

# Hydrothermal synthesis of copper complexes of 4'-pyridyl terpyridine: From discrete monomer to zigzag chain polymer

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Received 25 February 2006; accepted 25 April 2006

Available online 3 May 2006

## Abstract

Seven copper complexes [Cu(L1)I<sub>2</sub>] (**1**), [Cu<sub>2</sub>(L1)<sub>2</sub>I<sub>2</sub>]<sub>2</sub>[Cu<sub>2</sub>(μ-I)<sub>2</sub>I<sub>2</sub>] (**2**), [Cu(L2)I<sub>2</sub>] (**3**), [Cu<sub>2</sub>(L2)(μ-I)I(PPH<sub>3</sub>)] (**4**), [Cu<sub>4</sub>(L2)<sub>2</sub>(μ-I)<sub>2</sub>I<sub>2</sub>] (**5**), {[Cu(L2)I]<sub>2</sub>[Cu<sub>2</sub>(μ-I)<sub>2</sub>I<sub>2</sub>]}<sub>n</sub> (**6**) and [Cu<sub>2</sub>(L2)(μ-I)<sub>n</sub>] (**7**) have been prepared by reactions of ligands: 4'-(2-pyridyl)-2,2':6',2''-terpyridine (L1) and 4'-(3-pyridyl)-2,2':6',2''-terpyridine (L2) with CuI in hydrothermal conditions, respectively. By alternating the oxidation states of the metal centers, increasing stoichiometric metal/ligand ratio and introducing a second ligand, the compounds were successfully developed from mononuclear (**1** and **3**) to multinuclear (**2**, **4** and **5**) and polymers (**6** and **7**). The synthesis of these compounds may provide an approach for the construction of coordination compounds of 4'-pyridyl terpyridine with different nuclearity.

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**Keywords:** Terpyridine; Hydrothermal reaction; Copper mixed-valent complex; Copper iodide; Coordination polymer

## 1. Introduction

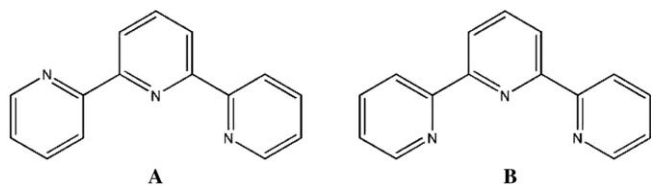
The design of complex molecular architectures is an important goal for synthetic chemistry as it provides the opportunity to control or encode the properties of a material at the molecular level [1]. Chemists have great interest in the design, synthesis and exploring the properties of coordination polymers. 2,2':6',2''-Terpyridine (terpy) and its derivatives have been intensively explored because of their versatility as building blocks for supramolecular assemblies and polymers [2,3] and the interesting electronic, photonic, magnetic, reactive and structural properties shown by the transition metal complexes of these ligands [4]. In the last decades, special attention has been drawn to the 4'-functionalized terpyridine ligands, since the appended substituents may be utilized not only to tailor the electronic properties of the ligand and its metal complexes, but also to incorporate new functionalities through

further derivative reactions, as well as to introduce terpyridine complexes into polymers [5].

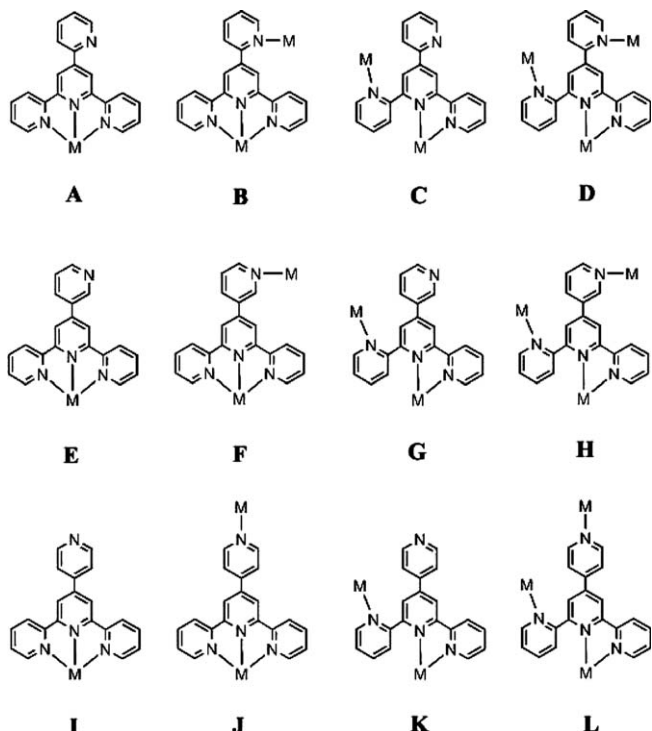
For 4'-functionalized terpyridines, the pyridyl-substituted 4'-pyridyl terpyridines (pyterpy) have been essentially ignored and scarcely reported [6,7]. As an oligopyridine ligand with multi-domain, 4'-pyridyl terpyridine is a potentially bridging ligand, incorporating a tridentate 2,2':6',2''-terpyridine functionality and an isolated monodentate pyridyl group. When the terpyridine is bonded to a metal, it isomerizes to a *cis*-configuration (Scheme 1, left), though preferably to *cis-cis*-configuration (Scheme 1, right). At the same time, the different N-donor pyridyl attached to the C(4') position of a 2,2':6',2''-terpyridine ligand may result in different coordination modes (Scheme 2). Constable [7] has reported that the 4'-pyridyl substituent is very weakly electron withdrawing when placed in the C(4') position of a 2,2':6',2''-terpyridine ligand and the extended conjugation make pyterpy a better π-acceptor ligand than terpyridine, such that it stabilizes the lower oxidation states. The pyterpy may be used in the assembly of coordination compounds because of their diverse coordination modes and bridging ability.

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Scheme 1. The different configurations of terpyridine.



Scheme 2. Coordination modes of pyterpys.

Our studies were induced by the interest in the development of different polynuclear complexes of the 4'-pyridyl terpyridine, in which the discrete complex entities are further assembled into larger entities or arrays of defined architectures. Self-assembly processes controlled by the multidentate ligands and the coordinated geometry prefer-

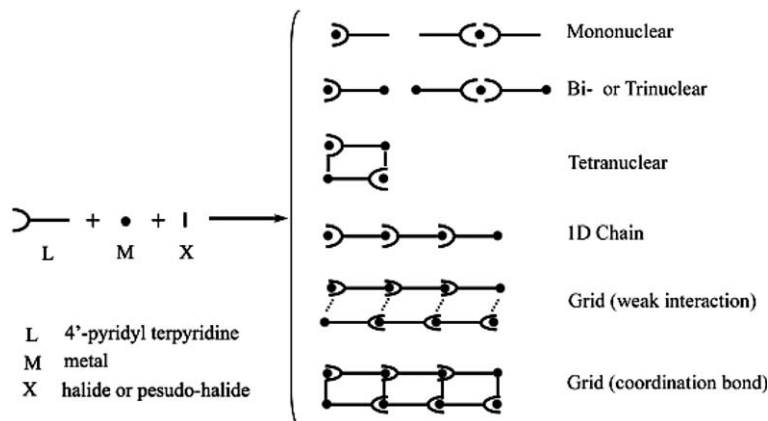
ences of the metal ions can lead to different fantastic polynuclear complexes such as molecular helicates, grids, rings and boxes [8–10]. Sauvage [11] have reported that the coordination preferences of copper in different oxidation states, e.g. four-coordinate copper(I), five- or six-coordinate copper(II), may be used to drive supramolecular systems. On the other hand, copper(I) halide were commonly selected as the metal source due to their ability to form neutral arrays [12], and the strong coordination nature of the halide anion which can bridge two or more copper centers and can be connected to form coordination polymers using diverse bridging ligands. It is reasonable to predict that the copper compounds based on pyterpy and an appropriate linkers, such as halide and pseudo-halide X (Cl, Br, I, SCN or CN), can be developed from monomers to polymers as shown in Scheme 3.

On the basis of our pervious work [13,14], we report the hydrothermal preparation of several compounds of 4'-(2-pyridyl)-2,2':6',2''-terpyridine (**L1**) and 4'-(3-pyridyl)-2,2':6',2''-terpyridine (**L2**) with copper(I) iodide. By changing the reaction conditions (temperature, stoichiometry, additives), the valence of copper varied from bivalence to mixed-valence and monovalence, the compounds developed from mononuclear to multinuclear and polymers. The result shows that it is an effective way to achieve coordination polymers of pyterpy by controlling the oxidation states of metal centers and selecting appropriate linkers.

## 2. Experimental

### 2.1. General

All chemicals and reagents are commercially available and were used as received without further purification. The ligand **L1** and **L2** were synthesized by a modified literature method [26,42]. FT-IR spectra (KBr pellets) were recorded on a Nicolet Avatar 360 FTIR spectrometer in the range 4000–400  $\text{cm}^{-1}$  region. Elemental analyses of C, H, and N were determined with a Perkin-Elmer 2400 C elemental analyzer.



Scheme 3. Topologies of some pyterpy compounds.

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