

Supporting Information

Mechanical switching of magnetic interaction by tweezers-type complex

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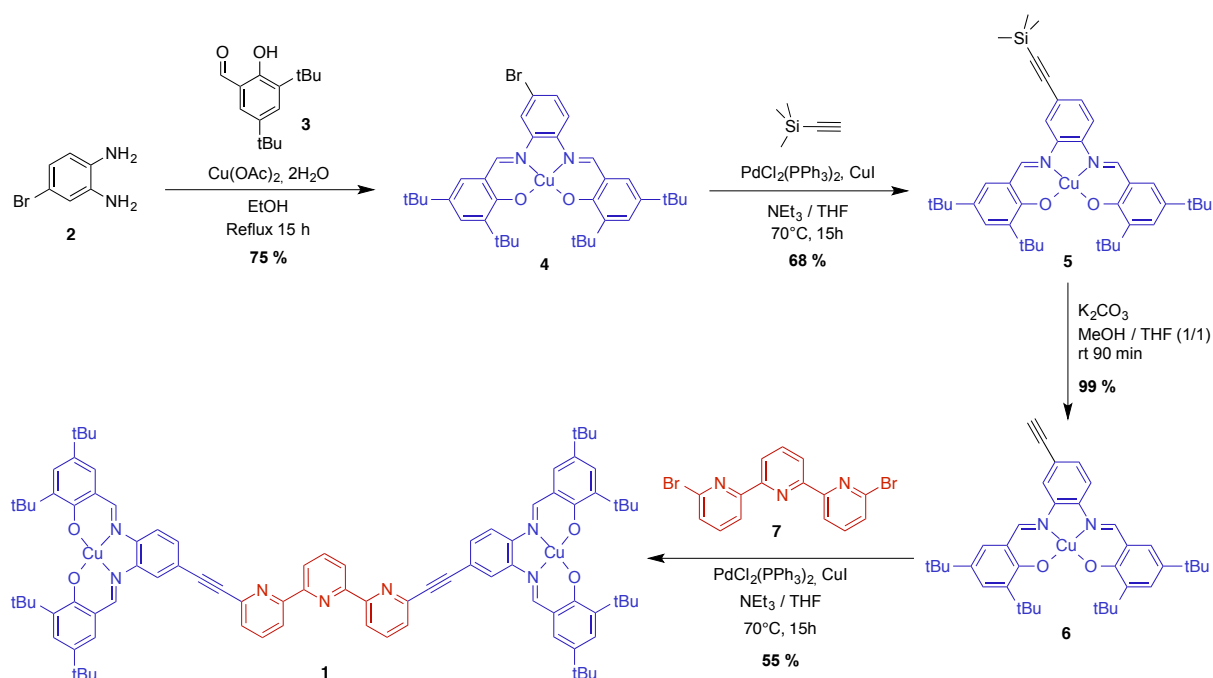
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General procedures

Reagent grade tetrahydrofuran was distilled from sodium and benzophenone. Tetrahydrofuran and triethylamine were degassed by three freeze-pump-thaw cycles before being used in the Sonogashira coupling reactions. All other chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed using silica gel from Merck (40-63 μm) or GraceResolv High Resolution Flash Cartridges (particle size 40 μm). Thin layer chromatography was performed using aluminium plates pre-coated with silica gel 60 F254 0.20 mm layer thickness purchased from VWR. Absorption spectra were recorded on a JASCO V-670 spectrophotometer. Infrared spectra were recorded on a Bruker tensor 27 ATR spectrometer. Electrospray ionisation (ESI) mass spectrometry was performed on a Bruker microTOF spectrometer.

Synthesis



The main challenge of the synthesis of **1** was to control the coordination of the two binding sites (salphen and terpyridine) and to avoid any metal exchange. Since a strategy involving the synthesis of the free ligand followed by metal coordination might lead to a mixture of products, we used a “Chemistry on complex” route by analogy with previously obtained Pt-based tweezers.¹ Cu-salphen complexes are enough inert to avoid metal exchange during the cross coupling and can be purified by column chromatography enabling the success of this strategy.

Complex 4

In a round bottom flask were introduced 4-bromo-1,2-diaminobenzene **2** (500 mg, 2.67 mmol, 1 eq), 3,5-diterbutyl-2-hydroxybenzaldehyde **3** (1.32 g, 5.61 mmol, 2.1 eq), Cu(OAc)₂·2H₂O (639 mg, 2.94 mmol, 1.1 eq), and absolute ethanol (30 mL). After 15 h refluxing, the mixture was cooled down, the crude product precipitated and was filtered. Then the brown crude product was dissolved in CH₂Cl₂, and passed through a plug of silica gel (CH₂Cl₂). The solvent evaporation under reduced pressure yielded complex **4** as a brown solid (1.39 g, 75 %).

ESI-HRMS *m/z* (%): [M+Na]⁺ calc (C₃₆H₄₅BrCuN₂O₂): 704.1834 (100), found: 704.1848 (100).

Elemental analysis calc (%) for C₃₆H₄₅BrCuN₂O₂: C 63.47, H 6.66, N 4.11; found: C 63.08, H 6.75, N 3.96.

IR (ATR; ν, cm⁻¹): 2950, 2904, 2866, 1592, 1570, 1546, 1520, 1478, 1461, 1428, 1384, 1356, 1256, 1234, 1195, 1174, 1161, 1130, 1120, 1025, 954, 904, 867, 835, 802, 789, 745, 635, 532, 378, 334.

Complex 5

In a Schlenk tube under argon were introduced complex **4** (900 mg, 1.32 mmol, 1 eq), PdCl₂(PPh₃)₂ (139 mg, 0.198 mmol, 15 mol %), CuI (75 mg, 0.396 mmol, 30 mol %). A mixture of NEt₃ (10 mL) and THF (20 mL) previously distilled and degased, was then added. The mixture was heated at 70°C, and TMSA (1.49 mL, 10.57 mmol, 8 eq) was added. The mixture was heated under argon at 70°C for 15 h. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (SiO₂: Cyclohexane / AcOEt (0-5 %)) yielding **5** as a dark orange solid (625 mg, 68 %).

ESI-HRMS *m/z* (%): [M+Na]⁺ calc (C₄₁H₅₄CuN₂O₂Si): 720.3143 (100), found: 720.3143 (100).

Elemental analysis calc (%) for (C₄₁H₅₄CuN₂O₂Si + ½ AcOEt): C 69.55, H 7.87, N 3.77; found: C 69.67, H 8.03, N 3.70.

IR (ATR; ν, cm⁻¹): 2953, 2904, 2867, 2151 (ν_{C≡C}), 1598, 1576, 1546, 1521, 1495, 1462, 1427, 1384, 1357, 1250, 1194, 1172, 1130, 1110, 979, 855, 838, 811, 790, 758, 705, 633, 622, 531, 337.

Complex 6

In a round bottom flask, complex **5** (400 mg, 0.573 mmol, 1eq) was dissolved in a mixture of THF (12 mL) and MeOH (10 mL), then K₂CO₃ (158 mg, 1.15 mmol, 2eq) was added. The mixture was stirred at room temperature during 90 min. The solvent was evaporated under reduced pressure, and the brown crude product was purified by plug filtration (SiO₂, CH₂Cl₂). After solvent evaporation, **6** was obtained as a dark orange solid (366 mg, 99 %). Single crystals were grown by slow evaporation of a solution of **6** in CH₂Cl₂.

ESI-HRMS *m/z* (%): [M+Na]⁺ calc (C₃₈H₄₆CuN₂O₂): 648.2748 (100), found: 648.2751 (100).

Elemental analysis calc (%) for C₃₈H₄₆CuN₂O₂: C 72.87, H 7.40, N 4.47; found: C 72.59, H 7.51, N 4.22.

IR (ATR; ν , cm^{-1}): 3316 ($\nu_{\text{C-H}}$), 2951, 2904, 2865, 1617, 1599, 1579, 1544, 1521, 1491, 1461, 1427, 1385, 1355, 1261, 1222, 1196, 1171, 1127, 1109, 1023, 865, 836, 812, 790, 636, 596, 567, 532, 493, 355.

Crystallographic structure:

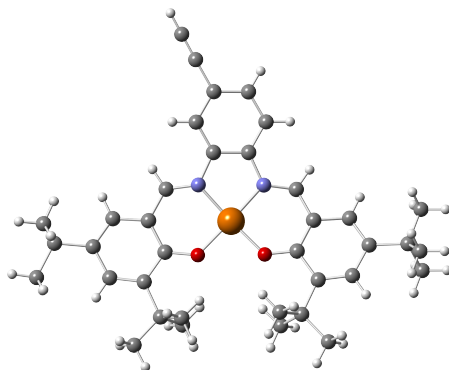


Figure S1. Crystallographic structure of the complex **6**

Tweezers 1

In a Schlenk tube under argon 6,6''-Dibromo-2,2':6',2''-terpyridine **7** (47 mg, 0.12 mmol, 1eq), **6** (300 mg, 0.479 mmol, 4 eq), $\text{PdCl}_2(\text{PPh}_3)_2$ (17 mg, 0.024 mmol, 20 mol %) and CuI (9 mg, 0.048 mmol, 40 mol %) were introduced. A mixture of NEt_3 (6 mL) / THF (12 mL) previously distilled and degassed by freeze pump thaw was then added. The mixture was heated at 70 °C under argon during 15 h. After solvent evaporation, CH_2Cl_2 (30 mL) and 10 drops of tris(2-aminoethyl)amine were added. The mixture was then washed with water (3×50 mL), dried over MgSO_4 , filtered, and evaporated. The crude product was purified by column chromatography (SiO_2 : Cyclohexane / CH_2Cl_2 / AcOEt (100/0/0)-(0/100/0)-(0/80/20)), then recrystallized in CHCl_3 yielding tweezers **1** as a dark orange solid (98 mg, 55 %). Single crystals were grown by slow evaporation of a solution of **1** in chloroform/acetonitrile (8/2).

ESI-HRMS m/z (%): $[\text{M}+\text{Na}]^+$ calc ($\text{C}_{91}\text{H}_{99}\text{Cu}_2\text{N}_7\text{O}_4\text{Na}$): 1504.6232 (100), found: 1504.6254 (100).

Elemental analysis calc (%) for ($\text{C}_{91}\text{H}_{99}\text{Cu}_2\text{N}_7\text{O}_4 + \text{H}_2\text{O}$): C 72.87, H 6.79, N 6.54; found: C 72.98, H 6.80, N 6.50.

IR (ATR; ν , cm^{-1}): 2950, 2905, 2867, 2212 ($\nu_{\text{C}\equiv\text{C}}$), 1600, 1576, 1562, 1521, 1497, 1462, 1424, 1384, 1358, 1255, 1195, 1172, 1129, 1110, 864, 812, 791, 743, 636, 527, 367.

UV-Visible titration procedure

UV-visible absorption spectra were recorded on a JASCO V-670 spectrophotometer at 25°C. H₃CCN was distilled before use, CHCl₃ was dried over molecular sieves 4 Å and neutralized on neutral Al₂O₃. Metal salts and tris(2-aminoethyl)amine were used without any purification. Solutions of tweezers, metals and ligands, used for titrations were prepared in volumetric flasks, and additions were made with Hamilton syringes. The metal salt concentrations in the stock solutions were checked by titration with a terpyridine solution. Curve fits were performed by a nonlinear least-squares fit of the absorbance versus the concentration of guest added using the Matlab program developed by P. Thordarson.²

The titrations monitored by UV-Visible spectroscopy have been performed according to the following general procedures:

Tweezers 1 closing: To 3.0 mL of open tweezers (5.0×10^{-6} M) dissolved in CHCl₃ in a quartz cell (10 mm), were added 0.1 eq (1.5 μL of solution 1.0×10^{-3} M) of metal salt dissolved in a mixture H₃CCN / CHCl₃ (2 / 8). After each addition, a UV-Visible absorption spectrum (250 – 700 nm, 400 nm/min, 25°C) was recorded immediately and after 5 minutes to check that the equilibrium was reached.

[Zn(1)]²⁺ reopening: To 3.0 mL of open tweezers (5.0×10^{-6} M) dissolved in CHCl₃ in a quartz cell (10 mm), were added 1.0 eq (15 μL of solution 1.0×10^{-3} M) of zinc salt dissolved in a mixture H₃CCN / CHCl₃ (2 / 8). A UV-Visible absorption spectrum (250 – 700 nm, 400 nm/min, 25°C) was recorded after 10 minutes. Then were added 0.1 eq (1.5 μL of solution 1.0×10^{-3} M) of tris(2-aminoethyl)amine dissolved in CHCl₃. After each ligand addition, a UV-Visible absorption spectrum (250 – 700 nm, 400 nm/min, 25°C) was recorded immediately and after 5 minutes to check that the equilibrium was reached.

EPR measurements procedure

EPR measurements were performed with a Bruker Elexsys spectrometer, at X-Band frequency, in the 4K to 300K temperature range. The magnetic field was modulated with a frequency of 100 kHz.

CHCl₃ was dried over molecular sieves 4 Å, neutralized on Al₂O₃, and degased by argon bubbling. Distilled or spectrograde H₃CCN was used. Solutions of tweezers, metals, or ligands, were prepared in volumetric flasks, then degased by argon bubbling for 20 min. Solution additions were performed with Hamilton syringes.

Sample preparation for perpendicular mode EPR:

The X band perpendicular mode EPR measurements have been performed in Suprasil quartz tube (diameter 2 mm), on frozen and degased solutions (150 μL, 1.0×10^{-4} M).

Tweezers 1: In a volumetric flask under argon the tweezers 1 was dissolved in CHCl₃ previously degased. The resulting solution was degased 20 additional minutes by argon bubbling. 150 μL of this solution (1.0×10^{-4} M) were introduced in the EPR tube under argon, before freezing in liquid nitrogen.

[Zn(1)](ClO₄)₂: Same procedure than for 1 with additional 1.2 eq of Zn(ClO₄)₂ (9 μL of solution at 5.0×10^{-3} M) added before freezing in liquid nitrogen.

Distance evaluation

The D values were used to evaluate the distance between the two interacting paramagnetic metal ions in dipolar coupling according to equation:³

$$D = \frac{3}{2} \frac{\mu_0}{4\pi h} \frac{g^2 \mu_B^2}{R^3} \approx 19.47 \frac{g^2}{R^3} \quad \text{Equation 1}$$

with D in MHz and R in nm.

SQUID Magnetometry

The magnetic measurements were performed in the laboratory on a Superconducting QUantum Interference Device (SQUID): Quantum Design MPMS-XL. The applied maximum field is 70 kOe, and the sample temperature range is 1.8 – 300 K. The solid samples of **1** (3.2 mg), and [Zn(**1**)]Cl₂ (3.9 mg), were immobilized in a capsule, which was then locked in a straw. The samples were introduced in the SQUID under inert atmosphere of helium.

XRD crystal structures

A single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Data collection were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections.

The structure were solved either with SUPERFLIP,⁴ Sir92⁵ or ShelxT⁶ programs and refined by full-matrix least-squares methods using SHELXL-13,⁷ in the WinGX⁸ suite or in Olex2⁹ suite.

All non-hydrogen atoms were refined anisotropically while some atoms of solvent molecules were refined isotropically. Hydrogen atoms were placed at calculated positions with a riding model. In [Zn(**1**)]Cl₂ structure, the chloroform molecules undergo a few restraints.

CCDC 1052163-1052165, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data

	Compound 6	Tweezers 1	[Zn(1)]Cl ₂
Crystallization conditions	Brown single crystals were grown by slow evaporation of CH ₂ Cl ₂	Orange single crystals were grown by slow evaporation of chloroform/acetonitrile (8/2)	Brown single crystals were grown by slow evaporation of chloroform/acetonitrile (8/2) solution.
Chemical formula	C ₃₈ H ₄₆ CuN ₂ O ₂ ·C ₂ H ₃ N	C ₉₁ H ₉₉ Cu ₂ N ₇ O ₄ ·6(H ₂ O)	C ₉₁ H ₉₈ Cl ₂ Cu ₂ N ₇ O ₄ Zn·3(CHCl ₃)
<i>M_r</i>	667.36	1577.85	1975.21
Crystal system, space group	Monoclinic, <i>P2₁/c</i>	Orthorhombic, <i>Pbcn</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	200	200	200
<i>a</i>	14.9821 (3)	11.3594 (2)	69.071 (3)
<i>b</i>	27.9247 (7)	40.7108 (6)	14.7327 (6)
<i>c</i> (Å)	18.0471 (4)	19.0962 (3)	19.7966 (8)
α	90	90	90
β	107.420 (1)	90	98.123 (2)
γ (°)	90	90	90
<i>V</i> (Å ³)	7204.1 (3)	8831.0 (2)	19942.9 (14)
<i>Z</i>	8	4	8
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α
μ (mm ⁻¹)	1.14	1.06	3.88
Crystal size (mm)	0.5 × 0.15 × 0.1	0.25 × 0.2 × 0.02	0.41 × 0.22 × 0.07
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	50720, 12681, 12053	54737, 7827, 5084	84593, 18504, 15500
<i>R</i> _{int}	0.017	0.072	0.040
(sin θ / λ) _{max} (Å ⁻¹)	0.595	0.596	0.610
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.104, 1.03	0.091, 0.288, 1.10	0.071, 0.208, 1.05
No. of reflections	12681	7827	18504
No. of parameters	855	510	1178
No. of restraints	0	0	42
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.74, -0.44	1.02, -0.71	1.84, -1.11
CCDC	1052163	1052164	1052165

UV-Visible titration

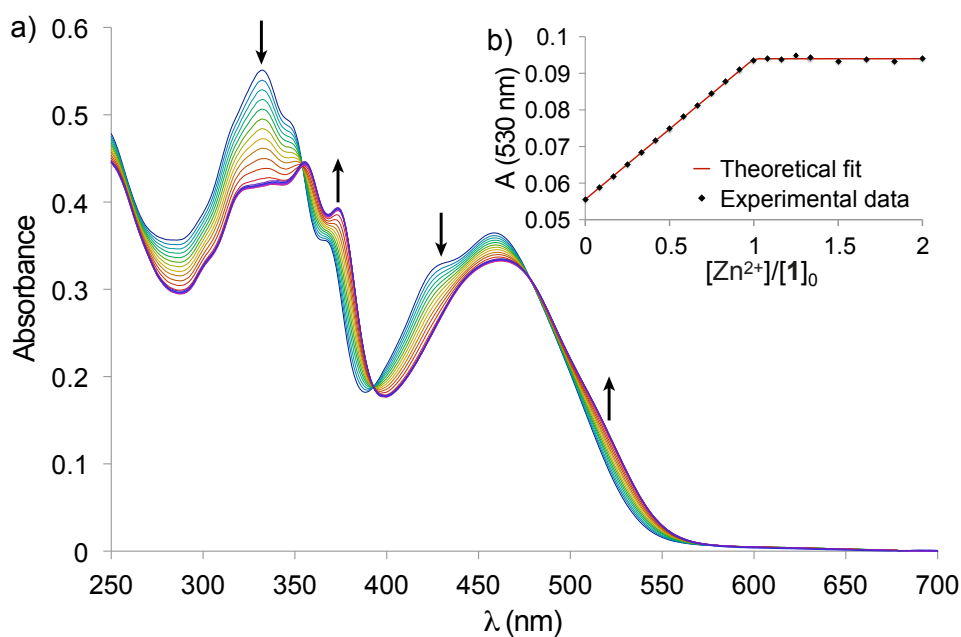


Figure S2. a) UV-Vis titration of tweezers **1** ($5.0 \times 10^{-6} \text{ mol.l}^{-1}$) with $ZnCl_2$ in $CHCl_3$. b) Absorbance at 530 nm and fitting with a 1:1 binding model.

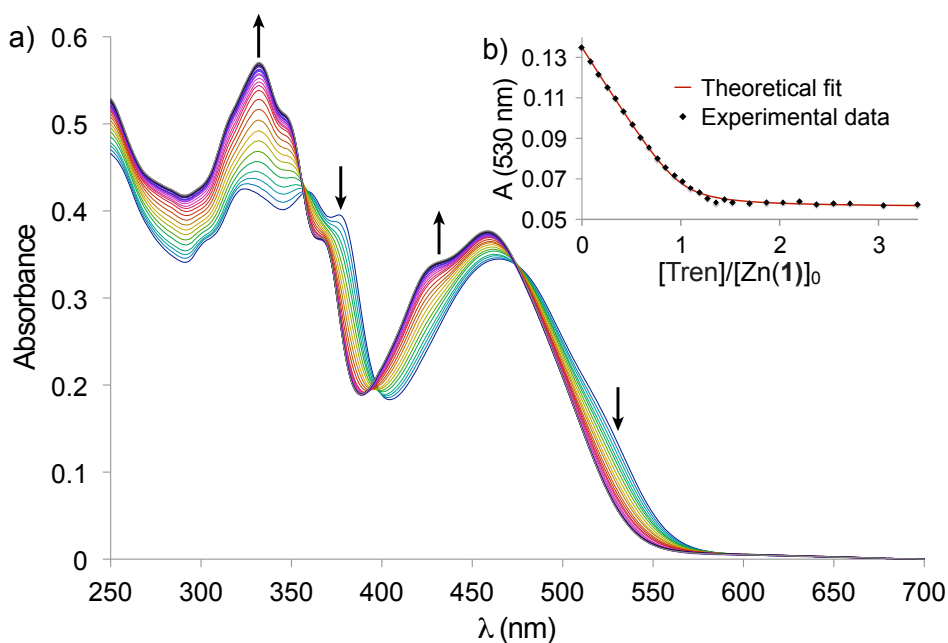


Figure S3 a) UV-Vis titration of complex $[Zn(1)](ClO_4)_2$ ($5.0 \times 10^{-6} \text{ mol.L}^{-1}$) upon addition of tren in $CHCl_3$. b) Absorbance at 530 nm and 1:1 binding model fit.

Mass spectrum of the closed tweezers by zinc $[\text{Zn}(\mathbf{1})]\text{Cl}_2$

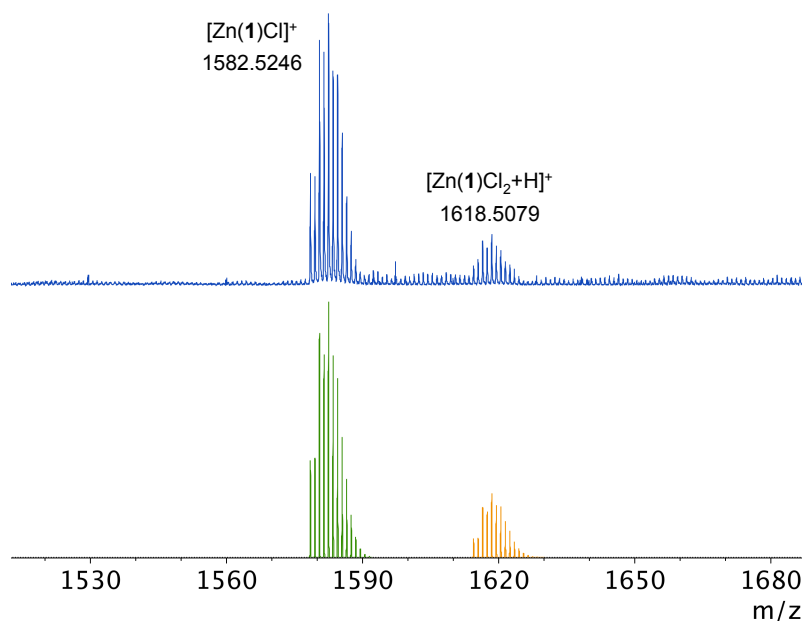


Figure S4. Mass spectrum of the closed tweezers by zinc $[\text{Zn}(\mathbf{1})]\text{Cl}_2$; experimental (top) and calculated (bottom)

Full scale EPR spectrum of the closed tweezers complex $[\text{Zn}(\mathbf{1})](\text{ClO}_4)_2$

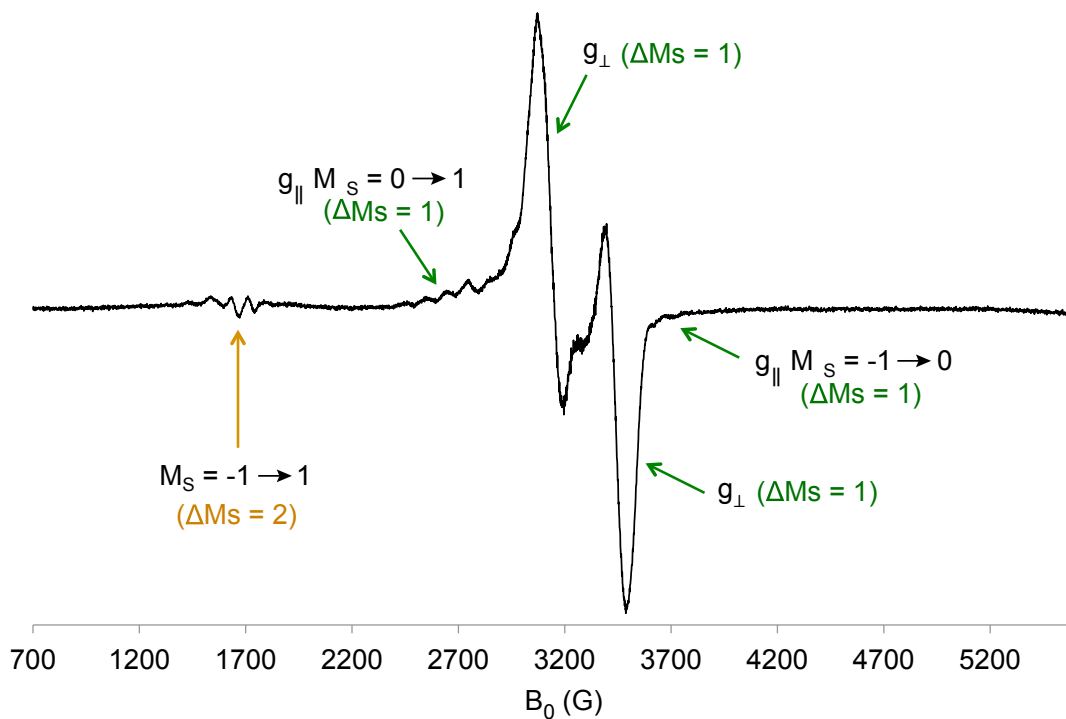


Figure S5. EPR spectrum of the closed tweezers complex $[\text{Zn}(\mathbf{1})](\text{ClO}_4)_2$ in frozen solution of CHCl_3 ($1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) at 5 K; allowed transitions (green), forbidden transition (orange)

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