge-on monolayer structures. On the basis of the combined data from GI-FTIR, ellipsometry, and contact angle measurements, we conclude that increasing the chain length of conjugated dithiol molecules results in a less tilted molecular orientation with respect to the surface normal. GI-FTIR showed a more than linear increase of the aromatic C–C stretch modes when the chain length increased from two to four phenyl rings, indicating that the longer p-phenylenes system is oriented along the surface normal. Similarly, increasing the length of the thiophene oligomers from two to four rings resulted in a more than linear increase of the intensity of the C–C stretch and C–H bend modes, again implying that the longest oligothienedithiol molecules are aligned very close to the surface normal, which is also corroborated by ellipsometry measurements.

### Experimental Section

**General Methods.** All chemical reagents were purchased from Aldrich Chemical Co. unless otherwise stated. 1,4-Benzendithiol was purchased from Tokyo Kasei Kogyo Co., Ltd. Elemental analysis was performed by Robertson Microlit Laboratories (Madison, NJ). Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 360 MHz spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm. UV–vis spectra were obtained on a HP-8453 spectrometer. Mass spectra were taken on a VG/Micromass Autospec with a 70 eV source (200 °C).

**Self-Assembled Monolayer Formation.** Gold-coated (1000 Å thickness) silicon wafers with a 100 Å titanium adhesion layer were prepared by e-beam deposition. Prior to submersion into the thiol-containing THF (anhydrous) solution, the gold sub-

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**Table 3. Preparation Conditions, Calculated Molecular Length, and Ellipsometry and Contact Angle Goniometry Data on Conjugated Mono- and Dithiols**

<table>
<thead>
<tr>
<th>compound</th>
<th>conc ( \times 10^{-5} ) M</th>
<th>dissolves or precipitates</th>
<th>calculated molecular length</th>
<th>measured layer thickness</th>
<th>contact angle H(_2)O</th>
<th>contact angle hexadecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>cleaned gold</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)SH</td>
<td>50 S</td>
<td>24.7</td>
<td>17.2</td>
<td>93</td>
<td>38</td>
<td>58</td>
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<tr>
<td>22a</td>
<td>5 S</td>
<td>9.4</td>
<td>9.9 ± 0.7</td>
<td>75</td>
<td>36</td>
<td>66</td>
</tr>
<tr>
<td>33a</td>
<td>5 P</td>
<td>13.3</td>
<td>9.7 ± 1.1</td>
<td>81</td>
<td>40</td>
<td>68</td>
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<td>1 P</td>
<td>21.8</td>
<td>22.1 ± 1.3</td>
<td>87</td>
<td>48</td>
<td>74</td>
</tr>
<tr>
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<td>5 S</td>
<td>12.3</td>
<td>7.2 ± 1.3</td>
<td>92</td>
<td>66</td>
<td>80</td>
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<tr>
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<td>5 S</td>
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<td>17.9 ± 1.3</td>
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<td>73</td>
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<tr>
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<td>11.2 ± 0.8</td>
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<td>12.5 ± 1.3</td>
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<td>5 S</td>
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<td>11.1 ± 2.2</td>
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<td>7.3 ± 0.6</td>
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<tr>
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<td>5 S</td>
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<td>10.9 ± 1.0</td>
<td>78</td>
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<td>73</td>
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<tr>
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<td>1 P</td>
<td>20.1</td>
<td>18.7 ± 1.2</td>
<td>95</td>
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<td>75</td>
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<td>11.9 ± 2.9</td>
<td>77</td>
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<td>17.1</td>
<td>19.3 ± 0.9</td>
<td>84</td>
<td>36</td>
<td>72</td>
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<tr>
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<td>5 P</td>
<td>15.7</td>
<td>21.0 ± 0.8</td>
<td>97</td>
<td>45</td>
<td>74</td>
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<tr>
<td>20a</td>
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<td>13.5</td>
<td>5.3 ± 0.8</td>
<td>78</td>
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<tr>
<td>32a</td>
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<td>27.1 ± 1.3</td>
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<td>53</td>
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<tr>
<td>12a</td>
<td>5 S</td>
<td>9.7</td>
<td>9.3 ± 1.0</td>
<td>79</td>
<td>48</td>
<td>70</td>
</tr>
<tr>
<td>26a</td>
<td>5 S</td>
<td>15.8</td>
<td>19.5 ± 0.4</td>
<td>96</td>
<td>58</td>
<td>71</td>
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\( ^{a} \) The structure is given in the text; compounds are arranged by similarity. \( ^{b} \) In THF. \( ^{c} \) Indicates whether the deprotected compound is soluble (S) or whether it precipitates (P) after several weeks at given concentration in THF. \( ^{d} \) Defined as the distance from Au to the farthest hydrogen atom of the molecule, optimized by the PM3 semiempirical method (see Experimental Section). \( ^{e} \) Measured by ellipsometry assuming a refractive index of 1.55. \( ^{f} \) \( \theta_{h} \) = advancing contact angle, \( \theta_{c} \) = receding contact angle, \( \theta_{s} \) = static contact angle. \( ^{g} \) Refractive index of 1.45.

strates were cleaned for 30 min in a mixture of water/NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub> (5:1:1) held at 75 °C, rinsed with deionized water (3 times), and blown dry with N<sub>2</sub>. In a glovebox under argon, the acetyl-

Grazing Incidence FT-IR. The GI-FITR data were recorded under a nitrogen atmosphere in a Nicolet 760 spectrometer equipped with a grazing incidence module containing gold-coated silicon wafers as mirrors at an 85° angle. Before measurement of the gold-coated silicon wafers, the gold layer was recorded on a freshly cleaned (the cleaning procedure is described above) gold substrate. Two thousand consecutive scans were averaged before the spectrum was corrected for the gold substrate by plotting the absorbance as \(-\log(R_{j}/R_{0})\), where \(R\) is the reflectivity of the substrate with the monolayer and \(R_{0}\) is the reflectivity of the reference gold substrate. The nominal spectral resolution was set at 4 cm\(^{-1}\).

**Ellipsometry.** Layer thicknesses were measured on a Rudolph research/auto EL ellipsometer equipped with a He–Ne laser (\(\lambda = 632.8\) nm) at an incidence angle of 70° with respect to the surface normal. Optical constants of the gold-coated substrates were measured prior to the SAM measurements and calculated from the ellipsometric parameters delta (\(\Delta = \delta_{1} - \delta_{0}\), defined as the phase difference between the p-wave and the s-wave before (\(\delta_{0}\)) and after (\(\delta_{1}\)) the deposition (\(\delta_{j}\)), and \(\psi\) = \(\arctan(R_{p}/R_{s})\), where \(\psi\) is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients with \(R_{p}\) being the reflection coefficient of the p-wave and \(R_{s}\) the reflection coefficient for the s-wave.\(^{87}\) The SAMs were rinsed with deionized water and 2-propanol three times and dried for 5 min with \(N_{2}\) before collecting the data. All layer thicknesses reported were calculated after averaging over at least five measurements. The refractive indices of gold and bare silicon wafer were measured by averaging on at least five spots.

Cyclic Voltammetry (CV) Measurements. CV experiments were performed on a BAS 100B electrochemical analyzer in an argon-filled glovebox with a three-electrode cell in a CH<sub>2</sub>Cl<sub>2</sub> solution (0.2 M Bu<sub>4</sub>NPF<sub>6</sub>, as an electrolyte) at different scan rates (10–1000 V s\(^{-1}\)). A platinum wire and a Ag/Ag<sup>+</sup> electrode were used as the counter and reference electrodes, respectively. The oxidation of ferrocene under our conditions occurs at 1.95 V (vs Ag/Ag<sup>+</sup>). The self-assembled thiols were measured prior to the SAM measurements and calculated from the ellipsometric parameters delta (\(\Delta = \delta_{1} - \delta_{0}\), defined as the phase difference between the p-wave and the s-wave before (\(\delta_{0}\)) and after (\(\delta_{1}\)) the deposition (\(\delta_{j}\)), and \(\psi\) = \(\arctan(R_{p}/R_{s})\), where \(\psi\) is the angle whose tangent is the ratio of the magnitudes of the total reflection coefficients with \(R_{p}\) being the reflection coefficient of the p-wave and \(R_{s}\) the reflection coefficient for the s-wave.\(^{87}\) The SAMs were rinsed with deionized water and 2-propanol three times and dried for 5 min with \(N_{2}\) before collecting the data. All layer thicknesses reported were calculated after averaging over at least five measurements. The refractive indices of gold and bare silicon wafer were measured by averaging on at least five spots.


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4.62 ppm. \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 7.73, 7.18 (b, 8 H), 3.46 (s, 2 H) ppm. \(^{13}C\) NMR (CDCl<sub>3</sub>): \(\delta = 157.5, 131.8, 124.1, 119.6 ppm). Anal. Calcld for C<sub>75</sub>H<sub>72</sub>O<sub>2</sub>S<sub>2</sub> (366 g/mol): C, 57.56; H, 4.03; S, 38.42. Found: C, 56.30; H, 3.89; S, 29.07.

Dithioacetyl 8. This compound was prepared using similar procedures as for compound 5a from dithiol 4 (yield, 83%), mp 174 °C. Anal. Calcld for C<sub>75</sub>H<sub>72</sub>O<sub>2</sub>S<sub>2</sub> (366 g/mol): C, 57.45; H, 4.22; S, 28.76. Found: C, 57.54; H, 4.54; S, 28.55.

Dithioal 5a. Dithioal 5 (8.5 g, 0.023 mol) was added to a solution of sulfuric acid (98%, 100 g) in water (200 mL) with vigorous stirring at room temperature, followed by a freshly prepared zinc dust amalgam (50 g, excess).\(^{25}\) After being stirred for 2 h, the mixture was refluxed for an additional 3 h. The reaction mixture was then cooled to room temperature and extracted with benzene. The solvent was evaporated to yield a white solid, which was purified by sublimation to give dithio 5a (4.1 g, 78%), mp 100–102 °C. \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 7.29 (d, J = 7.3 Hz, 4 H), 6.90 (d, J = 7.3 Hz, 4 H), 3.43 (2, H) ppm. \(^{13}C\) NMR (CDCl<sub>3</sub>): \(\delta = 133.0, 131.7, 130.1, 127.1 ppm). Anal. Calcld for C<sub>38</sub>H<sub>28</sub>O<sub>2</sub>S<sub>2</sub> (540 g/mol): C, 57.56; H, 4.03; S, 38.42. Found: C, 56.30; H, 3.89; S, 36.03.

Dithioal 6a. This compound was prepared using similar procedures as for compound 5a from dithiol 4 (yield, 89%), mp 104–105 °C. \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 234 (M+, 100%). \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 133.0, 131.7, 130.1, 127.1 ppm). Anal. Calcld for C<sub>75</sub>H<sub>72</sub>O<sub>2</sub>S<sub>2</sub> (366 g/mol): C, 57.56; H, 4.03; S, 38.42. Found: C, 56.50; H, 3.89; S, 36.03.

Dithioal 5. This compound was prepared using similar procedures as for compound 3 from diphenylsulfide (2) (yield, 80%), \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 382 (M+, 100%). \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 8.01 (d, J = 7.7 Hz, 4 H), 7.57 (d, J = 7.7 Hz, 4 H) ppm. \(^{13}C\) NMR (CDCl<sub>3</sub>): \(\delta = 143.8, 143.6, 131.3, 128.1 ppm.

Dithioal 6. This compound was prepared using similar procedures as for compound 5a from dithiol 4 (yield, 89%), mp 104–105 °C. \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 234 (M+, 100%). \(^{1}H\) NMR (CDCl<sub>3</sub>): \(\delta = 133.0, 131.7, 130.1, 127.1 ppm). Anal. Calcld for C<sub>75</sub>H<sub>72</sub>O<sub>2</sub>S<sub>2</sub> (366 g/mol): C, 57.56; H, 4.03; S, 38.42. Found: C, 56.50; H, 3.89; S, 36.03.
The precipitate was washed with a saturated solution of NaCl (3 × 30 mL) and dried over night at 60 °C in vacuo to give sodium fluoride, 2,7-disulfonato (13.0 g, 70%). 1H NMR (D2O): δ 7.68 (s, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 7.3 Hz, 2 H), 7.04 (d, J = 7.4 Hz, 2 H). 13C NMR (D2O): δ 144.0, 142.9, 142.0, 142.7, 124.3, 121.0, 36.8 ppm. The salt (3.7 g, 0.010 mol) was mixed with phosphorus pentachloride (5.2 g, 0.025 mol) and stirred at 110 °C for 2 h. 88 The phosphorus oxychloride formed during the reaction was distilled off, and the resulting dry residue was pulverized in a mortar and then treated with water. The precipitate was filtered off and washed with water to give dithiol 10 (2.9 g, 69%) as a light-red-brown powder. m/z (EI): 362 (M+ , 60%). 1H NMR (CDCl3): δ 8.30 (s, 1 H), 8.19 (d, J = 8.3 Hz, 2 H), 8.11 (d, J = 8.3 Hz, 2 H), 4.20 (s, 2 H) ppm. 13C NMR (CDCl3): δ 194.0, 142.8, 141.0, 124.2, 121.6, 119.8, 34.7 ppm. 

**Dithiol 11a.** Stannous chloride dihydrate (25 g, 0.22 mol) dissolved in a mixture of acetic anhydride (100 mL) and phosphorus pentachloride (5.2 g, 0.25 mol) and stirred at 120 °C for 2 h. The phosphorus oxychloride formed during the reaction was distilled off, and the residue was purified by flash chromatography on silica gel with hexanes/methylene chloride (1:1 v/v) as the eluent followed by recrystallization from hexane to give a light-yellow solid 16 (0.50 g, 31%), m/z (EI): 396 (M+ , 100%). 1H NMR (CDCl3): δ 7.25 (s, 4 H), 7.13 (d, J = 3.8 Hz, 2 H), 7.05 (d, J = 3.8 Hz, 2 H), 2.41 (s, 6 H) ppm. 13C NMR (CDCl3): δ 193.4, 142.8, 136.3, 136.2, 121.5, 124.5, 124.2, 29.3 ppm. Anal. Calcd for C16H12O2Se (396.5 g/mol): C, 56.43; H, 3.61; Se, 39.96. Found: C, 55.43; H, 3.61; Se, 39.95. 

**1,4-Bis(2-thienyl)benzene 17** was prepared from 2-bromothiophene and 1,4-benzenediboron acid according to standard procedures for Suzuki reactions: 89 orange-yellow solid (yield, 90%), mp 197−200 °C. 1H NMR (CDCl3): δ 7.61 (s, 4 H), 7.32 (d, J = 3.6 Hz, 1.1 Hz, 2 H), 7.27 (d, J = 3.6 Hz, 1.1 Hz, 2 H), 7.07 (m, 2 H) ppm. 13C NMR (CDCl3): δ 143.9, 133.5, 128.0, 126.3, 124.8, 123.9, 29.3 ppm. Anal. Calcd for C16H12O2Se (390.5 g/mol): C, 55.35; H, 3.61; Se, 32.64. Found: C, 55.43; H, 3.61; Se, 32.62. 

**Dithioacetylbis (1,5-naphthalenedithiol) 18.** 1,4-Bis(2-thienyl)benzene (1 g, 4 mmol) was refluxed at 180 °C with 78 °C, and acetyl chloride (0.52 g, 7.5 mmol) was added in one portion. After warming up to 20 °C, stirring overnight the residue was dissolved in dichloromethane and the residue was purified by flash chromatography on silica gel with hexanes/methylene chloride (1.1 v/v) as the eluant followed by recrystallization from hexane to afford a light-yellow solid 20 (1.50 g, 67%), m/z (EI): 446 (M+ , 100%). 1H NMR (CDCl3): δ 7.59 (s, 4 H), 7.64 (s, 6 H) ppm. 13C NMR (CDCl3): δ 193.6, 149.8, 136.6, 133.5, 126.4, 124.8, 123.8, 29.3 ppm. Anal. Calcd for C16H12O2Se (446.3 g/mol): C, 43.06; H, 1.35; S, 14.37; F, 34.05. Found: C, 43.01; H, 1.41; S, 14.43; F, 33.85. 

**1,4-(Diacytethylseleno)benzene 22.** To a solution of n-BuLi (2.5 M solution in THF, 50.0 mL, 0.13 mol) in dry THF (50 mL) at −78 °C was added dropwise a solution of 19 (2.3 g, 5.0 mmol) in dry THF (20 mL). The mixture was warmed to 20 °C stirred for 2 h, and then cooled to −78 °C. Sulfur powder (0.48 g, 0.015 mol) was then added in one portion. The reaction mixture was warmed to 0 °C, stirred for 30 min, and then cooled to −78 °C. Acetyl chloride (1.2 g, 0.015 mol) was added in one portion. After warming up to 20 °C, stirring overnight the residue was dissolved in dichloromethane and the residue was purified by flash chromatography on silica gel with hexanes/methylene chloride (1.1 v/v) as the eluant followed by recrystallization from hexane to afford a light-yellow solid 20 (1.50 g, 67%), m/z (EI): 446 (M+ , 100%). 1H NMR (CDCl3): δ 7.59 (s, 4 H), 7.64 (s, 6 H) ppm. 13C NMR (CDCl3): δ 193.6, 149.8, 136.6, 133.5, 126.4, 124.8, 123.8, 29.3 ppm. Anal. Calcd for C16H12O2Se (446.3 g/mol): C, 43.06; H, 1.35; S, 14.37; F, 34.05. Found: C, 43.01; H, 1.41; S, 14.43; F, 33.85.


Dithioacetyl 31a. To a mixture of 4-(methylthio)phenylboronic acid and potassium carbonate, the solvent in THF, 8 mL, 0.020 mol) at 20 °C, and the mixture was refluxed overnight. After quenching with 10% HCl, the mixture was extracted with toluene (20 mL). The solution was cooled to 78 °C, and methyl iodide (9.0 g, 0.066 mol) was added. The mixture was stirred at 78 °C overnight and then poured into water and extracted with diethyl ether (3 × 50 mL). The combined organic solution was washed with water and saturated NaCl solution and dried over MgSO4. After removal of the solvent, the residue was distilled in vacuo to give white solid (yield, 83%). 1H NMR (CDCl3): δ 7.21 (dd, J = 5.1 Hz, 1.1 Hz, 1 H), 7.13 (dd, J = 3.6 Hz, 1.1 Hz, 1 H), 7.01–7.00 (m, 1 H), 7.00 (d, J = 5.1 Hz, 1 H), 6.98 (d, J = 3.6 Hz, 1 H), 2.50 (s, 3 H) ppm. 13C NMR (CDCl3): δ 139.6, 137.0, 136.2, 131.8, 127.8, 124.5, 123.8, 123.7, 22.1 ppm. Anal. Calc'd for C20H16OS2 (371.4 g/mol): C, 65.40; H, 4.91; S, 19.99. Found: C, 65.40; H, 4.91; S, 19.99.

Dithioacetyl 31a. This compound was synthesized using the same procedures as for compound 31a. The crude product was sublimed in vacuo to give a light-yellow powder (yield, 51%), which is insoluble in common organic solvents, mp 380–385 °C. m/z (EI): 370 (M+), 60%, 338 (M+, 100%).

Dithioacetyl 31. Dithiobutyl ether 31 (2.50 g, 8.0 mmol) in dry chloroform (50 mL) was treated with methyl chloride (1.33 g, 0.017 mol) and triethylamine (1.72 g, 0.017 mol), and the product was purified by flash column chromatography on silica gel with hexane/methylene chloride (1:1 v/v) as the eluant to give a light-yellow powder of 2,5-bis[4-(methylthio)phenyl]thiophene (5.78 g, 88%). mp 212–215 °C. m/z (EI): 228 (M+, 70%), 186 (M+, 100%). 1H NMR (CDCl3): δ 7.66 (m, 4 H), 7.46 (m, 4 H), 7.34 (d, J = 3.6 Hz, 1 H), 1.19 (s, 6 H) ppm. 13C NMR (CDCl3): δ 139.5, 137.0, 136.2, 131.8, 127.8, 124.5, 123.8, 123.7, 22.1 ppm. Anal. Calc'd for C20H16S2 (318.5 g/mol): C, 68.28; H, 5.41; S, 26.31. Found: C, 68.08; H, 5.41; S, 26.31.
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