Chapter 2

A visible light driven molecular motor based on pyrene

To red-shift the excitation wavelength of overcrowded alkene-based molecular motors, a visible light-driven motor with an extended aromatic core is presented. In this motor, the naphthalene moiety in the upper half is changed to pyrene. Its photochemical and thermal isomerization processes were initially studied using DFT calculations and were followed by NMR and UV/vis studies. Combined, these studies show that extension of the \( \pi \) system on the upper half successfully shifts the excitation wavelength into the visible region, while retaining proper rotary function.

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2.1 Introduction

One of the major drawbacks for the field of photoresponsive switches and motors is that they are usually operated with harmful UV light.\(^{[1-3]}\) To fully exploit their potential application in biology\(^{[4,5]}\) or smart materials\(^{[6-9]}\) it is necessary to red-shift their excitation wavelength to the visible light region.\(^{[2,10]}\) Various strategies for the visible light activation of existing photoswitches have been developed in recent years, mostly by making changes to the design in such a way that the photochromic unit can directly absorb visible light. Examples are push-pull systems,\(^{[11,12]}\) extension of the \(\pi\) system\(^{[13,14]}\) and ortho-functionalization (applied to azobenzenes).\(^{[15-17]}\) Alternatively, photosensitizers\(^{[18,19]}\) or upconverting nanoparticles\(^{[20]}\) have been used to operate photoswitches with visible light or even near infrared. Additionally, new types of photoswitches are emerging that allow for switching with visible light.\(^{[21-24]}\)

Molecular motors based on overcrowded alkenes are unique photoswitches in the sense that they are able to perform rotary motion around their central double bond axle.\(^{[3,25,26]}\) Their rotary cycle is based on two photochemical steps and two thermally activated steps (Scheme 2.1a). An initial light-induced \(E\)-\(Z\) isomerization yields a metastable isomer with opposite helicity. Subsequently, a thermal helix inversion (THI) occurs, in which the upper half passes the lower half. The photogenerated state is often referred to as an ‘unstable’ state. The second half of the cycle proceeds in a similar manner, resulting in 360° rotation. Owing to the unique properties of these molecular motors, they have found applications in diverse fields, such as responsive soft materials,\(^{[9,27-29]}\) liquid crystals,\(^{[30,31]}\) anion binding\(^{[32,33]}\) and responsive catalysis.\(^{[34,35]}\)

\[\text{Scheme 2.1. a) Rotary cycle of second generation molecular motor 1. Note the isomer obtained after 180° rotation is identical to the initial isomer but viewed from the opposite side. b) Extension of the } \pi \text{ system of the upper half of the molecular motor to red-shift its excitation wavelength.} \]
To red-shift the excitation wavelength of these motors, for example, a tetraphenylporphyrin triplet sensitizer was attached to a second generation molecular motor as a triplet sensitizer.\textsuperscript{[36]} Hence, irradiation with 530 nm light resulted in triplet-triplet energy transfer from the porphyrin to the molecular motor, driving the rotation. In a related example, a molecular motor was incorporated into a Ru(II)-bipyridine complex.\textsuperscript{[37]} Here, irradiation into the metal-to-ligand charge transfer band with 450 nm light resulted in rotation.

Other methods have been applied in which changes in the motor design were made in such a way that it absorbs visible light. Even though this seems to be a more straightforward method, these changes might also inhibit the rotary function. The earliest successful example of a molecular motor able to absorb visible light features a push-pull substituent pattern.\textsuperscript{[38]} The motor, bearing a nitro and a dimethylamino substituent, showed photoisomerization with 425 nm light. Recently, our group demonstrated that also by extending the \(\pi\) system of the lower half, the excitation wavelength can be shifted to the visible region (up to 490 nm).\textsuperscript{[39]} As this lower half aromatic extension led to successfully red-shifting of the excitation wavelength, we became interested in studying whether this strategy could be also applied the upper half. Overcrowded alkene \textbf{2} was designed (Scheme 2.1b), in which the naphthalene moiety in the upper half of parent motor \textbf{1} is changed to pyrene. Additionally, alkyl chains are attached to the lower half to improve solubility.

### 2.2 DFT calculations

To predict whether target compound \textbf{2} would function as a visible light-driven molecular motor, TD-DFT calculations were performed first. The structure was optimized and the vertical transitions were calculated using B3LYP/6-31G(d,p), which was shown before to be a reliable method for the prediction of geometries and UV/vis spectra of overcrowded alkene based molecular motors.\textsuperscript{[39,40]} To reduce calculation time, methyl instead of hexyl substituents were introduced in the lower half. The first calculated transition at 431 nm has low oscillator strength (0.0038) and therefore most likely will not cause significant absorption. The second transition, being the HOMO-LUMO transition located at 420 nm, has a much higher oscillator strength (0.4818) (Figure 2.1a). Analysis of the orbitals involved showed a typical \(\pi-\pi^*\) transition located at the central double bond which is likely to lead to photochemical isomerization.

The same functional and basis set were used to predict the thermal barrier for THI. The ground states and transition state geometries were identified and the geometries were optimized, and subsequently verified with a frequency analysis (Figure 2.1b). A barrier (\(\Delta^\text{G}_{\text{calc}}\)) of 90.9 kJ mol\(^{-1}\) was found, which is slightly higher than the experimentally determined barrier for THI of parent motor \textbf{1} (\(\Delta^\text{G}_{\text{exp}} = 85\) kJ mol\(^{-1}\)).\textsuperscript{[41]} As these results
indicated that this pyrene-based overcrowded alkene would function as a visible light-driven motor, so we devised a strategy to synthesize this compound.

Figure 2.1. a) TD-DFT calculated HOMO-LUMO transition of motor 2. b) side and top views of optimized structures of motor 2.

2.3 Synthesis

The synthesis of 2 started with a palladium catalyzed Negishi cross-coupling of hexahydropyrene 6 with organozinc reagent 5 (Scheme 2.2). This organozinc reagent was prepared from ester 3, in which the bromide in 3 was substituted for iodide using a Finkelstein reaction to give 4. Subsequently, 4 was transformed into the organozinc reagent 5 by reaction with a zinc-copper couple, after which it was directly submitted to the cross-coupling reaction. The ester in 7 was then hydrolyzed and transformed into an acid chloride by using thionyl chloride, which was followed by an AlCl₃ mediated intramolecular Friedel-Crafts acylation to form ketone 9. Oxidation of 9 with DDQ afforded pyrene 10, which was subsequently converted into thioketone 11 and submitted to a Barton-Kellogg reaction with diazo compound 12 to provide overcrowded alkene 13. In the last step, hexyl chains were introduced on the lower half using a double palladium-
catalyzed organolithium cross-coupling, which was developed in our group.\cite{42,43} The structure of motor 2 was determined with \textsuperscript{1}H and \textsuperscript{13}C-NMR and composition by HRMS.

\begin{center}
\includegraphics[width=\textwidth]{Scheme_2.2.png}
\end{center}

\textbf{Scheme 2.2. Synthetic route for pyrene-based molecular motor 2}

\section*{2.4 UV/vis and \textsuperscript{1}H-NMR spectroscopy of motor 2}

Next, the photochemical and thermal isomerization behavior of motor 2 were investigated using UV/vis spectroscopy. The UV/vis spectrum of motor 2 in CH\textsubscript{2}Cl\textsubscript{2} showed an absorption maximum in the visible region, at $\lambda = 414$ nm, which is close to the predicted maximum of $\lambda = 420$ nm (Figure 2.2). Upon irradiation at 455 nm at 0 °C, a clear bathochromic shift was observed, which is characteristic for the formation of the unstable state upon photochemical E-Z isomerization. A clear isosbestic point was observed at $\lambda = 425$, indicative of a unimolecular process. Notably, even though pyrene is well-known to be fluorescent,\cite{44,45} no significant fluorescence was observed for motor 2. When the irradiated UV/vis sample was allowed to warm to room temperature, the original absorption spectrum was reobtained. The unstable state underwent thermal isomerization to afford the stable state. An Eyring analysis was performed to determine the activation parameters for this thermal process. The rate of isomerization was determined at five different temperatures between 0 °C and 20 °C by following the decrease in absorption at $\lambda = 470$ nm (Figure 2.3). The Gibbs free energy of activation was found to be $(\Delta^\ddagger G) = 88.5 \pm 0.1$ kJ mol\textsuperscript{-1}, which is in good agreement with the calculated value of 91 kJ mol\textsuperscript{-1} for THI obtained by DFT. As expected, this value is also in the same range as the barrier for THI of parent motor 1 ($\Delta^\ddagger G = 85$ kJ mol\textsuperscript{-1}).
Figure 2.2. Photochemical and thermal isomerization of motor 2 (top). UV/vis spectra of motor 2 in CH$_2$Cl$_2$ (c = 2.3 x 10$^{-3}$ M) upon irradiation with $\lambda_{\text{max}} = 455$ nm (bottom left) and $\lambda_{\text{max}} = 395$ nm (bottom right)

The photochemical and thermal isomerization were also followed by $^1$H-NMR spectroscopy. Irradiation of a sample of motor 2 in CD$_2$Cl$_2$ at 455 nm at -25 °C led to the appearance of a new set of signals, indicative of the formation of the unstable state (Figure 2.4). The sample was irradiated until no further changes were observed and at this photostationary state (PSS) the ratio of unstable to stable was determined to be 28:72. Irradiation of the same sample at 395 nm led to a PSS ratio of 90:10, because the unstable state absorbs less strongly at this wavelength (*vide infra*). When the sample was allowed to warm to room temperature, the original spectrum was obtained, illustrating that the THI had taken place. Combined, these studies show that pyrene based motor 2 functions as a visible light-driven molecular motor.
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Figure 2.3. Eyring plot analysis of the THI of unstable 2 to stable 2 monitored by the decrease in absorption at λ = 470 nm in CH₂Cl₂ (c = 2.6 x 10⁻⁵ M). ΔG (20 °C) = 88.5 ± 0.1 kJ mol⁻¹; ΔH = 77.8 ± 1.6 kJ mol⁻¹; ΔS = -36.5 ± 5.6 J mol⁻¹ K⁻¹

Figure 2.4. Selected region of ¹H-NMR spectra of motor 2 in CD₂Cl₂ (c = 1.7 x 10⁻³ M) at -25 °C. For atom labeling see Figure 2.2. i) stable 2 b) PSS λ_max = 455 nm iii) THI, 20 °C.

Additionally, the quantum yield for the photochemical E-Z isomerization (Φ_{s→u}) was estimated. By comparing the rate of formation of the unstable state to the formation of Fe⁺⁺ ions from potassium ferrioxalate under identical conditions (see experimental procedures for details), a quantum yield of 1.4% was determined. Using the PSS ratio, the quantum yield for the reverse photochemical isomerization (Φ_{u→s}) was calculated to be 0.38%.
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2.5 Conclusions

In summary, aromatic extension of the upper half, from naphthalene to pyrene, is shown to be a viable method to shift the excitation wavelength of a molecular motor into the visible light region ($\lambda_{irr} = 455$ nm). The photochemical and thermal isomerization processes were first explored by DFT calculations, and was followed by the synthesis of this pyrene-based molecular motor. Combined UV/vis and $^1$H-NMR studies revealed that the excitation wavelength is shifted into the visible region, while proper rotary motion is retained. Interestingly, despite the well-known fluorescence of pyrene, no significant fluorescence was observed when it is incorporated in a molecular motor.

2.6 Experimental procedures

General procedures

Reagents were purchased from Sigma-Aldrich, Combi-Blocks or TCI and were used as provided unless stated otherwise. Anhydrous solvents were obtained from a solvent purification system (MBRAUN SPS systems, MBSPS-800). Solvents were degassed by purging with N$_2$ for at least half an hour. All reactions involving air-sensitive reagents were performed under a N$_2$ atmosphere. Flash column chromatography was performed using silica gel (SiO$_2$) purchased from Merck (type 9385, 230-400 mesh) or on a Büchi Reveleris purification system with Büchi cartridges. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica 60 F253 obtained from Merck. Compounds were visualized with a UV lamp (254 nm) or by staining with CAM. Melting points (m.p.) were determined using a Büchi-B545 capillary melting point apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury-Plus 400 MHz or a Varian Inova 500 MHz spectrometer at 298K unless indicated otherwise. Chemical shifts are quoted in parts per million (ppm) relative to the residual solvent signal (for CDCl$_3$ $\delta$ 7.26 for $^1$H, $\delta$ 77.16 for $^{13}$C and for CD$_2$Cl$_2$ $\delta$ 5.32 for $^1$H, $\delta$ 53.84 for $^{13}$C). For $^1$H-NMR spectroscopy, the splitting pattern of peaks is designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), or dd (doublet of doublets). High resolution mass spectrometry (ESI or APCI-MS) was performed on a LTQ Orbitrap XL spectrometer. UV/Vis absorption spectra were recorded on a Agilent 8453 or a Specord S600 UV/Vis Spectroscopy System in a 10 mm quartz cuvette. The CD spectra were recorded on a Jasco J-810 spectrometer. The UV/Vis and NMR irradiation experiments were performed with Thorlabs fiber-coupled LEDs.

The Eyring analysis was performed by following the thermal isomerization step from unstable to stable by monitoring the decrease in absorption at 470 nm. The rate constant ($k$) of the first order decay at five temperatures (0, 5, 10, 15 and 20 °C) were obtained by fitting to the equation $Y = Ae^{(k\cdot t)} + Y_0$ using Origin Software. The obtained rates were used to perform a least-squares analysis with the Eyring equation $k = k_BT/h \cdot e^{(\Delta\Delta G/RT)}$ using direct weighting ($1/k^2$) to obtain the activation parameters. Subsequently, the
standard errors were obtained from a Monte Carlo error analysis on the linearized Eyring equation using calculated standard errors on rates an estimated standard error on temperature of 0.5 K.

**methyl-3-iodo-2-methylpropanoate (4)**

![](image)

NaI (375 mg, 2.5 mmol) was added to a solution of methyl (R)-3-bromo-2-methylpropanoate (0.25 ml, 2.0 mmol) in acetone (1.5 ml). The mixture was stirred while heated at reflux for 2 h, after which water was added (5 ml). The mixture was extracted three times with Et₂O and the combined organic layers were dried over MgSO₄. The volatiles were carefully removed in vacuo (>500 mbar) and the residue was filtered over a plug of silica (Et₂O) and dried in vacuo to yield 4 (417 mg, 92%) as a red oil. ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 3.38 (dd, J = 9.8, 6.6 Hz, 1H), 3.26 (dd, J = 9.8, 6.2 Hz, 1H), 2.80 (h, J = 6.8 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H). Spectroscopic data are in agreement with those reported in the literature.[46]

**methyl-3-(1,2,3,6,7,8-hexahydropyren-4-yl)-2-methylpropanoate (7)**

![](image)

A solution of iodide 4 (240 mg, 1.05 mmol) in dry toluene/DMA (15:1, 4.3 ml) was added to Zn-Cu couple (126 mg) under a N₂ atmosphere. The mixture was stirred at 60 °C for 4 h after which it was cooled to rt. Then, 4-bromo-1,2,3,6,7,8-hexahydropyrene (271 mg, 0.945 mmol), Pd₂dba₃ (11 mg, 0.012 mmol) and QPhos (17 mg, 0.024 mmol) were added and the mixture was stirred overnight at rt. The suspension was filtered over celite (washed with CH₂Cl₂) and the volatiles were removed in vacuo. The residue was purified by column chromatography (SiO₂, pentane/EtOAc 30:1) to yield 7 (208 mg, 71%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 7.1 Hz, 1H), 7.13 (d, J = 7.1 Hz, 1H), 7.06 (s, 1H), 3.70 (s, 3H), 3.29 – 3.18 (m, 1H), 3.15 – 3.02 (m, 8H), 2.91 – 2.79 (m, 2H), 2.13 – 2.03 (m, 4H), 1.23 (d, J = 6.3 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 176.9, 134.0, 134.0, 133.7, 132.2, 131.3, 130.4, 129.1, 126.4, 123.7, 123.0, 121.6, 40.5, 36.9, 31.5, 31.5, 31.4, 27.7, 23.3, 23.1, 16.8. HRMS (ESI+, m/z): Calcd for C₂₃H₂₃O₂⁺: 309.18491 [M+H]⁺, found 309.18478.

**3-(1,2,3,6,7,8-hexahydropyren-4-yl)-2-methylpropanoic acid (8)**
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Methyl ester 7 (364 mg, 1.18 mmol) was dissolved in a mixture of 25 ml THF and 25 ml aqueous 0.1M NaOH. The solution was stirred overnight at rt. and acidified with 2M aq. HCl. The mixture was extracted with CH$_2$Cl$_2$ and the combined organic layers were dried over MgSO$_4$. The volatiles were removed in vacuo to yield 8 (340 mg, 97%) as a colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.14 (d, $J = 7.1$ Hz, 1H), 7.11 (d, $J = 7.1$ Hz, 1H), 7.05 (s, 1H), 3.33 – 3.20 (m, 1H), 3.07 (q, $J = 5.4$ Hz, 8H), 2.94 – 2.75 (m, 2H), 2.12 – 2.00 (m, 4H), 1.22 (d, $J = 6.5$ Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 182.9, 134.2, 134.2, 133.9, 132.0, 131.5, 130.5, 129.3, 126.5, 123.9, 123.2, 40.6, 36.6, 31.6, 31.5, 27.8, 23.4, 23.2, 16.6. HRMS (ESI+, m/z): C$_{20}$H$_{22}$O$_2^+$: 295.16926 [M+H]$^+$, found 295.16913.

10-methyl-1,2,3,6,7,8,10,11-octahydro-9H-cyclopenta[e]pyren-9-one (9)

Acid 8 (340 mg, 1.15 mmol) was dissolved in dry CH$_2$Cl$_2$ (25 ml) under N$_2$ atmosphere. Thionyl chloride (0.20 ml, 2.74 mmol) was added and the mixture was stirred at reflux for 4h. The volatiles were removed in vacuo and the residue was redissolved in dry CH$_2$Cl$_2$ (25 ml) under N$_2$ atmosphere. AlCl$_3$ (231 mg, 1.73 mmol) was added in portions at 0 °C and the mixture was stirred at reflux for 3h. The mixture was allowed to cool to rt overnight after which water was carefully added. The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with water and dried over MgSO$_4$. The volatiles were removed in vacuo and the residue was purified using column chromatography (SiO$_2$, pentane/EtOAc 20:1) to yield 9 (200 mg, 63%) as a colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.23 (d, $J = 7.0$ Hz, 1H), 7.11 (d, $J = 7.0$ Hz, 1H), 3.62 (t, $J = 6.3$ Hz, 2H), 3.39 (dd, $J = 16.7, 8.4$ Hz, 1H), 3.07 (t, $J = 6.2$ Hz, 4H), 3.03 – 2.95 (m, 2H), 2.83 – 2.71 (m, 1H), 2.67 (dd, $J = 16.7, 4.9$ Hz, 1H), 2.14 – 1.99 (m, 4H), 1.36 (d, $J = 7.3$ Hz, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 211.6, 142.6, 137.4, 137.2, 133.7, 133.0, 129.6, 129.5, 128.1, 126.4, 123.5, 43.0, 32.9, 31.2, 31.2, 27.0, 26.6, 22.9, 22.6, 16.9. HRMS (ESI+, m/z): Calcd for C$_{20}$H$_{12}$O$: 277.15869 [M+H]$^+$, found 277.15903.

10-methyl-10,11-dihydro-9H-cyclopenta[e]pyren-9-one (10)
Ketone 9 (280 mg, 1.01 mmol) was dissolved in dry toluene (50 ml) under N\textsubscript{2} atmosphere and DDQ (722 mg, 3.18 mmol) was added. The mixture heat at reflux for 2h and then allowed to cool to rt. The suspension was filtered over celite (washed with CH\textsubscript{2}Cl\textsubscript{2}) and the volatiles were removed \textit{in vacuo}. The residue was purified by column chromatography (SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}) to yield 10 (225 mg, 82\%) as a yellow oil. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 9.50\) (d, \(J = 7.7\) Hz, 1H), \(8.37 - 8.31\) (m, 2H), \(8.22\) (d, \(J = 7.5\) Hz, 1H), \(8.14 - 8.03\) (m, 4H), \(3.86\) (dd, \(J = 17.6, 7.3\) Hz, 1H), \(3.16\) (dd, \(J = 17.6, 3.1\) Hz, 1H), \(3.02\) (pd, \(J = 7.4, 3.0\) Hz, 1H, 1.51 (d, \(J = 7.5\) Hz, 3H). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 212.8, 160.3, 134.0, 133.4, 132.1, 131.0, 130.7, 130.5, 129.6, 129.2, 128.8, 128.7, 128.4, 128.4, 126.8, 125.0, 124.7, 124.7, 44.5, 36.0, 19.5). HRMS (ESI\textsuperscript{+}, \(m/z\)): Calcd for C\textsubscript{20}H\textsubscript{15}O\textsuperscript{+}: 271.11174 [M+H]\textsuperscript{+}, found 271.11092.


Ketone 10 (196 mg, 0.725 mmol) and Lawesson reagent (441 mg, 1.09 mmol) were dissolved in dry toluene (5 ml) under N\textsubscript{2} atmosphere. The resulting suspension was heated to 95 °C and the conversion was followed by TLC. After 2.5h the mixture was allowed to cool to rt. and directly purified using column chromatography (SiO\textsubscript{2}, pentane/CH\textsubscript{2}Cl\textsubscript{2} 4:1 – 2:1) to yield the corresponding thioketone (161 mg, 78\%), which was used directly in the following reaction.

Thioketone 11 (160 mg, 0.559 mmol) and diazo 12 (294 mg, 0.839 mmol) were dissolved in dry toluene under a N\textsubscript{2} atmosphere. The mixture was stirred 16h at rt and subsequently 24h at 70 °C after which full conversion of the thioketone was observed by TLC. HMPT (0.17 ml, 0.923 mmol) was added and the mixture was stirred for 4h at 70 °C, after which water was added and the layers were separated. The aqueous layer was extracted twice with CH\textsubscript{2}Cl\textsubscript{2} and the combined organic layers were washed with brine and dried over MgSO\textsubscript{4}. The volatiles were removed \textit{in vacuo} and the resulting solid was washed with EtOAc. The crude product was used in the following reaction without further purification.
Compound 13 (50 mg, 0.087 mmol) and Pd[P(tBu)₃]₂ (4.4 mg, 0.0087 mmol) were loaded in a dry Schlenk flask under N₂ atmosphere. Dry toluene (4 ml) was added and the mixture was purged with O₂ and stirred overnight. In a separate dry Schlenk flask, n-hexyllithium (2.2M, 0.5 ml) was diluted with toluene (4.5 ml) to reach a final concentration of 0.22M. The diluted n-hexyllithium (0.8 ml) was added over 1 h via a syringe pump to the mixture of compound 13 and catalyst at rt and stirred for an additional 30 min. The reaction mixture was treated with MeOH (0.1 ml) and the volatiles were removed in vacuo. The residue was purified by column chromatography to yield 2 (33 mg, 65%) as a dark yellow solid.

1H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 7.7 Hz, 2H), 8.21 (d, J = 7.9 Hz, 1H), 8.18 – 8.07 (m, 4H), 7.88 (s, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.22 (dd, J = 7.8, 1.3 Hz, 1H), 6.96 (dd, J = 7.6, 1.5 Hz, 1H), 6.39 (s, 1H), 4.57 (p, J = 6.5 Hz, 1H), 3.87 (dd, J = 15.2, 5.6 Hz, 1H), 3.31 (d, J = 15.2 Hz, 1H), 2.79 (t, J = 7.6 Hz, 2H), 2.04 – 1.86 (m, 2H), 1.77 (p, J = 7.5 Hz, 2H), 1.54 (d, J = 6.6 Hz, 3H), 1.50 – 1.31 (m, 6H), 1.10 (p, J = 6.9 Hz, 2H), 1.05 – 0.68 (m, 12H). 13C NMR (101 MHz, CDCl₃) δ 153.0, 148.8, 143.9, 142.9, 142.7, 140.8, 140.1, 140.0, 138.8, 134.3, 134.1, 133.6, 132.0, 130.8, 130.0, 129.0, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 127.8, 127.6, 127.0, 126.9, 125.0, 121.8, 120.9, 47.6, 43.0, 39.2, 38.4, 34.5, 34.5, 34.2, 33.4, 31.7, 31.5, 25.4, 25.1, 22.3, 16.8, 16.8. HRMS (ESI+; m/z): Calcd for C₄₅H₄₇[+]: 587.36723, found 587.36603.

Quantum yield determination

The photon flux of the Thorlabs M420F2 LED was estimated by measuring the production of ferrous ions from potassium ferrioxalate. An aqueous 0.05 M H₂SO₄ solution containing 12 mM K₃[Fe(C₂O₄)₃] (2 mL, quartz cuvette) was irradiated at 20 °C for 2, 4, 6, 8 and 10 min in the dark at 420 nm at 20 °C. At every time interval, a volume of 10 μL was taken and diluted to 2.0 mL with an aqueous 0.5 M H₂SO₄ solution containing phenanthroline (1 g/L) and NaOAc (122.5 g/L). The absorption at λ = 517 nm was measured and compared to an identically prepared non-irradiated sample. The concentration of [Fe(phenanthrolin)e₃]²⁺ complex was calculated using its molar absorptivity (ε = 11100 M⁻¹ cm⁻¹). This concentration corresponded to the concentration of Fe²⁺ ions that had formed upon irradiation divided by 200. The difference in Fe²⁺ ion concentration was plotted versus time and the following slope, obtained by linear fitting...
to the equation $y = ax + b$ using Origin software, equals the rate of formation at standardized conditions (Figure 2.5). This rate can be converted into a photon flux by taking into account the quantum yield ($\Phi_{420} = 1.12$) of the formation of the Fe$^{2+}$ ion, resulting in a flux of $5.31 \times 10^{-5}$ mmol photons per second.

A sample of motor 2 was irradiated at 420 nm under identical conditions as with the actinometry at a concentration high enough to absorb all incident light ($\text{Abs}_{420} > 2, c = 2.28 \times 10^{-4}$ M in CH$_2$Cl$_2$) at 0 °C. The formation of the unstable state was monitored over time by following the absorbance increase at $\lambda = 475$ nm. The molar absorptivity of the unstable state at $\lambda = 475$ nm ($\varepsilon = 1.56 \times 10^4$ M$^{-1}$ cm$^{-1}$) was used to calculate the concentration increase. The initial concentration increase was plotted versus time (Figure 2.6) and the slope, the rate of formation of the unstable state, was obtained by linear fitting to the equation $y = ax + b$ using Origin software. The photochemical quantum yield ($\Phi_{s\rightarrow u} = 1.4\%$) 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 ($\Phi_{u\rightarrow s} = 0.38\%$) at $\lambda = 420$ nm can then be calculated using equation 1, in which $[\text{stable}]/[\text{unstable}]$ is the ratio of both states at PSS$_{420}$.
\[
\frac{[\text{stable}]}{[\text{unstable}]} = \frac{\Phi_{(M \rightarrow s)} \varepsilon_u}{\Phi_{(s \rightarrow u)} \varepsilon_s}
\] (1)

Figure 2.6. Linear fit of the photochemical formation of unstable 2 over time by irradiation of a sample of motor 2 with \( \lambda_{\text{max}} = 420 \) nm. The slope, obtained from the linear fit corresponds to the rate of formation of the unstable state \( (3.84 \times 10^{-7} \text{ M s}^{-1} \) or \( 7.71 \times 10^{-7} \text{ mmol s}^{-1} \)).

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