

## On the Correlation between Electronic Intramolecular Delocalization and Au-S Bonding Strength of Ruthenium Tetraammine SAMs

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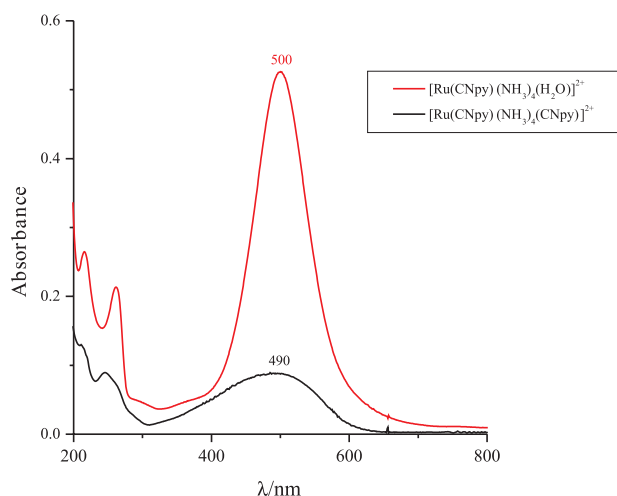
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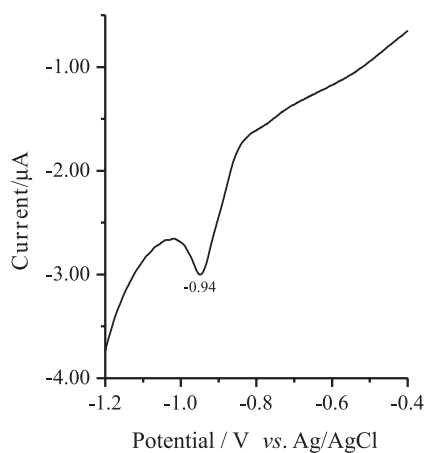
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The energies of the CNpy( $p_{\pi}^*$ )  $\leftarrow$  ( $d_{\pi}$ )Ru<sup>II</sup> MLCT transitions of the isolated compounds were determined on the basis of the observation of an additional MLCT transition at higher energy, which was assigned to an MLCT transition involving the second ligand as acceptor (*Inorg. Chem.* **1983**, 22, 224). In addition, the electronic spectra of the [(CNpy)Ru(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)]<sup>2+</sup> and [(CNpy)Ru(NH<sub>3</sub>)<sub>4</sub>(CNpy)]<sup>2+</sup> complexes, which are presented in Figure S1, were also used to determine the energy of the CNpy( $p_{\pi}^*$ )  $\leftarrow$  ( $d_{\pi}$ )Ru<sup>II</sup> MLCT transitions.



**Figure S1.** Electronic spectra of [(CNpy)Ru(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)]<sup>2+</sup> ( $5.2 \times 10^{-5}$  mol L<sup>-1</sup>) and [(CNpy)Ru(NH<sub>3</sub>)<sub>4</sub>(CNpy)]<sup>2+</sup> ( $5.8 \times 10^{-6}$  mol L<sup>-1</sup>) in water.

Linear sweep voltage (LSV) at 50 mV s<sup>-1</sup> of the gold electrode modified with [Ru(CNpy)(NH<sub>3</sub>)<sub>4</sub>(tna)]<sup>2+</sup> in 0.5 mol L<sup>-1</sup> KOH solution is presented in Figure S2. Similar curves were obtained for the monolayers formed onto gold with the complexes that contain sulfur. The desorption curve obtained for the non-coordinated tna can be found in a previous publication (*Electroanalysis* **2009**, 21, 1081). The surface coverage,  $\Gamma$ , was determined upon the integration of the area under the reductive peak which gives the reductive charge,  $Q_{rd}$ , and using the Equation  $\Gamma = \sigma_{rd}/nF$ , where  $\sigma_{rd}$  is the density of the reductive charge ( $\sigma_{rd} = Q_{rd}/A$ ),  $n$  is the number of electrons of the electrode reaction,  $F$  is the Faraday constant, and  $A$  is the electroactive area of the gold electrode.



**Figure S2.** LSV curve at 50 mV s<sup>-1</sup> of the gold electrode modified with [Ru(CNpy)(NH<sub>3</sub>)<sub>4</sub>(tna)]<sup>2+</sup> in 0.5 mol L<sup>-1</sup> KOH solution. The gold electrode was modified after 30 min of immersion in 2.0 mmol L<sup>-1</sup> aqueous solution of the complex.

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