

Molecular Motors | Hot Paper |

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

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Abstract: Efficiency and performance of light triggered molecular motors are crucial features that need to be mechanistically understood to improve the performance and enable conscious property tailoring for specific applications. In this work, three different hemithioindigo-based molecular motors are investigated and all four steps in their complete unidirectional rotation are unraveled fully quantitatively. Transient absorption spectroscopy across twelve orders of magnitude in time is used to probe the fs nuclear motions up to the ms thermal kinetics, covering the timeframe of the whole motor rotation. The newly known full mechanisms allow simulation of the motor systems to scrutinize their performance at realistic illumination conditions. This highlights

the importance of photoisomerization quantum yields for the rotation speed. The substitution pattern in close proximity to the rotation axle influences the excited and ground state properties. Reduction of electron donation and concomitant increase of steric hindrance leads to faster photoisomerization reactions with quasi-ballistic behavior, but also to a slight decrease in the quantum efficiency. The expected decelerating effects of increased sterics are primarily manifested in the ground state. A promising approach for next-generation hemithioindigo motors is to elevate electron donation at the rotor fragment followed by an increase of steric hindrance.

Introduction

The ambition to control the motion of inanimate matter at the molecular scale has initiated considerable progress over the past two decades. A major achievement was the advancement of elementary molecular switching units towards molecular motors, which are able to convert light input into unidirectional motion.^[1] Purely light-driven variants take a distinct position

in the field as they allow instant fueling without producing waste and at the same time provide the opportunity for precise spatio-temporal control. These motors are therefore of central importance to the field of molecular machines.^[2] To date, many intriguing functions have been explored with overcrowded stilbene derivatives of the seminal Feringa-type motor systems,^[1a] for example, changing the properties of materials such as liquid crystals,^[3] nanofibers,^[4] and gels,^[5] mechanical opening of cells,^[6] responsive stereocontrol in catalysis,^[7] or regulating molecular folding.^[8]

Only recently have alternative purely light-fueled motor designs become available by using different core chromophore structures, that is, the imine motors introduced by Greb and Lehn^[1i, j] and hemithioindigos (HTI) introduced by our own group.^[9] HTI-based motors allow high rates and completely unidirectional rotation at ambient temperature under non-damaging visible light irradiation, which opens up a great potential for applications in biology and medicine related fields. The first reported type of HTI motors function as four-step motors with alternating photo and thermal steps.^[9a] Owing to their fast motion, not all four intermediate states could be evidenced immediately in the first-generation system. Therefore, slower rotating variants with increased steric hindrance close to the rotating axle were developed as a second-generation system enabling observation of all ground state intermediates populated during motor rotation at low temperatures.^[9b] Subsequently, a combined ultrafast spectroscopy and quantum chemical study provided a comprehensive and quantitative mechanistic picture of the faster first-generation HTI motor at

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ambient temperature.^[9c] By applying a multiscale broadband transient absorption (TA) technique, it was possible to decipher both the ultrafast excited state processes as well as the so far elusive faster ground state transformations. For related time-resolved measurements of the excited state or of fast ground state processes of Feringa-type motors, see references [10] and [11].

When scrutinizing our first HTI motor and reporting quantum yields and kinetic constants for all motional processes, it was found that an unproductive triplet state slightly diminishes the quantum yield for the *Z* to *E* photoisomerization step, but does not disturb the directionality.^[9c] A kinetic model emphasized the importance of increased efficiencies of the photo-induced isomerization steps for the overall rate of HTI motor rotation. To obtain further insight into the unidirectional rotation mechanism and reveal design principles for property tuning of this novel type of molecular machine, we have now quantified the excited state and ground state processes of two differently substituted HTI motors by using TA spectroscopy and present the results in this work. Comparison of their mechanistic features with the first-generation HTI motor delivers many valuable insights into the influence of substitution on the different steps of the rotation cycle with important implications for future improvement of HTI motor performance and assessment.

Owing to the complexity of the motor rotation and its spectral signatures, we have to combine various methods. Slow thermal motions can best be studied with NMR spectroscopy, particularly at low temperature. This is augmented by quantum chemical calculations. The photoinitiated steps can best be studied by TA in an extremely wide range from femtoseconds to milliseconds. This even allows the study of faster thermal steps at ambient temperature. Finally, all observed mechanistic and quantitative information has to be incorporated into a

comprehensive model. After studying each motor variant, the comparison enables the desired new insights into the influence of different substitutions on motor behavior.

Results and Discussion

Ground state energy profile and thermal kinetics

The ground state energy profile has previously been investigated thoroughly for motor derivatives 1–3 (Figure 1).^[9a,b] The unidirectional motion is powered by visible light input triggering two photoisomerization reactions (A to B and C to D). They are separated each by a thermal helix inversion (B to C and D to A). The B to C thermal helix inversion generally encounters a much lower energy barrier compared with the corresponding D to A inversion. Motor 3 enabled a first low-temperature observation of the B to C transition. Increased steric bulk at the aromatic position next to the photoisomerizable double bond was thus found to be a suitable access point for the needed speed decrease. By using ultrafast transient absorption (TA) measurements at ambient temperature, the corresponding B to C helix inversion of the fastest motor 1 could subsequently also be proven experimentally.^[9c]

So far, the thermal B to C conversion of motor 2 was not experimentally observable. Likewise, experimental evidence for the completeness of both helix inversion steps B to C and D to A at ambient temperature was still missing for motors 2 and 3. In this work, we have analyzed the TA measurements on ns– μ s timescales with regard to the fast ground state kinetics, which are now quantified consistently at 22 °C for motors 2 and 3 (see Figure 1, Figure 2b, as well as section 3 in the Supporting Information). Two features are particularly noteworthy in comparison to motor 1 (see Figure 1):

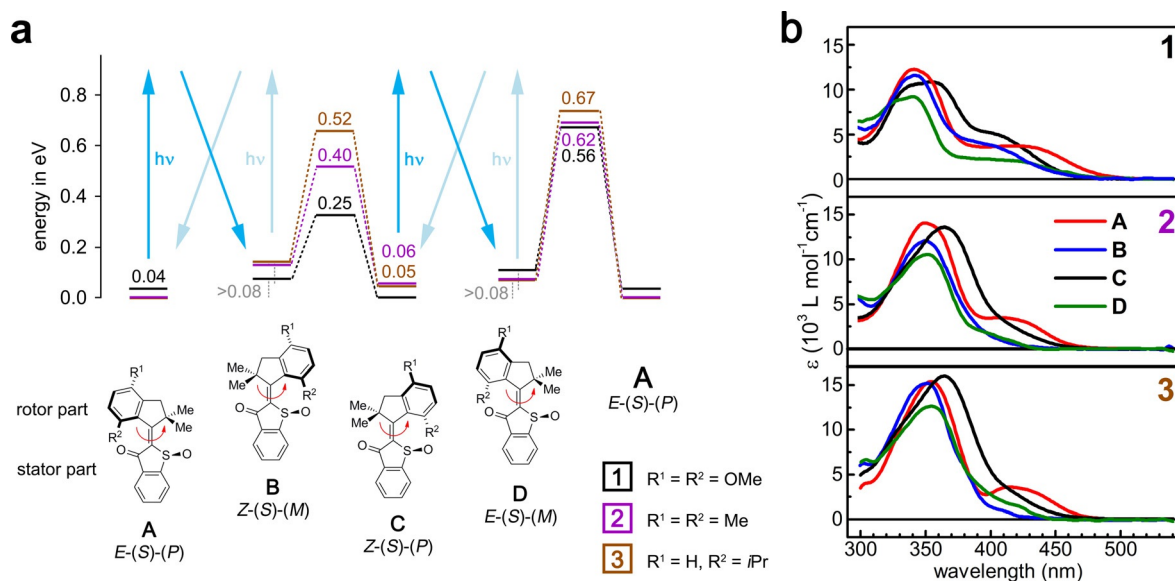


Figure 1. (a) Experimentally determined ground state energy profiles of HTI-based molecular motors 1 (black), 2 (purple), and 3 (brown). Only (S) configured isomers are shown for clarity. (b) Molar absorption spectra of all isomers. Molar absorption spectra of short-lived intermediates B and D were obtained by spectral reconstruction from the TA measurements.

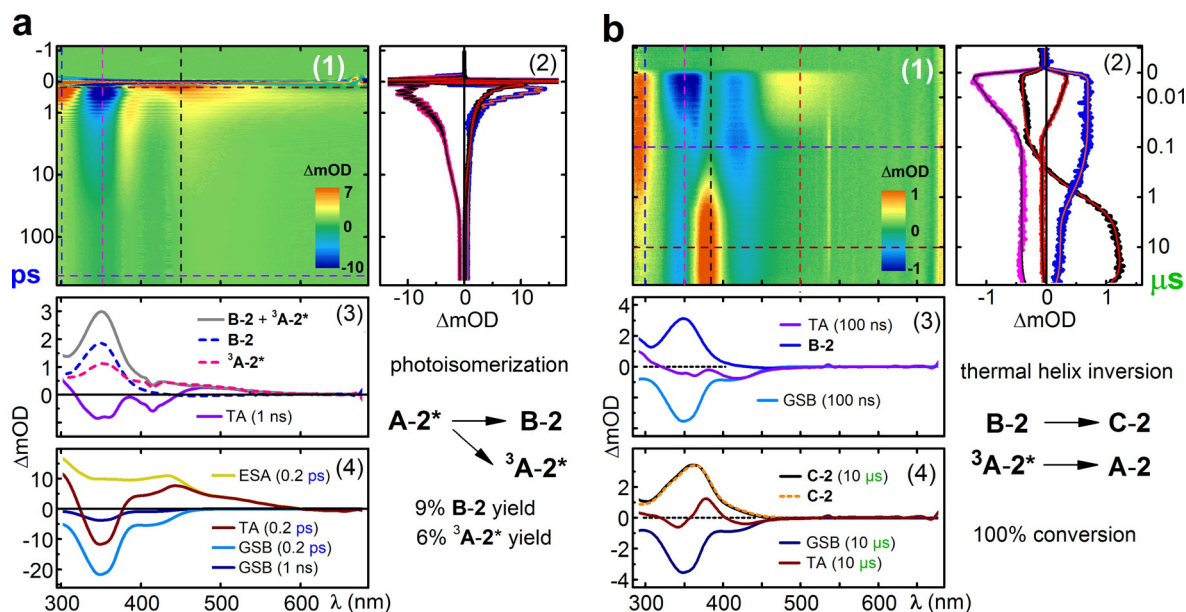


Figure 2. TA spectra after 420 nm excitation of **A-2** in CH_2Cl_2 at 22 °C. (a) (1) TA spectra on the fs/ps timescale. (2) Fits for the kinetics at selected wavelengths indicated (color coded vertical dashed lines) in part (a)–(1). (3) Reconstruction of the absorption spectrum of species **B-2** and $^3\text{A-2}^*$ from the sum spectrum obtained at 1 ns (bottom horizontal dashed line in (a)–(1)). (4) Comparison of the GSB bleach at 0.2 ps (top horizontal dashed line in (a)–(1)) and 1 ns (bottom horizontal dashed line in (a)–(1)) to determine the isomerization quantum yield. (b) (1) TA spectra on the ns/ μs timescale. (2) Fitted kinetic data of the **B-2** and $^3\text{A-2}^*$ decay. (3) Reconstruction of the **B-2** spectrum from the TA at 100 ns (top horizontal dashed line in (b)–(1)). (4) Reconstruction of the product spectrum (compared with **C-2**) at 10 μs delay (bottom horizontal dashed line in (b)–(1)).

1. Increased steric hindrance in the vicinity to the photoisomerizable double bond leads to a significant increase of the thermal **B** to **C** barriers whereas the barrier for the corresponding **D** to **A** conversion is affected much less.
2. Increasing the steric hindrance slightly from a methoxy group to a methyl group already results in a reversed stability of isomers **A** and **C**. In motor **1**, isomer **C** is thermodynamically the most stable one whereas in **2** and **3** isomer **A** is the most stable.

Both observations provide evidence for a significantly greater steric influence of the substituent in the *Z* isomers compared with the *E* isomers.

Transient absorption measurements

To probe the ultrafast excited state dynamics as well as consecutive thermal processes in the ground state, TA spectroscopy on the fs to ms timescale^[12] was used. All measurements were performed in CH_2Cl_2 solution at 22 °C with 35 fs pump pulses at about 420 nm. The data evaluation was done by kinetic analysis using multi-exponential fitting in a selected wavelength range or globally^[12b,13] and a thorough spectral analysis. For details and a discussion of the setup, experimental conditions, and the evaluation procedures refer to the Supporting Information section 2 or reference [9c]. The thermal **D** to **A** conversion of motors **2** and **3** proceeds on longer timescales, exceeding the limits of the TA measurements. Therefore, these reactions have been investigated by low-temperature ^1H NMR spectroscopy.^[9b] The previous time-resolved spectroscopic in-

vestigation of motor **1**^[9c] is included in the present discussion for comparison.

The TA measurements of motors **2** and **3** reveal strong similarities to the behavior of the methoxy-bearing motor **1**. In the following, motor **2** is discussed in more detail. After excitation of pure isomer **A-2**, a fast change of the ESA spectrum within 120 fs is assigned to structural relaxation. The main spectral decay with a time constant of 330 fs is assigned to the **A-2** to **B-2** photoisomerization reaction and return to the ground state. Slower subsequent absorption changes with a time constant of 8 ps can be attributed to thermal cooling in the ground state. As previously observed for motor **1**, the spectral analysis reveals the remaining spectrum to be the sum of the spectrum of intermediate **B-2** as well as a second redshifted spectrum (see Figure 2a, part (3)). Disentanglement of the two spectra was possible because of their significantly different decay dynamics (see below and section 3.2 in the Supporting Information). Assessment of the excited state of motor **1** at the CASSCF level of theory strongly supports the assignment of a similarly redshifted absorption to a triplet state $^3\text{A-1}^*$ populated after intersystem crossing near the Frank–Condon region.^[9c] As the absorption features and decay kinetics of the long-lived redshifted absorption of photoexcited **A-2*** show very high similarity to the ones of $^3\text{A-1}^*$, they can safely be assigned to a related triplet state $^3\text{A-2}^*$. At a delay time of 1000 ps, a comparison of the ground state bleaching (GSB) intensity with 200 fs delay time reveals that 15% of the initially excited molecules are in the excited triplet state or the **B-2** photoproduct (see Figure 2a, inset 4). The ratio of $^3\text{A-2}^*$ and **B-2** was determined to be 40:60 (see below) and correspondingly a quantum yield $\phi_{\text{A/B}}$ of $9 \pm 2\%$ for the **A-2** to **B-2** photoisomerization

as well as $\phi_{A/\beta A}$ of $6 \pm 2\%$ for $^3A-2^*$ triplet generation are extracted (see Figures S7–S9 in the Supporting Information).

The mixed $^3A-2^*$ and **B-2** absorption spectrum further decays on the ns timescale (see Figure 2b for ns data). Global analysis reveals two different processes with distinct time constants. These are the triplet decay back to the **A-2** ground state and the helix inversion of **B-2** to **C-2**. In contrast to motor **1**, the increased barrier for thermal helix inversion and the shorter triplet lifetime of $^3A-2^*$ clearly separates the two processes spectroscopically. For the $^3A-2^*$ state, the decay time of 25 ns is accompanied by a recovery of 40% of the GSB. The triplet state $^3A-2^*$ is thus found to be entirely nonproductive in terms of motor rotation—similar to motor **1**. Both the very fast ISC to the triplet and the fast return to the ground state can be attributed to the similar energy of the triplet state to the singlet states and to conical intersections with the latter. The lack of change in the GSB during the 990 ns decay of the **B-2** absorption and the concurrent appearance of the **C-2** spectral features are proof that the helix inversion from **B-2** to **C-2** is completely quantitative at 22 °C.

The second part of the unidirectional rotation cycle starting from **C-2** is discussed in the following (for details refer to sections 3.3–3.4 in the Supporting Information). The main differences to the first 180° rotation are the apparent lack of the involvement of a $^3C-2^*$ triplet state and the longer lifetime of the **D-2** intermediate compared with **B-2**. Otherwise, high similarity is found to the **A-2** photoreaction. In the beginning, rapid structural changes are observed via the ESA on the 100 fs timescale followed by excited state decay with a time constant of 370 fs. After thermal cooling with 5.2 ps is completed, the only identified photoproduct is the **D-2** intermedi-

ate formed with a quantum yield of ϕ_{CD} of $15 \pm 3\%$. The **D-2** isomer is identified by its significant thermal stability compared with **B-2** and its absorption spectrum, which is sufficiently different to the spectra of the other three isomers to be recognized as a distinct species. The quantum yield is confirmed by controlled continuous-wave (cw) illumination by LEDs.^[14] The slow thermal decay of **D-2** to **A-2** is not observed by TA spectroscopy for motor **2** because it exceeds the time range of the TA setup, but has been measured by low-temperature NMR spectroscopy.^[9b]

For motor **3**, an analogous picture is obtained from the time-resolved data (see sections 3.5–3.8 in the Supporting Information for details). Similar to **2**, the photoisomerization reactions are very fast and proceed on the fs timescale. Again, a slowly decaying (20 ns) nonproductive triplet state is observed after photoexcitation of **A-3**. The thermal decay from **B-3** to **C-3** proceeds quantitatively and with a time constant of 125 μ s at 22 °C. In the case of the photogenerated isomer **D-3** no dynamics can be observed on the μ s timescale, as is expected from the high energy barrier (0.67 eV) accompanying the **D-3** to **A-3** helix inversion process.^[9b] Motor derivative **3** shows much more similar ESA dynamics and decay times to motor **2** as opposed to motor **1**.

In Figure 3, a comparison of the ultrafast behavior of motor **1** and **2** is shown. The very fast decay of the excited state **A-2*** ESA and stimulated emission (SE) signals around 100 fs suggests that after excitation to the Franck–Condon region, the molecules change their geometries significantly while concomitantly propagating directly downhill on the potential energy surface towards an excited state minimum. This ballistic behavior is obscured for motor **1** although theoretically predicted.^[9c]

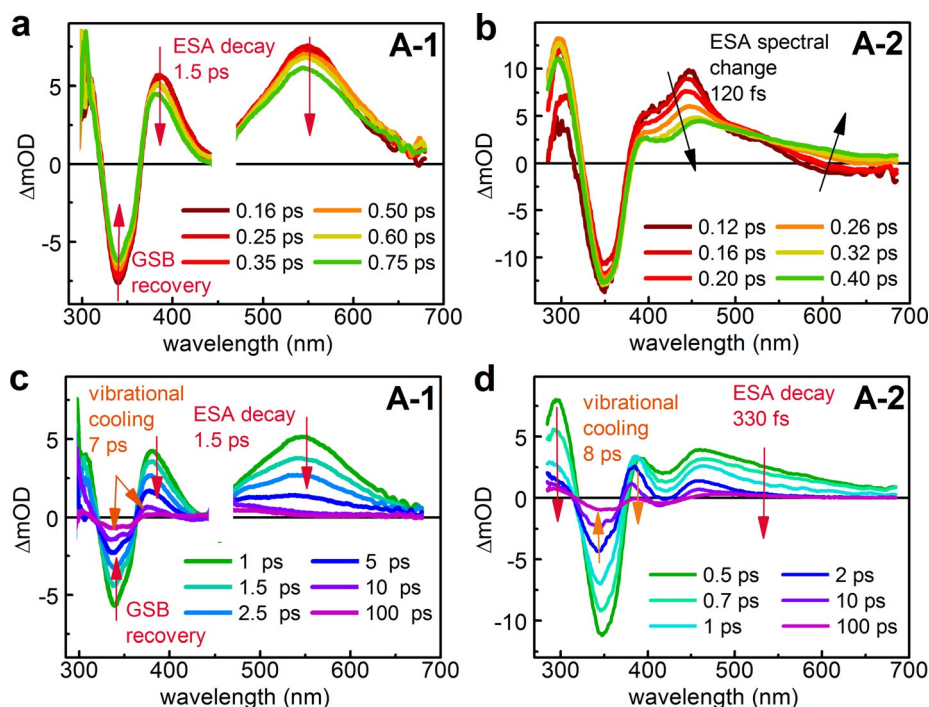


Figure 3. Spectral development of the transient spectra in time-resolved measurements of **A-1*** (a and c) and **A-2*** (b and d) in CH_2Cl_2 at 22 °C.

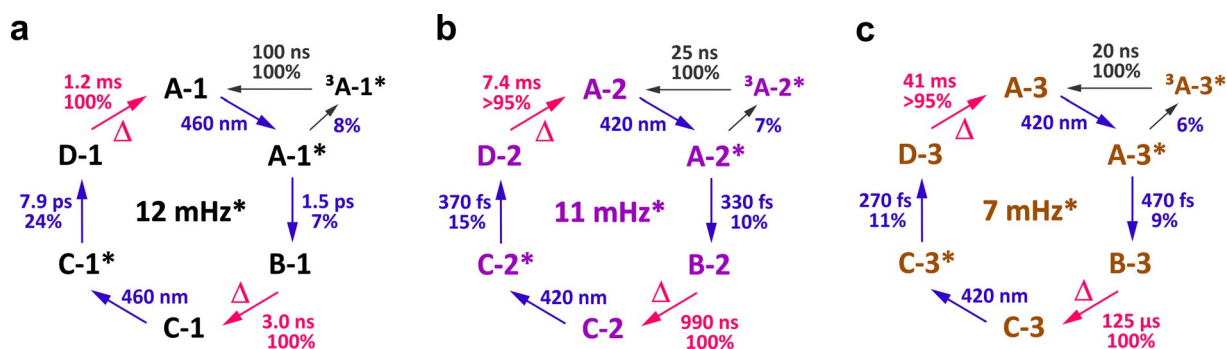


Figure 4. Quantitative mechanism of the unidirectional rotation cycle of HTI motors 1–3 determined in CH_2Cl_2 solution at 22°C . Only the life times of the D isomers of motors 2 and 3 were determined by low-temperature ^1H NMR spectroscopy in $\text{CD}_2\text{Cl}_2/\text{CS}_2$ (4:1) and then extrapolated to 22°C . Excited state processes are indicated as blue and black arrows, thermal processes in the ground state are shown in red. Actual rotation frequencies at ambient irradiation conditions are given in the centers. (a) Motor 1. (b) Motor 2. (c) Motor 3. *Rotation frequencies calculated at 100 mW cm^{-2} light power at 350 nm for 2 mL of a 0.1 mM solution in a $10\times 10\text{ mm}$ cuvette at 22°C .

Additionally, the photoisomerization is significantly faster compared with motor 1. This hints at the presence of a lower excited state barrier in A-2^* . The spectral analysis of the transient measurements of excited isomers C-1^* and C-2^* reveals again much faster dynamics for motor 2 compared with 1 (see also Supporting Information section 4, and Figure S27). The excited state behavior of motor 3 is very similar to motor 2 and an even faster photoisomerization of C-3^* with 270 fs was found. Taking into account the sizable photoisomerization quantum yields, this renders the photoisomerization speed of C-2 and C-3 the fastest measured for HTI derivatives so far.

Conclusion

The integral experimental quantification of the rotation mechanism of HTI motors 1–3 and the subsequent application of a kinetic model allows us to quantify the effects of the varying quantum yields, molar absorptions, and temperature on the overall rotation frequency (see Figure 4 and also Supporting Information section 7). The calculation delivers 12 mHz for 1, 11 mHz for 2, and 7 mHz for 3 under 100 mW cm^{-2} irradiation at 350 nm (absorption maximum). This light level corresponds to slightly concentrated and properly filtered solar irradiation. The derived rotation frequencies are much lower than the maximal attainable frequencies predicted by the highest ground state energy barriers, that is, 1 kHz for 1 and 114 Hz and 20 Hz for 2 and 3 (extrapolated to 22°C). Molar absorptions do not have a strong influence owing to their high similarity for all motors and isomers. Considering both the maximal attainable frequencies as well as the actual rotation frequency under constant illumination reveals motor design 1 as being overall superior to motors 2 and 3. In particular, at decreased temperature, this motor maintains rotation activity whereas 2 and 3 will effectively stop working.

The reason why we limit the irradiation to moderate intensities is the readily observable and expected heating of a solution with an optical density suited for optical detection. If this is not needed, one could use a much lower motor concentration and apply drastically higher light intensities, for example, with a focused laser. Two scenarios come to mind: motors at-

tached to biological cells or experiments on surfaces. Then, we can envision effective rotation frequencies in the low Hz range.

The transient absorption measurements of motors 1–3 allow several conclusions for future improved design of HTI-based motors. Increasing the quantum yields of the photoreactions and the molar absorption coefficients are both found to be especially important to increase the overall efficiency. Decreasing the barriers for the thermal helix inverting steps is important to rapidly remove thermally unstable states and avoid their unproductive excitation. In general, the frequencies of molecular motors with low ground state barriers are dominated by the quantum yields for both photoisomerizations. For HTI motors, substitution of the methoxy group in vicinity to the central double bond by larger groups resulted in only small changes of the A to B photoisomerization quantum yields. However, a strong decrease of the C to D photoisomerization quantum yield is observed if the methoxy group is replaced by sterically more hindered alkyl groups. Taken together, these combined effects suggest increasing the electronic density and also increasing the steric hindrance moderately at the rotor fragment to improve the quantum yield of both photoisomerization reactions at the same time. With respect to lifetimes, clear trends were observed. In general, the excited state lifetimes of singlet states decrease considerably when removing electron density and increasing sterics (motors 2 and 3 versus 1), whereas the triplet states experience less reduction in their lifetime. In the ground state the thermal B to C helix inversion is affected most and shows a reverse trend where removal of electron density and increase of steric hindrance leads to a strongly increased lifetime of the metastable B isomers.

In summary, we presented a comprehensive comparative study of the working mechanism of three HTI-based molecular motors 1 to 3. By using time-resolved absorption spectroscopy as the main experimental technique, we elucidated the kinetic and thermodynamic aspects of the HTI motor rotation in the ground as well as the excited state. We found that both the ground and excited state are strongly altered for the three motor derivatives. Increase of steric hindrance and reduced electron density of the altered substituent promotes significantly faster excited state dynamics but at the same time sig-

nificantly slower ground state dynamics. Quantum yields appear not to be correlated with changes in the excited state dynamics. The current work stresses the importance of the photoisomerization steps over the thermal ground state ratcheting processes for increasing the efficiency and speed at the current performance stage. A promising way to increase quantum yields of the photoreactions is incorporation of electron-donating substituents with increased steric hindrance at the rotor fragment of HTI motors and our current efforts are inter alia aimed in this direction.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: excited states · ground states · hemithioindigo · molecular motors · rotation mechanisms

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