1. General Methods

Synthetic reactions were conducted under a dry argon atmosphere. Dry solvents were purchased from ACROS Organics and used as received. Diethylether (Et₂O), hexane and ethylacetate were purchased from VWR and destilled prior to use by common laboratory methods. Ethanol (EtOH), dichloromethane (DCM), dimethylformamide (DMF), and acetonitrile (ACN) used for surface experiments were purchased from Carl Roth or VWR in HPLC grade and used as received. Silica gel 60M (0.04-0.063 mm, Macherey-Nagel) was used for column chromatography. Dialysis was performed using cellulose ester tubes (MWCO 1000 and 2000 Da; Spectrumlabs) from Roth. All gold substrates were purchased from Georg Albert PVD and stored under argon prior to use. Gold substrates used for XPS and NEXAFS were prepared onto polished single-crystal Si(100) wafers which have been coated with a 9 nm titanium adhesion layer and 30 nm gold (rms-roughness < 0.5nm). Semi-transparent Au substrates (20 nm) used for transmission-UV/Vis-spectroscopy were prepared on borosilicate glass with a 1 nm titanium adhesion layer . All surface experiments were performed in gamma-sterilized tubes (Orange Scientific).

Multilayers were prepared on pyridine-terminated self-assembled monolayers (PST) as template layer. As metal sources, tetrakis(acetonitrile)palladium(II) tetrafluoroborate and iron(II) tetrafluoroborate hexahydrate were used, respectively. For iron(II) deposition, the samples
were immersed in a 1 mM solution of the metal salt in ethanol for 30 min at r.t. For palladium(II) deposition, the samples were immersed in a 1 mM acetonitrile solution of the metal salt for 10 min at r.t. Deposition of the rotaxane took place by immersing the samples in a 1 mM solution of Rot6 in dichloromethane for 24 h at r.t. For multilayer construction, both steps were alternatingly repeated until the desired layer number was reached. Chloride addition was obtained by immersing the samples in a 1 mM solution of tetrabutyl ammonium chloride in dichloromethane for 2 h at r.t. Removal of the chloride ion was performed by immersing the sample in a 1 mM solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in dichloromethane for 2 h at r.t. After each deposition step, the samples were immersed in the corresponding solvent (ethanol, DMF or dichloromethane) for another 10 min, dried vigorously in a stream of argon and stored under argon before characterization. For deposition of the terpyridine-terminated monolayer consisting of one part 12-(2,2′:6′,2″-terpyridin-4′-yl)dodecane-1-thiol (TDT) and three parts decanethiol (DT) as well as the azide-terminated SAM 1,2-bis(11-azidoundecyl)disulfide (AUD) the gold surfaces were immersed for 24 h in a 1mM ethanol solution of these molecules after cleaning with HCl. The deposition of Rot3 was performed in DCM (1 mM) with 1 mol-% of the Cu(I)-catalyst Cat.

Microcontact printing (µCP) was performed using stamps patterned with dots (diameter = 10 µm; spacing = 5 µm) which were produced from polydimethylsiloxane and the Sylgard 184 curing agent (Dow Corning) by casting them against a silicon master and curing for 16 h at 60 °C. The master was produced photolithographically under clean-room conditions at MESA+. Previous to inking and µCP, the corresponding stamps and surfaces have been rinsed vigorously using MiliQ-water and EtOH for 30 s each. Inking of the PDMS stamps was carried out using a 1 mM solution of octadecanethiol ODT in ethanol for 15 min followed by drying in an argon stream. Transfer of the pattern to the surfaces was done manually by contacting the stamp and the gold substrate for 10 min. Afterwards, the substrates were rinsed with MiliQ-water and EtOH for 30 s each. Backfilling of the spacings between the dots was carried out by immersing the patterned substrates into 1 mM solutions of PST in DMF.

2. Instrumentation and Data Processing

**NMR spectra** were acquired on a Bruker ECX 400 (1H at 400 MHz, 13C at 101.8 MHz), a Joel Eclipse 500 (1H: 500 MHz; 13C: 125.8 MHz) and a Bruker 700 (1H: 700 MHz; 13C: 175 MHz) spectrometer at r.t.

**Exact masses** were measured on either an Agilent 6210 ESI-ToF mass spectrometer or an ESI-FTICR Ionspec QFT-7, Varian Inc. instrument.

**Transmission UV/Vis spectra** were recorded on a Varian Cary 50 UV/Vis spectrophotometer. A spectrum of the underlying SAM was used as background and subtracted from all multilayer spectra.

**XPS measurements** were carried out with an AXIS Ultra DLD electron spectrometer manufactured by Kratos Analytical, UK. XP spectra were recorded using monochromated Al Kα excitation at a pass energy of 40 eV for all detail spectra and 80 eV for the survey spectrum. The source-to-analyser angle was 60°. Emission angles of 0° and 60° with respect to the surface normal were used. The binding energy scales of XP spectra were corrected for charging using an electron binding energy of 83.96 eV for the Au 4f7/2 level of the gold substrate. XP spectra were analyzed with Unifit 2013 fitting software (Unifit Scientific Software GmbH, Leipzig, Germany) and all peak fits were performed with a Lorentzian-Gaussian sum function peak-shape model. The FWHM values in the N 1s and C 1s spectra were constrained to be equal for each component per spectrum. Peak fits and integrated peak areas were obtained after subtraction of Shirley backgrounds (Au 4f7/2, C 1s, F 1s Fe 2p3/2 and Ni 2p3/2). In case of N 1s, this approach was not applicable because that low intensity peak is superimposed by the intense loss
structure of the Au 4d photoemission doublet. The application of a Shirley background requires a higher count rate at the upper binding energy limit of the energy window used for background determination, but in the given case (due to superposition of Au 4d) we have a lower count rate at the upper binding energy limit. As a workaround, a linear background was used in this case. The uncertainty of measurement stays at an acceptable level.

**AFM analysis** was performed using a Multimode Nanoscope V (Bruker, Nanoscope 8.10) in tapping mode under ambient conditions. The data obtained from the patterned substrates was analysed using the open-source Gwyddion software.

**ToF-SIMS imaging** was performed on a reflectron-type ToF-SIMS IV instrument (ION-TOF, Münster, Germany) equipped with a 25 keV bismuth liquid metal ion gun (LMIG) as the primary ion source mounted at 45° with respect to the sample surface. The LMIG was operated at 0.5 μA emission current using the novel „collimated burst alignment“ (CBA) mode optimized to achieve high lateral (< 200 nm) as well as a high mass resolution (R ~ 5000). Bi\(^{3+}\) was selected as the primary ion by appropriate mass filter settings. The scanned surface area for each image was 25 × 25 μm\(^2\) with 256 x 256 pixels. The analysis chamber was operated at a pressure of 10\(^{-9}\) mbar. ToF-SIMS spectra and images were acquired in positive and negative ion mode. The mass scale was internally calibrated to errors < 10 ppm using easily assignable secondary ions (positive mode: C\(_2\)H\(_5\)+, C\(_4\)H\(_3\)+, C\(_6\)H\(_5\)+, C\(_7\)H\(_7\)+, Au\(^+\); negative mode: C\(_3\), C\(_4\), Au\(^-\)).

**Contact angle measurements** were performed with a Dataphysics Contact Angle System OCA. The images were analyzed with the software SCA 20 (Dataphysics, version 3.12.11).

**NEXAFS** spectra were measured at the HESGM CRG dipole magnet beam line at the synchrotron radiation source BESSY II (Berlin, Germany). The spectra were acquired in the partial electron yield (PEY) mode using a channel plate detector with a retarding voltage of -150 V and incident angles of linearly polarized synchrotron light of 30° (electric field vector upright to surface plane) and 90° (electric field vector parallel to the surface plane). The resolution \(E/\Delta E\) of the monochromator at the carbonyl π\(^*\) resonance of CO (\(h\nu = 287.4\) eV) was in the order of 2500. Raw spectra were divided by ring current and monochromator transmission function. The latter was obtained with a fresh surface of highly ordered pyrolytic graphite (HOPG; Advanced Ceramic, Cleveland, USA) at 285.4 eV.
3. Preparation and Characterization of New Compounds

The synthesis of diterpyridine rotaxane Rot6 was realized by a modified literature known synthesis of Rot5 followed by a Suzuki cross-coupling. The precursors were synthesized according to literature-known procedures.7-10

**Synthesis of Rot1.** Macrocycle MC1 (65 mg, 59 µmol) and the 2,5-diketopiperazine station I (34 mg, 178 µmol) were added to 50 mL chloroform. The solution was stirred at 45°C for 2d. Subsequently, the stopper unit (206 mg, 570 µmol), triethylamine (26 mg, 27 µmol) and tris(triphenylphosphine) copper(I) bromide (68.7 mg, 75 µmol) were added. The mixture was then stirred for another 2 d. The mixture was washed with water and the aqueous phase was extracted three times with DCM, the organic phases dried, filtered and the solvent evaporated. Preparative thin layer chromatography on silica with dichloromethane/methanol (96:4) as the eluent and dialysis (24 h, MWCO=1000, DCM/MeOH 3:1) afforded 75 mg (38 µmol) of pure product. Yield: 63%; 1H-NMR (400 MHz, CDCl3): δ = 8.59 (d, J = 1.3 Hz, isophth.-H, 2H), 8.56 (bs, isophth.-H, 1H), 8.45 - 8.42 (m, amide and isophth.-H, 3H), 8.38 (s, amide-H, 2H), 8.30 (d, J = 1.4 Hz, isophth.-H, 2H), 7.58 (s, triazole-H, 2H), 7.33 (d, J = 8.8 Hz, trityl-Ph-H, 4H), 7.30 - 7.17 (m, trityl-Ph-H, 30 H), 7.00 (d, J = 8.8 Hz, trityl-Ph-H, 4H), 6.88 (bs, Ar-H, 8H), 3.56 (s, CH2 (dp-axle), 4H), 3.26 (s, CH2 (dp-axe), 4H), 2.22 (bs, Cy, 8H), 1.98 (s, CH3, 12H), 1.93 (s, CH3, 12H), 1.61 (bs, Cy, 8H) 1.50 (bs, Cy, 4H), 1.42 (s, tBu, 9H) ppm. 13C NMR (176 MHz, CDCl3) δ = 165.4, 163.5, 162.9, 154.0, 149.3, 146.1, 142.2, 140.9, 136.0, 135.4, 134.3, 133.9, 132.5, 131.6, 131.1, 131.1, 131.0, 129.3, 128.0, 126.5, 126.4, 122.2, 120.5, 96.0, 65.0, 53.6, 49.8, 45.4, 39.7, 35.5, 35.2, 31.4, 26.4, 22.9, 18.8, 18.7 ppm. HR-MS (ESI-ToF, pos. mode, DCM/MeOH) m/z calcd. for [C124H119N12O6INa]+: 2021.8313 [M+Na]+; found: 2021.8322; ∆ = 0.4 ppm; calcd. for [C124H120N12O6I]+: 1999.8493 [M+H]+; found: 1999.8485; ∆ = -0.4 ppm.

**Synthesis of Rot2.** Bis(triphenylphosphine)palladium(II) dichloride (0.82 mg, 1.17 µmol) and copper(I) iodide (0.74 mg, 3.9 µmol) were dissolved in 10 mL of dry toluene. After the addition of 5 µL of diisopropyl ethyl amine (DIPEA) and 4 µL of trimethylsilyl acetylene, Rot1 (78 mg, 39 µmol) was added to the mixture. The solution was stirred at room temperature for 24h. Subsequently, the starting materials were added again in the same amount. The mixture was then heated to 40°C for another 24 h. The solvent was evaporated. The resulting solid was dissolved in DCM and washed with water (3 x 50 mL). The crude product was purified via preparative TLC (SiO2, DCM/MeOH 100:1) which afforded 43 mg of a light brown solid. Yield: 55%; 1H NMR (500 MHz, CDCl3): δ = 8.53 (s, para-TMSA-isophth.-H, 1H), 8.45 (s, para-tBu-isophth.-H, 1H), 8.39 (d, amide-H, 4H), 8.33 (s, ortho-TMSA-isophth.-H, 2H), 8.30 (s, ortho-tBu-isophth.-H, 2H), 7.59 (s, triazole-H, 2H), 7.33 (d, J = 8.7 Hz, ortho-triazole-stopper-H, 4H), 7.30 – 7.19 (m, stopper, 30H), 7.01 (d, J = 8.6 Hz, meta-triazole-stopper-H, 4H), 6.88 (s, Ar-H, 8H), 3.57 (s, CH2 (dp-axle), 4H), 3.26 (s, CH2 (dp-axe), 4H), 2.23 (s, Cy, 7H), 1.96 (d, J = 15.0 Hz, CH3, 25H), 1.67 – 1.46 (m, Cy, 18H), 1.42 (s, tBu-H, 9H), 0.25 (s, TMS-H, 10H). 13C NMR (101 MHz, CDCl3) δ = 165.4, 164.2, 153.9, 149.2, 148.6, 146.3, 146.0, 142.1, 135.4, 135.4, 135.2, 134.7, 134.3, 133.9, 132.5, 131.5, 131.2, 131.0, 129.3, 127.9, 127.8, 126.5, 125.8, 123.9, 122.3, 121.9, 120.5, 103.2, 97.3, 64.9, 49.8, 45.4, 39.6, 35.5, 35.1, 31.4, 29.8, 26.4, 22.9, 18.8, 18.7 ppm. HR-MS (ESI-ToF, pos. mode, DCM): m/z calcd. for [C129H128N12O6SiNa]+: 1992.9972 [M+Na]+; found: 1993.0060; ∆ = 4.4 ppm.
Synthesis of Rot3. Rot2\(^{(0.053\text{g}, 0.026 \text{mmol})}\) is dissolved in a 1:1 mixture of MeOH/DCM (5 mL) and KOH\((0.068\text{g}, 9.860 \text{mmol})\) is added. The mixture is stirred overnight and subsequently the solvent is evaporated. The solid is dissolved in DCM and washed with water (deionized, 3 x 20 mL). After purification by preparative TLC, 11 mg of a white solid is obtained. Yield: 23%. \(^{1}H\)-NMR (400 MHz, CDCl\(_3\)): δ = 8.57 (s, para-TMSA-Isophth.-H, 1H), 8.44 (s, amide + para-tBu-isophth.-H, 3H), 8.42 (s, amide-H, 2H), 8.36 (d, \(J = 1.2 \text{ Hz}\), ortho-TMSA-isophth.-H, 2H), 8.30 (d, \(J = 1.2 \text{ Hz}\), ortho-tBu-isophth.-H, 2H), 7.58 (s, triazole-H, 2H), 7.34 (d, \(J = 8.8 \text{ Hz}\), ortho-triazole-stopper-H, 4H), 7.30 – 7.03 (m, Stopper, 30H), 7.01 (d, \(J = 8.8 \text{ Hz}\), meta-triazole-stopper-H, 4H), 6.88 (s, Ar-H, 8H), 3.57 (s, -CH\(_2\)-(dp-axle), 4H), 3.27 (s, CH\(_2\) (dp-axle), 4H), 3.18 (s, CH\(_2\) (dp-axle), 4H) 2.22 (s, Cy, 8H), 1.98 (d, \(J = 10.8 \text{ Hz}\), CH\(_3\), 24H), 1.67 – 1.46 (m, Cy, 12H), 1.42 (s, tBu-H, 9H), 1.25 (s, amine, 1H) ppm. 13C-NMR (101 MHz, CDCl\(_3\)): δ = 165.3, 164.0, 149.2, 146.0, 142.1, 135.37, 134.8, 134.2, 133.8, 132.4, 130.9, 129.3, 127.9, 127.7, 126.4, 124.7, 122.2, 120.5, 81.9, 64.8, 49.7, 39.6, 35.1, 31.3, 26.3, 22.8, 18.7 ppm. HR-MS (ESI-ToF, pos. mode): m/z calcd. for \([\text{C}_{126}\text{H}_{120}\text{N}_{12}\text{O}_{6}\text{Na}]^{+}\): 1920.9385 [M+Na]\(^{+}\); found: 1920.9378; ∆= -0.4 ppm.

Synthesis of Rot4. Together with caesium carbonate (46 mg, 0.144 mmol) and tetrakis(triphenylphosphine)palladium(0) (10 mg, 8.6 µmol), the precursor rotaxane Rot1\((0.195 \text{g}, 0.089 \text{mmol})\) was dissolved in 60 mL of toluene and DMF (1:1). After the mixture was heated to 60°C, 4'-(4-boropinakolatophenyl)-2,2':6',2''-terpyridine 3 (46.27 mg, 0.11 mmol) was added. The solution was stirred for 1d at 60°C. Subsequently, caesium carbonate (46 mg, 0.144 mmol), 4' -(4-boropinakolatophenyl)-2,2':6',2''-terpyridine 3 (46.27 mg, 0.11 mmol), and tetrakis(triphenylphosphine)palladium(0) (10 mg, 8.6 µmol) are added again. The solution was stirred for another 2d at 60 °C and afterwards another batch of caesium carbonate (46 mg, 0.144 mmol), 4' -(4-borpinakolatophenyl)-2,2':6',2''-terpyridine 3 (46.27 mg, 1.15 mmol), and tetrakis(triphenylphosphine)palladium0) (10 mg, 8.6 µmol) was added. After 5 d, the solvent was evaporated under reduced pressure. The crude product was filtered through AlOx with dichloromethane/methanol 9:1 and 5% triethylamine as the eluent. Dialysis (24 h, MWCO 1000 Da, dichloromethane/methanol 2:1) afforded 23 mg (0.0105 mmol) of pure product. Yield: 18%; \(^{1}H\)-NMR (700 MHz, CDCl\(_3\)): δ = 8.80 (s, CH tpy, 2H), 8.75 (d, \(J = 4.6 \text{ Hz}\), CH tpy, 2H), 8.69 (s, CH tpy, 2H), 8.63 (s, CH Ph-MC, 2H), 8.59 (s, CH Ph-MC, 2H), 8.51 (bs, NH, 2H), 8.47 (s, CH Ph-MC, 1H), 8.40 (bs, NH, 2H), 8.31 (s, CH Ph-MC, 1H), 8.03 (d, \(J = 8.3 \text{ Hz}\), CH Ph-tpy, 2H), 7.91 (d, \(J = 8.3 \text{ Hz}\), CH Ph-tpy, 2H), 7.90 – 7.86 (m, CH tpy, 2H), 7.60 (s, CH triazole, 2H), 7.36 (mc, CH tpy, 2H), 7.34 (d, \(J = 8.6 \text{ Hz}\), CH Ph-stopper, 4H), 7.29 – 7.18 (m, CH Ph-stopper, 30 H), 7.02 (d, \(J = 8.6 \text{ Hz}\), CH Ph-stopper, 4H), 6.92 – 6.88 (m, CH Ph-MC, 8H), 3.59 (s, CH\(_2\) dp-axle, 4H), 3.30 (s, CH\(_2\) dp-axle, 4H), 2.24 (s, Cy, 8H), 2.00 (s, CH\(_3\), 12H), 1.99 (s, CH\(_3\), 12H), 1.62 (s, Cy, 8H), 1.52 (s, Cy, 4H), 1.43 (s, tBu-CH\(_3\), 9H) ppm. \(^{13}C\) NMR (176 MHz, CDCl\(_3\)): δ = 165.3, 164.8, 162.8, 156.3, 156.1, 153.8, 149.6, 149.2, 149.1, 146.0, 145.9, 142.1, 136.9, 135.3, 135.2, 134.2, 133.9, 132.7, 132.4, 132.3, 131.5, 131.3, 131.0, 130.9, 130.9, 130.5, 129.2, 128.0, 127.9, 127.9, 127.8, 127.8, 126.5, 126.4, 126.3, 123.9, 122.1, 121.4, 120.4, 119.6, 118.8, 64.9, 49.8, 45.3, 39.6, 35.4, 35.1, 31.3, 26.3, 22.8, 18.7 ppm. HR-MS (ESI-FTICR, pos. mode, DCM/MeOH): m/z calcd. for \([\text{C}_{145}\text{H}_{135}\text{N}_{15}\text{O}_{6}]^{2+}\): 1091.5370 [M+2H]\(^{2+}\); found: 1091.5389; ∆= -1.7 ppm.

Synthesis of Rot5. Macrocycle MC2 \( (250 \text{ mg}, 215 \text{ µmol}) \) and the 2,5-diketopiperazine station 1 \( (103 \text{ mg}, 540 \text{ µmol}) \) were added to 50 mL chloroform. The solution was stirred at 45°C for 2d. Subsequently, the stopper unit 2 \( (600 \text{ mg}, 1.6 \text{ mmol}) \), triethylamine \( (0.1 \text{ mL}, 0.72 \text{ mmol}) \) and tris(triphenylphosphine)copper(I) bromide \( (68.7 \text{ mg}, 75 \text{ µmol}) \) were added. The mixture was then stirred for another 6 d at 60 °C. The
solvent was removed under reduced pressure. Preparative thin layer chromatography on silica with dichloromethane/methanol (96:4) as the eluent and dialysis (24 h, MWCO=1000, DCM/MeOH 1:1) afforded 132 mg (64 µmol) of pure product. Yield: 29%; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 8.59 (s, NH, 4H) 8.56 (s, isoth.-H, 2H), 8.41 (s, isoth.-H, 4H), 7.59 (s, triazole-H, 2H), 7.34 (d, $J = 8.8$ Hz, Ph-H(trityl), 4H), 7.30–7.18 (m, Ph-H(trityl), 30H), 7.00 (d, $J = 8.8$ Hz, Ph-H(trityl), 4H), 6.88 (s, Hunter-Ph-H, 8H), 3.55 (s, CH$_2$ (dp-axle), 4H), 3.28 (s, CH$_2$ (dp-axle), 4H), 2.21 (s, Cy, 8H), 1.94 (s, CH$_3$, 24H), 1.55 (bs, Cy, 12H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 163.4, 162.9, 149.3, 148.8, 146.0, 140.9, 135.9, 135.3, 133.8, 132.5, 131.1, 131.1, 131.0, 127.9, 127.8, 127.7, 126.5, 126.1, 120.5, 96.0, 77.3, 64.9, 45.4, 35.1, 29.8, 22.9, 18.7 ppm. HR-MS (ESI-ToF, pos. mode): m/z calcd. for [C$_{120}$H$_{111}$I$_2$N$_{12}$O$_6$]+: 2070.6865 [M+H]$^+$; found: 2070.6757; $\Delta = -5.2$ ppm.

**Synthesis of Rot6.** The precursor rotaxane Rot5 (100 mg, 0.048 mmol), caesium carbonate (46 mg, 0.144 mmol) and tetrakis(triphenylphosphine)palladium(0) (10 mg, 8.6 µmol), were dissolved in 40 mL toluene and DMF (1:1). After the mixture was heated to 60 °C, 4’-(4-boropinakolatophenyl)-2,2’:6’,2’’-terpyridine 3 (46.27 mg, 0.11 mmol) was added. The solution was stirred for 1d at 60 °C. Subsequently, caesium carbonate (46 mg, 0.144 mmol), 4’-(4-boropinakolatophenyl)-2,2’:6’,2’’-terpyridine 3 (46.27 mg, 0.11 mmol), and tetrakis(triphenylphosphine)palladium(0) (10 mg, 8.6 µmol) were added again. The solution was stirred for another 2d at 60 °C. The solvent was evaporated under reduced pressure. The crude product was filtered through silica with dichloromethane/methanol 9:1 with 5% triethylamine as the eluent. Dialysis (24 h, MWCO 1000 Da, dichloromethane/methanol 2:1) afforded 42 mg (0.017 mmol) of pure product. Yield: 35%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.80 (s, tPy-H, 4H), 8.75 (d, $J = 4.5$ Hz, tPy-H, 4H), 8.69 (d, $J = 7.9$ Hz, tPy-H, 8H), 8.60 (s, amide-H, 4H), 8.54 (s, isoth.-H, 6H), 8.04 (d, $J = 8.2$ Hz, tPy-H, 4H), 7.97–7.83 (m, Ar-H, 8H), 7.64 (s, triazole-H, 2H), 7.40–7.32 (m, Ph-H (trityl) + Ph-H (tPy-Ph-isophth.), 38H), 7.04 (d, $J = 8.6$ Hz, Ph-H (trityl), 4H), 6.93 (s, Ar-H, 8H), 3.63 (s, CH$_2$ (dp-axle), 4H), 3.33 (s, CH$_2$ (dp-axle), 4H), 2.26 (s, Cy, 8H), 2.03 (s, CH$_3$, 24 H), 1.58 (bs, Cy, 12H) ppm. $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ = 164.8, 162.9, 156.3, 156.1, 149.2, 146.0, 142.1, 139.9, 138.3, 136.9, 135.3, 135.2, 132.4, 131.3, 130.9, 127.9, 126.4, 123.9, 121.4, 120.4, 118.8, 64.9, 49.8, 45.3, 39.6, 35.1, 26.3, 22.9, 18.7. HR-MS (ESI-FTICR, pos. mode, DCM/MeOH): m/z calcd. for [C$_{162}$H$_{140}$N$_{18}$O$_6$]$:^2+$: 2070.6862 [M+2H]$^2+$; found: 2070.6762; $\Delta = -4.8$ ppm.
4. Original NMR and Mass Spectra of New Compounds

Fig. S1: $^1$H NMR spectrum of Rot1.

Fig. S2: $^{13}$C NMR spectrum of Rot1.
Fig. S3: $^1$H NMR spectrum of Rot2.

Fig. S4: $^{13}$C NMR spectrum of Rot2.
Fig. S5: $^1$H NMR spectrum of Rot3.

Fig. S6: $^{13}$C NMR spectrum of Rot3.
Fig. S7: ESI-ToF spectrum of Rot3: isotope patterns for [M+Na]$^+$ (m/z 1920) and [M+K]$^+$ (m/z 1936).

Fig. S8: ESI-FTICR mass spectrum of Rot$_4$Fe: isotope pattern for [Rot$_4$Fe]$^{2+}$. 
Fig. S9: $^1$H NMR spectrum of Rot5.

Fig. S10: $^{13}$C NMR spectrum of Rot5.
Fig. S11: $^1$H NMR spectrum of Rot6.

Fig. S12: $^{13}$C NMR spectrum of Rot6.
Fig. S13: ESI-FTICR mass spectrum of Rot6: isotope pattern of [M+2H]^{2+} (m/z 1217).
Fig. S14: Chloride-induced switching of Rot5. Rot5 exhibits very similar switching-induced signal shifts as those described in the main text for Rot6.
Fig. S15: Temperature-dependent H-NMR spectra of the chloride-induced switching of Rot5. Temperature-dependent H NMR has been used to determine the exchange rate between the two triazol-stations upon switching after chloride addition, it has been shown that the shuttling process as well as the rotation of the axle are both fast processes at least on the NMR timescale, as we could not reach the coalescence temperature of both processes at 223 K (which is the lowest temperature, we can get with our instrument) the rates could not be determined.
Fig. S16: SR-XP survey spectrum of AUD-Rot3 (top) and AUD (bottom) (excitation energy: 700 eV). One can easily see that the C 1s as well as the O 1s signal increase after click-reaction. The C 1s increase is clearly due to the deposition of the rotaxane. In contrast, the increase of the O 1s signal is rather surprising. One reasonable explanation is the following: Not all azides are used to click Rot3 to the AUD surface as the size of the rotaxane is certainly significantly larger than that of an azidoalkylthiol. Consequently, some azides should be left. According to the XPS data, this is however not the case and we conclude that remaining azides decomposed by nitrogen loss. According to earlier data,¹¹ this decomposition process leads to the formation of imines by 1,2-H shifts within the nitrene intermediate. In the presence of traces of water, imines are prone to hydrolysis yielding aldehydes thus rationalizing the increased signal for oxygen in the XPS spectra.
Fig. S17: SR-XP C 1s spectrum of AUD-Rot3 (top) and AUD (bottom) (excitation energy: 350 eV). The spectrum at the top exhibits the expected signals for amide (~288 eV), nitrogen-bound (~287 eV), aliphatic (~285 eV), as well as aromatic carbon (284.5 eV). The spectrum at the bottom exhibits two peaks for nitrogen-bound (~287 eV) and aliphatic (~285 eV) carbon.12

Fig. S18: N K-edge NEXAFS spectra of AUD-Rot3 (top) and AUD (bottom). The two spectra agree well with experimental data as well as theoretical simulations previously obtained for other azide-terminated surfaces before and after click reactions.13
Fig. S19: SR-XP Survey spectrum of the PST-PdRot₆ monolayer (excitation energy: 700 eV).

Fig. S20: SR-XP C 1s core-level spectrum of the PST-PdRot₆ monolayer (excitation energy: 350 eV). Three signals are present representing aromatic (284.5 eV), aliphatic (285 eV) and nitrogen-bound carbon (286.5 eV).¹²
Fig. S21: SR-XP N 1s core-level spectrum of the PST-PdRot6 monolayer (excitation energy: 500 eV). The signals represent triazole (401.5 eV), a superposition of the second triazole N with complexed terpyridine N atoms (400.8 eV), and the third triazole N superimposed with the uncomplexed terpyridine and amide N atoms (399.5 eV).\textsuperscript{12}

Fig. S22: SR-XP Survey spectrum of PST-PdRot6-(FeRot6)\textsubscript{2} (excitation energy: 700 eV).
Fig. S23: SR-XP C 1s core level spectrum of PST-PdRot6-(FeRot6)$_2$ (excitation energy: 350 eV).

Fig. S24: SR-XP N 1s core level spectrum of PST-PdRot6-(FeRot6)$_2$ (excitation energy: 500 eV). The signals represent triazole (401.5 eV), a superposition of the second triazole N atom with complexed terpyridine N (400.8 eV), and the third triazole with uncomplexed terpyridine and amide nitrogen atoms (399.5 eV).
Fig. S25: Transmission UV/Vis spectra of Rot6 multilayers on a TDT/DT (1:3) surface. Layer growth is observed. The dotted spectrum is the solution spectrum of control complex (Rot4)2Fe(II) used for comparison.

Fig. S26: XP Fe 2p core-level spectra of TDT/DT (1/3)-(Fe-Rot6) multilayer and the normalized peak areas (excitation energy: Al Kα emission). Alternating, but overall growing signals for iron show the subsequent deposition of Rot6 and Fe(II) layers. When Fe(II) is deposited, the signal increases, when the next macrocycle is added, inelastic scattering of photoelectrons originating from the Fe(II) ions attenuates the signal.
Fig. S27: XPS C/Au ratios determined after each Rot6 and Fe(II) deposition on TDT/DT (1:3) (excitation energy: Al Kα emission).

Fig. S28: XP N 1s core-level spectra of TDT/DT (1/3)-(Fe-Rot6)2 (bottom) and TDT/DT (1/3)-(Fe-Rot6)2Fe (top) (excitation energy: Al Kα emission). The signals represent triazole (402 eV), a superposition of the second triazole with complexed terpyridine N (400.8 eV), and the third triazole with non-complexed terpyridine and amide (399.8 eV).12
Fig. S29: Tapping-mode AFM pictures of (a) a blank gold surface and patterned surfaces after the subsequent deposition steps: (b) ODT stamped, (c) backfilled with PST, (d) after deposition of one and (e) two layers Fe(II)-Rot6 on the PST template layer.

Fig. S30: Height distribution of the blank gold surface as obtained from AFM experiments.

Fig. S31: Height distribution of the ODT dots (left) and the free spaces (right) in between them as obtained from AFM experiments. Clearly, material has been deposited within the dots, while the spaces in between are not covered by ODT.
Fig. S32: Height distribution of the ODT dots (left) and the PST-backfilled spaces (right) in between them as obtained from AFM experiments. Both heights are similar with the PST molecules being somewhat shorter than ODT. The height of the dots is therefore slightly higher than that of the PST-filled voids.

Fig. S33: Height distribution of the ODT dots (left) and the spaces with one Fe-Rot6 layer (right) in between them as obtained from AFM experiments. The additional rotaxane layer causes the spaces between the dots to be higher now than the ODT-covered dots by ca. 1.6 nm.

Fig. S34: Height distribution of a blank gold surface treated with a 1 mM solution of Rot6 without underlying template layer as a control.
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