Molecular conductance
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We have synthesized an anthraquinone-based redox switch along with anthracene-based and dihydroanthracene-based analogues. The molecules have thioacetate terminals to anchor them to gold electrodes. During the synthesis of the core, the thiols were protected as tert-butyl thioethers, which were converted into acetyl thioesters in the last step. We show that the UV-Vis absorption spectra mainly depend on the conjugation pattern and that the anthracene compounds fluoresce about three orders of magnitude stronger than the anthraquinone compounds. Most important: the anthraquinone-based redox switch can be switched reversibly by electrochemistry or by chemical reduction and oxidation with TDAE and oxygen respectively, as we have shown by cyclic voltammetry, spectroelectrochemistry and NMR experiments.
Chapter 2

2.1 Introduction

In Chapter 1 we have briefly described the principles of π-logic, a concept based on conductance differences between cross-conjugated and linear conjugated pathways between two terminals. This concept can be investigated with a molecule in which the pathway between the terminals can be switched between cross-conjugated and linear conjugated. We have chosen reduction and oxidation as the trigger for this switching, because it fits the best in the electrical concept of π-logic, the conformational changes of the molecule are minimized and it is compatible with several methods of conductance measurements. This resulted in the design of our anthraquinone-based redox switch in 2004 (Figure 2.1). The pathway from one sulfur terminal to the other is cross-conjugated in this anthraquinone containing wire. Upon reduction, the anthraquinone is reduced to the hydroquinone dianion and the pathway between the sulfur terminals becomes linear conjugated. This change in conjugation pattern is expected to cause a change in conductance from low ("off") to high ("on").

In this chapter we will first introduce examples of molecules in which the π-conjugation is switched by external inputs. We will then describe the synthesis of our anthraquinone-based redox switch and reference compounds. The synthetic methodology as developed in this chapter is applied in the syntheses described in the next chapters. After discussing the optical properties we will show that our anthraquinone-based switch can be switched reversibly by electrochemical and chemical methods. In the last sections we will comment on the energy levels and report a crystal structure of our switch.

Figure 2.1 Schematic of the anthraquinone-based redox switch attached to gold electrodes.
2.1.1 π-Conjugation Switches in the Literature

A switch is used in an electronic circuit to open or close this circuit. It always needs a “trigger”, for instance someone pushing a button to close the circuit, which turns on the light. A conducting state and an isolating (less conducting) state are therefore required. Furthermore, this switching should be reversible. Examples of reversible switching systems in the molecular world are the diarylethene switches. UV-light is the trigger to switch from the cross-conjugated (open) to the linear conjugated (closed) state and visible light is used to switch back to the open state (Figure 2.2a). The change of conductance of these diarylethene switches upon irradiation was studied by several methods.

The first diarylethene switches were anchored to the gold surface via thiophene spacers and these were found to switch only from the closed to the open state in mechanically controllable break junctions and STM experiments. This is probably due to quenching of the excited state of the open switch by the gold electrode. The use of a phenylene spacer instead of a thiophene improved the reversibility of the switch when contacted to gold. Separating the conjugated system from the thiol anchoring group by a meta-substituted phenylene allowed reversible switching of the molecule inside molecular junctions. The linear conjugated (closed) state had a higher conductance than the cross-conjugated (open) state and reversible switching between this high and low conductance was possible (Figure 2.2b). The switching amplitude decreased over time, since not all molecules switched from one state to the other: photostationary states were obtained. Measuring a high conductance means that a larger fraction of switches is closed in comparison to the lower conductance. An advantage of this optical switch is that it can be addressed dry and inside a junction as long as there is optical access. Disadvantages are the aforementioned incomplete switching, the fundamental difficulty to address one single switch that is embedded in an array of switches by a photon (although these...
switches can also be addressed electrochemically\textsuperscript{15}, the conformational changes of the system (conductance switching cannot be attributed to changes in conjugation patterns only), and the requirement to decouple the system from the electrodes (the best working switch has cross-conjugated spacers, thus the system is not completely linear conjugated from one thiol to the other).

The energy levels of a molecule can be shifted by electrochemical oxidation and reduction. This concept -referred to as electrochemical gating- is widely used in electrochemical STM measurements, for instance with oligothiophene and bipyridyl containing structures.\textsuperscript{13,14} Several wires containing a tetrathiafulvalene (TTF) redox center have been synthesized\textsuperscript{15-17} and studied in conductance measurements.\textsuperscript{17,18} Even though electrochemical switching was observed, the conjugation pattern does not change between cross-conjugated and linear conjugated in these examples, neither in the redox-active molecular wires synthesized in the groups of Mayor\textsuperscript{19} and Bryce.\textsuperscript{20} The π-conjugation does change in the structures based on extended tetrathiafulvalene (TTF) as presented in Figure 2.3a and b. In contrast to our anthraquinone-based switch, the molecular wires in Figure 2.3a are linear conjugated from one sulfur terminal to the other and become cross-conjugated upon oxidation.\textsuperscript{21,22} Similar to our anthraquinone-based switch, the structures in Figure 2.3b are cross-conjugated and turn linear conjugated upon oxidation of the extended TTF.\textsuperscript{23} For all these extended TTF wires quasi-reversible oxidation in solution was found, and to the best of our knowledge, no conductance studies have been published yet.\textsuperscript{24}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.3.png}
\caption{Examples of reported molecules that switch between cross-conjugation and linear conjugation upon reduction or oxidation.}
\end{figure}
Tour et al. have reported a benzoquinone containing molecular wire (Figure 2.3c), but did not investigate conductance switching based on reduction and oxidation. More recently, oligo phenylene vinylene (OPV) based wires with a hydroquinone head group were synthesized (Figure 2.3d) and the thioacetate terminated molecules were inserted into an octanethiol SAM on gold. The conductance of the OPV wires was found to decrease upon oxidation to the benzoquinone state as was shown by electrochemical STM imaging.

2.1.2 Anthraquinone- and Anthracene-based Wires and Switches

We have synthesized the anthraquinone-based redox switch (Figure 2.1) with two, one, and without thioacetate terminals for anchoring to gold electrodes (compounds 2.1A, 2.2A, and 2.3, see Figure 2.4). The redox-active anthraquinone unit is separated from the thioacetate anchoring groups by phenyl-ethynyl spacers, to have a linear and rigid molecule.

Besides these cross-conjugated anthraquinone containing compounds, we made

cross-conjugated

linear conjugated

![Chemical structures](image)

**Figure 2.4** Overview of the anthraquinone- and anthracene-based molecules of which the synthesis and properties will be reported in this chapter.
linear conjugated analogues with anthracene-based cores (2.4A, 2.5A, and 2.6A) to have stable compounds of which the conductance could be compared with that of 2.1A. Furthermore, we have synthesized compound 2.7A, of which the π-conjugation is broken by sp³ hybridized methylene groups. The syntheses and analyses of these compounds will be described in the next sections.

Other possible approaches to switch between a cross-conjugated and a linear conjugated pathway that were investigated in our group are a pH-switch and a Diels-Alder switch. The pH-switch is the acridone analogue of the anthraquinone-based redox switch: the core of the molecule is a cross-conjugated N-methyl acridone unit, which becomes linear conjugated upon protonation (Figure 2.5a). This acridone-switch was successfully synthesized by Dr. Daniel J. T. Myles, it was protonated with one equivalent of triflic acid and isolated. Attempts to show reversible switching by UV-Vis spectroscopy failed however. Furthermore, since this switch includes a heteroatom (with a lone pair) in its π-conjugated core, reasonable resonance structures can be drawn in which the acridone state is linear conjugated (with a positively charged nitrogen atom and a negatively charged oxygen atom) and the protonated state is cross-conjugated (with a positively charged oxygen atom and a neutral nitrogen atom). Thus, the question arises if this system actually switches from cross-conjugated to linear conjugated.

![Figure 2.5 Schematic of an acridone-based pH-switch (a) and an anthracene-based Diels-Alder switch (b) attached to gold electrodes.](image-url)
Switching of the conjugation pattern could also be achieved by a Diels-Alder reaction on an anthracene-core (Figure 2.5b) of a linear conjugated wire: reaction with a dienophile will give a wire with broken conjugation. Heating should result in a retro-Diels Alder reaction, thus switching back to the linear conjugated wire. Treatment of compound 2.6B with N-phenylmaleimide gave the Diels-Alder adduct, which was stable up to at least 180 °C.\textsuperscript{31} Tuning the properties of the anthracene-core by varying the substituents at the 9,10-positions and a proper choice of a dienophile should result in a switching system that is compatible with conductance measurements.

### 2.2 Synthesis of the Anthraquinone- and Anthracene-based Molecular Wires

The most convenient synthesis strategy for the arylene ethynylene type compounds as listed in Figure 2.4 is by Sonogashira cross-couplings: a terminal acetylene is coupled to an aryl (or vinyl) halide by a palladium catalyst and a copper(I) salt as co-catalyst.\textsuperscript{32,33} For all Sonogashira cross-couplings in this thesis we have used dichlorobis(triphenylphosphine)palladium(II) and copper iodide as the catalytic system in THF, with a secondary or tertiary amine as co-solvent. The Pd(II) catalyst is reduced \textit{in situ} to Pd\textsuperscript{0}(PPh\textsubscript{3})\textsubscript{2} by the amine or by oxidative coupling of the terminal acetylenes.\textsuperscript{34} This Pd(0) complex then oxidatively inserts in the aryl-bromide or -iodide bond. In the meanwhile, the terminal acetylene is activated by the copper iodide. Transmetallation of the Pd(II) complex and the copper acetylide results in a Pd(II) complex with the acetylide and the arene. The C-C bond between the two parts is then formed by reductive elimination and the Pd(0) can start another cycle.

In a convergent synthesis approach to wires 2.1-2.7, their cores were synthesized in parallel to the phenylacetylene-based compounds. Cross-conjugated compounds 2.1-2.3 were made by Sonogashira cross-couplings with 2,6-dibromo-9,10-anthraquinone, as will be discussed in Section 2.2.1. 2,6-dibromo-9,10-anthraquinone was reduced to various 2,6-dibromo-anthracenes, from which linear conjugated compounds 2.4-2.6 were synthesized (Section 2.2.2), or to 2,6-dibromo-9,10-dihydroanthracene, being the core of compound 2.7 (Section 2.2.3).
2.2.1 Cross-conjugated Molecular Wires

The most direct route towards anthraquinone wire 2.1A is a Sonogashira coupling between 2,6-dibromo-9,10-anthraquinone (2.14) and 4-ethynyl-1-thioacetylbenzene (2.10). 2.14 was prepared from commercially available 2,6-diamino-9,10-anthraquinone by a Sandmeyer reaction in 64% yield. Acetylene 2.10 was synthesized in three steps from pipsyl chloride (4-iodobenzenesulfonyl chloride), which was reduced by zinc and dichlorodimethylsilane to 4-iodothiophenol, and then protected with acetyl chloride to give compound 2.8 in 81% yield (Scheme 2.1). Trimethylsilylacetylene was then cross-coupled to 2.8 by a Sonogashira reaction to give 2.9 in 77% yield and the thiol as a side product. The acetylene was deprotected by tetrabutylammonium fluoride (TBAF) at low temperature and under mild acidic conditions to prevent deacylation and 2.10 was obtained in 97% yield.

A first attempt to cross-couple 2.14 with 2.10 under the conditions that were used by Leventis et al. for Sonogashira cross-couplings on bromo-anthaquinones failed, while the cross-coupling with phenylacetylene to give 2.3 was reproduced with a yield of 56% (Scheme 2.2). In a second attempt we used a tertiary amine (diisopropylethylamine) instead of a secondary amine (diisopropylamine) to prevent hydrolysis of the thioester. However, no pure 2.1A was isolated. These problems are similar to those reported by Mayor et al. regarding the Sonogashira cross-coupling of 9,10-dibromoanthracene with 2.10 in a yield of only 5%. To overcome this problem, they used a tert-butyl protected thiol in the cross-coupling, and subsequently converted the tert-butyl protected thiol into an acetyl protected thiol by boron tribromide and acetyl chloride. We have adopted this approach and started with the alkylation of 4-bromothiophenol to 2.11 according to the literature procedure on 100 g-scale in 85% yield (Scheme 2.3). We have cross-coupled 2.11 with trimethylsilylacetylene in yields up to 85%, however, larger scale reactions tended to give lower yields and we had difficulties to reproduce previous results. This is most likely due to the low boiling point of

\[
\begin{align*}
\text{Scheme 2.1 Synthesis of acetylene 2.10:} & \quad (i) & \text{Zn, Me}_2\text{SiCl}_2, \text{DMA}, \text{(CH}_2\text{Cl})_2, 75^\circ\text{C}, \text{2. AcCl, 75}^\circ\text{C, 81} chances; & \quad (ii) & \text{Pd(PPh}_3)_2\text{Cl}_2, \text{CuI, trimethylsilylacetylene, iPr}_2\text{EtN, THF}, 77\%; & \quad (iii) & \text{TBAF, AcOH, Ac}_2\text{O, THF, 0}^\circ\text{C, 97}\%. \\
\end{align*}
\]
trimethylsilylacetylene (53°C), compared to the temperature required for the cross-coupling (refluxing THF, 66°C). This problem was overcome by using the higher boiling (triisopropylsilyl)acetylene for the Sonogashira cross-coupling, followed by deprotection of the acetylene by TBAF. This highly reproducible procedure gave 4.6 g of 2.13 in 83% yield over two steps.

Acetylene 2.13 was conveniently cross-coupled with 2.14 to 2.1B in 84% yield. All attempts to replace the tert-butyl protecting group by an acetyl protecting group with boron tribromide and acetyl chloride failed: 2.1A could not be separated from the side products that were formed. However, a modification of the bromine catalyzed reaction described by Mayor et al. gave the desired compound 2.1A. A drawback of this method is the low reproducibility: some of the attempts resulted in insoluble material only (most likely disulfides). For this reason we chose to apply this reaction only on quantities up to 100 mg. Larger amounts were obtained
by combining several batches, after the reaction and before the purification by
column chromatography, with an average yield of 46%.

Asymmetric compound 2.2A was synthesized by similar methods: only 1.1
equivalent of 2.13 was used in the cross-coupling with 2.14, to obtain a mixture of
products (30% unreacted 2.14, 45% asymmetric product, 25% 2.1B), from which
the asymmetric product was isolated by column chromatography in 38%. This was
then cross-coupled to phenylacetylene and 2.2B was obtained in 71% yield.
Conversion of the tert-butyl group into an acetyl group by catalytic amounts of
bromine resulted in 2.2B in 83% yield.

2.2.2 Linear Conjugated Molecular Wires

To compare the properties of the cross-conjugated anthraquinone with its linear
conjugated, though unstable hydroquinone, we decided to provide this
hydroquinone with an acetyl or methyl protecting group. The synthesis of 2,6-
dibromo-9,10-diacetoxyanthracene (2.15) from 2.14 and Sonogashira cross-
couplings with this compound were described in the aforementioned article of
Leventis et al. The anthraquinone was reduced by zinc powder to the
hydroquinone, which then formed the bisacetyl ester upon reaction with acetic
anhydride, and 2.15 was isolated in 81% (Scheme 2.4).

Scheme 2.4 Syntheses of the linear conjugated anthracene-based compounds 2.4A-2.6A: (i) Zn,
NaOAc, Ac₂O, reflux, 81%; (ii) 1. Na₂S₂O₄, Bu₄NBr, CH₂Cl₂, H₂O, 2. NaOH, 3. CH₃I, 24%; (iii) 1. NaBH₄,
MeOH, toluene, 2. HCl, H₂O, 3. NaBH₄, iPrOH, reflux, 18%; (iv) 2.13, Pd(PPh₃)₂Cl₂, CuI, iPr₂NH, THF,
reflux; (v) Br₂, AcCl, AcOH, CHCl₃; (vi) BBr₃, AcCl, CHCl₃, toluene.
A Sonogashira cross-coupling with 2.13 gave 2.4B in 75% yield and the tert-butyl thioethers were converted into acetyl thioesters (2.4A) by the bromine catalyzed reaction in 27% yield, following the same strategy as for the anthraquinone compounds 2.1A and 2.2A.\textsuperscript{42,43}

Anthraquinone 2.14 was also reduced to its hydroquinone by sodium dithionite\textsuperscript{36} and then, after deprotonation, trapped by iodomethane as bismethyl ether 2.16, which was isolated in 24% yield. Compound 2.16 was then cross-coupled with 2.13, resulting in 2.5B in 56% yield, which was converted into thioester 2.5A in 43% yield. We found that the $^1$H NMR spectra of compound 2.5B changed upon time when the solution was exposed to light (on air). The peak at 4.15 ppm had disappeared after 3 days and a new peak at 4.0 ppm was found instead. After 13 days the peak at 4.0 ppm had shifted to 3.5 ppm. In both solutions we found signals of 2.1B, together with other (small) peaks. The observed changes could be attributed to a [4 + 4] cycloaddition to form the dimer of 2.5B (Scheme 2.5), which can be oxidized to 2.1B, as reported for 2,3-ethynyl-9,10-dimethoxyanthracenes.\textsuperscript{44}

We have synthesized the parent anthracene wire 2.6A as linear conjugated analogue to 2.1A, to enable the formation of densely packed self-assembled monolayers (which could be hindered by the acetyl or methoxy groups of 2.4A and 2.5A), see Chapter 5. Anthraquinone 2.14 was reduced with sodium borohydride to 2,6-dibromoanthracene (2.17) according to literature procedures.\textsuperscript{45,46} After several unsuccessful or low-yielding attempts, the best result was obtained by addition of toluene as a co-solvent in the first step of the reaction and 2.17 was isolated in 18%. The cross-coupling with 2.13 to 2.6B, and subsequent conversion to 2.6A by boron tribromide and acetyl chloride\textsuperscript{47} went smoothly (80% and 61% yield respectively).
2.2.3 A Molecular Wire with Broken Conjugation

We completed our series of anthracene-based molecules with different conjugation patterns by preparing a molecular wire of which the π-conjugation is broken: molecule 2.7A consists of two π-conjugated parts that are separated by sp\(^3\) hybridized carbon atoms. The dihydroanthracene core of this molecule can be obtained from a reduction of anthraquinone 2.14. Many common reducing agents result in anthracenes as described in the previous section. However, the reduction with red phosphorus, iodine, and aqueous hydroiodic acid in a sealed ampule was reported to yield the corresponding dihydroanthracene from chloro substituted anthraquinones.\(^{48,49}\) We have used these conditions to obtain 2.18 in 58% yield (Scheme 2.6), contaminated with 2-bromo-6-diodo-9,10-dihydroanthracene (~20%). Another side product was debrominated 9,10-dihydroanthracene, which was removed by recrystallization. Attempts at the synthesis of 2.18 with red phosphorus and aqueous hydroiodic acid in refluxing acetic acid\(^{50}\) resulted in larger amounts of 2-bromo-6-iodo-9,10-dihydroanthracene (35-50%) in the recrystallized product. Kwon et al. have reported the reduction of 2.14 to 2.18 by hydroiodic acid and hypophosphorous acid in acetic acid in 50% yield.\(^{51}\) However, with identical reagents, but slightly different concentrations, a high yielding synthesis of anthracene 2.17 from 2.14 was reported.\(^{52,53}\)

![Scheme 2.6 Synthesis of dihydroanthracene-wire 2.7A: (i) P\(_{\text{red}}\), I\(_2\), HI, 135°C, 58%; (ii) 2.13, Pd(PPh\(_3\))\(_2\)Cl\(_2\), CuI, Et\(_3\)N, THF, reflux, 25%; (iii) BBr\(_3\), AcCl, CHCl\(_3\), toluene, 45%.](image)

A Sonogashira cross-coupling of 2.18 and 2.13 under the conditions as used for the syntheses of 2.1B-2.6B, gave only 16% conversion to 2.7B (the crude product contained 36% 2.18 and 47% monosubstituted product). This is probably due to deactivation of the C-Br bonds of 2.18 towards the oxidative insertion of the Pd\(^0\)(PPh\(_3\))\(_2\) catalyst by the two CH\(_2\) substituents of the phenyl rings.\(^{33}\) Replacing the solvent (17% diisopropylamine in THF) by pure triethylamine improved the conversion to 33% 2.7B (with only 16% 2.18 and 50% monosubstituted product). Compound 2.7B was isolated from this mixture in 25% yield. The reaction of 2.7B with boron tribromide and acetyl chloride to 2.7A gave no problems. However,
during the purification on a silica gel column, part of the material was converted into \textit{2.6A}, hence \textit{2.7A} was obtained in only 47\% yield.

### 2.3 Optical Properties

#### 2.3.1 UV-Vis Absorption Spectroscopy

We have measured the UV-Vis absorption spectra of the different molecular wires discussed in this chapter. Since the \textit{tert}-butyl protected thiols (\#B) have a higher solubility, higher chemical stability, and higher similarity with thiol than the acetyl-protected thiols (\#A), we have used the \textit{tert}-butyl protected thiols in our optical studies. The UV-Vis absorption spectra are given in Figure 2.6. Spectra of \textit{2.2B} and \textit{2.3} are not shown: their shapes are identical to that of \textit{2.1B} with blue-shifts of 3 and 6 nm respectively. This means that each (donating) thioether group gives rise to a slight decrease of the optical HOMO-LUMO gap. Compounds \textit{2.4B, 2.5B,} and \textit{2.6B} have absorption spectra of similar shape. The absorption spectrum of \textit{2.4B} is red-shifted by 6-14 nm compared to spectrum \textit{2.6B} (the parent anthracene wire), due to its acetoxy groups at the anthracene core. The stronger donating methoxy groups of compound \textit{2.5B} result in a larger shift of 10-26 nm. Whereas the absorption of compounds \textit{2.1B-2.6B} exceeds 420 nm, the absorption of \textit{2.7B} ends abruptly around 335 nm, showing clearly that the molecule is divided in two small chromophores (phenyl-ethynyl-phenyl), that have an absorption spectrum very similar to that of compound \textit{4.1B} (diStBu-OPE2, see Chapter 4). The optical HOMO-LUMO gaps as determined from the onsets of the absorption spectra are

![Figure 2.6 UV-Vis absorption spectra of compounds 2.1B (blue), 2.7B (dark red), 2.4B (black), 2.5B (green), and 2.6B (red) as $10^{-5}$ M solutions in CH$_2$Cl$_2$.](image)
listed in Table 2.1 (page 22). Though this gap is significantly larger for 2.7B (with its broken conjugation) than for compounds 2.1B-2.6B, the differences between cross-conjugated wires 2.1B-2.3 and linear conjugated wires 2.4B-2.6B are only marginal.

To gain more insight in these UV-Vis data, we calculated the electronic spectra of 2.1, 2.6, and 2.7 with methyl protected thiols, using the semi-empirical ZindoS method in Hyperchem™ with an orbital criterion of 10 occupied and 10 unoccupied orbitals. We found a good agreement between the trends in the electronic spectra and the experimental trends, even though the absolute values are blue-shifted by 0.2-0.4 eV. The relevant orbitals are shown in Figure 2.7, which we will discuss from right to left. Dihydroanthracene wire 2.7 has two nearly degenerate HOMO orbitals, which are obtained from a symmetric and an asymmetric combination of two parts, each of which resembles the HOMO of OPE2 (4.1B). The same holds for the two LUMO orbitals of 2.7. The nearly degeneracy of these HOMOs and LUMOs indicates only little electronic coupling between both parts of the molecule, reflecting its broken conjugation. The absorption at 318 nm is attributed to combined transitions of the HOMO-1 to LUMO and HOMO to LUMO+1.

All relevant orbitals of linear conjugated anthracene wire 2.6 extent over the entire molecular wire. The absorptions at 417 and 393 nm are attributed to the HOMO to LUMO transition and the combined transitions of HOMO to LUMO and HOMO to LUMO+1 respectively. All four orbitals given in Figure 2.7 are involved in the strong absorption at 325 nm.

The two nearly degenerate HOMO levels of cross-conjugated anthraquinone wire 2.1 resemble those of 2.7, indicating also here little electronic coupling between both parts. However, the LUMO level of 2.1 is located on the anthraquinone unit, as expected, since anthraquinone is a strong acceptor. The absorption at 373 nm is attributed to the transition of the HOMO-1 to the LUMO, whereas the absorption at 334 nm is attributed to the HOMO to LUMO+1 transition. The broad nature of the absorption at 373 nm (which results in the relatively low value for the HOMO-LUMO gap as determined from the onset of that absorption) could originate from the charge-transfer character of that absorption.54
An alternative explanation could be that, even though calculated to have an oscillator strength (intensity) of zero in the gas phase, the HOMO to LUMO transition contributes to the spectrum measured in solution. We note that the calculated energy difference between the HOMO and LUMO levels of 2.1 and 2.6 differs only 60 meV, in agreement with the nearly identical onsets of both UV-Vis absorption spectra. It is known that this optoelectronic HOMO-LUMO gap does not clearly distinguish the difference in electronic properties between cross-conjugated and linear conjugated molecules, especially if the cross-conjugated molecule has both strong electron donating and electron accepting groups.\textsuperscript{55,56}

**Figure 2.7** ZindoS-calculated orbitals of 2.1, 2.6, and 2.7 (all with methyl-protected thiols), that are involved in the electronic transitions corresponding to the measured absorptions.

**Figure 2.8** Excitation (dotted) and emission (solid) spectra of 2.1B (blue), 2.2B (green) and 2.3 (red) as $10^{-6}$ M solutions in CH$_2$Cl$_2$ and of 2.4B (black) as $10^{-8}$ M solution in CH$_2$Cl$_2$. The photo in the inset shows $10^{-5}$ M solutions of 2.1B (left flask) and 2.4B (right flask) upon irradiation with a 365 nm UV lamp.
2.3.2 Fluorescence Spectroscopy

A larger difference between cross-conjugated wires 2.1B-2.3 and linear conjugated wire 2.4B was observed in the fluorescence measurements. We observed the strong fluorescence of compound 2.4B already during its synthesis: a solution of the yellow compound appeared as dark blue. After measuring its fluorescence spectra (excitation and emission) and comparing these with those of 2.1B-2.3 (Figure 2.8), we measured fivefold higher intensity for 2.4B using as solution that was diluted hundred times more. Thus, its fluorescence is about 500 times stronger than that of the anthraquinone wires. This is also shown by the photo in the inset of Figure 2.8, which shows solutions 2.1B and 2.4B under irradiation with a 365 nm UV-lamp: 2.4B (right flask) emits blue light, whereas no strong emission from 2.1B is visible.

Even though the fluorescence intensity of anthraquinone compounds 2.1B-2.3 is much lower compared to anthracene compound 2.4B, the spectra of especially 2.1B and 2.2B show a very large Stokes shift, caused by the large polarization differences between the excited state and the ground state of these molecules. This effect was the main emphasis of the aforementioned study of Leventis et al.\textsuperscript{35} The fluorescence lifetime of 2.1B was found to be 706 ps by time resolved photoluminescence measurements,\textsuperscript{57} which is in the same order as that of anthracene wire 2.6B (1.78 ns), excluding the possibility that the measured signals arise from phosphorescence.

2.4 Redox-Switching of the Anthraquinone Wire

Anthraquinone compound 2.1 is designed as a redox switch: anthraquinone can be reduced to its hydroquinone, which turns the cross-conjugated wire 2.1 into its linear conjugated analogue (see Figure 2.1) and vice versa. This section presents the measurements that prove this switching behavior.

2.4.1 Cyclic Voltammetry and DPV

We have measured cyclic voltammograms of compounds 2.1B, 2.3, 2.4B, 2.14, and parent 9,10-anthraquinone in ODCB/acetonitrile (4:1), using 0.1 M Bu\textsubscript{4}NPF\textsubscript{6} as the electrolyte in a three electrode cell, with platinum working and counter electrodes and a silver wire as reference electrode. Contrary to compound 2.4B, all
Anthraquinone-containing compounds showed two reversible reductions; the representative cyclic voltammogram of 2.1B is shown in Figure 2.9. First the anthraquinone is reduced to the semiquinone anion radical and then to the hydroquinone dianion (see inset Figure 2.9). With the reversibility of both reductions, an important requirement of our switch is fulfilled.

![Cyclic Voltammogram and DPV](image)

**Figure 2.9** Cyclic Voltammogram (left) of 2.1B in ODCB/acetonitrile (the inset shows the redox processes to which the waves in the spectrum are attributed) and DPV (right) of 9,10-anthraquinone (black), 2.1B (blue), 2.3 (red), and 2.14 (green) solutions in ODCB/acetonitrile, to which ferrocene was added.

We have used Differential Pulse Voltammetry (DPV) to compare the positions of these reductions and added ferrocene (Fc) as an internal reference (Fc/Fc\(^+\) = 0.64 V vs. SHE). The first reduction appears at -1.24 V (vs. Fc/Fc\(^+\)) for 2.1B and at -1.25 V, -1.24 V and -1.43 V, for 2.3, 2.14, and anthraquinone respectively. The second reduction is similar to the first reduction- nearly identical for compounds 2.1B, 2.3, and 2.14 (-1.80 V, -1.79 V, and -1.79 V) and significantly more negative for anthraquinone (-2.00 V). These results indicate that the positions of the redox waves are influenced by substitution at the 2- and 6-positions of the anthraquinone, but that the identity of these substituents is less important: the reduction is localized at the anthraquinone unit. These results are very promising for the functionality of our anthraquinone-based redox-switch inside a junction, *i.e.* with its thiols attached to gold electrodes.
2.4.2 Spectroelectrochemistry

In the electrochemical measurement we observed a color change of the solution of 2.1B from yellow to red. This change of color was measured by spectroelectrochemistry: UV-Vis absorption spectra were measured while changing the potential of the solution. The spectrum measured at 0 V vs. SCE (+0.24 V vs. SHE; -0.40 vs. Fc/Fc⁺; see Figure 2.10, red line) was identical to the spectrum measured in CH₂Cl₂ without electrochemical control (Figure 2.6, blue line). When the potential was set at -1.6 V vs. SCE (-2.0 V vs. Fc/Fc⁺), new absorptions around 460 and 670 nm appeared, which are attributed to the hydroquinone dianion. The original spectrum was obtained again after setting the potential back to 0 V (the increased intensity between 300 and 450 nm is attributed to evaporation of the solvent over time). Thus, spectroelectrochemical experiments gave additional prove for the reversible switching of our anthraquinone wire.

![Figure 2.10 Absorption and differential absorption spectra of 2.1B in ODCB/acetonitrile 4:1 at a potential of 0 V (vs SCE) (red), -1.6 V (blue), and back at 0 V (green).](image)

2.4.3 Chemical reduction and oxidation

We have investigated chemical reduction of the anthraquinone switch as an alternative for electrochemical reduction. Chemical reduction is of interest for applications in a junction with a liquid cell, but without electrodes and electrolyte solution, which complicate the experimental setup and could give rise to leakage currents in electrical measurements. The use of metals (like zinc) or sulfur-
containing reducing agents (like \( \text{Na}_2\text{S}_2\text{O}_4 \)) is not desired for chemical reduction of the anthraquinone switch inside a junction, since these reducing agents are heterogeneous (they do not dissolve) or could modify the electrode material. Amines are better candidates for this chemical reduction. Although most amines are not strong enough to reduce anthraquinones,\(^{59}\) tetrakis(dimethylamino)ethylene (TDAE, see inset Figure 2.11) is an exception. This electron-rich amine easily releases two electrons to form its dication, in which the charges are highly delocalized. TDAE is known to have a reducing power comparable to zinc,\(^{60,61}\) and since zinc can be used to reduce anthraquinones (see for example the synthesis of 2.15), TDAE is expected reduce the anthraquinone-based switch to its dianion state.

![TDAE](image)

We have added TDAE to a solution of 2.1B in CDCl\(_3\) in a sealed NMR tube and measured a \(^1\)H NMR spectrum different from that of the starting compound, with broad signals in the aromatic region (Figure 2.11). This broadening could be caused by the formation of paramagnetic species in the sample or exchange processes (for instance proton exchange with the solvent). The signals became slightly sharper after two hours and did not change in the next two days. Opening

**Figure 2.11** \(^1\)H NMR spectra (8.65-7.35 ppm) of (a) anthraquinone 2.1B in CDCl\(_3\), (b) 2 mM 2.1B and 18 mM TDAE in CDCl\(_3\) after 10 minutes, (c) the same solution after 150 minutes, and (d) after bubbling air through this solution (a suspension was formed). The inset shows the structure of TDAE and its oxidation.
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the NMR tube for about 10 seconds had no effect on the solution, however, the spectrum of 2.1B was obtained again upon bubbling air through the solution. This experiment shows that we can “switch” anthraquinone 2.1B with TDAE to another state and that we can “switch” back with oxygen. Based on the reducing power of TDAE we expect the product from the reaction between 2.1B and TDAE to be the hydroquinone dianion of 2.1B (stabilized by the dication of TDAE). However, we cannot exclude the possibility that the semiquinone radical anion state of 2.1B is formed instead of the hydroquinone dianion. Attempts to further analyze the product of the reaction of TDAE with anthraquinone 2.1B by UV-Vis spectroscopy were not successful: the UV-Vis absorption spectra that were obtained upon dilution of the solutions used in the NMR experiments were a superposition of the spectrum of 2.1B and that of TDAE. This could either be due to trace amounts of oxygen in the dried and degassed CHCl₃ used for the dilution or to decreased stability of the salt at low concentrations. Even though the product was not identified and the use of an excess of TDAE and the absence of oxygen appear to be important conditions for the reduction of the anthraquinone, the reversible chemical switching as observed in the NMR experiments is still promising for applications in electrical junctions.

2.5 Energy Levels

Knowing the positions of the energy levels of our molecules with respect to the electrodes is useful for the interpretation of conductance measurements. In Table 2.1 we have listed the values of the HOMO-LUMO gap as determined from the onsets of the UV-Vis spectra (section 2.3.1). In order to obtain information about the positions of the energy levels, we have performed semi-empirical calculations, using the AM1-RHF method for structure optimization on the molecules with methyl-protected thiols. Table 2.1 shows the obtained lengths of the molecules and energies of the HOMO levels (EₑHOMO). These calculations are known to give accurate trends of EₑHOMO for a series of molecules, however the absolute values from these calculations are not reliable. Therefore, we have determined the EₑHOMO of 2.3 by an Ultraviolet Photoelectron Spectroscopy (UPS) measurement. In this measurement UV photons from a Helium lamp (21.2 eV) hit a surface, from which electrons are released with a kinetic energy (Eₑkin) which is 21.2 eV minus the binding energy (Eₑbinding). Thus, Eₑbinding can be determined from measuring Eₑkin.
Table 2.1 Molecular Length and Energy Levels.

<table>
<thead>
<tr>
<th>Wire</th>
<th>HOMO-LUMO gap (eV)$^a$</th>
<th>Length$^b$ calculated (Å)</th>
<th>$E_{\text{HOMO}}$ calculated (eV)</th>
<th>$E_{\text{HOMO}}$ UPS (eV)</th>
<th>$E_{\text{HOMO}}$ corrected$^d$ (eV)</th>
<th>$E_{\text{LUMO}}$ EC$^e$ (eV)</th>
</tr>
</thead>
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<td>-3.56</td>
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<tr>
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<td>-6.04</td>
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<td></td>
</tr>
<tr>
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<td>23.07</td>
<td>-9.045*</td>
<td>-6.1±0.1</td>
<td>-6.10</td>
<td>-3.55</td>
</tr>
<tr>
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<td>2.79</td>
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<td>-5.39</td>
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<td></td>
</tr>
<tr>
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<td>24.26</td>
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<td>-5.36</td>
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</tr>
<tr>
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<td>-5.74</td>
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<td></td>
</tr>
<tr>
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<td>3.75</td>
<td>24.06</td>
<td>-8.041</td>
<td>-5.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Determined from the onsets of the UV-Vis spectra of the 2.##B compounds in CH$_2$Cl$_2$.
b. The distance from S- to S-atom (we used the outer H-atoms in absence of S-atoms for 2.2B and 2.3).
c. Hyperchem$^TM$ Release 7.52 for Windows Molecular Modeling Systems. Structures were optimized using the AM1-RHF method. We used methyl-substituted thiols in the calculations.
d. All levels were shifted by +2.16 eV to get agreement with the HOMO level as determined by the UPS measurement.
e. determined from electrochemical measurements (DPV), with $E_{\text{HOMO}}$ of ferrocene at -4.8 eV.$^62$

* This value is much lower than $E_{\text{HOMO}}$ of 2.1 and 2.2, probably because this molecule is symmetric in the calculations, due to the lack of substituted thiols that bend out of the plane. When comparing the HOMO-LUMO gap and $E_{\text{LUMO}}$ from solution measurements on 2.1B and 2.3, $E_{\text{HOMO}}$ of 2.3 is expected to be only 70 meV lower in energy than that of 2.1B.

Figure 2.12 UPS spectra of ~20 nm thermally evaporated 2.3 on a gold substrate (solid line) and of 150 nm gold on mica (dotted line) at a bias of -4 V.
We have thermally evaporated a layer of about 20 nm of 2.3 onto a substrate of 150 nm gold on mica. The UPS spectrum was recorded at a bias of -4 V, to accelerate the electrons between sample and detector. For comparison we also measured the gold substrate without evaporated compound (without cleaning the substrate prior to the measurement). Both UPS spectra are given in Figure 2.12. The energy level of the HOMO \(E_{\text{HOMO}}\) of 2.3 is determined by subtraction of the width of the spectrum \(i.e.\) the right onset minus the left onset) from the energy of the photons, which gives \(E_{\text{HOMO}} = -6.1\pm0.1\) eV. The Fermi level of the gold layer was determined by the same method, to give \(E_{\text{Fermi}} = -4.5\) eV. This latter value deviates from values measured by others,\(^{63}\) most likely due to adsorbed species from the ambient on the gold surface. The value of \(-6.1\pm0.1\) eV was used to adjust the energy levels from the semi-empirical calculations (see Table 2.1). We will discuss the alignment of our molecular levels with the electrode materials and the implication for the electrical conductance in Chapters 4 and 5.

### 2.6 Crystal Structure

We obtained a crystal structure from anthraquinone wire 2.3 and found that the molecule is nearly flat (Figure 2.13), in contrast to the regioisomer 2,7-bis(phenylethynyl)-9,10-anthraquinone, which is bent.\(^{35}\) The outer phenyl rings of 2.3 are twisted only 7.26° with respect to the anthraquinone core. When we look at the packing in the crystal structure, we find two spacing distances: there are rows of molecules in which the phenyl-acetylene-phenyl unit of one molecule lays on top of the anthraquinone unit of the next molecule with a distance of 3.494 Å. In between these rows there are slides of molecules of which the phenyl-acetylene-phenyl unit of one molecule lays on top of the phenyl-acetylene-phenyl unit of the

![Figure 2.13 Crystal Structure of 2.3 (a and b) and its packing (c and d).](image-url)
next molecule, with the much larger spacing of 10.261 Å. Especially the finding that the molecule is nearly flat -in agreement with gas phase calculations- is of great importance for conductance measurements, since the electronic communication between the different parts of the conjugated molecule will be optimal if they lay in one plane (i.e. all \( p_z \)-orbitals are parallel).

2.7 Conclusions

We have synthesized an anthraquinone-based redox switch, along with anthracene and dihydroanthracene analogues. The conjugation pattern of these compounds varies from cross-conjugation to linear conjugation and broken conjugation, which is reflected by their spectroscopic properties. We have shown that the anthraquinone-based redox switch can be reversibly switched by electrochemistry and by chemical reduction and oxidation. With these compounds at hand, we can start comparing the electronic transport through these molecular wires to find the influence of the conjugation pattern on the conductance by various methods (see Chapter 5).
2.8 Experimental Section

2.8.1 General

All reactions were performed under a nitrogen atmosphere, using oven-dried glassware (150°C) and dry solvents (solvents for reactions towards 2.8, and 2.14-2.18 were not dried). All chemicals were purchased from Aldrich, Acros, or AlfaAesar and used as received. Diisopropylamine and triethylamine were distilled over NaOH. Copper iodide was heated and dried under vacuum. TBAF refers to tetrabutylammonium fluoride trihydrate. Silica gel was purchased from Screening Devices b.v. as SilicaFlash P60, with particle sizes of 40-63 μm and a pore size of 60Å. 

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Varian VXR-300 (300 MHz), a Varian AMX400 (400 MHz), or a Varian unity plus (500 MHz) at room temperature, unless depicted otherwise. Spectra were referenced to the solvent line (CDCl\(_3\): H, 7.26 ppm; C, 77.0 ppm; C\(_2\)D\(_2\)Cl\(_4\): H, 5.95 ppm; C, 72.5 ppm) relative to tetramethylsilane. FT-IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer, using the SMART iTR for ATR measurements (diamond). Indicated solids were measured in KBr using a Smart Collector DRIFT setup and indicated liquids were measured in the transmission mode between NaCl windows. Mass spectra were recorded on a Thermo Scientific Orbitrap XL or on a Jeol JMS-600H.

UV-Vis absorption spectra were measured on a Perkin/Elmer Lambda 900 UV-Vis-NIR Spectrometer at 10\(^{-5}\) M in dichloromethane in a quartz cuvet with a pathlength of 1 cm. Fluorescence measurements were performed on a Fluorolog 3 (Jobin Yvon Horiba) in dichloromethane, using filters of 370 and 399 nm. Time-resolved photoluminescence measurements were performed, exciting the solutions at 380 nm by a 150 fs pulsed Kerr mode locked Ti-sapphire laser and the photoluminescence was recorded by a Hamamatsu streak camera working in synchroscan mode, with a photocathode sensitive in the visible spectral range. Cyclic Voltammetry spectra were recorded at 10 mV/s on an Autolab PGstat 100 with Pt working and counter electrodes and a Ag reference electrode. Concentrations in analyte were mM in a mixture of o-dichlorobenzene (ODCB) and acetonitrile (4:1) containing Bu\(_4\)NPF\(_6\) (0.1 M) as supporting electrolyte. Solutions were purged with nitrogen prior to the measurement. Ferrocene was used as a reference compound. For spectroelectrochemical measurements a CHI630B electrochemical analyzer and a HP8453 UV-Vis spectrometer were used. A thin cell (1 mm) was supported with a Pt gauze working electrode, a Pt wire counter electrode and a SCE reference electrode.

For the UPS measurement 20 nm 2.3 was thermally evaporated onto gold (150 nm) on mica (see Experimental Section of Chapter 3). The UPS measurement was run in a homebuilt UHV system with a Helium lamp (50 mA, 0.58 kV, 0.2 mbar). The detector was grounded and a bias of -4 V was applied on the sample. The UPS spectrum was recorded within 10 minutes after positioning the UV beam on the sample.
2.8.2 Synthesis and Analysis of the Molecular Wires (2.1-2.7)

2,6-Bis[(4-tert-butylthiophenyl)ethynyl]-9,10-anthraquinone (2.1B)

To a suspension of 2.14 (579 mg, 1.58 mmol), dichlorobis(triphenylphosphine)palladium(II) (110 mg, 0.16 mmol), and copper iodide (34 mg, 0.18 mmol) in THF (65 mL) were added diisopropylamine (13 mL) and 2.13 (748 mg, 3.93 mmol). The reaction mixture was refluxed for 21 hours and poured into water (400 mL). This was extracted with CH$_2$Cl$_2$ (4 x 200 mL) and the combined organic layers were washed with water (4 x 400 mL) and brine (400 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude solid was preadsorbed onto silica and purified by column chromatography twice (silica gel, CH$_2$Cl$_2$; silica gel, CH$_2$Cl$_2$/heptane 1:1). The obtained solid was recrystallized from toluene to yield 627 mg (1.07 mmol, 84%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, $J = 1.7$, 2H), 8.33 (d, $J = 8.1$, 2H), 7.92 (dd, $J = 8.1$, 1.7, 2H), 7.60-7.50 (m, 8H), 1.32 (s, 18H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 181.92, 137.28, 136.56, 134.58, 133.50, 132.27, 131.74, 130.33, 129.61, 127.53, 122.48, 93.95, 89.35, 46.72, 31.02.

IR (cm$^{-1}$): 2974, 2863, 2214, 1671, 1593, 1586, 1473, 1365, 1324, 1165, 982, 916, 880, 847, 835, 740, 709. HRMS (APCI) calculated for [M+H]$^+$ 585.1916, found 585.1870. Calcld for C$_{38}$H$_{32}$O$_2$S$_2$: C, 78.05; H, 5.52; S, 10.97. Found: C, 78.42; H, 5.56; S, 10.88.

2,6-Bis[(4-acetylthiophenyl)ethynyl]-9,10-anthraquinone (2.1A)

Chloroform (18 mL) was added to 2.1B (102 mg, 0.17 mmol) and heated for a moment to obtain a yellow solution, to which acetyl chloride (5.5 mL) was added. A solution of bromine (0.2-0.5 mL, 0.3 M) in acetyl chloride/acetic acid (1:1) was added dropwise in the dark. The reaction mixture was stirred for 2-4 hours and poured into 250 mL ice water and stirred for 1 hour. The mixture was extracted with CH$_2$Cl$_2$ (3 x 200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. This reaction was repeated 3 times. The combined yellow solids (0.30 g) were preadsorbed onto silica and purified by column chromatography (silica gel, CH$_2$Cl$_2$) to yield 181 mg (0.324 mmol, 46%) of the title compound as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.45 (d, $J = 1.2$, 2H), 8.33 (d, $J = 8.0$, 2H), 7.92 (dd, $J = 8.0$, 1.7, 2H), 7.62 (d, $J = 8.3$, 4H), 7.45 (d, $J = 8.3$, 4H), 2.46 (s, 6H). $^{13}$C NMR (125 MHz, CHCl$_3$): δ 193.16, 181.87, 136.63, 134.31, 133.50, 132.42, 132.35, 130.41, 129.45, 129.27, 127.54, 123.37, 93.60, 89.45, 30.36. IR (cm$^{-1}$): 3065, 2923, 2219, 1702, 1670, 1589, 1324, 1303, 1276, 1245, 1121, 1101, 1090, 981, 957, 919, 881, 863, 827, 741, 711. HRMS (APCI) calculated for [M+H]$^+$ 557.0876, found 557.0834. Calcld for C$_{34}$H$_{20}$O$_4$S$_2$: C, 73.36; H, 3.62; S, 11.52. Found: C, 72.96; H, 3.72; S, 11.32.

2-bromo-6-[(4-tert-butylthiophenyl)ethynyl]-9,10-anthraquinone

To a suspension of 2.14 (736 mg, 2.01 mmol), dichlorobis(triphenylphosphine)palladium(II)
(75.9 mg, 0.108 mmol), and copper iodide (27.7 mg, 0.145 mmol) in THF (80 mL) were added diisopropylamine (12 mL) and 2.13 (422 mg, 2.22 mmol). The reaction mixture was refluxed for 22 hours and all volatiles were removed. The crude solid was dissolved in CH$_2$Cl$_2$ (400 mL), washed with water (2 x 200 mL) and brine (200 mL), dried over Na$_2$SO$_4$, filtered, and preadsorbed onto silica. This reaction was repeated and the combined material was purified by column chromatography twice (silica gel, CH$_2$Cl$_2$; silica gel, CH$_2$Cl$_2$/heptane 2:3) to afford 737 mg (1.55 mmol, 38%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (d, $J = 1.9$, 1H), 8.44 (d, $J = 1.4$, 1H), 8.30 (d, $J = 8.0$, 1H), 8.19 (d, $J = 8.3$, 1H), 7.93 (ddd, $J = 9.6$, 8.2, 1.8, 2H), 7.61-7.50 (m, 4H), 1.32 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$): 181.83, 181.30, 137.27, 137.24, 136.65, 134.64, 134.53, 133.23, 131.99, 131.94, 131.74, 130.31, 130.00, 129.76, 129.09, 127.56, 122.40, 94.11, 89.25, 46.72, 31.01. IR (KBr, cm$^{-1}$): 3322, 3065, 2977, 2961, 2865, 2215, 1672, 1599, 1580, 1327, 1314, 1305, 1283, 1167, 980, 865, 850, 832, 737, 710, 546, 540.

2-[(4-tert-butylthiophenyl)ethynyl]-6-(phenylethynyl)-9,10-anthraquinone (2.2B)

To a suspension of 2-bromo-6-[(4-tert-butylthiophenyl)ethynyl]-9,10-anthraquinone (399 mg, 0.84 mmol), dichlorobis(triphenylphosphine)palladium(II) (66 mg, 0.093 mmol), and copper iodide (21 mg, 0.11 mmol) in THF (42 mL) were added diisopropylamine (8 mL) and phenylacetylene (161 mg, 1.58 mmol). The reaction mixture was refluxed for 20 hours and all volatiles were removed. The residue was dissolved in 300 mL CH$_2$Cl$_2$, washed with water (3 x 200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude solid was preadsorbed onto silica and purified by column chromatography twice (silica gel, CH$_2$Cl$_2$; silica gel, CH$_2$Cl$_2$/heptane 1:1, gradually increasing to 3:2). The obtained solid was recrystallized from toluene to yield 296 mg (0.60 mmol, 71%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.44 (d, $J = 1.6$, 2H), 8.32 (dd, $J = 8.0$, 1.8, 2H), 7.91 (dt, $J = 8.0$, 1.7, 2H), 7.62-7.51 (m, 6H), 7.44-7.37 (m, 3H), 1.32 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 181.83, 137.27, 136.55, 136.52, 134.57, 133.52, 133.48, 132.30, 132.15, 131.91, 131.74, 130.31, 130.29, 129.88, 129.56, 129.21, 128.53, 127.51, 127.49, 122.50, 122.23, 94.58, 93.90, 89.37, 88.01, 46.71, 31.02. IR (KBr, cm$^{-1}$): 3346, 2980, 2958, 2937, 2895, 2861, 2217, 1681, 1598, 1336, 1304, 1169, 922, 856, 835, 756, 740, 712, 691, 579, 544, 533. HRMS (APCI) calculated for [M+H]$^+$ 497.15698, found 497.15661. Calcd for C$_{34}$H$_{22}$O$_2$S: C, 83.23; H, 4.87; S, 6.46. Found: C, 81.75; H, 4.82; S, 6.38.

2-[(4-acetylthiophenyl)ethynyl]-6-(phenylethynyl)-9,10-anthraquinone (2.2A)

To a suspension of 2-bromo-6-[(4-acetylthiophenyl)ethynyl]-9,10-anthraquinone (399 mg, 0.84 mmol), dichlorobis(triphenylphosphine)palladium(II) (66 mg, 0.093 mmol), and copper iodide (21 mg, 0.11 mmol) in THF (42 mL) were added diisopropylamine (8 mL) and phenylacetylene (161 mg, 1.58 mmol). The reaction mixture was refluxed for 20 hours and all volatiles were removed. The residue was dissolved in 300 mL CH$_2$Cl$_2$, washed with water (3 x 200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude solid was preadsorbed onto silica and purified by column chromatography twice (silica gel, CH$_2$Cl$_2$; silica gel, CH$_2$Cl$_2$/heptane 1:1, gradually increasing to 3:2). The obtained solid was recrystallized from toluene to yield 296 mg (0.60 mmol, 71%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.44 (d, $J = 1.6$, 2H), 8.32 (dd, $J = 8.0$, 1.8, 2H), 7.91 (dt, $J = 8.0$, 1.7, 2H), 7.62-7.51 (m, 6H), 7.44-7.37 (m, 3H), 1.32 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 181.83, 137.27, 136.55, 136.52, 134.57, 133.52, 133.48, 132.30, 132.15, 131.91, 131.74, 130.31, 130.29, 129.88, 129.56, 129.21, 128.53, 127.51, 127.49, 122.50, 122.23, 94.58, 93.90, 89.37, 88.01, 46.71, 31.02. IR (KBr, cm$^{-1}$): 3346, 2980, 2958, 2937, 2895, 2861, 2217, 1681, 1598, 1336, 1304, 1169, 922, 856, 835, 756, 740, 712, 691, 579, 544, 533. HRMS (APCI) calculated for [M+H]$^+$ 497.15698, found 497.15661. Calcd for C$_{34}$H$_{22}$O$_2$S: C, 83.23; H, 4.87; S, 6.46. Found: C, 81.75; H, 4.82; S, 6.38.
A nthraquinone- and Anthracene-based Molecular Wires and Switches

readsorbed onto silica and purified by column chromatography (silica gel, CH$_2$Cl$_2$) to yield 233 mg (0.483 mmol, 83%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (dd, $J = 1.2, 0.5, 2H$), 8.32 (dd, $J = 8.0, 2.3, 2H$), 7.92 (dd, $J = 8.1, 1.7, 2H$), 7.64-7.57 (m, 4H), 7.46-7.44 (m, 2H), 7.43-7.38 (m, 3H), 2.46 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): 193.15, 181.92, 181.87, 136.57, 136.55, 134.29, 133.49, 133.45, 132.41, 132.36, 132.12, 131.90, 130.38, 130.28, 129.87, 129.38, 129.25, 129.21, 128.52, 127.50, 123.21, 94.58, 93.55, 89.47, 88.01, 30.35. IR (cm$^{-1}$): 3060, 2923, 2211, 1697, 1671, 1584, 1323, 1300, 1274, 983, 950, 857, 827, 754, 741, 710, 687, 624. HRMS (APCI) calculated for [M+H]$^+$ 483.10494, found 483.10485. Calcd for C$_{32}$H$_{18}$O$_3$: C, 79.65; H, 3.76; S, 6.64. Found: C, 78.82; H, 3.99; S, 6.19.

2,6-Bis(phenylethynyl)-9,10-anthraquinone (2.3)

This compound was prepared by a modification of literature methods.$^{35}$ To a suspension of 2.14 (597 mg, 1.63 mmol), dichlorobis(triphenylphosphine)palladium(II) (113 mg, 0.16 mmol), and copper iodide (36.4 mg, 0.19 mmol) in THF (80 mL) were added diisopropylamine (12 mL) and phenylacetylene (410 mg, 4.02 mmol). The reaction mixture was refluxed for 21 hours and all volatiles were removed. The residue was suspended in 800 mL CH$_2$Cl$_2$ and washed with water (3 x 200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The crude solid was preadsorbed onto silica and purified by column chromatography twice (silica gel, CH$_2$Cl$_2$; silica gel, CH$_2$Cl$_2$/heptane 1:1, gradually increasing to 2:1). The obtained solid was recrystallized from toluene to yield 373 mg (0.91 mmol, 56%) of the title compound as dark yellow needles.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.47 (s, 2H), 8.34 (d, $J = 8.0, 2H$), 7.94 (d, $J = 8.0, 2H$), 7.62 (d, $J = 3.4, 4H$), 7.43 (bd, $J = 2.4, 6H$).

$^{13}$C NMR (125 MHz, CDCl$_3$): 181.98, 136.53, 133.50, 132.17, 131.90, 130.28, 129.85, 129.21, 128.53, 127.49, 122.23, 94.53, 88.02. IR (cm$^{-1}$): 3315, 3067, 2205, 1667, 1586, 1444, 1323, 1299, 1272, 1249, 1177, 984, 910, 880, 847, 757, 742, 708, 681, 660. HRMS (APCI) calculated for [M+H]$^+$ 409.12231, found 409.12279. Calcd for C$_{30}$H$_{16}$O$_2$: C, 88.22; H, 3.95. Found: C, 88.22; H, 3.86.

2,6-Bis[(4-tert-butylthiophenyl)ethynyl]-9,10-diacetoxyanthracene (2.4B)

To a suspension of 2.15 (0.474 g, 1.05 mmol), dichlorobis(triphenylphosphine)palladium(II) (72.2 mg, 0.103 mmol) and copper iodide (57.5 mg, 0.302 mmol) in THF (80 mL) were added 2.13 (0.640 g, 3.36 mmol) and diisopropylamine (16 mL). The reaction mixture was refluxed for 24 hours and the solvent was removed by rotary evaporation. The crude material was suspended in CH$_2$Cl$_2$ (100 mL) and poured into water (200 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (100 mL) and the combined organic layers were washed with water (4 x 200 mL), dried over Na$_2$SO$_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to give 0.629 g of a yellow-brown solid. This was dissolved in hot chloroform (30 mL) and upon addition of hexane (30 mL) a yellow precipitate was formed. The solution was cooled, the precipitate was filtered off, washed with hexane and dried to afford 532 mg (0.79 mmol, 75%) of
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the title compound as a yellow solid.

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz): } \delta 8.12 (s, 2H), 7.91 (d, J = 8.8 \text{ Hz}, 2H), 7.59 (d, J = 8.8 \text{ Hz}, 2H), 7.57-7.54 (m, 8H), 2.69 (s, 6H), 1.32 (s, 18H). \]

\[ ^{13}C \text{NMR (CDCl}_3, 100 \text{ MHz): } \delta 169.3, 140.2, 137.3, 133.8, 129.0, 125.4, 124.4, 123.6, 123.2, 122.2, 121.5, 91.1, 91.0, 46.6, 31.0, 20.84. \]

IR (KBr, cm\(^{-1}\)): 2972, 2959, 2922, 2897, 2862, 2210, 1761, 1618, 1364, 1192, 1158, 1045, 829.

MS (EI): \( m/z \) 670 (M\(^+\), 35%). Calcd for C\(_{42}\)H\(_{38}\)O\(_4\)S\(_2\): C, 75.19; H, 5.71. Found: C, 75.20; H, 5.63.

2,6-Bis[(4-acetylthiophenyl)ethynyl]-9,10-diacetoxyanthracene (2.4A)

2.4B (100 mg, 0.20 mmol) was dissolved in chloroform (17 mL) and acetyl chloride (5.0 mL) was added. A solution of bromine (0.2 mL, 0.3 M) in acetyl chloride/acetic acid (1:1) was added dropwise in the dark. The reaction mixture was stirred for 1.5 hours and poured into 250 mL ice water and stirred for 1 hour. The mixture was extracted with CH\(_2\)Cl\(_2\) (4 x 200 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated. The crude material was preadsorbed onto silica and purified by column chromatography (silica gel, CH\(_2\)Cl\(_2\)) to yield 27 mg (0.042 mmol, 27%) of the title compound as a yellow solid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3): \delta 8.12 (d, J = 0.9, 2H), 7.92 (d, J = 9.1, 2H), 7.63 (d, J = 8.4, 4H), 7.59 (d, J = 9.0, 1.4, 2H), 7.44 (d, J = 8.4, 4H), 2.69 (s, 6H), 2.45 (s, 6H). \]

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3): \delta 192.36, 168.21, 138.70, 132.94, 130.96, 127.77, 127.26, 124.05, 122.82, 122.42, 122.06, 120.79, 120.04, 89.79, 89.67, 29.10, 19.58. \]

IR (cm\(^{-1}\)): 2921, 2851, 2212, 1749, 1689, 1360, 1206, 1144, 1046, 1004, 954, 885, 826, 811, 790, 741, 625. HRMS (APCI) calculated for [M+H]\(^+\) 643.12436, found 643.12429.

2,6-Bis[(4-tert-butylthiophenyl)ethynyl]-9,10-dimethoxyanthracene (2.5B)

To a suspension of 2.16 (317 mg, 0.80 mmol), dichlorobis(triphenylphosphine)palladium(II) (58.0 mg, 0.083 mmol), and copper iodide (19.2 mg, 0.101 mmol) in THF (40 mL) were added diisopropylamine (8 mL) and 2.13 (402 mg, 2.11 mmol). The reaction mixture was refluxed for 16 hours and poured into water (200 mL). This was extracted with CH\(_2\)Cl\(_2\) (4 x 100 mL) and the combined organic layers were washed with water (6 x 100 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated. The crude solid was preadsorbed onto silica and purified by column chromatography twice (silica gel, CH\(_2\)Cl\(_2\); silica gel, CH\(_2\)Cl\(_2\)/heptane 1:1). The obtained solid was recrystallized from toluene to yield 276 mg (0.45 mmol, 56%) of the title compound as a yellow solid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3): \delta 8.49 (s, 2H), 8.27 (d, J = 8.9, 2H), 7.61-7.53 (m, 10H), 4.15 (s, 6H), 1.32 (s, 18H). \]

\[ ^{13}C \text{NMR (125 MHz, CDCl}_3): \delta 148.48, 137.30, 133.49, 131.58, 127.90, 126.55, 125.16, 124.32, 123.50, 123.01, 120.31, 91.66, 90.27, 63.68, 46.57, 31.00. \]

IR (cm\(^{-1}\)): 3072, 2957, 2938, 2838, 2208, 1617, 1487, 1450, 1359, 1302, 1162, 1126, 1059, 953, 902, 832, 718. HRMS (APCI) calculated for [M+H]\(^+\) 615.23860, found 615.23833. Calcd for C\(_{40}\)H\(_{38}\)O\(_2\): C, 78.14; H, 6.23; S, 10.43. Found: C, 78.77; H, 6.21; S, 10.21.
2,6-Bis[(4-acetyltiophenyl)ethynyl]-9,10-dimethoxyanthracene (2.5A)

Chloroform (20 mL) was added to 2.5B (107 mg, 0.17 mmol) and heated for a moment to obtain a yellow solution, to which acetyl chloride (5 mL) was added. A solution of bromine (0.25 mL, 0.3 M) in acetyl chloride/acetic acid (1:1) was added dropwise in the dark. The reaction mixture was stirred for 2-3 hours and poured into 250 mL ice water and stirred for 1 hour. The mixture was extracted with CH$_2$Cl$_2$ (3 x 150 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. This reaction was repeated once. The combined yellow solids (0.22 g) were preadsorbed onto silica and purified by column chromatography (silica gel, CH$_2$Cl$_2$) to yield 78 mg (0.13 mmol, 43%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.49 (s, 2H), 8.27 (d, $J = 9.0$, 2H), 7.65 (d, $J = 8.0$, 4H), 7.57 (d, $J = 9.0$, 2H), 7.44 (d, $J = 8.0$, 4H), 4.16 (s, 6H), 2.46 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.44, 148.52, 134.26, 132.26, 128.25, 127.88, 126.68, 125.17, 124.40, 124.34, 123.03, 120.20, 91.83, 90.04, 63.69, 30.32. IR (cm$^{-1}$): 2997, 2940, 2834, 2209, 1694, 1443, 1354, 1301, 1127, 1060, 983, 962, 881, 828, 810, 714, 627. HRMS (APCI) calculated for [M+H]$^+$ 587.13453, found 587.13472. Calcd for C$_{36}$H$_{26}$O$_4$S$_2$: C, 73.70; H, 4.47; S, 10.93. Found: C, 72.13; H, 4.46; S, 10.44.

2,6-Bis[(4-tert-butylthiophenyl)ethynyl]anthracene (2.6B)

To a suspension of 2.17 (404 mg, 1.20 mmol), dichlorobis(triphenylphosphine)palladium(II) (85.2 mg, 0.121 mmol), and copper iodide (36.4 mg, 0.191 mmol) in THF (60 mL) were added diisopropylamine (12 mL) and 2.13 (555 mg, 2.91 mmol). The reaction mixture was refluxed for 18 hours and all volatiles were removed. The residue was suspended in 150 mL CH$_2$Cl$_2$ and poured into 350 mL water. The aqueous phase was extracted with CH$_2$Cl$_2$ (2 x 150 mL). The combined organic layers were washed with water (3 x 200 mL), dried over Na$_2$SO$_4$, filtered, and part of the solvent was removed under reduced pressure. The concentrated solution was run over a column (silica gel, CH$_2$Cl$_2$). The obtained solid was recrystallized from toluene to yield 533 mg (0.96 mmol, 80%) of the title compound as slightly green needles.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.38 (s, 2H), 8.22 (s, 2H), 7.99 (d, $J = 8.7$, 2H), 7.58-7.52 (m, 10H), 1.32 (s, 18H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.29, 133.43, 131.94, 131.55, 131.12, 128.43, 127.97, 126.39, 123.54, 120.31, 91.44, 90.17, 46.56, 31.00. IR (cm$^{-1}$): 2960, 2939, 2919, 2893, 2958, 2211, 2163, 1918, 1619, 1486, 1474, 1454, 1395, 1365, 1279, 1170, 1154, 1098, 1015, 909, 867, 829, 797, 730, 657. HRMS (APCI) calculated for [M+H]$^+$ 555.2175, found 555.2131. Calcd for C$_{38}$H$_{34}$S$_2$: C, 82.26; H, 6.18; S, 11.56. Found: C, 82.27; H, 6.19; S, 11.43.

2,6-Bis[(4-acetylthiophenyl)ethynyl]anthracene (2.6A)

2.6B (302 mg, 0.545 mmol) was dissolved in chloroform (50 mL) and toluene (50 mL) upon heating and stirring. After cooling to room temperature acetyl chloride (10 mL) was added. While stirring, BBr$_3$ (1 M in CH$_2$Cl$_2$, 15 mL, 15
mmol) was added slowly. The reaction mixture was stirred for 5 hours and poured into ice water (600 mL). This was extracted with CH$_2$Cl$_2$ (4 x 200 mL), dried over Na$_2$SO$_4$, filtered, and all volatiles were removed by rotary evaporation. The crude material was preadsorbed onto silica gel and purified by column chromatography (silica gel, CH$_2$Cl$_2$/heptane, gradually increased from 2:1 to 4:1) yielding 174 mg (0.33 mmol, 61%) of the title compound as a dark yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): 8.38 (s, 2H), 8.23 (s, 2H), 7.99 (d, $J$ = 8.8, 2H), 7.63 (d, $J$ = 8.2, 4H), 7.55 (d, $J$ = 8.6, 2H), 7.44 (d, $J$ = 8.2, 4H), 2.45 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.42, 134.27, 132.24, 132.09, 131.59, 131.17, 128.47, 128.24, 127.96, 126.44, 124.46, 120.23, 91.63, 89.95, 30.31. IR (cm$^{-1}$): 3371, 3058, 2957, 2921, 2851, 2211, 1913, 1691, 1615, 1486, 1396, 1352, 1280, 1110, 948, 908, 822, 802, 626. HRMS (APCI) calculated for [M+H]$^+$ 527.1134, found 527.1092. Calcd for C$_{34}$H$_{22}$O$_2$S$_2$: C, 77.54; H, 4.21; S, 12.18. Found: C, 77.90; H, 5.34; S, 10.48.

2,6-Bis[(4-tert-butylthiophenyl)ethynyl]-9,10-dihydroanthracene (2.7B)

To a suspension of 2.18 (395 mg, 2.06 mmol), dichlorobis(triphenylphosphine)palladium(II) (147 mg, 0.21 mmol), and copper iodide (55.4 mg, 0.29 mmol) in triethylamine (35 mL) was added 2.13 (937 mg, 4.93 mmol). The reaction mixture was refluxed for 16 hours and all volatiles were removed. The resulting solid was preadsorbed onto silica and run over a plug of silica gel, eluted with CH$_2$Cl$_2$. The product was preadsorbed onto silica and further purified by column chromatography (silica gel, CH$_2$Cl$_2$/heptane 1:2). The obtained solid was recrystallized form diethyl ether to yield 288 mg (0.52 mmol, 25%) of the title compound as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$): 7.53-7.46 (m, $J$ = 8.1, 10H), 7.39 (dd, $J$ = 7.8, 1.2, 2H), 7.29 (d, $J$ = 7.8, 2H), 3.96 (s, 4H), 1.30 (s, 18H).

$^{13}$C NMR (125 MHz, CDCl$_3$): 137.24, 136.84, 136.37, 133.05, 131.44, 130.52, 129.60, 127.55, 123.76, 123.76, 120.87, 90.97, 88.40, 46.47, 35.85, 30.97. IR (cm$^{-1}$): 2960, 2919, 2894, 2859, 2209, 1500, 1417, 1369, 1169, 1152, 1014, 922, 829, 810, 803, 716. HRMS (APCI) calculated for [M+H]$^+$ 557.23312, found 557.23256. Calcd for C$_{38}$H$_{36}$S$_2$: C, 81.97; H, 6.52; S, 11.52. Found: C, 82.04; H, 6.53; S, 11.53.

2,6-Bis[(4-acetylthiophenyl)ethynyl]-9,10-dihydroanthracene (2.7A)

2.7B (188 mg, 0.334 mmol) was dissolved in chloroform (21 mL) and toluene (20 mL) and acetyl chloride (4 mL) was added. While stirring, BBr$_3$ (1 M in CH$_2$Cl$_2$, 8 mL, 8 mmol) was added slowly. The reaction mixture was stirred for 5 hours and poured into ice water (400 mL). This was extracted with CH$_2$Cl$_2$ (4 x 125 mL), dried over Na$_2$SO$_4$, filtered, and all volatiles were removed by rotary evaporation. The crude material was preadsorbed onto silica gel and purified by column chromatography (silica gel, CH$_2$Cl$_2$/heptane 2:1) yielding 83 mg (0.157 mmol, 47%) of the title compound as a light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): 8.35 (d, $J$ = 8.1, 4H), 7.49 (s, 2H), 7.43-2.7.37 (m, 6H), 7.29 (d, $J$ = 7.8, 2H), 3.96 (s, 4H), 2.44 (d, $J$ = 1.0, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.50, 136.93, 136.35, 134.20, 132.11, 130.57, 129.64, 127.84, 127.55, 124.66, 120.71, 91.17, 88.19, 35.82, 30.27. IR (cm$^{-1}$): 3057, 2926, 2859, 2209, 1705, 1498, 1415, 1396, 1124, 1109, 1100, 1089, 949.
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920, 829, 811, 619. HRMS (APCI) calculated for [M+H]+ 529.12905, found 529.12893. Calcd for C_{34}H_{24}O_{2}S_{2}: C, 77.24; H, 4.58; S, 12.13. Found: C, 77.25; H, 4.65; S, 12.03.

2.8.3 Synthesis and Analysis of the Acetylene Precursors (2.8-2.13)

4-Iodophenylthioacetate (2.8)

This compound was prepared according to a literature procedure. A solution of pipsyl chloride (5.01 g, 16.6 mmol) and N,N-dimethyl acetamide (4.6 mL, 49 mmol) in 1,2-dichloroethane (130 mL) was added to a suspension of zinc powder (3.85 g, 58.9 mmol) and dichlorodimethylsilane (7.0 mL, 58 mmol) in 1,2-dichloroethane (130 mL). The gray suspension was stirred for 2.5 hours at 70-75 °C to give a yellow-green solution. This solution was cooled to 50 °C and acetyl chloride (1.52 mL, 21.4 mmol) was added. The mixture was stirred for 30 minutes at 45-50 °C, cooled to 40 °C, filtered and poured into water (300 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 200 mL) and the combined organic layers were dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation to give a yellow liquid, which was purified by column chromatography (silica gel, CH$_2$Cl$_2$/hexane 1:4). 3.73 g (13.4 mmol, 81 %) of the title compound was obtained as a white solid.

Mp: 52-54 °C. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.74 (dd, J = 7.7, J = 1.5, 2H), 7.14 (dd, J = 7.5, J = 1.8, 2H), 2.43 (s, 3H).

13C NMR (CDCl$_3$, 75 MHz): δ 193.07, 138.29, 135.89, 127.69, 95.90, 30.20. IR (KBr, cm$^{-1}$): 2962, 2922, 1907, 1695, 1466, 1354, 1260, 1122, 811.

1-Thioacetyl-4-[(trimethylsilyl)ethynyl]benzene (2.9)

This compound was prepared by a modification of the literature method. 2.8 (1.34 g, 4.80 mmol) was dissolved in THF (7 mL). Diisopropylethylamine (1.04 g, 8.04 mmol) and trimethylsilylacetylene (0.731 g, 7.44 mmol) were added and the mixture was stirred for 1 hour. Dichlorobis(triphenylphosphine)palladium(II) (0.179 g, 0.26 mmol) and copper iodide (0.053 g 0.28 mmol) were added, all in the glovebox, and the reaction mixture was stirred 46 hours, after which it was poured into water (30 mL). This mixture was extracted with ether (3 x 50 mL) and the combined organic layers were washed with a NH$_4$Cl solution (2 x 75 mL) and brine (2 x 75 mL). The combined aqueous layers were extracted with ether (75 mL). All combined organic layers were dried over Na$_2$SO$_4$. The solvent was removed by rotary evaporation to give 1.69 g of a red oil. This crude product was purified by column chromatography twice (silica gel, hexane gradually increasing to hexane/CH$_2$Cl$_2$ 4:1; then silica gel, hexane/CH$_2$Cl$_2$ 1:1). 0.912 g (3.71 mmol, 77 %) of the title compound was obtained as a yellowish oil that crystallized upon standing.

Mp: 48-49 °C. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.49 (dd, J = 7.5, J = 1.1, 2H), 7.34 (dd, J = 7.5, J = 1.5, 2H), 2.41 (s, 3H), 0.26 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 75 MHz): δ 193.18, 134.00, 132.45, 128.29, 124.29, 104.13, 96.15, 30.18, -0.16. IR (KBr, cm$^{-1}$): 2962, 2160, 1705, 1483, 1256, 1111, 869, 834.
4-Ethynyl-1-thioacetylbenzene (2.10)

The conditions that were used for the preparation and the purification of this compound were based on literature procedures.\(^{57,64}\) A solution of 2.9 (0.901 g, 3.63 mmol) in THF (16 mL) was cooled to 0 °C. A solution of TBAF (5.97 g, 18.9 mmol), acetic acid (0.92 mL, 16 mmol) and acetic anhydride (1.50 mL, 16 mmol) in THF (18 mL) was added dropwise, while keeping the temperature below 0 °C. The reaction mixture was stirred for an additional 1.5 hours without cooling. Subsequently the mixture was filtered through a plug of silica and poured into water (50 mL). This mixture was extracted with CH\(_2\)Cl\(_2\) (4 x 20 mL) and the combined organic layers were washed with sat. NaHCO\(_3\) solution (3 x 40 mL), water (40 mL), and brine (40 mL). The combined aqueous layers were extracted with CH\(_2\)Cl\(_2\) (30 mL). All combined organic layers were washed one more time with brine (40 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed by rotary evaporation to yield 0.617 g (3.50 mmol, 97 %) of the title compound as an orange-red oil.

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.51 (d, \(J = 8.1, 2H\)), 7.36 (d, \(J = 8.1, 2H\)), 3.16 (s, 1H), 2.41 (s, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 75 MHz):\(\delta\) 193.10, 134.07, 132.59, 128.66, 123.21, 82.71, 78.85, 30.18.

IR (NaCl, cm\(^{-1}\)): 3286, 2960, 2927, 2104, 1708, 1483, 1397, 1353, 1124, 951, 829.

1-Bromo-4-\(\text{tert}\)-butylthiobenzene (2.11)

This compound was prepared by a literature method.\(^{40}\) A slurry of 4-bromothiophenol (99.18 g, 0.525 mol) in \(\text{tert}\)-butylchloride (400 mL) was stirred for 30 minutes. Aluminium chloride (3.53 g, 26.5 mmol) was added in portions over one hour. The reaction mixture started to foam and HCl was formed. The reaction mixture was stirred an additional hour and then poured into water (700 mL). The aqueous layer was extracted with pentane (3 x 150 mL). The combined organic layers were washed with water (2 x 100 mL), dried over Na\(_2\)SO\(_4\) and the solvents were removed by rotary evaporation. Vacuum distillation (80 °C, 9 mTorr) afforded 109.3 g (0.446 mmol, 85%) of the title compound as a colorless liquid.

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.46-7.36 (m, 4H), 1.27 (s, 9H).\(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta\) 138.85, 131.82, 131.58, 123.39, 46.02, 30.84. IR (NaCl, cm\(^{-1}\)): 2961, 2940, 2922, 2896, 2861, 1468, 1363, 1168, 1092, 1071, 1011, 820.

1-\(\text{tert}\)-Butylthio-4-[\(\text{triisopropylsilyl}\)ethynyl]benzene (2.12)

This compound was prepared by a modification of literature methods.\(^{41}\) A mixture of 2.11 (7.40 g, 30.2 mmol), dichlorobis(triphenylphosphine) palladium(II) (600 mg, 0.855 mmol) and copper iodide (396 mg, 2.08 mmol) was suspended in THF (210 mL). Diisopropylamine (30 mL) and (triisopropylsilyl)acetylene (11.14 g, 61.1 mmol) were added and the reaction mixture was refluxed for 19 hours. The reaction mixture was poured into water (400 mL) and extracted with diethylether (3 x 200 mL). The organic layers were washed with water (3 x 200 mL), dried over Na\(_2\)SO\(_4\), filtered and the solvents were removed. Column chromatography (silica gel, heptane) yielded 10.38 g (29.9 mmol, 99%) of the title compound as a yellowish liquid.

\(^1\)H NMR (CDCl\(_3\), 400MHz): \(\delta\) 7.51-7.39 (m, 4H), 1.28 (s, 9H), 1.13 (s, 21H).\(^{13}\)C NMR (CDCl\(_3\),
100MHz): δ 137.09, 133.20, 131.91, 123.86, 106.45, 92.31, 46.39, 30.94, 18.65, 11.29. IR (cm⁻¹): 2957, 2942, 2922, 2893, 2864, 2155, 1480, 1458, 1363, 1218, 1166, 1017, 996, 882, 832, 696, 673, 659. HRMS (APCI) calculated for [M+H]+ 347.22232, found 347.22342.

1-\textit{tert}-Butylthio-4-ethynylbenzene (2.13)

This compound was prepared by a modification of literature methods.41 1.12 (10.0 g, 28.8 mmol) was dissolved in THF (100 mL) and cooled to 0 °C. A solution of TBAF (18.5 g, 58.5 mmol) in THF (50 mL) was added dropwise over 30 minutes. The reaction mixture was stirred for 15 minutes at 0 °C and for 4 more hours without cooling. The reaction mixture was filtered through a plug of silica gel, eluted with CH₂Cl₂, which yielded 17.7 g brown oil. This was purified by column chromatography (silica gel, heptane/CH₂Cl₂ 4:1) to yield 4.58 g (24.1 mmol, 84%) of the title compound as a yellowish liquid, that became a white solid in the fridge.

1H NMR (CDCl₃, 400MHz): δ 7.53-7.41 (m, 4H), 3.14 (s, 1H), 1.28 (s, 9H).

13C NMR (CDCl₃, 100MHz): δ 137.12, 133.91, 131.99, 122.40, 83.07, 78.59, 46.43, 30.94. IR (cm⁻¹): 3291, 2960, 2921, 2896, 2863, 2110, 1918, 1480, 1456, 1394, 1363, 1164, 1093, 1017, 833, 648, 638, 614. HRMS (APCI) calculated for [M+H]+ 191.08890, found 191.08879.

2.8.4 Synthesis and Analysis of the Anthraquinone and Anthracene Precursors (2.14-2.18)

2,6-Dibromo-9,10-anthraquinone (2.14)

This compound was prepared by literature methods.35,36 A mixture of anhydrous copper(II)bromide (28.0 g, 125 mmol), \textit{tert}-butyl nitrite (17.2 mL, 145 mmol) and acetonitrile (200 mL) was heated to 60 °C and 2,6-diamino-9,10-anthraquinone (11.60 g, 48.7 mmol) was added in portions over 10 minutes. The reaction mixture stirred for 2 hours at 57 °C and for 1.5 hours at 70 °C, cooled and poured into 18% HCl solution (1 L). The brown precipitate was filtered, washed with water (10 x 200 mL) and acetonitrile (10 x 200 mL), and dried in the vacuum oven. The crude product was recrystallized from bromobenzene (1 L) with hot filtration to give 11.34 g (31.0 mmol, 64%) of the title compound as a dark yellow crystals.

Mp: 276-281 °C. 1H NMR (300 MHz, CDCl₃) δ 8.44 (d, J = 2.0, 2H), 8.17 (d, J = 8.3, 2H), 7.95 (dd, J = 8.3, 2.0, 2H). 13C NMR (CDCl₃, 125 MHz, 80 °C): δ 79.66, 135.89, 132.97, 130.41, 128.83, 128.68, 127.60. IR (KBr, cm⁻¹): 3086, 3065, 1673, 1574, 1309, 1286, 1163, 1106, 1069, 956, 914, 858, 816, 732, 711, 666.

2,6-Dibromo-9,10-diacectoxyanthracene (2.15)

This compound was prepared by a literature procedure.35 Acetic anhydride (75 mL) was added to 2.14 (1.84 g, 5.03 mmol), zinc dust (1.79 g, 27 mmol, activated by stirring for 1 hour in 10% HCl solution, and then filtering and washing with water and acetone) and anhydrous sodium acetate (0.65 g, 7.9 mmol) and the reaction mixture was stirred for 80 minutes. Then the reaction mixture was
refluxed for 90 minutes and cooled to room temperature. Water (60 mL) was added and the mixture was refluxed again for 10 minutes. After cooling, the yellow precipitate was filtered off and washed with water (6 x 120 mL). The crude product was dried in the vacuum oven to give 2.28 g of a yellow powder. This was dissolved in CH$_2$Cl$_2$ (600 mL) and filtered to remove traces of zinc powder. The CH$_2$Cl$_2$ was removed by rotary evaporation and 1.84 g (4.07 mmol, 81%) of the title compound was obtained as a yellow solid.

Mp: 298-301 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.08 (d, $J = 1.8$, 2H), 7.79 (d, $J = 9.2$, 2H), 7.58 (dd, $J = 9.3$, $J = 1.6$, 2H), 2.65 (s, 6H). $^{13}$C NMR (C$_2$D$_2$Cl$_4$, 100 MHz): $\delta$ 168.04, 138.27, 129.37, 123.52, 122.41, 122.26, 121.63, 120.32, 19.49. IR (KBr, cm$^{-1}$): 3072, 3027, 2935, 1755, 1611, 1446, 1429, 1365, 1356, 1200, 1164, 1049, 896, 860, 801, 754.

2,6-Dibromo-9,10-dimethoxyanthracene (2.16)

This compound was prepared by a modification of the literature methods.$^{36}$

$^2$14 (2.00 g, 5.48 mmol), tetrabutylammonium bromide (1.68 g, 5.21 mmol), and sodium dithionite (2.18 g, 14.8 mmol) were suspended in water (50 mL, purged with N$_2$). CH$_2$Cl$_2$ (60 mL, purged with N$_2$) was added and the dark green emulsion was stirred for 2.5 hours. Then 20% NaOH was added (50 mL, 257 mmol) and the reaction mixture turned magenta, after which it was stirred for another 2.5 hours. Iodomethane (53 mL, 858 mmol) was added and the reaction mixture was stirred for 20 hours, and poured into water (250 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 x 100 mL) and the organic layers were washed with water (5 x 200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The resulting 2.3 g orange solid was preadsorbed onto silica and purified by column chromatography (silica gel, heptane/CH$_2$Cl$_2$ 2:1), to afford 561 mg (1.42 mmol, 24%) of the title compound as a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.43 (d, $J = 1.5$, 2H), 8.15 (d, $J = 9.2$, 2H), 7.55 (dd, $J = 9.2$, 1.9, 2H), 4.09 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 147.89, 129.51, 125.80, 124.65, 124.53, 123.80, 120.46, 63.64. IR (cm$^{-1}$): 3086, 3004, 2964, 2936, 2842, 1604, 1449, 1435, 1348, 1071, 1051, 964, 880, 813, 793, 711. HRMS (APCI) calculated for [M+H]$^+$ 396.92563, found 396.92652. Calcd for C$_{16}$H$_{12}$Br$_2$O$_2$: C, 48.52; H, 3.05. Found: C, 48.26; H, 2.93.

2,6-Dibromoanthracene (2.17)

This compound was prepared by a modification of literature methods.$^{45,46}$

$^2$14 (3.23 g, 8.83 mmol) was suspended in a mixture of methanol (50 mL) and toluene (40 mL) and cooled to 0 °C. NaBH$_4$ (10.7 g, 283 mmol) was added in portions over 2.5 hours. Toluene (15 mL) and methanol (15 mL) were added and the reaction mixture was stirred for 16 hours and subsequently refluxed for 2.5 hours. After cooling to room temperature the reaction mixture was poured into N$_2$ purged ice water (600 mL), filtered and washed with water (500 mL). The obtained solid was stirred for 17 hours in 5 M HCl (100 mL), filtered, washed with water (500 mL), and dried. The dried solid was suspended in isopropanol (30 mL) and NaBH$_4$ (8.31 g, 220 mmol) was added. The reaction mixture was refluxed for 70 hours, poured into N$_2$ purged ice water (400 mL), filtered and washed with water (500 mL) and dried. Recrystallization from toluene afforded 543 mg (1.62 mmol, 18%) of the title compound as yellow crystals.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (s, 2H), 8.17 (d, $J = 2.0$, 2H), 7.87 (d, $J = 9.0$, 2H), 7.53 (dd,
2,6-Dibromo-9,10-dihydroanthacene (2.18)

2,6-Dibromo-9,10-dihydroanthacene (2.18) (5.27 g, 14.4 mmol), red phosphorus (4.20 g, 136 mmol) and iodine (1.00 g, 4.0 mmol) were placed in an ampule and HI (50 mL, 57% w/w in water) was added. The ampule was sealed and heated to 130-142 °C for 3 days. After cooling an opening of the ampule, the suspension was poured into water (400 mL) and filtered. The residue was washed with cold water (200 mL) and hot water (200 mL) and dried on air. The resulting solid was dissolved in CH$_2$Cl$_2$ (400 mL), dried over Na$_2$SO$_4$, filtered, and all volatiles were removed to afford 4.1 g white solid. This was recrystallized from ethanol to yield 2.81 g (8.31 mmol, 58%) of the title compound as white needles.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J = 1.9$, 2H), 7.32 (dd, $J = 8.0$, 2.0, 2H), 7.14 (d, $J = 8.0$, 2H), 3.85 (s, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 138.35, 134.77, 130.28, 129.25, 128.96, 119.89, 35.28. IR (cm$^{-1}$): 3082, 3052, 3024, 2933, 2853, 2806, 1593, 1474, 1414, 1391, 1173, 1129, 1076, 957, 913, 885, 871, 802, 724. Calcd for C$_{14}$H$_{14}$Br$_2$: C, 49.74; H, 2.98. Found: C, 48.74; H, 2.82.
2.9 References and Notes


24. Conductance measurements in gated electromigration junctions have been performed recently on a molecule from the family in Figure 2.3a by Jeppe Fock in the group of prof. Herre van der Zant at University of Delft (poster communication at the ElecMol'10 conference, 6-10 December 2010, Grenoble).


30. The protonated acridone wire was analyzed by $^1$H NMR spectroscopy (in DMSO-d6) and IR. Washing of a suspension of this protonated acridone in chloroform with water yielded the acridone-wire back.


34. Addition of the amine to the reaction mixture in general turned the yellow suspension into an orange-red solution, before the acetylene was added. This observation indicates that Pd(II) is reduced to Pd(0) by the amine.


42. No pure 2.4A could be obtained from a direct Sonogashira cross-coupling between 2.15 and 2.10.

43. See for the synthesis of the asymmetric analogue of 2.5B (with one thiol terminal only): E. H. van Dijk, *MSc Thesis* “An Anthraquinone-Based Switch for Molecular π-Logic”, *University of Groningen*, 2006.


54. Partial charge transfer could take place from the electron rich thio-functionalized phenylacetylene units to the electron poor anthraquinone unit.
57. Time resolved photoluminescence measurements were performed by Jia Gao and Jochem Smit, University of Groningen.