Chiral Two Bladed ML 2 Metallamacrocycles: Design, Structures and Solution Behavior

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Paper

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Hannah Soudry,[a] Christophe Desmarets*[a] Geoffrey Gontard[a] Tiffany Edgington,[b] Andrew L. Cooksy,[b] and Hani Amouri*[a]

Chiral two bladed complexes of [Co(L)$_2$][BF$_4$]$_2$ (1) and [Zn(L)$_2$][BF$_4$]$_2$ (2) containing an atropoisomeric semi-rigid bidentate ligand L were synthesized and characterized. They are obtained as homochiral species but in racemic mixture via a ligand self-sorting mechanism. These enantiomers can be differentiated in solution using optically active anions.

The design and the construction of well-defined discrete molecular architectures have attracted intense interest due to their wide range of potential applications.[1] Metal-assisted self-assembly of complementary subunits has been intensively used to prepare fascinating metal-organic complexes, polyhedra, cages, bowls, capsules, interlocked molecules etc…[2] Another interesting challenge is to be able to control the stereochemistry of the final nanostructure.[3] The use of an optically active ligand to assure chiral transfer to the metal centre is the most appropriate approach; however it is tedious and requires the preparation of the optically active ligands beforehand.[4] However chirality can also arise at the metal centre using achiral bidentate ligands; for instance helicoïdal chirality (Δ or Λ) in octahedral metal complexes arises upon coordination of the metal centre by at least two achiral bidentate ligands.[4] A more convenient approach consists in the preparation of racemic molecules or metallacycles followed by separation using chiral auxiliaries to obtain the target optically active supramolecules.

In this context, our group has developed the use of 1,3-(bis(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6 dimethylbenzene to construct a variety of appealing supramolecular structures such as coordination polymers, metallamacrocycles, and cages.[5] We have established the synthesis of some discrete self-assembled metalla-supramolecular 3D capsules of type M$_2$L$_4$ based on Co(II) and Cu(II) that are able to encapsulate weakly coordinated anions such as BF$_4^-$ and PF$_6^-$. More recently, the introduction of a highly rigid luminescent ligand in our systems leads to the formation of silver polymers and Pd$_2$L$_4$ luminescent nanocapsules capable of accommodating neutral organic molecules and/or anionic organometallic complexes as guests.[6] As part of our research program, we sought to introduce a chiral spacer ligand in our systems to design and prepare new metallasupramolecular assemblies in which internal cavities could be used for enantioselective recognition and separation of small molecules. The present work describes our preliminary results using this novel chiral assembling ligand to construct chiral coordination assemblies.

Herein we describe the formation of homochiral two bladed ML$_2$ metallamacrocycles (M = Co(II), Zn(II)) but obtained as racemates *R,R* /*S,S* in 50/50 ratio starting from racemic ligand and the metal salts. No *meso*-complexes were obtained, illustrating a ligand sorting mechanism. Conversion of this racemic material to a mixture of diastereoisomeric salts using chiral anion metathesis is also reported.

The semi-rigid bidentate assembling ligand **L** contains two peripheral methyl benzimidazole moieties connected to 5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl as a central spacer.[7] Ligand **L** displays intrinsic *C2* symmetry and was prepared in good yield (Scheme 1) by nucleophilic substitution[5f] of the known compound 3,3'-bis(chloromethyl)-2,2-dimethoxy-5,5',6,6'tetramethyl-1,1'-biphenyl and was fully characterized by IR, NMR and elemental analysis.

Treatment of **L** (2 equiv) with Co(II)(BF$_4$)$_2$.6H$_2$O in CH$_3$CN solution gave immediately a violet solution. After 12h of reaction the solution was concentrated and yielded a purple solid material that was isolated quantitatively and analysed elementally as {[Co(**L**)$_2$(BF$_4$)$_2$]}(**1**) (Scheme 2). Interestingly, this result contrasts with those obtained previously by our group where M$_2$L$_4$ metallacages were obtained when the achiral semi-rigid bis(benzimidazole) ligand was employed.

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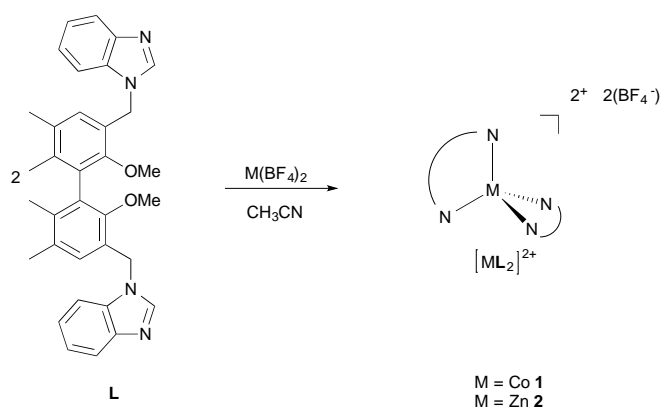b. *Department of Chemistry, San Diego State U., San Diego CA 92182-1030, USA.*

The latter lacks the chiral spacer 5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl but instead the two benzimidazole arms are attached to a central arene.
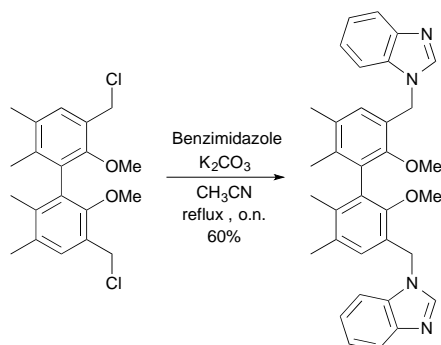
Scheme 1. Synthesis of the ligand 1,1-((5,5',6,6'-tetramethyl—2,2'dimethoxy-3,3'(methylene))bis(1H-benzimidazole) **L**.

Scheme 2. Synthesis of the chiral complexes {[Co(**L**)$_2$(BF$_4$)$_2$]}(**1**) and {[Zn(**L**)$_2$(BF$_4$)$_2$]}(**2**).

The infrared spectrum shows the presence of tetrafluoroborate anions with ν(B-F) at 1053 cm^{-1}. The electrospray mass spectrum shows a peak at m/z = 1206.46 which corresponds to the formation of [Co(**L**)$_2$BF$_4$]$^+$ species in solution. Due to the paramagnetic nature of the cobalt complex **1** the ^{1}H NMR spectrum was not informative. To ascertain the identity of complex **1**, convenient crystals for X-ray structural determination were prepared from CH$_3$CN/Et$_2$O solution after several attempts.

The compound crystallized in the monoclinic space group C2/c. The structure shows the formation of a Co**L**$_2$ dicationic complex (Figure 1) where the cobalt centre adopts a *pseudo*-tetrahedral geometry; each position is filled by a benzimidazole from the two bridging ligands **L**. The Co---N bond lengths lie in the range of 2.00-1.98(2) Å typical to those reported in the literature.[5] Interestingly, the X-ray structural determination reveals the formation of a racemic mixture of homochiral complexes (R, R)-{[Co((R_{ax})-**L**)$_2$(BF$_4$)$_2$]}(**1**) and (S,S)-{[Co((S_{ax})-**L**)$_2$(BF$_4$)$_2$]}(**1**) (Figure 1).

Hence the heterochiral (R, S) complex was not formed. A self sorting ligand recognition process mediated by the cobalt(II) metal centre seems to operate and hence favours the formation of the homochiral compound.
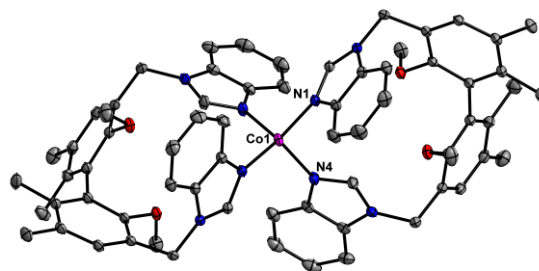

Figure 1. View of the cationic part of the homochiral complex (R,R)-[Co(**L**)$_2$][BF$_4$]$_2$ (**1**) (C grey, O red, N blue, Co pink; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°) : Co(1)-N(1) = 2.003(2), Co(1)-N(4) = 1.983(2), N(1)-Co(1)-N(1) = 114.33, N(4)-Co(1)-N(4) = 106.35, N(1)-Co(1)-N(4) = 108.73.

In order to confirm our hypothesis we envisioned to prepare another assembly but using Zn(II) instead of Co(II). Moreover the presence of a diamagnetic metal centre allows us to investigate its solution behaviour. Thus when Zn(II)(BF$_4$)$_2$.xH$_2$O was stirred with the bidentate ligand **L** under similar experimental conditions to those used for **1**, a pale yellow precipitate was quantitatively isolated after reaction work-up (Scheme 2). The spectroscopic data and elemental analysis are in accordance with the formation of [Zn(**L**)$_2$][BF$_4$]$_2$ (**2**). As previously, the electrospray (ES) mass spectrum demonstrates the integrity of the compound in solution since the fragment [Zn(**L**)$_2$HCO$_2$]$^+$ at m/z = 1169.46 is observed. Furthermore the ^{1}H NMR spectrum of {[Zn(**L**)$_2$(BF$_4$)$_2$]} (**2**) was recorded in CD$_3$CN, and we note that upon coordination to the Zn center a symmetric pattern with a downfield shift relative to ligand **L** is observed mainly for Ha, CH$_2$ and OMe protons.(Figure 2)

To ascertain the molecular structure of **2,** an X-ray structural determination was carried out. Crystals of **2** were grown by vapor diffusion of diethyl ether into a solution of the complex in CH$_3$CN. Compound **2** turned out to be isostrucural to **1** and exhibited a similar distorted tetrahedral geometry around the metal centre. The Zn---N bond lengths lies in the range of 1.99-2.00Å (Figure 3).
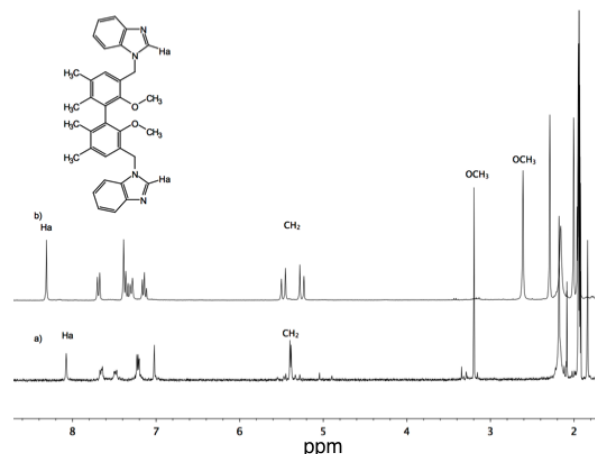
Figure 2. ^{1}H NMR spectra in CD$_3$CN for a) ligand **L** and b) complex [Zn(**L**)$_2$][BF$_4$]$_2$ (**2**).

In a similar way to **1**, the formation of a racemic mixture of homochiral complexes (R,R)-[Zn(**L**)$_2$][BF$_4$]$_2$ (**2**) and (S,S)-[Zn(**L**)$_2$][BF$_4$]$_2$ (**2**) is observed.
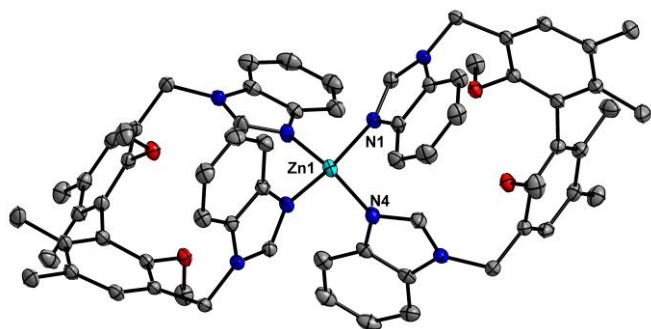

Figure 3 View of the cationic part the homochiral (R,R)-[Zn(**L**)$_2$][BF$_4$]$_2$ (**2**) (C grey, O red, N blue, Zn turquoise blue; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°) : Zn(1)-N(1) = 2.00 (2), Zn(1)-N(4) = 1.988(2), N(1)-Zn(1)-N(1) = 114.77(13), N(4)-Zn(1)-N(4) = 112.19(14), N(1)-Zn(1)-N(4) = 106.21(9), N(1)-Zn(1)-N(4) = 108.79(9).

We then examined the solution behavior of this chiral two bladed complex **2** and its differentiation using a chiral auxiliary anion.[8] To attain this objective, the racemic mixture [Zn(**L**)$_2$][BF$_4$]$_2$ (**2**) was treated by [Na][Δ-TRISPHAT] and subsequent anion metathesis resulted in the formation of the two diastereomeric compounds (R,R)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3a**) and (S,S)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3b**). Indeed complex {[Zn(**L**)$_2$(BF$_4$)$_2$]} (**2**) was mixed and stirred with two equivalents of [Na] [Δ-TRISPHAT] in CH$_3$CN under argon for one hour to lead to the formation of a white precipitate of NaBF$_4$. After filtration, the solution was concentrated, the precipitate isolated and washed with dichloromethane. A white solid was obtained and identified in good yield as {[Zn(**L**)$_2$(Δ-TRISPHAT)$_2$]} (**3**). (Scheme 3)
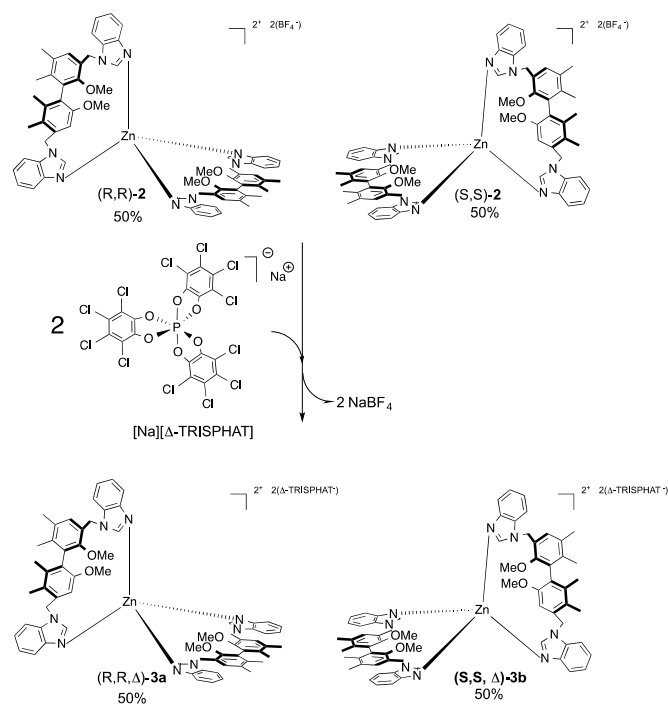
Scheme 3. Anion metathesis of rac-[Zn(**L**)$_2$][BF$_4$]$_2$ (**2**) and formation of the pair of diastereoisomers (R,R)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3a**) and (S,S)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3b**)

The infrared spectrum of the resulting material confirmed the disappearance of the bands of BF$_4$ anions at 1053 cm^{-1} and the presence of novel bands at 989 cm^{-1} and 669 cm^{-1} that we attribute to Δ-TRISPHAT. Moreover the ^{31}P NMR spectrum recorded in CD$_3$CN showed a singlet at -81.1 ppm assigned to Δ-TRISPHAT as reported in the literature.[8f] The ^{1}H NMR spectrum of (R,R)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3a**) and (S,S)-[Zn(**L**)$_2$][Δ-TRISPHAT]$_2$ (**3b**) recorded in CD$_3$CN shows the presence of two sets of signals which is in agreement with the formation of two diastereoisomers (see Figure SI), in particular the presence of two signals for Ha for both isomers at 8.20 ppm and 8.30 ppm respectively. This base-to-base line separation observed in the ^{1}H NMR spectrum can be attributed to the ion-pairing between the dicationic complexes and the Δ-TRISPHAT anion.

Unfortunately all our attempts either by chromatography or fractional crystallization to separate both diastereoisomers were not successful.

At this stage a comment on the homochiralty issue in these metallamacrocycles is required. For instance Wang et al. have demonstrated in an elegant work the formation of 3D homochiral polyhedra with rotational faces.[9] The authors show that the polyhedra self assemble from four truxene-based building blocks acting as faces and six diamine units that form the vertices. Depending on the rotational sense in which the –C=N- linkages are bent the truxene turns clockwise or anti-clockwise and therefore the assembly becomes homochiral. Their studies on the kinetics and mechanism revealed that the

non-covalent interaction among the faces is essential to the facial homochirality.

Thus we then studied the kinetic formation of **2** by adding a sequential amount of ligand **L** to Zn(BF$_4$)$_2$ in CD$_3$CN and monitored the formation of the assembly by ^{1}H-NMR (See Supporting information). At a [1+1] **L**/Zn mixture, broad signals are observed in the aromatic region; however upon addition of another equivalent of the ligand a rapid formation of sharp signals in the aromatic region becomes visible, suggesting the formation of the target homochiral metallacage (see Figure SII). No formation of the other heterochiral diastereomer was detected. This data suggest indeed that homochiral metallamacrocycles are favoured by kinetic and thermodynamic factors which might originate from the geometry of the metal centre (tetrahedral) and also the nature of the atropoisomeric chiral ligands.

A computational investigation[10a] of the complex supports a small but consistent thermodynamic preference for the observed enantiopure diastereomer over the racemic form. Initially, because experiments had not confirmed the spin of the organometallic complex, we optimized geometries of (**1**) with doublet, quartet, and sextet multiplicities using the B3LYP density functional method[10b] and a small 3-21G(H,C,N,O),LANL2DZ(Co) basis set,[10c] confirming that the quartet state is significantly (>28 kcal/mol) more stable than the others, as expected. The geometries were then re-optimized with a larger cc-pVDZ(C,H,N,O),CEP-121G(Co) basis set,[10d] and vibrational frequencies were calculated in order to obtain the free energy corrections. For both basis sets, the free energy of the enantiopure form at 298 K lies only 1.0 to 1.1 kcal/mol below the R,S free energy. However, additional corrections for solvation (using COSMO or IEFPCM methods[10e]) and for dispersion forces (Grimme's GD2 method[10f]) using the larger basis set increase this free energy gap to 3.7 kcal/mol. This difference would cause a measurable preference for the enantiopure diastereomer in experiments, but is not much greater than the expected error in these methods. This predicted free energy difference is also smaller than the 12 kcal/mol gap found for the similar system investigated by Wang et al.,[9] which suggests that the enantioselectivity of the present case may arise from kinetic as well as thermodynamic considerations.

Conclusions

In this communication, we reported the efficient preparation and characterization of chiral two bladed dicationic complexes [Co(L)$_2$][BF$_4$]$_2$ (**1**) and [Zn(L)$_2$][BF$_4$]$_2$ (**2**). Interestingly, due to a ligand self-sorting process the formation of homochiral chiral metallacages is favoured to give (*R*,*R*)-[M(**L**)$_2$][BF$_4$]$_2$ M = Co, (**1a**); M = Zn, (**2a**) and (*S*,*S*)-[M(**L**)$_2$][BF$_4$]$_2$ M = Co, (**1b**); M = Zn, (**2b**) but obtained in racemic mixture. These compounds can be converted to the corresponding diastereomeric mixture by anion metathesis using the chiral Δ-TRISPHAT anion as shown by ^{1}H-NMR analysis. Our future objectives will be devoted to separate the diastereomers as well as to prepare optically

active Co(II) and Zn(II) complexes starting from the enantiopure form of ligand **L** .

Experimental Section

General experimental methods

All solvents used were reagent grade or better. Commercially available reagents were used as received. 3,3'-bis(chloromethyl)-2,2-dimethoxy-5,5',6,6'tetramethyl-1,1'-biphenyl[7] and [Na]Δ-[TRISPHAT][11] were prepared according to published methods. All experimental manipulations were carried out under argon using Schlenk techniques. IR spectra were recorded on a Bruker Tensor 27 equipped with a Harrick ATR. Elemental analyses were performed by the microanalytical laboratory of ICSN, Gif-sur Yvette. NMR experiments were carried out on a Bruker Avance 300 MHz spectrometer operating at 300 K with chemical shifts references to residual solvent peaks. Chemical shifts are reported in parts per million (ppm) and coupling constant (*J*) in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, t = triplet, d = doublet, s = singlet, b = broad.

Synthesis

Ligand Synthesis. 1,1'-((5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl-3,3'-(methylene))bis(1H-benzimidazole) **L**: A round bottom flask was charged with benzimidazole (0.339 g, 2.86 mmol, 2.1 eq.), K$_2$CO$_3$ (0.563 g, 4.08 mmol, 3 eq.). 3,3'-bis(chloromethyl)-2,2-dimethoxy-5,5',6,6'tetramethyl-1,1'-biphenyl (0,5 g, 1.36 mmol, 1 eq.) was then solubilized in acetonitrile (15mL) freshly distilled on CaH$_2$ and was transferred to the flask. The solution was stirred at room temperature during 1h. The reaction mixture is then heated to reflux and is maintained under stirring 18 h. After cooling, the crude product was firstly filtered. The solid obtained, was extracted with CH$_3$CN (3x15 mL). The pale yellow solution was then concentrated and purified by column chromatography (AcOEt/MeOH : 100/0; 90:10; 80/20) to afford a white solid (0.432 g, 0.81 mmol, 60 %) ^{1}H NMR (300 MHz, CD$_3$CN, 300 K) (δ ppm) : 8.0 (s, 2H, H-Ar) ; 7.7-7.6 (m, 2H, H-Ar) ; 7.5-7.4 (m, 2H, H-Ar) ; 7.3-7.2 (m, 4H, H-Ar) ; 7.0 (s, 2H, H-Ar) ; 5.4 (d, ^{2}J = 4.2 Hz, 4H, CH$_2$) ; 3.2 (s, 6H, OCH$_3$) ; 2.2 (s, 6H, CH$_3$) ; 1.8 (s, 6H, CH$_3$). ^{13}C NMR (100 MHz, CD$_3$CN) (δ ppm) : 153.7 ; 143.6 ; 136.8 ; 133.7 ; 132.6 ; 131.3 ; 129.5 ; 126.1 ; 122.2 ; 121.4 ; 119.3 ; 110.4 ; 59.7 ; 43.3 ; 18.8 ; 15.6, IR (ATR): (ν, cm^{-1}) 2930 (ν CH$_3$) ; 1493 ; 1456 (ν C=C Ar) ; 1363 ; 1284 (ν C-N Ar) ; 1199; 1076 ; 1006 ; 740 ; 427. ES-MS m/z (CH$_3$CN) [LH$^+$]: 531.27, 531.27(found) ; Anal. calcd for C$_{34}$H$_{34}$N$_4$O$_2$.H$_2$O: C 74.93 ; H 6.46 ; N 10,14; Found: C 74.48 ; H 6.61 ; N 10.21.

{[Co(L)$_2$(BF$_4$)$_2$]}(1): Ligand **L** (30 mg, 0.05 mmol, 2 eq.) was added to a pink solution of Co(BF$_4$)$_2$.6H$_2$O (8.5 mg, 0.025 mmol, 1 eq.) in CH$_3$CN (5 mL). The solution was stirred at room temperature for 12 h, during which time a purple color appeared. The solvents were then removed. The purple precipitate obtained, was washed with ether (3 x15 ml) and dried under vacuum to afford {[Co(**L**)$_2$(BF$_4$)$_2$]}

(1) (39 mg, 0.028 mmol, 100%). **1** was recrystallized from CH_3CN/Et_2O to afford quantitatively purple crystals. IR (ATR): (v, cm^{-1}) 2940 (v CH_3) 1514 ; 1462 (v C=C Ar) ; 1289 (v C-N Ar) ; 1197, 1050 (v B-F) ; 1006 ; 742 ; 425, ES-MS (m/z): $[Co(\mathbf{L})_2BF_4]^+$: 1206.46; found 1206.47, Anal. calcd for $C_{68}H_{68}B_2F_8N_8O_4Co.4H_2O.CH_3CN$: C 59.00, H 5.73, N 8.85; found: C 59.25, H 5.44, N 8.75.

$\{[Zn(\mathbf{L})_2(BF_4)_2]\}$ (2) : Ligand **L** (105 mg, 0.18 mmol, 2 eq.) was added to a pink solution of $Zn(BF_4)_2.xH_2O$ (21.5 mg, 0.09 mmol, 1 eq.) in CH_3CN (15 mL). The solution was stirred at room temperature for 12 h. The solvents were then removed. The pale yellow precipitate obtained, was washed with ether (3 x15 ml) and dried under vacuum to afford $\{[Zn(\mathbf{L})_2(BF_4)_2]\}$ **(2)** (127 mg, 0.09 mmol, 100%). **2** was recrystallized from CH_3CN/Et_2O to afford quantitatively pale yellow crystals. ^1H NMR (300 MHz, CD_3CN, 300 K) (δ ppm) : 8.3 (s, 4H, H-Ar) ; 7.7 (d, ^3J = 8.4 Hz, 4H, H-Ar); 7.5-7.4 (m, 4H, H-Ar) ; 7.3 (dd, ^2J = 24.6 Hz ^3J = 8.4 Hz , 8H, H-Ar) ; 7.1 (t, ^3J = 7.7 Hz, 4H, H-Ar) ; 5.5 (d, ^2J = 14,8 Hz, 4H, CH_2) ; 5.2 (d, ^2J = 14,8 Hz, 4H, CH_2) ; 2.6 (s, 12H, OCH_3) ; 2.3 (s, 12H, CH_3) ; 2.0 (s, 12H, CH_3). ^{13}C NMR (100 MHz, CD_3CN) (δ ppm) : 155.0 ; 146.3 ; 137.8 ; 132.8 ; 132.6 ; 130.9 ; 130.6 ; 124.1 ; 123.7 ; 111.9 ; 59.1 ; 45.9 ; 29.6 ; 18.7; 15.8; IR (ATR): (v, cm^{-1}) 2924 (v CH_3) 1519 ; 1464 (v C=C Ar) ; 1274 (v C-N Ar) ; 1197 ; 1053 (v B-F) ; 742 ; 625, ES-MS (m/z): $[Zn(\mathbf{L})2(HCO_2)]^+$: 1169.46; found 1168.46, Anal. calcd for $C_{68}H_{68}B_2F_8N_8O_4Zn.2H_2O$: C 61.12, H 5.43, N 8.39; found: C 60.82, H 5.31, N 8.36.

Diastereomeric pair $\{[Zn((R_{ax})\text{-}\mathbf{L})_2(\Delta\text{-TRISPHAT})_2]\}$ (3a) and $\{[Zn((S_{ax})\text{-}\mathbf{L})_2(\Delta\text{-TRISPHAT})_2]\}$ (3b) A schlenck was charged with $[Na][\Delta\text{-TRISPHAT}]$(24 mg, 0.03 mmol, 2 eq.) and dissolved with freshly distilled CH_3CN (4 mL). $\{[Zn(\mathbf{L})_2(BF_4)_2]\}$ **(2)** (21 mg, 0.015 mmol, 1 eq.). A white precipitate is formed. The mixture is stirred at room temperature under argon during 3 h. The suspension was filtered through a pad of celite. Subsequent evaporation of the solvent afforded a white microcrystalline solid identified as the pair ad diastereomers $\{[Zn((R_{ax})\text{-}\mathbf{L})_2(\Delta\text{-TRISPHAT})_2]\}$ **(3a)** and $\{[Zn((S_{ax})\text{-}\mathbf{L})_2(\Delta\text{-TRISPHAT})_2]\}$ **(3b)** (27 mg, 0.01 mmol, 68%). ^1H NMR (300 MHz, CD_3CN, 300 K) (δ ppm) : 8.4 (s, 2H, H-Ar) ; 8.3 (s, 2H, H-Ar) 7.8-7.7 (m, 8H, H-Ar); 7.5-7.4 (m, 4H, H-Ar) ; 7.4-7.3 (m, 6H, H-Ar) ; 7.3-7.2 (m, 2H, H-Ar) ; 7.2-7.1 (m, 4H, H-Ar) ; 5.5 (d, ^2J = 14,6 Hz, 4H, CH_2) ; 5.2 (d, ^2J = 14,6 Hz, 4H, CH_2) ; 2.5 (s, 12H, OCH_3) ; 2.3 (s, 12H, CH_3) ; 2.1 (s, 12H, CH_3). ^{31}P NMR (121 MHz, CD_3CN) (δ ppm) :-81.1 (s, Δ-TRISPHAT); IR (ATR): (v, cm^{-1}) 2936 (v CH_3) ; 1446 (v C=C Ar) ; 1389 ; 1236 (v C-N Ar) ; 1080 ; 1034 ; 989 (v P-O) , 742 ; 718 ; 669(v C-Cl) ; 620 ; 552 ; 424 ; CD (0.05 mM, CH_3CN) (nm) : (+) 211, (-) 220, (-) 243 ; $[\alpha]^D_{293}$: -202 (0.1 ; EtOH)

X-ray crystal structures determination of $\{[Co(\mathbf{L})_2(BF_4)_2]\}$(1) and $\{[Zn(\mathbf{L})_2(BF_4)_2]\}$(2)

Suitable crystals were mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with Bruker Kappa-APEX2 systems using fine-focus sealed tube Mo-Kα (**1**) or micro-source Cu-Kα (**2**) radiations. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structures were solved with SIR92[12] (**1**) or SHELXT-2014[13] (**2**) and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[14] using the WinGX suite.[14] The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 1534238-1534239 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Crystal data for $[Co(\mathbf{L})_2(BF_4)_2]$, 2CH$_3$CN (1): violet prism, $C_{68}H_{68}N_8O_4Co$, 2(BF$_4$), 2(C$_2$H$_3$N), monoclinic C 2/c, a = 35.9304(11) Å, b = 9.2813(2) Å, c = 21.8455(7) Å, α = 90°, β = 112.173(1)°, γ = 90.0°, V = 6746.3(3) Å^3, Z = 4, T = 200(1) K, μ = 0.334 mm^{-1}, 59038 reflections measured, 10317 independent (R$_{int}$ = 0.0385), 7515 observed [I > 2σ(I)], 445 parameters, final R indices R1 [I > 2σ(I)] = 0.0515 and wR2 (all data) = 0.1479, GOF(on F^2) = 1.023, max/min residual electron density 1.20/-0.28 e·Å^{-3}.

Crystal data for $[Zn(\mathbf{L})_2(BF_4)_2]$, 2CH$_3$CN (2): colourless prism, $C_{68}H_{68}N_8O_4Zn$, 2(BF$_4$), 2(C$_2$H$_3$N), monoclinic C2/c, a = 35.9399(12) Å, b = 9.2811(3) Å, c = 21.8244(7) Å, α = 90° , β = 112.179(3)°, γ = 90°, V = 6741.1(4) Å^3, Z = 4, T = 200(1) K, μ = 1.176 mm^{-1}, 24622 reflections measured, 5906 independent (R$_{int}$ = 0.0705), 4037 observed [I > 2σ(I)], 445 parameters, final R indices R1 [I > 2σ(I)] = 0.0480 and wR2 (all data) = 0.1246, GOF(on F^2) = 1.016, max/min residual electron density 0.64/-0.29 e·Å^{-3}.

Acknowledgements

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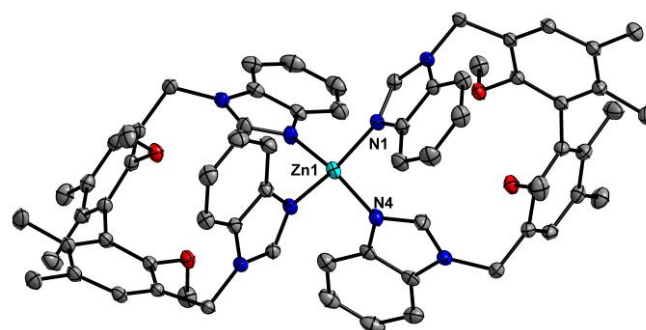
Chiral two bladed ZnL$_2$ metallacage.