Selective Self-Assembly of a Sequential Bipyridine−Bipyrazine Ligand Strand into a Double-Stranded Cu^{I} Helicate

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In this paper new aspects on the self-assembly processes of didentate coordinating ligands leading to a double-stranded helicate are described. It was reported, that directionality in the self-recognition of Cu^{I} ions could be driven by factors relating to the electronic configuration of heterocycles in carefully designed heterotopic ligands. If the sequential bipyrazine–bipyridine ligand strand **4** reacts with 1 equiv. of Cu^{I} the dimetallic complex $[Cu_2(\mathbf{L4})_2][PF_6]_2$ is formed in a cooperative process. In this coordination compound the two strands are oriented in opposite directions (HT) as illustrated by the X-ray structure of $[Cu_2(\mathbf{L4})_2][PF_6]_2$.

Introduction

In recent years, intensive research on self-assembling processes has been derived. Among numerous structures published in the literature[1] the spontaneous formation of double-stranded or more complex organometallic helical complexes was extensively studied. The formation of a helicate depends on the nature of the metal and ligands, and sometimes on additional information introduced by appropriate templating.[2]

Some years ago, papers dealt with the self-assembly of a class of directional ligands, which led to saturated double-stranded heterotopic helicates with Cu^{I} [3] or Pd^{II}.[4] In the latter case the two strands selectively adopt a head-to-tail arrangement which leads to a C_2-symmetrically saturated heterotopic double-stranded helicate, with each Pd^{II} lying in a distorted five-coordinated environment, produced by the coordination of one bipyridine and one terpyridine subunit in each strand. In the former case introduction of bulky substituents in the basic quaterpyridine by Constable and co-workers[5,5a] was shown to induce a distinction between head-to-head (HH) and head-to-tail (HT) conformers leading to the exclusive formation of an (HH) C_2-symmetrical double-stranded Cu^{I} helicate in solution and in the solid state. In a previous study, Albrecht and Fröhlich synthesized a sequential ligand which contains one catecholate and one aminophenolate unit, in which the ability of the two nucleophilic sites to control the metal-directed self-assembly of chelates was reported.[6]

The aim of this work was to pursue the research to resolve unknown features on the Cu^{I} complexing behavior, concerning saturated heterotopic ligands, which here provide an original example, since they may be separated into one didentate "bipyridine" segment and one didentate "bipyrazine" segment upon complexation to metal ions. This means that only the same number of four inner nitrogen atoms could be engaged in the coordination with Cu^{I} to form a helicate, which is a coordination complex and not a chelate. Thus, a potentially induced directionality cannot come from outside modifications on the strand as reported for quaterpyridine examples[5] or from different nucleophilic centers as in the case of catecholate vs. aminophenolate,[6] but probably from the different electronic configuration of the bipyrazine nucleus[7] vs. bipyridine.

Results and Discussion

Because of a poor reproducibility of reactions leading to the rather difficult functionalization of 6,6′-dimethyl-2,2′-bipyrazine (**1**) into the 6-(hydroxymethyl)-6′-methyl-2,2′-bipyrazine (**3**), our concern was first to improve the synthesis of **4**. Using an unusual reagent like the tetrachloro-diphenylglycouril (Scheme 1) in the radical chlorination limiting step, we selectively obtained the 6-(chloromethyl)-6′-methyl-2,2′-bipyrazine in good yield (58%). Compared with

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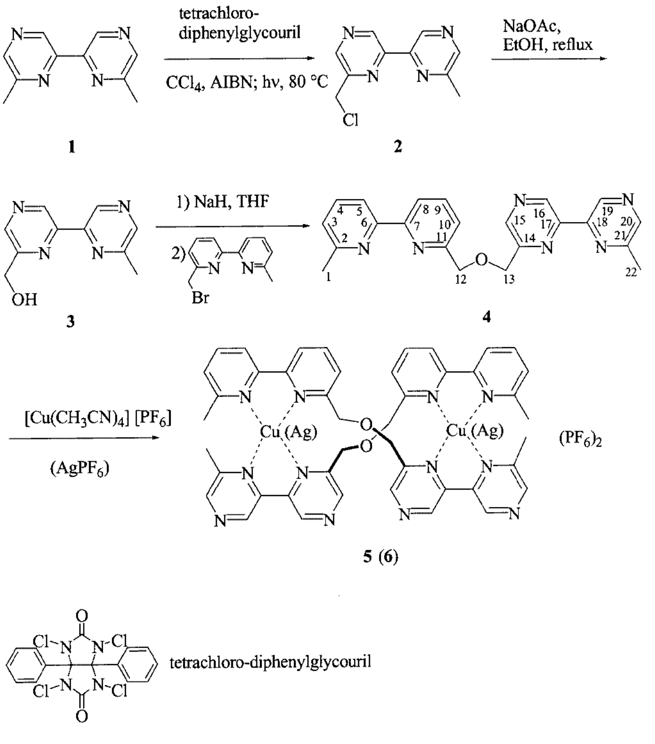
our previously reported synthesis[7a] the changes in the synthetic pathway led to a better yield (70%) of **4**. An equimolar amount of $[Cu(CH_3CN)_4][PF_6]$ added to **4** in anhydrous CH_3CN spontaneously led to a deep-red solution which confirmed the occurrence of the Cu^I coordination process. A thin layer chromatographic control showed that the ligand was totally consumed in the reaction. The crude material was recrystallized by slow diffusion of ether through an acetonitrile solution of the copper complex giving deep-red crystals that were stable in air.



Scheme 1

The ligand **4** (or **L4**) spontaneously forms the desired $[L_2Cu_2][PF_6]_2$ dinuclear double-stranded helical structure (see Exp. Sect.) as indicated by X-ray diffraction in the solid state. This structure persists in the dissolved state as established by various spectroscopic techniques (UV/Vis, ^1H NMR, ^{13}C NMR, and ES MS). An UV/Vis spectrophotometric titration of the ligand **4** by $[Cu(CH_3CN)_4][PF_6]$ in CH_3CN solution (see B in Figure 1) exhibits a clear isosbestic point indicating that a single species was formed and the appearance of an MLCT at 450 nm indicates the effective coordination of the Cu^I atoms. The titration plots (see A in Figure 1) assess that this species has a composition of ca. 1 Cu atom for 1 equiv. of **4** in agreement with the stoichiometry expected for the dihelicate $[Cu_2(\mathbf{L4})_2]^{2+}$.[8] The formation of the dinuclear helicate proceeds with a positive cooperativity as indicated by the increasing values of the calculated binding constants $\log\beta_{\text{metal-ligand}}$:[9] $\log\beta_{11} = 5.93$·for $[Cu(\mathbf{L4})]^+$; $\log\beta_{12} = 9.35$·for $[Cu(\mathbf{L4})_2]^+$; $\log\beta_{22} = 15.29$·for $[Cu_2(\mathbf{L4})_2]^{2+}$. This means that the formation of the final helicate is highly favored. In addition, preliminary results with other metal ions like Ag^I giving the $[Ag_2(\mathbf{L4})_2]$ complex **6** (Figure 2) show that the double-stranded helix formation with **4** is probably a more extended phenomenon.

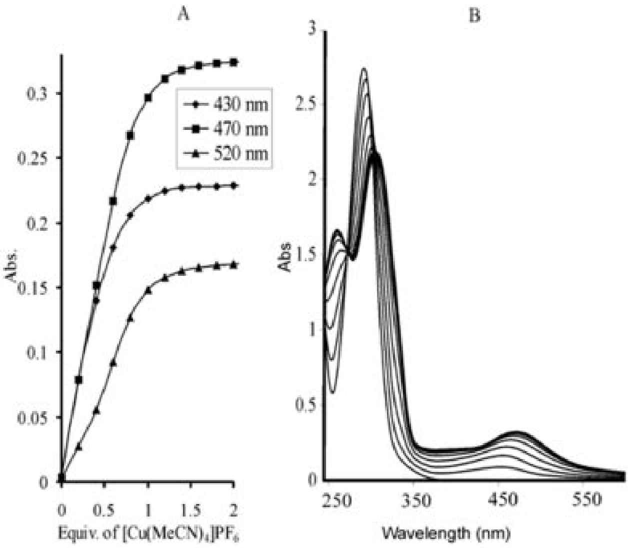


Figure 1. Spectrophotometric titration of the ligand **4** with $[Cu(MeCN)_4]PF_6$ (0.2−2.0 equiv.) in MeCN: A) plots of absorbance vs. added salt at three wavelengths and B) UV/Vis absorption spectra

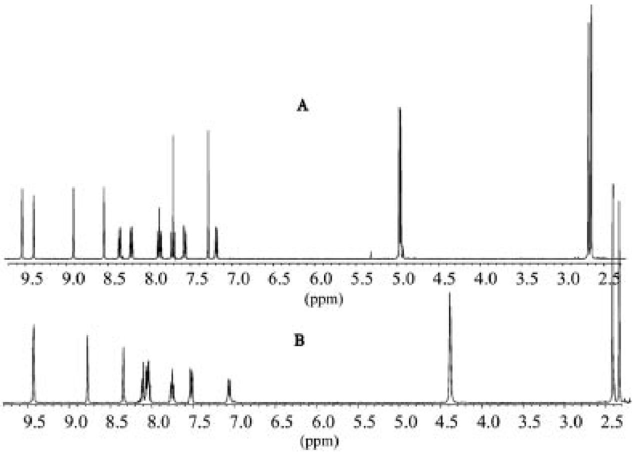


Figure 2. ^1H NMR spectra (400 MHz) of the free ligand **4** (A) and $[Ag_2(\mathbf{L4})_2][PF_6]_2$ in CD_3CN (B)

As previously established by Lehn and co-workers,[10] the ^1H NMR spectra of ligand **4** and its Cu^I complex (Figure 3) show the splitting of the enantiotopic methylene protons of the oxopropylene bridges in **4** (A_2 spin systems) to diastereotopic protons and doublets (AB spin systems) in the copper complex, on lowering the temperature. Methylene protons are also very useful for the estimation of the dynamic interconversion between dinuclear right-handed (*P*) and left-handed (*M*) enantiomeric helicates.[11] An investigation of the helical interconversion of complex **5** in a CD_3CN solution was realized using variable-temperature ^1H NMR experiments with analysis of the lateral methylene proton pattern between δ = 4.2 and 3.4 ppm (Figure 3). The free energy for the (*P*)/(*M*) interconversion in solution was estimated by the Eyring equation as $\Delta G^{\ddagger} = 66.9\ \text{kJ·mol}^{-1}$, this value is close to those found for analogous copper helicates.[12]

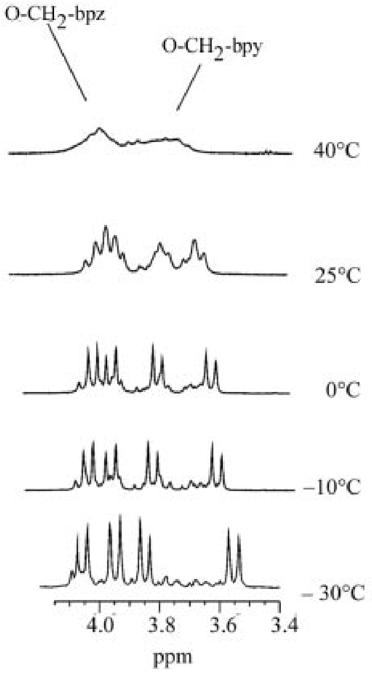


Figure 3. Variable-temperature ^1H NMR spectra of $[Cu_2(\mathbf{L4})_2][PF_6]_2$ in CD_3CN; selected region of methylene proton signals; each group of methylene protons is split into two distinct AB systems

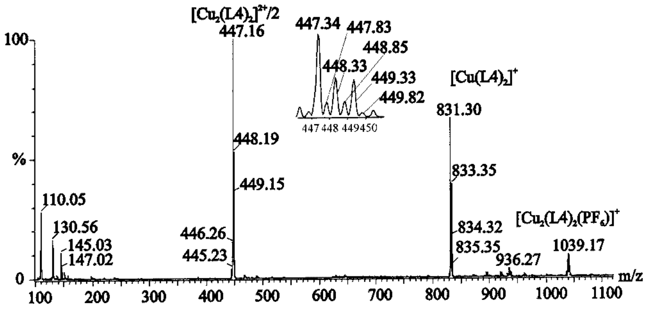


Figure 4. ES mass spectrum of the dinuclear double-stranded helical complex $[Cu_2(\mathbf{L4})_2][PF_6]_2$ (**5**) in acetonitrile

Finally, ES mass spectra (Figure 4) of **5** led to the observation of the $[Cu_2(\mathbf{L4})_2]^{2+}$ doubly charged ion (*m*/*z* = 447 a.m.u.) and the $[Cu_2(\mathbf{L4})_2(PF_6^-)]^+$ singly charged ion (*m*/*z* = 1040 a.m.u.). The isotopic distribution of the *m*/*z* = 447 ion shows peaks separated by 0.5 Da which is only compatible with a doubly charged species and the formation of the double-stranded helicate.[13] Similar results were obtained with the silver complex **6**. ES mass spectra exhibit the $[Ag_2(\mathbf{L4})_2]^{2+}$ doubly charged ion (*m*/*z* = 491 a.m.u.) and the $[Ag_2(\mathbf{L4})_2(PF_6^-)]^+$ singly charged ion (*m*/*z* = 1128 a.m.u.) with an isotopic distribution of the *m*/*z* = 491 ion showing peaks separated by 1.0 Da compatible with a doubly charged species.

X-ray diffraction analysis of a single crystal of the salt of the copper complex shows the presence of a double-stranded head-to-tail heterotopic helicate (Figure 5) which could be obtained by slow diffusion of diethyl ether into an acetonitrile solution containing **L4** and $[Cu(CH_3CN)_4][PF_6]$ in a 1:1 molar ratio. This structure represents the first example of such a helicate, having a strong directionality in self-assembly without external steric induction. The compound crystallizes in the triclinic $P\bar{1}$ space group with two dinuclear Cu^I complexes (a and b) and four PF_6^- disordered counterions in the asymmetric unit. Figure 5 depicts an ORTEP[14] view of the Cu^I complex structures displaying left- and right-handed helices. The Cu−Cu distances are 6.45 and 6.20 Å in the a and b complexes, respectively. The angle between the two corresponding Cu−Cu axes is 21°. Each Cu^I cation is in a distorted tetrahedral coordination and is attached to two pairs of N atoms belonging to one bipyridine and one bipyrazine molecule, respectively. All Cu−N bond lengths are equal to 2 Å within a narrow deviation interval (caption of Figure 5). The N−Cu−N angle values range from 80 to 135°, the most distorted helicate complex being the b one. All the bond lengths and angles are in good agreement with those obtained for (4,4′-bipyrimidine)- and (2,2′-bipyrazine)copper complexes.[15] In the present study, bipyrazine and bipyridine molecules are not ideally planar, the corresponding torsion angle between the two connected rings varies by up to 10° in order to accommodate the copper coordination on one hand and the outer interactions on the other. However, in each dinuclear complex, the bipyridine molecule mean planes are almost parallel. This is not true for the bipyrazine molecules which are attracted to each other in both the a and b complexes enhancing the metal tetrahedron distortions. Such an attraction of heterocycle molecules has been reported in our pre-

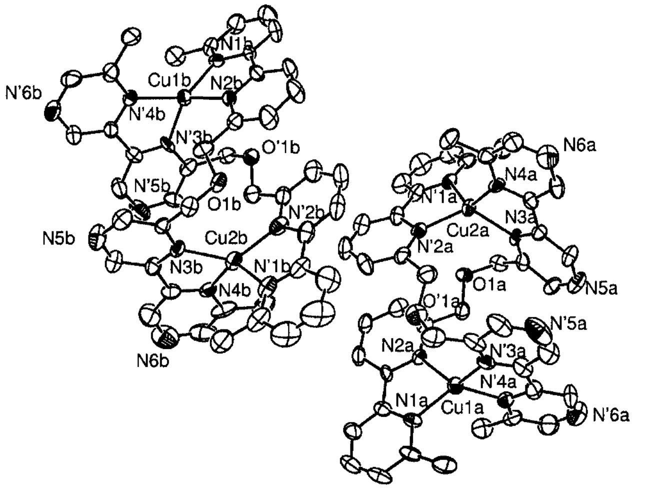


Figure 5. Structure (ORTEP view) of the two helicates in the asymmetric unit; the hexafluorophosphate anions and hydrogen atoms have been omitted for clarity; selected distances [Å] and angles [°]: Cu1a−N′3a 1.99 (1), Cu2a−N′2a 2.00(1), Cu1a−N1a 2.01(1), Cu2a−N3a 2.02(1), Cu1a−N2a 2.04(1), Cu2a−N4a 2.03(1), Cu1a−N′4a 2.06(1), Cu2a−N′1a 2.03(1), N′3a−Cu1a−N2a 123.7(5), N′2a−Cu2a−N3a 123.2(5), N1a−Cu1a−N′4a 124.7(5), N4a−Cu2a−N′1a 127.9(5), N′3a−Cu1a−N′4a 82.6(6), N3a−Cu2a−N4a 81.8(5), N1a−Cu1a−N2a 81.6(5), N′2a−Cu2a−N′1a 82.6(5); Cu1b−N′3b 2.01(1), Cu2b−N′2b 2.01(1), Cu1b−N1b 2.00(1), Cu2b−N3b 2.05(1), Cu1b−N2b 2.03(1), Cu2b−N4b 2.04(1), Cu1b−N′4b 2.01(1), Cu2b−N′1b 2.03(1), N′4b−Cu1b−N1b 134.6(5), N′1b−Cu2b−N4b 122.8(5), N′3b−Cu1b−N′4b 81.2(5), N3b−Cu2b−N4b 80.9(5), N2b−Cu1b−N1b 82.0(5), N′2b−Cu2b−N′1b 80.7(6), N2b−Cu1b−N′3b 120.8(5), N′2b−Cu2b−N3b 129.6(5)

vious work.[15] The crystal packing (see CCDC supplementary material) shows how the disordered PF_6^- counterions are distributed in the interstices.

In addition to the high atomic thermal vibration (room-temperature data in this study), the PF_6^- anion disorder probably breaks down a symmetry operation (center of inversion) which can hypothetically relate the two heterotopic helicates of the asymmetric unit. Furthermore, PF_6^- anions interact with the dinuclear complexes as revealed by the close F···H contacts ranging from 2.3 to 2.6 Å. Therefore, in the solid state, the PF_6^- counterion found close to the two bipyrazine heterocycles, belonging to the same helicate, can explain the non-parallelism of the corresponding molecular mean planes. The other counterions are found approximately in the same plane as the bipyridine molecule of one complex and are connected to the methyl group attached to the bipyrazine heterocycle of the second helicate.

Conclusions

In contrast to other helicates previously described, a directional selective double-stranded head-to-tail spontaneous assembly has been obtained from a heterotopic ligand without the help of external hindered factors, stereochemical requirements or the electronic nature of a chelating center[6] belonging to the coordination preference of the metal ions. In the asymmetric unit Cu−N bond lengths (2 Å) of the same distance were found whatever the nature of the biheterocycle involved in the coordination with the copper atom. The PF_6 disorder in the solid state induces a geometrical distinction of two double-stranded dinuclear complexes in the asymmetric unit. Furthermore, particular interactions between the PF_6 counteranions and biheterocycle protons of the ligand **4** through F−H hydrogen bonds were observed. In this study, it was reported that a careful design of the ligands can lead to a new class of helicates, which appear to be driven in their assembling process by the electronic configuration of the biheterocyclic units. Previous results of the experimental electron density,[7] which clearly pointed to the greater non-aromatic character of the 2,2′-bipyrazine compared to other diazines or monoazines, corroborate this hypothesis. Further work is in progress to analyze the general character of these results with other sequential heterotopic ligands.[16]

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX 400 spectrometer. UV/Vis spectra were recorded with a UVmC^2 Safas spectrometer. Mass spectra (ES) were taken with a Micromass Platform spectrometer. Elemental analyses were obtained with a Perkin−Elmer 240C CHN-O-S analyzer. The solvents were purified by standard methods.

6-Chloromethyl-6′-methyl-2,2′-bipyrazine (2): To a solution of 6,6′-dimethyl-2,2′-bipyrazine (1 g, 5.38 mmol) in CCl_4 (100 mL) under Ar, tetrachloro-diphenylglycouril {1,3,4,6-tetrachloro-3a,6a-diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione} (1 g, 2.32 mmol) and AIBN were added. The mixture was refluxed and irradiated by a tungsten lamp (100 W) for 24 h. The resulting precipitate was filtered, washed with CH_2Cl_2, and the solvent was removed in vacuo. The crude product was purified by chromatography on silica gel (elution: CH_2Cl_2/Et_2O, 95:5) to give two fractions. Fraction 1: **2:** Yield 683 mg (58%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.54 (s, 1 H), 9.38 (s, 1 H), 8.81 (s, 1 H), 8.53 (s, 1 H), 4.78 (s, 2 H), 2.66 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 153.1, 151.0, 148.5, 147.7, 145.2, 144.4, 143.1, 142.4, 43.9, 21.6 ppm. Fraction 2: **6,6′-Bis(chloromethyl)-2,2′-bipyrazine:** Yield 257 mg (19%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.57 (s, 2 H), 8.84 (s, 2 H), 4.80 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 151.1, 147.8, 144.8, 142.6, 43.8 ppm.

6-(Hydroxymethyl)-6′-methyl-2,2′-bipyrazine (3): To a solution of **2** (477 mg, 2.16 mmol) in anhydrous EtOH (20 mL), NaOAc (1.77 g, 21.60 mmol) was added. The mixture was refluxed for 24 h. The resulting precipitate was filtered and the solvent was removed in vacuo. The crude product was purified by chromatography on silica gel (elution: CH_2Cl_2/MeOH, 95:5) to give two fractions. Fraction 1: **3:** Yield 250 mg (57%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.50 (s, 1 H), 9.36 (s, 1 H), 8.73 (s, 1 H), 8.52 (s, 1 H) 4.95 (d, J = 4.2 Hz, 2 H), 3.66 (s, 1 H), 2.67 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 153.9, 153.3, 148.1, 148.0, 145.0, 143.0, 141.8, 140.0, 63.0, 21.6 ppm. Fraction 2: **6-(Acetoxymethyl)-6′-methyl-2,2′-bipyrazine:** Yield 102 mg (19%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.50 (s, 1 H), 9.34 (s, 1 H), 8.68 (s, 1 H), 8.51 (s, 1 H), 5.34 (s, 2 H), 2.64 (s, 3 H), 2.19 (s, 3 H) ppm, ^{13}C NMR ($CDCl_3$, 25 °C): δ = 170.3, 153.0, 150.1, 148.5, 147.8, 145.0, 143.4, 142.3, 140.2, 64.6, 21.5, 20.7 ppm.

6-Methyl-6′-[(6′-methyl-2,2′-bipyridin-6-yl)methoxymethyl]-2,2′-bipyrazine (4): To NaH (54 mg, 2.24 mmol) in anhydrous THF (5 mL) under Ar at 0 °C **3** (268 mg, 1.32 mmol) in THF (10 mL) was added. The mixture was stirred at 0 °C for 1 h. 6-(Bromomethyl)-6′-methyl-2,2′-bipyridine (348 mg, 1.32 mmol) in THF (10 mL) was then added, and the mixture was allowed to warm to room temp. The mixture was stirred at 40 °C for 24 h. After cooling to room temp., H_2O (10 mL) was added to the mixture and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by chromatography on alumina gel (elution: CH_2Cl_2) to give a white powder. Yield 353 mg (70%); m.p 142 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.52 (s, 1 H, bpz), 9.39 (s, 1 H, bpz), 8.90 (s, 1 H, bpz), 8.53 (s, 1 H, bpy), 8.35 (d, $^3J_{8,9}$ = 7.8 Hz, 1 H, bpy), 8.20 (d, $^3J_{5,4}$ = 7.8 Hz, 1 H, bpy), 7.86 (t, $^3J_{9,10}$ = 7.8 Hz, 1 H, bpy), 7.70 (t, $^3J_{4,3}$ = 7.8 Hz, 1 H, bpy), 7.55 (d, $^3J_{10,9}$ = 7.6 Hz, 1 H, bpy), 7.17 (d, $^3J_{3,4}$ = 7.6 Hz, 1 H, bpy), 4.96 (s, 2 H), 4.94 (s, 2 H), 2.67 (s, 3 H), 2.64 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 157.9 (C^{21}), 157.1 (C^{14}), 155.9 (C^{18}), 155.3 (C^{17}), 153.0 (C^{2}), 152.5 (C^{11}), 148.3 (C^{6}), 148.1 (C^{7}), 145.0 (C^{19}), 143.7 (C^{20}), 142.0 (C^{15}), 140.2 (C^{16}), 137.5 (C^{9}), 137.0 (C^{4}), 123.2 (C^{3}), 121.2 (C^{10}), 120.0 (C^{8}), 118.2 (C^{5}), 74.2 (C^{13}), 71.8 (C^{12}), 24.6 (C^{1}), 21.6 (C^{22}) ppm. UV/Vis (CH_3CN): λ_{max} $(\varepsilon)_{max}$ = 292 nm (27339). $C_{22}H_{20}N_6O$ (384.4): calcd. C 68.72, H 5.24, N 21.86; found C 68.64, H 5.22, N 21.73.

$[Cu_2(L4)_2][PF_6]_2$ (5): $[Cu(CH_3CN)_4][PF_6]$ (194 mg, 0.52 mmol) was added to the ligand **4** (200 mg, 0.52 mmol) in anhydrous CH_3CN (50 mL) solution under Ar. The mixture was stirred at room temp. and spontaneously led to a deep-red solution. After evaporation of the solvent, the solid residue was crystallized by slow diffusion of diethyl ether into an acetonitrile solution, which gave deep-red crystals. ^{1}H NMR (CD_3CN, −30 °C): δ = 9.68 (s, 4 H, bpz), 8.91 (s, 2 H, bpz), 8.34−8.32 (m, 4 H, 2 H-bpz, 2 H-bpy), 8.19−7.96 (m, 6 H, bpy), 7.57 (d, $^3J_{10,9}$ = 7.5 Hz, 2 H, bpy), 7.01 (d, $^3J_{3,4}$ = 7.4 Hz, 2 H. 1 H-bpy and 1 H-bpy′), 4.09−3.54 (m, 8 H, 4 CH_2), 2.42 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.15 (t, ^2J = 8.8 Hz; CH_3), 2.05 (s, 3 H,CH_3)

ppm. ^{13}C NMR (CD_3CN, −30 °C): δ = 158.4 (q), 154.8 (q), 152.4 (2 q), 150.6 (2 q), 149.3 (2 q), 149.0 (C^{19}), 145.5 (C^{20}), 143.6 (C^{15}), 142.0 (C^{16}), 139.9 (C^{9}), 139.6 (C^{4}), 127.0 (C^{3}), 126.1 (C^{10}), 122.5 (C^{8}), 120.5 (C^{5}), 71.7 (C^{13}), 68.4 (C^{12}), 24.1 (C^{1}), 21.5 (C^{22}) ppm. ^{13}C CPMAS NMR (75 MHz, 7 kHz, 20 °C): δ = 156.0 (q), 149.0 (q), 142.0 (C^{15}, C^{16}), 139.0 (C^{9}, C^{4}), 128.0 (C^{3}, C^{10}), 122.0−120.0 (C^{8}, C^{5}), 70.0 (C^{13}, C^{12}), 25.0 (C^{1}), 22.0 (C^{22}) ppm. UV/Vis (CH_3CN): λ_{max} $(\varepsilon)_{max}$ = 306 nm (21680). ES MS: *m/z* (%) = 1040.2 (20) $[Cu_2(\mathbf{L4})_2(PF_6^-)]^+$, 831.3 (90) $[Cu_2(\mathbf{L4})]^+$, 447.3 (100) $[Cu_2(\mathbf{L4})_2]^{2+}/2$. $C_{44}H_{40}Cu_2F_{12}N_{12}O_2P_2$ (1185.9): calcd. C 44.56, H 3.40, N 14.17; found C 44.52, H 3.37, N 13.95.

$[Ag_2(L4)_2][PF_6]_2$ (6): $AgPF_6$ (65.84 mg, 0.26 mmol) was added to the ligand **4** (100 mg, 0.26 mmol) in anhydrous CH_3CN (20 mL) solution under Ar. The mixture was stirred at room temp. and after evaporation of the solvent, the solid residue was crystallized by slow diffusion of diethyl ether into an acetonitrile solution, which gave white crystals. ^{1}H NMR (CD_3CN, 25 °C): δ = 9.43 (s, 1 H, bpz), 9.42 (s, 1 H, bpz), 8.77 (s, 1 H, bpz), 8.34 (s, 1 H, bpz), 8.11 (m, 3 H, bpy), 7.75 (t, ^3J = 7.8 Hz, 1 H, bpy), 7.52 (d, ^3J = 7.8 Hz, 1 H, bpy), 7.06 (d, ^3J = 7.6 Hz, 1 H, bpy), 4.39 (s, 2 H, CH_2), 4.38 (s, 2 H, CH_2), 2.41 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = 158.8 (q), 156.0 (q), 154.8 (q), 151.3 (q), 150.8 (q), 147.9, 145.7, 143.6, 141.7, 140.2, 140.0 (CH bpy), 126.1, 124.6, 122.5, 120.8 (CH bpz), 74.0 (CH_2 bpz), 70.5 (CH_2 bpy), 26.2 (CH_3 bpz), 22.4 (CH_3 bpy) ppm. UV/Vis (CH_3CN): λ_{max} $(\varepsilon)_{max}$ = 298 nm (25379). ES MS: *m/z* (%) = 1128.9 (10) $[Ag_2(\mathbf{L4})_2(PF_6^-)]^+$, 491.2 (100) $[Ag_2(\mathbf{L4})_2]^{2+}/2$.

X-ray Structural Analysis of $[Cu(C_{22}H_{20}N_6O)]_2[PF_6]_2$: The crystal structure of $[Cu(C_{22}H_{20}N_6O)]_2[PF_6]_2$, $\rho_{calcd.}$ = 1.61 Mg·m^{-3}, μ(Mo-K_α) = 1.036 mm^{-1}, was determined from a single-crystal X-ray diffraction experiment. The deep-red crystals obtained are plate-like and very fragile. A crystalline fragment sample was mounted on an Enraf−Nonius CAD-4F diffractometer. Several attempts were made because of the diffraction-limited power of the samples. Therefore, data collection was performed at room temp. on a large crystal fragment (approximately 0.5 × 0.9 × 0.2 mm) with Mo-K_α X-ray radiation (λ = 0.71073 Å). $[Cu(\mathbf{L4})]_2[PF_6]_2$ crystallizes in the triclinic $P\bar{1}$ space group, $Z = 4$ (two dinuclear complexes in the asymmetric unit). The unit cell parameters were obtained by least-squares fit to setting angles of 25 reflections in the range $12° < 2\theta < 26°$. The cell parameters are a = 13.912(2), b = 19.903(4), c = 20.062(3) Å, α = 97.67(2), β = 105.49(1), γ = 109.89(2)°, V = 4877.2(17) Å^3. The ω-2θ scan mode was used to record the diffracted intensities. Three standard reflections (−5 −1 2), (−5 0 0) and (−3 1 −1) were monitored every 2 h in order to control the intensity decay, which is not significant. 25304 reflections were collected up to $2\theta_{max}$ = 55.9°. Lorentz polarization corrections and data reduction was performed by using the WINGX package[17] for CAD4-collected intensities. The structure was solved by direct methods by using the SIR92 program.[18] Due to a large amount of weak intensities, only 22843 observed reflections were taken into account in order to refine the structure by full-matrix least squares based on $|F^2|$ by using the SHELX97[19] program. Thermal displacements of non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at their idealized positions but not refined. Three of the four PF_6^- counterions in the asymmetric unit are disordered. Two atomic positions were assigned to one phosphorus and 16 fluorine atoms, respectively. The site occupancy factors of these disordered atomic positions were refined. During the last cycles of refinement, an empirical absorption correction was applied (T_{min} = 0.040, T_{max} = 0.441) using the DIFABS program in the WINGX package.[17] The final statistical factors are $R1$(all observed data) = 0.319, $wR2$ = 0.387 for 22843 data and 1495 parameters, $R1$ $[I > 2\sigma(I)]$ = 0.127 for 6758 data with $I > 2\sigma(I)$. The weak ratio N_{obs}/N_{par} is assigned to the high disorder of the PF_6^- counterions in the solid state. The final residual densities in the unit cell are +0.85 and −0.80 e·Å^{-3}. CCDC-176336 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +b 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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