



Structure and spectroscopy of two new bases for building block: Terpyridine derivatives

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ABSTRACT

Two new terpyridine compounds are reported: 4'-(3-methyl-2-thienyl)-4,2':6',4''-terpyridine, C₂₀H₁₅N₃S, (**I**) and 4'-(4-quinolinyl)-4,2':6',4''-terpyridine, C₂₅H₁₇C₁₃N₄, (**II**). Both structures crystallize in centrosymmetric space groups and present weak H-bonds, which gives greater stability to their structures. Light absorption by both molecules is firmly established on the experimental and the TDDFT analysis as coming from $\pi \rightarrow \pi^*$ transitions. The fluorescence of both compounds has a small Stokes shift, which is also consistent with the emission from highly rigid molecules. Furthermore, the thermal stability observed for both compounds, until about 280 °C, making these molecules interesting candidates for use as complex ligands, which are obtained by means of solvothermal synthesis (technique with temperatures of about 150 °C).

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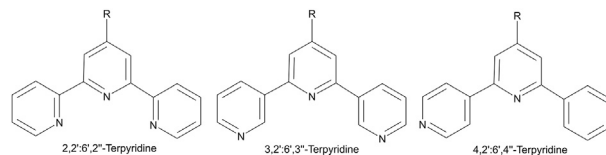
1. Introduction

One of the first steps in metallosupramolecular chemistry is to find versatile building blocks [1–6]. On the other hand, much effort has been focused on the purposeful design and controllable synthesis of coordination systems employing multidentate ligands [7–10]. Systems such as pyridine, 2,2'-bipyridine, 1,10-phenanthroline or similar have a desired ability to coordinate hard and medium metal ions; then, the formed structures are stabilized thanks to the pi conjugated system and also due to its aromatic ring stacking. However, these systems are discrete in nature. In order to obtain a chain or planar type system, it is required a ligand wherein the donor atoms arrangement ensures the spread of the molecular structure: this requirement is met by some terpyridines.

Along the years, n,2':6',n'' Terpyridines (Tpy) as well as all their 4'-substituted derivatives have been the subject of intensive structural study, in any of their current forms, viz., n = 2, 3 and 4 (Scheme 1).

The different spatial disposition of the nitrogen donors in these forms confers them a striking diversity of coordinative capabilities, as a search in the CSD (v5.13 plus Feb. 2014 updates [11]) easily discloses. Table 1 presents a summary of the results obtained for the three types of Tpy-based compounds, pointing out the number of reported moieties, either complexes or unbound, and among the former, the polymeric ones are prominent.

The most numerous, by far, is the 2,2':6',2'' group that coordinates almost exclusively as $\mu_1\text{-}\kappa^3$ chelating ligands due to the convergent disposition of the N donors. The few polymeric reported cases are the result of the bridging capabilities of the eventual R substituent. On the other hand, the 3,2':6',3'' group is the less frequently reported; the stereo-disposition of the pyridyl



Scheme 1. 2,2':6',2'', 3,2':6',3'' and 4,2':6',4''-terpyridine molecules.

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Table 1
Number of terpyridine based structures in the CSD [11].

Tpy type	Uncomplexed	Complexed (Any metal)	Complexed (Polymeric)	Polymeric percentage
2,2':6',2''-	114	678	136	20%
3,2':6',3''-	2	11	8	73%
4,2':6',4''-	10	61	54	89%

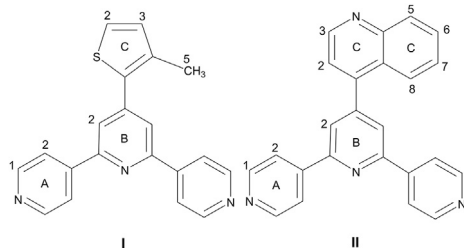
N's, somehow intermediate between the other two, allows both monomeric as well as polymeric coordination arrangements. Finally, the 4,2':6',4'' case ranks second in the number of entries, though far from the 2,2'. All these ligands appear as very versatile in their coordination modes: their divergent nature allows them to connect to metal centers acting either as bidentate-bridging (using the 4,4'' pyridyl groups to give an infinite chain structure [3,4,6] or a 3D network structure [8]) or as tridentate (using the three external 4-pyridyl groups to engage in a 3D structural motif [9] or molecular capsules [7]). This versatility turns this type of ligands particularly attractive for the generation of complex networks, in particular open 3D coordination structures (metal-organic framework, MOF's). Their particular structural nature and versatile coordination possibilities of these ligands could lead to interesting physical properties such as luminescence [12,13] or the cooperative type, as the magnetic ones [14–16]. The aim of our research line is to obtain ligands that result in complexes with cooperative magnetic properties.

As an initial step in order to explore new 4,4'' divergent terpyridine-based ligands and further analyze their coordination capabilities and supramolecular properties, we present herein two new free ligands (Scheme 2) obtained when changing the R substituent, viz.: 4'-(3-methyl-2-thienyl)-4,2':6',4''-terpyridine (I) and 4'-(4-quinoliny)-4,2':6',4''-terpyridine (II).

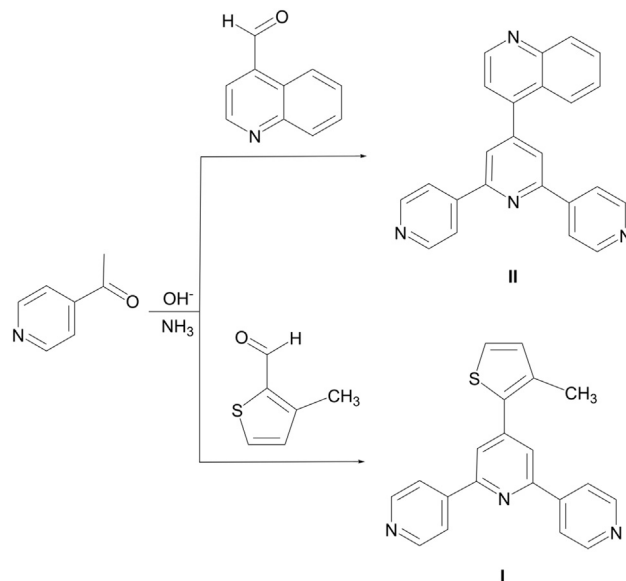
Both structures crystallize in centrosymmetric space groups $P2_1/n$ for I and $P\bar{1}$ for II; with one single molecule per asymmetric unit. We have studied the fluorescence behavior for both systems, in order to eventually compare, with the respective transition metal complexes for these compounds. With this in mind, we have studied the absorption and emission spectra for both systems; indicating that this electronic transitions are $\pi \rightarrow \pi^*$ type. Then, as mentioned before, the expected continuity is to obtain coordination compounds, considering that these ligands are thermally stable up to about 280 °C the solvothermal synthesis techniques could also be implemented.

2. Experimental

I.- Syntheses. The terpyridine systems were prepared according to the Aldol condensation and Michael addition [17] methods (Scheme 3) with minimal modifications; the chemical reagents were used without further purification.



Scheme 2. Molecular structure diagram for I and II, with ring labeling and numbering.



Scheme 3. Synthetic pathway for I and II.

4'-(3-methyl-2-thienyl)-4,2':6',4''-terpyridine (I). 4-acetylpyridine (1.211 g, 10 mmol) was added to 25 mL of 3-methylthiophenecarboxaldehyde ethanolic solution (0.6309 g, 5 mmol). The solution was stirred for 10 min, then KOH (0.5611 g, 10 mmol) and concentrated NH_3 were added (14.5 mL). The mixture was stirred overnight (ca.18 h). A yellow precipitate was obtained and then filtered and washed with water (4×10 mL). Recrystallization of the ligand was done in CH_3Cl (15 mL). Pale yellow needles was obtained: $\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}$ (770 mg, 2.337 mmol, 46.74%). *Anal.* Calc: C, 72.92; H, 4.59; N, 12.76; S, 9.73. Found: C, 73.0; H, 4.7; N, 13.0; S, 9.5.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.79 (d, $J = 6.0$ Hz, 4H, H^{A1}), 8.04 (d, $J = 6.0$ Hz, 4H, H^{A2}), 7.91 (s, 2H, H^{B2}), 7.40 (d, $J = 5.0$ Hz, 2H, H^{C2}), 7.04 (d, $J = 5.0$ Hz, 2H, H^{C3}), 2.50 (s, 3H, H^{C5}). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 155.13 (C^{B1}), 150.60 (C^{A1}), 145.89 (C^{A3}), 145.03 (C^{B3}), 136.14 (C^{C1}), 134.17 (C^{C4}), 132.01 (C^{C3}), 125.94 (C^{C2}), 121.16 (C^{A2}), 120.10 (C^{B2}), 15.50 (C^{C5}).

FT-IR (KBr, cm^{-1}) 3085, 3026 (merged ν_{CH} pyridine and thiophene rings), 2976 (ν_{CH} methyl), 1591, 1539 and 1400 (ν_{CC} pyridine and thiophene rings), 1065(w), 996(w), 826(m), 739(m), 629(m), 490(w).

4'-(4-quinoliny)-4,2':6',4''-terpyridine (II). 4-acetylpyridine (0.9691 g, 8 mmol) was added to 20 mL of 4-quinoliny-carboxaldehyde ethanolic solution (0.6287 g, 4 mmol). The solution was stirred by 10 min, then KOH (0.449 g, 8 mmol) and concentrated NH_3 were added (11.6 mL). The mixture was stirred ca 4 h. A white precipitate was obtained and then filtered and washed with water (3×10 mL) and ethanol (2×10 mL).

Recrystallization of the ligand was done in CH_3Cl (18 mL). White crystals plates were obtained: $\text{C}_{24}\text{H}_{16}\text{N}_4$ (750 mg, 2081 mmol, 39.08%). *Anal.* Calc: C, 79.98; H, 4.47; N, 15.55. Found: C, 78.0; H, 4.3; N, 15.0.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.06 (d, $J = 4.2$ Hz, 1H, H^{C3}), 8.80 (d, $J = 6.0$ Hz, 4H, H^{A1}), 8.26 (d, $J = 8.4$ Hz, 1H, H^{C5}), 8.09 (d, $J = 6.0$ Hz, 4H, H^{A2}), 8.00 (s, 2H, H^{B2}), 7.83 (dd overlapping, $J = 14.8, 8.0$ Hz, 2H, $\text{H}^{\text{C6+C8}}$), 7.60 (t, $J = 7.6$ Hz, 1H, H^{C7}), 7.45 (d, $J = 4.2$ Hz, 1H, H^{C2}).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.26 (C^{B1}), 150.72 (C^{A1}), 150.01 (C^{C3}), 148.73 (C^{C4}), 148.61 (C^{C9}), 145.44 (C^{A3}), 145.06 (C^{B3}), 130.41 (C^{C5}), 130.06 ($\text{C}^{\text{C6/C8}}$), 127.70 (C^{C7}), 125.70 (C^{C1}), 124.73 ($\text{C}^{\text{C6/C8}}$), 121.25 (C^{C2}), 121.16 (C^{A2}), 120.93 (C^{B2}).

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