Chapter 4
Light-Gated Rotation in a Molecular Motor Functionalized with a Dithienylethene Switch

A multiphotochromic hybrid system is presented in which a light-driven overcrowded alkene-based molecular rotary motor is connected to a dithienylethene photoswitch. Ring closing of the dithienylethene moiety, using an irradiation wavelength different from the wavelength applied to operate the molecular motor, results in the inhibition of the rotary motion as is demonstrated by detailed $^1$H-NMR and UV/Vis experiments. For the first time, a light-gated molecular motor is thus obtained. Furthermore, the excitation wavelength of the molecular motor is red-shifted from the UV into the visible light region upon attachment of the dithienylethene switch.

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4.1 Introduction

Inspired by the wealth of molecular machines found in Nature, which drive and regulate a wide range of processes such as muscle contraction and ATP synthesis, a large collection of synthetic molecular machines has been developed over the last decades.[1–8] Prominent examples of such artificial machines include a molecular elevator,[9] a molecular brake,[10] a nanocar,[11] an adaptive catalyst,[12] a molecular walker[13] and a synthesizer,[14] which are all powered by either chemical fuel, redox processes or light. The use of light as a stimulus offers the advantage that it is non-invasive and does not produce any waste products.[6,8] Moreover, it can be easily tuned in terms of wavelength and intensity and it can be applied with high spatio-temporal control. These advantages have stimulated the application of light-driven molecular switches[15] and motors in functional materials[8,16–21] and in biological systems.[22–25] However, potentially harmful UV light is typically used for their operation while, for practical applications, the use of visible light is often desired.[26–32]

One of the major contemporary challenges in the development of light-driven switches and motors is to design systems that can be controlled by more than one stimulus, offering a higher level of control. Gated photochromism, which is the ability to turn photoswitching processes on and off using a stimulus that is complementary to light, provides such control. Different stimuli have been used in the past to achieve gated photochromic systems, for example by ion complexation,[33–36] pH change,[37,38] redox processes,[39–41] or host-guest interactions.[42] We envisioned that the use of light, of a different wavelength than the wavelength that is used for photoswitching, could be a viable alternative. However, to our best knowledge, no successful examples of light-gated photochromism have been reported so far, which is most probably due to a lack of orthogonality.[43]

Light-driven molecular motors based on overcrowded alkenes represent unique photoresponsive systems in the sense that they undergo unidirectional rotation around their central double bond (Scheme 4.1 a) Full 360° rotary cycle of molecular motors 1 and 2 (note that the isomer generated after 180° rotation is identical to the starting isomer, but has a different viewpoint). b) Representation of light-gated rotary motion via switching between the open and closed form of the appending DTE moiety.[44–46] Promising applications have been demonstrated in nanotechnology,[11,47,48] catalysis,[12,49] and anion binding,[50,51] amongst others. Unidirectional rotation is achieved by sequential photochemical E-Z-isomerization and thermal helix inversion steps (Scheme 4.1a). In the first step, an unstable isomer is generated photochemically in which the methyl-substituent at the stereocentre adopts an energetically unfavored pseudo-equatorial orientation. The strain that is built up around the double bond is subsequently released by a thermal helix inversion (THI) process, in which the aromatic moieties of the upper and lower half slide along each other. After this thermal step, the thermodynamically favored
pseudo-axial orientation of the methyl group is restored. A second photochemical $E$-$Z$-isomerization, followed by a THI, completes a full 360° rotation.

Scheme 4.1 a) Full 360° rotary cycle of molecular motors 1 and 2 (note that the isomer generated after 180° rotation is identical to the starting isomer, but has a different viewpoint). b) Representation of light-gated rotary motion via switching between the open and closed form of the appending DTE moiety.

Several approaches have been taken to dynamically control the rotary behavior of molecular motors with a second stimulus, all of which required chemical additives. Illustrative examples are the locking of rotation using an acid-base responsive self-complexing pseudorotaxane\cite{52} and the reversal of the rotary direction by base-catalyzed epimerization.\cite{53} More recently, we reported an allosteric approach in which the rotational speed can be regulated by metal complexation.\cite{54} Whereas all of these approaches rely on chemical additives, we considered the development of a non-invasive approach an important next step. We now present the first example in which the rotary behavior of a light-driven molecular motor can be controlled by an additional light source.
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In our design, a second generation molecular motor is connected to a dithienylethene (DTE) switch to give a multiphotocromic hybrid system (Scheme 4.1b). Interestingly, the molecular motor can be operated with visible light ($\lambda_{irr} = 455$ nm) instead of the generally used UV light. Upon closing of the DTE switch by UV light ($\lambda_{irr} = 312$ nm), the rotation of the molecular motor is inhibited, a process which can be reversed by irradiation with light of a longer wavelength ($\lambda_{irr} = 528$ nm), which opens the switch.

4.2 Synthesis

For the synthesis of target molecule 2, the molecular motor moiety was first synthesized using a Barton-Kellogg reaction (Scheme 4.2). Coupling partners diazo 3 and thioketone 4 were freshly prepared following literature procedures.\cite{47,55} For the synthesis of the DTE switch moiety, unsymmetric dithienylethene 6 was first synthesized according to literature procedures.\cite{56} Due to the poor reactivity of chlorides in Sonogashira coupling reactions, the chloride was first exchanged for an iodide by lithium-halogen exchange followed by quenching with iodine. The TMS protected acetylene moiety could then be installed using a Sonogashira coupling, yielding switch 8. Subsequent TMS deprotection followed by a second Sonogashira coupling with bromo-substituted motor 5 afforded hybrid 2.
4.3 \textsuperscript{1}H-NMR and UV/vis studies

The possible photochemical and thermal isomerization steps of 2, as illustrated in Scheme 4.3, were first followed by \textsuperscript{1}H-NMR spectroscopy. Figure 4.1i shows the \textsuperscript{1}H-NMR spectrum of the stable open (so) isomer of hybrid 2 in CD2Cl2. Upon irradiation at 455 nm at \(-25 \, ^\circ\text{C}\), a new species appeared (Figure 4.1ii). In analogy to the unsubstituted parent motor 1,\textsuperscript{[57]} the clear shifts of \textsuperscript{1}H-NMR signals H\textsubscript{a}, H\textsubscript{c}, and H\textsubscript{c'} are characteristic for the photochemically induced formation of the unstable 2uo (Scheme 4.3). Moreover, the doublet signal for H\textsubscript{d} has a clearly distinct chemical shift for each isomer. The sample was irradiated until no further changes were observed, that is, the photostationary state had been reached. The ratio of unstable:stable at this photostationary state (PSS\textsubscript{455}) was found to be 66:34. When the sample was warmed up to room temperature, the THI was allowed to take place, resulting in quantitative conversion to the stable state (that is, isomer 2so). The same NMR sample was then irradiated at 312 nm at room temperature to isomerize the DTE moiety to its closed isomer 2sc (Figure 4.1iii). The expected formation of isomer 2sc was evident from the shifts of protons H\textsubscript{e}, belonging to the methyl substituents of the...
thiophene moieties, and proton H_d. At the PSS 312, the ratio of closed:open isomer was found to be approximately 70:30. The sample was subsequently irradiated at 455 nm at −25 °C to test whether the closed hybrid 2sc could be isomerized to the unstable state 2uc (Figure 4.1.iv). If isomerization would be allowed, the unstable 2uc should be observed beside the unstable 2uo, which are the photochemical isomerization products of 2sc and 2so respectively, which were present in a 70:30 ratio. After irradiation the sample contained 2uo, but 2uc was absent, revealing inhibition of isomerization in the closed form. It should be noted that at the same time also some opening of the DTE switch occurs when the sample is irradiated at 455 nm which is unusual for DTE switches at this wavelength. The rate of the opening of the DTE switch is, however, significantly lower than when the sample is irradiated at 528 nm.

Figure 4.1. ^1H-NMR spectra of 2 in CD_2Cl_2. (i) before irradiation; (ii) PSS 455 nm; (iii) PSS 312 nm; (iv) sample of iii irradiated at 455 nm; (v) sample of ii irradiated at 312 nm.
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The unstable closed isomer 2uc could be accessed via another route. That is, by first irradiating a sample of 2so at 455 nm at −25 °C, to give isomer 2uo, and subsequently at 312 nm at the same temperature to close the DTE switch (Scheme 4.3). Figure 4.1v corresponds to this experiment and reveals a fourth doublet of H₄ belonging to the unstable closed isomer. Allowing the sample to warm up to room temperature leads to quantitative conversion of 2uc back to 2sc and of the remaining 2uo back to 2so. These combined NMR experiments reveal that the motor functions as usual when the DTE switch is in the open state, but that rotation is impeded when it is closed. Thus, the rotary function can be controlled by light of a different wavelength than the wavelength that is used to operate the molecular motor. This gated photochromic behavior is most likely due to an energy transfer process from the motor to the DTE moiety in analogy to other multiphotochromic systems.[43,59]

Scheme 4.3 Photochemical and thermal isomerization steps of hybrid 2.

The isomerization behavior of hybrid 2 was additionally studied by UV/Vis spectroscopy. The UV/Vis spectrum of a solution of 2so in CH₂Cl₂ shows an absorption band with a maximum at λ = 423 nm (Figure 4.2). This absorption band is bathochromically shifted compared to the parent unsubstituted molecular motor 1, which has an absorption maximum at λ = 395 nm.[56] Most likely, this bathochromic shift is caused by the extension of the π system. Aromatic extension has been shown before to be suitable to shift the excitation wavelength of molecular motors into the visible light region.[60]
Figure 4.2 a) UV/Vis spectra of hybrid 2 upon irradiation at 455 nm. b) Eyring plot analysis of the thermal isomerization step from unstable to stable 2. c) UV/vis spectra of hybrid 2 upon irradiation at 455 nm (-9 °C) followed by 312 nm (-9 °C) and 528 nm (20 °C). c) after irradiation at 312 nm (20 °C) followed by 455 nm (-9 °C) and 528 nm (20 °C).

Upon irradiation of a UV/Vis sample of 2so with 455 nm light at -9 °C a bathochromic shift was observed (Figure 4.2a), which is characteristic for the formation of the unstable isomer 2uo. A clear isosbestic point at λ = 447 nm revealed that this photochemical isomerization is a unimolecular process. The quantum yield for this photochemical step (Φso→uo) was estimated by comparing the rate of formation of 2uo, which was determined by following the absorption increase at λ = 505 nm at a concentration high enough to absorb all incident light, with that of Fe²⁺ ion formation from potassium ferrioxalate, under identical conditions (see Experimental Procedures for details). A quantum yield of Φso→uo = 5.6% was measured and the quantum yield for the reverse photochemical isomerization step (Φuo→so) was then calculated using the PSS455 ratio, giving Φuo→so = 3.3%. These values are in similar range as the quantum yields that have been measured for structurally related molecular motors with and without substituents in the same position. When the UV/Vis sample was allowed to warm to room temperature, the original spectrum was recovered, indicating that the THI had taken place. The rates for this thermal isomerization step were determined at five different temperatures (ranging from 0 to 20...
°C) by monitoring the decrease in absorption at λ = 500 nm. Using the Eyring equation (Figure 4.2b), the activation parameters for this process were determined (ΔH° = 74.9 ± 1.7 kJ mol⁻¹; ΔS° = -41.5 ± 5.9 J K⁻¹ mol⁻¹). The Gibbs free energy barrier (ΔG°(20 °C)) was found to be 87.1 ± 0.1 kJ mol⁻¹, corresponding to a half-life (t₁/₂(20 °C)) of 370 s. These values are in the same order of magnitude as the ones determined for the unsubstituted parent molecular motor 1, for which an energy barrier of 85 kJ mol⁻¹ and a half-life of 190 s have been reported. Moreover, multiple cycles of these photochemical and thermal isomerization steps could be performed without any major signs of fatigue.

When a UV/vis sample of 2so was first irradiated at 312 nm at 20 °C, a broad band around λmax = 602 nm appeared (Figure 4.2c, green line). This band is characteristic for the formation of the closed, more conjugated isomer of the DTE switch (isomer 2sc), of which the formation was also observed by ¹H-NMR spectroscopy (vide supra). This closed state of the DTE switch is thermally stable under the experimental conditions used and multiple close/open isomerization cycles showed only minor signs of fatigue. Subsequent irradiation of this sample, containing a mixture of 2so and 2sc, at 455 nm at −9 °C caused relatively small changes in the absorption band located around λmax = 423 nm. The broad band in the visible region decreased, revealing some concomitant opening of the DTE switch. These results are fully consistent with the ¹H-NMR studies, showing that only the open isomer 2so is able to undergo E-Z-isomerization whereas this process is inhibited for the closed isomer 2sc. Subsequent irradiation at 528 nm triggered almost quantitative opening of the DTE switch as is clear from the disappearance of the absorption around λmax = 602 nm.

As also described for the ¹H-NMR studies, isomer 2uc could be accessed by irradiation of a sample containing 2so at 455 nm to afford 2uo, followed by irradiation at 312 nm, showing the emergence of a broad band in the visible region (Figure 4.2d, red line). The emergence of this band is indicative of the formation of the closed DTE moiety. Again, opening of the DTE switch could be triggered by irradiation at 528 nm.

4.4 Conclusions

In summary, we have presented a photochromic hybrid system consisting of an overcrowded alkene-based molecular motor and a DTE switch. Interestingly, by aromatic extension, the excitation wavelength is red-shifted into the visible region. Visible light excitation leads to the usual rotary motor behavior when the DTE is in the open form. However, when closed, the rotary motion is inhibited and thus, light-gated photochromism is observed. This is the first system in which the rotary function can be switched on and off in a non-invasive manner by using an additional light source. Gated systems, like the one presented here, offer an increased level of control over photoswitching processes, which will prove essential for the development of more complex and sophisticated molecular machinery in the future. Studies on the exact
mechanism of the inhibition of the rotary motion by the closed isomer of the DTE switch, which require detailed investigation of the electronic coupling of both photochromes, are underway in our lab.

4.5 Experimental procedures
For general remarks regarding experimental procedures see Chapter 2.
Compounds 3, 4, and 6 were synthesized according to literature procedures and all spectroscopic properties were in agreement with reported spectra.

9-(5-bromo-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene (5)

Freshly prepared diazo compound 3 (405 mg, 2.11 mmol) and thioketone 4 (613 mg, 2.11 mmol) were dissolved in dry toluene (80 ml) under N₂ atmosphere in a flame-dried Schlenk flask and stirred overnight at rt. HMPT (0.44 ml, 2.41 mmol) was added and the resulting mixture was stirred for 3h at 50 °C. The volatiles were evaporated and the residue was purified using column chromatography (SiO₂, pentane/EtOAc 20:1) followed by layered crystallization with CH₂Cl₂/MeOH to yield 5 (520 mg, 57%) as yellow crystals.

M. p. 213 °C; H NMR (400 MHz, CDCl₃): δ 8.36 (d, J = 8.6 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.92 (s, 1H), 7.86 – 7.81 (m, 2H), 7.75 (d, J = 7.5 Hz, 1H), 7.57 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.36 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.22 (td, J = 7.5, 1.0 Hz, 1H), 6.79 (td, J = 7.6, 1.2 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 4.34 (m, 1H), 3.58 (dd, J = 15.1, 5.7 Hz, 1H), 2.74 (d, J = 15.2 Hz, 1H), 1.39 (d, J = 6.7 Hz, 3H); C NMR (101 MHz, CDCl₃): δ 149.9, 147.5, 140.3, 139.9, 139.8, 137.1, 136.8, 131.3, 131.0, 130.8, 128.4, 128.1, 128.0, 127.5, 127.4, 127.3, 127.2, 126.9, 126.2, 125.9, 125.5, 124.3, 119.9, 119.2, 45.6, 41.8, 19.4; HRMS (APCI⁺, m/z): Calcd for C₂₇H₂₀Br [M+H⁺]: 423.07429, found: 423.07431.

3-[3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenyl-3-thienyl)-1-cyclopenten-1-yl]-5-iodo-2-methylthiophene (7)
Under a N₂ atmosphere, dithienylethene 6 (50 mg, 0.10 mmol, 1.0 equiv.) was dissolved in dry THF (2 mL) in a flame dried schlenk tube and the mixture was cooled to −78 °C. t-Butyl lithium (1.9 M in hexane, 0.12 mL, 0.23 mmol, 2.2 equiv.) was slowly added and the mixture was stirred for 45 min at the same temperature. Then, iodine (58.4 mg, 0.23 mmol, 2.2 equiv.) was added and the mixture was stirred for 45 min at −78 °C and then at rt for a further 30 min. The mixture was diluted with CH₂Cl₂ and the organic layer was washed with water, Na₂S₂O₃ and brine. The organic phase was dried (MgSO₄) and volatiles were removed in vacuo. The residue was purified using column chromatography (SiO₂, pentane) to give aryl iodide 7 (53 mg, 90%) as a blue oil.

**1H-NMR (400 MHz, CDCl₃):** δ 7.54 (dd, J = 7.4, 1.6 Hz, 2H), 7.39 (dd, J = 7.6, 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.24 (s, 2H), 1.95 (s, 3H), 1.93 (s, 3H).

**19F NMR (376 MHz, CDCl₃):** δ -110.16 (t, J = 5.5 Hz), -131.90 (p, J = 5.6 Hz).

Spectroscopic data are in agreement with those reported in the literature.⁶

3-[3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenyl-3-thienyl)-1-cyclopenten-1-yl]-2-methyl-5-trimethylsilylethynylthiophene (8)

Under a N₂ atmosphere, aryl iodide 7 (40 mg, 0.07 mmol, 1.0 equiv.), tetrakis(triphenylphosphine)palladium(0) (6.0 mg, 5.3 μmol, 0.075 equiv.), copper(I) iodide (1.0 mg, 5.3 μmol, 0.075 equiv.) and triethylamine (3 mL) were placed into a Schlenk flask and the mixture was degassed. Then, trimethylsilylacetylene (20 μL, 0.014 mmol, 2.0 equiv.) was added and the mixture was stirred at 70 °C overnight in the dark. The progress of the reaction was followed by TLC and once the reaction was completed, the mixture was diluted with EtOAc and washed with aq. NH₄Cl, water and brine. The organic phase was dried (MgSO₄) and concentrated in vacuo. The residue was purified using column chromatography (SiO₂, pentane) to give alkyne 8 (30 mg, 79%) as a blue oil.

**1H-NMR (400 MHz, CDCl₃):** δ 7.56 – 7.51 (m, 2H), 7.39 (dd, J = 8.4, 6.8 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.25 (s, 2H), 1.93 (s, 3H), 1.89 (s, 3H), 0.25 (s, 9H).

**19F NMR (376 MHz, CDCl₃):** δ -110.2 (s), -131.9 (s).

Spectroscopic data are in agreement with those reported in the literature.⁶

5-Ethynyl-3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenyl-3-thienyl)-1-cyclopenten-1-yl]-2-methylthiophene (9)
Alkyne 8 (30 mg, 55.4 μmol, 1.0 equiv.) was dissolved in THF (1 mL), potassium hydroxide (100 mg, 1.78 mmol, 32 equiv.), water (1 mL) and MeOH (1.5 mL) were added and the mixture was stirred at room temperature for 2 h. The mixture was diluted with CH₂Cl₂ and the organic layer was washed with water and brine. The organic phase was dried (MgSO₄) and concentrated in vacuo to give alkyn 9 (25 mg, quant) as a purple oil.

**1H-NMR (400 MHz, CDCl₃):** δ 7.53 (dd, J = 7.6, 1.6 Hz, 2H), 7.38 (dd, J = 8.4, 6.8 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 3.35 (s, 1H), 1.93 (s, 3H), 1.92 (s, 3H);

**19F NMR (376 MHz, CDCl₃):** δ -110.23 (t, J = 5.7 Hz), -131.91 (p, J = 5.1 Hz);

**13C NMR (101 MHz, CDCl₃):** δ (16 signals were observed, signals of the central perfluorocyclopentene are not observed as is commonly found in the literature[56]) 143.8, 142.7, 141.4, 133.4, 132.9, 129.2, 128.1, 125.8, 125.7, 125.0, 122.3, 120.5, 82.3, 76.0, 14.7, 14.6. HRMS (APCI+, m/z): Calcd for C₂₃H₁₅F₆S₂ [M+H⁺]: 469.05139 found: 469.05060.

**5-((1-(9H-fluoren-9-ylidene)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)ethynyl)-2-methyl-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-en-1-yl)thiophene (2)**

Compound 5 (14 mg, 32 μmol, 1.0 equiv.), alkyne 9 (15 mg, 32 μmol, 1.0 equiv.), and triethylamine (2 mL) were placed into a Schlenk flask under N₂ atmosphere and the mixture was degassed. Then, tetrakis(triphenyl-phosphine)palladium(0) (2.0 mg, 1.6 μmol, 0.05 equiv.) and copper(I) iodide (0.30 mg, 1.6 μmol, 0.05 equiv.) were added and the mixture was stirred at 70 °C in the dark overnight. The mixture was diluted with CH₂Cl₂ and the organic layer was washed with aq. NH₄Cl, water and brine. The organic phase was dried (MgSO₄) and concentrated in vacuo. The residue was purified using column chromatography (SiO₂, pentane) to give hybrid 2 (20 mg, 77%) as a yellow solid. m.p. 145 °C (dec.); **1H-NMR (400 MHz, CDCl₃):** δ 8.46 (d, J = 8.4 Hz, 1H), 8.02 – 7.94 (m, 1H), 7.87 –
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7.82 (m, 3H), 7.76 (d, J = 7.5 Hz, 1H), 7.55 – 7.62 (m, 3H), 7.45 – 7.28 (m, 8H), 7.22 (t, J = 7.4 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.69 (d, J = 7.9 Hz, 1H), 4.31 – 4.39 (m, 1H), 3.57 (dd, J = 15.1, 5.7 Hz, 1H), 2.77 (d, J = 15.1 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H);

\( ^{19}\text{F} \text{NMR (376 MHz, CDCl}_3\text{): } \delta = -110.08 \text{ (t, } J = 5.5 \text{ Hz), } -110.15 \text{ (t, } J = 5.5 \text{ Hz), } -131.85 \text{ (tt, } J = 5.5 \text{ Hz); } ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3\text{: } \delta = \text{43 signals were observed, signals of central perfluorocyclopentene are not observed as is commonly found in literature}}^{[56]} \text{ 150.2, 146.3, 144.0, 142.7, 141.5, 140.4, 139.9, 139.8, 138.0, 137.1, 133.4, 132.4, 131.9, 131.8, 129.8, 129.2, 128.3, 128.1, 128.1, 127.4, 127.4, 127.3, 127.2, 126.9, 126.5, 126.2, 126.0, 125.8, 125.5, 124.4, 122.4, 122.3, 121.8, 119.9, 119.2, 93.1, 88.1, 45.4, 41.8, 19.4, 14.8, 14.7. HRMS (APCI+, m/z): Calcd for C\text{50}H\text{33}F\text{6}S\text{2} [M+H\text{+}]: 811.19224, found: 811.19286.

Quantum yield determination

The photon flux of the Thorlabs M455F1 LED was estimated by measuring the production of ferrous ions from potassium ferrioxalate.\(^{[63]}\)

![Graph showing linear fit of the photochemical formation of Fe\(^{2+}\) ions over time by irradiation with \(\lambda_{\text{max}} = 455\) nm. The slope, obtained from the linear fit, corresponds to the rate of formation of Fe\(^{2+}\) ions (4.81 \times 10^{-5} \text{ M s}^{-1} \text{ or } 9.62 \times 10^{-5} \text{ mmol s}^{-1}).

A sample of 2so was irradiated with \(\lambda_{\text{max}} = 455\) nm light under identical conditions as with the actinometry at a concentration high enough to absorb all incident light (Abs\(_{455} > 2, c = 6.9 \times 10^{-5}\) M). The formation of 2uo was monitored over time by following the absorbance increase at \(\lambda = 505\) nm. The molar absorptivity of 2uo at \(\lambda = 505\) nm (\(\varepsilon = 2.17 \times 10^4\) m\(^{-1}\) cm\(^{-1}\)) was used to calculate the concentration increase. The initial concentration increase was plotted versus time and the slope, the rate of formation of 2uo, was obtained by linear fitting to the equation \(y = ax + b\) using Origin software. The photochemical quantum yield
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of \(2\text{so} \) \((\Phi_{\text{so}-\text{uo}} = 6.3\%)\) was then calculated using the photon flux of this specific light source
previously determined at identical conditions in the actinometry. The quantum yield of
the reverse reaction at \(\lambda = 455\) nm \((\Phi_{\text{so}-\text{uo}} = 3.3\%)\) can then be calculated using equation 1,
in which \([\text{so}], [\text{uo}]\) are the concentrations at PSS\(_{455}\).

\[
\frac{[\text{so}]}{[\text{uo}]} = \frac{\phi_{\text{uo}-\text{so}} \epsilon_{\text{uo}}}{\phi_{\text{so}-\text{uo}} \epsilon_{\text{so}}}
\]  
(eq. 1)

Figure 4.4 Linear fit of the photochemical formation of \(2\text{so}\) over time by irradiation \(\lambda_{\text{max}} = 455\) nm. The slope, obtained from the linear fit, corresponds to the rate of formation \(2\text{so}\) \((2.78 \times 10^6 \text{ M s}^{-1} \text{ or } 5.56 \times 10^6 \text{ mmol s}^{-1})\).

4.6 References

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[58] Irradiation with 312 nm also causes isomerization of the molecular motor to form isomer 2uo. The THI is however relatively fast at this temperature and as a result only the stable isomer is observed.


