DYE-SENSITIZATION OF NANOCRYSTALLINE TiO_2 ELECTRODES WITH NEWLY PREPARED RUTHENIUM (II) COMPLEXES

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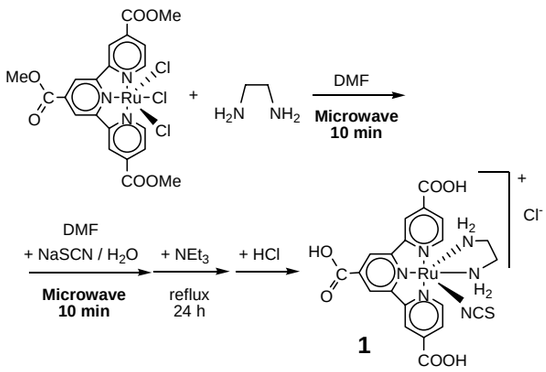
Dye-sensitized solar cells (DSSCs) composed of Ru(II) polypyridyl compounds, nanocrystalline TiO_2 thin film photo-electrodes and the redox electrolyte (I^-/I_3^-) have been studied because of their high performance and possible economical manufacturing process.[1] In order to improve the efficiency of such systems further, photosensitizer should have an absorption spectrum that overlaps with the solar spectrum while maintaining sufficient thermodynamic driving force for the electron transfer as well as the dye regeneration processes.

One of the most effective sensitizers reported so far is Ru(tctpy)(NCS)$_3$ (Black-Dye) which can absorb a wide range of light.[2]

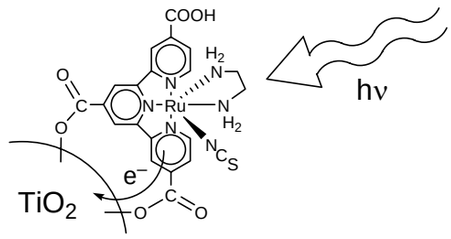
We reported β-diketonato Ru(II) tricarboxyterpyridine complexes that can absorb a wider range of light than black dye.[3] However, when used in DSSCs, the β-diketonato complexes have not shown high open-circuit voltage, probably because their LUMO energy, ca –0.9 V vs. SCE, are to close to the TiO_2 conduction band edge.

In this paper, we present the synthesis and application of the ethylenediamine ruthenium(II) tricarboxyterpyridine complex [Ru(tctpy)(en)(NCS)]Cl (en-Dye, **1**) as a new sensitizer for DSSCs

Complex **1** was synthesized using microwave synthesis techniques, which shortened the duration of the ligand replacement reactions, and hydrolyzed methoxycarbonyl groups by a conventional method. (Scheme 1). The UV–vis absorption spectra of **1** and Black-Dye exhibit intense, broad metal-to-ligand charge transfer (MLCT) bands with absorption maxima at 560 nm.



The cyclic voltammogram of **1** measured in ethanol containing 2 eq of TBA(OH) and 0.1 M TBA(ClO_4) shows one irreversible wave for the Ru^{3+}/Ru^{2+} couple at +0.60 V vs. SCE. An emission maximum was observed at around 800 nm, when **1** was measured in ethanol at 298 K, and the lifetime was 47 ns. The 0-0 transition energy (E^{00}) of **1** was calculated to be approximately 1.63 eV, therefore, the excited-state oxidation potential (E_{ox}^*) of **1** was estimated to be –1.03 V vs. SCE, which is 0.08 eV more negative than that of Black-Dye.



Photoelectrochemical experiments on the dye-sensitized semiconductor electrode films were performed in a sandwich-type solar cell. The effectiveness for light to electronic enerrgy conversion in a solar cell device of this new Ru(II) complex when anchored to nanocrystalline TiO_2 film electrodes will be discussed.

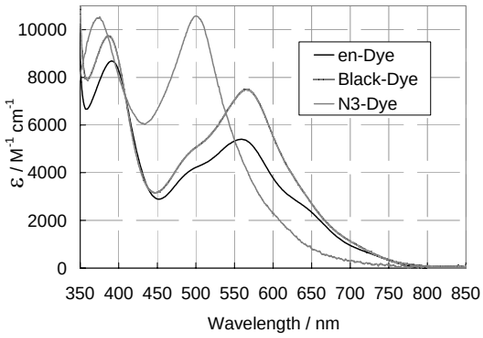


Fig.1 Absorption spectra of dye complexes in aqueous NaOH (pH=12)

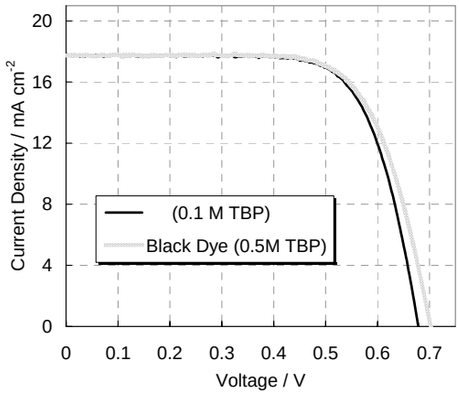


Fig.2 I-V curves of DSSCs sensitized with **1** and Black-Dye

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2) Md. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, **123**, 1613, (2001).
3) A. Islam, H. Sugihara, M. Yanagida, K. Hara, G. Fujihashi, Y. Tachibana, R. Katoh, S. Murata and H. Arakawa, *New J. Chem.*, **26**, 966, (2002).