# An Easy Entry into Schiff Base Molecules Bearing a Pendant Primary Alcohol Function for Hydrogen Bonding

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**Abstract:** A series of mono-oxidized pyridine, bipyridine, terpyridine and pyridine/pyridazine frameworks were prepared using $MnO_2$ as oxidant. Corresponding Schiff bases were prepared with aromatic or aliphatic amines carrying various functions such as paraffin chains, terminal acrylates and a second nitrogen atom. Various flexible tethers have been used for the ditopic ligands synthesis. These ligands formed dinuclear helicates for the shorter chains. The dinuclear copper(I) complex prepared from the $CH_2$–$CH_2$ bridge is aggregated in the solid state by a hydrogen bonded network of the residual primary alcohol groups. For the longer spacers the ditopic ligand wraps around a single copper(I) centre forming a mononuclear complex. A significant merit of this work is that it allows the preparation of ligands and complexes retaining the hydroxymethyl function, which are likely to help to stabilize multidimensional networks in the solid state.

**Key words:** oligopyridines, Schiff bases, helicates, primary alcohols, hydrogen bonds

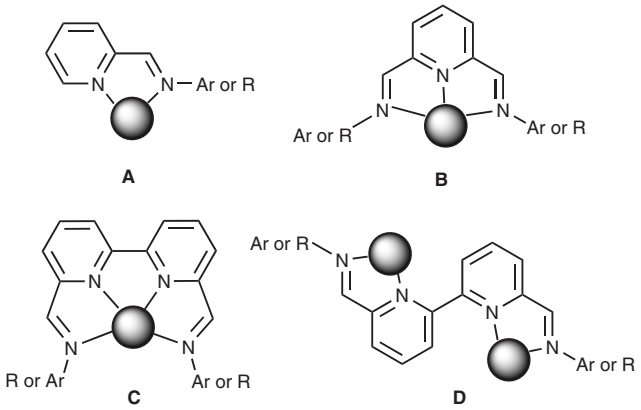


**Figure 1** Binding behavior of imino-pyridine ligands

The development of the so-called Schiff base compounds has attracted a lot of interest in the fields of coordination chemistry and material sciences.[1,2] Metal complexes derived from such useful derivatives are known to form a large variety of molecular architectures, ranging from macrocyclic helicates to infinite coordination polymers.[3,4] In particular, 2-iminopyridine, 2,6-diiminopyridine and 6,6′-diimino-2,2′-bipyridine, readily formed via reversible reaction between an achiral or chiral amine and appropriate aldehydes, are attractive building blocks for assembling intricate supramolecular species and highly stable metallo-helicates.[5,6] The presence of a lone pair on the nitrogen atom of the imino group enables the coordination of numerous metal cations, especially when the imine function is located at the *ortho* position of the heterocycle such as pyridine.[7] These ligands can display specific binding behavior towards metal cations, some are reminiscent of 2,2′-bipyridine as in **A**, 2,2′:6′,2″-terpyridine as in **B** and 2,6,2′,6′-quaterpyridine as in **C** (Figure 1). Notice that in this last case the ligand can adopt a bridging mode of coordination of type **D**. Recently, various molecules found interesting applications as ligands in various homogeneous catalytic reactions such as hydrosilation, Mukaiyama aldolization and cyclopropanation,[8] homologation of aromatic aldehydes,[9] and ethylene polymerization.[10–12]

In the domain of material science, the main advantage in the use of Schiff base ligands relates to the availability of a free imino site that can be functionalized with a wide variety of appendages, such as paraffin tails, highly polarized molecular units or fragments bearing specific physical properties. Along these lines we discovered that assembling non-mesomorphic but lipid-like ligands bearing in close proximity to the central core of two imino functions around d-block transition metals promotes the formation of a liquid-crystalline state.[13–15] One of the key element of this approach lies in the helix rigidity and polarizability to counterbalance the flexibility and non-polarizability imported by the paraffin chains. It becomes clear from the few examples we have in hand, that the use of segmented ligands carrying hybrid function such as pyridines/imines certainly facilitate the interlocking of rigid conformations. The ready availability of these Schiff-based ligands, the simplicity of the purification procedures, the mildness of the reaction conditions, and the high yields allow the preparation of multigram scale materials.

Furthermore, the engineering of ligands carrying additional organizing vectors such as potential hydrogen bond donors or π-π stacking facilities will promote the organization of matter in the liquid-crystalline or solid-phase. The present work is motivated by such a concept targeting the preparation of ligands retaining a hydroxymethyl function on one side of the molecule. The easy way to

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generate such molecules would be to find a selective mono-oxidation of dihydroxymethyl oligopyridinic platforms.

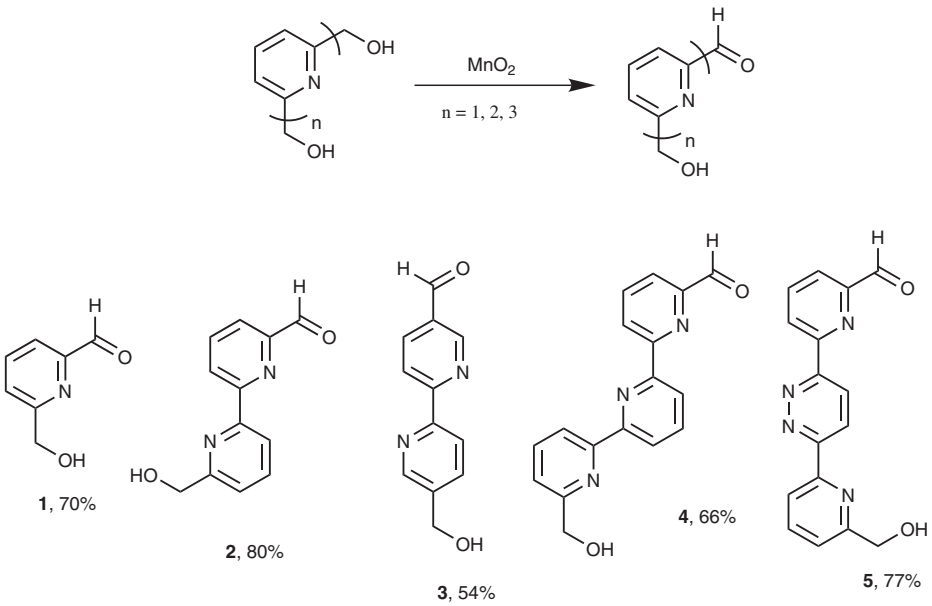
Indeed, the selective oxidation of a single primary alcohol in 2,6-hydroxymethylpyridine is feasible but remains difficult and feasible only under harsh conditions. Typical literature procedures utilize $SeO_2$ (0.5 equiv) under refluxing pyridine.[16] This is a major problem due to the toxicity, cost, product purity and low isolated yields. In our hands, this was a significant issue that could not be overcome by manipulating the experimental conditions. We desired conditions that would be practical, inexpensive, environmentally friendly, amenable to large-scale synthesis and allow for substrate generality.

The use of other metal reagents or catalysts has also been developed to address this issue and manganese dioxide has proved to be a valuable oxidizing agent for many functional groups.[17–19] However, we noticed that 2,6-dihydroxymethylpyridine was doubly oxidized to the dialdehyde in acceptable yield.[20] Also, the hydroxymethyl substituted aromatic heterocyles, including pyridines, furans, and thiophenes are oxidized smoothly to the corresponding aldehydes by 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxoammonium perchlorate as reagent.[21] Alternatively, 6-formyl-2-methylpyridine could be generated by heterogeneous oxidation,[22] whereas 6-formyl-6′-methyl-2,2′-bipyridine and 6-formyl-5′-methyl-2,2′-bipyridine could be prepared by a mono-oxidation of a single methyl substituent by selenium dioxide in refluxing dioxane.[23]

We found that depending of the source of commercially available manganese dioxide, the selective mono-oxidation of oligopyridine carrying dihydroxymethyl functions could be achieved in appreciable yields. In particular, the use of $MnO_2$ from Rhône-Poulenc (Prolabo No. 25259296) in a stoichiometric ratio with 2,6-dihydroxymethylpyridine was weakly active and solely provided the mono-oxidized derivative **1**, in $CHCl_3$ at 60 °C. Other sources such as $MnO_2$ from Merck (No. 805958) was very active and provided solely the di-oxidized compounds. After some experimentation, we were pleased to find that we could isolate compound **1** in 70% using a large excess of $MnO_2$ from Prolabo and extend the protocol to a family of oligopyridine derivatives as depicted in Scheme 1. Chloroform gave the best yields probably due to a correct mismatch between the solubility of products, the kinetic of the reaction and the selectivity. In all cases the formation of the bis-aldehydes is inefficient (<5%) and the unreacted compounds could be easily recovered. Similar trends were found for bipyridine, terpyridine and pyridine/pyridazine derivatives (Scheme 1), opening an avenue for the synthesis of sophisticated ligands.

It is likely that the difference of activity between the different $MnO_2$ suppliers is due the different nature of the crystalline phase and surface area. By mean of X-ray powder diffraction it was possible to determined the nature of the $MnO_2$ phase, likely to be a Pyrolusite phase for the Prolabo sample and Akhtenskite for the $MnO_2$ purchased from Merck.[24] Also significant is the weak surface area found by the Brunaüer–Emmett–Teller technique (BET), for the Prolabo sample (3.8 $m^2/g$) and 46.7 $m^2/g$ for the Merck sample. Furthermore, the morphology of both samples is different and it is concluded that the larger crystal and lower surface area present in the Prolabo sample favor a weaker activity resulting in the mono-oxidized sample. The more dispersed Merck sample is highly active and provide exclusively doubly oxidized derivatives.

One of the objectives of this study was to develop a concise and practical synthesis of Schiff-based molecules and their analogues to facilitate further evaluation in coordination chemistry and material sciences. The remaining hy-




**Scheme 1**

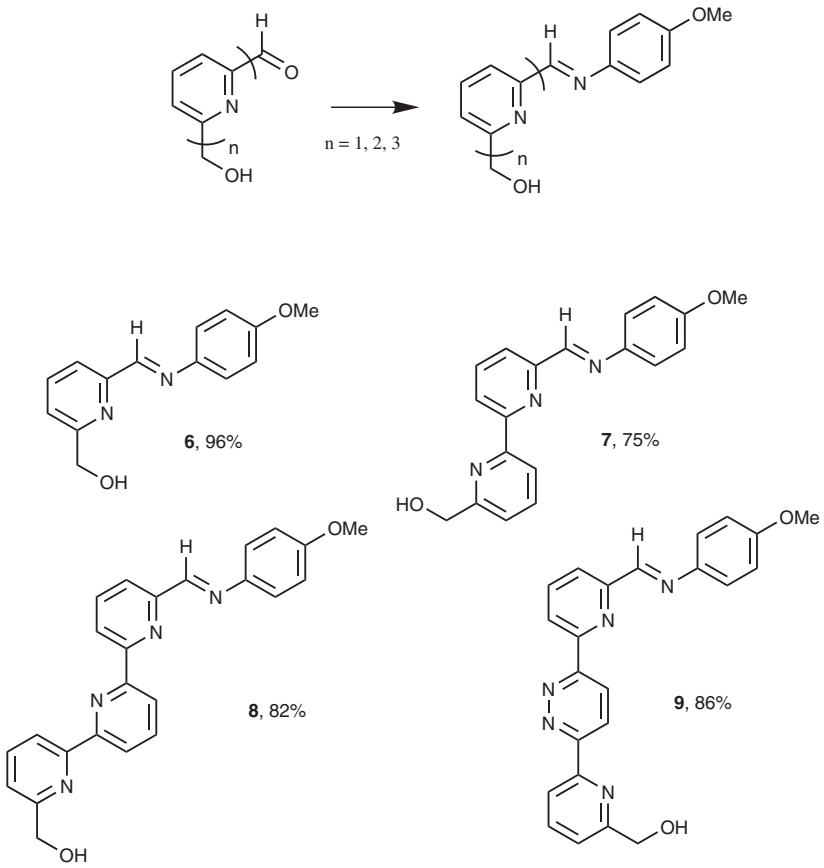
droxy groups will act as organizing vectors in the solid state in order to stabilize three-dimensional structures via hydrogen bonds (vide infra). This has led us to devise a flexible synthetic strategy, which employs the model compound *p*-methoxyaniline as a template (Scheme 2). The condensations are straightforward when realized under stoichiometric conditions, in hot ethanol, in the presence of trace amounts of acetic acid. The desired imino derivatives were recovered pure by filtration at room temperature.

In analogy to our previous work,[25] and also stimulated by our involvement in a program devoted to the engineering of mesomorphic nanostructures, 2-formyl-6-hydroxymethylpyridine was condensed with aniline derivative bearing in the *para* position an additional phenyl ester dipole and carrying in its periphery three paraffin chains. In one case, one of these alkyl chain is substituted by an acrylate function, a potential module for controlled polymerization reactions (Figure 2). Photo- or radical-initiated polymerization reactions have already been applied to generate stable anisotropic networks from reactive rod like liquid crystals in the nematic, cholesteric or smectic phases. In this processes, monomers with reactive end groups such as acrylates could be macroscopically aligned and polymerized in order to freeze the molecular organization in a rigid material.[26,27]

After some experimentation, we were pleased to find that these condensations can effectively been performed under mild conditions and in fair yields. To avoid the transesterification by-product with the free methyl alcohol function and to achieve a better yield in the imine formation, we turned our attention to the use of trace amounts of *p*-toluenesulfonic acid instead of acetic acid. Despite its obvious advantages and potential utility, *p*-TsOH enabled the formation of the acrylate derivatives only in modest to good yields (Figure 2).

Encouraged by the successful preparation of the imino derivatives, we moved to the more ambitious goal of expanding the methodology to the use of aliphatic diamino compounds in order to produce ditopic ligands for copper complexation. Ligands **14** and **15** were successfully prepared in almost quantitative yields, by condensation of two equivalents of 2-formyl-6-hydroxymethylpyridine or 2-formyl-6-hydroxymethyl-2,2′-bipyridine with ethylenediamine in the presence of trace amounts of acetic acid (Scheme 3).

In addition, in order to test the potential of the pyridine-based diimino ligands to bridge two cations or to wrap around a single metal we have increase the size of the spanning diamine from n = 2 to n = 5 (Scheme 4). Here also the condensation is straightforward in the presence of trace amounts of acetic acid, but we noticed a progressive




**Scheme 2**

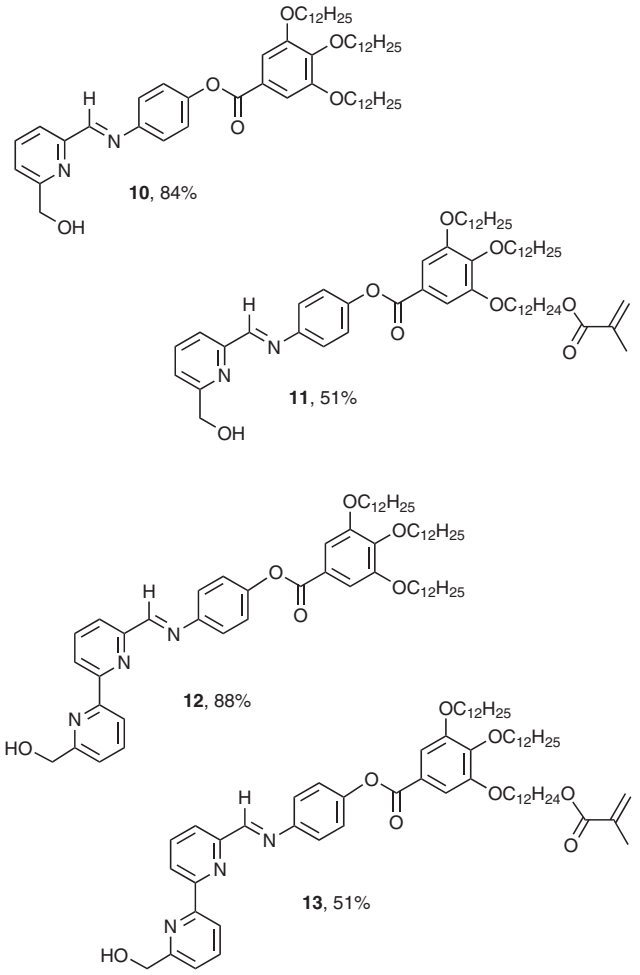
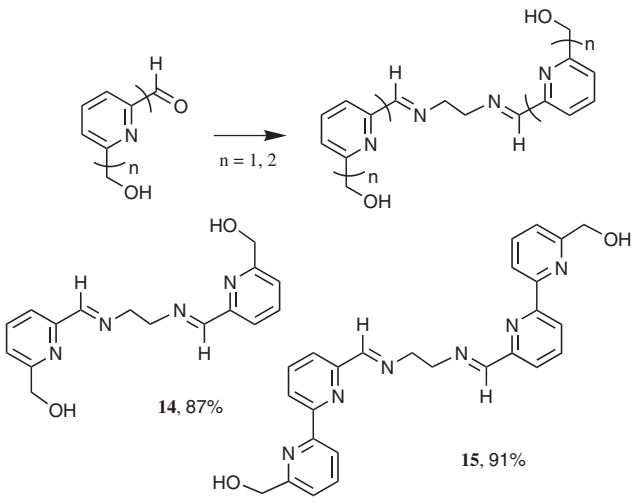


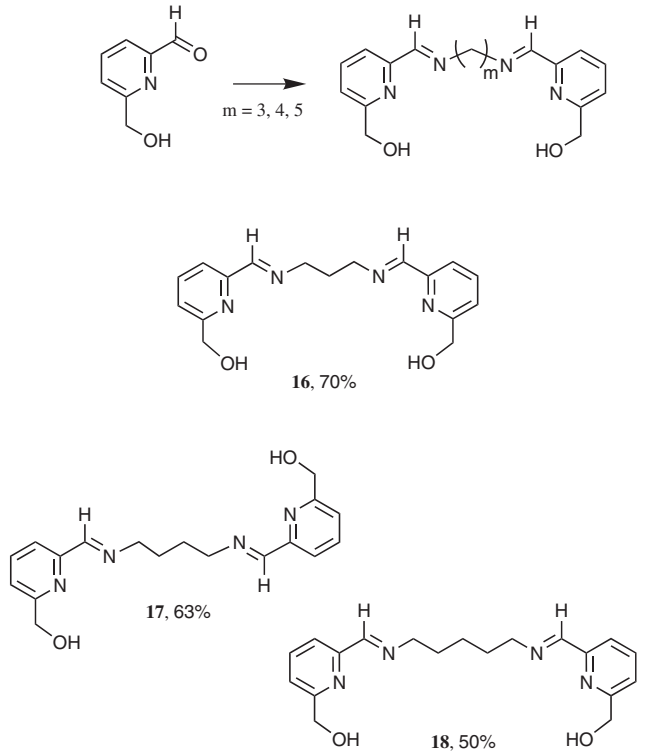

**Figure 2** Pyridine or bipyridine Schiff bases **10**–**13**




**Scheme 3**

decrease of the isolated yields on increasing the number of carbon atoms (Scheme 4).

In order to test the coordination abilities of such ligands towards transition metal and to generate simple metal induced self-organized structures, ligand **14** was allowed to




**Scheme 4**

react under stoichiometric conditions with $[Cu(CH_3CN)_4](BF_4)$ salts[28] under anaerobic conditions. Immediately after mixing the ligand with the metal salt, a deep-red color characteristic of Cu-imino derivatives develops in the solution. This coloration is indicative of a Cu(I) cation surrounded by four nitrogen donor atoms.[29] FT-IR studies in solution and the solid state of the resulting complex show a 21 $cm^{-1}$ shift of the imino stretching vibration, confirming that no free imino function is present at 1650 $cm^{-1}$ (C=N). Furthermore, the $^1H$ NMR spectrum of the isolated Cu-complex **19**, reveals the presence of an AB system (*exo*-H: 4.57 ppm, $J = 15.3$ Hz; *endo*-H: 3.77 ppm, $J = 15.3$ Hz), while in the free ligand a singlet is found at 4.89 ppm. This prochirality of the methylene protons is consistent with rigidification of the iminopyridine fragments due to the coordination to the metal centre, but is not a tool to determine the helical nature of the resulting complex.[30] ES-MS reveals the presence of an intense molecular peak at 809.2 $[M - BF_4]^+$ and 361.1 $[M - 2BF_4]^{2+}$ typical of a binuclear species (Figure 3). A X-ray crystal structure unambiguously confirmed the formation of a binuclear metallohelicate with the two copper(I) centers being separated by 3.902 Å. The ligands wraps around the two metal centers to give a double strand helicate complex (Figure 4). The bond lengths and angles around the copper cation are in good agreement with the values found in similar copper complexes.[29] As expected, the crystal structure is stabilized by hydrogen bond interactions involving the four alcohol functions forming a tight multidimensional H-bonded network. Two different hydrogen bonds interlink the dimeric structure along the axis c; d = 2.874(9) Å and d = 2.944(11) Å (Figure 5). Re-

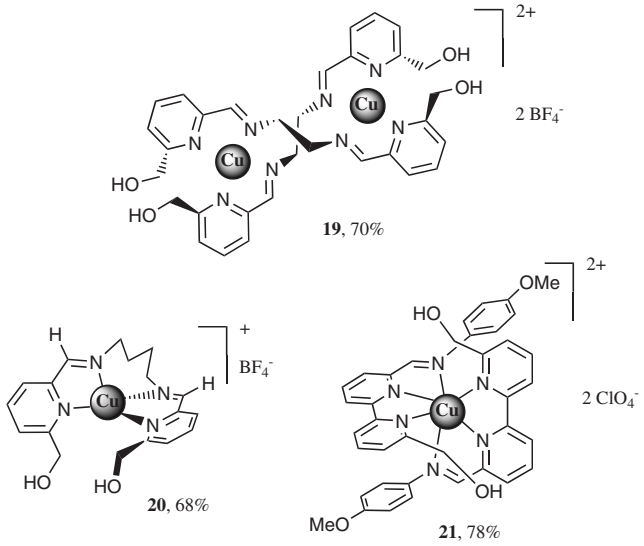



**Figure 3** Various copper complexes **19**–**21**: top, double strand helicate; bottom, mononuclear species

cently, similar polymeric arrays self-assembled by hydrogen bond aggregation have been evidenced.[31]

At this stage, it was interesting to test the pyridine based ligands **16**, **17** and **18** in the formation of copper(I) complexes. Interestingly, we found that ligand **17** bearing a flexible 1,4-diiminobutane tether does not form the double stranded helicate but rather give rise to a stable and deep-red mono-nuclear complex **20** in which a single ligand **17** wraps around a single copper(I) cation. ES-MS reveals the presence of an intense molecular peak at 389.2 $[M - BF_4]^+$ and the absence of a peak at higher mass typical of a dicationic species. The proton NMR of complex **20** reveals the presence of a single complex but does not give the stoichiometry of the formed complex. Surprisingly, with ligands bearing a 1,2-diiminopropane or 1,5-diiminopentane spacer, mixtures of complexes were observed under the standard conditions of reaction. Based on $^1H$ NMR and ES-MS data, it can be stated that in the case of ligand **16** both mononuclear and binuclear are simultaneously formed, whereas, in the case of ligand **18** a mixture of the mononuclear and polymeric complexes was formed. Attempts to grow single crystals or to properly separate these complexes remain elusive.

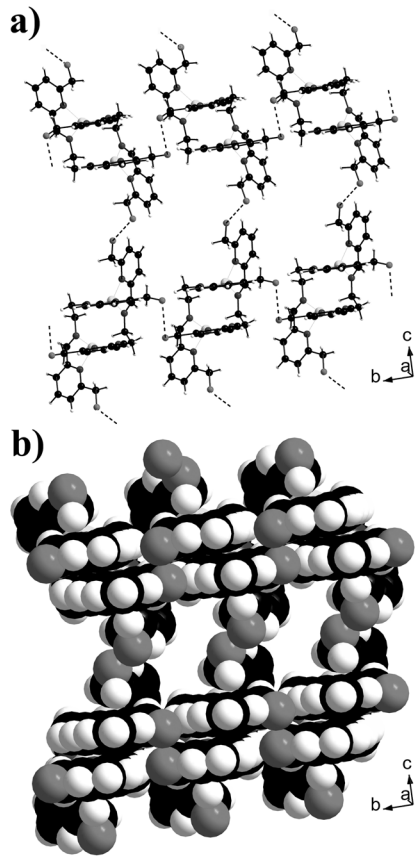



**Figure 5** Interlinked hydrogen bonded network running along the c axis. (a) ball and stick view of the network. (b) CPK view.

Finally, in order to test the coordination abilities of a potential tridentate ligand we mixed together two equivalents of the tritopic ligand **7** with one equivalent of $Cu(H_2O)_6 \cdot ClO_4$. The instantaneous formation of the complex was followed by observation of a deep-red color. As expected for a copper(II) species in an octahedral environment, the resulting complex is paramagnetic and the FT-IR reveal a 25 $cm^{-1}$ decrease of the C=N stretching vibration, a value typical for a strong interaction with the metal center. $FAB^+$ analysis is in keeping with a two ligand/one copper stoichiometry with intense molecular peaks at 800.2 $[M - ClO_4]^+$, 350.6 $[M - 2\ ClO_4]^{2+}$. A schematic

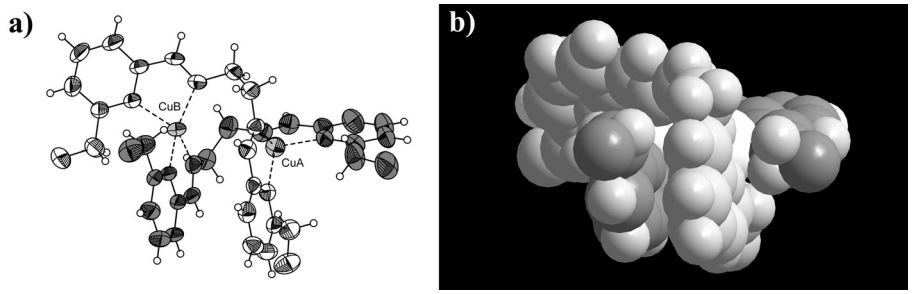



**Figure 4** (a) ORTEP drawing of the $[Cu_2(\mathbf{14})_2]^{2+}$ helicate **19** showing the 30% probability thermal ellipsoids. The hydrogen atoms are drawn as small spheres of arbitrary radii. (b) CPK view of the binuclear complex. The counter anions were deleted for the sake of clarity.

representation of the copper(II) complex is given in Figure 3.

In summary, we have described the preparation of monoformyl/monohydroxymethylpyridine based molecules. Condensation with adequate primary amine or aniline derivatives allows the facile formation of multitopic ligands bearing a controlled number of donor atoms and methylene units in the spacer. When additional ester functions are present on the anilines, the use of *p*-TsOH versus acetic acid is preferred in order to avoid transesterification of the compounds. Some of these ligands formed stable mono- and dinuclear complexes with Cu(I) salts. A copper helicate was characterized by an X-ray diffraction study. The tuning of the complex stoichiometry is feasible by varying the flexibility and length of the bridging carbon chain. This approach has considerable potential benefits in terms of simplifying the covalent synthesis. Some of these new ligands carry suitable acrylate fragments for polymerization reactions, which makes these compounds an attractive and available template for material science. We are currently exploring how to integrate further supramolecular interactions to design even more sophisticated templates based on multiple recognition events in which hydrogen bonding and π-π stacking interactions are privileged.

6,6′-Di(hydroxymethyl)-2,2′-bipyridine, 5,5′-dihydroxymethyl-2,2′-bipyridine, 6,6′-dihydroxymethyl-2,2′:6′,2″-terpyridine, 3,6-di-(6-hydroxymethyl-2-pyridyl)-pyridazine,[32] 4-{[3,4,5-tri(dodecadecyloxy)benzoyloxy]}aniline,[33] 4-{[3,4-di(dodecadecyloxy)-5-(11′-methylacrylatedodecadecyloxy)]benzoyloxy}aniline,[34] $[Cu(CH_3CN)_4](BF_4)$[28] were prepared and purified according to the literature procedure. 2,6-Di(hydroxymethyl)pyridine, *p*-anisidine, ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, and $Cu(ClO_4)_2·6H_2O$ are commercially available.

**Monocarbaldehydes 1–5 (Scheme 1); General Procedure**

In a round-bottomed flask equipped with a condenser, the dihydroxymethyl substrate was dissolved in the given amount of $CHCl_3$ and $MnO_2$ was added as a solid. The mixture vigorously stirred under reflux for several days until most of the starting material was consumed. After cooling to r.t., the suspension was filtered over Celite with a glass frit. The mono-oxidized products were purified by flash chromatography over silica gel using a mixture of solvents, gradient $CH_2Cl_2$–MeOH (0 to 5%) as eluent. In some cases the silica gel support was pre-treated with $Et_3N$. Most of the target molecules were directly obtained pure. In some cases, recrystallization from a mixture of $CH_2Cl_2$ and hexane was required.

**2-Formyl-6-hydroxymethylpyridine (1)**

2,6-Di(hydroxymethyl)pyridine (2.00 g, 14.37 mmol) was oxidized with $MnO_2$ (81.00 g, 0.93 mol) in $CHCl_3$ (200 mL) for 4 days. After purification, a white solid (1.35 g, 70%) was obtained.

FT-IR (KBr): 3437s (OH), 2920s, 2851m, 1619m (C=O), 1384, 1333, 1259, 1113, 1037 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.09 (s, 1 H), 7.89 (d, 2 H, $^3J$ = 4.3 Hz), 7.52 (t, 1 H, $^3J$ = 4.3 Hz), 4.88 (br s, 2 H), 3.59 (br s, 1 H).

$^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 193.0, 160.2, 152.3, 138.2, 125.0, 121.3, 64.2.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 138.2 $[M + H]^+$.

Anal. Calcd for $C_7H_7NO_2$ (137.14): C, 61.31; H, 5.14; N, 10.21. Found: C, 61.17; H, 4.87; N, 10.04.

**6-Formyl-6′-hydroxymethyl-2,2′-bipyridine (2)**

6,6-Di(hydroxymethyl)-2,2′-bipyridine (0.100 g, 0.463 mmol) was oxidized with $MnO_2$ (2.65 g, 30 mmol) in $CHCl_3$ (100 mL) for 3 days. After purification by chromatography (silica gel, pretreated with $Et_3N$), 0.079 g of a white solid (80%) was obtained.

FT-IR (KBr): 3437s (OH), 2923s, 2863m, 1619m (C=O), 1384, 1179, 1083 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.15 (s, 1 H), 8.67 (dd, 1 H, $^3J$ = 7.5 Hz, $^4J$ = 1.8 Hz), 8.50 (d, 1 H, $^3J$ = 7.5 Hz), 8.00 (m, 2 H), 7.88 (t, 1 H, $^3J$ = 7.5 Hz), 7.32 (d, 1 H, $^3J$ = 7.5 Hz), 4.86 (s, 2 H), 3.62 (br s, 1 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 193.6, 158.5, 152.4, 138.0, 137.8, 125.0, 121.5, 121.1, 120.0, 64.0.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 215.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{10}N_2O_2$ (214.22): C, 67.28; H, 4.71; N, 13.08. Found: C, 66.96; H, 4.53; N, 12.78.

**5-Formyl-5′-hydroxymethyl-2,2′-bipyridine (3)**

5,5′-Di(hydroxymethyl)-2,2′-bipyridine (0.300 g, 1.39 mmol) was oxidized with $MnO_2$ (7.95 g, 90 mmol) in $CHCl_3$ (100 mL) for 2 days. After purification by chromatography (silica gel, pretreated with $Et_3N$), 0.160 g of a white solid (54%) was obtained.

FT-IR (KBr): 3437s (OH), 2923s, 2863m, 1619m (C=O), 1384, 1179, 1083 $cm^{-1}$.

$^1H$ NMR (200 MHz,$CDCl_3$, 25 °C) : δ = 10.17 (s, 1 H), 9.12 (d, 1 H, $^4J$ = 2 Hz), 8.71 (d, 1 H, $^4J$ = 2 Hz), 8.61 (d, 1 H, $^3J$ = 8.0 Hz), 8.52 (d, 1 H, $^3J$ = 8.0 Hz), 8.31 (dd, 1 H, $^3J$ = 8.0 Hz, $^4J$ = 2.0 Hz), 7.91 (d, 1 H, $^3J$ = 8.0 Hz), 4.86 (s, 2 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 190.6, 160.4, 154.1, 151.7, 148.2, 137.2, 136.9, 135.8, 122.1, 122.1, 121.3, 62.5.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 215.1 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{10}N_2O_2$ (214.22): C, 67.28; H, 4.71; N, 13.08. Found: C, 67.00; H, 4.62; N, 12.86.

**6-Formyl-6″-hydroxymethyl-2,2′:6′,2″-terpyridine (4)**

6,6′-Dihydroxymethyl-2,2′:6′,2″-terpyridine (0.500 g, 1.70 mmol) was oxidized with $MnO_2$ (9.72 g, 110 mmol) in $CHCl_3$ (100 mL) for 2 days. After purification by chromatography (silica gel, pretreated with $Et_3N$), 0.338 g of a white solid (66%) was obtained.

FT-IR (KBr): 3437s (OH), 2923s, 2863m, 1619m (C=O), 1384, 1179, 1083 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.11 (s, 1 H), 8.65 (d, 1 H, $^3J$ = 8.0 Hz), 8.51 (d, 2 H, $^3J$ = 8.0 Hz), 7.97 (m, 3 H), 7.88 (t, 2 H, $^3J$ = 8.0 Hz), 7.32 (d, 1 H, $^3J$ = 8.0 Hz,), 4.86 (s, 2 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 192.4, 160.7, 158.2, 154.5, 151.7, 150.5, 150.2, 137.9, 136.8, 124.1, 122.9, 121.8, 120.4, 120.2, 119.8, 119.3, 64.3.

FAB$^+$-MS (m-NBA): *m*/*z* = 292.1 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{13}N_3O_2$ (291.30): C, 70.09; H, 4.50; N, 14.42. Found: C, 69.73; H, 4.26; N, 14.19.

**3-(6′-Formylpyridyl)-6-(6′-hydroxymethylpyridyl)pyridazine (5)**

3,6-Di(6-hydroxymethyl-2-pyridyl)pyridazine (0.300 g, 1.02 mmol) was oxidized with $MnO_2$ (7.50 g, 86.27 mmol) in $CHCl_3$ (200 mL) for 3 days. The oxidized monoproduct was purified by chromatography (silica gel, pretreated with $Et_3N$), affording 0.230 mg (77%) of a white solid.

FT-IR (KBr): 3438s (OH), 2923s, 2857m, 1619m (C=O), 1432, 1384, 1149, 1083 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.20 (s, 1 H), 8.81 (m, 4 H), 8.02 (m, 3 H), 7.40 (d, 1 H, $^3J$ = 8.0 Hz), 4.90 (s, 2 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 193.6, 160.4, 146.6, 140.8, 138.4, 138.1, 125.7, 125.5, 121.8, 120.5, 64.2.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 293.2 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{12}N_4O_2$ (292.29): C, 65.75; H, 4.14; N, 19.17. Found: C, 65.46; H, 3.94; N, 18.96.

**Schiff Bases 6–9 (Scheme 2); General Procedure**

In a round-bottomed flask equipped with a condenser, the monocarbaldehyde derivative was dissolved in a minimum volume of EtOH, and a stoichiometric amount of *p*-anisidine was added. After stirring for 5 min at r.t., AcOH (one drop) was added and the mixture was heated overnight at 80 °C. During the cooling process, a voluminous precipitate appeared. After 1 h at –30 °C, the solid was collected by filtration using a glass frit and washed with a minimum amount of cold EtOH and $Et_2O$. In all cases the recovered pale yellow solids were analytically pure.

**2-Hydroxymethyl-6-(4-iminomethoxybenzene)pyridine (6)**

Reaction of 2-hydroxymethyl-6-formylpyridine (0.100 g, 0.729 mmol) with *p*-methoxyaniline (0.0987 g, 0.802 mmol) in EtOH (20 mL) containing AcOH (one drop) afforded 0.177 mg (96%) of **6**.

FT-IR (KBr): 3437s (OH), 2918m, 2850m, 1619m (C=N), 1596s, 1448s, 1384s, 1112s, 791s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.72 (s, 1 H), 7.93 (m, 2 H), 7.56 (t, 1 H, $^3J$ = 4.5 Hz), 7.32 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.96 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 4.89 (s, 2 H), 3.84 (s, 3 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 160.8, 158.6, 154.7, 152.5, 152.3, 138.4, 125.4, 124.7, 120.9, 120.6, 64.3, 55.7.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 243.2 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{14}N_2O_2$ (242.27): C, 69.41; H, 5.82; N, 11.56. Found: C, 69.21; H, 5.64; N, 11.19.

**6-Hydroxymethyl-6′-(4-iminomethoxybenzene)-2,2′-bipyridine (7)**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.100 g, 0.467 mmol) with *p*-methoxyaniline (0.164 g, 0.560 mmol) in EtOH (25 mL) containing AcOH (one drop) afforded 0.112 g (75%) of **7**.

FT-IR (KBr): 3437s (OH), 2918m, 2850m, 1619m (C=N), 1596s, 1448s, 1384s, 1112s, 791s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.73 (s, 1 H), 8.46 (t, 2 H, $^3J$ = 7.5 Hz), 8.25 (d, 1 H, $^3J$ = 7.5 Hz), 7.94 (m, 1 H), 7.89 (m, 1 H), 7.36 (m, 1 H), 7.28 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.97 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 4.87 (s, 2 H), 3.86 (s, 3 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 162.6, 158.4, 158.9, 158.2, 153.4, 145.6, 139.8, 138.9, 126.8, 124.7, 123.5, 123.0, 121.8, 120.5, 64.6, 55.9.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 320.2 $[M + H]^+$.

Anal. Calcd for $C_{19}H_{17}N_3O_2$ (319.37): C, 71.46; H, 5.37; N, 13.16. Found: C, 71.19; H, 5.11; N, 13.00.

**6-Hydroxymethyl-6″-(4-iminomethoxybenzene)-2,2′:6′,2″-terpyridine (8)**

Reaction of 6-hydroxymethyl-6″-formyl-2,2′:6′,2″-terpyridine (0.100 g, 0.332 mmol) with *p*-methoxyaniline (0.117 g, 0.398 mmol) in EtOH (30 mL) containing AcOH (one drop) afforded 0.108 g (82%) of **8**.

FT-IR (KBr): 3437s (OH), 2918m, 2850m, 1619m (C=N), 1596s, 1448s, 1384s, 1112s, 791s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.75 (s, 1 H), 8.68 (d, 1 H, $^3J$ = 8.0 Hz), 8.55 (d, 2 H, $^3J$ = 8.0 Hz), 7.96 (m, 3 H), 7.86 (t, 2 H, $^3J$ = 8.0 Hz), 7.38 (d, 1 H, $^3J$ = 8.0 Hz), 7.34 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.99 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 4.87 (s, 2 H), 3.86 (s, 3 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 162.9, 159.6, 158.6, 158.5, 158.0, 157.7, 155.7, 153.4, 143.6, 139.8, 138.9, 138.6, 126.5, 126.3, 124.5, 124.1, 123.5, 123.0, 121.8, 120.5, 64.4, 55.8.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 397.2 $[M + H]^+$.

Anal. Calcd for $C_{24}H_{20}N_4O_2$ (396.16): C, 72.71; H, 5.08; N, 14.13. Found: C, 72.54; H, 5.00; N, 13.95.

**3-[6-(4-Iminomethoxybenzene)-2-pyridyl]-6-[6-hydroxymethyl-2-pyridyl)]pyridazine (9)**

Reaction of 3-(6′-formylpyridyl)-6-(6′-hydroxymethylpyridyl)pyridazine (0.100 g, 0.342 mmol) with *p*-methoxyaniline (0.120 g, 0.410 mmol) in EtOH (40 mL) containing AcOH (one drop) afforded 0.117 g (86%) of **9**.

FT-IR (KBr): 3438s (OH), 2983m, 2956m, 1619m (C=N), 1503s, 1421s, 1382s, 1265s, 1092s, 896s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.74 (m, 5 H), 8.33 (d, 1 H, $^3J$ = 7.9 Hz), 8.01 (m, 2 H), 7.40 (d, 1 H, $^3J$ = 7.9 Hz), 7.39 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.98 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 4.89 (s, 2 H), 3.86 (s, 3 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 160.1, 158.1, 157.9, 154.8, 153.1, 152.2, 137.9, 137.9, 125.1, 124.9, 122.9, 122.6, 122.3, 121.6, 120.3, 114.5, 64.2, 55.5.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 398.2 $[M + H]^+$.

Anal. Calcd for $C_{23}H_{19}N_5O_2$ (397.44): C, 69.51; H, 4.82; N, 17.62. Found: C, 69.32; H, 4.56; N, 17.41.

**Schiff Bases 10–13 (Figure 2); General Procedure**

In a round-bottomed flask equipped with a condenser, the monocarboxyaldehyde derivative was dissolved in a minimum volume of EtOH, and stoichiometric amount of 4-[3,4,5-tri(dodecadecyloxy)benzoyloxy]aniline or 4-{[3,4-di(dodecadecyloxy)-5-(11′-methylacrylatedodecadecyloxy)]benzoyloxy}aniline was added. After stirring for a few min at r.t., one crystal of *p*-TsOH (ca. 1 mg) was added and the solution was heated overnight at 80 °C. During the heating process a voluminous precipitate appeared. After 1 h at –30 °C, the solid was collected by filtration using a glass frit and washed with a minimum amount of cold EtOH and $Et_2O$. In all cases the recovered pale yellow solids were analytically pure.

**Ligand 10**

Reaction of 2-formyl-6-hydroxymethylpyridine (0.100 g, 0.729 mmol) with 4-[3,4,5-tri(dodecadecyloxy)benzoyloxy]aniline (0.558 mg, 0.729 mmol) in EtOH (30 mL) in the presence of *p*-TsOH (one crystal) afforded 0.542 g (84%) of **10**.

FT-IR (KBr): 3437s (OH), 2918m, 2850m, 1619m (C=N), 1596s, 1448s, 1384s, 1112s, 791s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.64 (s, 1 H), 8.14 (d, 2 H, $^3J$ = 7.5 Hz), 7.84 (t, 1 H, $^3J$ = 7.5 Hz), 7.32 (m, 6 H), 4.85 (s, 2 H), 4.03 (m, 6 H), 1.83 (m, 60 H), 0.84 (m, 9 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 167.2, 163.4, 158.7, 155.9, 152.3, 145.6, 145.4, 140.2, 139.3, 126.4, 124.9, 123.1, 122.9, 121.4, 119.7, 73.2, 72.8, 69.5, 64.6, 31.7, 30.4, 30.0, 29.6, 29.5, 29.3, 29.2, 29.1, 28.5, 26.1, 25.9, 25.6, 25.4, 24.7, 22.6, 18.2, 18.0, 14.0.

$FAB^+$-MS (*m*-NBA): *m*/*z* (%) = 885.2 (100, $[M + H]^+$), 763.2 (30).

Anal. Calcd for $C_{56}H_{88}N_2O_6$ (885.31): C, 75.97; H, 10.02; N, 3.16. Found: C, 75.65; H, 9.81; N, 2.90.

**Ligand 11**

Reaction of 2-hydroxymethyl-6-formylpyridine (0.100 g, 0.729 mmol) with 4-{[3,4-di(dodecadecyloxy)-5-(11′-methylacrylate-dodecadecyloxy)]benzoyloxy}aniline (0.621 g, 0.729 mmol) in EtOH (30 mL) in the presencd of *p*-TsOH (one crystal), afforded 0.360 g (51%) of **11**.

FT-IR (KBr): 3437s (OH), 2918m, 2850m, 1619m (C=N), 1596s, 1448s, 1384s, 1112s, 791s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.65 (s, 1 H), 8.17 (d, 2 H, $^3J$ = 7.5 Hz), 7.90 (t, 1 H, $^3J$ = 7.5 Hz), 7.38 (s, 2 H), 6.97 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.71 (d, AB system, $^3J$ = 7.9 Hz, 2 H), 6.09 (m, 1 H), 5.54 (m, 1 H), 4.85 (s, 2 H), 4.13 (m, 2 H), 4.03 (m, 6 H), 1.93 (s, 3 H), 1.65 (m, 60 H), 0.88 (m, 6 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 167.3, 163.5, 158.7, 155.9, 152.3, 145.6, 145.4, 140.2, 139.3, 126.4, 125.1, 124.3, 122.0, 115.6, 108.5, 73.3, 69.0, 65.3, 64.6, 31.7, 30.7, 30.6, 30.2, 29.6, 29.5, 29.4, 29.3, 29.1, 28.5, 26.0, 25.9, 25.6, 25.5, 24.7, 22.6, 18.2, 18.1, 14.1. $FAB^+$-MS (*m*-NBA): *m*/*z* (%) = 969.1 (100, $[M + H]^+$), 847.2 (20).

Anal. Calcd for $C_{60}H_{92}N_2O_8$ (969.41): C, 74.34; H, 9.57; N, 2.89. Found: C, 74.02; H, 9.34; N, 2.49.

**Ligand 12**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.100 g, 0.467 mmol) with 4-[3,4,5-tri(dodecadecyloxy)benzoyloxy]aniline (0.358 g, 0.467 mmol) in EtOH (25 mL) in the presence of *p*-TsOH (one crystal) afforded 0.396 g (88%) of **12**.

FT-IR (KBr): 3220s (OH), 2904m, (CH), 2844m (CH), 1650m (C=N), 1593s, 1459s, 1027s, 999s, 970s, 789s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.73 (s, 1 H), 8.52 (d, 1 H, $^3J$ = 8.0 Hz), 8.46 (d, 1 H, $^3J$ = 8.0 Hz), 8.27 (d, 1 H, $^3J$ = 8.0 Hz), 7.99 (d, 1 H, $^3J$ = 8.0 Hz), 7.92 (d, 1 H, $^3J$ = 8.0 Hz), 7.85 (d, 1 H, $^3J$ = 8.0 Hz), 7.40 (m, 4 H), 7.29 (d, 2 H, $^3J$ = 8.0 Hz), 4.86 (br s, 2 H), 4.03 (m, 6 H), 3.94 (br s, 1 H), 1.87–1.26 (m, 60 H), 0.87 (m, 9 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 165.5, 161.5, 158.7, 156.0, 154.8, 154.6, 153.4, 150.2, 149.0, 143.5, 138.0, 124.2, 123.0, 122.8, 122.6, 122.0, 121.1, 120.3, 109.0, 73.9, 73.5, 32.3, 30.6, 30.1-29.7, 26.5, 26.4, 23.1.

$FAB^+$-MS (*m*-NBA): *m*/*z* (%) = 962.2 (100, $[M + H]^+$), 763.2 (15).

Anal. Calcd for $C_{61}H_{91}N_3O_6$ (962.39): C, 76.13; H, 9.53; N, 4.37. Found: C, 75.78; H; 9.23; N, 4.03.

**Ligand 13**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.100 g, 0.467 mmol) with 4-{[3,4-di(dodecadecyloxy)-5-(11′-methylacrylatedodecadecyloxy)]benzoyloxy}aniline (0.398 mg, 0.467 mmol) in EtOH (30 mL) in the presence of *p*-TsOH (one crystal) afforded 0.239 mg (51%) of **13**.

FT-IR (KBr): 3220s (OH), 2904m, 2844m, 1650m (C=N), 1593s, 1459s, 1027s, 999s, 970s, 789s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.74 (s, 1 H), 8.54 (d, 1 H, $^3J$ = 8.0 Hz), 8.43 (d, 1 H, $^3J$ = 8.0 Hz), 8.25 (d, 1 H, $^3J$ = 8.0 Hz), 7.93 (d, 1 H, $^3J$ = 8.0 Hz), 7.93 (d, 1 H, $^3J$ = 8.0 Hz), 7.91 (d, 1 H, $^3J$ = 8.0 Hz), 7.80 (m, 4 H), 7.36 (d, 2 H), 6.10 (m, 1 H), 5.54 (m, 1 H), 4.90 (br s, 2 H), 4.15 (m, 2 H), 4.05 (m, 6 H), 3.97 (br s, 1 H), 1.95 (br s, 3 H), 1.90–1.23 (m, 60 H), 0.88 (m, 6 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 166.4, 165.3, 158.7, 156.0, 154.8, 154.6, 153.4, 152.9, 150.2, 144.5, 142.9, 142.7, 136.4, 125.0, 124.2, 122.1, 115.5, 108.4, 73.4, 73.2, 69.1, 65.4, 64.7, 31.8, 30.6, 30.7, 30.2, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.5, 26.0, 25.9, 25.6, 25.4, 24.7, 22.6, 18.2, 18.0, 14.0.

$FAB^+$-MS (*m*-NBA): *m*/*z* (%) = 1046.2 (100, $[M + H]^+$), 847.2 (10).

Anal. Calcd for $C_{65}H_{95}N_3O_8$ (1046.47): C, 74.60; H, 9.15; N, 4.02. Found: C, 74.27; H; 9.01; N, 3.87.

**Schiff Bases 14–18 (Schemes 3 and 4); General Procedure**

In a round-bottomed flask equipped with a condenser, the monocarbaldehyde derivative was dissolved in a minimum volume of EtOH, and half an equivalent of ethylenediamine was added. After stirring for a few min at r.t., AcOH (one drop) was added and the solution was heated overnight at 80 °C. After cooling to r.t., the solvent was removed by rotary evaporation and the crude solid was triturated with a minimum amount of cold EtOH, filtered and washed with $Et_2O$. The resulting yellowish solids were analytically pure.

**Bis(6-hydroxymethyl-2-iminopyridine)ethylenediamine (14)**

Reaction of 2-formyl-6-hydroxymethylpyridine (0.400 g, 2.9 mmol) with ethylenediamine (0.096 g, 1.6 mmol) in EtOH (10 mL) containing AcOH (one drop) afforded 0.376 g (87%) of **14**.

FT-IR (KBr): 3220s (OH), 2904m, 2844m, 1650m (C=N), 1593s, 1459s, 1027s, 999s, 970s, 789s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.41 (s, 2 H), 7.90 (d, 2 H, $^3J$ = 7.7 Hz), 7.74 (dd, 2 H, $^3J$ = 7.7 Hz), 7.28 (d, 2 H, $^3J$ = 7.7 Hz), 4.89 (s, 4 H), 4.07 (s, 4 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 161.9, 158.8, 157.4, 138.8, 123.9, 123.6, 64.5, 54.7.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 299.1 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{18}N_4O_2$ (298.35): C, 64.41; H, 6.08; N, 18.78. Found: C, 64.12; H, 5.86; N, 18.44.

**Bis(6-hydroxymethyl-6′-imino-2,2-bipyridine)ethylenediamine (15)**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.200 g, 0.934 mmol) with ethylenediamine (0.028 g, 0.467 mmol) in EtOH (20 mL) in the presence of AcOH (one drop) afforded 0.385 g (91%) of **15**.

FT-IR (KBr): 3220s (OH), 2904m, 2844m, 1650m (C=N), 1593s, 1459s, 1027s, 999s, 970s, 789s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.52 (s, 2 H), 8.44 (dd, 2 H, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz), 8.36 (d, 2 H, $^3J$ = 7.7 Hz), 8.06 (dd, 2 H, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz), 7.84 (m, 4 H), 7.24 (d, 2 H, $^3J$ = 7.7 Hz), 4.83 (s, 4 H), 4.12 (s, 4 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 161.9, 158.6, 157.4, 156.7, 137.9, 137.8, 123.9, 123.2, 118.9, 118.6, 64.5, 54.7.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 453.2 $[M + H]^+$.

Anal. Calcd for $C_{26}H_{24}N_6O_2$ (452.52): C, 69.01; H, 5.35; N, 18.57. Found: C, 68.75; H, 5.12; N, 18.19.

**Bis(6-hydroxymethyl-6′-imino-2,2′-bipyridine)propylenediamine (16)**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.200 g, 0.934 mmol) with 1,3-diaminopropane (0.035 g, 0.467 mmol) in EtOH (20 mL) containing AcOH (one drop) afforded 0.102 g (70%) of **16**.

FT-IR (KBr): 3222s (OH), 2906m, 2850m, 1652m (C=N), 1595s, 1462s, 1029s, 1000s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.43 (s, 2 H), 7.92 (d, 2 H, $^3J$ = 7.7 Hz), 7.78 (dd, 2 H, $^3J$ = 7.7 Hz), 7.31 (d, 2 H, $^3J$ = 7.7 Hz), 4.92 (s, 4 H), 3.97 (t, $^3J$ = 6.9 Hz, 4 H), 2.79 (m, 2 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 162.3, 158.6, 157.5, 138.9, 124.0, 123.8, 64.7, 54.7, 36.0.

$FAB^+$-MS (*m*-NBA): *m*/*z* = 313.1 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{20}N_4O_2$ (312.37): C, 65.37; H, 6.45; N, 17.94. Found: C, 65.20; H, 6.26; N, 17.74.

**Bis(6-hydroxymethyl-6′-imino-2,2′-bipyridine)butylenediamine (17)**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.200 g, 0.934 mmol) with 1,4-diaminobutane (0.041 g, 0.467 mmol) in EtOH (20 mL) containing AcOH (one drop) afforded 0.096 g (63%) of **17**.

FT-IR (KBr): 3218s (OH), 2907m, 2840s, 1652m (C=N), 1595m, 1462s, 1029s, 1002s $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.44 (s, 2 H), 7.92 (d, 2 H, $^3J$ = 7.8 Hz), 7.75 (dd, 2 H, $^3J$ = 7.8 Hz), 7.32 (d, 2 H, $^3J$ = 7.8 Hz), 4.93 (s, 4 H), 3.99 (t, $^3J$ = 6.8 Hz, 4 H), 2.81 (m, 4 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 161.6, 158.9, 157.6, 138.7, 123.7, 123.9, 64.7, 54.6, 29.7.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 327.1 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{22}N_4O_2$ (326.39): C, 66.24; H, 6.79; N, 17.17. Found: C, 66.03; H, 6.53; N, 17.00.

**Bis(6-hydroxymethyl-6′-imino-2,2′-bipyridine)pentylenediamine (18)**

Reaction of 6-hydroxymethyl-6′-formyl-2,2′-bipyridine (0.200 g, 0.934 mmol) with 1,5-diaminopentane (0.048 g, 0.467 mmol) in EtOH (20 mL) containing AcOH (one drop) afforded 0.079 g (50%) **18**.

FT-IR (KBr): 3225s (OH), 2906m, 2848m, 1654m (C=N), 1599m, 1464m, 1024s, 1004m $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.40 (s, 2 H), 7.93 (d, 2 H, $^3J$ = 7.7 Hz), 7.74 (dd, 2 H, $^3J$ = 7.7 Hz), 7.29 (d, 2 H, H, $^3J$ = 7.7 Hz), 4.90 (s, 4 H), 4.02 (t, $^3J$ = 6.8 Hz, 4 H), 2.74 (m, 6 H).

$^{13}C$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 161.7, 158.9, 157.3, 138.9, 124.2, 123.7, 64.7, 54.8, 32.8, 27.3.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 341.1 $[M + H]^+$.

Anal. Calcd for $C_{19}H_{24}N_4O_2$ (340.42): C, 67.04; H, 7.11; N, 16.46. Found: C, 66.87; H, 6.96; N, 16.33.

**Dinuclear Copper(I) Complex 19**

Ligand **14** (0.100 g, 0.335 mol) was dissolved in argon-degassed $CH_2Cl_2$ (15 mL) and added dropwise to a solution of $[Cu(CH_3CN)_4](BF_4)$ (0.106 g, 0.338 mol) in MeCN (10 mL). Immediately after mixing at r.t., a deep-red solution formed that is characteristic of a fast complexation process. After complete addition, the solution was stirred for 1 h and $Et_2O$ was allowed to slowly diffuse through the solution. The deep-red mono-crystals were collected and dried under high vacuum; yield: 89%.

FT-IR (KBr): 3445s (OH), 2906m, 2855m, 1629m (C=N), 1593s, 1463s, 1084s, 999s, 973s $cm^{-1}$.

$^1H$ NMR (200 MHz, acetone-$d_6$, 25 °C): δ = 8.82 (s, 2 H), 8.13 (dd, 2 H, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz), 7.90 (d, 2 H, $^3J$ = 7.7 Hz), 7.59 (d, 2 H, $^3J$ = 7.7 Hz), 4.71 (s, 4 H), 4.45 (d, AB system, *J* = 15.3 Hz, 2 H), 4.17 (d, AB system, *J* = 15.3 Hz, 2 H).

FAB$^+$-MS (*m*-NBA): *m*/*z* (%) = 809.2 $[M - BF_4]^+$, 361.1 $[M - 2BF_4]^{2+}$.

Anal. Calcd for $C_{32}H_{36}B_2Cu_2F_8N_8O_4$ (897.38): C, 42.83; H, 4.04; N, 12.49. Found: C, 42.54; H, 3.89; N, 12.14.

**Mononuclear Copper(I) Complex 20**

Ligand **17** (0.100 g, 0.306 mol) was dissolved in argon degassed $CH_2Cl_2$ (15 mL) and added dropwise to a solution of $[Cu(CH_3CN)_4](BF_4)$ (0.048 g, 0.153 mol) in MeCN (10 mL). Immediately after mixing at r.t., a deep-red solution was formed characteristic of a fast complexation process. After complete addition, the solution was stirred for 1 h and $Et_2O$ was allowed to slowly diffuse through the solution. The precipitate was collected and dried under high vacuum; yield: 68%.

FT-IR (KBr): 3445s (OH), 2906m, 2855m, 1629m (C=N), 1593s, 1463s, 1084s, 999s, 973s $cm^{-1}$.

$^1H$ NMR (200 MHz, acetone-$d_6$, 25 °C): δ = 8.86 (s, 2 H), 8.21 (d, 2 H, $^3J$ = 7.7 Hz), 8.00 (dd, 2 H, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz), 7.72 (d, 2 H, $^3J$ = 7.7 Hz), 4.75 (s, 4 H), 4.49 (m, 2 H), 4.21 (m, 2 H), 3.03 (m, 4 H).

FAB$^+$-MS (*m*-NBA) *m*/*z* = 389.2 $[M - BF_4]^+$.

Anal. Calcd for $C_{18}H_{22}BCuF_4N_4O_2 \cdot MeCN$ (476.74 + 41.05): C, 46.39; H, 4.87; N, 13.53. Found: C, 46.21; H, 4.65; N, 13.34.

**Mononuclear Copper(II) Complex 21**

An MeCN solution (10 mL) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (0.056 g, 0.144 mmol) was added dropwise to a $CH_2Cl_2$ solution (5 mL) containing ligand **7** (0.092 g, 0.288 mmol). After 2 h, $Et_2O$ was layered over the previous solution and after a few days the solid formed was collected by filtration over a glass frit affording complex **21**; yield: 78% (0.101 g).

FT-IR (KBr): 3398s (OH), 2974m, 2857m, 1598m (C=N), 1505s, 1466s, 1434s, 1252s, 1085s, 999s, 975s $cm^{-1}$.

FAB$^+$-MS (*m*-NBA): *m*/*z* = 800.2 $[M - ClO_4]^+$, 350.6 $[M - 2 ClO_4]^{2+}$.

Anal. Calcd for $C_{38}H_{34}Cl_2CuN_6O_8$ (901.18): C, 50.65; H, 3.80; N, 9.33. Found: C, 50.57; H, 3.55; N, 9.00.

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