Luminescent molecular wires with 2,5-thiophenediyl spacers linking $\{Ru(terpy)_2\}$ units

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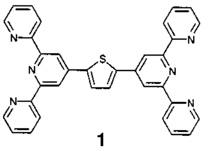
Whereas $\{Ru(terpy)_2\}^{2+}$ salts are essentially non-luminescent in fluid solution luminescent molecular wires with $\{Ru(bpy)_3\}^{2+}$-like activity result when these units are connected by 2,5-thiophenediyl spacers.

Multinuclear oligopyridine complexes are important in metallosupramolecular chemistry and species such as rods or wires,[1] helicates[2] and dendrimers[3] are well established.[4,5] The investigation of photoinduced energy- and electron-transfer in geometrically well defined polynuclear systems allows the electronic and nuclear factors governing these processes to be investigated.[6–8] The exploitation of the spectroscopic (particularly luminescence) properties of transition metal–oligopyridine complexes for ion-sensing,[4,5,9] light-harvesting or energy-collection using high-nuclearity dendrimers is of intense current interest.[6] The $\{Ru(terpy)_2\}^{2+}$ chromophore is often employed in such assemblies[10] even though its luminescence properties are poor (room temperature, MeCN solution: $\phi \approx 10^{-5}$, $\tau \leqslant 0.3 \times 10^{-9}$ s[10,11]) in comparison to $\{Ru(bpy)_3\}^{2+}$. Substituents on the terpy ligand significantly improve the luminescence properties[6,8,10,12] and we now describe a new ligand in which a 2,5-thiophenediyl spacer[13] connecting $\{Ru(terpy)_2\}$-chromophores modifies the properties such that di- and tri-nuclear complexes exhibit $\{Ru(bpy)_3\}^{2+}$-like luminescence.



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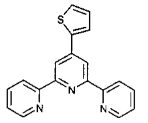

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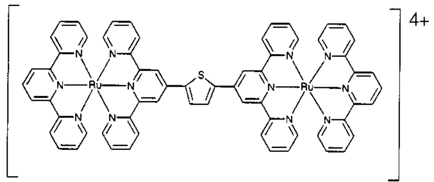
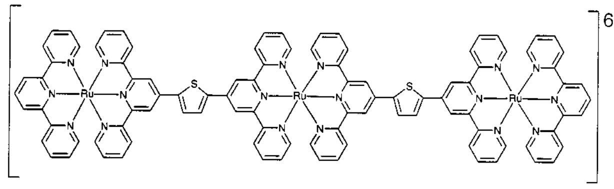


$[(terpy)Ru(\mathbf{1})Ru(terpy)]^{4+}$



$[(terpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(terpy)]^{6+}$

The new dinucleating ligand **1** was prepared in a two step process from 2-acetylpyridine and thiophene-2,5-dicarbaldehyde in *ca.* 30% yield as a white solid.† The reaction of $[Ru(terpy)Cl_3]$ with a stoichiometric amount of **1** in EtOH containing *N*-ethylmorpholine (NEM) gave the mononuclear *ligand-complex* $[(terpy)Ru(\mathbf{1})]^{2+}$ isolated as a red PF_6^- salt in 60% yield [MALDI-TOF MS: *m/z* 1024 (M − PF_6), 879 (M − $2PF_6$)]. All ruthenium complexes were purified by chromatography over SiO_2 using MeCN–H_2O–saturated aqueous KNO_3 mixtures as the mobile phase. The direct reaction of 3 equivalents of $[Ru(terpy)Cl_3]$ with **1** in ethanol containing NEM gave the dinuclear complex $[(terpy)Ru(\mathbf{1})Ru(terpy)][PF_6]_4$ [95%, MALDI-TOF MS: *m/z* 1362 (M − $3PF_6$), 1212 (M − $4PF_6$)] together with $[(terpy)Ru(\mathbf{1})][PF_6]_2$ (39%). The trinuclear complex $[(terpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(terpy)][PF_6]_6$ was obtained in 48% yield from the reaction of the ligand-complex $[(terpy)Ru(\mathbf{1})][PF_6]_2$ with $RuCl_3\cdot 3H_2O$ in $HOCH_2CH_2OH$ containing NEM in a 600 W microwave oven. All of the complexes are electrochemically active, but in their cyclic voltammograms (MeCN, Fc/Fc^+ reference) exhibit only a single Ru(II)/Ru(III) process $\{[(terpy)Ru(\mathbf{1})][PF_6]_2$ and $[(terpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(terpy)][PF_6]_6$ +0.87 V, $[(terpy)Ru(\mathbf{1})Ru(terpy)][PF_6]_4$ +0.88 V$\}$. Preliminary structural data for the complex $[(terpy)Ru(\mathbf{1})Ru(terpy)][PF_6]_2[NO_3]_2$ indicate a planar bridging ligand and a Ru···Ru distance of 14.4 Å.[14]

Table 1 lists room temperature absorption and luminescence data for MeCN solutions of the dinuclear and trinuclear complexes, together with those for mononuclear reference

Table 1 Spectroscopic and photophysical parameters[a]

	Absorption		Luminescence		
	λ_{max}^{abs}/nm	$(10^{-4}\ \varepsilon/dm^3\ mol^{-1}\ cm^{-1})$	λ_{max}^{em}/nm[b]	τ/ns	$10^4\ \phi$[c]
$[Ru(bpy)_3][PF_6]_2$	288(7.7)	452(1.5)	615	170	160
$[Ru(terpy)_2][PF_6]_2$[d]	306(7.2)	490(2.8)	*ca.* 640	0.25	$\leqslant$0.3
$[(terpy)Ru(\mathbf{2})][PF_6]_2$	307(6.5)	486(2.4)	664	5.9	0.53
$[Ru(\mathbf{2})_2][PF_6]_2$	316(5.5)	498(2.9)	664	8.5	0.88
$[(terpy)Ru(\mathbf{1})Ru(terpy)][PF_6]_4$	307(10.6)	517(5.8)	738	340	6.9
$[(terpy)Ru(\mathbf{1})Ru(\mathbf{1})Ru(terpy)][PF_6]_6$	308(15.1)	532(10.8)	736	330	6.8

[a] Room temperature, air-equilibrated acetonitrile solvent. [b] Band maxima for uncorrected spectra. [c] Luminescence efficiency obtained from corrected spectra. [d] Refs. 10 and 11.

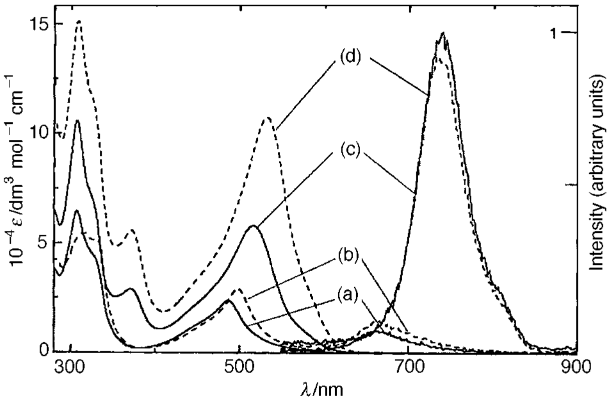


Fig. 1 Absorption and luminescence spectra of the ruthenium complexes: (a) [(terpy)Ru(**2**)][PF_6]$_2$, (b) [Ru(**2**)$_2$][PF_6]$_2$, (c) [(terpy)Ru(**1**(terpy)][PF_6]$_4$ and (d) [(terpy)Ru(**1**)Ru(**1**)(terpy)][PF_6]$_6$; excitation was at 480 nm.

complexes;‡ absorption and luminescence spectra of the complexes are presented in Fig. 1.§ All of the complexes display intense UV absorption bands (306–316 nm, ε = 5–15 10^4 dm^3 mol^{-1} cm^{-1}) and less intense bands in the visible region (485–532 nm, ε = 2.4–11 10^4 dm^3 mol^{-1} cm^{-1}). The former bands are due to ligand centered (^{1}LC) transitions and those in the visible are due to metal-to-ligand charge-transfer (^{1}MLCT).[6,10] For the mononuclear model complexes [(terpy)-Ru(**2**)][PF_6]$_2$ and [Ru(**2**)$_2$][PF_6]$_2$ the 2-thienyl group causes significant changes in the band maximum and minor changes of the band intensity with respect to [Ru(terpy)$_2$][PF_6]$_2$ (Table 1). In contrast, on passing from mononuclear [(terpy)Ru(**2**)][PF_6]$_2$ to the di- and tri-nuclear species, the band associated with the lowest lying ^{1}MLCT transition moves sequentially to longer wavelengths with a concomitant increase in ε (Table 1). This behaviour is consistent with the increasing numbers of {Ru-(terpy)$_2$}$^{2+}$ chromophores and may indicate that the 2,5-thiophenediyl spacer allows some intermetal electronic communication, allowing a stablisation of the MLCT levels through electronic and electrostatic effects.[8,15] The polynuclear complexes also exhibit a band at *ca.* 360 nm not present in the mononuclear compound; we are currently investigating the origin of this band which could arise from CT or LF states.

The excited states responsible for the luminescence are formally triplet Ru → terpy CT levels[10] and the luminescence maxima in Table 1 are consistent with their sequential stabilisation on passing from the mono- to the di- and tri-nuclear complexes (Table 1). What is remarkable is that for the polynuclear species the luminescence lifetime and efficiency increase by two and one order of magnitude, respectively, with respect to the mononuclear complexes. This effect is presumably related to the stabilisation of the cluster of ^{3}MLCT levels responsible for the luminescence leading to a large energy gap between these and the upper lying ^{3}MC levels which offer very effective pathways for non-radiative processes.[15]

The 2,5-thiophenediyl linker is chemically inert, in contrast to polyalkyne spacers, and offers new possibilities for building up high-nuclearity luminescent {Ru(terpy)$_2$}$^{2+}$-based molecular wires with photochemical properties akin to those of {Ru(bpy)$_3$} derivatives. Work is in progress to prepare and study mixed Ru(II)/Os(II) heteropolynuclear species where photoinduced RuOs energy transfer may allow a detailed understanding of the properties of the 2,5-thiophenediyl spacers.

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Notes and references

† **1**: δ_H($CDCl_3$) 8.76 (4H, d, H^{6A}), 8.75 (4H, s, H^{3B}), 8.65 (4H, d, *J* 8.3 Hz, H^{3A}), 7.87 (4H, dt, *J* 7.8, 1.8 Hz, H^{4A}), 7.84 (2H, s, H^{3C,4C}), 7.36 (4H, m, H^{5A}); δ_C($CDCl_3$) 156.2, 155.9, 149.2, 143.2, 142.8, 136.9, 126.9, 124.0, 121.3, 116.9; *m/z* 546.1628 (high resolution: calc. for $C_{34}H_{22}N_6S$, 546.1627).

‡ Full details of ligand **2** and its complexes will be reported later.

§ Absorption and luminescence spectra of dilute solutions (10^{-5} M) in MeCN were recorded with a PE Lambda 5 spectrophotometer and with a Spex Fluorolog II spectrofluorimeter (λ_{exc} = 480 nm) respectively. Uncorrected luminescence band maxima (±2 nm) are quoted. Corrected band maxima and luminescence quantum efficiencies (±20%) were determined using the procedure described in ref. 15. Luminescence lifetimes (±8%) were obtained with IBH single-photon counting equipment or with a picosecond fluorescence spectrometer based on a ND : YAG laser (Continuum PY62-10) and a Hamamatsu C1587 streak camera.[15]

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