

PANCHROMATIC SENSITIZATION FOR THE DYE SENSITIZED NANOCRYSTALLINE SOLAR CELL

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The development of ruthenium(II) polypyridyl complexes sensitized solar cell exhibiting a light-to-electrical conversion efficiency of 10% has brought of the sensitization of large band gap semiconductor oxides to the forefront of photoelectrochemical research^{1, 2}. However, relatively weak absorption of commonly utilized sensitizers in the 700 to 800 nm ranges inhibits a further improvement of the solar cell efficiency. One of the important goals for the next generation of solar cells based on this technology is to prepare sensitizers that could harvest light through the visible region and into the near IR. A black trithiocyanato-ruthenium complex was first reported to enhance spectral response in the red and near-IR region^{3,4}.

For ruthenium diimine sensitizers, there are two design strategies to systematically shift the metal-to-ligand charge transfer (MLCT)($d\pi \rightarrow \pi^*$) absorption bands toward the red region of the solar spectrum. One is to lower the energy of the π^* orbital by adding electron-withdrawing groups to a polypyridyl ligand^{4,5}, and the other is to increase that of the $d\pi$ orbital by decreasing the $d\pi-\pi^*$ back-bonding donation to nonchromophoric ligands^{5,6}. However, based on energy gap considerations, the former approach may result in lowering of the quantum yield for interfacial charge separation since the rate of nonradiative decay would compete effectively with electron injection^{4,5}.

Here, two new black sensitizers, [Ru(ttp-COOH)(NCS)₃] (**1**), and [*trans*-Ru(pby-COOH)₂(SCN)₂] (**2**) were designed and synthesized. The absorption spectra of the above two complexes in acetone show intense metal-to-ligand charge transfer bands at 600 nm and 562 nm, respectively. The MLCT bands of the above two coomplexes are red shifted when compared to that of [*cis*-Ru(pby-COOH)₂(SCN)₂] (535nm), which is the most efficient sensitizer so far. The red shift is due to an increase in the energy of the metal t_{2g} orbital by weakening of the ligand field. For the complex **1**, the relatively weak ligand field results from the twisted distortion which serves to relieve the steric repulsive interactions between the 6,6'-hydrogen atoms of

the bipyridine ligands⁸, whereas for the complex **2**, it is the consequence of the unfavorable bite angles associated with the terpyridine ligand⁸⁻¹⁰. In addition, thiocanato anionic ligands stabilize the excited states by electron donation to ruthenium causing a red shift in the MLCT band^{11,12}.

For tuning of t_{2g} and π^* levels, a new Ru complex, Ru[bpy-(COOH)₂][5-(4 dimethyl-aminophenylimino)quinoline-8-one], was synthesized also. Its absorption maximum is at 870 nm in acetone. In addition, two new Ru complex supermolecules bearing one or two electron donating groups -(4-N-methyl-aminophenyl) on the polypyridine were synthesized for repressing charge recombination. The photophysical and photoelectrochemical properties of these new compounds are under investigating.

Acknowledgement

The NNSFC (29971031, 29733100) is gratefully acknowledgement for financial support.

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