On/off electrochemical switches based on quinone-bisketals[†]

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The synthesis and anodic oxidation of a variety of 2,5-diaryl or dialkynylaryl substituted 1,4-dialkoxybenzenes to quinone bisketals is described. The study of the X-ray structures and electrochemical and spectroscopic properties evidenced that these pairs constitute a first approach to the concept of a molecular nanofuse.

The control over the flow of electrons between electron reservoirs by a molecular conductor would be highly valuable in many scientific fields.¹ Thus for example, there are excellent examples of conjugated molecules facilitating the connection between metallic centers in electronic homogeneous enzymatic systems.² In solid state, the control of conductivity opens the possibility to simulate the behavior of standard circuitry at the molecular level.³ To date, some successful approaches using electrical stimuli have been reported. Nevertheless, they are voltage dependent, reversible and work in the off/on sense.⁴ Development of systems working in the on/off sense with an irreversible behavior towards the voltage, mimicking a macroscopic fuse, is much less extended. Ideally, when situated in a molecular circuit, a fuse could: (a) detect an overvoltage, thus protecting complex electronic systems from over-oxidation or reduction, (b) trigger other processes in a controlled manner or (c) act as binary components of Read Only Memories (ROMs).⁵

Following previous studies on the synthesis and applications of quinone bisketals⁶ we reasoned that *p*-dialkoxybenzene derivatives such as I (Scheme 1) could behave as an



Scheme 1 Working hypothesis.

electrochemical on/off pair in the presence of a nucleophilic oxygen.⁷ Our working hypothesis, summarized in Scheme 1, assumed that the initial aromatic conductor I can be electrochemically transformed into the insulator quinone bisketal II at a controlled voltage.⁸

We report herein the synthesis of different substituted p-dialkoxybenzene/quinone bisketal pairs, as well as a computational study to establish their geometry, later confirmed in some cases, by X-ray crystallography. We also measured their electrochemical and spectroscopic properties. Our results provide evidence that these couples may work as irreversible on/off electrochemical pairs, which could be considered a primitive prototype of a nanofuse.

We first synthesized *p*-dialkoxybenzenes 1 and 2 (Table 1) because they show a poly-p-phenylene or an expanded alkyndiyl poly-p-phenylene structure, which have been extensively used in fundamental studies of molecular conductivity.⁹ Although the requirement of a nucleophilic oxygen would not be critical in homogeneous environments, it could avoid their use in solid state devices, where no exogenous oxygen source is available. In this sense we prepared compounds 3-4, which include a nucleophilic oxygen atom in the alkoxy side chains. Compounds 5-8, bearing a heteroatomic substituent at the para-position of the phenyl groups, were designed to have in hand different systems with functional groups capable of acting as linkers between the organic molecule and the electrodes.¹⁰ Compounds 9-10 were prepared to carry out some key spectroscopic studies. The synthesis of compounds 1-10 was achieved by Suzuki or Sonogashira coupling reactions.¹¹ Their anodic oxidation in methanol afforded the corresponding quinone bisketals **1a–10a** in good yields (Table 1).

The retention of shape and length in the on and off states may be particularly relevant for molecular electronics, guaranteeing that there is not any mechanical stress in the global system when the switching process takes place. For instance, photoswitches based on dithienylethene derivatives, which have shown excellent switching properties, suffer changes in length and geometry in the switching event provoking the subsequent reorganization in the junction to accommodate the new situation.¹² The computational studies¹¹ predicted closely related geometries for all the pairs 1-10/1a-10a. The calculated lengths in all cases were very similar with differences smaller than 0.7%.11 A virtually linear geometry was maintained both in the oxidized and reduced forms.¹³ The only significant differences observed were related with the torsion angles between the phenyl groups and the central aromatic ring or the 1,4cyclohexadiene core.11 The single crystal X-ray structures

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 Table 1
 Anodic
 oxidation
 of
 2,5-diaryl-1,4-dimethoxybenzene

 derivatives 1–10



^{*a*} Electrolysis was carried out in a single cell apparatus. ^{*b*} Two steps overall yield.^{11 *c*} Based on the starting material recovered.

obtained for the pairs 1–1a, 2–2a and 5–5a as well as for the dioxolane 3a are shown in Fig. 1.¹⁴

As can be seen, the length of the molecules 1 (13.2 Å) and 1a (13.4 Å) in the solid structure reflected a slight expansion (1.6%) from the reduced to the oxidized form. It is also remarkable that 1a is almost linear (178.8°) . The X-ray diffraction of bisketal 3a also evidenced a length of 13.3 Å, which corresponds to a slight expansion (1.0%) with respect to structure 1. X-Ray structures of expanded *p*-terphenyls 2 and 2a also showed that the main geometrical parameters are conserved in both structures. The length is almost the same (2, 18.3 Å; 2a, 18.4 Å) and both are almost linear



Fig. 1 X-Ray structures of 1, 1a, 3a, 2, 2a, 5 and 5a. The lengths are in Å.

(2, 179.0°; 2a, 174.5°). In the X-ray structures of the *p*-trifluoromethylsulfanyl substituted *p*-terphenyls 5 and 5a, we could see that the distances between the terminal sulfur atoms differ by only 0.12 Å and the deviation from linearity is less than 2° . Thus, the geometrical parameters theoretically predicted matched with those experimentally determined.

Electrochemical studies (cyclic voltammetry, CV, and, in some cases, square wave voltammetry, SWV) were used to learn the oxidative and reductive properties of the compounds that were prepared. The electrochemical studies of compounds 1–10 were carried out in acetonitrile. 2,5-Diphenyl-1,4-dimethoxybenzene 1 showed a reversible oxidation wave at $E_{1/2} = 0.8$ V and an irreversible one at $E_{1/2} = 1.34$ V (Fig. 2).¹⁵

A similar behavior was observed for the substituted analogue 3. A reversible peak at 0.80 V appeared in the cyclic voltammogram and an irreversible peak at 1.35 V. In contrast, the CV of the oxidized tetramethyl bisketal 1a and the related dioxolane 3a did not show any oxidation or reduction peaks from -2.5 to +1.7 V vs. Fc/Fc⁺.¹⁶ This is a consequence of a stabilization of the HOMO level due to the loss of the conjugation of the 1,4-cyclohexadiene structure, in agreement with the theoretical energy calculated for the HOMO of 1 (-5.19 eV, DFT level) and 1a (-6.14 eV).¹¹ Taking into account the electrochemical stability of compounds 1a and 3a, we can relate their formation with the irreversible second anodic peak at 1.34 V. Therefore, the system would be stable, retaining the electronic properties until such overvoltage occurred. Although the first peak is probably associated with the formation of a radical-cation in the electron rich central aromatic ring, its exact structure is not known.⁷



Fig. 2 Cyclic and square wave voltammograms for the oxidation of **1** (MeCN, 0.15 M TBAPF₆, 25 °C). CV: $v = 0.1 \text{ V s}^{-1}$ (blue and red). SWV: scan increment = 2 mV, SW amplitude = 25 mV, frequency = 15 Hz (green). CV of a solution of **1a** is also shown (brown).



Fig. 3 Comparison between the UV-vis spectra of *off* structures 4a, 9a and 10a (0.00001 M in CH₂Cl₂).

The phenyl alkyndiyl substituted dimethoxybenzene derivative **2** showed a cyclic voltammogram where the first reversible peak appeared at 0.91 V. We also observed two irreversible peaks at 1.12 and 1.32 V which must be related also with the *on/off* voltage. Similar anodic peaks (0.91 rev., 1.10 irrev. and 1.30 irrev.) were obtained in the cyclic voltammogram of compound **4**. The corresponding *off* states **2a** and **4a** showed a similar behavior to **1a** and **3a**. Both were electrochemically inert from -2.2 to +1.7 V vs. Fc/Fc⁺. The electrochemical behaviour of compounds **5–10** possessing substituents showed the same trend.¹¹

In the standard theory of quantum transport through molecules, the conductivity at low bias is related to the HOMO-LUMO energy gap, being maximized with small values of such gap. Consequently, the measure of the HOMO-LUMO difference of energy could help to predict the different ability of our systems to transfer the electrons through the reduced and oxidized molecules I and II depicted in Scheme 1. The HOMO-LUMO energy gap could be deduced from the CV studies considering the difference between the first oxidation and reduction potentials, or from the UV-vis absorption wavelengths. These two values were similar, showing an increase in the HOMO-LUMO gap of about 1.2 eV for tri-p-phenylene-type structures (1a, 3a, 5a-8a) and 0.85 eV from expanded alkyndiyl tri-p-phenylene-type structures (2a, 4a, 9a and 10a) with respect to the corresponding on structures (1-10).11 These electrochemical and optical gap values and our previous theoretical calculations¹⁷ support our hypothesis that structures 1-10 have conductivity values higher than **1a-10a**. This fact is also supported by the comparison between UV-vis spectra of off structures 2a, 9a and 10a (Fig. 3). It can be observed that the UV-vis spectrum of asymmetric 10a is, within the experimental error, a simple addition of the UV-spectra of symmetric 2a and **9a**. This fact strongly suggests that an electronic disconnection between the two ends of the molecule is taking place owing to the expected insulating character of the quinone bisketal moiety.

In conclusion, we have synthesized a series of dialkoxybenzene/ quinone bisketals, which mimic some properties of a macroscopic fuse. The key synthetic processes used warrant a trouble-free incorporation of these pairs in more elaborated structures for future applications in molecular circuitry. The X-ray structures of different pairs showed that no significant geometrical changes occurred from the reduced to the oxidized forms, which, to our knowledge, has no precedent in the literature. CV studies also determined that quinone bisketals show differences between oxidation and reduction peaks/waves that at least exceed 4 V, evidencing the irreversibility of the system. The electrochemical and optical gaps, deduced from the CV and UV-Vis spectra, strongly suggest differences of magnitude in conductivity between the *on* (dialkoxybenzenes I) and *off* (quinone bisketals II) states at low voltage. Although the proposed *off* state II is electrochemically irreversible, it can be changed again to the *on* state using some known chemical or physical processes.¹⁸

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