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Optically Active Metallo-Supramolecular Polymers Derived from Chiral *Bis*-terpyridines

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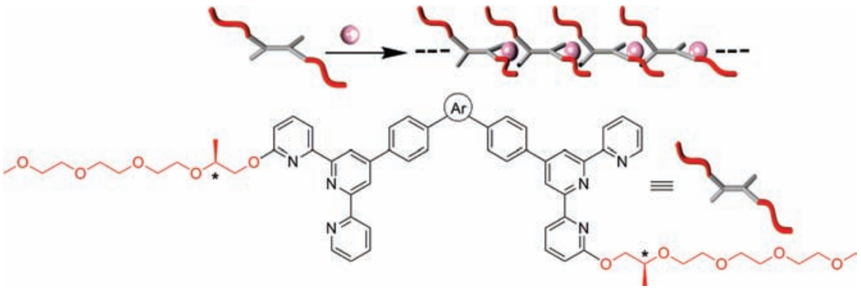
ABSTRACT



The optically active metallo-supramolecular polymers were successfully synthesized *via* complexation of Fe(II) ions with new *bis*-terpyridines containing chiral tetra-ethylene glycol units at the *ortho*-position of the peripheral pyridine rings. In addition, we also revealed solvent and temperature effects toward assembly and dis-assembly behavior of polymers.

The self-assembly of organic ligands with metal ions has afforded many fascinating architectures[1] that are of interest in various fields including catalysis,[2] functional materials,[3] and chemical biology.[4] Recently, several reports[5] covered the development of optically active metallo-supramolecular assemblies through tailored ligand systems and transition metal ions, some of their derivatives are of great interest in the field of asymmetric catalysis.[6] However, there are only limited reports[7] dealing with synthesis of ditopic chiral *bis*-terpyridines (**btpy**) and their optically active coordination polymers. Although there have been reports on chiral btpy and chiral metallo-supramolecular polyelectrolytes (**MEPE**s), the detailed studies of solvent and temperature effects on the optical activities have not been reported so far. We expect that the introduction of chirally substituted tetra-ethylene glycol (**TEG**),[8] chains at the pyridine periphery will not only influence the solubility but will also influence the architecture

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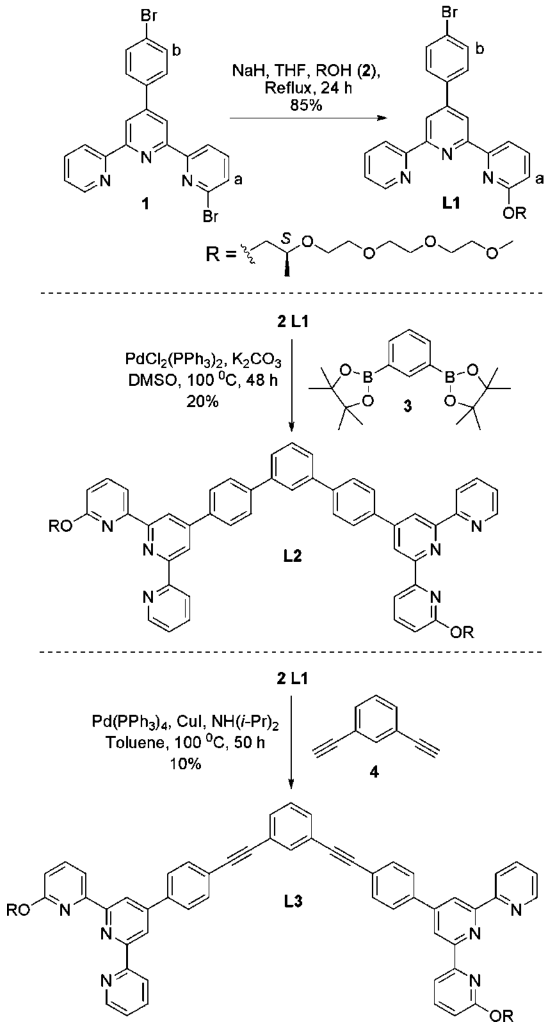
of the resulting **MEPE**. Thus, the presence of chiral **TEG** chain in **btpy** encourages us for studies of solvent and temperature effects on chiral **MEPE**s.

On the basis of these perspectives, we present an approach for the formation of self-assembled helical metallo-supramolecular polyelectrolytes ($\boldsymbol{\eta}$-**MEPE**). In contrast to previous reports,[9] the ditopic **btpy** ligand itself is not chiral but we employ a chiral **TEG** chain at the 6-position of the pyridine ring to induce the chirality at the next level of the supramolecular architecture. To allow the formation of helical **MEPE**s, we employ a 1,3-substituted phenyl unit to connect the two chiral **tpy** metal ion receptors. In order to prevent steric crowding in the coordination sphere, only one peripheral pyridine ring is functionalized.

The synthetic scheme of enantiopure **btpy** containing a chiral **TEG** chain at the *ortho*-position of the pyridine ring is shown in Scheme 1. The 6-Bromo-4′-(4-bromo-phenyl)-[2,2′;6′,2″] terpyridine, **1**, was synthesized according to a previously reported procedure,[10] which is a useful protocol for synthesis of new chiral synthon **L1**. The chemoselective synthesis of ligand **L1** was achieved using compound **1** and 1.2 equivalent of chiral **TEG** in the presence of two equivalents of NaH as base. Ligand **L1** was obtained in good chemical and optical yield and characterized by ^{1}H, ^{13}C NMR, 2D-COSY NMR, and mass spectrometry (Supporting Information). The ^{1}H NMR of compound **1** shows peaks for proton $\mathbf{H_a}$ at $\delta = 7.71$ ppm (dd, $J = 7.25$ Hz) and $\mathbf{H_b}$ at $\delta = 7.76$ ppm (d, $J = 15.9$ Hz), whereas chiral ligand **L1** shows peaks for proton $\mathbf{H_a}$ at $\delta = 6.85$ ppm (d, $J = 8.25$ Hz) and $\mathbf{H_b}$ at $\delta = 7.70$ ppm (Supporting Information, Figure S1). The upfield shift of the $\mathbf{H_a}$ proton and the unchanged peak position of $\mathbf{H_b}$ in NMR confirm chemoselective synthesis of chiral ligand **L1**. This new synthon opens up the door for the synthesis of new chiral **btpy** using different synthetic methodologies.

The chiral **btpy** ligand **L2** was synthesized by Suzuki bis-coupling[11] of 1,3-benzenediboronic acid bis(pinacol) ester **3** with two equivalents of ligand **L1** in modest yield. Additionally, the chiral ligand **L3** was synthesized by Sonogashira cross-coupling[12] of 1,3-diethynyl benzene **4** with two equivalent of ligand **L1** in low yield. The ligands **L2** and **L3** were purified by alumina column chromatography and preparative GPC. All products were characterized by NMR, mass spectrometry, and optical polarimetry.

Scheme 1. Synthesis of Chiral *bis*-Terpyridine Ligands



The self-assembly process of **btpy** was investigated with **Fe**$^{2+}$ as a central metal ion, since it forms well-defined (achiral) octahedral complexes with well-distinguishable metal-to-ligand charge transfer (**MLCT**) band in UV−vis spectra.[10a,c,13] The coordination reaction of **L1** (Supporting Information, Figure S6a)[14] and **L2** (Figure 1a) with **Fe(II)** to give rise dimer and polymer were monitored through UV−vis spectrophotometric titration, respectively. These experiments clearly showed that the coordination reaches end point at 1:0.5 (Supporting Information, Figure S6b) and 1:1

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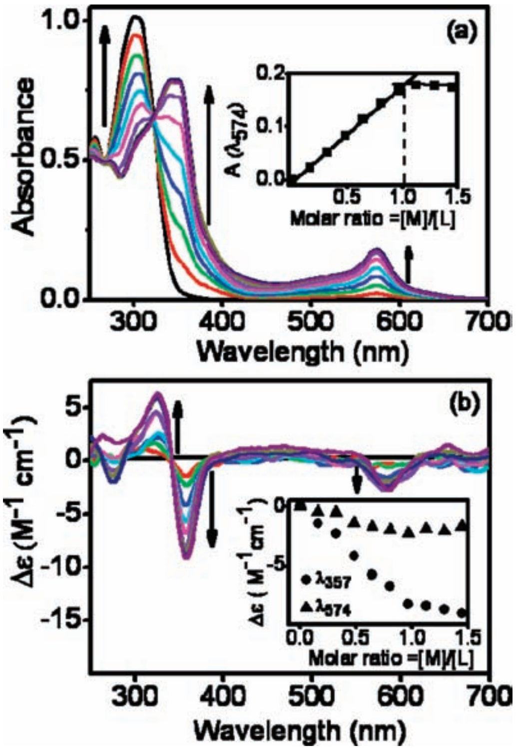

Figure 1. (a) UV−vis and (b) CD spectral changes in the titration of **L2** solution ($CHCl_3$, $c = 1.10 \times 10^{-5}$ M, $l = 1$ cm) with $\mathbf{Fe(ClO_4)_2}$ solution (CH_3CN, $c = 4.42 \times 10^{-5}$ M) at 20 °C. Arrows indicate the direction of spectral changes. The inset (a) shows the change in absorbance at 574 nm and inset (b) shows the increase in CD intensities at 357 and 574 nm as a function of added $\mathbf{Fe^{2+}}$.

(inset, Figure 1a) ratio of **L1**:**Fe(II)** and **L2**:**Fe(II)** for **tpy** and **btpy**, respectively. The presence of a very well-defined isosbestic point at 321 nm also indicates that there is simple equilibrium involved in case of **L2**. This result confirms the formation of coordination polymer. Results from the spectrophotometric titration were corroborated by titrations followed by Circular dichroism (CD) study. As depicted in Figure 1b, clear spectral changes are observed upon addition of **Fe(II)** metal ions. Interestingly, we are unable to observe a CD signal for the neat ligands in chloroform. However, upon addition of different amount of $\mathbf{Fe^{2+}}$ solution in acetonitrile (CH_3CN) to the solution of **L2** in chloroform ($CHCl_3$), we observe a CD signal, which gradually increases in intensity as $\mathbf{Fe^{2+}}$ is added to solution. The observed CD signal is clearly an indication for the formation of optically active structures upon metal ions coordination. As is evident from the Job plots (inset, Figure 1b) the Cotton effect at the **MLCT** band indicates the formation of an asymmetric environment of the otherwise optically inactive $\mathbf{Fe(tpy)_2}$. Furthermore, new peaks appeared at 357 nm (negative) and 320 nm (positive), which also show a function with respect to added metal ions.

It was well reported[10] that, the solubility of a metallo-supramolecular polymer largely depends on counteranions. Hence, for study of solvent effects, we need **MEPE**s with different counteranions. Therefore, after conformation of stiochiometric ratio of metal to ligand (**L2**), further self-assembly of chiral ligands (**L1**, **L2**, **L3**) were carried out by refluxing an equimolar amount of ligand and $\mathbf{Fe(OAc)_2}$ in acetic acid (CH_3COOH) under argon atmosphere. The color of the solution turned purple during complexation, indicating the formation of the corresponding **MEPE**s. The **MEPE**s with $\mathbf{CH_3COO^-}$ as counteranions are soluble in acetic acid, methanol (CH_3OH) and water (H_2O). We also synthesized **FeL2′-MEPE** with $\mathbf{PF_6^-}$ as counteranions to study the optically active structures in CH_3CN solvent. The coordination of **Fe(II)** and ligands (**L1**, **L2**) were confirmed by ^1H NMR, UV−vis spectroscopy and the molecular weights determination in methanol solvents (**FeL2-MEPE** $= 1.7 \times 10^4$ and **FeL3-MEPE** $= 1.4 \times 10^4$) by SEC-Viscometry-RALLS method.[14]

The conformation of optically active polymers or oligomers largely depends on the solvent media,[8a,b,15] metal to ligand coordination[16] and their counteranions.[16b,c] As there are no reports for different solvent effects on chiral **MEPE**s, hence we elaborated our attention to this respect. The absorption spectra of **FeL2-MEPE** (CH_3OH) with $\mathbf{CH_3COO^-}$ counteranions and **FeL2′-MEPE** (CH_3CN) with $\mathbf{PF_6^-}$ counteranions shows their characteristics **MLCT** band almost at the same position (λ_{573}) (Supporting Information, Figure S8a) as in case of **FeL2-MEPE** with $\mathbf{ClO_4^-}$ counteranions (λ_{574}) (Figure 1b). Whereas, the absorption spectra of different polymers **FeL2-MEPE** and **FeL3-MEPE** show change in the **MLCT** band at 573 and 575 nm due to increase in conjugation. The CD spectra of these polymers show nearly the same type of signal at the **MLCT** band ($\Delta\varepsilon_{570} = -0.13$ M^{-1} cm^{-1}), ($\Delta\varepsilon_{570} = -0.03$ M^{-1} cm^{-1}), followed by a positive ($\Delta\varepsilon_{340} = 0.79$ M^{-1} cm^{-1}), ($\Delta\varepsilon_{340} = 0.52$ M^{-1} cm^{-1}) and a negative signal ($\Delta\varepsilon_{293} = -0.25$ M^{-1} cm^{-1}), ($\Delta\varepsilon_{293} = -0.39$ M^{-1} cm^{-1}), respectively (Supporting Information, Figure S7b). Surprisingly, we observed a very interesting result in water as compared to organic solvents of **FeL2-MEPE** with $\mathbf{CH_3COO^-}$ counteranions.

The UV−vis spectra showed a depression of overall optical intensity with a shift of the **MLCT** band from λ_{573} to λ_{577}, which is associated with the difference in the dielectric constants (Supporting Information, Figure S8a). In contrast, we observe strong changes in the CD spectra, a negative Cotton effect with a very sharp increase in CD intensity at 357 nm ($\Delta\varepsilon_{357} = -9.15$ M^{-1} cm^{-1}), followed by a positive Cotton effect ($\Delta\varepsilon_{316} = 1.52$ M^{-1} cm^{-1}). This solvent also shows an enhancement of the CD intensity of the **MLCT** band ($\Delta\varepsilon_{577} = -1.03$ M^{-1} cm^{-1}). The CD spectra of **FeL2-MEPE** in water show strong Cotton effects over the absorption ranges (Supporting Information, Figure S8b), as it was obtained in case of titration of **L2** with $\mathbf{Fe(ClO_4)_2}$ (Figure 1b), indicating the formation of a optically active stable structures. Further, the CD sepctra of **FeL2-MEPE**

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in aqueous solution show different sign around 340 nm and same sign for the **MCLT** band from that in organic solvents. This result suggests that **FeL2-MEPE** adopts a different conformation in water as compared to organic solvents. The possible explanation for strong changes in CD intensity of **MEPE** is due to hydrogen bonding[17] between water molecules and ethylene oxide chains of chiral **TEG** units of btpy, but the possibility of aggregation of aromatic parts in water is not ruled out as reported by Lee *et al.*[18] for coordination polymers.

It is well-known that the changes in temperature affect chiral conformations.[8b,c,15,19a,b] Recently, Schubert *et al.*[5d,19c,d] have reported the temperature effect on metallo-supramolecular polymers. Inspired from these reports, the temperature dependent CD spectra will allow us to study the self-assembly of **MEPE**. The temperature dependent studies of optically active **FeL2-MEPE** was carried out in a temperature range from 10−50 °C in water. The UV−vis spectra (Supporting Information, Figure S9) show a gradually decrease in the absorption intensity of the **MLCT** band with increasing temperature, and at 50 °C we note the almost complete absence of this band indicating that **MEPE** has dis-assembled. A similar effect is observed in the CD spectra, which are shown in Figure 2. The CD intensity decreases without change in shape of spectra with increasing temperature. The changes of CD spectra by increasing temperature may be due to the decomposition of metallosupramolecular polymers by the cleavage of metal complexes. The temperature dependent peak intensities of the **MLCT** band of **FeL2-MEPE** in the UV−vis (Supporting Information, Figure S9) and CD spectra (Figure 2) are shown in the insets. These results show that the **MEPE**s are equilibrium structures. At elevated temperatures the **MEPE** dis-assembled, which is indicated by the loss of the characteristic **MLCT** band. While we did not observe a reversible effect in water, we do note that in methanol the **MLCT** band is recovered upon cooling. As we noted above, equilibrium in water is slow at room temperature and, therefore, recovery of the **MLCT** band is not observed under the experimental conditions (Supporting Information, Figure S10).

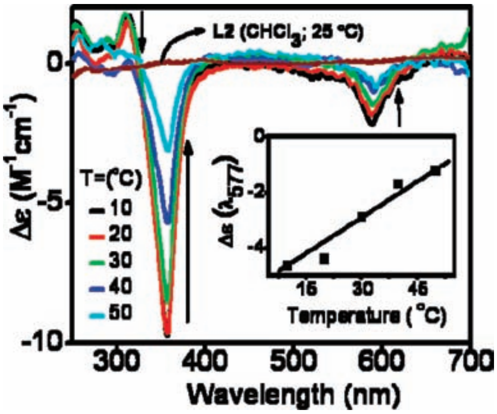

Figure 2. CD spectra of **FeL2-MEPE** in water ($c = 2.00 \times 10^{-5}$ M, $l = 1$ cm) at different temperatures. Arrows indicate the direction of spectral changes. The inset shows the relationship of CD intensity of the **MLCT** band ($\lambda = 577$ nm) with increasing temperature.

In conclusion, we synthesized a new chiral synthon **L1**, which is the basis for the development of chiral **btpy**s. The chiral **btpy** ligands **L2** and **L3** with a 1,3-connectivity and chiral **TEG** chains at the *ortho*-position of periphery were synthesized and applied for generation of metal ion induced new optically active metallo-supramolecular polymers. The change in CD intensities as a function of added **Fe^{2+}** confirm the formation of optically active coordination polymers. The strong CD intensities of **MEPE**s indicate that they adopt chiral conformations and the temperature dependence of UV−vis and CD spectra indicates the dis-assembling of optically active metallo-architectures at higher temperature. Studies to determine the conformational change of **FeL2-MEPE** in water to organic solvent are in progress.

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Supporting Information Available: Experimental procedures, full spectroscopic data for all new compounds, UV−vis, CD spectra and proton NMR data of ligands and MEPEs. This material is available free of charge via the Internet at http://pubs.acs.org.

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