

Synthesis and Photochemical Properties of a New Substituted Phenol Covalently Linked to Ruthenium (II) *Tris*-bipyridine Containing Four Ester Groups as Sensitizer

Feng SHI, Hong Yang LI, Xiao Jun PENG*, Rong ZHANG, Xiao Qiang CHEN,
Jiang Li FAN, Li Cheng SUN*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012

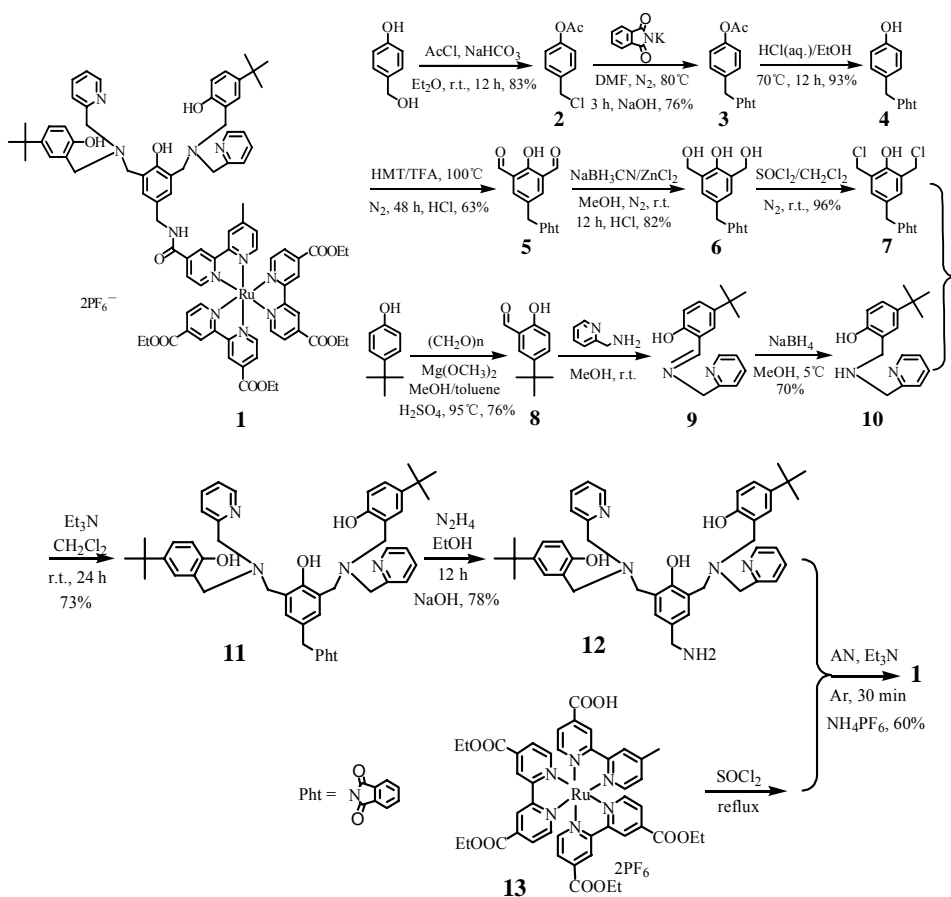
Abstract: As photosensitizer for solar cell, a new ruthenium (II) complex with four ester groups had been synthesized, in which a phenol substituted by {(2-hydroxy-5-*tert*-butylbenzyl)(pyridyl-2-methylamino)methyl} is covalently linked to ruthenium (II) *tris*-bipyridine. The structures of the new compounds were confirmed by NMR and ESI-MS spectra. The electrochemical and photochemical properties were also studied.

Keywords: Photosensitizer, ruthenium complex, phenolate ligand, nanocrystalline TiO₂, solar cell.

Much research efforts have aimed at exploring light-induced charge separation in natural or artificial molecular systems and designing model systems, which are capable of converting light into chemical and electric energy¹. These efforts have largely been motivated by the impressive solar energy devices developed by Grätzel and co-workers with ruthenium polypyridyl sensitizers anchored to porous colloidal TiO₂ films². Polypyridyl Ru(II) complexes can efficiently absorb visible light, pump an electron into the conduction band of TiO₂ and accept an electron from the solution redox couple, and repeat the cycle, thus they have high yield of the conversion of solar light into electricity. Charge recombination from the nanocrystalline TiO₂ to sensitizer is a crucial process limiting the efficiency of a regenerative solar cell^{3,4}. This electron-sensitizer recombination flux can be reduced if the lifetime of the charge-separated state (S⁺ | (e⁻) TiO₂ S | TiO₂) is increased. Based on our former work⁵, long-lived photo-induced charge separation had been obtained by replacing the simple sensitizer with molecular dyads as donor. Now, a new dyad based on ruthenium (II) *tris*-bipyridine was designed. The hydrogen-bonding between the arms and substituted phenol of this molecule is expected to promote the electron transfer rate from the phenol to photo-generated Ru (III) analogous to the proposed interaction between tyrosine and His 190 in PSII and the substituted phenol can stabilize the "hole" at Ru (III) in the MLCT state after the electron transfer from Ru (II) to acceptor (such as TiO₂), all which could compete with the charge recombination between oxidized sensitizer and reduced semiconductor in order to provide a possibility for a long-lived charge separation.

* E-mail: pengxj@chem.dlut.edu.cn

Scheme 1



Experimental

Complex **1** was synthesized *via* the route presented in **Scheme 1**. 4-Hydroxybenzyl alcohol was treated with acetyl chloride followed by potassium phthalimide to obtain **3**. After substitution with phthalimide, the acetyl group was hydrolyzed under acidic conditions to form **4**. Through functionalization in the *ortho*-positions of the phenol, **5** was achieved by formylation *via* the Duff reaction^{6,7}. **5** was reduced to the corresponding alcohol **6** with NaBH₃CN/ZnCl₂^{8,9}. **6** was then chlorinated with thionyl chloride to form **7**. The synthesis of **8** was described by Aldred *et al.*¹⁰ **8** was successfully converted to the corresponding Schiff base **9** by condensation with 2-(aminomethyl)pyridine. **10** was obtained by the reduction of **9** with NaBH₄. Reaction between **10** and **7** gave the substituted phenol **11**. Mild hydrolytic condition gave the desired amine **12** in 78 % yield. The compound **13** was synthesized according to the literature¹¹. The amine **12** was then linked to the ruthenium part **13** *via* an amide bond to give **1**.

Results and Discussion

The UV-Vis absorption spectra were recorded with HP8453. Emission spectra were obtained by PTI-700 fluorescent spectrophotometer. Cyclic voltammetry (CV) was performed on BAS100W potentiostat.

Table 1 The molar extinction coefficients and band assignments of UV-Visible absorption

Compound	λ_{ab} / nm	$\epsilon / 10^3 \cdot \text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$	Band Assignment
[Ru(bpy) ₃] ₂ PF ₆	450	19.2	d $\pi_M \rightarrow \pi_L^*$ (bipyridyl ligand)
	360	10.0	$\pi_M \rightarrow \delta_M^*$ (metal)
	288	76.8	$\pi_L \rightarrow \pi_L^*$ (bipyridyl ligand)
	244	32.3	d $\pi_M \rightarrow \pi_L^*$ (bipyridyl ligand)
1	474	24.5	d $\pi_M \rightarrow \pi_L^*$ (bipyridyl ligand)
	362	17.5	$\pi_M \rightarrow \delta_M^*$ (metal)
	307	67.5	$\pi_L \rightarrow \pi_L^*$ (bipyridyl ligand)
	244	45.0	d $\pi_M \rightarrow \pi_L^*$ (bipyridyl ligand)

The maximum of the MLCT band at 474 nm of **1** is red-shifted by 24 nm compared to the typical MLCT band in [Ru(bpy)₃]²⁺ (λ_{max} at 450 nm). Similar red shifts also occurred at the LC band¹², which was possible to improve the absorption efficiency in the harvesting of sunlight.

Table 2 Fluorescent data in degassed acetonitrile at room temperature

Compound	λ_{ex} / nm	λ_{em} / nm	Φ_{em}
[Ru(bpy) ₃] ₂ PF ₆	450	608	0.062
1	474	642	0.138

The red shift of the MLCT band and the higher luminescence quantum yield compared to [Ru(bpy)₃]₂PF₆ are due to the presence of the carboxylic acid groups and the donor ligand; the withdrawing nature of the carboxylic acids groups lowers the energy of the π^* transition to occur at lower energy, and the donor ligand destabilize the metal t_{2g} orbital to tune the spectra.

Table 3 Electrochemical data of [Ru(bpy)₃-phenol]²⁺ complex in acetonitrile

Compounds as PF ₆ ⁻ salts	$E_{1/2} / \text{V}^{[a,b]}$			
	[Ru(bpy) ₃] ^{0/+}	[Ru(bpy) ₃] ⁺⁰	[Ru(bpy) ₃] ^{2+/+}	[Ru(bpy) ₃] ^{3+/2+}
1	-1.314	-1.519	-1.866	1.286
[Ru(bpy) ₃] ²⁺	-1.698	-1.911	-2.177	0.944

The first reduction potential for the ligand of compound **1** occurs at $-1.314 \text{ V vs Fc}^{+/0}$, which is about 400 mV less negative than that of the compound [Ru(bpy)₃]₂PF₆, and the

oxidation potential of the Ru³⁺/Ru²⁺ was also enhanced, which provide high driving-force for electron transfer.

The results presented that the sensitizer had high redox potential, broad absorbance of spectra, which is thus interesting for further photoelectrochemical study to analyze its performance as photosensitizer for solar cell.

Acknowledgment

This work was supported by “973 program” of the Ministry of Science and Technology of China and the National Natural Science Foundation of China (Project 20376010, 20128005).

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Received 20 October, 2003