

New Charge-Transfer Salts for Reversible Resistive Memory Switching

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ABSTRACT

We found novel organic charge-transfer salts that exhibit reversible resistive memory switching phenomena. Homogeneous layers of these complexes can be easily fabricated using solution processing. The copper–2,3-dichloro-5,6-dicyano-*p*-benzoquinone complex was investigated in more detail. Devices made of this complex can be reversibly switched between a high and a low resistance state by applying voltage pulses as short as 1 μ s. The memory states remain stable for more than 15 h without an electricity source.

With recent advancements in the miniaturization of memory technology, increasing importance is being placed on the development of new methods for the fabrication of highly integrated and yet competitively priced memory. In addition to several new memory concepts based on inorganic materials, such as magnetic random access memory (MRAM) and ferroelectric random access memory (FeRAM),^{1,2} conjugated organic materials are also coming increasingly under investigation. The utilization of organic materials in memory systems offers much promise: not only can such materials be easily tailored, but they can also usually be deposited quite easily by solution processing.³

A number of organic materials that exhibit memory behavior are known today.^{4–11} These materials fall into two categories: those that mainly exhibit capacitive memory switching and those that mainly exhibit resistive memory switching. The latter materials, on which we focus here, are favorable for commercialization because resistive memory states are easier to detect and reading of the memory is usually nondestructive. In capacitive memories, this is generally speaking not the case. A further advantage of the resistive memory behavior is that the fabricated memory cells can be operated without transistors in every cell (passive matrix) and therefore can in principle be stacked on top of each other, which in turn makes a very high memory density possible.³

Many materials exhibit nonvolatile resistive memory phenomena, including charge-transfer (CT) salts. CT salts are complexes of at least two compounds that form an aggregation without forming a covalent bond. One of the compounds acts as an electron donor, the other one as an acceptor. Reversible conduction switching phenomena of CT

salts were first discovered by Potember et al.⁹ in a copper–charge-transfer salt, similar to the one presented in our work. Since this initial discovery, much research has been dedicated to this topic.^{9,11–13} The memory cells fabricated with Potember's material consist of a relatively thick (> 100 nm) layer of the CT salt, which is why they are usually called bulk memories. These CT-based bulk memories can be easily fabricated by solution processing.⁹ This is a significant advantage over molecular memories, which are considerably more difficult to produce. A major problem that must be overcome with Potember's system, however, is the substantial degree of roughness of the organic layers.⁹ The material does not form smooth layers, but rather grows as a polycrystalline film with a grain size larger than 50 nm.¹¹

In this work, we present CT salts that form comparably smooth layers and, which, to our knowledge, have been examined neither as a complex in and of themselves, nor in terms of their memory properties. The complex we investigated in most detail consists of copper and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), or CuDDQ. Sandwich cells of this complex can be fabricated easily by solution processing. They show memory type switching with threshold voltages lower than 4 V and a ratio between the high and low resistive state of more than 10³. The measured electrical characteristics are very promising for possible future memory applications. Furthermore, we investigated the complexes that copper forms with tetracyano-*p*-benzoquinone (4CQ) and tetrachloro-*p*-benzoquinone (CA) respectively. The Cu4CQ complex exhibits switching phenomena, whereas no such phenomena were observed for CuCA.

Because, to our knowledge, the complex CuDDQ has not been reported in the literature, we initially investigated the reaction between copper and DDQ. Indeed, when a thin

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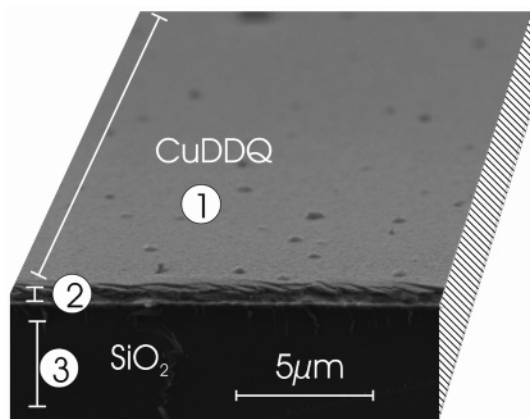


Figure 1. Tilted cross-section scanning electron microscope image of a Cu/CuDDQ device. The number (1) denotes a homogeneous CuDDQ layer, (2) an area where the device has been broken apart in order to reveal the cross section, and (3) a silicon wafer substrate.

copper rod is submerged to a DDQ–acetonitrile solution (at room temperature under ambient conditions), a reaction takes place that causes the initially yellow solution to turn red. The copper is probably oxidized by the DDQ: UV–vis spectroscopy of the now-red solution reveals the typical absorption spectrum of the DDQ anion.¹⁴ This is in accordance with the formation of a CT-salt by means of a redox reaction:¹⁵ the DDQ acts as an acceptor and is reduced, and the copper is in turn oxidized: $\text{Cu} + \text{DDQ} \rightarrow \text{Cu}^+ \text{DDQ}^-$.

To deposit layers of this complex on top of a test structure, the following procedure is used. A silicon wafer is coated with a 500 nm thick copper film by electroplating. The wafer is cleaned and dipped in a DDQ–acetonitrile solution for 1 min. A detailed procedure has been described elsewhere.⁹ In this solution, a 200 nm thick, very homogeneous layer forms on the copper surface (Figure 1). It is assumed to be composed of the CuDDQ complex and residues of the solvent. A titanium top electrode is deposited by positioning a shadow mask on top of the CuDDQ-coated substrate and RF sputtering of a 50 nm thick Ti layer. The shadow mask contains round and square holes approximately 500 μm in diameter that define the lateral geometry of the device.

The thus fabricated structures were characterized electrically; typical results are shown in Figure 2a,b. These measurements were performed with a Keithley SourceMeter 2400. Figure 2a shows a measured current voltage curve. If a voltage larger than 2.6 V (corresponding to an electric field of $2.6 \times 10^5 \text{ V/cm}$) is applied to the structure, the current spontaneously jumps from about 7 μA (corresponding to a resistance of $10^6 \Omega$; labeled “OFF” state) to 2 mA ($10^3 \Omega$; labeled “ON” state). This corresponds to an ON/OFF resistance ratio of 10^3 and is similar to the ON/OFF ratio found for other organic memory systems.^{6,11,16} Once in the ON state, the structures can be switched back to the OFF state by ramping the voltage below -3.7 V (corresponding to an electric field of $-3.7 \times 10^5 \text{ V/cm}$).

To confirm that both magnitude and polarity of the voltage are responsible for the switching, we tested the device’s current response to repeated voltage ramps of the same polarity. Figure 2b shows the measured current as a function

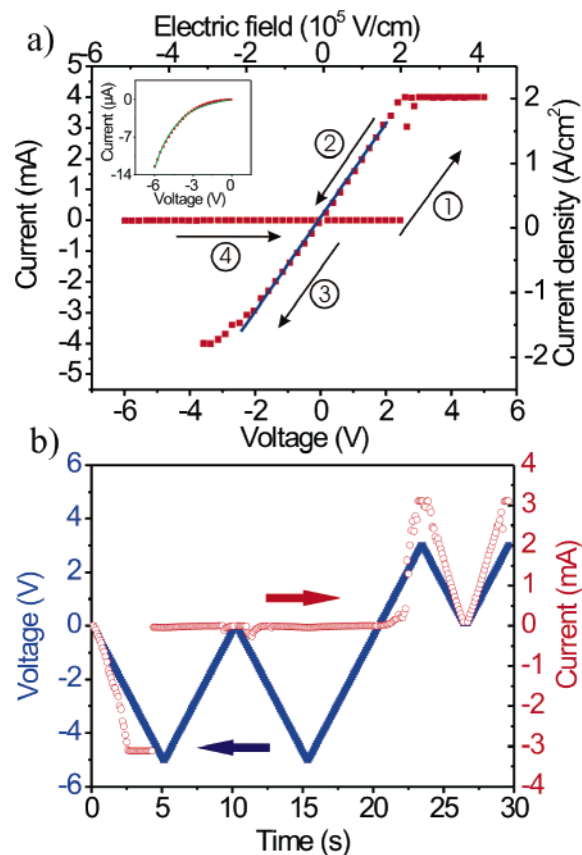


Figure 2. Electrical testing of the devices. (a) I–V characteristics of a Cu/CuDDQ(127 nm)/Ti cell. The current was limited to a maximum of 4 mA to protect the device. The voltage was ramped as indicated by the arrows. The sweep speed was 1 V/s. The current measured in the high resistance state is shown on a magnified scale in the inset. (b) The time dependence of the current through the cell (red circles, right scale) upon applying the voltage (blue squares, left scale) is shown. The respective memory state does not change on application of the same voltage ramp that has been used for switching, as can be seen in the current trace. Switching can only be performed by changing the polarity of the applied voltage.

of time for the shown voltage ramp. The switching from the ON to the OFF state can only be performed by applying a negative voltage to the copper electrode, the reverse switching from OFF to ON can be only achieved by applying a positive voltage. The cell can only be switched by applying a voltage with the opposite sign from the voltage that induced the memory state. From this, we deduce that heat alone cannot be responsible for the switching mechanism. To verify this hypothesis, we calculated the increase in temperature during the switching of the cells, using the method described by Zellers et al.⁸ When short voltage pulses (-7 V , 1 μs) are applied to switch the cells, even while switching from the ON to the OFF state, the cell temperature only increases by approximately 3 $^\circ\text{C}$.

We fabricated and tested 40 cells in the described manner. More than 50% of these showed the described switching phenomenon. The cells can also be switched using short voltage pulses. As shown in Figure 3a, the switching speed of the cell can be increased if short pulses with higher voltage are applied, which is in accordance with the results of Potember et al.⁹ The switching time of the cell can be made

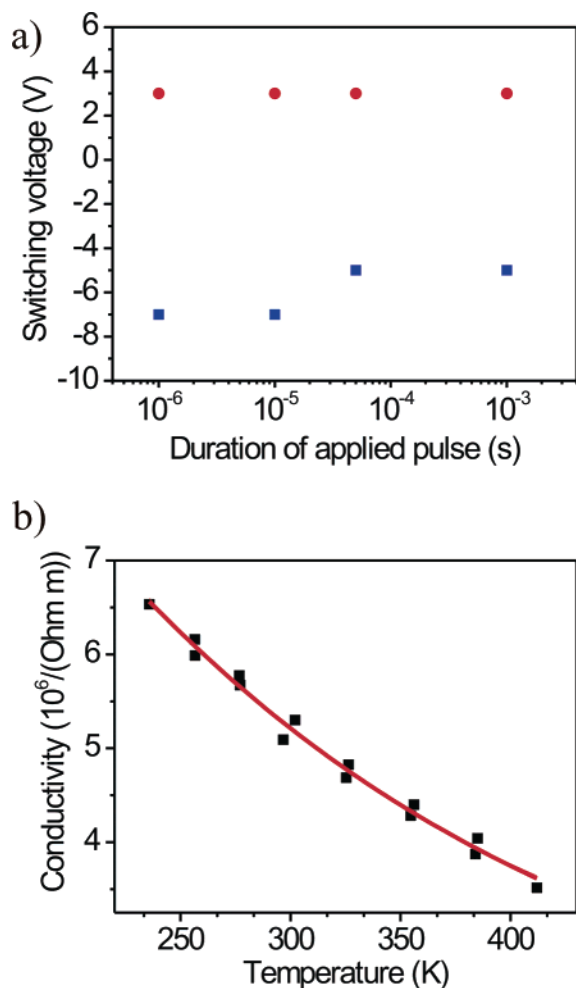


Figure 3. (a) Dependence of the switching voltage on the duration of the applied voltage pulse. The red circles (OFF → ON) and blue squares (ON → OFF) indicate the height of the pulse needed to switch the cell. (b) Temperature dependence of the conductivity in the high resistance state (OFF). The conductivity decreases with increasing temperature. The red line is a fit with the expected temperature dependence of the conductivity for CT complexes.

as short as 1 μs if the switching voltage is raised up to -7 V. We also tested the endurance of the cells. The structures could be switched back and forth between their high and low resistance states over 2000 times with the help of short voltage pulses ($\Delta t = 100 \mu\text{s}$, $V = 5$ V). An endurance this high is quite promising, although it still has to be increased in comparison to values found in similar systems in the literature.^{6,16} The ratio between the ON and OFF state shrinks during these cycles to 10^2 . We have also evaluated retention and found that the cells retain either memory state for more than 15 h without an external electricity source. Considering the early development stage of research being done in this field and in comparison to results obtained with similar systems,⁶ these results appear very promising.

To elucidate if the observed resistance switching is due to a bulk phenomenon (i.e., the organic material is responsible for the switching mechanism) or to a surface phenomenon (i.e., the switching occurs at the organic/electrode interface), we investigated the temperature dependence of

the resistance of the cell in the OFF state. The temperature-dependent measurements were performed in an argon-filled oven. The temperature was monitored using a PT 100 thermoelement positioned in close proximity to the wafer. We found that the conductivity decreases with increasing temperature, as shown in Figure 3b. This behavior is typical for CT salts.¹⁷ The measured data was fit with the standard temperature relationship for CT salts: $\sigma = \sigma_0 T^{-\alpha} \exp(-\Delta/T)$. The fit yielded the parameters: $\sigma_0 = 0.3$, $\alpha = 1.8$, $\Delta = 217.5$, all of which are typical for CT salts. This suggests that, in the high resistance state, the main contribution to the resistance comes from the CT salt, not from the electrode/CuDDQ interface. From this, we conclude that the switching process is a bulk process. The widely acknowledged bulk-switching phenomenon for these types of charge-transfer salts is a field-induced redox reaction,¹² which may be responsible for our system as well; in the high resistance state, the CT salt conducts the electrons at room temperature via some form of hopping conduction. The current–voltage curve in the high resistance state can be fitted well to the relation for the hopping conductance (inset Figure 2a) $I = I_0 \sinh(U/U_0)$ with $U_0 = 2kTd/(ea)$, and k being the Boltzmann's constant, T the temperature, d the layer thickness, e the electron's charge, and a the hopping distance. The fit yields a hopping distance of 3.8 nm. Values as large as this have been observed in earlier work.¹⁸ In this context, if the electric field applied exceeds a certain critical value, the ionic bond between the copper and the DDQ is destroyed, and neutral copper and DDQ are formed. In this state, the conduction takes place via the highly conductive copper, leading to the low memory state with ohmic conduction, as can be discerned from Figure 2a. The observed temperature dependence of the high resistance state, however, cannot be accounted for by hopping conduction. This is why we think that other transport phenomena must be considered in order to explain the OFF state temperature dependence. Further experiments, such as thickness and electrode radius dependence of the resistance in the different memory states, as well as Raman spectra in both states, would provide further evidence of whether the suggested mechanism is correct.

Because of the success with CuDDQ, it seemed plausible that other benzoquinones, especially quinones containing cyano groups, would exhibit the same switching behavior. Indeed, using the same technique as used for CuDDQ, we managed to grow homogeneous layers of copper and tetracyano-*p*-benzoquinone (4CQ) and of copper and tetrachloro-*p*-benzoquinone (CA). Cu4CQ showed switching behavior similar to that discovered for CuDDQ. A typical current–voltage curve is shown in Figure 4a. Scanning electron microscopy (SEM) on the Cu4CQ revealed the formation of a smooth layer of the complex on a copper surface (Figure 4b). Our layers of the CuCA, on the other hand, did not show switching behavior (Figure 4a).

To answer the question why CuDDQ and Cu4CQ show switching, while CuCA does not show switching in our experiments, we would like to point out two important differences between CuDDQ and Cu4CQ on one hand and CuCA on the other hand. First, we note that CuDDQ and

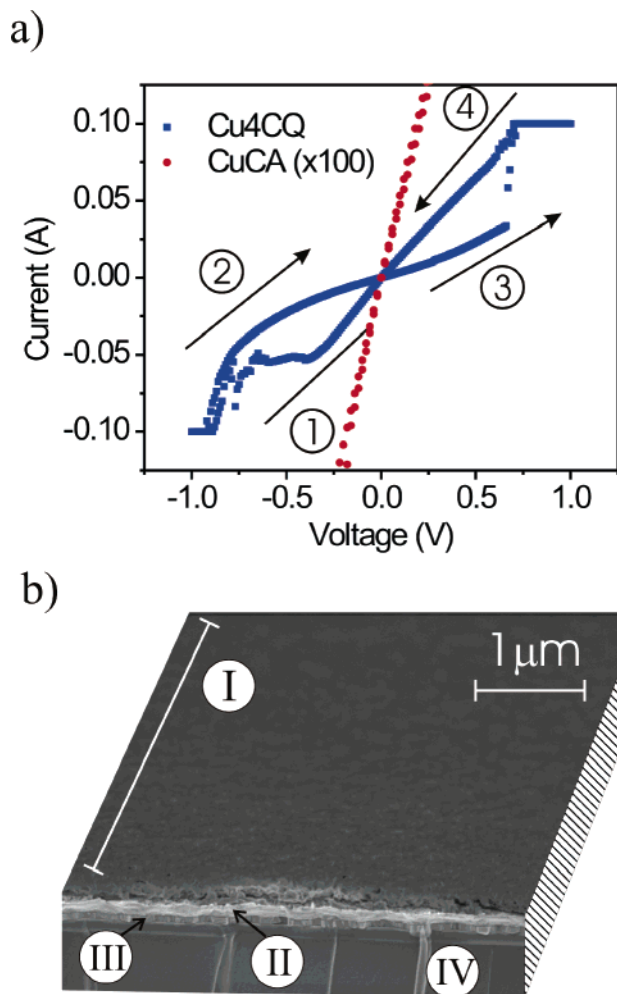


Figure 4. (a) Current–voltage characteristics of the Cu4CQ and of the CuCA cell. In the case of the CuCA, the data is multiplied by a factor 100 to enhance the visibility. The voltage is swept as indicated by the numbers. In the case of the Cu4CQ cell, the current was limited to a maximum of 100 mA to protect the device. (b) Tilted cross-section SEM picture of the Cu4CQ device. The number (I) denotes the homogeneous Cu4CQ layer, (II) the copper bottom electrode, (III) the adhesive layer made of TiW, and (IV) the silicon wafer substrate.

Cu4CQ contain nitrile groups, while CuCA does not contain nitrile groups. Interestingly, the only other copper-containing CT salt that has been reported to show resistive memory switching also relies on a nitrile-containing organic acceptor.⁹ It seems that the presence of nitrile groups is required for the observation of bistability. Second, it appears that the electron affinity of the CT salts determines whether the system shows switching behavior or not: When the electron affinity of the organic acceptor is 2.8 eV or greater, switching is observed (DDQ: 3.13 eV; 4CQ: 2.87 eV);¹⁹ when it is 2.5 eV or less, switching is not observed (CA: 2.48 eV).¹⁹ This finding is supported by results from other groups,⁹ where organic acceptors with an electron affinity of 2.84 eV (ref 19) show switching behavior.

In summary, we demonstrated that the CT salt CuDDQ exhibits reversible resistive memory switching with a ratio

between the high and the low resistance state of about 10^2 – 10^3 . The cells can be fabricated very easily using solution processing. The layers obtained in this manner are very smooth. The structure can be repeatedly switched between the high and the low resistance state. We believe that further process optimization can improve the already promising electrical data of the devices significantly. Furthermore, we discovered that the complex Cu4CN also shows reversible switching phenomena, while no such switching effects were observed for the complex Cu4CA. An interesting goal for future work would be to investigate whether other organometallic CT salts exhibit comparable reversible memory phenomena.

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