

Syntheses

Materials

2,3-Bis(2-pyridyl)pyrazine (dpp; Aldrich 98%), ammonium hexafluorophosphate (Aldrich 99%), triethylamine (Aldrich), titanium isopropoxide (Aldrich), and polyethylene glycol (Aldrich, 2000 TM Carbowax) were used as supplied. Trimethylamine N-oxide (TMNO) was obtained by vacuum sublimation of the hydrate (Fluka purum) at 120 °C. Ethanol was freshly distilled from magnesium turnings prior to use unless used as a co-solvent with water. Sephadex LH-20 and CM Sephadex C25 chromatographic materials were obtained from Pharmacia. $\text{Ru}^{\text{III}}(\text{tpy})\text{Cl}_3$ was prepared as previously described (Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845) as was $[\text{Ru}(4,4'\text{-Me}_2\text{bpy})(4,4'\text{-(CO}_2\text{Et)}_2\text{bpy})(\text{CO})_2](\text{PF}_6)_2$ (Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145.).

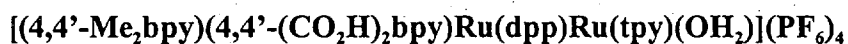
$[\text{Ru}(\text{tpy})(\text{dpp})\text{Cl}]\text{Cl}$

$\text{Ru}(\text{tpy})\text{Cl}_3$ (0.45 g, 1.0 mmol) was dissolved in 3:1 (v/v) ethanol/water (75 mL) containing lithium chloride (45 mg, 1.0 mmol), dpp (1.2 g, 5.1 mmol), and triethylamine (1 mL). The solution was heated at reflux for 4 h then hot filtered and cooled to room temperature. The reaction volume was reduced by two-thirds under reduced pressure and the resulting solution refrigerated for 72 h. The resulting dark purple crystals were collected by vacuum filtration and washed with small amounts of cold 2 M HCl, acetone, and finally ether. The product thus obtained was purified by passage down an LH-20 size exclusion column eluted with methanol.

The leading black edge was discarded and the main band collected by concentration of the solvent and precipitation into ether. The chromatographic step was repeated once.



[Ru(4,4'-Me₂bpy)(4,4'-(CO₂Et)₂bpy)(CO)₂] (0.15 g, 0.16 mmol) and trimethylamine N-oxide (36 mg, 0.48 mmol) were heated at reflux under Ar in ethanol. Over the course of 2 h, [Ru(tpy)(dpp)Cl](Cl) was added. The reaction was continued at reflux for 8 h; then cooled to room temperature and the solvent was removed under reduced pressure. The resulting solid was taken up in a small amount of acetonitrile and precipitated into ether. The resulting precipitate was eluted twice on a Sephadex LH-20 column using methanol. The first dark band was collected in both cases. The solvent was removed and the complex eluted on a CM Sephadex C25 column by using a gradient of 0 - 500 mM aqueous sodium chloride. The desired band only began to move when the sodium concentration reached 300 mM. The solid product was precipitated by addition of a saturated aqueous solution of NH₄PF₆ and collected by filtration.



The hydrolysis of the ester groups and replacement of chloride with water were carried out in the same step starting with [(4,4'-Me₂bpy)(4,4'-(CO₂Et)₂bpy)Ru(dpp)Ru(tpy)Cl](PF₆)₃. The complex was heated at reflux for 12 h in a minimum of 1:1 v/v ethanol/water which had been adjusted to pH = 1 with H₂SO₄. The reaction was forced to completion by the addition of silver nitrate and continued reflux for another 4 h. After filtering the solution to remove silver chloride, ammonium hexafluorophosphate was added and the complex was extracted into ethyl acetate. The ethyl acetate was washed repeatedly with water to remove hexafluorophosphoric acid, dried over sodium sulfate, and evaporated to yield a red powder. Analytical HPLC analysis

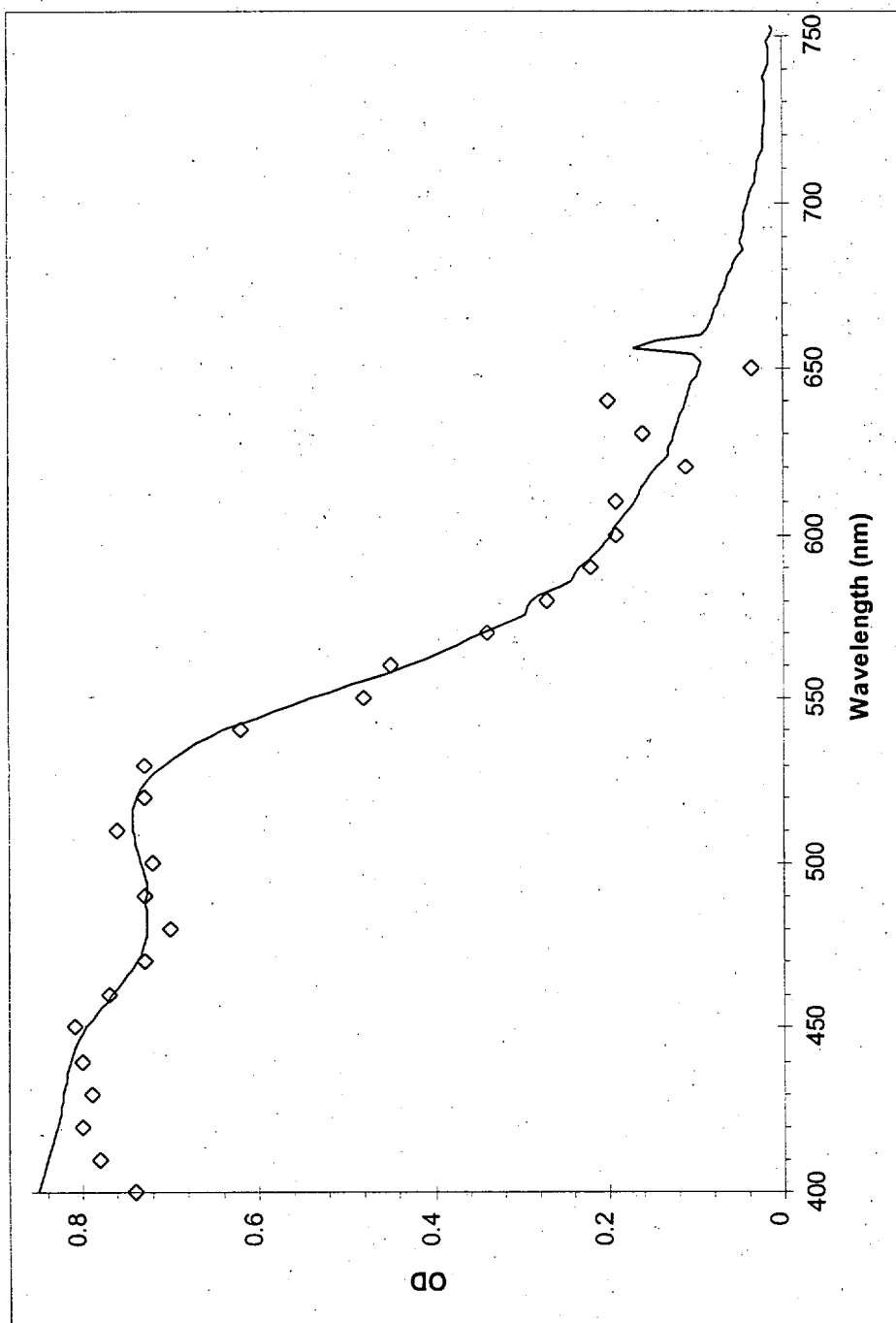
only a single sharp peak was observed at all wavelengths. The complex was further characterized by UV-visible absorption spectroscopy and electrochemical analysis as described in the text.

Electrode Preparation

This method is also described in Trammell, S. A.; Moss, J. A.; Yang, J. C.; Nakhle, B.; Slate, C. A.; Odobel, F.; Sykora, M. Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 3665. Titanium isopropoxide (25 mL, Aldrich) was added dropwise with stirring to approximately 150 mL distilled water containing 1.05 mL 70% HNO₃. The sol was heated with stirring in an open round bottom flask at 85 °C until the solution volume was 50 mL (135 g TiO₂ per L). The resulting sol was autoclaved by sealing approximately 35 mL TiO₂ sol in a 5 in. × 1.5 in. glass vessel and heating in an oven at 200 °C for ~14 h, inducing precipitation of the TiO₂. After cooling, the glass was opened and 40% w/w polyethylene glycol was added to the stirring TiO₂ suspension. The suspension was stirred overnight resulting in a thick viscous mixture.

Tin(IV)-doped indium oxide (ITO) electrodes (Delta Technologies, 20 Ω/sq) were cleaned by sonicating 15 min in 1:1:5 NH₄OH : H₂O₂ : H₂O (v/v/v) and rinsing with water and ethanol. A 75 mm × 50 mm ITO sheet was masked by placing two pieces of Scotch tape lengthwise on the surface, leaving a 1 cm wide exposed area between them. Several drops of the TiO₂ mixture were placed at one end of the electrode and spread evenly across the exposed area with a test tube in one sweep. The TiO₂ film was allowed to dry in air 30 min. The electrode was cut into ~ 7 mm x 50 mm pieces and heated in a Lindberg furnace at 400 °C under a continuous flow of O₂ for 30 min. The molecular assembly was added by immersion of the warm electrodes into a saturated ethanolic solution overnight. The derivatized electrodes were rinsed with ethanol, water, and finally the electrolyte solution used in the experiment.

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Figure S1. Photo-action spectrum (\diamond) of $[\text{Ru}(\text{bpy}(\text{CO}_2\text{H})_2)(4,4'\text{-Me}_2\text{bpy})(\text{dpp})\text{Ru}(\text{tpy})(\text{OH}_2)]^{4+}$ adsorbed onto a $\text{TiO}_2/\text{ITO}/\text{glass}$ electrode immersed in propylene carbonate with 0.5 M NaI and 0.05 M I_2 . The plot has been normalized to overlay with the light harvesting efficiency (LHE) spectrum (---) of the same electrode. LHE is the fraction of incident light absorbed by the sample.