JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

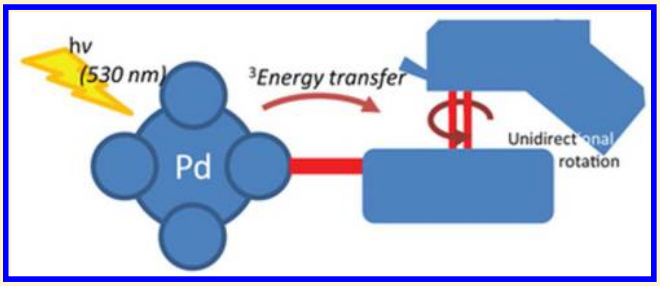
Driving Unidirectional Molecular Rotary Motors with Visible Light by Intra- And Intermolecular Energy Transfer from Palladium Porphyrin

Arjen Cnossen, Lili Hou, Michael M. Pollard,[‡] Philana V. Wesenhagen, Wesley R. Browne,* and Ben L. Feringa*

Centre for Systems Chemistry, Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, Faculty of Mathematics and Natural Sciences, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands

Supporting Information

ABSTRACT: Driving molecular rotary motors using visible light (530−550 nm) instead of UV light was achieved using palladium tetraphenylporphyrin as a triplet sensitizer. Visible light driven rotation was confirmed by UV/vis absorption, circular dichroism and ^{1}H NMR spectroscopy and the rotation was confirmed to be unidirectional and with similar photostationary states, despite proceeding via a triplet instead of a singlet excited state of the molecular motor. Energy transfer proceeds in both inter- and intramolecular fashion from the triplet state of the porphyrin to the motor. Stern Volmer plots show that the rate of intermolecular quenching of the porphyrin excited state by the molecular motor is diffusion-controlled.



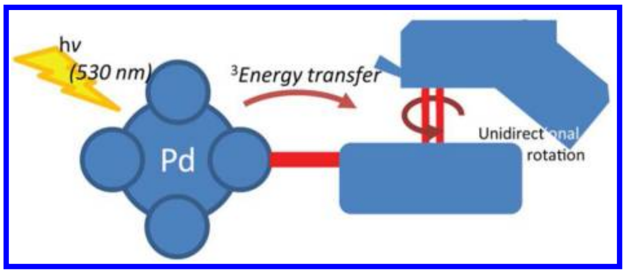
INTRODUCTION

Light driven molecular switches and, more recently, linear and rotary motors show promise in future nanosystems and devices based on integrated molecular components.[1−5] Near- and mid-UV light is typically required to operate most photoactive molecular systems, such as azobenzene[6,7] and diarylethene[8,9] switches and overcrowded alkene-based motors.[10,11] Red and near-IR light-driven molecular components are, however, highly desirable, in expanding for instance their application to biological systems, where UV light can trigger undesirable responses, including cellular apoptosis. Shifting to longer wavelength also reduces irradiation-induced damage to soft material devices based on organic molecules. In certain cases, this has been achieved by shifting the absorption spectrum to the visible region through the use of substituents[12] or Lewis acids.[13] However, to provide sufficient energy to drive photochemical reactions with red light, typically it is expected that two-photon absorption would be required.[14] One solution is sensitization of switches through energy transfer from appended chromophores to induce isomerization. An example in nature is found in the exogenous chromophore used to trigger rhodopsin with long wavelength light, used by deep-sea fish for vision.[15,16] Some examples in the recent literature illustrate the use of sensitized photochemistry in azobenzenes,[17,18] diarylethene switching[19] and in a catenane-based molecular rotor.[20] Stoddart, Balzani, Credi and co-workers used an energy transfer relay to drive a rotaxane-based linear molecular motor with visible light.[21]

The incorporation of molecular motors into more complex systems is desirable as it allows for advanced functions to be driven with external stimuli. However, the dynamic properties in systems combining molecular switches or motors with other chromophores can be affected by crosstalk. For example, when four azobenzenes were attached to the meso-positions of a porphyrin, it was found that *E*-*Z* photoisomerization no longer took place.[22] A recent study by Tour showed that the incorporation of a second generation molecular motor into a molecular car equipped with wheels derived from fullerenes leads to complete quenching of the photochemistry of the motor by the fullerenes.[23]

Motivated by the rich literature on the photoisomerization of stilbene and related olefin chromophores,[24,25] we considered using an exogenous chromophore to drive the molecular motor function. In this way, visible light that is not (directly) absorbed by the molecular motor can be used to drive the rotary cycle by employing, for example, a porphyrin chromophore to harvest and relay photochemical energy (Scheme 1).[26,27] A number of examples of metalloporphyrins that can sensitize the isomer-

Scheme 1. Rotation of a Molecular Motor Driven by Energy Transfer from a Sensitizer That Absorbs Visible Light



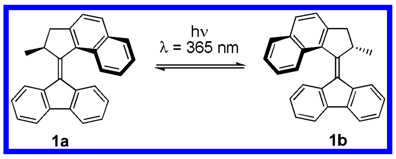
Received: July 17, 2012
Published: October 4, 2012

dx.doi.org/10.1021/ja306986g | *J. Am. Chem. Soc.* 2012, 134, 17613−17619

ization of stilbene and its derivatives by irradiating at wavelengths longer than the lowest absorption of stilbene have been reported.[28−30] In the present study, both inter- and intramolecular energy transfer as a means of driving a rotary motor was examined.

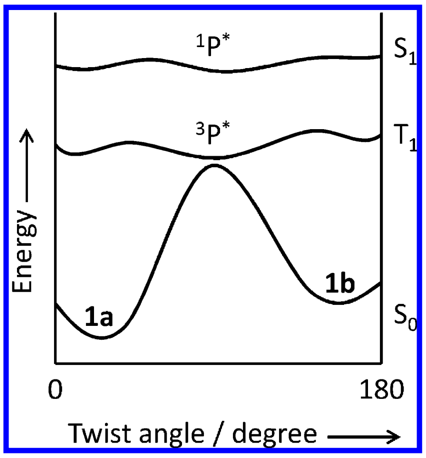
In our previous studies, motors such as **1** operated by the direct absorption of a photon to excite the molecules to a singlet excited state, followed by relaxation to a twisted state (^{1}p*) that may either decay forward to give the thermally unstable isomer **1b** or backward to give the starting alkene **1a** (Scheme 2).[31,32] By using a triplet sensitizer, a lower lying triplet excited state of the molecular motor can be accessed. Following this excitation pathway, the molecule can adopt a twisted state (^{3}p*).

Scheme 2. Photoisomerization of 1a to 1b Driven by UV Light



Taking this approach is nontrivial, however, since in addition to competing electron-transfer processes, achieving equally favorable photostationary states is challenging.[34] This twisted state does not necessarily have the same geometry as that reached on the singlet excited state surface, and in principle could have a different preference for relaxing toward the unstable or the stable form (Scheme 3).[35]

Scheme 3. Schematic Energy Profile along the Rotation Reaction Coordinate of an Asymmetrically Substituted Alkene[33]

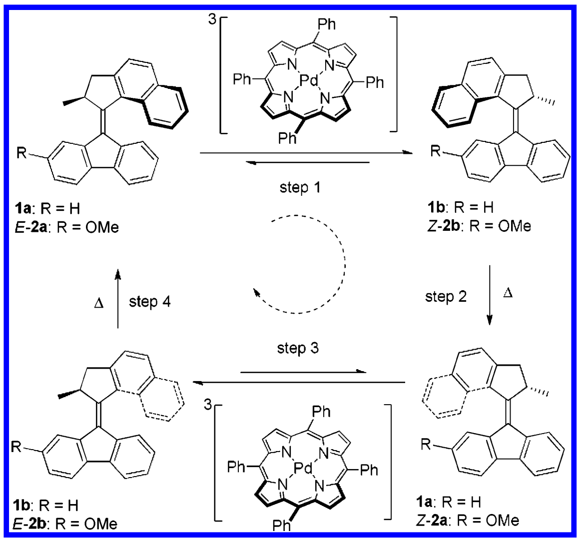


The photostationary state that is obtained depends on the efficiency of the excitation and the decay ratio. If there is a large energy difference between the triplet excited state of the stable and the unstable forms, the energy transfer efficiency to both forms will be different. Furthermore, if the excited state has a preference for decay to either the stable or the unstable form, it will influence the photostationary state obtained also.

The overall rate of the rotation of the molecular motor depends on the rate of the thermal helix inversion step, because it is much slower than the photoisomerization step, although at high rates the irradiation intensity and concentration also start to play a role.[36] If the photoisomerization proceeds via a triplet mechanism, the photochemistry might take place over a longer time scale, but since the thermal helix inversion of **1** has a half-life of several minutes,[31] the thermal step will still be rate limiting.

An important aspect in this approach is whether the rotation of the motor remains unidirectional. If the photoisomerization via the triplet state proceeds analogously to that of the singlet process, it is expected that overall the rotation will still be unidirectional. Indeed, even though the photoisomerization is reversible, the subsequent thermal helix inversion is essentially one-way, which ensures that the rotation can only operate in one overall direction (Scheme 4). However, one can envision that in the triplet excited state other processes can take place, which could allow ill-defined interconversion of the stable or unstable forms.

Scheme 4. Excitation of Palladium Tetraphenylporphyrin with Visible Light Followed by Efficient Intersystem Crossing Generates the Triplet Porphyrin Excited State[a]



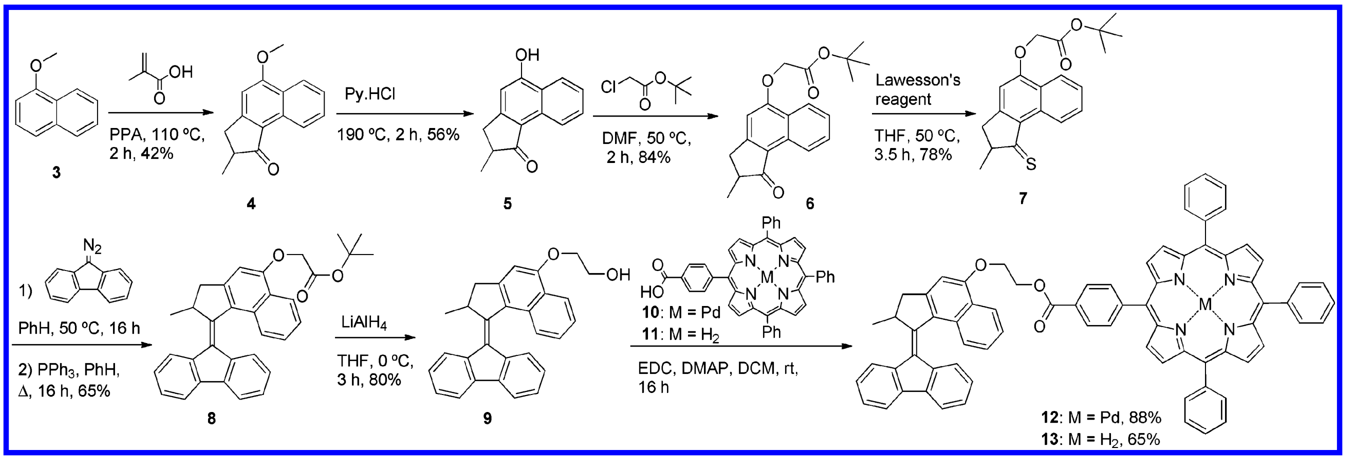
[a] Intermolecular energy transfer to the molecular motor drives photoisomerization of the central olefinic bond. Thermal helix inversion of the unstable form completes one half rotation.

RESULTS AND DISCUSSION

Molecular Design. We selected palladium tetraphenylporphyrin (PdTPP) as a sensitizer to investigate the possibility of harnessing longer wavelength light to drive the rotary cycle of **1** through intermolecular energy transfer. This chromophore is well suited for the purpose because it has a relatively long-lived triplet state lifetime (up to 2 ms)[37] and has a strong absorption at wavelengths longer than those of the motor, allowing for selective excitation of PdTPP in the presence of **1**. With a triplet energy of 178 kJ/mol,[37] the excited state energy of ^{3}[PdTPP] is significantly lower than that of the singlet excited state of motor **1** (~300 kJ/mol). The triplet excited state energy of motor **1** is unknown; however, it can be estimated using time-dependent density functional theory (TD-DFT) calculations. TD-DFT calculations on the B3LYP/6-31G-(d,p)[38−40] level of theory gives a value of 182 kJ/mol, which is comparable with that of PdTPP.[41]

In addition to intermolecular energy transfer[42] from the sensitizer and the molecular motor, a covalent system was

Scheme 5. Synthesis of TPP Motor Conjugates 12 and 13



designed to allow for intramolecular energy transfer, to increase the effective molarity and thus the efficiency of energy transfer. In energy transfer processes, the distance and orientation between the donor and acceptor is important.[43] In the covalent system employed (Scheme 5), a flexible, nonconjugated linker is used, which precludes through-bond interactions, with an ester formation as the final coupling step. Substitution on this position of the motor has no effect on the thermal helix inversion, although the photostationary state is affected by electron donating or withdrawing substituents.[44] In a different molecular motor, the effect of substitution with large alkyl groups was also reported to be minimal,[45] so we do not expect a significant difference in behavior between the motor unit in **12** and compound **1**.

Synthesis. The synthesis of target motor **9** with an ethylene glycol spacer for attachment of the porphyrin is shown in Scheme 5. Starting from 1-methoxynaphthalene **3**, ketone **4** was synthesized in a one pot Friedel–Crafts acylation/Nazarov cyclization in moderate yield. Deprotection of the phenol could be carried out conveniently by heating with pyridine hydrochloride. Purification of the resulting naphthol **5** was somewhat hampered by poor solubility; however, the crude product could be used directly in the next step. Alkylation of **5** with *tert*-butyl chloroacetate gave **6** in good yield. Conversion of the ketone moiety to a thioketone was effected by Lawesson's reagent.

Thioketone **7** was found to be stable toward column chromatography and could be stored for several days at ambient conditions without noticeable degradation. The sterically overcrowded olefinic bond was introduced by a Barton-Kellogg coupling between **7** and 9-diazofluorene. A mixture of olefin **8** and the corresponding episulfide was obtained, which was not separated but instead treated with triphenylphosphine yielding functionalized motor **8** in 65% yield. The ^{1}H NMR spectrum of **9** shows the typical splitting pattern of the protons on the cyclopentene ring. Further characterization was performed with ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HR-MS). Attempts to hydrolyze the ester functionality in **8** for subsequent coupling to an alcohol substituted porphyrin failed under both acidic and basic conditions. However, reduction of the ester to an alcohol using $LiAlH_4$ proceeded in good yield. Acid functionalized porphyrin **10** was synthesized in three steps to allow coupling to **9** (see Supporting Information). The alcohol moiety in **9** was reacted with **10** in a carbodiimide-mediated esterification to give **12** in 88% yield. Compound **12** was characterized by ^{1}H and ^{13}C NMR spectroscopy and HR-MS. For control experiments, free-base analogue **13** was also synthesized by coupling motor **9** to **11**.

Photoisomerization by Intermolecular Energy Transfer. Sensitization of the photoisomerization of **1** by collisional energy transfer from PdTPP was studied in 1,2-dichloroethane at 293 K. The UV/vis absorption spectra of **1a** and the PSS mixture of **1a** and **1b** obtained after irradiation at 365 nm is shown in Figure 1. The absorption spectra of **1** overlap partially with the absorption spectrum of PdTPP, with the Soret band of the porphyrin dominating the absorption spectrum.

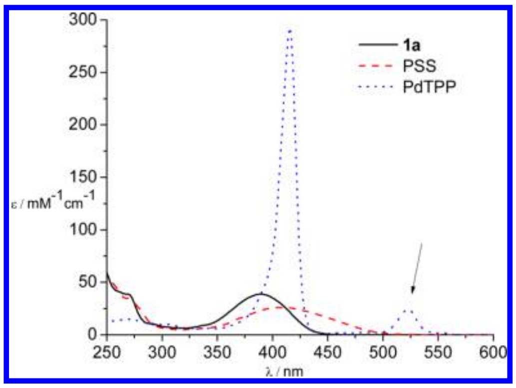


Figure 1. UV/vis absorption spectra of **1a** (full line), the PSS mixture of **1a** and **1b** obtained after irradiation at 365 nm (dashed line) and PdTPP (dotted line).

Irradiation of the porphyrin at 420 nm would also lead to direct excitation and isomerization of **1**. Hence, irradiation was carried out at a wavelength resonant with one of the Q-bands (indicated by the arrow in Figure 1) of the porphyrin, at longer wavelength than the absorption of both the stable and the unstable forms of **1**. Excitation at 530–550 nm was achieved by the use of a visible light source with an appropriate band-pass filter or a 532 nm pulsed laser.

An argon purged solution of **1** alone and a 1:1 mixture of PdTPP and **1** (5 μM) were irradiated at 532 nm (pulsed laser, 6 ns, 10 Hz). A red shift in the absorption was observed, corresponding to the photoisomerization of motor **1** (Figure 2), as observed before upon direct irradiation of **1** with UV light. The change in absorption is minor and partially obscured by the overlap with the porphyrin absorption, but is nevertheless reproducible. In contrast, when a solution of **1**

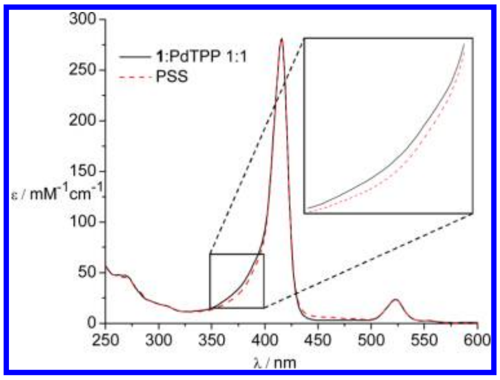


Figure 2. UV/vis absorption spectra of a mixture of **1** and PdTPP (full line) and the same mixture after irradiation at 532 nm (dashed line). Inset: expansion of the 350−400 nm region.

only was irradiated under the same conditions no changes were observed in the UV/vis absorption spectrum, confirming that the photochemistry of **1** cannot be driven directly at 532 nm.

CD spectroscopy was employed to further characterize the photoisomerization of **1**. Enantiomerically pure (*S*)-**1** was obtained by preparative chiral stationary phase HPLC. The absolute configuration was assigned based on comparison of the CD spectrum to the spectrum predicted by TD-DFT calculations on the B3LYP/6-31G(d,p) level of theory (Figure 3).

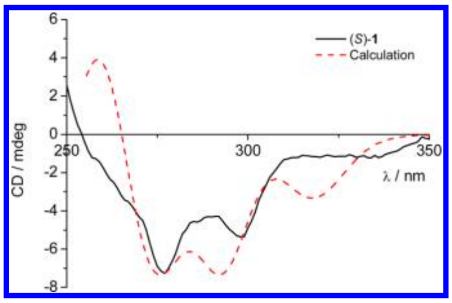


Figure 3. CD spectrum measured for **1** (full line) in dichloromethane and normalized calculated CD spectrum for (*S*)-**1** (dashed line). It should be noted that the spectrum is solvent dependent as can be seen by comparison with the spectrum of **1** in hexane.[31].

Upon irradiation at 532 nm of a 1:1 mixture of (*S*)-**1** and PdTPP in chloroform, the major bands in the CD spectrum start to decrease in intensity, which implies the formation of the unstable form with opposite helicity (Figure 4). The bands do not invert fully, even upon prolonged irradiation, which can be rationalized by a relatively low PSS; from the decrease in signal intensity, a ratio **1a**/**1b** of about 75:25 can be estimated. Upon heating to 40 °C for 20 min, the spectral changes in both the UV/vis absorption and the CD spectra are reversed.

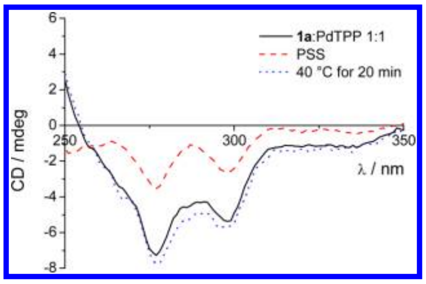


Figure 4. CD spectra of a mixture of **1** and PdTPP (full line) and the same mixture after irradiation at 532 nm (dashed line) and subsequent heating to 40 °C for 20 min (dotted line). Note that the spectrum after heating is slightly more intense due to a small change in concentration during heating.

Unidirectionality of the Sensitized Rotation Process. A central question in driving photoisomerization by triplet sensitization rather than direct excitation is whether or not the unidirectionality of the rotary motor function is retained. Previously, the unidirectionality of the rotary motor function of **1** under direct excitation (365 nm) was established by CD and ^{1}H NMR spectroscopy.[31] To be able to distinguish the four distinct steps in the rotary cycle of the motor, a methoxy substituent was introduced in the lower half. Compound **2** was synthesized according to literature procedures,[31] analogous to **1**, and the *E* and *Z* isomers were separated by column chromatography.

A 1:1 mixture of PdTPP and **2** (18 mM) was irradiated at −40 °C in toluene-d_8 at 546 nm (±5 nm). The initial isomer *E*-**2a** of the molecular motor was converted to the thermally unstable *Z*-**2b** (Scheme 4, step 1). Characteristic changes in the ^{1}H NMR spectrum are the shift of the alkyl signals and the appearance of a signal of the methoxy group at 2.6 ppm (Figure 5). At the PSS, the ratio of *E*-**2a** to *Z*-**2b** was 64:36. Warming the mixture at 40 °C for 20 min resulted in the conversion of *Z*-**2b** to *Z*-**2a** (Scheme 4, step 2). The alkyl signals recover at their original positions, while the intensity of the new methoxy signal remains unchanged, indicating the formation of the *Z*-**2a** isomer.

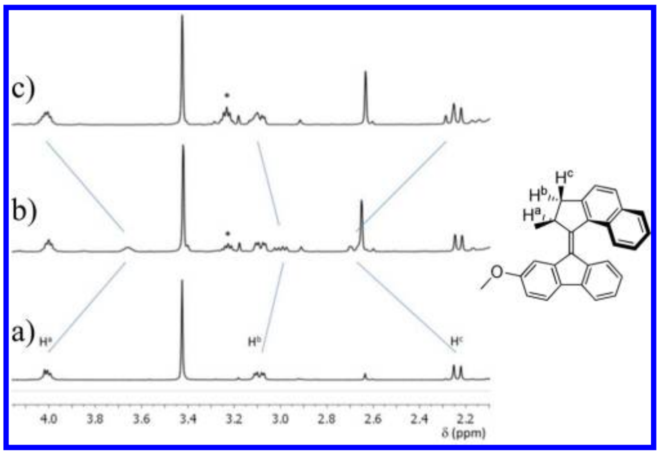


Figure 5. Partial ^{1}H NMR spectrum (−40 °C, toluene-d_8) of (a) a mixture of PdTPP and *E*-**2a** before irradiation, (b) mixture of *E*-**2a** and *Z*-**2b** obtained upon irradiation at 546 nm at −40 °C, and (c) mixture of *E*-**2a** and *Z*-**2a** obtained upon warming to 40 °C for 20 min. * = ethanol.

A similar series of experiments was performed with *Z*-**2a** (Figure 6). When a mixture of *Z*-**2a** and PdTPP was irradiated at 546 nm, the signal of the alkyl protons shifted, indicating the formation of thermally unstable *E*-**2b** (Scheme 4, step 3). Likewise, the signal of the methoxy group at 2.6 ppm decreases with an increase in the intensity of the methoxy signal (3.4 ppm) of *E*-**2b** (Figure 6). At the PSS, the ratio of *Z*-**2a** to *E*-**2b** was 65:35. Upon warming, the alkyl signals shift back to their original position, while the intensity of the methoxy signal remains the same (Scheme 4, step 4). This shows that all of the thermally unstable form generated by photoisomerization in

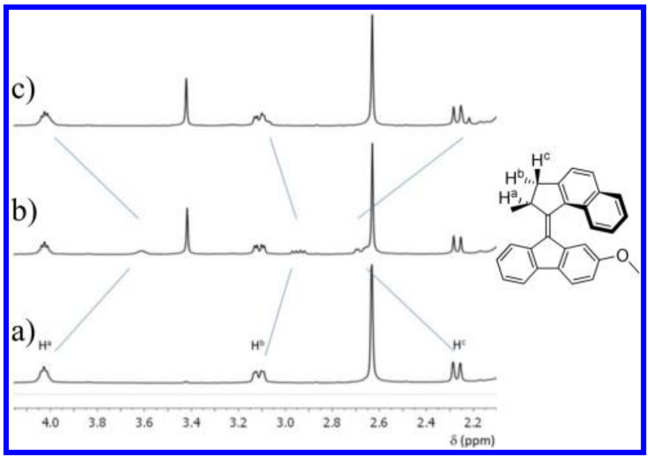
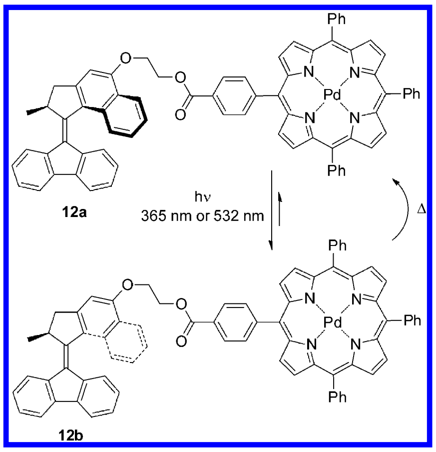


Figure 6. Partial ^{1}H NMR spectrum (−40 °C, toluene-d_8) of (a) a mixture of PdTPP and *Z*-**2a** before irradiation, (b) mixture of *Z*-**2a** and *E*-**2b** obtained upon irradiation at 546 nm at −40 °C, and (c) mixture of *Z*-**2a** and *E*-**2a** obtained upon warming to 40 °C for 20 min.

steps 1 and 3 is converted to the expected thermally stable form and that the rotation is unidirectional. During the isomerization steps, the same changes in helicity were observed for compound **2** as for compound **1** (see Supporting Information).

Photoisomerization by Intramolecular Energy Transfer. In motor-porphyrin hybrid **12**, the energy transfer is expected to take place in an intramolecular fashion to drive the photoisomerization of the motor (Scheme 6). Because the motor is linked covalently to the sensitizer, the effective molarity will be high and energy transfer should proceed more efficiently than in the intermolecular case.

Scheme 6. Expected Isomerization Behavior of 12



When irradiated with visible light (532 nm, 6 ns, 10 Hz) for 10 s, the photostationary state of an argon purged solution of **12** was reached, and this resulted in an increase in the absorbance between 450 and 500 nm with a concomitant minor red-shift of the shoulder around 375 nm (Figure 7), similar to what was observed for **1**. The isomerization was performed repeatedly: the same sample was irradiated at 532 nm for 10 s and left in the dark for 20 min for four cycles, with the change in absorbance monitored at 460 nm (Figure 7, inset). The excellent repeatability of the UV/vis absorption spectral changes of **12** indicates that the photoisomerization of the motor part is reversible and degradation does not occur.

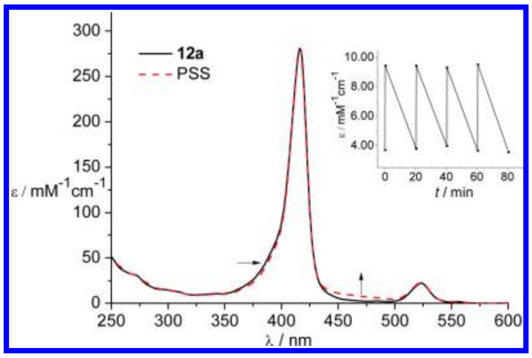


Figure 7. UV/vis absorption spectrum of **12a** (full line) and the mixture of **12a** and **12b** obtained after irradiation at 532 nm (dashed line). Inset: Molar absorptivity at 460 nm of a solution of **12** alternately irradiated at 532 nm for 10 s and left in the dark at rt for 20 min.

The changes in the UV/vis absorption spectrum upon irradiation are somewhat obscured by overlap of the strong Soret band of the porphyrin. However, with CD spectroscopy characteristic spectral changes are also expected in the 250−350 nm region, where the porphyrin has negligible absorption. Indeed, when a solution of (*R*)-**12a** is irradiated at 532 nm, a distinct decrease in the intensity of the CD signal is observed (Figure 8). As was the case for **1**, complete inversion is not observed, presumably due to a relatively modest PSS (vide infra). The observed spectral changes are fully reversible when thermal helix inversion is allowed to take place by heating to 40 °C for 20 min. If the palladium-free porphyrin **13** is used instead of **12**, no changes are observed in either the UV/vis absorption or the CD spectrum. Prolonged irradiation led to irreversible changes in the CD spectrum, which are attributed to degradation (see Supporting Information).

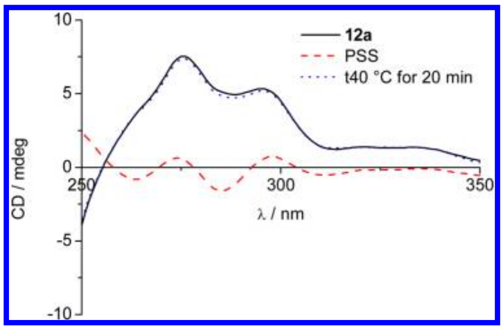


Figure 8. CD spectra of **12a** (full line) and the mixture of **12a** and **12b** obtained after 10 s irradiation at 532 nm (dashed line) and the mixture after the thermal step (dotted line). Note that the opposite stereoisomer is used compared with **1** (Figure 4).

At 138 kJ/mol, the triplet excited state energy of free-base tetraphenylporphyrin (H_2TPP) is considerably lower than that of both PdTPP and motor **1**, so triplet energy transfer is not expected in this case.[46] Energy transfer from the porphyrin in the singlet excited state cannot take place because it is too low in energy relative to the singlet excited state of **1**. These results indicate that the energy transfer in the case of the palladated porphyrin goes via triplet energy transfer.

The photostationary state for the sensitized isomerization between **12a** and thermally unstable **12b** was determined by ^{1}H NMR spectroscopy. A solution of **12a** in toluene-d_8 was irradiated (532 nm) at −40 °C until further changes were not observed. By comparing the integrals of the absorptions of **12a** and **12b** in the alkyl region, the photostationary state ratio **12a**/**12b** was determined to be 67:33. This is similar to the 57:43 ratio obtained under direct irradiation (365 nm) for a methoxy-substituted analogue of **1**,[44] and to the ratio obtained for the intermolecular process (vide supra), with the slight difference being within experimental uncertainty.

A more important parameter, however, is the photochemical quantum yield for the visible light-driven photoisomerization. This was determined to be 0.11 ± 0.02 (using the reference potassium reineckate as a standard).[47,48] This is close to the quantum yield obtained for direct excitation, 0.14, showing that similar efficiency can be reached using visible light.[49]

Luminescence Lifetime and Quenching. The results of the irradiation experiments using nonmetalated motor–porphyrin hybrid **13** implied that the rotation upon visible light irradiation proceeds via triplet energy transfer. To demonstrate this conclusively, the luminescence lifetimes of the porphyrins were measured. Steady-state emission spectra of PdTPP, a mixture of PdTPP and **1** with a ratio of 1:2.5 and motor–PdTPP hybrid **12** in 1,2-dichloroethane under an argon atmosphere were recorded (Figure 9). PdTPP, irradiated with visible light (532 nm), gives fluorescence at 610 nm and phosphorescence at 710 nm.[50] The phosphorescence quantum yield for PdTPP is significantly reduced by the molecular motor, both in an inter- and intramolecular fashion, which is attributed to the energy transfer from PdTPP to the motor (Table 1). The quenching of phosphorescence in **12** was greater than in the mixture of **1** and PdTPP under the same conditions. In contrast, the fluorescence quantum yield for PdTPP was not influenced by the presence of the molecular motor. This confirms that energy transfer is not via singlet energy transfer but via triplet energy transfer. As a control, the steady-state fluorescence of H_2TPP was compared to that of **13**; singlet energy transfer was not observed and there was no change in the fluorescence quantum yield (see Supporting Information).

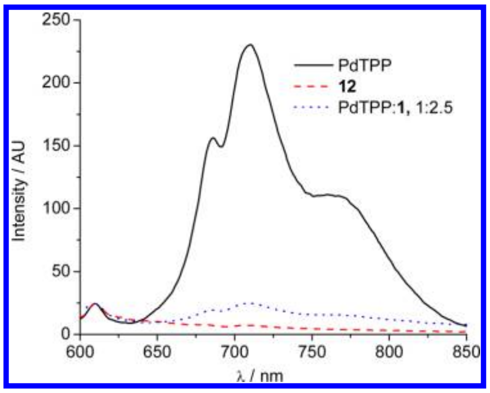


Figure 9. Emission spectra of PdTPP (2 × 10^{-5} M, full line), a 1:2.5 mixture of PdTPP and **1** (PdTPP 2 × 10^{-5} M, **1** 5 × 10^{-5} M, dashed line), and **12** (2 × 10^{-5} M, dotted line) under Ar atmosphere, λ_{exc} = 532 nm.

Table 1. Photophysical Properties of PdTPP and 3 in 1,2-dichloroethane[a]

	fluor. λ_{max} (nm)	phosphor. λ_{max} (nm) {τ_T in μs}	Φ_f(%)[b]	Φ_p (%)[b]
PdTPP	610	710 (36 ± 4)	~0.01	0.5 ± 0.1
PdTPP:**1**	610	710 (9 ± 1)	~0.01	~0.05
12	610	710 (0.41)	~0.01	<0.04

[a] All the measurement were performed in Ar-saturated environment. Fluorescence quantum yield Φ_f, phosphorescence quantum yield Φ_p and triplet lifetime τ_T. [b] The quantum yields were determined using $[Ru(bpy)_3]$ $(PF_6)_2$ in water as a reference (Φ = 0.028).

The intra- and intermolecular energy transfer were further studied by means of time-resolved emission spectroscopy. The phosphorescence decay curves of PdTPP, a 1:2.5 mixture of PdTPP and **1**, and **12** were recorded at 710 nm (Table 1, see also Supporting Information). The lifetimes were fitted using first-order exponential decay kinetics. The phosphorescence lifetime was reduced from 34 μs for PdTPP to 9 μs for the mixture, and to 0.41 μs for **12**, which confirms that quenching of PdTPP triplet excited state occurs. As expected, the covalent system **12** shows more efficient energy transfer than the mixture of PdTPP and **1**.

The phosphorescence lifetime of PdTPP in the presence of the motor at concentrations between 0.0 and 0.5 mM in (argon-saturated) 1,2-dichloroethane was determined and the data is shown in the form of a Stern–Volmer plot (τ_0/τ versus motor concentration, Figure 10). A linear fit yielded a bimolecular quenching rate constant k_q of 1.8 × 10^9 M^{-1} s^{-1} for the quenching of ^{3}PdTPP* by **1**. The diffusion-controlled rate constant in 1,2-dichloroethane is approximately 8.9 × 10^9 M^{-1} s^{-1} at 25 °C.[51] This indicates that energy transfer is diffusion controlled in the present intermolecular system also.

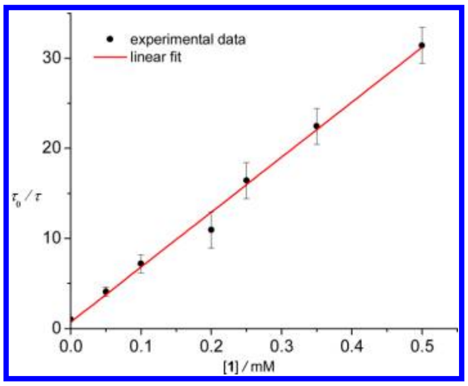


Figure 10. Stern–Volmer plot for quenching of PdTPP by **1** (points) and linear fit (red line).

■ CONCLUSION

In conclusion, the photoisomerization in second generation molecular motors can be driven by visible light when a suitable triplet sensitizer is employed. Energy transfer from the triplet excited state of PdTPP to the motor leads to the formation of the unstable form, which subsequently undergoes thermal helix inversion resulting in rotation of the upper half relative to the lower half. The photoisomerization was characterized by UV/vis, CD and ^{1}H NMR spectroscopy and it was found that the sensitized photoisomerization proceeds similar to photoisomerization by direct irradiation; the main difference is that the PSS is decreased to a minor extent with respect to the unstable form. Energy transfer from the porphyrin to the motor takes place conveniently in an intermolecular fashion to drive the photoisomerization. However, covalent linking of the motor to the porphyrin increases the efficiency substantially.

Using excitation at longer wavelengths than 546 nm is in principle possible. However, energy transfer to motor **1** requires that the triplet excited state energy of the sensitizer be higher than that of **1**. Considering the triplet excited state energies of PdTPP (178 kJ/mol) and H_2TPP (138 kJ/mol), the current limit is between 672 and 872 nm. An alternative approach is to use motor structures with lower triplet excited state energies. Ultimately, driving the photoisomerization of overcrowded alkene-based motors with IR light would expand their use in biological systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, compound characterization data, control experiments, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

w.r.browne@rug.nl; b.l.feringa@rug.nl

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the European Research Council (Advanced Investigator grant 227897; A.C., B.L.F.), The Netherlands Organization for Scientific Research (VIDI grant 700.57.428, W.R.B.) and the Ubbo Emmius fund (L.H.).

■ DEDICATION

‡In Memoriam; Febuary 27, 2010

■ REFERENCES

(1) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191.

(2) Coskun, A.; Banaszak, M.; Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2012**, *41*, 19−30.

(3) Faiz, J. A.; Heitz, V.; Sauvage, J. P. *Chem. Soc. Rev.* **2009**, *38*, 422−442.

(4) Balzani, V.; Credi, A.; Venturi, M. *Chem. Soc. Rev.* **2009**, *38*, 1542−1550.

(5) *Molecular Switches*; Feringa, B. L., Browne, W. R., Eds.; Wiley-VCH: Weinheim, 2011.

(6) Dhammika Bandara, H. M.; Burdette, S. C. *Chem. Soc. Rev.* **2012**, *41*, 1809−1825.

(7) Barrett, C. J.; Mamiya, J.; Yager, K. G.; Ikeda, T. *Soft Matter* **2007**, *3*, 1249−1261.

(8) Matsuda, K.; Irie, M. *J. Photochem. Photobiol., C* **2004**, *5*, 169−182.

(9) Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327−336.

(10) Feringa, B. L. *J. Org. Chem.* **2007**, *72*, 6635−6652.

(11) Pollard, M. M.; Klok, M.; Pijper, D.; Feringa, B. L. *Adv. Funct. Mater.* **2007**, *17*, 718−729.

(12) Beharry, A. A.; Sadovski, O.; Woolley, G. A. *J. Am. Chem. Soc.* **2011**, *133*, 19684−19687.

(13) Yang, Y.; Hughes, R. P.; Aprahamian, I. *J. Am. Chem. Soc.* **2012**, *134*, 15221−15224.

(14) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3244−3266.

(15) Douglas, R. H.; Partridge, J. C.; Dulai, K. S.; Hunt, D. M.; Mullineaux, C. W.; Hynninen, P. H. *Vision Res.* **1999**, *39*, 2817−2832.

(16) Okada, T.; Ernst, O. P.; Palczewski, K.; Hofmann, K. P. *Trends Biochem. Sci.* **2001**, *26*, 318−324.

(17) Venkataramani, S.; Jana, U.; Dommaschk, M.; Sönnichsen, F. D.; Tuczek, F.; Herges, S. *Science* **2011**, *331*, 445−448.

(18) Sakamoto, R.; Kume, S.; Sugimoto, M.; Nishihara, H. *Chem.—Eur. J.* **2009**, *15*, 1429−1439.

(19) Brayshaw, S. K.; Schiffers, S.; Stevenson, A. J.; Teat, S. J.; Warren, M. R.; Bennett, R. D.; Sazanovich, I. V.; Buckley, A. R.; Weinstein, J. A.; Raithby, P. R. *Chem.—Eur. J.* **2011**, *17*, 4385−4395.

(20) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174−179.

(21) Balzani, V.; Clemente-Léon, M.; Credi, A.; Ferrer, B.; Venturi, M.; Flood, A. H.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 1178−1183.

(22) Hunter, C. A.; Sarson, L. D. *Tetrahedron Lett.* **1996**, *37*, 699−702.

(23) Morin, J.-F.; Shirai, Y.; Tour, J. M. *Org. Lett.* **2006**, *8*, 1713−1716.

(24) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197−3217.

(25) Benson, R.; Williams, D. F. *J. Phys. Chem.* **1977**, *81*, 215−220.

(26) Lukas, A. S.; Wasielewski, M. R. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001; pp 1−35.

(27) Gust, D.; Moore, T. A.; Moore, A. L. *Chem. Commun.* **2006**, 1169−1178.

(28) Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 2620−2625.

(29) Brink, M.; Wennerström, O. *J. Photochem. Photobiol., A* **2001**, *143*, 201−208.

(30) Möllerstedt, H.; Wennerström, O. *J. Photochem. Photobiol., A* **2001**, *139*, 37−43.

(31) Vicario, J.; Meetsma, A.; Feringa, B. L. *Chem. Commun.* **2005**, 5910−5912.

(32) Vicario, J.; Walko, M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 5127−5135.

(33) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausolito, CA, 1991; pp 473−481.

(34) Wang, J.; Kulago, A.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2010**, *132*, 4191−4196.

(35) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23−39.

(36) Klok, M.; Browne, W. R.; Feringa, B. L. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9124−9131.

(37) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359−375.

(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

(39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(40) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(41) These calculations are known to have a significant margin in the determination of the energy of electronically excited states, see: Grimme, S.; Neese, F. *J. Chem. Phys.* **2007**, *127*, 154116.

(42) For a review on inter- and intermolecular energy transfer, see Raymo, F. M.; Tomasulo, M. *Chem. Soc. Rev.* **2005**, *34*, 327−336.

(43) See for example: Aratani, N.; Kim, D.; Osuka, A. *Acc. Chem. Res.* **2009**, *42*, 1922−1934.

(44) Pollard, M. M.; Wesenhagen, P. V.; Pijper, D.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, *6*, 1605−1612.

(45) Caroli, G.; Kwit, M. G.; Feringa, B. L. *Tetrahedron* **2008**, *64*, 5956−5962.

(46) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83−126.

(47) *Handbook of Photochemistry*; Montalti, M., Credi, A., Prodi, L., Gandolfi, M. T., Eds.; CRC Press: Boca Raton, FL, 2006; pp 609−610.

(48) Szychlinski, J.; Bilski, P.; Martuszewski, K.; Blazejowski, J. *Analyst* **1989**, *114*, 739−741.

(49) Conyard, J.; Addison, K.; Heisler, I. A.; Cnossen, A.; Browne, W. R.; Feringa, B. L.; Meech, S. R. *Nat. Chem.* **2012**, *4*, 547−551.

(50) Rogers, J. E.; Nguyen, K. A.; Hufnagle, D. C.; Mclean, D. G.; Su, W.; Gossett, K. M.; Burke, A. R.; Vinogradov, S. A.; Pachter, R.; Fleitz, P. A. *J. Phys. Chem. A* **2003**, *107*, 11331−11339.

(51) *Handbook of Photochemistry*; Montalti, M.. Credi, A.. Prodi, L.. Gandolfi, M. T., Eds.; CRC Press: Boca Raton, FL, 2006; p 424.