DEVELOPMENT OF NEW EFFICIENT RUTHENIUM(II) POLYPYRIDYL PHOTOSENSITIZERS FOR NANOCRYSTALLINE TIO2 SOLAR CELLS

H. Arakawa, A. Islam and H. Sugihara
Photoreaction Control Research Center (PCRC),
National Institute of Advanced Industrial Science and Technology (AIST)
AIST Tsukuba, Central 5, Tsukuba, Ibaraki 305-8565, Japan

Dye-sensitized solar cells composed of Ru(II) polypyridyl complexes, nanocrystalline TiO2 thin film photo-electrodes and the redox electrolyte (I^-/I_3^-) have been studied intensively because of their high performances. In order to improve the efficiency of such systems further, photosensitizer should have an absorption spectrum that overlaps with the solar spectrum while maintaining sufficient thermodynamic driving forces for the electron transfer as well as the dye regeneration processes.

We have systematically tuned the HOMO and LUMO energy levels of Ru(II) polypyridyl complexes by introducing ligands with a low-lying π * molecular orbital (for examples, 4,7-dicarboxy-1,10-phenanthroline [1], 2-(2-Pyridyl)-4-carboxyquinoline, and 4,4'-dicarboxy-2,2'-biquinoline[2]) or by destabilization of the metal t_{2g} orbital with a strong donor ligand [3]. From this result, we have estimated the optimal threshold value of 1.45eV for maximum power conversion. The most successful charge transfer sensitizer employed so far in these solar cells is Ru(tctpy)(NCS)$_3$ (tctpy = 4,4',4"-tricarboxy-2,2":6',2"-terpyridine)[4].

We previously reported remarkably high energy conversion efficiency using -diketonato ruthenium(II) polypyridyl sensitizer such as Ru(dcbpy)$_2$(acac) (dcbpy = 4,4' -dicarboxy-2,2'-bipyridine, acac = acetylacetonate) [5]. The strong σ -donating nature of negatively charged oxygen donor in the diketonate ligand destabilizes the ground state energy level of the dye, leading to lower energy shift of MLCT transitions. Moreover, the chelating structure of this ligand makes the complex resistant against the ligand loss processes.

Recently, we have developed a new class of ruthenium(II) polypyridyl photosensitizers of Ru(tctpy)(L)(NCS) type where L is one of the four β -diketonate ligands: acetylacetonate (acac), 2,2,6,6-tetramethyl-3,5-heptanedionato (dpmo), 6,8-tridecanedionato (tdd), 1,3-diphenyl-1,3-propanedion (dbmo). The photosensitizers have intense metal-to-ligand charge-transfer (MLCT) absorption bands in over the whole visible range. These complexes, when anchored to nanocrystalline TiO2 film electrodes achieve very efficient sensitization over the whole visible range extending into the near IR region.

Figure 1 shows the absorption spectra of Ru(tctpy)(NCS)3 and newly developed three Ru(tctpy)(L)(NCS) complexes. To suppress dye aggregation on TiO2 we used different types of substituted β -diketonate ligands. The effectiveness for light to electric energy conversion in a solar cell device of these new Ru(II) polypyridyl complexes when anchored to nanocrystalline TiO2 film electrodes will be discussed.

References

[1] K.Hara, et al., *Langmuir*, **17**,5992(2001).
[2] A.Islam et al., *Inorg.Chim.Acta*, **322**,7(2001).
[3] A.Islam et al., *J.Photochem.Phtobio.A:***145**,135(2001).
[4] Md.K.Nazeeruddin et al., *J.A.C.S.*, **123**,1613 (2000).
[5] Y.Takahashi, et al., *Inorg.Chim.Acta*, **310**,169(2000).

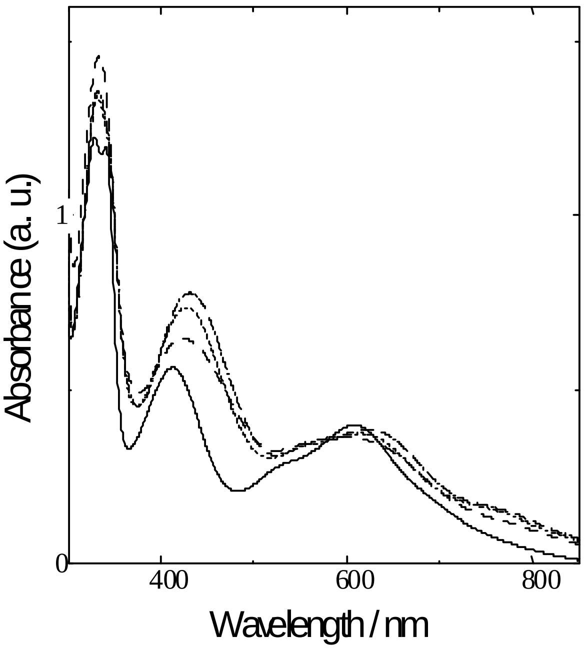
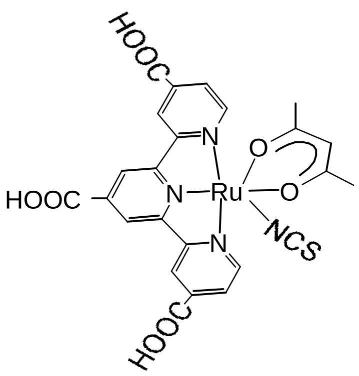
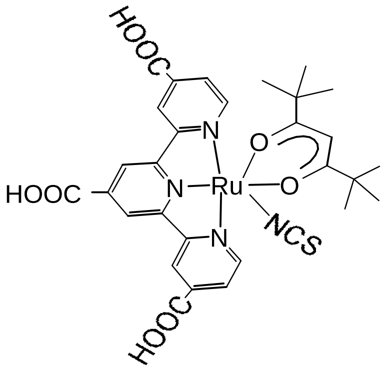


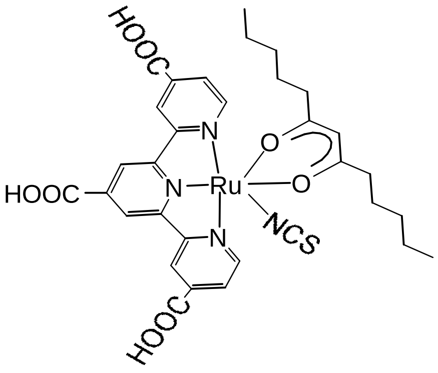
Figure 1. Absorption spectra of Ru(tctpy)(NCS)$_3$ (———), Ru(tctpy)(acac)(NCS) (– – –), Ru(tctpy)(dpmo)(NCS) (— —), Ru(tctpy)(tdd)(NCS) (—·—).



Ru(tctpy)(acac)(NCS)



Ru(tctpy)(dpmo)(NCS)



Ru(tctpy)(tdd)(NCS)