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A New Luminescent and Redox-Active Ruthenium Complex

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INTRODUCTION

Much effort has been devoted to the synthesis and characterization of luminescent and redox-active polynuclear metal complexes largely because of their fascinating properties. Trinuclear Ru(II) complexes containing tetrathiafulvalene(TTF)-substituted polypyridine ligands have been reported as coupled antennas and charge-separation systems. Herein, we briefly discuss the synthesis and properties of a Ru(II) complex based on the TTF-2py ligand.

RESULTS

The air-stable $[Ru(bpy)_2(ET-2py)](PF_6)_2$ {TTF-2py = 4,5-bis(2-pyridyl-methylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene} was obtained by the reaction of $[Ru(bpy)_2Cl_2]$ with equimolar ET-2py in anhydrous ethanol followed by addition of aqueous NH_4PF_6 . Slow evaporation of its solution in CH_3CN afforded some brown single crystals. The X-ray crystal structure exhibits a distorted octahedral geometry about Ru(II) ion (Figure 1), with the coordination polyhedron defined by five nitrogen atoms and a sulfur atom: two N, N-chelate bipy ligands are cis to each other and a molecule of ET-2py behaves as bidentate through S(5)

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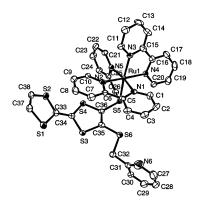


FIGURE 1 Crystal structure of [Ru(bpy)₂(ET-2py)]²⁺.

and N(5). The two unoccupied donor sites and their relative orientation suggest that this complex should be able to bind to a second metal ion as a bidentate N, S donor ligand, and such a possibility is currently being explored. Electrochemical oxidation involves the TTF moiety of ET-2py and the Ru center, occurring reversibly in CH₃CN at 0.73, 1.03 and 1.31 V vs. Ag/AgCl, respectively. The absorption spectrum is essentially similar to the parent $[Ru(bpy)_3]^{2+}$ species and can be interpreted accordingly. Moreover, luminescence band maxima, emission quantum yield, and lifetime are also very close to those featured by the parent complex, indicating that changes introduced by the ligand ET-2py don't modify the chromophore properties.

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