

**Electronic Supplementary Information**

**for**

**Drastic Difference in the Photo-Driven Hydrogenation Reactions of Ruthenium  
Complexes Containing NAD Model Ligands**

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## Experimental

**Materials.** All chemicals used for the synthesis of the ligands and complexes were commercial products of the highest available purity and were further purified by the standard methods.<sup>1</sup> Solvents were also purified by standard methods before use.<sup>1</sup>

**Syntheses.** All ligands and complexes used in this study were prepared according to the following procedures and the structures of the products were confirmed by the analytical data (*vide infra*).

**2-(3-methylpyridin-2-yl)benzo[*b*][1,5]naphthyridine (3Me<sub>1</sub>-pbn).** This ligand was prepared in the same manner as that for the synthesis of pbn<sup>2</sup> using the 3-methyl-2-acetyl-pyridine<sup>3</sup> instead of 2-acetyl-pyridine. ESI-MS: *m/z* 271.1 [M+H]<sup>+</sup>; (Found: C, 79.70; H, 4.92; N, 15.38. C<sub>18</sub>H<sub>13</sub>N<sub>3</sub> requires C, 79.68; H, 4.83; N, 15.49%); δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>): 9.06 (1 H, s), 8.63 (2 H, m), 8.37 (1 H, d, *J* 9.1), 8.30 (1 H, d, *J* 8.8), 8.12 (1 H, d, *J* 8.3), 7.86 (1 H, m), 7.72 (1 H, d, *J* 7.6), 7.62 (1 H, t, *J* 7.5), 7.32 (1 H, dd, *J* 7.9 and 4.7) and 2.75 (3 H, s).

**[Ru(bpy)<sub>2</sub>(3Me<sub>1</sub>-pbn)](PF<sub>6</sub>)<sub>2</sub> (1).** To a 2-methoxyethanol solution (20 mL) of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] (121 mg, 0.25 mmol) was added AgPF<sub>6</sub> (126 mg, 0.50 mmol) in 2-methoxyethanol, and the mixture was stirred for 2 h at 70 °C. The resulting mixture was cooled to room temperature, and insoluble material was removed by filtration through celite. After the addition of the ligand 3Me<sub>1</sub>-pbn (67.6 mg, 0.25 mmol) to the filtrate, the reaction mixture was stirred for 12 h at 70 °C. The solution was concentrated to *ca.* 1 mL and poured into aqueous NH<sub>4</sub>PF<sub>6</sub> solution. The solid formed was collected and dried *in vacuo*. Recrystallization from acetonitrile / diethylether gave **1** as reddish purple crystals (190 mg, 78.3%). ESI-MS: *m/z* 342.6 [M-2PF<sub>6</sub>]<sup>2+</sup>; (Found: C, 47.15; H, 3.24; N, 11.04. C<sub>40</sub>F<sub>12</sub>H<sub>32</sub>N<sub>8</sub>P<sub>2</sub>Ru requires C, 47.30; H, 3.18; N, 11.03%); δ<sub>H</sub> (500 MHz, CD<sub>3</sub>CN): 8.70 (1 H, d, *J* 9.3), 8.64 (1 H, d, *J* 7.9), 8.62-8.59 (2 H, m), 8.35 (1 H, s), 8.30 (1 H, d, *J* 5.5), 8.17 (1 H, d, *J* 8.1), 8.15-8.10 (4 H, m), 8.08 (1 H, d, *J* 8.6), 8.02 (1 H, td, *J* 8.0 and 1.3), 7.98 (1 H, d, *J* 7.8), 7.88 (1 H, m), 7.84 (1 H, td, *J* 7.9 and 1.3), 7.65 (2 H, t, *J* 5.6), 7.59-7.53 (3 H, m), 7.36-7.27 (5 H, m) and 3.00 (3 H, s).

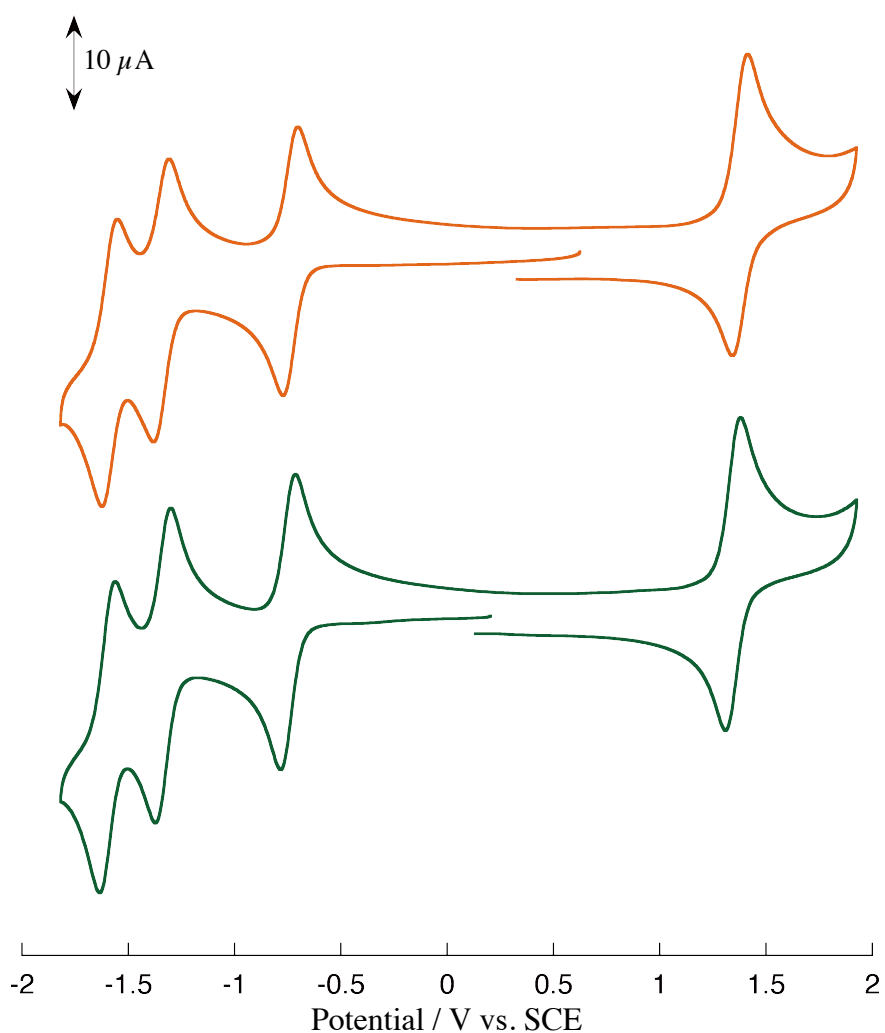
**[Ru(bpy)<sub>2</sub>(3Me<sub>1</sub>-pbnHH)](PF<sub>6</sub>)<sub>2</sub> (2).** An aqueous solution (15 mL) of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (182 mg, 1.05 mmol) was added to a solution of **1** (102 mg, 0.10 mmol) in acetonitrile (15 mL) under a nitrogen atmosphere. After stirring the mixture for 2 h at room temperature, the solution was concentrated and added to an aqueous solution of NH<sub>4</sub>PF<sub>6</sub>. Orange powder was collected by filtration and recrystallized from acetonitrile/diethylether under nitrogen atmosphere (78.3 mg, 76.5%). ESI-MS: *m/z* 343.6 [M–2PF<sub>6</sub>]<sup>2+</sup>; (Found: C, 47.49; H, 3.85; N, 9.47. C<sub>41</sub>F<sub>12</sub>H<sub>39</sub>N<sub>7</sub>OP<sub>2</sub>Ru requires C, 47.50; H, 3.79; N, 9.46%); δ<sub>H</sub> (500 MHz, CD<sub>3</sub>CN): 8.52 (1 H, d, *J* 8.2), 8.48–8.46 (2 H, m), 8.43 (1 H, d, *J* 7.9), 8.23 (1 H, d, *J* 5.2), 8.15 (1 H, d, *J* 9.2), 8.10–8.04 (2 H, m), 8.03–7.98 (2 H, m), 7.85 (1 H, d, *J* 4.9), 7.77 (1 H, d, *J* 7.6), 7.71 (1 H, d, *J* 5.5), 7.66 (1 H, s), 7.45–7.40 (3 H, m), 7.38 (1 H, ddd, *J* 7.9, 5.5 and 1.2), 7.33 (1 H, dd, *J* 5.5 and 1.0), 7.29 (1 H, ddd, *J* 7.9, 5.5 and 1.2), 7.23 (1 H, d, *J* 9.2), 7.06–7.00 (2 H, m), 6.72 (1 H, td, *J* 7.9 and 1.0), 6.69 (1 H, d, *J* 8.5), 6.23 (1 H, d, *J* 7.6), 3.97 (1 H, d, *J* 20), 2.99 (1 H, d, *J* 20) and 2.79 (3 H, s).

**Physical measurements.** NMR measurements were performed with a JEOL GX-500 (500 MHz) NMR spectrometer. Electronic spectra were measured with a Hewlett-Packard 8453 diode array spectrophotometer. Emission spectra were recorded on a JASCO FP-6600 spectrofluorometer. ESI-mass spectra were obtained with a micromass LCT time of flight mass spectrometer. Cyclic voltammetry measurements were performed at 293 K on an ALS/Chi model 660 electrochemical analyzer in deaerated solvent containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte. A conventional three-electrode cell was used with a glassy-carbon working electrode and a platinum wire as the counter electrode. The glassy-carbon working electrode was routinely polished with a BAS polishing alumina suspension and rinsed with acetone before use. The reversibility of the electrochemical processes were evaluated by standard procedures and all potentials were recorded against a Ag/Ag<sup>+</sup> reference electrode which was calibrated using an SCE reference. All electrochemical measurements were carried out under an atmospheric pressure of argon. Photochemical hydrogenation reaction experiments were conducted in nitrogen-bubbled CH<sub>3</sub>CN/TEOA (4 : 1, v/v) at 293 K. The

solution containing 0.1 mM of complexes was irradiated with light through a 450 nm cut-off filter (TOSHIBA Y-45) using a 150 W Xenon lamp. Elemental analyses were carried out at Research Center for Molecular-scale Nanoscience, Institute for Molecular Science.

**X-ray crystal structure determinations.** Well-shaped single crystals of **1** and **2**, which are suitable for X-ray crystallographic analysis, were grown by slow evaporation of methanol from a methanol/water solution of **1** and by slow vapour diffusion of diethylether into an acetonitrile solution of **2** under nitrogen atmosphere, respectively. Data for **1** and **2** were collected on a Rigaku/MSK Saturn CCD diffractometer using graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.710747 \text{ \AA}$ ) at 123 K and processed using Crystal Clear program (Rigaku). The structures were solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$  using SHELX-97<sup>4</sup>. The absorption corrections were done using the multi-scan technique. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in the refinement process as per the riding model.

Fig. S1



**Fig. S1** Cyclic voltammograms of (orange)  $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$  and (green) **1** in acetonitrile (1.0 mM) containing 0.1 M TBAPF<sub>6</sub> at 293 K (working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/Ag<sup>+</sup>; scan rate, 50 mV s<sup>-1</sup>).

## References

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