Chapter 6

MACROSCOPIC TRANSPORT BY SYNTHETIC MOLECULAR MACHINES

This chapter describes a synthetic system composed of molecular machines that converts external energy (light) into motion to transport a macroscopic cargo and do measurable work. The system is composed of rotaxanes grafted on a self-assembled alkanethiol monolayer on Au(111) and was studied by X-ray photoelectron spectroscopy, scanning tunnelling microscopy and contact angle techniques. The light-switchable rotaxane components can expose or conceal fluoroalkane residues and thereby modify the surface tension. This principle proves to be useful for the directional macroscopic transport of a liquid droplet on the surface, thanks to the collective operation of the rotaxane sub-layer. The system could have applications such as lab-on-a-chip for performing chemical reactions without reaction vessels on a tiny scale where the transported drop acts as carrier of different reagents.
6.1 Introduction

As already mentioned in Chapter 1, rotaxanes can present reversible linear motion of the macrocycle respect to the thread in response to external stimuli when they are in solution. For example, the change in position of the rotaxane subunits has been used as a nanoscale mechanical switch to vary physical properties such as conductivity, induced circular dichroism and fluorescence. However, their use as building blocks for the development of advanced materials seems to be possible by controlling their properties on surfaces. For this purpose, we have studied a light-switchable rotaxane that can isomerize a fumaramide station (E-I, which has a high binding affinity for the macrocycle) to maleamide (Z-I, which has a low binding affinity for the macrocycle) under the influence of UV-light irradiation, causing the shuttling of the macrocycle respect to the thread. The two isomers are special because they expose or conceal fluoroalkane residues present in the rotaxane thread, leading to a more polarophobic or polarophilic molecule, respectively (Figure 6.1). The shuttling process was observed in solution by Nuclear Magnetic Resonance (NMR).

![Figure 6.1. Chemical structure of the light-switchable rotaxane. Photo-isomerization of the fumaramide group (green) generates the maleamide station (gray). The tetrafluorosuccinamide station (red) is exposed (E-I) or concealed (Z-I) by the macrocycle.](image)

The selected rotaxane was used to produce a photo-responsive surface by grafting it on a 11-MUA SAM on Au(111) via interactions between carboxylic and pyridine groups, following the methods described in Chapter 2 (see scheme in Figure 6.2). The system will be called E-I.11-MUA.Au(111) or Z-I.11-MUA.Au(111) for simplicity. Since the contact angles of both polar and apolar liquids are highly sensitive to small variations in the concentrations of fluoroalkane groups on the surface, it seemed possible that the mechanical shuttling associated with an E-I to Z-I transformation could be used to create a rotaxane-terminated surface with switchable wettability characteristics.
This chapter summarizes the surface characterization by XPS, STM and contact angle, the working principle of the synthetic molecular system and prospective applications.

![Diagram](image.png)

**Figure 6.2.** A photo-responsive surface based on switchable fluorinated molecular machines. Light-switchable rotaxanes with the fluoroalkane region (red) exposed (E-1) were physisorbed onto a SAM of 11-MUA on Au(111) to create a polarophobic surface (left), E-1.11-MUA.Au(111). (Right) Illumination with 240-400 nm light isomerizes some of the E olefins to Z, causing a nanometer displacement of the rotaxane threads in the Z-shuttles which encapsulates the fluoroalkane units leaving a more polarophilic surface, E/Z-1.11-MUA.Au(111). The rotaxanes are not directionally aligned or necessarily linear as depicted in this cartoon for clarity.

### 6.2 Characterization of the E-1.11-MUA.Au(111) surface

#### 6.2.1 Are the rotaxanes on the 11-MUA surface?

After careful preparation of the E-1.11-MUA.Au surface, it was checked by XPS in order to verify that the rotaxane was successfully grafted on the 11-MUA SAM.

The clearest evidence for successful grafting comes from the detection of the nitrogen ls and fluorine ls core levels in the photoemission spectrum of E-1.11-MUA.Au, since these elements are obviously not present in 11-MUA. Figure 6.3 (left) shows the N ls photoemission line and its fit, where the single peak at 400.4 eV corresponds to amide and pyridine groups. Although nitrogen atoms are located in several distinct chemical environments in the rotaxane, in practice XPS can not distinguish between all of them, therefore the symmetric peak is fitted with...
only one single component. However, it is worth noting that the FWHM of 2.2 eV is larger than the experimental resolution (1.5 eV) reflecting the presence of nitrogen atoms in non-equivalent chemical environments. Likewise, Figure 6.3 (right) presents the F 1s photoemission spectrum, where the symmetric photoemission line was reconstructed by one peak centered at 688.6 eV with a FWHM of 2.2 eV. The broadening of this signal can be attributed again to the different chemical surroundings of the fluorine atoms.

![Figure 6.3](image.png)

**Figure 6.3.** X-ray photoemission spectra of the N 1s and F 1s core levels of E-1.11-MUA.Au. Row data (■) and fits to the experimental lines (—).

To facilitate the analysis of the carbon 1s core level, samples of E-I directly deposited on Au(111) and of 11-MUA.Au were studied separately and used as references, since the overlap of signals arising from both rotaxane and 11-MUA molecules would make the direct interpretation of the E-1.11-MUA.Au(111) spectrum rather complex. As already discussed in Chapter 5, the C 1s core level lineshape of 11-MUA (Figure 6.4, top panel) can be fitted by a minimum of three components, one at 284.7 eV binding energy, corresponding to aliphatic carbon, a second one at 285.6 eV originating from carbon atoms next to sulfur and carboxylic groups, and one at 289.2 eV, deriving from carboxylic carbon. The C 1s spectrum of E-I on Au (Figure 6.4, middle panel), is reconstructed by a minimum of six components. The peak at 284.4 eV binding energy, accompanied by the shake-up feature due to π-π* transitions (290.5 eV) is assigned to aromatic carbons.

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8 The experimental resolution in the C 1s spectrum of E-1.11-MUA.Au is 1.5 eV, which is different from the C 1s spectra of E-I on Au and 11-MUA.Au (1.2 eV). It was chosen in this way to maximize the signal intensity and minimize data acquisition time.
The peak at 285.4 eV arises from carbon atoms of the aliphatic chains and from aromatic carbon atoms bound to electronegative groups. The component at 286.5 eV is due to aliphatic carbon atoms bound to both electronegative moieties and amide groups. The peak at 287.9 eV is a sign of the presence of amide groups.\textsuperscript{8–10} Carbon atoms bound to fluorine show the highest chemical shift and give rise to the component at 293.1 eV. The relative areas of the various components in C 1$s$ photoemission line are in good agreement with the stoichiometry of the rotaxane. With these references in mind, we can now focus on the C 1$s$ spectrum of E-1.11-
MUA.Au(111) (Figure 6.4, bottom panel): the presence of the rotaxane is confirmed by the peak at 284.5 eV, accompanied by the shake-up feature at 290.5 eV, and by the amide signal at 287.9 eV. The peak at 285.4 eV originates from different contributions, namely, from carbon atoms of the aliphatic chains of both rotaxane and 11-MUA, and from aromatic carbon atoms bound to electronegative groups. This explains why its intensity is so important after functionalization with rotaxanes. A similar explanation can be given for the component at 286.3 eV, which derives from both 11-MUA and \( E^{-} \) molecules. The characteristic peak of carboxyl groups of 11-MUA is always observed at 289.2 eV. The signal of carbon bound to fluorine, expected at 293.1 eV, is too weak to be identified in this spectrum.

### 6.2.2 Estimation of the rotaxane coverage

<table>
<thead>
<tr>
<th>Coverage of ( E^{-} ) on 11-MUA SAM</th>
<th>1%</th>
<th>2%</th>
<th>3%</th>
<th>5%</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N )</td>
<td>0.7</td>
<td>1.2</td>
<td>1.8</td>
<td>2.6</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>( F )</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
<td>1.1</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>( C )</td>
<td>78.5</td>
<td>78.5</td>
<td>78.5</td>
<td>78.4</td>
<td>77.8 ± 1.6</td>
</tr>
<tr>
<td>( S )</td>
<td>6.7</td>
<td>6.2</td>
<td>5.9</td>
<td>5.3</td>
<td>6.1 ± 0.6</td>
</tr>
<tr>
<td>( O )</td>
<td>13.9</td>
<td>13.5</td>
<td>13.2</td>
<td>12.6</td>
<td>14.7 ± 0.7</td>
</tr>
<tr>
<td>( F/S )</td>
<td>0.04</td>
<td>0.08</td>
<td>0.12</td>
<td>0.2</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>( N/S )</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>( F/N )</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.40 ± 0.05</td>
</tr>
</tbody>
</table>

**Table 6.1.** Comparison between experimental atomic percentages derived from the photoemission peak areas of an 11-MUA SAM film functionalized with \( E^{-} \) and theoretical values calculated for different functionalization yields.

The coverage is defined here as the amount of 11-MUA acid groups that are functionalized with rotaxanes. It can be estimated by comparing the experimentally determined atomic percentages as derived from the photoemission line area with those values calculated taking into account the stoichiometry of the molecules. In the calculation, we considered a model in which the surface is composed of 100 11-MUA with one, two, three or five adsorbed \( E^{-} \). This corresponds to 1, 2, 3 or
5% of functionalization yield of the acid groups. Table 6.1 summarizes the experimental and theoretical results obtained by this method. The error in the measurements was estimated to be 2% for C, 5% for O and 12% for S, N, and F. The photoelectrons coming from atoms that are closer to the Au substrate are more attenuated than the photoelectrons from the top-most layer. For this reason, the intensity of the S 2p signal was corrected in the quantification taking into account the attenuation length that the electrons experience when travelling through 15 Å layer thickness (Chapter 5, Table 5.1). We assume that the attenuation is only due to the presence of 11-MUA and consider that the inelastic mean free path of S 2p electrons is 38 Å. The experimental values are in reasonably good agreement with a coverage of about 2%. The C and especially the O signals always contain a contribution of atmospheric contaminants, which affects all percentages.

### 6.2.3 \( E \text{-}1.11\text{-MUA.Au} \) investigated by STM

STM was employed to investigate the distribution of rotaxane molecules on the 11-MUA SAM in the nanometer range. Figure 6.5 shows images of 11-MUA.Au and \( E \text{-}1.11\text{-MUA.Au} \) surfaces. The detailed structure of the 11-MUA monolayer has been described in Chapter 5. Briefly, 11-MUA molecules self-assemble on the Au(111) substrate leading to a compact monolayer ordered in a \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure with acid-groups pointing towards the air side. Figure 6.5a presents a large area image where ordered domains of 11-MUA molecules arranged in striped-like structures are clearly seen. The darker areas are single-atom-deep etch pits in the gold terrace, i.e. vacancy islands of monoatomic depth formed during the self-assembly process. Figure 6.5b shows a higher magnification image where both ordered and non-ordered regions are present. The striped-like domains are due to the formation of a c(4x2) superlattice with respect to the fundamental \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure.

The images of rotaxane-functionalized SAMs are shown in Figures 6.5c and 6.5d. The surface is decorated by bright features of uniform size (diameter ~ 2 nm) that do not form ordered structures and do not change position after several scans. Since their dimensions are comparable to the size of the rotaxane, most probably each feature corresponds to an individual molecule. Although it is hard to distinguish the ordered arrays of the 11-MUA monolayer below the rotaxanes, etch pits – characteristic of alkanethiol adsorption on Au(111) – are clearly visible as dark regions in the higher magnification image (Figure 6.5d) demonstrating that we are indeed in presence of a functionalized 11-MUA monolayer. The
functionalization yield, estimated statistically from several STM measurements, is in agreement with the values obtained by XPS.

Figure 6.5. (a) Large area STM image of 11-MUA SAM on Au(111) on mica showing gold terraces uniformly covered with ordered domains of alkanethiols (87x87 nm$^2$, $V = 800$ mV, $I = 10$ pA), (b) higher resolution image of 11-MUA striped-like ordered domains (32x32 nm$^2$, $V = -515$ mV, $I = 20$ pA), (c) large area STM image of $E$-1.11-MUA.Au(111) (70x70 nm$^2$, $V = 560$ mV, $I = 20$ pA), (d) higher magnification image of $E$-1.11-MUA.Au(111) (45x45 nm$^2$, $V = 560$ mV, $I = 20$ pA) with the etch-pits in the alkanethiol monolayer visible below the rotaxane molecules.
6.2.4 Stability under UV irradiation

Since the rotaxane configuration can be switched by UV-light, a stability test was performed to determine whether UV irradiation caused any damage to the $E$-1.11-MUA.Au(111) surfaces. The photo-irradiation experiments on the $E$-1.11-MUA.Au surfaces were carried out in air using 240–400 nm light emitted by a 300 W Xe lamp (Thermo Oriel, Model 66902) using a combination of Thermo Oriel glass filters, 57396 and 51650. The beam was focused on the sample using Thermo Oriel 77376 fibres positioned 1 cm above the substrate. Light intensity was measured using a 2 W broadband power/energy meter, 13 PEM 001/J Mellers Griot. The intensity of the ultraviolet light measured 1 cm from the optical fibres was 2.9 mW.

![Graph showing the evolution of the S 2p core level of $E$-1.11-MUA.Au after UV-light irradiation.](image)

**Figure 6.6.** Evolution of the S 2p core level of $E$-1.11-MUA.Au after UV-light irradiation.
Figure 6.6 presents the evolution of sulphur $2p$ signal of a freshly prepared $E$-1.11-MUA.Au surface and the same sample after 5, 10 and 15 min of UV-light irradiation. Every experimental line was mathematically reconstructed by a combination of doublets with a splitting of 1.18 eV.\textsuperscript{11} The signal of the non-irradiated $E$-1.11-MUA.Au surface can be fitted by two components. The main component peak at 162.0 eV corresponds to S bound to Au.\textsuperscript{11, 13, 17} The second component at 163.9 eV could be due to a small amount of alkanethiols not bound to the Au substrate but only intercalated between the chemisorbed 11-MUA molecules or physisorbed as a double layer.\textsuperscript{18} Alternatively, the second component might derive from disulfides formed under the influence of the X-ray during spectra acquisition.\textsuperscript{19, 20} When 11-MUA.Au was measured, the peak at 163.9 eV does not appear (see Chapter 5). From this observation and taking into account that the acquisition time was very short, we can conclude that the second component in the rotaxane spectrum is not due to X-ray damage but to physisorbed alkanethiols. Indeed, during the sample preparation, 11-MUA.Au was immersed in a rotaxane solution for several days and during this procedure some alkanethiol chains can desorb and re-adsorb no longer as chemisorbed but as physisorbed molecules.\textsuperscript{21, 22} However, the presence of weakly bound alkanethiols did not affect the reproducibility of the results in terms of stability.

After 5 min of UV irradiation, the S $2p$ core level presents the same features as for the fresh surface and there is no evidence of damage induced by the UV light. After 10 min of irradiation, the main peak at 162.0 eV remains very intense but a new peak starts to appear at 167.9 eV. This signal originates from the oxidation of sulphur (RSO$_3^-$) and is a clear indication of degradation induced by the UV light.\textsuperscript{23} From these data, we can conclude that after 10 minutes less than 1/5 of the alkanethiol chains are damaged.

After 15 min of irradiation, the N $1s$ and F $1s$ core levels look like the spectra presented in Figure 6.3. Thus, there are no evidences of changes in the rotaxane itself. The C $1s$ core level can not give useful information for this particular test because the sample can get traces of environmental contamination after every removal from the UHV chamber that influence the C $1s$ core level signal.

In addition, the samples can be used several times for the transport experiments that will be described later in this Chapter, even after storage in air for weeks.
6.2.5 The photo-responsive $E$-1.11-MUA.Au surface

Contact angle measurements with several liquids were performed to investigate the surface properties before and after 5 min of UV-light irradiation. The results are summarized in Table 6.2. Irradiation for longer periods had no further effect on the contact angles. The results show that the rotaxane functionalized substrate is indeed a photo-responsive surface. The significant change in contact angles after irradiation provides evidence that positional switching of the macrocycle relative to the thread of the rotaxane was occurring on the surface. As a control experiment, 11-MUA.Au surfaces without rotaxane functionalization and samples prepared with a similar non-fluorinated rotaxane were tested (i.e. a rotaxane in which fluorine atoms were replaced by hydrogen atoms and should not produce strong polarity changes after shuttling; see Figure 6.7). None of the control samples manifested changes in contact angles after UV-light irradiation, suggesting that the lowering in contact angles in the case of the fluorinated rotaxane surface is caused by a reduction in the number of exposed fluoroalkane residues.

![Figure 6.7. The non-fluorinated rotaxane used to prepare control samples for determining the photo-responsive properties of $E$-1.11-MUA.Au.](image)

6.3 Macroscopic transport

Surface energy heterogeneity\(^{24-28}\) brought about by photoinduced wetting/de-wetting has previously\(^{29,30}\) been used to move droplets of liquids across surfaces. In a two-stage process, an azobenzene-terminated surface was photoisomerized to cis (wetting the surface) and then asymmetrically irradiated at the rear of the droplet at a second wavelength (cis-to-trans isomerization), selectively de-wetting the back edge of the droplet and pushing it forward.
<table>
<thead>
<tr>
<th>Liquids</th>
<th>Before UV-irradiation</th>
<th>After UV-irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diiodomethane</td>
<td>35</td>
<td>13</td>
</tr>
<tr>
<td>Water</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>Formamide</td>
<td>40</td>
<td>31</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48</td>
<td>40</td>
</tr>
<tr>
<td>Bromoform</td>
<td>18</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 6.2. Contact angles of various low-volatility liquids deposited on the E-1.11-MUAAu surface. The liquid droplets were deposited before and after irradiation of the surface with UV-light for 5 min. * Experimental error was ± 2°.

Similarly, the photoresponsive properties of E-1.11-MUAAu due to the nanometer molecular shuttling might be useful for the transport of a macroscopic object. In order to test this possibility, the following experiment was carried out: a 1.25 µl drop of diiodomethane, the liquid that produces the greatest contrast in contact angle between the pristine and the irradiated surface (Table 6.2), was deposited on a freshly prepared E-1.11-MUAAu on glass and the sample was irradiated with a perpendicular beam of 240-400 nm light focused on one side of the drop and the adjacent area to produce a gradient in the surface free energy across the length of the drop. The results are summarized in Figure 6.8. After irradiation for 80 s the front of the drop started to advance at a dynamic contact angle of 30 ± 2°, which continued to decrease during the wetting of the surface. The advancing contact angle remained at least 1° lower than the receding contact angle during this initial extension period, the inequality of contact angles illustrating the difference in surface properties caused by the irradiation. If irradiation was stopped at any point, no further changes to the droplet were observed until irradiation was re-started. After a total of 900 s irradiation time (Figure 6.8b), the droplet had elongated by 0.8 mm and the advancing dynamic contact angle decreased to 13 ± 2°. From 900 to 1010 s transport of the entire droplet occurred at a mean speed of ~1 µm s⁻¹, during which time the contact angles on the illuminated and the non-illuminated side of the drop were essentially equivalent (Figure 6.8c). By 1110 s (Figure 6.8d), the contact angle had reduced to its minimum value of 12 ± 2° and irradiation produced no further changes until evaporation became significant.

At a simple level, the mechanism of drop transport seems straightforward: as the right-hand side (as shown in Fig. 6.8a) of the drop and adjacent section of the surface is irradiated with ultraviolet light, the E/Z ratio of shuttles on that part of
Figure 6.8. Lateral photographs of light-driven transport of a 1.25 μl diiodomethane drop along the surface of a $E$-1.11-MUA$\cdot$Au(111) substrate on glass. The direction of transportation was controlled by irradiation with a perpendicular beam of 240-400 nm light focused on one side of the drop and the adjacent surface. (a) Before irradiation (pristine $E$-1.11-MUA$\cdot$Au(111)), contact angle 35 ± 2°. (b) After 900 s irradiation, contact angle 13 ± 2° (illuminated side) 15 ± 2° (non-illuminated side). The diiodomethane drop has spread from the high $E/Z$-1 ratio area in the direction of the low $E/Z$-1 ratio region, increasing the total wetted area, and is about to be transported. (c) After 1010 s irradiation (just after transport), contact angle 13 ± 2°. (d) After 1110 s irradiation (at the photostationary state), contact angle 12 ± 2°.

The surface starts to decrease and that part of the surface becomes less polarophobic. The contact angle at the right-hand side of the drop decreases, causing a Laplace pressure gradient inside the droplet$^{31,32}$ and the forward edge creeps along the surface, elongating the droplet and wetting the surface. As the $E/Z$ ratio on the irradiated region of the surface progressively decreases, the droplet
spreads further along the surface. A necessary consequence of the forward movement of the front edge of the droplet is that the back edge of the droplet is forced to make a thermodynamic contact angle with the unchanged polarophobic surface that is shallower than the original preferred angle. Consequently, at a critical point the original position of the rear end of the droplet becomes so energetically unfavourable that the progressive driving force for increasing wetting at the front end of the drop causes contraction of the droplet from the rear to occur, leading to sudden and reasonably rapid transport of the droplet towards the low E/Z ratio region of the surface. Further irradiation only slightly reduces the contact angle until a photostationary state is reached.

The E-1.11-MUA.Au(111) surfaces are stable and the same sample can be used repeatedly for transport experiments with reproducible results over the course of several weeks. In contrast, diiodomethane droplets on SAMs made from the control non-fluorinated shuttle or other shuttles or heptadecafluorodecanethiol did not undergo contact angle change or transportation even after 20 min ultraviolet irradiation. Nevertheless, it was investigated whether other (photo)chemistry of E- or Z-1 and CH2I2, rather than just photoisomerization and shuttling of the fluorinated rotaxane, might be contributing to the observed effects. (i) Neither E- nor Z-1 showed any trace of alkylation of the pyridine groups when dissolved in a 1:1 mixture of CH2I2/CH2Cl2 (the rotaxanes are not soluble in neat CH2I2) at room temperature for 24 h. (ii) The iodine atoms of CH2I2 do not act as a 'heavy atom' triplet sensitizer for the olefin in E-1; the rate of isomerization and the E/Z ratio in the photostationary state is the same in CH2I2/CH2Cl2 solution as it is in CH2Cl2. (iii) X-ray photoemission spectroscopy (XPS) reveals no damage or change in elemental composition after 5 min ultraviolet irradiation of the E-1.11-MUA.Au and after 10 min less than 1/5 of the molecules might be damaged (111) surface (see section 6.2.4) and also shows that the shuttle is intact on the surface after the droplet transport (the spectra look like those of Figures 6.3 and 6.4). (iv) Although the photo-induced cyclopropanation of electron-rich olefins with CH2I2 is known to occur over 2–60 h using strong ultraviolet sources, the olefin in E-1 is electron poor and no degradation, side product or reaction of E-1 besides isomerization was observed when the solution photo-isomerization experiment (254 or 312 nm) was carried out for 20 min (4× longer than normal) in CH2I2/CH2Cl2. No discolouration of CH2I2 was observed (indicative of the formation of I2) either in solution or in the liquid droplet experiments. (v) Finally, we note that the contact angle of the droplet

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** Measurements of the rotaxane in solution were carried out by José Berná and Emilio M. Perez (Prof. Dr. David A. Leigh’s research group). School of Chemistry, University of Edinburgh, The King’s Buildings, West Mains Road, Edinburgh EH9 3JJ, United Kingdom.
in Fig. 6.8b–d (that is, just before and after transport) is similar to that of a non-irradiated CH$_2$I$_2$ droplet deposited on the irradiated surface (see Table 6.2), suggesting that any photochemistry of CH$_2$I$_2$ during the experiment does not significantly effect the fluorophobicity of the droplet. However, we cannot rule out that it may play some role in altering the viscosity, surface tension or interaction with the monolayer.

Figure 6.9. Lateral photographs of light-driven directional transport of a 1.25 µl diiodomethane drop across the surface of a E-1.11-MUA.Au(111) substrate on mica. a) Before irradiation (pristine E-1). b) After 215 s of irradiation (20 s before transport). c) After 370 s of irradiation (just after transport). d) After 580 s of irradiation (at the photostationary state).

Mica provides a flatter and more regular surface than glass (Chapter 2.4.1) and consequently SAMs are generally more ordered using Au(111) deposited on mica.
Although the contact angles were found to be the same for the SAMs on the different substrates, the transport of CH$_2$I$_2$ was significantly more facile using mica (Figure 6.9). Indeed, the rear end of the droplet could be transported more than 1.5 mm (compared with 0.8 mm using Au(111) on glass, Figure 6.8) on the new photo-responsive surface (Figure 6.9d).

**Figure 6.10.** Lateral photographs of light-driven transport of a 1.25 µl diiodomethane drop on a $E$-$1.11$-MUA.Au(111) substrate on mica up a 12° incline. For clarity, on photographs b-d a white line is used to indicate the surface of the substrate. a) Before irradiation. b) After 160 s of irradiation (just before transport). c) After 245 s of irradiation (just after transport). d) After 640 s irradiation (at the photostationary state). Note how the drop moves slightly back downhill under the effect of gravity from c to d as the $E/Z$ ratio of the lower part of the incline decreases and the droplet progressively wets more of the surface down to slope. The experimental set-up does not permit accurate contact-angle measurements on an incline.
Finally, the ability of the monolayer of molecular shuttles to do macroscopic work against gravity by driving a droplet up a 12° incline using $E$-1.11-MUA.Au(111) on mica was investigated (Figure 6.10).37

The capillary length, $\kappa^{-1} = (\gamma/\rho g)^{1/2}$ (where $\gamma$ is the surface tension of the liquid, $\rho$ is its density, and $g$ is gravity), above which gravity effects should appear is 1.25 mm for CH$_2$I$_2$ and the influence of gravity is clearly seen in the Figure 6.10 photographs (for example, the directional wetting of the surface and downhill movement of the droplet between Fig. 6.10c and d). However, even moving uphill, photo-induced wetting and subsequent transport using $E$-1.11-MUA.Au(111) on mica proved much more rapid than on glass. Between 160 and 245 s, the 1.25 µl of CH$_2$I$_2$ ($\rho = 3.325$ g/ml) moves 1.38 mm (at ~ 16 µm/s) up the 12° incline. The work done against gravity by the collective action of the monolayer of molecular machines is thus $(1.25 \times 10^{-3}$ ml $\times 3.325 \times 10^{-3}$ kg/ml) $\times (1.38 \times 10^{-3}$ m $\times \sin 12^\circ) \times (9.8$ m/s$^2) = 1.2 \times 10^{-8}$ J. The molecular shuttles each occupy an area of ~ 3 nm$^2$, so ~ $2 \times 10^{12}$ molecules are under the elongated drop just before transport. Therefore, if around 40% of the shuttles have been isomerized by the time the droplet is transported uphill, each molecular machine’s contribution to the collective work against gravity – energy stored as potential energy by their action – is ~ $1.5 \times 10^{-20}$ J, that is ~ 9 kJ/mol. Extra work, lost as heat, also has to be done to overcome the viscous forces that resist transport of the droplet. NMR experiments6 and studies on related rotaxanes38 indicate that the energy available to do work through the macrocycle in $E$-1 hydrogen bonding to the fumaramide station rather than the fluoroalkane group is of the order 15–18 kJ/mol. So even if the 12° slope would be the maximum they can overcome, the efficiency of the molecular machines in elevating a droplet by biased Brownian motion to store potential energy is at least 50% of the total free energy made available by the nanometre movements of the individual machine parts.

The extrapolation across the length scales from mechanical motion at the molecular level to macroscopic transport is considerable. However, the mechanism by which it occurs is not a continuous mechanical process. Light fuels isomerization, which causes nanometre positional changes in individual molecules by biased Brownian motion, which collectively cause a change in the physical properties of the surface, ultimately leading to transport of an object on a length scale a million times larger than the initial change in molecular co-conformation. In doing so, the rotaxane molecules are not individually well described as ‘motors’. In both olefin diastereomers $E/Z$-1 the macrocycle is in equilibrium between the binding sites at either end of the thread, the light-fuelled chemical reaction simply changes the position of this equilibrium. If the thread is converted back to its
original structure (Figure 6.1) the net change in position of the macrocycle is undone, that is the rotaxane acts a mechanical switch not a motor. A key difference between a ‘switch’ and a ‘motor’ is in fact, that the former is simply a function of state. The property of the system it is influencing does not depend on the trajectory of how the system evolved, merely on what the current state of the switch is. However, the collective action of the monolayer of molecular mechanical switches does act as a motor, transporting the diiodomethane droplet to a position that it did not sample previously through Brownian motion.

6.4 Reactions-without-vessels performed on the *E*-1.11-MUA.Au(111) surface

Although methods for the injection and pumping of fluids inside microchannels and the connecting and interfacing of microreactors with other system components have significantly improved over recent years, the preparation of new systems for performing analysis or chemical reactions on the micro- and nano-litre scale is still a very active area of research. Nearly all of the microreactors reported to date rely on the flow of streams of reagents through capillaries or microchannels, which effectively sets a lower limit on the volumes utilized due to the contaminating effects of diffusion and surface adsorption. The use of two or three phase flows in which aqueous plugs of the reagents are submerged in an immiscible carrier fluid have been demonstrated to minimize these problems. In order to continue decreasing the size of microreactors, sensors and lab-on-a-chip devices, the use of discrete droplets of reagents might be advantageous, but the intrinsic difficulties in the manipulation and directional transport of single droplets complicates their use. In this respect, the utilization of molecular motors or switches for analyte and reactant transport may be a suitable alternative. The rotaxane-based system presented in this Chapter permits the light-directed transport of discrete microlitre droplets of reagents over non-structured surfaces, thus eliminating the need for previously carved micro-channels or capillaries. Its simplicity and versatility might prove useful in the design of a new generation of lab-on-a-chip devices. Since the changes in wettability properties upon UV-light irradiation of this photo-responsive surface can be used to transport a macroscopic cargo, the switching behaviour of the surface to perform chemical reactions on a microlitre scale is tested. For easier visualization of the process, we chose a chemical reaction which results in a colour change: the reaction between bromothymol blue (see Figure 6.11) and an aqueous solution of sodium
hydroxide (NaOH$_{aq}$). We used diiodomethane as a carrier liquid, which does not take part (react) or influence (catalyze) the chemical reaction. Both reagents are insoluble in diiodomethane, in which only bromothymol blue forms a stable dispersion, so we deposited a tiny droplet (~ 0.2 µl) of NaOH$_{aq}$ on top of the second diiodomethane drop. Figure 6.11 shows the lateral photographs of light-driven directional transport of two microliter-size diiodomethane droplets (2.5 µl each) each carrying a reactant, across the surfaces of E-1.11-MUA.Au(111) at different stages of the experiment. Both drops, Drop1, a diiodomethane drop with a droplet (~ 0.2 µl) of NaOH$_{aq}$ deposited on top, and Drop2, a suspension of bromothymol blue in diiodomethane, were deposited onto E-1.11-MUA.Au(111) (Fig. 6.11a). The area between the drops was then irradiated with a perpendicular beam of 240-400 nm light, focused on one side of each drop and the adjacent area in between the two drops. After 20 seconds of irradiation, the drops start to elongate towards each other (Fig. 6.11b). We observed that Drop2 moves slower

![Image of experimental setup and photographs](image)

**Figure 6.11.** Lateral photographs of the colour reaction driven by the collective work of rotaxanes on the surface. Two drops with reagents (1 and 2) are placed on E-1.11-MUA.Au(111). (a) Before UV-light irradiation, (b) 25 seconds after irradiation (drops start to elongate), (c) 52 seconds after irradiation (drops are in intimate contact), (d) final state (aqueous droplet coloured blue). The chemical structure of bromothymol blue before (top) and after (bottom) the reaction is also shown.
than Drop 1. This can be explained by the change in surface tension of the diiodomethane droplet caused by addition of bromothymol blue. While it is difficult to predict or measure the exact surface properties of a dispersed system like Drop 2, addition of bromothymol blue does not seem to have altered them dramatically since we were still able to observe the directional motion of the droplet on the photo-responsive surface. Similarly, the presence of the small droplet of NaOH\textsubscript{aq} onto the diiodomethane drop, Drop 1, does not appear to influence the properties of the carrier liquid at all. After 52 seconds of irradiation the two drops reach each other and mix, leading to the diffusion of bromothymol blue from Drop 2 to Drop 1 (Fig. 6.11c). At this point, the ultraviolet light irradiation was switched off. Although the NaOH\textsubscript{aq} droplet remained in the same place after the irradiation, 80 seconds after Drop 1 and Drop 2 mixed, bromothymol blue molecules reached the aqueous medium and gave a clearly detectable blue coloration (Fig. 6.11d).

6.5 Conclusions

In this Chapter it was shown that one layer of synthetic molecular machines driven by light is enough to move a macroscopic object: the collective operation of the rotaxanes power the movement of microlitre droplets. The millimetre-scale directional transport of diiodomethane on the \textit{E}-1.11-MUA.Au(111) surface is achieved by using the biased Brownian motion of stimuli-responsive rotaxanes to expose or conceal fluoroalkane residues and thereby modify surface tension.

The light-induced changes in surface wettability allow chemical reactions to be performed on the microlitre scale by bringing individual drops containing different reactants together. Both dissolved and suspended reagents in a diiodomethane droplet can be used to carry out chemical reactions.

The transport of microlitre droplets on a non-structured photo-responsive surface may prove useful for delivering reagents in lab-on-a-chip environments, potentially minimizing problems associated with diffusion and surface absorption compared to structured micro-reactors.

References

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[51] Bromothymol blue or 4,4’-(3H-2,1 Benzoxathiol-3-ylidene) bis [2 bromo-3-methyl-6-(1-methylethyl)phenol] S,S-dioxide, chemical formula: C_{27}H_{32}Br_{2}O_{5}S, CAS No.: 76-59-5, is a commonly used acid-base indicator. It is yellow in acidic aqueous solutions and blue in basic solutions.