Electronic Supporting Information (ESI)

Fast and slow walking driven by chemical fuel

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1. Synthesis

1.1 General Information

All commercial reagents were used without further purification. Solvents were dried with the appropriate desiccants and distilled prior to use. Bruker Avance (400 MHz), Jeol ECZ (500 MHz) and Varian (600 MHz) spectrometers were used to measure ^{1}H and ^{13}C NMR spectra employing a deuterated solvent as the lock and residual protiated solvent as internal reference ($CDCl_3$: δ_H 7.26 ppm, δ_C 77.0 ppm; CD_2Cl_2: δ_H 5.32 ppm, δ_C 53.8 ppm, THF-d8: δ_H 1.72 ppm, 3.58 ppm, δ_C 25.3 ppm, 67.2 ppm). The following abbreviations were used to describe NMR peak pattern: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, brs = broad singlet, brd = broad doublet, m = multiplet. The coupling constant values are given in Hertz (Hz) and, wherever possible, assignment of protons is provided. The numbering of different carbons in different molecular skeletons does not necessarily follow IUPAC nomenclature rules; it was exclusively implemented for assigning NMR signals. All electrospray ionization (ESI-MS) spectra were recorded on a Thermo-Quest LCQ deca and the theoretical isotopic distributions of the mass signals were calculated using IsoPro 3.0 software. Melting points of compounds were measured on a BÜCHI 510 instrument and are not corrected. Elemental analysis was performed using the EA-3000 CHNS analyzer. Column chromatography was performed either on silica gel (60-400 mesh) or neutral alumina (Fluka, 0.05-0.15 mm, Brockmann Activity 1). Merck silica gel (60 F254) or neutral alumina (150 F254) sheets were used for thin layer chromatography (TLC). The multi-component assembly of complexes was performed directly in the NMR tube with CD_2Cl_2 as solvent. Compounds **3**,[1] **5**,[2] **8**,[3] **6**,[4] **9**,[5] **10**,[6] **12**,[7] **13**,[8] and complexes [**12•14**][9] and [DB24C8•**12**•$(H)_2$]PF_6[10] were prepared/characterized according to reported procedures available in the literature.

1.2 Ligands used in this study and synthetic schemes

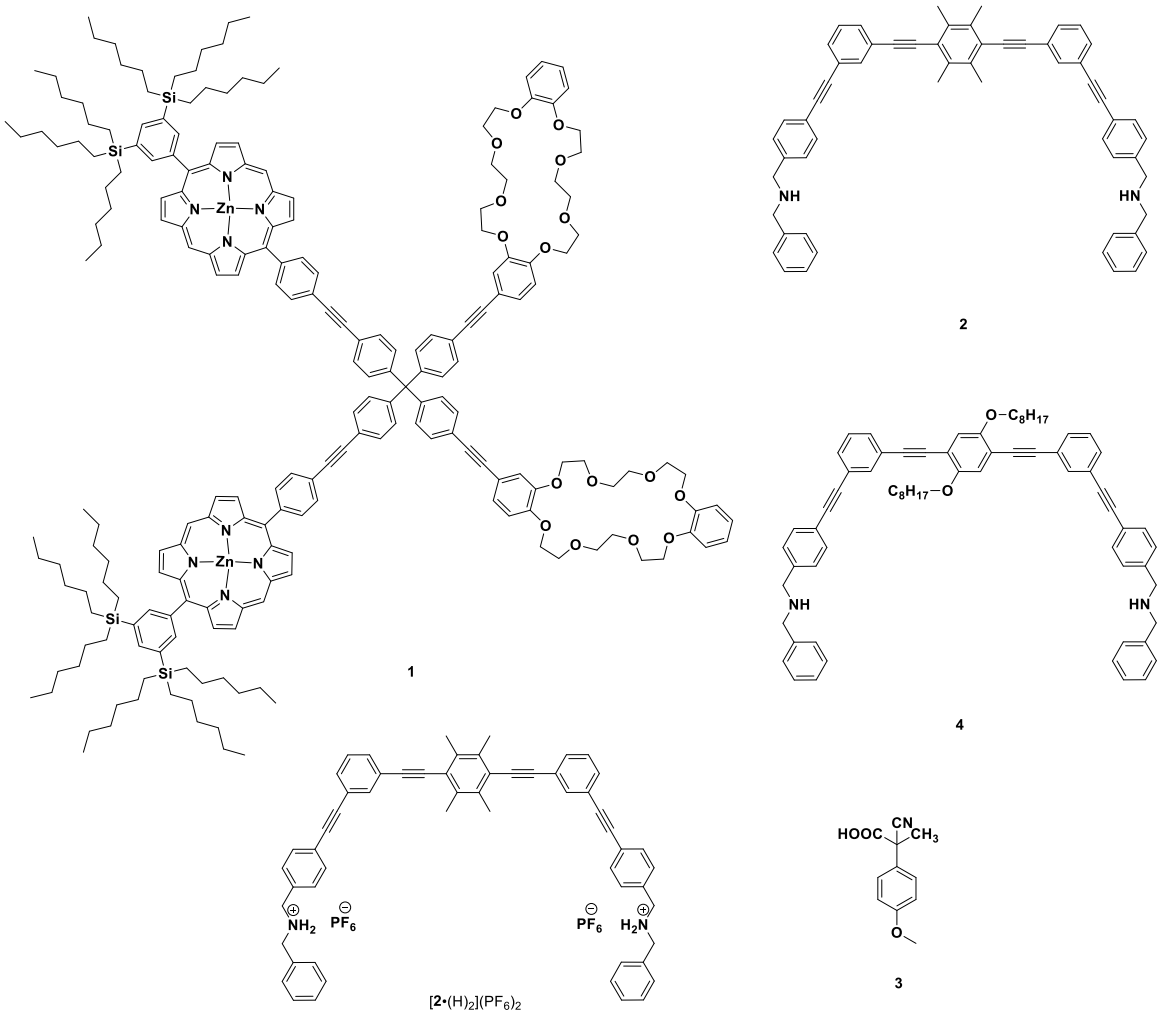
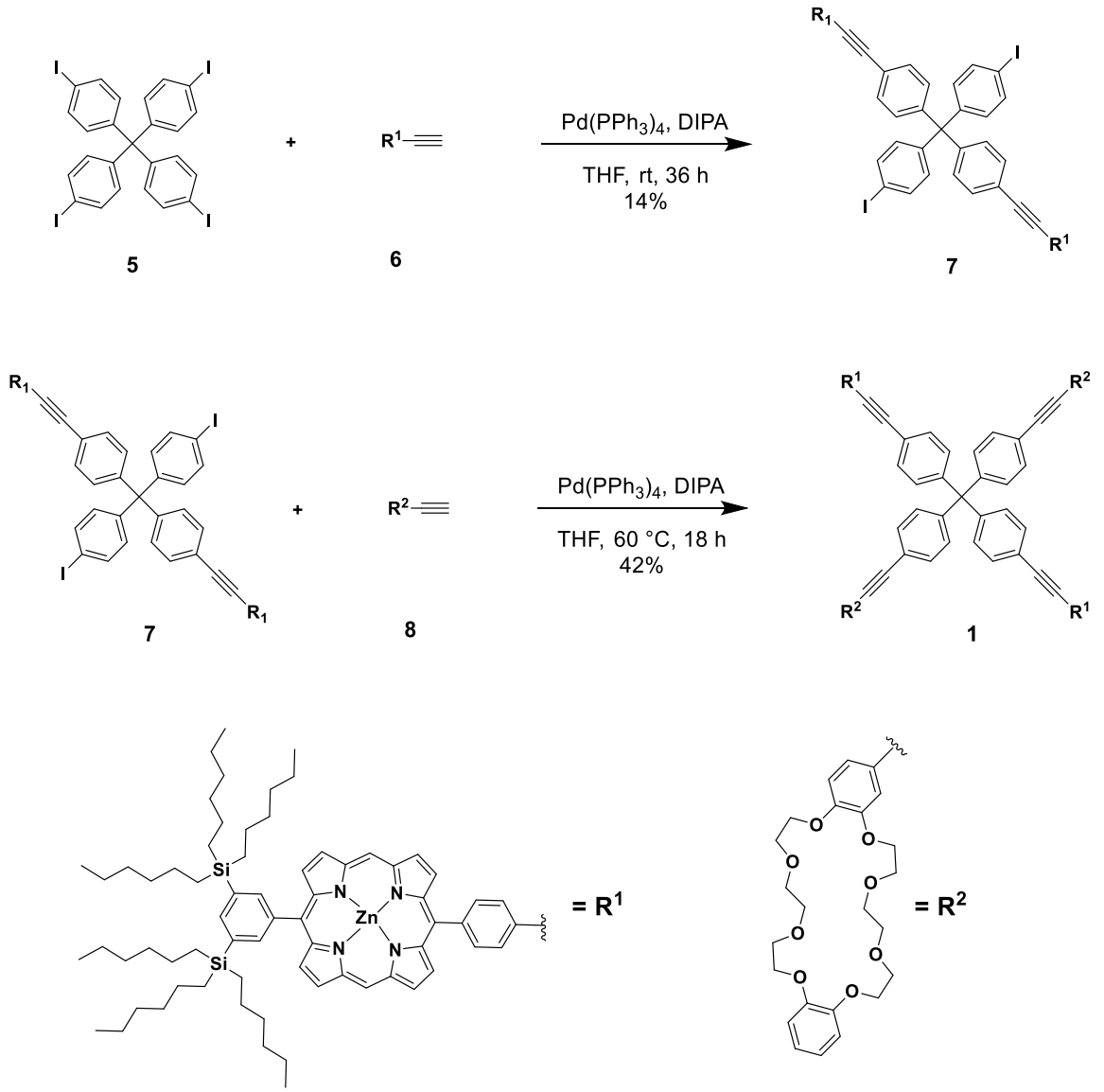
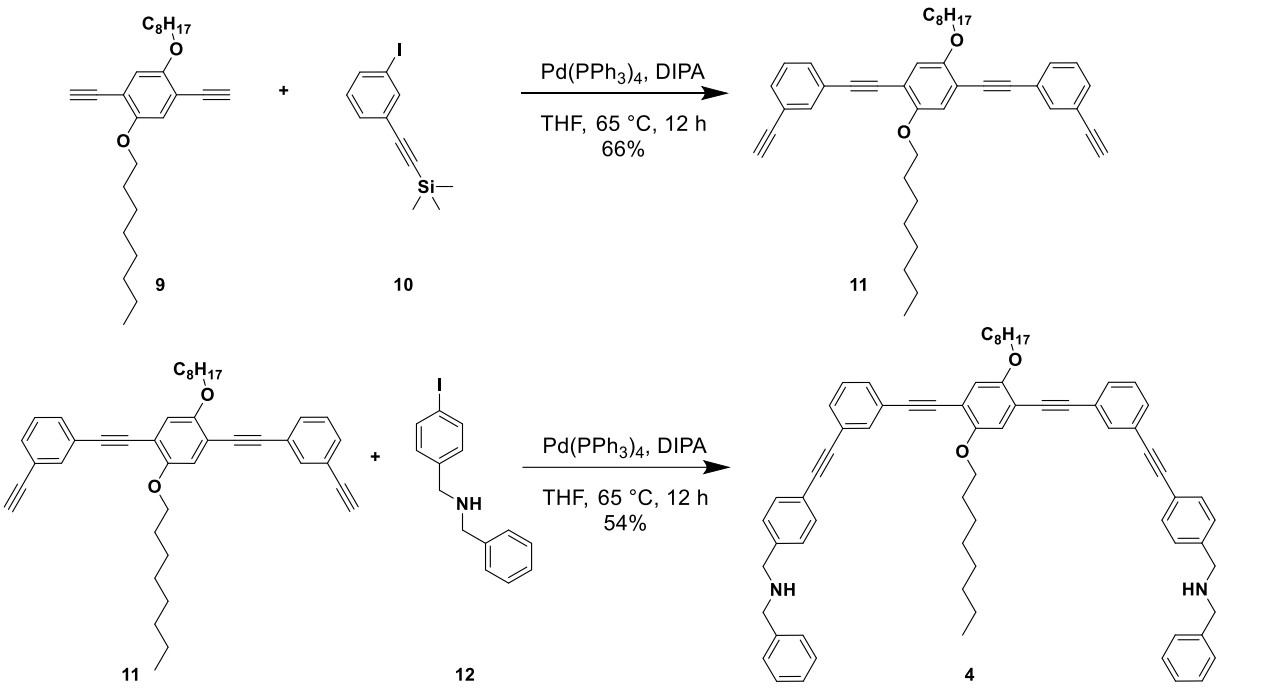


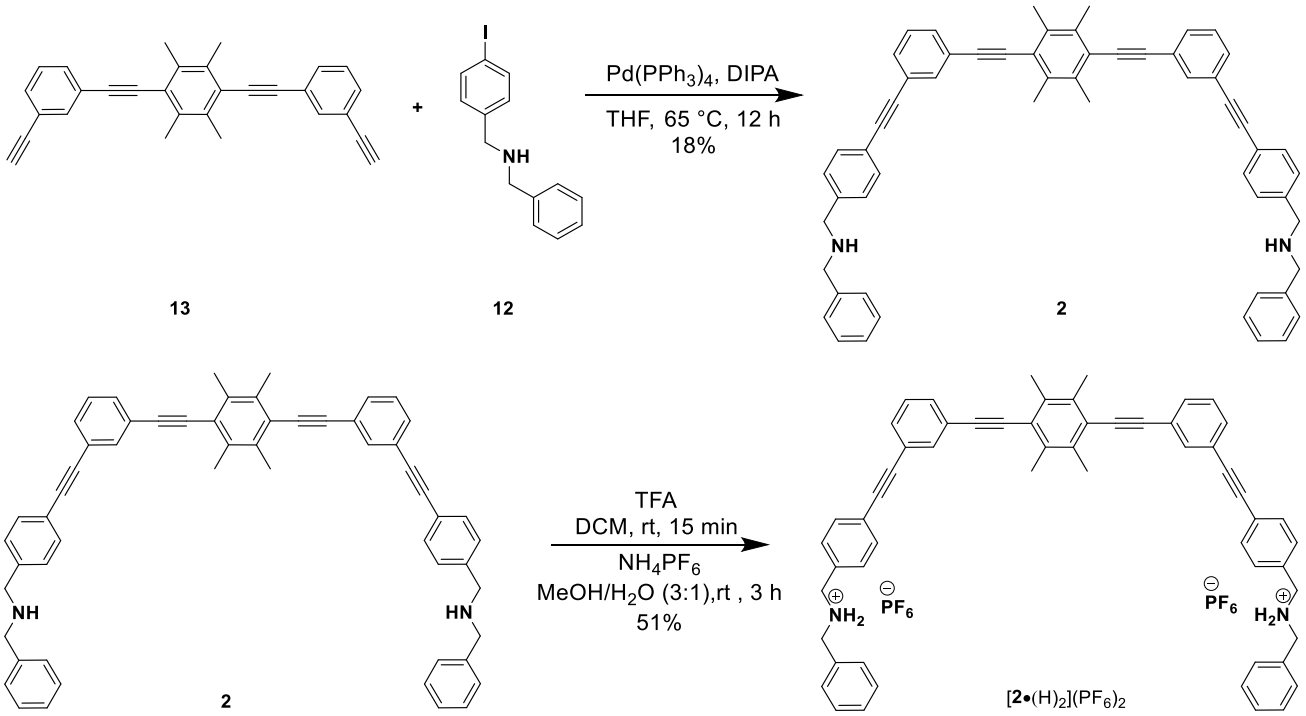
Figure S1: Ligands used in this study.



Scheme S1: Synthetic route to ligand **1.**



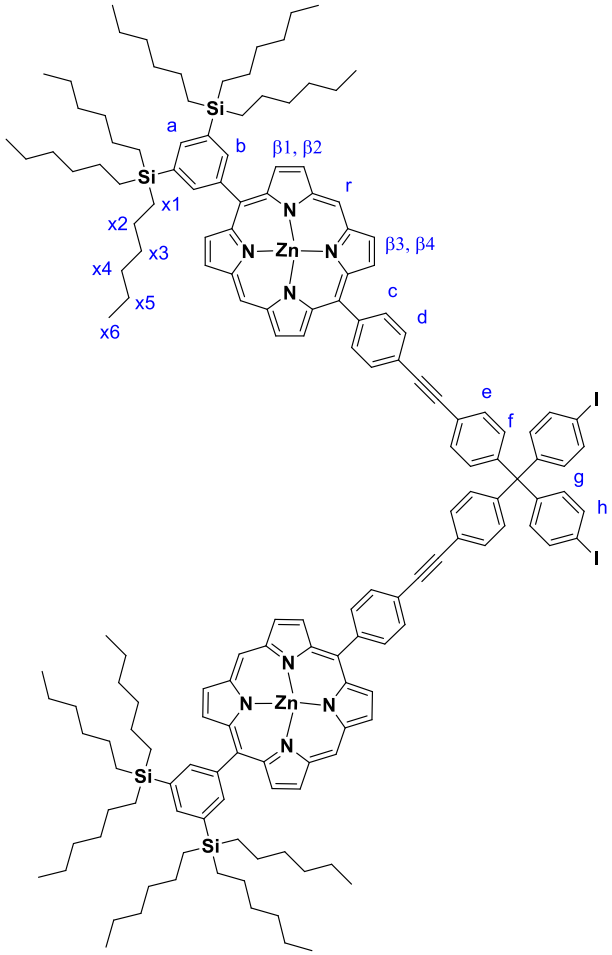
Scheme S2: Synthetic route to biped **4.**



Scheme S3: Synthetic route to **2** and [**2**•$(H)_2$]$(PF_6)_2$.

1.3 Synthesis of organic ligands

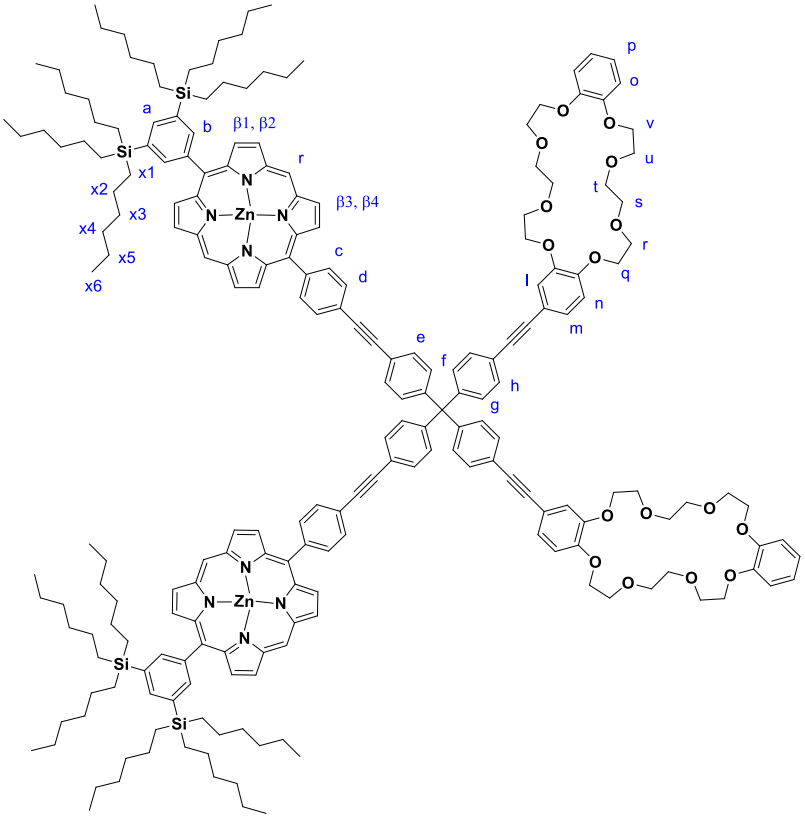
Synthesis of compound 7



In a reaction tube, compounds **5** (89.5 mg, 109 μmol) and **6** (230 mg, 219 μmol) were dissolved in THF and diisopropylamine (30 mL, 1:4, v/v). The solution was subjected to 15 min of sparging with N_2. Then, $Pd(PPh_3)_4$ (13 mg, 11 μmol) was added under an inert N_2 atmosphere. The tube was sealed with a screw cap and stirred at rt for 36 h (TLC). After evaporation of the solvents, the crude pink residue was dissolved in DCM, washed with H_2O, brine and subsequently dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a pink solid which was further purified by size-exclusion column chromatography on Biobeads®-SX1 using distilled THF as the eluent to obtain the desired compound **7** (R_f = 0.45 in 50% chloroform in hexane on SiO_2) as a dark-pink glassy solid (80.0 mg, 29.4 μmol, 14%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 10.40 (s, 4H, r-H), 9.53 (d, ^3J = 4.6 Hz, 4H, β3-H), 9.49 (d, ^3J = 4.6 Hz, 4H, β2-H), 9.20 (d, ^3J = 4.6 Hz, 4H, β4-H), 9.16 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.36 (d, ^4J = 1.0 Hz, 4H, b-H), 8.31 (d, ^3J = 8.2 Hz, 4H, c-H), 8.07 (t,

^4J = 1.0 Hz, 2H, a-H), 8.01 (d, ^3J = 8.2 Hz, 4H, d-H), 7.74 (d, ^3J = 8.6 Hz, 4H, h-H), 7.70 (d, ^3J = 8.6 Hz, 4H, e-H), 7.37 (d, ^3J = 8.6 Hz, 4H, g/f-H), 7.12 (d, ^3J = 8.6 Hz, 4H, f/g-H), 0.93-1.53 (m, 120H, x1-, x2-, x3-, x4-, x5-H), 0.86 (t, ^3J = 6.4 Hz, 36H, x6-H) ppm. **^{13}C NMR (125 MHz, THF-d8):** δ 150.9, 150.5, 150.4, 150.3, 146.9, 146.5, 144.6, 142.5, 141.6, 139.5, 137.9, 135.6, 135.2, 133.7, 132.6, 132.3, 132.2, 132.0, 131.9, 131.7, 130.3, 123.0, 122.5, 121.3, 119.0, 106.4, 92.9, 90.6, 90.4, 67.7, 34.3, 32.4, 24.9, 23.3, 14.3, 13.3 ppm. **Elemental analysis** ($C_{160}H_{198}I_2N_8Si_4Zn_2$•$H_2O$): Calcd. C, 70.37; H, 70.44; N, 3.98. Found, C, 70.24; H, 7.25; N, 3.71.

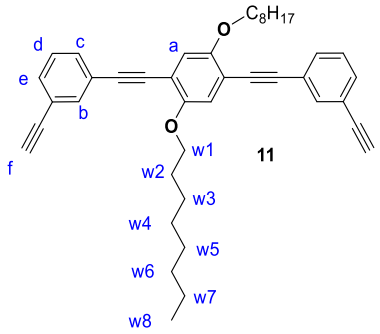
Synthesis of compound 1



In a reaction tube, compounds **7** (75.0 mg, 27.4 μmol) and **8** (38.7 mg, 82.2 μmol) were dissolved in THF and diisopropylamine (30 mL, 1:4, v/v). The solution was subjected to 15 min of sparging with N_2. Then, $Pd(PPh_3)_4$ (5 mg) was added under an inert N_2 atmosphere. The tube was sealed with a screw cap and stirred at 60 ºC for 18 h (TLC). After cooling to rt and evaporation of the solvents, the crude pink residue was dissolved in DCM, washed with H_2O, brine and subsequently dried over anhydrous $MgSO_4$. The solvent was evaporated to furnish a pink solid which was further purified by size-exclusion column chromatography on Biobeads®-SX1 using distilled

THF as the eluent to obtain a sticky, pink solid which was subsequently precipitated using DCM/MeOH affording the desired compound **1** (40.0 mg, 11.5 µmol, 42%) as a dark-pink crystalline solid (R_f = 0.2 in 50% EtOAc in DCM on SiO_2). **Mp** = 168-170 °C. **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.40 (s, 4H, r-H), 9.52 (d, ^3J = 4.6 Hz, 4H, β3-H), 9.48 (d, ^3J = 4.6 Hz, 4H, β2-H), 9.19 (d, ^3J = 4.6 Hz, 4H, β4-H), 9.15 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.36 (d, ^4J = 1.0 Hz, 4H, b-H), 8.30 (d, ^3J = 8.2 Hz, 4H, c-H), 8.07 (t, ^4J = 1.0 Hz, 2H, a-H), 8.02 (d, ^3J = 8.2 Hz, 4H, d-H), 7.71 (d, ^3J = 8.6 Hz, 4H, e-H), 7.55 (d, ^3J = 8.6 Hz, 4H, h-H), 7.43 (d, ^3J = 8.6 Hz, 4H, g/f-H), 7.37 (d, ^3J = 8.6 Hz, 4H, f/g-H), 7.15 (dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz, 2H, m-H), 7.08 (d, ^3J = 2.0 Hz, 2H, l-H), 6.89-6.85 (m, 10H, o-, p-, n-H), 4.14-4.09 (m, 16H, q-, v-H), 3.86-3.82 (m, 16H, r-, u-H), 3.74 (s, 16H, s-, t-H), 0.94-1.53 (m, 120H, x1-, x2-, x3-, x4-, x5-H), 0.86 (t, ^3J = 6.4 Hz, 36H, x6-H) ppm. **^{13}C NMR (125 MHz, THF-d8):** δ 150.9 (2C), 150.5, 150.4, 149.9, 147.2, 146.6, 144.6, 142.5, 141.7, 139.5, 135.6, 135.2, 132.7 (2C), 132.3, 132.2, 132.0, 131.9 (2C), 131.7, 131.5, 130.4, 125.8, 123.1, 122.9, 122.5, 121.8, 121.3, 119.0, 117.9, 116.4, 115.3, 115.2, 114.5, 106.4, 90.9, 90.6, 90.5, 87.9, 71.9, 70.5, 70.4 (2C), 70.3 (2C), 70.2, 34.3, 32.3, 24.8, 23.3, 14.3, 13.3. **Elemental analysis** $C_{217}H_{268}N_8O_{16}Si_4Zn_2$•$H_2O$•$CH_2Cl_2$): Calcd. C, 72.92; H, 7.64; N, 3.12. Found, C, 72.62; H, 7.24; N, 2.85.

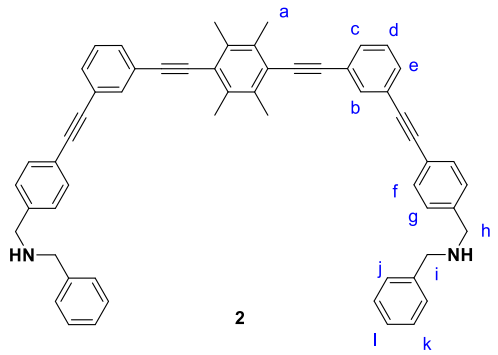
Synthesis of compound 11



In a reaction tube, compounds **9** (505 mg, 131 µmol) and **10** (118 mg, 393 µmol)) were dissolved in THF and diisopropylamine (30 mL, 1:4, v/v). The solution was subjected to 15 min of sparging with N_2. Then, $Pd(PPh_3)_4$ (7.5 mg, 6.5 µmol) was added under an inert N_2 atmosphere. The tube was sealed with a screw cap and stirred at 65 °C for 12 h (TLC). After cooling to rt and evaporation of the solvents, the crude brown residue was dissolved in DCM, washed with H_2O, brine and subsequently dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain a crude-yellow solid which was subsequently dissolved in 50 mL THF/MeOH (3:1). To this solu-

tion, K_2CO_3 (1.00 g as granules) was added and stirred at rt for 4 h until completion (TLC). The suspension was then filtered and the resultant filtrate was evaporated to afford a yellow solid which was further purified by column chromatography (R_f = 0.45 in 5% EtOAc in hexane on SiO_2) on silica gel (60-120 mesh) using EtOAc/hexane (5:95) as the eluent to furnish the desired compound **11** as a bright-yellow sticky solid (510 mg, 880 µmol, 66%). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.66 (t, ^4J = 1.5 Hz, 2H, b-H), 7.50 (td, 2H, ^3J = 7.8 Hz, ^4J = 1.5 Hz, c/e-H), 7.45 (td, 2H, ^3J = 7.8 Hz, ^4J = 1.5 Hz, e/c-H), 7.30 (t, 2H, ^3J = 7.8 Hz, ^5J = 0.5 Hz, d-H), 7.06 (s, 2H, a-H), 4.03 (t, ^3J = 6.5 Hz, 4H, w1-H), 3.09 (s, 2H, f-H), 1.86-1.26 (m, 24H, (w2-w7)-H), 0.86 (t, ^3J = 6.8 Hz, 6H, w8-H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 153.9, 135.2, 131.9, 128.5, 123.9, 122.6, 117.1, 114.0, 93.9, 86.8, 82.9, 77.8, 69.8, 32.0, 29.6 (2C), 29.5 (2C), 26.3, 22.8, 14.2 ppm. **Elemental analysis** ($C_{42}H_{46}O_2$•1.5H_2O): Calcd. C, 82.72; H, 8.10. Found, C, 82.69; H, 7.75.

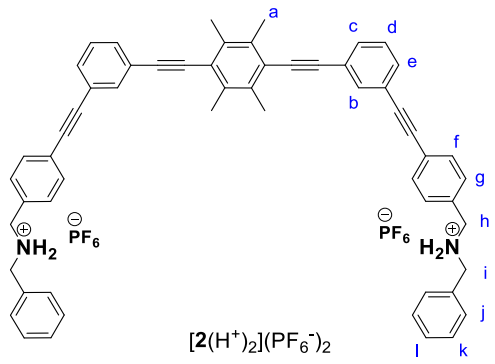
Synthesis of compound 2



In a reaction tube, compounds **13** (121 mg, 314 µmol) and **12** (304 mg, 941 µmol)) were dissolved in THF and diisopropylamine (30 mL, 1:4, v/v). The solution was subjected to 15 min of sparging with N_2. Then, $Pd(PPh_3)_4$ (21 mg, 17 µmol) was added under an inert N_2 atmosphere. The tube was sealed with a screw cap and stirred at 65 °C for 12 h (TLC). After cooling to rt and evaporation of the solvents, the crude pale yellow residue was dissolved in DCM, washed with H_2O, brine and subsequently dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain a yellow solid which was further purified by column chromatography (R_f = 0.45 in 4% MeOH in DCM on SiO_2) on silica gel (60-120 mesh) using MeOH/DCM (2:98) as the eluent to obtain **2** as a pale yellow solid (45 mg, 59 µmol, 18%). **Mp** = decomposition (turns dark brown) at 125 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.73 (t, ^3J = 1.6 Hz, 2H, b-H), 7.52 (d, ^3J = 8.00 Hz, 4H, f/g-H), 7.52-7.48 (m, 4H, c-, e-H), 7.36-7.32 (m, 14H, g/f-, d-, j-, k-H), 7.28-7.26 (m, 2H, l-H), 3.83 (s,

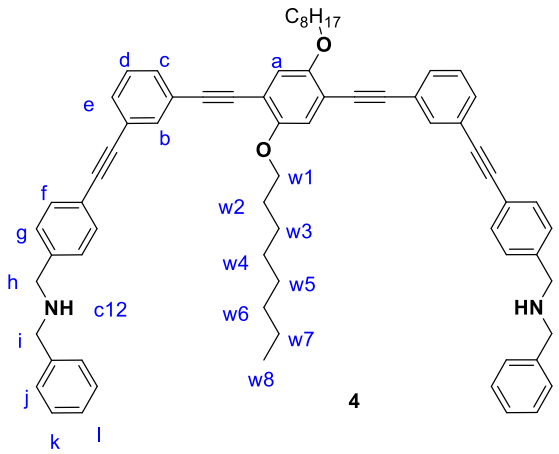
4H, i/h-H), 3.82 (s, 4H, h/i-H), 2.51 (s, 12H, a-H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 141.0, 140.2, 135.9, 134.4, 131.9, 131.3, 131.2, 128.7, 128.6, 128.4, 128.3, 127.2, 124.3, 123.9, 123.4, 121.7, 97.5, 90.2, 89.3, 88.6, 53.3, 53.0, 18.6. **Elemental analysis** ($C_{58}H_{48}N_2$•$0.5CH_2Cl_2$): Calcd. C, 86.16; H, 6.06; N, 3.44. Found, C, 86.44; H, 5.96; N, 3.34. **ESI-MS:** *m/z (%)* = 773.1 (100) [**2**+H]$^+$.

Synthesis of compound [**2**$(H^+)_2$]$(PF_6^-)_2$



A solution of trifluoroacetic acid (73.5 mg, 646 µmol) in CH_2Cl_2 was added dropwise to a solution of **2** (50.0 mg, 64.6 µmol) in 20 mL of CH_2Cl_2. After stirring for 15 min at rt, NH_4PF_6 (104 mg, 639 µmol) in 10 mL of MeOH/H_2O (3:1) was added dropwise and the solution was stirred at rt for another 3 h. The solution was then evaporated in vacuo to obtain a brown suspension. The suspension was filtered, the filtrate was washed several times with MeOH and Et_2O. The residue was then dried in ambient conditions for 2 h to furnish product [**2**$(H^+)_2$]$(PF_6^-)_2$ as an orange solid **(**35 mg, 32 µmol, 51%). **Mp** = >250 °C. **^{1}H NMR (500 MHz, CD_3CN):** δ 7.77 (t, ^3J = 1.5 Hz, 2H, b-H), 7.64 (d, ^3J = 8.0 Hz, 4H, f/g-H), 7.62 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 2H, c/e-H), 7.57 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 2H, e/c-H), 7.51 (d, ^3J = 8.0 Hz, 4H, g/f-H), 7.49-7.45 (m, 12H, j-, k-, l-, d-H), 4.27-4.23 (m, 8H, i-, h-H), 2.52 (s, 12H, a-H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 137.0, 134.8, 132.9, 132.5, 132.3, 131.9, 131.5, 131.3, 131.1, 130.7, 130.1, 130.0, 125.0, 124.9, 124.1, 124.0, 98.1, 90.4, 89.8, 89.7, 52.4, 51.9, 18.6. **Elemental analysis** ($C_{58}H_{50}F_{12}N_2P_2$): Calcd. C, 65.41; H, 4.73; N, 2.63. Found, C, 65.15; H, 4.74; N, 2.59. **ESI-MS:** *m/z (%)* = 773.0 (100) [**2**+H]$^+$.

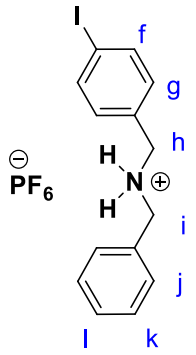
Synthesis of compound 4



4

In a reaction tube, compounds **11** (200 mg, 343 µmol) and **12** (332 mg, 1.03 mmol)) were dissolved in THF and diisopropylamine (30 mL, 1:4, v/v). The solution was subjected to 15 min of sparging with N_2. Then, $Pd(PPh_3)_4$ (21 mg, 17 µmol) was added under an inert N_2 atmosphere. The tube was sealed with a screw cap and stirred at 65 °C for 12 h (TLC). After cooling to rt and evaporation of the solvents, the crude yellow residue was dissolved in DCM, washed with H_2O as well as brine and subsequently dried over anhydrous $MgSO_4$. The solvent was evaporated to furnish a yellow solid that was further purified by column chromatography (R_f = 0.45 in 2% MeOH in DCM on SiO_2) on silica gel (60-120 mesh) using MeOH/DCM (2:98) as the eluent to afford **4** as a bright-yellow solid (181 mg, 185 µmol, 54%). **Mp** = 130-132 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.69 (t, ^3J = 1.6 Hz, 2H, b-H), 7.52-7.49 (m, 8H, f/g-, c-, e-H), 7.37 (d, ^3J = 8.0 Hz, 4H, g/f-H), 7.36-7.31 (m, 10H, d-,j-,k-H), 7.25 (t, ^3J = 6.8 Hz, 2H, l-H), 7.05 (s, 2H, a-H), 4.05 (t, 4H, w1-H), 3.83 (s, 4H, i/h-H), 3.80 (s, 4H, h/i-H), 1.87-1.26 (m, 24H, (w2-w7)-H), 0.84 (t, ^3J = 6.8 Hz, 6H, w8-H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 154.2, 141.9, 141.0, 134.7, 132.0, 131.7, 131.6, 129.0, 128.7, 128.6, 128.5, 127.3, 124.2, 121.7, 117.3, 114.3, 94.3, 90.4, 88.5, 87.0, 70.1, 53.5, 53.2, 32.2, 29.8 (2C), 29.8, 29.7, 26.5, 23.1, 14.3 ppm. **Elemental analysis** ($C_{70}H_{72}N_2O_2$•$0.5CH_2Cl_2$): Calcd. C, 83.36; H, 7.24; N, 2.76. Found, C, 82.96; H, 6.87; N, 2.40. **ESI-MS:** *m/z (%)* = 973.3 (100) [**4**+H]$^+$.

Synthesis of compound [**12**(H^+)](PF_6^-)

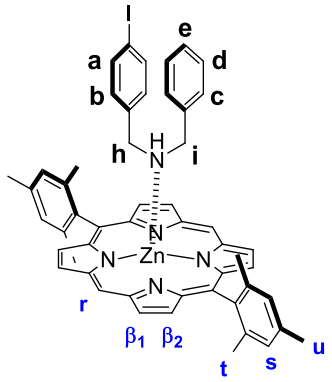


[**12**(H^+)](PF_6^-)

To compound **12** (2.00 g, 6.19 mmol), dissolved in 75 mL of CH_2Cl_2, HPF_6 was added dropwise at 0 °C resulting in a white precipitation. HPF_6 was added until no further precipitation was observed. The mixture was filtered, washed with CH_2Cl_2, and then dried under high vacuum to afford [**12**(H^+)](PF_6^-) (2.45 g, 5.25 mmol, 85%). **Mp** = 223-225 °C. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.83 (d, ^3J = 8.5 Hz, 2H, f-H), 7.46 (s, 5H, j-,k-,l-H), 7.24 (d, 2H, ^3J = 8.5 Hz, g-H), 4.22 (s, 2H, h-H), 4.18 (s, 2H, i-H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ 139.2, 133.2, 131.3, 131.2, 131.1, 130.8, 130.0, 52.5, 51.8 ppm. **Elemental analysis** ($C_{14}H_{15}F_6INP$): Calcd. C, 35.84; H, 3.22; N, 2.99. Found, C, 35.64; H, 3.09; N, 2.91. **ESI-MS:** *m/z (%)* = 324.0 (100) [**12**+H]$^+$.

2. Synthesis and characterization of complexes

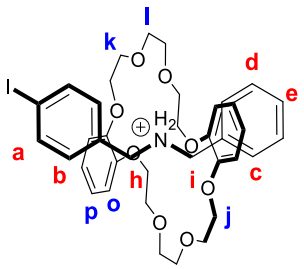
Model complex [**12•14**][9]



[12•14]

In an NMR tube, compound **12** (462 µg, 757 nmol) and zinc porphyrin **14**[8] (244 µg, 757 nmol) were dissolved in 560 µL of CD_2Cl_2 to furnish a clear pink solution. The sample was submitted for NMR measurement. Data were in close agreement with those reported.[9] **Yield:** Quantitative (by NMR). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 10.16 (s, 2H, r-H), 9.36 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.88 (d, ^3J = 4.6 Hz, 4H, β2-H), 7.44 (d, ^3J = 8.2 Hz, 2H, a-H), 7.33 (s, 4H, s-H), 7.14-7.07 (m, 3H, d-,e-H), 6.70-6.67 (m, 2H, c-H), 6.41 (d, ^3J = 8.2 Hz, 2H, b-H), 2.66 (s, 6H, u-H), 2.59 (s, 2H, i/h-H), 2.57 (s, 2H, h/i-H) 1.80 (s, 12H, t-H) ppm.

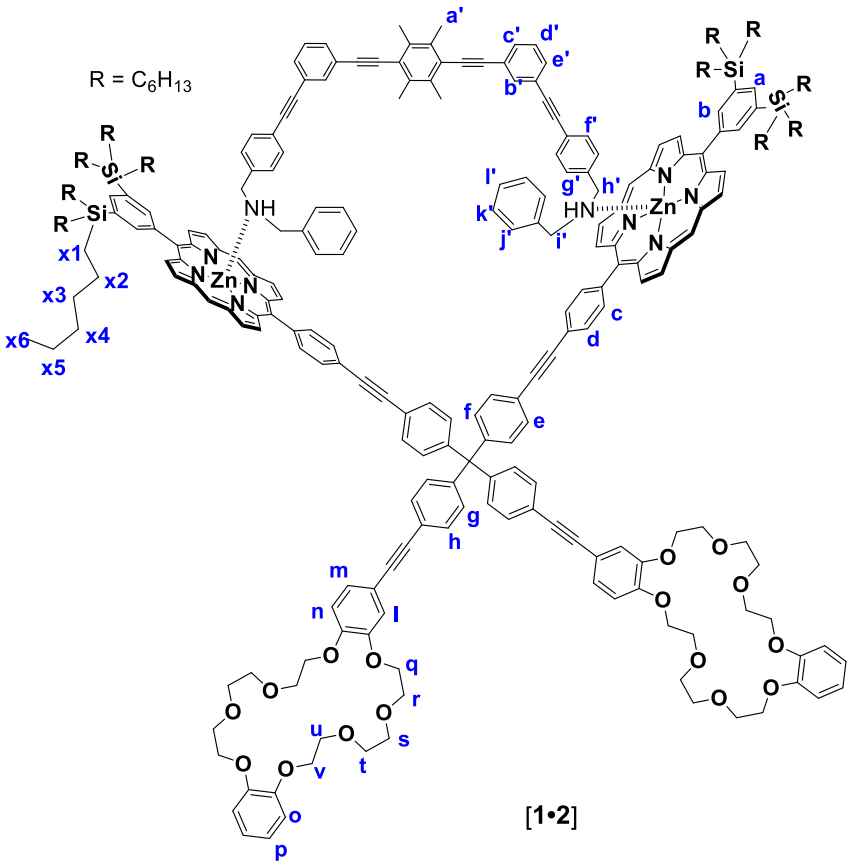
Model complex **C1**[10]



C1

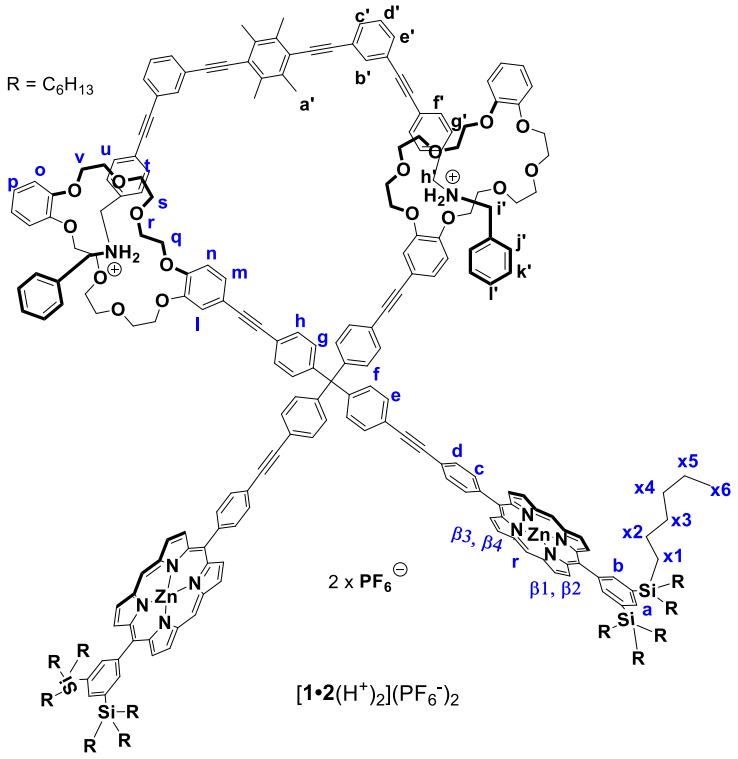
In an NMR tube, crown ether **DB24C8** (339 μg, 756 nmol) and [**12**•$(H)_2$]PF_6 (355 μg, 756 nmol) were dissolved in 50 μL of CD_3CN to obtain a clear solution. The solution was then evaporated to dryness using a stream of dry N_2 gas. The resultant residue was dissolved in 560 μL of CD_2Cl_2 and submitted for NMR measurement. Data were in close agreement with those reported.[10] **Yield:** Quantitative (by NMR). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.42 (d, ^3J = 8.2 Hz, 2H, b-H), 7.34-7.25 (m, 5H, d-,e-H), 7.00 (d, ^3J = 8.2 Hz, 2H, a-H), 6.91-6.89 (m, 4H, o-,p-H), 6.77-6.75 (m, 4H, o-,p-H), 4.64-4.61 (m, 2H, h-H), 4.59-4.56 (m, 2H, i-H), 4.09-4.04 (m, 8H, j-H), 3.76-3.74 (m, 8H, k-H), 3.52-3.43 (m, 8H, l-H) ppm.

Complex [1•2]



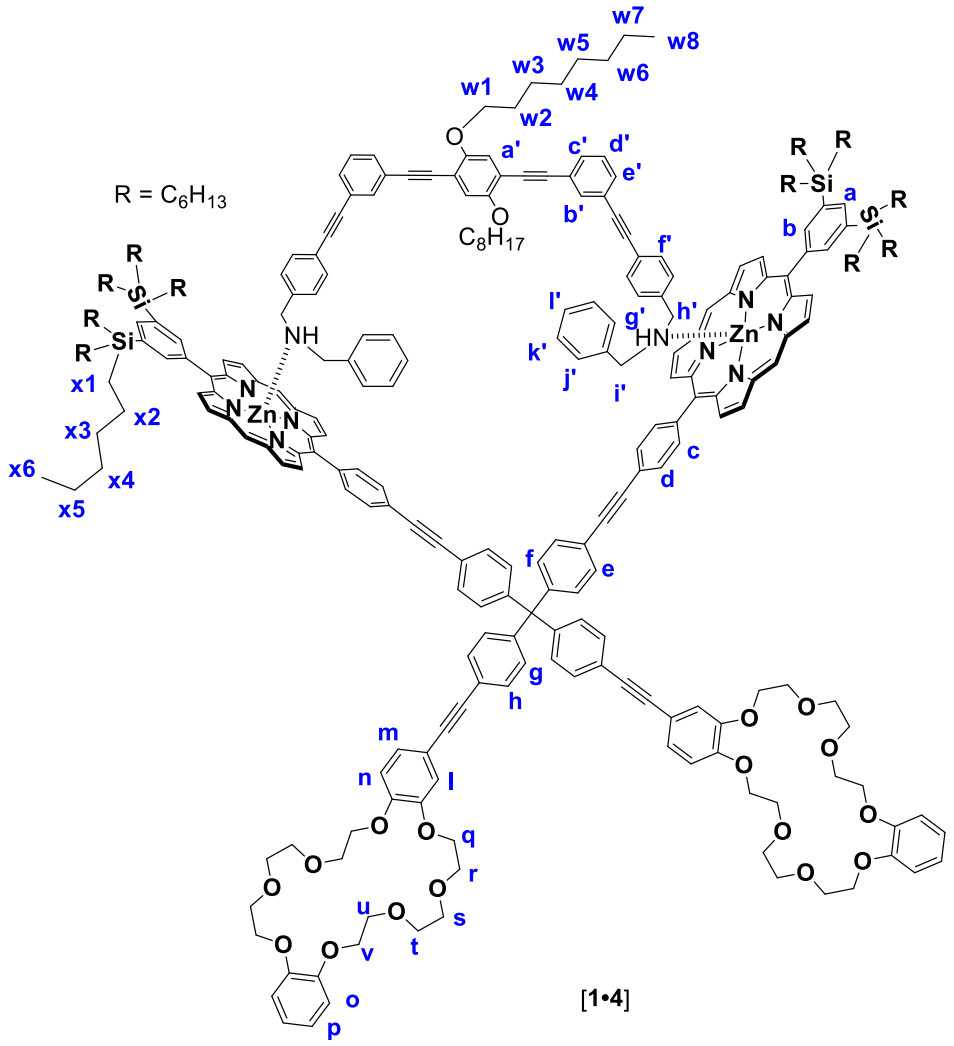
In an NMR tube, compounds **1** (616 µg, 176 µmol) and **2** (136 µg, 0.176 µmol) were dissolved in 560 µL of CD_2Cl_2 furnishing a dark pink solution. The sample was submitted for NMR measurement. **Yield:** Quantitative (by NMR). **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.37 (s, 4H, r-H), 9.50 (d, ^3J = 4.6 Hz, 4H, β3-H), 9.46 (d, ^3J = 4.6 Hz, 4H, β2-H), 9.17 (d, ^3J = 4.6 Hz, 4H, β4-H), 9.14 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.36 (s, 4H, b-H), 8.27 (d, ^3J = 8.2 Hz, 4H, c-H), 8.06 (s, 2H, a-H), 8.01 (d, ^3J = 8.2 Hz, 4H, d-H), 7.70 (m, 6H, e-, b'-H), 7.55 (d, ^3J = 8.6 Hz, 4H, f/g-H), 7.52 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, c'/e'-H), 7.48 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, e'/c'-H), 7.42-7.35 (m, 10H, g/f-, d'-, h-H), 7.31 (brd, ^3J = 8.0 Hz, 4H, f'-H), 7.16-7.11 (m, 8H, m-, k'-, l'-H), 7.08 (d, ^3J = 2.0 Hz, 2H, l-H), 6.89-6.85 (m, 10H, o-, p-, n-H), 6.70 (brs, 4H, j'-H), 6.63 (brs, 4H, g'-H), 4.14-4.09 (m, 16H, q-, v-H), 4.03 (t, ^3J = 6.5 Hz, 4H, w1-H), 3.86-3.82 (m, 16H, r-, u-H), 3.74 (s, 16H, s-, t-H), 2.51 (s, 12H, a'-H), 2.49 (s, 4H, i'/h'-H), 2.47 (s, 4H, h'/i'-H), 0.94-1.88 (m, 120H, (x1-x5)-H), 0.87 (t, ^3J = 6.4 Hz, 36H, x6-H) ppm. **Elemental analysis** ($C_{275}H_{316}N_{10}O_{16}Si_4Zn_2$•3.5$H_2O$•4$CH_2Cl_2$): Calcd. C, 71.86; H, 7.15; N, 3.00. Found, C, 71.56; H, 7.31; N, 3.06.

Complex [**1**•**2**$(H^+)_2$]$(PF_6^-)_2$



Compounds **1** (0.476 µg, 0.134 µmol) and [**1**•**2**$(H^+)_2$]$(PF_6^-)_2$ (143 µg, 0.134 µmol) were dissolved in 50 µL of CD_3CN:CD_2Cl_2 (1:1). This solution was evaporated to dryness using a stream of dry N_2 gas and the pink residue was then redissolved in 560 µL of CD_2Cl_2 furnishing a clear, pink solution. The sample was submitted for NMR measurement. **Yield:** Quantitative (by NMR). **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.40 (s, 4H, r-H), 9.52 (d, ^3J = 4.6 Hz, 4H, β3-H), 9.48 (d, ^3J = 4.6 Hz, 4H, β2-H), 9.18 (d, ^3J = 4.6 Hz, 4H, β4-H), 9.15 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.35 (s, 4H, b-H), 8.31 (d, ^3J = 8.2 Hz, 4H, c-H), 8.07 (s, 2H, a-H), 8.02 (d, ^3J = 8.2 Hz, 4H, d-H), 7.82 (s, 2H, b'-H), 7.73-7.68 (m, 4H, e-H), 7.65 (d, ^3J = 7.8 Hz, 2H, e'/c'-H), 7.62 (d, ^3J = 7.8 Hz, 2H, c'/e'-H), 7.58 (d, ^3J = 8.6 Hz, 4H, f/g-H), 7.54-7.48 (m, 10H, g'-, d'-, j'-H), 7.43-7.38 (m, 8H, g/f-, k'-H), 7.35-7.28 (m, 6H, h-,l'-H), 7.21 (d, ^3J = 8.0 Hz, 4H, f'-H), 7.16 (d, ^3J = 8.5 Hz, 2H, m-H), 7.00 (s, 2H, l-H), 6.93-6.70 (m, 10H, o-, p-, n-H), 4.74 (brs, 8H, i'-, h'-H), 4.14-3.43 (m, 48H, q-, v-, r-, u-, s-, t-H), 2.56 (s, 6H, a'-H), 2.55 (s, 6H, a'-H), 0.94-1.88 (m, 120H, (x1-x5)-H), 0.87 (t, ^3J = 6.4 Hz, 36H, x6-H) ppm. **ESI-MS:** *m/z* (%) = 2162.1 (100) [**1**•**2**•$(H)_2$•$(CH_3OH)_2$]$^{2+}$. **Elemental analysis** ($C_{275}H_{318}F_{12}N_{10}O_{16}P_2Si_4Zn_2$•$3CH_2Cl_2$•$3.5H_2O$): Calcd. C, 68.56; H, 6.85; N, 2.88. Found, C, 68.84; H, 6.70; N, 2.49.

Complex [1•4]



In an NMR tube, compounds **1** (621 µg, 178 nmol) and **4** (172 µg, 178 nmol) were dissolved in 560 µL of CD_2Cl_2 furnishing a dark pink solution. The sample was submitted for NMR measurement. **Yield:** Quantitative (by NMR). **^{1}H NMR (500 MHz, CD_2Cl_2):** δ 10.37 (s, 4H, r-H), 9.50 (d, ^3J = 4.6 Hz, 4H, β3-H), 9.46 (d, ^3J = 4.6 Hz, 4H, β2-H), 9.17 (d, ^3J = 4.6 Hz, 4H, β4-H), 9.14 (d, ^3J = 4.6 Hz, 4H, β1-H), 8.36 (d, ^4J = 1.0 Hz, 4H, b-H), 8.27 (d, ^3J = 8.2 Hz, 4H, c-H), 8.06 (s, 2H, a-H), 8.01 (d, ^3J = 8.2 Hz, 4H, d-H), 7.70 (d, ^3J = 8.6 Hz, 4H, e-H), 7.68 (t, ^3J = 1.6 Hz, 2H, b'-H), 7.55 (d, ^3J = 8.6 Hz, 4H, f/g-H), 7.49 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, c'/e'-H), 7.48 (td, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, e'/c'-H), 7.41 (d, ^3J = 8.6 Hz, 4H, g/f-H), 7.37-7.34 (m, 6H, d'-, f'-H), 7.29 (d, ^3J = 8.6 Hz, 4H, h-H), 7.15 (dd, ^3J = 8.6 Hz, ^4J = 2.0 Hz, 2H, m-H), 7.12-7.09 (m, 6H, k'-, l'-H), 7.08 (d, ^3J = 2.0 Hz, 2H, l-H), 7.03 (s, 2H, a'-H), 6.89-6.85 (m, 10H, o-, p-, n-H),

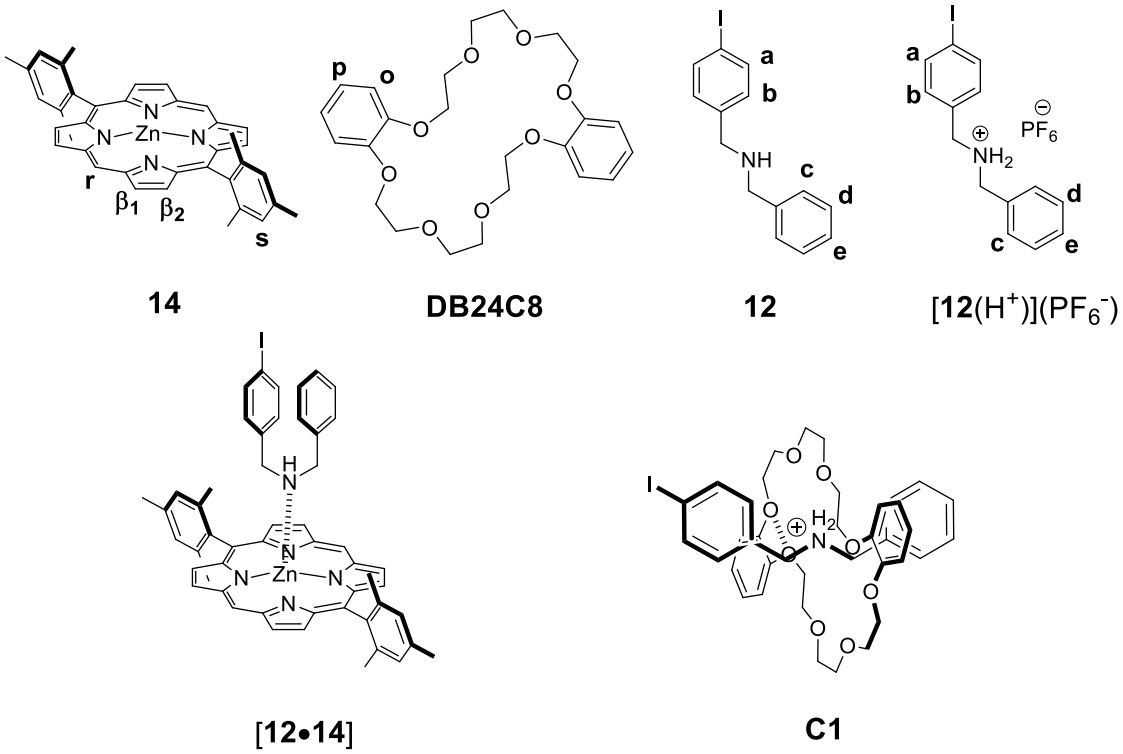
6.65 (brd, ^{3}J = 7.2 Hz, 4H, j'-H), 6.58 (brd, ^{3}J = 7.2 Hz, 4H, g'-H), 4.14-4.09 (m, 16H, q-, v-H), 4.03 (t, ^{3}J = 6.5 Hz, 4H, w1-H), 3.86-3.82 (m, 16H, r-, u-H), 3.74 (s, 16H, s-, t-H), 2.54 (s, 4H, i'/h'-H), 2.44 (s, 4H, h'/i'-H), 1.88-0.86 (m, 144H, (x1-x5)-H, (w2-w7)-H), 0.87 (t, ^{3}J = 6.4 Hz, 36H, x6-H), 0.83 (t, ^{3}J = 6.5 Hz, 6H, w8-H) ppm. **Elemental analysis** ($C_{287}H_{340}N_{10}O_{18}Si_4Zn_2$•2.5 H_2O•5CH_2Cl_2): Calcd. C, 71.13; H, 7.26; N, 2.84. Found, C, 70.92; H, 7.02; N, 2.95.

3. Model studies

Firstly, self-sorting was tested by mixing ligands **12, DB24C8** and **14** in a 1:1:1 molar ratio in CD_2Cl_2 at 298 K. The ^{1}H-NMR spectrum measured subsequently was compared with those of the ligand **12** (Fig. S2e), mixture of free **14**, **DB24C8** (Fig. S2f) and [**12•14**] (Fig. S2d), which indicated quantitative formation of [**12•14**] and free **DB24C8** (Fig. S2c)**.**

Secondly, ligands **14, DB24C8** and [**12**(H^+)](PF_6^-) were mixed in a 1:1:1 molar ratio in CD_2Cl_2 at 298 K. The ^{1}H-NMR spectrum when compared with that of the mixture containing the free ligands **DB24C8**, **14** and complex **C1** (Fig. S2a) indicated the quantitative formation of complex **C1** and free **14** (Fig. S2b).

The study confirms the orthogonality of the NH_{Amine}→ZnPor and the ammonium ⊂ crown ether pseudo-rotaxane interactions.



Scheme S4: Ligands **12**, **14**, **DB24C8** and [**12**(H^+)](PF_6^-) and the resultant complexes [**12•14**] and **C1** formed in this model study.

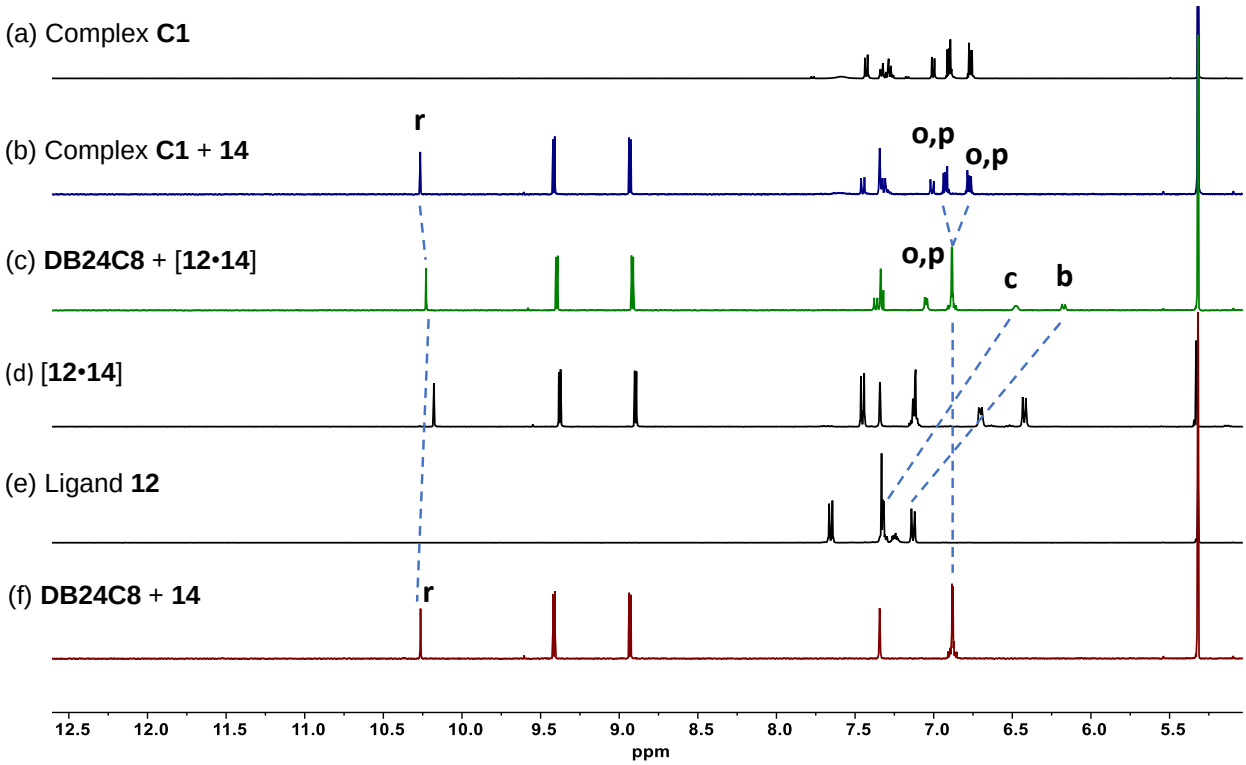


Figure S2: Comparison of ^{1}H-NMR spectra (CD_2Cl_2, 500MHz) of complex **C1**, the mixture **C1+14**, the mixture **DB24C8** + [**12•14**], complex [**12•14**], ligand **12**, and the mixture **14+DB24C8.**

4. NMR Spectra: ^{1}H, ^{13}C, ^{1}H-^{1}H COSY

Compound 7

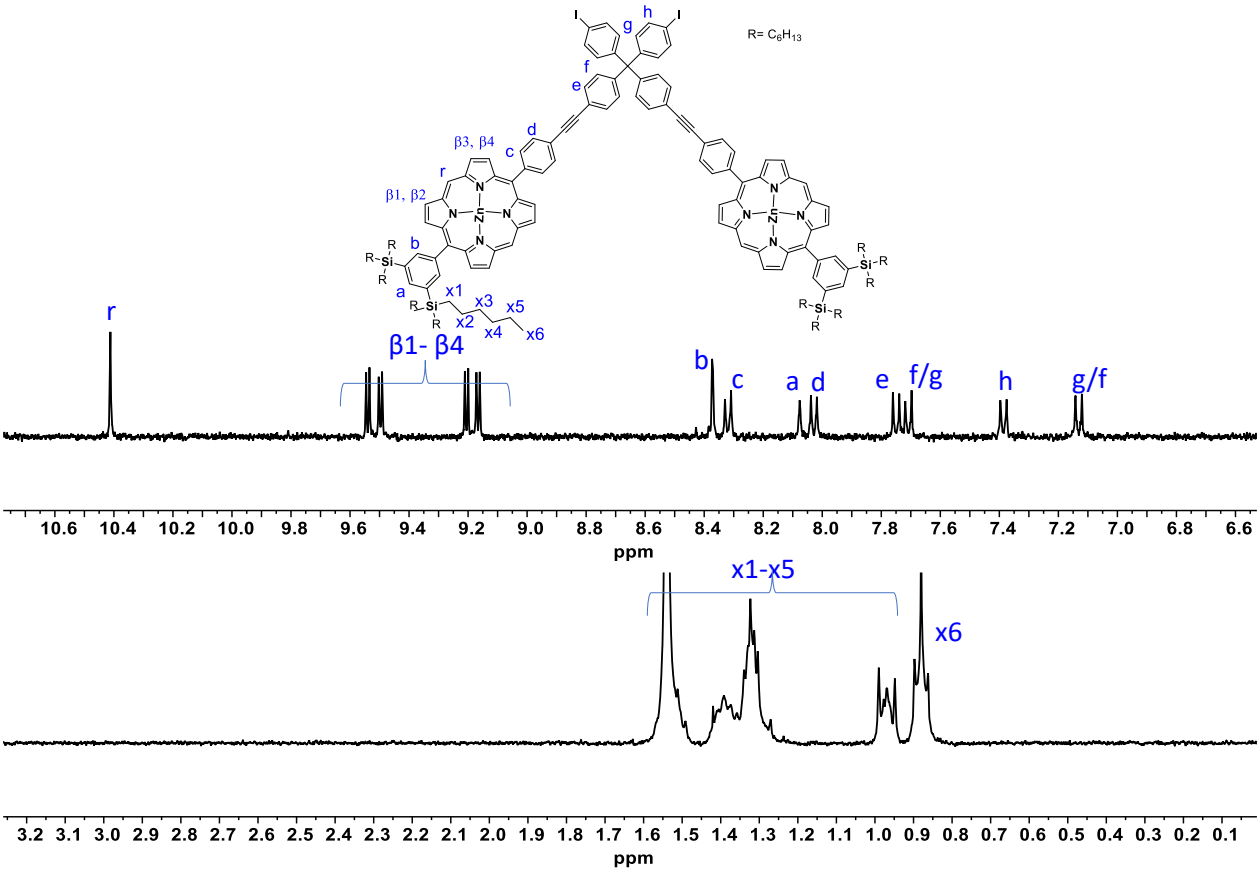


Figure S3 : ^{1}H-NMR spectrum of compound **7** (CD_2Cl_2, 500 MHz, 298 K).

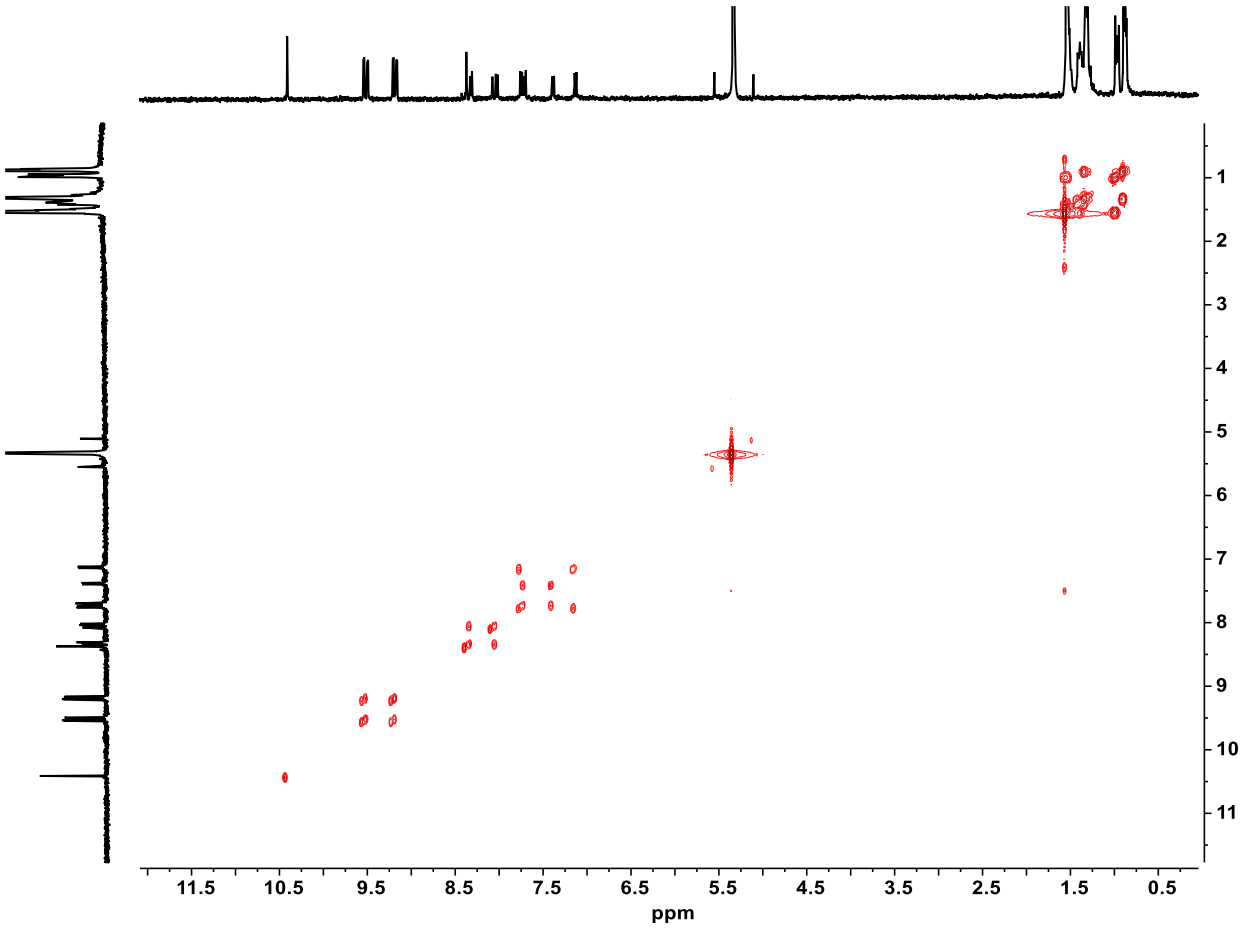


Figure S4: ^{1}H-^{1}H COSY spectrum of compound **7** (CD_2Cl_2, 400 MHz, 298 K).

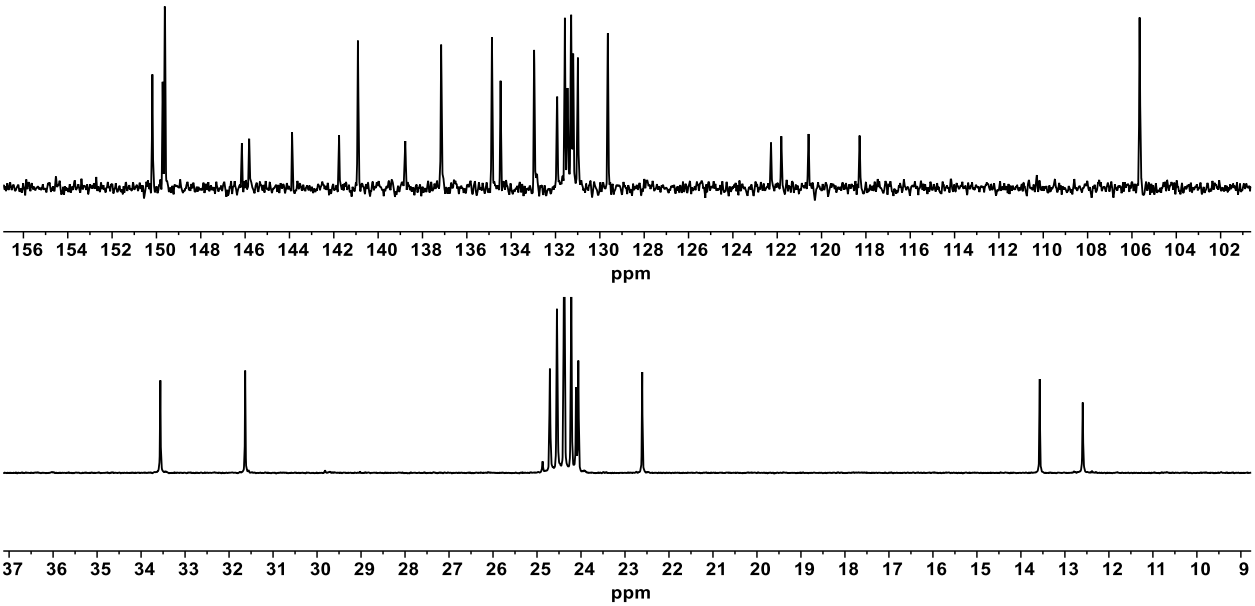


Figure S5: ^{13}C spectrum of compound **7** (THF-d_8, 125 MHz, 298 K).

Compound 1

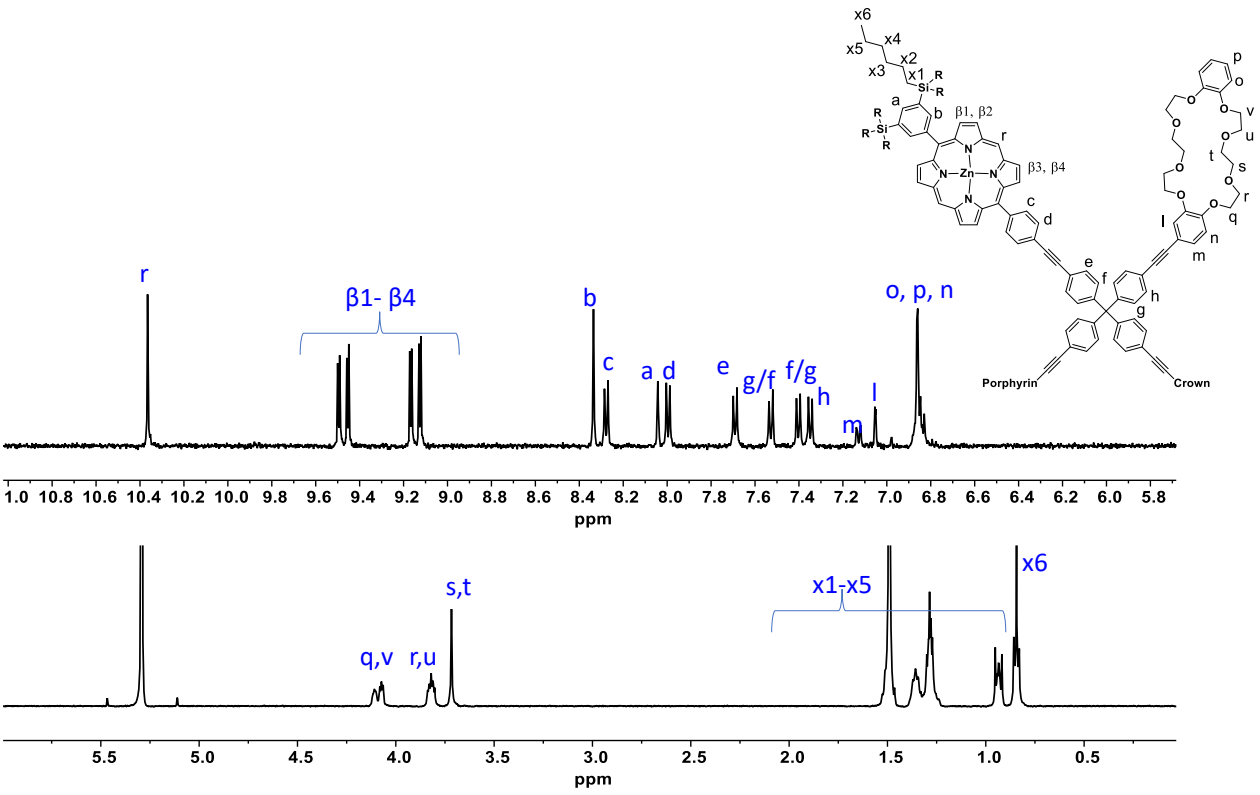


Figure S6: ^{1}H-NMR spectrum of compound **1** (CD_2Cl_2, 500 MHz, 298 K).

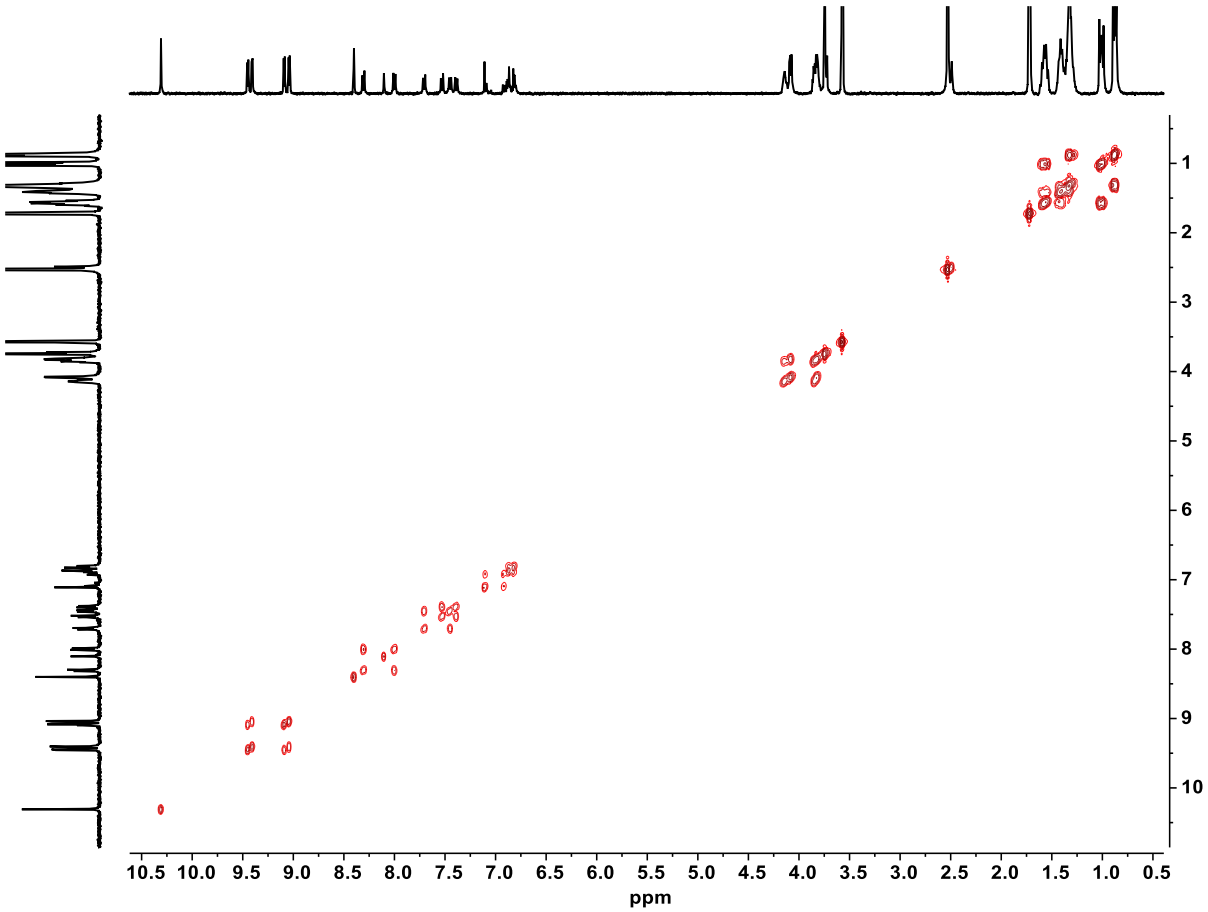


Figure S7: ^{1}H-^{1}H COSY spectrum of compound **1** (THF-d_8, 400 MHz, 298 K).

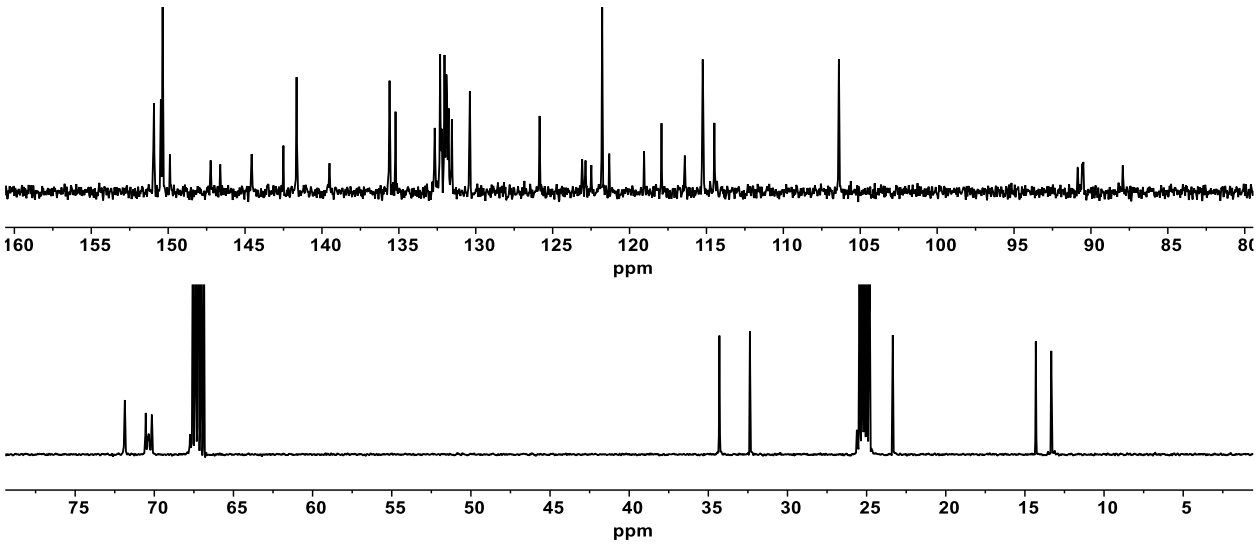


Figure S8: ^{13}C spectrum of compound **1** (THF-d_8, 125 MHz, 298 K).

Compound 2

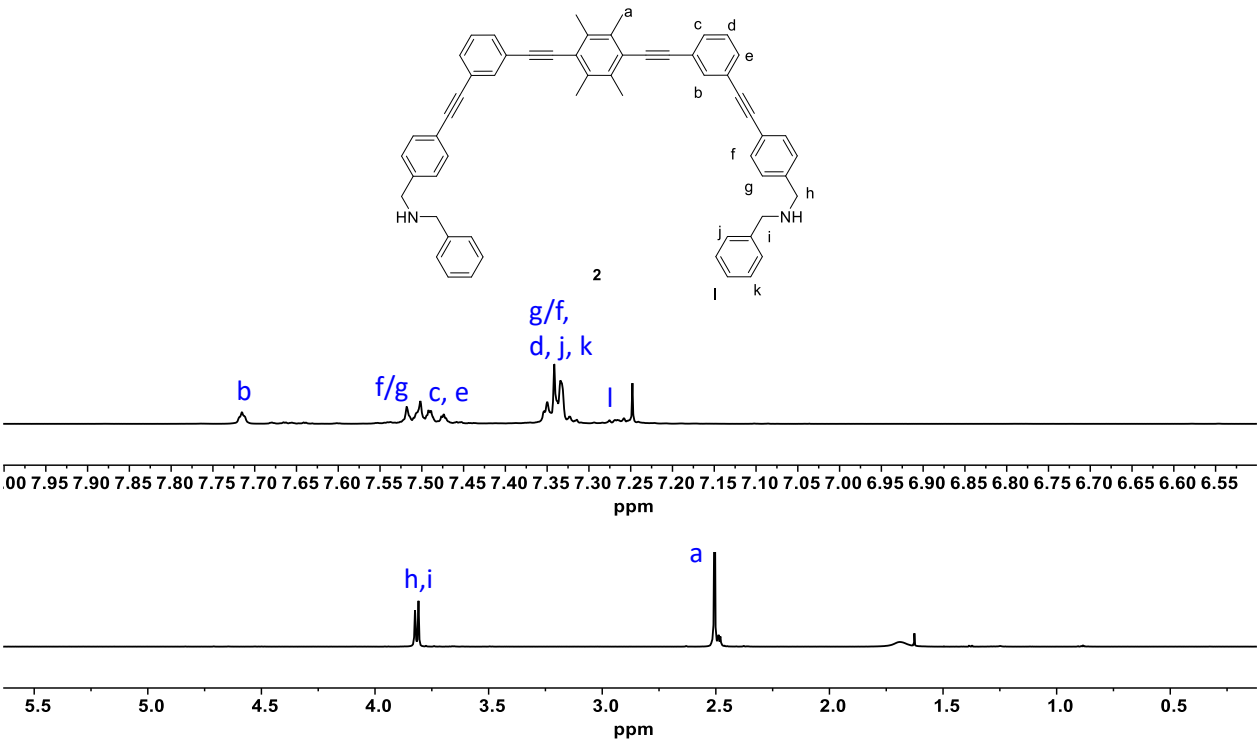


Figure S9: ^{1}H-NMR spectrum of compound **2** ($CDCl_3$, 500 MHz, 298 K).

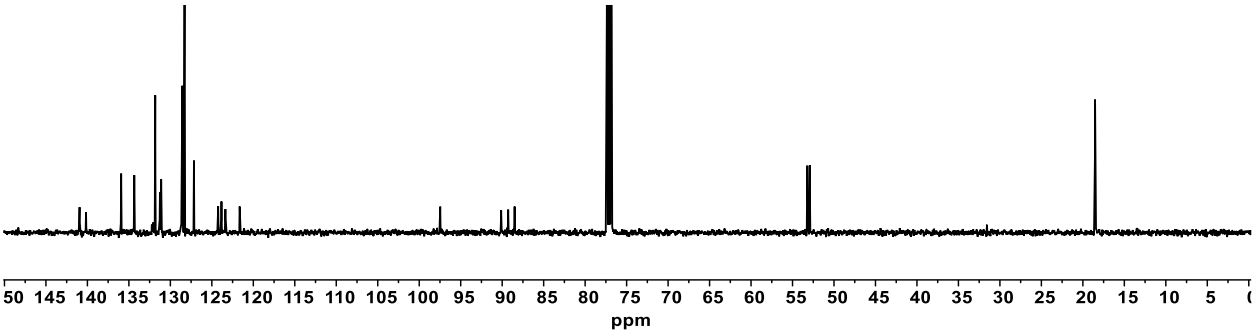


Figure S10: ^{13}C spectrum of compound **2** (CD_2Cl_2, 125 MHz, 298 K).

Compound $[\mathbf{2}(H^+)_2](PF_6^-)_2$

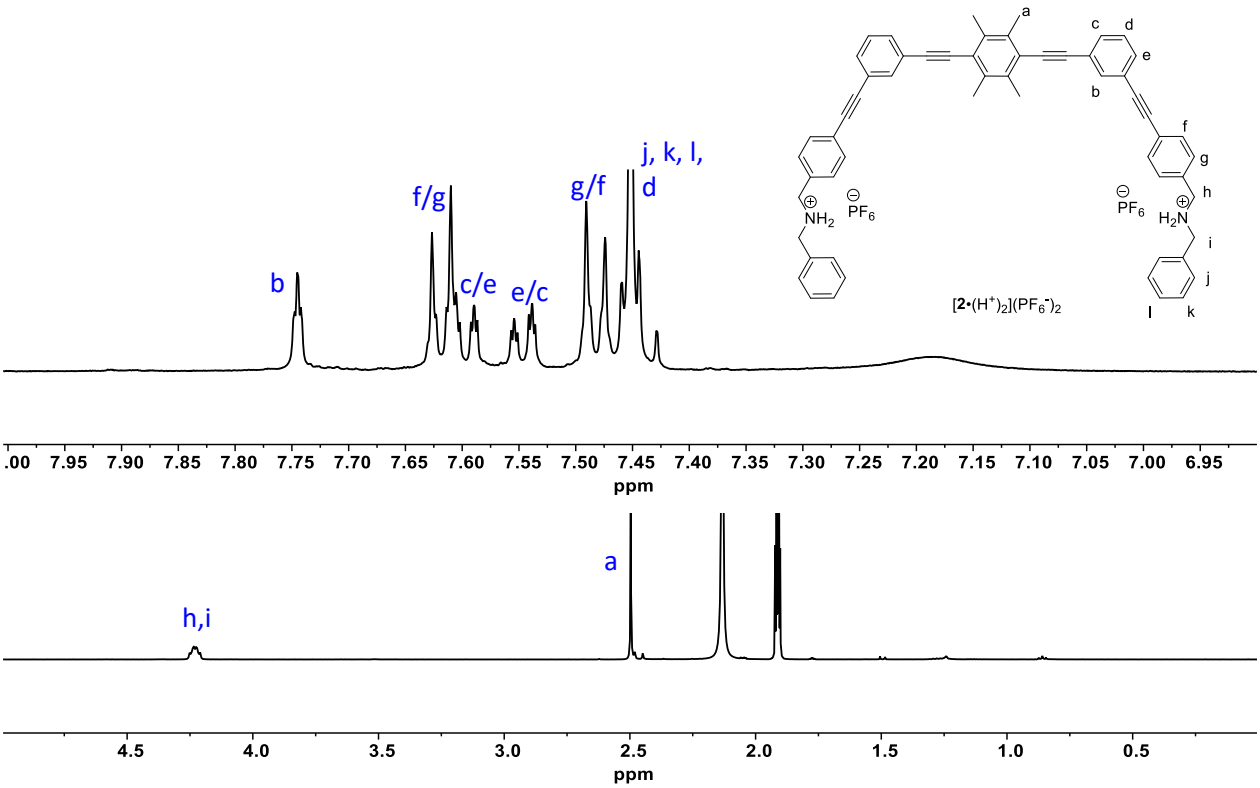


Figure S11: ^{1}H-NMR spectrum of compound $[\mathbf{2}(H^+)_2](PF_6^-)_2$ (CD_3CN, 500 MHz, 298 K).

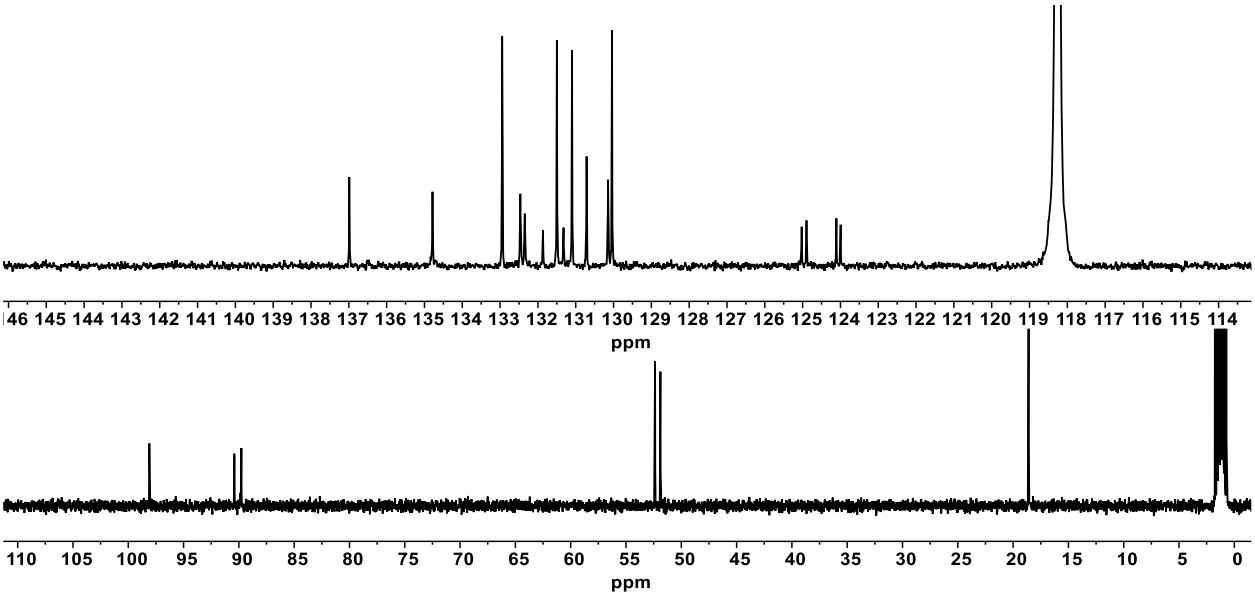


Figure S12: ^{13}C spectrum of compound $[\mathbf{2}(H^+)_2](PF_6^-)_2$ (CD_3CN, 125 MHz, 298 K)

Compound 4

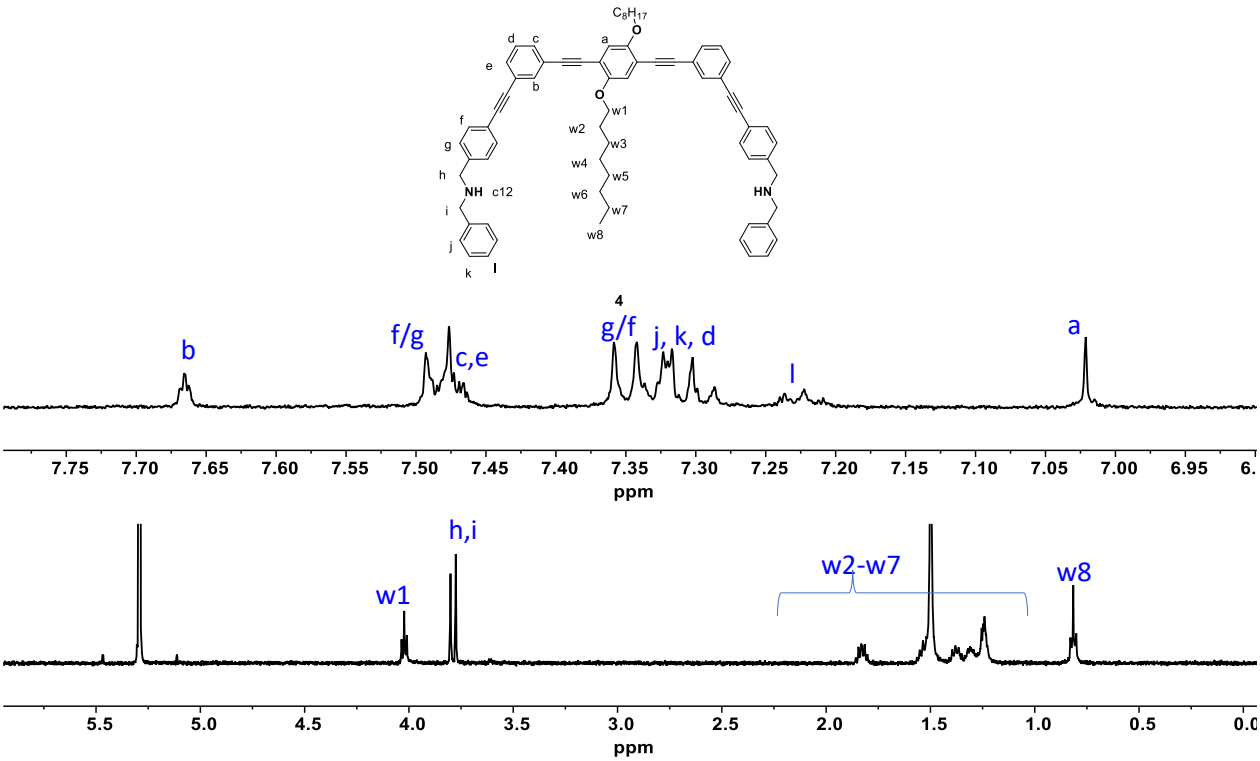


Figure S13: ^{1}H-NMR spectrum of compound **4** (CD_2Cl_2, 500 MHz, 298 K).

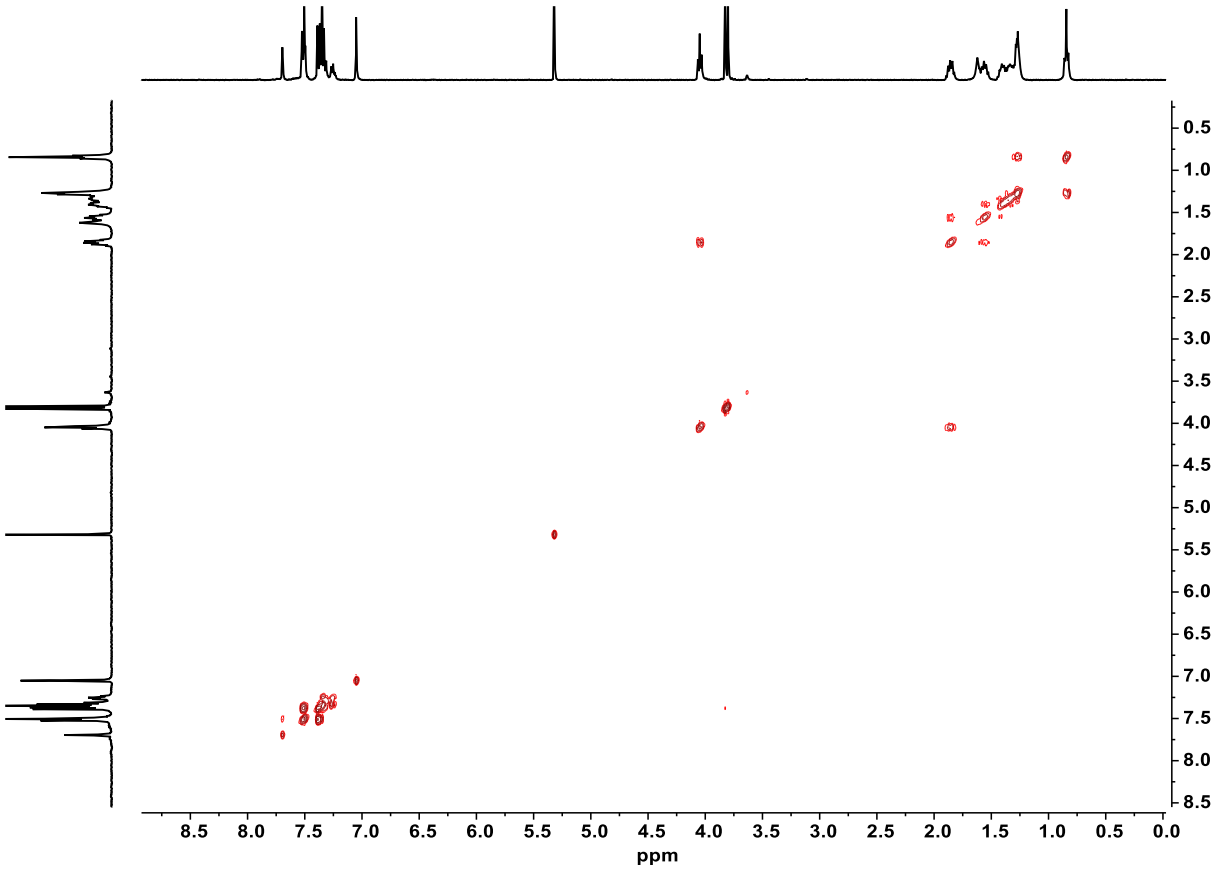


Figure S14: ^{1}H-^{1}H COSY spectrum of compound **4** (CD_2Cl_2, 400 MHz, 298 K).

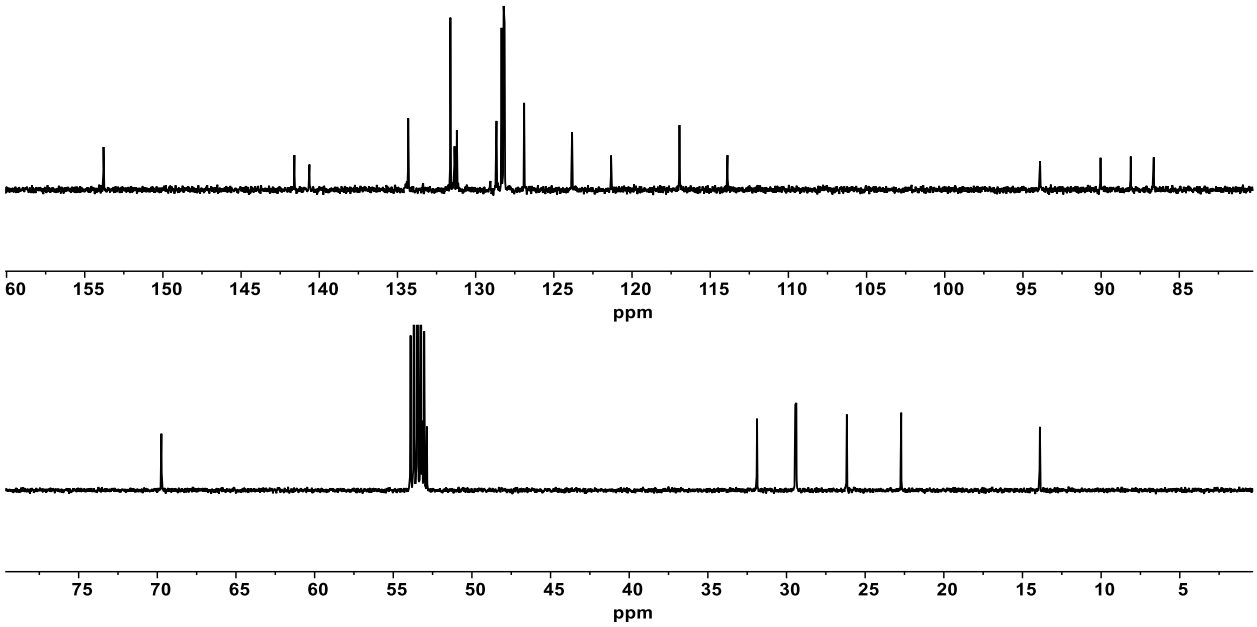


Figure S15: ^{13}C spectrum of compound **4** (CD_2Cl_2, 125 MHz, 298 K).

Compound 11

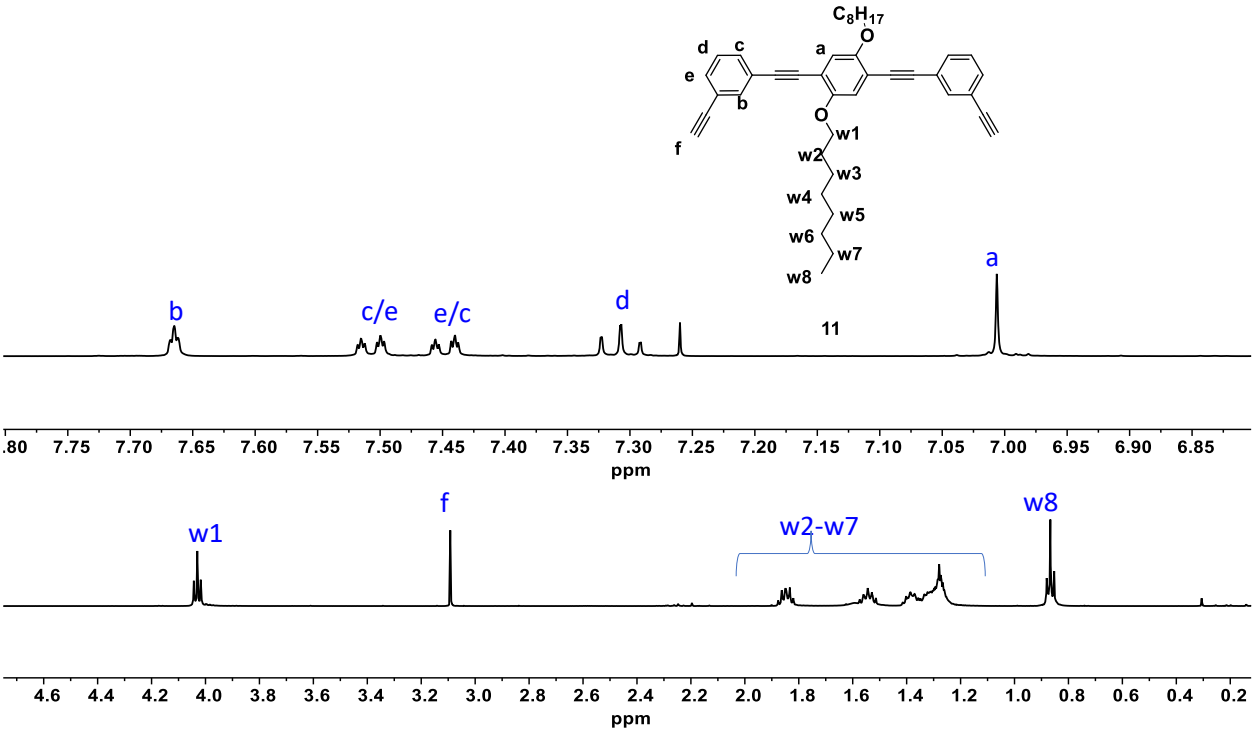


Figure S16: ^{1}H-NMR spectrum of compound **11** ($CDCl_3$, 500 MHz, 298 K)

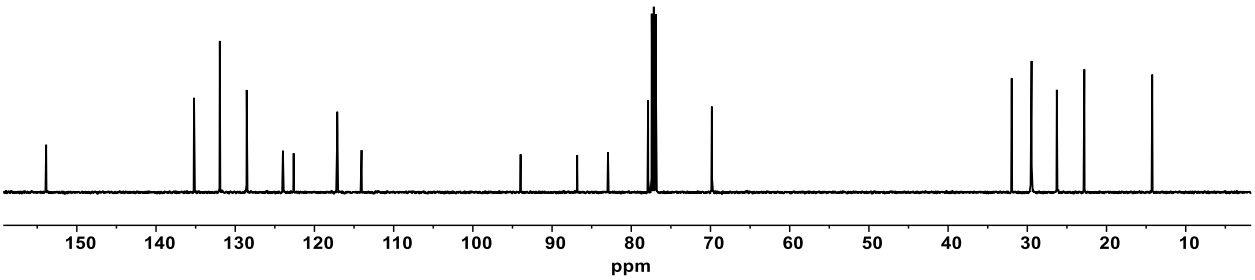


Figure S17: ^{13}C spectrum of compound **11** ($CDCl_3$, 125 MHz, 298 K)

Compound [**12**(H^+)](PF_6^-)

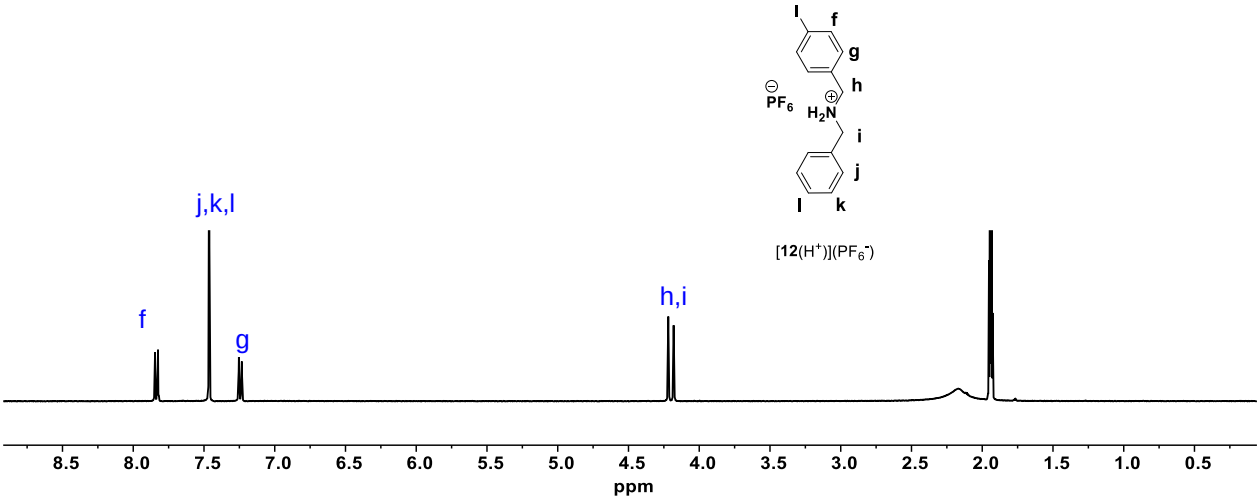


Figure S18: ^{1}H-NMR spectrum of compound [**12**(H^+)](PF_6^-) (CD_3CN, 500 MHz, 298 K).

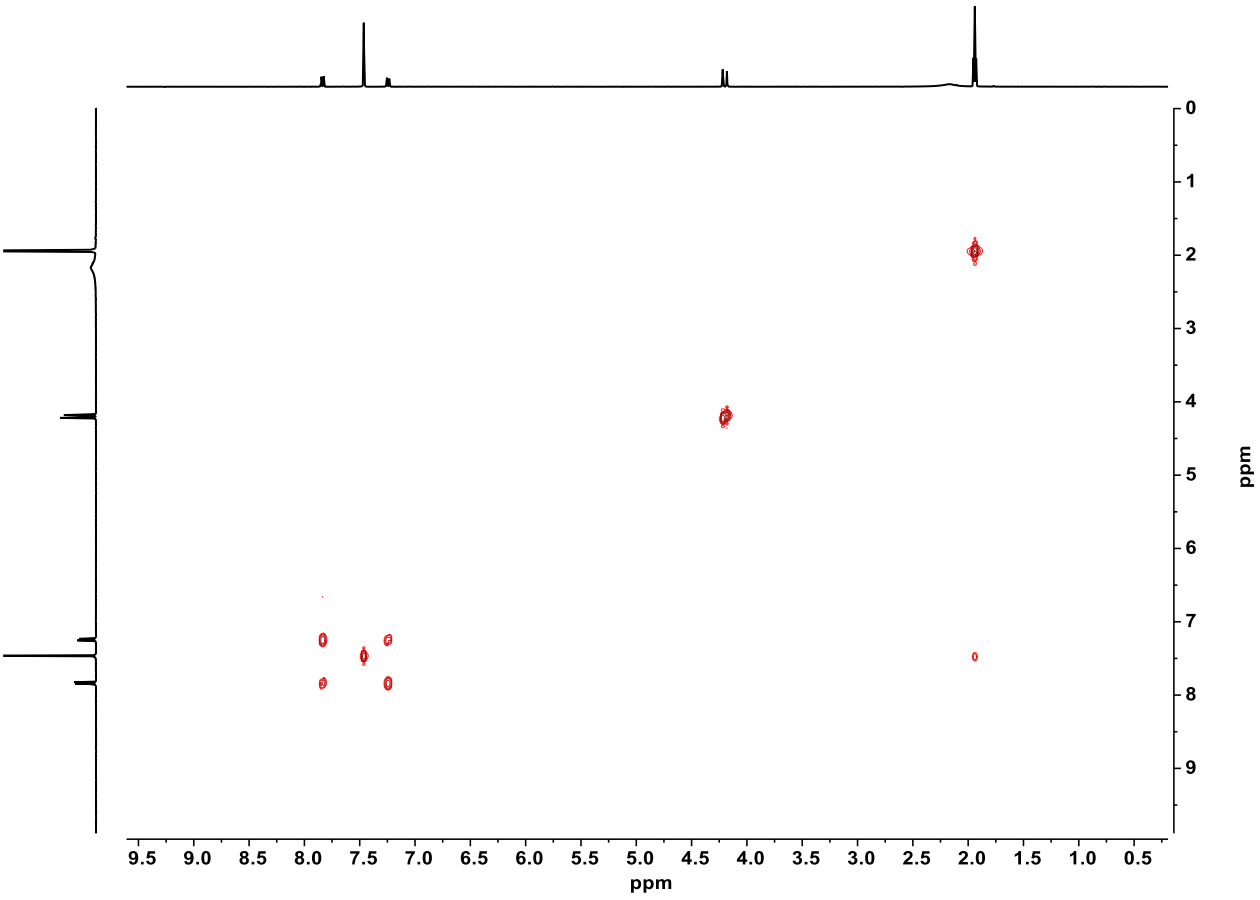


Figure S19: ^{1}H-^{1}H COSY spectrum of compound [**12**(H^+)](PF_6^-) (CD_3CN, 400 MHz, 298 K).

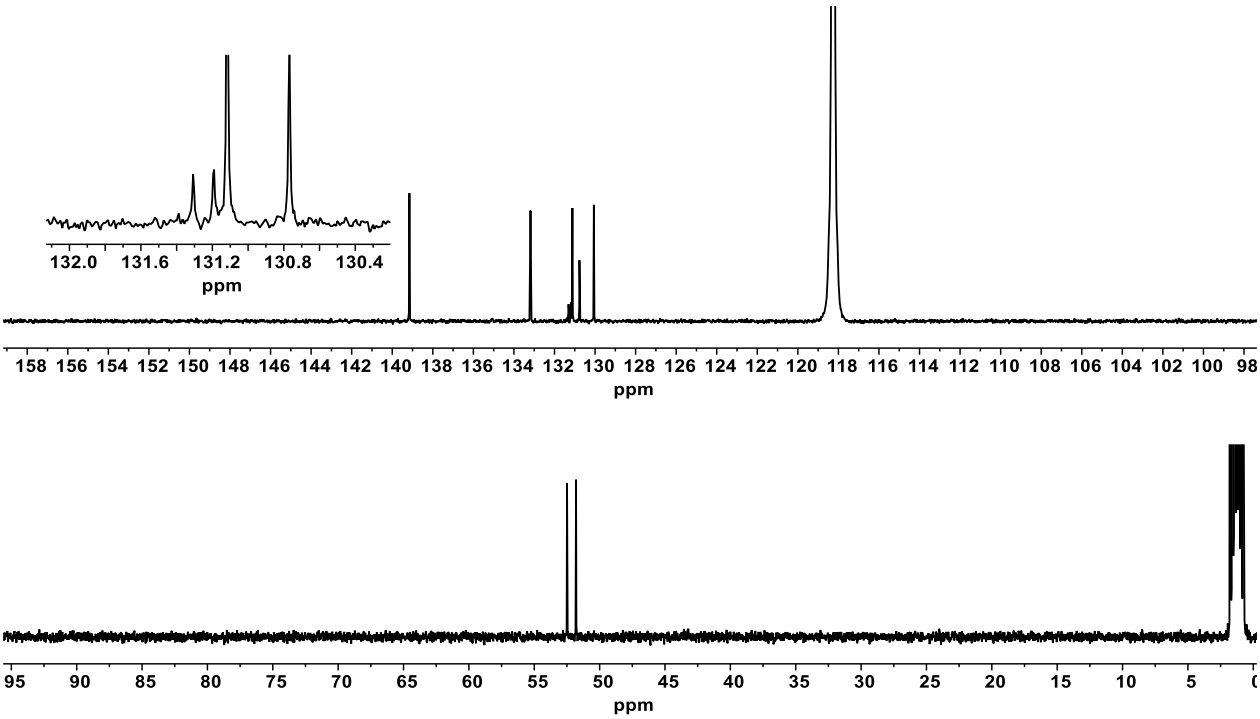


Figure S20: ^{13}C spectrum of compound [**12**(H^+)](PF_6^-) (CD_3CN, 125 MHz, 298 K).

Complex [1•2]

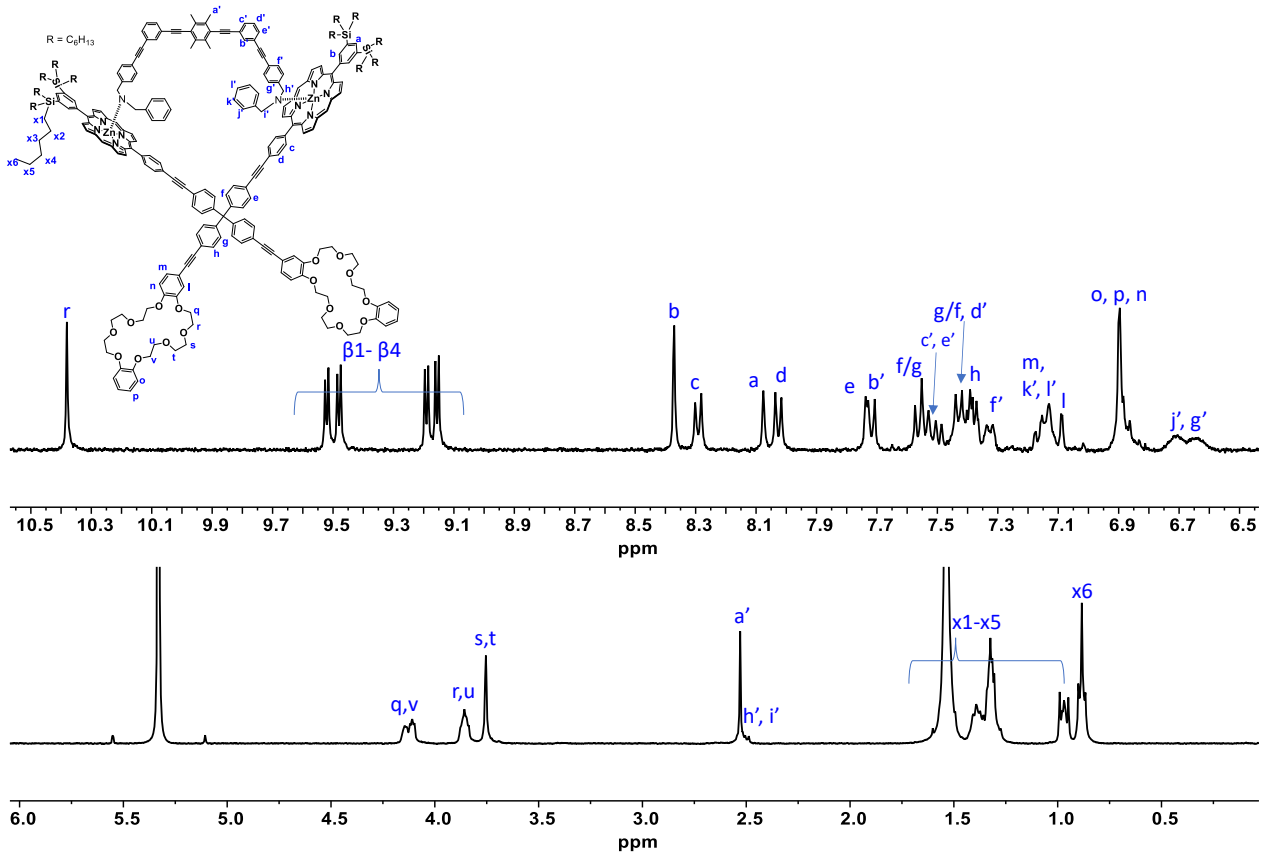


Figure S21: ^{1}H-NMR spectrum of complex [**1•2**] (CD_2Cl_2, 500 MHz, 298 K).

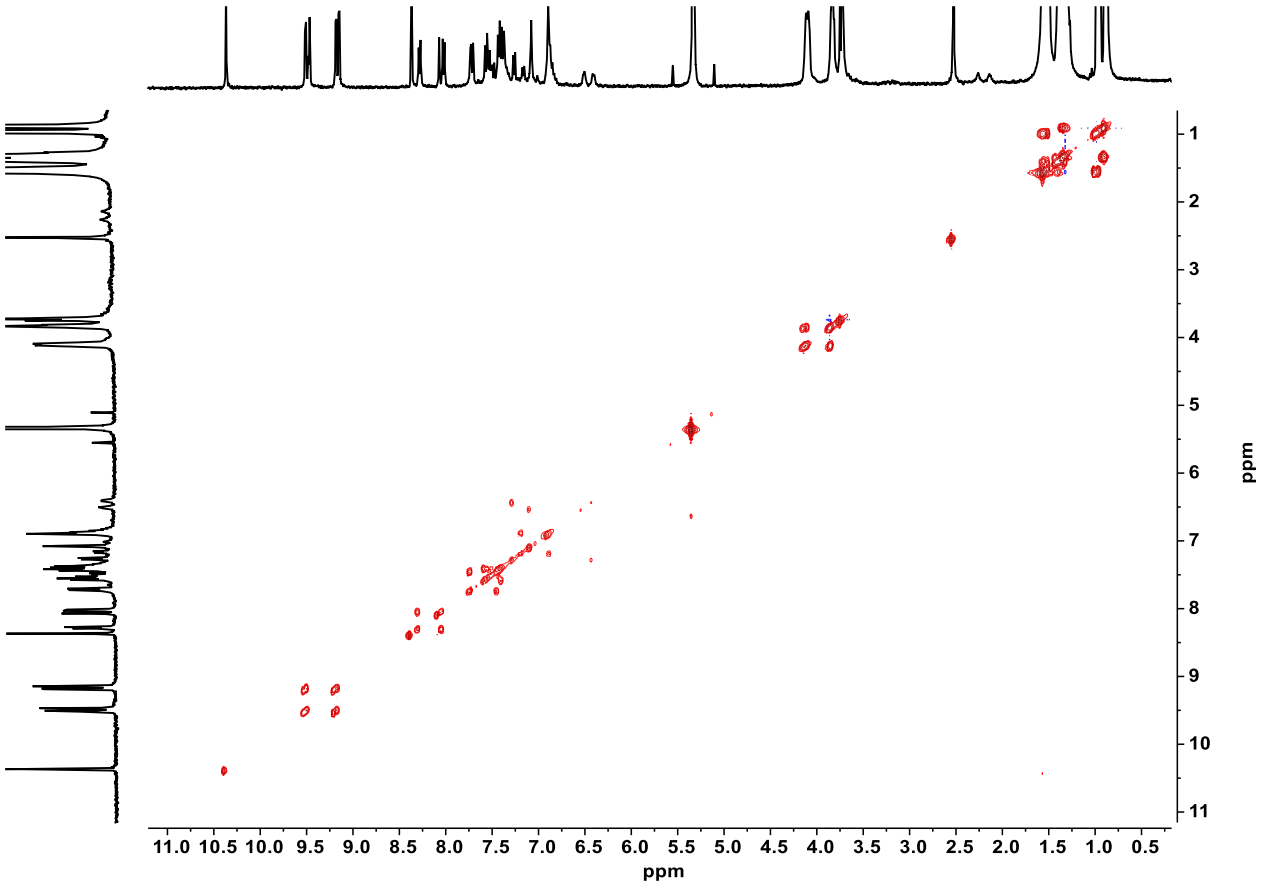


Figure S22: ^{1}H-^{1}H COSY spectrum of complex [**1•2**] (CD_2Cl_2, 400 MHz, 298 K).

Complex [**1•2**$(H^+)_2$]$(PF_6^-)_2$

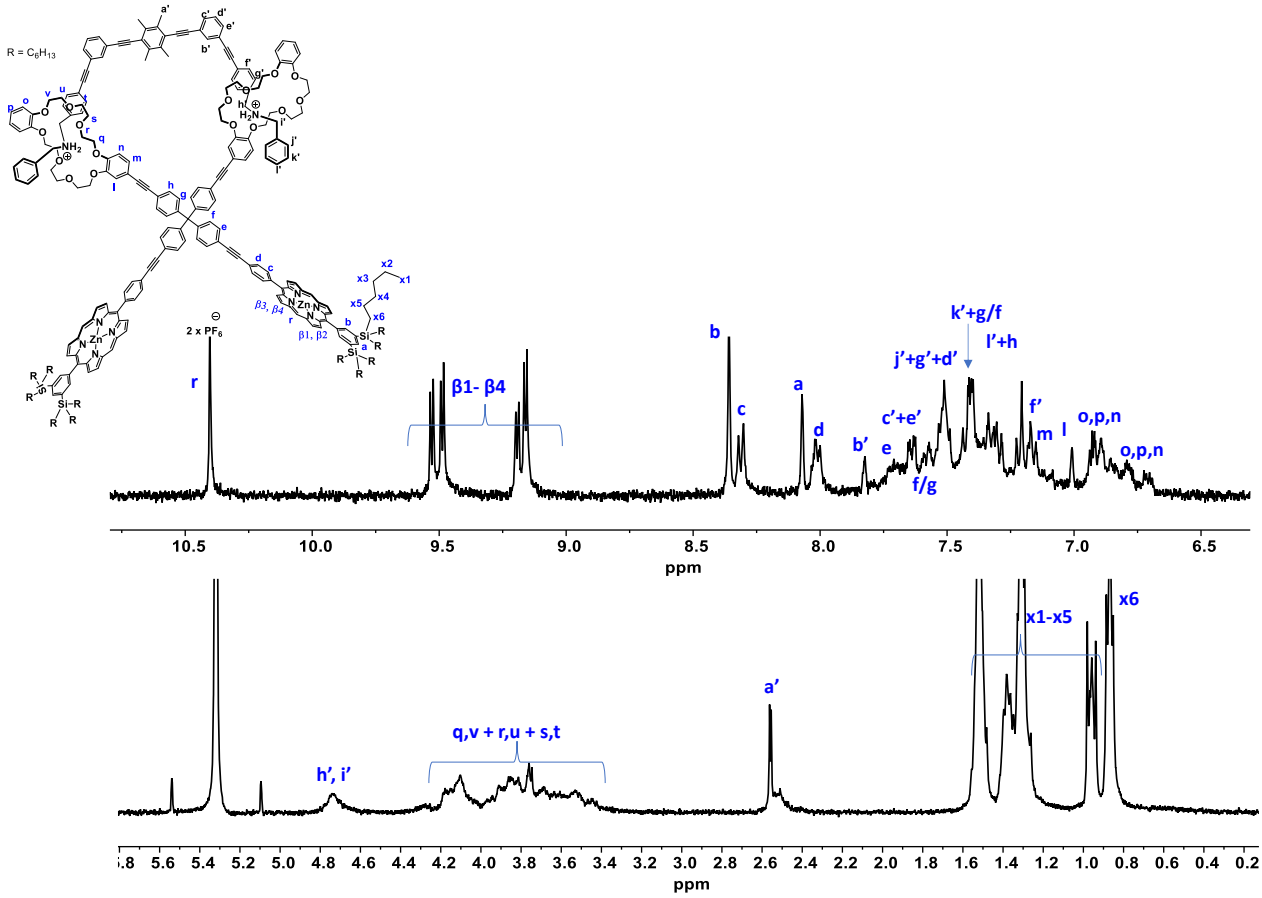


Figure S23: ^{1}H-NMR spectrum of complex [**1•2**$(H^+)_2$]$(PF_6^-)_2$ (CD_2Cl_2, 500 MHz, 298 K).

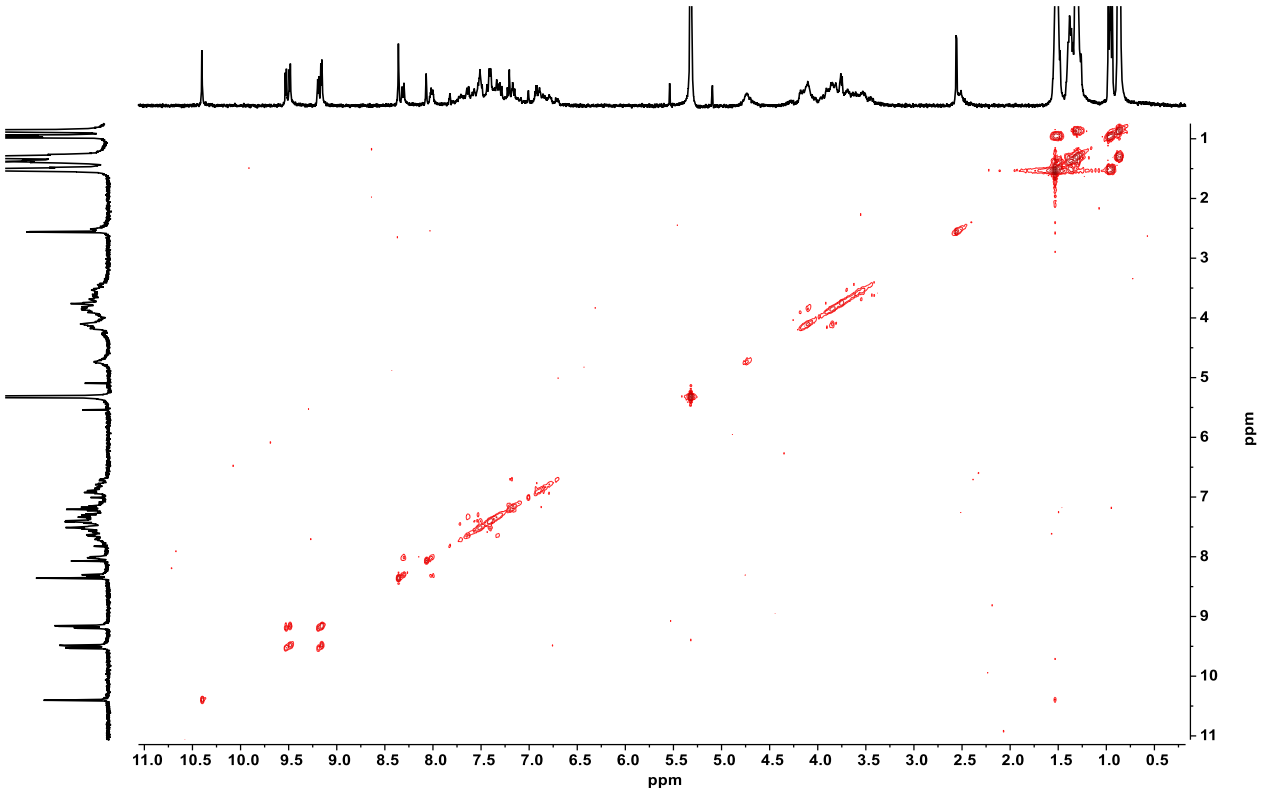


Figure S24: ^{1}H-^{1}H COSY spectrum of complex [**1•2**$(H^{+})_2$]$(PF_6^{-})_2$ (CD_2Cl_2, 400 MHz, 298 K).

Complex [1•4]

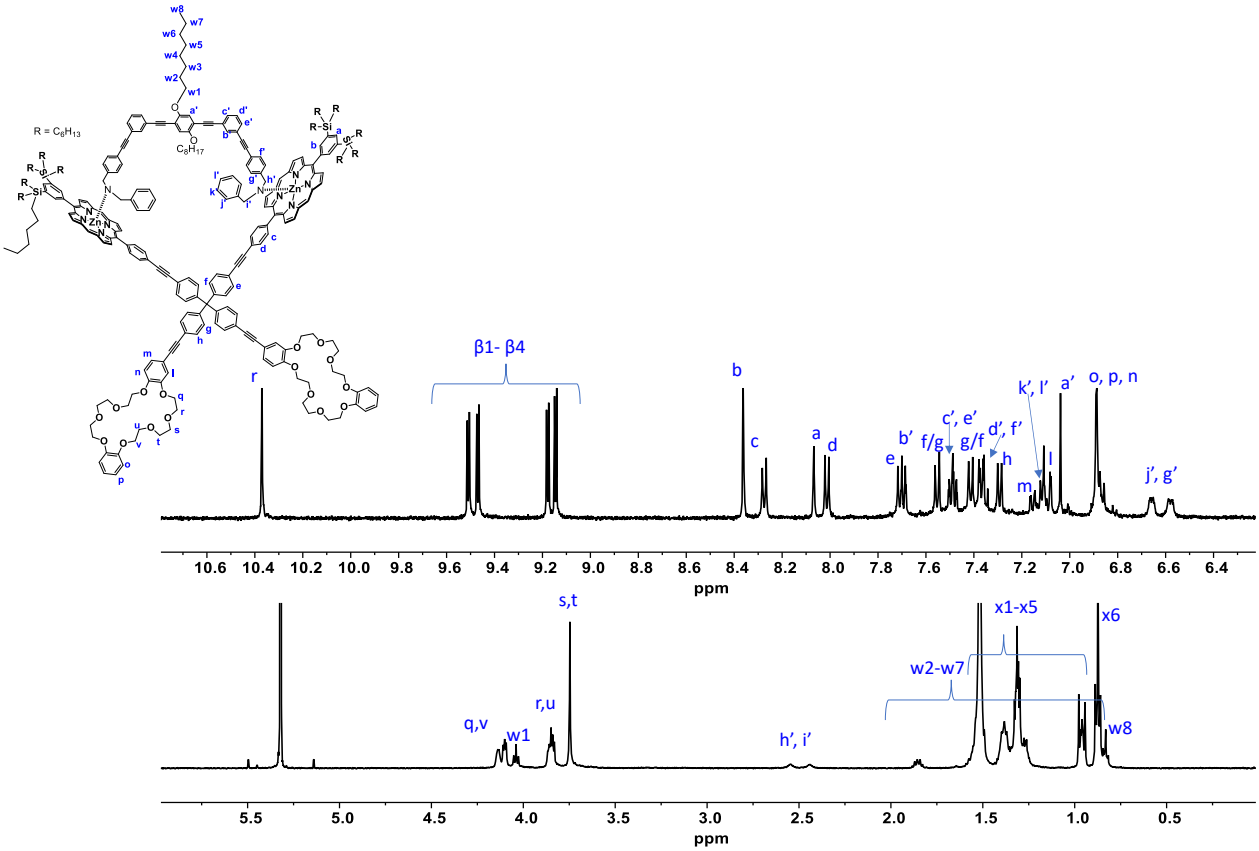


Figure S25: ^{1}H-NMR spectrum of complex [**1•4**] (CD_2Cl_2, 500 MHz, 298 K).

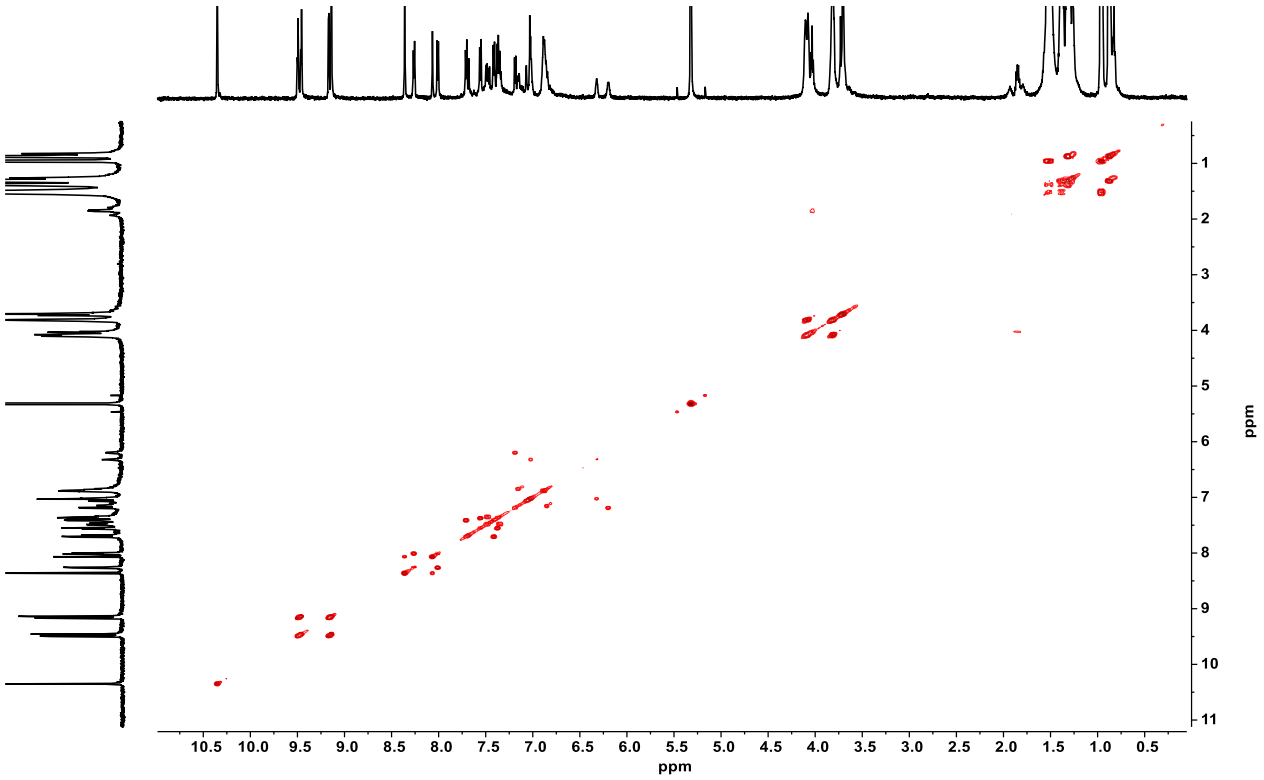


Figure S26: ^{1}H-^{1}H COSY spectrum of complex [**1•4**] (CD_2Cl_2, 600 MHz, 298 K).

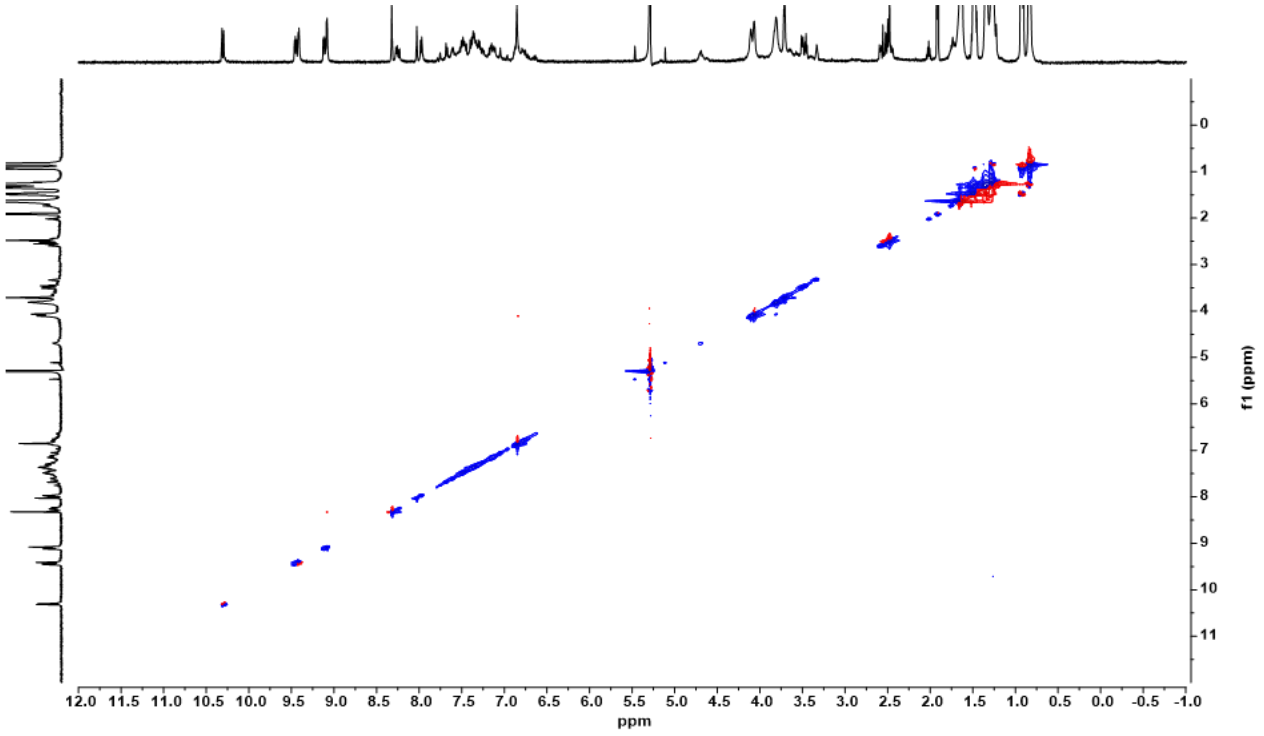


Figure S27: ^{1}H-^{1}H ROESY NMR spectrum of complex [**1•2**(H^+)] (CD_2Cl_2, 500 MHz, mixing time= 500 ms, 298 K) The complex [**1•2**(H^+)] was generated *in situ* by adding 1 eq DBU to [**1•2**(H^+)$_2$] and a ROESY-NMR was recorded for the sample.

5. ^{1}H-^{1}H DOSY NMR

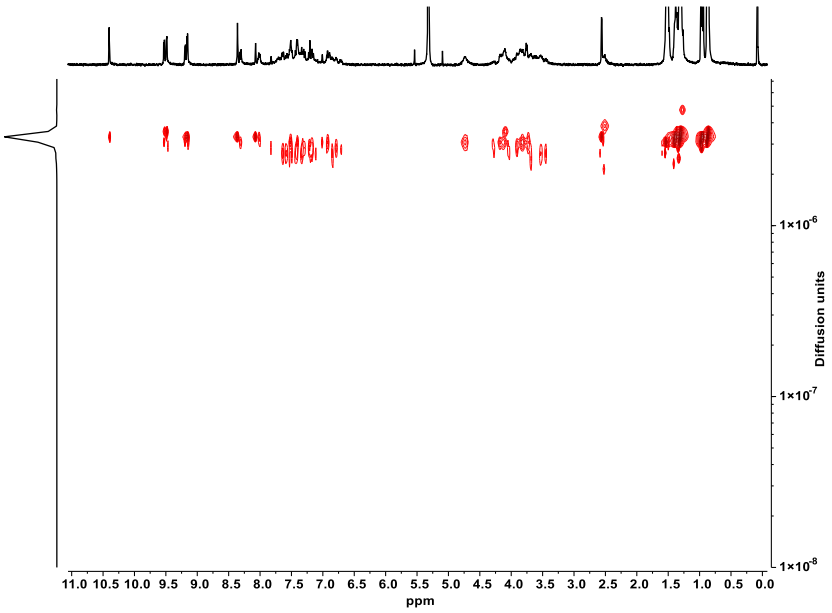


Figure S28: ^{1}H-DOSY NMR of [**1•2**$(H^{+})_2$]$(PF_6^{-})_2$ in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient D = 3.30 × 10^{-10} m^2 s^{-1} and experimental hydrodynamic radius r = 16.0 Å.

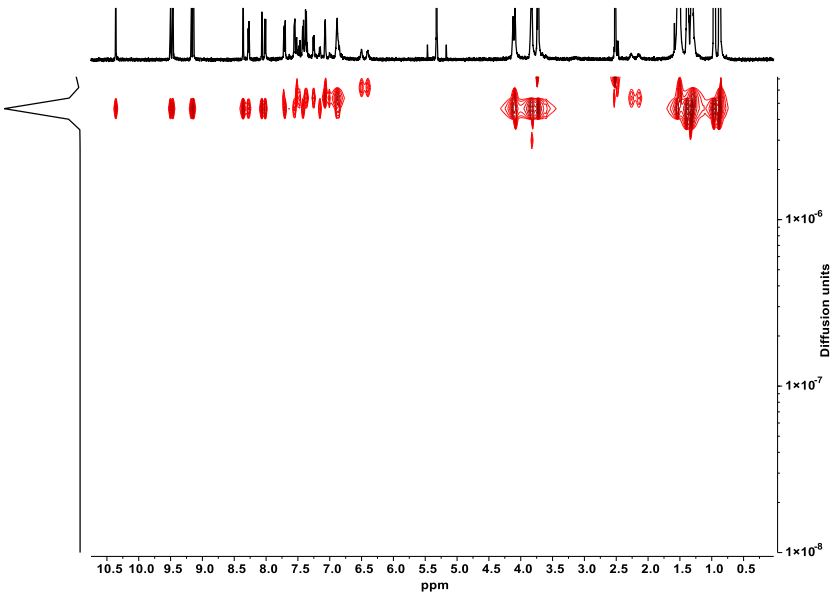


Figure S29: ^{1}H-DOSY NMR of [**1•2**] in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient D = 4.40 × 10^{-10} m^2 s^{-1} and experimental hydrodynamic radius r = 12.0 Å.

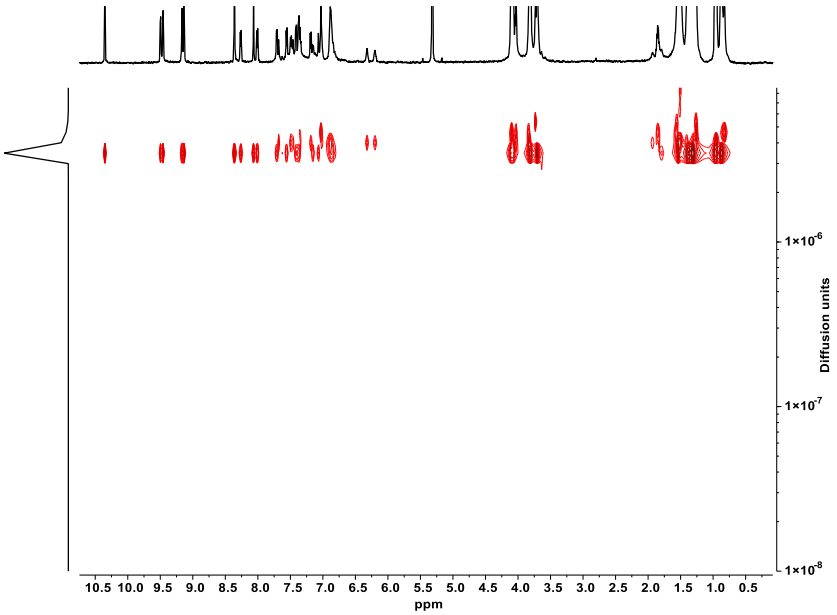


Figure S30: ^{1}H-DOSY NMR of [**1•4**] in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient $D = 3.50 \times 10^{-10}$ m^2 s^{-1} and experimental hydrodynamic radius $r = 15.2$ Å.

6. Stepwise walking using DBU titration

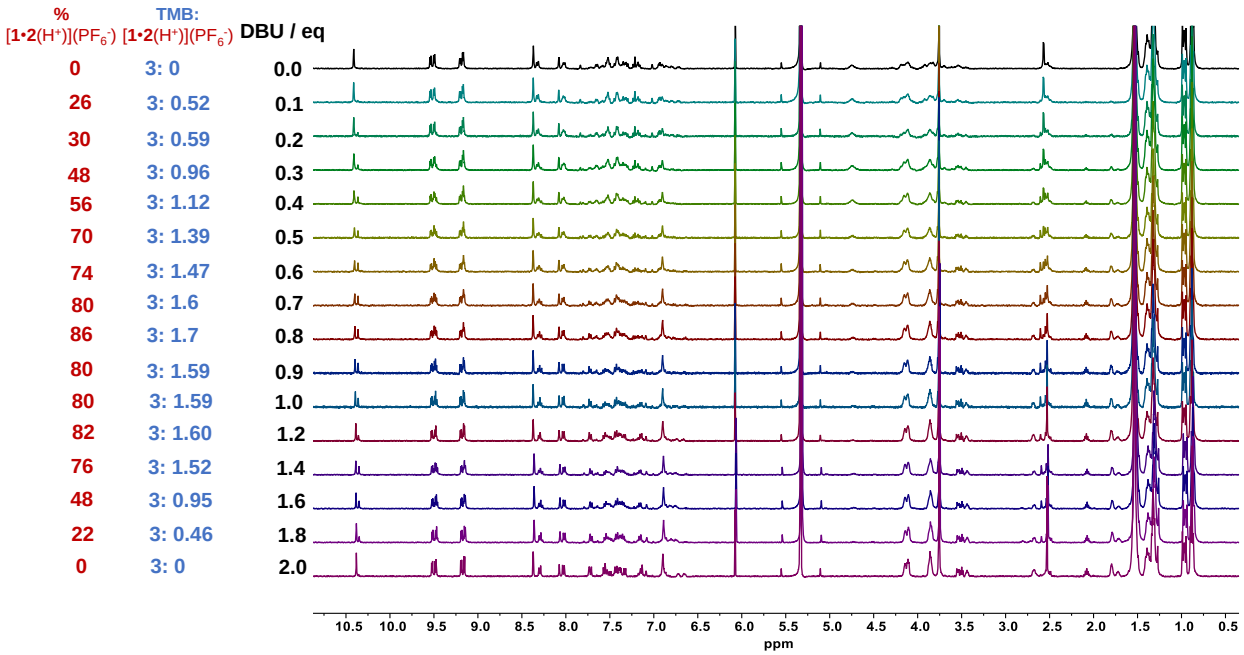


Figure S31: ^{1}H-NMR of titration of 2.0 eq of DBU against equimolar (0.35 mM) mixture of [**1•2**$(H^+)_2$]$(PF_6^-)_2$ and 1,3,5-trimethoxybenzene (TMB, internal standard) in CD_2Cl_2 at 298 K. Ratio of TMB : [**1•2**(H^+)](PF_6^-) is calculated by integration of characteristic peak of TMB (integration set to 3; constant) at 6.01 ppm and integration of the r-H signal of formed [**1•2**(H^+)](PF_6^-) at 10.36 ppm in the mixture. Since, the signal at 10.36 ppm only represents exactly half of the total r-H signals of [**1•2**(H^+)](PF_6^-), the % [**1•2**(H^+)](PF_6^-) is calculated using the equation below. Other possible assemblies in this mixture during the course of the titration are: [**1•2**$(H^+)_2$]$(PF_6^-)_2$ and [**1•2**].

Equation 1. Formula used to calculate the %: [**1•2**(H^+)](PF_6^-) (Fig S26) formed in the titration using integration of r-H signal at 10.36 ppm vs TMB as shown in Fig 3a in manuscript.

$$\%\ [\mathbf{1\bullet 2}(H^+)](PF_6^-) = \frac{\text{Integration of r-H signal (10.36 ppm)} * 2}{\text{Integration of r-H for all assemblies}}$$

** Integration of r-H for all assemblies is a constant and equal to 4*

7. Stepwise walking using chemical fuel (two cycles)

A mixture of **1** (645 µg, 185 nmol) and **4** (179 µg, 185 nmol) were dissolved in 500 µL of CD_2Cl_2 in an NMR tube with**.** Then, the assembly [**1•4**] was treated with chemical fuel **3** (94.8 µg, 462 nmol) at room temperature.

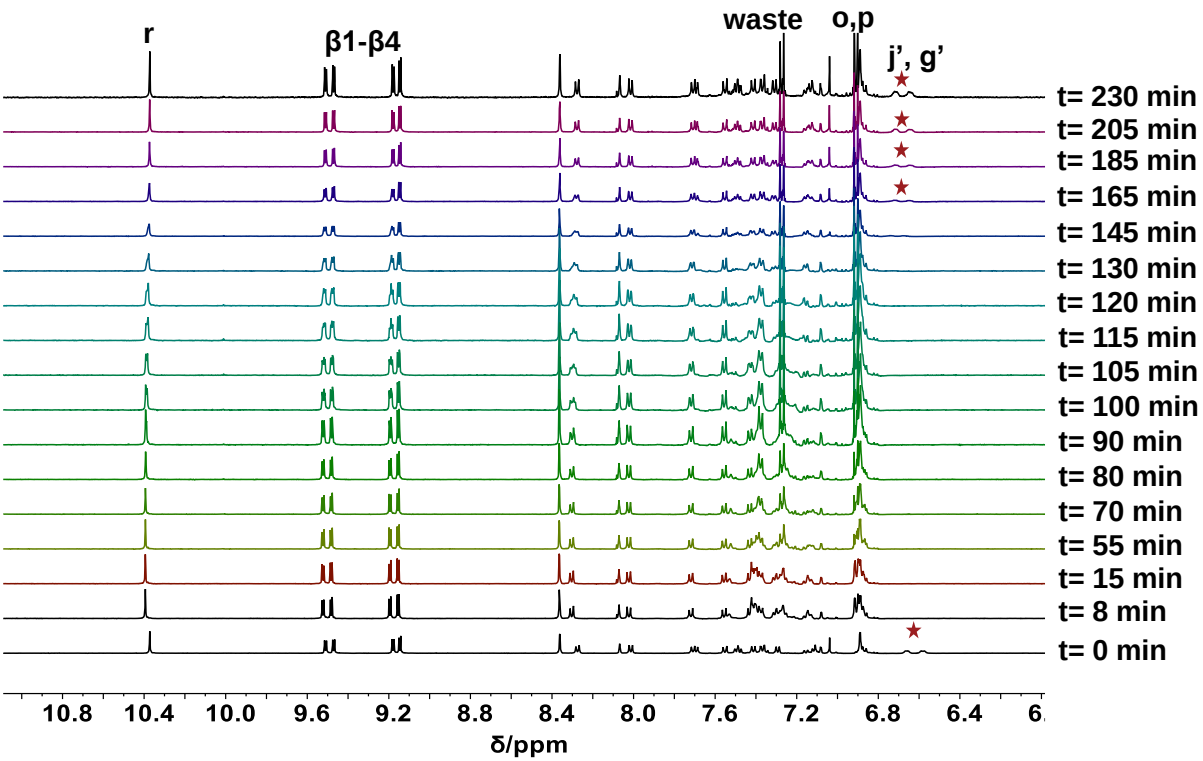


Figure S32: Partial ^{1}H NMR spectra (CD_2Cl_2, 298 K) recorded at various times (after start) as shown by time stamps on the right. Marked proton signals r-H split into two sets approximately during the middle of the full cycle. Signals marked with asterisks are j', g'-H which are attributed to reformation of the starting state/assembly [**1•4**] after consumption of all the fuel that was added in the beginning of cycle 1.

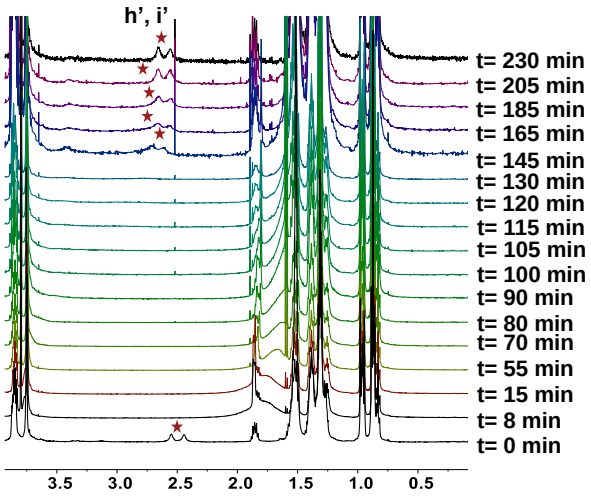


Figure S33: Partial ^{1}H NMR spectra (CD_2Cl_2, 298 K) recorded at various times (after start) as shown by time stamps on the right. Proton signals of h',i'-H marked with asterisks are attributed to regeneration of the starting state/assembly [**1•4**] (in Phase-3) after consumption of all the fuel added in the beginning of cycle 1.

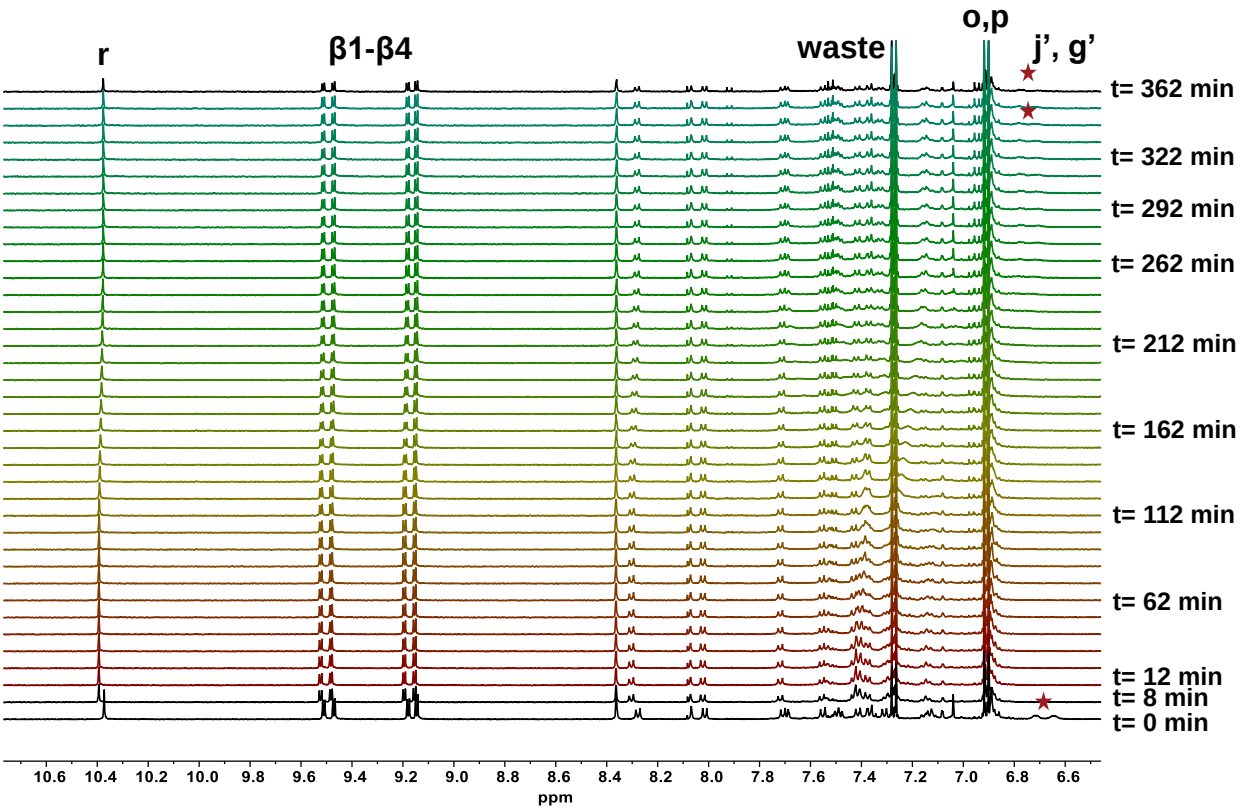


Figure S34: Partial ^{1}H NMR spectra (CD_2Cl_2, 298 K) recorded at various times (after start) as shown by time stamps on the right. Marked proton signals r-H don't clearly split into two sets (only lateral shifting of the r-H signal) during the second cycle. Signals marked with asterisks are j', g'-H which are attributed to reformation of the starting state/assembly [**1•4**] after consumption of all the fuel that was added in the beginning of cycle 2. Signal of the chemical waste/byproduct accumulated in the system is shown at 7.25 ppm.

8. ESI-MS Spectra

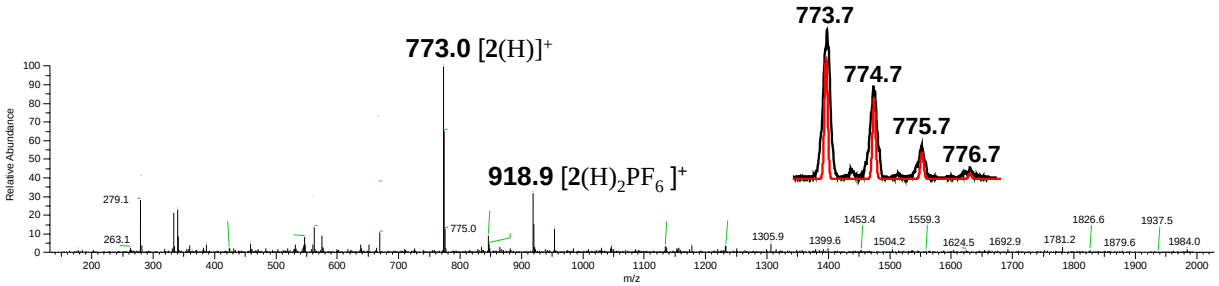


Figure S35 : ESI-MS of ligand $[\mathbf{2}(H^+)_2](PF_6^-)_2$. Inset: The experimental and theoretical (red) isotopic distributions are in good agreement.

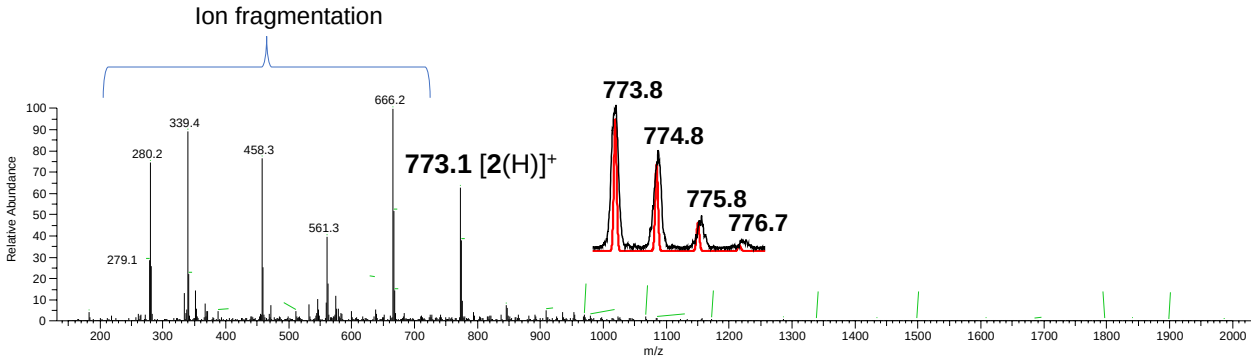


Figure S36: ESI-MS of ligand **2** after protonation. Inset: The experimental and theoretical (red) isotopic distributions correlate well.

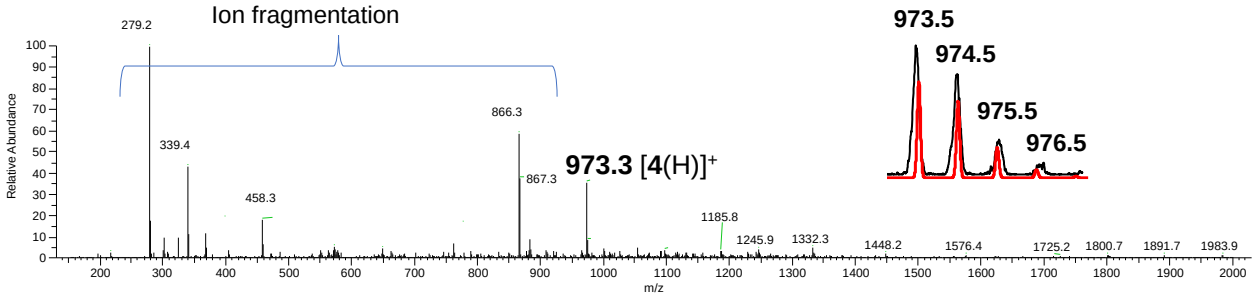


Figure S37: ESI-MS of ligand **4** after protonation. Inset: The experimental and theoretical (red) isotopic distributions correlate well.

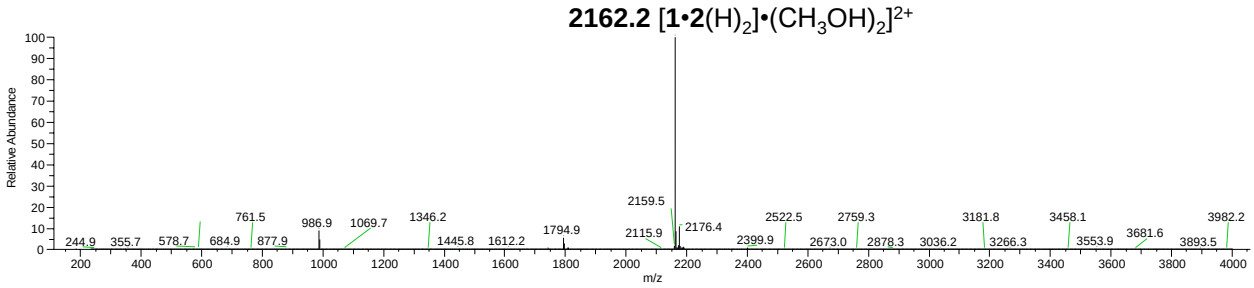


Figure S38: ESI-MS of complex [**1•2**$(H^+)_2$]$(PF_6^-)_2$ dissolved in DCM/MeOH (4:1). No isotopic distribution available above *m/z* > 2000.

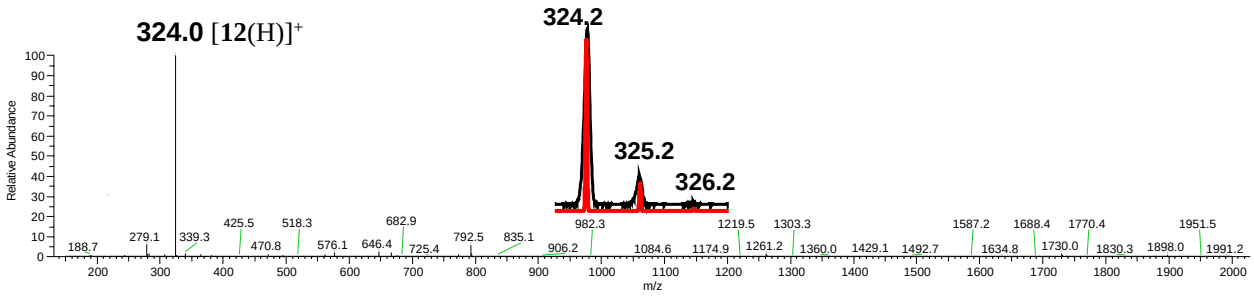


Figure S39: ESI-MS of ligand [12(H^+)](PF_6^-). Inset: The experimental and theoretical (red) isotopic distributions correlate well.

9. References

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