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Linear Bilateral Extended 2,2′:6′,2″-Terpyridine Ligands, Their Coordination Complexes and Heterometallic Supramolecular Networks

Janis Veliks, Jui-Chang Tseng, Karla I. Arias, Florian Weisshar, Anthony Linden and Jay S. Siegel*

Octahedral metal complexes of tridentate 2,2′:6′,2″-terpyridine (terpy) fused with five-membered furan rings mimic the topology of tetrahedral metal complexes of bidentate 5,5′-functionalized 2,2′-bipyridine (bipy). Herein, we report the robust synthesis of 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-yl)pyridine based ligands to access series of linear bilateral extended terpy derivatives. This molecular design of alternating five- and six-membered rings has been applied to extend the applicability of terpy as a building block in supramolecular chemistry. The complexation of 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-yl)pyridine derivatives with metal ions preferring octahedral geometry (Fe²⁺, Ru²⁺, and Zn²⁺) gives molecular “crossings” and “corners”. Such design elements, functionalized with 4-aryl groups, allowed the construction of 3D and 2D heterometallic supramolecular networks containing Fe²⁺, Ag⁺ or Fe²⁺, Cu⁺ metal centers.

Introduction

De novo design and synthesis of functional supramolecular architectures benefit from ready access to components with well-defined assembly geometries. A mainstay component of supramolecular and materials chemistry, 2,2′:6′,2″-terpyridine (terpy) ligands form coordination complexes with various metals and have photophysical and electrochemical properties suitable for supramolecular chemistry, nanotechnology, solar cells, catalysis, and antibacterial research. A vast range of accessible terpy derivatives incorporate into geometrically well-defined supramolecular assemblies. Examples include the synthesis of Borromean link precursors, metal-organic dendrimers, and molecular grids.

Bifunctional molecular strings of terpy and bipy structural units, used in rotaxane-based molecular machines, switches and muscles, and multi-component assemblies, such as coordination polymers, and metal-organic frameworks (MOFs), reveal system properties dependent on the geometry building blocks and motivate the synthesis of ligands with new geometries. Specifically, this study addresses the synthesis and characterization of linear bilateral extended terpyridines (Fig. 1) mimicking the linear geometry of 5,5′-functionalized 2,2′-bipyridine (bipy in which sites for skeletal substitution are perpendicular to the metal coordination vector). Such ligands would allow the introduction of terpy into “linear molecular assemblies – a complement to the "stub", "W", "V or Λ", and "C" motifs stemming from substituents at positions 4′, 4/4″, 5/5″, and 6/6″ with angles relative to the coordination vector of 180°, 120°, 60°, and 0°, respectively (Fig. 1A).

Fusion of a five-membered ring to the six-membered flanking rings of terpy specifically addresses the linear bilateral geometry mentioned above (Fig. 1B), and focuses this work on the practical and versatile synthesis of 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-yl)pyridines (Fig. 2). Complexation of these ligands with octahedrally coordinating metal ions gives access to molecular “crossings” and “corners” suitable to the design of heterometallic supramolecular networks.
Results and discussion

Retrosynthetic analysis of linear terpyridine 1 leads to the opening of fused five-membered rings at a heteroatom Y, giving a disubstituted ethynyl derivative 2, which could be prepared by Sonogashira coupling20 between dihalide 3 and acetylene 4 (Scheme 1). Terpyridine 5 stems from 6 with ortho-directing groups at the 5- and 5′-positions to enable ortho-lithiation,21 and subsequent addition of a halide electrophile would lead to compound 7. For Y = O, 6 is 5,5′-hydroxy-2,2′:6′,2′′-terpyridine and the target ligands are 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-y]pyridines.

Scheme 1 Retrosynthesis of Linear Terpyridine 1.

Synthesis of acetylenes

The pursuit of 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-y]pyridine-based ligands motivated the development of an efficient chromatography-free synthesis (Scheme 2) of the key intermediate 4,4′-diido-5,5′-bis(methoxy-methoxy)-2,2′:6′,2′′-terpyridine (14). The route to 14 follows a Stille22 cross-coupling strategy via 8 and 10. Regioselective lithiation23 of commercially available 2,5-dibromopyridine (7) with n-butyllithium and subsequent addition of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave 5-borylated pyridine 824 in good yield.

Synthesis of the terpy core

The precursor of the central ring, 2,6bis(trimethylstannyl)pyridine (10), was synthesized by nucleophilic stannylation of 2,6-dichloropyridine (9) with freshly prepared NaSnMe3 in good yield.25 26 Terpy 11 was prepared by Stille coupling between bromide 8 and bistannane 10 according to the procedure reported by Schlüter.24 Oxidation/hydroxydeboronation27 of 11 resulted in 5,5′-dihydroxyterpyridine 12 in excellent yield.28 These reactions were performed routinely on a 40 g to 90 g scale and have the potential for further scale-up. Subsequent deprotonation of hydroxy groups with NaH and treatment with MOMCl (prepared in situ)29 afforded terpy 13, with ortho-directing groups at the 5,5′-positions. Regioselective ortho-lithiation30 with n-BuLi in the presence of TMEDA and subsequent quenching with iodine gave the desired diido-terpy 14. During iodine addition, a thick precipitate formed complicating both stirring and appropriate cooling. Therefore, an optimal yield was obtained when the reaction was run on a 1–3 g scale per batch. Straightforward trituration of crude product with hot ethanol afforded pure 14.

Synthesis of terpy ligands

The modular synthesis of linear bilateral terpy ligands requires functionalized acetylenes to incorporate desired moieties in the flanking positions. The introduction of manisyl groups31 improves the solubility of polypyridine ligands and facilitates later homologation; therefore, several acetylenes containing this group were prepared. The synthesis of 2-ethynyl-5-methoxy-1,3-dimethylbenzene 1832 was accomplished according to Scheme 3. The bromide 1533 was converted to the iodide 16 by lithiation and subsequent quenching with iodine. Under optimized conditions for Sonogashira coupling, 16 reacted smoothly with trimethylsilylacetylene to produce silyl-protected acetylene 17. Deprotection with KF in methanol gave 18 in high yield (Scheme 3).
positions, Sonogashira coupling was performed with 1.05 equivalents of acetylene (Table 1, entries 7-9), giving 23.

Scheme 3 Synthesis of acetylene 18.

The focus.

26a

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Manisyl substituted 5-ethynylbipyridines 22a and 22b were synthesized from known bromopyridines 19a and 19b (Scheme 4). Negishi coupling with 2,5-dibromopyridine (7) afforded bromopyridines 20a and 20b, which coupled well with trimethylsilylacetylene to give 21a and 21b. Subsequent deprotection with KF formed ethynylbipyridines 22a and 22b in good yields over 2 steps.

Ligand Synthesis

Simple symmetric ligand precursors—bisethynyl-terpyridines 23a, 23b, and 23c, as well as a mixed variation with bipyridine 23f, were prepared by Sonogashira coupling with an excess amount (>2 eq) of corresponding alkynes in good to high yields (Table 1, entries 1, 2, 5, and 6). Due to the instability of 4-ethynlypyridine, 24d was prepared in a stepwise fashion. First, bisethynyl-terpyridines 23a, 23b, and 23c, were synthesized in two steps by Sonogashira coupling between 14 and trimethylsilylacetylene following one-pot deprotection of silyl groups in the presence of KF (Table 1, entry 3). A subsequent coupling reaction with 4-isodopyridine (25) under standard conditions (Table 1, entry 4) gave 23d in good yield.

To incorporate two different substituents into the 4- and 4’-positions, Sonogashira coupling was performed with 1.05 equivalents of acetylene (Table 1, entries 7-9), giving a statistical mixture of mono- and bis-coupled products 24a-c and 23f-h, respectively, as well as unreacted diiodoterpyridine 14. These mixtures were easily separated by column chromatography, and pure monosubstituted intermediates 24a-c were obtained. The non-symmetric terpyridine/bipyridine conjugates 24a and 24b were further subjected to coupling with manisyl acetylene 18 to give products 26a and 26b in good yields (Scheme 5).

With the library of 4,4’-disubstituted terpyridines 23a-h, 26a and 26b in hand, developing general cyclization conditions to access the 2-substituted-furo[2,3-c]pyridine motif became the focus.

Scheme 4 Synthesis of 5-ethynyl-2,2’-bipyridines 22.

Manisyl substituted 5-ethynylbipyridines 22a and 22b were synthesized from known bromopyridines 19a and 19b (Scheme 4). Negishi coupling with 2,5-dibromopyridine (7) afforded bromopyridines 20a and 20b, which coupled well with trimethylsilylacetylene to give 21a and 21b. Subsequent deprotection with KF formed ethynylbipyridines 22a and 22b in good yields over 2 steps.

Manisyl substituted 5-ethynylbipyridines 22a and 22b were synthesized from known bromopyridines 19a and 19b (Scheme 4). Negishi coupling with 2,5-dibromopyridine (7) afforded bromopyridines 20a and 20b, which coupled well with trimethylsilylacetylene to give 21a and 21b. Subsequent deprotection with KF formed ethynylbipyridines 22a and 22b in good yields over 2 steps.

Table 1 Synthesis of 23 and 24 by Sonogashira coupling

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<td></td>
<td>2.5</td>
<td>20</td>
<td>23b 92</td>
</tr>
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<td></td>
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<td>4.5°18°</td>
<td>23c 86</td>
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<td>23f 90</td>
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<td>15</td>
<td>24a 40</td>
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Recovery 14.

In order to obtain ligand L4, conditions for acidic deprotection of the MOM group7, followed by base-assisted cycloisomerization were tested on the mixed terpyridine/bipyridine 26a. Various reaction conditions, like varying the acid, base, solvent, and reaction time, were tried (Table 2, entries 1-5). The use of HCl, CeCl3, and DMF resulted in the isolation of L4 in high yield (Table 2, entry 5). These conditions also led to the isolation of L1-L3, L5, and L6 (Table 2, entries 6-10) in good to high yields.
Metal complexes

A linear bilateral extended conformation of ligands can be acquired by formation of complexes with a 2:1 ligand-to-metal ratio (2:1 complexes). Initially, complexation of simple symmetric ligands $L_{1-3}$ was tested with divalent octahedral metals ($Ru^{2+}$, $Zn^{2+}$, and $Fe^{2+}$) to form molecular “crossings” (Scheme 3). Ruthenium(II) complexes $[L_{1-3}, Ru](PF_6)_2$ were prepared by heating the corresponding ligands with RuCl$_2$(DMSO)$_4$ in ethylene glycol at 120 °C,$^5$ resulting in high product yields (Table 3, entries 1, 4, and 7). Simple phenyl-substituted ligand $L_1$ and $n$-hexyl-substituted ligand $L_2$ formed 2:1 zinc(II) complexes with zinc(II) triflate in a mixture of tetrahydrofuran and methanol at room temperature (Table 3, entries 2 and 5). As 4-pyridyl-substituted ligand $L_3$ is less soluble, heating at 50 °C was necessary to facilitate formation, as shown in Table 3, entry 8. Similarly, $Fe^{2+}$-complexes were prepared by reacting iron(II) tetrafluoroborate with the corresponding ligand in a mixture of tetrahydrofuran and water at room temperature (Table 3, entries 3 and 6), but, in the case of $L_3$, addition of acetonitrile to the reaction mixture was necessary to improve solubility and yield (Table 3, entry 9). All resulting metal complexes were precipitated with aqueous KPF$_6$ and were obtained in good to high yield.

Analogous to simple ligands $L_{1-3}$, mixed terpyridine/bipyridine ligands $L_{4-6}$ reacted with Zn(OTf)$_2$ and Fe(BF$_4$)$_2$:6H$_2$O selectively at the terpyridine coordination site (Table 4), forming either “corner” complexes with $L_4$ and $L_5$, or “crossing” complexes with $L_6$, leaving the bipyridine coordination site unreacted. This selectivity can be explained by the kinetic lability of Zn(II) and Fe(II) complexes and the thermodynamic stability of the highest order chelate. In contrast, the kinetically inert character of Ru(II) led to a complicated mixture of oligomers when $L_{4-6}$ were used (Table 4, entries 3, 6, and 9). Isolation of the desired 2:1 complexes was not successful. Therefore, an alternative approach towards ruthenium(II) complexes was considered for the mixed ligand systems $L_{4-6}$. By first introducing ruthenium(II) and then functionalizing the obtained complex with bipyridine moieties, the desired “corner” and “crossing” complexes were obtained (Scheme 6 and 7). Diiodoterpyridine $L_{48L_6}$ was subjected to complexation with 0.5 equivalents of RuCl$_2$(DMSO)$_4$ by heating in ethylene glycol (Scheme 6).

Unexpectedly, during the reaction, the MOM protecting groups were cleaved, leading to the formation of compound 27. This finding obviated harsh acidic conditions$^3$ for MOM-deprotection.

Crude complex 27 was used in the next step, where Sonogashira cross-coupling$^{22b}$ with acetylene $22a$ in situ ring closure$^{22a}$ afforded compound $[L_6Ru](PF_6)_2$ directly, thus, leading to the desired complexes in just two steps starting from 14 with a 48% overall yield.

The corresponding non-symmetric Ru(II) complexes $[L_{4}Ru](PF_6)_2$ and $[L_{5}Ru](PF_6)_2$ were prepared similarly (Scheme 7). Complexation of manisyl-substituted iodoterpyridine $24c$ with 0.5 eq of Ru(DMSO)$_2$Cl$_2$ in EtOH in one step gave complexed, deprotected, and partially cyclized product 28, which was used without further purification in the subsequent reaction. The Sonogashira coupling with ethynylbipyridine $22a$ or $22b$ and one-pot cyclization gave the desired complexes with 43% or 40% isolated yields over two steps, respectively.

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**Table 2** One-pot MOM-deprotection/cycloisomerisation of 23 and 26

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<th>solvent</th>
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<td>NaOMe</td>
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<td>40</td>
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<td>Cs$_2$CO$_3$</td>
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<td>Cs$_2$CO$_3$</td>
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<td>72</td>
<td>1.6 73</td>
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$^a$ 32% aq. HCl was added to the starting material (SM) in the indicated solvent and heated to 80 °C until the deprotection of MOM was complete (followed by LC-MS). Then the base was added, and the reaction mixture was heated to 90 °C for the corresponding time, unless otherwise stated. $^b$ Heated to reflux. $^c$ 5.4 M NaOMe in MeOH.
Table 3 Synthesis of metal complexes with simple symmetric ligands L1-L3

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<tr>
<th>entry</th>
<th>ligand</th>
<th>R'=R''=</th>
<th>metal source</th>
<th>solvent</th>
<th>time (h)</th>
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* A solution of metal source (0.5 eq) was added to a solution of L1-L3 (1.0 eq) and stirred at the indicated temperature. After the stated reaction time, sat. aq. KPF₆ was added to induce precipitation and the solid was collected by filtration.

Table 4 Synthesis of metal complexes with mixed terpyridine/bipyridine ligands L4-L6

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<tr>
<th>entry</th>
<th>ligand</th>
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</tbody>
</table>

* A solution of metal source was added to a solution of L4-L6 and stirred at the indicated temperature. After the stated reaction time, sat. aq. KPF₆ was added to induce precipitation and the solid was collected by filtration. * A complicated mixture, product could not be isolated.
The \(^1\)H NMR spectra of \([L_4Zn](PF_6)_2\) and \([L_4Fe](PF_6)_2\) (Figure 3, spectra b and c) parallel that of \([L_4Ru](PF_6)_2\) (spectrum d). Given that \([L_4Ru](PF_6)_2\) is synthesized by grafting bipy units on to the preformed terpy ruthenium(II) complex \(28\), it seems reasonable to conclude that Fe(II) and Zn(II) also bind at the terpy unit of \(L_4\). Terpyridine transition metal complexes exhibit characteristic strong upfield shifts of the proton \(o\) and \(j\) signals (d-\(\pi^*\) back-donation) and downfield shift for the signal of proton \(l\) (deshielding due to the conformational change of terpyridine) compared to the shifts observed for the free ligand (Figure 3, spectrum a). The proton signals corresponding to the bipyridine moiety are less affected. These observations hold true for all Zn\(^{2+}\), Fe\(^{3+}\), and Ru\(^{2+}\) complexes in the ligand series \(L_4-L_6\).

Structure

Single crystals of the free ligands \(L_1\) and \(L_4\) suitable for X-ray crystallography were obtained by diethyl ether vapor diffusion into a saturated dichloromethane solution. In Figure 4, the molecular structures clearly show the presence of furo[2,3-c]pyridine-5-yl motifs linked by the central 2,6-substituted pyridine ring, thus forming the desired ligand architecture. The usual conformation of uncoordinated terpyridine has a “\(\Lambda\) shaped” structure with the flanking substituents placed almost perpendicular to each other, as seen for \(L_1\) (Fig. 4a). One arm of the mixed ligand \(L_4\) consists of furo[2,3-c]pyridine-5-yl, bipyridine and manisyl groups in a linear disposition and the second arm is the 2-manisyl-furo[2,3-c]pyridine-5-yl unit (Fig. 4b). The manisyl rings in \(L_4\) adopt a clinal conformation to the mean plane of the ligand, in contrast to the periplanar conformation of the simple phenyl substituents of \(L_1\). This deviation from planarity seen in the crystal structure of \(L_4\), correlates with the much better solubility of the manisyl substituted ligands \(L_4-L_6\) in common organic solvents.

The complexation of linear terpy ligands with metal ions preferring octahedral geometry transforms the overall ligand conformation from “\(\Lambda\) shaped” to a “linear bilateral” one, as illustrated by the molecular structures of the Fe\(^{2+}\), Ru\(^{2+}\), and Zn\(^{2+}\) complexes with \(L_1\) depicted in Fig. 5. Crystals for complexes \([L_1Zn](PF_6)_2\), \([L_1Ru](PF_6)_2\), and \([L_1Fe](PF_6)_2\) were obtained by diffusion of diethyl ether vapor into the corresponding acetonitrile solutions.

These crystal structures possess triclinic symmetry and belong to space group \(P\bar{1}\). In each case, the asymmetric unit consists of one cation, two PF\(_6^–\) anions, and a cavity situated about a center of inversion containing disordered solvent molecules. The three structures are essentially isomorphous except that the contents of the solvent cavities may differ (for the treatment and estimation of the solvent content, see the deposited CIF files in the ESI†).
Fig. 5 The switching of L1 conformation from "Λ-shaped" to the "linear bilateral" and the structures of the cations of a) [L1₂Zn](PF₆)₂·Et₂O·6MeCN; b) [L1₂Ru](PF₆)₂·2Et₂O·3MeCN; c) [L1₂Fe](PF₆)₂·2Et₂O·MeCN (hydrogen atoms, PF₆⁻ and solvent molecules removed for clarity, displacement ellipsoids drawn at the 50% probability level).

Table 5 Selected bite angles and bond lengths of L₁ metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>C(2)-N(2)-C(2) (°)</th>
<th>N(2)-M-C(2) (°)</th>
<th>M-N(1) (Å)</th>
<th>M-N(2) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PF%E2%82%86">L1₂Fe</a>₂</td>
<td>142.1(3)</td>
<td>92.8(1)</td>
<td>1.971(3)</td>
<td>1.882(3)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">L1₂Ru</a>₂</td>
<td>146.2(4)</td>
<td>89.9(2)</td>
<td>2.061(5)</td>
<td>1.983(4)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">L1₂Zn</a>₂</td>
<td>150.1(2)</td>
<td>87.13(6)</td>
<td>2.183(2)</td>
<td>2.080(2)</td>
</tr>
</tbody>
</table>

* Average of two such parameters in the molecule.  
* Average of four such parameters in the molecule.

Photophysical properties

The UV/Vis spectra of the free ligands L₁-L₆ display absorption maxima in a range of 239 to 338 nm (Fig. 6A; see ESI† Table S1). These absorptions can be attributed to π-π* transitions. The ligands L₁-L₆ are fluorescent with emission maxima from 338 to 426 nm and quantum yields ranging from 0.14 to 0.62.

The absorption spectra of all zinc(II), iron(II), and ruthenium(II) complexes with L₁-L₆ (Fig. 6B; see ESI† Table S2, Fig. S16, and S17) display pronounced ligand-centered (LC) transitions. However, the complexes with iron(II) and ruthenium(II) also show characteristic lower energy bands from 360 to 600 nm which can be attributed to MLCT transitions. The zinc(II) complexes exhibit a fluorescence comparable to that of the parent ligands with quantum yields ranging from 0.10 to 0.63.

The MLCT bands of the iron(II) and ruthenium(II) complexes with L₁-L₆ are non-luminescent at room temperature. However, excitation at the LC bands shows weak but detectable fluorescence.
The free ligands and their zinc(II) complexes exhibit solid-state emission with moderate to medium quantum yields (ESI† Tables S1 and S2). A more detailed description about the solution and solid-state photophysical properties of the bilateral extended terpy ligands L1-L6 and their corresponding Zn(II), Fe(II), and Ru(II) complexes can be found in the Supporting Information (Table S1, S2 and Fig. S15, S16, and S17).

Heterometallic supramolecular networks

A solution of AgPF₆ in ethanol was layered over a solution of the 4-pyridyl substituted [L₃Fe(PF₆)₂] complex in acetonitrile. A small amount of cyclohexane between the layers was used to slow down the diffusion process. In a few days fine needle-like crystals formed which over two weeks transformed into dark purple blocks that were separated by filtration to give coordination polymer [L₃FeAg]ₙ(PF₆)₃n·6.5nMeCN (further referred to as L₃FeAg) (Scheme 8).

![Scheme 8 Synthesis of 3D L₃FeAg and 2D L₃FeCu heterometallic supramolecular networks.](image)

Similarly, a [Cu(CH₃CN)₄]PF₆ solution was slowly diffused into the acetonitrile solution of [L₃Fe(PF₆)₂] using a small amount of cyclohexane between the layers. Dark purple block-like crystals were obtained over three weeks, and the resulting product [L₃FeCu(MeCN)]ₙ(PF₆)₃n·4.5nMeCN (further referred to as L₃FeCu) was separated by filtration (Scheme 8).

The X-ray crystal structures of complexes L₃FeAg and L₃FeCu revealed that they are coordination polymers. The asymmetric unit of L₃FeAg contains two repeats of the chemically unique portion of the polymeric cation (Fig. 7), six disordered PF₆⁻ ions and a cavity situated about a center of inversion containing disordered solvent molecules. The cationic structure is a three-dimensional doubly interpenetrating coordination framework with (6,4) diamondoid net (dia-b) topology. The nodes of this framework are tetrahedral silver(I) centers (Fig. 8, light blue balls) and octahedral iron(II) centers (magenta balls), where the four arms of the molecular “crossing” act as linkers. The inversion related network is interpenetrated in a manner characteristic of diamondoid type networks.

![Fig. 8 The diamondoid net (dia-b) topology of L₃FeAg and interpenetration.](image)

The structure of the iron(II) based molecular “crossings” reveal that the furo[2,3-c]pyridine arms of the ligand are significantly tilted; therefore, the angle between the N atoms of both flanking 4-pyridyl groups and the N atom of the central ring of terpy, N(4)-N(2)-N(5), is 134.43(5)°. The shortest Ag(1)···Ag(2) and Fe(1)···Fe(2) distances within a single net are 16.9095(6) and 16.7399(8) Å, respectively. This causes significant voids and channels within the structure. Each unit cell contains one solvent-filled centrosymmetric cavity which comprises 31.5% of the total volume (calculated using PLATON).

The X-ray crystal structure of L₃FeCu shows that Fe(II) based molecular “crossings” in the presence of Cu(I) assemble into a structure similar to that of L₃FeAg. However, one coordination site of the tetrahedral Cu(I) center is occupied by acetonitrile (Fig. 9). Consequently, one of four 4-pyridyl...
groups, which is disordered, is not coordinated to the copper atom and the cationic structure of \( \text{L3FeCu} \) consists of stacked 2D polymeric layers with a (6,3) honeycomb \(^{41}\) net topology (Fig. 10). Adjacent layers are related by inversion symmetry. The nodes of this framework are tetrahedral copper(I) centers (Fig. 10, dark red balls) and octahedral iron(II) centers (magenta balls), where only three arms of the molecular “crossing” act as linkers.

The shortest Fe(1)···Fe(1) and Cu(1)···Cu(1) distances within each net are 16.7466(6) and 18.3235(6) Å, respectively. The angle between the N atoms of flanking 4wpyridyl groups at the N atom of the central ring of terpy, N(10)-N(7)-N(9), is 135.23(5)°.

While the \( \text{L3FeAg} \) and \( \text{L3FeCu} \) structures are similar (Fig. 11), the 3D topology in \( \text{L3FeAg} \) is reduced to a 2D layer network by replacing a pyridine connection to silver with a competing MeCN ligand in \( \text{L3FeCu} \). Interestingly, in \( \text{L3FeAg} \), the Ag–N(pyridyl) bond lengths at each unique Ag(I) cation are grouped into two pairs of distinctly different distances, one with an average distance of 2.25 Å and the other pair at 2.41 Å.

The \(^{1}H\) and \(^{13}C\) NMR spectra of vacuum dried and dissolved crystals of \( \text{L3FeAg} \) and \( \text{L3FeCu} \) in acetonitrile-\( d_{3} \) are almost identical to that of \( [\text{L3Fe(PF}_6]_2 \), suggesting that the solid state structure disassociates in solution. The proton signals of the 4-pyridyl groups are slightly shifted due to the presence of Ag\(^{+}\) or Cu\(^{2+}\) ions.

Fig. 11 Schematic representation of the 3D cationic structure of \( \text{L3FeAg} \) and 2D layered cationic structure of \( \text{L3FeCu} \).

Conclusions

The concept of a linear bilateral extended terpyridine was developed by fusing five-membered rings to the flanking pyridine rings of the terpy ligand, thus mimicking the extended geometry of 5,5′-functionalized 2,2′-bipyridine. It was realized synthetically by developing a modular synthesis of 2,6-bis(2-substituted-furo[2,3-c]pyridine-5-yl)pyridine based ligands. This modular synthesis allowed for the introduction of alkyl, aryl, and heteroaryl functionalities in the flanking positions of these ligands. The molecular “crossings” were synthesized by coordinating simple symmetric ligands to divalent metal cations (Fe\(^{2+}\), Ru\(^{2+}\) and Zn\(^{2+}\)) forming 2:1 complexes. In the case of mixed bipyridine/terpyridine ligands, zinc(II) and iron(II) selectively form complexes at the terpyridine coordination site. The corresponding ruthenium(II) complexes were prepared through an indirect methodology. First, unfunctionalized ruthenium(II) terpyridine 2:1 complexes were prepared, then bipyridyl groups were introduced through a one-pot Sonogashira coupling with an in situ furan ring formation. In this way, the terpy and bipy moieties arrange themselves in a linear rod motif. These complexes resemble molecular “crossings” and “corners”, depending on whether symmetric or non-symmetric starting materials were used in the reaction. The X-ray crystal structures of symmetric phenyl substituted analogues showed that a proper “linear bilateral” conformation of terpy ligands is acquired by complexation with metal ions, so that flanking substituents are spanned relative to each other with an obtuse angle. This angle increases in the sequence of Fe\(^{2+}\)~Ru\(^{2+}\)~Zn\(^{2+}\). The free ligands show high to medium fluorescence quantum yields that are significantly quenched by complexation with Fe\(^{2+}\) and Ru\(^{2+}\) ions. The zinc(II) complexes still retain a fluorescence efficiency similar to that of their parent ligands. The free ligands and their zinc(II) complexes exhibit solid-state emission with moderate to medium quantum yields, so could find an application as optoelectronic materials. This molecular design has potential in supramolecular chemistry giving new topological features to terpyridine, which now mimics the linear geometry of 5,5′-disubstituted 2,2′-bipyridine. It has been shown that linear bilateral extended terpy based Fe(II) “crossings” functionalized with 4-pyridyl groups at the flanking positions are able to assemble into 3D and 2D heterometallic supramolecular networks by using Ag(I) or Cu(I), respectively. Substitution of the flanking positions of linear bilateral extended terpy with directionally functional
groups allows the construction of supramolecular assemblies and extended networks. Given the fact that a convenient synthesis of these ligands has been developed, various functional groups can easily be introduced to address other supramolecular interactions like hydrogen or donor-acceptor bonding, as well as strong metal-carboxylate bonds, which are used extensively in the field of MOFs.

Therefore, linear bilateral extended terpy based fundamental building blocks with “crossing” and “corner” character are new tools in the hands of chemists and could inspire the creation of new designed molecular architectures.

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Notes and references


19 The term “linear bilateral extended 2,2′:6′,2′′-terpyridine” was chosen to describe terpy based scaffold represented in Fig. 1B, because it mimics the linear or extended geometry of 5,5′-disubstituted 2,2′-bipyridine and has “two-sided” or bilateral character. For definition of “bilateral,” see: The Oxford English Dictionary. 7th ed. OUP, Oxford, 2005.


