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# Synthesis, electrochemistry, and photophysical properties of binuclear ruthenium(II)–terpyridine complexes comprising redox-active ferrocenyl spacer

Teng-Yuan Dong *, Mei-Ching Lin, Shu-Wei Chang, Chih-Chien Ho, Shu-Fan Lin, Liangshiu Lee

*Department of Chemistry, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan*

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**Abstract**

In attempting to perturb the electronic properties of the spacer, we now describe an interesting example of $Ru^{2+}$–tpy (tpy = terpyridine) complexes with 1,1′-bis(ethynyl)polyferrocenyl moiety attached directly to the 4′-position of the tpy ligand (tpy–C≡C–$(fc)_n$–C≡C–tpy; fc = ferrocenyl; $n = 2$–3). Complexes of $Ru^{2+}$–tpy have room-temperature luminescence in $H_2O/CH_3CN$ (4/1) solution. The ground-state HOMO and LUMO energies were probed by electrochemical measurements and the excited-state photophysical properties were probed by UV–Vis absorption spectroscopy and luminescence spectroscopy. The redox behavior of $[(tpy)Ru^{II}$–tpy–C≡C–$(fc)_n$–C≡C–tpy–$Ru^{II}(tpy)]^{4+}$ complex is dominated by the $Ru^{2+}/Ru^{3+}$ redox couple ($E_{1/2}$ from 1.35 to 1.39 V), $Fe^{2+}/Fe^{3+}$ redox couples ($E_{1/2}$ from 0.4 to 1.0 V) and $tpy/tpy^{-}/tpy^{2-}$ redox couples ($E_{1/2}$ from −1.3 to −1.5 V). Electrochemical data, UV absorption and emission spectra indicate that the π-delocalization in the spacer is enhanced by the insertion of ethynyl unit. Interestingly, the insertion of ethynyl unit into the main chain causes a dramatic increase of phosphorescence yield ($1.48 \times 10^{-4}$ for $n = 2$; $1.13 \times 10^{-4}$ for $n = 3$), triplet lifetime (67 ns for $n = 2$; 24 ns for $n = 3$), and emission intensity. The biferrocenyl spacer can be converted into mixed-valence biferrocenium spacer, which gives a more effective π-delocalization along main chain, by selective chemical oxidation of ferrocenyl unit. In deoxygenated $H_2O/CH_3CN$ (4/1) solution at 25 °C, the oxidized complex of $[(tpy)Ru^{II}$–tpy–C≡C–$(fc)_2$–C≡C–tpy–$Ru^{II}(tpy)]^{5+}$ is nonemissive. The presence of lower energy ferrocenium-centered $[Ru_a^{II}$–$tpy^{-}$–$fc^{III}$–$fc^{III}$–tpy–$Ru_b^{II}]$excited-state provides an additional channel for excited-state decay. The mixed-valence biferrocenium center acts as an efficient quencher for the MLCT excited-state.
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*Keywords:* Molecular wire; Time-resolved spectroscopy; Luminescence; Electrochemistry; Metallocene

## 1. Introduction

Over the past decade, complexes containing unsaturated form of organic linear spacers end-capped by various transition metal centers have been proposed as models for molecular wires. In this context, end-capping of unsaturated organic spacers with redox-active groups, such as ruthenium(II) polypyridine metal centers, have been most studied where they are intended to promote long-range electron or energy transfer [1–3]. An important issue concerns how best to design the spacer that permits controlled transfer of electron or energy along the molecular axis. In principle, this issue can be resolved by careful manipulation of the energetics of the end-capping metal centers and the connecting spacer. In general, the design principle combines the most unsaturated form of organic linear spacer with the most stable redox- or photo-active terminals [4–21]. The design of interesting bis-2,2′:6′,2″-terpyridine ligands (tpy–tpy) by connecting two terpyridine moieties via a rigid organic spacer attached to their 4′-positions has found applications in energy conversion systems such as dye-sensitized solar cells [4] and electroluminescent devices [5]. The tpy–tpy ligands which have been reported

* Corresponding author. Tel.: +886 7 5253937; fax: +886 7 525 3908.
*E-mail address:* dty@mail.nsysu.edu.tw (T.-Y. Dong).

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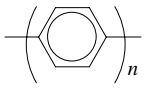
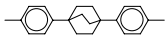
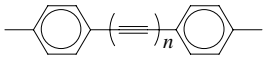
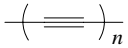
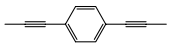
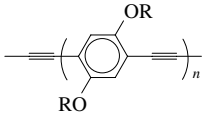
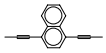
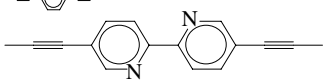
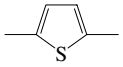
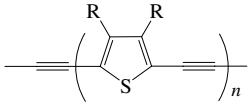
and used further to make dinuclear ruthenium(II) complexes are illustrated in Table 1.

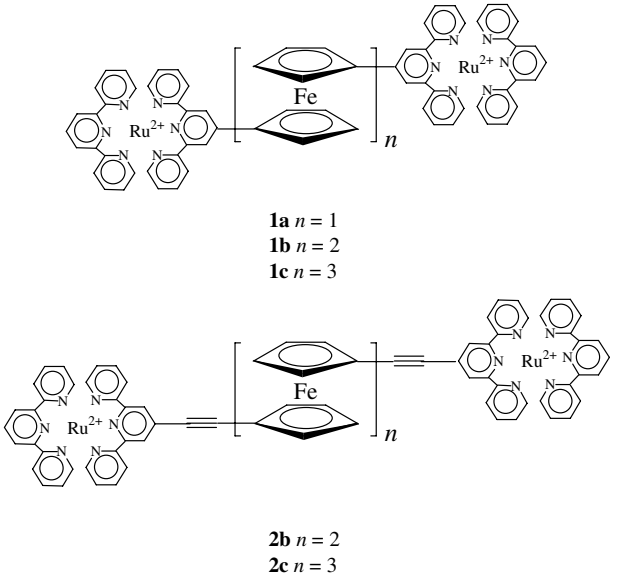
Our design principle for a wire-like molecule has to fulfill following criteria: (i) organometallic redox-active spacer to enhance the capability of transfer information along the molecular axis and (ii) modular synthetic approach to control the length of the wire [21,22]. We have earlier published electrochemical and photophysical studies for a series of complexes containing bis-(2,2′:6′,2″-terpyridyl)polyferrocene redox-active spacers end-capped with photoactive $Ru^{2+}$–terpyridine terminals to address these issues ($[(tpy)Ru^{II}–(tpy–(fc)_n–tpy)–Ru^{II}(tpy)]^{4+}$ complexes **1a**–**c** in Scheme 1; fc = ferrocenyl; $n = 1$–3) [22]. The polyferrocenyl spacers themselves are insulators, but can be converted into semiconducting materials by selective oxidation of ferrocenyl units to form mixed-valence polyferrocenium spacers. In our earlier reports, a rapid intramolecular electron-transfer process in mixed-valence biferrocenium was observed [23]. Thus, mixed-valence polyferrocenium spacers, which possibly give an effective π-delocalization along main chain, can serve as model systems for molecular wires. The redox behavior of **1a**–**c** was dominated by the $Ru^{2+}/Ru^{3+}$ redox couple ($E_{1/2}$ from 1.35 to 1.38 V), $Fe^{2+}/Fe^{3+}$ redox couples ($E_{1/2}$ from 0.4 to 1.0 V) and $tpy/tpy^{-}/tpy^{2-}$ redox couples ($E_{1/2}$ from −1.3 to −1.5 V).

Table 1
Photophysical properties of the various $(tpy)Ru^{2+}$–tpy-spacer-tpy$Ru^{2+}$(tpy) complexes at 25 °C ($\lambda_{max}^{em}$: emission maximum; $\Phi$: emission quantum yield; $\tau$: triplet lifetime)

| Spacer | $n$ | $\lambda_{em}$ | $\tau$ (ns) | $\Phi \times 10^4$ |
|---|---|---|---|---|
|  | 0 | n.d. | | |
| | 1 | n.d. | | |
| | 2 | n.d. | | |
|  | | n.d. | | |
|  | 1 | 670 | 3.2 | <1 |
| | 2 | 665 | 5.5 | <1 |
|  | 1 | 722 | 565 | 14 |
| | 2 | 735 | 720 | 23 |
|  | | 685 | 110 | 26 |
|  | 1 | 693 | 135 | 28 |
| | 2 | 695 | 125 | 25 |
| | 3 | 692 | 140 | 30 |
| | 4 | 694 | 130 | 27 |
| | 5 | 695 | 130 | 28 |
|  | | 702 | 475 | 40 |
|  | | 678 | 100 | 6 |
|  | | 738 | 340 | 6.9 |
|  | 1 | 713 | 140 | 2.38 |
| | 2 | 730 | 164 | 0.42 |
| | 3 | 732 | 135 | 0.14 |
| | 4 | 726 | 121 | 0.08 |
| | 5 | 703 | 99 | 0.18 |

Attachment of ferrocenyl moiety to the 4′-position of tpy unit in the $Ru^{2+}$ complexes has minimal influence on the $Ru^{2+}/Ru^{3+}$ redox potential (from 1.35 to 1.38 V). These $Ru^{2+}$-centered oxidation processes are more positive by at least 80 mV compared to that of monomeric $[Ru(tpy)_2]^{2+}$ complex. For the binuclear $Ru^{2+}$ complexes of tpy–$(fc)_n$–tpy, a single wave was found for the $Ru^{2+}/Ru^{3+}$ redox couple. It might indicate that the electronic coupling between the two $Ru^{2+}$ centers is relatively weak. Attention has also been focused on complexes illustrated in Table 1 in which a single wave of the $Ru^{2+}/Ru^{3+}$ redox couple was also found. Recently, the physical properties of a series of linearly arranged $Ru^{2+}$ complexes, $[(tpy)Ru^{II}–(tpy–(DEDBT)_n–tpy)–Ru^{II}(tpy)]^{4+}$ ($n = 1$, 2, 3, 4, 5), featuring $Ru^{2+}$–tpy chromophores connected to π-conjugated organic 2,5-diethynyl-3,4-dibutylthiophene oligomeric fragments (DEDBT), were reported [16]. The distance between two chromophoric centers was estimated from 18.5 Å ($n = 1$) to 42 Å ($n = 5$). In these diethynyl-thiophene bridged complexes, a single wave of the $Ru^{2+}/Ru^{3+}$ redox couple was also found at ~1.36 V. The electronic coupling between the $Ru^{2+}$ centers in the tpy–DEDBT–tpy system is also relatively weak.

In attempting to perturb the electronic properties of the spacer, we now describe an interesting example of $Ru^{2+}$–tpy complexes (complexes **2b**–**c** in Scheme 1) with 1,1′-bis(ethynyl)polyferrocenyl moiety attached directly to the 4′-position of tpy ligand (tpy–C≡C–$(fc)_n$–C≡C–tpy; $n = 2$–3). Complexes of **2b**–**c** have room-temperature luminescence. We expect that the insertion of ethynyl unit in the main chain could enhance the effective π-delocalization. The preparation, structural determination, and electrochemical characteristics of the $Ru^{2+}$ free tpy–C≡C–$(fc)_n$–C≡C–tpy spacer were reported in our previous paper [24]. Spacers of tpy–C≡C–$(fc)_n$–C≡C–tpy have the capa-




**1a** $n = 1$
**1b** $n = 2$
**1c** $n = 3$

**2b** $n = 2$
**2c** $n = 3$

Scheme 1. Structures of the discussed ferrocenyl-bridged $Ru^{2+}$ complexes (counterion: $PF_6^-$).

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