

Flow : a study of electron transport through networks of interconnected nanoparticles

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6.1 INTRODUCTION

6.1.1 **Prediction of enhanced switching**

In the previous chapter, we stated that cotunneling in nanoparticle networks does not give a significant contribution to the total current, even at low temperatures. This has an important impact on the expectation by Dayen *et al.*^[1], who predicted that the ON-OFF ratio of a device incorporating molecular switches should scale with the cotunneling distance. Indeed, if cotunneling does not occur, no direct enhancement of the ON-OFF ratio should be expected, assuming that switching only changes $G_{\mathcal{T}}$. However, switching also has an indirect effect, as changing $G_{\mathcal{T}}$ changes ϵ and hence E_{C} . This in turn changes the current at low temperature.

To investigate if this can lead to sizeable effects, we calculated IV curves for two systems (one high-conductance, one low-conductance) with parameters similar to those used in the previous chapter. The parameters are defined as shown in the table below. We discarded all currents lower than 10 fA, to replicate the noise floor in our set-up. We then calculated the ratio of the currents and plotted the maximum ratio versus the temperature, as can be seen in Fig. 6.1.

	E_{C}	$E_{\rm C,var}$	$G_{\mathcal{T}}$	$A\!R$	N
High conductance	20 meV	4 meV	$G_{T}=4.40\cdot10^{-5}~{\rm G_{0}}$	430	33
Low conductance	25 meV	5 meV	$G_{T} = 8.80 \cdot 10^{-7} \text{ G}_{0}$	430	33



Fig. 6.1: Calculated (using the alternative model from chapter 5) maximum resistance ratio of two systems with a factor of 50 difference in G_{τ} and a 20% difference in E_{c} and $E_{c,var}$ versus temperature. To increase the speed of computation, (multiple) cotunneling was ignored, and only values for j = 1 were calculated. The blue line shows the calculated maximum of the resistance ratio, the dashed black line shows the expected ratio if transport was only Ohmic. As can be seen from the graph, the resistance ratio increases dramatically as the temperature decreases, even without cotunneling.

This figure shows that even without cotunneling, the maximum resistance ratio increases rapidly with decreasing temperature. This is similar to an analogous result found by Dayen *et al.*^[1] and shown in Fig. 2.12, which shows that the resistance ratio between a pre- and a post-exchange device increases with decreasing temperature. We found that increasing $E_{\rm C}$



increases the maximum ratio and additionally saw that increasing $E_{C,var}$ decreases the maximum ratio at lower temperatures. These results seem to suggest that nanoparticle networks can indeed be used to enhance the ON-OFF ratio of molecular switches, without even needing cotunneling to explain this phenomenon.

6.2 MOLECULAR SWITCHES

As discussed in chapter one, molecular switches are arguably among the most interesting types of functional molecules^[2,3]. These are molecules that can switch between multiple states, where each state has distinct optical, electronic or chemical properties. They are interesting from a fundamental point of view, as the quantum mechanical nature of the switching can be studied in the lab. Additionally, they have many possible applications, such as chemical sensors (*e.g.* pH sensors^[4]) or optoelectronic circuits^[5]. In these two cases, the resistance of the molecule changes upon capture of a chemical species or upon absorption of light, respectively. It is of course important that the change in resistance is large enough to measure. The switchable molecular device discussed briefly in chapter one has a resistance that only changes by 20% upon illumination^[2], much lower than the orders of magnitude difference between the ON and OFF states of the average transistor.

This resistance ratio could be improved chemically, by altering the molecule. However, a molecule can only be changed so much before it loses its functionality. As discussed in the previous section, a Coulomb blockaded network of nanoparticles has an enhanced sensitivity to the molecules between the particles. By incorporating the molecular switch into the network, the ON-OFF ratio of the entire network can become larger than the ON-OFF ratio of the individual switches.

This chapter focuses on the trans-10b,10c-dimethyl-10b,10c-dihydropyrene molecular switch, as seen in Fig. 6.2. This molecule has two stable states: a closed DHP state, and an open CPD state*, the cores of which are illustrated in Fig. 6.3. The DHP isomer is the most stable of the two and has a deep red color, contrasting with the open metastable CPD state, which is colorless. Illumination of the DHP state with visible light breaks the center bond in the molecule, causing the two phenyl rings on either side to snap out of plane. The resulting CPD state has less orbital overlap, causing both sides of the molecule to be electronically separated, and hence has a lower conductance^[6]. Switching back to the DHP state can be accomplished by illumination with UV-radiation, or by thermal excitation, illustrated in Fig. 6.3. An important reason for choosing this particular switch is the fact that the change in length upon switching is negligible. Hence, mechanical hampering of the switching process is not expected.

^{*}DHP and CPD are abbreviations of DiHydroPyrene and CycloPhaneDiene respectively, referring to the cores of the molecules.



DHF

Fig. 6.2: Schematic depiction of the DHP based molecular switch (trans-10b,10c-dimethyl-10b,10c-dihydropyrene). The two thiol groups on either end facilitate the binding to the gold nanoparticles. The pyridine rings are present to decouple the core of the molecule from the contacts, while still allowing electronic transport through the molecule^[7].

Fig. 6.3: Schematic depiction of the two states of the cores of the molecular switch. The high-conductance DHP state can be switched to the low-conductance CPD state by illumination with visible light. Switching back can be done by applying heat or illuminating with UV radiation. Adapted from Roldan *et al.*^[6].

This change in conductance upon switching was tested in solution using a MCBJ by Roldan *et al.*^[6] on a very similar molecule[†]. For the DHP state, they found a conductance of 10^{-4} G₀. Upon illumination with visible light however, the conductance changed to $\approx 10^{-8}$ G₀, a change of almost four orders of magnitude. This change was reversible, as the conductance changed back to the original value of 10^{-4} G₀ upon heating of the solution. These results suggest that both states are stable when connected to electrodes. Moreover, the two states have very different conductances.

There is a caveat however, as it is not clear if switching occurs when the molecule is contacted. As the measurements are done in solution, each conductance trace is most probably a measurement of a different molecule. It is therefore likely that the molecules switch in solution, before being contacted to the MCBJ where they are measured. This means that although switching is observed in this particular setting, it is likely that the ON and the OFF states are not the same molecule. Therefore, it is not clear whether or not the molecules can be switched after being contacted.

6.3 **Device Fabrication**

Device fabrication was done analogously to the procedure in section 4.3.1. Prior to exchange, the room temperature resistance of the devices was checked in a probe station. As the molecular switch, trans-10b,10c-dimethyl-10b,10c-dihydropyrene (DHP) was used. Due



[†]The only difference is the presence of the thiol groups, which are present in our molecule, but are not present in the cited research. Roldan *et al.* ^[6] used pyridine anchoring groups for binding to the contacts of the MCBJ.

to the small available quantity of the molecule, only around half a milligram was dissolved in a mixture of THF with 20% triethylamine. Since this switch reacts irreversibly with oxygen upon illumination^[8,9], special care was taken when the network was in contact with oxygen. To minimize contact with the ambient environment, the device was attached to the chip carrier under nitrogen atmosphere and transported to the cryostat wrapped in aluminum foil. Loading the sample was done in the dark.

6.4 Optical measurements

First, the switchable molecules were tested for switchability in solution. For that, a tiny amount of material was dissolved in acetonitrile to create a solution with an estimated concentration of 1.2 μ M, which was placed into a 1 cm quartz cuvette. The solution was illuminated using a tungsten halogen light source (5 W) to measure the optical absorption spectrum as a function of time. The results can be seen in Fig. 6.4.

At the start of the measurement (indicated by the topmost dark blue curve), the spectrum shows two peaks at 530 nm and 683 nm, in agreement with previous results^[6]. Illuminating with visible light should switch the molecule to the colorless CPD state. This is indeed observed, as the initial spectrum shows distinct peaks at 530 nm and 683 nm, which decrease in height over time (time progression is indicated by the color of the curves changing from blue to yellow to red). This is more clearly seen in the inset, which shows the normalized absorption at three different wavelengths. The absorption at the chosen wavelengths all decrease over time, corresponding to conversion of the DHP state to the CPD state.

In order to see if this transition is reversible by illumination with UV radiation, another set of optical experiments was done. The molecule was stored in the dark to allow thermal relaxation to the DHP state. Subsequently, the solution was illuminated by a mercury arc lamp (100 W) with a high-pass filter at 400 nm, only allowing larger wavelengths to pass. The spectrum of the light source can be seen in Fig. 6.5, including the two used filters (high-pass and low-pass). At the start of the experiment, and successively after every ten minutes, the light source was turned off and the absorption spectrum was measured using the tungsten light source. After taking one spectrum, the tungsten light source was turned off, and illumination with the Hg source was resumed





Fig. 6.4: Change over time in the absorption spectrum of DHP dissolved in acetonitrile at 25 °C. Blue is the first absorption curve, red shows the spectrum after 67 minutes. The inset shows the normalized absorption at 450 nm, 530 nm and 683 nm (indicated by the lines of the same color in the spectrum) over time. The curves are normalized to the absorption at the respective wavelength at t = 0 and t = 67 min. The decrease in the absorption corresponds to conversion from the closed DHP state to the open CPD state, caused by illumination by the tungsten light source used to measure the spectrum. The absorption below 450 nm could not be measured accurately, as the intensity of the light source at these wavelengths is too low to give reliable data.

After this experiment, the high-pass filter was replaced by a low-pass filter, only allowing wavelengths smaller than 450 nm to pass[‡], and the experiment was repeated. As visible light causes the DHP \rightarrow CPD transition, and UV radiation causes the CPD \rightarrow DHP transition, we expect to see a decrease in absorption during the first experiment, and an increase in absorption during the second. This is exactly what can be seen in Fig. 6.6.

^{\ddagger}The low-pass filter becomes transparent again above 630 nm. However, the intensity of the light source is low at these wavelengths, and we found that it does not interfere with the CPD \rightarrow DHP transition.



Fig. 6.5: Optical spectra of the Hg light source, black shows the unfiltered source, red shows the high-pass filtered source, and purple shows the low-pass filtered source. The high-pass filter starts transmitting above 400 nm, whereas the low-pass filter becomes transparent below 450 nm. Moreover, the low-pass filter again becomes slightly transparent above 630 nm. We found that the transmission at these wavelengths do not significantly affect our results.

The left figure shows the absorption spectra of the first experiment, where the inset shows the change in absorption over time at the indicated wavelengths. The right figure shows the results of the second experiment. As expected, illumination with long-wavelength light shows a decrease in absorption, agreeing with the DHP \rightarrow CPD transition, whereas illumination with short-wavelength light shows the reverse. Moreover, the switching in either direction is very fast, as most of the conversion is already complete before the second measurement.

These results show that this particular batch of molecules indeed show reversible switching behavior, and that the switching can be controlled by illumination with a chosen frequency of light. In order to confirm that the switches can be incorporated into a network of nanoparticles, an array was stamped on a glass substrate. The transparent glass substrate allowed us to measure the UV-VIS transmission through the network. The absorption before exchange and after exchange was measured, the results of which can be seen in Fig. 6.7.





Fig. 6.6: Change over time in the absorption spectra of the switch dissolved in acetonitrile at 42 °C. Progression of time is indicated by change in color of the curves from red to blue, the inset shows normalized absorption over time at chosen wavelengths. In the left figure, the solution is illuminated by the Hg light source using the high-pass filter, on the right, the low-pass filter is used instead. Left plot shows that the absorption decreases over time, corresponding to the DHP \rightarrow CPD, obtained when illuminating with long wavelengths (> 400 nm). We attribute the dip in the first and second measurement points to a misalignment of the fiber optic cable. The right plot shows an increase in absorption, indicating the reverse transition upon illumination with short wavelengths (< 450 nm).



As can be seen in the figure, molecular exchange shifts the absorption peak by 10 nanometers and also broadens it. This indicates that exchange on this sample is indeed successful and that the switches are present in the network.

6.5. INITIAL RESULTS IN DARK ENVIRONMENT

Fig. 6.7: Absorption spectra of the nanoparticle array before (red) and after (blue) exchange with the DHP based molecular switch, the black dashed lines show the Lorentzian fits. The absorption peak shifts by almost 10 nanometers after exchange and also increases in width. Both of these factors indicate successful insertion of the molecules.



6.5 INITIAL RESULTS IN DARK ENVIRONMENT

Prior to exchange, the IV behavior was checked at room temperature in a probe station to ensure that fabrication was successful. After exchange, the one-volt resistance of the network changed from 10 G Ω to 100 k Ω , indicating successful crosslinking of the nanoparticles. This was followed by investigation at variable temperatures in a dark environment, the results of which can be seen in Fig. 6.8.

As the room temperature conductance of the network is large ($\approx 30 \,\mu$ S), we assume that the molecule is initially in the DHP state and did not switch during transfer to the cryostat. The current is similar to the post-exchange result obtained in the previous chapter, albeit roughly an order of magnitude smaller. Fits using the new model can be found in Fig. F.1 in the appendix.





Fig. 6.8: Current versus voltage plots of a nanoparticle network interlinked by molecular switches at various temperatures, plotted on a double-log scale. The data points below the noise floor were removed by hand. The IV curves are similar to those observed in the previous chapter, indicating successful insertion of the switches into the array. See appendix F for fits to these curves using our alternative model.

6.6 EFFECT OF LIGHT AT CONSTANT TEMPERATURE

In order to check the switchability of the network interconnected by the molecular switches, the sample was heated to room temperature under helium atmosphere inside the cryostat. As the insert was fitted with a fiber optic cable, we were able to illuminate the sample *in situ* using various light sources. The resistance at 1 V was measured over time and the sample was illuminated with the mercury light source using the high-pass filter. This should initiate the DHP \rightarrow CPD transition, causing an increase in resistance. Fig. 6.9 shows the one-second averaged resistance versus time.





Fig. 6.9: One-second averaged resistance at 1 V of the nanoparticle network interconnected by molecular switches at room temperature versus time. The sample was illuminated using a mercury light source through a high pass (> 400 nm) filter during the time indicated by the orange window. The illumination should facilitate the DHP \rightarrow CPD transition, corresponding to a decrease in resistance of four order of magnitude. However, no significant change is observed.

The illumination was started after 120 seconds and stopped after 800 seconds, as indicated by the orange window. From Fig. 6.6, left plot, we expect that the conversion should be almost complete after 600 seconds. However, during this time, no significant change in resistance is observed. If all molecules were in the DHP state before the measurement, illumination should trigger the DHP \rightarrow CPD transition, which is paired with an increase in resistance. However, if the molecules are already in the CPD state, the resistance should not change. Therefore, the observation that the resistance does not change might indicate that all molecules are already in the CPD state, not allowing further switching. To check if this is indeed the case, a second measurement was done, this time illuminating using a low-pass filter, allowing only high energy light to pass. The results can be seen in Fig. 6.10.



6. NANOPARTICLE NETWORK DEVICES INTERLINKED BY MOLECULAR SWITCHES



Fig. 6.10: One-second averaged resistance at 1 V of the nanoparticle network interconnected by molecular switches at room temperature versus time. The sample was illuminated using a mercury light source through a high pass (> 400 nm) filter during the entire measurement. The illumination should facilitate the DHP \rightarrow CPD transition, corresponding to an increase in resistance of four order of magnitude. Even after 900 minutes, no significant change in resistance is observed.

Illumination was started after 120 seconds and stopped after 830 seconds, indicated by the first purple window. During illumination, there is no significant change in the resistance. This is confirmed by the trend in the resistance without illumination, indicated by the white window. We found earlier that the switches should complete the CPD \rightarrow DHP transition within ten minutes. However, as the environment might affect the transition rate, we again start the illumination after 50 minutes, in order to see slower changes in the resistance. However, even after three hours of illumination, no change in the resistance was observed.

As the DHP \rightarrow CPD transition might also be slower when the switch is integrated in a nanoparticle network, we change the filters in order to illuminate only with a wavelength larger than 400 nm, identical to the experiment from Fig. 6.9. However, we now illuminate for 15 hours to ensure that even a slower transition rate is captured. The results of this can be seen in Fig. 6.11.





6.6. EFFECT OF LIGHT AT CONSTANT TEMPERATURE

Fig. 6.11: One-second averaged resistance at 1 V of the nanoparticle network interconnected by molecular switches versus time. The sample was illuminated using a mercury light source through a low pass (< 450 nm) filter during the time indicated by the purple windows. The illumination should facilitate the CPD \rightarrow DHP transition, corresponding to an increase in resistance of four order of magnitude. However, no significant change is observed.

Although the resistance changes slightly over the course of 900 minutes, no clear switching is observed. As illumination at these wavelengths should facilitate the DHP \rightarrow CPD transition, we expect to see an increase in resistance of four order of magnitude, which is clearly not observed.

To summarize: neither illumination with large, as with small wavelengths results in a change in resistance, even after extended periods of illumination. This could be due to several reasons. The first of which is the absence of the molecule itself. If molecular place-exchange was unsuccessful, illumination should not have any effect.

In order to study if the molecules are present, we measured the optical spectra before and after exchange. We saw a clear change between the pre-exchange and the post-exchange spectra in Fig. 6.7, indicating that exchange was indeed successful. Moreover, exchange was paired with a change in resistance, supporting this conclusion. Additionally, we used Raman spectroscopy (facility at Dublin City University, group of Prof. Tia Keyes) to determine the presence of the switches. However, the measured signal was too low to provide a definite conclusion.



by the dim light of an LCD computer monitor and took no longer than a minute. These conditions should be insufficient to realise the DHP \rightarrow CPD transition.

Moreover, chemically bonding the molecule to the gold nanoparticles could alter the electronic structure of the molecule. These effects are not uncommon, and as we saw in chapter 1, can indeed prohibit switching in molecules. Alternatively, as the switching requires an electronically excited transition state, this excited state can lose its energy to the surrounding nanoparticles, pacifying the switch. Vice versa, the nanoparticles could be optically excited and transfer the excitation to the molecules. In our system, it could be that the excitation is quenched by the nanoparticles, preventing the molecules from switching.

6.7 Conclusion

We attempted to explore the enhancement of the ON-OFF ratio of nanoparticle networks interlinked with molecular switches. We predict that this ratio should increase with decreasing temperature, due to a change in $E_{\rm C}$ of the nanoparticles between the ON and OFF states. To experimentally confirm this, we fabricated a nanoparticle network interlinked by trans-10b,10c-dimethyl-10b,10c-dihydropyrene, a molecule that can switch between two resistance states upon irradiation with visible light (ON \rightarrow OFF) or UV radiation (OFF \rightarrow ON). Although we observed reversible switching of the molecule in solution and also found a change in SPR frequency and resistance after molecular exchange (indicating successful insertion of the molecule), we observed no change in the resistance of the interlinked network. Neither UV radiation or visible light had a significant effect, even after prolonged illumination.

Although the exact cause of this is unclear, it might be due to passivation of the functionality of the molecule due to chemical bonding with the nanoparticles. This chemical bond might allow the excited transition state to be quenched due to interaction with the nanoparticles. As the length change of the molecule upon switching is negligible, mechanical inhibition of the switch is not expected. Future experiments involving the same molecule should rule out these predictions, possibly by directly measuring switching in a MCBJ while the molecule switches when connected, directly observing the switching. Moreover, other tried and tested molecules, such as diarylethylenes^[2] might provide a better alternative to the molecule used in this research.



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