A redesign of light-driven rotary molecular motors†‡

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Received 11th October 2007, Accepted 23rd November 2007
First published as an Advance Article on the web 13th December 2007
DOI: 10.1039/b715652a

Structural modification of unidirectional light-driven rotary molecular motors in which the naphthalene moieties are exchanged for substituted phenyl moieties are reported. This redesign provides an additional tool to control the speed of the motors, and should enable the design and synthesis of more complex systems.

Introduction

Rotary molecular motors are ubiquitous in biological systems where they provide the essential mechanochemical driving force for cellular functions including ion and proton pumping, cellular translocation, and ATP synthesis.[1] Synthetic molecular motors would allow chemists the possibility to mimic their biological functions as well as to invent new applications in, for instance, smart materials and nanodevices.[2] Successful designs for synthetic rotary molecular motors have been reported, including those powered by light energy,[3–5] and chemical energy.[6,7]

One of the most promising designs is based on chiral overcrowded alkenes, comprising a naphthalene chromophore linked through a central alkene to an identical or different aromatic chromophore to give the 'first-generation' (*e.g.* **1** and **2**, Fig. 1) and 'second-generation' molecular motors, respectively.[3,4] Two major challenges to overcome to be able to harness work from these systems include accelerating the speed of rotation, and functionalization to allow incorporation into more complex molecular systems. Addressing these challenges has been deceptively difficult. Several recent investigations on the modification of these motors have revealed that minor alterations in their structure can lead to a dramatic enhancement,[8–10] as well as sometimes undesired[11,12] effects on the motor's speed, in some cases destroying the function as a motor altogether.[11,13] Moreover, the synthesis of functionalized versions of these systems is mired by the necessity to incorporate functionalized naphthalene moieties into the system.

Here we report the redesign of both our first- and second-generation motors, wherein the naphthalene moiety is exchanged for a substituted phenyl ring (structure **3** illustrates this modification to first-generation motor **2**, Fig. 1). This simplification is anticipated to both provide a convenient handle for tuning the speed of the motor,[14] as well as facilitating the synthesis of functionalized motors by avoiding the need to derivatize the naphthalene moiety through multistep syntheses.[15] Key challenges to achieving this goal include tuning of the structure to avoid photocyclization of the *cis* isomer,[11] and to maintain the necessary steric interactions that lead to the formation of the metastable intermediates upon photoirradiation of both *cis* and *trans* isomers.

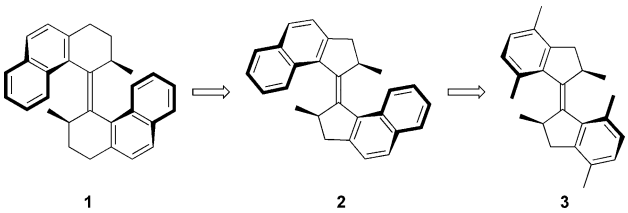

Fig. 1 Design modifications of the original molecular motor **1**, accelerated motor **2**, and new motor **3**.

In addition to *cis* → *trans* photoisomerization, a number of rigidified stilbenes undergo photocyclization as the predominant side reaction.[16] However, this photocyclization does not occur in stilbene derivatives in which the geminal substituents of the central alkene are fused through 5-membered rings.[17] Thus, it was anticipated that a motor based on this core would not suffer from photochemical cyclization side reactions. In **3**, the naphthalene function of **2** was exchanged with a dimethyl-substituted phenyl ring to preserve the steric interactions in the *fjord* region which are necessary to generate conformational bistability.

Results and discussion

Overcrowded alkene **3** was conveniently prepared in two steps by a tandem Friedel–Crafts/Nazarov cyclization of methacrylic acid onto *p*-xylene in polyphosphoric acid to give 2,4,7-trimethylindan-1-one,[18] followed by a McMurry coupling to give a 3.5 : 1 mixture of *cis*-**3** and *trans*-**3** in 32% overall yield (Fig. 2). Key data supporting the structural assignment include the upfield shift of the ^{1}H NMR absorptions ($CDCl_3$) of the aryl methyl groups located in the *fjord* region of the *cis* isomer (1.51 ppm) relative to the *trans* isomer

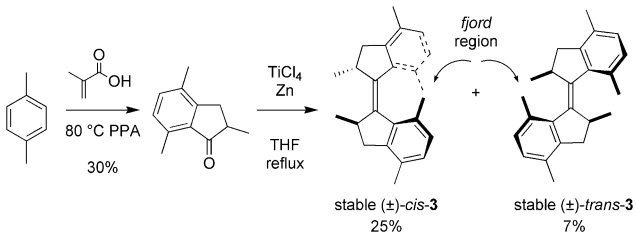

Fig. 2 Tandem Friedel–Crafts/Nazarov cyclization, followed by a McMurry coupling in the synthesis of *cis*-**3** and *trans*-**3**.

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† Electronic supplementary information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra of *cis*-**3**, *trans*-**3** and **6**, in addition to ^{1}H NMR spectra of the PSS mixtures. See DOI: 10.1039/b715652a

‡ CCDC reference numbers 666199 and 666200. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715652a

(2.04 ppm), which are consistent with the expected shielding caused by their close proximity to the adjacent aromatic rings.

X-Ray crystallography‡ showed that in both *cis* and *trans* isomers, the stereogenic methyl group adopts a pseudo-axial conformation to minimize steric strain imposed by the adjacent substituents on the overcrowded central alkene (Fig. 3). Comparison of the X-ray structures of the stable isomers of **3** with the analogous isomers of **2** show how the increased steric demands of the sp^3 centers in the *fjord* region (due to the presence of the methyl substituents) relative to sp^2 centers (as in **2**) influences the geometry around the central olefin moiety of both isomers.

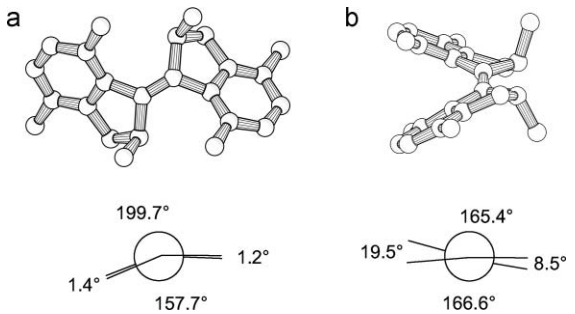

Fig. 3 (a) Pluto drawing (top) and Newman projection (bottom) of stable *trans*-**3**. (b) Pluto drawing (top) and Newman projection (bottom) of stable *cis*-**3**.

The X-ray structure of stable *trans*-**3** (Fig. 3) reveals that it adopts a twisted, *syn*-folded conformation, similar to the *trans* isomer of **2**. However, in *trans*-**3**, the fold angle of the double bond (199.7°) is slightly larger than that observed in the *trans* isomer of **2** (197.8°), hinting at an increase in strain generated by the bulkier sp^3 hybridized methyl substituent. This might in turn cause a greater destabilization of the unstable form of *trans*-**3** compared with **2** (*vide infra*).

In contrast to the *cis* isomer of **2**, which adopts an *anti*-folded conformation, *cis*-**3** adopts an *anti*-twisted conformation (Fig. 3). This is attributed to the additional steric demands generated by the two interfering sp^3 centers of the methyl groups present in the *fjord* region of the *cis* isomer.

By analogy with **1** and **2**, it was anticipated that **3** should function as a light-powered molecular rotary motor which proceeds through 4 distinct steps in a unidirectional fashion (Fig. 4). Starting with stable *cis*-**3**, a photochemical isomerization generates

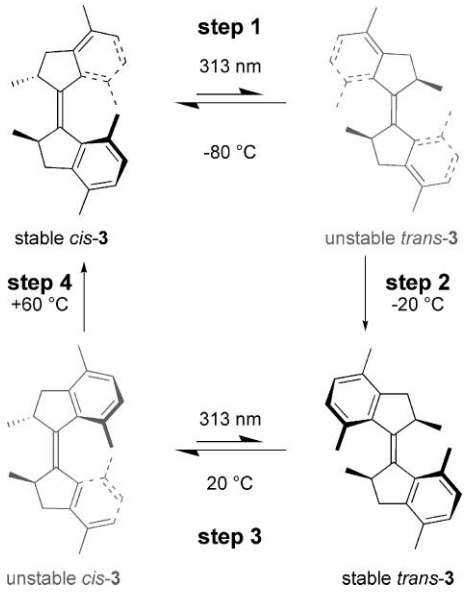

Fig. 4 Rotary cycle of molecular motor **3**.

unstable *trans*-**3** in which the stereogenic methyl substituents are forced into a conformationally strained pseudo-equatorial conformation (step 1). This strain is released during the thermal helix inversion step (step 2) whereby the molecule isomerizes to give stable *trans*-**3**, in which the stereogenic methyl groups resume an energetically favoured axial orientation. A second photochemical double bond isomerization (step 3) generates unstable *cis*-**3**, which is followed by a second thermal helix inversion (step 4) which ultimately regenerates stable *cis*-**3**. The two photochemical and two thermal steps add up to a full 360° rotation of the upper part relative to the lower part. The unidirectionality of the rotary cycle is dictated by the helicity of the overcrowded alkene and the absolute configuration of the stereogenic centers.

Irradiation of a solution of stable *cis*-**3** in hexane with 313 nm light at −80 °C showed a red-shift of the major long wavelength band in the UV spectrum from 310 nm to an absorption centered at 325 nm (Fig. 5). This red-shift is consistent with increased strain on the central double bond, and hence the generation of a higher energy isomer.[12]

After irradiation (λ_{max} = 313 nm, −80 °C) of stable *cis*-**3** in $CDCl_3$, its ^1H NMR spectrum showed that the photostationary

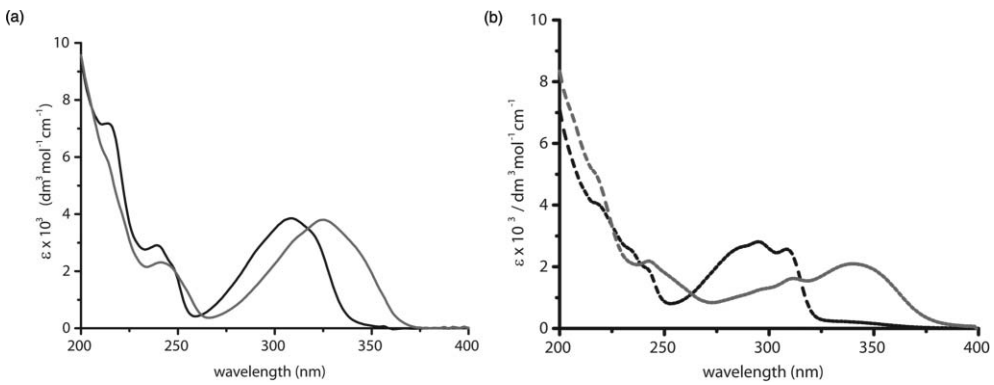

Fig. 5 Left: UV spectra of hexane solutions of stable *cis*-**3** at −50 °C (black, solid), the PSS_{313nm} containing unstable *trans*-**3** at −50 °C (grey, solid). Right: stable *trans*-**3** (black, dashed) at rt, and a PSS_{365nm} containing unstable *cis*-**3** at rt (grey, dashed).

state (PSS) contained a mixture of stable *cis*-**3** and unstable *trans*-**3** in a 8 : 1 ratio. The identity of unstable *trans*-**3** was evident from the appearance of a new set of absorptions which were consistent with the *trans* structure, including the benzylic methyl protons in the *fjord* region which no longer experience shielding by the adjacent aromatic rings. This change in their environment leads to a downfield shift from 1.51 ppm in stable *cis*-**3** to 2.11 ppm in unstable *trans*-**3**. Informative changes also include the upfield shift of the doublet generated by the stereogenic methyl group from 1.05 ppm§ in stable *cis*-**3** to 0.82 ppm in unstable *trans*-**3**. This shift is consistent with analogous changes in the ^{1}H NMR spectrum of **2**.[12]

Upon warming the sample at −20 °C for 20 min, the ^{1}H NMR spectrum revealed that unstable *trans*-**3** had undergone a quantitative thermal helix inversion to generate stable *trans*-**3**. Each of the absorptions from the unstable isomer were replaced by signals from the stable isomer, including the doublet from the stereogenic methyl at 0.82 ppm shifting to 1.08 ppm upon going from an equatorial to an axial conformation. These data demonstrate that this structurally modified motor undergoes the crucial thermal conversion from its unstable isomer to the stable isomer in an irreversible, unidirectional fashion.

The thermal isomerization was followed by monitoring the change in absorption at 335 nm at four different temperatures (−45, −40, −35 and −30 °C). Using the Eyring equation, it was determined that the isomerization has a Gibbs free energy of activation ($\Delta^{\ddagger}G^{\circ}$) of 71 kJ mol^{-1}. This value corresponds to a half-life at rt of 1.2 s, which shows that the helix inversion is faster than the analogous helix inversion of the related motor **2**, of which the unstable *trans* to stable *trans* isomerization occurs with a half-life of 18 s under identical conditions. It is possible that a slight increase in steric crowding between the stereogenic methyl groups and the benzylic methyl groups in the *fjord* region (compared with the aromatic ring present in **2**) results in subsequent destabilization of unstable *trans*-**3** relative to unstable *trans*-**2**.

The UV spectrum of stable *trans*-**3** and unstable *cis*-**3**, generated by irradiation (λ_{max} = 313 nm) of pure stable *trans*-**3** at rt, also shows a dramatic red-shift of the major absorption band. This includes a red-shift of the absorption at 290 nm to a broad absorption with a maximum at 340 nm, which is consistent with the generation of unstable *cis*-**3**, reflecting the increased torsional strain on the central double bond.

Irradiation of a benzene-d_6 solution of stable *trans*-**3** at 313 nm generated a PSS comprising a mixture of stable *trans*-**3** : unstable *cis*-**3** in a 1.1 : 1 ratio.[19] Photoconversion to the unstable *cis* isomer was apparent from the upfield shift of the aryl methyl groups in the *fjord* region from 2.04 ppm in stable *trans*-**3** to 1.61 ppm in unstable *cis*-**3**. Additionally, the doublet from the methyl group at the stereogenic center shifted upfield from 1.12 ppm to 1.35 ppm, consistent with the analogous shifts observed in **2**. The ^{1}H NMR spectrum of the sample after heating (60 °C for 2 h) revealed that all of the absorptions of unstable *cis*-**3** were replaced by the absorptions expected from stable *cis*-**3**, exemplified by the shift of the doublet from the stereogenic methyl group from 1.35 to 1.10 ppm. These ^{1}H NMR data indicated that the thermal isomerization quantitatively gave stable *cis*-**3**.

§ This value was obtained at low temperature, and is slightly shifted from the corresponding absorption measured at rt.

The kinetic parameters of the thermal conversion of unstable *cis*-**3** to stable *cis*-**3** in heptane solution were determined by monitoring the change in absorption at 350 nm at four temperatures (T = 70, 80, 90, 100 °C). Using the Eyring equation, the Gibbs free energy of activation was determined to be 101.2 kJ mol^{-1}, indicating that isomerization is slow (at rt: $t_{1/2}$ >1.5 d, at 60 °C: $t_{1/2}$ = 20 min) compared with the thermal isomerization in step 2 (unstable *trans*-**3** → stable *trans*-**3**). This isomerization step of **3** is also much slower than the isomerization of the analogous unstable *trans*-**2** to stable *trans*-**2**, which has a half-life of 74 min at rt.

We then investigated the effect of exchanging the naphthalene for a substituted phenyl moiety on second-generation motors (Fig. 6). The original second-generation motor **4**[4] has a half-life of 233 h at rt, and has been the subject of intense efforts to reduce this time.[14] It was found that when the naphthalene moiety in the upper half of **4** was exchanged with a benzene, irradiation lead to photocyclization.[11] The alkenes containing a lower half derived from fluorenone have proven to be attractive for study because they exhibit a large change in their UV–vis spectrum upon isomerization between the stable and unstable isomers, and generally have good photoequilibria. We believed that the same redesign could be used as a means to adjust the speed of second generation motors (*i.e.* **5** → **6**) as well as to expand the range of structures that function as unidirectional molecular motors.

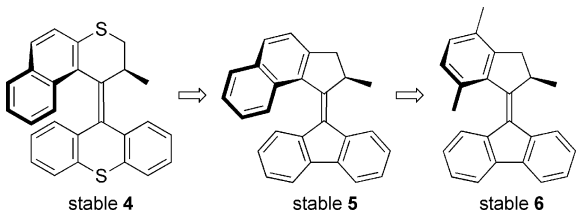

Fig. 6 Design modifications of the original second-generation molecular motor **4**, accelerated motor **5**, and redesigned **6**.

Alkene **6** was prepared in 3 steps using a Staudinger-type diazothioketone synthesis.[20] 2,4,7-Trimethylindan-1-one[18] was treated with Lawesson's reagent to give the thioketone **7** (Fig. 7) that is unstable and degrades on silica gel.[21] Therefore, most of the Lawesson's reagent was removed by precipitation with pentane, and the crude filtrate was treated with diazofluorenone to give alkene **6**. Our previous experience with related derivatives that contain the naphthalene function suggests that electron donating substituents on the aromatic moiety should improve the stability of the intermediate thioketone.

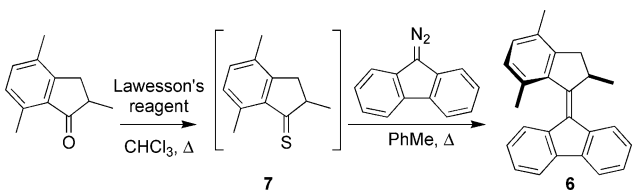

Fig. 7 Synthesis of **6**.

Like **3**, it was anticipated that **6** would avoid photocyclization side reactions due to insufficient π-orbital overlap because it also contains 5-membered rings fused to the central olefin (Fig. 8).

The UV–vis spectrum of stable **6** in hexane contains a major band centered at 360 nm (Fig. 9). Irradiation (λ_{max} = 365 nm)

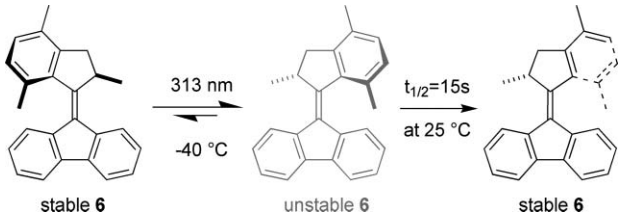

Fig. 8 Photochemical and thermal isomerization of **6**.

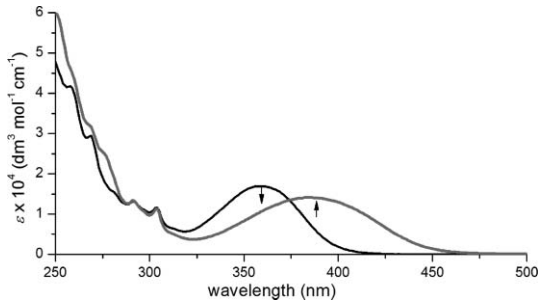

Fig. 9 UV spectra of stable **6** (black) and unstable **6** (grey) in hexane at −40 °C.

of this sample at −40 °C resulted in a thermally reversible red-shift of the major band to a broad absorption centered at 385 nm, analogous to related motor **5**.[22] The reversion of the PSS spectrum (grey) back to its original spectrum (black) was monitored by the change in absorption at 410 nm at four different temperatures (−15, −10, 0 and 10 °C); using the Eyring equation[23] we could establish that the thermal step of **6** had a $\Delta^{\ddagger}G^{\circ}$ of 79.1 kJ mol^{-1}, and a $t_{1/2}$ at rt of 15 s, which is over 12 times faster than that reported for **5**.

Irradiation (λ_{max} = 365 nm) of stable **6** in toluene-d_8 at −40 °C to its PSS allowed ^{1}H NMR spectroscopic characterization of unstable **6**. A 3 : 1 ratio of unstable **6** and stable **6** was present at the PSS. The identity of unstable **6** is evident from the downfield shift of the absorption from the stereogenic methyl group from 1.13§ to 1.39 ppm upon changing from a pseudo-axial to pseudo-equatorial conformation. This change in conformation is also supported by the upfield shift of the methine proton from 3.94§ to 3.54 ppm which is consistent with $H_{ax} \rightarrow H_{eq}$. Warming this sample to rt resulted in the rapid regeneration of the original spectrum of stable **6**.

Conclusion

The naphthalene group in first- and second-generation light-driven rotary molecular motors can be exchanged for a dimethyl-substituted phenyl group, while preserving the photochemical and thermal steps crucial to their 4-step rotary cycles. The change in structure from **2** → **3** leads to a modest acceleration of the thermal isomerisation step from the unstable to the stable *trans* isomer, but a significant deceleration of the corresponding unstable → stable *cis* isomer. When the same structural alteration was applied to the second-generation motors possessing a fluorene-derived lower half (**5** → **6**), the motor function was preserved with a modest acceleration of the thermal helix inversion.[24] It is anticipated that this simplification of the original structure without compromising the motor function will guide future efforts of motor design, by providing a new handle to control the motors' speed as well as facilitating the design and synthesis of systems functionalized in ways which were previously impractical.

Experimental

General remarks

Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary Analytical TLC was performed with Merck silica gel 60 F254 plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). 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, for the ^{1}H nucleus or at 100.57 and 125.70 MHz, respectively, for the ^{13}C nucleus. Chemical shifts are reported in δ units (ppm) relative to the residual deuterated solvent signals of $CHCl_3$ (^{1}H NMR: δ 7.26 ppm; ^{13}C NMR: δ 77.0 ppm). MS (EI) spectra were obtained with a Jeol JMS-600 spectrometer, C_7D_7H (^{1}H NMR: δ 2.09 ppm) and C_6D_5H (^{1}H NMR: δ 7.15; ^{13}C NMR: 128.0 ppm). UV measurements were performed on a Hewlett-Packard HP 8543 FT spectrophotometer in conjunction with an Oxford Optistat using Uvasol grade solvents (Merck). Solvents were distilled and dried before use by standard methodology. Irradiation experiments were performed with a Spectroline model ENB-280C/FE lamp. Photostationary states (PSS) were ensured by monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed. Thermal helix inversions were monitored by UV–vis spectroscopy using the apparatus described above with a cut-off filter (313 nm for *cis*-**3** and *trans*-**3**, 350 nm for **6**) to minimize irradiation by the analysis lamp, as well as 20 s interval times of data point collection. 2,4,7-Trimethylindan-1-one[18] and diazofluorenone[25] were synthesized by following literature procedures.

Synthesis

***cis*-3 and *trans*-3.** $TiCl_4$ (1.10 mL, 10.0 mmol) was added dropwise to a vigorously stirred suspension of Zn (20.0 mmol, 1.30 g) in THF (15 mL). This mixture was heated to reflux for 2 h, and cooled to rt. 2,4,7-Trimethylindan-1-one (871 mg, 5.00 mmol) was added (2 × 0.5 mL THF to rinse the flask), and the mixture was heated to reflux for 2 d. This mixture was then cooled, diluted with EtOAc (15 mL) and washed with aq. HCl (0.1 N, 3 × 5 ml). The mixture was then washed with water (2 × 5 mL), brine, dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by flash chromatography (SiO_2, $R_{f\text{-}trans} = 0.6$, $R_{f\text{-}cis} = 0.68$, heptane, *trans* isomer is less soluble) to give the *cis* (197 mg, 25%) and *trans* (56 mg, 7%) isomers, both as white solids. X-Ray quality crystals were obtained by slow evaporation from MeOH (*cis*) or heptane (*trans*). Stable *cis*-**3**: mp 181–182 °C; λ_{max}(hex)/nm 213 sh (ε/dm^3 mol^{-1} cm^{-1} 7150), 308 sh (3850); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (d, J = 7.0 Hz, 6H), 1.51 (s, 6H), 2.26 (s, 6H), 2.44 (d, J = 15.0 Hz, 2H), 3.09 (dd, J = 15.0, 6.5 Hz, 2H), 3.35 (quin., J = 6.5 Hz, 2H), 6.85 (d, J = 7.5 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H); ^{13}C NMR (APT, 100 MHz, C_6D_6) δ 18.5, 20.6, 21.0,

39.0, 42.2, 128.6, 128.7, 130.8, 133.6, 141.1, 141.2, 144.3; HRMS (EI) calcd for $C_{24}H_{28}$; 316.2191, found 316.2201. Stable *trans*-**3**: dec. ~135 °C; λ_{max}(hex)/nm 295 (ε/dm^3 mol^{-1} cm^{-1} 2800), 308 sh (2570); ^{1}H NMR (400 MHz, C_6D_6) δ 1.12 (d, J = 6.4 Hz, 6H), 2.04 (s, 6H), 2.13 (d, J = 14.8 Hz, 2H), 2.46 (s, 6H), 2.64 (dd, J = 6.0, 14.8 Hz, 2H), 2.98 (quin, J = 6.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 17.5, 18.8, 21.4, 38.4, 41.6, 127.9, 128.4, 130.6, 130.9, 140.7, 141.3, 141.9; HRMS (EI) calcd for $C_{24}H_{28}$; 316.2191, found 316.2199.

9-(2,4,7-Trimethyl-2,3-dihydro-1*H*-inden-1-ylidene)-9*H*-fluorene 6. ,4,7-Trimethylindan-1-one (944 mg, 4.00 mmol) was heated with Lawesson's reagent (1.78 g, 4.00 mmol) in $CHCl_3$ in a sealed tube to 95 °C for 4 h. The thioketone appears as a dark purple spot on TLC (heptane–toluene; 10 : 1) and runs faster than the starting material ketone (this product degrades to some extent on TLC). Other byproducts are evident as slower eluting spots on the TLC (possibly the vinyl sulfide). The crude ^{1}H NMR spectrum suggested a mixture of compounds were present, including the starting material ketone and the thioketone in a ratio of 13 : 1. The mixture was cooled, concentrated to a volume of ~5 mL, diluted with heptane (10 mL), filtered, concentrated *in vacuo*, diluted again with heptane (with trituration of the solid material), decanted, then concentrated *in vacuo*, diluted with toluene (10 mL) and treated directly with the diazofluorenone at 50 °C for 1 h, then 80 °C for 5 h. (Efforts to purify the thioketone by flash chromatography gave an impure product in <10% yield due to the instability of the thioketone.) This material was then filtered over silica gel, concentrated, and purified by flash chromatography (SiO_2 doped with 10% $AgNO_3$, 10% toluene in heptane, though the eluent required is sensitive to the amount of $AgNO_3$ employed). This yields the desired motor **6** (240 mg, 18%) as a yellow solid as well as bifluorene (~500 mg). Recrystallization from EtOH gave fine yellow needles: mp 147–148 °C; λ_{max}(hex)/nm 213 (ε/dm^3 mol^{-1} cm^{-1} 62 100), 241 (56 800), 268 sh (29 300), 291 (13 100), 304 (11 500), 359 (16 900); ^{1}H NMR (400 MHz, toluene-d_8) δ 1.15 (d, J = 6.4 Hz, 3H), 2.10 (s, 3H, hidden by solvent peak, can be observed in $CDCl_3$), 2.27 (s, 3H), 2.29 (d, J = 14.0 Hz, 1H), 2.89 (dd, J = 6.0, 14.4 Hz, 1H), 3.97 (quin., J = 6.8 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.20–7.28 (m, 2H), 7.59 ($d_{apparent}$, J = 8.0 Hz, 2H), 7.65 (d, J = 7.2 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.2 (CH_3), 19.0 (CH_3), 21.1 (CH_3), 39.9 (CH_2), 43.9 (CH), 119.1 (CH), 119.6 (CH), 120.3 (CH), 123.6 (CH), 123.9 (CH), 126.5 (CH), 126.76 (CH), 128.81 (CH), 127.0 (CH), 128.7 (CH), 130.08 (CH), 130.11 (CH), 131.5 (CH), 134.5 (CH), 137.8 (C), 139.4 (C), 139.6 (C), 139.7 (C), 139.8 (C), 145.2 (C), 152.3 (C). HRMS (EI) calcd $C_{25}H_{22}$ 322.1712, found 322.1731.

^{1}H NMR characterization of unstable intermediates

Photochemical generation of PSS of unstable *trans*-3. Unstable *trans*-**3**: A solution of 2.4 mg of stable *cis*-**3** in C_7D_8 (0.7 mL) was irradiated at 313 nm for 8 h at −80 °C, with periodic analysis of its ^{1}H NMR spectrum throughout. No further changes were observed after 6 h. ^{1}H NMR (500 MHz, −80 °C, $CDCl_3$) δ 0.82 (d, J = 6.5 Hz, 6H), 2.11 (s, 6H), 2.33 (d, J = 14.0 Hz, 2H), 2.43 (s, 6H), 2.62 (dd, J = 5.3, 14.8 Hz, 2H), 2.83 (quin., J = 6.0 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 7.04 (d, J = 7.5 Hz, 2H).

Photochemical generation of PSS sample of unstable *cis*-3. A solution of 3 mg of stable *trans*-**3** in C_6D_6 (0.7 mL) was irradiated at 313 nm for 2 h at 0 °C, with intermittent analysis of its ^{1}H NMR spectrum throughout. No further changes were observed after 1.5 h. Unstable *cis*-**3**: ^{1}H NMR (400 MHz, C_6D_6) δ 1.35 (d, J = 6.0 Hz, 6H), 1.61 (s, 6H), 2.14 (d, J = 14.0 Hz, 2H), 2.13 (s, 6H), 2.53 (dd, J = 5.6, 14.4 Hz, 2H), 2.80–3.00 (unresolved peak due to overlap with an absorption from remaining stable *trans*-**3**, 2H), 6.81 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H).

Photoirradiation of stable 6 to give a PSS mixture containing unstable 6 and stable 6. A solution of stable **6** (4 mg) in toluene-d_8 (0.7 mL) was irradiated (λ_{max} = 365 nm) in an NMR tube at −40 °C for 3 h. The photochemical conversion was followed by intermittent analysis by ^{1}H NMR at −40 °C. When no additional changes were apparent in the ^{1}H NMR spectrum, the mixture contained a 3 : 1 mixture of unstable **6** : stable **6**. Unstable **6**: ^{1}H NMR (500 MHz, toluene d_8 at −60 °C) δ 1.33 (d, J = 6.4 Hz, 3H), 2.05 (s, hidden by solvent peak, 3H), 2.10 (s, 3H), 2.35 (dd, J = 6.0, 14.0 Hz, 2H), 2.79 (dd, J = 16.0, 8.5 Hz, 2H), 3.48 (sext., J = 6.7 Hz, 2H), 6.83 (d, J = 7.5 Hz, 2H), 6.86–7.11 (2H, overlapped with solvent), 7.18 ($quin_{apparent}$, J = 7.3 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.50–7.62 (m, 3H).

Acknowledgements

Wesley R. Browne, Edzard Geertsema, and Dirk Pijper are gratefully acknowledged for their helpful suggestions. Financial support from the Netherlands Organization for Scientific Research (NWO-CW) through a NWO-CW Top-grant, Spinoza grant from NWO and a Nanoned grant is gratefully acknowledged.

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