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Temperature-dependent and time-resolved emission studies of *cis*-Ru(bpy)$_2$(N$_3$)$_2$ HELEN K. GERARDI, NRL, NRC Postdoctoral Research Associate, DOUGLAS J. BROWN, US Naval Academy, RYAN COMPTON, NRL, NRC Postdoctoral Research Associate, WALTER J. DRESSICK, NRL, EDWIN J. HEILWEIL, NIST, JEFFREY C. OWRUTSKY, NRL — The electronic properties of a Ru^{II} cyclometalated dye complex, *cis*-Ru(bpy)$_2$(N$_3$)$_2$, were examined with time-resolved and temperature-dependent visible emission measurements. Compared to two related solar cell dye-sensitizer species, *cis*-Ru(bpy)$_2$(NCS)$_2$ and *cis*-Ru(bpy)$_2$(CN)$_2$, the azide (N$_3$) pseudohalide ligand dramatically changes the electronic properties of the dye. The uv-vis absorption spectra of *cis*-Ru(bpy)$_2$(N$_3$)$_2$ in various solvents reveal that its metal-to-ligand charge transfer band (MLCT) is located more than 50 nm to the red of the MLCT bands found for the other two complexes. Furthermore, while room temperature emission is readily observed for *cis*-Ru(bpy)$_2$(NCS)$_2$ and *cis*-Ru(bpy)$_2$(CN)$_2$, the emission is much weaker for *cis*-Ru(bpy)$_2$(N$_3$)$_2$. We report the first observation of luminescence from *cis*-Ru(bpy)$_2$(N$_3$)$_2$ by measuring it in 4:1 EtOH:MeOH matrices at temperatures below 140 K. Emission bands are observed at 665 nm and 620 nm (514 nm excitation). The quantum yield of this species was estimated by comparing the integrated emission signal of *cis*-Ru(bpy)$_2$(N$_3$)$_2$ to that of *cis*-Ru(bpy)$_2$(CN)$_2$ at 77 K and was determined to be exceptionally low (6 x 10^{-4}). The luminescence lifetime of *cis*-Ru(bpy)$_2$(N$_3$)$_2$ at 77 K was measured to be approx. 800 ns, implying an extremely slow radiative rate of 780 s^{-1}. The long radiative rate and low quantum yield led us to further investigate the photolability and electrochemical behavior of the azide complex.

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