

Synthesis and Properties of an Anthraquinone-Based Redox Switch for Molecular Electronics

Elisabeth H. van Dijk, Daniel J. T. Myles, Marleen H. van der Veen, and Jan C. Hummelen*

Molecular Electronics, Materials Science Centre^{Plus}, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

j.c.hummelen@rug.nl

Received March 14, 2006

ABSTRACT



The synthesis of a molecular wire bearing an anthraquinone core and thioacetyl end groups for gold electrode binding is described. A model anthraquinone system, substituted with *tert*-butylthio groups, can be reversibly switched electrochemically from cross conjugated (low conductance “off”) to linear conjugated (high conductance “on”) via two-electron reduction/oxidation reactions. This feature holds promise for the anthraquinone-based wires to be used as redox-controlled switches in molecular electronic devices.

The understanding of electronic-transport properties through single molecules between metal contacts has recently become possible, for example, by the mechanically controllable break junction (MCBJ) technique¹ and STM.² A large number of conjugated molecular wires containing terminal sulfur groups based on oligo(thiopheneethynylene)s, oligo(phenyleneethynylene)s (OPEs), and oligo(phenylenevinylene)s (OPVs) have been synthesized,³ some of which have been embedded as passive elements in MCBJs.⁴ Mayor et al.⁵ have shown

(1) (a) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252. (b) van Ruitenbeek, J. M.; Alvarez, A.; Piñeyro, I.; Grahmann, C.; Joyez, P.; Devoret, M. H.; Esteve, D.; Urbina, C. *Rev. Sci. Instrum.* **1996**, *67*, 108.

(2) (a) Moth-Poulsen, K.; Patrone, L.; Stuhr-Hansen, N.; Christensen, J. B.; Bourgoïn, J.-P.; Bjørnholm, T. *Nano Lett.* **2005**, *5*, 783 and references therein. (b) van der Molen, S. J.; van der Vegte, H.; Kudernac, T.; Amin, I.; Feringa, B. L.; van Wees, B. J. *Nanotechnology* **2006**, *17*, 310. (c) Moore, A. M.; Dameron, A. A.; Mantooth, B. A.; Smith, R. K.; Fuchs, D. J.; Ciszek, J. W.; Maya, F.; Yao, Y. X.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **2006**, *128*, 1959.

(3) (a) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376. (b) Wang, C. S.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2006**, *71*, 108. (c) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem.-Eur. J.* **2001**, *7*, 5118. (d) Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. *J. Org. Chem.* **2003**, *68*, 1275.

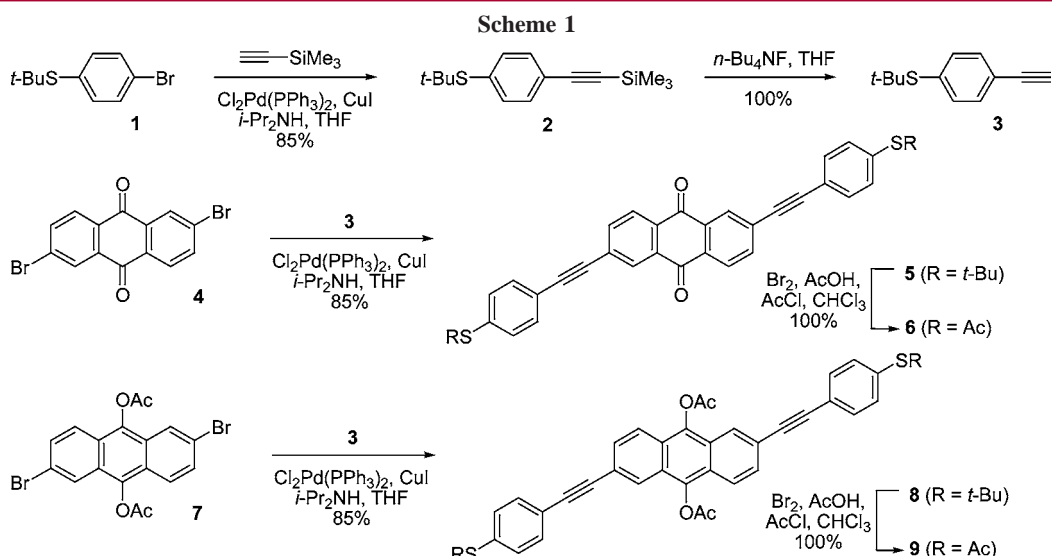
that the electronic properties of bis-9,10-phenylethynyl-anthracenes largely depend on whether the thiol anchors are situated at the para or meta positions. An approximate 2-order magnitude drop in the current was observed in going from the para- to the meta-substituted compound. This example clearly illustrates how the conductivity is influenced by the molecular topology (i.e., linear vs cross conjugated). Active elements such as multiterminal molecular junctions, switches, and logic gates are also being investigated for molecular electronics.⁶ In this vein, diarylethene-based photochromic switches have been studied in MCBJs by the group of Van Wees.⁷ The “closed” (linear conjugated) form of the switch was assembled into a break junction and illuminated with light ($\lambda = 546$ nm), resulting in a 10^3 increase of the

(4) Kergueris, C.; Bourgoïn, J.-P.; Palacin, S.; Esteve, D.; Urbina, C.; Magoga, M.; Joachim, C. *Phys. Rev. B* **1999**, *59*, 12505.

(5) Mayor, M.; Weber, H. B.; Reichert, J.; Elbing, M.; von Hänisch, C.; Beckmann, D.; Fischer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5834.

(6) (a) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541. (b) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486.

(7) Dulić, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402.



resistance (i.e., from the $M\Omega$ to the $G\Omega$ range). This is due to switching of the molecule from the closed to the open state and thus from linear to cross conjugated. Upon illumination of the open form in the break junction with 313 nm light, no reverse switching was observed. This is attributed to quenching of the first excited state of the open form by gold. However, it has been shown that reversible switching can be achieved for a diarylethene containing methylene spacers between the conjugated system and the sulfur end groups.⁸

Very recently, Nielsen and co-workers reported an oligo-(phenyleneethynylene)-tetrathiafulvalene cruciform for its use in molecular electronics.⁹ The linear-conjugated pathway along the OPE could be irreversibly switched electrochemically to a cross-conjugated one via a two-electron oxidation of the flanking TTF moieties.

In this paper, we present the synthesis of an anthraquinone-based molecular switch (**6**) that has thioacetyl end groups for attachment to gold surfaces. The long-term objective is to use these molecules in electronic devices whereby the conductivity is reversibly switched from low (off) to high (on) and vice versa.

Anthraquinone-based redox switch **6** and reference anthracene compound **9** were synthesized as shown in Scheme 1. Compound **2** was previously prepared by Mayor et al. using different starting materials, although no experimental details were reported.⁵ More recently, Nielsen and co-workers developed a method for its preparation in 75% yield, but by employing a rather elaborate catalytic system ($\text{Cl}_2\text{Pd}(\text{PhCN})_2/\text{P}(t\text{-Bu})_3/\text{CuI}$).¹⁰ We have found that **2** can be prepared in 85% by a standard¹¹ ($\text{Cl}_2\text{Pd}(\text{PPh}_3)_2/\text{CuI}$) Sonogashira cross-coupling reaction of known **1**¹² with trimethylsilylacetylene.

By modification of the literature methods,^{5,10,13} the trimethylsilyl protecting group of **2** was then removed using TBAF in THF affording key building block **3** in quantitative yield. Compounds **4** and **7** were prepared according to the literature.¹⁴ Acetylene **3** was then independently cross-coupled to **4** and **7**, yielding products **5** and **8**, respectively. Both **5** and **8** contain *tert*-butyl-protected thiol end groups, which were converted to the more labile thioacetyl groups by a modified bromine-catalyzed deprotection protocol that was initially developed by the group of Mayor.¹³ Because of the poor solubility of **5** and **8** in acetyl chloride, we found it necessary to use chloroform as cosolvent for the reactions. Target compounds **6** and **9** were obtained in quantitative yields. The ¹H and ¹³C NMR spectra are in agreement with their symmetrical structures, and after the thiol protecting group conversion (i.e., *t*-Bu to Ac), both displayed an additional carbonyl stretch (1705 cm^{-1} for **6** and 1692 cm^{-1} for **9**). The thioacetyl terminated compounds **6** and **9** can in principle be assembled onto gold¹⁵ and studied, for example, by the MCBJ technique or by STM. However, because the thioacetyl compounds are much less soluble than their *tert*-butyl congeners **5** and **8**, the latter are used for the spectroscopic and electrochemical measurements reported herein.

The UV–vis absorption spectrum of **5** shows maxima at 305, 334, and 373 nm, whereas the spectrum of **8** shows maxima at 319, 331, 385, 406, and 430 nm (see Supporting Information). The linear-conjugated compound **8** absorbs more strongly in the UV region than **5** and has anthracene-

(11) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(12) Stühr-Hansen, N. *Synth. Commun.* **2003**, *33*, 641.

(13) Błaszczczyk, A.; Elbing, M.; Mayor, M. *Org. Biomol. Chem.* **2004**, *2*, 2722.

(14) Yang, J. H.; Dass, A.; Rawashdeh, A.-M. M.; Sotiropoulos, C.; Panzner, M. J.; Tyson, D. S.; Kinder, J. D.; Leventis, N. *Chem. Mater.* **2004**, *16*, 3457.

(15) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(8) He, J.; Chen, F.; Liddell, P. A.; Andréasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; Lindsay, S. M. *Nanotechnology* **2005**, *16*, 695.

(9) Sørensen, J. K.; Vestergaard, M.; Kadziola, A.; Kilså, K.; Nielsen, M. B. *Org. Lett.* **2006**, *8*, 1173.

(10) Stühr-Hansen, N.; Sørensen, J. K.; Moth-Poulsen, K.; Christensen, J. B.; Bjørnholm, T.; Nielsen, M. B. *Tetrahedron* **2005**, *61*, 12288.

like absorptions appearing at lower energies due to the extended conjugation. Cross-conjugated compound **5** shows a broad fluorescence emission peak at 675 nm. Conjugated compound **8** is approximately 1000 times more fluorescent and emits blue light (440 and 470 nm). These spectroscopic experiments show that the electronic properties of the linear-conjugated (on) and cross-conjugated (off) compounds show substantial differences. These findings are in good agreement with those found by Leventis et al. on similar types of compounds.¹⁴

Cyclic voltammetry measurements on **5** showed two fully reversible reduction waves at a scan rate of 10 mV/s (Figure 1). The anthraquinone core is first reduced to the semi-

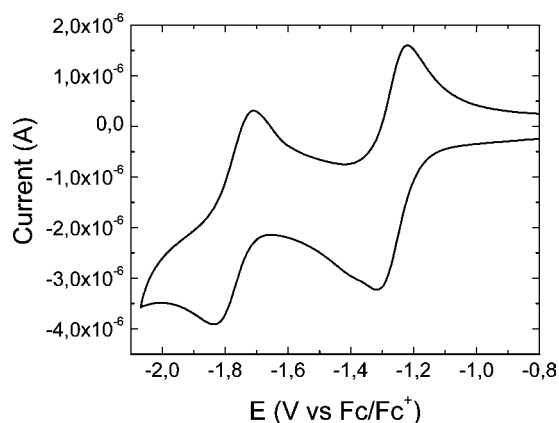


Figure 1. Cyclic voltammogram of **5** in ODCB/CH₃CN.

quinone at -1.27 V and then to the hydroquinone dianion at -1.80 V vs F_c/F_c^+ . The potentials of anthraquinone **5** were compared with the redox potentials of 9,10-anthraquinone, 2,6-dibromoanthraquinone, and 2,6-bis(phenylethynyl)-9,10-anthraquinone by differential pulse voltammetry (DPV), and these data can be found in the Supporting Information. The measurements showed that the reduction potentials of these 2,6-disubstituted anthraquinones are nearly identical to each other but considerably different when compared to unsubstituted 9,10-anthraquinone. This is a promising feature for the switching behavior of compound **6** while attached to gold because the nature of the substituents appears to have little if any effect on the redox chemistry of the anthraquinone core.

UV-vis spectroelectrochemical experiments on **5** were performed in a thin cell setup with a path length of 1 mm that was supported with a platinum gauze working electrode, a platinum wire counterelectrode, and a SCE reference electrode. A UV-vis spectrum was first recorded on a pale yellow solution of neutral **5** at 0 V (Figure 2). Applying a potential of -1.6 V (vs SCE) resulted in significant changes in the absorption spectrum. The absorption at 373 nm disappeared, and broad absorptions at 460 and 670 nm arose with a concomitant color change of the solution to green. These findings are qualitatively the same as those found for the hydroquinone dianion of unsubstituted 9,10-anthraquino-

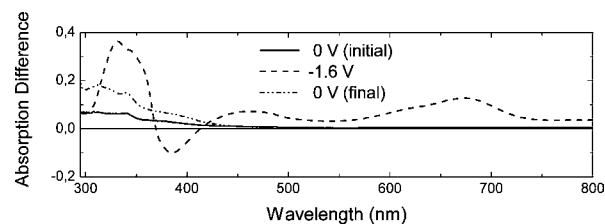


Figure 2. Differential absorption spectra of **5** in ODCB/CH₃CN.

ne, which has its principle absorptions at 470 and 622 nm in DMF.¹⁶ The differences in the positions of absorption maxima for **5** with respect to 9,10-anthraquinone are ascribed to a combination of substituent and solvent polarity effects. When the potential was subsequently set back at 0 V, the original absorption spectrum was obtained. The experiment proved that anthraquinone **5** could be switched reversibly between its neutral and dianionic states.

The π -electron delocalization within the frontier orbitals provides a suitable observable to obtain insight into the charge-transport properties of single molecules.¹⁷ We have performed molecular orbital calculations to qualitatively determine whether the conductivity could change from low to high when the anthraquinone system is switched from a cross- to a linear-conjugated state. All molecular orbital calculations and geometry optimizations were performed for the single molecules in a vacuum, using the semiempirical Austin Model 1 (AM1)¹⁸ level of theory implemented in the HyperChem 7.5 program package of Hypercube Inc.¹⁹ The conjugated hydroquinone dianion was simulated by imposing a total charge of -2 on the structure during the semiempirical calculations.

Figure 3 shows the electron probability distribution $\varphi(x,y)^2$ within the frontier orbitals for the neutral and hydroquinone dianion of thiol (SH) end-capped **5**. The frontier orbitals of the neutral cross-conjugated state are mainly localized to certain parts of the molecule (here, the HOMO and HOMO-1 are close to degenerate, as expected for symmetry reasons). On the other hand, the HOMO and LUMO of the conjugated hydroquinone dianion are fully delocalized across the molecule far into the terminals. Hence, the spatial extent of the LUMO demonstrates that there is enough delocalization to allow for efficient transport of electrons between the termini of the dianionic conjugated form. An even more enhanced π -electron delocalization was observed within the frontier orbitals of the neutral conjugated compound **9**. The reference anthracene **9** would therefore be an ideal charge-transport medium for holes and/or

(16) Babaei, A.; Connor, P. A.; McQuillan, A. J.; Umapathy, S. *J. Chem. Educ.* **1997**, *74*, 1200.

(17) (a) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015. (b) Karzazi, Y.; Cornil, J.; Brédas, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 10076. (c) Heurich, J.; Cuevas, J. C.; Wenzel, W.; Schön, G. *Phys. Rev. Lett.* **2002**, *88*, 256803.

(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(19) *HyperChem*, release 7.5 for Windows, Molecular Modeling System; Hypercube, Inc. and Autodesk, Inc.

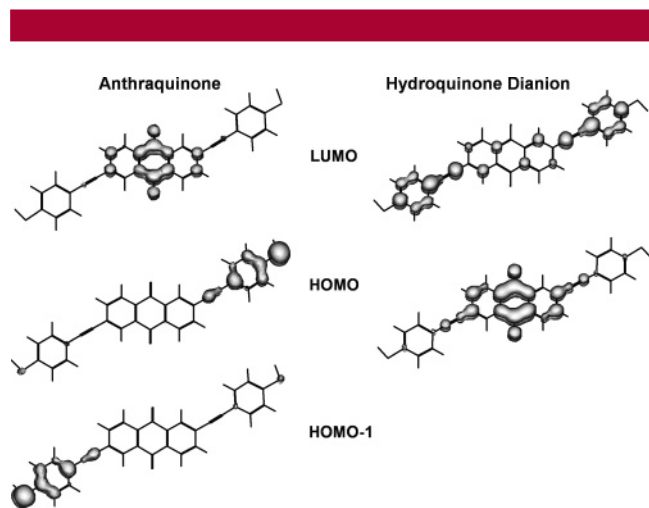


Figure 3. AM1-calculated representations of the electron probability distribution within the frontier orbitals of the neutral and hydroquinone dianion of thiol end-capped **5**.

electrons and could serve as an important model system for MCBJ experiments. These results suggest that we have designed a well-defined redox-active switch and a switching

mechanism solely determined by the topology (linear or cross conjugated) of the conductive path.

In summary, we have prepared an anthraquinone-based molecular wire that can be reversibly switched from cross conjugated (low conductance “off”) to linear conjugated (high conductance “on”). We are currently investigating the electronic-transport properties of this redox-controlled switch while attached to gold electrodes, for example, by electrochemistry, STM, and the MCBJ technique. Results of these studies will be reported in due course.

Acknowledgment. The financial support of the Materials Science Centre^{Plus} is greatly appreciated. The authors wish to thank Dr. Wesley Browne for help with the spectroelectrochemical measurements. The group of Professor Bart J. van Wees and also Dr. Alex Sieval (University of Groningen) are thanked for valuable discussions.

Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL0606278