Supporting Information

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General remarks for synthetic procedures
Reagents were purchased from Sigma-Aldrich and Strem and were used as provided unless stated otherwise. All solvents were reagent grade and were dried and distilled before use according to standard procedures. All reactions were performed in oven- or flame-dried round bottom or modified Schlenk (Kjeldahl shape) flasks fitted with rubber septa under a positive pressure of nitrogen, unless stated otherwise. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at 40 ºC. Flash column chromatography was performed as described by Still et al.[1] Chromatography: silica gel, Merck type 9385 230-400 mesh. TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or exposure to ceric ammonium molybdate solution (CAM) or an acidic solution of p-anisaldehyde (anisaldehyde) followed by brief heating with a heating gun.

General remarks for instrumentation
1H and 13C NMR spectra were recorded on a Varian VXR-300, a Varian Mercury Plus 400, or a Varian Inova 500 operating at 300, 400, and 500 MHz, respectively, for the 1H nucleus, and at 75, 100 and 125 MHz for the 13C nucleus. Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (CHCl3: δ 7.26). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl3: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant in Hz, and assignment.
Mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Orbitrap XL. Contact Angles were measured under ambient conditions on a Dataphysics contact angle goniometer with SCA20, version 3.60.2, and software supplied by Dataphysics. Equilibrium contact angles were obtained on 1 µL water droplets on amine-coated quartz, MS1, and MS2 using the sessile drop method. The contact angle was measured at four different locations on each surface and the results were averaged.
UV/vis absorption spectra were measured with a Jasco V-630 spectrophotometer attached with NCP-706 Cell holders for maintaining samples at a fixed and uniform temperature. To generate the motors in the unstable forms, samples were irradiated with UV light (Spectroline model ENB-280C/FE lamp, λmax = 365 nm; intensity ≈ 1.0 mW/cm²) at a distance of 3 cm from the centre of the lamp. For monitoring the decay of the UV signals for unstable-1 → stable-1, unstable-2 → stable-2, unstable-MS1 → stable-MS1, and unstable-MS2 → stable-MS2 at 475 nm as a function of time, a high-pass filter was mounted between the UV light source and the sample to cut off light with wavelengths below 460 nm to minimize photochemical isomerization occurring upon data recording.
Synthesis

3,6-dibromo-9-diazo-9H-fluorene (4).
To a solution of dibromo fluorenone 3[2] (800 mg, 2.4 mmol) in EtOH (280 mL), N₂H₄•H₂O (20 mL) was added and the solution was heated at 80 °C for 6 h. Addition of water (10 mL) to the hot mixture followed by cooling to rt resulted in the precipitation of a pale yellow solid. The solid was filtered, washed with cold MeOH and dried in vacuo. MnO₂ (0.5 g, 5.75 mmol) was added to a stirred solution of this pale yellow solid in THF (20 mL) at rt for 2 h. The mixture was then filtered over a plug of SiO₂ and the solvent was removed under reduced pressure to afford diazo 4 (435 mg, 1.2 mmol, 60%) as an orange solid. (This compound is not stable under ambient conditions and was used immediately for the synthesis of 6). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 1.5 Hz, 2H, Ar-H), 7.51 (dd, J = 8.3, 1.4 Hz, 2H, Ar-H), 7.36 (d, J = 8.3 Hz, 2H, Ar-H); ¹³C NMR (101 MHz, CDCl₃) δ 132.7, 131.8, 129.7, 125.7, 124.3, 124.1, 120.5, 118.3; HRMS (APCI-ion trap) m/z: [M – N₂ + H]⁺ Calcd for C₁₃H₁₂Br₂ 320.8909, found 320.8919.

3,6-dibromo-9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphtalen-1-ylidene)-9H-fluorene (6).
Diazao 4 (400 mg, 1.15 mmol) was added to a solution of thiketone 5[3] (485 mg, 2.30 mmol) in toluene (120 mL). The mixture was heated at 90 °C for 12 h and then PPh₃ (300 mg, 1.15 mmol) was added, followed by an additional 4 h heating at 90 °C. The mixture was cooled down to rt and CH₃I (3 mL, 48 mmol) was added, followed by stirring at rt for 1 h. The mixture was concentrated in vacuo and purified by flash column chromatography (SiO₂, 20:1 pentane:CH₂Cl₂) affording dibromo 6 (169 mg, 0.34 mmol, 29%) as an orange oil. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.91 (m, 3H, Ar-H), 7.86 – 7.80 (m, 2H, Ar-H), 7.66 (d, J = 8.4 Hz, 1H, Ar-H), 7.59 (d, J = 8.2 Hz, 1H, Ar-H), 7.55 – 7.46 (m, 2H, Ar-H), 7.36 (m, 1H, Ar-H), 6.94 (dd, J = 8.5, 1.9 Hz, 1H, Ar-H), 6.56 (d, J = 8.5 Hz, 1H, Ar-H), 4.26 (p, J = 6.6 Hz, 1H, C-H), 3.57 (dd, J =...
6.7 H2O (5 mL) was added. THF and MeOH were removed by rotary evaporation. NaOH
Ester C 52.4, 52.3, 45. 131.9, 131.4, 131.3, 131.1, 130.9, 130.1, 130.0, 129.7, 129.2, 129.1, 128.7, 127.3, 124.1, 123.1, 122.3, 121.0, 120.9, 45.5, 42.0, 19.3; HRMS (APCI-ion trap) m/z: [M + H]+ Calcd for C25H19Br2 500.9848, found 500.9895.

**Tetramethyl 5,5’-(9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-3,6-diyldiisophthalic acid (8).**

A mixture of 6 (161 mg, 0.32 mmol), pinacol ester 7[4] (323 mg, 0.96 mmol), K2PO4 (407 mg, 1.9 mmol), and Pd(PPh3)4 (33 mg, 0.032 mmol) was stirred in 1,4-dioxane (20 mL) at 100 °C for 16 h. After the mixture was cooled to rt, it was diluted with ethyl acetate (30 mL) and filtered. After removal of the solvent, the residue was purified by flash column chromatography (SiO2, pentane: CH2Cl2= 1:20) to yield ester 8 as a brown oil (152 mg, 65%). 1H NMR (400 MHz, CDCl3) δ 8.53 (s, 2H, Ar-H), 8.27 (s, 4H, Ar-H), 7.93 – 7.90 (m, 1H, Ar-H), 7.85 (t, J = 8.8 Hz, 2H, Ar-H), 7.80 – 7.74 (m, 1H, Ar-H), 7.72 – 7.64 (m, 1H, Ar-H), 7.51 (d, J = 8.2 Hz, 1H, Ar-H), 7.39 (t, J = 7.5 Hz, 1H, Ar-H), 7.35 – 7.28 (m, J = 5.6, 3.1 Hz, 2H, Ar-H), 7.25 (t, J = 7.7 Hz, 1H, Ar-H), 7.14 (t, J = 7.4 Hz, 1H, Ar-H), 6.73 (t, J = 7.5 Hz, 1H, Ar-H), 6.65 (d, J = 7.9 Hz, 1H, Ar-H), 4.33 – 4.22 (m, 1H, C-H), 3.88 (s, 12H, CO2C-H3), 3.51 (dd, J = 15.0, 5.6 Hz, 1H, C-H), 2.69 (d, J = 15.1 Hz, 1H, C-H), 1.31 (d, J = 6.7 Hz, 3H, C-H3); 13C NMR (101 MHz, CDCl3) δ 166.2, 166.1, 165.8, 152.8, 147.9, 141.8, 141.7, 140.3, 140.0, 139.8, 139.7, 137.5, 137.4, 137.3, 135.9, 133.2, 132.6, 132.1, 131.9, 131.4, 131.3, 131.1, 130.9, 130.1, 130.0, 129.7, 129.2, 129.1, 128.8, 127.3, 126.8, 126.3, 126.2, 125.4, 125.1, 124.5, 123.9, 118.3, 117.6, 84.4, 67.0, 52.5, 52.4, 52.3, 45.4, 41.9, 24.8, 19.4; HRMS (ESI-ion trap) m/z: [M + H]+ Calcd for C43H32O8 729.2410, found 729.2473.

5,5’-(9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-3,6-diyldiisophthalic acid (1).

Ester 8 (154 mg, 0.20 mmol) was dissolved in THF (5 mL), MeOH (5 mL) and NaOH(aq) (1 M, 5 mL) and heated at 75 °C for 12 h. The mixture was cooled to rt and water (5 mL) was added. THF and MeOH were removed by rotary evaporation. A brown precipitate was formed upon titration of the mixture with HCl(aq) (1 M) until pH = 1. After filtration, the brown solid was washed with cold water(aq) (10 mL) and dried in vacuo, affording compound 1 as a solid (103 mg, 0.15 mmol, 77%). M.p. 72 – 74 °C; 1H NMR (500 MHz, CD3OD) δ 8.55 (s, 4H, Ar-H), 8.46 (s, 1H, Ar-H), 8.38 (s, 2H, Ar-H), 8.15 (s, 1H, Ar-H), 8.03 (d, J = 8.1 Hz, 1H, Ar-H), 7.90 (d, J = 8.0 Hz, 1H, Ar-H), 7.67 (d, J = 8.0 Hz, 1H, Ar-H), 7.61 (d, J = 8.2 Hz, 1H, Ar-H), 7.56 – 7.52 (m, 1H, Ar-H), 7.39 (t, J = 7.2 Hz, 1H, Ar-H), 7.27 (t, J = 7.4 Hz, 1H, Ar-H), 7.02 (d, J = 8.3 Hz, 1H, Ar-H), 6.66 (d, J = 8.1 Hz, 1H, Ar-H), 4.28 (dd, J = 10.2 Hz, 4.4 Hz, 1H, C-H), 3.51 (d, J = 10.4 Hz, 1H, C-H), 2.74 (d, J = 15.0 Hz, 1H, C-H), 1.31 (d, J = 6.7 Hz, 3H, C-H3); 13C NMR (101 MHz, DMSO-d6) δ 164.4, 151.5, 148.1, 139.7, 139.5, 139.4, 136.7, 136.2, 135.7, 132.7, 132.5, 131.6, 129.5, 129.4, 128.7, 127.7, 127.5, 127.5, 127.1, 126.9, 126.3, 125.8, 125.4, 124.6, 124.3, 122.6, 120.3, 119.8, 53.2, 45.5, 41.9, 19.5; HRMS (ESI-ion trap) m/z: [M]+ Calcd for C43H28O8 672.1874, found 672.1810.
Dimethyl-3,3′-(9-((2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-3,6-diyldibenzoate) (10).

A stirred mixture of 6 (300 mg, 0.60 mmol), Pd(PPh₃)₄ (92 mg, 0.09 mmol), EtOH (1.5 mL), aqueous Na₂CO₃(aq.) (2 m, 3 mL), and toluene (80 mL) was purged with argon for 15 min and then heated to 95 °C. Pinacol ester 9 (438 mg, 1.67 mmol) was added and the resulting mixture was heated at reflux for 16 h under argon atmosphere. The mixture was cooled down to rt and the water layer was removed. The remaining organic layers were dried over MgSO₄ and concentrated in vacuo. Column chromatography (SiO₂, 1:1 pentane: CH₂Cl₂) afforded diester 10 as an orange sticky oil (190 mg, 0.31 mmol, 52%). ¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H, Ar-H), 8.35 (s, 1H, Ar-H), 8.21 (d, J = 1.2 Hz, 1H, Ar-H), 8.14 – 8.04 (m, 3H, Ar-H), 8.02 – 7.93 (m, 4H, Ar-H), 7.84 (dd, J = 14.7, 8.1 Hz, 2H, Ar-H), 7.72 (dd, J = 8.1, 1.5 Hz, 1H, Ar-H), 7.64 – 7.55 (m, 2H, Ar-H), 7.50 (t, J = 7.9 Hz, 2H, Ar-H), 7.38 (t, J = 7.6 Hz, 1H, Ar-H), 7.15 (dd, J = 8.2, 1.6 Hz, 1H, Ar-H), 6.82 (d, J = 8.3 Hz, 1H, Ar-H), 4.39 (dd, J = 12.7, 6.5 Hz, 1H, C-H), 4.00 (s, 3H, CO₂C-H₃), 3.95 (s, 3H, CO₂C-H₃), 3.63 (dd, J = 15.1, 5.5 Hz, 1H, C-H), 2.81 (d, J = 15.1 Hz, 1H, C-H), 1.44 (d, J = 6.7 Hz, 3H, C₃H₃); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 167.1, 152.2, 147.8, 141.5, 141.4, 140.5, 140.0, 139.7, 138.7, 138.5, 137.1, 136.2, 132.7, 131.6, 131.5, 131.2, 130.8, 130.6, 129.8, 129.6, 129.0, 128.8, 128.4, 128.2, 128.1, 127.4, 126.8, 126.3, 126.2, 125.4, 125.1, 124.5, 124.0, 118.4, 117.6, 53.4, 52.3, 52.2, 45.5, 42.0, 19.5; HRMS (ESI-ion trap) m/z: [M + H]⁺ Calcd for C₄₃H₃₂O₄ 613.2365, found 613.2373.

3,3′-(9-((2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-3,6-diyldibenzoic acid (2).

Diester 10 (300 mg, 0.49 mmol), NaOH (196 mg, 4.90 mmol), MeOH (3 mL), and H₂O (1 mL) were heated to 95 °C for 12 h. The resulting mixture was then cooled to 5 °C for 3 h and white precipitates were formed. The precipitates were filtered, washed with cold MeOH (5 mL), and redissolved in water (2 mL). The solution was acidified with HCl(aq.) (2 m) until pH = 1, and the solid was isolated by filtration, washed with cold water (10 mL) and dried in vacuo affording diacid 2 as a brown solid (140 mg, 0.24 mmol, 49%). ¹H NMR (500 MHz, DMSO-d₆) δ 8.65 (s, 1H, Ar-H), 8.57 (s, 1H, Ar-H), 8.45 (s, 1H, Ar-H), 8.30 (s, 1H, Ar-H), 8.17 (d, J = 7.7 Hz, 1H, Ar-H), 8.14 – 8.09 (m, 3H, Ar-H), 8.02 (t, J = 7.9 Hz, 2H, Ar-H), 7.94 (d, J = 7.7 Hz, 1H, Ar-H), 7.85 (d, J = 8.1 Hz, 1H, Ar-H), 7.76 (d, J = 8.2 Hz, 1H, Ar-H), 7.71 – 7.66 (m, 2H, Ar-H), 7.62 – 7.53 (m, 2H, Ar-H), 7.44 (t, J = 7.6 Hz, 1H, Ar-H), 7.23 (d, J = 8.3 Hz, 1H, Ar-H), 6.70 (d, J = 8.3 Hz, 1H, Ar-H), 4.40 – 4.30 (m, 1H, C-H), 3.63 (dd, J = 15.4, 5.3 Hz, 1H, C-H), 3.35 (brs, 3H, CO₂H₂), 2.85 (d, J = 15.5 Hz, 1H, C-H), 1.37 (d, J = 6.6 Hz, 3H, C₃H₃); ¹³C NMR (101 MHz, DMSO-d₆) δ 167.9, 167.8, 152.4, 148.5, 140.9, 140.7, 140.6, 140.4, 139.4, 138.5, 138.4, 136.7, 135.7, 132.8, 132.1, 132.0, 131.9, 131.6, 131.5, 129.7, 129.6, 129.5, 129.3, 128.8, 128.7, 127.9, 127.8, 127.3, 127.0, 126.5, 126.0, 126.0, 124.9, 124.8, 124.7, 119.2, 118.6, 45.5, 41.9, 19.7; HRMS (ESI-ion trap) m/z: [M + H]⁺ Calcd for C₄₁H₂₈O₄ 585.2050, found 585.2060.
Thermal behaviour and kinetic studies of unstable-1 → stable-1 and unstable-2 → stable-2 by UV/vis spectroscopic measurements in solution

The activation parameters of the thermal isomerization of unstable-1 → stable-1 were determined at different temperatures (273, 275.5, 278, and 280.5 K) in MeOH by UV/vis absorption spectroscopy. The thermal isomerization was followed by monitoring the change in absorption at 475 nm as a function of time (Figure S2a). The obtained data can be fitted with a monoexponential decay and the rate constants (k) for the thermal isomerization steps and the Eyring plots were obtained (Figure S2a-2). Using the Eyring equation, it was determined that this isomerization has a Gibbs free energy of activation (Δ‡G°) of 84.5 kJ/mol (unstable-1 → stable-1). This value corresponds to a half-life of 130 s at 293 K.

Using the same procedure, the activation parameters of the thermal isomerization of unstable-2 → stable-2 were determined at different different temperatures (273, 278, 283, 288, and 293 K) in MeOH. The thermal isomerization was followed by monitoring the change in absorption at 475 nm as a function of time (Figure S2b). Using the Eyring equation (Figure S2b-2), it was determined that this isomerization has a Gibbs free energy of activation (Δ‡G°) of 86.0 kJ/mol (unstable-2 → stable-2). This value corresponds to a half-life of 227 s at 293 K.

S2 Thermal decay of UV/vis signal at 475 nm (in the dark) of motor 1 (a) and motor 2 (b) after it reached the PSS upon irradiation at λmax = 365 nm at various temperatures; Eyring plot for thermal isomerization of unstable-1 → stable-1 (a-2) and unstable-2 → stable-2 (b-2).
Perparation of motor functionalized monolayers M1 and M2

Quartz slides (Ted Pella, Inc) were cleaned by immersing in a piranha solution (3/7 ratio of 30% H2O2 in H2SO4) at 90 °C for 1 h and rinsed copiously first with doubly distilled water (3 times), then with MeOH and dried under a stream of N2 before surface modification. (Caution! Piranha solution is highly corrosive and reactive toward organics)

The piranha-cleaned quartz slides were silanized by immersing in a 1 mM solution of 3-aminopropyl(diethoxy)methylsilane in freshly distilled toluene at rt for 12 h, then rinsed copiously with toluene and MeOH, sonicated first in toluene, then in MeOH and dried under a stream of argon.

The amine-coated quartz were immersed in dried CH2Cl2 solution (10 mL) containing 1 or 2 (10⁻⁴ M) at rt for 6-24 h, then the slides were removed, washed with copious CH2Cl2 and dried under a stream of argon.

S3 Thermal decay of UV/vis signals at 475 nm (293 K, in the dark, N2 atmosphere) during thermal isomerization of the motors as a function of time. The thermal decay of the signals were fitted (red line in S3a as equation 1; red line in S3b as equation 2), and hence the half-lives for the rate of thermal isomerization for unstable-MS1 → stable-MS1 (t1/2= 161 s at 293 K) and unstable-MS2 → stable-MS2 (T1= 544 s; T2= 3855 s at 293 K) were extracted.

\[
y = 0.001090 \exp(-x/161.2) - 0.000047 \quad \text{ (equation 1)}
\]

\[
y = 0.000288 \exp(-x/543.9) + 0.000431 \exp(-x/3854.5) + 0.000004 \quad \text{ (equation 2)}
\]

S4 UV/vis absorption spectra of MS1 (a) and MS2 (b) after reaction with amine-coated quartz slides for various amounts of time. The signal increases with reaction time.
$^1$H NMR spectrum of compound 4

$^{13}$C NMR spectrum of compound 4
$^1$H NMR spectrum of compound 6

$^{13}$C NMR spectrum of compound 6
$^1$H NMR spectrum of compound 8

$^{13}$C NMR spectrum of compound 8
$^1$H NMR spectrum of compound 1

$^{13}$C NMR spectrum of compound 1
$^{1}$H NMR spectrum of compound 10

$^{13}$C NMR spectrum of compound 10
$^1$H NMR spectrum of compound 2

$^{13}$C NMR spectrum of compound 2
References