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Approaches to wired terpyridine: Bithienyl alkynyl derivatives of 2,2′:6′,2″-terpyridine and their ruthenium(II) complexes

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ABSTRACT

Two approaches to the formation of ruthenium(II) complexes containing ligands with conjugated 2,2′:6′,2″-terpyridine (tpy), alkynyl and bithienyl units have been investigated. Bromination of 4′-(2,2′-bithien-5′-yl)-2,2′:6′,2″-terpyridine leads to 4′-(5-bromo-2,2'-bithien-5′-yl)-2,2′:6′,2″-terpyridine (**1**), the single crystal structure of which has been determined. The complexes $[Ru(\mathbf{1})_2][PF_6]_2$ and $[Ru(tpy)(\mathbf{1})][PF_6]_2$ have been prepared and characterized. Sonogashira coupling of the bromo-substituent with (TIPS)C≡CH did not prove to be an efficient method of preparing the corresponding complexes with pendant alkynyl units. The reaction of 4′-ethynyl-2,2′:6′,2″-terpyridine with 5-bromo-2,2′-bithiophene under Sonogashira conditions yielded ligand **2**, and the heteroleptic ruthenium(II) complex $[Ru(\mathbf{2})(tpy)][PF_6]_2$ has been prepared and characterized.

1. Introduction

A recurrent theme in metallosupramolecular chemistry is the incorporation of redox active and photoactive species into photonic devices, with the hope of achieving applications in, for example, solar energy conversion [1], biomolecule sensing [2,3] and dye-sensitized solar cells [4,5]. The $\{M(tpy)_2\}^{n+}$ unit provides a structurally rigid building block, functionalization of which is readily achieved, allowing this unit to be central to the development of a range of supramolecular architectures [6–9]. We and others have demonstrated that the conjugation of thienyl units to $\{M(tpy)\}^{n+}$ domains has beneficial consequences for the photophysical properties [10–17]. We are currently seeking ways of enhancing the photophysical properties [18] of $\{Ru(tpy)_2\}^{2+}$-based systems, by functionalizing the tpy ligand in the 4′-position with thienyl and alkynyl substituents which are covalently linked to each other. Ultimately, these units will serve as spacers between the tpy domain and a pendant functionality and should enhance electronic communication between the latter components of the assembly [13,16,19–26]. There have been only a few reports of tpy ligands carrying conjugated thienyl and alkynyl [27–34], and in this paper, we describe our initial synthetic approaches to coupling tpy, bithienyl and alkynyl units and the formation of ruthenium(II) complexes of ligands **1** and **2** (Scheme 1).

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2. Experimental

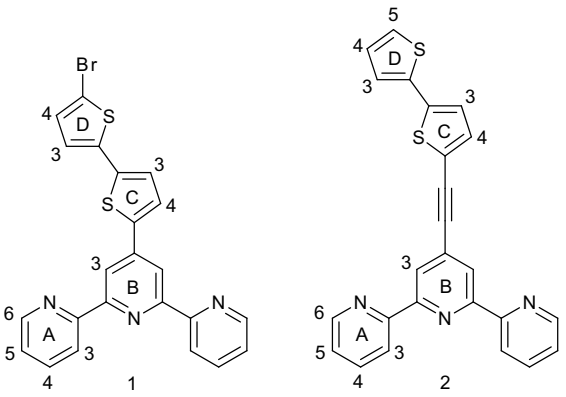
2.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker Avance DRX-500 or DPX-400 spectrometers; the ring labelling and numbering schemes adopted for the ligands and heteroleptic complexes are shown in Schemes 1 and 2. Chemical shifts for ^1H and ^{13}C NMR spectra are referenced to residual solvent peaks with respect to TMS = δ 0 ppm. Electron impact, FAB and electrospray ionisation mass spectra were recorded using Finnigan MAT 95, MAT 8400 and MAT LCQ mass spectrometers, respectively. Reactions were carried out under argon.

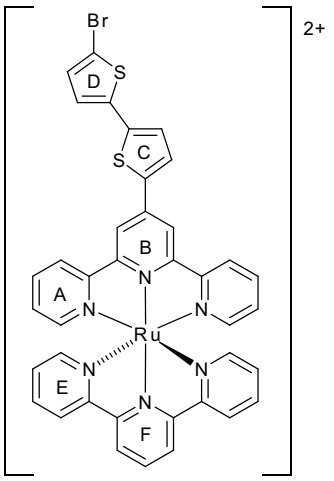
$[Ru(tpy)Cl_3]$ [35] and 4′-ethynyl-2,2′:6′,2″-terpyridine [36] were prepared as previously reported. (TIPS = triisopropylsilyl).

2.2. 5-Bromo-2,2′-bithiophene

5-Bromo-2,2′-bithiophene was prepared by NBS bromination of 2,2′-bithiophene, as reported by Wu et al. [37]. Optimum yields were obtained by using neat acetic acid as solvent rather than the acetic acid and chloroform as previously reported. ^1H NMR spectroscopic data were in agreement with those reported [37] although the spectra were consistent with the presence of 5,5′-dibromo-2,2′-bithiophene [38] as an impurity which was difficult to separate.



Scheme 1. Structures of ligands **1** and **2**, and numbering scheme used for the NMR spectroscopic assignments.



Scheme 2. Ring labelling for the NMR spectroscopic assignments in $[Ru(tpy)(1)]^{2+}$. The same scheme is used in $[Ru(tpy)(2)]^{2+}$.

2.3. 4′-(5-Bromo-2,2′-bithien-5′-yl)-2,2′:6′,2″-terpyridine (*1*)

4′-(2,2′-Bithien-5′-yl)-2,2′:6′,2″-terpyridine [39] (0.31 g, 0.81 mmol) was dissolved in a mixture of glacial acetic acid (5 cm^3) and *N*-bromosuccinimide (0.17 g, 0.97 mmol) and stirred at room temperature overnight in the absence of light. The reaction mixture was neutralised with aqueous $NaHCO_3$ and the solution was extracted into CH_2Cl_2 (3×25 cm^3). The CH_2Cl_2 extracts were dried over Na_2SO_4 and the solvent was removed. Compound **1** was isolated as a yellow solid (0.26 g, 0.55 mmol, 68%). m.p. = 185.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.72 (ddd, *J* 4.8, 1.8, 0.9 Hz, 2H, H^{A6}), 8.64 (s, 2H, H^{3B}), 8.63 (dt, *J* 7.5, 1.0 Hz, 2H, H^{A3}), 7.86 (dt, *J* 7.7, 1.8 Hz, 2H, H^{A4}), 7.68 (d, *J* 3.9 Hz, 1H, H^{C4}), 7.35 (ddd, *J* 7.5, 4.8, 1.2 Hz, 2H, H^{A5}), 7.15 (d, *J* 3.9 Hz, 1H, H^{C3}), 7.00 (s, 2H, H^{D3+D4}). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm 156.2 (C^{B2}), 156.0 (C^{A2}), 149.3 (C^{A6}), 143.0 (C^{B4}), 140.9 (C^{C5}), 138.7 (C^{D2}), 138.2 (C^{C2}), 137.2 (C^{A4}), 131.0 (C^{D4}), 126.9 (C^{C4}), 125.1 (C^{C3}), 124.5 (C^{D3}), 124.2 (C^{A5}), 121.6 (C^{A3}), 116.9 (C^{B3}), 111.9 (C^{C5}). EI MS *m/z* 476 $[M]^+$. $C_{23}H_{14}BrN_3S_2 \cdot 1.5H_2O$ requires C, 54.87; H, 3.40; N, 8.35. Found: C, 54.26; H, 2.83; N, 8.25%.

2.4. $[Ru(tpy)(\mathbf{1})][PF_6]_2$

$[Ru(tpy)Cl_3]$ (0.12 g, 0.27 mmol) was added to a stirring solution of compound **1** (0.13 g, 0.25 mmol) in EtOH (20 cm^3) with a few drops of *N*-ethylmorpholine. The mixture was stirred at room temperature for 15 min, and then heated at reflux for 5 h in the absence of light. The mixture was cooled to room temperature, and was added to aqueous NH_4PF_6 and the solution diluted with water (100 cm^3). The resulting precipitate was collected and dissolved in MeCN and purified by column chromatography (SiO_2, MeCN:H_2O:aqueous KNO_3 9:0.9:0.1). The second (red) band was collected, excess aqueous NH_4PF_6 was added and solvent was removed. The solid was dissolved in acetonitrile, and the product precipitated by addition to water. Recrystallization from MeCN/Et_2O gave $[Ru(tpy)(1)][PF_6]_2$ as a red solid (40 mg, 0.036 mmol, 13%). ^{1}H NMR (500 MHz, CD_3CN) δ/ppm 8.88 (s, 2H, H^{B3}), 8.75 (d, *J* 8.2 Hz, 2H, H^{F3}), 8.64 (d, *J* 8.1 Hz, 2H, H^{A3}), 8.49 (d, *J* 8.0 Hz, 2H, H^{E3}), 8.41 (t, *J* 8.2 Hz, 1H, H^{F4}), 8.11 (d, *J* 3.9 Hz, 1H, H^{C4}), 7.95 (dt, *J* 7.8, 1.3 Hz, 2H, H^{A4}), 7.92 (dt, *J* 7.9, 1.4 Hz, 2H, H^{E4}), 7.51 (d, *J* 3.9 Hz, 1H, H^{C3}), 7.43 (d, *J* 5.5 Hz, 2H, H^{A6}), 7.34 (d, *J* 5.6 Hz, 2H, H^{E6}), 7.29 (d, *J* 3.9 Hz, 1H, $H^{D3/D4}$), 7.22 (d, *J* 3.9 Hz, 1H, $H^{D3/D4}$), 7.17 (m, 4H, H^{A5+E5}). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ/ppm 159.1 ($C^{A2/E2}$), 158.9 ($C^{A2/E2}$), 156.5 ($C^{B2/F2}$), 156.4 ($C^{B2/F2}$), 153.6 ($C^{A6/E6}$), 153.5 ($C^{A6/E6}$), 141.7 (C^{B4}), 140.6 ($C^{C2/D2}$), 139.8 (C^{C5}), 139.2 ($C^{A4/E4}$), 139.1 ($C^{A4/E4}$), 138.8 ($C^{C2/D2}$), 136.9 (C^{F4}), 132.9 (C^{D4}), 130.4 (C^{C4}), 128.6 ($C^{A5/E5}$), 128.5 ($C^{A5/E5}$), 127.2 (C^{C3}), 126.8 (C^{D3}), 125.7 ($C^{A3/E3}$), 125.5 ($C^{A3/E3}$), 124.8 (C^{F3}), 120.3 (C^{B3}), 113.2 (C^{D5}). ESI MS *m/z* 957 $[M-PF_6]^+$, 405 $[M-2PF_6]^{2+}$. $C_{38}H_{25}Br_1F_{12}N_6P_2Ru_1S_2 \cdot H_2O$ requires C, 40.80; H, 2.43; N, 7.51. Found: C, 41.10; H, 2.77; N, 7.18%.

2.5. $[Ru(\mathbf{1})_2][PF_6]_2$

$RuCl_3 \cdot 3H_2O$ (31 mg, 0.12 mmol), **1** (110 mg, 0.23 mmol) and $AgNO_3$ (0.06 g, 0.35 mmol) were added to DMF (15 cm^3). The solution was stirred at room temperature for 15 min, after which time it was heated at reflux for 8 h in the absence of light. The reaction mixture was filtered to remove AgCl, and then saturated aqueous NH_4PF_6 (excess) was added to the filtrate to precipitate the product which was purified by column chromatography (SiO_2, MeCN:aqueous KNO_3, 15:1). The main red fraction was collected and saturated aqueous NH_4PF_6 was added to effect nitrate/hexafluorophosphate exchange. Solvent was removed, the solid residue dissolved in MeCN, and the product precipitated by addition of water. $[Ru(1)_2][PF_6]_2$ was recrystallized from MeCN/Et_2O and was isolated as an orange-red solid (80 mg, 0.060 mmol, 52%). ^{1}H NMR (400 MHz, CD_3CN) δ/ppm 8.89 (s, 4H, H^{B3}), 8.64 (d, *J* 8.0 Hz, 4H, H^{A3}), 8.11 (d, *J* 4.0 Hz, 2H, H^{C4}), 7.95 (dt, *J* 7.9, 1.5 Hz, 4H, H^{A4}), 7.51 (d, *J* 3.9 Hz, 2H, H^{C3}), 7.43 (d, *J* 4.8 Hz, 4H, H^{A6}), 7.29 (d, *J* 3.9 Hz, 2H, $H^{D3/D4}$), 7.23 (d, *J* 3.9 Hz, 2H, $H^{D3/D4}$), 7.18 (m, 4H, H^{A5}). ESI MS *m/z* 1198 $[M-PF_6]^+$.

2.6. Ligand *2*

4′-Ethynyl-2,2′:6′,2″-terpyridine (100 mg, 0.388 mmol), 5-bromo-2,2′-bithiophene (100 mg, 0.408 mmol), $[Pd(PPh_3)_2Cl_2]$ (14 mg, 0.020 mmol) and CuI (4 mg, 0.021 mmol) were dissolved in Et_3N (8 cm^3). The solution was heated under reflux for 48 h. The solvent was then evaporated under reduced pressure. The crude material was dissolved in hexane (200 cm^3). After filtration, solvent from the filtrate was removed under reduced pressure. The crude product was purified by several, sequential column chromatographic separations (see text) (Al_2O_3, hexane:ethyl acetate 1:1), and the third band was collected. Compound **2** was isolated as a yellow solid (45 mg, 0.11 mmol, 28%). M.p. = 152.4 °C. ^{1}H NMR (500 MHz, CD_3CN) δ/ppm 8.70 (d, *J* 4.6 Hz, 2H, H^{A6}), 8.60 (d, *J* 7.9 Hz, 2H, H^{A3}), 8.53 (s, 2H, H^{B3}), 7.85 (dt, *J* 7.8, 1.7 Hz, 2H, H^{A4}), 7.33 (dd, *J* 7.2, 4.8, 0.7 Hz, 2H, H^{A5}), 7.25 (dd, *J* 5.0, 1.0 Hz, 1H, H^{D3}), 7.24 (d, *J* 3.9 Hz, 1H, H^{C4}), 7.21 (d, *J* 3.7 Hz, 1H, H^{D5}), 7.08 (d, *J* 3.8 Hz, 1H, H^{C3}), 7.02 (dd, *J* 3.8, 5.0 Hz, 1H, H^{D4}). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ/ppm 155.8 ($C^{A2/B2}$), 155.7 ($C^{A2/}$