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Photochemical and thermal behavior of light-driven unidirectional molecular motor with long alkyl chains

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ABSTRACT

In order to utilize molecular motors in a molecular device or smart materials, their dynamic behavior when other groups are introduced at key positions has to be examined. A C_{16} hydrocarbon chain has been introduced at the stereogenic centers of the first generation light-driven molecular motor based on sterically overcrowded biphenanthrylidene. It was found that this derivatization does not affect the unidirectional rotary capability of the motor and does not cause a reduction of its speed, opening new possibility for future functionalizations and applications.

1. Introduction

Inspired by the natural molecular motors abundantly present in biological systems[1–3] and molecular switches[4] as trigger elements, several artificial molecular systems have been designed and synthesized[5–17] where rotor functions are present or external stimuli induce controlled translational or rotary motion. The remarkable progress in recent years is clearly demonstrated by the number of reviews recently published.[18] To power future nanomachines, new and more complex molecular motors should be developed that can operate in the presence of a range of other functionalities, while the factors governing motor function have to be established.

In 1999, we reported the first light-driven unidirectional molecular motor (**1**)[19] (Chart 1). It consists of a sterically overcrowded symmetric biphenanthrylidene, the main features of which are its intrinsic helical shape, the central C=C bond, which works as axis of rotation, two stereogenic centers with a methyl substituent that, due to steric hindrance, adopt an energetically preferred pseudo-axial orientation, whereas the molecule undergoes a stereoselective stilbene-type photoisomerization. In this system, repetitive unidirectional rotation around the central double bond (the axis of rotation) is achieved in four steps: two energetically uphill photochemical steps, each followed by an energetically downhill thermal step. Upon irradiation, *cis*/*trans* isomerization occurs, with inversion of the helicity and simultaneous change in the conformation of the six-membered ring, forcing the methyl substituents to adopt a less favored pseudo-equatorial orientation. To revert to the most favored pseudo-axial conformation of the methyl substituents, the naphthalene upper part must slip past the lower part of the molecule, resulting in an irreversible thermal isomerization with simultaneous helix inversion. The half-life time for the thermal helix inversion from (*P*)-*trans* to (*M*)-*trans* was 1908 s at room temperature.

The five-membered ring version of this motor (**2**)[20,21] (Chart 1) was found to show faster thermal inversions due to the considerable reduction of the steric hindrance in the 'fjord region' of the molecule. The half-life time for the thermal helix inversion from (*P*)-*trans* to (*M*)-*trans* has been determined to be only 18 s at room temperature.

Moreover, we have recently reported that changing the substituent at the stereogenic centers has a profound influence on the

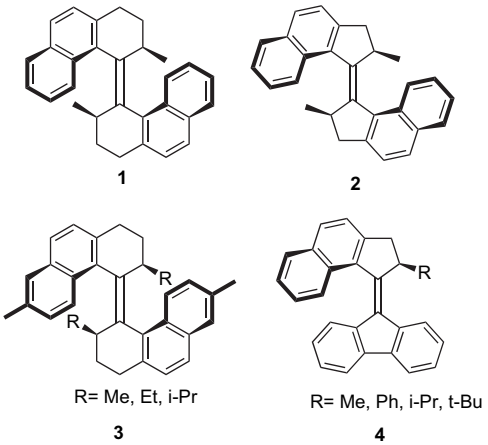

Chart 1.

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energy barriers for the thermal helix inversion as in **3**[22] and **4**[23] (Chart 1). In fact, not only the steric hindrance in the 'fjord region', but also conformational effects are involved in governing the thermal isomerization process using fine tuning of steric parameters cumulated in light-driven molecular motors[23] that rotate at 83 rpm approaching the speed of the natural ATPase rotary motor.[1]

Future application of molecular motors will rely on more complex systems, where the motor will have additional groups attached to it, and/or experience a reduced space in which to move, or when the motor operates when assembled on a surface.

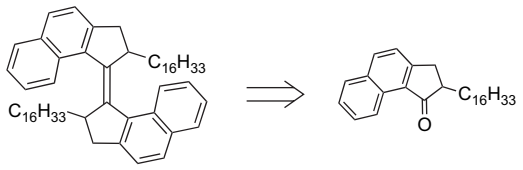
Therefore, it is of fundamental importance to study the behavior of modified versions of molecular motors, in order to examine particular features, for instance the effect on the rotary motion of attached groups. Especially the introduction of long alkyl chains, that can be used to tether larger objects or polymers to be moved through a solution or along a surface, is an important goal.

Herein we report the synthesis and study of a first generation five-membered ring molecular motor **5** derivatized at the stereogenic center with a C_{16} alkyl chains. The key point of this study is whether long chains attached to the motor affect or prevent its rotation. They could, for example, increase the friction with the solvent, or just make the motor 'experience' entanglement or the weight of the substituents.[24]

2. Results and discussions

2.1. Synthesis

We envisioned that the target molecular motor **5**, with two pending C_{16} alkyl chains, might be readily accessible through McMurry coupling of the corresponding ketone **6** (Chart 2). This is indeed the key step in the synthesis of the symmetrical motors we have reported so far,[19,20,25] as this method offers a strong driving force necessary to lead to the sterically crowded product.



5 6

Chart 2.

The synthesis of the ketone **6** started with the α-alkylation of octadecanoic acid methyl ester with 2-bromomethylnaphthalene employing LDA in dry THF to provide **7** in 72% yield (Scheme 1). Hydrolysis of **7** with LiOH in a H_2O/MeOH/THF solution provided acid **8** in 72% yield. After conversion into the corresponding acyl chloride (not isolated) with thionyl chloride, it readily reacted with aluminum chloride in a regioselective intramolecular Friedel–Crafts reaction leading to ketone **6**. The yield for this last step was as high as 91%, and exclusively **6** was obtained from substitution at the α-position of the naphthalene moiety. The ketone **6** was then coupled in the presence of low valent titanium (McMurry coupling) in refluxing THF over a period of 3 days, leading to overcrowded alkene **5** in 76% yield with a *cis*/*trans* ratio of about 2:3, as determined by ^{1}H NMR.

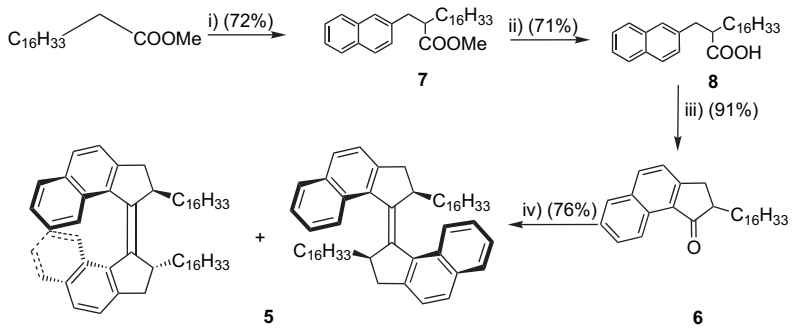
In order to study the dynamic behavior of these molecules, separation of the *cis* and *trans* isomers was required. Due to the high apolar nature of the compound, the R_f values of the two isomers were found to be very similar, so the separation was performed on silica loaded with silver nitrate according to a literature procedure.[26] Due to the coordination between the metal and the olefinic double bond, the separation of the isomers was indeed improved.

The discrimination between *trans*-**5** and *cis*-**5** is easily accomplished based on ^{1}H NMR analysis. The proton resonances in the aromatic region of *trans*-**5** are found at values between δ 7.4 and 8.3 ppm, while those of *cis*-**5** are found between δ 6.3 and 7.7 ppm, in agreement with the data previously reported for **2**.[20] The reason that the ^{1}H NMR resonances for the indicated protons are observed at higher field in *cis*-**5** is the aromatic ring current anisotropy due to the close proximity of the naphthalene moieties with each other. It should be emphasized that only the *R*,*R* and *S*,*S* (and not *R*,*S*) diastereomers were observed as products from the McMurry coupling. This conclusion comes from the fact that the ^{1}H NMR spectrum of **5** showed resonance frequencies similar to those of **2**, where COSY, NOESY, and X-ray analysis were performed and the molecular geometry unequivocally proved.[20]

2.2. Isomerization processes

2.2.1. NMR measurements

In order to demonstrate the unidirectionality of the rotary motion of **5** (Fig. 1), ^{1}H NMR measurements were performed using pure *trans*-**5** and *cis*-**5** (Figs. 2 and 3). The ^{1}H NMR spectrum of *trans*-**5** in toluene-d_8 (Figure 2a) in the range 2–4 ppm shows the absorbtions of the three protons of the five-membered rings (namely H_a, H_b, and H_c, see Fig. 1). This sample was irradiated at 365 nm in an ethanol bath at −80 °C till the PSS (photostationary state), leading to the unstable-*cis* form. This is defined as the *cis* isomer where the first methylene of the alkyl chains at the stereogenic center is in a pseudo-equatorial position. The assignment of the *cis* geometry is based on the low field shift of all the three protons shown (Fig. 2b). The conversion from stable-*trans* to unstable-*cis* at the PSS was quantitative. The sample was then allowed to warm up to 50 °C until the thermal conversion to the stable-*cis* isomer (the *cis* isomer where the first methylene of the alkyl chains at the stereogenic center is in a pseudo-axial orientation) was complete (Fig. 2c). Here H_a shifts even further downfield, while H_b



Scheme 1. Synthesis of **5**. Reagents and conditions: (i) LDA, THF, −78 °C; 2-bromomethylnaphthalene, THF, −78 °C→rt (72%); (ii) aq LiOH (71%); (iii) thionylchloride, DCM, reflux, $AlCl_3$, DCM, 0 °C→rt (91%); (iv) Zn, $TiCl_4$, THF (76%; *cis*/*trans*=2:3).

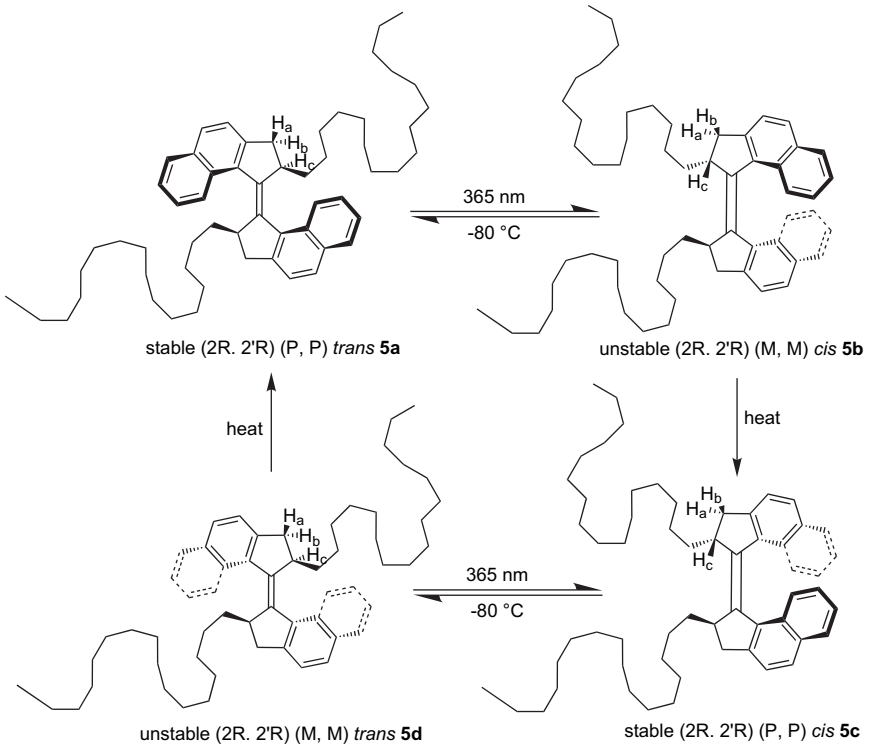


Figure 1. Rotary cycle of molecular motor **5**. In the NMR study, all the steps were performed in toluene-d_8; for the thermal steps a maximum temperature of 50 °C was reached.

moves to slightly higher field, and H_c does not shift significantly. The thermal conversion of unstable-*cis* to stable-*cis* completes the first half of the rotary cycle. The same procedure was followed for pure *cis*-**5**; a sample was measured in toluene-d_8 (Fig. 3a), and subsequently irradiated in an ethanol bath at −80 °C till the PSS was reached. This time, incomplete conversion was found; the unstable-trans/stable-*cis* ratio at the PSS was about 3:1, as calculated from the NMR integrations (Fig. 3b). Again we observed a shift of all the three protons; H_a and H_c to higher field, while H_b shifted to lower field. Warming up the sample, the unstable-*trans* converted into the stable-*trans* form, exhibiting a high field shift for all the three protons considered, while the spectrum of the stable-*cis*

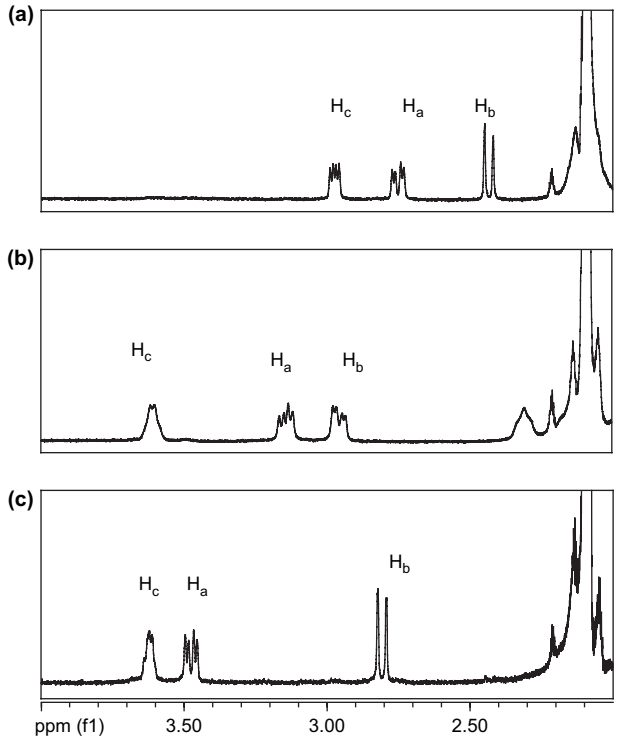


Figure 2. (a) ^{1}H NMR spectrum of the motor *trans*-**5** in toluene-d_8 in the range 2–4 ppm; (b) PSS after irradiation at 365 nm; (c) after thermal step. All the spectra are acquired at −50 °C.

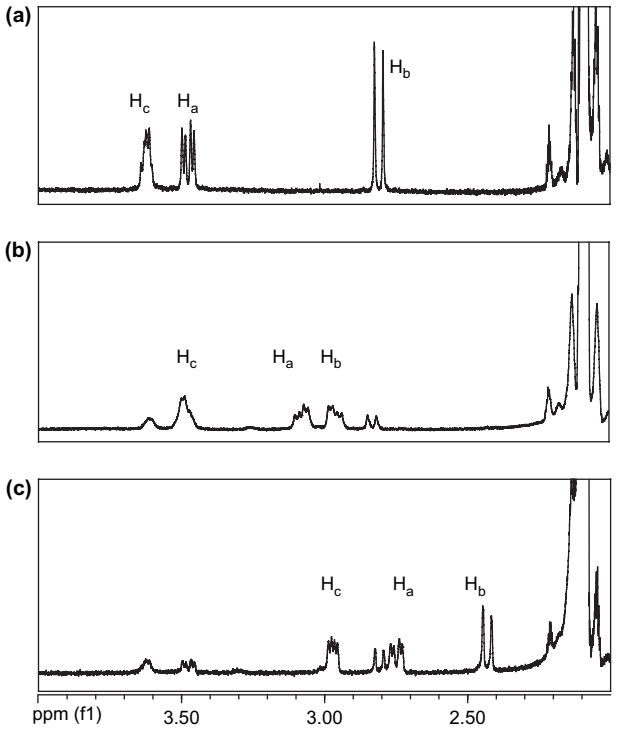


Figure 3. (a) ^{1}H NMR spectrum of the motor *cis*-**5** in toluene-d_8 in the range 2–4 ppm; (b) PSS after irradiation at 365 nm; (c) after thermal step. All the spectra are acquired at −50 °C.

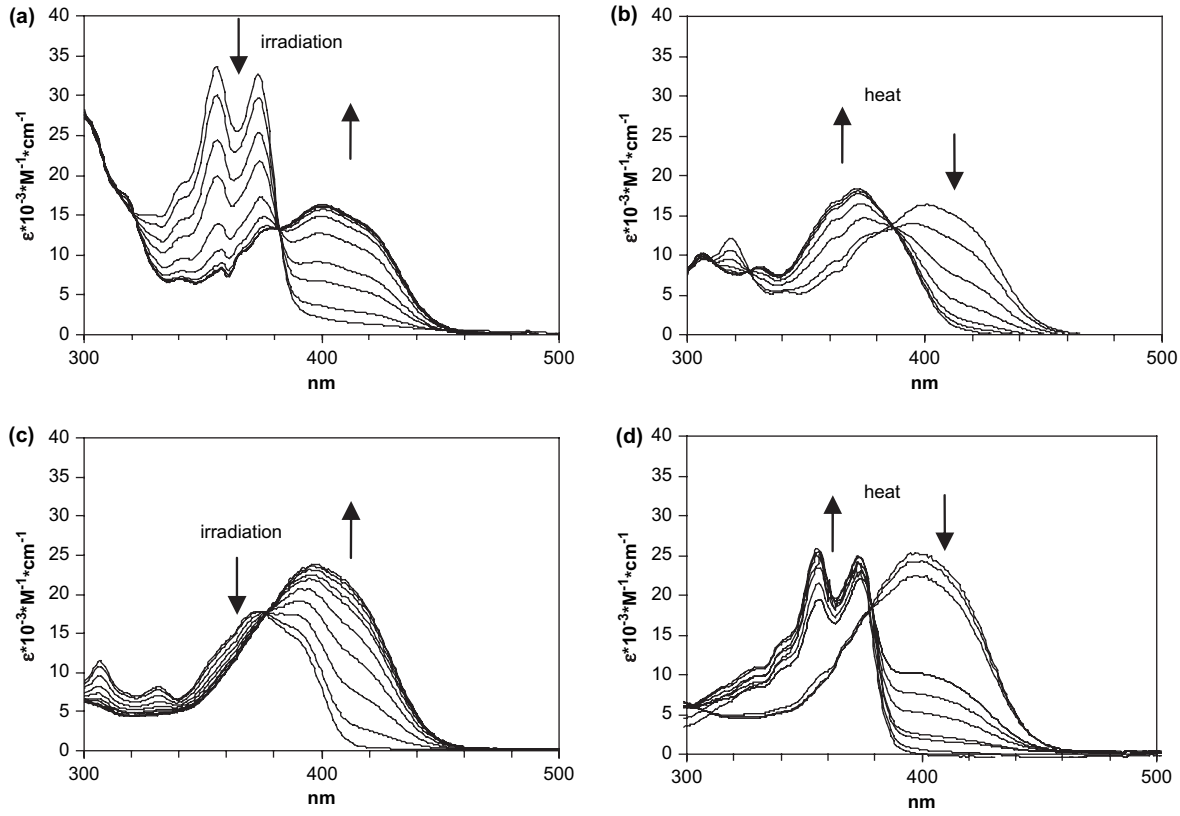


Figure 4. UV–vis spectroscopy of the molecular motor **5**: (a) *trans* isomer in *n*-hexane irradiated at −15 °C at 365 nm and (b) heated to 35 °C; (c) *cis* isomer irradiated at −50 °C at 365 nm and (d) heated to 25 °C.

did not undergo any modification (Fig. 3c). A complete 4-step cycle involving two photochemical and two thermal steps has therefore been established.

2.2.2. UV measurements

Solutions in *n*-hexane of the pure *cis* and the pure *trans* isomers of motor **5** were used for UV–vis spectroscopy measurements. In Figure 4 the UV–vis spectral changes during all four steps of the isomerization cycle are shown. A solution of *trans*-**5** in hexane was irradiated at −15 °C with a mercury lamp equipped with a Pyrex filter (λ>280 nm) till the PSS was reached, and the conversion followed by UV–vis spectroscopy. The presence of isosbestic points (Fig. 4a) indicated that the photochemical process is a unimolecular conversion. The UV spectrum of the unstable-*cis* shows a red shift, as is typical for the unstable forms of this class of molecules.[19,20] The sample was then allowed to warm to room temperature and in this thermal process isosbestic points were again found (Fig. 4b). Going from the unstable-*cis* to the stable-*cis*, a blue shift was observed in the UV–vis spectrum.

The same route was followed starting from the *cis* isomer (Fig. 4c,d). The only difference is that the irradiation was performed at −50 °C, as the isomerization of unstable-*trans*-**5** is predicted to be much faster than the thermal conversion of the unstable-*cis*-**5**.[20,27] Again, in both photochemical and thermal steps isosbestic points were observed (Fig. 4c,d).

By HPLC analysis (OD column, solvent: heptane 100%), the PSSs were determined to be 16:84 for the stable-*trans*-**5**/unstable-*cis*-**5**, and 12:88 for the stable-*cis*-**5**/unstable-*trans*-**5** mixtures. Therefore it was possible to calculate the UV spectra of the unstable forms (Fig. 5).[28]

2.2.3. CD measurements

In order to verify the inversion in helicity in each isomerization step and to study the kinetics of the two thermal helix inversion steps, CD measurements were performed. Pure enantiomers were readily obtained by resolution using preparative HPLC applying a Chiracel-OD column and heptane as eluent.

The CD spectrum of the first enantiomer of *trans*-**5** in hexane at −50 °C is shown in Figure 6a. According to the absolute configuration determination of **2** reported by Harada et al.[21] on related molecules, this enantiomer was assigned the (2*R*,2′*R*)-(*P*,*P*) configuration. Upon irradiation with a mercury lamp equipped with a Pyrex filter (λ>280 nm) till the PSS was reached, the CD spectrum changed significantly because of the presence of a major quantity of (2*R*,2′*R*)-(*M*,*M*) unstable-*cis*-**5b** of opposite helicity then the stable-*trans*-**5a**. The CD spectrum of (2*R*,2′*R*)-(*M*,*M*) unstable-*cis*-**5** is not a mirror image of that of (2*R*,2′*R*)-(*P*,*P*) stable-*trans*-**5a**, because

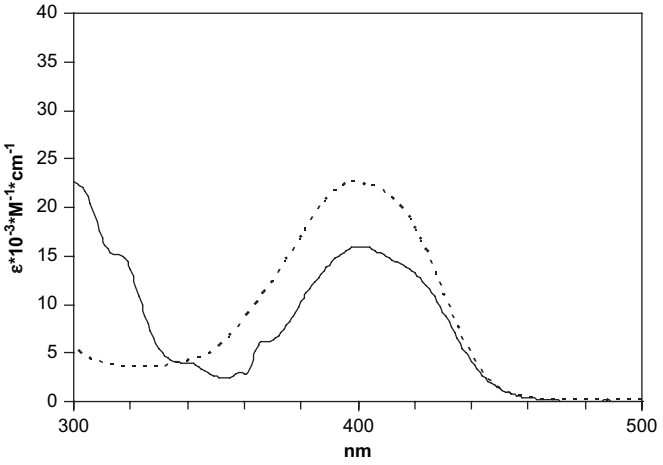


Figure 5. UV–vis spectra of unstable forms of motor **5** in *n*-hexane. Solid line: unstable-*cis*-**5** at −15 °C, dotted line: unstable-*trans*-**5** at −50 °C.

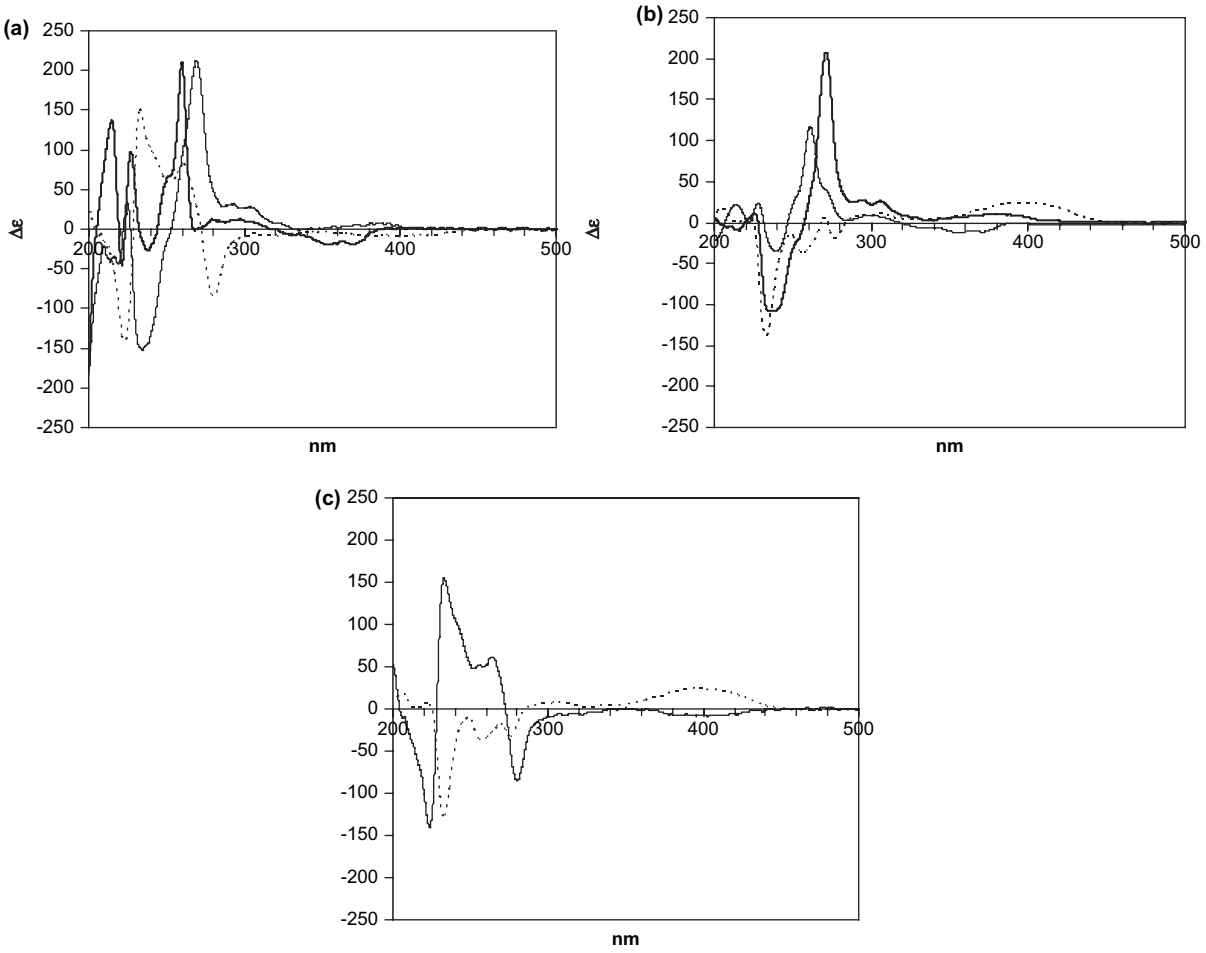


Figure 6. CD spectra of molecular motor **5**: (a) thick line: *trans* (2*R*,2′*R*)-(*P*,*P*) **5a**, dotted line: photostationary state after irradiation at λ>280 nm, thin line: after warming; (b) thick line: *cis* (2*R*,2′*R*)-(*P*,*P*) **5c**, dotted line: photostationary state after irradiation at λ>280 nm, thin line: after warming; (c) solid line: unstable *cis*-**5b**, dotted line: unstable *trans*-**5d**.

although the helicity is inverted, the chirality at the two stereogenic centers is unchanged. Subsequently, the sample was allowed to warm in order to complete the thermal inversion leading to the (2*R*,2′*R*)-(*P*,*P*) stable-*cis*-**5c**. In doing so, the helicity changes once more and again *P*-helicity was observed, as in the case of pure stable-*trans*-**5a**. We observed, indeed, that the Cotton effect for (2*R*,2′*R*)-(*P*,*P*) stable-*cis*-**5c** is similar to the Cotton effect for the pure (2*R*,2′*R*)-(*P*,*P*) stable-*trans*-**5a**.

Next, enantiopure *cis*-**5** was studied. The CD spectrum of the solution in hexane at −50 °C of the first enantiomer eluted (which in analogy with the results reported by Harada et al.[21] for **2** was assigned as the (2*R*,2′*R*)-(*P*,*P*) isomer) is shown in Figure 6b. The solution of (2*R*,2′*R*)-(*P*,*P*)-*cis*-**5** was irradiated with a mercury lamp equipped with a Pyrex filter (λ>280 nm) till the PSS was reached. As in the former case, the CD spectrum now was significantly different because of the presence of a major quantity of (2*R*,2′*R*)-(*M*,*M*) unstable-*trans* of opposite helicity than (2*R*,2′*R*)-(*P*,*P*) stable-*cis* (ratio of stable-*cis*-**5**/unstable-*trans*-**5**=12:88 by HPLC, vide supra). Again we observed that the CD spectrum of this isomer is not a mirror image of the initial one, because although the helicity is inverted, the chirality at the two stereogenic centers is unchanged. Subsequently, the sample was allowed to warm till the thermal inversion was completed, leading to (2*R*,2′*R*)-(*P*,*P*) stable-*trans*. The helicity changes once more, returning to a spectrum with a Cotton effect almost similar to that observed for the pure (2*R*,2′*R*)-(*P*,*P*) stable-*cis* isomer.

Based on the CD spectra at the PSSs and the results from HPLC analysis, it was possible to calculate the CD spectra of the unstable forms[28] (Fig. 6c).

The changes in CD absorption as a function of time due to the thermal inversion at the specific wavelengths at different temperatures 25, 35, 45, and 55 °C for the thermal step of unstable-*cis*-**5b** to stable-*cis*-**5c** and at temperatures 20, 10, 0, and 10 °C for the thermal step of unstable-*trans*-**5d** to stable-*trans*-**5a** were measured. From these data the rate constants (k) for the first-order thermal helix inversion processes at different temperatures were obtained. The enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were determined from the rate constant by means of the Eyring plot, and from this the Gibbs free energy of activation ($\Delta^{\ddagger}G^{0}$) and the half-life time ($t_{1/2}$) at room temperature were calculated (in the Eyring plot the correlation coefficients R were 0.976 and 0.987, respectively, for the thermal step of unstable-*cis*-**5b** to stable-*cis*-**5c** and unstable-*trans*-**5d** to stable-*trans*-**5a**). The results are summarized in Table 1, including the PSS ratios discussed above. The corresponding data determined for the methyl substituted molecular motor **2** previously reported[20] are included for comparison. It was observed that motor **5** provided better PSSs in all the examined cases. The half-life times at room temperature for the thermal helix inversion were of the same order of magnitude for **2** and **5** (Table 1).

3. Conclusions

A derivatized molecular motor with long alkyl chains at the two stereogenic centers has been synthesized and characterized. The experimental results show that this new molecule still works as a unidirectional light-driven molecular motor.

Even though it is tempting to say that it is slightly faster (see Table 1) than the methyl analog (probably this is due to an

Table 1
Photostationary state ratios and kinetic and thermodynamic parameters of thermal isomerization processes for motors **2** and **5**

Motor		**2**	**5**
PSS stable-*trans*/unstable-*cis* (hexane, λ>280 nm)		21:79	16:84
PSS stable-*cis*/unstable-*trans* (hexane, λ>280 nm)		22:78	12:88
PSS stable-*trans*/unstable-*cis* (toluene, λ=366 nm)		10:90	>5:95
Thermal step unstable–stable-*cis*	$t_{1/2}$ 20 °C	78 min	37 min
	$\Delta^{\ddagger}G^0$ (20 °C) (kJ mol^{-1})	93	91
	$\Delta^{\ddagger}H$ (kJ mol^{-1})	84	77
	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	−31	−47
Thermal step unstable–stable-*trans*	$t_{1/2}$ 20 °C	18 s	16 s
	$\Delta^{\ddagger}G^0$ (20 °C) (kJ mol^{-1})	80	79
	$\Delta^{\ddagger}H$ (kJ mol^{-1})	73	55
	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	−24	−81

increased steric hindrance of the C_{16} alkyl groups in **5** at the stereogenic centers compared with the methyl groups in **2**, slightly raising the ground states[29]) we believe that the most important outcome from the kinetic studies is that motor **5** and **2** have comparable speeds in both thermal steps. Finally, motor **5** exhibited more selective photostationary states compared to motor **2**, with respect to the unstable form in all the considered cases. These findings set the stage for tethering larger units to the motor molecule.

4. Experimental section

4.1. General

Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. Solvents were distilled and dried before use by standard methodology. NMR spectra were obtained using a Varian Mercury Plus and a Varian Unity Plus Varian-500, operating at 399.93 and 499.86 MHz, respectively. Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signals of $CDCl_3$ (^{1}H NMR, δ 7.26 ppm; ^{13}C NMR, δ 77.0 ppm) or toluene-d_8 (^{1}H NMR, δ 2.09 ppm). Melting points were taken on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope and are uncorrected. MS (EI) and HRMS (EI) spectra were obtained with a JEOL JMS-600 spectrometer. The IR spectroscopy measurements were performed on a Nicolet Nexus FT-IR apparatus. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Column chromatography was performed on silica gel (Aldrich 60, 230–400 mesh). Preparative HPLC was performed on a Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, a 811C dynamic mixer, a 805 manometric module, with a 119 UV–vis detector, and a 202 fraction collector, using the Chiralcel OD (Daicel) column. Elution speed was 1 ml/min. Irradiation experiments were performed with a Spectroline ENB-280C/FE UV lamp at 365 nm. The photostationary states were determined by monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed using a Hewlet–Packard HP 8543 FT spectrophotometer. Thermal helix inversions were monitored by CD spectroscopy using a JASCO J-715 spectropolarimeter and a JASCO PFD-350S/350L Peltier-type FDCD attachment with temperature control. Uvasol-grade solvents (Merck) were used.

4.1.1. 2-Bromomethylnaphthalene

Prepared according to a literature procedure.[30]

4.1.2. 2-Heptadecyl-3-naphthylpropionic acid methyl ester (**7**)

An LDA solution in THF (100 ml) was prepared at −78 °C by adding *n*-BuLi (10 ml, 16 mmol) to diisopropylamine (2.25 ml, 16 mmol) followed by stirring for 20 min at −78 °C. A solution of methyl stearate (4.74 g, 15.9 mmol) in THF (50 ml) was added dropwise at −50 °C and the resulting mixture was stirred for 1.5 h at −78 °C. A solution of 2-bromomethylnaphthalene (3.9 g, 17.6 mmol) in THF (20 ml) was added slowly and the reaction mixture was allowed to warm overnight to room temperature. Addition of saturated aqueous solution of NH_4Cl (200 ml), extraction with diethyl ether (3×100 ml), drying of the organic layers over $MgSO_4$ followed by evaporation of the solvent gave a solidified oil. Purification by column chromatography (SiO_2, ethylacetate/pentane 1:16) gave a waxy solid (5.0 g, 72%), which was used immediately in the next step.

4.1.3. 2-Heptadecyl-3-naphthylpropionic acid (**8**)

2-Heptadecyl-3-naphthylpropionic acid methyl ester (5.0, 11.4 mmol) was dissolved in a mixture of THF (100 ml) and ethanol (100 ml) and a solution of LiOH (1.8 g) in water (100 ml) was slowly added. The reaction mixture was refluxed for 24 h. After cooling to room temperature, diluted aq HC1 was added and the mixture was extracted with diethyl ether (3×150 ml). The organic layers were collected and washed with brine, dried over Na_2SO_4, and the solvent evaporated. Purification by column chromatography (SiO_2, ethylacetate/pentane 1:16; R_f=0.23 in ethylacetate/pentane 1:4) gave a waxy solid (3.41 g, 71%); mp 67.0–67.5 °C. IR (KBr): 3054, 2922, 2852, 1696, 1467 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (br, 3H), 1.19 (br, 28H), 1.50 (br, 1H), 1.61 (br, 1H), 2.72 (br, 1H), 2.82–2.89 (m, 1H), 3.04–3.11 (m, 1H), 7.34 (d, *J*=8.4 Hz, 1H), 7.44–7.49 (m, 2H), 7.64 (s, 1H), 7.76–7.82 (m, 3H), 10.0 (br, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.03, 22.62, 27.21, 29.50 (br), 31.75, 31.94, 38.10, 47.51, 125.40, 125.45, 127.22, 127.27, 127.53, 127.59, 128.01, 132.21, 133.50, 136.61; HRMS EI: calcd for $C_{29}H_{44}O_2$, 424.3341; found, 424.3356. Anal. Calcd for $C_{29}H_{44}O_2$: C, 82.02; H, 10.44; O, 7.53. Found: C, 82.10; H, 10.45; O, 7.30.

4.1.4. 2-Heptadecyl-2,3-dihydro-1H-cyclopenta[a] naphthalen-1-one (**6**)

To a solution of 2-heptadecyl-3-naphthylpropionic acid (2.2 g, 5.2 mmol) in dichloromethane (100 ml), thionyl chloride (2.6 ml) and 4 drops of DMF were added, and the mixture refluxed for 6 h. After evaporation of all volatiles dichloromethane was added (200 ml) and the mixture cooled to 0 °C, and at this temperature $AlCl_3$ (1.4 g, 10.4 mmol) was added. Stirring was continued overnight and a saturated aqueous solution of NH_4Cl (100 ml) was added. After separation of phases, the water layer was extracted twice with dichloromethane (100 ml). The organic layers were collected, washed with water, and dried over $MgSO_4$. After evaporation of solvent, the crude product was purified by column chromatography (SiO_2, 5% ethylacetate in pentane; R_f=0.56) to give a viscous oil (1.96 g, 91%). IR (KBr): 2919, 2849, 1684, 1462 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86–0.90 (m, 3H), 1.10–1.54 (m, 29H), 2.00–2.06 (m, 1H), 2.72–2.79 (m, 1H), 2.87 (d, *J*=3.3 Hz, 1H), 2.93 (d, *J*=3.3 Hz, 1H), 3.36–3.47 (q, *J*=7.3 Hz, 1H), 7.49–7.69 (m, 3H), 7.85 (d, *J*=8.1 Hz, 1H), 8.03 (d, *J*=8.4 Hz, 1H), 9.16 (d, *J*=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.11, 21.95, 27.83, 29.50 (br), 32.06, 33.84, 48.81, 124.03, 126.13, 128.21, 129.16, 129.87, 131.12, 132.89, 135.94, 157.21, 209.92; HRMS EI: calcd for $C_{29}H_{42}O$, 406.3236; found, 406.3238. Anal. Calcd for $C_{29}H_{42}O$: C, 85.66; H, 10.41; O, 3.93. Found: C, 85.65; H, 10.45; O, 4.10.

4.1.5. (2R*,2′R*)-(P*,P*)-(E)-(±)- and (2R*,2′R*)-(P*,P*)-(Z)-(±)-2,2′-Diheptadecyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[a]naphthalenylidene (**5**)

This structure does not express the absolute stereochemistry of the molecule. To a stirred suspension of zinc powder (0.78 g, 11.5 mmol) in THF (5 ml) was added slowly $TiCl_4$ (0.66 ml, 6 mmol) at 0 °C. The resulting black slurry was then heated at reflux for 2 h. A solution of 2-heptadecyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (1.22 g, 3 mmol) in THF (4 ml) was added and heating was

continued for 3 days. The reaction mixture was poured into a saturated aqueous solution of NH_4Cl (100 ml) and extracted with ethylacetate (3×80 ml). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield impure product as brown oil. The first purification was performed by column chromatography (SiO_2, 2% ethylacetate in pentane; R_f (*cis*)=0.45 in pentane, R_f (*trans*)=0.54 in pentane), yielding **5** (0.85 g, 76%) as a mixture of *cis* and *trans* isomers in a ratio of about 2:3. Further purification was performed by column chromatography with SiO_2 pretreated with a 10% solution of $AgNO_3$ in CH_3CN.[26] (2*R**,2′*R**)-(*P**,*P**)-(*E*)-(±)-2,2′-diheptadecyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]-naphthalenylidene: waxy solid; mp 73.9–75.0 °C. IR (KBr): 3049, 2924, 2847, 1475 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.85–0.90 (m, 6H), 1.20–1.25 (m, 58H), 2.01–2.05 (m, 2H), 2.52 (d, *J*=15.6 Hz, 2H), 2.82–2.88 (m, 4H), 7.37 (d, *J*=8.4 Hz, 2H), 7.43–7.51 (m, 4H), 7.74 (d, *J*=8.0 Hz, 2H), 7.89 (d, *J*=8.7 Hz, 2H), 8.25 (d, *J*=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 78 MHz) δ 14.44, 23.00, 28.31, 29.68, 30.02, 30.24, 32.23, 35.07, 38.10, 48.26, 123.69, 124.28, 126.99, 127.86, 128.54, 129.83, 132.44, 138.14, 139.80, 144.49; HRMS EI: calcd for $C_{58}H_{84}$, 780.6573; found, 780.6551. Anal. Calcd for $C_{58}H_{84}$: C, 89.16; H, 10.84. Found: C, 88.35; H, 10.82. Chiral separation: Chiralcel OD (heptane 100%), retention times: (2*R*,2′*R*)-(*P*,*P*) 15.92 min and (2*S*,2′*S*)-(*M*,*M*)[26] 19.85 min; $[\alpha]_D^{20}$ +195 (*c* 0.00205, hexane) for the second enantiomer eluted. (2*R**,2′*R**)-(*P**,*P**)-(*Z*)-(±)-2,2′-diheptadecyl-2,2′,3,3′-tetrahydro-1,1′-bicyclopenta[*a*]naphthalenylidene: waxy solid; mp 52.4–53.1 °C. IR (KBr): 3048, 2923, 2851, 1466 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86–0.88 (m, 6H), 1.20–1.62 (m, 60H), 2.82 (m, 2H), 3.45–3.49 (m, 4H), 6.31–6.36 (m, 2H), 6.52 (d, *J*=8.4 Hz, 2H), 7.46 (d, *J*=8.4 Hz, 2H), 7.61–7.70 (m, 4H); ^{13}C NMR ($CDCl_3$ 78 MHz) δ 14.74, 23.30, 29.54, 29.98, 30.31, 30.71, 32.53, 34.82, 38.46, 49.37, 97.59, 124.73, 125.23, 125.83, 126.95, 128.34, 129.05, 130.59, 133.59, 141.40, 142.72; HRMS EI: calcd for $C_{58}H_{84}$, 780.6573; found, 780.6569. Anal. Calcd for $C_{58}H_{84}$: C, 89.16; H, 10.84. Found: C, 88.90; H, 10.90. Resolution: Chiralcel OD (heptane 100%), retention times: (2*R*,2′*R*)-(*P*,*P*) 8.82 min and (2*S*,2′*S*)-(*M*,*M*)[21] 12.64 min; $[\alpha]_D^{20}$ +200 (*c* 0.015, hexane) for the second enantiomer eluted.

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