Supporting Information

Molecular Spur Gears with Triptycene Rotators and a Norbornane-Based Stator

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Section A. General Information

Unless otherwise notified all commercially available compounds were used as received without further purification. 9-(bromoethynyl)-triptycene **S1a** and 9-(2,2'-dibromovinyl)-triptycene **S1b** were prepared as reported in the literature.¹ Thin-layer chromatography (TLC) plates pre-coated with silica gel 60 F254 were purchased and were visualized using a UV lamp. Flash column chromatography was performed using silica gel (230–400 mesh) as the stationary phase. Anhydrous tetrahydrofuran (THF) was distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Melting points of solids were measured without calibration of the apparatus. ¹H NMR and ¹³C NMR spectra in solution were recorded at 500 MHz and 126 MHz, respectively. Chemical shifts are reported in ppm and the (residual) solvent signals of CDCl₃ (¹H NMR: δ 7.26 ppm; ¹³C NMR: δ 77.0 ppm) were used as reference. Multiplicities of the peaks are reported as singlet (s), doublet (d), triplet (t), or multiplet (m). The coupling constants J are reported in Hz. Infrared spectra (IR) were recorded with a HATR-FTIR instrument. High-resolution mass spectra were acquired using ESI/APCI ionization methods and the signal was detected with a TOF detector.

Section B .Synthesis and Characterization



In an oven dried seal tube was added 9-anthraldehyde (4.53 g, 22.0 mmol), norbornadiene (920 mg, 10.0 mmol), and toluene (3 mL) under Argon. The tube was sealed and the reaction mixture was heated to 200 °C in a sand bath for 3 days before it was allowed to cool down to room temperature. The reaction mixture was transferred to a round bottom flask and the solvent was removed *in vacuo*. Flash column chromatography of the residue using a 15:1 (v/v) mixture of hexanes and DCM as the eluent provided the desired regioisomer **5** (1.907 g, 38%) and the undesired isomer **6** (2.901 g, 57%).

5: white solid, m.p. 283–284 °C; ¹H NMR (500 MHz, CDCl₃, ppm): δ –1.08 (s, 2H), 1.91 (dd, *J* = 8.6, 2.7 Hz, 2H), 2.03 (d, *J* = 8.6 Hz, 2H), 2.06–2.11 (m, 2H), 4.25 (d, *J* = 2.7 Hz, 2H), 7.01–7.16 (m, 12H), 7.23–7.27 (m, 2H), 7.29–7.35 (m, 2H), 10.80 (s, 2H); ¹³C NMR (126 MHz, CDCl₃, ppm): δ 26.9, 41.5, 48.3, 50.7, 51.4, 58.6, 121.0, 122.3, 123.8, 124.7, 125.5, 126.0, 126.4, 126.6, 138.9, 141.9, 142.1, 144.4, 203.5; IR (powder, cm⁻¹): *v* 653(w), 695 (m), 734(s), 748(s), 781(w), 878(w), 917(w), 986(w), 1036(m), 1135(m), 1165(w), 1223(w), 1263(w), 1295(w), 1457(s), 1484(w), 1717(s), 2732(w), 2825(w), 2937(w), 3019(w), 3040(w); HRMS (DART, TOF): m/z calculated for C₃₇H₂₉O₂ (MH⁺): 505.2168, found: 505.2154.



Figure S2. ¹³C NMR spectra of compound 5 at 126 MHz in CDCl₃.

6: white solid, m.p. 288–289 °C; ¹H NMR (500 MHz, CDCl₃) δ –1.04 (s, 2H), 1.89 (dd, J = 8.7, 2.7 Hz, 2H), 1.99 (s, 1H), 2.11 (d, J = 8.7 Hz, 2H), 2.18 (s, 1H), 4.18 (d, J = 2.7 Hz, 2H), 7.02–7.15 (m, 12H), 7.21–7.25 (m, 2H), 7.33–7.39 (m, 2H), 10.76 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.0, 40.0, 43.3, 48.5, 51.0, 51.5, 58.5, 76.7, 77.0, 77.3, 121.2, 122.6, 123.6, 124.5, 125.6, 126.1, 126.3, 126.5, 138.8, 142.0, 142.0, 144.3, 203.0; IR (powder, cm⁻¹): v 657(w), 703 (m), 747(s), 781(w), 859(w), 930(w), 980(w), 1035(m), 1139(m), 1202(w), 1265(w), 1290(w), 1456(s), 1483(w), 1722(s), 2722(w), 2824(w), 2934(w), 3020(w), 3063(w); HRMS (ESI/APCI, TOF): m/z calculated for C₃₇H₂₉O₂ (MH⁺): 505.2168, found: 505.2151.



Figure S3. ¹H NMR spectra of compound 6 at 500 MHz in CDCl₃.





In a 100-mL round bottom flask with a stir bar were added 4-acetamidobenzenesulfonyl azide (1.64 g, 6.83 mmol), dimethyl (2-oxopropyl)phosphonate (1.13 g, 6.83 mmol), K_2CO_3 (2.05 g, 14.9 mmol) in acetonitrile (20 mL). The resulting mixture was stirred at room temperature for 2 h before a solution of 7 (1.50 g, 2.97 mmol) in a mixture of DCM (10 mL) and methanol (10 mL) was added into the flask. The reaction mixture was stirred overnight before it was filtered through a short plug of silica to remove the insoluble solids. The solvent was removed *in vacuo*, and the residue was purified by flash column chromatography using a mixture of hexanes and DCM (3:1, v/v) as the eluent to give the desired product 7 (1.21 g, 82%).

7: white solid, m.p. 197–199 °C; ¹H NMR (500 MHz, CDCl₃) δ –0.99 (s, 2H), 1.81–1.89 (m, 4H), 1.97 (d, J = 1.5 Hz, 1H), 2.54 (s, 1H), 2.92 (s, 2H), 4.17 (d, J = 2.5 Hz, 2H), 6.99–7.12 (m, 10H), 7.16 (dd, J = 7.0, 1.5 Hz, 2H), 7.47–7.53 (m, 2H), 7.55–7.61 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.4, 40.7, 44.2, 47.5, 47.7, 51.2, 56.4, 77.1, 81.8, 121.9, 122.8, 123.2, 123.8, 125.6, 126.0, 126.4, 140.2, 140.8, 143.2, 143.3; IR (powder, cm⁻¹): ν 731(s), 748(s), 781(w), 906(m), 934(w), 979(w), 1027(w), 1157(w), 1190(w), 1291(w), 1456(s), 1480(w), 2932(w), 3020(w), 3067(w), 3299(s); HRMS (ESI/APCI, TOF): m/z calculated for C₃₉H₂₉ (MH⁺): 497.2269, found: 497.2252.



Figure S6. ¹³C NMR spectra of compound 7 at 126 MHz in CDCl₃.



To a solution of 9-ethynyltriptycene **S1a** (140 mg, 0.50 mmol) in acetone (5 mL) in a 25-mL round bottom flask were added NBS (163 mg, 0.91 mmol) and AgNO₃ (51 mg, 0.30 mmol). The reaction mixture was stirred at room temperature for 2 h and TLC showed a clean conversion. Thus the reaction mixture was filtrated through a short plug to give pure product **8a** (179 mg, >99%).

8a: white solid, m.p. 232–233 °C; ¹H NMR (500 MHz, CDCl₃) δ 5.40 (s, 1H), 7.01–7.08 (m, 6H), 7.35–7.40 (m, 3H), 7.67–7.71(m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 50.9, 53.1, 54.0, 75.1, 122.3, 123.4, 125.2, 125.8, 144.0, 144.2; IR (powder, cm⁻¹): ν 606(w), 639(s), 678(w), 742(s), 748(s), 857(w), 875(w), 1025(w), 1186(w), 1295(w), 1456(s), 2211(w), 3033(w), 3065(w); HRMS (ESI/APCI, TOF): m/z calculated for C₂₂H₁₄Br (MH⁺): 357.0279, found: 357.0279.



Figure S7. ¹H NMR spectra of compound 8a at 500 MHz in CDCl₃.



Figure S8. ¹³C NMR spectra of compound 8a at 126 MHz in CDCl₃.



The dibromoalkene **S1b** (230 mg, 0.45 mmol) was dissolved in THF (3 mL) and a TBAF solution (1.0 M in THF, 4 mL, 4.0 mmol) was slowly added into the flask. TLC analysis was performed immediately after the addition and more than half of the starting material has been consume. The reaction was stirred overnight at 45 °C and was quenched by adding a saturated NH₄Cl solution (20 mL) into the reaction flask. The mixture was extracted with DCM (20 mL) twice and the organic layers were combined and concentrated to give a crude. Flask column chromatography with a 10:1 (v/v) hexanes-DCM mixture as the eluent provided the desired product **8b** (139 mg, 72%).

8b: white solid, m.p. 191–192 °C; ¹H NMR (500 MHz, CDCl₃) δ 5.89 (q, J = 1.8 Hz, 1H), 7.05–7.18 (m, 5H), 7.33 (app. d, J = 7.8 Hz, 1H), 7.40–7.47 (m, 2H), 7.68–7.74 (m, 2H), 7.88 (app. d, J = 7.6 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 49.7 (q, J = 2.0 Hz), 51.8, 54.1, 74.6, 122.4 (q, J = 4.9 Hz), 122.4, 124.0, 124.3 (q, J = 273.4 Hz, -CF₃), 125.1, 125.1 (q, J = 31.1 Hz), 125.7, 125.8, 126.2, 142.8, 143.1 (q, J = 2.1 Hz), 143.6, 146.2; IR (powder, cm⁻¹): v 615(w), 626(m), 640(m), 665(s), 685(w), 733(m), 747(s), 762(m), 803(m), 869 (w), 927 (w), 1026(w),

1068(m), 1089(s), 1105(s), 1124(s), 1149(m), 1267(w), 1294(m), 1326(s), 1435(m), 1457(m), 1609(w), 2216(w), 2854(w), 2924(w), 3072(w); HRMS (ESI/APCI, TOF): m/z calculated for $C_{23}H_{13}BrF_3$ (MH⁺): 425.0153, found: 425.0146.



Figure S9. ¹H NMR spectra of compound 8b at 500 MHz in CDCl₃.



Figure S10. ¹³C NMR spectra of compound 8b at 126 MHz in CDCl₃.



To a 25 mL round bottom flask were added 7 (108 mg, 0.22 mmol) and 9-(bromoethynyl)triptycene (390 mg, 1.09 mmol) and benzene (5 mL) under Argon. The solution was degased for 10 min before $Pd_2(dba)_3$ (21 mg, 0.023 mmol) and copper(I) iodide (4.4 mg, 0.023 mmol) were added into the flask. The reaction mixture was degased for another 5 min before triethylamine (0.3 mL) was added in. The reaction was stirred at room temperature overnight before the solvent was removed *in vacuo*. The residue was absorbed on silica. Flash column chromatography with a 3:1 (v/v) hexanes-DCM mixture as the eluent provided the desired product with a small amount of impurities. The obtained solids were washed with a 10:1 (v/v) hexanes-DCM mixture (2 mL) to remove the impurities and provide the desired product **9a** (146 mg, 64 %).

9a: white solid, m.p. > 272 °C (dec.); ¹H NMR (500 MHz, CDCl₃) δ –0.82 (s, 2H), 1.97 (dd, *J* = 8.5, 2.9 Hz, 2H), 2.05 (s, 1H), 2.14 (d, *J* = 8.5 Hz, 2H), 2.79 (s, 1H), 4.26 (d, *J* = 2.9 Hz, 2H), 5.27 (s, 2H), 6.54 (td, *J* = 7.4, 1.1 Hz, 6H), 6.65 (td, *J* = 7.4, 1.1 Hz, 6H), 7.09–7.27 (m, 18H), 7.70 (d, *J* = 7.4 Hz, 6H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 7.4 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.7, 41.2, 44.0, 47.7, 48.4, 51.6, 53.1, 53.5, 55.8, 73.4, 73.8, 76.2, 78.0, 122.2, 122.3, 122.9, 123.0, 123.5, 124.0, 125.1, 125.4, 125.9, 126.3, 126.4, 126.8, 140.2, 140.7, 143.2, 143.3, 143.6, 143.9; IR (powder, cm⁻¹): *v* 606(w), 640(s), 653(w), 695(w), 746(s), 864(w), 941(w), 1027(w), 1156(w), 1292(w), 1456(m), 1608 (w), 2839(w), 3019(w), 3067(w); HRMS (ESI/APCI, TOF): m/z calculated for C₈₃H₅₆N (MNH₄⁺): 1066.4413, found: 1066.4445.



Figure S11. ¹H NMR spectra of compound **9a** at 500 MHz in CDCl₃.



Figure S12. ¹³C NMR spectra of compound 9a at 126 MHz in CDCl₃.



To a 30-mL round bottom flask were added 7 (50 mg, 0.10 mmol) and **8b** (138 mg, 0.33 mmol) and benzene (10 mL) under Argon. The solution was degased for 20 min before $Pd_2(dba)_3$ (21 mg, 0.023 mmol), CuI (4.4 mg, 0.023 mmol), and triethylamine (0.3 mL) were added into the flask. The reaction mixture was degased for another 5 min before it was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was absorbed on silica to be purified by flash column chromatography. A 3:1 (v/v) hexanes-DCM mixture as the eluent provided the desired product with a small amount of fluorescent impurities. The obtained solids were washed with a 10:1 (v/v) hexanes-DCM mixture (1 mL) twice to remove the residual impurities and provide the desired product **9b** (81 mg, 68 %).

9b: white solid, m.p. > 266 °C (dec.); ¹H NMR (500 MHz, CDCl₃) δ –0.79 (s, 2H), 1.97 (dd, J = 8.5, 2.6 Hz, 2H), 2.08 (s, 1H), 2.16 (d, J = 8.5 Hz, 2H), 2.83 (s, 1H), 4.28 (d, J = 2.6 Hz, 2H), 5.79 (s, 2H), 5.95 (dd, J = 7.7, 7.6 Hz, 2H), 6.51 (d, J = 7.7 Hz, 2H), 6.76–6.84 (m, 4H), 6.91 (t, J = 7.4 Hz, 4H), 7.10–7.31 (m, 12H), 7.37 (d, J = 7.4 Hz, 4H), 7.66 (d, J = 7.6 Hz, 2H), 7.74–7.90 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ 27.7, 41.2, 44.0, 47.7, 48.4, 49.6, 51.5, 53.5, 55.9, 72.8, 73.0, 76.7, 78.5, 121.7 (q, J = 4.7 Hz), 122.1, 122.5, 123.0, 123.4, 123.7, 124.0, 124.2 (q, J = 273.4 Hz, **-C**F₃), 124.5 (q, J = 31.2 Hz), 124.6, 125.5, 125.5 (app. d, J = 2.2 Hz), 125.9, 126.1, 126.3, 126.5, 126.9, 140.0, 140.7, 142.2, 142.7 (app. d, J = 1.4 Hz), 143.0, 143.2, 143.4 (app. d, J = 1.3 Hz), 145.4; ¹⁹F NMR (376 MHz, CDCl₃) δ –62.65; IR (powder, cm⁻¹): v 627(w), 652(m), 685(w), 698(w), 744(s), 802(w), 1028(w), 1070(w), 1090(m), 1117(s), 1155(m), 1293(w), 1326(s), 1434(w), 1457(m), 1609(w), 2926(w), 3072(w); HRMS (ESI/APCI, TOF): m/z calculated for C₈₅H₅₄F₆N (MNH4⁺): 1202.4160, found: 1202.4193.

¹³C NMR (126 MHz, CDCl₃) δ 27.7, 41.2, 44.0, 47.7, 48.4, 49.6, 51.5, 53.5, 55.9, 72.8, 73.0, 76.7, 78.5, 120.9, 121.7, 121.7, 122.1, 122.5, 123.0, 123.1, 123.4, 123.7, 124.0, 124.1, 124.3, 124.6, 124.8, 125.2, 125.5, 125.5, 125.5, 125.9, 126.1, 126.3, 126.5, 126.9, 127.4, 140.0, 140.7, 142.2, 142.7, 142.7, 143.0, 143.2, 143.4, 143.5, 145.4.







Figure S14. ¹³C NMR spectra of compound 9b at 126 MHz in CDCl₃.

Section C. X-Ray Diffraction

For structural determination, a colorless crystal was picked out from the mother liquor and mounted on the diffractometer immediately for data collection. The diffractometer was equipped with Mo-K α radiation ($\lambda = 0.71073$ Å) and an area detector. Diffraction was collected at 100 K and the structures were solved and refined with the SHELXTL program. All heavy atoms were refined anisotropically while the hydrogen atoms were placed at the calculated positions.





Section E. Computational Methods

Metadynamics molecular dynamics (MD) simulations were performed using the NAMD v2.11 program.² Force field parameters were generated with the antechamber module using the General Amber Force Field (GAFF), and the atomic partial charges were assigned using the RESP method. Single point charges were computed with HF/6-31G* theory. We used Gaussian09 for the quantum mechanical (QM) computations and the antechamber module in Amber14 to process atomic partial charges from the QM computations. In the simulation, the structures of each spur gear system were first minimized in vacuum with no solvent model. Well-tempered metadynamics in conjunction with multiple-walker algorithm were used to accelerate convergence of the free energy landscape computed from the metadynamics simulations. The Langevin thermostat controlled the temperature at 300 K and the Langevin barostat kept at the pressure at 1 atm. The collective variables were chosen to be the dihedral angle of the two triptycenes of each molecular gear, with the range constrained to be -180° to 180°. The gear systems were first minimized and equilibrated for 20 ns. We simulated the rotations of each spur gear for 180 ns and 2D potentials of mean force were generated.

Section F. References

- Frantz, D. K.; Linden, A.; Baldridge, K. K.; Siegel, J. S. Molecular Spur Gears Comprising Triptycene Rotators and Bibenzimidazole-Based Stators. J. Am. Chem. Soc. 2012, 134, 1528– 1535.
- 2) NAMD code is available for download at https://www.ks.uiuc.edu/Research/namd/.