Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Dynamic topomerization of Cu(I)-complexed pseudorotaxanes

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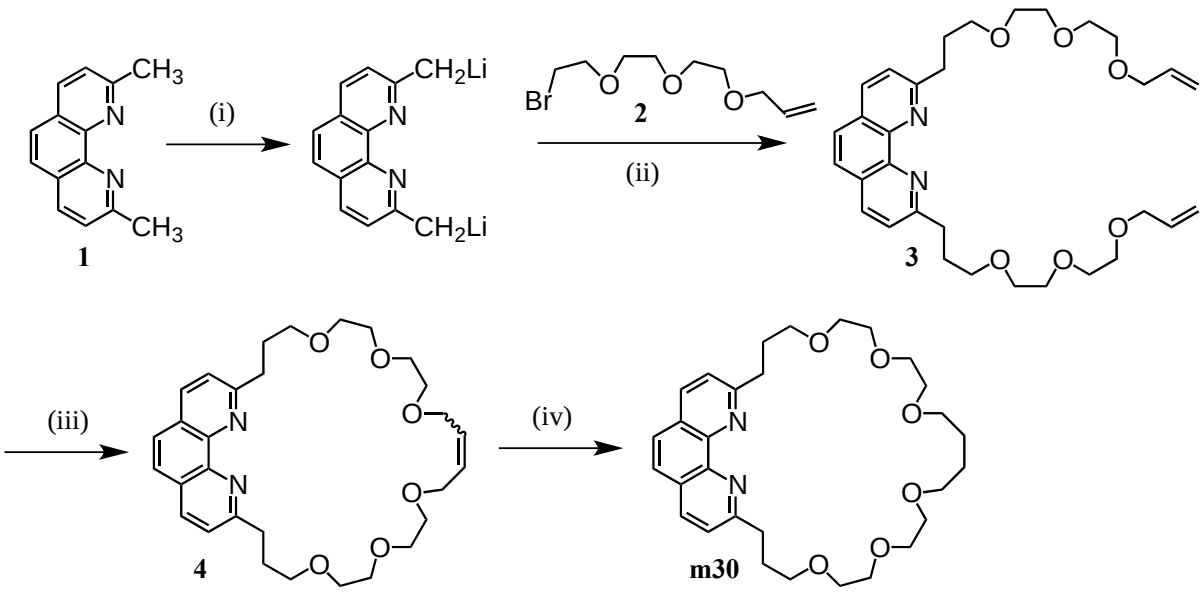
Preparation of m30

The synthesis of macrocycle **m30** is depicted in Scheme S1. Compound **2** was prepared in three steps from ethylene glycol according to a reported procedure.[1] Phenanthroline **3** was obtained in 41% yield from the reaction of the dicarbanion derived from neocuproine (**1**) with bromide **2** in THF. The macrocyclization was then performed under ring closing metathesis reaction conditions using the first generation Grubbs' catalyst. Macrocycle **4** was thus prepared in a remarkable 86% isolated yield. Close inspection of the ^{1}H NMR of **4** revealed that this compound was obtained as an *E*/*Z* isomeric mixture, one isomer being largely major (*ca*. 90%). Finally, hydrogenation of the carbon-carbon double bond was carried out using Pd/C.



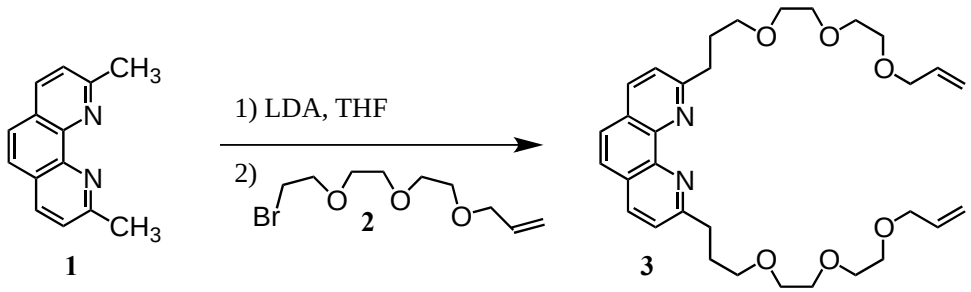
Scheme S1. Reagents and conditions: (i) LDA, THF, (ii) **2**, THF (41%); (iii) first generation Grubbs' catalysts, CH_2Cl_2 (86%); (iv) H_2, Pd/C, THF (60%).

[1] M. Gonçalves, K. Estieu-Gionnet, T. Berthelot, G. Laïn, M. Bayle, X. Canron, N. Betz, A. Bikfalvi and G. Déléris, *Pharm Res.*, 2005, **8**, 1411.

Experimental section

General. Acetonitrile (CH_3CN) was distilled over CaH_2 under Ar. Dichloromethane (CH_2Cl_2) was distilled over CaH_2 under Ar. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} purchased from E. Merck. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer Spectrum One Spectrophotometer. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. The ^1H signals were assigned by 2D experiments (COSY and ROESY). MALDI-TOF-mass spectra were carried out on a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer. ESI-MS mass spectra were carried out on a Bruker MicroTOF spectrometer.

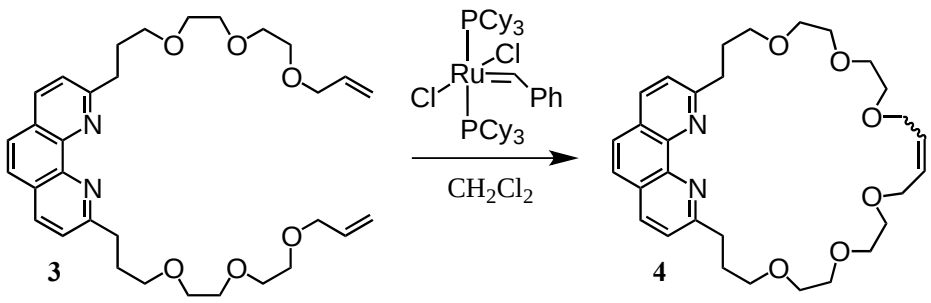
Compound 3.



A 2 M solution of LDA in THF (9 mL, 18 mmol) was added slowly to a stirred solution of **1** (1.87 g, 8.97 mmol) in anhydrous THF (50 mL) at -78 °C under Ar. After 4 h, a solution of **2** (5.0 g, 19.75 mmol) in THF (10 mL) was added dropwise. The resulting mixture was stirred for 2 h at -78°C, then for 16 h at room temperature. The solution was then poured into ice water (150 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2/1 to 2% MeOH) gave **3** (2.02 g, 41% yield) as a pale yellow glassy product. ^1H NMR (CD_2Cl_2, 400 MHz): 8.15 (d, J = 7 Hz, 2H), 7.72 (s, 2H), 7.54 (d, J = 7 Hz, 2H), 5.91 (m, 2H), 5.29-5.13 (m, 4H), 3.99-3.97 (m, 4H), 3.63-3.55 (m, 20H), 3.20 (m, 4H), 2.17 (m, 4H). ^{13}C {^1H} NMR (CD_2Cl_2, 75 MHz): 163.0, 146.4, 136.9, 135.9, 127.9, 126.3, 123.4, 117.1, 72.8, 71.45, 71.4, 71.35, 71.1, 70.4, 36.6, 30.9. MALDI-TOF MS: 553.12 (MH^+, calcd for

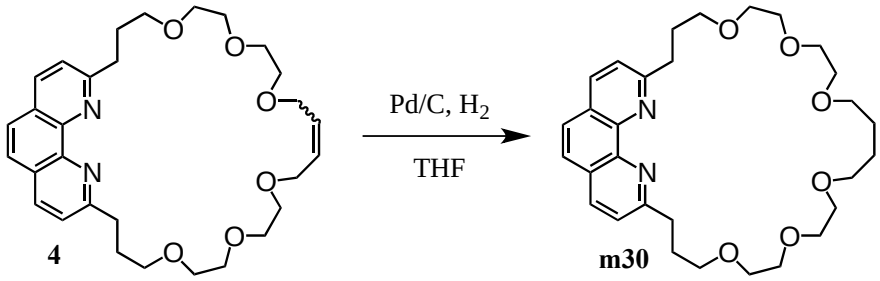
$C_{32}H_{45}N_2O_6$: 553.33). Anal. Calcd. for $C_{32}H_{44}N_2O_6$: C, 69.54; H, 8.02; N, 5.07. Found: C, 69.67; H, 7.96; N, 4.97.

Compound 4.



Grubb's 1st generation catalyst (5 mol%) was added to a 0.01M solution of **3** (600 mg, 1.09 mmol) in CH_2Cl_2. After 6h at room temperature, an additional portion of catalyst (5 mol%) was added. After 6 h, the solvent was removed under vacuum. Column chromatography on SiO_2 (CH_2Cl_2/1 to 3% MeOH) gave **4** (490 mg, 86% yield) as a pale yellow glassy product that was used as received in the next step. ^{1}H NMR ($CDCl_3$, 300 MHz): 8.12 (d, *J* = 7 Hz, 2H), 7.68 (s, 2H), 7.49 (d, *J* = 7 Hz, 2H), 5.79 (m, 2H), 4.02 (m, 4H), 3.70-3.55 (m, 20H), 3.26 (m, 4H), 2.24 (m, 4H). MALDI-TOF MS: 525.11 (MH^+, calcd for $C_{30}H_{41}N_2O_6$: 525.29).

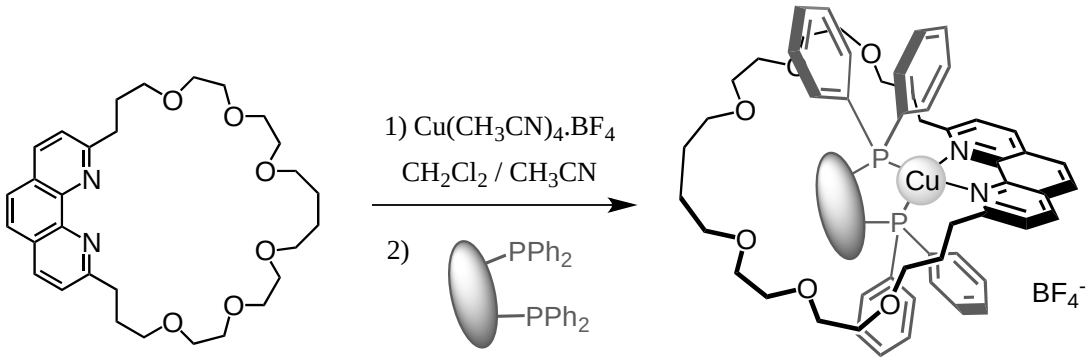
Compound m30.



A mixture of **4** (550 mg, 1.05 mmol) and Pd/C (10 wt. % loading, 55 mg) in THF (50 mL) was stirred at room temperature under positive H_2 atmosphere. After 4 h, the mixture was filtered (Celite) and evaporated. Column chromatography on SiO_2 (CH_2Cl_2/1 to 3% MeOH) gave **3** (330 mg, 60% yield) as a colorless glassy product. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.17 (d, *J* = 7 Hz, 2H), 7.73 (s, 2H), 7.53 (d, *J* = 7 Hz, 2H), 3.67-3.58 (m, 16H), 3.53 (m, 4H), 3.45

(m, 4H), 3.21 (m, 4H), 2.18 (m, 4H), 1.61 (m, 4H). ^{13}C {^{1}H} NMR (CD_2Cl_2, 75 MHz): 163.1, 146.4, 136.9, 127.9, 126.2, 123.3, 71.7, 71.6, 71.5, 71.4, 71.2, 70.9, 36.7, 30.9, 27.2. MALDI-TOF MS: 527.15 (MH^+, calcd for $C_{30}H_{43}N_2O_6$: 527.31). Anal. Calcd. for $C_{30}H_{42}N_2O_6$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.51; H, 8.22; N, 5.02.

Preparation of pseudorotaxanes [Cu(m30)(PP)]BF_4



m30 [Cu(**m30**)(PP)]BF_4

Pseudorotaxane [Cu(m30)(dppe)]BF_4. A solution of **m30** (70 mg, 0.13 mmol) and $Cu(CH_3CN)_4BF_4$ (42 mg, 0.13 mmol) in CH_2Cl_2/CH_3CN (7 : 3, 10 mL) mixture was stirred for 0.5 h, then dppe (53 mg, 0.13 mmol) was added. After 1 h, the solvents were evaporated. Recrystallization by slow diffusion of Et_2O into a CH_2Cl_2 solution of the crude product gave [Cu(**m30**)(dppe)]BF_4 (90 mg, 63%) as yellow-orange crystals (m.p.: 144-145°C). ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.57 (d, *J* = 7 Hz, 2H), 8.09 (s, 2H), 7.68 (d, *J* = 7 Hz, 2H), 7.30 (m, 20H), 3.54 (m, 16H), 3.25 (m, 10H), 2.82 (m, 4H), 2.48 (m, 4H), 1.72 (m, 4H), 1.39 (m, 2H). ^{31}P {^{1}H} NMR (CD_2Cl_2, 162 MHz): -6.87. MALDI-TOF MS: 987.2 ($[M - BF_4]^+$, calcd for $C_{56}H_{66}N_2P_2O_6Cu$: 987.37). Anal. Calcd. for $C_{56}H_{66}N_2P_2O_6CuBF_4$: C, 62.54; H, 6.19; N, 2.60. Found: C, 62.70; H, 6.44; N, 2.39.

Pseudorotaxane [Cu(m30)(POP)]BF_4. A solution of **m30** (110 mg, 0.21 mmol) and $Cu(CH_3CN)_4BF_4$ (66 mg, 0.21 mmol) in CH_2Cl_2/CH_3CN (7:3, 10 mL) mixture was stirred for 0.5 h, then POP (113 mg, 0.21 mmol) was added. After 1 h, the solvents were evaporated. Column chromatography (SiO_2, CH_2Cl_2/1% MeOH) followed by recrystallization (slow diffusion of Et_2O into a CH_2Cl_2 solution of the product) gave [Cu(**m30**)(POP)]BF_4 (191 mg,

75% yield) as yellow crystals (m.p.: 172-173°C). ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.43 (d, *J* = 7 Hz, 2H), 7.98 (s, 2H), 7.68 (d, *J* = 7 Hz, 2H), 7.31 (m, 6H), 7.15 (m, 8H), 7.05-6.82 (m, 14H), 3.15-3.07 (m, 20H), 2.92 (t, *J* = 6 Hz, 4H), 2.67 (t, *J* = 6 Hz, 4H), 1.32 (m, 8H). ^{31}P {^{1}H} NMR (CD_2Cl_2, 162 MHz): -13.57. ES-MS: 1127.39 ($[M - BF_4]^+$, calcd for $C_{66}H_{70}N_2O_7P_2Cu$: 1127.40). Anal. Calcd. for $C_{66}H_{70}N_2O_7P_2CuBF_4$: C, 65.21; H, 5.80; N, 2.30. Found: C, 64.99; H, 6.01; N, 2.24.

X-Ray crystal structures of [Cu(m30)(dppp)]BF_4 and **[Cu(m30)(POP)]BF_4**.

The resolution of both structures is only moderate, mainly because of the disorder in the flexible chain subunit of the **m30** ligand. For this reason, the bond lengths and bond angles have not been described in detail. The identity of both Cu^I-complexed pseudo-rotaxanes is, however, in no doubt.

[Cu(**m30**)(dppe)]BF_4.0.5Et_2O. Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of [Cu(**m30**)(dppe)]BF_4. Data were collected at 173 K on a Bruker APEX-II CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. It is noted that (i) one phenyl group is disordered on 2 positions and (ii) the residual electronic density attributed to half a molecule of unresolved Et_2O solvent has been squeezed. Crystallographic data: formula: $C_{56}H_{66}CuN_2O_6P_2.BF_4.(C_4H_{10}O)_{1/2}$ (M = 1075.40 $g.mol^{-1}$); yellow crystal, 0.50 × 0.25 × 0.15 mm; crystal system: triclinic, space group P-1; a = 11.7950(7) Å; b = 13.2034(7) Å; c = 19.7058(11) Å; α = 106.642(1)°; β = 106.201(1)°; γ = 91.402(1); V = 2805.3(3) $Å^3$; Z = 2; F(000) = 1128; a total of 36543 reflections collected; 2.24° < θ < 28.09°, 13553 independent reflections with 8630 having I > 2σ(I); 553 parameters; Final results : $R_1(F^2)$ = 0.0905; $wR_2(F^2)$ = 0.2668, Goof = 1.102. Full data collection parameters and structural data are available as CIF file (Cambridge Crystallographic Data Centre deposition number CCDC 905751).

[Cu(**m30**)(POP)]BF_4. Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of [Cu(**m30**)(POP)]BF_4. Data were collected at 173 K on a Bruker APEX-II CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined against F^2 using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The high residual electronic density results from the disorder in the BF_4 counteranion as well as from the disorder in the flexible

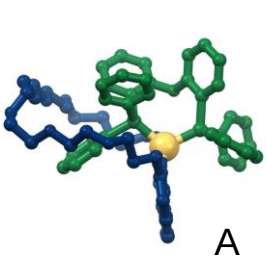
chain subunit of the **m30** ligand. Crystallographic data: formula: $C_{66}H_{70}CuN_2O_7P_2.BF_4$ (M = 1215.53 g.mol^{-1}); yellow crystal, 0.30 × 0.25 × 0.20 mm; crystal system: triclinic, space group P-1; *a* = 13.6380(5) Å; *b* = 14.9380(5) Å; *c* = 15.6669(6) Å; α = 78.733(1)°; β = 72.898(1)°; γ = 83.964(1); V = 2988.29(19) Å^3; Z = 2; F(000) = 1272; a total of 47180 reflections collected; 2.04° < θ < 30.09°, 14418 independent reflections with 17435 having I > 2σ(I); 634 parameters; Final results : $R_1(F^2)$ = 0.1250; $wR_2(F^2)$ = 0.3530, Goof = 1.484. Full data collection parameters and structural data are available as CIF file (Cambridge Crystallographic Data Centre deposition number CCDC 905746).

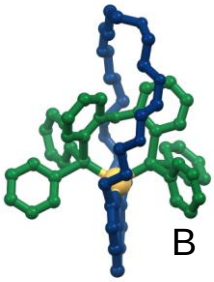
Computational studies

The molecular modeling was performed with *Spartan'10* Macintosh Parallel Edition (Wavefunction Inc., USA) at the semi-empirical PM6 level.

For both [Cu(**m30**)(dppe)]$^+$ and [Cu(**m30**)(POP)]$^+$, the molecular geometry was optimized for the two possible conformers: **A** and **B** for [Cu(**m30**)(POP)]$^+$ / **C** and **D** for [Cu(**m30**)(dppe)]$^+$

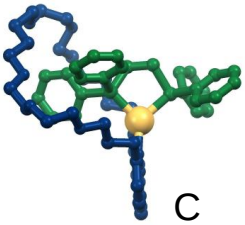
The calculated structures (**m30**: blue, PP ligand: green, Cu: yellow, the H atoms have been omitted for clarity) and the corresponding heat of formation are indicated bellow.

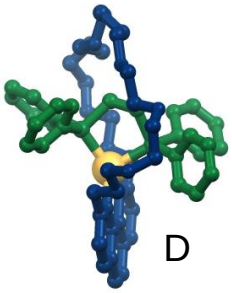




917.0 kJ/mol 938.9 kJ/mol

DE = 21.9 kJ/mol (= 5.2 kcal/mol)





891.4 kJ/mol 865.7 kJ/mol

DE = 25.7 kJ/mol (= 6.1 kcal/mol)

Fig. S1. Crystal packing showing the dimeric arrangment of the [Cu(**m30**)(dppe)]$^{+}$ cations in the crystal lattice.

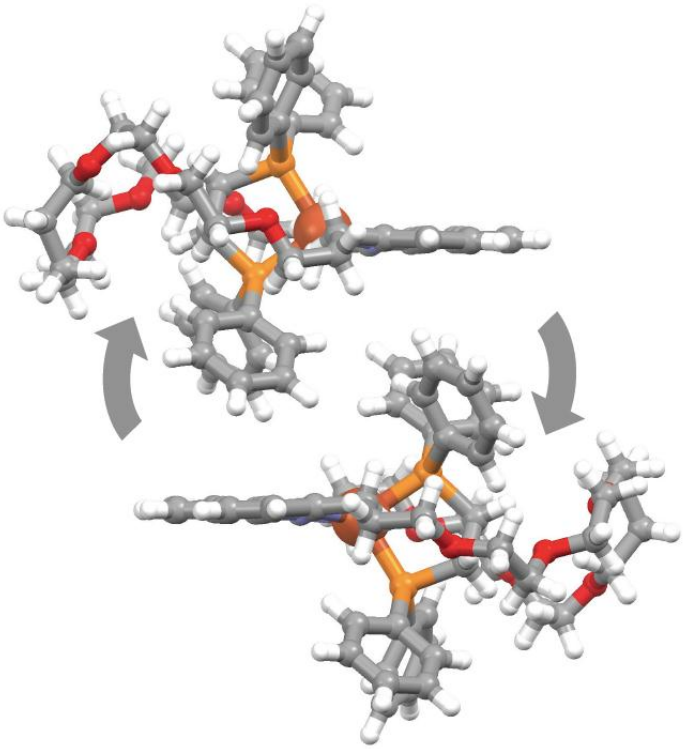


Fig. S2. ^{1}H NMR spectra (400 MHz) of [Cu(**m30**)(POP)]BF_4 recorded at different temperatures in $CDCl_2CDCl_2$ (left) and CD_2Cl_2 (right).

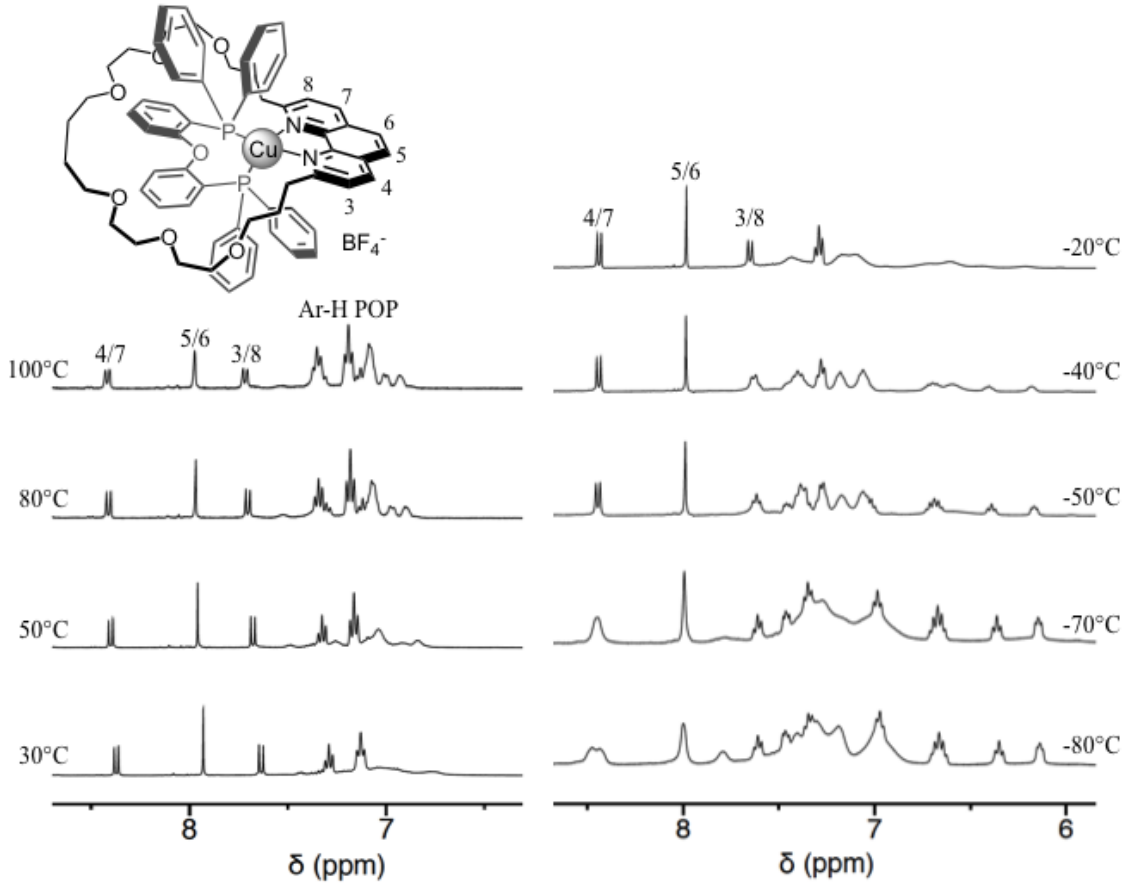


Fig. S3. ^{31}P NMR spectra (CD_2Cl_2, 162 MHz) of [Cu(**m30**)(POP)]BF_4 (left) and [Cu(**m30**)(dppe)]BF_4 (right) recorded at different temperatures.

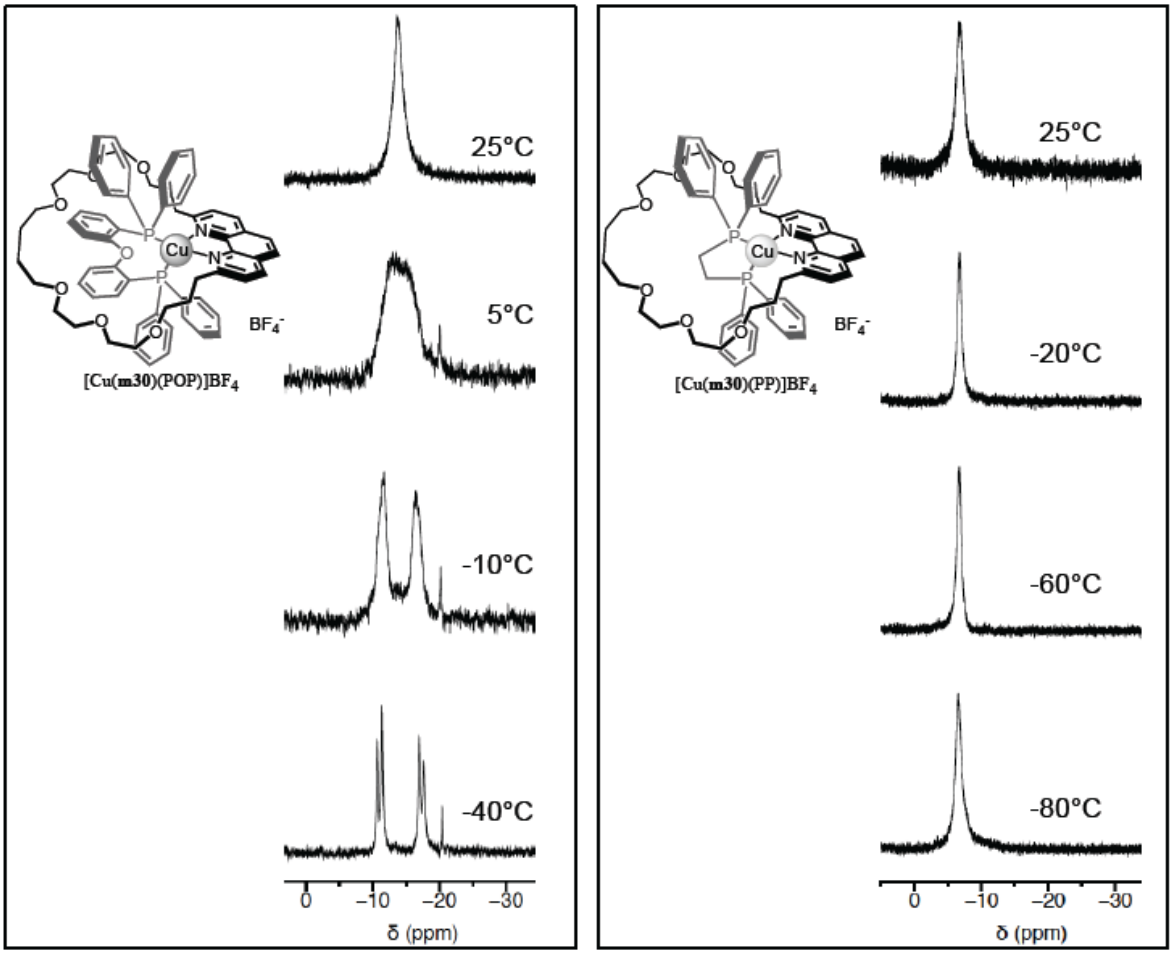


Fig. S4. Calculated structures of the different topomers of [Cu(**m30**)(POP)]$^{+}$ (top) and [Cu(**m30**)(dppe)]$^{+}$ (bottom); **m30**: blue, PP ligand: green, Cu: yellow; the H atoms have been omitted for clarity. A potential energy diagram is proposed to explain the dynamic exchange between topomers, *i.e.*, topomerization, evidenced for [Cu(**m30**)(POP)]BF_4 by the variable temperature ^{31}P and ^{1}H NMR studies. In the case of [Cu(**m30**)(dppe)]BF_4, only topomer **D** was detected and no dynamic exchange was evidenced.