

Supplementary Information for

Braiding two polymer chains into a double helix with a molecular rotor

Maxime Ledent,¹ Damien Sluysmans,¹ Philippe Schiel,² Damien Dattler,² Quan Li,² Thomas Ellis,² Nicolas Giuseppone,^{2,3} Anne-Sophie Duwez¹

¹ UR Molecular Systems, Department of Chemistry, University of Liège, Liège, Belgium

² SAMS Research Group, Université de Strasbourg, CNRS, Institut Charles Sadron UPR 22, Strasbourg, France.

³ Institut Universitaire de France (IUF), Paris, France.

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1. General synthetic methods

Solvents and chemical reagents: All solvents and all commercially available reagents were purchased at the highest quality and used as received unless otherwise noted. Dry solvents were obtained by passing them through a double column SolvTech purification system. Water was deionized by using a milli-gradient system (Millipore, Molsheim, France). Yields refer to spectroscopically purified (^1H Nuclear Magnetic Resonance) homogeneous materials. Compound **3** was synthesized according to a previously reported procedure.¹

Chromatographic methods: Thin Layer Chromatographies (TLC) were performed using silica on TLC Al foils (silica gel matrix with fluorescent indicator 254 nm, thickness: 500 μm , Sigma-Aldrich). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm) as well as potassium permanganate stain were used for visualization. Flash Column Chromatographies were performed using silica gel (60 Å, 230 - 400 mesh, 40 - 63 μm , Sigma-Aldrich). Ultra-performance liquid chromatography with mass spectrometry (UPLC-MS) analyses were conducted on a Waters Acquity UPLC-SQD apparatus equipped with a SQD mass spectrometer, a PDA detector (190 – 500 nm, 80 Hz), using a reverse phase column (Waters, BEH C18 1.7 μm , 2.1 $\times$ 50 mm), the MassLynx 4.1 – XP software and a gradient of water/acetonitrile + 0.1 % TFA as eluent.

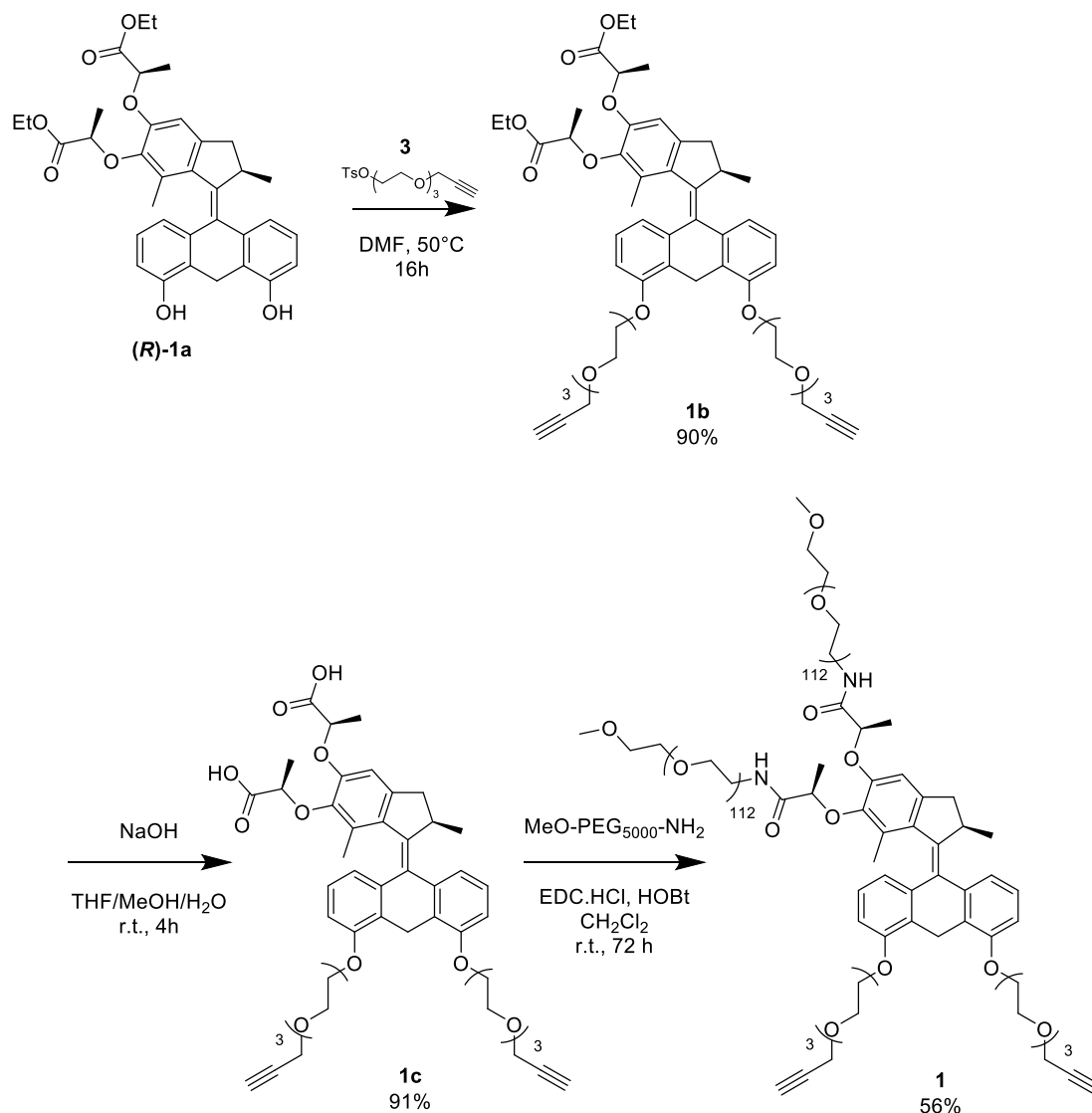
Nuclear magnetic resonance (NMR): All the spectra were recorded on a Bruker Avance 400 at 25°C unless otherwise noted. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz. The observed signals are reported as follows: chemical shift in ppm from the signal of TMS, with the residual solvent signal as internal standard (^1H NMR: CDCl_3 δ 7.26 ppm, CD_3OD δ 3.31 ppm; ^{13}C NMR: CDCl_3 δ 77.16 ppm, CD_3OD δ 49.00 ppm); multiplicity (singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br)); integration. Coupling constants J are given in Hz.

Mass spectrometry. Electron Spray Ionization (ESI) was recorded on a SQD mass spectrometer from Waters either by direct injection or after chromatography.

2. Synthesis of molecular motors

Here we describe the synthesis of the polymer-motor and polymer-episulfide conjugate. We established a synthetic pathway starting from the previously reported tetrasubstituted second-

generation Feringa motor **1** (ref [xx] in the main text), followed by its derivation with a pair of PEO chains. Silane was chosen to act as ligand on silicon wafers.



Scheme S1. Synthetic pathway for molecular motor **1**.

Compound **1b**

To a solution of motor **(R)-1a** (130.0 mg, 0.215 mmol) and K₂CO₃ (89.3 mg, 0.65 mmol) in DMF (15 mL) was added a solution of compound **3** (220.7 mg, 0.656 mmol) in DMF (4 mL) and the reaction mixture was stirred at 50 °C for 16 h. The reaction mixture was diluted with water (40 mL) and extracted with DCM (3 x 50 mL). The combined organic phases were dried over Na₂SO₄ and purified by flash column chromatography (silica gel, cyclohexane/ EtOAc 5:1 → 1:1) affording compound **1b** (182.2 mg, 90% yield) as a yellowish solid.

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.93 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.53 (s, 1H), 4.79 (q, *J* = 6.8 Hz, 1H), 4.76 (q, *J* = 6.8 Hz, 1H), 4.35 – 4.08 (m, 13H), 4.03 – 3.91 (m, 4H), 3.88 – 3.80 (m, 4H), 3.78 – 3.61 (m, 12H), 3.34 (dd, *J* = 14.9, 6.1 Hz, 1H), 2.45 – 2.39 (m, 2H), 2.32 (d, *J* = 14.9 Hz, 1H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 172.5, 172.0, 155.8, 155.3, 149.6, 145.9, 144.4, 141.9, 141.7, 138.2, 133.4, 131.0, 127.6, 126.7, 126.4, 124.9, 124.6, 120.9, 120.3, 109.5, 109.0, 108.0, 79.7, 77.2, 76.8, 74.5, 72.9, 71.1, 70.8, 70.4, 69.7, 69.6, 69.1, 68.8, 61.2, 60.7, 58.4, 39.5, 38.1, 18.9, 18.6, 18.4, 14.5, 14.1, 14.0.

MS (ESI): calculated for C₅₂H₆₅O₁₄S [M+H]⁺ *m/z* = 945.41, found: 945.51.

Compound 1c

To a solution of compound **1b** (80.0 mg, 0.085 mmol) in THF/MeOH (2 mL/2 mL) was added a solution of NaOH (17.0 mg, 0.43 mmol) in water (2 mL). The mixture was stirred at room temperature for 4 hours and then quenched with a 1 M HCl (0.5 mL) solution at 0 °C. The mixture was then extracted with DCM (3 x 10 mL), the combined organic phases dried over Na₂SO₄ and concentrated under vacuum to afford the compound **1c** (68.5 mg, 0.077 mmol, 91% yield) as a slightly green solid, which was pure enough to be used as such in the next step.

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.96 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.78 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.65 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.81 (q, *J* = 6.9 Hz, 1H), 4.39 (q, *J* = 6.9 Hz, 1H), 4.29 (m, 2H), 4.24 – 4.07 (m, 8H), 4.05 – 3.90 (m, 4H), 3.84 (dt, *J* = 5.1, 3.4 Hz, 4H), 3.77 – 3.57 (m, 14H), 3.36 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.43 – 2.42 (m, 1H), 2.42 – 2.41 (m, 1H), 2.38 (d, *J* = 15.2 Hz, 1H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.44 (s, 3H), 1.13 (s, 3H), 0.63 (d, *J* = 6.7 Hz, 3H).

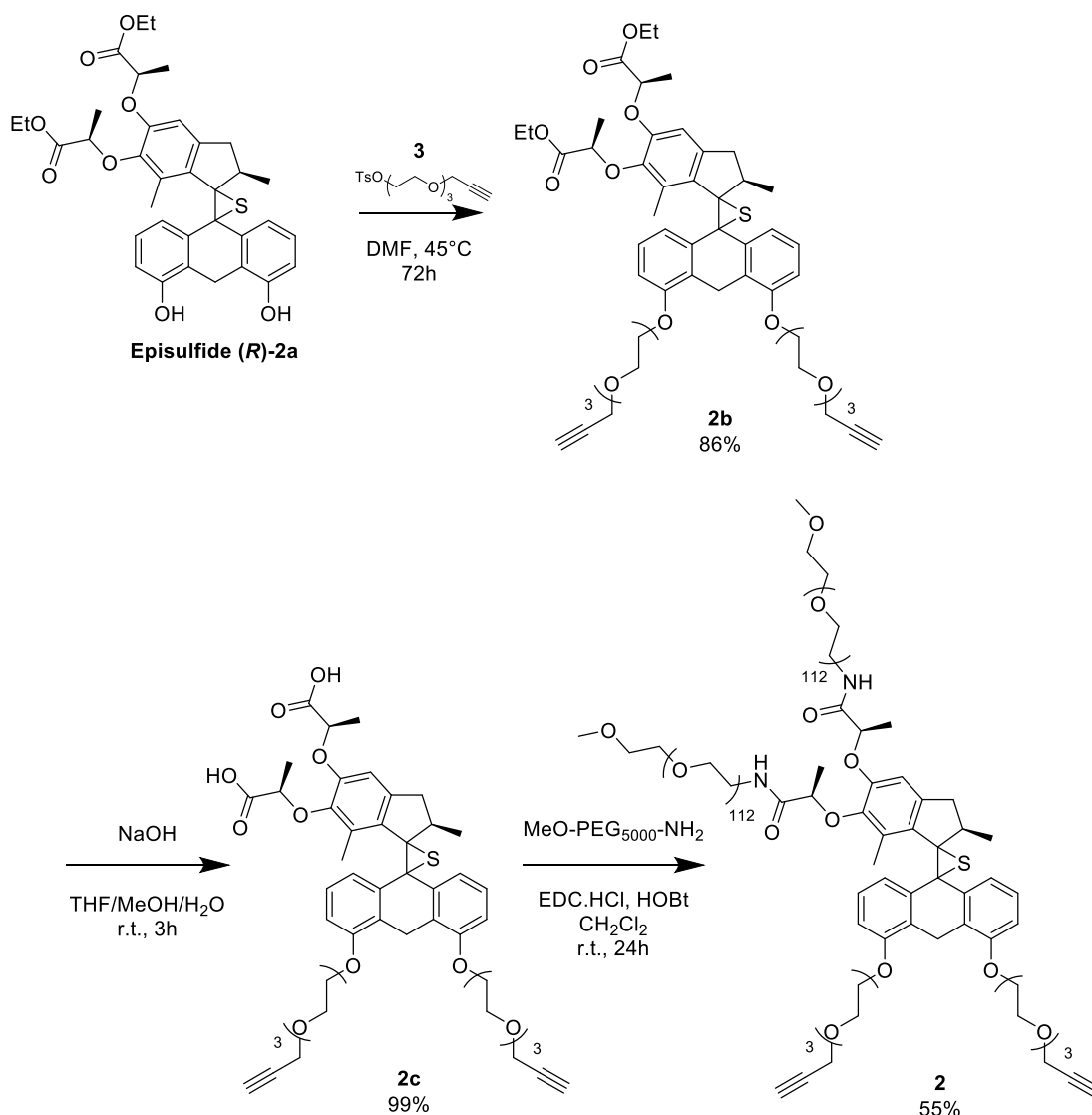
¹³C NMR (100 MHz, CDCl₃) δ 172.1, 175.2, 157.4, 156.8, 151.5, 147.2, 145.5, 143.8, 143.2, 139.5, 138.1, 134.5, 131.9, 129.3, 128.0, 126.4, 125.6, 122.0, 121.3, 110.8, 110.6, 109.5, 80.7, 78.4, 76.0, 74.3, 73.7, 72.1, 71.7, 71.6, 71.4, 70.9, 70.8, 70.2, 70.1, 62.3, 59.1, 40.4, 39.3, 19.3, 19.1, 18.8, 15.2.

MS (ESI): calculated for C₄₈H₅₆O₁₄S [M+H]⁺ *m/z* = 889.35, found: 889.18.

Compound 1

To a solution of compound **1c** (13.0 mg, 14.6 μmol) in CH₂Cl₂ (1 mL) was added HOBt (7.9 mg, 58.5 μmol) and EDC.HCl (22.4 mg, 117.0 μmol) at room temperature. After 10 min stirring, a solution of MeO-PEG-NH₂ (5000 Da, 182.8 mg, 36.6 μmol) in CH₂Cl₂ (2 mL) was added and the reaction mixture was stirred for 72 h at room temperature. The solvent was removed under vacuum and the crude purified by reversed phase column chromatography (C₁₈, MeOH/H₂O 3:7 - > 4:1) to afford compound **1** (89 mg, 8.19 μmol, 56%) as a slightly yellow solid.

¹H NMR (400 MHz, CD₃OD) δ 7.41 (d, J = 7.8 Hz, 1H), 7.32 (dd, J = 8.0, 8.0 Hz, 1H), 7.05 (dd, J = 7.9, 7.9 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.75 (s, 1H), 6.65 (d, J = 7.6 Hz, 1H), 4.73 (q, J = 6.6 Hz, 1H), 4.42 (q, J = 6.7 Hz, 1H), 4.36 – 4.14 (m, 11H), 4.03 – 3.34 (m, 910H), 2.90 – 2.83 (m, 2H), 2.42 (d, J = 15.1 Hz, 1H), 1.54 (d, J = 6.7 Hz, 3H), 1.33 – 1.29 (m, 3H), 1.18 (s, 3H), 0.63 (d, J = 6.6 Hz, 3H).



Scheme S2. Synthetic pathway for episulfide **2**.

Compound **2b**

To a mixture of compound **Episulfide (R)-2a** (1 eq., 310 mg, 0.513 mmol) and K₂CO₃ (239 mg, 1.74 mmol) in DMF (20 mL) was added a solution of compound **3** (3.62 eq., 634 mg, 1.85 mmol) in DMF (15 mL). The mixture was stirred at 45 °C over the weekend. Then the mixture was diluted with water (20 mL) and extracted with CH₂Cl₂ (3 x 40 mL). The combined organic phases were

dried over Na₂SO₄ and purified by flash column chromatography (silica gel, n-hexane:EtOAc=3:1--2:1---1:1, *R_f* = 0.2 (EtOAc/n-hexane (1/1))) affording compound **2b** (415 mg, 0.439 mmol, 86 %) as a yellowish solid.

¹H NMR (400 MHz, CDCl₃, 25°C) δ 7.32 (d, 1H, *J*=7.6 Hz), 7.21 (t, 1H, *J*=8.0 Hz), 6.93 (t, 1H, *J*=8.0 Hz), 6.76 (d, 1H, *J*=7.6 Hz), 6.69 (dd, 1H, *J*=8.0, 1.0 Hz), 6.64 (dd, 1H, *J*=7.6, 1.2 Hz), 6.54 (s, 1H), 4.77 (sext, 2H, *J*=6.8 Hz), 4.31-4.08 (m, 13H, 1-H), 3.98-3.93 (m, 4H, 2-H), 3.85-3.82 (m, 4H, 3-H), 3.72-3.67 (m, 12H, 4-H), 3.34 (m, 1H, *J*=15.2, 6.0 Hz), 2.43-2.40 (dt, 2H, *J*=2.4 Hz), 2.32 (d, 1H, *J*=14.8 Hz), 1.61 (d, 3H, *J*=6.8 Hz), 1.46 (d, 3H, *J*=6.8 Hz), 1.22 (t, 3H, *J*=7.2 Hz), 1.20 (s, 3H), 1.19 (t, 3H, *J*=7.2 Hz), 0.62 (d, 3H, *J*=6.8 Hz).

¹³C NMR (400 MHz, CDCl₃, 25°C) δ 172.5, 172.0, 155.8, 155.3, 149.6, 145.9, 144.4, 141.9, 141.7, 138.2, 133.4, 131.0, 127.6, 126.7, 126.4, 124.9, 124.6, 120.9, 120.3, 109.5, 109.0, 108.0, 79.7, 77.2, 76.8, 74.5, 72.9, 71.1, 70.8, 70.4, 69.7, 69.6, 69.1, 68.8, 61.2, 60.7, 58.4, 39.5, 38.1, 18.9, 18.6, 18.4, 14.5, 14.1, 14.0.

MS (ESI⁺): Calculated for [M+H]⁺ C₅₂H₆₅O₁₄S₂ [M+H]⁺ 877.47 Found: 877.47

Compound 2c

To a solution of episulfide **2b** (1 eq., 410 mg, 0.434 mmol) in THF/MeOH (2 mL/2 mL) was added a NaOH (5.59 eq., 96.8 mg, 2.42 mmol) solution (in 2 mL H₂O). The mixture was stirred at room temperature for 3 h and then quenched with 1 M HCl at 0 °C. The mixture was then washed with CH₂Cl₂ (3x15 mL). The combined organic phase was dried over Na₂SO₄, concentrated in vacuum and further purified by flash column chromatography (silica gel, CH₂Cl₂ -> CH₂Cl₂:MeOH=100:1->20:1, *R_f* = 0.1 (CH₂Cl₂/MeOH (100/1))) affording episulfide **2c** (381 mg, 0.429 mmol, 99 %) as a slightly yellow solid.

¹H NMR (CD₃OD, 400 MHz, 25 °C) δ = 7.37 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.81 (q, *J* = 7.2 Hz, 1H), 4.62 (q, *J* = 6.8 Hz, 1H), 4.30-4.10 (m, 9H), 3.92-3.89 (m, 4H), 3.78-3.77 (m, 4H), 3.66-3.60 (m, 12H), 3.40-3.35 (m, 1H), 2.80 (t, *J* = 2.4 Hz, 1H), 2.79 (t, *J* = 2.4 Hz, 1H), 2.36 (d, *J* = 15.2 Hz, 1H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.17 (s, 3H), 0.60 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (CD₃OD, 100 MHz, 25 °C) δ = 176.1, 175.5, 157.4, 156.8, 151.5, 147.2, 145.5, 143.8, 143.2, 139.5, 134.5, 131.9, 129.3, 128.0, 126.4, 125.6, 122.0, 121.3, 110.8, 110.6, 109.5, 80.7, 78.4, 76.0, 74.3, 73.7, 72.1, 71.7, 71.6, 71.4, 70.9, 70.8, 70.2, 70.1, 62.3, 59.1, 40.4, 39.3, 19.3, 19.1, 18.8, 15.2.

MS (ESI⁺): calculated for C₄₈H₅₆O₁₄S₂ [M+Li]⁺ 927.41, found: 927.42.

Compound 2

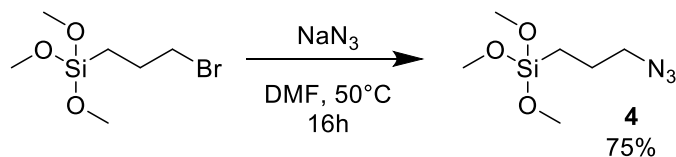
To a solution of compound **2c** (1 eq., 10 mg, 0.0112 mmol) in CH₂Cl₂ (1.03 mL) was added HOBt (3.04 eq., 4.77 mg, 0.0342 mmol) and N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide (7.85 eq.,

16.9 mg, 0.0883 mmol) at room temperature. After 40 min, a solution of NH₂-PEG-OMe (2.1 eq., 129 mg, 0.0237 mmol) in CH₂Cl₂ (1 mL) was added. The mixture was stirred at room temperature for 24 hours. After removal of the solvent, the residue was purified by reversed phase column chromatography (C₁₈, Merck, MeOH/H₂O 3:7→8 :2) affording compound **2** (65 mg, 0.00622 mmol, 55 %) as a slightly yellow solid.

¹H NMR (CDCl₃, 400 MHz, 298 K) δ 7.36 (d, ³J=7.6 Hz, 1H), 7.23-7.13 (m, 2H), 7.09 (dd, ³J = 7.9, 7.9 Hz, 1H), 6.91 (brs, 1H), 6.79 (d, ³J = 6.6 Hz, 1H), 6.69 (d, ³J = 8.3 Hz, 1H), 6.42 (s, 1H), 4.51 (q, ³J = 6.6 Hz, 1H), 4.25-4.20 (m, 1H), 4.15-3.97 (m, 9H), 3.92-3.84 (m, 4H), 3.82-3.48 (m, 1300H), 3.44 – 3.37 (m, 12H), 3.23 (t, J = 6.8 Hz, 1H), 3.13 (dd, J = 15.2, 6.2 Hz, 1H), 2.07 (d, J = 15.2 Hz, 1H), 1.47-1.37 (m, 6H), 1.08 (d, ³J = 7.0 Hz, 3H), 0.92 (d, ³J = 6.8 Hz, 3H).

3. Grafting of molecular motors on silicon surfaces

Functionalization of silicon surfaces with molecular motor **1** or episulfide **2** requires the synthesis of an azido-functionalized silane as follows:



Scheme S3. Synthetic pathway for (3-azidopropyl)trimethoxysilane **4**.

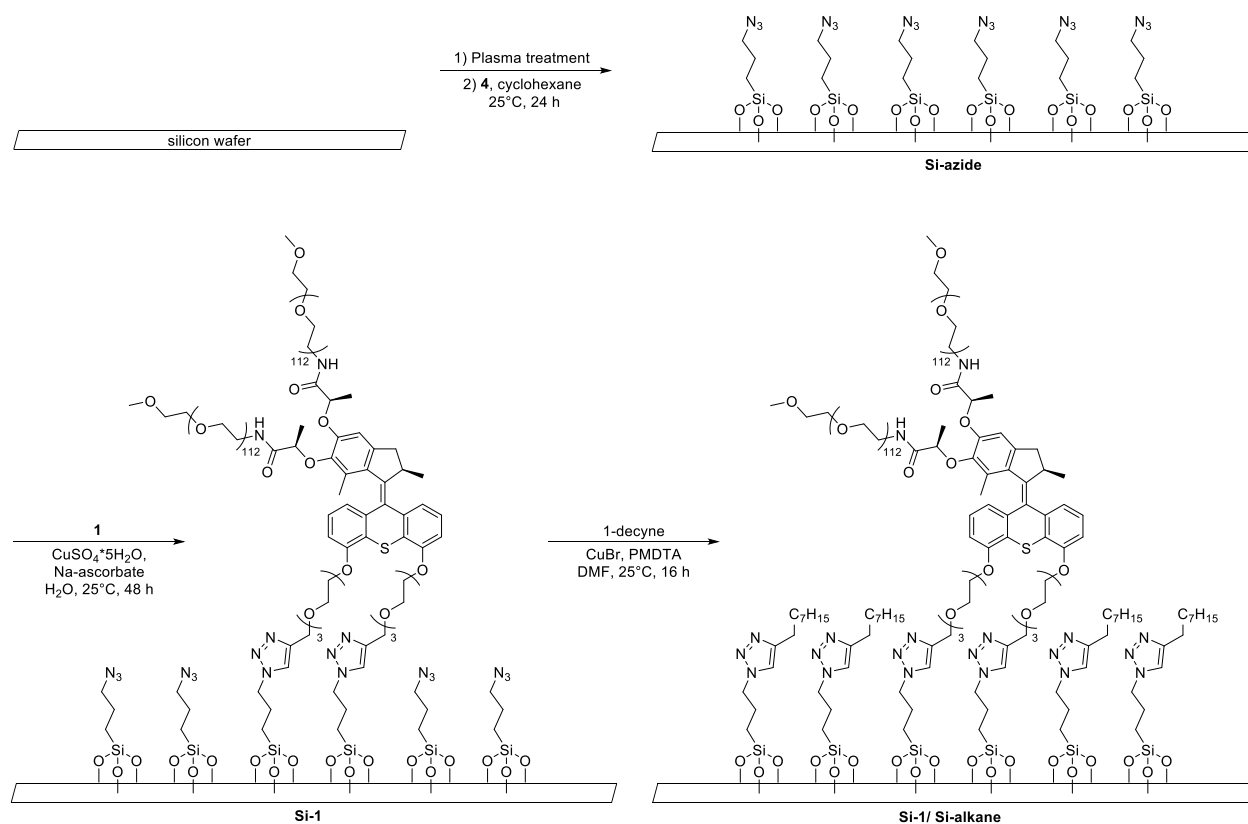
Compound **4**

A solution of (3-bromopropyl)trimethoxysilane (2.0 g, 4.11 mmol) and sodium azide (0.64 g, 4.93 mmol) in DMF (16 mL) was stirred at 50°C for 16 h. The reaction was quenched with water (10 mL) and the aqueous solution was extracted with diethyl ether (3 x 10 mL). The organic phase was washed with water (2 x 50 mL) and brine (50 mL) and dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give compound **4** (1.26 g, 6.14 mmol, 75% yield) as a slightly yellow liquid.

¹H NMR (400 MHz, CDCl₃) δ 3.55 (s, 9H), 3.25 (t, J = 7.0 Hz, 2H), 1.74 – 1.65 (m, 2H), 0.73 – 0.64 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 53.82, 50.69, 22.61, 6.41.

MS (ESI⁺): calculated for C₆H₁₅N₃O₃Si [M+H]⁺ m/z = 206.09, found: 206.17.



Scheme S4. Surface functionalization steps for the self-assembled monolayers of polymer-motor conjugate.

The following surface functionalization protocols are for two silicon wafer surfaces (cut in 2 x 2 cm) placed in a sample holder.

Si-azide functionalized surfaces

The silicon surfaces were first sonicated in a deionised water/ethanol mixture (5 mL/ 5mL) for 10 minutes and dried under a nitrogen flow. Afterwards, they were treated in a plasma chamber for 2 minutes.

Thickness determined by ellipsometry: 24.06 +/- 0.43 Angströms; Contact angle: 4.7°.

Then, a solution with 3-Azidopropyltrimethoxysilane **4** (17.3 mg, 0.08 mmol) in THF (1 mL) with deionised water (10.3 µL) and HCl (37%, 1.3 µL) was prepared. This mixture was added to cyclohexane (9 mL) to obtain a hazy solution. The previously activated silicon surfaces were added to this solution and put on a shaking plate for 24 h. The surfaces were then sonicated for 5 minutes in acetone (10 mL) and ethanol (10 mL) successively and dried under a nitrogen flow.

Thickness determined by ellipsometry: 94.90 +/- 7.76 Angströms; Contact angle: 54.9°.

Si-1 (surfaces functionalized with molecular motor 1)

Two silanised surfaces were added to a solution of motor **1** (5 mg, 0.46 μmol) with copper sulfate pentahydrate (1.15 mg, 4.6 μmol) and sodium ascorbate (0.92 mg, 4.6 μmol) in degassed, deionised water (10 mL). The reaction mixture with the surfaces were put on a shaking plate for 48 h. The surfaces were then sonicated for 5 minutes in water (10 mL) and ethanol (10 mL) successively and dried under a nitrogen flow.

Thickness determined by ellipsometry: 143.31 +/- 12.84 Angströms; Contact angle: 34.7°.

Si-1/ Si-alkane (surfaces functionalized with molecular motor 1 and alkyl chains)

Two surfaces of **Si-1** were added to a solution of 1-Decyne (18 μL , 0.1 mmol) with CuBr (14.3 mg, 0.1 mmol) and PMDTA (20.9 μL , 0.1 mmol) in dry, degassed DMF (10 mL). The reaction mixture with the surfaces were put on a shaking plate for 16 h. The surfaces were then sonicated for 5 minutes in acetone (10 mL) and ethanol (10 mL) successively and dried under a nitrogen flow.

Thickness determined by ellipsometry: 163.21 +/- 15.02 Angströms; Contact angle: 59.9°.

The density of functionalization was approximated by knowing the surface of the silicon wafer 2x4 cm², and the mass of motor that was attached to the surface (4.1 mg attached and 0.9 mg recovered from solution), leading to the average attachment of 1 motor on 4 nm².

4. SMFS experiments

a. Experimental setup

SMFS experiments were performed using an MFP3D Origin+ (Asylum Research, Oxford Instruments) AFM with OBL-10 Biolevers (Bruker) with a nominal spring constant of $\sim 0.03 \text{ N.m}^{-1}$. Prior to the experiments, the cantilevers were calibrated in air using the thermal noise method in combination with the Sader method to determine the exact spring constant k . Grafted surfaces were placed in the fluid cell and immersed in anhydrous, filtered DMF. The cantilever was then immersed in the fluid cell away from the surface for 1 h prior to SMFS measurements, allowing the system to reach equilibrium. Approach–retraction cycles were then performed at a constant tip velocity of 200 nm.s^{-1} . During the approach phase, the AFM tip was brought into contact with the surface until a force of 500 pN was reached, enabling physisorption of the polymer chains onto the tip. The tip was then retracted to a distance of 100 nm from the surface to ensure full extension of the molecule and desorption between successive cycles (total system length $\approx 40 \text{ nm}$). Raw cantilever deflection versus piezo displacement curves were converted into force–distance curves using Hooke's law:

$$F = -kx = -k(z-d)$$

with F the force experienced by the molecule, k the spring constant of the cantilever determined by Sader's method, x the cantilever deflection, z the piezo-movement and d the tip-substrate distance.

The same setup was used for irradiated surfaces. Prior to SMFS measurements, surfaces were irradiated in DMF for 1 minute with UV light (0.43 mW cm^{-2} at 366 nm).

b. Analysis of force-distance curves

Raw force– piezo-movement curves were sorted using a homemade routine implemented in IgorPro software. Only experiments exhibiting an event occurrence of approximately 5% (i.e., polymer chain stretching events) were retained, ensuring measurements at the single-molecule level.² The selected curves were further analysed using a custom routine enabling curve transformation, extraction of force–distance parameters, and mathematical fitting. For all curves, the rupture force and corresponding extension were determined to construct histograms. For plateau-containing curves, the force and extension values at the onset and end of the plateau were also extracted to calculate the plateau length (Δx). Automatic fitting of the force–distance curves using the worm-like chain (WLC) model was performed in the entropic regime (typically below $\sim 100 \text{ pN}$). The WLC equation can be expressed as follows:

$$F(D) = \frac{k_B T}{l_p} \left[\frac{D}{L} + \frac{1}{4(1 - \frac{D}{L})^2} - \frac{1}{4} \right]$$

where k_B is the Boltzmann constant and T is the temperature. The persistence length (l_p) and the contour length (L) are treated as fitting parameters during the curve analysis.

Histograms of force, extension, l_p and Δx were constructed using IgorPro. Probability density functions (PDF) were obtained by fitting the data by a Kernel smoothing function ($N = 1000$ points) using MatLab (MathWorks). Raw data were further analysed using a Gaussian mixture model (GMM), corresponding to a weighted sum of M Gaussian components ($i = 1-3$), expressed as:

$$P(x|\lambda) = \sum_{i=1}^M p_i G(x|\mu_i, \sigma_i)$$

where x is the vector of the observable, $G(x|\mu_i, \sigma_i)$ is the normalized Gaussian component with mean μ_i and variance σ_i , and p_i is the weight of the i^{th} component. The weights satisfy the normalization condition $\sum_{i=1}^M p_i = 1$, and λ represents the set of all the parameters $\lambda = \{p_i, \mu_i, \sigma_i\}$ for $i=1, 2$ or 3 .

Each population is reported with its 95% confidence interval estimated as $\pm 1.96 \sqrt{\frac{\sigma^2}{(p_i N)}}$ where σ^2 is the variance of the i^{th} component, and $p_i N$ represents the effective size of the population.

5. Supplementary figures

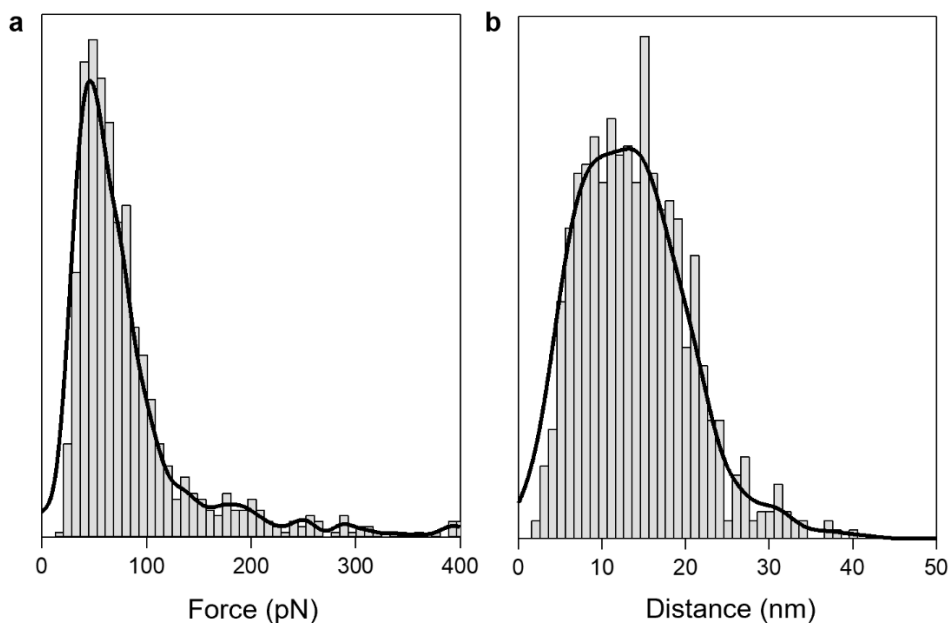


Figure S1. Histograms of rupture forces and corresponding extension distances measured for tip–polymer detachment events in DMF on the polymer–motor conjugate prior to UV irradiation ($N = 638$). The rupture forces fall within the expected range for physisorption interactions, while the measured extension distances are in good agreement with the length of the polymer–motor conjugates.

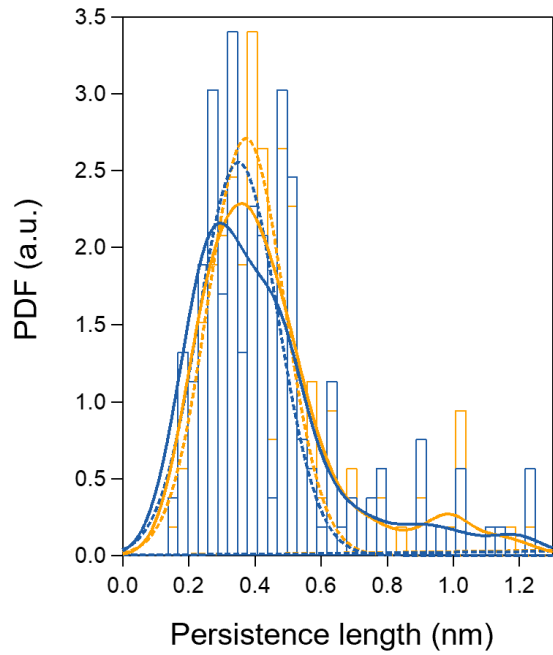


Figure S2. Persistence length (l_p) distributions extracted from force–distance curves before (blue) and after (orange) the plateau. Gaussian fits (dashed lines) yield values of 0.37 ± 0.02 nm and 0.35 ± 0.02 nm, respectively. The similarity between the persistence lengths in both regimes indicates that a single polymer chain is stretched throughout the plateau.

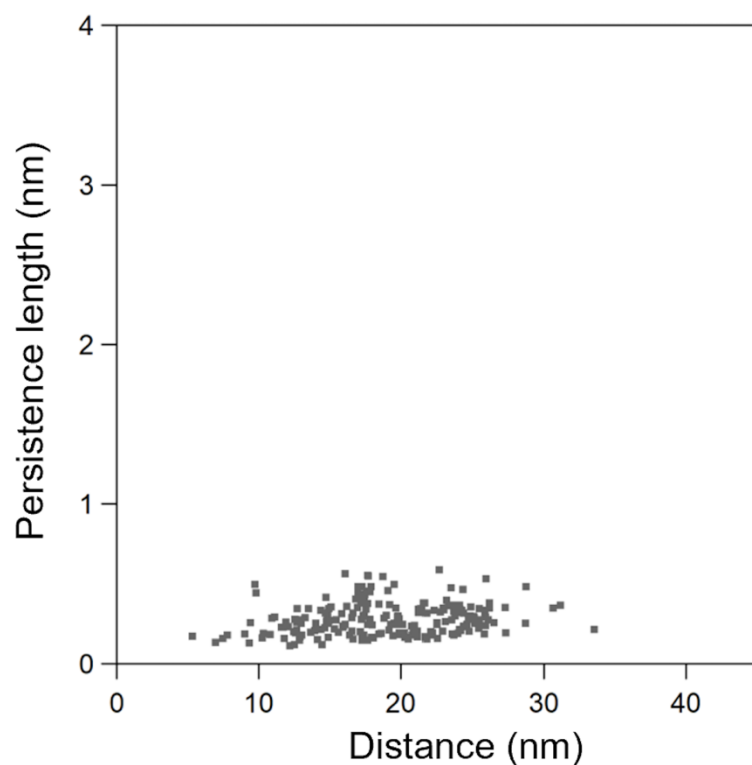


Figure S3 Persistence length (l_p) values extracted from force–distance curves recorded after UV irradiation of the episulfide-based control system, plotted as a function of rupture distance ($N = 196$). In contrast to the active polymer–motor conjugate, no elevated l_p values (> 1 nm) are observed, indicating the absence of highly rigid, entangled structures.

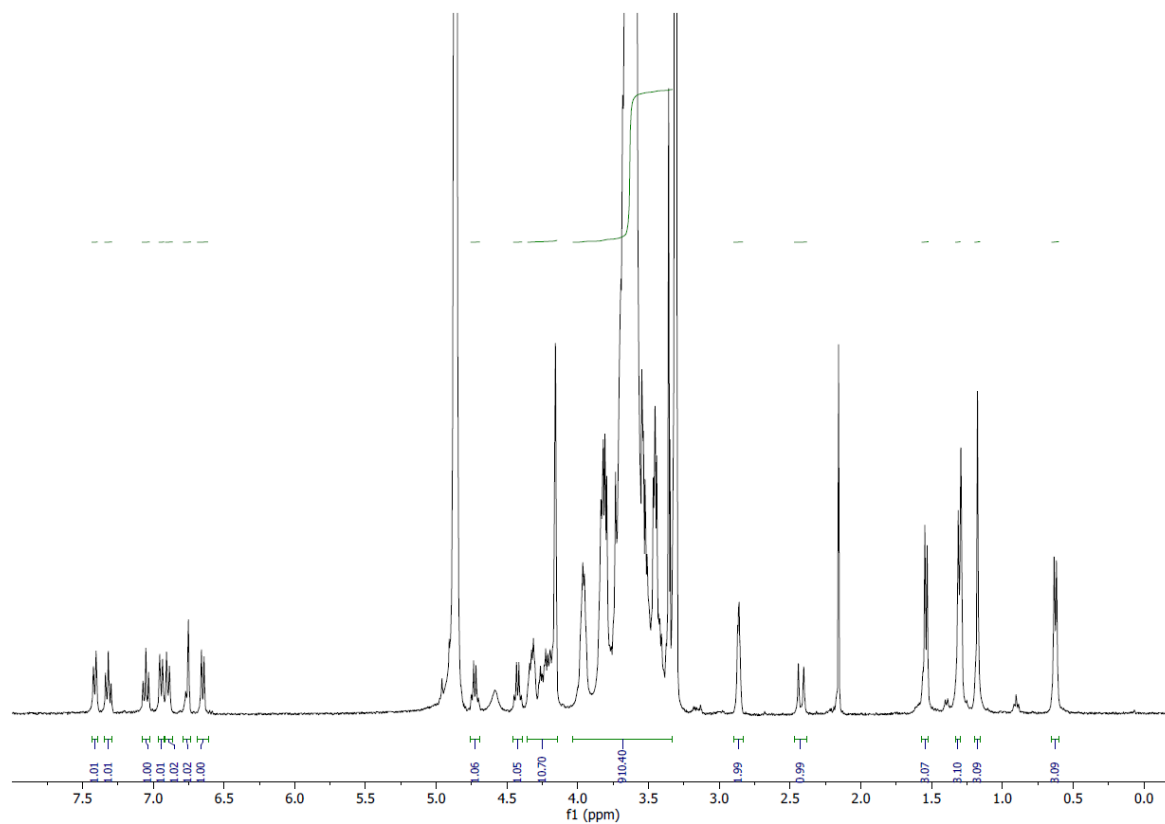


Figure S4. ^1H NMR (400 MHz, CD_3OD , 298 K) spectrum of molecular motor **1**.

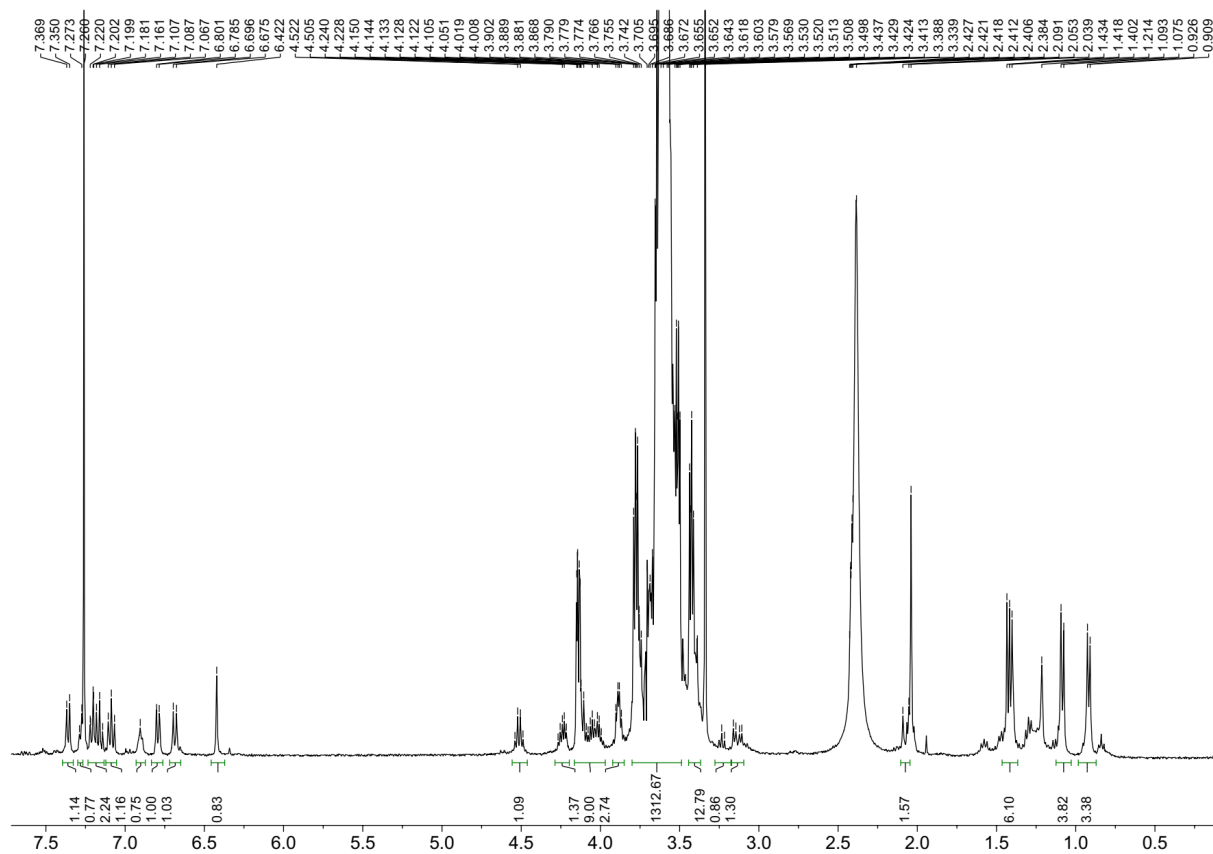


Figure S5. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of episulfide **2**.

6. References

1. Li, Q., Fuks, G., Moulin, E., Maaloum, M., Rawiso, M., Kulic, I., Foy, J. T. & Giuseppone, N. Macroscopic contraction of a gel induced by the integrated motion of light-driven molecular motors. *Nature Nanotechnology* **10**, 161–165 (2015).
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