Inorganic Chemistry

Communication

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Thiocyanate-Free Ruthenium(II) Sensitizer with a Pyrid-2-yltetrazolate Ligand for Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: The synthesis of the new complex [Ru(Tetrazpy)(dcbpy)$_2$]Cl is reported, along with its spectroscopical, electrochemical, and theoretical characterization. The first dye-sensitized solar cell device with this complex has been prepared, leading to a 3% of conversion efficiency, promising data considering the simplicity of the Tetrazpy ligand.

The use of renewable energy sources instead of fossil fuel is a necessity of humanity. The Sun is a green and cheap source of energy: 10 min of solar irradiation onto the Earth's surface is equal to the total yearly human energy consumption.[1,2] The world energy challenge can be won by harnessing the Sun's power with photovoltaic technologies. Dye-sensitized solar cells (DSSCs) have been extensively studied as sunlight-to-electricity conversion systems[3,4] with power conversion efficiencies exceeding a value of 12%.[5]

The most commonly used photosensitizers are 2,2′-bipyridineruthenium(II) (2,2′-bipyridine = bpy) complexes with thiocyanate (NCS) ligands, such as *cis*-dithiocyanatobis(2,2′-bipyridine-4,4′-dicarboxylate)ruthenium(II) (N3 and N719);[6,7] a limitation of such ruthenium(II) complexes is the presence of NCS ancillary ligands. NCS is an ambidentate ligand that can be easily replaced by other competing ligands, yielding less efficient species. Often, 4-*tert*-butylpyridine is used as an additive in the electrolyte solution,[8,9] but NCS-based ruthenium dyes[10,11] may release a NCS ligand by ligand exchange with 4-*tert*-butylpyridine or with the solvent. The efficiency of a N719−4-*tert*-butylpyridine cell compared to N719 in a similar DSSC is 50% lower because of the ca. 30 nm blue shift in its optical absorption spectrum.[12] Clearly, it is crucial to develop NCS-free ruthenium sensitizers.[1,13]

Cyclometalated ruthenium complexes are an alternative for DSSCs. In fact, cyclometalating ligands give stability to complexes often used for organic light-emitting diodes (OLEDs)[14] or organic light-emitting electrochemical cells.[15] Graetzel et al.,[16] Berlinguette et al.,[17] van Koten et al.,[18] and our team[19] have studied ruthenium complexes with cyclometalated-ligand-based DSSCs. Also, other ligands were used instead of NCS ligands, for example, oxyquinolate,[20] pyridylpyrazole, and triazole.[21]

To our knowledge, pyrid-2-yltetrazolate (Tetrazpy) ligands have never been used in ruthenium dyes for DSSCs, although they have been used for the preparation of luminescent organometallic complexes for OLEDs,[22] as ligands for polymeric coordination materials,[23a] and for lanthanide ions, as contrast agents.[23b] The stronger electron-withdrawing character of the tetrazolate ligand with respect to phenylpyridine can increase the oxidation potential of ruthenium(II) dyes containing these ligands, a tool for the facile regeneration of oxidized sensitizers by the redox couple. This observation prompted us to synthesize the first ruthenium dye with a Tetrazpy ligand for DSSCs (see Figure 1).

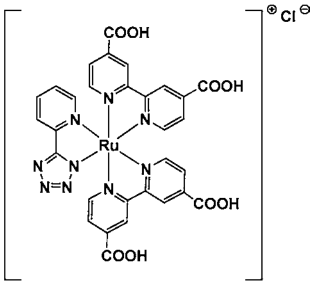

Figure 1. Ruthenium dye with a Tetrazpy ligand.

The synthesis involves two steps: (i) preparation of [RuCl$_2$(dcbpy)$_2$] (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid);[24] (ii) substitution of the chlorides in [RuCl$_2$(dcbpy)$_2$] with 5-(pyrid-2-yl)tetrazole[25] (see the Supporting Information).

The good agreement between the experimentally and computed UV−vis spectra of the ruthenium dye in dimethyl sulfoxide (DMSO) is presented in Figure 2. There are three bands in the visible region, instead of the two bands seen for NCS−Ru dyes, allowing a broad harvesting of solar radiation, although the ε values are not high (λ = 377 nm, ε = 9950 M^{-1} cm^{-1}; λ = 444 nm, ε = 6450 M^{-1} cm^{-1}; λ = 496 nm, ε = 10100

Received: July 12, 2013
Published: September 11, 2013

dx.doi.org/10.1021/ic401794g | *Inorg. Chem.* 2013, 52, 10723−10725

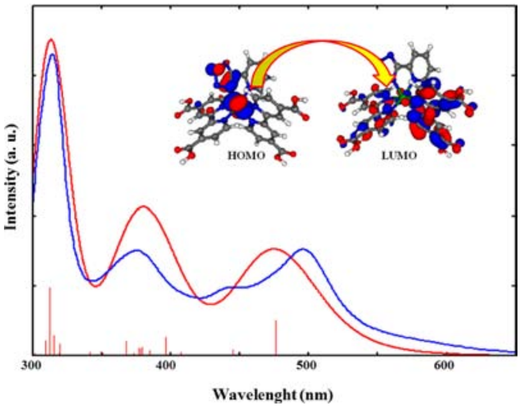

Figure 2. Computed (red lines) and experimental (blue lines) UV−vis spectra in DMSO. Red vertical lines correspond to calculated excitation energies and oscillator strengths. Inset: isodensity surface plots (isodensity counter = 0.035) of molecular orbitals involved in the lowest intense transition that gives the absorption band at 474 nm.

M^{-1} cm^{-1}). We computed the first band at 475 nm, slightly blue-shifted with respect to the experiment (0.11 eV), with metal-to-ligand charge-transfer character.

A cyclic voltammetry (CV)/differential pulse voltammetry (DPV) study of the tetrazole-based complex was performed; in order to clarify its electrochemical behavior, the free ligands 5-(pyrid-2-yl)-1*H*-tetrazole (TetrazHpy) and dcbpy have also been investigated. The main voltammetric results are shown in Table 1 (see also the Supporting Information).

Table 1. Main CV Parameters

	oxidation		reduction	
	$E_p{}^a$	$\Delta E_p{}^b$	$E_{p,I}{}^a$	$\Delta E_p{}^b$
TetrazHpy			−1.99	0.106
dcbpy			−1.82	0.115
[Ru(Tetrazpy)(dcbpy)$_2$]Cl	0.54	0.088	−1.49	0.069

[a] Peak potential (E_p/V vs Fc$^+$|Fc) in *N*,*N*-dimethylformamide (DMF) with 0.1 M TBAPF$_6$. [b] $\Delta E_p = E_p - E_{p/2}$.

[Ru(Tetrazpy)(dcbpy)$_2$]Cl presents an oxidation peak at 0.54 V (Fc$^+$|Fc), at 0.05 V s^{-1} scan rate potential (Figure 3), due to a monoelectronic, chemically reversible, and electrochemically irreversible process that can be assigned to the Ru$^{3+/2+}$ redox reaction (see the Supporting Information). As expected, the high-electron-withdrawing tetrazolate ligand stabilizes the bivalent state of the metal with respect to complexes with phenylpyridine and oxyquinolate ligands.[20] In the cathodic window, the first electrochemical process can be attributed to a reduction localized on the dcbpy ligand, as suggested by the relative energy of the two free ligands (Figure 3) and by density functional theory calculations (Figure 2).

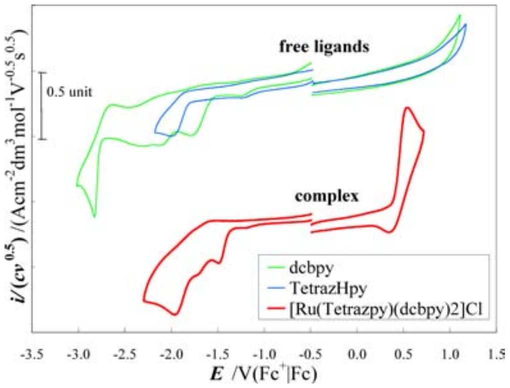

Figure 3. Synopsis of cyclic voltammograms for free ligands (top) and [Ru(Tetrazpy)(dcbpy)$_2$]Cl (bottom) on a glassy carbon electrode (0.071 cm^2). Sample concentration = 0.001 M in DMF with 0.1 M TBAPF$_6$; potential scan rate = 0.05 V s^{-1}; positive feedback (200−210 Ω).

The $E_{1/2}$ value for the couple dye$^{+/0}$, $E_{1/2(\text{dye+|dye})}$ = 0.9 V (SHE) (see the Supporting Information), is more positive (ca. 0.4 V) than that of the I$^-$|I$_3{}^-$ redox shuttle, affording a significant thermodynamic driving force to reduction of the oxidized dye.

The photovoltaic performances obtained with [Ru(Tetrazpy)(dcbpy)$_2$]Cl are reported in Table 2 and Figure 4. We obtain a maximum conversion efficiency η of 3.0% (cell 4) using both chenodeoxycholic acid (CDCA) as the coadsorbent and LiI as the electrolyte additive. From the absorption spectra of the dye on TiO$_2$, with and without CDCA (see the Supporting Information), we do not observe a strong difference, suggesting that only weak aggregation issues are present. The improvement of all of the photovoltaic parameters may be due to reduction of the recombination processes between I$_3{}^-$ ions in the electrolyte and the injected electrons.[26,27] Unexpectedly, there is a simultaneous increase of the photocurrent and a decrease of V_{oc} for the LiI additive because the Li$^+$ ions are able to downshift the TiO$_2$ conduction band.[28] Overall, a considerable improvement in the photocurrent (>30%) with respect to cell 1, without additives, was obtained, despite a slight reduction in V_{oc} and FF. For N719-based devices, made in analogous conditions, we reached an efficiency of 6.1%. The lower performances of [Ru(Tetrazpy)(dcbpy)$_2$]Cl with respect to N719 is caused by the strong reduction in the photocurrent and V_{oc} values. This can be explained by the lower amount of absorbed light, as can be

Table 2. Photovoltaic Parameters for DSSCs with [Ru(Tetrazpy)(dcbpy)$_2$]Cl, under Simulated AM 1.5 Sun Illumination

cell	additive	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
1		5.6	626	0.68	2.4
2	0.01 M CDCA	5.9	655	0.70	2.7
3	0.1 M LiI	6.4	598	0.67	2.6
4	0.01 M CDCA and 0.1 M LiI	7.6	609	0.65	3.0
N719		12.4	734	0.67	6.1

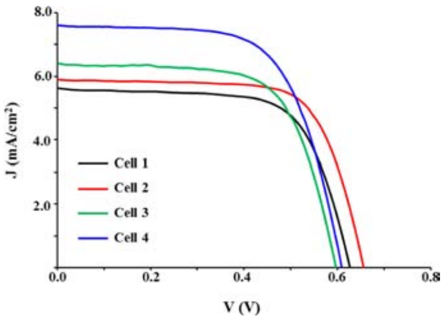

Figure 4. *JV* characteristic of DSSCs: cell 1, black line; cell 2, red line; cell 3, green line; cell 4, blue line.

observed from the absorption spectra of the dyes on TiO_2 (see the Supporting Information) and a resulting less efficient electron injection process, even if the dye loading measurements have shown an amount of adsorbed dye comparable or also greater for $[Ru(Tetrazpy)(dcbpy)_2]Cl$ (5.1×10^{-8} mol cm^{-2}) with respect to N719 (4.1×10^{-8} mol cm^{-2}).

The achievement of 3% efficiency is remarkable for the first member of this new family of dyes. The use of highly π-delocalized substituted 5-(pyrid-2-yl)tetrazoles should enhance solar light harvesting, improving the cell's efficiency. The efficiency for $[Ru(ppy)(dcbpy)_2]^+$ (ppy = phenylpyridine) is 2%,[19b] whereas that of related complexes with adequately substituted ppy is much higher[19] and, in one case, reaches 10%.[16] In conclusion, our work unveils the potential of a new class of ruthenium complexes for convenient DSSCs. The first member gives a good efficiency that will be surely improved in the near future by using adequately substituted 5-(pyrid-2-yl) moieties.

ASSOCIATED CONTENT

Supporting Information

Materials, synthesis, computational details, solar cell fabrication and characterization, and electrochemical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Fondazione Cariplo (Grant 2010-0525) and by MIUR (FIRB 2004: RBPR05JH2P). P.S., M.G.L., and F.D. are also thankful for FP7-ENERGY-2010 Project 261920 "ESCORT" for financial support.

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