

# Preparation, characterization, and electrochromic properties of novel Co(II)-bis-2,2':6',2''-terpyridine metallo-supramolecular polymers

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## Abstract

A rich variety of novel ditopic bis-terpyridines, by symmetric and unsymmetric introduction of functional groups in the pyridine rings, as well as tuning the spacers for bridging the two terpyridine moieties, is described. These bis-terpyridines are useful ligands for developing new metallo-supramolecular materials with novel functions, as well as for investigating the structure–property relationships. In order to investigate the structural factors of bis-terpyridine based metallo-supramolecular materials, such as the functional groups in the ring periphery of the ligands and the spacers between the two terpyridine coordination components, several different types of Co<sup>II</sup>-bis-terpyridine supramolecular polymers were prepared from various bis-terpyridine functional modules and Co(OAc)<sub>2</sub>. The absorption and the electrochemical behavior of these new supramolecular polymers were studied by UV/Vis spectroscopy and differential pulse voltammetry (DPV), respectively. The results showed that the introduction of electron donating groups at the pyridine ring affects remarkably the charge transfer and electrochemical properties of the coordination polymers. In addition, the electrochromic properties of the coordination polymers were also studied. Significant color change and high reversibility were observed from these polymers.

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## 1. Introduction

In the search for new functional materials, metallo-supramolecular polymers associated with ditopic bis-terpyridines have become of increasing interest in the last few years due to the structural advantages. This type of ligands is generally chemical and thermal stable, and has very high binding affinity towards a large variety of transition metal ions by forming an octahedral geometries (Fig. 1) [1]. Furthermore, the bis-terpyridine based coordination polymers possess in many cases distinct magnetic, photochemical and electrochemical properties, as well as interest of chemical biology [1,2].

So far, numerous functional polymer materials based on 2,2':6',2''-terpyridine metal complexes have been reported, and significant contributions from these pioneer studies are observed not only in the academic community, but also in industrial applications [1–3]. However, studies on such type of functional

materials have not been investigated thoroughly, and still a great deal remains to be learned about the structural factors of the ligands for instance. Most of the previous studies are focused on the ligands by modification the spacer region. Examples concerning the coordination component functionalized have been rarely reported. It is anticipated that the introduction of a functional group into the pyridine rings, such as electron donating or withdrawing groups, may perturb the charge density distribution over the conjugated coordination scaffold, which in turn would result in alterations of properties of the polymer materials.

In this paper, we describe the preparation of two novel Co<sup>II</sup>-bis-terpyridine polymers prepared from a pyridine ring substituted and unsubstituted ligand, respectively. Owing to the two ligands have same biphenyl spacer, it would therefore facilitate an investigation into the effect of functional group in pyridine ring on the property of the coordination polymer. On the other hand, to study the influence of spacer of the ligands, a coordination polymer based on 1,4-bis(2,2':6',2''-terpyridine-4-yl) benzene, which is commercially available, was also prepared. Following the preparation of metallo-supramolecular polymers,

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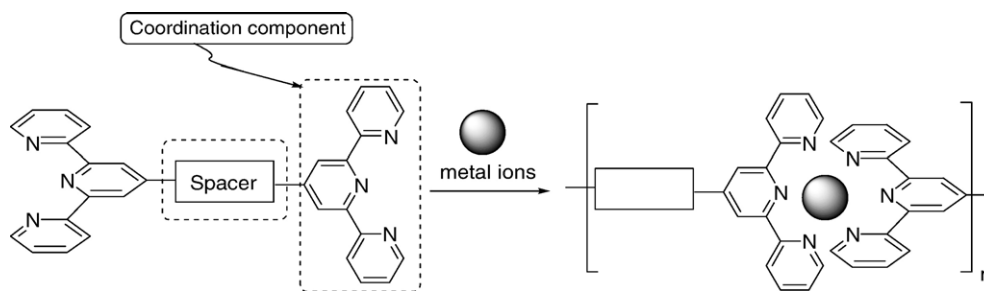


Fig. 1.

detailed studies on their absorption and electrochemical properties, as well as the electrochromic applications are also presented.

## 2. Experimental procedures

### 2.1. General methods

Unless otherwise noted, all reagents were reagent grade and were used without purification. Methanol, acetic acid, were dehydrated, and were purchased from Wako or Kanto Chemical Co. Inc. UV/Vis spectra were obtained by using a Shimadzu UV-2550 UV–visible spectrophotometer. Differential pulse voltammetry (DPV) and amperometric experiments were measured on an electrochemical analyzer, ALS/H CH instruments, with a platinum wire as counter electrode and Ag/AgCl reference electrode in an anhydrous and argon saturated 0.1 mol L<sup>-1</sup> acetonitrile solution of tetra-*n*-butylammonium perchlorate (*n*-Bu<sub>4</sub>NClO<sub>4</sub>). Films of the polymers for DPV measurements were prepared by casting the MeOH solution (0.5 mM) on a glassy carbon working electrode and slowly evaporating the solvent, and films for electrochromic experiments were prepared by casting the same solution on an ITO plate (ca. 25 × 12 × 1.1 mm, 8–12 Ω, optical trans. >83%, Aldrich), and slowly evaporating the solvent and a further dry at 60 °C for 10 min. 1,4-bis(2,2':6',2''-terpyridine-4-yl)benzene (**4**) was purchased from Aldrich (97%), and was directly used without further purification.

### 2.2. Preparation of CoII-bis-terpyridine metallo-supramolecular polymers

#### 2.2.1. Preparation of polymer 5

**1a** (21.02 mg, 0.0310 mmol) and Co(OAc)<sub>2</sub> (5.49 mg, 0.0310 mmol) was refluxed in an argon saturated mixture of acetic acid (20 mL) and MeOH (5 mL) under argon atmosphere for 1 d. The solution was cooled to room temperature and filtered to remove the insoluble residues. The filtrate was slowly evaporated to remove the solvent, and the product was further dried under vacuum overnight to give polymer **5** (24.1 mg, 91%).

#### 2.2.2. Preparation of polymer 6

**1b** (19.90 mg, 0.0323 mmol) and Co(OAc)<sub>2</sub> (5.71 mg, 0.0323 mmol) was refluxed in an argon saturated acetic acid

(20 mL) under argon atmosphere for 1 d. The solution was cooled to room temperature and filtered to remove the insoluble residues. The filtrate was slowly evaporated to remove the solvent, and the product was further dried under vacuum overnight to give polymer **6** (22.6 mg, 89%).

#### 2.2.3. Preparation of polymer 7

**4** (50.00 mg, 0.0925 mmol) and Co(OAc)<sub>2</sub> (16.37 mg, 0.0925 mmol) was refluxed in an argon saturated MeOH (50 mL) under argon atmosphere for 1 d. The solution was cooled to room temperature and filtered to remove the insoluble

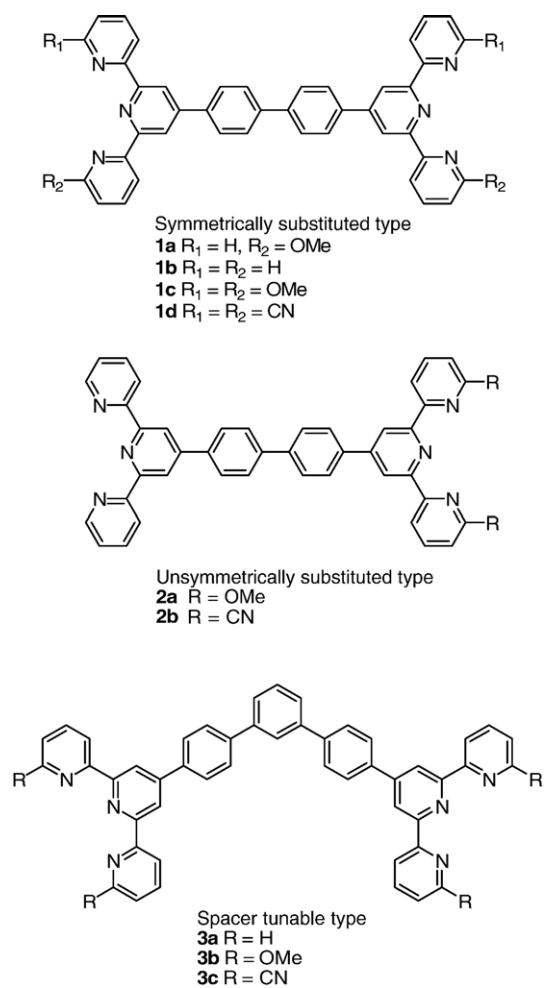


Fig. 2.

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