Enantiomerically Pure C_2-symmetric Dinuclear Silver(I) and Copper(I) Complexes from a Bis(2,2′-bipyridine)-substituted 9,9′-Spirobifluorene Ligand

Torsten Piehler and Arne Lützen

Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany

Reprint requests to Prof. Dr. Arne Lützen. Fax: +49 228 73 9608. E-mail: arne.luetzen@uni-bonn.de

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Dedicated to Professor Rolf Saalfrank on the occasion of his 70^th^ birthday

We have prepared a new bis(bipyridyl) ligand **1** based on a chiral 9,9′-spirobifluorene core in both enantiomerically pure forms. This ligand was found to undergo diastereoselective self-assembly to optically pure dinuclear coordination compounds upon coordination to copper(I) and silver(I) ions. Surprisingly, however, the resulting diastereomer was not found to be D_2-symmetric which is usually found for similar bis(bidentate) ligands, but rather C_2-symmetric with differently configurated metal centers.

Key words: Self-assembly, Helicates, 2,2′-Bipyridines, 9,9′-Spirobifluorene, Diastereoselectivity

Introduction

Nowadays self-assembly is a widely accepted method to build up sophisticated molecular architectures [1]. Besides the formation of cage-like structures with cavities of a certain size and a distinct chemical nature (provided *e. g.* by functional groups pointing inside the cavity) [2, 3], one of the most challenging aspects of these efforts is the implementation of chiral information into the different moieties employed to form the supramolecular structures. There are quite a number of beautiful examples where (dia-)stereoselective self-assembly could indeed be achieved [4]. Helicates are among the chiral objects that can be used for this purpose [5]. Such metallosupramolecular aggregates can be produced in a stereocontrolled manner through diastereoselective self-assembly from chiral ligands as demonstrated in many examples in recent years [5 – 10]. However, it is still very difficult to predict the degree of stereoselectivity and the resulting relative configuration of the newly formed stereogenic metal centers that are programmed in a given ligand structure.

Some time ago we reported on a BINOL-based bis(bipyridyl) ligand which undergoes completely diastereoselective self-assembly to dinuclear double- and triple-stranded D_n-symmetric helicates upon coordination to late transition metal ions [11a]. Since then we have been able to show that other dissymmetric building blocks like differently substituted BINOLs [11], Tröger's base derivatives [12], or D-isomannit [13] can also be used in this way. Here, we report on the synthesis of a new type of enantiomerically pure bis(bipyridyl) ligand (**1**, Fig. 1) that bears a 9,9′-spirobifluorene, and on its extraordinary self-assembly to C_2-symmetric dinuclear coordination compounds with differently configurated copper(I) or silver(I) centers in a completely diastereoselective manner.

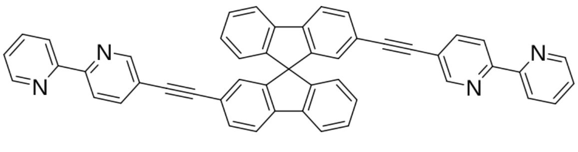

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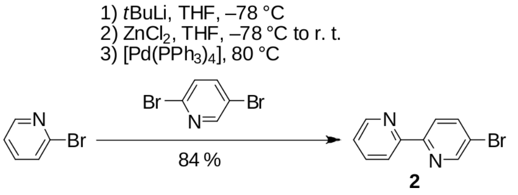
Fig. 1.

Results and Discussion

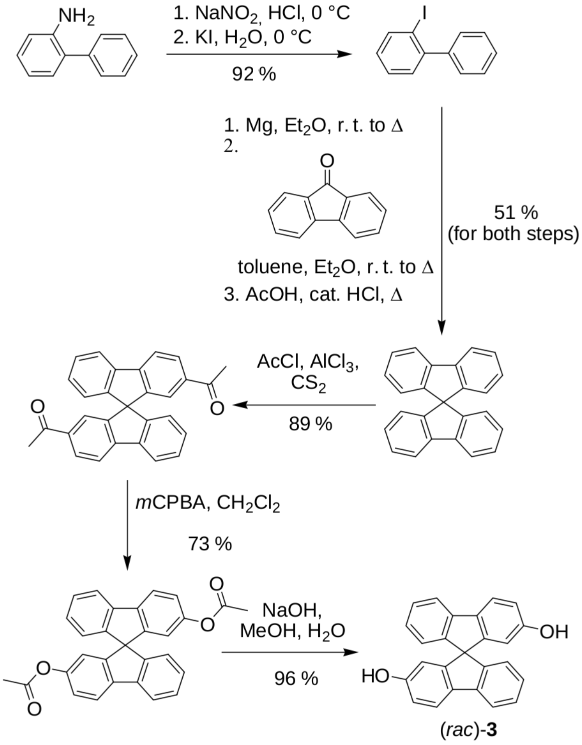
Synthesis

The synthesis of (*R*)- and (*S*)-**1** asked for the preparation of enantiomerically pure 2,2′-disubstituted 9,9′-spirobifluorene building blocks and an orthogonally 5-functionalized 2,2′-bipyridine. The synthesis of 5-bromo-2,2′-bipyridine (**2**) was achieved starting from 2-bromopyridine which was transformed into the corresponding organozinc compound and then reacted with 2,5-dibromopyridine using a Negishi cross-coupling protocol that we were able to develop recently (Eq. 1) [14].

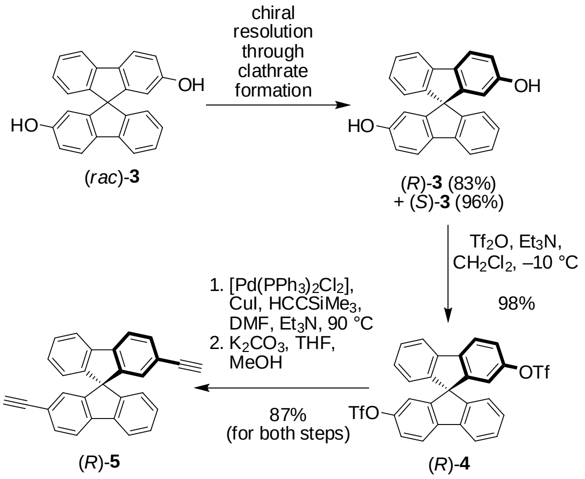


(1)

The synthesis of the spirobifluorene building block started from 2-aminobiphenyl following the established procedures of J. M. Tour [15], M. Gomberg [16], and V. Prelog [17] and led to (*rac*)-2,2′-dihydroxy-9,9′-spirobifluorene ((*rac*)-**3**) in six consecutive steps. This sequence involved a Sandmeyer-like iodination, followed by a Grignard reaction with fluorenone to give the corresponding tertiary alcohol. This was subjected to an acid-mediated condensation reaction to give the 9,9′-spirobifluorene. Friedel-Crafts acylation with acetyl chloride afforded the diketone which was transformed to a diester using a Baeyer-Villiger oxidation. Finally, saponification of the ester function gave rise to the desired (*rac*)-**3** (Scheme 1).



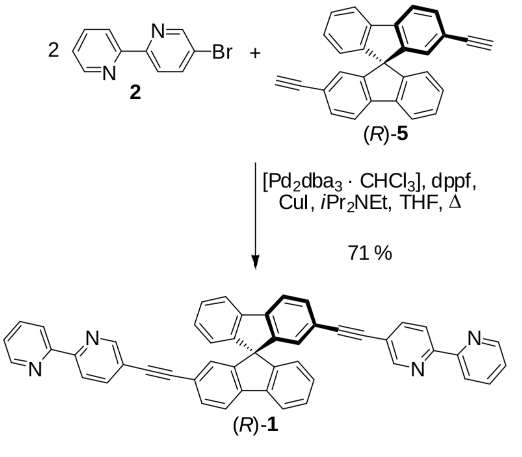
Scheme 1.



Scheme 2. (Tf_2O = trifluoromethanesulfonic acid anhydride)

(*rac*)-**3** was then resolved by clathrate formation with (*R*,*R*)-2,3-dimethoxy-*N*,*N*,*N*′,*N*′-tetracyclohexylsuccinamide before the enantiomerically pure diols were transformed into the corresponding optically pure bistriflates (*R*)- and (*S*)-**4**. These were then reacted with trimethylsilylacetylene in a Sonogashira cross-coupling reaction to give the desired diethynylated 9,9-spirobifluorenes (*R*)- and (*S*)-**5** after removal of the silyl protecting group (Scheme 2) [18].

Finally, twofold Sonogashira reaction of **2** and (*R*)- and (*S*)-**5** afforded the optically pure bis(bipyridyl) ligands (*R*)- and (*S*)-**1**, respectively (Eq. 2).



(2)

Metal coordination

After the successful synthesis of both enantiomers of ligand **1** we studied their complexation behavior towards late transition metal ions. Given the fact that ligand **1** has a very rigid V-shaped structure that seems almost ideally preorganized for the formation of double-stranded dinuclear coordination complexes, we chose copper(I) and silver(I) ions for this purpose because these diamagnetic ions prefer a tetrahedral coordination geometry by four *N*-donor centers of two 2,2′-bipyridine ligands and allowed us to investigate the coordination behavior of **1** not only by mass spectrometry and CD spectroscopy but also by NMR spectroscopy.

In order to prepare the complexes we generated solutions of the ligands in dichloromethane, and of $[Ag(CH_3CN)_2](BF_4)$ and $[Cu(CH_3CN)_4](BF_4)$ in acetonitrile. Upon mixing of ligand and salt solutions immediate color changes indicated the successful formation of bipyridine complexes: pale-yellow for silver(I), and red-brown for copper(I), typical for these types of complexes.

For the analysis of the stoichiometric composition of the complexes we performed ESI MS measurements. These did indeed show the expected peaks at *m/z* = 735.2 and 781.1 with matching isotope patterns for the doubly-charged dinuclear complexes $[Cu_2(\mathbf{1})_2]^{2+}$ and $[Ag_2(\mathbf{1})_2]^{2+}$, and also peaks at *m/z* = 1559.4 and 1648.3 with matching isotope patterns that could be assigned to the singly charged complexes still carrying one counterion $\{[Cu_2(\mathbf{1})_2](BF_4)\}^+$ and $\{[Ag_2(\mathbf{1})_2](BF_4)\}^+$, respectively [19], thus, confirming the formation of discrete dinuclear complexes rather than oligo- or polymeric species (Fig. 2).

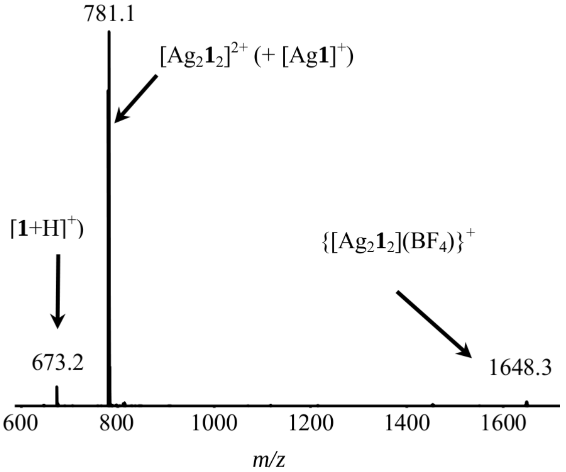
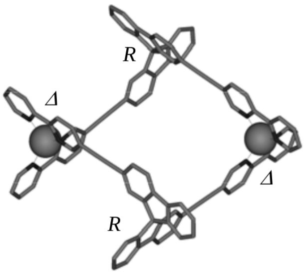
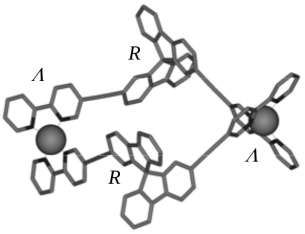


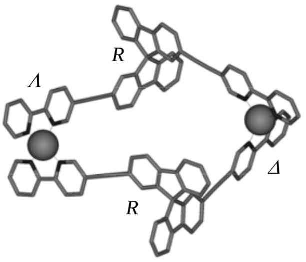
Fig. 2. Pos. ESI MS of a 1 : 1 mixture of $[Ag(CH_3CN)_2]BF_4$ and (*R*)-**1** in CH_2Cl_2/CH_3CN 3 : 1.



(Δ,Δ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$



(Λ,Λ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$



(Λ,Δ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$

Fig. 3. PM3-TM-minimized structures of the three possible diastereomeric dinuclear copper(I) complexes (Δ,Δ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$, (Λ,Λ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$, and (Λ,Δ)-$[Cu_2\{(R)\text{-}\mathbf{1}\}_2]^{2+}$ formed upon self-assembly of (*R*)-**1** and $[Cu(CH_3CN)_4](BF_4)_2$.

MS studies can help to elucidate the selectivity of self-assembly processes in terms of stoichiometry but provide no information about the stereoselectivity of these processes. NMR spectroscopy, however, can address this problem. A simple ^{1}H-NMR spectrum can already give information about the selectivity and also the symmetry of the dinuclear coordination compounds with newly formed stereogenic metal centers generated from enantiomerically pure C_2-symmetric ligands: in principle three diastereomeric complexes can form in such cases, one where both metal centers are (Δ)-configurated, one where both are (Λ)-configurated, and one where one is (Δ)- and the other one (Λ)-configurated, as illustrated in Fig. 3. The first two would be D_2-symmetric. Thus, the two halves of each of the ligands remain magnetically equivalent.

Although the third one represents a “*meso*”-form with respect to the coordination geometry at the two metal centers it is, however, still chiral and even less symmetric (C_2-symmetric) due to the fact that we use enantiomerically pure ligands. Thus, in this case the two halves of the ligands are no longer magnetically equivalent because they are bound to differently configurated metal centers, which makes their relative orientation to the stereogenic center of the spirobifluorene different from each other.

Fig. 4 shows the spectra that were obtained for ligand **1** and its silver(I) and copper(I) complexes. Like with all other chiral ligands that we have investigated so far [11 – 13], we indeed arrived at a completely diastereoselective self-assembly of dinuclear double-stranded coordination compounds as we observed only a single set of signals which all belong to a single species. However, in view of our previous results these spectra were really surprising because they clearly reveal that the two halves of the ligand are no longer magnetically equivalent in the dinuclear aggregates since now the number of signals is doubled compared to the free ligand. Thus the presence of the two D_2-symmetric diastereomers can be ruled out, and therefore the dinuclear complexes must be the (Δ,Λ)-configurated C_2-symmetric aggregate.

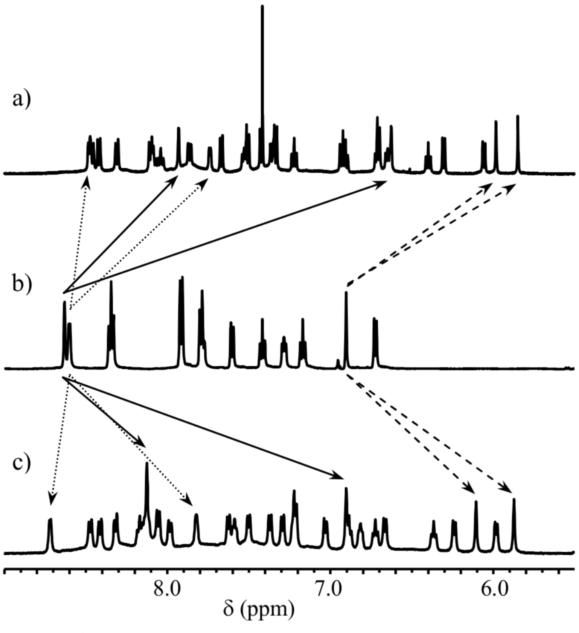


Fig. 4. ^{1}H-NMR spectra (500.1 MHz, 298 K, in CD_2Cl_2/CD_3CN 3 : 1) of a) (Δ,Λ)-[Cu_2{(*R*)-**1**}$_2$](BF_4)$_2$, b) (*R*)-**1**, and c) (Δ,Λ)-[Ag_2{(*R*)-**1**}$_2$](BF_4)$_2$. Arrows indicate shifts and splitting of some of the ligands’ proton signals in the dinuclear complexes (dotted arrows 25-H, dashed arrows 1-H, normal arrow 20-H; for the numbering see Fig. 6).

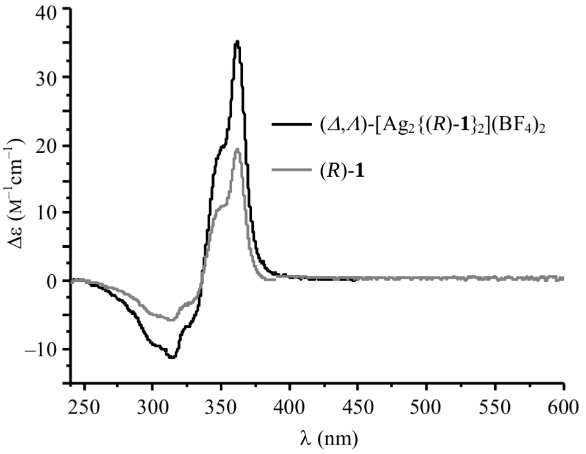


Fig. 5. CD spectra (5 × 10^{-5} M solutions in CH_2Cl_2/CH_3CN) of (*R*)-**1** (grey) and (Δ,Λ)-[Ag_2{(*R*)-**1**}$_2$](BF_4)$_2$ (black).

This was further corroborated by *e*lectron *c*ircular *d*ichroism (ECD) spectroscopy [20]. As shown exemplarily in Fig. 5 for the silver complex of (*R*)-**1**, the CD spectra obtained for the complexed ligands are very similar to the spectra of the free ligands because the signals arising from the differently configurated bis(bipyridyl) metal complexes cancel each other out. The difference in intensity is merely a result of the fact that all samples were measured at the same concentration which means that there is the double amount of the spirobifluorene ligand in the solutions of the complexes.

Conclusion

We have synthesized a new bis(bipyridyl) ligand **1** based on a chiral 9,9′-spirobifluorene core in both enantiomerically pure forms in an effective manner *via* a 12-step reaction sequence. The self-assembly of dinuclear metal coordination compounds from **1** and copper(I) and silver(I) ions was studied by ESI mass spectrometry, and NMR and ECD spectroscopy. These experiments have clearly demonstrated that the self-assembly processes are not only selective in terms of the formation of discrete dinuclear complexes, but they were also found to occur in a completely diastereoselective manner. Surprisingly, however, the resulting diastereomer was not found to be D_2-symmetric but rather C_2-symmetric with metal centers of different configuration. Such a behavior has never been observed before for this type of ligands.

Experimental Section

All solvents were distilled and thoroughly dried prior to use according to standard procedures. All syntheses with air- and moisture-sensitive compounds were performed under Schlenk conditions, with argon as the inert gas. For purification purposes column chromatography on silica gel was applied. Solvents for mobile phases were distilled prior to use. Detection was done under UV light (254 and 366 nm). ^{1}H- and ^{13}C-NMR spectra were recorded at 298 K and at 500.1 and 125.8 MHz, or at 400.1 and 100.6 MHz, respectively. ^{1}H-NMR chemical shifts are reported on the δ scale (ppm) relative to residual non-deuterated solvent as the internal standard. ^{13}C-NMR chemical shifts are given in δ values (ppm) relative to the deuterated solvent as the internal standard. Signals were assigned on the basis of ^{1}H-, ^{13}C-, HMQC-, and HMBC-NMR experiments. Numbering of the ^{1}H and ^{13}C nuclei is according to Fig. 6. Melting points are not corrected. Chemicals and reagents (except for the solvents) obtained from commercial sources were used as received. The following compounds were prepared according to published procedures: 5-bromo-2,2′-bipyridine (**2**) [14c], 2-iodobiphenyl [15], 9,9′-spirobifluorene [16], (*rac*)-2,2′-diacetyl-9,9′-spirobifluorene [17], (*rac*)-2,2′-diacetoxy-9,9′-spirobifluorene [17], (*rac*)-2,2′-dihydroxy-9,9′-spirobifluorene (*rac*)-**3**) [17], (*R*)-2,2′-dihydroxy-9,9′-spirobifluorene ((*R*)-**3**) [18], (*S*)-2,2′-dihydroxy-9,9′-spirobifluorene ((*S*)-**3**) [18], (*R*)-2,2′-bis(trifluoromethylsulfonyloxy)-9,9′-spirobifluorene ((*R*)-**4**) [18], (*S*)-2,2′-bis(trifluoromethylsulfonyloxy)-9,9′-spirobifluorene ((*S*)-**4**) [18], (*R*)-2,2′-diethynyl-9,9′-spirobifluorene ((*R*)-**5**) [18], and (*S*)-2,2′-diethynyl-9,9′-spirobifluorene ((*S*)-**5**) [18].

*(R)- and (S)-2,2′-Bis(5-ethynyl-2,2′-bipyridyl)-9,9′-spirobifluorene ((R)- and (S)-**1**)*

A two-neck flask equipped with a condenser was charged with 64 mg (178 mmol) of (*R*)-2,2′-diethinyl-9,9′-spirobifluorene ((*R*)-**5**), 2 mg (0.01 mmol) of CuI, 105 mg (446 mmol, 2.5 equiv.) of 5-bromo-2,2′-bipyridine, 6 mg (6 mol-%) of 1,1′-bis(diphenylphosphino) ferrocene (dppf), and 6 mg (3 mol-%) of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct ($Pd_2(dba)_3 \cdot CHCl_3$). The flask volume was evacuated and flushed with argon twice. 5 mL of abs. THF and 0.06 mL (2.4 equiv.) diisopropylamine were added *via* syringe. The mixture was heated to 60 °C for 48 h. After that time TLC monitoring (eluent toluene/THF 20 : 1 + 5 % Et_3N) revealed the complete consumption of the starting material. The reaction was quenched by adding 5 mL of brine, and the mixture was filtered through Celite. The filtrate was collected and washed with sat. aq. $NaHCO_3$ solution. After drying the organic phase with Na_2SO_4 the solvents were evaporated *in vacuo*, and the residue was subjected to column chromatography on silica gel (eluent: toluene/THF 20 : 1 + 5 % Et_3N) to give the desired product as a yellow solid. Yield: 85 mg (71 %). $[\alpha]_D^{27.6}$ ((*R*)-**1**) = +740° (c = 0.73; $CHCl_3$), $[\alpha]_D^{28.8}$ ((*S*)-**1**) = −675° (c = 0.74; $CHCl_3$). – CD (λ ($\Delta\varepsilon$), CH_2Cl_2/CH_3CN 1 : 1, $c = 5 \times 10^{-5}$ mol/L): (*R*)-**1** = 315 (−5.2), 362 (19.7), (*S*)-**1** = 315 (5.3), 362 (−19.6). – R_f: 0.20 (toluene/THF 20 : 1 + 5 % Et_3N, silica gel). – MS (EI): *m/z* (%) = 673.1 (100) $[M]^{+\bullet}$. – HRMS (EI) *m/z* = 673.2362 (calcd. 673.2314 for $[C_{49}H_{28}N_4]^{+\bullet}$, $[M]^{+\bullet}$). – ^{1}H NMR ($CDCl_3$, 298.0 K, 500.1 MHz): δ = 6.78 (d, J = 7.7 Hz, 2 H, 8-H), 6.97 (d, J = 1.1 Hz, 2 H, 1-H), 7.16 (ddd, J = 7.1 Hz, J = 7.7 Hz, J = 1.1 Hz, 2 H, 7-H), 7.26 – 7.29 (2 H, 24-H), 7.41 (ddd, J = 7.1 Hz, J = 7.7 Hz, J =1.1 Hz, 2 H, 6-H), 7.60 (dd, J = 7.7 Hz, J = 1.1 Hz, 2 H, 3-H), 7.77 – 7.79 (m, 2 H, 23-H), 7.81 (dd, J = 8.2 Hz, J = 1.7 Hz, 2 H, 17-H), 7.86 (d, J = 7.7 Hz, 2 H, 4-H), 7.87 (d, J = 7.7 Hz, 2 H, 5-H), 8.34 (d, J = 8.2 Hz, 2 H, 18-H), 8.37 (d, J = 8.2 Hz, 2 H, 22-H), 8.65 (d, J = 4.4 Hz, 2 H, 25-H), 8.69 (m, 2 H, 20-H). – ^{13}C NMR ($CDCl_3$, 298.0 K, 125.8 MHz): δ = 65.6 (C-9), 86.8 (C-15), 93.8 (C-14), 120.2 (C-4), 120.3 (C-18), 120.5 (C-5), 121.3 (C-22), 121.8 (C-16), 123.8 (C-24), 124.1 (C-8), 127.3 (C-1), 128.1 (C-6), 128.6 (C-7), 131.7 (C-3), 136.8 (C-17), 139.2 (C-23), 140.9 (C-12), 142.4 (C-11), 148.4 (C-10*), 148.5 (C-13*), 149.2 (C-25), 151.4 (C-20), 154.7 (C-19), 155.4 (C-21) (assignment might be interchanged).

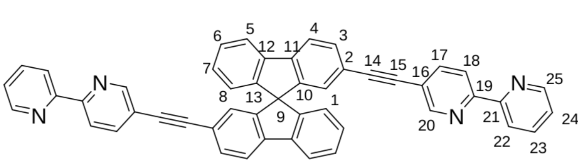


Fig. 6. Labeling of the carbon nuclei in ligand **1** (the magnetically non-equivalent nuclei in the complexes are labeled C-1, C-1′ *etc.*).

(Δ,Λ)-$[Ag_2\{(R)\text{-}\mathbf{1}\}_2](BF_4)_2$/$(\Delta,\Lambda)$-$[Ag_2\{(S)\text{-}\mathbf{1}\}_2](BF_4)_2$

6.00 mg (8.92 mmol) of (*R*)-**1** was dissolved in 0.6 mL of CD_2Cl_2. 2.81 mg (8.92 mmol) of $[Ag(CH_3CN)_2](BF_4)$ was dissolved in 0.2 mL CD_3CN. The two solutions were combined and mixed. The resulting light-yellow solution was transferred into an NMR tube. Likewise, solutions for measurement of ESI and CD spectra were generated. For ESI-MS and CD studies a 5×10^{-5} mol L^{-1} solution was prepared (CH_2Cl_2/CH_3CN 1 : 1). The complexes of (*S*)-**1** were prepared and characterized likewise.

CD (λ ($\Delta\varepsilon$)): (Δ,Λ,R) = 315 (−10.7), 351 (20.0), 362 (35.4); (Δ,Λ,S) = 315 (10.8), 351 (−19.9), 362 (−35.4). – MS ((+)-ESI, CD_2Cl_2/CD_3CN): *m/z* = 781.1 ($[Ag_2\mathbf{1}_2]^{2+}$, $[Ag\mathbf{1}]^+$), 1648.3 $\{[Ag_2\mathbf{1}_2](BF_4)\}^+$). – ^{1}H NMR ($CD_2Cl_2/CD_3CN$ 2 : 1, 298.0 K, 500.1 MHz): δ = 5.87 (s, 1 H, H-1′), 5.98 (d, J = 7.2 Hz, 1 H, 8′-H), 6.11 (s, 1 H, 1-H), 6.24 (d, J = 7,7 Hz, 1 H, 8-H), 6.37 (dd, J = 7.2 Hz, J = 7.2 Hz, 1 H, 7′-H), 6.66 (d, J = 8.2 Hz, 1 H, 3′-H), 6.72 (dd, J = 7.3 Hz, J = 7.7 Hz, 1 H, 6′-H), 6.81 (m, 1 H, 24-H), 6.88 (m, 1 H, 7-H), 6.90 (s, 1 H, 20-H), 7.03 (d, J = 7,7 Hz, 1 H, 3-H), 7.22 (m, 1 H, 6-H), 7.23 (d, J = 7.7 Hz, 1 H, 4-H), 7.29 (d, J = 7.7 Hz, 1 H, 17′-H), 7.37 (d, J = 8.2 Hz, 1 H, 4′-H), 7.50 (d, J = 7.7 Hz, 1 H, 5′-H), 7.59 (m, 1 H, 24′-H), 7.62 (d, J = 7.7 Hz, 1 H, 5-H), 7.82 (s, 1 H, 25-H), 7.98 (d, J = 8.2 Hz, 1 H, 17-H), 8.06 (d, J = 7.7 Hz, 1 H, 18′-H), 8.13 (m, 1 H, 23-H), 8.13 (s, 1 H, 20′-H), 8.17 (m, 1 H, 23′-H), 8.32 (d, J = 7.7 Hz, 1 H, 22′-H), 8.41 (d, J = 8.2 Hz, 1 H, 18-H), 8.47 (d, J = 8.2 Hz, 1 H, 22-H), 8.72 (d, J = 4.4 Hz, 1 H. 25′-H).

$(\Delta,\Lambda)\text{-}[\mathrm{Cu_2}\{(R)\text{-}\mathbf{1}\}_2](\mathrm{BF_4})_2/(\Delta,\Lambda)\text{-}[\mathrm{Cu_2}\{(S)\text{-}\mathbf{1}\}_2](\mathrm{BF_4})_2$

6.00 mg (8.92 mmol) of (R)-**1** was dissolved in 0.6 mL of CD_2Cl_2. 2.81 mg (8.92 mmol) of $[Cu(CH_3CN)_4](BF_4)$ was dissolved in 0.2 mL CD_3CN. The two solutions were combined and mixed. The resulting light-yellow solution was transferred into an NMR tube. Likewise, solutions for measurement of ESI and CD spectra were generated. For ESI-MS and CD studies a 5×10^{-5} mol L^{-1} solution was prepared (CH_2Cl_2/CH_3CN 1 : 1). The complexes of (S)-**1** were prepared and characterized likewise.

CD (λ ($\Delta\varepsilon$)): ($\Delta\Lambda$,R) = 297 (−5.2), 364 (11.7); (Δ,Λ,S) = 297 (5.2), 364 (−11.6). – MS ((+)-ESI, pos., CD_2Cl_2/CD_3CN): m/z = 735.2 ($[Cu_2\mathbf{1}_2]^{2+}$, $[Cu\mathbf{1}]^{+}$), 1559.4 ($\{[Cu_2\mathbf{1}_2](BF_4)\}^{+}$). – ^{1}H NMR ($CD_2Cl_2/CD_3CN$ 2 : 1, 298.0 K, 500.1 MHz): δ = 5.85 (s, 1 H, 1′-H), 5.98 (s, 1 H, 1-H), 6.06 (d, J = 7.7 Hz, 1 H, 8′-H), 6.30 (d, J = 7.5 Hz, 1 H, 8-H), 6.40 (dd, J = 7.0 Hz, J = 7.7 Hz, 2 H, 7′-H), 6.62 (s, 1 H, 20-H), 6.65 (m, 1 H, 24-H), 6.70 (d, J = 7.9 Hz, 1 H, 3′-H), 6.71 (m, 1 H, 6′-H), 6.91 (m, 1 H, 7-H), 6.93 (d, J = 8.2 Hz, 1 H, 3-H), 7.22 (dd, J = 7.7 Hz, J = 7.7 Hz, 2 H, 6-H), 7.33 (d, J = 8.2 Hz, 1 H, 4-H), 7.56 (dd, J = 8.4 Hz, J = 1.7 Hz, 17′-H), 7.42 (d, J = 8.2 Hz, 1 H, 4′-H), 7.51 (d, J = 8.0 Hz, 1 H, 5′-H), 7.53 (m, 1 H, 24′-H), 7.67 (d, J = 7.7 Hz, 1 H, 5-H), 7.74 (d, J = 4.8 Hz, 1 H, 25-H), 7.86 (dd, J = 8.6 Hz, J = 1.7 Hz, 1 H, 17-H), 7.93 (s, 1 H, 20′-H), 8.04 (m, 1 H, 23-H), 8.08 (m, 1 H, 23′-H), 8.10 (d, J = 8.4 Hz, 1 H, 18′-H), 8.31 (d, J = 8.4 Hz, 1 H, 22′-H), 8.42 (d, ^3J = 8.6 Hz, 1 H, 18-H), 8.46 (m, J = 8.3 Hz, 2 H, 22-H), 8.48 (d, J = 5.0 Hz, 1 H, 25′-H). – ^{13}C NMR (CD_2Cl_2/CD_3CN 2 : 1, 298.0 K, 125.8 MHz): δ = 64.5, 84.8, 85.0, 95.3, 95.9, 119.0 (2 C), 119.1, 120.1 (2C), 120.3, 120.5, 121.1, 121.6, 121.9, 122.4, 122.8, 123.5 (3 C), 125.4 (2 C), 125.7, 126.7, 127.6, 128.1, 128.4, 131.1, 131.3, 138.2, 138.4, 139.1, 140,4, 140.6, 141.5, 142.6, 146.4, 147.5, 147.6 (2 C), 147.7, 147.8, 148.3, 148.4, 148.9, 149.3, 149.8, 151.1, 151.3.

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