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Short Note

4′-(5-*N*-Propylthiophen-2-yl)-2,2′:6′,2″-terpyridine

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Abstract: A new thiophene-substituted terpyridine derivative has been prepared through the reaction between 5-*N*-propylthiophene-2-carboxaldehyde and 2-acetylpyridine. This terpyridine derivative bears an alkyl chain linked via a thiophene heterocycle.

Keywords: chalcogenophene; heterocycles; ligands; pyridine derivatives; thiophene derivatives

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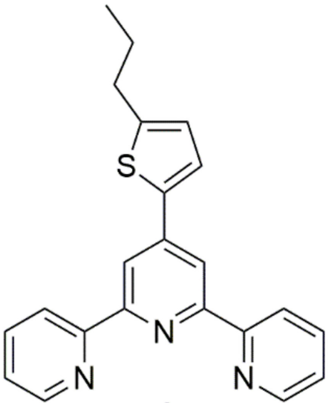
1. Introduction

2,2′:6′,2″-Terpyridine (terpy) ligands and their metal complexes have been widely studied [1] owing to the broad range of applications for such molecules. Varying the nature of the substituents on the ligands and/or the metallic centre offers the possibility to prepare an enormous number of different substances. In particular, terpyridines that contain the five membered heterocycle thiophene [2] have attracted widespread of attention. In fact, they can be used in the preparation of materials for solar cells [3–5], for the functionalization of nanoparticles [6], as fluorescent probes [7,8], as antimicrobial agents [9], as electrochromic materials [10] or as chromophores [11], just to name a few. The substituents that are present on the thiophene ring have an important impact, especially on properties of thiophene-substituted terpyridine-based materials [12]. Therefore, the preparation of new thiophene-substituted terpyridines is still of interest. This paper presents the synthesis of the novel 4′-(5-*N*-propylthiophen-2-yl)-2,2′:6′,2″-terpyridine ligand (**1**) (Figure 1).



1

Figure 1. Chemical structure 4′-(5-*N*-propylthiophen-2-yl)-2,2′:6′,2″-terpyridine (**1**).

2. Results and Discussion

Many synthetic methods are available for the preparation of terpyridine derivatives [13–15]. In order to prepare 4′-(5-*N*-propylthiophen-2-yl)-2,2′:6′,2″-terpyridine, the method described by Wang and Hanan in 2005 [16] was selected. This procedure allowed the facile preparation of **1** from 2-acetylpyridine and 5-*N*-propylthiophene-2-carboxaldehyde.

As in many cases with this synthetic protocol, the crude product was sufficiently pure (>98% by quantitative NMR [17,18] and by combustion analysis) to be used (e.g., for the preparation of metal complexes) without purification.

Ligand **1** was characterized by ^{1}H and ^{13}C-NMR as well as by HR-MS. Firstly, the ^{1}H-NMR spectrum agrees with the chemical structure. NMR spectra of 4′-functionalized terpyridines exhibit a typical singlet for proton 3′ and 5′. In the present molecule, this singlet is seen at δ = 8.63 ppm. Furthermore, as expected, hydrogens that belong to the thiophene heterocycle (a and b) appear as doublets centered at 7.60 and 6.84 ppm, respectively, with a coupling constant of 3.6 Hz. Finally, signals for the propyl chain can be observed as two triplets (at 2.84 and 1.02 ppm) and a multiplet at 1.76 ppm (Figure 2).

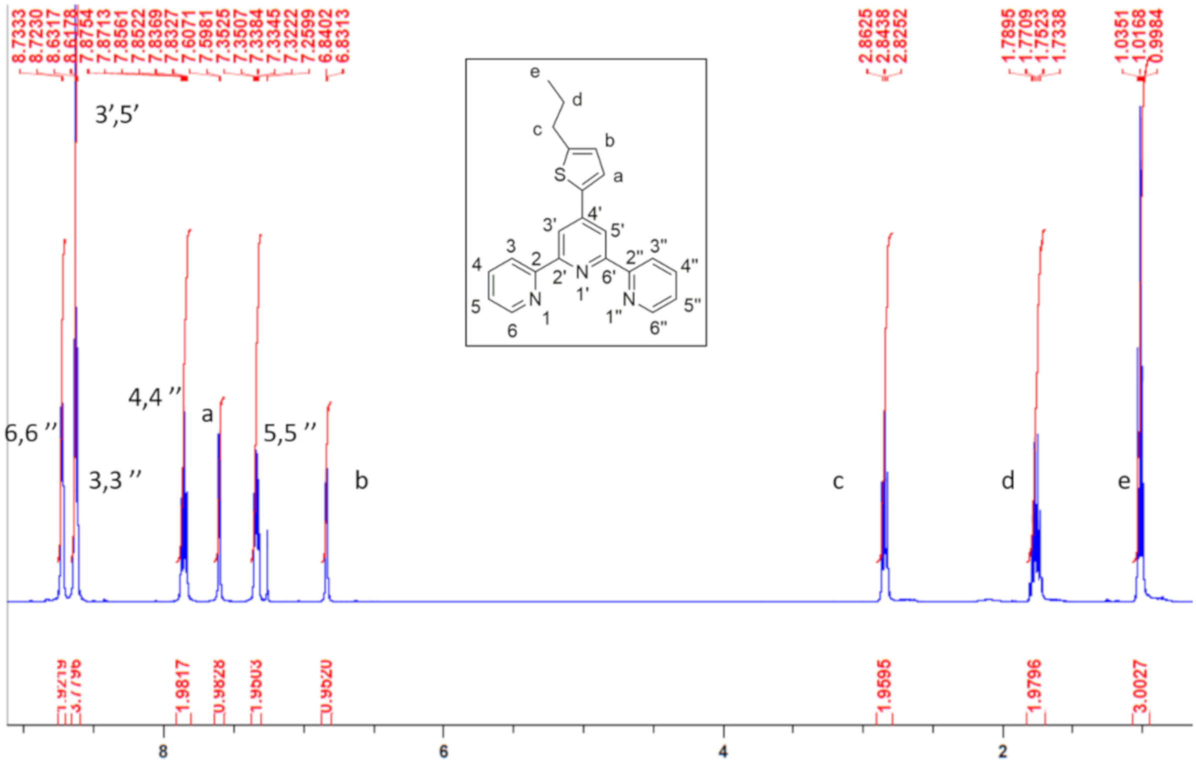


Figure 2. ^{1}H-NMR spectra of compound **1** (inset: structure and atom numbering of **1**).

Additionally, the structure of **1** was further confirmed by ^{13}C-NMR as well as by HR-MS (Supplementary Materials). For instance, the ^{13}C-NMR spectrum features 15 signals due to the symmetry of the molecule, while mass spectra exhibit the molecular ion peak at 358.13703 (calc. for $[C_{22}H_{19}N_3S + H]^+$: 358.13724). The UV-Vis spectrum of compound **1** recorded in acetonitrile exhibits bands at 231, 252, 286 and 314 nm (Figure 3).

The strong absorption band can be assigned to $\pi - \pi^*$ transitions of the terpyridine part, and the shape of the spectrum is similar to previously reported ones for such five-membered heterocycle-substituted terpyridines [11,19].

As expected, introduction of an aliphatic chain onto the thiophene ring subsequently lowered the melting point of the product (98–99 °C) when compared to other non-functionalized chalcogenophene-substituted terpyridine molecule [20–23]. This phenomenon is also observed in an hexylthiophene-functionalized 2,2′:2′,2″-terpyridine [11] (Table 1).

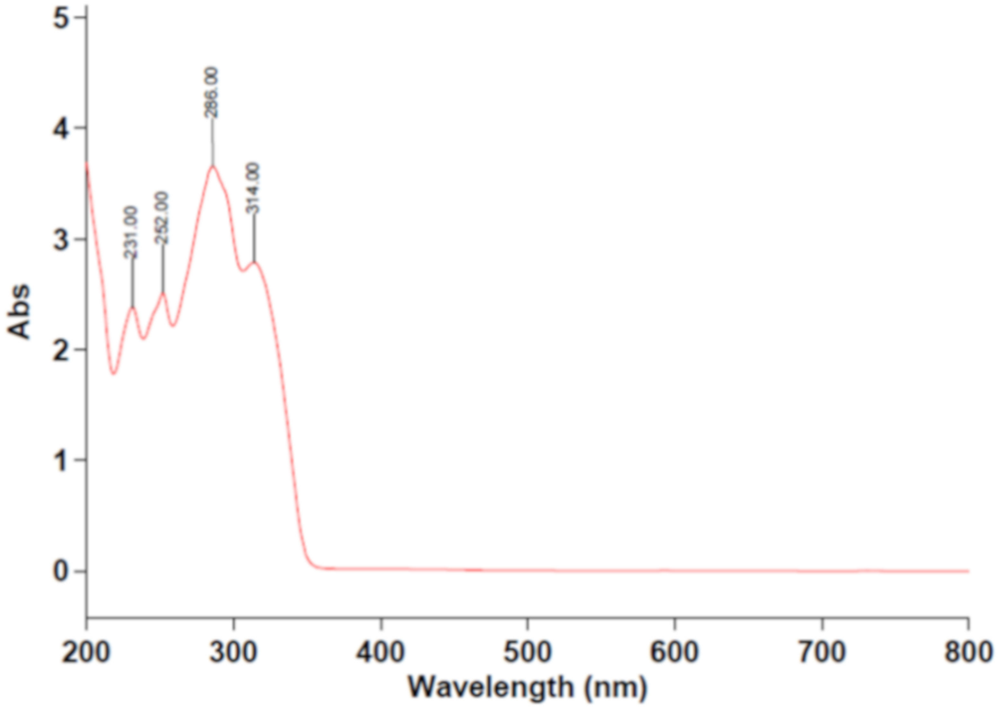
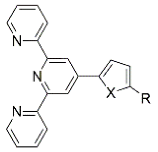


Figure 3. UV-Vis. spectrum of terpyridine **1** (1.21×10^{-4} M in acetonitrile).

Table 1. Comparison of melting points for some chalcogenophene-substituted terpyridines. [a] Values from literature.



X=	S			O	Se	Te
R=	$n\mathrm{C}_6\mathrm{H}_{13}$	$n\mathrm{C}_3\mathrm{H}_7$	H	H	H	H
Mp (°C)	70–72 [a]	98–99	197–199 [a]	219 [a]	215–218 [a]	196–200 [a]

3. Materials and Methods

All reagents were purchased from commercial suppliers (ACROS Organics, Geel, Belgium and TCI Chemicals, Zwijndrecht, Belgium) and used as received. Starting material 5-*N*-propylthiophene-2-carboxaldehyde [24] was prepared from thiophene via 2-*N*-propylthiophene [25] and 1-(thiophen-2-yl)-propan-1-one [26] according to literature procedures. ^{1}H and ^{13}C-NMR spectra were recorded on a Brucker AC 400 (Bruker, Wissembourg, France) at 400 and 100 MHz, respectively, using $\mathrm{CDCl_3}$ as a solvent. Melting point was recorded with a Stuart SMP 10 melting point apparatus (Bibby Sterilin, Stone, UK) and was uncorrected. The UV-Vis spectrum was recorded on a Cary 300 (Agilent Technologies, Santa Clara, CA, USA) using acetonitrile ($C = 1.21 \times 10^{-4}$ M) as solvent. HR-MS was recorded at Sayence SATT, Dijon, France. Elemental analysis was performed at Service d'Analyse Élémentaire, Vandoeuvre-les-Nancy, France.

4′-(5-*N*-Propylthiophen-2-yl)-2,2′:6′,2″-terpyridine (**1**): to a solution of 2-acetylpyridine (7.43 g; 61 mmol) in ethanol (154 mL), 5-*N*-propylthiophene-2-carboxaldehyde (4.73 g; 31 mmol), 85% potassium hydroxide pellets (4.73 g; 72 mmol) and 25% aqueous ammonia (89 mL) were added. The reaction mixture was stirred at room temperature for 24 h. The solid was then filtered on a glass sintered funnel and washed with ice-cold 50% ethanol until washings were colorless. The product was dried under vacuum over phosphorus pentoxide. Compound 1 was obtained as a light-yellow solid (4.25 g; 39%). Mp= 98–99 °C. ^{1}H-NMR (CDCl$_3$, 400 MHz), δ (ppm): 8.73 (d, 2H H6, 6″, *J* = 4.2 Hz), 8.63 (d, 2H, H3, 3″, *J* = 7.6 Hz), 8.63 (s, 2H, H3′, 5′), 7.85 (m, 2H, H4, 4″), 7.60 (d, 1H, Ha, *J* = 3.6 Hz), 7.34 (dd, 2H, H5, 5″, *J* = 6.5 Hz, *J* = 4.9 Hz), 6.84 (d, 1H, Hb, *J* = 3.6 Hz),2.84 (t, 2H, Hc, *J* = 7.5 Hz), 1.76 (m, 2H, Hd), 1.02 (t, 3H, He, *J* = 7.3 Hz). ^{13}C-NMR (CDCl$_3$, 100 MHz), δ (ppm): 156.2, 155.9, 149.1, 148.1, 143.8, 139.1, 136.8, 125.7, 125.6, 123.8, 121.3, 116.7, 32.4, 24.8, 13.7. HR-MS: calc. for $[C_{22}H_{19}N_3S + H]^+$ 358.13724, found 358.13703. Elemental analysis for $C_{22}H_{19}N_3S$: C, 73.92; H, 5.36; N, 11.75; S, 8.97, found C, 73.27; H, 5.39; N, 11.90; S, 8.96. UV-Vis (nm): λ_{abs} = 231, 252, 286, 314.

4. Conclusions

A new thiophene-containing terpyridine was prepared and characterized. This ligand features an alkyl chain on the thiophene ring. This resulted in a lowering of the melting point of this type of molecule, a feature that can be interesting in view of future applications (e.g., for the preparation of low melting complexes).

Experiments are currently in progress to incorporate this ligand into organometallic materials. Results will be reported in due course.

Supplementary Materials: The following are available online, ^{1}H and ^{13}C-NMR, HR-MS, UV-Vis and IR spectra of terpyridine **1**.

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Data Availability Statement: The data from this study are available in this paper and in its Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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