Electronic Supplementary Information

Proton transfer network with luminescence display controls OFF/ON catalysis that generates a high-speed slider-on-deck

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‡ Sohom Kundu and Isa Valiyev contributed equally.

1. Synthesis

1.1 General information

All reagents were received from commercial suppliers and used without further purifications. Technical grade solvents were distilled prior to use. Bruker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian (600 MHz) spectrometers were used to record ^{1}H-, ^{13}C-, ^{1}H-^{1}H-COSY spectra at 298 K employing the deuterated solvent as the lock. The chemical shifts are referenced to the residual protiated fraction of the solvent ($CHDCl_2$: δ_H = 5.32 ppm, δ_C = 53.8 ppm; CHD_2CN: δ_H = 1.94 ppm). Abbreviations were used in ^{1}H NMR assignments to describe splitting patterns (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublets of doublets, brs: broad singlet, td: triplet of doublets, tt: triplet of triplets, m: multiplet), the value of coupling constant(s) is reported in Hertz (Hz) and the number of protons is implied. The carbon atoms numbering is typically not in accordance with IUPAC nomenclature guidelines. Compounds **1**,[1] **2**,[2] **3**,[3] were synthesized according to known protocols, sometimes using slightly modified procedures. Column chromatography was performed on silica gel 60 (60−230 mesh). Thin Layer Chromatography (TLC) was performed on Merck silica gel (60 F254) sheets. The spectral data of these compounds were in full agreement with those in the literature. Melting points were measured on a Büchi SMP-20 and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum-Two FT-IR spectrometer. UV-vis spectra were measured on a Cary Win 50. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer.

1.2 Ligands

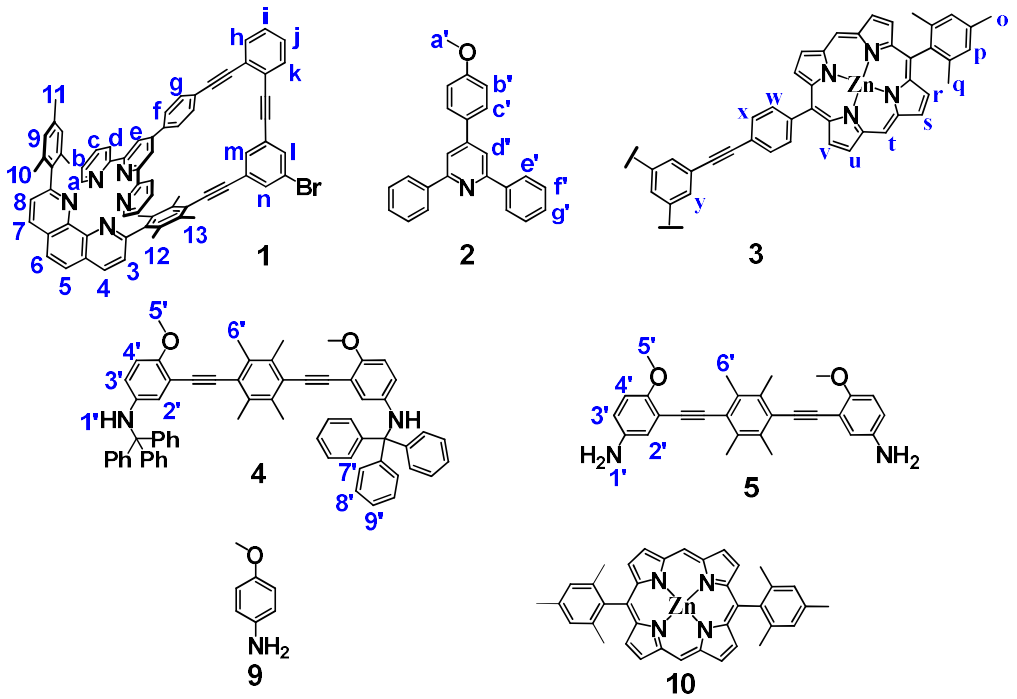
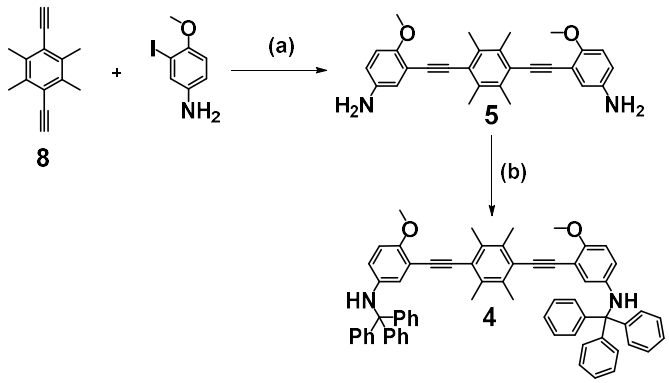


Chart 1. Structure of ligands **1-10**.

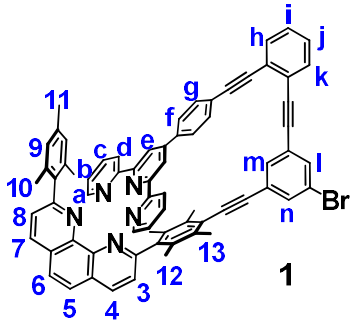
1.3 Synthesis scheme of ligands 4 & 5



Scheme 1. Synthesis of **4** & **5**. Reagents and conditions: (a) $Pd(PPh_3)_4$, Et_3N, 60 °C, 12 h, 74% ; (b) Triphenylmethyl chloride, Et_3N, rt, DCM, 82%.

1.4 Synthesis and characterization of ligands

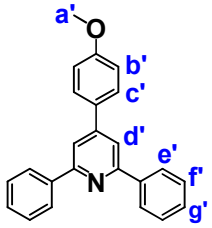
Characterization data of the known ligand **1**[1]



1

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.79 (s, 6H, 13-H), 2.01 (s, 6H, 10-H), 2.30 (s, 3H, 11-H), 2.44 (s, 6H, 12-H), 6.92 (s, 2H, 9-H), 7.33 (ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.39-7.42 (m, 2H, [i+j]-H), 7.43 (d, ^3J = 8.2 Hz, 1H, 8/3-H), 7.55 (d, ^3J = 8.2 Hz, ^{1}H, 3/8-H), 7.61-7.65 (m, 2H, [h+k]-H), 7.71-7.74 (m, 3H, [l+m+n]-H), 7.78 (d, ^3J = 8.6 Hz, 2H, f/g-H), 7.86 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2H, c-H), 7.90 (s, 2H, [5+6]-H), 7.96 (d, ^{3}J = 8.6 Hz, 2H, g/f-H), 8.29 (d, ^3J = 8.2 Hz, 1H, 7/4-H), 8.33 (d, ^3J = 8.2 Hz, 1H, 4/7-H), 8.65-8.69 (m, 4H, [a+d]-H), 8.77 (s, 2H, e-H) ppm.

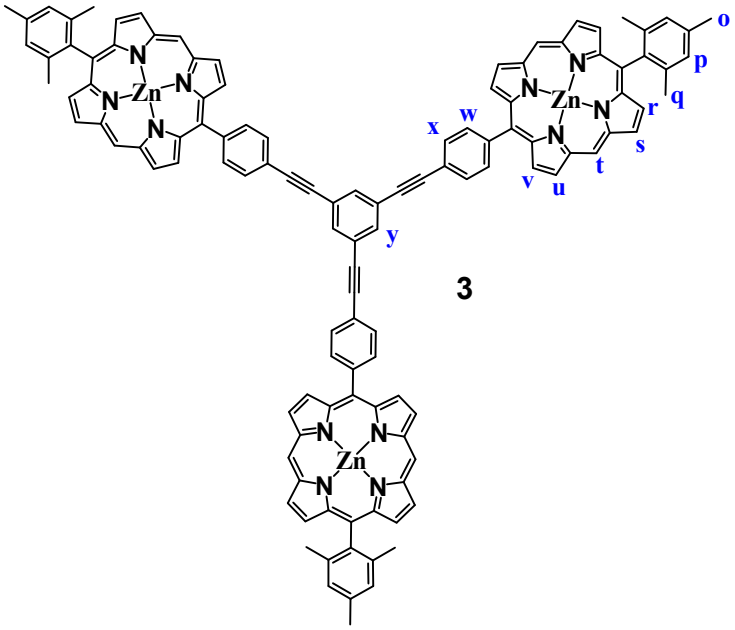
Characterization data of the known ligand **2**[2]



2

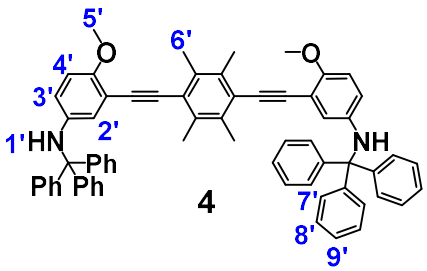
^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 3.89 (s, 3H, a'-H), 7.07 (d, ^3J = 8.5 Hz, 2H, c'-H), 7.43 – 7.56 (m, 6H, f'-, g'-H), 7.76 (d, ^3J = 8.5 Hz, 2H, b'-H), 7.92 (s, 2H, d'-H), 8.21 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 4H, e'-H) ppm. **UV-vis** (CH_2Cl_2): λ_{max} = 260 nm (ε = 5.18 × 10^4 M^{-1} cm^{-1}).

Characterization data of the known ligand **3**[3]



^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.84 (s, 18H, q-H), 2.67 (s, 9H, o-H), 7.34 (s, 6H, p-H), 8.14 (d, ^3J = 8.0 Hz, 6H, x-H), 8.15 (s, 3H, y-H), 8.39 (d, ^3J = 8.0 Hz, 6H, w-H), 8.99 (d, ^3J = 4.5 Hz, 6H, r-H), 9.22 (d, ^3J = 4.5 Hz, 6H, v-H), 9.46 (d, ^3J = 4.5 Hz, 6H, s-H), 9.53 (d, ^3J = 4.5 Hz, 6H, u-H), 10.36 (s, 6H, t-H) ppm.

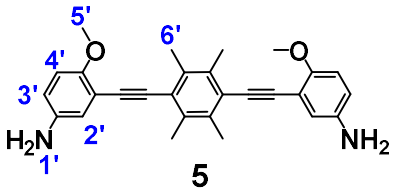
Synthesis and characterization data of ligand **4**



In a one necked round bottomed flask, ligand **5** (100 mg, 236 µmol) was dissolved in mixture of 15 mL of DCM and 15 mL of TEA. After 5 min of stirring chlorotriphenylmethane (262 mg, 943

μmol) was added into the solution and kept for stirring at rt for 24 h. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, EtOAc/DCM = 1:5, R_f = 0.5) providing 172 mg of **4** as brownish yellow solid (189 μmol, 80%). **MP:** > 250 °C. **IR** (KBr): 3943, 3755, 3690, 3598, 3053, 2986, 2832, 2685, 2521, 2410, 2343, 2305, 2125, 2054, 1605, 1550, 1491, 1421, 1275, 1266, 1253, 1155, 1029, 986, 895, 766, 739, 690 cm^{-1}. **^{1}H-NMR** (500 MHz, CD_2Cl_2): δ = 2.39 (s, 12H, 6′-H), 3.73 (s, 6H, 5′-H), 4.88 (brs, 2H, 1′-H), 6.31 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 2H, 3′-H), 6.51 (d, ^3J = 8.4 Hz, 2H, 4′-H), 6.60 (d, ^4J = 1.4 Hz, 2H, 2′-H), 7.23 (tt, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 6H, 9′-H), 7.27-7.32 (m, 12H, 7′-H), 7.39-7.42 (m, 12H, 8′-H) ppm. **^{13}C-NMR** (125 MHz, CD_2Cl_2): δ = 18.3, 56.6, 71.9, 92.3, 95.3, 111.7, 113.0, 117.8, 121.0, 123.7, 127.2, 128.3, 129.5, 135.8, 140.4, 145.8, 152.9 ppm. **Elemental analysis:** Calcd. for $C_{66}H_{56}N_2O_2$•0.5H_2O•0.5CH_2Cl_2 C, 83.06; H, 5.97; N, 2.91. Found: C, 83.17; H, 5.83; N, 2.92. Due to facile deprotection of trityl functional group during gas phase ionization preventing mass determination.

Synthesis and characterization data of ligand **5**



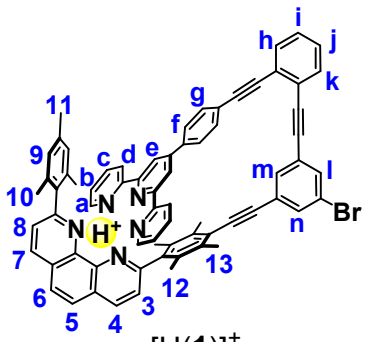
5

Under nitrogen atmosphere, 1,4-diethynyl-2,3,5,6-tetramethylbenzene (**8**)[3] (114 mg, 628 μmol) and 3-iodo-4-methoxyaniline (468 mg, 1.88 mmol) were dissolved in 15 mL of THF and 15 mL of diisopropylamine. Subsequently, the solution was deaerated by bubbling nitrogen through the solution for 15 min. Then the solution was charged with $Pd(PPh_3)_4$ (36.0 mg, 31.3 μmol) and heated at 55 °C for 24 h. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, EtOAc/DCM = 1:6, R_f = 0.3) providing 186 mg of **5** as brownish yellow solid (439 μmol, 70%). **MP:** > 200-202 °C. **IR** (KBr): 3944, 3757, 3689, 3447, 3054, 2987, 2685, 2521, 2410, 2305, 2126, 1606, 1551, 1501, 1421, 1264, 1156, 896, 747, 705 cm^{-1}. **^{1}H-NMR** (500 MHz, CD_2Cl_2): δ = 2.51 (s, 12H, 6′-H), 3.51 (brs, 4H, 1′-H), 3.84 (s, 6H, 5′-H), 6.67 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 2H, 3′-H), 6.78 (d, ^3J = 8.4 Hz, 2H, 4′-H),

6.86 (d, ^{4}J = 1.4 Hz, 2H, 2′-H) ppm. **^{13}C-NMR** (125 MHz, CD_2Cl_2): δ = 18.4, 56.8, 92.7, 95.1, 112.9, 113.9, 116.8, 119.5, 123.8, 135.9, 140.6, 153.8 ppm. **ESI-MS:** m/z (%) = 425.3 (100) [(**5**+H)]$^{+}$. **Elemental analysis:** Calcd. for $C_{28}H_{28}N_2O_2$•0.5H_2O C, 77.57; H, 6.74; N, 6.46. Found: C, 77.92; H, 6.40; N, 6.71.

1.5 Synthesis and characterization of complexes

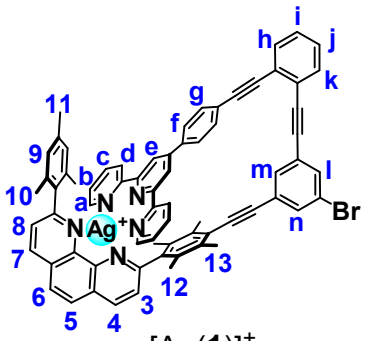
Characterization data of the known complex[1] [H(**1**)]$^{+}$



[H(**1**)]$^{+}$

^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 1.26 (s, 6H, 13-H) 1.87 (s, 6H, 10-H), 1.89 (s, 6H, 12-H), 2.13 (s, 3H, 11-H), 6.60 (s, 2H, 9-H), 7.23 (dd, ^{3}J = 8.0 Hz, ^{3}J = 4.8 Hz, 2H, b-H), 7.41 (d, ^{3}J = 8.2 Hz, 1H, 8/3-H), 7.42-7.44 (m, 2H, [i+j]-H), 7.56 (t, ^{4}J =1.4 Hz, 1H, l-H), 7.59-7.64 (m, 4H, [h+k+c]-H), 7.68 (t, ^{4}J =1.4 Hz, 1H, n/m-H), 7.74 (t, ^{4}J =1.4 Hz, 1H, m/n-H), 7.79 (d, ^{3}J = 8.2 Hz, 1H, 3/8-H), 7.87 (d, ^{3}J = 8.4 Hz, 2H, g-H), 7.92 (d, ^{3}J = 8.0 Hz, 2H, d-H), 8.06 (d, ^{3}J = 8.4 Hz, 2H, f-H), 8.10 (d, ^{3}J = 8.4 Hz, 2H, 6/5-H), 8.22 (d, ^{3}J = 8.4 Hz, 1H, 5/6-H), 8.43 (d, ^{3}J = 8.2 Hz, 1H, 7/4-H), 8.48 (br, 2H, e-H), 8.60 (dd, ^{3}J = 4.8 Hz, ^{4}J = 1.2 Hz, 2H, a-H), 8.69 (d, ^{3}J = 8.2 Hz, 1H, 4/7-H) ppm.

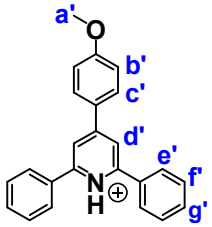
Characterization data of the known complex[1] $[Ag(\mathbf{1})]^+$



$[Ag(\mathbf{1})]^+$

^{1}H-NMR (500 MHz, CD_2Cl_2:CD_3CN (15:1)): δ= 1.38 (s, 6H, 13-H), 1.77 (s, 6H, 12-H), 1.86 (s, 6H, 10-H), 1.91 (s, 3H, 11-H), 6.55 (s, 2H, 9-H), 7.11 (t, ^4J = 1.6 Hz, 1H, l-H), 7.22 (ddd, ^3J = 7.8, 4.8 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.42-7.44 (m, 2H, [i+j]-H), 7.57-7.63 (m, 4H, [h+k+n/m+8/3]-H), 7.69 (t, ^4J = 1.6 Hz, 1H, m/n-H), 7.80 (dd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 2H, a-H), 7.84 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, c-H), 7.86 (d, ^3J = 8.2 Hz, 2H, g/f-H), 7.92 (d, ^3J = 8.4 Hz, 1H, 3/8-H), 7.98 (d, ^3J = 8.2 Hz, 2H, f/g-H), 8.06 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, d-H), 8.16 (d, ^3J = 9.0 Hz, 1H, 6/5-H), 8.21 (d, ^3J = 9.0 Hz, 1H, 5/6-H), 8.23 (s, 2H, e-H), 8.54 (d, ^3J = 8.4 Hz, 1H, 7/4-H), 8.71 (d, ^3J = 8.4 Hz, 1H, 4/7-H) ppm.

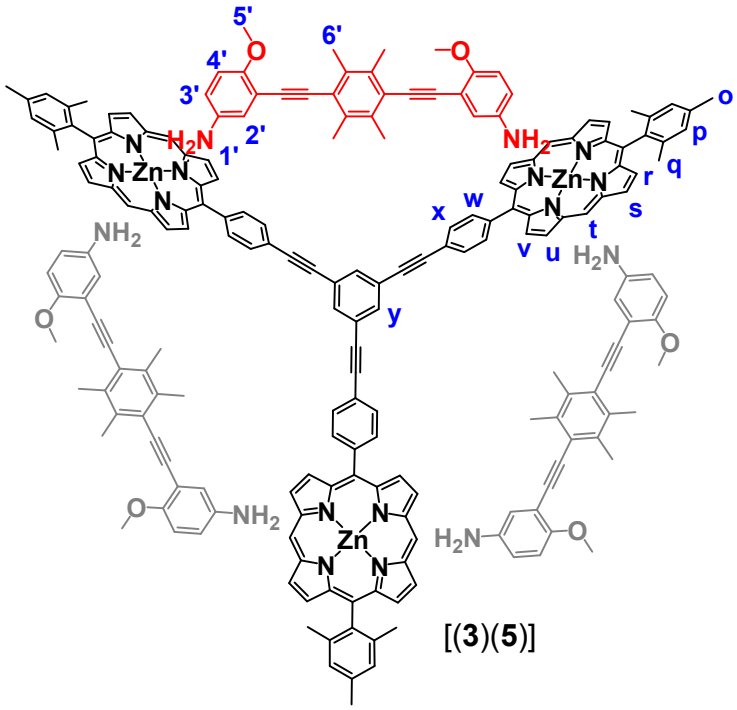
Characterization data of the known complex[4] $[H(\mathbf{2})]^+$



$[H(\mathbf{2})]^+$

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 3.91 (s, 3H, a'-H), 7.12 (d, ^3J = 8.5 Hz, 2H, c'-H), 7.56 – 7.62 (m, 6H, f'-, g'-H), 7.84 (d, ^3J = 8.5 Hz, 2H, b'-H), 8.00 (s, 2H, d'-H), 8.01-8.04 (m, 4H, e'-H) ppm. **UV-vis** (CH_2Cl_2): λ_{max} = 335 nm ($\varepsilon = 5.18 \times 10^4$ M^{-1} cm^{-1}).

Synthesis and characterization of complex [(**3**)(**5**)]



Ligand **3** (850 µg, 450 nmol) was dissolved in 500 µL of CD_2Cl_2 into an NMR tube and ligand **5** (191 µg, 450 nmol) was added into the solution and subsequently the NMR was recorded. **Yield**: Quantitative. **MP:** > 250 °C. **^{1}H-NMR** (500 MHz, CD_2Cl_2): δ = 1.84 (s, 18H, q-H), 2.59 (s, 12H, 6'-H), 2.68 (s, 9H, o-H), 3.65 (brs, 2H, 2'-H), 3.67 (s, 6H, 5'-H), 4.00 (brs, 2H, 3'-H), 5.84 (d, 2H, 4'-H), 7.36 (s, 6H, p-H), 8.10 (d, ^3J = 8.0 Hz, 6H, x-H), 8.12 (s, 3H, y-H), 8.32 (d, ^3J = 8.0 Hz, 6H, w-H), 8.96 (d, ^3J = 4.5 Hz, 6H, r-H), 9.15 (d, ^3J = 4.5 Hz, 6H, v-H), 9.43 (d, ^3J = 4.5 Hz, 6H, s-H), 9.47 (d, ^3J = 4.5 Hz, 6H, u-H), 10.29 (s, 6H, t-H) ppm. **Elemental analysis:** Calcd. for $C_{145}H_{106}N_{14}O_2Zn_3$•$2H_2O$ C, 75.44; H, 4.80; N, 8.49. Found: C, 75.04; H, 4.46; N, 8.19. Due to facile dissociation during gas phase ionization preventing mass determination, [(**3**)(**5**)] was characterized by DOSY measurements.

1.6 Synthesis of NetStates

Synthesis of NetState-I ($[H(\mathbf{1})]^+ + \mathbf{2}$)

In an NMR tube, ligand **1** (950 µg, 913 nmol) and ligand **2** (308 µg, 913 nmol) were dissolved in 500 µL of CD_2Cl_2, then TFA (104 µg, 913 nmol) in CD_2Cl_2 (10.0 µL) was added. After 1 min of mixing the ^{1}H-NMR was recorded. **Yield**: Quantitative

Synthesis of NetState-II ($[Ag(\mathbf{1})]^+ + [H(\mathbf{2})]^+$)

In an NMR tube, ligand **1** (950 µg, 913 nmol) and ligand **2** (308 µg, 913 nmol) were dissolved in 500 µL of CD_2Cl_2, then TFA (104 µg, 913 nmol) in CD_2Cl_2 (10.0 µL) was added. After 1 min of mixing $AgBF_4$ (178 µg, 913 nmol) in CD_3CN (15.0 µL) was added and subsequently the ^{1}H-NMR was recorded. **Yield**: Quantitative.

2. NMR spectra: ^{1}H, ^{1}H-^{1}H COSY

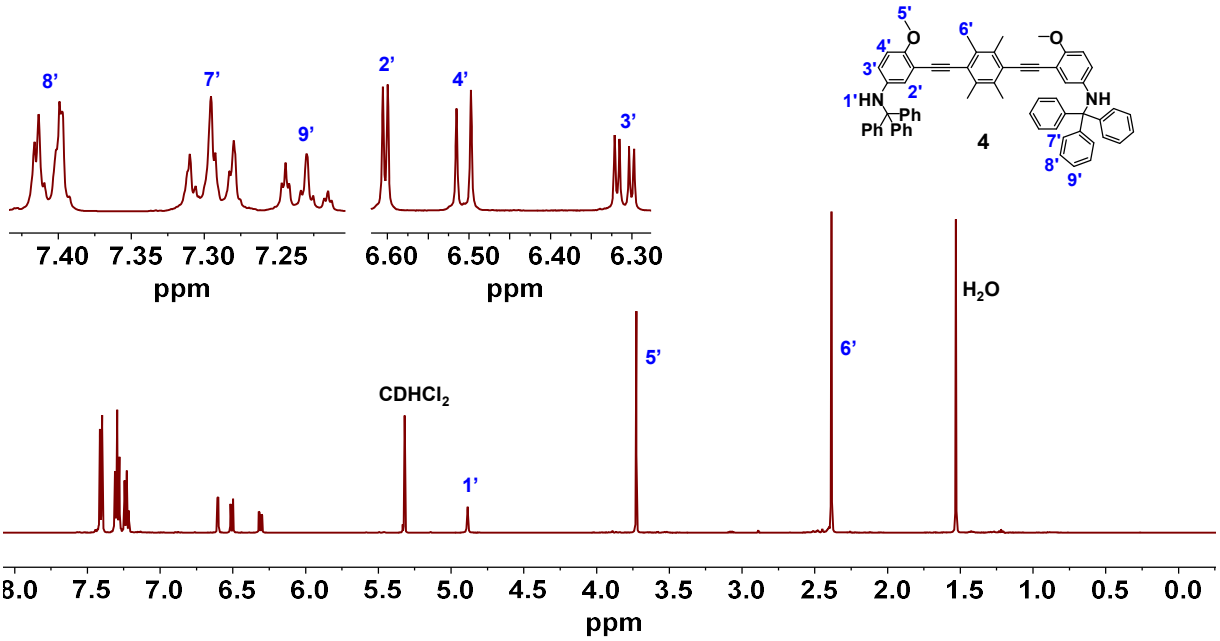


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of ligand **4**.

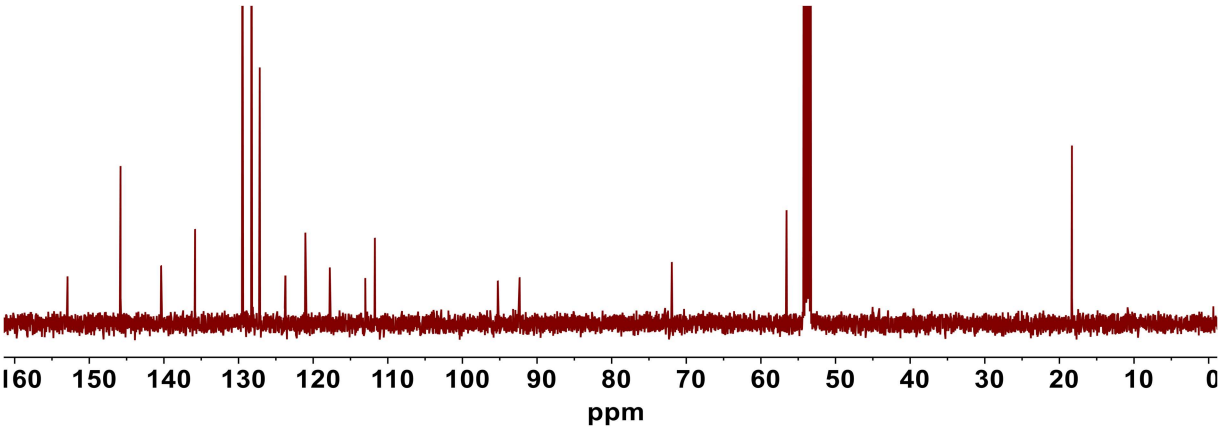


Figure S2. ^{13}C NMR spectrum (CD_2Cl_2, 125 MHz) of ligand **4**.

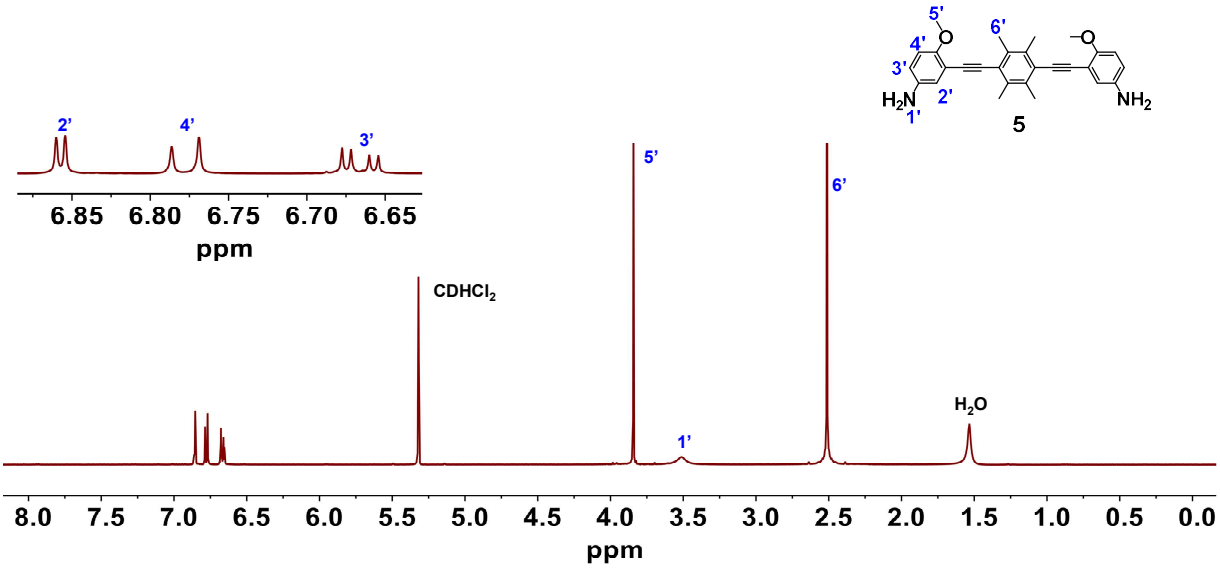


Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of ligand **5**.

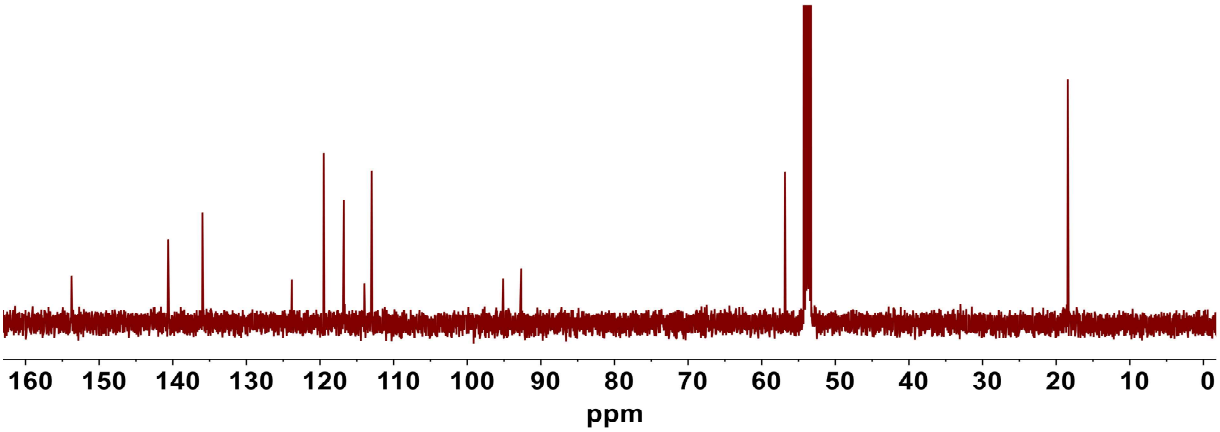


Figure S4. ^{13}C NMR spectrum (CD_2Cl_2, 125 MHz) of ligand **5**.

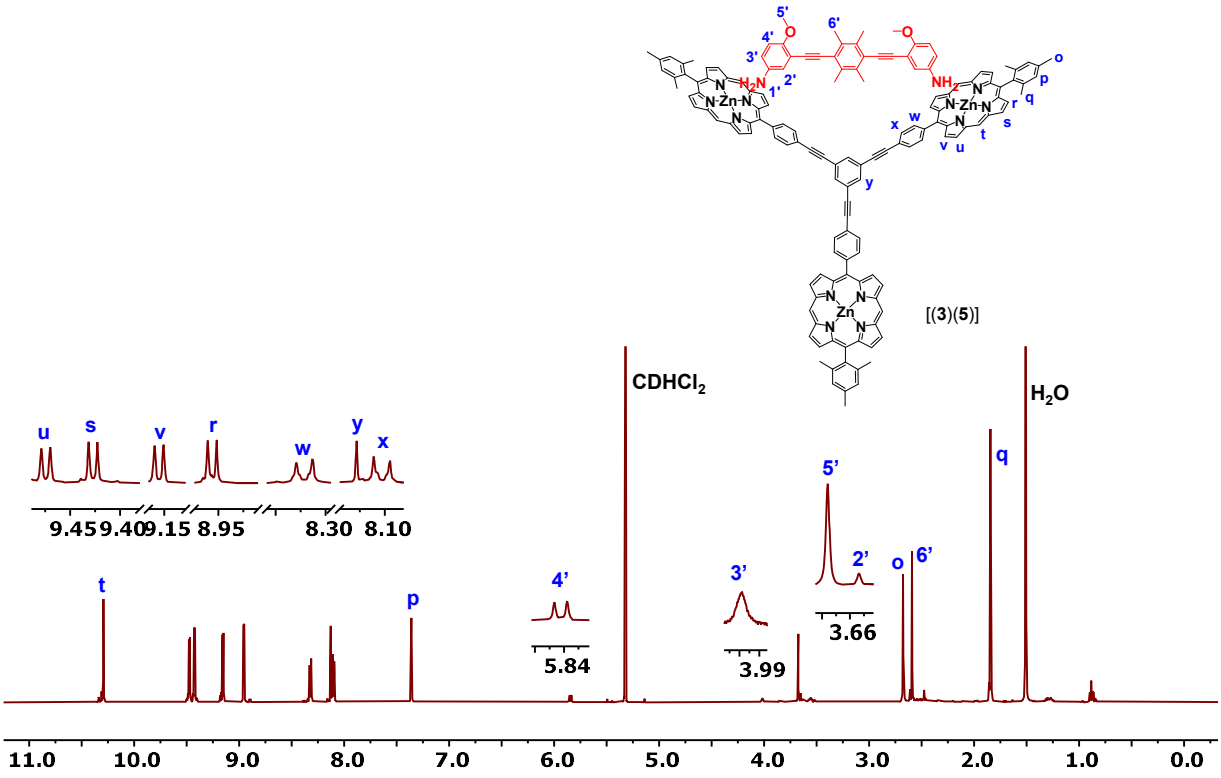


Figure S5. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of complex [(**3**)(**5**)].

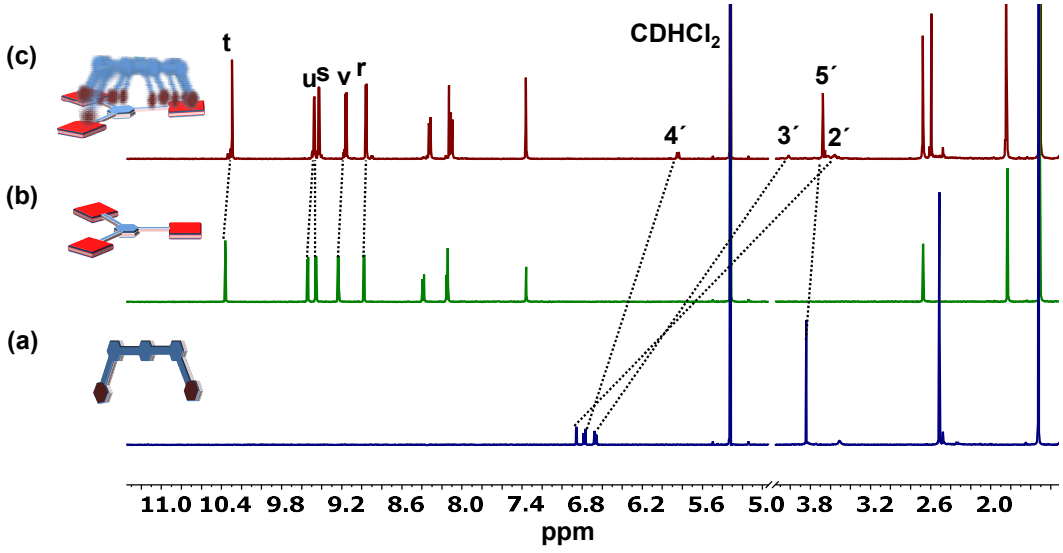


Figure S6. Partial ^{1}H NMR comparison spectra (500 MHz, CD_2Cl_2, 298 K) of (a) biped **5**, (b) deck **3** and (c) nanoslider [(**3**)(**5**)].

3. Variable temperature ^{1}H NMR studies

The kinetics of the sliding motion at various temperatures was analyzed through simulation of the experimental ^{1}H NMR spectra using the program WinDNMR.[5] The spectra simulation using the model of a 2-spin system undergoing mutual exchange provided the rate constants at the given temperatures. Activation parameters were determined from an Eyring plot.

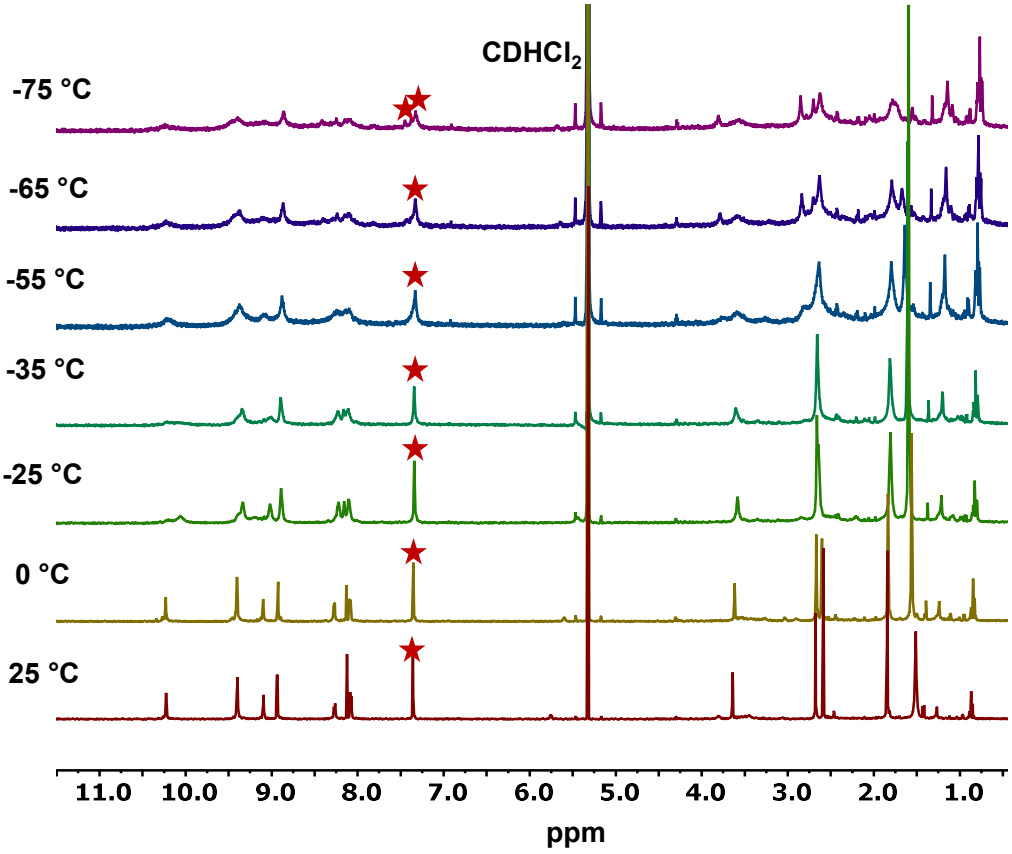


Figure S7. Partial ^{1}H VT-NMR (CD_2Cl_2, 600 MHz) of slider-on-deck showing the splitting of proton p-H at different temperatures.

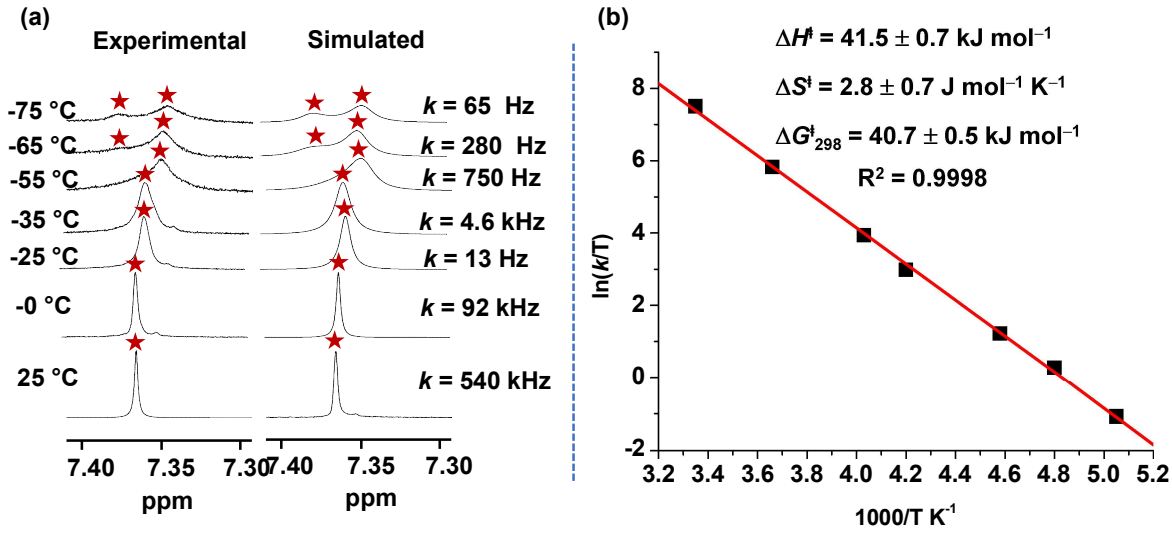


Figure S8. (a) Experimental and simulated ^{1}H VT-NMR (CD_2Cl_2, 600 MHz) of slider-on-deck shows the splitting of p-H (red asterisk marked) and (b) Eyring plot for rotational exchange in slider-on-deck.

4. DOSY NMR spectra

Calculation of hydrodynamic radius from DOSY

The diffusion coefficient *D* for slider-on-deck was obtained from the DOSY spectrum. The corresponding hydrodynamic radius was calculated by using the Stokes-Einstein equation:

$$r = kBT/6\pi\eta D$$

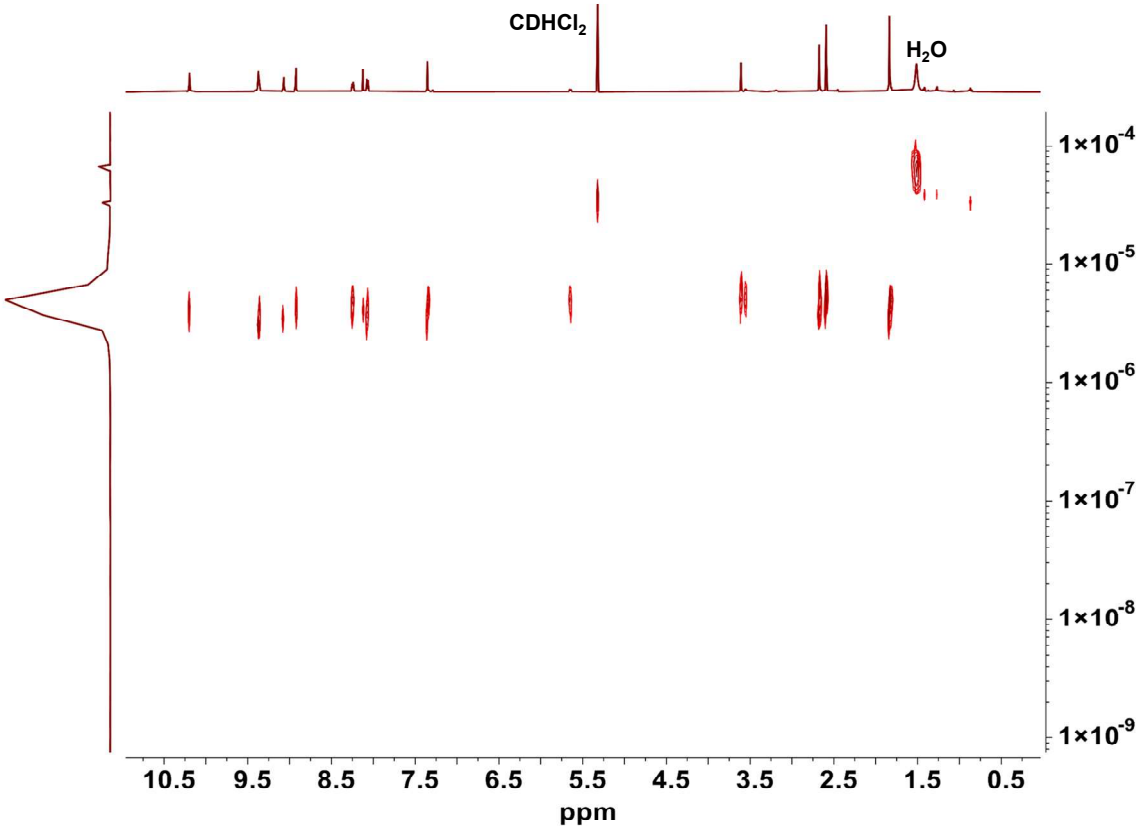


Figure S9. ^{1}H-DOSY NMR of [(**3**)(**5**)] in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient D = 4.75×10^{-10} m^2s^{-1}, hydrodynamic radius r = 10.4 Å.

5. Switching studies

Switching between NetState-I and NetState-II

In an NMR tube, ligand **1** (950 µg, 913 nmol) and ligand **2** (308 µg, 913 nmol) were dissolved in 500 µL of CD_2Cl_2, then TFA (104 µg, 913 nmol) in CD_2Cl_2 (10.0 µL) was added. After 1 min of mixing $AgBF_4$ (178 µg, 913 nmol) in CD_3CN (15.0 µL) was added and it resulted in NetState-II. After formation of NetState-II, tetrabutylammonium iodide (337 µg, 913 nmol) was added into the NMR tube and it resulted in NetState-I formation and AgI precipitation. The reversibility of the system examined over 3 cycles.

6. Catalytic experiments

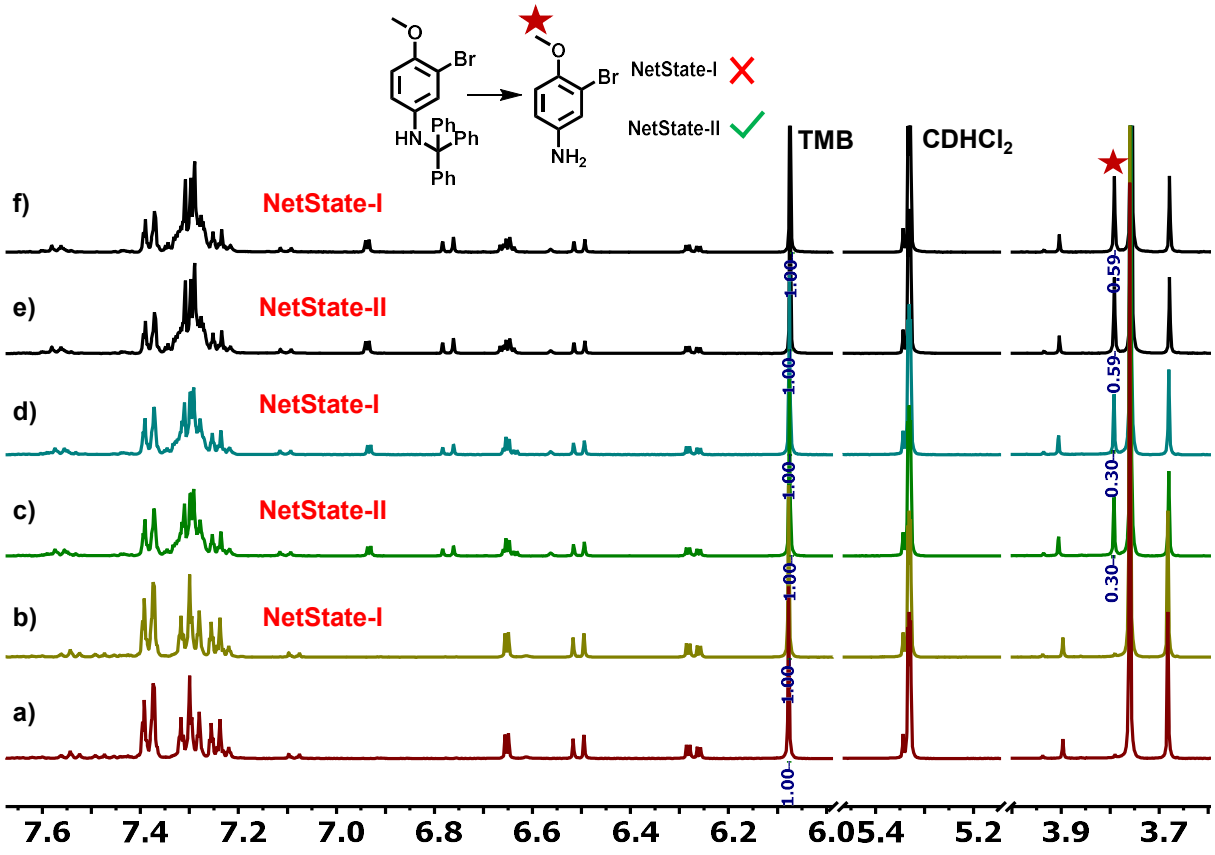


Figure S10. Reversible switching between the networking states furnishes reproducible amounts of the product **7** in NetState-II at 40 °C during 2 h. Consumed amounts of substrates were added. a) Ligands **1** + **2** + **6** + TMB (1:1:10:10 ratio respectively), no product formation; b) NetState-I + TMB + **6** (1:10:10 ratio respectively), no product formation; c) NetState-II + TMB + **6** (1:10:10 ratio respectively), 30% yield of **7**; d) NetState-I + TMB + **6** (1:10:10 ratio respectively), no product formation, overall 30% yield of **7**; e) NetState-II + TMB + **6** (1:10:10 ratio respectively), 29% yield of **7**; overall 59% yield of **7**; f) NetState-I + TMB + **6** (1:10:10 ratio respectively), no product formation, overall 59% yield of **7**. Concentrations of the networking states are identical for all experiments (see page S10). The red asterisk marked proton signal at 3.79 ppm was integrated with respect to TMB for yield calculation.

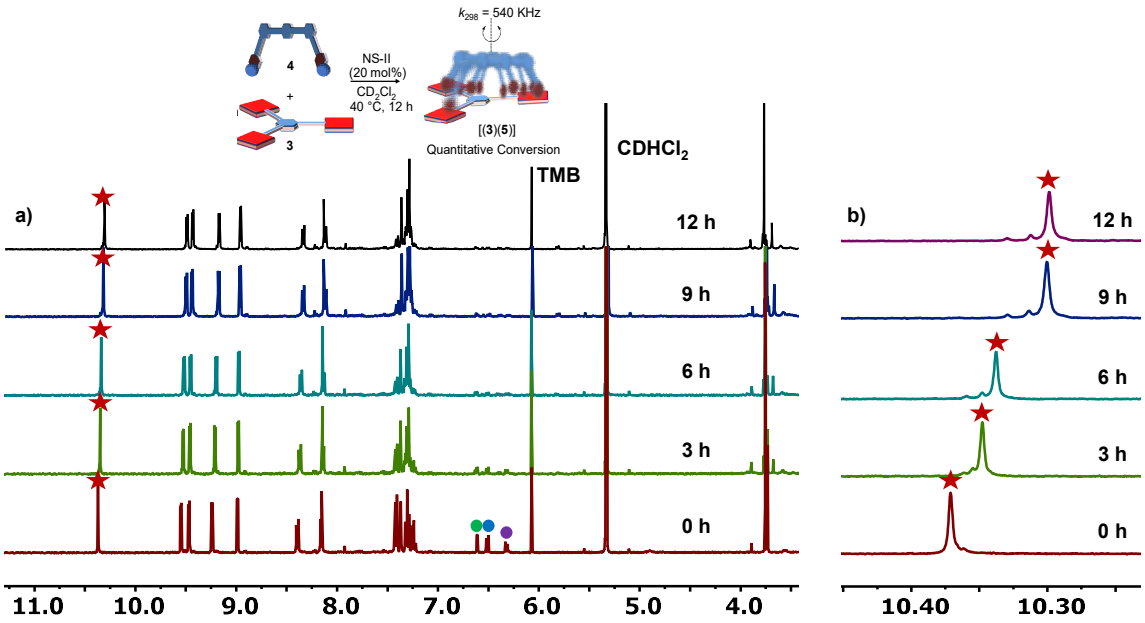


Figure S11. a) Partial ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of the conversion of **3** and **4** to [(**3**)(**5**)] as catalyzed by NetState-II. Red asterisk marked proton signal shows quantitative conversion after 12 h catalyzed by NetState-II; b) close-range partial ^{1}H NMR spectra of the t-H proton. Concentrations of the networking states are identical for all experiments (see page S10).

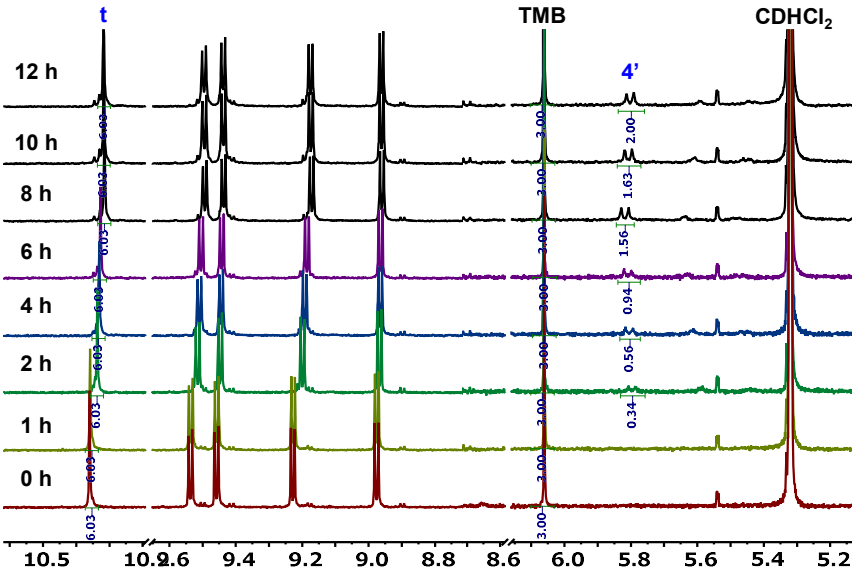


Figure S12. Partial ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of the conversion of **3** and **4** to [(**3**)(**5**)] as catalyzed by NetState-II. Gradual evolution of 4'-H proton signal at 5.84 ppm (integrated with respect to TMB) of porphyrin deck bound biped **5** After 12 h, t-H:4'-H appeared at 3:1 ratio.

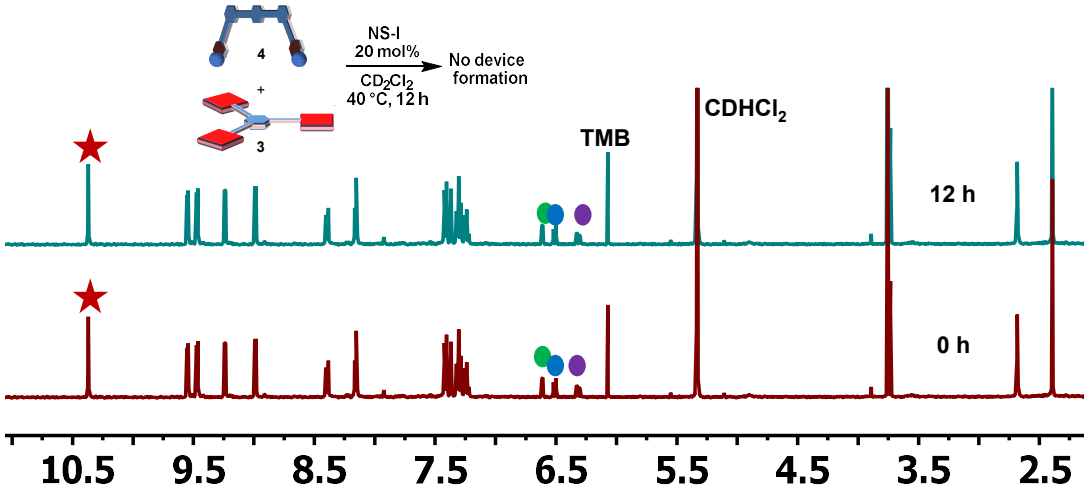


Figure S13. Partial ^{1}H NMR spectra of the OFF state of the conversion of **3** and **4** to [(**3**)(**5**)] as catalyzed by NetState-I. Concentrations of the networking states are identical for all experiments (see page S10).

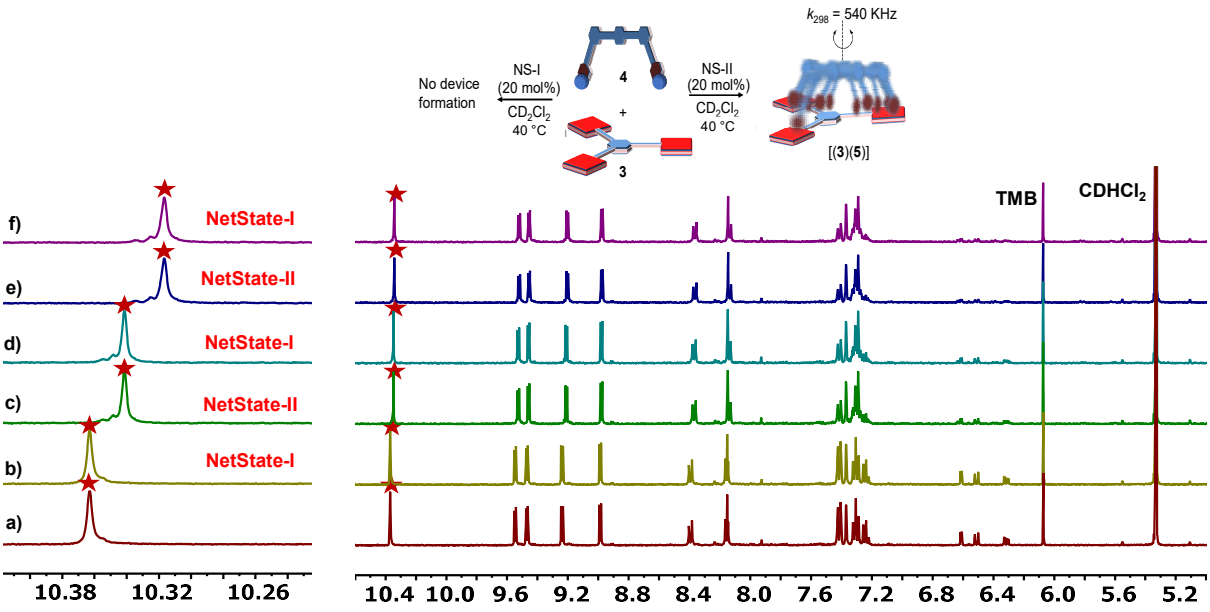


Figure S14. OFF/ON catalysis cycle by alternate formation of NetState-I/NetState-II states. a) Ligands **1** + **2** + **3** + **4** + TMB (1:1:5:5:5 ratio respectively), b) OFF state of the conversion of **3** and **4** to [(**3**)(**5**)] in presence of 20 mol% NetState-I after 3 h at 40 °C (overall time is 3 h) c) ON state of the conversion of **3** and **4** to [(**3**)(**5**)] in presence of 20 mol% NetState-II after 3 h at 40 °C (overall time is 6 h) d) OFF state of the conversion of **3** and **4** to [(**3**)(**5**)] in presence of 20

mol% NetState-I after 3 h at 40 °C (overall time is 9 h) e) ON state of the conversion of **3** and **4** to [(**3**)(**5**)] in presence of 20 mol% NetState-II after 3 h at 40 °C (overall time is 12 h) f) OFF state of the conversion of **3** and **4** to [(**3**)(**5**)] in presence of 20 mol% NetState-I after 3 h at 40 °C (overall time is 15 h). Concentrations of the networking states are identical for all experiments (see page S10).

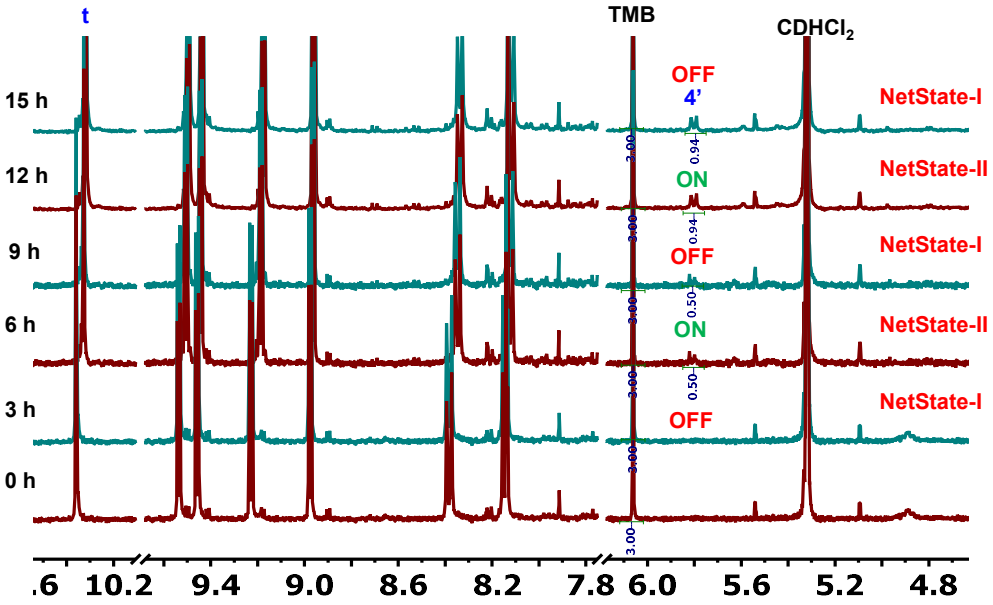


Figure S15. Partial ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of the OFF/ON catalysis cycle for conversion of **3** and **4** to [(**3**)(**5**)] with alternative NetState-I⇆NetState-II switching. Evolution of 4'-H proton signal at 5.84 ppm (integrated with respect to TMB) of porphyrin deck bound deprotected biped **5** provided evidence about the ON state of the reaction catalyzed by NetState-II. No further evolution of 4'-H proton signal attested the OFF state of catalysis with NetState-I.

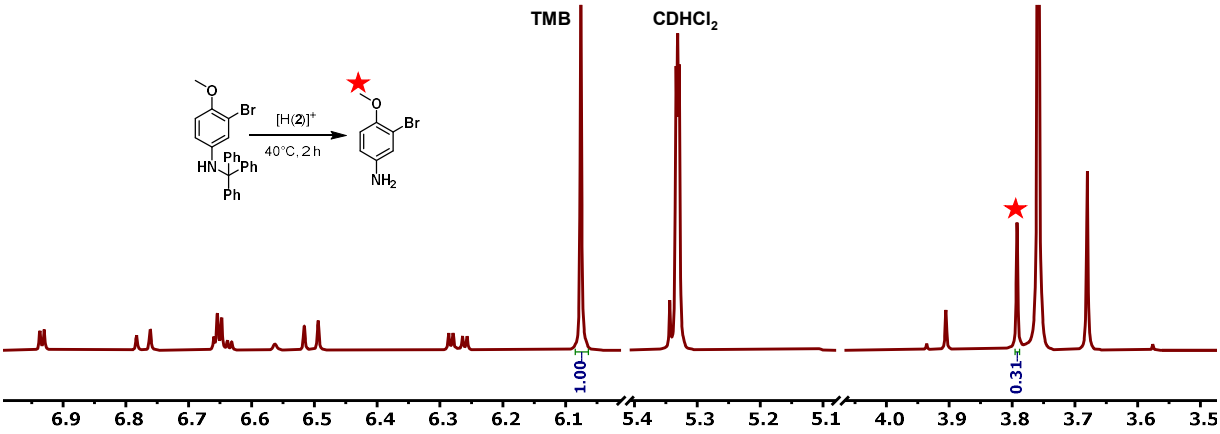


Figure S16. Partial ^{1}H NMR spectrum of the conversion of compound **6** to product **7** catalyzed by [H(**2**)]$^{+}$ complex during 2 h at 40 °C. TMB used as internal standard. The red asterisk marked proton signal at 3.79 ppm was integrated with respect to TMB for yield calculation.

7. ESI-MS spectra

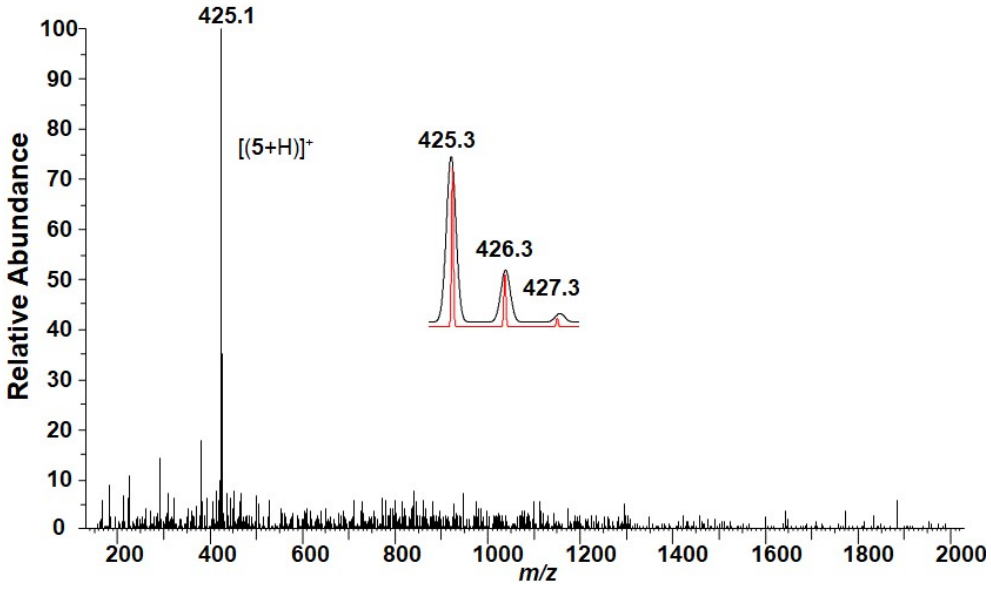


Figure S17. ESI-MS spectrum of [(**5**+H)]$^{+}$.

8. Fluorescence spectra

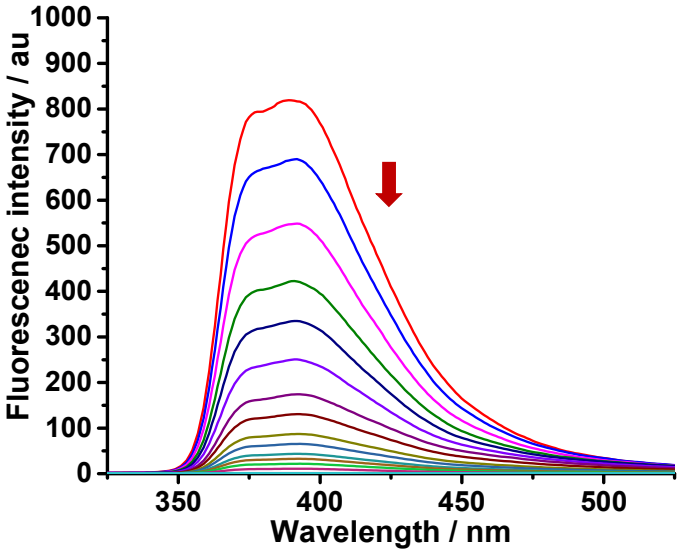
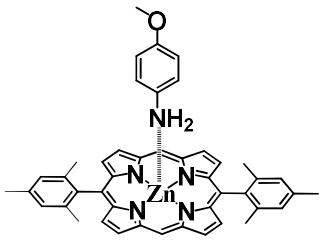


Figure S18. Fluorescence spectra of $([H(\mathbf{1})]^+$ (c = 7.69 × 10^{-6} M) in CH_2Cl_2 (2 mL) upon addition of $AgBF_4$ (3.82 × 10^{-3} M) at 298 K to afford the complex $[Ag(\mathbf{1})]^+$.

9. Measurement of binding constant

The UV-vis titration technique was used to measure binding constants of complexes. The full data of a selected wavelength region was analyzed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA).



[(9)(10)]

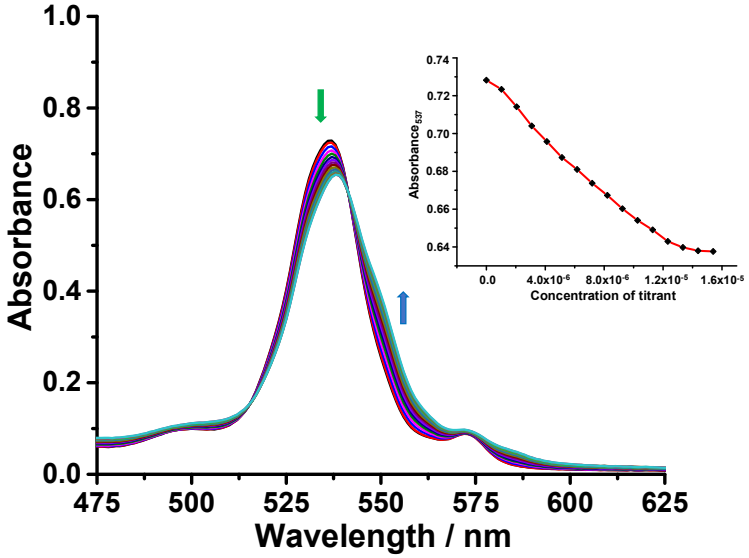


Figure S19. UV-vis spectra of **10** (c = 1.54 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon addition of **9** (3.85 × 10^{-3} M) in CH_2Cl_2 at 298 K to afford the complex [(**9**)(**10**)]. The wavelength region 475-625 nm was analyzed.

Result: log K = 2.87 ± 0.31.

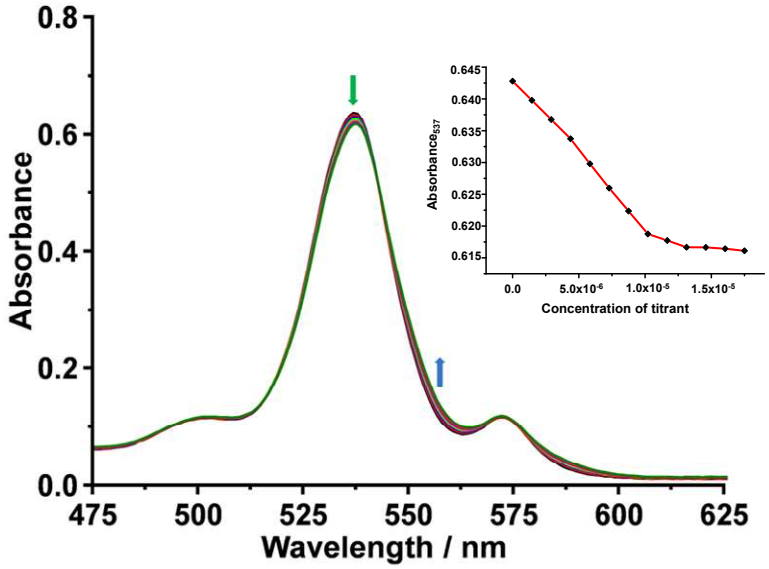


Figure S20. UV-vis spectra of **3** (c = 1.75 × 10^{-5} M) in CH_2Cl_2 (2 mL) upon titration with a solution of **5** (3.51 × 10^{-3} M) in CH_2Cl_2 at 298 K to afford the complex [(**3**)(**5**)]. The wavelength region 475-625 nm was analyzed. Result: log K = 6.31 ± 0.27.

10. Control catalytic experiment

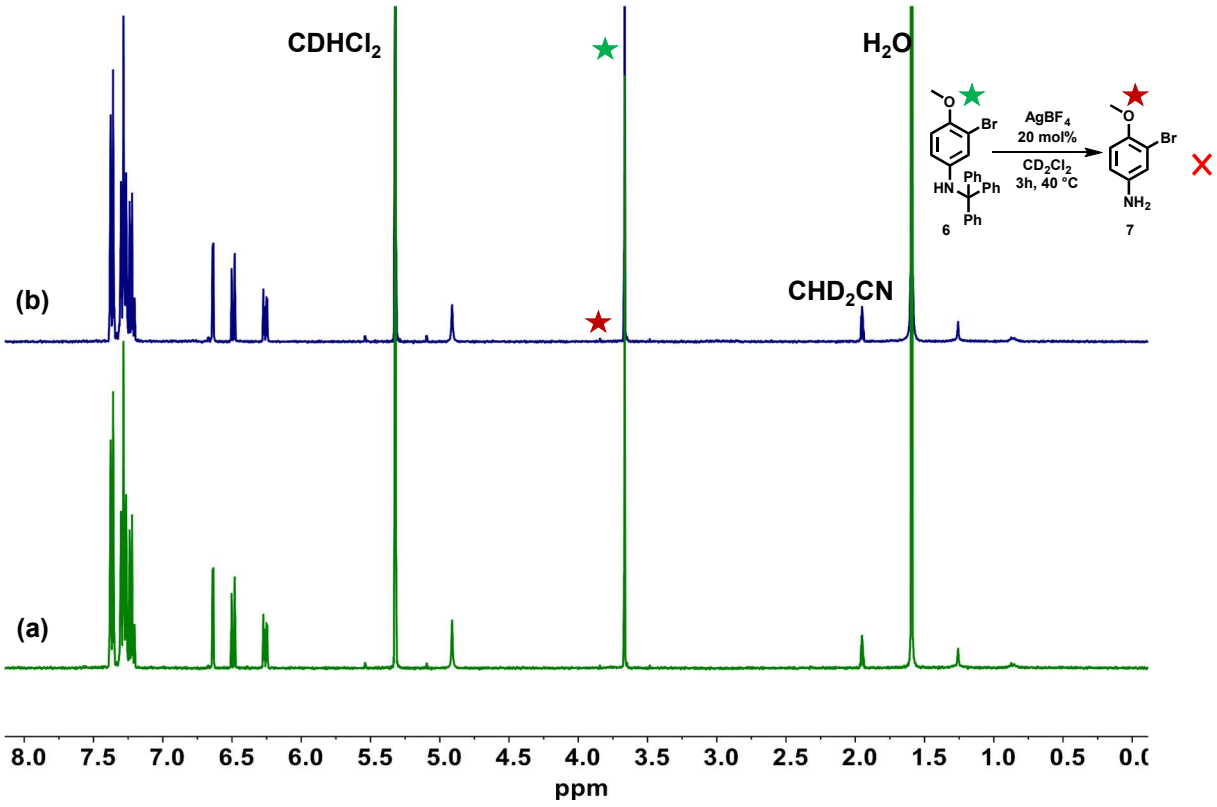


Figure S21. ^{1}H NMR spectrum of the putative deprotection of compound **6** to product **7** in presence of 10 mol% of $AgBF_4$ ions after 3 h at 40 °C. Absence of a proton signal at 3.79 ppm (red asterisk) confirms that the reaction is in an OFF state.

11. References

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