

Supporting Information

Surface-Mounted Altitudinal Molecular Rotors

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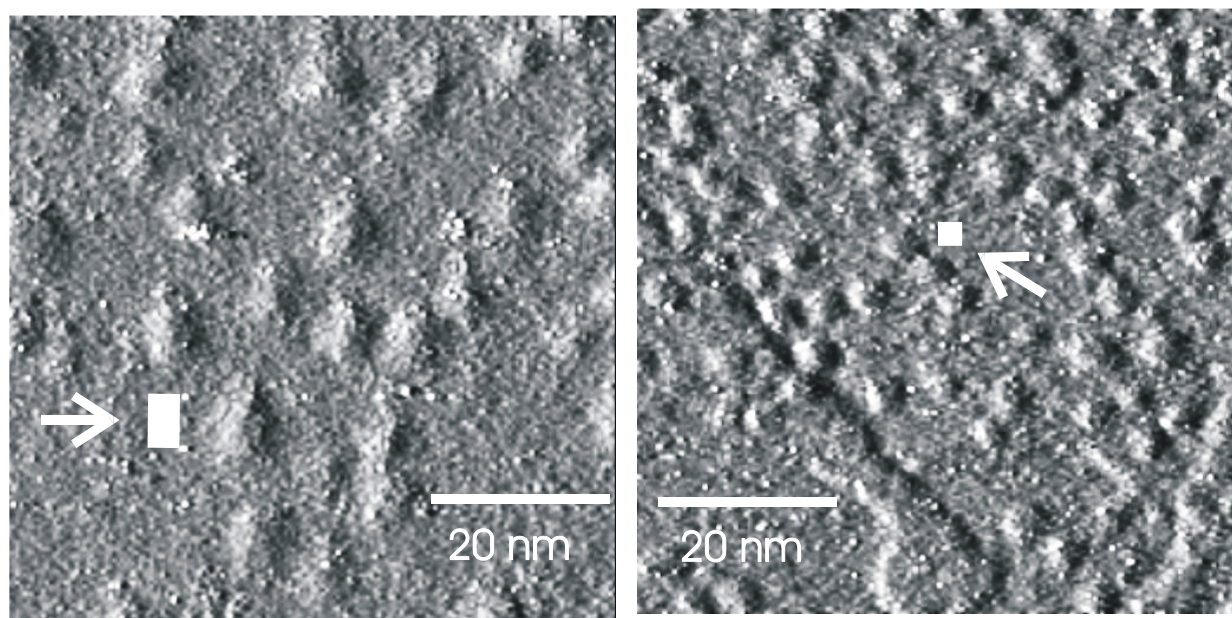
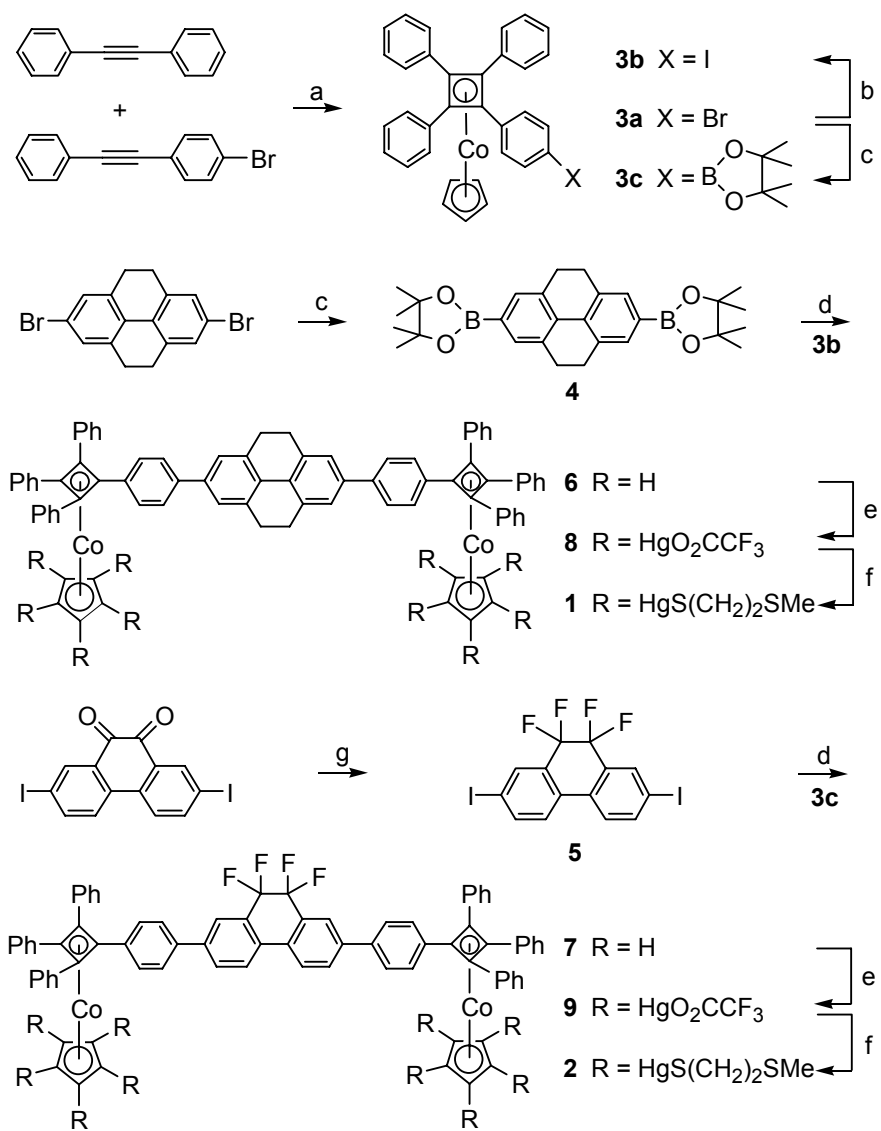


Figure S1. Constant-current (1.5 nA) STM of **2** (left) and **10** (right) on Au(111) imaged in air (shadow mode). The dimensions of the white areas are 2.5 nm \times 5 nm and 2.5 nm \times 2.5 nm, respectively.



Key: a) CpCo(CO)₂; b) *t*-BuLi, I₂; c) bis(pinacolato)diboron, PdCl₂(dppf), KOAc; d) Pd black, KF; e) Hg(O₂CCF₃)₂; f) HS(CH₂)₂SMe; g) F₃SNEt₂.

Scheme S1.

Synthetic Pathway to Altitudinal Molecular Rotors

General Procedures. All reagents were purchased from Aldrich, except for dicarbonylcyclopentadienylcobalt (Strem), and were used as received. Solvents were of analytical grade and were dried by standard methods and freshly distilled before use. 2,7-Dibromo-4,5,9,10-tetrahydropyrene,¹ 2,7-diiodophenanthrenequinone,² 2-methylthioethanethiol,³ and tetraphenylcyclobutadienepentakis(2-methylthioethanethiolmercurio)cyclopentadienylcobalt⁴ were prepared according to established procedures. NMR spectra were acquired with a Varian Unity Inova 500 (¹H, 500.3 MHz; ¹³C, 125.8 MHz) and a Varian Unity Inova 400 (¹H, 400.2 MHz; ¹³C, 100.6 MHz; ¹⁹F, 376.5 MHz) spectrometers. Chemical shifts are reported in ppm and are referenced to the corresponding residual nuclei in deuterated solvents (CDCl₃ unless stated otherwise) for ¹H and ¹³C NMR and to external CFCl₃ for ¹⁹F NMR. Variable-temperature ¹⁹F NMR spectra in THF-*d*₈ were acquired with a Varian Unity Inova 500 spectrometer, keeping the sample for 20 min at each temperature, which was calibrated using methanol.⁵ The activation energy was calculated from the Eyring equation.⁶ IR spectra were recorded with a Nicolet Avatar 320 FT-IR spectrometer. UV-vis spectra were measured with an HP 8452A spectrometer. Mass spectra were recorded with a VG 7070 EQ-HF hybrid tandem mass spectrometer. Melting points were determined with a Laboratory Devices MEL-TEMP II apparatus and are uncorrected.

4-Bromodiphenylacetylene. 1-Bromo-4-iodobenzene (40.0 g, 0.141 mol), PdCl₂(PPh₃)₂ (0.50 mg, 0.71 mmol), CuI (135 mg, 0.71 mmol), NEt₃ (100 mL), and THF (200 mL) were charged to a 500 mL flask. After the system was purged with argon, phenylacetylene (14.4 g, 0.141 mol) was slowly injected into the reaction vessel. The reaction mixture was stirred at rt for 24 h and a large amount of white solid, presumably Et₃NHI, precipitated. All volatile material was removed under vacuum and the residue was dissolved in CH₂Cl₂ (200 mL). The solution was washed with dilute hydrochloric acid (2 M, 200 mL) and then water (2 × 100 mL), and dried over MgSO₄. After the solvent was removed,

the crude brown material was chromatographed on silica gel (CH₂Cl₂). Crystallization of the product from a mixture of CH₂Cl₂ and hexanes (60:40) gave 4-bromodiphenylacetylene (33.8 g, 94%) as white microcrystals. Mp: 83! 84 /C (lit.⁷ 82! 83 /C). ¹H NMR: * 7.35! 7.37 (m, 3 H, Ph), 7.40 (d, *J* = 8.4 Hz, 2 H, Ph), 7.49 (d, *J* = 8.4 Hz, 2 H Ph), 7.52! 7.54 (m, 2 H, Ph). ¹³C NMR: * 88.45, 90.65 (ethynyl), 122.41, 122.63, 123.06, 128.56, 128.57, 131.75, 131.77, 133.18 (Ph).

(4-Bromophenyltriphenylcyclobutadiene)cyclopentadienylcobalt (3a). A mixture of 4-bromodiphenylacetylene (2.57 g, 10.0 mmol), diphenylacetylene (1.78 g, 10.0 mmol), and CpCo(CO)₂ (2.18 g, 12.0 mmol) in xylene (80 mL) was stirred in the dark at 130 /C for 48 h under argon atmosphere. After the solvent and excess CpCo(CO)₂ were evaporated under vacuum, flash chromatography of the residue on silica gel (40:60 CH₂Cl₂/petroleum ether) afforded a mixture of CpCo[C₄Ph₃(4-BrC₆H₄)] (**3a**), CpCo(C₄Ph₄), and cis-/trans-CpCo[C₄Ph₂(4-BrC₆H₄)₂]. The monobromide **3a** (1.40 g, 25%) was separated from the byproducts by repeated chromatography in a long column (20:80 CH₂Cl₂/petroleum ether) as a yellow powder. Mp: 206! 208 /C. ¹H NMR: * 4.64 (s, 5 H, Cp), 7.22! 7.29 (m, 9 H, Ph), 7.33 (m, 4 H, Ph), 7.43! 7.47 (m, 6 H, Ph). ¹³C NMR: * 73.47, 75.02, 75.23 (Cb), 83.40 (Cp), 119.82, 126.42, 126.51, 128.12, 128.18, 128.90, 129.03, 130.35, 131.26, 136.00, 136.20, 136.29 (Ph). IR (KBr): < 3079 (w), 3057 (w), 3027 (w), 1596 (m), 1497 (s), 1444 (m), 1007 (s), 806 (s), 748 (s), 717 (s), 699 (s) cm⁻¹. MS (EI): *m/z* (*I*_{rel}) 560 (100, M⁺), 480 (2, CpCoC₄Ph₄⁺), 302 (50), 241 (12), 178 (25, PhCCPh⁺). Anal. Calcd for C₃₃H₂₄BrCo: C, 70.86; H, 4.32. Found: C, 70.99; H, 4.46.

(4-Iodophenyltriphenylcyclobutadiene)cyclopentadienylcobalt (3b). *t*-BuLi (1.7 M in pentane, 0.32 mL, 0.54 mmol) was added dropwise from a syringe to a solution of **3a** (0.20 g, 0.36 mmol) in absolute ether (10 mL) under argon at -78 /C. The reaction mixture was kept at -40 /C for 60 min to give a red-brown slurry. Freshly sublimed iodine crystals (0.36 g, 1.43 mmol) were added

in one portion. After additional 60 min of stirring at 0 °C, the deep brown reaction mixture was poured into an aqueous solution of sodium sulfite (1 M, 20 mL). The aqueous phase was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic phase was dried over magnesium sulfate and all solvent was evaporated. The crude product was purified by chromatography on silica gel (20:80 CH₂Cl₂/petroleum ether) to give **3b** (178 mg, 82%) as a yellow powder. Mp: 205–206 °C. ¹H NMR: * 4.64 (s, 5 H, Cp), 7.20 (d, *J* = 8.5 Hz, 2 H, Ph), 7.23–7.28 (m, 9 H, Ph), 7.43–7.47 (m, 6 H, Ph), 7.53 (d, *J* = 8.5 Hz, 2 H, Ph). ¹³C NMR: * 73.42, 75.03, 75.29 (Cb), 83.40 (Cp), 91.17, 126.42, 126.51, 128.11, 128.17, 128.88, 129.04, 130.57, 136.18, 126.27, 136.69, 137.18 (Ph). IR (KBr): < 3078 (w), 3047 (w), 3026 (w), 1595 (m), 1497 (s), 1443 (m), 1384 (m), 1005 (s), 825 (s), 811 (s), 753 (s), 717 (s), 697 (s) cm⁻¹. MS (EI): *m/z* (*I*_{rel}) 606 (100, M⁺), 480 (1, CpCoC₄Ph₄⁺), 302 (32), 241 (10), 178 (18, PhCCPh⁺). Anal. Calcd for C₃₃H₂₄CoI: C, 65.36; H, 3.99. Found: C, 65.53; H, 3.96.

[4-(4',4',5',5'-Tetramethyl-1',3',2'-dioxoborolan-2'-yl)phenyl-2,3,4-triphenylcyclobutadiene]cyclopentadienylcobalt (3c). The bromide **3a** (420 mg, 0.75 mmol), bis(pinacolato)diboron (210 mg, 0.83 mmol), PdCl₂(dppf) (31 mg, 0.038 mmol), and potassium acetate (223 mg, 2.25 mmol) were charged to a 25 mL flask under argon. After the solvent DMSO (10 mL) was added, the reaction system was heated to 80 °C and stirring was continued for 24 h. The mixture was cooled to rt and was then poured into water to precipitate a brown solid. The solid was collected on a frit, washed with water (3 × 30 mL), and dried in an oven at 60 °C. The crude product was transferred to a column charged with silica gel. A small amount of impurities was eluted first (40:60 CH₂Cl₂/petroleum ether), followed by an orange band of the main product (80:20 CH₂Cl₂/petroleum ether). The compound **3c** (378 mg, 83%) was further purified by a second column chromatography (80:20 CH₂Cl₂/petroleum ether) as a yellow-brown powder. Mp: 115–118 °C. ¹H NMR: * 1.36 (s, 12 H, Me), 4.61 (s, 5 H, Cp), 7.18–7.26 (m, 8 H, Ph), 7.44–7.46 (m, 9 H, Ph), 7.65 (d, 2 H, *J* = 8.2

Hz, Ph). ^{13}C NMR: * 25.13 (Me), 74.33, 75.23, 75.49 (Cb), 83.49 (Cp), 84.00 (OC), 126.42, 128.13, 128.18, 128.25, 128.32, 129.09, 129.13, 134.45, 136.52, 136.55, 140.28 (Ph); the carbon atom next to the boron atom was not observed. IR (KBr): < 3079 (w), 3058 (w), 3028 (w), 2975 (m), 2927 (w), 1604 (s), 1499 (s), 1397 (s), 1359 (s), 1319 (m), 1144 (s), 1090 (m), 809 (m), 740 (m), 696 (m) cm^{-1} . MS (EI): m/z (I_{rel}) 606 (100, M^+), 480 (4, $\text{CpCoC}_4\text{Ph}_4^+$), 328 (10), 302 (25), 178 (12, PhCCPh^+). Anal. Calcd for $\text{C}_{39}\text{H}_{36}\text{BCoO}_2$: C, 77.24; H, 5.98. Found: C, 77.11; H, 6.09.

2,7-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-4,5,9,10-tetrahydropyrene (4).

2,7-Dibromo-4,5,9,10-tetrahydropyrene¹ (728 mg, 2.0 mmol), bis(pinacolato)diboron (1.12 g, 4.4 mmol), $\text{PdCl}_2(\text{dppf})$ (163 mg, 0.20 mol), and potassium acetate (1.18 g, 12.0 mol) were charged to a 50 mL flask under argon. DMSO (20 mL) was added and the reaction system was heated at 85 $^{\circ}\text{C}$ for 24 h. The mixture was poured into benzene (40 mL) and water (40 mL) and the aqueous phase was extracted with benzene (2×40 mL). The combined organic phase was dried over magnesium sulfate and evaporated to dryness. The solid residue was dissolved in CH_2Cl_2 and chromatographed on silica gel (CH_2Cl_2). Further purification of the product by crystallization from CH_2Cl_2 /hexanes (50:50) gave **4** (440 mg, 48%) as colorless crystals. Mp: 332! 334 $^{\circ}\text{C}$. ^1H NMR: * 1.36 (s, 24 H, Me), 2.88 (s, 8 H, CH_2), 7.54 (s, 4 H, 1,3,6,8-H). ^{13}C NMR: * 25.01 (Me), 28.18 (CH_2), 83.92 (OC), 132.46 (C-1,3,6,8), 133.43 (C-10b,10c), 135.25 (C-3a,5a,8a,10a); the carbon atoms (C-2,7) next to boron atoms were not observed. IR (KBr): < 3043 (w), 3022 (w), 2977 (s), 2936 (m), 2887 (m), 2838 (m), 1610 (s), 1470 (s), 1429 (s), 1374 (s), 1334 (s), 1275 (s), 1218 (s), 1143 (s), 1115 (s), 964 (s), 894 (m), 849 (s), 696 (s) cm^{-1} . MS (EI): m/z (I_{rel}) 458 (100, M^+), 410 (10), 359 (15), 331 (6, $\text{M}^+ - \text{BO}_2\text{C}_2\text{Me}_4$), 258 (12), 204 (8, $\text{C}_{16}\text{H}_{12}^+$). Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{B}_2\text{O}_4$: C, 73.40; H, 7.92. Found: C, 72.98; H, 8.05.

9,9,10,10-Tetrafluoro-9,10-dihydrophenanthrene.⁸ Diethylaminosulfur trifluoride⁹ (DAST,

2.42 g, 15.0 mmol) was added from a syringe to a solution of phenanthrenequinone (1.04 g, 5.0 mmol)

in 1,4-dioxane (40 mL) under argon. After the reaction mixture was stirred at 90 °C for 48 h, it was poured into water (20 mL) and the aqueous phase was extracted with CH₂Cl₂ (4 × 30 mL). The organic phases were combined, dried over magnesium sulfate, and evaporated to dryness. The residue was chromatographed on silica gel (10:90 CH₂Cl₂/petroleum ether). The crude product was further purified by crystallization from CH₂Cl₂/hexanes (20:80) at -30 °C to give 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene (0.59 g, 47%) as colorless plates. Mp: 96–98 °C (lit.⁸ 95–96 °C). ¹H NMR: * 7.47 (t, *J* = 7.6 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.82 (d, *J* = 7.7 Hz, 2 H), 7.86 (s, *J* = 7.7 Hz, 2 H). ¹³C NMR: * 113.64 (tt, ¹*J*_{FC} = 251 Hz, ²*J*_{FC} = 30 Hz, CF₂), 124.59, 125.69 (C-1,8), 127.85 (C-8a,10b), 129.32, 132.56 (C-4a,4b), 132.58. ¹⁹F NMR: * -122.0 (s, CF₂). IR (KBr): < 3081 (w), 1609 (m), 1574 (m), 1486 (m), 1456 (m), 1403 (m, br), 1296 (m), 1260 (s), 1230 (m), 1151 (m), 1089 (s), 1071 (s), 1046 (s), 1006 (s), 956 (m), 924 (s), 766 (s), 730 (s) cm⁻¹. MS (EI): *m/z* (*I*_{rel}) 252 (100, M⁺), 233 (15, M⁺ ! F), 202 (30, M⁺ ! CF₂), 183 (15, M⁺ ! CF₃), 116 (15). HRMS Calcd: 252.0562. Found: 252.0554.

9,9,10,10-Tetrafluoro-2,7-diiodo-9,10-dihydrophenanthrene (5). Diethylaminosulfur trifluoride⁹ (DAST, 484 mg, 3.0 mmol) was added from a syringe to a solution of 2,7-diiodophenanthrenequinone² (460 mg, 1.0 mmol) in 1,4-dioxane (10 mL) under argon. After the reaction mixture was stirred at 90 °C for 48 h, it was poured into water (20 mL) and the aqueous phase was extracted with CH₂Cl₂ (4 × 30 mL). The organic phases were combined, dried over magnesium sulfate, and evaporated to dryness. The residue was chromatographed on silica gel (10:90 CH₂Cl₂/petroleum ether). The crude product was further purified by crystallization from CH₂Cl₂/hexanes (30:70) at -30 °C to give **5** (272 mg, 54%) as colorless plates. Mp: 245–247 °C. ¹H NMR: * 7.53 (d, *J* = 8.3 Hz, 2 H, 4,5-H), 7.94 (d, *J* = 8.3 Hz, 2 H, 3,6-H), 8.12 (s, 2 H, H-1,8). ¹³C NMR: * 94.80 (C-2,7), 112.36 (tt, ¹*J*_{FC} = 250 Hz, ²*J*_{FC} = 28 Hz, CF₂), 125.94 (C-3,6), 129.18

(C8a,10a), 131.22 (C-4a,4b), 134.80 (C-1,8), 141.72 (C-4,5). ^{19}F NMR: δ -122.0 (s, CF_2). IR (KBr): < 3070 (w), 1461 (m), 1412 (m, br), 1263 (s), 1228 (m), 1101 (s), 1067 (s), 1020 (s), 892 (m), 820 (m), 732 (m), 695 (m) cm^{-1} . MS (EI): m/z (I_{rel}) 504 (100, M^+), 485 (2, $\text{M}^+ - \text{F}$), 454 (2, $\text{M}^+ - 2\text{F}$), 377 (6, $\text{M}^+ - \text{I}$), 351 (34), 250 (20, $\text{M}^+ - 2\text{I}$), 200 (15). HRMS Calcd: 503.8495. Found: 503.8497. Anal. Calcd for $\text{C}_{14}\text{H}_6\text{F}_4\text{I}_2$: C, 33.36; H, 1.20. Found: C, 33.74; H, 1.20.

Synthesis of 6 via Suzuki Coupling Reaction. The iodide **3b** (206 mg, 0.34 mmol), the boronic ester **4** (73 mg, 0.16 mmol), palladium black (34 mg, 0.32 mmol), and potassium fluoride (112 mg, 1.92 mmol) were charged to a 25 mL flask. After THF (10 mL) and methanol (10 mL) were added, the reaction mixture was refluxed in the open air for 24 h, during which time, some yellow solid formed. All solvents were evaporated and the residue was separated by gradient chromatography on silica gel with chloroform/petroleum ether (20:80 to 80:20) to give **6** (121 mg, 65%) as a yellow powder. Mp: > 350 $^{\circ}\text{C}$. ^1H NMR: δ 3.01 (s, 8 H, CH_2), 4.66 (s, 10 H, Cp), 7.22! 7.26 (m, 18 H, Ph), 7.39 (s, 4 H, 1,3,6,8-H), 7.46! 7.48 (m, 4 H, Ph), 7.50! 7.54 (m, 16 H, Ph). ^{13}C NMR: δ 28.75 (CH_2), 74.63, 75.13, 75.25 (Cb), 83.45 (Cp), 124.61, 126.38, 126.42, 126.59, 128.15, 128.17, 129.05, 129.18, 129.29, 129.85, 135.79, 136.02, 136.68, 136.69, 138.87, 139.76. IR (KBr): < 3078 (w), 3056 (w), 3026 (w), 2928 (m), 2888 (w), 2831 (w), 1597 (m), 1498 (s), 1457 (m), 1400 (s), 1107 (m), 838 (m), 807 (m), 744 (m), 695 (s) cm^{-1} . MS (LSIMS, 3-NOBA): m/z 1162 (M^+). Anal. Calcd for $\text{C}_{82}\text{H}_{60}\text{Co}_2$: C, 84.67; H, 5.20. Found: C, 84.51; H, 5.46.

Synthesis of 7 via Suzuki Coupling Reaction. The diiodide **5** (101 mg, 0.20 mmol), the boronic ester **3c** (255 mg, 0.42 mmol), palladium black (43 mg, 0.40 mmol), and potassium fluoride (140 mg, 2.4 mmol) were charged to a 50 mL flask. After tetrahydrofuran (15 mL) and methanol (15 mL) were added, the reaction mixture was refluxed in the open air for 4 h and a yellow precipitate developed in the system. The solid was collected on a frit and washed thoroughly with a

CH₂Cl₂/hexanes mixture (40:60, 3 × 20 mL). The crude product was purified by flash chromatography over a short column of silica gel with CH₂Cl₂ to give **7** (215 mg, 89%) as a yellow powder. Mp: 225! 227 /C. ¹H NMR (CD₂Cl₂): * 4.67 (s, 10 H, Cp), 7.21! 7.29 (m, 18 H, Ph), 7.44! 7.46 (m, 4 H, Ph), 7.50! 7.53 (m, 8 H, Ph), 7.56 (m, 8 H, Ph), 7.93 (d, *J* = 8.2 Hz, 2 H, Phen), 8.02 (d, *J* = 8.2 Hz, 2 H, Phen), 8.10 (s, 2 H, Phen). ¹³C NMR (CD₂Cl₂): * 74.42, 75.84, 76.02 (Cb), 83.76 (Cp), 113.50 (t, ¹*J*_{FC} = 250 Hz, CF₂), 124.03, 125.74, 126.79, 126.88, 126.99, 128.52, 128.58, 129.32, 129.56, 129.77, 131.00, 131.21, 136.81, 136.85, 137.08, 137.84, 142.28; two peaks are coincident. ¹⁹F NMR (CD₂Cl₂): * -121.9 (s, CF₂). IR (KBr): < 3079 (w), 3057 (w), 3029 (w), 1598 (s), 1498 (s), 1482 (s), 1401 (s), 1228 (m), 1107 (s), 1078 (s), 1009 (m), 821 (m), 807 (m), 740 (m), 698 (s) cm⁻¹. MS (LSIMS, 3-NOBA): *m/z* 1208 (M⁺). Anal. Calcd for C₈₀H₅₄Co₂F₄: C, 79.47; H, 5.98 Found: C, 79.22; H, 5.86.

Synthesis of 8 via Decamercuration of 6. Mercury(II) trifluoroacetate (252 mg, 0.59 mmol) was added in portions to a suspension of **6** (65.1 mg, 0.056 mmol) in 1,2-dichloroethane (20 mL) under argon. The reaction mixture became a homogeneous red solution in seconds and some yellow solid developed gradually. After the mixture was stirred at rt for 24 h, it was heated at 70 /C for additional 24 h. The solid was collected on a frit, washed with a mixture of CH₂Cl₂ and pentane (50:50, 3 × 20 mL), and dried under high vacuum to afford **8** (192 mg, 80%) as a yellow powder. Mp: 210! 215 /C (dec., change of color). ¹H NMR (DMSO-*d*₆): * 2.92 (s, 8 H, CH₂), 7.20! 7.30 (m, 18 H, Ph), 7.43 (s, 4 H, 1,3,6,8-H), 7.55! 7.57 (m, 4 H, Ph), 7.68! 7.70 (m, 4 H, Ph), 7.77! 7.83 (m, 12 H, Ph). ¹³C NMR (THF-*d*₈): * 29.28 (CH₂), 77.64, 78.11, 78.39 (Cb), 110.68 (Cp), 120.08 (q, ¹*J*_{FC} = 288 Hz, CF₃), 124.00, 128.35, 128.74, 129.97, 130.17, 130.24, 130.26, 130.34, 130.84, 135.55, 136.60, 136.69, 136.81, 139.77, 141.17, 161.14 (q, ²*J*_{FC} = 38 Hz, C=O), two peaks are coincident. ¹⁹F NMR (THF-*d*₈): * -73.0 (s, CF₃). IR (KBr): < 3081 (w), 3060 (w), 3026 (w), 2934 (w), 2826 (w), 1684 (s,

br), 1436 (m), 1419 (m), 1399 (m), 1189 (s, br), 1148 (s, br), 734 (m) cm^{-1} . UV-vis (THF): λ_{max} (ϵ_{max}) 236 (108 000), 360 (90 000) nm. Anal. Calcd for $\text{C}_{102}\text{H}_{50}\text{Co}_2\text{F}_{30}\text{Hg}_{10}\text{O}_{20}$: C, 28.56; H, 1.17. Found: C, 28.68; H, 1.11.

Synthesis of 9 via Decamercuration of 7. Mercury(II) trifluoroacetate (470 mg, 1.10 mmol) was added in portions to a suspension of **7** (121 mg, 0.10 mmol) in 1,2-dichloroethane (30 mL) under argon. The reaction mixture became a homogeneous red solution in seconds and some yellow solid formed gradually. After the mixture was stirred at rt for 24 h, it was heated at 70 $^{\circ}\text{C}$ for additional 24 h. The solid was collected on a frit, washed with a mixture of CH_2Cl_2 and pentane (50:50, 3 \times 40 mL), and dried under high vacuum to give **9** (320 mg, 74%) as a yellow powder. Mp: 215! 220 $^{\circ}\text{C}$ (dec., change of color). ^1H NMR ($\text{DMSO}-d_6$): * 7.19! 7.30 (m, 18 H, Ph), 7.66! 7.70 (m, 8 H, Ph), 7.80! 7.82 (m, 8 H, Ph), 7.85! 7.87 (m, 4 H, Ph), 8.06 (d, $J = 8.3$ Hz, 2 H, Phen), 8.09 (s, 2 H, Phen), 8.31 (d, $J = 8.3$ Hz, 2 H, Phen). ^{13}C NMR ($\text{THF}-d_8$): * 77.08, 78.34, 78.57 (Cb), 110.68 (Cp), 114.55 (t, $^1J_{\text{FC}} = 250$ Hz, CF_2), 120.05 (q, $^1J_{\text{FC}} = 288$ Hz, CF_3), 124.03, 126.53, 128.58, 128.85, 129.32, 129.94, 130.19, 130.27, 130.31, 130.38, 131.18, 132.14, 136.44, 136.60, 137.15, 138.51, 138.97, 141.98, 161.17 (q, $^2J_{\text{FC}} = 38$ Hz, $\text{C}=\text{O}$). ^{19}F NMR ($\text{THF}-d_8$): * -72.7 (s, 30 F, CF_3), -120.6 (s, 4 F, CF_2). IR (KBr): < 3077 (w), 3060 (w), 3026 (w), 1677 (s, br), 1497 (m), 1482 (m), 1437 (m), 1402 (m), 1208 (s, br), 1187 (s, sh), 1141 (s, br), 839 (m), 806 (m), 724 (m), 707 (m) cm^{-1} . UV-vis (THF): λ_{max} (ϵ_{max}) 236 (98 000), 328 (69 000), 360 (79 000) nm. Anal. Calcd for $\text{C}_{100}\text{H}_{44}\text{Co}_2\text{F}_{34}\text{Hg}_{10}\text{O}_{20}$: C, 27.71; H, 1.02. Found: C, 27.78; H, 1.05.

Synthesis of Altitudinal Rotor 1. A solution of 2-methylthioethanethiol³ in THF (1.0 M, 0.22 mL, 0.22 mmol) was injected slowly from a syringe to a mixture of **8** (85.8 mg, 0.020 mmol) and triethylamine (22.3 mg, 0.22 mmol) in THF (2 mL) at 0 $^{\circ}\text{C}$ under argon. An orange powder precipitated almost immediately. After the reaction mixture was stirred for 5 min, anhydrous ether

(5 mL) was added. The solid was collected on a frit and washed with ether (3 × 20 mL). The crude product was dissolved in CH₂Cl₂ solution (5 mL) and reprecipitated with ether (10 mL) to give **1** (78 mg, 92 %) as an orange powder. Mp: 140! 145 /C (dec.). ¹H NMR (DMSO-*d*₆): * 1.96 (s, 30 H, Me), 2.64 (t, br, *J* = 6.1 Hz, 20 H, SCH₂), 2.94 (s, 8 H, CH₂), 3.05 (t, br, *J* = 6.1 Hz, 20 H, SCH₂), 7.18! 7.28 (m, 18 H, Ph), 7.49 (s, 4 H, 1,3,6,8-H), 7.52! 7.54 (m, 4 H, Ph), 7.64! 7.66 (m, 4 H, Ph), 7.70! 7.76 (m, 12 H, Ph). ¹³C NMR (CD₂Cl₂): * 15.43 (Me), 28.36 (SCH₂), 29.10 (CH₂, Phen), 40.27 (SCH₂), 74.230, 75.15, 75.22 (Cb), 124.82, 127.22, 127.33, 127.62, 127.93, 129.25, 129.28, 129.39, 129.62, 129.66, 130.17, 136.44, 137.10, 137.85, 137.92, 139.15, 139.76. IR (KBr): < 3028 (w), 3054 (m), 3023 (w), 2970 (w), 2910 (s), 2828 (m), 1696 (m), 1495 (s), 1425 (s), 1401 (s), 1384 (m, sh), 1258 (m), 1196 (m), 838 (m), 744 (m), 704 (m) cm⁻¹. UV-vis (THF): λ_{\max} (ϵ_{\max}) 230 (198 000), 362 (92 000) nm. Anal. Calcd for C₁₁₂H₁₂₀Co₂Hg₁₀S₂₀: C, 31.79; H, 2.86. Found: C, 31.53; H, 2.94.

Synthesis of Altitudinal Rotor 2. A solution of 2-methylthioethanethiol³ in THF (1.0 M, 0.22 mL, 0.22 mmol) was injected slowly from a syringe to a mixture of **8** (86.7 mg, 0.020 mmol) and triethylamine (22.3 mg, 0.22 mmol) in THF (2 mL) at 0 /C under argon. An orange powder precipitated almost immediately. After the reaction mixture was stirred for 5 min, anhydrous ether (5 mL) was added. The solid was collected on a frit and washed with ether (3 × 20 mL). The crude product was dissolved in CH₂Cl₂ solution (5 mL) and reprecipitated with ether (10 mL) to give **2** (80 mg, 94 %) as an orange powder. Mp: 135! 140 /C (dec.). ¹H NMR (DMSO-*d*₆): * 1.96 (s, 30 H, Me), 2.64 (s, br, 20 H, CH₂), 3.05 (s, br, 20 H, CH₂), 7.18! 7.28 (m, 18 H, Ph), 7.60! 7.63 (m, 8 H, Ph), 7.73! 7.79 (m, 12 H, Ph), 8.10 (d, *J* = 8.2 Hz, 2 H, Phen), 8.20 (s, 2 H, Phen), 8.32 (d, *J* = 8.2 Hz, 2 H, Phen). ¹³C NMR (CD₂Cl₂): * 15.33 (Me), 28.22 (CH₂), 40.22 (CH₂), 73.46, 75.44, 75.72 (Cb), 114.33 (t, ¹*J*_{FC} = 260 Hz, CF₂), 124.23, 125.74, 127.32, 127.48, 127.97, 128.03, 129.21, 129.33, 129.58, 129.89, 129.96, 131.12, 131.24, 137.13, 137.66, 137.91, 138.42, 138.97, 142.29. ¹⁹F NMR

(CD₂Cl₂): * -121.6 (s, CF₂). IR (KBr): < 3074 (w), 3056 (w), 3025 (w), 2974 (w), 2910 (s), 2828 (w), 1596 (m), 1496 (m), 1481 (s), 1401 (s), 1259 (m), 1196 (m), 1100 (m), 1075 (m), 1050 (m), 823 (m), 705 (m) cm⁻¹. UV-vis (THF): δ_{\max} (ϵ_{\max}) 232 (180 000), 319 (73 000), 372 (67 000) nm. Anal. Calcd for C₁₁₀H₁₁₄Co₂F₄Hg₁₀S₂₀: C, 30.89; H, 2.69. Found: C, 31.16; H, 2.52.

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