

Studies of a Series of Novel Rhenium(I) Bipyridyl Dyes for Solar Cells

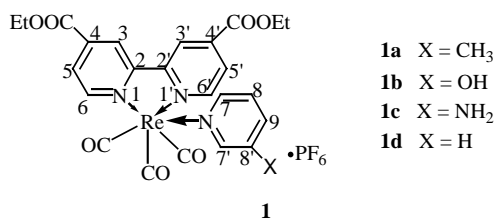
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Abstract: A series of novel rhenium(I) 2,2'-bipyridyl complexes [*fac*-Re(4,4'-di-COOEt-bpy)-(CO)₃(Xpy)PF₆], where bpy is 2,2'-bipyridine, py is pyridine and X is 3-methyl, 3-hydroxy, or 3-amino, were synthesized, their photophysical and electrochemical properties were studied. The Re(II/I) oxidation potentials decreased as the X group becomes more electron donating from H to 3-methyl, 3-hydroxy, or 3-amino, which might be a very convenient ways for adjusting the electron transfer driving force.

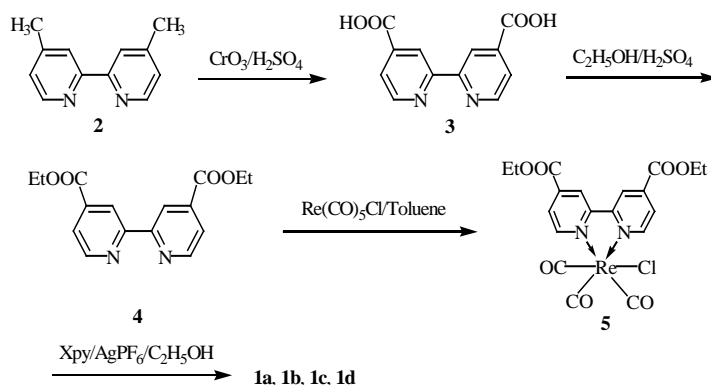
Keywords: Rhenium(I) bipyridyl complex, redox potential, electron transfer driving force.

Rhenium(I) bipyridyl complexes¹ could be used as photosensitizers in the dye-sensitized nanocrystalline photovoltaic solar cells² due to their high stability and intense metal-to-ligand charge transfer transitions. The Re(II/I) oxidation potentials are significantly positive which could not only provide a larger driving force than the ruthenium(II) bipyridyl complexes, such as N3 dyes³, for interfacial charge recombination, but also result in serious backward electron transfer and reduce the IPCE (Incident Photon-to-current Conversion Efficiency) of the cells. In order to find a simple way to adjust the electron transfer driving force by ligand modification, we have synthesized a series of novel complexes **1a**, **1b**, and **1c** (see structures below) by introducing electron-donating group X (X = CH₃, OH, or NH₂) on the pyridyl ligand, the result demonstrated that the Re(II/I) oxidation potential could be decreased as the X group becomes more electron donating, which might be a potential means for improving the efficiency of the cells. In this letter, we want to report the synthesis, the electrochemical and photophysical properties of the complexes **1a-1c** in comparison with that of the existing non-substituted complex **1d**⁴.



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Scheme 1

Table 1 UV-Visible and fluorescent spectral data in acetonitrile at 23 ± 2 °C

Complex	λ_{max} (nm)	ϵ ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	τ (ns)	ϕ_{em} (10^{-3})
1a	381	8.1	383	621	71	5.6
1b	382	8.3	383	616	65	5.0
1c	382	8.5	383	613	0.7	0.5
1d	380	8.5	383	616	80	5.8

As shown in **Scheme 1**, 4,4'-dimethyl-2,2'-bipyridine **2** was oxidized to get **3** in 92% yield, then **3** was esterified with absolute ethanol to give **4** in 93% yield. A mixture of $\text{Re}(\text{CO})_5\text{Cl}$ and **4** in toluene was refluxed for 1 h to give an orange solid residue of crude **5**, which was further reacted with different Xpy ligand, resulted in the corresponding **1a**, **1b**, **1c** and **1d** in a good yield.

They all show typical absorption properties of the rhenium(I) bipyridyl complex⁵. The intense low-energy absorption bands in the spectra were assigned to metal-to-ligand charge-transfer (MLCT), namely the transition of $d\pi(\text{Re}) \rightarrow \pi^*(\text{bipyridyl ligand})$. The MLCT absorption maxima, molar extinction coefficients and the fluorescent spectral data are listed in **Table 1**.

As the X group becomes more electron donating from H to 3-methyl, 3-hydroxy, or 3-amino, the MLCT absorption maximum and the emission maximum were changed little, the quantum yield ϕ and the fluorescence lifetime τ were decreased gradually, which was in accordance with the energy gap law⁶.

A chemically irreversible oxidation wave appeared at about 1.5 V was for the $\text{Re}(\text{II})/\text{Re}(\text{I})$ couple, and the reversible reduction wave at about -1.4 V was a bpy-based one electron reduction⁷. The $\text{Re}(\text{II}/\text{I})$ oxidation potential was decreased as the X group becomes more electron donating from H to 3-methyl, 3-hydroxy, or 3-amino; but the the bpy ligand reduction potential was changed little as the electron-donating groups introduced, some of the larger wave such as that in **1c** was mainly caused by the reduction potential of the 3-hydroxypyridyl ligand overlapped, which means that the adjusting of the $\text{Re}(\text{II}/\text{I})$ oxidation potential through ligand modification has nearly no in-

Table 2 Redox potentials of complex **1** (vs. Ag/Ag⁺)

Complex	1a	1b	1c	1d
Re(II/I) (V)	1.53	1.51	1.47	1.53
bpy ^{0/-} (V)	-1.44	-1.43	-1.46	-1.44

fluence on the bpy ligand reduction potential, that could be much satisfied. The reasons might be that the electron-donating group increased the electronic density of the N atom on the pyridine ring, which neutralized the positive charge of the rhenium to some extent, decreased the energy level of the $d\pi(\text{Re})$ orbital, but generated little affection on the energy level of the bpy ligand. The redox potentials measured by cyclic voltammetry are tabulated in Table 2.

NMR spectra were obtained on a Varian INOVA 400 MHz spectrometer, using TMS as internal standard. ESI-MS was performed on a HP1100 LC/MSD. HRMS were detected on a Q-ToF Micromass spectrometer (England). The absorption spectra were recorded on a HP 8453 spectrophotometer and the fluorescent spectra were recorded using a PTI-C-700 fluorometer. Cyclic voltammetry was recorded on a BAS 100 B/W instrument using a three-electrode system consisting of a Ag/Ag⁺ (0.01 mol/L AgNO₃, 0.1 mol/L tetrabutylammonium hexafluorophosphate TBAPF₆, CH₃CN) as reference electrode, a platinum wire as counter electrode and a freshly polished glassy carbon (diameter 2 mm) as working electrode. The data are as follows.

1a: bright yellow powder, yield 92 %; ¹H NMR (acetone-d₆, δ ppm): 1.43 (t, 6H, J = 7.0 Hz, -OCH₂CH₃), 2.23 (s, 3H, -CH₃), 4.50 (q, 4H, J = 7.0 Hz, -OCH₂CH₃), 7.34 (t, 1H, J = 5.8 Hz, H₈), 7.82 (d, 1H, J = 7.2 Hz, H₉), 8.31 (d, 1H, J = 5.2 Hz, H₇), 8.40 (d, 2H, J = 5.6 Hz, H₅, H₅), 8.46 (s, 1H, H₇), 9.20 (s, 2H, H₃, H₃), 9.71 (d, 2H, J = 5.6 Hz, H₆, H₆); ¹³C NMR (acetone-d₆, δ ppm): 14.26 (-OCH₂CH₃), 18.00 (-CH₃), 63.50 (-OCH₂CH₃), 125.14 (C₃, C₃), 127.21 (C₈), 128.99 (C₅, C₅), 138.35 (C₈), 141.55 (C₉), 142.69 (C₄, C₄), 149.94 (C₇), 152.86 (C₇), 156.05 (C₆, C₆), 157.36 (C₂, C₂), 163.55 (-COO-), 191.53 (CO), 195.89 (CO); ESI-MS Positive: [M-PF₆]⁺ (m/z 664.1); HRMS calcd. for C₂₅H₂₃N₃O₇Re: 664.1093, found: 664.1081.

1b: yellow powder, yield 91%; ¹H NMR (DMSO-d₆, δ ppm): 1.44 (t, 6H, J = 7.0 Hz, -OCH₂CH₃), 4.50 (q, 4H, J = 7.0 Hz, -OCH₂CH₃), 7.19 (dd, 1H, J = 8.5 Hz, 5.4 Hz, H₈), 7.29 (ddd, 1H, J = 8.5 Hz, 2.3 Hz, 1.1 Hz, H₉), 7.80 (d, 1H, J = 2.3 Hz, H₇), 7.82 (d, 1H, J = 5.4 Hz, H₇), 8.26 (dd, 2H, J = 5.6 Hz, 1.4 Hz, H₅, H₅), 9.18 (s, 2H, H₃, H₃), 9.50 (d, 2H, J = 5.6 Hz, H₆, H₆), 10.51 (d, 1H, -OH); ¹³C NMR (DMSO-d₆, δ ppm): 13.75 (-OCH₂CH₃), 62.24 (-OCH₂CH₃), 124.16 (C₃, C₃), 125.93 (C₉), 126.85 (C₈), 127.69 (C₅, C₅), 139.38 (C₇), 140.98 (C₄, C₄), 142.34 (C₇), 154.62 (C₆, C₆), 155.45 (C₈), 155.54 (C₂, C₂), 162.19 (-COO-), 190.14 (CO), 194.49 (CO); ESI-MS Positive: [M-PF₆]⁺ (m/z 666.1); HRMS calcd. for C₂₄H₂₁N₃O₈Re: 666.0886, found: 666.0878.

1c: yellow powder, yield 93%; ¹H NMR (acetone-d₆, δ ppm): 1.43 (t, 6H, J = 7.0 Hz, -OCH₂CH₃), 4.51 (q, 4H, J = 7.0 Hz, -OCH₂CH₃), 5.30 (s, -NH₂), 7.05 (dd, 1H, J = 5.4 Hz, H₉), 7.15 (d, 1H, J = 5.0 Hz, H₈), 7.64 (d, 1H, J = 5.4 Hz, H₇), 7.94 (s, 1H, H₇), 8.39 (d, 2H, J = 5.6 Hz, H₅, H₅), 9.23 (s, 2H, H₃, H₃), 9.63 (d, 2H, J = 5.4 Hz, H₆, H₆); ¹³C NMR (acetone-d₆, δ ppm): 14.30 (-OCH₂CH₃), 63.53 (-OCH₂CH₃), 124.21 (C₉),

125.17 (C₃, C₃), 127.57 (C₈), 128.92 (C₅, C₅), 138.59 (C₇), 140.37 (C₇), 142.66 (C₄, C₄), 148.09 (C₈), 155.86 (C₆, C₆), 157.38 (C₂, C₂), 163.55 (–COO–), 194.96 (CO), 196.26 (CO); ESI-MS Positive: [M-PF₆]⁺ (*m/z* 665.1); HRMS calcd. for C₂₄H₂₂N₄O₇Re: 665.1046, found: 665.1055.

1d: bright yellow powder, yield 91%; ¹H NMR (DMSO-d₆, δ ppm): 1.43 (t, 6H, J = 7.2 Hz, –OCH₂CH₃), 4.49 (q, 4H, J = 7.2 Hz, –OCH₂CH₃), 7.42 (dd, 2H, J = 7.6 Hz, 6.5 Hz, H₈, H₈), 7.97 (t, 1H, J = 7.6 Hz, H₉), 8.25 (dd, 2H, J = 5.8 Hz, 1.1 Hz, H₅, H₅), 8.41 (dd, 2H, J = 6.5 Hz, 1.4 Hz, H₇, H₇), 9.16 (d, 2H, J = 1.1 Hz, H₃, H₃), 9.53 (d, 2H, J = 5.8 Hz, H₆, H₆); ¹³C NMR (DMSO-d₆, δ ppm): 13.87 (–OCH₂CH₃), 62.41 (–OCH₂CH₃), 124.22 (C₃, C₃), 126.74 (C₈, C₈), 127.78 (C₅, C₅), 139.90 (C₉), 141.00 (C₄, C₄), 151.70 (C₇, C₇), 154.93 (C₆, C₆), 155.52 (C₂, C₂), 162.45 (–COO–), 190.52 (CO), 194.58 (CO); ESI-MS Positive: [M-PF₆]⁺ (*m/z* 650.1); HRMS calcd. For C₂₄H₂₁N₃O₇Re: 650.0937, found: 650.0953.

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