Light-to-Energy Conversion in Organic Solar Cells and Molecular Motors

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Electronic Supporting Information (ESI) for

Chapter 4

Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

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**Table of Contents**

S1. Methods and General Information .................................................................................................... 3  
  S1.1. Preparation and Characterization of Compounds ........................................................................ 3  
  S1.2. Difference Absorption Measurements ......................................................................................... 3  
  S1.3. Transient Absorption Spectroscopy ............................................................................................ 3  
  S1.4. Time-Resolved Photoluminescence Spectroscopy ....................................................................... 7  
S2. Preparation and Characterization of Compounds ........................................................................... 8  
  S2.1. Sensitizer Azide .......................................................................................................................... 8  
  S2.2. Motor .......................................................................................................................................... 12  
S3. Density Function Theory (DFT) Calculations .............................................................................. 18  
S4. NMR Studies ..................................................................................................................................... 19  
  S4.1. NOESY and ROESY NMR ......................................................................................................... 19  
  S4.2. Determination of PSS Ratios ...................................................................................................... 21  
  S4.3. Comparison of $^1$H NMR Spectra ............................................................................................ 24  
S5. Steady-State Absorption ..................................................................................................................... 24  
  S5.1. Absorption Spectra ...................................................................................................................... 24  
  S5.2. Isomerization Studies ................................................................................................................... 25  
  S5.3. Eyring Plots ................................................................................................................................ 27  
  S5.4. Quantum Yields of Isomerization ............................................................................................. 28  
S6. Difference Absorption Spectroscopy ................................................................................................. 29  
  S6.1. Difference Absorption Spectra ................................................................................................... 30  
  S6.2. Concentration Dependence ........................................................................................................ 31  
  S6.3. Time Evolution of $\Delta$OD Spectra .......................................................................................... 33  
S7. Transient Absorption (TA) Spectroscopy ......................................................................................... 34  
  S7.1. TA Maps and Spectra Under One-Photon Excitation ................................................................. 34  
  S7.2. TA Transients at 620 nm ............................................................................................................ 35  
  S7.3. Intensity Dependence at 620 nm ................................................................................................ 37  
  S7.4. TA Transients at 510 nm ........................................................................................................... 39  
  S7.5. Intensity Dependence at 510 nm ............................................................................................... 42  
S8. Time-Resolved PL Spectroscopy ..................................................................................................... 42  
  S8.1. PL Maps and Mean Energies ..................................................................................................... 43  
  S8.2. PL Transients ............................................................................................................................. 44  
  S8.3. PL Intensity Dependence ........................................................................................................... 46  
S9. Resonance Energy Transfer ............................................................................................................... 47  
  S9.1. PL Quantum Yield of AF-343 .................................................................................................... 47  
  S9.2. Energy Transfer Rate ................................................................................................................ 47  
S10. NMR Spectra .................................................................................................................................. 49  
S11. References ........................................................................................................................................ 61
S1. Methods and General Information

S1.1. Preparation and Characterization of Compounds

Reagents were purchased from Sigma Aldrich, Acros or TCI Europe and were used as received. Solvents were reagent grade and used without prior water removal unless otherwise indicated. Anhydrous solvents were obtained from an MBraun SPS-800 solvent purification system or directly bought from Acros. Solvents were degassed by purging with N$_2$ for a minimum of 30 min or by three freeze-pump-thaw cycles.

Flash column chromatography was performed on silica gel (Merck, type 9385, 230–400 mesh) or on a Büchi Reveleris purification system using Büchi silica cartridges. Thin layer chromatography was carried out on aluminum sheets coated with silica gel 60 F254 (Merck). Compounds were visualized with a UV lamp and/or by staining with KMnO$_4$, CAM or vanillin.

Motor 2 was prepared as described in the literature$^1$.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury-Plus 400 or a Bruker Avance 600 NMR spectrometer at 298 K unless otherwise indicated. PSS studies were performed on a Varian Unity Plus 500 NMR spectrometer. Chemical shifts are given in parts per million (ppm) relative to the residual solvent signal. Multiplets in $^1$H NMR spectra are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), br (broad). High resolution mass spectrometry was performed on an LTQ Orbitrap XL spectrometer. Steady-state UV-vis absorption spectra were recorded on an Agilent 8453 UV-vis Diode Array System, equipped with a Quantum Northwest Peltier controller, in 10 mm quartz cuvettes. Irradiation experiments were performed using fiber-coupled LEDs (M420F2, M455F1, M470F3, M490F3, M505F3, M530F2) obtained from Thorlabs Inc.

S1.2. Difference Absorption Measurements

Difference absorption measurements were performed using a UV-vis-NIR spectrometer (Lambda 900) and two different types of light sources for one- and two-photon absorption experiments at 455 nm and 800 nm, respectively. The one-photon irradiation was provided by a fiber-coupled LED (M455F1, Thorlabs) with a maximum output power of 11 mW. The two-photon irradiation was implemented using an amplified mode-locked Ti:sapphire laser (Legend Elite Duo, Coherent) centered at 800 nm with a 1 kHz repetition rate.

S1.3. Transient Absorption Spectroscopy

Transient absorption (TA) spectroscopy was performed in a pump-probe arrangement (Fig. S1) based on an amplified mode-locked Ti:sapphire laser (Legend Elite Duo, Coherent) centered at 800 nm (1 kHz repetition rate). The laser output was split into pump (~90%) and probe (~10%) beams. For 400 nm excitation, the pump beam frequency was doubled in a β-barium borate (BBO) crystal. A mechanical translation stage (LS-180, Physik Instrumente) with 508 mm excursion was used to delay the probe pulse with respect to the pump pulse. The probe beam was focused into a 2 mm sapphire crystal to generate a white-light (400–850 nm) continuum (WLC). A short-pass filter with a cut-off wavelength of 750 nm placed in the probe beam, was used to remove residual fundamental frequency radiation from WLC.
Both the pump and the probe beams were focused and spatially overlapped in a 0.2 mm flow cell (Starna Scientific Ltd.), connected to a peristaltic pump (Masterflex, Cole-Parmer) to refresh the sample in the excitation spot. The total volume of the system (including connection tubing and the cell) was ~5 mL. The diameters of the pump and probe beams at the sample position were ~260 μm and ~170 μm, respectively. The polarization of the pump and probe beams was linear and set to be parallel to each other. The delay of the probe pulse was scanned in 30 fs steps within 0–10 ps range, 0.5 ps steps for 10–100 ps range, and 2 ps steps for 100–2600 ps range.

TA of the probe beam in the flow cell was recorded using two different types of detector, a 500–1000 nm compact spectrometer (CCS175/M, Thorlabs) and a silicon photodiode (DET36A, Thorlabs). The spectrometer detected the TA spectra in the range of 500–750 nm; however, it had a lower signal-to-noise ratio as compared to the lock-in referenced photodiode.

For spectrometer detection, the pump beam was chopped at 20 Hz by an asynchronous mechanical chopper (Stanford Research Systems, Inc.), with the spectrometer locked to the chopper electronics. The differential absorption (ΔOD) of the probe with the pump on and off was calculated for each time delay. Conventionally, negative (ΔOD) signals represent stimulated emission and/or ground-state bleaching, while positive values represent pump-induced excited state absorption. Finally, ΔOD of each pump-probe delay scan was compiled as a function of time and wavelength (for a
TA map). This arrangement typically allowed obtaining $\Delta OD \approx 10^{-3}$ which is more than sufficient in the case of one-photon excitation.

For photodiode detection, the pump beam was synchronously chopped at 500 Hz, i.e., every other pump pulse was blocked. The photodetector output was amplified by a lock-in amplifier referenced to the chopper electronics, digitized and fed to the computer. To obtain the TA signals at a particular probe wavelength (510 nm and 620 nm) band-pass filters with a full width at half maximum of 10 nm and 20 nm, respectively, were placed in front of the photodiode. This arrangement improved the sensitivity down to $\Delta OD \approx 4 \cdot 10^{-5}$ which allowed obtaining the signals under two-photon excitation conditions.

Due to the strong solvent response at early time (<0.5 ps), the TA kinetics under two-photon excitation were corrected by direct subtraction of the separately recorded solvent response (Fig. S3). The TA maps and TA kinetics under one-photon excitation were also corrected for the optical density of the sample following the Lambert-Beer law, using the following equation (Eq. S1):

$$\{\Delta OD\}_{corr} = \frac{\Delta OD}{1 - 10^{-6OD(\lambda=400 \text{ nm})}}$$  \hspace{1cm} (Eq. S1)

For two-photon excitation the correction was not needed and the pump did not experience any direct (one-photon) absorption.

As the WLC was not compressed, the time when the pump and probe pulses overlap at a particular probe wavelength, was wavelength-dependent. For finding the correction curve (i.e., the dependence of the group delay on the wavelength), a TA measurement was performed on chloroform under a sufficiently high peak intensity of >18 GW/cm$^2$ (corresponding to an experimental average intensity of 1.8 W/cm$^2$) of the pump pulse, so that a non-resonant TA signal was clearly observed. Then the transient non-resonant signal was fitted to a combination of a Gaussian—a derivative of the Gaussian function which yielded the zero delay time$^3$. This time was used to determine the zero position of the TA kinetics at 510 nm and 620 nm.

For spectrometer detection, the transient spectra were extracted from the raw TA map of chloroform by taking spectral slices of 30 fs width at different times (Fig. S2A). Each transient spectrum was fitted to a Gaussian function (Fig. S2B) to obtain the peak position. The peak positions were fitted to a second-order polynomial function$^4$, yielding the group delay at each particular probe wavelength (gray line in Fig. S2A). This function was used to correct the raw TA maps by shifting the data along the time coordinate.
Fig. S2. Transient absorption of chloroform (solvent). A TA map of chloroform under 400 nm pump. The open dots show the mean values (the wavelengths of the group delays) of Gaussian functions fitted to the transient spectra. The error bars refer to the standard deviations. The gray curve shows the fit to a second-order polynomial function. B An example of a transient spectrum at 0.25 ps. The black curve shows the fit to the Gaussian function with a mean value of 577 nm and a standard deviation of 16 nm.

Solvent contribution around zero delay time

In femtosecond TA experiments, a non-resonant solvent response is typically observed when the pump and probe pulses overlap in time. This is especially important for the two-photon excitation conditions as the intensities are higher than for the one-photon ones (even though the detuning from the solvent resonances in UV is larger).

Figure S3 shows the TA traces of chloroform solutions of 1, 2, AF-343, and neat chloroform under one- and two-photon excitation (pump wavelengths of 400 nm and 800 nm, respectively). The signals were recorded right one after another to maintain identical experimental conditions. Evidently, for two-photon excitation the solvent response has a similar (albeit noticeably lower) amplitude as any of the signals from the sample solutions. Because the TA signals are additive, in the following, the solvent contribution was subtracted from sample TA signals (similar to the insets in Fig. S3B and S3D). We note, however, that this procedure does not fully remove the so-called coherent artefact near zero delay as it originates from the sample solutions, too. Note also, that in the case of one-photon excitation the solvent contribution did not exceed 10% (estimated in Fig. S3A and S3C) and therefore was disregarded.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

Fig. S3. Solvent contribution around zero delay time. TA traces of chloroform solutions of 1s (green), 2s (blue), AF-343 (red) and neat chloroform (orange) at 510 nm (A, B) and 620 nm (C, D) probe wavelengths under one-photon, 400 nm, (left panels) and two-photon, 800 nm, (right panels) excitation. The pump intensity under one-photon excitation was 1.8 W/cm² for neat chloroform and 0.13 W/cm² for 1s, 2s, and AF-343; under two-photon excitation it was fixed at 9 W/cm² for all samples. The black curves show fits to a combination of a Gaussian — a derivative of the Gaussian function with standard deviations, $\sigma = 110 \pm 30$ fs (140 $\pm$ 30 fs) and $\sigma = 100 \pm 30$ fs (90 $\pm$ 30 fs) for 510 nm (620 nm) chloroform transients under one- and two-photon excitation, respectively. The insets show the traces of the solution samples with the solvent contribution subtracted. The molar concentration of all compounds was set to be similar as $\sim 1.7 \cdot 10^{-5}$ M.

S1.4. Time-Resolved Photoluminescence Spectroscopy

Time-resolved photoluminescence (PL) spectroscopy was carried out using a Hamamatsu C5680 streak camera equipped with a Ti:Sapphire laser (Mira 900, Coherent). To obtain the excitation wavelength of 390 nm, the laser output (wavelength of 780 nm at 76 MHz repetition rate) was doubled in a β-barium borate (BBO) crystal. For measurements with a time window above 2 ns, the repetition rate was lowered to 2 MHz by a pulse picker. The excitation beam was focused by a 7.6 cm lens into a 1 mm quartz cuvette, containing the studied compounds dissolved in chloroform. The apparatus functions of the setup were $\sim 6$ ps and $\sim 4$ ps (standard deviations of a Gaussian function) for excitation wavelengths of 390 nm and 780 nm, respectively. The former was measured directly (see Section 8.2) while the latter was calculated by squaring the response function of the former.
S2. Preparation and Characterization of Compounds

S2.1. Sensitizer Azide

*2,7-Dibromo-9H-fluorene (S1)*

![Chemical Structure]

To a stirred solution of fluorene (16.62 g, 100.0 mmol) and iodine (279 mg, 1.10 mmol) in DCM (110 mL), bromine (10.9 mL, 212 mmol) dissolved in DCM (15 mL) was added dropwise at room temperature over 1.5 h. After stirring for an additional 30 min a solution of NaHSO₃ (2.00 g) in H₂O (15 mL) was added and the biphasic mixture was stirred vigorously for another 30 min. H₂O was added, the layers were separated and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give compound S1 (32.32 g, 99.7 mmol, quant.) as an off-white solid, which was used without further purification. Data is in accordance with literature⁵.

**¹H NMR** (600 MHz, CDCl₃) δ 7.66 (d, J = 1.6 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.50 (dd, J = 8.2, 1.8 Hz, 2H), 3.85 (s, 2H); **¹³C NMR** (151 MHz, CDCl₃) δ 144.9, 139.9, 130.3, 128.5, 121.3, 121.1, 36.7.

*2,7-Dibromo-9,9-diethyl-9H-fluorene (S2)*

![Chemical Structure]

To a mechanically stirred solution of S1 (31.25 g, 96.44 mmol), powdered KOH (26.41 g, 470.6 mmol) and KI (1.60 g, 9.64 mmol) in DMSO (70 mL) at 0 °C, EtBr (18.6 mL, 251 mmol) was added dropwise over 20 min. The ice bath was subsequently removed and after 1 h a second batch of EtBr (4.00 mL, 54.0 mmol) was added dropwise over 5 min at room temperature. After stirring for 2 h at room temperature the mixture was cooled to 0 °C, quenched with H₂O and extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give S2 (33.68 g, 88.59 mmol, 92%) as a white solid. Data is in accordance with literature⁶.

**¹H NMR** (600 MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 2H), 7.46 (dd, J = 8.0, 1.8 Hz, 2H), 7.44 (d, J = 1.7 Hz, 2H), 1.99 (q, J = 7.4 Hz, 4H), 0.32 (t, J = 7.4 Hz, 6H); **¹³C NMR** (151 MHz, CDCl₃) δ 151.9, 139.6, 130.4, 126.4, 121.6, 121.2, 56.9, 32.8, 8.6.

*7-Bromo-9,9-diethyl-9H-fluorene-2-carbaldehyde (S3)*

![Chemical Structure]

ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light
To a solution of S2 (13.68 g, 35.98 mmol) in anhydrous THF (62 mL) at −78 °C, n-BuLi (2.5 M in hexanes, 15.1 mL, 37.8 mmol) was added dropwise over 5 min to give a dark orange solution. After 30 min anhydrous DMF (3.88 mL, 50.4 mmol) was added dropwise over 2 min and the resulting solution was stirred at −78 °C for 20 min before the cooling bath was removed to let the mixture slowly warm up to room temperature. After 1 h at room temperature the reaction was quenched with sat. aqueous NH₄Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give S3 (11.81 g, 35.88 mmol, quant.) as a pale yellow solid, which was used without further purification. Data is in accordance with literature⁷.

\[ \text{S3} \quad (\text{Bromo-9,9-diethyl-9H-fluoren-2-yl)benzo[d]thiazole (S4)} \]

A solution of S3 (11.81 g, 35.88 mmol) and 2-aminobenzenethiol (4.80 mL, 44.9 mmol) in anhydrous DMSO (36 mL) was heated to 195 °C. After 1.5 h the mixture was allowed to cool to room temperature and separated between H₂O and EtOAc. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with H₂O, AcOH/H₂O (1:4), H₂O, sat. aqueous NaHCO₃ and brine, dried over Na₂SO₄ and concentrated in vacuo. Purification by flash column chromatography (SiO₂, dry load on celite, 5% EtOAc in pentane) gave S4 (9.78 g, 22.5 mmol, 63%) as a pale yellow solid.

\[ \text{S4} \]

\[ \text{1H NMR} \quad (600 MHz, CDCl₃) \delta 10.06 (s, 1H), 7.88 – 7.84 (m, 2H), 7.81 (dd, J = 7.5, 1.0 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.53 – 7.50 (m, 2H), 2.14 – 2.07 (m, 2H), 2.07 – 1.99 (m, 2H), 0.31 (t, J = 7.4 Hz, 6H); \]

\[ \text{13C NMR} \quad (151 MHz, CDCl₃) \delta 192.2, 153.6, 150.5, 146.9, 139.1, 135.8, 130.7, 130.7, 126.7, 123.4, 123.3, 122.4, 120.2, 56.8, 32.7, 8.6. \]

3-(Benzylxy)-N-phenylaniline (S5)

To a solution of 3-hydroxydiphenylamine (18.52 g, 100.0 mmol) and K₂CO₃ (27.64 g, 200.0 mmol) in anhydrous DMF (100 mL) at 0 °C, BnBr (13.1 mL, 110 mmol) was added dropwise over 15 min. The resulting mixture was slowly allowed to warm to room temperature overnight before it was separated between H₂O and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Purification by flash column
chromatography (SiO₂, dry load on celite, 10% DCM in pentane) gave S5 (26.66 g, 96.84 mmol, 97%) as a pale yellow solid. Data is in accordance with literature⁸.

³¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.40 (m, 2H), 7.38 (dd, J = 8.4, 6.8 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.28 – 7.20 (m, 2H), 7.16 (t, J = 8.1 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.93 (tt, J = 7.4, 1.1 Hz, 1H), 6.71 (t, J = 2.3 Hz, 1H), 6.64 (ddd, J = 8.0, 2.2, 0.9 Hz, 1H), 6.55 (ddd, J = 8.3, 2.4, 0.8 Hz, 1H), 5.73 (br s, 1H), 5.03 (s, 2H); ³¹C NMR (151 MHz, CDCl₃) δ 160.0, 144.7, 142.9, 137.2, 130.3, 129.5, 128.7, 128.0, 127.6, 121.5, 118.5, 110.6, 107.4, 104.3, 70.1; HRMS (ESI pos) m/z calcd for C₁₉H₁₈NO [M+H]⁺ 276.13829, found 276.13870.

7-(Benzo[d]thiazol-2-yl)-N-(3-(benzoxyl)phenyl)-9,9-diethyl-N-phenyl-9H-fluoren-2-amine (S6)

A Schlenk flask was charged with S4 (2.92 g, 6.71 mmol), S5 (2.18 g, 7.92 mmol), Pd₂(dba)₃ (61 mg, 0.067 mmol) dpdf (74 mg, 0.13 mmol), and NaOt-Bu (903 mg, 9.40 mmol). Anhydrous, degassed (bubbling N₂ for 45 min) toluene was added and the mixture was heated at 110°C overnight. It was then cooled to room temperature, quenched with sat. aqueous Na₂SO₄ and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Flash column chromatography (SiO₂, dry load on celite, 30–50% DCM in pentane) gave S6 (2.45 g, 3.89 mmol, 58%) as a yellow solid. Data is in accordance with literature⁸.

³¹H NMR (600 MHz, CDCl₃) δ 8.14 – 8.05 (m, 2H), 8.03 (dd, J = 7.9, 1.6 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.50 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.33 – 7.27 (m, 3H), 7.21 – 7.12 (m, 4H), 7.09 – 7.02 (m, 2H), 6.78 (t, J = 2.3 Hz, 1H), 6.73 (dd, J = 8.0, 2.1 Hz, 1H), 6.67 (dd, J = 8.2, 2.4 Hz, 1H), 4.97 (s, 2H), 2.10 (dq, J = 14.5, 7.3 Hz, 2H), 1.96 (dq, J = 14.5, 7.4 Hz, 2H), 0.40 (t, J = 7.3 Hz, 6H); ³¹C NMR (151 MHz, CDCl₃) δ 169.0, 159.8, 154.4, 152.2, 150.9, 149.3, 148.1, 147.8, 144.6, 137.0, 135.7, 135.1, 131.7, 130.0, 128.7, 128.1, 127.7, 127.4, 126.4, 125.1, 124.6, 123.8, 123.2, 123.1, 121.7, 121.6, 121.2, 119.5, 119.3, 116.6, 110.6, 109.3, 70.1, 56.6, 32.8, 8.8; HRMS (ESI pos) m/z calcd for C₃₈H₃₇N₂OS [M+H]⁺ 629.26211, found 629.26084.

3-((7-(Benzo[d]thiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)(phenyl)amino)phenol (S7)

A pressure tube was charged with pyr·HCl (6.89 g, 55.6 mmol) and heated until the solid had melted (m.p. 146 °C). S6 (750 mg, 1.19 mmol) was added and the resulting mixture was heated to 200 °C for 3 h before cooling to room temperature and separating between H₂O and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Flash column chromatography (SiO₂, dry load on celite, 10–50% EtOAc in pentane) gave S7 (529 mg, 0.982 mmol, 82%) as a yellow solid. Data is in accordance with literature⁸.
A Schlenk flask was charged with **AF-343** (100 mg, 0.155 mmol), NaN₃ (50 mg, 0.77 mmol) and anhydrous DMF (1.7 mL). The mixture was heated to 60 °C for 7.5 h, cooled to room temperature and separated between H₂O and EtOAc. The aqueous layer was extracted with EtOAc before the combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Flash column chromatography (SiO₂, dry load on celite, 3% EtOAc in pentane) gave **S8** (88 mg, 0.14 mmol, 97%) as a yellow solid.
A three-neck flask equipped with a mechanical stirrer was charged with polyphosphoric acid (PPA, 115% H₃PO₄, 80 mL), heated to 80 °C and 1-methoxynaphthalene (13.1 mL, 90.0 mmol) was added over 3 min. After 5 min methacrylic acid (13.0 mL, 153 mmol) was added over 3 min and the resulting mixture was stirred at 80 °C for 2.5 h. The dark red mixture was allowed to cool to room temperature and the reaction was quenched by adding ice. After stirring the mixture overnight it was extracted with 

Ethyl acetate and the combined organic layers were dried over MgSO₄ and the reaction was heated to 200 °C for 2.5 h. The dark red mixture was allowed to cool to room temperature and the solution was poured onto ice. After stirring the mixture overnight it was extracted with EtOAc and the combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified via recrystallization from hot EtOH (250 mL) to obtain S9 (14.94 g, 66.02 mmol, 73%) as a pale yellow solid. Data is in accordance with literature⁹. 

5-Hydroxy-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (S10) 

Pyr·HCl (69.5 g, 601 mmol) was melted (m.p. 146 °C) in a flask at 180 °C before S9 (4.00 g, 17.7 mmol) was added and the resulting mixture was heated to 200 °C. After 2 h the solution was poured onto ice and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. Flash column chromatography (SiO₂, dry load on celite, 50–90% EtOAc in pentane) gave S10 (3.346 g, 15.76 mmol, 89%) as an off-white solid. Data is in accordance with literature¹⁰.

¹H NMR (400 MHz, DMSO-d₆) δ 11.41 (s, 1H), 8.96 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 6.92 (s, 1H), 3.37 (dd, J = 18.4, 8.3 Hz, 1H), 2.64 (m, 2H), 1.36 (d, J = 14.4, 7.4 Hz, 2H), 1.96 (dq, J = 14.4, 7.4 Hz, 2H), 0.39 (t, J = 7.3 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 169.0, 159.3, 154.4, 152.2, 150.9, 149.4, 148.0, 147.8, 144.6, 135.8, 135.1, 131.7, 130.1, 129.4, 127.4, 126.4, 125.1, 124.7, 123.8, 123.3, 123.1, 121.7, 121.6, 121.2, 119.6, 119.3, 117.0, 110.0, 109.1, 66.9, 56.6, 50.3, 32.8, 8.8; HRMS (ESI pos) m/z calcd for C₃₈H₃₆N₂O₃ [M+H]+ 608.24782, found 608.24782.
2.80 – 2.61 (m, 2H), 1.21 (d, J = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 207.0, 160.4, 159.8, 130.5, 129.1, 125.4, 124.1, 122.9, 122.8, 121.1, 105.6, 41.4, 34.9, 16.6.

(3-Bromoprop-1-yn-1-yl)triisopropylsilane (S11)

A Schlenk flask was charged with NaHMDS (1.0 M in THF, 40.0 mL, 40.0 mmol) and THF (40 mL) and subsequently cooled to −78 °C. Propargyl bromide (80% in toluene, 4.46 g, 4.21 mmol) and the resulting mixture was heated to 50 °C for 18 h. It was then quenched by adding sat. aqueous NH$_4$Cl and extracted with DCM. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. Flash column chromatography (SiO$_2$, dry load on celite, pentane) gave S11 (6.09 g, 22.1 mmol, 55%) as a colorless oil. Data is in accordance with literature.$^{11}$

$^1$H NMR (600 MHz, CDCl$_3$) δ 3.94 (s, 2H), 1.07 (m, 21H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ 102.0, 89.3, 18.7, 15.2, 11.3.

2-Methyl-5-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-2,3-dihydro-1H-cyclopenta[a]napthalen-1-one (S12)

A Schlenk flask was charged with S10 (1.06 g, 5.00 mmol) and K$_2$CO$_3$ (2.76 g, 20.0 mmol). DMF (28 mL) was added followed by S11 (1.79 g, 6.50 mmol) and the resulting mixture was heated to 50 °C for 18 h. It was then cooled to room temperature and separated between H$_2$O and DCM. The aqueous layer was extracted with DCM and the combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo. Flash column chromatography (SiO$_2$, dry load on celite, 3–5% EtOAc in pentane) gave S12 (1.710 g, 4.21 mmol, 84%) as a light yellow oil that solidified upon standing at room temperature.

$^1$H NMR (600 MHz, CDCl$_3$) δ 9.13 (dd, J = 8.3, 1.1 Hz, 1H), 8.27 (dd, J = 8.4, 1.2 Hz, 1H), 7.67 (dd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.53 (dd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.02 (s, 1H), 5.01 (s, 2H), 3.40 (dd, J = 17.1, 7.2 Hz, 1H), 2.86 – 2.69 (m, 2H), 1.35 (d, J = 7.4 Hz, 3H), 1.04 (m, 21H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ 208.6, 159.6, 158.8, 130.8, 129.4, 126.1, 125.4, 124.0, 124.0, 122.7, 103.7, 100.9, 90.9, 57.4, 42.4, 36.0, 18.6, 17.1, 11.2; HRMS (ESI pos) m/z calcd for C$_{26}$H$_{32}$O$_2$Si [M+H]$^+$ 407.24008, found 407.24036.

2-Methyl-5-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-2,3-dihydro-1H-cyclopenta[a]napthalene-1-thione (S13)
A Schlenk flask was charged with Lawesson’s reagent (4.25 g, 10.5 mmol) and S12 (1.42 g, 3.50 mmol). Toluene (63 mL) was added and the mixture was heated to 95 °C for 1.5 h, cooled to room temperature and concentrated in vacuo. Flash column chromatography (SiO2, dry load on celite, 0–8% EtOAc in pentane) gave S13 (1.370 g, 3.24 mmol, 93%) as a dark red oil that solidified upon standing at 6 °C.

1H NMR (600 MHz, CDCl3) δ 10.18 (d, J = 8.4 Hz, 1H), 8.32 (dd, J = 8.4, 1.3 Hz, 1H), 7.74 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.56 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.05 (s, 1H), 5.03 (s, 2H), 3.44 (dd, J = 17.9, 6.5 Hz, 1H), 3.15 (pd, J = 7.2, 2.2 Hz, 1H), 2.86 (dd, J = 17.9, 2.2 Hz, 1H), 1.49 (d, J = 7.3 Hz, 3H), 1.05 (s, 21H); 13C NMR (151 MHz, CDCl3) δ 245.6, 161.6, 160.0, 134.1, 131.6, 130.8, 126.5, 125.7, 124.4, 122.9, 103.4, 100.6, 91.3, 57.6, 55.2, 40.5, 22.3, 18.7, 11.2; HRMS (ESI pos) m/z calc for C26H15OSSi [M+H]+ 423.21724, found 423.21683.

3,6-Dibromophenantherene-9,10-dione (S14)

9,10-Phenantherenedione (10.00 g, 48.03 mmol) and benzoyl peroxide (75 wt% in H2O, 465 mg, 1.44 mmol) were dissolved in nitrobenzene (50 mL). Bromine (5.44 mL, 106 mmol) was added over 2 min under vigorous stirring. The mixture was heated to 120 °C for 20 h. After cooling to room temperature the formed precipitate was filtered off and washed with pentane. The mother liquor was concentrated in vacuo and filtered to give a second batch of product. S14 (15.57 g, 42.54 mmol, 89%) was obtained as a yellow powder. Data is in accordance with literature12.

1H NMR (600 MHz, CDCl3) δ 8.12 (d, J = 1.7 Hz, 2H), 8.07 (d, J = 8.3 Hz, 2H), 7.67 (dd, J = 8.3, 1.7 Hz, 2H); 13C NMR (151 MHz, CDCl3) δ 179.0, 136.1, 133.6, 132.2, 130.0, 127.5.

3,6-Dibromo-9H-fluoren-9-one (S15)

H2O (58 mL) was added to a mixture of dibromophenantherene S14 (14.05 g, 38.39 mmol) and KOH (28.00 g, 499.0 mmol) and the mixture was heated to 100 °C. KMnO4 (32.16 g, 203.5 mmol) was added portion wise over 2 h to the suspension and the final mixture was kept at 100 °C for additional 3 h. It was then allowed to cool to room temperature and conc. H2SO4 was added until neutral pH was obtained. Na2SO3 was added until the solution turned light yellow. The solid product was filtered off and after drying in an oven at 90 °C overnight product S15 (8.27 g, 24.5 mmol, 64%) was obtained as a pale yellow solid. Data is in accordance with literature12.
3,6-Dibromo-9-diazo-9H-fluorene (S16)

To a mixture of S15 (3.00 g, 8.88 mmol) and absolute EtOH (90 mL) was added hydrazine monohydrate (50–60% in H2O, 11.7 mL, 133 mmol) and the resulting light yellow suspension was heated to 90 °C. After 4 h the mixture was allowed to cool to room temperature and H2O (10 mL) was added. The green suspension was put in the freezer at −25 °C to allow crystallization overnight. The solids were collected and a second batch was crystallized by adding water (15 mL) to the mother liquor and putting it in the freezer at −25 °C. The collection of both batches yielded a pale green solid as the corresponding hydrazone (1.94 g, 5.51 mmol, 62%). The crude hydrazone (1.67 g, 4.74 mmol) was dissolved in anhydrous THF (53 mL) and MnO2 (4.12 g, 47.4 mmol) was added. The black suspension was stirred at room temperature for 3 h and then filtered over a plug of celite. The orange solution was concentrated in vacuo to yield product S16 (946 mg, 2.70 mmol, 57%) as an orange solid. Note: This compound is not stable under ambient conditions for prolonged periods of time and should be stored at −20 °C. Data is in accordance with literature12.

\[ ^1\text{H} \text{ NMR} (600 \text{ MHz, CDCl}_3) \delta 8.03 (s, 2H), 7.52 (d, J = 8.5 \text{ Hz, } 2H), 7.37 (d, J = 8.2 \text{ Hz, } 2H); \]
\[ ^{13}\text{C} \text{ NMR} (151 \text{ MHz, CDCl}_3) \delta 131.9, 131.8, 129.9, 124.5, 120.6, 118.4, 64.0. \]

(3-[[1-(3,6-Dibromo-9H-fluoren-9-ylidene)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yloxy]prop-1-yn-1-yl]triisopropylsilane (S17)

A Schlenk flask was charged with S13 (1.30 g, 3.08 mmol) and S16 (861 mg, 2.46 mmol). A mixture of toluene and THF (2:1, 100 mL) was added and the mixture was heated to 65 °C for 18 h. HMPT (1.34 mL, 7.38 mmol) was added and the mixture as stirred at 65 °C for another 4 h before it was concentrated in vacuo. Flash column chromatography (SiO2, dry load on celite, 3–5% DCM in pentane) gave S17 (675 mg, 0.947 mmol, 39%) as a dark yellow solid.

\[ ^1\text{H} \text{ NMR} (600 \text{ MHz, CDCl}_3) \delta 8.37 (dd, J = 8.5, 1.3 \text{ Hz}, 1H), 7.94 (d, J = 1.9 \text{ Hz}, 1H), 7.85 (d, J = 1.9 \text{ Hz}, 1H), 7.82 (d, J = 8.4 \text{ Hz}, 1H), 7.59 (d, J = 8.4 \text{ Hz}, 1H), 7.52 (dd, J = 8.3, 1.9 \text{ Hz}, 1H), 7.48 (ddd, J = 8.3, 6.8, 1.2 \text{ Hz}, 1H), 7.37 (ddd, J = 8.3, 6.8, 1.3 \text{ Hz}, 1H), 7.20 (s, 1H), 6.94 (dd, J = 8.5, 1.9 \text{ Hz}, 1H), 6.55 (d, J = 8.5 \text{ Hz}, 1H), 5.07 (d, J = 16.1 \text{ Hz}, 1H), 5.02 (d, J = 16.1 \text{ Hz}, 1H), 4.22 (p, J = 6.6 \text{ Hz}, 1H), 3.54 (dd, J = 15.0, 5.6 \text{ Hz}, 1H), 2.72 (d, J = 15.1 \text{ Hz}, 1H), 1.37 (d, J = 6.7 \text{ Hz, } 3H), 1.04 (s, 21H); \]
\[ ^{13}\text{C} \text{ NMR} (151 \text{ MHz, CDCl}_3) \delta 156.4, 153.6, 149.6, 140.3, 139.8, 138.9, 136.2, 130.5, 130.2, 129.2, 128.7, 127.6, 127.1, 127.1, 126.7, 125.2, 125.1, 125.1, 123.2, 123.1, 122.3, 120.5, 120.5, 105.0, 101.5, 90.5, 57.4, 45.4, 42.6, 19.7, 18.7, 11.2; \]
\[ \text{HRMS (ESI pos) } m/z \text{ calcd for C}_{33}\text{H}_{36}\text{Br}_2\text{OSi}[\text{M+H}]^+ \text{ 711.12879, found 711.12813.} \]
3,6-Dibromo-9-(2-methyl-5-(prop-2-yn-1-yloxy)-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene (S18)

To a solution of S17 (350 mg, 0.491 mmol) in THF (5.0 mL) at room temperature was added TBAF (1.0 M in THF, 516 μL, 0.516 mmol) dropwise. The mixture was left to stir for 1 h and subsequently separated between H2O and DCM. The aqueous layer was extracted with DCM and the combined organic layers were dried over Na2SO4 and concentrated in vacuo. Flash column chromatography (SiO2, dry load on celite, 3–10% DCM in pentane) gave S18 (188 mg, 0.338 mmol, 69%) as a yellow solid.

7-(Benzo[d]thiazol-2-yl)-N-(3-(4-(((1-(3,6-dibromo-9H-fluorene-9-ylidene)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-5-yl)oxy)methyl)-1H-1,2,3-triazol-1-yl)ethoxy)phenyl)-9,9-diethyl-N-phenyl-9H-fluoren-2-amine (S19)

A Schlenk tube was charged with S18 (37 mg, 66 μmol), S8 (40 mg, 66 μmol) and tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (35 mg, 66 μmol). Anhydrous, degassed (three freeze-pump-thaw cycles) CHCl3 (1.3 mL) was added and the mixture was stirred at 25 °C for 1 h. [Cu(CH3CN)4]PF6 (25 mg, 66 μmol) was added and the reaction was stirred at 25 °C for 16 h before it was concentrated in vacuo. Flash column chromatography (SiO2, dry load on celite, 0–8% EtOAc in DCM) gave S19 (76 mg, 65 μmol, 99%) as a yellow solid.
= 12.0 Hz, 1H), 5.47 (d, J = 12.1 Hz, 1H), 4.77 (t, J = 5.0 Hz, 2H), 4.31 (t, J = 5.0 Hz, 2H), 4.20 (p, J = 6.6 Hz, 1H), 3.54 (dd, J = 15.2, 5.6 Hz, 1H), 2.74 (d, J = 15.1 Hz, 1H), 2.15 – 2.01 (m, 2H), 1.98 – 1.86 (m, 2H), 1.36 (d, J = 6.6 Hz, 3H), 0.45 – 0.33 (m, 6H); \(^{13}C\) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 168.9, 158.8, 157.1, 154.3, 153.5, 152.3, 150.8, 150.0, 149.5, 147.8, 147.6, 144.4, 144.0, 140.3, 139.8, 138.8, 136.2, 135.9, 135.0, 131.7, 130.5, 130.3, 130.2, 129.5, 129.2, 128.2, 127.7, 127.5, 127.1, 127.1, 126.6, 126.5, 125.2, 125.2, 125.1, 124.8, 124.7, 124.3, 123.8, 123.5, 123.1, 123.1, 123.1, 122.3, 121.7, 121.6, 121.2, 120.5, 120.5, 119.6, 119.4, 117.2, 109.8, 108.6, 104.0, 66.4, 62.7, 56.6, 50.1, 45.2, 42.6, 32.7, 19.7, 8.8; HRMS (ESI pos) \(m/z\) calcld for C\(_{68}\)H\(_{54}\)Br\(_2\)N\(_2\)O\(_3\)S [M+H]\(^+\) 1162.23595, found 1162.23765.

9-((1-[(2-3-((7-Benzo[d]thiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)(phenyl)amino)phenoxy)ethyl]-1H-1,2,3-triazol-4-yl)methoxy)-2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-3,6-dicarbonitrile (1)

A Schlenk flask was charged with S19 (11 mg, 9.4 \(\mu\)mol), tBuXPhos Pd G3 (7.5 mg, 9.4 \(\mu\)mol), tBuXPhos (6.7 mg, 16 \(\mu\)mol) and Zn(CN)\(_2\) (6.7 mg, 57 \(\mu\)mol). A degassed (three freeze-pump-thaw cycles) mixture of DMF/H\(_2\)O (99:1, 0.75 mL) was added and the mixture was heated to 70 °C for 3 h. It was then separated between H\(_2\)O and DCM, the aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. Flash column chromatography (SiO\(_2\), dry load on celite, 50–100% DCM in pentane followed by 2–8% EtOAc in DCM) gave 1, (10 mg, 9.4 \(\mu\)mol, quant.) as an orange solid.

\(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.36 (dd, \(J = 8.5, 1.4\) Hz, 1H), 8.14 (d, \(J = 1.5\) Hz, 1H), 8.07 (d, \(J = 1.5\) Hz, 1H), 8.06 – 8.03 (m, 3H), 7.98 (dd, \(J = 7.9, 1.6\) Hz, 1H), 7.94 (s, 1H), 7.88 (d, \(J = 7.9\) Hz, 1H), 7.71 (dd, \(J = 8.2, 1.6\) Hz, 1H), 7.68 (d, \(J = 7.9\) Hz, 1H), 7.61 (d, \(J = 8.2\) Hz, 1H), 7.51 – 7.44 (m, 3H), 7.40 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.20 (s, 1H), 7.17 – 7.10 (m, 5H), 7.08 – 7.02 (m, 2H), 6.78 – 6.70 (m, 2H), 6.68 (t, \(J = 2.3\) Hz, 1H), 6.53 (dd, \(J = 8.2, 2.4\) Hz, 1H), 5.53 (d, \(J = 12.1\) Hz, 1H), 5.50 (d, \(J = 12.1\) Hz, 1H), 4.78 (t, \(J = 5.0\) Hz, 2H), 4.32 (t, \(J = 5.0\) Hz, 2H), 4.26 (p, \(J = 6.5\) Hz, 1H), 3.60 (dd, \(J = 15.3, 5.5\) Hz, 1H), 2.84 (d, \(J = 15.3\) Hz, 1H), 2.12 – 2.00 (m, 2H), 1.98 – 1.83 (m, 2H), 1.42 (d, \(J = 6.7\) Hz, 3H), 0.38 – 0.32 (m, 6H); \(^{13}C\) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 168.8, 160.5, 158.8, 158.5, 154.3, 152.3, 152.3, 150.8, 149.5, 147.8, 147.6, 144.4, 143.6, 143.4, 140.6, 137.9, 137.3, 136.0, 135.0, 131.8, 131.3, 130.5, 130.3, 130.2, 129.5, 128.3, 127.9, 127.4, 126.7, 126.4, 125.9, 125.9, 125.7, 125.2, 125.0, 124.7, 124.4, 124.1, 123.9, 123.8, 123.6, 123.5, 123.2, 123.1, 121.7, 121.6, 121.2, 119.6, 119.5, 119.4, 117.2, 109.7, 109.5, 109.3, 108.5, 104.1, 66.4, 62.8, 56.6, 50.1, 45.7, 42.7, 32.8, 32.7, 20.2, 8.8; HRMS (ESI pos) \(m/z\) calcld for C\(_{70}\)H\(_{64}\)N\(_2\)O\(_3\)S [M+H]\(^+\) 1056.40542, found 1056.40707.
S3. Density Function Theory (DFT) Calculations

Structure optimizations of $1_s$, AF-343 and $2_s$ in the gas phase were performed in Gaussian 16 (B3LYP, 6-311G(d,p)) using the GaussView 5.0 add-on. Figure S4 shows the shape and energy of the obtained frontier orbitals.

The envisioned resonance energy transfer mechanism requires the frontier orbitals of the chromophores making up the sensitizer and motor domains to be confined to their respective parts of the molecule as seen in Fig. S4. It should be noted that the HOMO–1 and LUMO orbitals of $1_s$ are closely related to the HOMO and LUMO orbitals of $2_s$ whereas a similar relationship exists between HOMO and LUMO+1 of $1_s$ and HOMO and LUMO of AF-343. Due to the spatial separation of these two sets of orbitals in $1_s$, photoexcitation is only allowed for HOMO–1→LUMO and HOMO→LUMO+1 transitions.

Fig. S4. Frontier orbitals of $2_s$, AF-343 and $1_s$ obtained by DFT (B3LYP, 6-311G(d,p)).
S4. NMR Studies

S4.1. NOESY and ROESY NMR

NOESY spectra of compound 2 before and after irradiation to PSS with a 455 nm LED were recorded in CDCl₃ to assign alkyl proton signals of the stable and metastable isomers (Fig. S5 and S6).

Fig. S5. NOESY NMR of 2 in CDCl₃. Conditions: 2.5·10⁻³ M, 25 °C.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

Fig. S6. NOESY NMR of 2 in CDCl$_3$ after irradiation to PSS with a 455 nm LED. Conditions: 2.5·10$^{-3}$ M, 25 °C.

A ROESY spectrum of compound 1, was recorded in CDCl$_3$ to determine the regioselectivity of the click reaction (Fig. S7).
**Fig. S7. ROESY NMR of 1_s in CDCl_3. Conditions: 2.5·10^{-3} M, 25 °C.**

**S4.2. Determination of PSS Ratios**

A 1.0·10^{-3} M solution of 1_s or 2_s in CDCl_3 was prepared and transferred into an NMR tube which was subsequently fitted with a glass fiber cable for *in situ* irradiation. The sample was placed in a Varian Unity Plus 500 NMR spectrometer and cooled to −10 °C. ¹H NMR spectra were recorded before irradiation and after irradiation to PSS using an appropriate LED. An irradiation time of 120 min was used to ensure PSS would be reached at the comparably high concentration of these samples. This time was not optimized. Ratios of metastable:stable isomers at PSS were determined by comparing the integrals of the two signals corresponding to H^d. The sample was then warmed to room temperature for 150 min to allow for complete thermal helix inversion (THI) before recording another ¹H NMR spectrum at −10 °C. Spectra stacks are shown in Fig. S8 and S9 and PSS ratios of metastable:stable isomers are shown in Table S1.
Fig. S8. Stack of $^1$H NMR spectra of 1 before irradiation with a 455 nm LED (1$_a$), at PSS and after completed THI. Conditions: $1.0 \cdot 10^{-3}$ M, CDCl$_3$, –10 °C.

Fig. S9. Stack of $^1$H NMR spectra of 2 before irradiation with a 455 nm LED (2$_a$), at PSS and after completed THI. Conditions: $1.0 \cdot 10^{-3}$ M, CDCl$_3$, –10 °C.

Figures S8 and S9 show the formation of one new set of signals upon irradiation with 455 nm light corresponding to the formation of metastable isomers 1$_m$ and 2$_m$, respectively. Upon standing at rt for prolonged periods of time the original spectra were recovered confirming complete THI had occurred.
Table S1. Summary of ratios of metastable:stable isomers at PSS.
Summary of ratios of metastable:stable isomers of 1s and 2s at PSS obtained by irradiating NMR samples with LEDs of different wavelengths until no further change was observed.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>1m:1s</th>
<th>2m:2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>365</td>
<td>58:42</td>
<td>64:36</td>
</tr>
<tr>
<td>395</td>
<td>62:38</td>
<td>86:14</td>
</tr>
<tr>
<td>455</td>
<td>71:29</td>
<td>76:24</td>
</tr>
<tr>
<td>470</td>
<td>60:40</td>
<td>67:33</td>
</tr>
</tbody>
</table>

The ratio of 1m:1s at the photostationary state (PSS) was found to be similar to that of 2 for irradiation with 365 nm, 455 nm and 470 nm LEDs; however, significant differences were observed at 395 nm (Table S1) coinciding with the absorption maximum of the 2PA sensitizer domain (Fig. S11A). The lower percentage of metastable isomer (1m) in the PSS mixture of 1 can be explained by taking into account energy transfer from the sensitizer unit to the metastable isomer of the motor domain leading to photochemical back-reaction. This provides a first indication that energy transfer from the 2PA sensitizer to the motor unit is taking place. One might also expect similar behavior in the case of 365 nm irradiation. However, looking at the absorption spectrum of AF-343 (Fig. S11A) one can deduce that irradiation with 365 nm light, contrary to 395 nm light, also leads to the population of excited states higher than S1. The fast energy transfer from the sensitizer to the motor in 1 means that this energy could be transferred before the sensitizer relaxes to the S1 state. This would influence how well the excited state energy of the sensitizer at the moment of the energy transfer matches with those of the stable and metastable isomers of 1, respectively, shifting the observed PSS in favor of the latter.
S4.3. Comparison of $^1$H NMR Spectra

Figure S10 shows a comparison of the aromatic regions of the $^1$H NMR spectra of $1_s$, $2_s$ and AF-343 recorded at 25 °C in CDCl$_3$.

![Comparison of $^1$H NMR spectra of $1_s$, $2_s$ and AF-343. Conditions: CDCl$_3$, 25 °C.](image)

As can be seen in Fig. S10 the aromatic region of the $^1$H NMR spectrum of $1_s$ is largely simply the sum of the spectra of $2_s$ and AF-343. A significant deviation was found only for $H^a$ which occupies the position on the motor unit ortho to the anchor point of the linker. The signal corresponding to the triazole proton $H^b$ is also highlighted. Put together these observations rule out significant interactions between the π-systems of motor and sensitizer unit in $1_s$.

S5. Steady-State Absorption

S5.1. Absorption Spectra

$1.0 \cdot 10^{-5}$ M solutions of $1_s$, AF-343 and $2_s$ in CHCl$_3$ were prepared and UV-vis spectra were recorded at 20 °C. $1_s$ and $2_s$ were afterwards irradiated with a 455 nm LED until no further change was observed indicating PSS (Fig. S11). Spectra of pure metastable compounds were calculated using the ratios of stable:metastable isomers at PSS obtained by $^1$H NMR (see Section 4.2).
Fig. S11. Absorption spectra of 1, AF-343 and 2. A Absorption spectra of 1s, AF-343 and 2s and the sum of the latter two. Conditions: 1.0·10⁻⁵ M, CHCl₃, 20 °C. B Measured spectra of 1, before and after irradiation to PSS with a 455 nm LED and calculated spectrum of 1m. Conditions: 1.0·10⁻⁵ M, CHCl₃, 20 °C. C Measured spectra of 2, before and after irradiation to PSS with a 455 nm LED and calculated spectrum of 2m. Conditions: 1.0·10⁻⁵ M, CHCl₃, 20 °C.

Figure S11A reveals the steady-state absorption spectrum of 1s in the region >250 nm to be the almost exact sum of a 1:1 mixture of 2s and AF-343 ruling out significant interactions between the π-systems of the motor and sensitizer units. The band corresponding to HOMO–LUMO transition in absorption spectra of the metastable isomers 1m and 2m (Fig. S11B and C) is more red-shifted compared to the corresponding stable isomers, 1s and 2s, respectively.

S5.2. Isomerization Studies

1.0·10⁻⁵ M solutions of 1s and 2s in CHCl₃ were prepared. UV-vis spectra were recorded at 20 °C before and during irradiation with a 455 nm LED (Fig. S12A and C). The light source was removed and spectra were recorded during THI until no further change was observed (Fig. S12B and D).
Fig. S12 Isomerization studies on compounds 1 and 2. Conditions: 1.0·10^{-5} M, CHCl₃, 20 °C. A Photochemical (455 nm LED) formation of 1ₘ from stable isomer 1ₛ. B Thermal recovery of 1ₛ. C Photochemical (455 nm LED) formation of 2ₘ from stable isomer 2ₛ. D Thermal recovery of 2ₛ. E Fatigue study on compound 1. Conditions: 1.0·10^{-5} M, CHCl₃, 45 °C, 455 nm LED.

Identical spectral changes with clean isosbestic points at 471 nm were observed for both the photochemical and thermal isomerization of 1 and 2 (Fig. S12). This indicates a clean conversion of the stable to the metastable isomers and vice versa and demonstrates that the motor unit in 1 behaves analogous to the free motor 2.

To study the fatigue resistance of 1, a cuvette was charged with 2.5 mL of a 1.0·10^{-5} M solution of 1 in CHCl₃ and placed in the sample holder of a UV-vis spectrophotometer which had been warmed up to 45 °C. An absorption spectrum was recorded before the sample was irradiated to PSS using a
455 nm LED. Another spectrum was recorded, the sample was kept at 45 °C in the dark until no more spectral change was observed. This sequence of irradiating to PSS and subsequently waiting for complete thermal recovery was repeated five more times. The absorbance of the sample at 435 nm at the beginning of the study and after each subsequent step of irradiation as well as thermal recovery was plotted (Fig. S12E).

Only minor changes in absorption behavior were observed during this study confirming that 1 can undergo more than six 180° rotations without significant signs of fatigue.

### S5.3. Eyring Plots

A 1.0·10⁻⁵ M solution of the according molecular motor in CHCl₃ was prepared. Samples of each molecular motor at five different temperatures were at first irradiated to PSS using a 455 nm LED and the subsequent THI back to the stable isomer was followed on a UV-vis spectrophotometer. The absorbance at 520 nm was plotted over time (Fig. S13A and B).

Rate constants, \( k \), were determined by fitting a 1ˢᵗ order rate law. Thermodynamic parameters for the formation of the transition state were obtained by fitting the linearized form of the Eyring equation (Fig. S13C, Table S2).

![Eyring plots](image)

**Fig. S13. Eyring study of the thermal isomerization of 1ₘ and 2ₘ.** Conditions: 1.0·10⁻⁵ M, CHCl₃, 455 nm LED. A Change of absorbance at 520 nm observed over the course of the THI of 1ₘ at different temperatures. B Change of absorbance at 520 nm observed over the course of the THI of 2ₘ at different temperatures. C Linearized Eyring plots for THI of 1ₘ and 2ₘ. Dotted lines represent 95% confidence intervals.
Table S2. Summary of thermodynamic parameters of THI of metastable isomers 1\textsubscript{m} and 2\textsubscript{m}.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta^\ddagger G(20 , ^\circ\text{C})$ (kJ·mol\textsuperscript{-1})</th>
<th>$\Delta^\ddagger H(20 , ^\circ\text{C})$ (kJ·mol\textsuperscript{-1})</th>
<th>$\Delta^\ddagger S(20 , ^\circ\text{C})$ (J·mol\textsuperscript{-1}·K\textsuperscript{-1})</th>
<th>$\tau_{1/2}(20 , ^\circ\text{C})$ (min)</th>
<th>$\tau(20 , ^\circ\text{C})$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsubscript{m}</td>
<td>91.9 ± 0.1</td>
<td>87.5 ± 1.0</td>
<td>−14.8 ± 3.3</td>
<td>44.3 ± 0.5</td>
<td>63.9 ± 0.7</td>
</tr>
<tr>
<td>2\textsubscript{m}</td>
<td>91.7 ± 0.2</td>
<td>86.6 ± 0.9</td>
<td>17.3 ± 3.3</td>
<td>41.7 ± 1.0</td>
<td>60.2 ± 1.5</td>
</tr>
</tbody>
</table>

A standard Gibbs free energy of activation ($\Delta^\ddagger G^*$) of 91.9 ± 0.1 kJ·mol\textsuperscript{-1} was found for 1\textsubscript{m}, within error of that of the parent motor 2\textsubscript{m} (91.7 ± 0.2 kJ·mol\textsuperscript{-1}) (Fig. S13C). This fits well with the limited influence of an increased size of substituents on $\Delta^\ddagger G^*$ observed in earlier studies\textsuperscript{15}.

S5.4. Quantum Yields of Isomerization

At first, the photon flux of a 445 nm LED was determined using ferrioxalate actinometry\textsuperscript{16} following a modified standard protocol\textsuperscript{17}. An aqueous H\textsubscript{2}SO\textsubscript{4} solution (0.05 M) containing freshly recrystallized K\textsubscript{3}[Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}] (41 mM, 2 mL, 1 cm quartz cuvette) was irradiated at 20 °C for a given period of time in the dark with a 445 nm LED. The solution was then diluted with 1.0 mL of an aqueous H\textsubscript{2}SO\textsubscript{4} solution (0.5 M) containing phenanthroline (1 g L\textsuperscript{-1}) and NaOAc (122.5 g L\textsuperscript{-1}) and left to react for 10 min. The absorption at $\lambda = 510$ nm was measured and compared to an identically prepared non-irradiated sample. The concentration of [Fe(phenanthroline)]\textsuperscript{2+} complex was calculated using its molar absorptivity ($\varepsilon = 11100$ M\textsuperscript{-1}·cm\textsuperscript{-1}) considering the dilution. The quantity of Fe\textsuperscript{2+} ions (expressed in mol) was plotted versus time (expressed in seconds) and the slope, obtained by linear fit of the data points to the equation $y = ax + b$, equals the rate of formation of the Fe\textsuperscript{2+} ion at 445 nm. This rate can be converted into the photon flux ($I$) by dividing it by the quantum yield of [Fe(phenanthroline)]\textsubscript{3}\textsuperscript{2+} complex ($\phi_{445\text{nm}} = 1.06$) at 445 nm and by the probability of photon absorption at 445 nm of the Fe\textsuperscript{3+} complex (approximated to 1 as we were working in the total absorption regime). The obtained photon flux was $I = 2.62073 \cdot 10^{-5}$ E s\textsuperscript{-1}.

For the quantum yield (QY) determination, $1.0 \cdot 10^{-5}$ M solutions of 1\textsubscript{s} and 2\textsubscript{s} in CHCl\textsubscript{3} were prepared. Samples of 2.0 mL were irradiated under conditions identical to those used for the ferrioxalate actinometry to maintain the same photon flux, leading to the formation of the corresponding metastable isomers. These measurements were performed in triplicates for compounds 1 and 2. Figure S14 shows the plots of the obtained kinetic traces at 540 nm.
**ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light**

**Fig. S14. QY determination of compounds 1 and 2.** Plots showing the kinetic traces at 540 nm obtained during irradiation of CHCl₃ solutions of 1 (A) and 2 (B). Conditions: 1.0·10⁻⁵ M, CHCl₃, 20 °C, 445 nm LED.

QYs of isomerization were determined using the initial slope approximation. QYs for the formation of 1ₘ and 2ₘ from the corresponding stable isomers were determined as 13.4 ± 0.4% and 13.9 ± 0.8%, respectively. The fact that they are identical within the experimental margin of error is another reflection of the independent behavior of the motor chromophore in 1.

**S6. Difference Absorption Spectroscopy**

The output light source of LED (455 nm) and laser beam of 8 mm in diameter irradiated a 1 cm quartz cuvette, containing the studied compounds dissolved in chloroform (~1.7·10⁻⁵ M), for 5 min and 30 min, respectively. The irradiation time at 800 nm of 30 min was chosen close to the upper limit imposed by the back reaction with a half-life of ~40 min. The fiber output of the LED was placed at a distance of about 2 cm from the sample cell.

For intensity dependence experiments with two-photon excitation, the irradiation intensity was varied between 0.15 W/cm² and 0.44 W/cm²; in all other experiments it was fixed at 0.3 W/cm². Due to strong absorption under one-photon excitation, the irradiation power from the LED in intensity dependence experiments was kept low (≤1.2 mW) and the irradiation time was reduced to 1 min to avoid reaching the photostationary state.

The absorption of the samples was recorded before irradiation and from 10 s (the time to transfer the cuvette from the place of irradiation to the spectrometer) after irradiation at different times up to two and half hours; all in dark. Finally, difference absorption (ΔOD) spectra were obtained by subtracting the absorption spectra before irradiation from the ones after irradiation. As the difference spectra are extremely sensitive to temperature (Fig. S15), great care was taken to keep the temperature stable at ~22 °C over the course of these experiments.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

**Fig. S15.** Temperature dependence of the absorption spectrum of 1s. Absorption spectra of 1s ($c = 1.0 \cdot 10^{-5}$ M) in CHCl₃ at different temperatures. The inset shows absorption spectra of 1s at different temperatures (20–50 °C) subtracted from the one at 10 °C.

### S6.1. Difference Absorption Spectra

Figure S16 shows the difference absorption ($\Delta OD$) spectra of 1, 2, AF-343 and a mixture of 2 and AF-343 (denoted as TPA+M hereafter) under one-photon, 455 nm, and two-photon, 800 nm, irradiation, respectively.

**Fig. S16.** Difference absorption spectra from one- and two-photon irradiation. Difference absorption ($\Delta OD$) spectra before and right after (~10 s) one-photon (A) and two-photon (B) irradiation of 1s (green), TPA+M (violet), 2s (blue) and AF-343 (red). One-photon radiation was provided by a 455 nm LED for 5 min. Two-photon radiation at 800 nm was provided by a laser system for 30 min. The spectra are offset by 0.1 and 4 \cdot 10^{-3} in A and B, respectively. The molar concentration of all compounds was set to be similar as ~1.7 \cdot 10^{-5} M with CHCl₃ as the solvent.

The $\Delta OD$ spectra of 1 and 2 from one-photon, 455 nm irradiation are virtually identical, indicating the formation of metastable state isomers (1m and 2m, respectively). This signifies that both systems are operational under one-photon excitation so that it is difficult to factorize the contribution of the sensitizer antenna. The linear dependence on the excitation power confirms a one-photon character of the excitation (Fig. S17A). Not surprisingly, a simple mixture of AF-343 and 2s (referred to as TPA+M) with no chemical attachment between the two, shows a similar spectrum (violet curves in
Fig. S16). In the dark, metastable isomer $1_m$ over time reverts back to $1_s$, leading to recovery of the original spectrum following an overall 180° rotation (to be discussed in detail below).

**Fig. S17. Power (intensity) dependence of $\Delta OD$ of 1 under one-photon (two-photon) irradiation.** Difference absorption ($\Delta OD$) spectra of 1 under one-photon, 455 nm (A) and two-photon, 800 nm (B) irradiation with different irradiation power and intensity, respectively. For one-photon (two-photon) irradiation, the samples were measured after irradiation with a 455 nm LED for 1 min (30 min) and keeping in the dark for 10 s. The insets show the dependences of $\Delta OD$ of 1 averaged in the 500–520 nm spectral window on the irradiation power (intensity). The black lines show the fits to a power law function, $y = ax^n$ with $n = 0.97 \pm 0.03$ and $n = 2.0 \pm 0.2$ for one- and two-photon irradiation, respectively. The error bars refer to the standard deviation. The molar concentration of 1 was $\sim 1.7 \cdot 10^{-5}$ M with CHCl$_3$ as the solvent for both one- and two-photon irradiations.

Under two-photon, 800 nm irradiation, neither the motor core $2_s$ nor the sensitizer (AF-343) show any change in the $\Delta OD$ spectrum (Fig. S16B). In contrast, the response of $1_s$ is very similar to that under one-photon excitation (Fig. S16A) but it has a quadratic dependence on the excitation intensity (Fig. S17B). This provides clear evidence that the NIR excitation is accumulated by the sensitizer and further transferred to the motor core, making it rotate. The time evolution of the signal following irradiation was also similar to the one-photon excitation case (see below). However, a control experiment on the simple mixture TPA+M yielded a similar response, albeit with a factor of 2 lower amplitude. To reveal the mechanism of such a response, we performed concentration dependence experiments.

**S6.2. Concentration Dependence**

The reasoning behind the concentration dependence experiments is as follows: For the chemically attached motor core and sensitizer, the amount of metastable isomer being formed upon irradiation is linearly proportional to the concentration of the molecules (assuming low concentrations). For a simple mixture of the two compounds, if the concentration of the motor core or sensitizer or both is low enough to exclude diffusion-mediated ET, the only alternative mechanism is photon-mediated, i.e., the sensitizer after two-photon excitation emits an anti-Stokes photon which is subsequently re-absorbed by the motor core (Fig. S18A). The probability of both absorption and re-absorption is proportional to concentration; therefore, the amount of metastable-state isomer is proportional to the square of concentration. Therefore, the concentration dependence allows distinguishing between the two mechanisms: direct energy transfer and photon-mediated energy transfer.
To calculate the concentration dependence of a TPA+M sample more realistically (i.e., including propagation of the excitation and re-emitted PL photons), we performed the following Monte-Carlo simulations. In a simulation cube with a grid of 500x500x500 cells we randomly placed “chromophores” and “molecular motors”, both at the same concentration. “Excitation photons” arrived orthogonally to one side of the cube; the coordinates of the photons were also random. If the coordinates of a photon and a chromophore coincided, the chromophore was considered excited and produced a PL photon propagating into a random direction in the solid angle of 4π. If the coordinates of a molecular motor coincided with those of the propagating PL photon, the motor was considered activated. The procedure was repeated 10 times, and the number of PL photons and motors excited were averaged (Fig. S18B). As expected, at low concentrations dependences of the number of PL photons and motors activated follow linear and quadratic functions, respectively. At higher concentrations, the effect of depletion of the flux of photons upon propagation begins to become pronounced. For the excitation photons, the dependence is perfectly described by the Beer–Lambert law; however, for the activated motors the situation is more complex as the pathlength between emission and absorption events becomes to be random. This leads to an additional factor in front of the optical density.

Fig. S18. Energy transfer mechanism in TPA+M. A Schematic of photon-mediated energy transfer between the dye AF-343 and motor core 2. CI stands for conical intersection (see Fig. 4.1 in the main text of Chapter 4). B Monte-Carlo simulations of the concentration dependence for the formation of 2m in TPA+M. Black squares and red dots show the number of PL photons and excited motors, respectively. Dashed lines represent fits to a power function (y = Ax^n) at low (< 2 \cdot 10^{-3}) concentration with n = 0.97 and 1.98 for the number of PL photons and excited motors, respectively. Solid lines show fits to the Beer–Lambert law A_1(1 - 10^{10 \Delta OD}) and A_2(1 - 10^{10 \Delta OD})^2 with a = 1.13 for the number of PL photons and excited motors, respectively. The inset shows the same dependences in a linear scale.

Figures S19A and S19B show experimental ΔOD spectra of samples of 1 and TPA+M in CHCl₃, respectively, at different molar concentrations. The molar concentrations of 1 and TPA+M were varied with the same ratio so that ΔODs of 1 and TPA+M can be compared directly. The other experimental conditions such as irradiation time and light intensity were kept similar for each measurement. As expected, ΔOD of 1 at 510 nm decreases linearly with decreasing concentration (Fig. S19A, inset). In contrast, ΔOD of TPA+M at 510 nm decreases much faster, in an almost quadratic fashion (Fig. S19B, inset), as expected for the photon-mediated mechanism with moderate absorption (see Fig. S18B). Note that propagation effects are more pronounced for motor activation than for PL photons produced due to a longer propagating distance. This proves that the absorption-emission-reabsorption mechanism for energy transfer between chemically non-bound motor cores and sensitizers is possible and indeed observed in a sample of TPA+M. In Section 8, based on the time-resolved PL quenching of the sensitizer emission we will further demonstrate that direct resonance energy transfer (RET) is the dominant mechanism for the chemically-attached motor core and sensitizer (more specifically, strong
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

quenching for RET and no quenching for photon-mediated mechanism). This also excludes the diffusion-mediated mechanism mentioned above, where the two-photon excited chromophore and the motor diffuse towards each other with the Förster resonance energy transfer taking place when they are sufficiently close.

![Graph A](Image)

**Fig. S19.** Concentration dependence of $\Delta OD$ of 1 and TPA+M. Difference absorption ($\Delta OD$) spectra of 1 (A) and TPA+M (B) after two-photon irradiation (at 800 nm for 30 min and keeping in the dark for 10 s) with different molar concentrations in CHCl$_3$. The irradiation intensity was kept at 0.3 W/cm$^2$. The insets show the dependence of $\Delta OD$ averaged in the 500–520 nm spectral window on the molar concentration. The black lines show the fits to a power law function, $y = ax^n$ with $n = 0.8 \pm 0.2$ and $n = 1.6 \pm 0.3$ for 1 and TPA+M, respectively. Some deviations from the exact quadratic scaling in the latter is explained by the propagation effects under high optical density conditions (see Fig. S18B, inset). The error bars refer to the standard deviation.

To finalize this Section, we would like to make a few remarks concerning the photon-mediated energy transfer observed above. Potentially, this opens up new possibilities for utilizing IR radiation for driving molecular motor as no chemical linkage between the motor and IR light absorbing chromophore is required. However, there are a number of drawbacks inherently associated with this approach. First, the experimental conditions here were deliberately chosen close to ideal, and such conditions might not be compatible with bio-functionalities. Second, by using two separate compounds one has to solve the problem of co-localisation in the relevant parts of the studied organism. Third, under biological conditions other species will compete for the reabsorption of PL and due to potential side-effects caused by these compounds working under low conditions is crucial. Nonetheless, if the chemical attachment between the chromophore and motor is not feasible or impedes the motor functionality (e.g. in the case of upconverting nanoparticles$^{20}$), one might use this scheme for IR powering of the molecular motor.

S6.3. Time Evolution of $\Delta OD$ Spectra

To prove that the photogenerated metastable state isomers proceed to a second, identical stable state isomers, $\Delta OD$ spectroscopy measurements of 1 at different times after irradiation and keeping in the dark were performed for one- and two-photon excitation (Fig. S20). $\Delta OD$s at 510 nm (where the highest $\Delta OD$ signal occurs) over time are plotted in the insets of Fig. S20. The $\Delta OD$s at 510 nm under one-and two-photon irradiation decrease with a similar lifetime of $\sim 45$ min (temperature 22 °C), indicating that 1 proceeds to 1. Hence, we conclude that 1 functions properly under one-and two-photon irradiation.
**ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light**

Fig. S20. Time evolution of $\Delta OD$ spectra of 1 under one- and two-photon irradiation. Time evolution of difference absorption ($\Delta OD$) spectra of 1 after one-photon (A) irradiation (at 455 nm for 5 min and keeping in the dark between 10 s and 90 min) and two-photon (B) irradiation (at 800 nm for 30 min and keeping in the dark between 10 s and 160 min). The data in B are equivalent to Fig. 4.2b of the main text of Chapter 4. The magenta arrows depict the thermal recovery of 1 via thermal helix inversion from 1m. The insets show the respective decrease of $\Delta OD$ averaged in the 500–520 nm spectral window over time together with the exponential fit (black lines), $y = ae^{-t/\tau}$, with $\tau = 48 \pm 1$ min and $\tau = 43 \pm 3$ min for 1 under one- and two-photon excitation, respectively. The error bars refer to the standard deviation. The molar concentration of 1 was $\sim 1.7 \cdot 10^{-5}$ M with CHCl$_3$ as the solvent.

S7. Transient Absorption (TA) Spectroscopy

To study the dynamics of the excitation energy transfer and the subsequent formation of metastable isomer (as observed in the difference absorption data), fs TA spectroscopy was applied. Samples of AF-343, 2, and 1, in chloroform were used for the measurements under one- and two-photon excitation conditions at 400 nm and 800 nm, respectively. The optical densities at 400 nm of AF-343, 2, and 1, were 0.58, 0.14 and 0.71, respectively, corresponding to a concentration of $\sim 6 \cdot 10^{-4}$ M.

S7.1. TA Maps and Spectra Under One-Photon Excitation

Figure S21 shows TA maps and spectra of AF-343, 2, and 1 under one-photon excitation at 400 nm. The TA map of AF-343 (Fig. S21A) shows an intense, positive $\Delta OD$ band between 500 nm and 680 nm up to 2.6 ns and a weak, negative $\Delta OD$ region below 525 nm which begins to appear after $\sim 20$ ps. The former band is assigned to the excited state absorption (ESA) of AF-343 while the latter one is assigned to stimulated emission (SE) as PL of AF-343 occurs in this region (Fig. S28). At first, SE is counterbalanced by ESA but within the next 20 ps the balance shifts in favor of SE due to dynamical Stokes shift (Fig. S21D). For longer times (>20 ps), the relaxed ESA band remains unchanged in shape up to 2.6 ns. These results are in good agreement with the PL dynamics of AF-343 (see Section 8.2). It is worth noting that there is a compensation point around $\sim 525$ nm where the ESA is balanced with the SE.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

Fig. S21. TA maps and spectra under one-photon excitation. TA maps (upper panel) and transient spectra (lower panel) of AF-343 (A, D), 2 (B, E) and 1 (C, F) under one-photon excitation at 400 nm. The black arrows in D depict the dynamical Stokes shift of AF-343. The TA spectra were obtained from the TA maps by averaging the spectral slices at different times (as shown in the legends). The molar concentration of all compounds was set to be similar as ~6 \times 10^{-4} M with CHCl₃ as the solvent.

TA map of 2 (Fig. S21B) shows two intense ΔOD regions with a positive signal between 500 nm and 600 nm and a negative signal between 600 nm and 700 nm, respectively. They are assigned to ESA and SE of 2, respectively. The SE band vanishes completely within 1 ps while the ESA exhibits a much longer decay (Fig. S21E); the latter is consistent with the previous studies on a similar motor^{12,21}.

TA map of 1 (Fig. S21C) shows an intense, positive ΔOD band between 500 nm and 680 nm, similar to the ESA band of AF-343. However, this band decays much faster as compared to that of AF-343 (Fig. S21F).

The signal-to-noise ratio of the spectrometer-based detection was not adequate for two-photon excitation with sufficiently low excitation intensity which avoids photooxidation and photodegradation. Therefore, we switched to a more sensitive mode of detection based on a single photodiode with an interference filter in front of it, and a lock-in amplifier. Two wavelengths were selected based on the spectrally resolved one-photon excitation (Fig. S21): 620 nm near the maximum of the excited-state absorption of AF-343 and far from any 2 response, and 510 nm, where the strongest spectral change of the photogenerated metastable motor isomer occurs. To facilitate direct comparison between one- and two-photon excitation, we also repeated the one-photon excitation experiments with single-wavelength lock-in detection.

S7.2. TA Transients at 620 nm

Figure S22 shows TA traces of AF-343, 2 and 1 under one-photon (400 nm) and two-photon (800 nm) excitation at a probe wavelength of 620 nm. This probe wavelength is near the maximum of the excited-state absorption of AF-343 (Fig. S21A) and far from any 2 response (Fig. S21B), which means that the TA trace at this particular wavelength shows exclusively the excited-state dynamics of AF-343. Linear and quadratic dependences of ΔOD of AF-343 and 1 on the excitation intensity (Fig. S23) confirm the one- and two-photon absorption at 400 nm and 800 nm, respectively.
The 620 nm TA traces of **AF-343** under one- and two-photon excitation show an intense, long-lived signal. This result is in good agreement with time-resolved PL data (see Section 8.2). The kinetic traces of **AF-343** were fitted to four exponential decay components with the decay times provided in Table S3. The first two fastest decay components are attributed to the combined vibrational-solvent relaxation (dynamical Stokes shift), as discussed for the TA maps (Section 7.1). As polarization of the pump and probe beams was set parallel to each other, rotational contribution of the sensitizer with \( \tau_3 \approx 190 \) ps is also possible. The longest time component is assigned to the \( S_1 \) lifetime of **AF-343**.

The TA trace at 620 nm of **2** under one-photon excitation shows a negative signal (within 0.7 ps) followed by a positive signal. These signals are assigned to the SE and ESA, respectively, as discussed in the TA maps (Section 7.1). No observable signal of **2** under two-photon excitation at 800 nm was found. This result is consistent with the difference absorption data (Fig. S16) discussed above.

![Fig. S22. TA transients at 620 nm.](image) Solvent corrected TA kinetic traces of **AF-343** (red), **2** (blue) and **1** (green) at 620 nm probe under one-photon, 400 nm, (A) and two-photon, 800 nm, (B) excitation. The data in B are equivalent to Fig. 4.3 of the main text of Chapter 4. The gray curves represent the fits to exponential functions (the fitting functions and parameters are summarized in Table S3). The inset in B depicts the \( \Delta OD \) dependence of **AF-343** on the excitation intensity at a delay of 10 ps. The black line shows the fit to a power-law function \( y = ax^n \) with \( n = 1.9 \pm 0.1 \). The excitation intensities for one-photon and two-photon excitation were 0.13 W/cm\(^2\) and 9 W/cm\(^2\), respectively. The molar concentration of all compounds was set to be similar as \( \sim 6 \cdot 10^{-4} \) M with CHCl\(_3\) as the solvent.

The TA kinetics at 620 nm for both one-photon and two-photon excitations of **1** were substantially shortened indicating quenching of the excited state of the sensitizer (see also Section 8). The 620 nm traces of **1** under one-photon and two-photon excitations were fitted to three exponential decay components (decay times are provided in Table S3). The shortest time component of 1.5 ps (share of \( \sim 88\% \)) corresponds to the depopulation of the excited state of the sensitizer and is therefore assigned to the energy transfer from the sensitizer (to the motor core). It is worth noting that the timescale for energy transfer is faster than the excited-state equilibration time of the sensitizer, indicating that energy transfer to the motor core occurs before the sensitizer relaxes vibrationally. The second component of \( \sim 50 \) ps (share of \( \sim 7\% \)) is also attributed to the energy transfer which occurs most likely from less favorable conformations. Finally, the excited state of the remaining sensitzers – i.e., those which have not undergone energy transfer (share of \( \sim 5\% \)) – relaxes at a 1.5 ns time scale which is attributed to the \( S_1 \) lifetime. Hence, we conclude that excitation energy transfer away from the sensitizer (presumably to the motor core) occurs mainly within \( \sim 1.5 \) ps with an efficiency of \( \sim 90\% \).
The TA kinetics of AF-343 and 1 at 620 nm under one-photon, 400 nm, and two-photon, 800 nm, excitation were fitted to exponential functions convoluted with a Gaussian distribution (Eq. S2).

\[ y = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} \otimes \sum_i a_i e^{-\frac{t}{\tau_i}} \]  

(Eq. S2)

where \( \sigma \) is the standard deviation of the Gaussian distribution, and \( a_i \) and \( \tau_i \) are the amplitude and decay time of the \( i^{th} \) exponent, respectively. The fitting parameters for TA kinetic traces at 620 nm are listed in Table S3.

Table S3. Fitting parameters for TA transients at 620 nm. Summary of the decay times and amplitudes of 620 nm TA traces of AF-343 and 1 under one-photon (400 nm) and two-photon (800 nm) excitation. The sum of all amplitudes is normalized to unity.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AF-343</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One-photon excitation</td>
<td>Two-photon excitation</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>120 ± 30 fs</td>
<td>100 ± 30 fs</td>
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<tr>
<td>( a_1 )</td>
<td>0.24</td>
<td>0.25</td>
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<tr>
<td>( \tau_1 )</td>
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<td>0.9 ± 0.2 ps</td>
</tr>
<tr>
<td>( a_2 )</td>
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<td>0.28</td>
</tr>
<tr>
<td>( \tau_2 )</td>
<td>9 ± 1 ps</td>
<td>11 ± 1 ps</td>
</tr>
<tr>
<td>( a_3 )</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>( \tau_3 )</td>
<td>200 ± 10 ps</td>
<td>190 ± 10 ps</td>
</tr>
<tr>
<td>( a_4 )</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td>( \tau_4 )</td>
<td>1950 ± 100 ps</td>
<td>1525 ± 75 ps</td>
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</table>

S7.3. Intensity Dependence at 620 nm

To prove that TA kinetics at 620 nm of AF-343 and 1 follow one- and two-photon absorption processes at 400 nm and 800 nm, respectively, TA measurements with various excitation intensities were performed (Fig. S23). The dependences of the TA response at 100 ps and 18 ps for 1 and AF-343, respectively, on the excitation intensity are plotted in the insets of Fig. S23. At this time, all transient processes (the vibrational/solvent relaxation as for AF-343 or the energy transfer as for 1) have been completed. For 1, we also analyzed the early time of 1 ps when the energy transfer occurs. The fittings of the TA response as a function of the excitation intensity clearly show linear and quadratic dependences for one- and two-photon absorption processes at 400 nm and 800 nm, respectively. Fitting parameters are summarized in Table S4.
Fig. S23. Intensity dependence of TA signals at 620 nm under one- and two-photon excitation. TA traces of AF-343 (A, B) and 1 (C, D) at 620 nm under one-photon, 400 nm, (left panel) and two-photon, 800 nm, (right panel) excitation with different excitation intensities. The black arrows depict increasing extents of excitation. The insets show the $\Delta OD$ dependence of AF-343 and 1 averaged in the 0.8–1.2 ps interval (open dots) and in the 98–102 ps interval (filled dots) on the excitation intensity (the data in B in for AF-343 were averaged in the 17–19 ps interval instead of the 98–102 ps interval). The black lines show the fits to a power-law function $y = ax^n$ with $n$ summarized in Table S4. The transients were not corrected for the early-time solvent contribution as the signal intensities are analyzed at later times. The error bars refer to the standard deviation. The molar concentration of all compounds was set to be similar as $~6 \times 10^{-4}$ M with CHCl$_3$ as the solvent.

Table S4. Fitting parameters for intensity dependence of TA signals at 620 nm. Summary of $n$ values for the fits of the dependence of $\Delta OD$ on the excitation intensity at different times.

<table>
<thead>
<tr>
<th>Delay time</th>
<th>One-photon excitation</th>
<th>Two-photon excitation</th>
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<tr>
<td></td>
<td>AF-343</td>
<td>1</td>
</tr>
<tr>
<td>1 ps</td>
<td>-</td>
<td>0.97 ± 0.01</td>
</tr>
<tr>
<td>18 ps</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 ps</td>
<td>1.07 ± 0.01</td>
<td>0.94 ± 0.04</td>
</tr>
</tbody>
</table>
S7.4. TA Transients at 510 nm

Figure S24 shows TA kinetic traces of AF-343, 2 and 1 under one-photon (400 nm) and two-photon (800 nm) excitation at 510 nm where the strongest spectral change of the photogenerated metastable isomer occurs (Fig. S16). This wavelength is also close to the compensation point where ESA is balanced by SE at longer times (Section 7.1), which reduces possible contribution of the sensitizer response to the kinetic of 1 (as discussed below).

The 510 nm TA kinetic of AF-343 under one-photon excitation shows a positive, short-lived signal (<10 ps) followed by a negative, long-lived tail, which are attributed to the excited state absorption (ESA) and stimulated emission (SE), respectively (as discussed in Section 7.1). Note that there is no ground state bleaching contribution as the probe wavelength lies outside the absorption region. Under two-photon excitation, the TA kinetic of AF-343 displays a decay with two exponential components ($\tau_1 = 6$ ps and $\tau_2 = 35$ ps). The difference with the result from one-photon excitation can be explained by the fact that the 510 nm probe under two-photon excitation is closer to the compensation point because different states are excited and/or the interference filter was not aligned exactly at the normal incidence (and hence had a slightly shifted central wavelength). In either case, the 510 nm transient reflects mostly the interplay between ESA and SE during relaxation, and does not follow the excited state lifetime because of proximity of the compensation point.

The TA trace of 2 under one-photon excitation immediately shows a strong, positive signal decaying to a long-lived offset (share of ~2%), which is attributed to the ground state absorption of photogenerated 2m. The early signal was fitted to two exponential decay components with $\tau_1 = 0.9$ ps and $\tau_2 = 16$ ps. Following previous studies on similar motors\textsuperscript{12,21}, the 0.9 ps and 16 ps components were assigned to the photoinduced absorption of the S1 excited state while moving from the Frank-Condon region to the conical intersection, and vibrational cooling/structural relaxation of the ground state, respectively. Under two-photon excitation, no observable signal of 2 was obtained.
indicating that the bare motor core does not function under direct two-photon excitation. This result is consistent with the difference absorption spectra (Fig. S16) discussed above.

The TA kinetic traces of 1 under both one-photon and two-photon excitation show strong positive signals followed by an offset, which is similar to 2 under one-photon excitation. The intensity dependence of the amount of photoswitching (Fig. S25) demonstrates the one-photon and two-photon absorption character at 400 nm and 800 nm excitation, respectively. Due to direct excitation of the motor core under one-photon excitation conditions (400 nm), the excitation energy transfer from the sensitizer to the motor core and direct excitation of the motor core are hardly distinguishable.

In contrast, under two-photon excitation conditions the contribution of the direct excitation to the motor core in the TA trace of 1 is excluded as the bare motor core is not excited at 800 nm. To eliminate the contribution of the AF-343 signal from the motor core signal, the signal of AF-343 was subtracted from the signal of 1 (inset in Fig. S24B). Note that this operation is legitimate only at very short times (< 2 ps) when the sensitizer response can still be considered constant. The rising time of ~0.9 ps matches well to the depletion time of the sensitizer excited state of 1.5 ps (Fig. S22B) and therefore attributed to the energy transfer time between the sensitizer and the motor core.

The 510 nm TA trace of 1 under two-photon excitation was fitted to three exponential decay components with \( \tau_1 = 155 \) fs, \( \tau_2 = 2.1 \) ps, \( \tau_3 = 165 \) ps and an offset. The shortest component (155 fs) is ascribed to a coherent two-photon response of AF-343. The 2.1 ps component is attributed to convolution of the energy transfer time of 1.5 ps and the excited state relaxation towards the conical intersection (0.6–0.9 ps). The longest decay component is assigned to the structural relaxation of the ground state with a lifetime of 165 ps, which is also longer than that for the bare motor (2) core, presumably due to the larger size of 1. It is also conceivable that the systems which do not exhibit energy transfer (~10% of the total amount) contribute to this time, too. Finally, the offset is caused by the long-lived (~40 min) photoisomerized state. This also signifies the necessity of the sample renewal between the laser shots because otherwise the photoisomerized species would start to accumulate.

The TA kinetic traces at 510 nm of AF-343, 2 and 1 under one-photon (400 nm) and two-photon (800 nm) excitation were fitted to functions (Eq. S3 and S4) as summarized below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF-343 (one-photon excitation)</td>
<td>( y = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} \sum a_i e^{-\frac{t}{\tau_i}} + a_{ing} \left( 1 - e^{-\frac{t}{\tau_{ing}}} \right) ) (Eq. S3)</td>
</tr>
<tr>
<td>AF-343 (two-photon excitation)</td>
<td>( y = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{t^2}{2\sigma^2}} \sum a_i e^{-\frac{t}{\tau_i}} + a_o ) (Eq. S4)</td>
</tr>
<tr>
<td>1, 2</td>
<td></td>
</tr>
</tbody>
</table>

where \( \sigma \) is the standard deviation of the Gaussian distribution, \( a_i \) and \( \tau_i \) are the amplitude and decay time of the \( i \)th exponent, respectively. \( a_{ing} \) and \( \tau_{ing} \) are the amplitude and decay time of the ingrowing component. The fitting parameters for TA kinetic traces at 510 nm are listed in Table S5.
Table S5. Fitting parameters for TA transients at 510 nm. Summary of the decay times and amplitudes of 510 nm TA traces of **AF-343, 2** and **1** under one-photon (400 nm) and two-photon (800 nm) excitation. The sum of all amplitudes is normalized to unity.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>One-photon excitation</th>
<th>Two-photon excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AF-343</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>138 ± 30 fs</td>
<td>267 ± 30 fs</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.83</td>
<td>0.853</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>5.5 ± 0.1 ps</td>
<td>1.6 ± 0.1 ps</td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.13</td>
<td>0.132</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>620 ± 10 ps</td>
<td>12 ± 1 ps</td>
</tr>
<tr>
<td>$a_{ing}$</td>
<td>0.04 (<strong>i</strong>)</td>
<td>-</td>
</tr>
<tr>
<td>$\tau_{ing}$</td>
<td>15 ± 1 ps (<strong>i</strong>)</td>
<td>-</td>
</tr>
<tr>
<td>$a_0$</td>
<td>-</td>
<td>0.015</td>
</tr>
</tbody>
</table>

(*) Ingrowing component: $1 - \exp\left(-t/\tau\right)$

(**) Contribution from the coherent artefact as shown in Fig. S3.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

S7.5. Intensity Dependence at 510 nm

To prove that the transients of 1 follow one- and two-photon absorption processes at 400 nm and 800 nm, respectively, TA measurements at 510 nm probe wavelength with various excitation intensities were performed (Fig. S25). The dependences of the TA response at 1 ps, when RET and the formation of the metastable isomer occur, and 100 ps, when the metastable isomer is fully accumulated, on the excitation intensity were plotted in the insets of Fig. S25. Fitting of the TA response as a function of the excitation intensity clearly shows linear and quadratic dependences for one- and two-photon absorption processes, respectively.

**Fig. S25.** Intensity dependence of TA signals of 1 at 510 nm under one- and two-photon excitation. TA traces of 1 at 510 nm probe wavelength under one-photon, 400 nm, (A) and two-photon, 800 nm, (B) excitation with different excitation intensities. The black arrows depict increasing extents of excitation. The insets show the \( \Delta OD \) dependence of 1 at 1 ps (open dots) and 100 ps (filled dots) on the excitation intensity. The black lines show the fits to a power-law function \( y = ax^n \) with \( n = 1.0 \pm 0.1 \) (1.25 ± 0.08) and \( n = 2.0 \pm 0.2 \) (2.7 ± 0.5) at 1 ps (and 100 ps) under one- and two-photon excitation, respectively. The signals at early time (<0.5 ps) in B contain contributions from the solvent response (Fig. S3). The 1 ps and 100 ps data were averaged in the 0.8–1.2 ps (open dots) and 98–102 ps (filled dots) time windows, and the error bars refer to the standard deviations. The molar concentration of all compounds was set to be similar as \( \sim 6 \cdot 10^{-4} \) M with CHCl₃ as the solvent.

S8. Time-Resolved PL Spectroscopy

Even though the temporal resolution of time-resolved PL is generally not as good as for TA, it is the simplest and most straightforward way to demonstrate resonance energy transfer from the sensitizer in 1. Samples of AF-343, 1, and TPA+M in chloroform were used for the measurements under one- and two-photon excitation conditions using 390 nm and 780 nm light, respectively. The excitation average intensities did not exceed 0.08 W/cm² and 6 kW/cm² for one- and two-photon excitations, respectively. The optical density at 390 nm of the AF-343 solution was 0.07; the optical densities of 1 and TPA+M samples was set identical as 0.08 at 390 nm. All samples therefore had identical concentrations of \( 1.4 \cdot 10^{-5} \) M. For all experiments, the polarizations of the excitation and PL beams were set at the magic angle (54.7°). The PL signal was collected at a \( \sim 90° \) angle with respect to the excitation laser beam. A band-pass filter (Thorlabs, 420–700 nm transmission range) at the polychromator entrance slit was used to remove stray light coming from the excitation beam. Finally, PL intensity of the samples was recorded as a function of the wavelength and delay producing a PL map. In all measurements, the room temperature was kept at 20 °C.
S8.1. PL Maps and Mean Energies

Figure S26(A-F) shows PL maps of AF-343, 1 and TPA+M under one photon, 390 nm, and two-photon, 780 nm, excitation. All PL maps show a similar mean energy of 2.51 eV up to 5 ns for both one-photon and two-photon excitation (Fig. S26G and H), except at very early times (<50 ps) where vibrational relaxation occurs. This indicates that the PL of all samples originates from AF-343.

Fig. S26. Time-resolved PL maps under one- and two-photon excitation. PL maps of AF-343 (A, B), 1 (C, D) and TPA+M (E, F) under one-photon (left panel) and two-photon (right panel) excitation. The excitation wavelengths are 390 nm and 780 nm, respectively. The PL intensity in all maps was normalized to its maximum value. (G, H) Mean energies of AF-343 (red), 1 (green) and TPA+M (violet) under one-photon (G) and two-photon (H) excitation. The mean energies were calculated as \( \frac{1}{2\pi} \int \omega \langle S(\omega, t) \rangle d\omega / \int \langle S(\omega, t) \rangle d\omega \) of spectral slices \( S(\omega, t) \) at a particular time \( t \) (from the PL map). The molar concentration of all compounds was set to be similar as \( \sim 1.4 \times 10^{-5} \) M with CHCl₃ as the solvent.
S8.2. PL Transients

Figure S27 shows time-resolved PL transients of AF-343 and 1 under one- and two-photon excitation. PL of AF-343 under both one- and two-photon excitation shows a long decay with a lifetime of ~2 ns. Linear and quadratic dependences of the PL intensities on the excitation intensities were obtained as shown in Fig. S28, evidencing one-photon and two-photon excitation processes at 390 nm and 780 nm, respectively.

Upon attaching the motor to the sensitizer, the initial PL under both one-photon and two-photon excitations accelerates to ~8 ps. This indicates a strong PL quenching due to excitation energy transfer from AF-343 to (presumably) the motor core. However, due to limited temporal resolution of PL measurements, this PL quenching time (~8 ps) is larger than the time of excitation energy transfer (~1.5 ps from TA data, Fig. S22). The long-lived PL component exhibits a decay time similar to the sensitizer lifetime (~2 ns). The short-lived component of ~1.5 ps (Fig. S22) of AF-343 depopulation is not well-resolved by the streak camera which leads to the seemingly reduced ratio between the peak amplitude and the long-time tail.

With the same concentration of TPA+M as used for the difference absorption measurement (1.4 \cdot 10^{-5} M), PL of TPA+M is similar to that of AF-343 under both one- and two-photon excitation (violet curves in Fig. S27), indicating that there is no PL quenching in TPA+M. This supports our previous conclusion that the mechanism of excitation energy transfer from AF-343 to 2 to drive the motor rotation in TPA+M with that in 1, and it cannot be RET (see Section 6). The similarly long PL decay of AF-343 in the TPA+M sample strongly suggests the aforementioned photon-mediated energy transfer.

*Could the emission-reabsorption mechanism affect the TA transients (see e.g. Fig. S24) at long times?*

Following the “instantaneous” excitation with a 100-fs pulse, the energy transfer process is triggered simultaneously in all molecules (the so-called “zero time synchronization”). With the emission-reabsorption mechanism in action, residual PL from those 10% of 1 which have not undergone the energy transfer, is spread out in time over 2 ns. Therefore, even if we assume that all these secondary up-converted photons are re-absorbed, their impact onto delayed relaxation – such as e.g., photoinduced back-isomerization – is non-synchronized over the entire ensemble and hence can hardly have any effect on the transients.
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

Fig. S27. Time-resolved PL transients under one- and two-photon excitation. Time-resolved PL transients of AF-343 (red), 1 (green) and TPA+M (violet) under one-photon (A) and two-photon (B) excitation. The excitation wavelengths are 390 nm and 780 nm, respectively. The PL transients were obtained by integrating PL maps (Fig. S26) between 410–580 nm, where sensitizer PL occurs. For the sake of clarity, the PL transients of TPA+M are multiplied by 2. The black arrows depict the PL quenching upon attaching the motor core to the sensitizer. The gray lines show fits to exponential functions for the PL transients of AF-343, 1 and TPA+M. The fitting parameters are listed in Table S6. The black open dots depict the apparatus function at 390 nm.

The black curve in A shows the fit to the Gaussian distribution, \( y = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{t^2}{2\sigma^2}} \) with \( \sigma = 4.2 \) ps. The insets show the non-normalized data on linear scale for the first 150 ps. Small differences in PL intensities between AF-343 and TPA+M are caused by deviations in the cuvette’s position when changing the sample (typical for streak-camera measurements). The molar concentration of all compounds was set to be similar as \( \approx 1.4 \cdot 10^{-5} \) M with CHCl\(_3\) as the solvent.

The PL transients of AF-343, 1 and TPA+M were fitted to exponential functions convoluted to a Gaussian distribution (presenting the apparatus function) (Eq. S5):

\[
y = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{t^2}{2\sigma^2}} \otimes \sum_i a_i e^{-\frac{t}{\tau_i}}
\]

(Eq. S5)

where \( \sigma \) is the standard deviation of the Gaussian distribution, \( a_i \) and \( \tau_i \) are the amplitude and decay time of the \( i^{th} \) exponent, respectively. The fitting parameters for PL transients are listed in Table S6. The \( \sigma \) values are obtained from the fits to Eq. S5. \( \sigma \) for one-photon excitation is slightly longer than the one derived from the response function because of time jitter during the PL measurements. \( \sigma \) for two-photon excitation is slightly shorter than that for one-photon excitation as expected for the higher order nonlinearity. The lifetime of AF-343 amounts to \( 2.0 \pm 0.2 \) ns and is in good agreement with the TA data (Section S7.2).
Table S6. Fitting parameters of PL transients. Summary of the decay times and amplitudes of PL transients of AF-343, 1 and TPA+M under one-photon (390 nm) and two-photon (780 nm) excitation. The sum of all amplitudes is normalized to unity.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>One-photon excitation</th>
<th>Two-photon excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AF-343</td>
<td>1</td>
</tr>
<tr>
<td>σ</td>
<td>6 ± 1 ps</td>
<td>7 ± 1 ps</td>
</tr>
<tr>
<td>a₁</td>
<td>-</td>
<td>0.89</td>
</tr>
<tr>
<td>τ₁</td>
<td>-</td>
<td>8 ± 1 ps</td>
</tr>
<tr>
<td>a₂</td>
<td>1</td>
<td>0.11</td>
</tr>
<tr>
<td>τ₂</td>
<td>2.0 ± 0.1 ns</td>
<td>2.0 ± 0.1 ns</td>
</tr>
</tbody>
</table>

S8.3. PL Intensity Dependence

To confirm that PL of AF-343 follows one- and two-photon absorption processes at 390 nm and 780 nm excitations, respectively, time-resolved PL measurements with various excitation intensities were performed. The PL spectra integrated in the 450–550 ps time region are shown in Fig. S28. The dependences of the integrated PL intensity on the excitation intensity are plotted in the insets of Fig. S28. The fittings of the integrated PL intensity as a function of the excitation intensity clearly show linear and quadratic dependences for one- and two-photon absorption processes at 390 nm and 780 nm, respectively.

Fig. S28. Intensity dependence of AF-343 under one- and two-photon excitation. Time-integrated PL spectra of AF-343 under one-photon (A) and two-photon (B) excitation with different excitation intensities. The excitation wavelengths are 390 nm and 780 nm, respectively. The spectra were obtained by integrating PL maps of AF-343 in the 450–550 ps time range. The insets show the dependence of the PL intensity (integration of the PL spectrum) on the excitation intensity. The black lines show the fits to a power-law function, $y = ax^n$ with $n = 1.24 \pm 0.02$ and $n = 1.91 \pm 0.03$ for one-photon and two-photon excitation, respectively.
S9. Resonance Energy Transfer

S9.1. PL Quantum Yield of AF-343

To determine the PL quantum yield (PL QY) of AF-343, we used the well-known coumarin 102 (C102) dye with a PL QY of 76.4% as a reference because its absorption and PL spectra are similar to those of AF-343 (Fig. S29). The PL QY of the AF-343 dye is calculated using the following equation:

$$ Q_S = Q_{\text{ref}} \left( \frac{1 - 10^{-OD_{\text{ref}}(\lambda)}}{1 - 10^{-OD_S(\lambda)}} \right) \frac{\int F_S(\lambda) n_S^2}{\int F_{\text{ref}}(\lambda) n_{\text{ref}}^2} $$

(Eq. S6)

Here, $Q_S$ and $Q_{\text{ref}}$ are the PL QYs of AF-343 and C102, respectively. $OD_S$ and $OD_{\text{ref}}$ are the optical densities at the excitation wavelength of the AF-343 and C102 samples, respectively. $\int F_S(\lambda)$ and $\int F_{\text{ref}}(\lambda)$ are the integrals of the PLs of AF-343 and C102, respectively. $n_S$ and $n_{\text{ref}}$ are the refractive indexes of the solvent in the AF-343 ($n = 1.45$ for Chloroform) and C102 ($n = 1.36$ for Ethanol) samples, respectively.

To avoid PL reabsorption, samples were prepared with a low molar concentration so that the optical density at the excitation wavelength (390 nm) did not exceed 0.1. The PL measurements of the AF-343 dye and the C102 reference were performed five times one after another to reduce uncertainty, and then the PL spectra were averaged. The integrals of the PLs were obtained by integrating the PL spectra between 400 nm and 700 nm. The PL QY of AF-343 was calculated as $Q_S = 78\%$.

![Fig. S29. Absorption and PL spectra of dyes. Absorption (solid lines) and PL (dashed lines) spectra of C102 (grey) and AF-343 (red) upon excitation with 390 nm light. C102 and AF-343 were dissolved in ethanol and chloroform, respectively.](image)

S9.2. Energy Transfer Rate

As the interactions between the bare motor core and AF-343 are relatively weak (as follows from $^1$H NMR, Fig. S10 and absorption spectra, Fig. S11) we can use the well-known Förster relation to estimate the energy transfer rate, $k_T$, (or time, $\tau_T$) from the sensitizer to the motor core:

$$ k_T = \frac{1}{\tau_T} = \frac{1}{\tau_S} \left( \frac{R_0}{R} \right)^6 $$

(Eq. S7)
Here, $\tau_s$ is the excited state lifetime of the AF-343 dye (2 ns), $R$ is the distance between the sensitizer and the motor core (~1.3 nm counting center-to-center). The Förster radius, $R_0$, is defined as follows:

$$R_0^6 = \frac{2.07 N_A}{128 \pi^2 n^4} \int F_S(\lambda) \varepsilon_M(\lambda) \lambda^4 d\lambda$$

(Eq. S8)

where $Q_S$ is the PL QY of the AF-343 dye (~78%, Section 9.1), $N_A$ is Avogadro’s number, $n$ is the refractive index of the medium, and $\kappa$ is the orientation factor ($\kappa^2 \approx 2/3$ assuming a random distribution of orientation of the transition dipole moments). The integral is the spectral overlap integral where $F_D(\lambda)$ is the normalized PL spectrum of AF-343 (Fig. 4.1C of the main text of Chapter 4) and $\varepsilon_M(\lambda)$ is the molar extinction coefficient of the motor core (Fig. S11). Figure S30 illustrates the spectral overlap of the AF-343 PL and motor core absorption.

Eq. S8 can be recast as:

$$R_0^6 = 8.785 \times 10^{-11} \frac{\kappa^2 Q_S}{n^4} J$$

(Eq. S9)

Here, $J = \int F_S(\lambda) \varepsilon_M(\lambda) \lambda^4 d\lambda$ is evaluated over the wavelength expressed in nm, and the molar extinction coefficient has the units of M$^{-1}$ cm$^{-1}$, and $R_0$ is expressed in nm. These all result in a Förster radius of $R_0 = 4.5$ nm and energy transfer time of ~1.1 ps. The latter is in good agreement with the energy transfer time of ~1.5 ps obtained from the transient absorption data at 510 nm.

We would like to point out, however, that although the calculated energy transfer time matches the experimental value of 1.5 ps reasonably well, it should be taken with some caution. First, the point dipole approximation might not be valid as the distance between the dipoles is about their size. Second, energy transfer occurs well before the excited state is equilibrated (i.e., the steady-state PL spectrum is formed). If we consider a hypothetical case of zero Stokes shift (i.e., when the maxima of absorption and PL spectra coincide), the spectral overlap decreases by 40% and subsequently the Förster radius decreases to 4.1 nm, and the energy transfer time increases to 1.9 ps, still presenting a good prediction for the experimental value. All these reasons led us to avoid calling the process “Förster energy transfer” and instead use the more neutral term “resonance energy transfer” (RET).

**Fig. S30.** Spectral overlap of the sensitizer PL and motor core absorption spectra. Normalized absorption (blue solid curve) and PL (red dashed curve) spectra of the motor core $2_s$ and AF-343, respectively. The orange-shaded area illustrates the (normalized) spectral overlap of the AF-343 PL and motor core absorption.
S10. NMR Spectra
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light
ESI of Chapter 4. Powering Rotary Molecular Motors with Low-Intensity Near-Infrared Light

S11. References


