

## A Convenient Synthesis and Properties of Ru(bpy)<sub>2</sub>[bpy(CO<sub>2</sub>H)- (CO<sub>2</sub>Et)](PF<sub>6</sub>)<sub>2</sub> Photosensitive Dye

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**Abstract:** A novel Ru(II) *tris*-bipyridyl complex, Ru(bpy)<sub>2</sub>[bpy(CO<sub>2</sub>H)(CO<sub>2</sub>Et)](PF<sub>6</sub>)<sub>2</sub> is prepared in a simple and convenient process. It will be an alternative of Ru(bpy)<sub>2</sub>bpy(CO<sub>2</sub>Et)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> to be used in solar cells as photosensitive dyes.

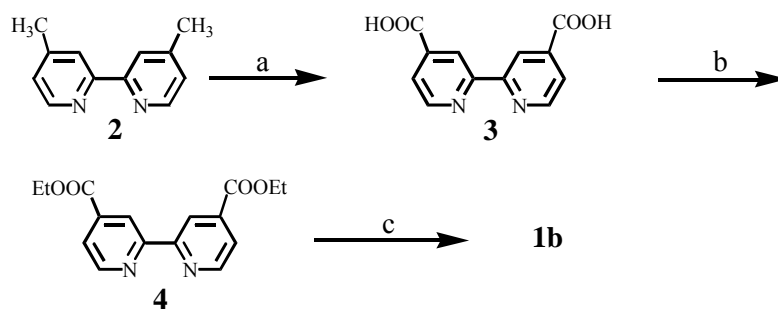
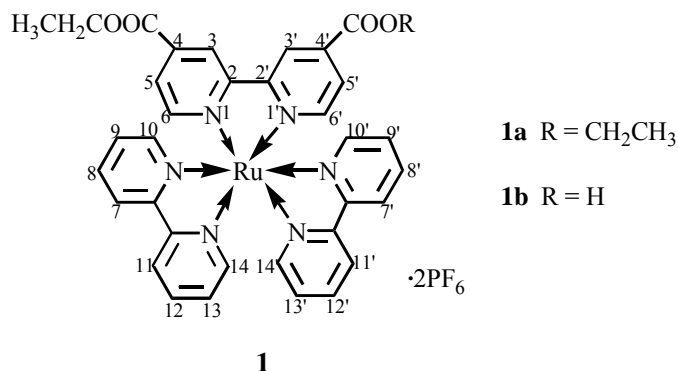
**Keywords:** Ruthenium(II) *tris*-bipyridyl complex, photosensitive dyes, light stability, electrochemistry.

Ruthenium(II) *tris*-bipyridyl complexes are mainly used as photosensitizers in the so-called "Grätzel solar cells"<sup>1</sup>, because they have suitable redox potentials and intense metal-to-ligand charge transfer transitions in the near UV and visible region. The well-known efficient photosensitive dyes, such as N3 dye<sup>2</sup> and black dye<sup>3</sup>, were all ruthenium(II) complexes. There are carboxylic groups in these molecules, attaching the dye to the surface of nanostructured TiO<sub>2</sub><sup>4</sup>. The carboxylic dyes are easy to dye the TiO<sub>2</sub>, but not easy to be handled. The dyes containing ethoxycarbonyl groups (such as deeb, 4,4'-(CO<sub>2</sub>Et)-2,2'-bipyridine) are often used, because they are more soluble in organic solvents, easier to be isolated, characterized, and purified than those containing carboxylic groups (such as dcb, 4,4'-(CO<sub>2</sub>H)-2,2'-bipyridine). The ethoxycarbonyl groups are often hydrolyzed to carboxylic groups before being dyed on the surface of nanostructured TiO<sub>2</sub>. Meyer and coworkers<sup>5</sup> reported that the synthesis of **1a** in darkness for 15 hours and the yield was 85%. Recently, we found that under ambient light, the reaction could be finished in less than 2.5 hours and a "by-product" **1b** was acquired in 88% yield. This compound is more convenient to be prepared, easier to be isolated, purified, and have higher yield than **1a**. We herein report the synthetic process, photochemical and electrochemical properties of **1b** in comparison with **1a**.

As shown in **Scheme 1**, 4,4'-dimethyl-2, 2'-bipyridine **2** was oxidized to get **3** in 92% yield, **3** was esterified with absolute ethanol to give **4** in 93% yield. Then *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O and **4** were refluxed together for 2.5 hour in 1:1 ethanol/water (v/v) to give the desired product **1b** in 88% yield and **1a** in less than 1% yield. When we prepared **1a** according to the literature, **1b** could not be obtained. It seems that there is photocatalysis in the process, the photocatalysis not only catalyzes the coordination, but

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a) CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. b) C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>SO<sub>4</sub>. c) *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O.

also catalyzes the hydrolysis of one ester group in **4**. The detailed mechanism is under investigation.

UV-Visible absorption data of **1a** and **1b** in aqueous solution at room temperature are collected in **Table 1**. **1b** showed typical absorption properties of the ruthenium(II) *tris*-bipyridyl complex. The band at 287 nm was assigned to ligand centered (LC) transition ( $\pi_L \rightarrow \pi_L^*$ ), while the other two intense bands at 476 nm and 246 nm were attributed to metal to ligand charge transfer (MLCT) transitions, namely the transition of  $d\pi_M \rightarrow \pi_L^*$ . The absorption spectrum of **1a** and **1b** matched pretty well within the experimental error.

**Table 1** UV-Visible absorption maxima in acetonitrile at room temperature

| Dye       | $\lambda_{\text{max}}$ (nm) | $\epsilon$ ( $10^3 \cdot \text{M}^{-1} \text{L} \cdot \text{cm}^{-1}$ ) | Assignment                   |
|-----------|-----------------------------|---|------------------------------|
| <b>1a</b> | 477                         | 13.5  | $d\pi_M \rightarrow \pi_L^*$ |
|           | 286                         | 56.4  | $\pi_L \rightarrow \pi_L^*$  |
|           | 246                         | 28.2  | $d\pi_M \rightarrow \pi_L^*$ |
| <b>1b</b> | 476                         | 13.5  | $d\pi_M \rightarrow \pi_L^*$ |
|           | 287                         | 56.2  | $\pi_L \rightarrow \pi_L^*$  |
|           | 246                         | 28.3  | $d\pi_M \rightarrow \pi_L^*$ |

Both complexes showed the same excitation maximum at 469 nm and emission maximum at 672 nm, and the same fluorescence quantum yield of 0.03 in acetonitrile at room temperature.

As listed in **Table 2**, the cyclic voltammograms of **1b** showed the features which were characteristic for ruthenium(II) *tris*-bipyridyl complexes<sup>7</sup>, with a reversible metal-based oxidation (Ru<sup>II/III</sup>) wave and three successive reversible reductions at negative potentials. The first reduction wave was due to the reduction of the carboxylated ligand (L), followed by two successive one-electron reductions of the two non-substituted bipyridyl ligands respectively. The redox potentials are nearly equaled to those of **1a**.

**Table 2** Electrochemical data of **1a** and **1b** at room temperature

| Dye       | E <sub>1/2</sub> (Ru <sup>II/III</sup> ) V | E <sub>1/2</sub> (L/L*) V | E <sub>1/2</sub> (bpy <sub>1</sub> /bpy <sub>1</sub> <sup>-</sup> ) V | E <sub>1/2</sub> (bpy <sub>2</sub> /bpy <sub>2</sub> <sup>-</sup> ) V |
|-----------|--|---------------------------|---|---|
| <b>1a</b> | 1.16                                       | -1.37*                    | -1.79   | -2.08   |
| <b>1b</b> | 1.16                                       | -1.35*                    | -1.79   | -2.08   |

\* the E<sub>p</sub> value, vs. Ag/Ag<sup>+</sup>.

<sup>1</sup>H NMR spectrum was recorded on a Varian INOVA 400 MHz spectrometer, using TMS as internal standard. Proton assignments are based on 2D-NMR (<sup>1</sup>H-<sup>1</sup>H COSY, HMQC and HMBC) spectra. The electro-spray ionization mass spectrometry (ESI-MS) was performed on a HP1100 LC/MSD with acetonitrile as solvent. The absorption and emission measurements were performed at room temperature in air saturated acetonitrile of spectroscopic grade. The absorption spectra were recorded on a HP 8453 spectrophotometer and the emission spectra were recorded by a PTI-C-700 fluorometer. The electrochemistry was performed under nitrogen and the electrolyte used was 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile. Cyclic voltammetry was recorded using a three-electrode system consisting of a Ag/Ag<sup>+</sup> (0.01 mol/L AgNO<sub>3</sub>, 0.1 mol/L TBAPF<sub>6</sub>, CH<sub>3</sub>CN) 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:** <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ 1.41 (t, 6H, *J* = 7.2 Hz, -OCH<sub>2</sub>CH<sub>3</sub>), 4.46 (q, 4H, *J* = 7.2 Hz, -OCH<sub>2</sub>CH<sub>3</sub>), 7.47 (ddd, 2H, *J* = 7.6 Hz, 5.6 Hz, 1.2 Hz, H<sub>10</sub>, H<sub>10'</sub>), 7.54 (ddd, 2H, *J* = 7.6 Hz, 5.6 Hz, 1.2 Hz, H<sub>6</sub>, H<sub>6'</sub>), 7.69 (dd, 2H, *J* = 5.6 Hz, 1.2 Hz, H<sub>11</sub>, H<sub>11'</sub>), 7.74 (dd, 2H, *J* = 5.6 Hz, 1.2 Hz, H<sub>7</sub>, H<sub>7'</sub>), 7.88 (dd, 2H, *J* = 5.8 Hz, 1.6 Hz, H<sub>2</sub>, H<sub>2'</sub>), 7.96 (d, 2H, *J* = 5.8 Hz, H<sub>3</sub>, H<sub>3'</sub>), 8.13 (dd, 2H, *J* = 7.8 Hz, 7.6 Hz, H<sub>9</sub>, H<sub>9'</sub>), 8.17 (dd, 2H, *J* = 7.8 Hz, 7.6 Hz, H<sub>5</sub>, H<sub>5'</sub>), 8.81 (dd, 2H, *J* = 7.8 Hz, 1.2 Hz, H<sub>8</sub>, H<sub>8'</sub>), 8.82 (dd, 2H, *J* = 7.8 Hz, 1.2 Hz, H<sub>4</sub>, H<sub>4'</sub>), 9.24 (d, 2H, *J* = 1.6 Hz, H<sub>1</sub>, H<sub>1'</sub>). ESI-MS positive (*m/z*): found mono-charged peak at 859.2 [M-PF<sub>6</sub>]<sup>+</sup>, double-charged peak at 357.0 [M-2PF<sub>6</sub>]<sup>2+</sup>.

**1b:** <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ 1.41 (t, 3H, *J* = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>), 4.45 (q, 2H, *J* = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>), 7.47 (t, 2H, *J* = 6.0 Hz, H<sub>10</sub>, H<sub>10'</sub>), 7.53 (t, 2H, *J* = 6.4 Hz, H<sub>6</sub>, H<sub>6'</sub>), 7.71 (t, 2H, *J* = 4.4 Hz, H<sub>11</sub>, H<sub>11'</sub>), 7.75 (t, 2H, *J* = 6.0 Hz, H<sub>7</sub>, H<sub>7'</sub>), 7.88 (dd, 2H, *J* = 5.4 Hz, 1.2 Hz, H<sub>2</sub>, H<sub>2'</sub>), 7.92-7.97 (d, 2H, *J* = 5.8 Hz, H<sub>3</sub>, H<sub>3'</sub>), 8.13 (d, 2H, *J* = 7.2 Hz, H<sub>9</sub>, H<sub>9'</sub>), 8.16 (d, 2H, *J* = 7.2 Hz, H<sub>5</sub>, H<sub>5'</sub>), 8.80 (d, 2H, *J* = 7.8 Hz, H<sub>8</sub>, H<sub>8'</sub>), 8.81 (d, 2H, *J* = 7.8 Hz, H<sub>4</sub>, H<sub>4'</sub>), 9.17-9.18 (s, 2H, H<sub>1</sub>, H<sub>1'</sub>). ESI-MS Positive *m/z*: found mono-charged peak at 831.2 ([M-PF<sub>6</sub>]<sup>+</sup>), double-charged peak at 343.0 ([M-2PF<sub>6</sub>]<sup>2+</sup>).

The stability of **1b** was tested. No noticeable change of the NMR spectrum and the absorption spectrum were observed when it was stored in DMSO-*d*<sub>6</sub> solution for two months under ambience. The test of the dyeing properties after the ethoxycarbonyl groups are hydrolyzed to carboxylic groups and incident photo to current conversion efficiency for TiO<sub>2</sub> system showed there were no difference between **1a** and **1b**. So this new dye **1b** will be an alternative of Ru(bpy)<sub>2</sub>bpy(CO<sub>2</sub>Et)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> to be used in solar cells as photosensitive dye.

### Acknowledgments

The work was supported by “973 project” of Ministry of Science & Technology of China and National Natural Science Foundation of China (project 20128005).

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Received 4 July, 2003