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COMMUNICATION

Terpyridinyl Dibenzo[b,d]furan and Dibenzo[b,d]thiophene based Tetrameric Bismetallomacrocycles

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Novel dibenzo[b,d]thiophene and dibenzo[b,d]furan-based bisterpyridine ligands have been synthesized and used to create unique metalloc macrocycles. Directly self-assembly between the bisterpyridine ligands and Fe(II) led to a mixture containing multiple homo-metalloc macrocycles. In terms of a coordination-driven approach to supramolecular chemistry, there is growing concern with the 2,2':6',2''-terpyridine core and its coordination with Fe(II) which could lead to a mixture containing multiple homo-metalloc macrocycles. However, utilizing the robust Tpy(TpyRu)2(Tpy)Tpy ligands, the metallo-organic ligands, coordination with Fe(II) resulted in the pure tetrameric bismetallomacrocycles. Structures were characterized by 1H NMR, 2D COSY, DOSY-NMR, ESI-TOF-MS and UV/vis spectrum.

Over the past two decades, the design and construction of highly ordered, supramolecular architectures have attracted considerable attention, especially metallic macrocycles. The innovative works of Lehrl, Stang, Fujita, Newkome and many others in the field of self-assembly have shown that understanding the nature of the intermediate is an important tool in determining the outcome of the final supramolecular structure. In terms of a coordination-driven approach to supramolecular structures, there is growing concern with the 2,2':6',2''-terpyridine core and its coordination with Fe(II) which could lead to a mixture containing multiple homo-metalloc macrocycles. Structures were characterized by 1H NMR, 2D COSY, DOSY-NMR, ESI-TOF-MS and UV/vis spectrum.

Herein, we describe our approach to synthesizing a unique set of macrocycles employing two novel bisterpyridine ligands (L1 and L2) based on dibenzo[b,d]thiophene and dibenzo[b,d]furan units. The angels of L1 and L2 are approximately 79.5° and 90°, respectively, and this becomes of apparent significance upon complexation. The ability of L1 to self-assemble with Fe(II) generated mixed macrocycles with metallocycles ranging from triangular to hexameric in nature; however, coordination of L2, due to its close 90° bond angle, with Fe(II) yielded only a tetrameric cycle and small amounts of a pentameric cycle (Scheme 1). In order to construct single quantities of metallo-macrocycles, a step-wise approach was employed. First, a half-square bracket metallo-organic ligand (D3 and D4, Scheme 2) with two uncomplexed free terpyridines was constructed; thereafter, when coordinated with Fe(II), nearly quantitative yields of two dinuclear tetrameric cycles were obtained.

Synthesis of the key organic building blocks (L1 and L2) began by altering commercially available dibenzo[b,d]thiophene and dibenzo[b,d]furan to give 2,8-dibromobenzeno[b,d]thiophene and 2,8-dibromobenzeno[b,d]furan. Subsequent reaction with 4-((2,2':6',2''-terpyridin)-4'-yl)phenyl)boronic acid via Suzuki-coupling yielded the desired ligands (see ESI, Scheme S1). The ligands were structurally confirmed by 1H-NMR (Fig S1-S2), 13C-NMR (Fig S11-S12) and LC-MS (Fig S15, Fig S16).

L1 reacted with 1 equiv. of FeCl2 in a mixed solvent (CHCl3/MeOH=1/1) to produce an inseparable metallo-macrocyclic mixture (Scheme 1 and Fig 1). The mixed structures were confirmed by 1H-NMR, (Fig 1, top) showing the most characteristic peak of tpyH9.5 revealed in multiple peaks. In addition, ESI-TOF-MS indicated the multi-macrocycles (L1Fe), by revealing the metallocrimmer [m/z= 427.266, 541.513, 713.136 and 999.179 corresponding to [[L1Fe]4-nPF6]n+, n=3-6), metallo-tetramer [m/z= 508.824, 617.79 and 779.344 corresponding to [[L1Fe]4-nPF6]n+, n=5-7), metallo-pentamer [m/z= 490.663, 570.117, 672.274 and 808.481 corresponding to [[L1Fe]4-nPF6]n+, n=6-9], and trace amounts of the
metallo-hexamer \((m/z = 835.724)\) corresponding to \([(\text{L1Fe})_6-7PF_6]^{2+}\) (Fig 2, top).

When treating \(\text{L2}\) with 1 equiv. of \(\text{FeCl}_3\), \(^1\text{H-NMR}\) showed multiple peaks corresponding to the \(\text{tpy}H^{3',5'}\) proving that the product also is a mixture, but more distinguishable than \([(\text{L1Fe})_6]\) (Fig 1, bottom). The ESI-TOF-MS spectrum confirmed a main product of the metallo-tetramer \((m/z = 419.34, 499.95, 607.44, 757.92, 983.65\) and \(1359.71)\) corresponding to \([(\text{L2Fe})_4nPF_6]^n, n=3-8\) and trace amounts of the metallo-pentamer \((m/z = 795.80)\) corresponding to \([(\text{L2Fe})_5-4PF_6]^6\) (Fig 2, bottom). The most likely reason is the extended phenyl group in \(\text{L1}\) increased the rotation and bending flexibility, leading to the diversity in the molecular coordination.\(^{21}\) In the results from \(\text{L2}\), the angel was much closer to 90° which decreased the rotational freedom during the self-assembly process.

It has been reported that the \([\text{tpyRu-tpy}]^{2+}\) structure\(^ {21}\) is strong enough to obstruct scrambling of ligands. Thus, a step-wise coordination method was used for the design and synthesis of metallo-dimmers \([(\text{L1RuL1})\text{Cl}_2]\) and \([(\text{L2RuL2})\text{Cl}_2]\) (\(\text{D3}\) and \(\text{D4}\)) from a one-pot reaction. \(^1\text{H-NMR}\) of dimer \(\text{D3}\) \((\text{D3}\) (Fig. 3, Fig. S5 and S9). The color denotes the respective metals, displayed two resonances of \(\text{tpy}H^{3',5'}\) at 9.54 ppm and 8.87 ppm with an integration ratio of 1:1. ESI-TOF-MS showed peaks at \(m/z = 566.5, 849.2\) for \([\text{M-2Cl+H}]^{3+}\), \([\text{M-2Cl}]^{2+}\) (ESI, Fig. S17) also provided evidence for the formation of \(\text{D3}\). In terms of \(\text{D4}\), along with consistent \(^1\text{H-NMR}\) spectra, two distinct resonances of \(\text{tpy}H^{3',5'}\) were at 9.54 ppm and 8.87 ppm with an integration ratio of 1:1. ESI-TOF-MS showed peaks at \(m/z = 417.1, 555.8\) and 833.2 for \([\text{M-2Cl+2H}]^{3+}\), \([\text{M-2Cl+H}]^{3+}\) and \([\text{M-2Cl}]^{2+}\) respectively (Fig S18).

Subsequently, \(\text{D3}\) and \(\text{D4}\) were treated with \(\text{FeCl}_3\) in MeOH. After the simple counterion exchange with \(\text{NH}_4\text{PF}_6\), two desired metallo-tetramers were obtained in nearly quantitative yield (Scheme 2). The \(^1\text{H-NMR}\) spectra for metallo-tetramer \(\text{S}\) \((\text{T5}, \text{Fig} 2)\), where the color denotes the respective metals, displayed two resonances of \(\text{tpy}H^{3',5'}\) for each assignable proton, all integrating 1:1. In comparison to \(\text{D3}\), protons at the 6,6'' position of Tpy-B (purple) exhibited a dramatic shift from 8.71 to 7.29 ppm due to the electron shielding effect after complexation with \(\text{Fe}^{3+}\) (Fig 3, Fig S5 and S9).

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It was observed that the \([\text{tpyRu-tpy}]^{2+}\) structure\(^{21}\) is strong enough to obstruct scrambling of ligands. Thus, a step-wise coordination method was used for the design and synthesis of metallo-dimers \([(\text{L1RuL1})\text{Cl}_2]\) and \([(\text{L2RuL2})\text{Cl}_2]\) (\(\text{D3}\) and \(\text{D4}\)) from a one-pot reaction. \(^1\text{H-NMR}\) of dimer \(\text{D3}\) \((\text{D3}, \text{Fig} 3, \text{Fig} \text{S5 and S9})\) also provided evidence for the formation of \(\text{D3}\). In terms of \(\text{D4}\), along with consistent \(^1\text{H-NMR}\) spectra, two distinct resonances of \(\text{tpy}H^{3',5'}\) were at 9.54 ppm and 8.87 ppm with an integration ratio of 1:1. ESI-TOF-MS showed peaks at \(m/z = 417.1, 555.8\) and 833.2 for \([\text{M-2Cl+2H}]^{3+}\), \([\text{M-2Cl+H}]^{3+}\) and \([\text{M-2Cl}]^{2+}\) respectively (Fig S18).

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characterization for molecules having relatively larger molecular weights and for monitoring self-assembly processes by correlating chemical resonances to diffusion coefficients in solutions.\textsuperscript{30} T5 and T6 (Fig 5) showed only one component in solution for each substance. The diffusion coefficients measured in CD$_3$CN at 298K are $2.796 \times 10^{-10}$ m$^2$/s for T5, and $2.759 \times 10^{-10}$ m$^2$/s for T6, respectively. Experimental hydrodynamic radius for T5 and T6 were calculated to be 2.13 nm and 2.16 nm via the Stoke-Einstein equation $D = \frac{k_B T}{6 \pi \eta r}$ ($k_B$, Boltzman constant; $T$, absolute temperature; $\eta = 0.367$ mPa·s, viscosity of CD$_3$CN at 298 K).\textsuperscript{31}

Further support for the formation of T5 was provided by ESI-TOF-MS signals for the multiply-charged species in charge states $+8$ (m/z 438.21), $+7$ (m/z 521.9673), $+6$ (m/z 633.2730), $+5$ (m/z 788.92), $+4$ (m/z 1022.39) and $+3$ (m/z 1401.22). The detected results and the isotope pattern of each peak agreed well with the corresponding theoretical distributions (Fig 6 top, also see ESI). In terms of T6, there are several unambiguous peaks for the multiply-charge states $+8$ (m/z 430.72), $+7$ (m/z 512.97), $+6$ (m/z 622.62), $+5$ (m/z 776.14) $+4$ (m/z 1006.41), $+3$ (m/z 1390.21). Likewise, slight differences between the detected isotope pattern and the corresponding theoretical distributions of each peak have been found (Fig 6 bottom, also see ESI).

UV-vis spectroscopy for the compounds were examined in MeCN. For D3, the major absorption band at $\lambda = 310$ nm originated from intra-ligand charge transfer in addition to the characteristic absorption band at $\lambda = 496$ nm indicating the MLCT of Ru$^{3+}$ to terpyridine ligands. Further, T5 revealed two MLCT bands, $\lambda = 494$ and 572 nm, representing Ru$^{3+}$ and Fe$^{3+}$, respectively (Fig 7 left, Fig S22). As well, the similar UV-vis spectra of D4 and T6 were illustrated in Fig 7 (right, Fig S23). The electrochemical properties of complexes T5 and T6 were investigated by cyclic voltammetry (see ESI, Fig. S24), all complexes illustrated one reversible oxidation couple of Ru$^{3+}$/Ru$^{2+}$ and the moderate onset oxidation potentials, which was determined to be 1.50 V (T5) and 1.70 V (T6) vs Hg/Hg$\textsubscript{2}$Cl$_2$, respectively. In addition, the reversible oxidation couple of Fe$^{3+}$/Fe$^{2+}$ were measured to be 0.73V in T5 and 1.15V in T6, respectively.

Conclusions

In conclusion, two dibenzo[b,d]thiophene and dibenzo[b,d]furan-based bisterpyridinyl ligands possessing uniquely
restricted angles, have been synthesized and proven to self-assemble with transition metals to form two dinuclear tetrameric metallamacrocycles by means of a step-wise strategy. The structures of the two metallo-tetramers were confirmed by H-NMR, COSY-NMR, DOSY-NMR, ESI-TOF-MS and UV-vis. This study demonstrates that controlling the angled metallo-ligands is possible for the purpose of preparing pure square-shaped supramolecular metallamacrocycles. It provides an effective method to further probe the characteristics, structure and stability of [TpyRuTpy] complexes in order to design and prepare Ru-based terpyridine complexes with enhanced photophysical properties.

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Notes and references
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Dibenzo[b,d]thiophene and dibenzo[b,d]furan based bisterpyridines having specific bend angles had been synthesized. Directly self-assembly between the bisterpyridines and Fe²⁺ led to the metallo-macrocyclic mixtures. Utilizing the robust metallo-organic-ligands result the pure tetrameric metallo-macrocycles.