Chiral stimuli-responsive metallo-supramolecular assembly induced by Cu^{II}/Cu^{I} redox change.

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Supporting Information

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1 GENERAL REMARKS

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques unless stated otherwise. Reagents were purchased from commercial chemical suppliers (mainly Acros, Aldrich, Alfa Aesar, TCI Europe and Strem) and used without further purification. Solvents were dried and degassed according to standard procedures. ^{1}H, ^{13}C [1] and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer and a Bruker Avance III HD - 500 MHz. ^{13}C assignments were confirmed when necessary with the use of DEPT 135 experiments. ^{1}H and ^{13}C-NMR spectra were referenced using the residual solvent peak ($CDCl_3$: δ H = 7.26 ppm; δ C = 77.16 ppm) at 295K. Chemical shifts δ are given in ppm whereas coupling constants *J* are stated in Hertz (Hz). The following abbreviations are used to classify the multiplicity of the observed signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, dd = doublet from doublet, dt = doublet from triplet, m = complex multiplet or broad signal. Positive mode electrospray ionization mass spectra (ESI-MS) were recorded on microTOF, Bruker Daltonics. All manipulations were conducted under an argon atmosphere unless otherwise stated.

2 SYNTHESIS OF MONOTOPIC & DITOPIC BISOXAZOLINE LIGANDS 1 & 4

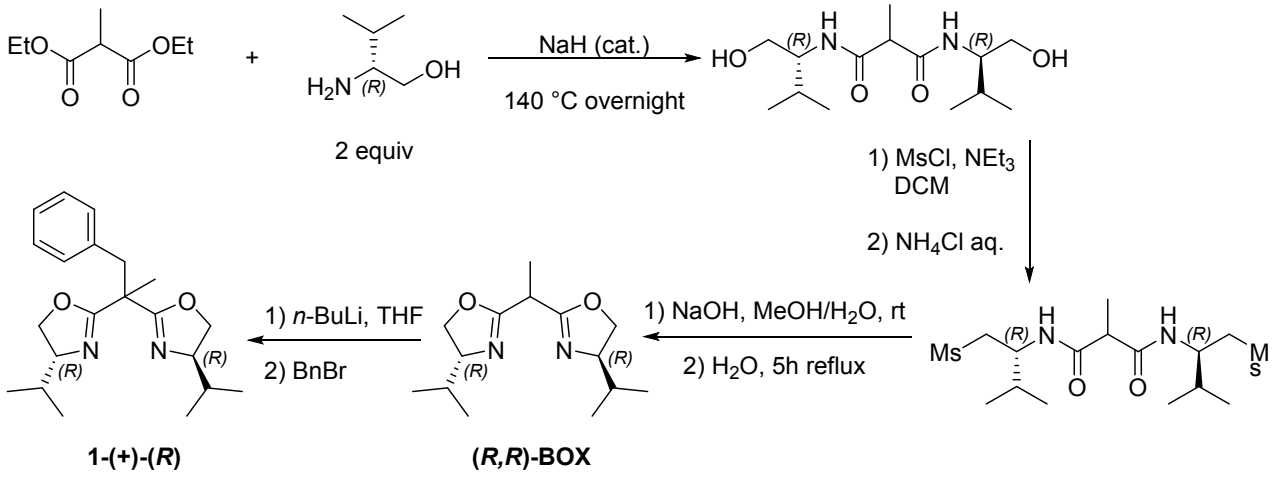
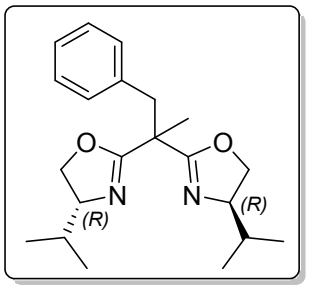


Figure S 1. Synthesis of bisoxazoline unit (*R,R*)-BOX.

(*R*)-1

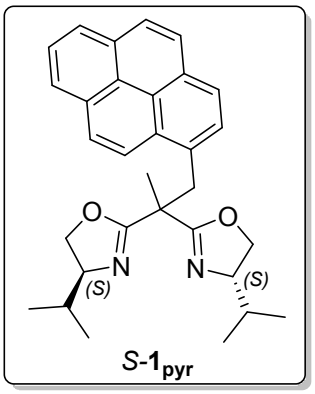


This monotopic (*R*)-Box ligand was synthesized according to the procedure reported in literature for (*S*)-Box.[1]: 58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28-7.11 (m, 5H; H_{Arom}), 4.29-4.15 (m, 2H; -NCH), 4.08-3.85 (m, 4H; -OCH_2), 3.29 (q, ^4J= 13.5 Hz, 2H; -CH_2), 1.88-1.65 (m, 2H; -C<u>H</u>$(CH_3)_2$), 1.43 (s, 3H; -C(C<u>H</u>$_3$), 0.92-0.79 (m,9H; -CH(C<u>H</u>$_3)_2$), 0.82 (d, J = 6.8 Hz, 3H, CH(C<u>H</u>$_3)_2$); IR (KBr): ṽ = 1659 cm-1 (s, free C=N); MS (ESI +): m/z: 343.23 $[M+H]^+$; elemental analysis calcd (%) for $C_{21}H_{30}N_2O_2$ (342.48): C 73.65, H 8.83, N 8.18; found C 73.43, H 8.72, N 7.95. $[\alpha]_D^{20}$ = +55 (*c* 1.14, $CHCl_3$).

(*S*)-1

This monotopic (*S*)-Box ligand was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[2] : IR (KBr): 1657 cm^{-1} (s, free C=N), $[\alpha]_D^{20}$ = -54 (*c* 1.14, $CHCl_3$).

(*S*)-1$_{pyr}$



The (*S,S*)-**BOX** was dissolved in dry THF, cooled down to -78 °C and BuLi was added. After 15 min at this temperature a THF solution of 1-(Bromomethyl)pyrene was added dropwise to the (*S,S*)-**BOX**-solution. The

reaction mixture is allowed to reach room temperature and stirred overnight. The crude was quenched with saturated solution of NH_4Cl, extracted with DCM and purified by column chromatography (eluent: Et_2O).The pyrene bisoxazoline ligand was isolated in 80% as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 9.3 Hz, 1H, H_{Ar}), 8.16 (dd, *J* = 7.6, 2.8 Hz, 2H, H_{Ar}), 8.07 (t, *J* = 8.1 Hz, 2H, H_{Ar}), 8.03 (s, 2H, H_{Ar}), 7.98 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 7.92 (d, *J* = 7.9 Hz, 1H, H_{Ar}), 4.29 – 4.22 (m, 1H, CH_2), 4.14 (dd, *J* = 15.0, 9.5 Hz, 3H, CH_2Ar, CH_2), 4.08 – 4.02 (m, 1H, CH(O)), 3.98 – 3.92 (m, 2H, CH(N), CH(O)), 3.87 (dt, *J* = 9.9, 6.5 Hz, 1H, CH (N)), 1.80 (dt, *J* = 13.2, 6.6 Hz, 1H, C<u>H</u>(CH_3)), 1.62 (dt, *J* = 13.1, 6.4 Hz, 1H, C<u>H</u>(CH_3)$_2$), 1.48 (s, 3H, CH_3), 0.92 (d, *J* = 6.8 Hz, 3H, CH(C<u>H</u>$_3$)$_2$), 0.87 (d, *J* = 6.7 Hz, 3H, CH(C<u>H</u>$_3$)$_2$), 0.81 (d, *J* = 6.7 Hz, 3H, CH(C<u>H</u>$_3$)$_2$), 0.76 (d, *J* = 6.8 Hz, 3H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.91 (C_{Ar}), 167.68 (C_{Ar}), 131.60 (C_{Ar}), 131.52 (C_{Ar}), 130.89 (C_{Ar}), 130.56 (C_{Ar}), 130.48 (C_{Ar}), 129.35 (CH_{Ar}), 127.62 (CH_{Ar}), 127.09 (CH_{Ar}), 127.01 (CH_{Ar}), 125.86 (CH_{Ar}), 125.15 (CH_{Ar}), 125.05 (C_{Ar}), 124.74 (CH_{Ar}), 124.53 (CH_{Ar}), 124.32 (CH_{Ar}), 72.13 (CH(N)), 71.76 (CH(N)), 70.28 (CH_2(O)), 70.02 (CH_2(O)), 44.37 (C(CH_3)), 38.13 (CH_2Ar), 32.55 <u>C</u>H(CH_3)$_2$), 32.39 <u>C</u>H(CH_3)$_2$), 21.97 CH(<u>C</u>H$_3$)), 18.83 2CH(<u>C</u>H$_3$)$_2$), 17.93 CH(<u>C</u>H$_3$)$_2$), 17.63 CH(<u>C</u>H$_3$)$_2$);. IR (neat): ṽ 1656.9 cm^{-1} (s, free C=N), elemental analysis calcd (%) for $C_{31}H_{34}B_2N_2O_2$: C 79.79, H 7.34, N 6.00; found C 79.20, H 7.40, N 6.03.

Synthesis of Ditopic ligand (*R*)-4

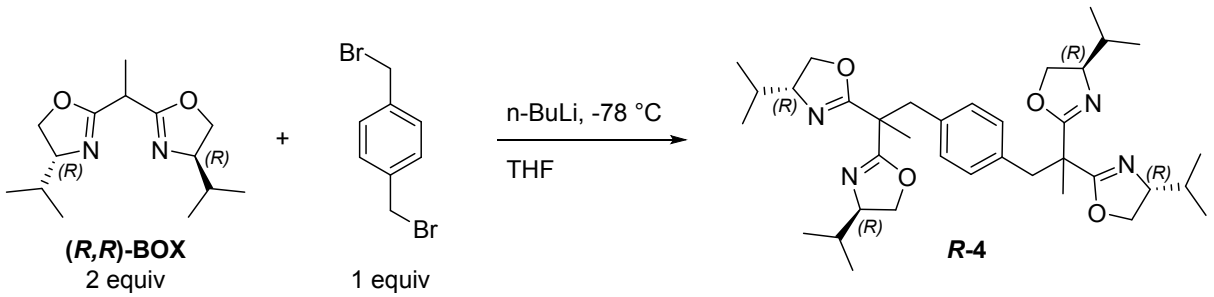
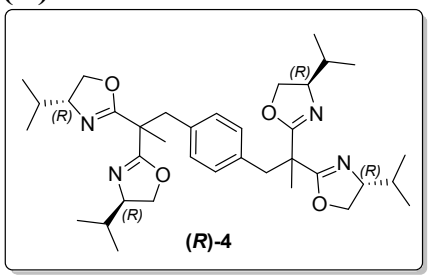


Figure S 2. Synthesis of bisoxazoline ditopic **(*R*)-4**.

(*R*)-4: [3]



1,1'-Bis[(4*R*)-4,5-dihydro-4-isopropyloxazol-2-yl]ethane (3.96 mmol, 1g)[1] was dissolved in dry tetrahydrofuran (25 mL). A solution of 1.6 M *n*-BuLi in hexane (4.31 mmol, 2.7 mL) was added drop-wise at -78°C. After stirring for 15 min, the bath was removed and α,α'-dibromo-*p*-xylene (1.96 mmol, 517.3 mg) was added. The mixture was then stirred at room temperature for 12 h. The resulting mixture was washed with a saturated NH_4Cl solution and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave colorless oil, which was purified by silica gel column chromatography (AcOEt/MeOH, 95:5) yielding a colorless viscous oil (1.56 mmol, 948 mg, 80%). $[\alpha]_D^{25}$: +0.84 (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (s, 4H; H_{Ar}), 4.22 (dt, ^3J= 8.0 Hz, ^3J= 1.3 Hz, 4H; -NC<u>H</u>), 4.05-3.90 (m, 8H; -OC<u>H</u>$_2$), 3.24 (s, 4H; -C<u>H</u>$_2$), 1.84-1.67 (m, 4H; -C<u>H</u>$(CH_3)_2$), 1.40 (s, 6H; -C(C<u>H</u>$_3$), 0.94-0.80 (m, 24H; -CH(C<u>H</u>$_3$)$_2$;

This ditopic Box ligand was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[4]

(*S*)-4. The same procedure was used with 1,1'-bis[(4*R*)-4,5-dihydro-4-isopropyloxazol-2-yl]ethane. $[\alpha]_D^{25}$: -0.81 (*c* 0.5, $CHCl_3$).

3 SYNTHESIS OF $[Cu(BOX)_2][BF_4]_2$ COMPLEXES

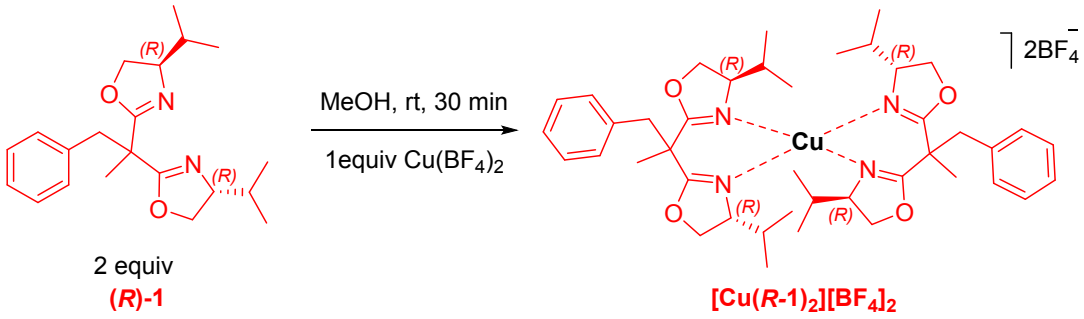


Figure S 3. Synthesis of homochiral $Cu^{II}(R\text{-}\mathbf{1})_2(BF_4)_2$ complexes

General procedure for synthesis of the enantiopure $[Cu^{II}\text{-}(\mathbf{1})_2][BF_4]_2$ complexes: The desired enantiopure **1-(-)-(*S*) or 1-(+)-(*R*) Box** ligand (0.030 g, 0.087 mmol) was dissolved in MeOH (0.5 mL), stirred for 15 min and then a solution of the $Cu(BF_4)_2$ (0.010g; 0.043mmol) in MeOH (0.5 mL) was added. The resulting turquoise solution was then stirred for 30 min at room temperature, after whom the solvent was concentrated and the complex was precipitated in Et_2O giving the corresponding complex $[Cu^{II}(R\text{-}\mathbf{1})_2][BF_4]_2$ or $[Cu^{II}(S\text{-}\mathbf{1})_2][BF_4]_2$ as a blue-green powder.

$[Cu^{II}(R\text{-}\mathbf{1})_2][BF_4]_2$ in nearly quantitative yield (0.038 g, 98%). IR: $\tilde{\nu}$ = 1629 cm^{-1} (s, C=N); elemental analysis calcd (%) for $C_{42}H_{60}B_2F_8N_4O_4Cu$ + CH_2Cl_2: C 51.29, H 6.21, N 5.56; found C 50.73, H 6.21, N 5.81. HRMS (ESI): m/z calcd for $[C_{42}H_{60}N_4O_4Cu]^+$: 747.3905, Found: 747.3871.

Synthesis of the Racemic complex of (+/-)-$\mathbf{Cu^{II}\text{-}(1)_2(BF_4)_2}$

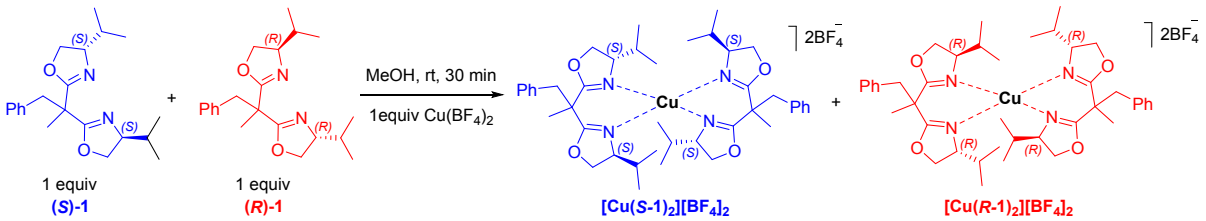


Figure S 4. Synthesis of homochiral $Cu^{II}(R\text{-}\mathbf{1})_2(BF_4)_2$ and $Cu^{II}(S\text{-}\mathbf{1})_2(BF_4)_2$complexes as racemic mixture

Ligands **1-(+)-(*R*)** (0.043 mmol, 15 mg) and **1-(-)-(*S*)** (0.043 mmol, 15 mg) were dissolved in 0.5 mL of MeOH, stirred for 15 min and then a solution of the $Cu(BF_4)_2$ (0.010g; 0.043 mmol) in MeOH (0.5 mL) was added. The resulting turquoise solution was then stirred for 30 min at room temperature, after whom the solvent was concentrated and the complex was precipitated in Et_2O giving the corresponding homochiral complex $(Cu^{II}(R\text{-}\mathbf{1})_2(BF_4)_2$ and $Cu^{II}(S\text{-}\mathbf{1})_2(BF_4)_2$ as a blue-green powder in 93% yield (0.037 g). IR (neat): $\tilde{\nu}$ = 1633 cm-1 (s, C=N), elemental analysis calcd (%) for $C_{42}H_{60}B_2F_8N_4O_4Cu + CH_2Cl_2$: C 51.29, H 6.21, N 5.56; found C 51.21, H 6.58, N 5.61. HRMS (ESI): m/z calcd for $[C_{42}H_{60}N_4O_4Cu]^+$: 747.3905, Found: 747.3865. Analytical pure monocrystal for X-ray analysis was obtained from DCM/Et_2O mixture.

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4 SYNTHESIS OF $[Cu(diBOX)_n][BF_4]_{2n}$ METALLOPOLYMERS

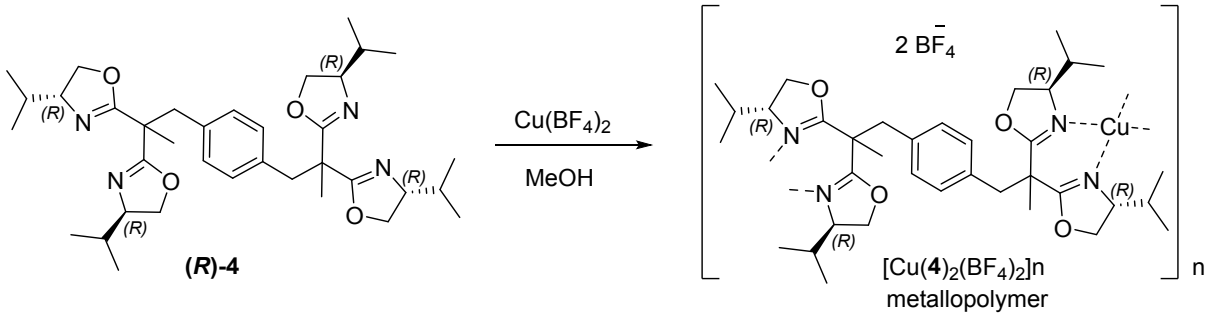

Figure S 5. Synthesis of homochiral enantiopur Cu^{II} metalloplymer

Enantiopure metallo-polymer $[Cu(R\text{-}\mathbf{4})_2(BF_4)_2]_n$

Chiral ditopic ligand **(*R*)-4** (0.07 mmol, 40 mg) was dissolved in 0.5 mL of MeOH. The resulting colorless solution was stirred for 10 min before adding drop-wise a previously prepared solution of $Cu(BF_4)_2$. (0.07 mmol, 16.6 mg) in MeOH (0.5 mL). The turquoise solution was stirred overnight at room temperature and the solvent was evaporated to dryness. The resulting turquoise powder was washed with diethyl ether and dried under vacuum giving the product in 95% yield (54 mg). ^1H NMR could not be recorded because Cu(II) is paramagnetic; IR (neat): $\tilde{\nu}$ = 1577 cm^{-1} (s, C=N). elemental analysis calcd (%) for $C_{72}H_{108}B_4Cu_2F_{16}N_8O_8.2(H_2O)_2$: C 49.13, H 6.64, N 6.37; found C 49.17, H 6.61, N 6.15.

Racemic metallo-polymer $[Cu(4)_2(BF_4)_2]_n$

Ligands ditopic **(*R*)-4** (0.035 mmol, 10 mg) and **(*S*)-4** (0.035 mmol, 10 mg) were dissolved in 0.5 mL of MeOH. The resulting colorless solution was stirred for 10 min before adding drop-wise a previously prepared solution of $Cu(BF_4)_2.xH_2O$ (0.07 mmol, 15.63 mg) in MeOH (0.5 mL). The turquoise solution was stirred overnight at room temperature and the solvent was evaporated to dryness. The resulting turquoise powder was washed with diethyl ether and dried under vacuum giving the product in nearly quantitative yield

5 SYNTHESIS OF RACEMIC $[Zn(BOX)_2][BF_4]_2$ COMPLEX 2

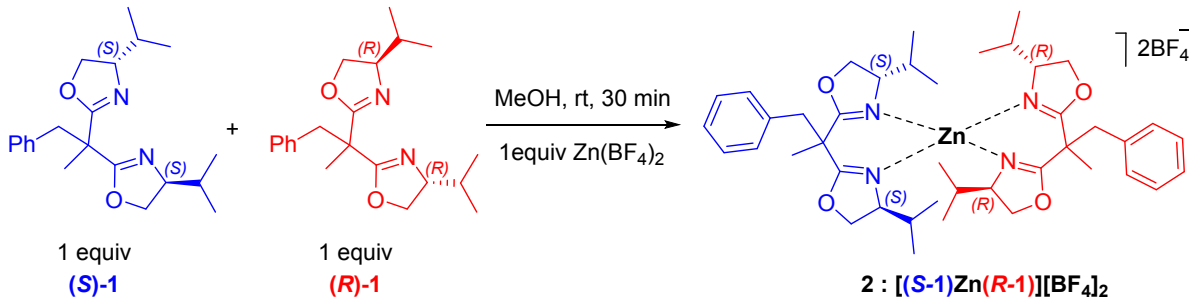

Figure S 6. Synthesis of heterochiral $[(S\text{-}\mathbf{1})Zn^{II}(R\text{-}\mathbf{1})][BF_4]_2$ complex

Procedure for the synthesis of the racemic Zn^{II} complex 2: Ligands box **(*R*)-1** (0.010 g, 0.0292 mmol) and **(*S*)-1** (0.010 g, 0.0292 mmol) were dissolved in MeOH (0.25 mL), stirred for 15 min and the solution of the $Zn(BF_4)_2$ (0.07 g, 0.0292 mmol) in MeOH (0.25 mL) was added. The reaction mixture was stirred for 1h, after whom the solvent was concentrated and the complex was precipitated in Et_2O giving the corresponding heterochiral complex $[(S\text{-}\mathbf{1})Zn^{II}(R\text{-}\mathbf{1})][BF_4]_2$ was isolated in a high yield (0.024, 89%). ^{1}H NMR (300 MHz, MeOD) δ 7.34-7.06 (m, 10H, H_{Ph}), 4.33 (q, J = 9.6 Hz, 4H, CH_2), 4.13 (q, J = 8.5 Hz, 4H, CH_2), 3.95 (s, 4H, CH(N)), 3.21 (q, J = 13.3 Hz, 2H, C*H*(CH_3)), 1.78 (dd, J = 14.3, 7.5 Hz, 4H, C*H* (CH_3)$_2$), 1.41 (s, 6H, CH_3), 0.99-0.57 (m, 24H, CH(C*H*$_3$)), IR (neat): $\tilde{\nu}$ = 1633 cm^{-1} (s, C=N), HRMS (ESI): m/z calcd for $[C_{42}H_{60}N_4O_4Zn]^+$: 748.3906, Found: 748.3609. Analytical pure monocrystal for X-ray analysis was obtained from DCM/Et_2O mixture.

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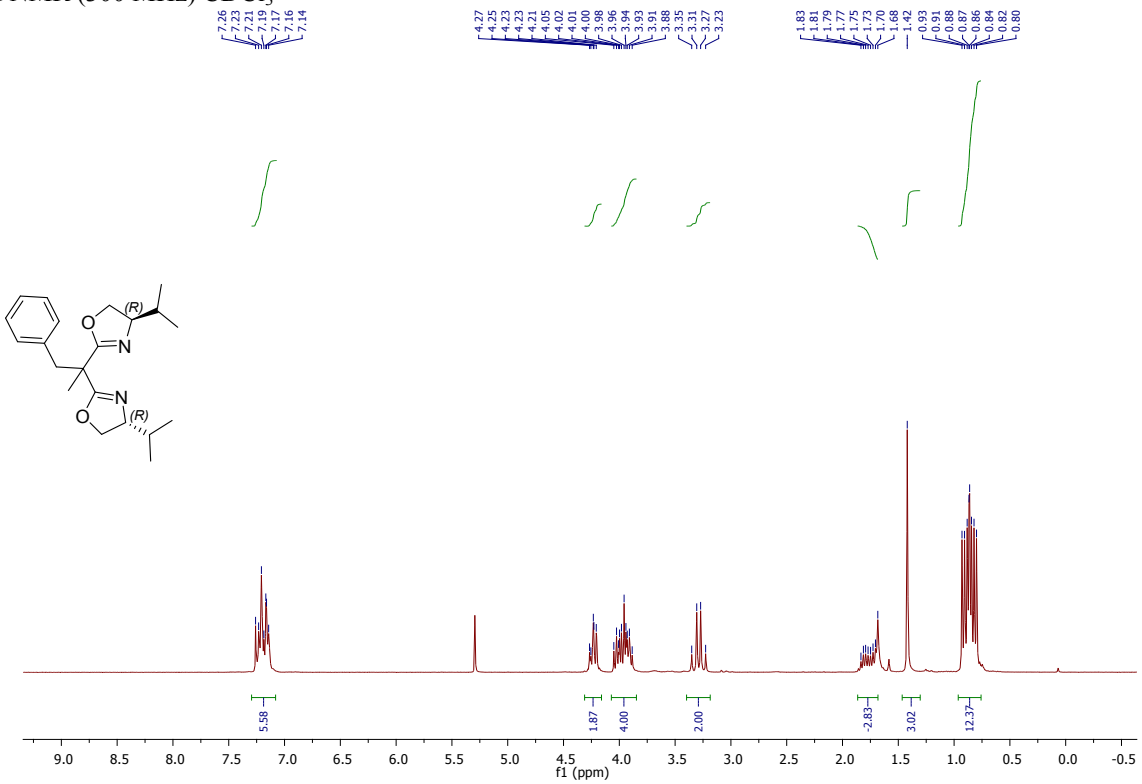
6 ^{1}H, NMR SPECTRA OF ALL COMPOUNDS & IR OF COPPER COOMPLEXES.

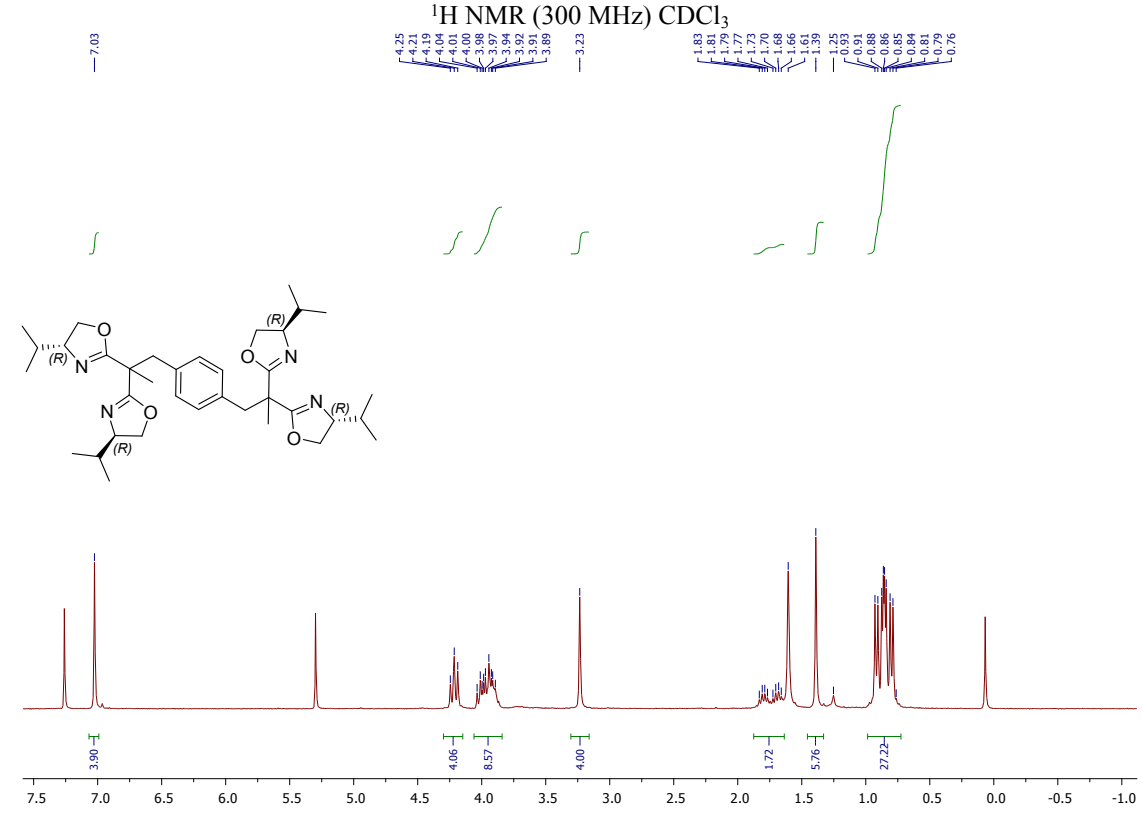
Ligand (*R*)-1

^{1}H NMR (300 MHz) $CDCl_3$



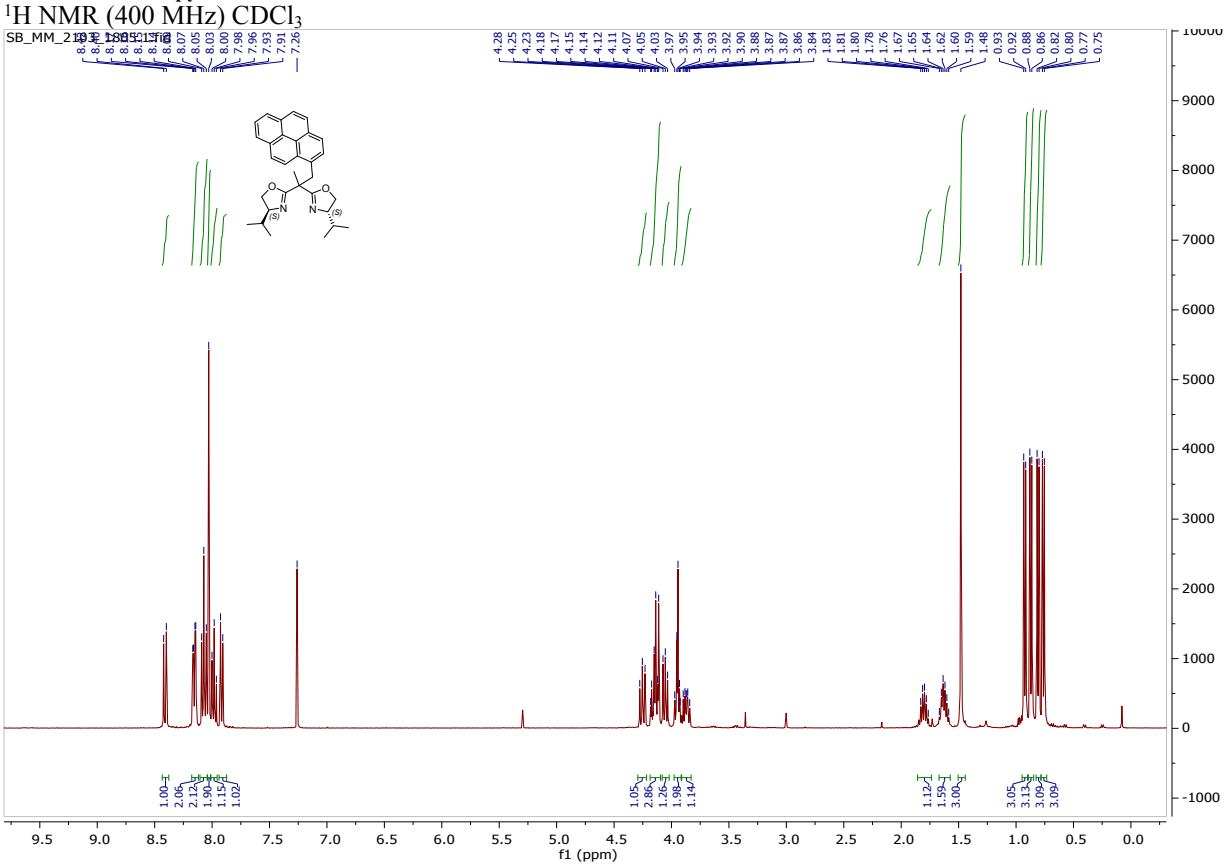
Ligand (*R*)-4

^{1}H NMR (300 MHz) $CDCl_3$

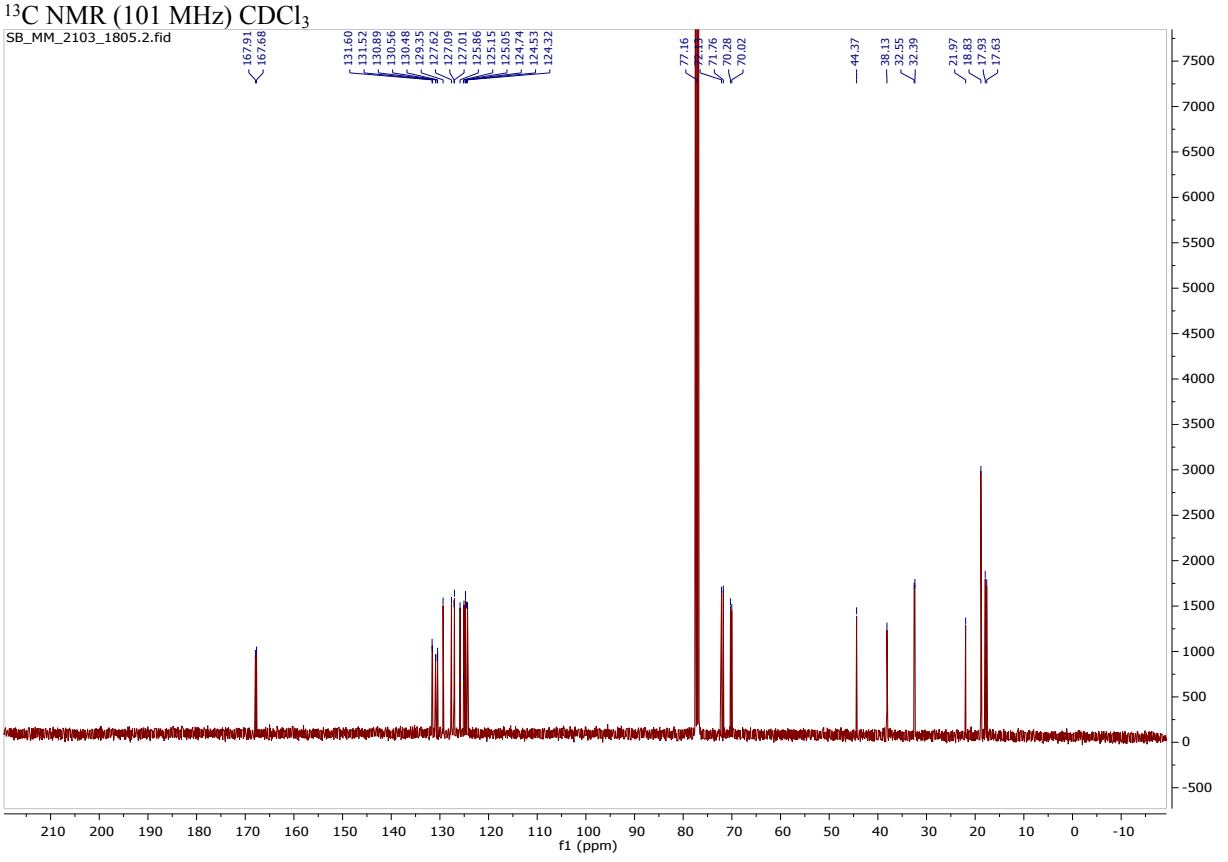


Ligand (*S*)-1_{pyr}

^{1}H NMR (400 MHz) $CDCl_3$

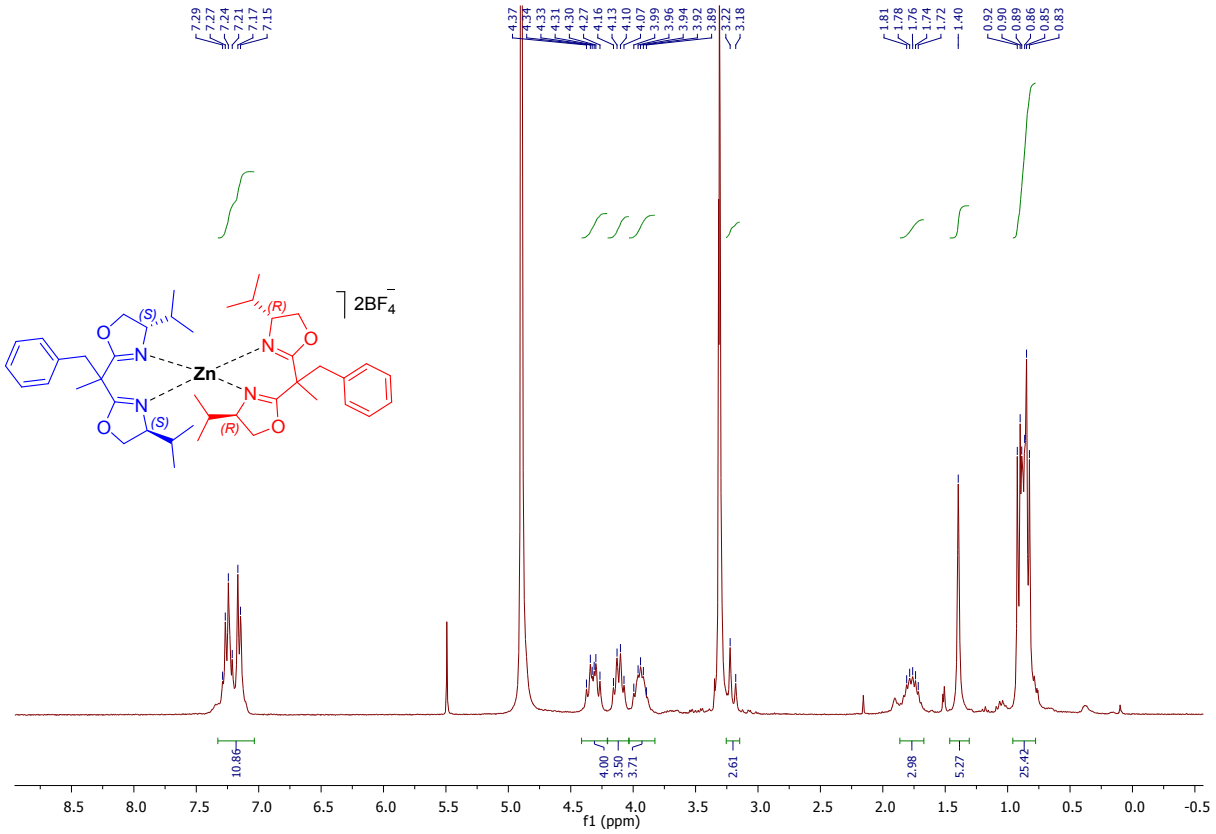


^{13}C NMR (101 MHz) $CDCl_3$



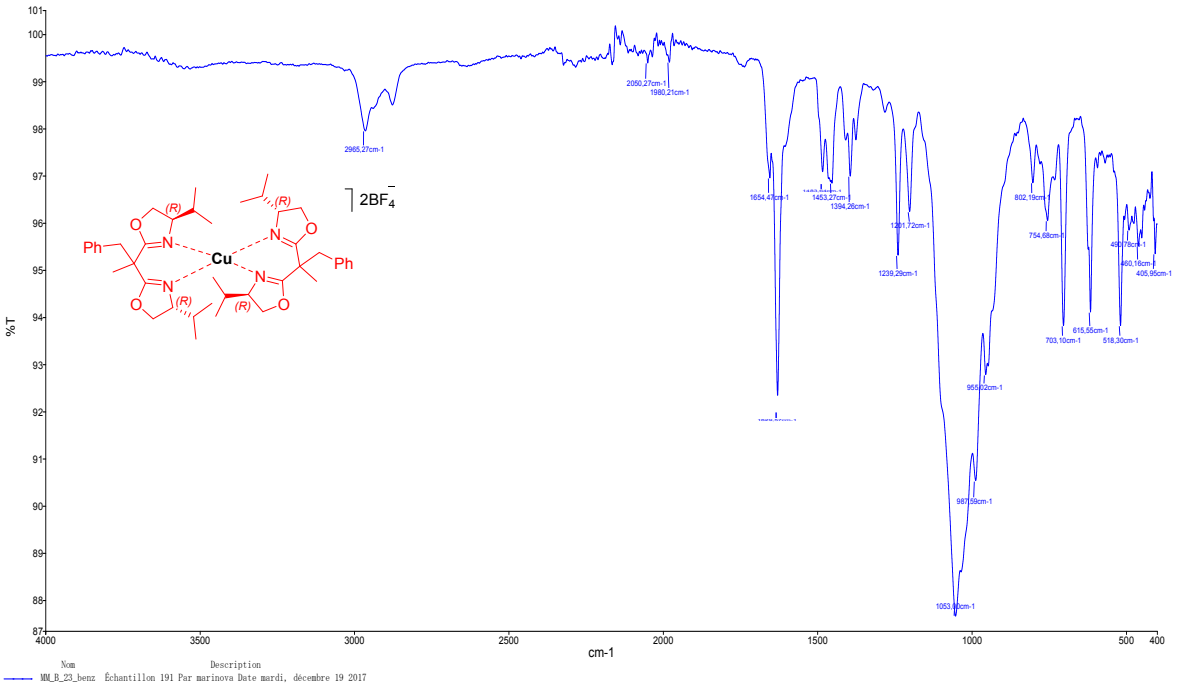
Complex 2 :[(*S*-1)Zn^{II}(*R*-1)][BF_4]$_2$

^{1}H NMR (300 MHz) MeOD



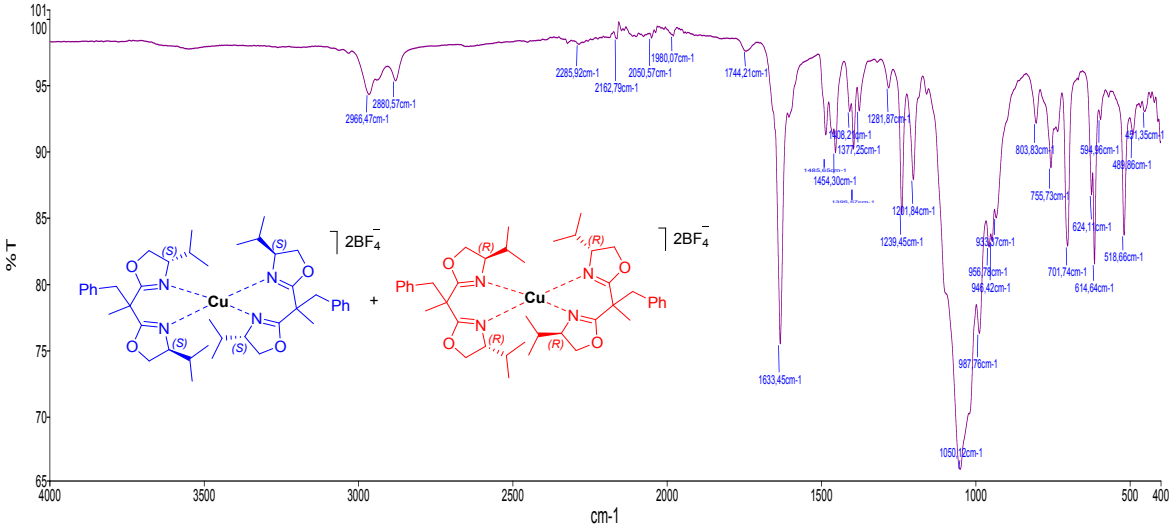
Complex (*R*)-3:[Cu(*R*-1)$_2$][BF_4]$_2$

Infra Red spectra (cm^{-1})



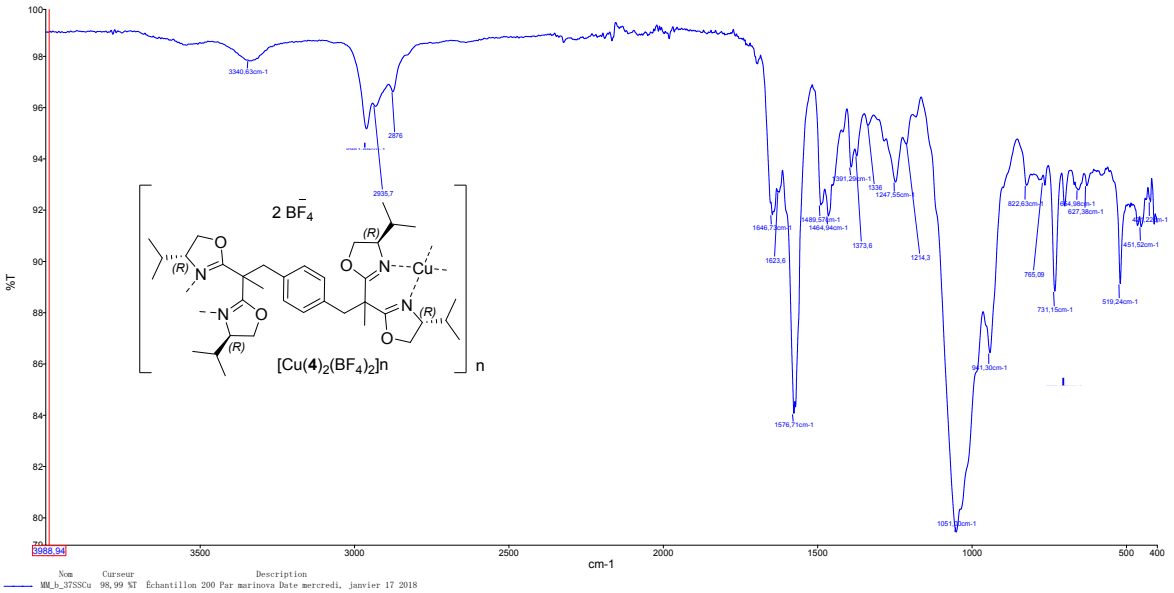
Complex Racemic -3: $[Cu(1)_2][BF_4]_2$

Infra Red spectra (cm^{-1})



Metallo-polymer $[Cu(\mathit{R}\text{-}4)_2(BF_4)_2]_n$

Infra Red spectra (cm^{-1})



7 ELECTROCHEMICAL MEASUREMENTS

The experiments were performed in a three-electrode electrochemical cell. A 3.0 mm diameter glassy carbon disk was used as working electrode and Pt wires as counter electrode and pseudo-reference electrodes. The solvent was dichloromethane containing 0.1 M $TBAPF_6$ (Fluka >99.0%, for electrochemical analysis) as supporting electrolyte. The cyclic voltammetry experiments were performed at room temperature using a PGSTAT30 Autolab potentiostat. The potential of the Ferrocene Fc+/Fc redox transition was used as reference of the potential scale. Before the measurements, the solutions were desaerated by argon bubbling.

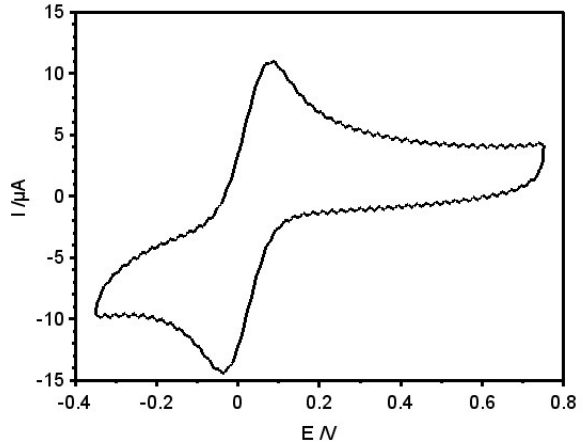


Figure S 7. Cyclic voltammetry of the homochiral enantiopure complex Cu(*S*-**1**)$_2$(BF_4)$_2$ on a glassy carbon electrode at a concentration of 1 mM in 0.1 M $TBAPF_6$ CH_2Cl_2 solution. Sweep rate 200 mV s^{-1}. The potential axis is referred to the Fc^+/Fc redox potential.

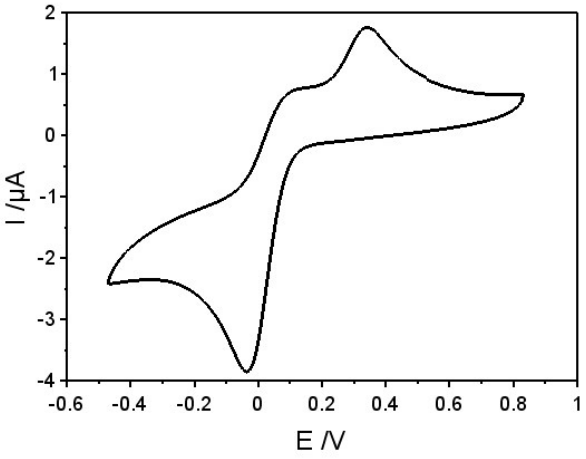


Figure S 8. Cyclic voltammograms at sweep rate of 20 mV s-1 with racemic Cu complex

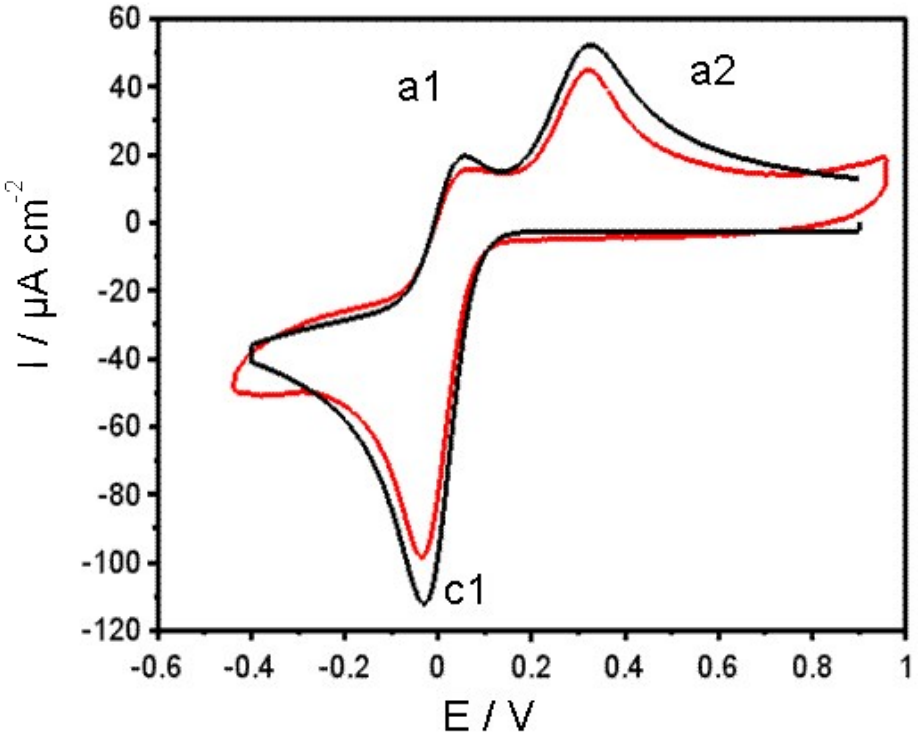


Figure S 9. Experimental (red line) and simulated (black line) cyclic voltammograms at 50 mV s^{-1} for the racemic complex. The simulated CV was obtained using digital simulations of an EC mechanism (cf. A. Bard and Faulkner, Electrochemical methods: Fundamental and Applications, 2nd Edition, Wiley Textbooks, 2000). Parameters: C= 8.5 10^{-7} mol cm^{-3}, D=5.5 10^{-6} mol cm^{-3}, k_0= 7 10^{-3} cm s^{-1} (electrochemical step), kc=0.2 s^{-1} (chemical step).

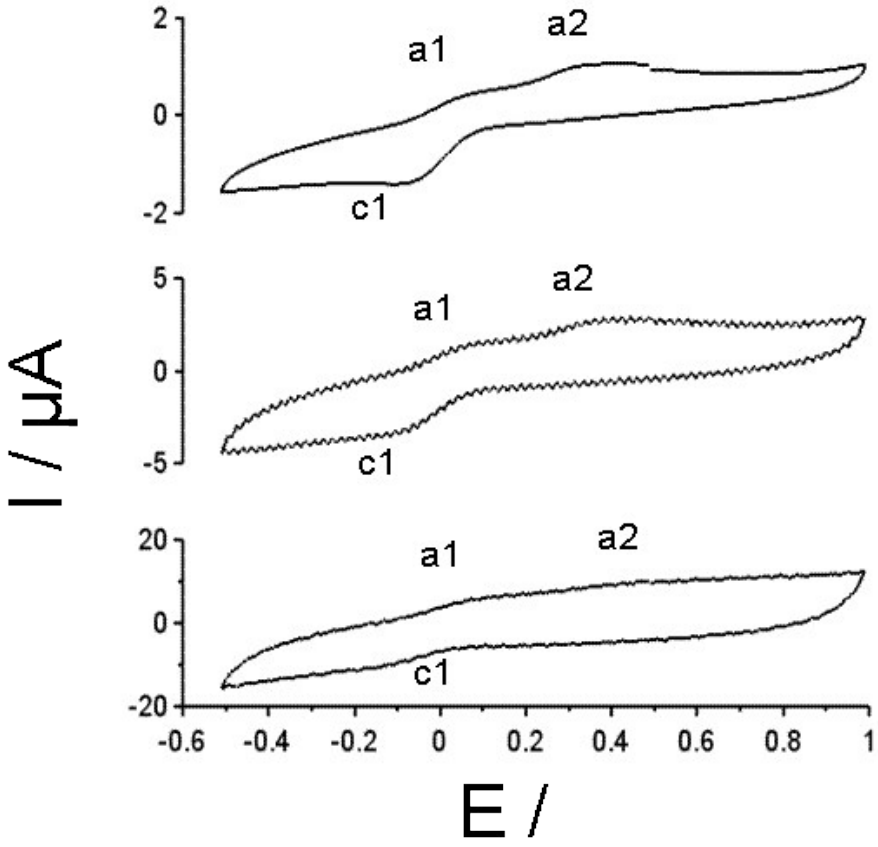


Figure S 10. Cyclic voltammograms at different sweep rates 20 mV s^{-1} (top), 500 mV s^{-1} (middle), 5000 mV s^{-1} (bottom) of the racemic mixture of $[Cu(\mathbf{4})_2(BF_4)_2]_n$

8 MASS SPECTROMETRY INVESTIGATIONS: FORMATION OF HETEROCHIRAL Cu^{I} COMPLEX

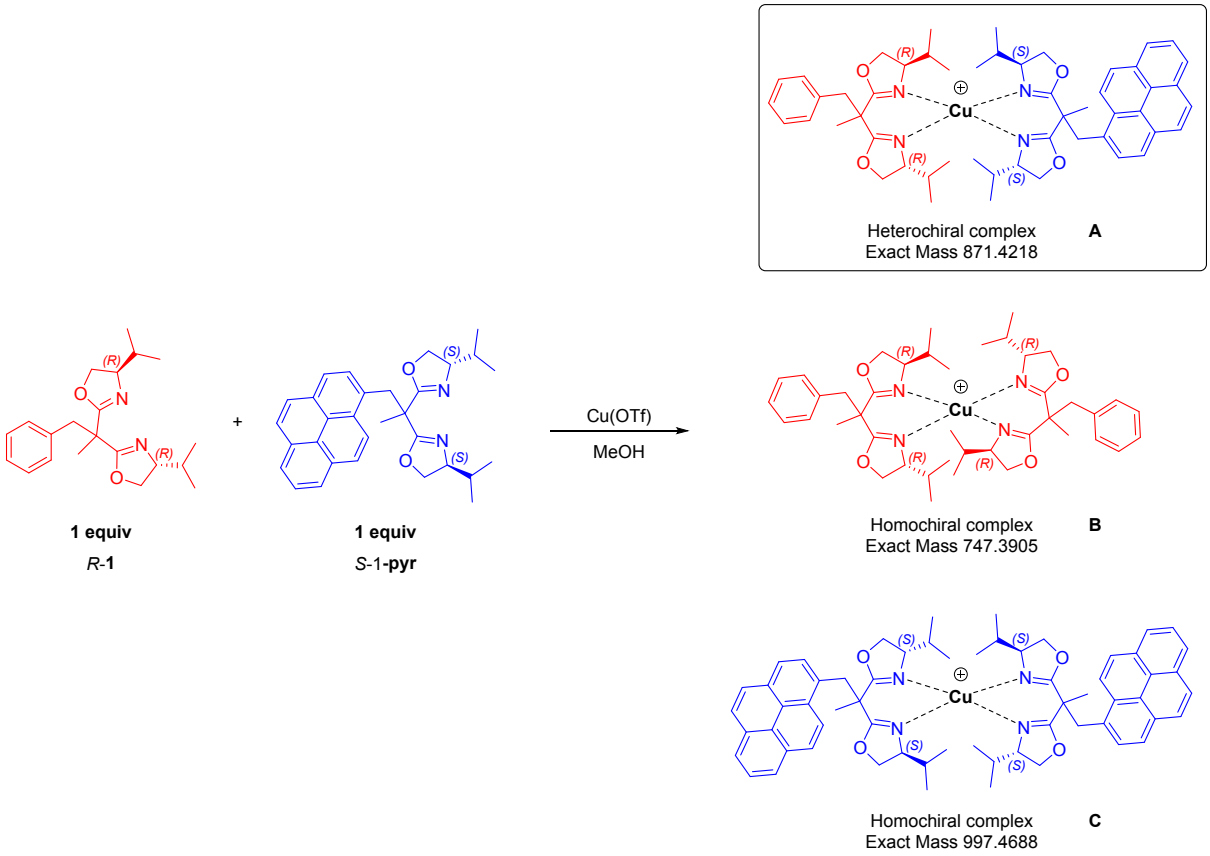


Figure S 11. Self-assembly of the Cu^{I} complexes upon addition of Cu(OTf), bisoxazoline ligand (*R*-**1**) and bisoxazoline ligand (S-**1-pyr**) in methanol.

Experimental procedure for heterochiral [(*R*-1)Cu^{I}(*S*-1_{pyr})][OTf] complex:

In a glove box, the *R*-**1** (5 mg, 14.6 µmol), *S*-$\mathbf{1}_{pyr}$ (6.8 mg, 14.6 µmol) and [Cu^{I}(OTf)]$_2$ •Toluene (7.5 mg, 14.6 µmol) were mixed all together in a sealed vial, then MeOH (0.3 mL) was added and the resulting brownish mixture was stirred for one hour. After this time, the solution was directly analyzed by high resolution electrospray ionization mass spectrometry (ESI-MS).

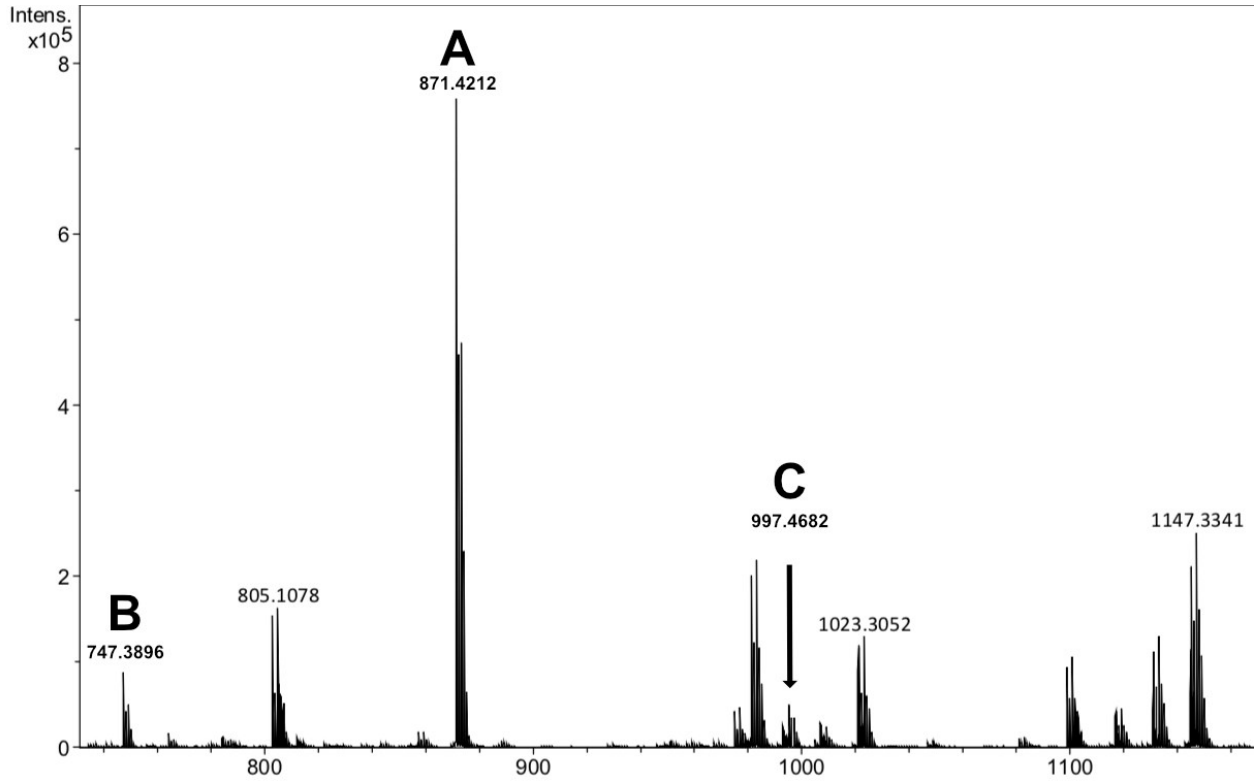


Figure S 12. Electrospray-ionization mass spectra (ESI-MS)

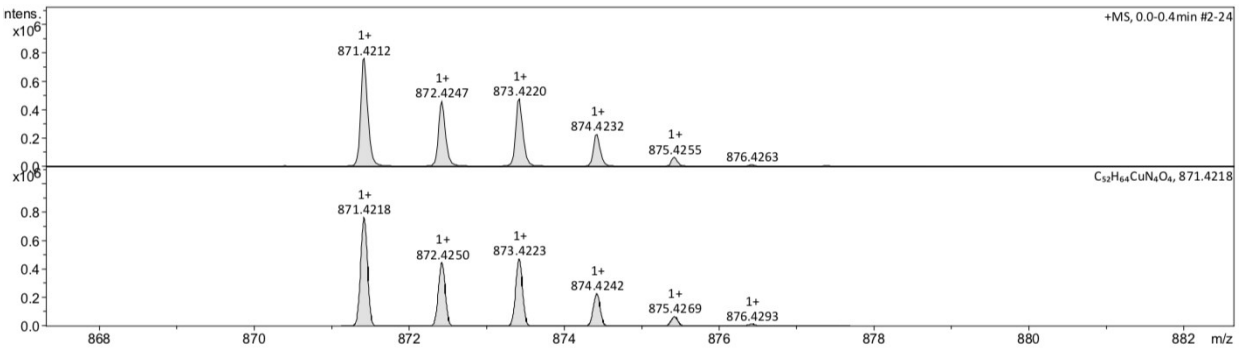


Figure S 13. Electrospray-ionization mass spectra (ESI-MS) of complex **A** and comparison of the isotope pattern for the observed M^+.

9 X-RAY STRUCTURES OF Cu & Zn COMPLEXES

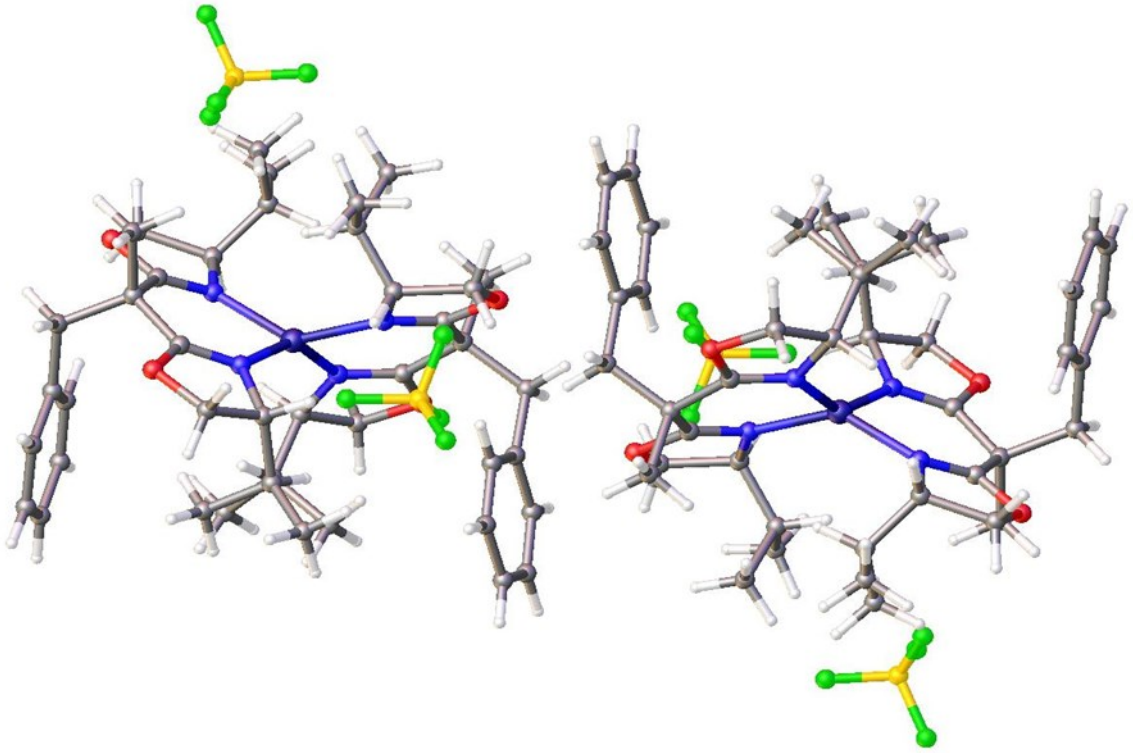


Figure S 14. X-ray structure of the racemic complex 2 with $Cu(BF_4)_2$. (CCDC Deposition Number 1984728)

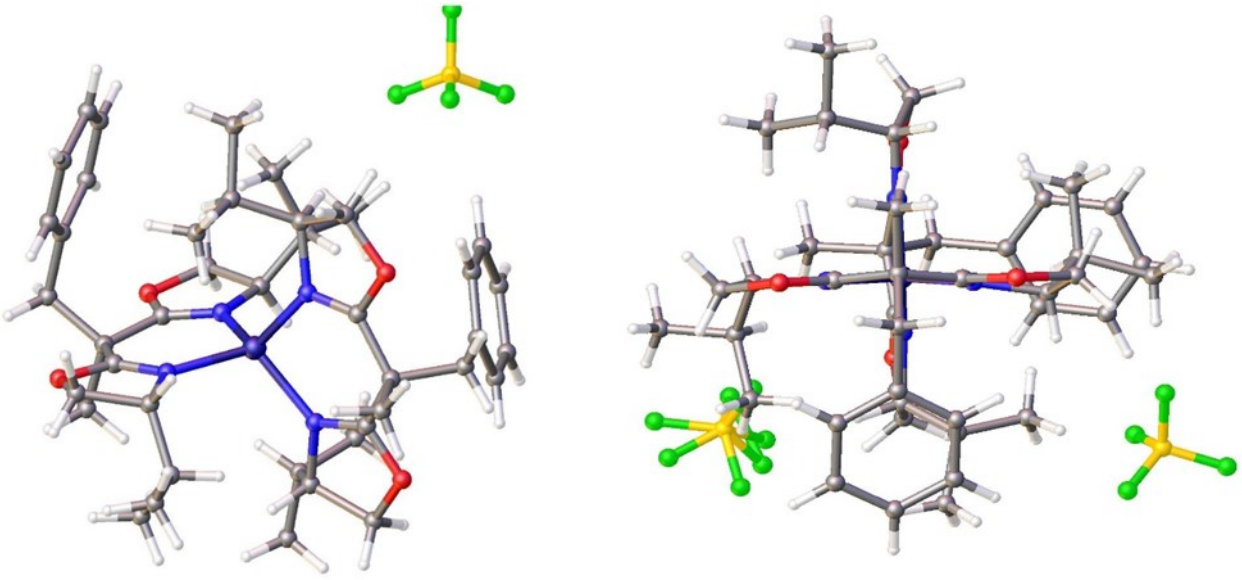


Figure S 15. X-ray structure of the heterochiral complex 3 with $Zn(BF_4)_2$. (CCDC Deposition Number 1984727)

10 REFERENCES.

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