Abstract: The field of molecular and organic electronics has seen rapid progress in recent years, developing from concept and design to actual demonstration devices in which both single molecules and self-assembled monolayers are employed as light-responsive components. Research in this field has seen numerous unexpected challenges that have slowed progress and the initial promise of complex molecular-based computers has not yet been realised. Primarily this has been due to the realisation at an early stage that molecular-based nano-electronics brings with it the interface between the hard (semiconductor) and soft (molecular) worlds and the challenges which accompany working in such an environment. Issues such as addressability, cross-talk, molecular stability and perturbation of molecular properties (e.g. inhibition of photochemistry) have nevertheless driven development in molecular design and synthesis as well as our ability to interface molecular components with bulk metal contacts to a very high level of sophistication. Numerous groups have played key roles in progressing this field not least teams such as those led by Whitesides, Aviram, Ratner, Stoddart and Heath. In this short review we will however focus on the contributions from our own group and those of our collaborators in employing diarylethene based molecular components.

Keywords: Diarylethene · Molecular electronics · Self-assembled monolayers

Introduction

Molecular design, synthesis and characterisation of potential functional molecular components for application in molecular and organic electronics is an iterative process in which even very well known compounds can surprise us by their versatility. It is the combination of theory, synthesis and characterisation of light and redox responsive molecules required in this research program that drives curiosity in our research team. Over the last decades, we, together with many groups around the world, have been captivated by the remarkable properties demonstrated by a relatively small yet diverse group of responsive molecular systems. As fascinating as these systems are in solution, it is at interfaces between non-molecular materials and on surfaces that attention has shifted to in recent years since application in molecular and organic electronic devices makes this next step inevitable. In this short review, we give a cursory overview of recent advances made by our research teams together with other groups from biochemistry to materials physics.

Design Rules for Light-controlled Molecular-based Electronic Components

At the heart of our research program is the development of light and redox switchable molecules in which at least two stable and often several addition meta-stable
Molecular-based photochromic switches can be 'switched' by irradiation with UV and/or visible light between two or more molecular states (A and B) in a reversible manner. The change in molecular structure induced is accompanied by a change in the energies of the frontier molecular orbitals and hence redox and electronic absorption spectra (Scheme 1).[7] It is this change that can be induced by external stimuli that makes these systems attractive as components in molecular-based electronic devices.[8] Furthermore the ability to tune these photochromic systems by synthetic modification together with their often high stability, reversibility and fast response times (i.e. high photochemical quantum yields) provides for a level of control that is unmatched in wholly non-molecular systems.[7]

The change in the energy of frontier orbitals that accompanies photoswitching offers the possibility of such photoswitches changing their conductivity in devices, thereby acting, for example, as memory units.[9,10] These photochromic systems, although highly promising, pose major technical challenges to their application in molecular electronics, not least in connecting them to conducting interfaces and in demonstrating that their photochromic state can control conductivity and charge transport significantly. These challenges are compounded by issues such as fatigue, photochemical quantum yields, readout and, critically, on defects. A further complication that is often overlooked is that when confined in a densely packed monolayer these systems can show intermolecular interactions that are not normally observed in solution.[11,12]

**Photoswitching of Conductance**

Achieving the full potential of photoswitchable molecular-based electronic devices necessitates that we can control charge transport across the electrode–electrode gap bridged by these systems. This requires that direct tunnelling currents are low relative to mediated charge transport (resonant tunnelling) ‘through’ molecular orbitals,[13,14] and that the mediated charge transport is significantly different between the two photochromic states.[15] Our own efforts in photo-switching of conductance has focused on the dithienylethene class of photochromes. Dithienylethenes exist in two stable forms; a colourless (open) isomer and a coloured (closed) isomer (Fig. 1).[7] In addition to differences in the electronic absorption spectra of the two isomers between the two forms, there are pronounced differences in redox chemistry and hence in the relative energy levels of the molecular orbitals.[16] It is these changes in frontier orbital energies induced photochemically that we have focused our attention on in developing molecular-based electronic devices in recent years.

**Light Switching of Molecules on Metallic Surfaces**

**Trans-cis** isomerization of azobenzenes,[17–19] stilbenes[20] and overcrowded alkenes[21] chemisorbed on gold nanoparticles via alkylthiol linkers with a range of chain lengths have been reported. In these studies the effect of immobilisation on photochemical properties was of considerable interest both from molecule–surface and molecule–molecule interactions. Self-assembly of photoswitches on metallic (nanoparticulate) surfaces can result in direct electronic coupling of a nanoparticle core with a chromophore due to their proximity.[22,23] This might result in complete inhibition of photoactivity. Furthermore steric constraints can limit the conformational freedom of the molecular entities. For diarylethene-based photochromic switches, however, inhibition of photochemical activity because of steric interactions arising from packing in a monolayer is not expected to be significant especially considering that photochemistry is seen for this class of compound even in crystalline states.[24] The earliest study of diarylethenes self-assembled on a surface of gold nanoparticles employed pentamethylenyl alkyl chains to isolate the photoactive unit from the gold surface and showed full retention of the photochemistry observed in solution.[25]

This approach to preserving photochemistry by insulation from the surface does have a drawback in that some degree of orbital interaction with the surface is perceived as being essential to achieving resonant tunneling. Hence we deemed it essential to assess the effect of direct attachment of the diarylethene photoswitches to metallic surfaces, both gold nanoparticles[26] and electrodes[27] using a range of conjugated aromatic spacers. For several spacer units the ring-opening process was retained.[23,26] However ring closure showed a considerable dependence on the spacer group employed. The quantum yields for ring closing for *meta*- and *para-*
substituted phenyl units were the same indicating that the π-conjugation pathway has no effect on the electronic coupling of the chromophore with the Au surface. By contrast with a thiényl spacer group ring closing was essentially absent.\[15,23,26\]

The distance between the surface and the dithienylethene is the same for all three systems and hence we can reasonably infer that the origin of differences in photochemical activity on the surface is due to perturbation of molecular orbital levels by the gold nanoparticles.\[27\]

**Light Switching of Conductance of Individual Molecules on Surfaces**

Achieving the goal of light-controlled molecular electronic devices is no simple feat. The first step is to observe photo-triggered changes in conductance where a molecule bridges two electrodes. Furthermore, this phenomenon needs to be demonstrated under conditions close to that which real molecular devices would operate, *i.e.* at ambient temperatures and self-assembled on nano-electrodes. The first challenges faced relate to discrimination of resonant tunnelling controlled by photoswitching from especially the stability of the molecule electrode interface and stochastic rearrangements of both surface and molecule. On a practical side placing individual molecules between electrodes is most easily achieved using scanning tunneling microscopy\[28,29\] (STM) and the mechanically controlled break-junction\[30\] (MCBJ). A further challenge is to avoid electrochemically induced switching, however by controlling the electrode potentials such voltage-induced switching can be avoided.\[31\]

With diarylethene photochromic switches (Fig. 2) rearrangement of double and single bonds upon photoswitching was expected to result in a significant change in conductance but without substantial change to their physical height when arranged vertically in a self-assembled monolayer. The first study of diarylenes as components in molecular electronic devices employed the MCBJ technique in which two gold electrodes were bridged by a dithienylethene switch with anchoring to the surface achieved using thiol end groups.\[15\]

These early experiments revealed two key results. The first was that upon changing from a ring closed to a ring open form the conductance dropped by three orders of magnitude. Secondly the immobilisation of the switch between two electrodes completely prevented ring closing of the dithienylethene. Further studies using a monothiol functionalised dithienylethene in an STM confirmed these observations.\[32\] These studies highlighted a further challenge to molecular electronics; stochastic switching, which was voltage dependent and believed to be related to the electrochemical switching observed for these systems as well as the mobility of gold atoms in MCBJ devices. The absence of reversibility has been explored theoretically by several groups and although the initial view was that this is due to excited state quenching by gold,\[33\] more recent analysis suggests it is more subtle a phenomenon where the interaction with gold serves to invert the relative ordering of molecular orbitals (*i.e.* lowering of a non-photoactive excited state upon binding to gold).\[27\]

One approach to overcoming this drawback is to reduce the efficiency of the contact between the gold surface and the dithienylethene using a methylene spacer group. The isolation of the switching unit with only a partly conjugated linker allowed for the retention of reversible photochromism.\[34\] Although the differences between the two states is dramatically reduced taking this approach a switch in resistance from 526 MΩ in the open form and 4 MΩ in the closed form could be achieved. Replacing the gold electrodes with carbon nanotubes as demonstrated recently by the group of Guo and Nuckolls\[35\] allows for further improvements in the approach by eliminating the problem of the mobility of gold atoms on the electrode surfaces.

Swapping isolated individual dithienylethene switches between an open and a closed state with UV and visible light has been demonstrated recently.\[36\] The individual molecules were isolated by dilution into self-assembled monolayers of n-dodecanethiol on Au(111) (Fig. 3). This approach simplified imaging the individual molecules. The state of the molecule (either ring opened or closed) was more readily observed due to the strong contrast with the surrounding alkyl thiols. The change in geometry *e.g.* height, observed for azobenzenes does not occur for dithienylethenes and hence the changes in tunnelling current observed reflect real changes in conductivity. A key advantage over the MCBJ...
technique is the ability to perform statistically large numbers of experiments.

**Molecular Redox Switches**

The connection between photochemical and electrochemical switching is perhaps an under appreciated advantage in efforts to achieve multi-addressable molecular-based functional components for molecular devices. Electrochemistry allows entire monolayers of redox active molecular switches to be addressed at electron transfer limited rates and with high sensitivity. An example of this is shown in Fig. 2 and Fig. 4. Cyclic voltammetry allows for changes in the energies of the HOMO and LUMO levels to be estimated and provides detailed insight as to whether it is the HOMO or LUMO orbitals or both change in energy upon switching. This information is key to interpreting the magnitude of changes in resonant tunnelling contributions in molecular electronic devices.

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radiation however redox-driven switching is typically only in one direction. Immobilisation on an ITO surface does not affect the photochemical properties of the dithienylethene shown in Fig. 4, however, in contrast to solution, on the surface it can be switched in both directions electrochemically. The difference in redox behaviour between in solution and on a surface is not due to changes in the properties of the switches or molecular orbital/surface state interactions. Instead it occurs because the intermolecular electron transfer rates between the individual molecules is not diffusion limited as in solution since the molecules are held in proximity to each other on the surface.

**Photoswitching of Conductance in Organic Electronics**

A macroscopic switching device using diarylethene photochromes based polymers was reported recently by Irie and coworkers. A conductive dithienylethene-based polymer was sandwiched between ITO and metallic electrodes. Importantly this study demonstrated that different metal electrodes, e.g. Al, showed rectifying behaviour while, e.g., Au provided for symmetric IV characteristics. Stability was a key problem in the polymer-based devices, however, this could be overcome by using a non-photochromic polystyrene polymer doped with diarylethene molecules.

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by Nuckolls and coworkers, in which a field-effect transistor (FET) was constructed from a single-walled carbon nanotube (SWCNT) on which photochromic spiro-pyran switches were self-assembled and the SWCNT contacted by gold electrodes. UV and visible light irradiation could be used to switch between low and high conductance.

Recently a large array device that employed monolayers of diarylethene photochromic switches on a gold electrode covered with a PEDOT:PSS conducting polymer layer and a second layer of gold has demonstrated that light switching of conductance in an organic device is now a reality (Fig. 5). Importantly, the photochromic monolayer was coated with a conducting polymer layer to preclude short circuits through the photoactive SAM. The devices were constructed using a two-dimensional lattice which served to interconnect individual nanolayers and the molecules must reach so that resonant tunnelling becomes the dominant parameter in controlling conductance; in this a collaborative multidisciplinary approach is paramount. Only once this has been established can we seriously consider more complex functionalities such as rectification. From the technical side, much more understanding of the phenomena which occur at the molecule/electrode interface both upon attachment and during operation is necessary also.

What makes molecular and organic electronics, in our view, so exciting and hold so much promise for the future is that we have only begun to access the molecular tool box in the use of diarylethenes, azobenzenes, spiropyrans and stilbenes. Photo/redox active systems such as the overcrowded alkenes, and multiple switching systems based on oligothiophenes, could open much greater complexity in function with minimal increase in synthetic complexity. To date, molecules containing only a single switching unit have been employed, however it is expected that future efforts will be directed to larger molecular systems which allow for multiple switching units to be incorporated between the metal contacts of junctions. This approach although synthetically challenging allows both for increasing the junction gap size (thereby reducing direct tunnelling), amplifying the effect of changes in molecular structure and conductivity and in allowing for several conductivity states to be accessed (i.e. non-binary). A key challenge from a molecular design perspective is to achieve switching of multiple chromophores without loss of electronic communication between the units. Ultimately the true power of molecular electronics will not be in mimicking conventional solid state devices but in providing new operations through the use of combinations of molecular switching components.

Photo and redox switchable components present a bright future in organic and molecular electronics and, although considerable challenges remain to be overcome, the leap from demonstration of physical phenomena in molecular-based devices, such as the working redox device based on rotaxanes by Stoddart, Heath and coworkers and more recent examples of light-driven solid-state molecular switching devices based on monolayers of photochromic diarylethene molecules, to application may be realised in the very near future.

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