Communication

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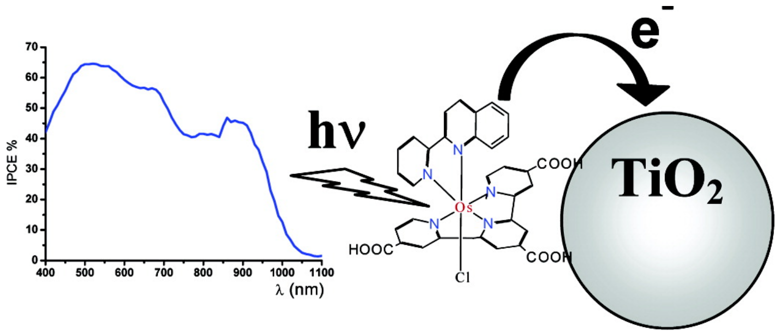
J. Am. Chem. Soc., **2005**, 127 (44), 15342-15343• DOI: 10.1021/ja053438d • Publication Date (Web): 15 October 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

Sensitization of Nanocrystalline TiO_2 with Black Absorbers Based on Os and Ru Polypyridine Complexes

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Dye-sensitized solar cells (DSSCs) are considered a valuable alternative to solid-state semiconductor devices.[1] They combine the advantages of low cost and molecular tunability with the material properties of wide band-gap semiconductors, such as stability toward corrosion, charge transport, and mechanical resilience. Although DSSCs made either of glass[2] or of plastic materials[3] are close to application, improvements in the conductive properties of the semiconductor support,[4,5] of the electron mediator,[6,7] and of the redox and spectroscopic properties of the dye sensitizer[8−10] are thought to still be needed in order to maximize their solar to electricity conversion efficiency. The electrochemical and spectroscopic properties of the dye, acting as an electron pump in the sensitization process, are crucial in determining the long-term stability and the light harvesting efficiency of the device. Many different dyes have been tried, the most well-known being a Ru bipyridine complex (red dye, $[Ru(Hdcbpy)_2(NCS)_2](TBA)_2)$[11] and a Ru terpyridine complex (black dye, $[Ru(Htcterpy)(NCS)_3](TBA)_3)$).[12] However, they suffer from limitation on cell efficiency (due to limited light harvesting) and lack of enough stability for hard outdoors applications, a topic still under discussion in the scientific community.[13] We report here the preparation and the photoelectrochemical properties of a new series of cationic dyes, corresponding to the general formulas $[M(H_3tcterpy)LY]^+$, where M = Os(II) or Ru(II); (H_3tcterpy) is the tridentate ligand 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine, L is a bidentate ligand of the type 2,2′-bipyridine (bpy) or 2-(2′-pyridylquinoline) (pyq), which can be substituted both in the 4 and 4′ positions by X = H, CH_3, COOH, or $C(CH_3)_3$ (ligand structures are reported in Table S1 of the Supporting Information (SI)), and finally, a monodentate ligand Y = Cl^-, I^-, or NCS^-. These dyes show reversible metal oxidations and, in the Os case, unprecedented photoconversion efficiency in the near-infrared (NIR).

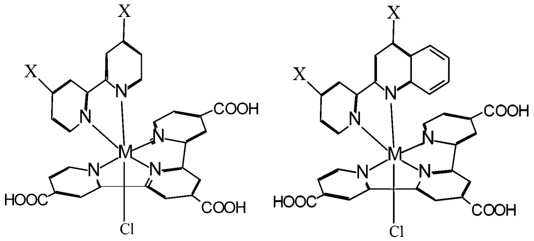

Figure 1. Structures of the investigated cationic dyes.

The syntheses (see SI, section S1) of the Os and Ru complexes have been carried out in *n*-butanol starting from the chloride species which were treated first with the (H_3tcterpy) ligand followed by reaction with the bidentate aromatic ligand L bearing the different substituents X. Substitution of the coordinated monodentate ligand Cl^- with I^- or NCS^- was preceded by treatment with Ag^+. The cationic complexes were finally precipitated mainly as hexafluorophosphate salts. A fine-tuning of the spectroscopic and electrochemical properties of the complexes was obtained by changing the substituents X at the bipyridine (X-bpy) and pyridylquinoline (X-pyq) ligands. Electrochemical and photoelectrochemical properties of the synthesized dyes, such as half-wave potential $E_{1/2}$, maximum IPCE,[11] short-circuit photocurrent J_{sc}, and open-circuit photovoltage V_{oc}, obtained from DSSCs, are reported in Table 1. For the Ru complexes, minor changes were observed by changing the coordinated Cl^- with I^- or NCS^-. The effect of systematic variations of the ligand environment on the spectroscopic properties of metal polypyridine complexes has previously been investigated and discussed.[14,15] Coordination at the metal center of acceptor ligands with low-lying π^* orbitals red shifts the energy of the corresponding $d\pi-\pi^*$ metal-to-ligand charge transfer (MLCT) transitions and anodically shifts the metal oxidation potential. The red sensitivity of the metal complex can further be increased by introducing σ- and π-donating ligands, which increase the electron density at the metal center.[16] These effects are magnified in the Os(II) complexes, where the high spin−orbit coupling constant (SO ca. 3000 cm^{-1})[20] allows the direct population of low energy, spin forbidden,[3] MLCT states. Osmium dyes showing high photoconversion efficiencies in the red part of the visible region have previously been studied.[17,18] The molecular design that we have explored allows one to further extend the light harvesting efficiency to the NIR.

The photoelectrochemical characterization of the dyes was performed in sandwich-type DSSCs by using I^-/I_3^- as electron mediator. The preparation of the photoanodes, the assembly of the cells, and the description of the photoelectrochemical measurements are given in section S2 of the SI. The photoaction spectra of some of the investigated Os and Ru dyes are reported in Figure 2 and Figure S2 of the SI, respectively.

Concerning the Os case, the photoaction spectra are quite broad; the conversion of photons to electrons starts at 1100 nm, with maxima of photoaction spectra, uncorrected for the absorption of the glass support, approaching 50% at 900 nm and 70% in the visible region. This is the first time that such high spectral efficiency at so large wavelengths has been achieved. As a result, even if the IPCE maximum is below that of the black dye, the integrated photocurrent for some of these dyes is close to that of the black dye and superior to that of red dye. We have to note, however, that these spectra were obtained with LiI-rich electrolyte (Electrolyte 1 made of 2 M LiI and 0.1 M I_2 in γ-butyrolactone), without alkaline additives such as 4-*tert*-butylpyridine, which always gives large IPCE but low V_{oc} and cell efficiencies. When using Electrolyte 2 (made of 0.7 M dimethylimidazolium iodide, 0.3 M LiI, 0.1 M I_2 + 0.5 M 4-*tert*-butylpyridine in γ-butyrolactone), the short-circuit

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10.1021/ja053438d CCC: $30.25 © 2005 American Chemical Society

Table 1. Electrochemical and Photoelectrochemical Properties of Os and Ru Dyes

			Electrolyte 1			Electrolyte 2		
dye code	dye formula	$E_{1/2}$[a] (V) vs NHE	IPCE[b] max (%)	J_{sc}[c] (mA/cm^2)	V_{oc}[d] (V)	IPCE[b] max (%)	J_{sc}[c] (mA/cm^2)	V_{oc}[d] (V)
Os bpy Cl	$[Os(H_3tcterpy)(bpy)Cl]PF_6$	0.76	58	15.4	0.22	18	2,5	0.40
Os dmbpy Cl	$[Os(H_3tcterpy)(dmbpy)Cl]PF_6$	0.78	50	14.4	0.19	17	2.7	0.42
OsH2dcbpyCl	$[Os(H_3tcterpy)(H_2dcbpy)Cl]PF_6$	0.91	68	18.7	0.25	21	3.5	0.42
Os tbbpy Cl	$[Os(H_3tcterpy)(tbbpy)Cl]PF_6$	0.79	50	13.3	0.21	31	5.8	0.45
Os pyq Cl	$[Os(H_3tcterpy)(pyq)Cl]PF_6$	0.89	65	18.5	0.23	12	1.9	0.40
Ru tbbpy Cl	$[Ru(H_3tcterpy)(tbbpy)Cl]Cl$	1.12	78	17.5	0.41	33	6.6	0.51
Ru tbbpy Cl	$[Ru(H_3tcterpy)(tbbpy)Cl]PF_6$	1.12	71	15.5	0.40	49	9.1	0.60
Ru tbbpy I	$[Ru(H_3tcterpy)(tbbpy)I]PF_6$	1.12	78	16.7	0.43	37	5.8	0.55
Ru tbbpy SCN	$[Ru(H_3tcterpy)(tbbpy)SCN]PF_6$	1.17	79	15.4	0.44	57	10.0	0.62
Ru pyq Cl	$[Ru(H_3tcterpy)(pyq)Cl]PF_6$	1.22	79	17.4	0.45	48	9.9	0.60
Ru pyq I	$[Ru(H_3tcterpy)(pyq)I]PF_6$	1.18	71	13.5	0.36	6	0.7	0.55
Ru dmpyq Cl	$[Ru(H_3tcterpy)(dmpyq)Cl]PF_6$	1.18	66	13.7	0.38	36	6.5	0.57
Ru dmpyq I	$[Ru(H_3tcterpy)(dmpyq)I]PF_6$	1.15	67	13.6	0.31	9	1.2	0.45
Ru Hmcpyq Cl	$[Ru(H_3tcterpy)(Hmcpyq)Cl]PF_6$	1.21	75	15.2	0.34	15	2.2	0.48
Ru Hcpyq Cl	$[Ru(H_3tcterpy)(Hcpyq)Cl]\ PF_6$	1.23	48	9.1	0.43	19	2.8	0.52
black[e]	$[Ru(Htcterpy)(SCN)_3]\ TBA_3$	0.85	82	19.5	0.52	73	16.5	0.70
red[e]	$[Ru(Hdcbpy)_2(SCN)_2]\ TBA_2$	0.81	85	16.5	0.49	80	14.8	0.69

[a] $E_{1/2}$ is the half-wave potential obtained from the CV curves and expressed versus the normal hydrogen electrode (NHE). [b] IPCE max is the maximum value of the IPCE plots collected under short-circuit condition. [c] J_{sc} is the integrated photocurrent of the IPCE plot from 400 to 1100 nm with respect to the standard AM1.5G solar cell spectrum. [d] V_{oc} is the open-circuit photovoltage. [e] The well-known Ru red and black dyes are included at the end for comparison.

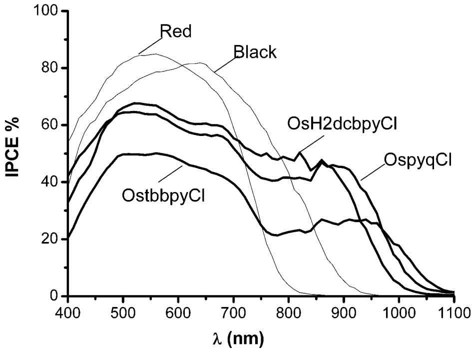

Figure 2. Photoaction spectra of Os dyes measured in sandwich-type solar cells (nanocrystalline TiO_2 films, electrolyte made of 2 M LiI + 0.1 M I_2 in γ-butyrolactone). $OsH_2dcpyCl = [Os(H_3tcterpy)(H_2dcbpy)(Cl)]^+$; $OstbbpyCl = [Os(H_3tcterpy)(tbbpy)(Cl)]^+$; $OspyqCl = [Os(H_3tcterpy)(pyq)(Cl)]^+$.

currents J_{sc} decreased significantly with respect to that obtained with Electrolyte 1, much more than in the case of the red or black dye, and the observed V_{oc} values were lower (Table 1) than the typical value of 0.7 V obtained with the red or black dye.[17] It is known that V_{oc} is kinetically limited by electron tunneling through the solid to acceptors at the interface or in the electrolyte,[11,21] and equations quantifying this kinetic control have been reported.[21] The low V_{oc} values obtained when using the Os dyes can be due either to efficient back electron transfer to the nascent Os(III) center or to back electron transfer from the conduction band to I_2 mediated by low-lying ligand orbitals, as previously observed by the Arakawa group.[19] This issue will be the object of further investigation.

The photoaction spectra of the new Ru dyes (Figure S2 of the SI) fall between the spectra of the red, $[Ru(Hdcbpy)_2(NCS)_2)](TBA)_2$, and the black, $[Ru(Htcterpy)(NCS)_3](TBA)_3$, dye. The onsets of the photoaction spectra are at wavelengths shorter than 950 nm, and the spectral efficiencies are lower than 10% at 900 nm. Consequently, the integrated photocurrents for many of these new Ru dyes are comparable to that of the red dye, but smaller than that of the black dye. Interestingly, it can be noted that the substitution of coordinated Cl^- or NCS^- with I^- does not affect the photoelectrochemical performances of the Ru dyes (Table 1), a feature which can be of relevance for DSSC operating with iodide as electron mediator since either thermal or photoinduced substitution of the coordinated anion by iodide can take place.[20] As in the case of Os, when we measured the performance with Electrolyte 2, the corresponding short-circuit currents J_{sc} decreased significantly with respect to that obtained with Electrolyte 1, and the V_{oc} values were rather low; however, the stability of the one-electron oxidized form, as shown by the reversible Ru(II)/(III) wave observed in CV, makes these dyes promising candidates for improving the long-term stability of DSSCs.

Acknowledgment. This work was supported by IMRA Europe and FIRB Contract RBNE019H9K.

Supporting Information Available: Ligand preparations, synthesis of ruthenium and osmium complexes, complete photoelectrochemical and electrochemical data, photoaction spectra of Ru dyes, and complete refs 12 and 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA053438D