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Control of rotor function in light-driven molecular motors

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Supporting Information

Pages S2-S6. General considerations, Pd/XPhos optimization table, structural analysis, kinetic studies of *cis*- and *trans*-**5**, and ¹H NMR spectra of photochemical and thermal isomerization experiments for molecular motor *cis*- and *trans*-**5**.

Pages S7-S17. ¹H and ¹³C NMR spectra, recorded on a 400 MHz spectrometer in CDCl₃ solution.

General Considerations. Column chromatography was performed on silica gel (230-400 mesh). ^{13}C NMR spectra were recorded on a 101 MHz or a 126 MHz spectrometer. ^1H NMR spectra were recorded on a 400 MHz or a 500 MHz spectrometer. 2D-EXSY NMR spectra were recorded on a 500 MHz spectrometer. Chemical shifts are denoted in δ -unit (ppm) relative to CDCl_3 (^1H δ = 7.26, ^{13}C δ = 77.0) or DCM-d_2 (^1H δ = 5.32, ^{13}C δ = 54.0). For ^1H NMR spectroscopy, the splitting parameters are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (double doublet). HRMS (ESI) spectra were obtained with an orbitrap mass spectrometer.

Table S1. Optimization of Pd/XPhos percentage in α -arylation with aryl halide.

Entry	Product	Mol% Pd	Mol% XPhos	% Yield
1 ^a	6.1	5	10	< 5%
2	6.1	20	40	36
3	6.1	50	100	62
4	6.2	20	40	32
5	6.2	50	100	67
6	6.3	20	40	36
7	6.3	50	100	70

a) No product 6.1 was obtained for $\text{Pd}(\text{OAc})_2/\text{XPhos}$ 1 mol%: 2 mol%

Structural analysis.

Figure S1. a) Structure of stable *cis*-**4** as calculated at the DFT B3LYP 6-31G(d,p) level of theory, b) PLUTO drawing of stable *cis*-**1**.

Figure S2. a) Structure of stable *trans*-**4** as calculated at the DFT B3LYP 6-31G(d,p) level of theory, b) PLUTO drawing of stable *trans*-**1**.

The assignment of the structures of motors **4** and **5** is based on related first-generation motors, such as motor **1**. This is supported by calculations at the DFT B3LYP 6-31G(d,p) level of theory, with the Gaussian 03W software package.¹ Comparison of these calculations with X-ray structures of stable *cis*-**1** (Figure S1) and stable *trans*-**1** (Figure S2) shows that motor **4** adopts the same configuration as motor **1**.² The introduction of a large substituent on the stereogenic center does not change the pseudo-axial orientation of the substituent in both stable isomers. Due to the steric similarity of motor **5** to motor **4**, the same configuration is predicted for **5**.

Discussion of the kinetic studies of motor and rotor moieties of compound **5** and the ^1H NMR experiments of photochemical and thermal isomerization of compound **5**:

Thermal behavior of a motor **5 by UV-vis spectroscopic measurements.** The kinetic parameters of the thermal helix inversions from unstable to stable of both *cis*- and *trans*-**5** were determined. In a UV-vis spectroscopic experiment, similar to that described in the main text, the thermal helix inversion step from unstable *trans*- to stable *trans*-**5** was observed at five different temperatures (−20, −15, −12, −10 and −5 °C) in dichloromethane. The thermal isomerization was followed by monitoring the change in absorption at 410 nm. Using the Eyring equation (Figure S3a), it was determined that the isomerization has a Gibbs free energy of activation ($\Delta^\ddagger G^\circ$) of 78.14 kJ·mol $^{-1}$ (unstable *trans*-**5**→stable *trans*-**5**). This value corresponds to a half-life at room temperature of 9.4 s, which shows that the thermal helix inversion is similar to the analogous helix inversion of the related motor **4**, of which the unstable *trans* to stable *trans* isomerization occurs with the half-life of 9.4 s at rt.

Figure S3. a) Eyring plot for thermal conversion of unstable to stable *trans*-**5** at 5 different temperatures. b) Eyring plot for thermal conversion of unstable to stable *cis*-**5** at 4 different temperatures.

On the other hand, in the transformation of unstable *cis*-**5** to stable *cis*-**5**, the kinetic parameters of the thermal conversion in 1,2-dichloroethane solution were determined by monitoring the change in absorption at 410 nm at four different temperatures (30, 40, 50 and 60 °C). Using the Eyring equation (Figure S3b), the Gibbs free energy of activation was determined to be 97.08 kJ·mol $^{-1}$, indicating that isomerization is a bit faster ($t_{1/2}$ = 6.2 h at rt) compared with the thermal isomerization of the analogous unstable *cis*-**3** to stable *cis*-**3** ($t_{1/2}$ = 8.2 h at rt).

Photochemical and thermal behavior of a motor **5 by ^1H NMR studies.** In order to confirm the results from the UV-vis measurements, supporting data using other techniques was required. ^1H NMR spectroscopy is a useful technique for monitoring the progress of the photochemical and thermal isomerization of motor **5**. As described in the main text of ^1H NMR spectroscopic studies from stable

trans-**5** to stable *cis*-**5** in CD₂Cl₂, it was found that the efficiency of the thermal helix inversion step from unstable *cis*-**5** to stable *cis*-**5** depends on the temperature. Consequently, more experiments for this process have been performed in another solvent (toluene-*d*₈) and at different temperatures to prove that even in different systems, during the thermal helix inversion process from unstable to stable *cis*-**5**, a competing backward rotation can occur. Starting with stable *trans*-**5** in toluene-*d*₈ (Figure S4a), ¹H NMR analysis of the photochemical step ($\lambda \geq 365$ nm), the conversion of stable *trans*-**5** to unstable *cis*-**5** indicated that a photostationary state (PSS) with stable *trans*-**5** < 5% and unstable *cis*-**5** > 95% was reached in 2 h at -40 °C (Figure S4b). After reaching the PSS, the thermal isomerization was performed by warming the sample of unstable *cis*-**5** to room temperature overnight (Figure S4c). Analysis of the ¹H NMR spectrum of molecular motor **5** after thermal helix inversion showed the ratio of stable *trans*-**5**: stable *cis*-**5** after thermal isomerization, as determined by ¹H NMR spectroscopy, was 37:63. In contrast, when the thermal helix inversion of unstable *cis*-**5** was performed at 70 °C for 30 min, a different ratio of stable *trans*-**5**: *cis*-**5** was obtained; 24:76 (Figure S4d).

Figure S4. ¹H NMR studies (500 MHz) in toluene-*d*₈ of a) Stable *trans*-**5**, b) Unstable *cis*-**5**, formed upon irradiation ($\lambda \geq 365$ nm) c) Stable *cis*-**5**, obtained by thermal helix inversion at rt d) Stable *cis*-**5**, obtained by thermal helix inversion at 70 °C (all spectra were obtained at -40 °C).

Even though the rotation of stable *trans*- to stable *cis*-**5** is not exclusively unidirectional, this compound is still able to function as a molecular motor.

Continuing with the other half of rotary cycle of motor **5**, stable *cis*-**5** in CD₂Cl₂ (Figure S5a) was irradiated to form unstable *trans*-**5** (75% conversion in PSS) (Figure S5b) and thermal helix inversion followed at rt for 20 min to provide stable *trans*: *cis*-**5** in the ratio 75:25 (Figure S5c). For this thermal helix inversion from unstable *trans*-**5** to stable *trans*-**5**, no backward rotation is observed.

Figure S5. ¹H NMR studies (500 MHz) in CD₂Cl₂ of a) Stable *cis*-**5**, b) Unstable *trans*-**5** obtained by irradiation ($\lambda \geq 365$ nm), c) Stable *trans*-**5**, formed upon thermal helix inversion at rt. (all spectra were performed at -40 °C).

Figure S4. ^1H NMR Spectrum (400 MHz, CDCl_3) of compound **7**.

Figure S5. APT NMR spectrum (101 MHz, CDCl_3) of compound **7**.

Figure S6. ¹H NMR Spectrum (400 MHz, CDCl₃) of compound **6.1**.

Figure S7. APT NMR spectrum (101 MHz, CDCl₃) of compound **6.1**.

Figure S8. ^1H NMR Spectrum (400 MHz, CDCl_3) of compound **6.2**.

Figure S9. APT NMR spectrum (101 MHz, CDCl_3) of compound **6.2**.

Figure S10. ¹H NMR Spectrum (400 MHz, CDCl₃) of compound **6.3**.

Figure S11. APT NMR spectrum (101 MHz, CDCl₃) of compound **6.3**.

Figure S12. ¹H NMR Spectrum (400 MHz, CDCl₃) of compound **6.4**.

Figure S13. APT NMR spectrum (101 MHz, CDCl₃) of compound **6.4**.

Figure S14. ^1H NMR Spectrum (400 MHz, CDCl_3) of compound **6.5**.

Figure S15. APT NMR spectrum (101 MHz, CDCl_3) of compound **6.5**.

Figure S16. ¹H NMR Spectrum (400 MHz, CDCl₃) of compound **6.7**.

Figure S17. APT NMR spectrum (101 MHz, CDCl₃) of compound **6.7**.

Figure S18. ^1H NMR Spectrum (400 MHz, CDCl_3) of molecular motor stable *trans*-4.

Figure S19. APT NMR spectrum (101 MHz, CDCl_3) of molecular motor stable *trans*-4.

Figure S20. ^1H NMR Spectrum (400 MHz, CDCl_3) of molecular motor stable *cis*-4.

Figure S21. APT NMR spectrum (101 MHz, CDCl_3) of molecular motor stable *cis*-4.

Figure S22. ^1H NMR Spectrum (400 MHz, CDCl_3) of molecular motor stable *trans*-5.

Figure S23. APT NMR spectrum (101 MHz, CDCl_3) of molecular motor stable *trans*-5.

Figure S24. ^1H NMR Spectrum (400 MHz, CDCl_3) of molecular motor stable *cis*-5.

Figure S25. APT NMR spectrum (101 MHz, CDCl_3) of molecular motor stable *cis*-5.

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