

Synthesis of Two Novel Rhenium(I) Bipyridyl Photosensitive Dyes

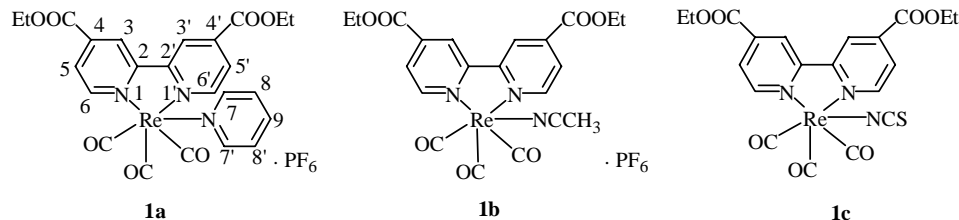
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Abstract: Two novel rhenium(I) 2, 2'-bipyridyl complexes, [(4,4'-di-COOEt-bipy) Re(CO)₃(NCCH₃)PF₆] and [(4,4'-di-COOEt-bipy) Re(CO)₃(NCS)], a model complex [(4,4'-di-COOEt-bipy) Re(CO)₃(pyridine)PF₆], were synthesized. Their ground state electronic spectra and emission spectra were measured in acetonitrile. The MLCT absorption maximum of the complex exhibited a considerable red shift as the ligand changed from pyridine to CNCH₃, or SCN.

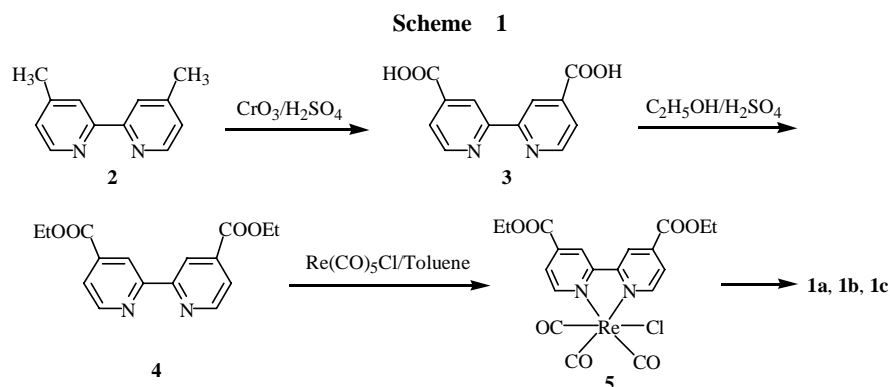
Keywords: Rhenium(I) 2, 2'-bipyridyl complex, photosensitizer, red shift.

Rhenium(I) bipyridyl complexes could be useful as photosensitizers in the nanocrystalline photovoltaic cells (NPC)¹, due to their high stability and intense metal-to-ligand charge transfer transitions². However, rhenium(I) bipyridyl complexes generally absorb light in the blue and ultraviolet regions, so they could not get efficient sunlight harvesting and solar energy conversion. Meyer and coworkers have synthesized the trifluoromethanesulfonate of **1a**³ (see structures below) but it showed a poor MLCT absorption maximum at 380 nm. In order to find a way to enlarge the absorption band range, we have designed and synthesized two novel complexes **1b** and **1c** by ligand modification. **1a** was also synthesized as a model in the meantime. In this paper, we report the synthesis, characterization and the ground state electronic spectra and emission spectra of the complexes **1a**, **1b** and **1c**.



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 1 mmol of Re(CO)₅Cl and **4** in toluene was refluxed for 1 h to give an orange

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solid residue of crude **5**, it was further reacted with different ligands, which resulted in the corresponding **1a**, **1b** and **1c** in a good yield.

NMR spectra were obtained on a Varian INOVA 400 MHz spectrometer, using TMS as internal standard. The electrospray ionization mass spectrometer (ESI-MS) experiments were performed on a HP1100 LC/MSD. IR spectra were acquired on a JASCO FT-IR 430 spectrometer. The absorption spectra were recorded on a HP 8453 spectrophotometer and the emission spectra were recorded using a PTI-C-700 fluorometer.

4,4'-Dicarboxyl-2,2'-bipyridine 3: As shown in **Scheme 1**, this compound was prepared according to the literature⁴. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.90 (dd, *J* = 4.8 Hz and 2H, 1.6 Hz, H₅, H₅), 8.83 (s, 2H, H₃, H₃), 8.90 (m, 2H, H₆, H₆).

4,4'-Bis(ethoxycarbonyl)-2,2'-bipyridine 4: The powder of **3** (0.35 g, 1.43 mmol) was suspended in a solution of 20 mL absolute ethanol and 0.8 mL of concentrated H₂SO₄ and refluxed for 10 h, then the solution was cooled to room temperature and poured into a mixture of ice/water. 25% aqueous NaOH solution was added under vigorous stirring until the solution became neutral, the white solid precipitate was collected by filtration, washed thoroughly with water and dried to give crude **4**. The product was recrystallized twice from 95% ethanol, yielding 0.40 g (93%) of white needle crystals with melting point at 160-161 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 1.40 (t, 6H, *J* = 7.0 Hz, -OCH₂CH₃), 4.42 (q, 4H, *J* = 7.0 Hz, -OCH₂CH₃), 7.89 (d, 2H, *J* = 4.5 Hz, H₅, H₅), 8.82 (s, 2H, H₃, H₃), 8.89 (d, 2H, *J* = 4.5 Hz, H₆, H₆); ESI-MS Positive: [M+H]⁺ (*m/z* 301.1).

Synthesis of 1a: The procedure for preparation of **1a** was according to a modification of the method described by Brent MacQueen and Schanze⁵. 1 mmol of Re(CO)₅Cl and 1 mmol of **4** were dissolved in 150 mL of toluene and the solution was refluxed for 1 h, the solvent was evaporated under vacuum, and an orange solid residue of crude **5** was obtained. It was redissolved in ethanol (20 mL) without purification, and 1.5 mmol of AgPF₆ together with 1.5 mmol of pyridine were added. The mixture was refluxed for 1 h then the ethanol was evaporated and the product was redissolved in 50 mL of CH₂Cl₂, the precipitate (AgCl) formed during the reaction and was removed by filtration and the CH₂Cl₂ was then evaporated. Purification was made by column chromatography on silica gel using CH₂Cl₂:CH₃OH 80:1 as eluent. The yield is 91%.

UV-Vis (CH₃CN) λ_{\max} 380 nm; ¹H NMR (δ ppm, DMSO-*d*₆) : 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, *H*₈, *H*₈), 7.97 (t, 1H, *J* = 7.6 Hz, *H*₉), 8.25 (dd, 2H, *J* = 5.8 Hz, 1.1 Hz, *H*₅, *H*₅), 8.41 (dd, 2H, *J* = 6.5 Hz, 1.4 Hz, *H*₇, *H*₇), 9.16 (d, 2H, *J* = 1.1 Hz, *H*₃, *H*₃), 9.53 (d, 2H, *J* = 5.8 Hz, *H*₆, *H*₆); ¹³C NMR (δ ppm, DMSO-*d*₆) : 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); IR (KBr) ν : 2038, 1936; ESI-MS Positive: [M-PF₆]⁺ (*m/z* 650.1).

Synthesis of **1b**: **1b** was prepared by refluxing **5** in CH₃CN containing excess AgPF₆ for 8 h under Ar. AgCl was removed by filtration and the solvent was evaporated⁶. Purification was made by column chromatography on silica gel using CH₃CN:H₂O:KNO₃ (saturated) 1000:1:1 as eluent. The yield is 85%. UV-Vis (CH₃CN) λ_{\max} 402 nm; ¹H NMR (δ ppm, CDCl₃) : 1.49 (t, 6H, *J* = 7.2 Hz, -OCH₂CH₃), 2.07 (s, 3H, CNCH₃), 4.55 (q, 4H, *J* = 7.2 Hz, -OCH₂CH₃), 8.08 (d, 2H, *J* = 5.8 Hz, *H*₅, *H*₅), 8.83 (s, 2H, *H*₃, *H*₃), 9.19 (d, 2H, *J* = 5.6 Hz, *H*₆, *H*₆); ¹³C NMR (δ ppm, CDCl₃) : 14.45 (-OCH₂CH₃), 29.85 (NCCH₃), 63.35 (-OCH₂CH₃), 117.83 (NCCH₃), 123.12 (C₃, C₃), 126.74 (C₅, C₅), 140.61 (C₄, C₄), 153.98 (C₆, C₆), 156.22 (C₂, C₂), 162.90 (-COO-), 188.35 (CO), 196.58 (CO); IR (KBr) ν : 2150, 2030, 1911; ESI-MS Positive: [M-PF₆]⁺ (*m/z* 612.1).

Synthesis of **1c**: **1c** was synthesized by refluxing a solution of NaNCS (1 mmol, 81.07 mg, in 5 mL of H₂O) and **5** (0.1 mmol, 60.6 mg, in 10 mL DMF) for 6 h⁷, then 10 mL H₂O was added, the resulting precipitate was filtrated and dried. Purification was made by column chromatography on silica gel using CH₂Cl₂ as eluent. The yield is 83%. UV-Vis (CH₃CN) λ_{\max} 430 nm; ¹H NMR (δ ppm, Acetone-*d*₆) : 1.46 (t, 6H, *J* = 7.2 Hz, -OCH₂CH₃), 4.53 (q, 4H, *J* = 7.2 Hz, -OCH₂CH₃), 8.32 (d, 2H, *J* = 5.8 Hz, *H*₅, *H*₅), 9.26 (s, 2H, *H*₃, *H*₃), 9.38 (d, 2H, *J* = 5.8 Hz, *H*₆, *H*₆); ¹³C NMR (δ ppm, Acetone-*d*₆) : 14.38 (-OCH₂CH₃), 63.46 (-OCH₂CH₃), 122.08 (NCS), 124.71 (C₃, C₃), 128.16 (C₅, C₅), 142.35 (C₄, C₄), 155.41 (C₆, C₆), 157.35 (C₂, C₂), 163.79 (-COO-), 191.99 (CO), 196.15 (CO); IR (KBr) ν : 2098, 2028, 1938, 1905, 856, 836; ESI-MS Positive: [M-NCS]⁺ (*m/z* 571.1).

1b and **1c** exhibited a considerable red shift of 22 and 30 nm compared with that of **1a**. The reasons may be that NCCH₃ and SCN are powerful σ electron donors that could increase the electron density of the $d\pi_M$ orbital and decrease the energy gap between the ground state and the MLCT transitions ($d\pi_M \rightarrow \pi_L^*$). Therefore, it can be definitely concluded that change of the ligand could modify the MLCT absorption band range.

The luminescence spectral data in degassed acetonitrile at room temperature are listed in **Table 1**. The emission maximum of **1b** showed a blue shift of 11 nm relative to that of **1a** and a higher quantum yield, but **1c** showed little emission at room temperature in solution. The reasons may be that NCCH₃ and SCN could form powerful π back-bond with the metal atom and the π electron accepting ability of the ligand could decrease the electron density and increase the stability of the MLCT excited state to some extent. But the reasons that **1c** showed little emission is under discussion now.

Table 1 Fluorescent spectral data in acetonitrile at 23 ± 2 °C

Complex	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	ϕ_{em} (10^{-3})
1a	383	616	5.8
1b	383	605	9.7
1c	383	-	-

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