A Trimer of Ultrafast Nanomotors
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Published in:
Chemistry

DOI:
10.1002/chem.200802718

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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A trimer of ultra-fast nanomotors: synthesis, photochemistry and self-assembly on graphite
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Synthesis

General
Chemicals were purchased at Aldrich or Acros. Solvents for chromatography and extractions were technical grade. Solvents for reactions were reagent grade and distilled and dried according to standard procedures. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh) using positive pressure. NMR spectra were recorded on a Varian Gemini-200 ($^1$H: 200 MHz, $^{13}$C: 50 MHz), Varian VXR-300 ($^1$H: 300 MHz), Varian AMX400 ($^1$H: 400 MHz, $^{13}$C: 100 MHz) or Varian Unity Plus ($^1$H: 500 MHz, $^{13}$C: 125 MHz) spectrometer. NOE spectra were recorded on a Varian Unity Plus (500 MHz). Chemical shifts are denoted in $\delta$-units (ppm) relative to the residual solvent peak (CDCl$_3$: $^1$H $\delta = 7.26$, $^{13}$C $\delta = 77.0$). The splitting parameters are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. HPLC analyses were performed on a Shimadzu 10AD-VP system using a Chiralcel OD column. Preparative HPLC was performed on a Gilson HPLC system consisting of a 231XL sampling injector, a 306 (10SC) pump, an 811C dynamic mixer, a 805 manometric module, with a 119 UV-vis detector and a 202 fraction collector. MS (EI) and HRMS (EI) spectra were obtained with a JEOL JMS-600. Melting points were taken on a Büchi Melting Point B-545 apparatus and are uncorrected. Thioketones S3 and S6$^1$, 2-methoxy-9-fluorenone S5$^2$, and 1,3,5-triethynylbenzene$^3$ were synthesized according to literature procedures.

Scheme S1 Synthesis of molecular motor 4.
4-bromo-7-methoxy-2-methyl-2,3-dihydro-1H-inden-1-one S1. To stirred polyphosphoric acid (50 mL) at 65 °C was added methacrylic acid (1.50 g, 17.4 mmol). After vigorous stirring for 5 min, 4-bromoanisole (3.16 g, 16.9 mmol) was added. The mixture was stirred for 1.5 h at 110 °C after which the reaction was quenched by pouring the mixture into 300 mL ice water and stirring overnight. The aqueous phase was extracted with Et₂O (2 x 150 mL). The combined organic layers were filtered, washed with water, brine, and dried over Na₂SO₄. After removal of the solvent in vacuo the crude product was purified by column chromatography (heptane:EtOAc, 2:1) yielding S1 (1.02 g, 24%) as a light yellow oil which solidified on standing. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 8.8 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 3.85 (s, 3H), 3.17 (dd, J = 17.6, 8.0 Hz, 1H), 2.62-2.53 (m, 1H), 2.49 (dd, J = 17.6, 4.4 Hz, 1H), 1.21 (d, J = 7.6 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 206.5 (C), 157.6 (C), 155.2 (C), 138.8 (CH), 126.3 (C), 111.9 (C), 111.5 (CH), 56.2 (CH₃), 42.2 (CH), 36.0 (CH₂), 16.7 (CH₃); HRMS (EI) calcd. for C₁₁H₁₁BrO₂ 253.9942, found 253.9930.

(4-bromo-7-methoxy-2-methyl-2,3-dihydro-1H-inden-1-ylidene)hydrazine S2. A solution of S1 (0.887 g, 3.47 mmol) in hydrazine monohydrate (20 mL) was heated to reflux for 1 h, during which a precipitate formed. The reaction mixture was allowed to cool and the light yellow precipitate was filtered off and washed twice with cold Et₂O. The mother liquor was diluted with EtOAc and washed with water. Drying over Na₂SO₄ and removal of the solvent in vacuo yielded a second portion of S2 as a light brown solid (combined yield 0.80 g, 86%). mp 154.5-155.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 5.35 (br s, 2H), 3.89 (s, 3H), 3.30-3.16 (m, 2H), 2.56 (d, J = 16.8 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 160.0 (C), 155.8 (C), 147.2 (C), 132.7 (CH), 126.7 (C), 111.7 (C), 111.5 (CH), 56.3 (CH₃), 39.9 (CH₂), 32.2 (CH), 17.3 (CH₃); HRMS (EI) calcd. for C₁₁H₁₁BrNO [M-NH₂]: 252.0024, found 252.0017; Anal. calcd. for C₁₁H₁₃BrN₂O C, 49.09; H, 4.87; N, 10.41. Found C, 48.80; H, 4.84; N, 10.31.

9-(4-bromo-7-methoxy-2-methyl-2,3-dihydro-1H-inden-1-ylidene)-9H-fluorene 3. To a stirred solution of 9-fluorenone (0.351 g, 1.95 mmol) in toluene (5 mL) was added Lawesson’s reagent⁴ (1.17 g, 2.89 mmol). The mixture was heated to reflux for 2.5 h. The toluene was removed by distillation in vacuo and the residue purified by column chromatography (CH₂Cl₂:pentane, 1:1, Rf = 0.8) yielding the thioketone S3 (with some impurities) as a green solid (0.200 g, ~50%) To a solution of S2 (0.204 g, 0.760 mmol) in DMF (5 mL) at -50 °C was added (diacetoxyiodo)benzene (0.293 g, 0.910 mmol). After 30 s of stirring a solution of 9-thiofluorenone (0.200 g, 1.02 mmol) in CH₂Cl₂ (5 mL) was added. The mixture was allowed to warm to room temperature and stirred overnight. Subsequently, the mixture was diluted with EtOAc, washed with water, 2 N aqueous HCl and brine and
concentrated *in vacuo*. Column chromatography (pentane:CH₂Cl₂, 9:1) yielded a yellow solid comprising episulfide S₃ (Rₗ = 0.4) and alkene 3 (Rₗ = 0.35), combined yield 0.14 g. Episulfide S₃: NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.45-7.20 (m, 5H), 7.08 (t, J = 7.8 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 3.94 (s, 3H), 2.99-2.95 (m, 1H), 2.47 (dd, J = 15.8, 5.9 Hz, 1H), 2.35 (d, J = 15.8 Hz, 1H), 1.25 (d, J = 6.9 Hz, 3H).

This mixture was dissolved in toluene (10 mL) and triphenylphosphine (0.78 g, 3.0 mmol) was added. The solution heated to reflux for 60 h, and the toluene was removed by distillation *in vacuo*. The residue was taken up in Et₂O (12 mL), and MeI (1.0 mL, 2.3 g, 16 mmol) was added. The reaction mixture was stirred overnight after which a white precipitate formed. The precipitate was filtered, and the filtrate was concentrated *in vacuo*. Column chromatography (pentane:CH₂Cl₂, 9:1) yielded 3 (0.123 g, 40%) as a yellow solid.

9-(7-methoxy-2-methyl-4-(phenylethynyl)-2,3-dihydro-1H-inden-1-ylidene)-9H-fluorene 4. In a flame-dried flask under N₂ was placed CuI (0.7 mg, 4 μmol), Pd(PhCN)₂Cl₂ (2.1 mg, 5.4 μmol), P(t-Bu)₃ (2.2 mg, 10.8 μmol), diisopropylamine (24 μL, 18 mg, 0.18 mmol), 3 (39 mg, 0.09 mmol), phenylacetylene (12 μL, 11 mg, 0.11 mmol) and dioxane (0.3 mL). The reaction mixture was stirred overnight at rt and diluted with EtOAc. The organic layer was washed with water, 2 N aqueous HCl and brine. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (pentane:CH₂Cl₂, 6:1) to yield 4 (33 mg, 86%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.86 (m, 1H), 7.80-7.77 (m, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.57-7.54 (m, 3H), 7.40-7.25 (m, 7H), 7.15 (t, J = 8.2 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 4.21-4.17 (m, 1H), 3.76 (s, 3H), 3.42 (dd, J = 15.6 Hz, 1H), 2.92 (d, J = 15.6 Hz, 1H), 1.40 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9 (C), 151.9 (C), 147.3 (C), 140.1 (C), 139.5 (C), 139.4 (C), 137.9 (C), 133.8 (CH), 131.5 (2CH), 130.8 (C), 128.9 (C), 128.3 (2CH), 128.1 (CH), 126.9 (CH), 126.8 (CH), 125.8 (CH), 125.2 (CH), 124.1 (CH), 123.5 (C), 119.6 (CH), 118.6 (CH), 113.1 (C), 109.6 (CH), 91.4 (C), 87.3 (C), 54.8 (CH₃), 43.7 (CH), 40.9 (CH₂), 19.1 (CH₃); HRMS (EI) calcd. for C₃₂H₂₄OBr: 424.1827, found: 424.1825. HPLC Chiralcel OD column, 95:5 n-heptane:2-propanol, T = 50 °C, flow rate 1 mL/min, retention times 8.0 min, 16.6 min.
1,3,5-tris((1-(9H-fluoren-9-ylidene)-7-methoxy-2-methyl-2,3-dihydro-1H-inden-4-yl)ethynyl)benzene 5. In a flame-dried flask under a N₂ atmosphere was placed CuI (1.0 mg, 5.2 μmol), Pd(PhCN)₂Cl₂ (2.8 mg, 7.3 μmol), P(t-Bu)₃ (3.6 μL, 3.0 mg, 14.8 μmol), diisopropylamine (33 μL, 24 mg, 0.24 mmol), 3 (50 mg, 0.12 mmol), 1,3,5-triethynylbenzene (5.3 mg, 0.035 mmol) and dioxane (0.3 mL). The solution was stirred overnight at 50 °C and then diluted with EtOAc. The organic layer was washed with water, 2 N aqueous HCl and brine, and dried on Na₂SO₄. The solvent was removed in vacuo and the crude product was purified by column chromatography (pentane:CH₂Cl₂, 3:1) to yield 5 as a yellow solid (25 mg, 56%). 5 was isolated as a mixture of diastereomers in a 1:3:3:1 (RRR:RRS:RSS:SSS) ratio as determined by HPLC. ¹H NMR (300 MHz, CDCl₃) δ 7.90-7.88 (m, 3H), 7.80-7.77 (m, 3H), 7.73 (d, J = 7.4 Hz, 3H), 7.68 (s, 3H), 7.57 (d, J = 8.5 Hz, 3H), 7.40-7.20 (m, 9H), 7.14 (t, J = 7.5 Hz, 3H), 6.89 (d, J = 8.6 Hz, 3H), 4.23-4.19 (m, 3H), 3.78 (s, 9H), 3.43 (dd, J = 15.7, 5.9 Hz, 3H), 2.93 (d, J = 15.6 Hz, 3H), 1.40 (d, J = 6.6 Hz, 9H); ¹³C NMR (50 MHz, CDCl₃) δ 157.3 (C), 152.2 (C), 147.4 (C), 140.4 (C), 139.7 (C), 139.7 (C), 138.2 (C), 134.1 (CH), 134.0 (CH), 131.5 (C), 129.4 (C), 127.3 (CH), 127.2 (CH), 127.3 (CH), 126.0 (CH), 125.4 (CH), 124.6 (C), 124.4 (CH), 120.0 (CH), 118.9 (CH), 110.0 (CH), 90.3 (C), 88.8 (C), 55.6 (CH₃), 44.2 (CH), 41.1 (CH₂), 19.7 (CH₃); MS (MALDI-TOF, no matrix) m/z: 1116.6 [M⁺]. HPLC: Chiralcel AD column, 90:10 n-heptane:2-propanol, T = 50 °C, flow rate 1 mL/min, retention times 11.8 min, 16.7 min, 22.0 min, 25.7 min.
9-(4-bromo-7-methoxy-2-methyl-2,3-dihydro-1H-inden-1-ylidene)-2-methoxy-9H-fluorene S8. To a solution of 2-methoxy-9H-fluoren-9-one S5 (0.138 g, 0.660 mmol) in toluene (3 mL) was added Lawesson’s reagent (0.4 g, 1 mmol). The mixture was heated to 80 °C for 3 h. The toluene was distilled in vacuo and the residue purified by column chromatography (pentane:CH2Cl2, 1:1). The first (wine-red) band was collected, concentrated and then immediately used in the next step.

To a solution of S2 (53 mg, 0.20 mmol) in DMF (2 mL) at -50 °C was added (diacetoxyiodo)benzene (76 mg, 0.24 mmol). After stirring for 20 s, a solution of 2-methoxyfluoren-9-thione S6 in CH2Cl2 (2 mL) was added. The mixture was allowed to warm to rt overnight and diluted with EtOAc. The organic layer was washed with water, 2 N aqueous HCl and brine and dried on Na2SO4. The solvent was removed in vacuo and the crude product was purified by column chromatography (pentane:CH2Cl2, 1:1) yielding a mixture of episulfides cis-S7 and trans-S7 (Rf = 0.3) and alkenes cis-S8 and trans-S8 (Rf = 0.25), combined yield 45 mg.

This mixture was dissolved in toluene (8 mL) and triphenylphosphine (0.24 g, 0.92 mmol) was added. The solution was heated at reflux overnight and the toluene was removed by distillation in vacuo. The residue was taken up in Et2O (12 mL) and MeI (1.0 mL, 2.3 g, 16 mmol) was added. The reaction mixture was stirred for 3 h; a white precipitate formed. The precipitate was filtered and the filtrate was concentrated. Column chromatography (pentane:CH2Cl2, 2:1) yielded S8 (38 mg, 44 % from S2) (45:55 mixture of cis and trans isomers) as a yellow solid. Separation of cis and trans isomers was not practical at this point.

H NMR (300 MHz, CDCl3) δ 7.81 (d, J = 7.7 Hz, 1H), 7.69-7.61 (m, 4H), 7.49 (d, J = 8.8 Hz, 1H), 7.29-7.22 (m, 4H), 7.14 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 4.03 (s, 3H), 2.37 (s, 3H).

Scheme S2 Synthesis of desymmetrized molecular motor 6.
Hz, 2H), 7.43 (s, 1H), 7.35-7.15 (m, 4H), 7.06 (t, J = 7.4 Hz, 1H), 6.95-6.70 (m, 5H), 4.17-4.11 (m, 2H), 3.91 (s, 3H), 3.74 (s, 3H), 3.71 (s, 6H), 3.29 (dd, J = 15.6, 6.0 Hz, 2H), 2.72 (d, J = 15.4 Hz, 2H), 1.38 (d, J = 6.6 Hz, 3H), 1.37 (d, J = 7.0 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 159.3 (C), 158.8 (2C), 156.1 (2C), 148.5 (2C), 148.4 (2C), 147.0 (C), 140.9 (C), 140.2 (C), 139.5 (C), 139.3 (C), 137.6 (C), 133.6 (C), 133.2 (CH), 133.1 (CH), 132.9 (C), 131.5 (C), 130.5 (C), 127.2 (CH), 127.1 (CH), 125.8 (CH), 125.0 (CH), 124.8 (CH), 124.1 (CH), 120.1 (CH), 119.2 (CH), 118.9 (CH), 118.0 (CH), 113.0 (CH), 112.4 (CH), 111.5 (C), 111.4 (C), 111.3 (CH), 111.1 (CH), 110.7 (CH), 55.6 (CH3), 55.4 (CH3), 51.1 (CH3), 54.9 (CH3), 43.3 (CH), 43.2 (CH), 42.4 (2CH2), 19.1 (CH3), 18.9 (CH3); HRMS (EI) calcd. for C25H21O2Br: 434.0705, found: 434.0700.

**cis-** and **trans-9-(7-methoxy-2-methyl-4-(phenylethynyl)-2,3-dihydro-1H-inden-1-ylidene)-2-methoxy-9H-fluorene 6a and 6b.** In a flame-dried flask under N2 was placed CuI (0.5 mg, 2.6 μmol), Pd(PhCN)2Cl2 (1.6 mg, 4.1 μmol), P(t-Bu)3 (2.0 μL, 2.2 mg, 8.3 μmol), diisopropylamine (19 μL, 14 mg, 0.14 mmol), S8 (19 mg, 0.044 mmol), phenylacetylene (9.1 μL, 8.5 mg, 0.083 mmol) and dioxane (0.25 mL). The solution was stirred overnight at 50 °C and then diluted with EtOAc. The organic layer was washed with water, 2 N aqueous HCl and brine, and dried on Na2SO4. The solvent was removed in vacuo and the crude product was further purified by column chromatography (pentane:CH2Cl2, 3:1) to yield 5 (15 mg, 75%) (mixture of cis and trans isomers). **Cis** and **trans** isomers were separated by column chromatography (pentane:tert-butyl methyl ether, 12:1) and stored in the dark. HRMS (EI) calcd. for C33H26O2: 454.1933, found: 454.1921. cis-6a: 1H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 7.3 Hz, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.56 (m, 3H), 7.40-7.25 (m, 5H), 6.87 (m, 3H), 4.18 (m, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.40 (dd, J = 15.5, 5.9 Hz, 1H), 2.90 (d, J = 15.5 Hz, 1H), 1.38 (d, J = 6.7 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 158.9 (C), 157.0 (C), 152.1 (C), 147.4 (C), 140.2 (C), 139.6 (C), 139.5 (C), 134.0 (CH), 133.0 (C), 131.6 (2CH), 131.0 (C), 128.9 (C), 128.4 (2CH), 128.1 (CH), 127.1 (CH), 125.8 (CH), 124.1 (CH), 123.6 (C), 119.2 (CH), 118.9 (CH), 113.2 (C), 113.0 (CH), 111.0 (CH), 109.7 (CH), 91.4 (C), 87.2 (C), 55.4 (CH3), 55.0 (CH3), 43.8 (CH), 40.8 (CH2), 19.1 (CH3). HPLC Chiralcel OD column, 95:5 n-heptane:2-propanol, T = 50 °C, flow rate 1 mL/min, retention times 7.2 min, 30.3 min. trans-6b: 1H NMR (200 MHz, CDCl3) δ 7.66 (d, J = 8.0 Hz, 1H), 7.6-7.15 (m, 10H), 7.05 (t, J = 7.2 Hz), 6.88 (t, J = 8.0 Hz), 4.16 (m, 1H), 3.91 (s, 3H), 3.76 (s, 3H), 3.41 (dd, J = 15.8, 5.6 Hz, 1H), 2.90 (d, J = 15.4 Hz), 1.39 (d, J = 6.8 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 159.2 (C), 156.9 (C), 151.9 (C), 147.3 (C), 141.0 (C), 139.4 (C), 137.8 (C), 133.8 (CH), 133.5 (C), 131.5 (2xCH), 130.8 (C), 128.9 (C), 128.3 (2CH), 128.1 (CH), 126.9 (CH), 125.0 (CH), 124.7 (CH), 123.5 (C), 120.1 (CH), 117.9 (CH), 113.1 (C), 112.3 (CH), 110.7 (CH), 109.7 (CH), 91.4 (C), 87.2 (C), 55.6 (CH3), 55.6 (CH3), 54.8 (CH3), 43.7 (CH), 40.9 (CH2), 18.9 (CH3). HPLC Chiralcel OD column, 95:5 n-heptane:2-propanol, T = 50 °C, elution rate 1 mL/min, retention times 9.4 min, 12.8 min.
UV-vis and CD spectroscopies

General
Low temperature spectroscopy was performed using an Optistat DN (Oxford Instruments, Tubney Woods, Abingdon, Oxon OX13 5QX, UK) cryostat equipped with an ITC 601 temperature controller. Irradiation experiments were performed with a 200 W Oriel Xe-lamp, adapted with a 300 nm cut-off filter and the appropriate band-pass filter (334 or 365 nm, typical bandwidth: 10 nm) in series, or a Spectroline lamp model ENB-280C/F (\(\lambda = 365\) nm). UV-vis measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer. CD spectra were recorded on a JASCO J-715 spectropolarimeter. Photostationary states were ensured by monitoring composition changes by taking UV spectra at distinct intervals until no changes were observed.

Determination of stable cis-6a/unstable trans-6b and stable trans-6b/unstable cis-6a at their PSS
A method to determine the ratio of two photochemically interconvertible species X and Y was reported by Fischer.\(^5\) The method is based on the assumption that the ratio of the quantum yield of photoconversion of X to Y (\(\Phi_X\)) over the quantum yield of photoconversion of Y to X (\(\Phi_Y\)) does not differ at two different wavelengths. The concentration of X and Y in the PSS obtained by irradiation at any given wavelength is given by equation S1:

\[
\frac{X}{Y}_\lambda = \frac{\Phi_Y}{\Phi_X} \times \left( \frac{A_X}{A_Y} \right)_\lambda
\]

(Equation S1)

In which \(A\) is the absorbance of pure X or Y at that wavelength. Because it is assumed that the ratio of the quantum yield of photoconversion for X and Y does not change, the ratio of two PSSs at different wavelengths is given by equation S2:

\[
\frac{\left( \frac{X}{Y} \right)_{\lambda_2}}{\left( \frac{X}{Y} \right)_{\lambda_1}} = \frac{\left( \frac{A_Y}{A_X} \right)_{\lambda_1}}{\left( \frac{A_Y}{A_X} \right)_{\lambda_2}}
\]

(Equation S2)

The extent of photoconversion of X to Y at any given wavelength \(\lambda\) can be denoted as \(\alpha\) (Equation S3) and the change in absorbance of the mixture starting from only X can be denoted as \(\Delta A\) (Equation S4):

\[
\left( \frac{X}{Y} \right)_\lambda = \left( \frac{1-\alpha}{\alpha} \right)_\lambda
\]

(Equation S3)

\[
\Delta A = A_{\text{obs}} - A_X
\]

(Equation S4)

By inserting these two equations into equation S2 this can be developed to equation S5:
\[
\alpha_{\lambda_2} = \frac{\left( \frac{\Delta A_{\lambda_1}}{A_{\lambda_1}} - \frac{\Delta A_{\lambda_2}}{A_{\lambda_2}} \right)}{1 + \frac{\Delta A_{\lambda_1}}{A_{\lambda_1}} - n \left( 1 + \frac{\Delta A_{\lambda_2}}{A_{\lambda_2}} \right)}
\]

(Equation S5)

In which \( n \) is the ratio of the two different PSS ratios obtained by irradiation at \( \lambda_1 \) and \( \lambda_2 \). In equation S5, the relative amount of \( Y \) in the PSS ratio of the photoequilibrium after irradiation at the wavelength of interest is expressed as a function of the relative change in absorbance at two particular wavelengths, when passing from only \( X \) to the PSS obtained by irradiation at the same wavelength, and the ratio of the PSS ratios resulting from irradiation at these two wavelengths. For a more extensive derivation of this equation, see ref. 5. This method can be applied to the photochemical isomerization step in our system, by using the stable form as \( X \) and the thermally unstable form as \( Y \).

A solution of stable \( cis\text{-}6a \) in iso-pentane at 150 K was irradiated with 365 ± 5 nm light, leading to a red-shift of the long-wavelength band in the UV-vis spectrum. Irradiation with 334 ± 5 nm light led to a slightly different change in the UV-vis spectrum (Figure S1, left). The maximum change in the absorbance \( \Delta A \) is observed around 360 nm and the ratio of the PSS ratios \( n \) was calculated to be 1.15. The relative change in absorbance \( (\Delta A/A)_{334} \) and \( (\Delta A/A)_{365} \) were determined to be -0.552 and -0.305, respectively. Using these values in equation S5 gives \( \alpha_{365} = 0.703 \). This corresponds to ratio of stable \( cis\text{-}6a \):unstable \( trans\text{-}6b \) of 30:70.

Repeating this experiment, employing stable \( trans\text{-}6b \), the ratio of the PSS ratios \( n \) was calculated to be 1.10. The relative change in absorbance \( (\Delta A/A)_{334} \) and \( (\Delta A/A)_{365} \) were determined to be -0.453 and -0.269, respectively. Using these values in equation S5 gives \( \alpha_{365} = 0.716 \). This corresponds to ratio of stable \( cis\text{-}6a \):unstable \( trans\text{-}6b \) of 28:72. An intrinsic error in the UV spectrum of ±0.005 is assumed, resulting in an error of ±2 in the \( cis\text{:}trans \) ratio.

**Speed of thermal helix inversion of 4**

To determine the kinetic parameters of the thermal isomerization step, kinetic studies were performed. A solution of 4 in iso-pentane at 150 K was irradiated (\( \lambda = 365 \pm 20 \) nm) to its
PSS and change of the CD absorption at $\lambda = 218$ nm was followed in time at 4 different temperatures between 167.5 K and 175 K. Using the Eyring equation, rate constants $k$ of the first order process allowed the determination of the Gibbs free energy of activation ($\Delta^\ddagger G^\circ$) to be 51 kJ/mol (Figure S2). The half-life ($t_{1/2}$) under standard conditions was obtained after extrapolation (Table S1).

![Figure S2](image)

**Figure S2** Eyring plot of the thermal step of the rotational cycle of molecular motor 4.

**Table S1** Kinetic parameters of the thermal helix inversion of motor 4.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$k$ (s$^{-1}$) (20 °C)</th>
<th>$\Delta^\ddagger G^\circ$ (kJ/mol)</th>
<th>$t_{1/2}$ (s) (20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$4.3 \times 10^3$</td>
<td>51</td>
<td>$1.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Scanning tunneling microscopy**

All STM experiments were performed at room temperature, using a PicoSPM machine (Molecular Imaging, Scientec). Pt/Ir STM tips were prepared mechanically from Pt/Ir wire (80:20, diameter 0.25 mm, Goodfellow). Prior to STM imaging, ($S$)-($M$)-($S'$)-($M'$)-($S''$)-($M''$)-5 was dissolved in 1-phenyloctane (Aldrich) at a concentration of ~0.1 mM by sonication (5 min) and heating at ~60 °C (10 min). A drop of the warm solution was applied to a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, Goodfellow) and the STM tip immersed into the solution for imaging. The parameters of the unit cells were measured after drift effects were corrected with the Scanning Probe Image Processor (SPIP) software (Image Metrology ApS).
The same procedure was applied to investigate the self-assembly of a mixture of diastereoisomers of 5 on HOPG. As in the case of enantiomerically pure (S)-(M)-(S’)-(M’)-(S’’)-(M’’)-5, large ordered areas are formed by a mixture of diastereoisomers on HOPG. However, the structure of the monolayer which is formed is drastically different, as evidenced by Figure S3. From this observation we conclude that enantio-specific van der Waals interactions are at the origin of the formation of the (S)-(M)-(S’)-(M’)-(S’’)-(M’’)-5 honeycomb lattice.

S1 400 MHz, CDCl₃
S1 50 MHz, CDCl₃
S2 75 MHz, CDCl₃
S3 400 MHz, CDCl₃
300 MHz, CDCl₃
S18

3 50 MHz, CDCl₃
400 MHz, CDCl₃
$^1$H NMR (100 MHz, CDCl$_3$)
$5$ 300 MHz, CDCl$_3$
$S_{22} \quad O \quad O \quad O \quad 5 \quad 50 \text{ MHz, CDCl}_3$
*cis* and *trans*-**S8** 300 MHz, CDCl$_3$
cis and trans-S8 75 MHz, CDCl₃
$\text{5a 400 MHz, CDCl}_3$
cis-6a 125 MHz, CDCl₃
trans-6b 200 MHz, CDCl₃
trans-6b 125 MHz, CDCl₃