Tuning the Ground and Excited State Dynamics of Hemithioindigo Molecular Motors by Changing Substituents

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Figure S1. Molecular structures of all four intermediates of HTI motors 1 – 3 with complete stereo assignment. Each isomer exists as pair of enantiomers, which were not separated for time resolved measurements.
2 Experimental setup and conditions for transient absorption

2.1 Transient absorption setup

For the transient absorption (TA) measurements of the molecular dynamics a multiscale, broadband setup was used. The setup is based on a 1 kHz Ti:sapphire amplifier system (CPA2001, Clark MXR). The pulses centered at 778 nm are frequency converted in non-collinear optical parametric amplifier (NOPA) to 840 nm.\(^1\) The NOPA pulses are overcompressed in a SF10 prism compressor and subsequently frequency doubled to 420 nm with a 140 µm thick BBO crystal (Type I, 30°). The pulse length was measured by autocorrelation with the TPA depletion method to 35 fs.\(^2\) The compressor was set for the shortest pulses at the sample. The pump was delayed by mechanical delay line to maximum delay of 2 ns. The pump pulse is focused into the sample to a 100 µm FWHM spot. The pulse energy varied between 200 and 500 nJ.

A part of the 778 nm beam is split off and focused into a circularly moved 5 mm CaF\(_2\) plate resulting in a supercontinuum pulse ranging from 285 to 720 nm.\(^3\) This pulse probes the sample and is focused to a 35 µm FWHM spot. A part of the probe pulse is split off before the sample with a reflective neutral density filter (reflective metallic FRQ-ND10; Newport Corp.) at 45° serving as a broadband beam splitter. Both sample and reference pulse are dispersed in a prism spectrograph and recorded by a double CCD-frame camera system (S7030-0906; Hamamatsu Inc.; electronics by Entwicklungsbüro Stresing) with single-shot spectral referencing for high sensitivity.\(^4,5\) A broadband wire-grid polarizer (UBB01A; LOT-QuantumDesign/MOXTEK) is used in the sample arm to suppress stray light from the pump pulse.

For longer delay times than 2 ns the Ti:sapphire system is electronically synchronized with a wavelength tunable ns light source at 1 kHz (NT242 SHG/SFG; EKSPLA uab).\(^6\) Using the ns pulse to pump the sample, delay times up to 700 µs can be achieved with an instrumental response function of 2.5 ns. The timing jitter is less than <200 ps. The ns pulses of 420 nm are focused to a 150 µm FWHM spot with a pulse energy of 1 µJ. To extend the delay times to the ms-range the ns light source was chopped down to a repetition rate of 50 Hz. After excitation the irradiated volume is probed multiple times.\(^7\) In this way delay times up to 18.7 ms can be achieved.
2.2 Experimental conditions

For the measurements racemic mixtures of the pure A-isomer or the pure C-isomer were used (see Fig. S1). The thermal interconversion between A and C encounters a very high energy barrier, which makes them stable for years at ambient temperature.\(^8\), \(^9\) Sample preparation and TA measurements were performed under red LED light to exclude room light induced A/C isomerization. The sample concentration was adjusted to ascertain that the optical density of the solution does not exceed OD = 0.3 throughout the probed spectral region. An optical path length of 100 µm was used. The sample was inserted into a flow circuit with a 100 µm flow cell of our own design.\(^3\) No degradation of the samples has been observed during the measurements. The flow speed is chosen for complete sample exchange within 1 ms (for ms-measurements the flow speed is reduced accordingly). At delay times longer than 100 µs the flow out is visible as decrease in the TA signal and is corrected numerically.

2.3 Data evaluation

The recorded raw transient absorption data was first chirp corrected and wavelength calibrated according to ref. [3]. Multiple scans were averaged if possible and a stray light correction was performed. To unravel the dynamics/kinetics, measured data were usually fitted with a sum of exponential functions or damped periodic functions (for oscillations) convoluted with the instrumental response function. The global analysis\(^10\) then gives the decay associated difference spectra (DADS) associated with a certain time constant/process. It should be noted that if very similar time constants are additionally associated with spectral dynamics the matrix components for the global analysis are no longer well separable. For example motor 2 and 3 show very fast kinetics with two components. This leads to a correlation of the time constants and the DADS amplitudes, therefore the latter can only be considered on a semiquantitative basis.

For further information a spectral analysis at selected delay times was used. This is described in ref. [11] In brief, adding the ground state bleach (GSB) spectra to the transient spectra at delay times with ideally only one photoproduct present, results in the product spectra and the products current concentration can be determined. Comparing the product concentration to the concentration of the initially excited molecules also gives the quantum yields for the species.
3 Transient absorption measurements

3.1 Motor A-2 - fs/ps dynamics

The transient absorption measurement of motor A-2 (see Fig. S2) shows a very fast decay of the excited state absorption (ESA) and an initial spectral change in the ESA that has not been observed in the photoisomerization of motor 1 (compare ref. [10]). Two main ESA bands are visible at 300 nm and around 470 nm. They are separated by the GSB at 350 nm. It can be seen right away that the decay of the ESA and the GSB is quite fast. Additionally, a significant change in the ESA spectrum is observed directly after the excitation. At 600-650 nm an initially negative signal is observed which is most likely associated with stimulated emission (SE) of the excited state. The spectral change in the ESA spectrum happens on the 100 fs timescale, which is easily visible between 450-650 nm. Within the same time the signal of the SE vanishes. These initial changes in the ESA spectrum are too drastic to be traced back to solvation or vibrational cooling effects alone. In these cases usually only a wavelength shift and a narrowing of the ESA band is expected.

Figure S2. Transient absorption measurement on the fs/ps timescale after 420 nm excitation of pure A-2 in CH₂Cl₂ at 22 °C. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
From theoretical calculations of motor 1 (ref. [7]) it is known that in the $S_1$ minimum the motor has already rotated almost 90° around the double bond from the starting conformation. This significant geometrical change is expected to result in significant changes in the ESA spectrum as well as in a shift or reduction of the SE. Therefore, the observed initial dynamics within 120 fs are assigned to a relaxation on the potential energy landscape from the Franck-Condon region to the $S_1$ minimum. This process explains the change in the ESA spectrum and the vanishing of the SE, although the latter could also be masked by overlapping ESA. Solvation effects are most likely of minor importance, as solvation in CH$_2$Cl$_2$ proceeds in 0.38 ps,\textsuperscript{[7]} i.e. much slower than the observed changes.

The subsequent decay of the ESA has a time constant of 330 fs, which is exceptionally fast for HTI-based photo switches. A series of two conical intersection to the ground state is the main deexcitation channel for motor 1, as it was shown by theoretical calculations. It is reasonable to expect a similar mechanism for motor 2. The very fast decay of the ESA of 2 suggests an almost barrier free and directly accessible conical intersection from the $S_1$ minimum to the $S_2$ state. The second conical intersection is also predicted to be barrierless.

After the fast decay of the excited state the thermal relaxation in the ground state can be readily observed with a typical time constant of 8 ps (see Fig. S3). Characteristic for this process is an apparent GSB recovery alongside a decaying absorption, which appears slightly red shifted to the GSB spectral features.

The remaining transient signals at later delay times are comprised of the triplet state of A-2* and of the photoproduct B-2. The combined quantum yield is $\phi = 15 \pm 3\%$. The triplet can be identified by an absorption tail of the product spectrum reaching up to 600 nm. For all ground state intermediates of HTI based motors an absorption above 500 nm is not expected and therefore this absorption features can be safely assigned to a triplet state. From the mixed spectrum alone the ratio of $^3A$-2* and B-2 cannot be determined. However, this can be done from the ns/µs timescale measurements (see below), which determined a ratio of $^3A$-2* : B-2 of 40 : 60. The individual quantum yields are thus $\phi_{A/B} = 9 \pm 2\%$ and $\phi_{A/A} = 6 \pm 2\%$. In addition to the pure B-2 absorption spectrum obtained from the measurement on the ns/µs timescale the combined product spectrum can be decomposed to get the triplet $^3A$-2* absorption spectrum (Fig. S4).
Figure S3. DADS from a global fit of the transient absorption data recorded at early times after photoexcitation of A-2. Note that the time constants of the two fast decaying components are very similar and the amplitudes start to correlate. The amplitudes can therefore not be evaluated in a quantitative way and are scaled to be more comparable to the actual signal strength. (b) Fitted kinetic traces at selected wavelengths. The rapid oscillations are due to a vibrational wavepacket induced in the solvent.

Figure S4. (a) Spectral decomposition at 200 fs delay time after photoexcitation of A-2. (b) Spectral reconstruction at 1000 ps delay time. The resulting product spectrum was further broken down by the ration of B-2 to the triplet $^3$A-2, which was obtained on the ns/μs timescale.
3.2 Motor A-2 - ns/μs dynamics

For motor 1 the lifetimes of the triplet $^3$A-1* (100 ns) and the intermediate B-1 (3 ns) were rather similar and therefore led to significant spectral overlap of these two species in the transient measurements. For motor 2 the steric hindrance is increased compared to motor 1 and theoretical calculations predict a higher barrier for the thermal helix inversion of B-2 leading to a lifetime of this metastable state of about 750 ns at 22 °C. This lifetime is significantly longer than the expected triplet decay in fully aerated solution and should allow for a clear spectral discrimination between the triplet $^3$A-2* decay and decay of the B-2 intermediate. In the transient absorption measurement of A-2 on the ns/μs timescale (Fig. S6) a decay of the band around 500 nm is observed with a time constant of 25 ns accompanied by a 40% GSB recovery. It should be noted that the absorption signal (B-2 absorption) at 300 nm stays constant during this process (see Fig. S6). Therefore this decay can be assigned to the $^3$A-2* triplet deexcitation.

Figure S5. Transient absorption measurement on the ns/μs timescale after 420 nm excitation of pure A-2 in CH$_2$Cl$_2$ at 22 °C. Signal decay after 100 μs is caused by the flow out. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
For the thermal helix inversion of $\text{B-2}$ to $\text{C-2}$ a time constant of 990 ns is found. The spectral reconstruction at 100 ns gives the absorption spectrum of pure $\text{B-2}$ (Fig. S8). The comparison of the GSB at 100 ns and 10 µs shows that the GSB stays constant during this conversion. The spectrum of the photoprocess observed at 10 µs is identical with the $\text{C-2}$ spectrum. Therefore it can be deduced that a quantitative thermal helix inversion from $\text{B-2}$ to $\text{C-2}$ occurs at 22 °C. Since the $\text{C-2}$ isomer is also thermally stable, the DADS component in Fig. 6a describing the flow-out is considered the infinity component of the global analysis.

An alternative pathway to the species spectra of the intermediate $\text{B-2}$ and the photoprocess $\text{C-2}$ in this measurement is the decomposition of the DADS (Fig. S9). The DADS curve with the time constant 990 ns is the difference of the $\text{B-2}$ and $\text{C-2}$ spectra. The DADS curve with the infinite time constant is the difference between the $\text{C-2}$ spectrum (product) and the $\text{A-2}$ spectrum (GSB). The concentration of the GSB is known from the spectral analysis and can be used to scale the known $\text{A-2}$ and $\text{C-2}$ spectra. The result is the spectrum of $\text{B-2}$, which is more reliable than the one from the reconstruction (no negative values). It also shows that the infinite DADS component is perfectly reproduced, which is a second confirmation that during the helix inversion from $\text{B-2}$ to $\text{C-2}$ no GSB recovery takes place.

Figure S6. (a) DADS received from a global fit of the transient absorption data recorded at later times after photoexcitation of $\text{A-2}$. (b) Fitted kinetic traces at selected wavelengths. The flow-out of the motor solution was fitted with an additional Gaussian function with a 400 µs half width at 1/e². The DADS for the latter is considered the infinity component in (a) due to the thermal stability of the resulting $\text{C-2}$ isomer.
Figure S7. (a) Spectral reconstruction at 5 ns delay time after photoexcitation of A-2. The product spectrum was further subtracted from the B-2/3A-2* mix spectrum received at later delay times leading to the 3A-2* triplet spectrum.

Figure S8. (a) Spectral reconstruction at 100 ns delay time after photoexcitation of A-2. At this delay time the triplet has completely decayed and the product spectrum exclusively represents the intermediate state B-2 absorption. (b) Spectral reconstruction at 10 μs delay time after photoexcitation of A-2. The resulting spectrum is identical with the known C-2 spectrum (scaled by the GSB concentration).
Figure S9.  (a) DADS decomposition of the 990 ns component. This component is the difference spectrum between the B-2 and C-2 spectrum representing the quantitative thermal helix inversion from B-2 to C-2. (b) DADS decomposition of the infinite (∞) component of the global fit. This component represents the difference spectrum between A-2 and C-2. Overall the decompositions show that excitation of A-2 leads to B-2, which converts thermally completely to C-2.
3.3 Motor C-2 - fs/ps dynamics

The ultrafast dynamics of C-2 (Fig. S10) after excitation with 420 nm light are similar to the dynamics observed for A-2. A fast initial change in the ESA spectrum is observed (82 fs) followed by a rapid decay with 370 fs (see Fig. S11). The thermal relaxation in the ground state proceeds with 5.2 ps. There is very little or no sign of a triplet signal in this measurement. For this reason, the spectrum of the photoproduct can directly be obtained by spectral analysis (Fig. S12) and be assigned to D-2. The quantum yield for the C-2 to D-2 photoisomerization is $\phi_{CD} = 15 \pm 3\%$.

![Transient absorption measurement](image)

**Figure S10.** Transient absorption measurement on the fs/ps timescale after 420 nm excitation of pure C-2 in CH$_2$Cl$_2$ at 22 °C. The rapid oscillations are due to a vibrational wavepacket induced in the solvent. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
Figure S11. (a) DADS received from a global fit of the transient absorption data recorded at early times after photoexcitation of C-2. Note that the time constants of the two fast components are very similar and the amplitudes start to correlate. The amplitudes can therefore not be evaluated in a fully quantitative way and are scaled to be more comparable to the actual signal strength. (b) Fitted kinetic traces at selected wavelengths. The rapid oscillations are due to a vibrational wavepacket induced in the solvent.

Figure S12. (a) Spectral reconstruction at 200 fs delay time after photoexcitation of C-2. (b) Spectral reconstruction at 100 ps delay time after photoexcitation of C-2 resulting in the D-2 spectrum.
3.4 Motor C-2 - ns/µs dynamics

The calculated time constant of the D-2/A-2 helix inversion is about 6.2 ms at ambient temperature and therefore out of the measurement range of the basic transient absorption setup. Accordingly on the ns/µs timescale no dynamics are observed (Fig. S13). The spectrum of pure D-2 can be obtained from the transient measurement at longer delay times (Fig. S14). It is slightly different from the one observed in the fs/ps timescale measurements but is considered to be more reliable for two reasons: On the one hand there is a very small signal at 500 nm that could hint at a low yield $^3$C-2* triplet state formation. This signal decays within 100 ns and contributes to the product spectrum of the ps measurements. Secondly the signal to noise ratio in the ns/µs measurement is better due to overall higher signal intensities.

Figure S13. Transient absorption measurement on the ns/µs timescale after 420 nm excitation of pure C-2 in CH$_2$Cl$_2$ at 22 °C. Signal decay after 100 µs is caused by the flow out. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
Figure S14. Spectral reconstruction at 200 ns delay time after photoexcitation of C-2 giving the D-2 spectrum.
3.5 Motor A-3 - fs/ps dynamics

The ultrafast dynamics of A-3 (see Fig. S15) are very much analogous to the behavior of A-2. The relaxation to the $S_1$ minimum happens within 140 fs with a subsequent fast decay to the ground state of 470 fs (Fig. S16). The thermal relaxation in the ground state has a time constant of 5.7 ps. After all dynamics are finished 13% of the initially excited molecules are still visible as GSB (see Fig. S17). The ratio between the triplet state $^3A-3^*$ and B-3 is almost 50:50 slightly in favor of B-3. The corresponding quantum yields are $\phi_{A,B} = 7 \pm 3\%$ and $\phi_{A/A} = 6 \pm 3\%$.

![Figure S15](image-url)

**Figure S15.** Transient absorption measurement on the fs/ps timescale after 420 nm excitation of pure A-3 in CH$_2$Cl$_2$ at 22 °C. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
Figure S16. (a) DADS obtained from a global fit of the transient absorption data recorded at early times after photoexcitation of A-3. Note that the time constants of the two fast decaying components are very similar and the amplitudes start to correlate. The amplitudes can therefore not be evaluated in a fully quantitative way and are scaled to be more comparable to the actual signal strength. (b) Fitted kinetic traces at selected wavelengths. The rapid oscillations are due to a vibrational wavepacket induced in the solvent.

Figure S17. (a) Spectral decomposition at 100 fs delay time after photoexcitation of A-3. (b) Spectral reconstruction at 1000 ps delay time. The resulting product spectrum was further broken down by the ratio of B-3 to the triplet ³A-3*, which was obtained from the measurement on the ns/µs timescale.
3.6 Motor A-3 - ns/µs dynamics

The behavior of A-3 on the ns/µs timescale is again analogous to A-2 (Fig. S18). The main difference is the even slower thermal helix inversion from B-3 to C-3 with a time constant of 125 µs (Fig. S19). This is on the edge where already some of the excited volume has flowed out of the probe area. The flow out was compensated by including it into the fit using a Gaussian function with a half width at 1/e² of 400 µs. With this information it can be calculated how many molecules have already flowed out during the measurement. The product spectrum at 150 µs matches the C-3 spectrum well. The scaled GSB is close to the concentration at 1 µs (see Fig. S21). The triplet state \(^3A\)-3\(^*\) decays back to the ground state A-3 with 20 ns. 50% auf the GSB are recovered in this process (Fig. S20-21). In the time window from 0.1 µs to 10 µs no dynamics take place. In this time window the absorption spectrum of pure B-3 can be extracted.

![Image of transient absorption measurement on the ns/µs timescale after 420 nm excitation of pure A-3 in CH₂Cl₂ at 22 °C. Signal decay after 100 µs is caused by the flow out. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.](image)

**Figure S18.** Transient absorption measurement on the ns/µs timescale after 420 nm excitation of pure A-3 in CH₂Cl₂ at 22 °C. Signal decay after 100 µs is caused by the flow out. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.
Figure S19. (a) DADS received from a global fit of the transient absorption data recorded at later times after photoexcitation of A-3. (b) Fitted kinetic traces at selected wavelengths.

Figure S20. Spectral reconstruction at 3 ns delay time. The product spectrum was further subtracted from the B-3/3A-3* mixture spectrum received at later delay times leading to the 3A-3* triplet spectrum.
Figure S21. (a) Spectral reconstruction at 1 µs delay time after photoexcitation of A-3. At this delay time the triplet state $^3A-3^*$ has completely decayed and the product spectrum represents exclusively absorption of the intermediate B-3 state. (b) Spectral reconstruction at 150 µs delay time. The resulting spectrum is very similar to the known C-3 spectrum (scaled according to the GSB concentration). Due to the flow out of excited molecules during the measurement with a half width at 1/e$^2$ of 400 µs, the GSB has to be scaled by a factor of 1.15 to be comparable to (a). This proves the completeness of the helix inversion from B-3 exclusively to C-3.
3.7 Motor C-3 - fs/ps dynamics

The dynamics of the C-3 to D-3 photoisomerization are similar to the ones observed after excitation of C-2 (Fig. S22). However, the decay of the ESA is even faster in this case and with 270 fs the fastest one observed in this study (Fig. S23). From the spectral reconstruction (Fig. S24) the quantum yield for the photoisomerization is found to be \( \phi_{C/D} = 9 \pm 3\% \).

![Figure S22. Transient absorption measurement on the fs/ps timescale after 420 nm excitation of pure C-3 in CH\(_2\)Cl\(_2\) at 22 °C. The rapid oscillations are due to a vibrational wavepacket induced in the solvent. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.](image-url)
Figure S23. (a) DADS received from a global fit of the transient absorption data recorded at early times after photoexcitation of C-3. Note that the time constants of the two fast components are very similar and the amplitudes start to correlate. The amplitudes can therefore not be evaluated in a quantitative way and are scaled to be more comparable to the actual signal strength. (b) Fitted kinetic traces at selected wavelengths. The rapid oscillations are due to a vibrational wavepacket induced in the solvent.

Figure S24. (a) Spectral reconstruction at 120 fs delay time after photoexcitation of C-3. (b) Spectral reconstruction at 100 ps delay time resulting in the D-3 absorption spectrum, which is compared to the corresponding spectrum obtained from the ns/μs measurement.
### 3.8 Motor C-3 - ns/µs dynamics

For motor 3 the helix inversion is expected to happen with a time constant of 30 ms at ambient temperature. This is too slow for the transient absorption setup used in this work. Consequently no change in the TA signal is observed on the ns/µs timescale (see Fig. S25). From the spectral reconstruction the D-3 spectrum can be obtained (Fig. S26).

**Figure S25.** Transient absorption measurement on the ns/µs timescale after 420 nm excitation of pure C-3 in CH$_2$Cl$_2$ at 22 °C. The colored bars in the 3D plot frame the area that was averaged to obtain the corresponding 1D spectrum or time trace represented in the upper and right graphs.

**Figure S26.** Spectral reconstruction at 3 µs delay time after photoexcitation of C-3 giving the D-3 spectrum.
Comparison of the ultrafast behavior of photoexcited C-1 and C-2

Figure S27. Spectral development of the ESA of C-1 and C-2 after excitation with 460 and 420 nm in CH₂Cl₂ at 22 °C. a) Spectral dynamics of C-1* at early times reveal only subtle spectral changes and the beginning of the excited state decay. b) The ESA spectrum of C-2* is changing rapidly within a few hundred fs and the GSB signal starts to change significantly after about 400 fs. c) Decay of the ESA spectrum of C-1* happens with a time constant of 7.9 ps. d) Decay of the ESA spectrum of C-2* is extraordinarily fast and happens with 370 fs. Subsequent hot ground state relaxation proceeds with a time constant of 5.2 ps.

Note: Wiggles above 600 nm result from the supercontinuum generation (probe pulse) due to phase variations near the fundamental wavelength (778 nm). They are adjustment dependent and vary from day to day - a measurement artifact without any molecular information. The additional wiggles in (d) result from the decaying stimulated Raman signal of CH₂Cl₂ with a frequency of 280 cm⁻¹. They appear in the spectrum because of a non-ideal chirp correction at delays far away from time zero - again an evaluation artifact without relevant information.
5 Quantum yield determination of motor 3 in CH₂Cl₂

For the confirmation of the quantum yields retrieved from the transient absorption measurements an additional method was used on the example of motor 3. This method is based on sample illumination with high power LEDs, a precise measurement of the absorbed photons and a spectroscopic measurement of the photoproduct concentration. For the illuminations an improved version of the quantum yield determination setup from ref. [12, 13] was used. The LED light is collected by a f = 25 mm best form lens and imaged into a 10 mm cuvette with a f = 150 mm lens. The light power is measured with a calibrated power meter (Coherent PowerMax USB - PS19Q). The samples are irradiated stepwise and for every step a spectrum of the sample is recorded with an absorption spectrometer (UV 2600; Shimadzu Corp.). The proper linear combination of the absorption spectra of pure A-3 and C-3 are fitted to the mixed spectrum to retrieve the concentrations at every time step. To the resulting concentration curves in dependence on the illumination time a numerical model is fitted that calculates the number of photons absorbed by either A-3 and C-3 for every wavelength in the LED spectrum at every infinitesimal time step. In the simulation the quantum yields are the only free parameters and optimized to fit the concentration curves. This gives the quantum yields for the A to C and C to A photoisomerizations. Details on this method for quantum yield determination will be given in a forthcoming publication.

Figure S28. (a) Absorption spectra obtained during a stepwise illumination of a sample of A-3 with a LED, whose emission spectrum is centered at 445 nm. (b) Fitted concentration changes occurring during the illumination and resulting quantum yields.
Starting from A-3 the illumination is done with an OSRAM LD-CQ7P-1U3U 455 nm LED. The spectrum is narrowed at 445 nm by a band pass filter (Edmund Optics 455 nm hard coated band pass filter, 10 nm FWHM, tilted to 20 °). The LED was driven by 2.7 V and 0.1 A, which results in an optical power of 3.29 mW at the sample as determined with a reference cell filled with pure CH$_2$Cl$_2$. The absorption spectra obtained during stepwise illumination and the LED emission spectrum are given in Fig. S28 (a). The plotted concentration changes and the corresponding fitted simulation curves are shown in Fig. S28 (b). The resulting quantum yields are $\phi_{A/C} = 9.1 \pm 1\%$ and $\phi_{C/A} = 10.8 \pm 1\%$.

Starting from a mixture containing mainly C-3 the illumination is done with a VIOSYS CUN8GF1A 385 nm LED. The LED was driven by 3.14 V and 0.17 A. To reduce the power a neutral density filter (metallic reflective ND1, Edmund Optics Inc.) with an optical density of about 1 is used, which results in an optical power of 2.13 mW, as determined with a reference cell filled with pure CH$_2$Cl$_2$. The absorption spectra obtained during stepwise illumination and the LED emission spectrum are given in Fig. S29 (a). The plotted concentration changes and the corresponding fitted simulation curve are shown in Fig. S29 (b). The resulting quantum yields are $\phi_{A/C} = 9.2 \pm 1\%$ and $\phi_{C/A} = 10.2 \pm 1\%$.

**Figure S29.** (a) Absorption spectra obtained during a stepwise illumination of a sample containing mainly C-3 with a LED, whose emission spectrum is centered at 385 nm. (b) Fitted concentration changes occurring during illumination and resulting quantum yields.

The (averaged) quantum yields (9 % and 10.5 %) are higher than the ones calculated from the TA data (7% and 9%), but within experimental error. This highlights that quantum yields from TA measurements are reliable.
6 Stationary absorption spectra of motors 1-3

From the time resolved measurements the absorption spectra of the thermally unstable intermediates B and D can be determined. Due to the known concentration of the GSB, the spectra can be converted to the molar absorption coefficients. The spectra of all four motor positions for motor 1-3 are shown in Figs. S30-33. Note that there are certain common features of the intermediates in the different motors. For example the spectra of isomers D are slightly lower in absorption compared to A and they have a wing/plateau in the red edge region similar to A. The B spectra are of similar shape compared to C but are usually blue shifted and slightly lower in the absorption.

Figure S30. Stationary absorption spectra of all four isomers of motor 1.
Figure S31. Stationary absorption spectra of all four isomers of motor 2.

Figure S32. Stationary absorption spectra of all four isomers of motor 3.
7 Calculation of motor rotation frequency under constant illumination

The average rotation frequency of an individual motor can be estimated from the number of photons absorbed by the sample per second and the number of motor molecules. As two photons are needed for a complete rotation, the number of photons has to be divided by 2. In addition, the finite quantum yields ($\phi_{A/B}$ and $\phi_{C/D}$) and the non-unity absorption $Abs$ have to be considered. As a result, the rotation frequency $f$ is determined by:

$$f = \frac{1}{2} \cdot \frac{Abs \cdot N_{ph}}{N_{mol}} \cdot \frac{\phi_{A/B} \cdot \phi_{C/D}}{}$$  \hspace{1cm} (S1)

Here $Abs$ is the overall absorption of the sample considering the concentration of all four states in the PSS:

$$Abs = 1 - 10^{-d \left[ \varepsilon_{A} c_{A} + \varepsilon_{B} c_{B} + \varepsilon_{C} c_{C} + \varepsilon_{D} c_{D} \right]}.$$  \hspace{1cm} (S2)

with $\varepsilon_{X}$ being the absorption coefficient of species X and $c_{X}$ the corresponding concentration. The photon flux $N_{ph}$ is calculated from the irradiation conditions, while the excitation is considered to be monochromatic:

$$N_{ph} = P_{0} \cdot \frac{\lambda}{h \cdot c}.$$  \hspace{1cm} (S3)

where $P_{0}$ is the incoming light power and $\lambda$ is the wavelength of irradiation. The number of molecules $N_{mol}$ is given by the overall concentration $conc$, the volume $V$ of the solution and the Avogadro number $N_{A}$ to give:

$$N_{mol} = conc \cdot N_{A} \cdot V.$$  \hspace{1cm} (S4)

It is assumed that the sample is slowly irradiated and that the exchange of the irradiated fraction with the rest of the solution is fast (excessive stirring).

Typical and realistic irradiation conditions are 100 mW/cm$^2$ light power at 350 nm and 2 mL of a 0.1 mM solution in a 10x10 mm cell. Under these conditions the effective rotation frequencies are 12 mHz for motor 1, 11 mHz for motor 2, and 7 mHz for motor 3 at 22°C. The observed differences mainly result from differences in the quantum yields, the slightly different absorptions only have a small effect. The products of the relevant quantum yields (see Tab. 1 in the main text) show the same order: 0.017 for motor 1, 0.015 for motor 2 and 0.010 for motor 3.
A rate model for the motor system has been presented earlier.\[7\] It was found that for the above illumination parameters, no significant population of the short lived intermediates B and D is found since their thermal decay (helix inversion) is much faster than the possibility of a photon absorption of these species. The maximum rotation speed of the motors can only be achieved at light intensities high enough to keep motor populations in the limiting thermal step. For motor 1 the light intensity necessary exceeds 1000 W/cm\(^2\), which would probably destroy the sample nearly instantaneously. At least it would evaporate the solution due to insufficient sample exchange. Only with very rapid sample flow and active cooling would one be able to go beyond a few W/cm\(^2\).

Note that for the calculation of the rotation speed in eq. S1 the rate constants are not considered. This estimate is therefore only valid as long as the overall rotation frequency is slower than any limiting rate constant \(k_{\text{lim}}\) of a thermal or photochemical step. For motor 1 the limiting rate constant is near 1 kHz – the inverse of the D-1 to A-1 decay time - and the light intensity to reach this it is not practical. For motors with much slower thermal steps the limiting rate(s) have to be considered. This can be done, e.g., by using a step function:

\[
  f = \begin{cases} 
    f & f \leq k_{\text{lim}} \\
    k_{\text{lim}} & f > k_{\text{lim}} 
  \end{cases}
\]

(S5)

or a function that approaches the limiting rate smoother like a sigmoidal function.

Focusing to \(A = 1 \text{ mm}^2\) and neglecting diffusion and stirring, increases \(f\) to 2.2 Hz (motor 1) at 100 mW light power. A value of 1.3 Hz is obtained for motor 3, which is already 1/20 of the maximum rotation rate due to the relatively slow thermal decay of D-3. Thus, it can be observed that if the first limiting step is reached by stronger illumination the speed differences are becoming much more pronounced in the series of motors 1 to 3.
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