

Design, Synthesis, and Application of Amphiphilic Ruthenium Polypyridyl Photosensitizers in Solar Cells Based on Nanocrystalline TiO₂ Films

S. M. Zakeeruddin,[†] Md. K. Nazeeruddin,^{*†}
R. Humphry-Baker,[†] P. Péchy,[†] P. Quagliotto,[‡] C. Barolo,[‡]
G. Viscardi,[‡] and M. Grätzel^{*†}

Laboratory for Photonics and Interfaces, Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, and Dipartimento di Chimica Generale ed Organica Applicata, Corso Massimo, D'Azeglio 48, 10125 Torino, Italy

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There is currently considerable interest in ruthenium(II) polypyridyl complexes because of their applications in nanocrystalline TiO₂ based solar cells,^{1–4} biosensors,⁵ molecular wires,⁶ and light-emitting diodes.⁷ The *cis*-dithiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) complex (referred to as N3) is widely used as a charge-transfer sensitizer in dye-sensitized solar cells and shows a high incident photon to current conversion efficiency (IPCE) yielding close to 10% under AM 1.5 solar conditions.⁸ Heteroleptic amphiphilic sensitizers are another interesting class of sensitizers for solar cell applications. In this paper we report a new series of heteroleptic amphiphilic ruthenium polypyridyl photosensitizers, [Ru(H₂dc bpy)(mhdbpy)(NCS)₂] (**1**), [Ru(H₂dc bpy)(dtdbpy)(NCS)₂] (**2**), and [Ru(H₂dc bpy)(mddbpy)(NCS)₂] (**3**) (where the ligands H₂dc bpy = 4,4'-dicarboxy-2,2'-bipyridine, mhdbpy = 4-methyl-4'-(hexadecyl-2,2'-bipyridine), dtdbpy = 4,4'-ditridecyl-2,2'-bipyridine, and mddbpy = 4-methyl-4'-(2-dodecyltetradecyl)-2,2'-bipyridine), and their stability toward water-based desorption from a TiO₂ surface.

* To whom correspondence may be addressed. E-mail: Mdkhaja.Nazeeruddin@epfl.ch. Phone: ++41-21-693 61 24. Fax: ++41-21-693 41 11.

[†] Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland.

[‡] Dipartimento di Chimica Generale ed Organica Applicata.

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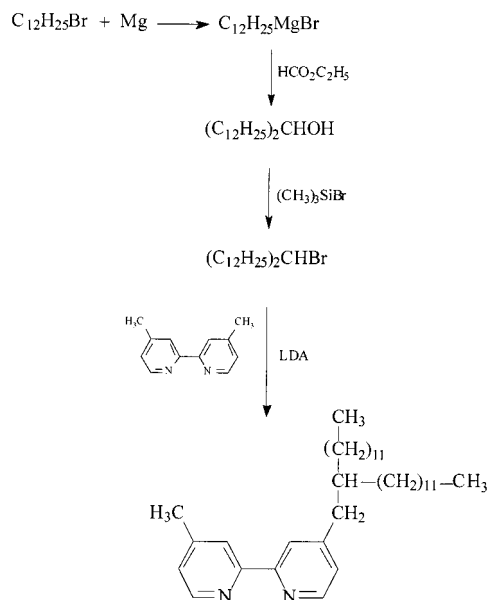
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Scheme 1



The ligands mhdbpy and dtdbpy were prepared using a literature procedure.⁹ Scheme 1 shows the synthetic strategy applied for synthesis of 4-methyl-4'-(2-dodecyltetradecyl)-2,2'-bipyridine. A solution of ethyl formate in anhydrous ethyl ether was added to an ether solution of the Grignard reagent of 1-bromododecane. After the reaction was quenched, the secondary alcohol was isolated as a white solid, which was then converted to its bromide derivative with bromotrimethylsilane. The solution of the bromide derivative was added to the solution of 4,4'-dimethyl-2,2'-bipyridine, which was selectively monolithiated using lithium diisopropylamide (2.0 M). After the reaction was quenched, the crude product was purified by flash chromatography, to obtain the asymmetric 2,2'-bipyridine ligand (see the Supporting Information for synthetic details).

Figure 1 shows the structures of complexes **1**, **2**, and **3**, which were obtained by refluxing an excess of NCS⁻ ligand with the corresponding heteroleptic dichloro complexes using a published procedure¹⁰ (see the Supporting Information for synthetic details). The elemental analysis and the spectroscopic data are consistent with the proposed structures.¹¹ Table 1 shows UV-vis, emission, and electrochemical data of complexes **1–3**, which were measured in ethanol. The complex **1** shows broad and intense visible bands between 390 and 530 nm regions due to metal-to-ligand charge transfer (MLCT) transitions. The low-energy MLCT band of complex **1** is blue shifted by 10 nm when compared to the *cis*-dithiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) complex (Table 1). The two distinct absorption bands in the UV region at 296 and 314 nm are due to the mhdbpy and H₂dc bpy

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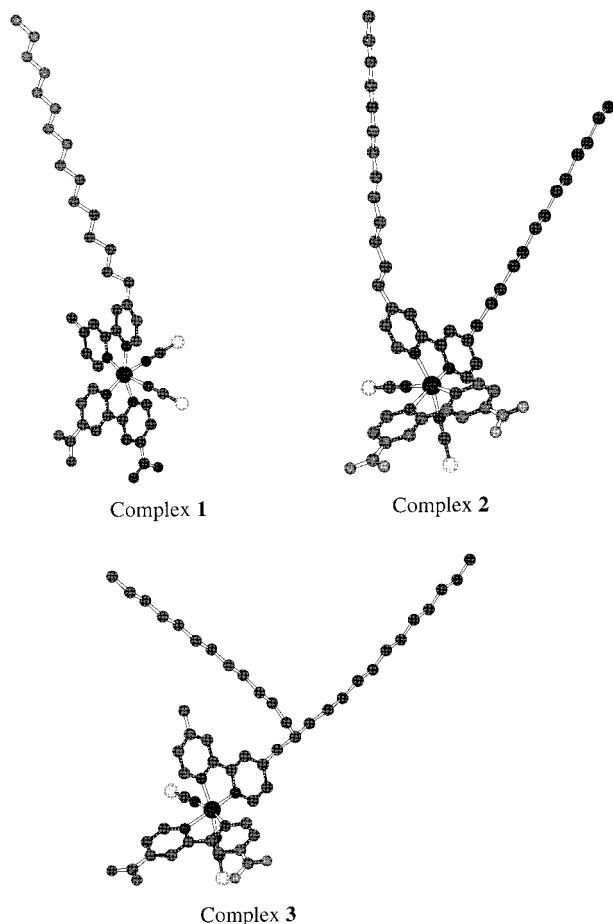
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(11) Anal. Calcd for [Ru(H₂dc bpy)(mhdbpy)(NCS)₂]-2H₂O (**1**), RuC₄₁H₅₄N₆S₂O₆: C, 55.22; H, 6.06; N, 9.43. Found: C, 55.57; H, 6.06; N, 9.38. Anal. Calcd for [Ru(H₂dc bpy)(dtdbpy)(NCS)₂]-3H₂O (**2**), RuC₅₀H₇₃N₆O₇S₂: C, 57.97; H, 7.15; N, 8.11. Found: C, 58.01; H, 6.96; N, 8.01. Anal. Calcd for [Ru(H₂dc bpy)(mddbpy)(NCS)₂]-2H₂O (**3**), RuC₅₁H₇₄N₆O₆S₂: C, 60.41; H, 7.10; N, 8.29. Found: C, 61.09; H, 7.90; N, 8.42.

Table 1. Absorption, Luminescence, Redox, and Photoelectrochemical Properties of Complexes 1–3

complex	abs max (nm) ^a ($\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$)			em ^b λ_{max} (nm)	τ^c (ns)	Ru(II/III) ^d	I_{sc}^f (mA/cm ²)	V_{oc}^g (mV)	FF ^h
	$\pi-\pi^* \text{ L}^1$	$\pi-\pi^* \text{ L}^2$	d $\pi-\pi^*$						
1	296 (3.65)	314 (2.53)	384 (1.0), 528 (1.01)	746	13	0.70	16.7	715	0.64
2	296 (3.60)	312 (2.50)	384 (1.01), 525 (1.11)	742	29	0.74	15.9	740	0.72
3	296 (3.77)	312 (2.61)	380 (1.03), 520 (1.10)	734	17	0.70	13.2	670	0.64
N3		314 (4.82)	398 (1.4), 538 (1.42)	830	20	0.85 ^e	16.5	640	0.65

^a Measured in ethanol, L1 = mhdbpy, dtdbpy, mddbpy; L2 = H₂dc bpy. ^b The emission spectra were obtained by exciting into the lowest MLCT band at 298 K in ethanol solution, values ± 2 nm. ^c At 298 K in ethanol solution ± 1 ns. ^d V vs Ag/AgCl, measured in DMF solution, under similar conditions ferrocene/ferrocenium redox couple was observed 0.46 V vs Ag/AgCl. ^e Value from ref 8. ^f Short circuit current under simulated AM 1.5 solar light. ^g Open circuit voltage under simulated AM 1.5 solar light. ^h Fill factor.

**Figure 1.** Structure of complexes **1**, **2**, and **3**.

ligands $\pi-\pi^*$ transitions, respectively. The UV absorption bands were assigned by comparing to the corresponding homoleptic complexes.

When the complexes **1–3** are excited within the low-energy MLCT transition bands in an air-equilibrated ethanol solution, they show luminescence maxima at 746, 742, and 734 nm, respectively. The excited-state lifetimes of these complexes, measured under similar conditions as the emission spectra are found to be in the range of 15–30 ns. The cyclic voltammogram of **1** in DMF shows a reversible wave at 0.7 V vs Ag/AgCl, on a glassy carbon electrode at a scan rate of 500 mV s⁻¹, which can be readily assigned to the Ru(II)/(III) couple. The ratio between the oxidation peak current and the reduction peak current is 0.9. On the cathodic side, there is a quasireversible peak at -1.57 V vs Ag/AgCl, assigned to the reduction of H₂-dc bpy ligand. The Ru(II)/(III) couple in complex **1** is 150 mV less positive than the value measured for [Ru(H₂-dc bpy)₂(NCS)₂].^{12,13}

The ¹H NMR spectra of **1**, **2**, and **3** show 12 resonance peaks in the aromatic region. In the aliphatic region, in

addition to the long-chain protons for **1** and **3**, there are two methyl resonance peaks at δ 2.50 and δ 2.80 ppm corresponding to two positional isomers (see Table 2 in the Supporting Information). The proton-decoupled ¹³C NMR spectra of these complexes show, besides the pyridine peaks, two resonance peaks at 133.52 and 134.01 ppm, which were assigned to the carbon of the N-coordinated NCS ligands.¹² The attenuated total reflectance Fourier transform IR (ATR-FTIR) spectrum of complex **2** measured as a powder shows the most prominent bands at 2105 cm⁻¹ (-NCS), 1710 cm⁻¹ (C=O), and 1240 cm⁻¹ (C-O).¹⁴ The adsorption of **2** onto TiO₂ from 2 \times 10⁻⁴ M solution gave a significantly altered spectrum in the 1300–1700 cm⁻¹ region while the -NCS group absorption remains at 2110 cm⁻¹. The IR spectrum of **2** adsorbed on TiO₂ clearly shows the bands at 1608 cm⁻¹ (-COO⁻_{as}) and 1383 cm⁻¹ (-COO⁻_s) indicating that the two carboxylic groups are deprotonated and are involved in the adsorption of the dye on the surface. The IR data show unambiguously that the dye is being adsorbed on the surface using the two carboxylate groups as a bidentate chelation or bridging mode rather than an ester type linkage.¹⁵

The nanocrystalline TiO₂ (anatase) films were prepared on conducting glass using a previously described procedure.¹⁶ The electrodes were heated to 450 °C for 10 min and then allowed to cool to \approx 50 °C before dipping into the dye solution (3 \times 10⁻⁴ M in ethanol) for 20 h. The dark red colored films exhibited \approx 80% incident photon to current conversion efficiency when tested in a photovoltaic cell in conjunction with a redox electrolyte 0.6 M dimethylpropylimidazolium iodide and 100 mM of iodine in methoxyacetonitrile. Figure 2 shows the photocurrent action spectrum of a cell containing sensitizer **1** where the incident photon to current conversion efficiency is plotted as a function of wavelength. The overlap integral of this curve with the standard global AM 1.5 solar emission spectrum yields a photocurrent density of 16 \pm 1 mA/cm²; the open circuit potential is 730 \pm 10 mV. The short circuit currents and open circuit voltages measured with **1**, **2**, and **3** are collected in Table 1.

The rate of electron transport in dye-sensitized solar cell is a major element of the overall efficiency of the cells. The electrons, injected into the conduction band from optically excited dye, can traverse the TiO₂ network and be collected at the transparent conducting glass or can react with a redox mediator. The reaction of conduction band electrons with a redox mediator gives undesirable

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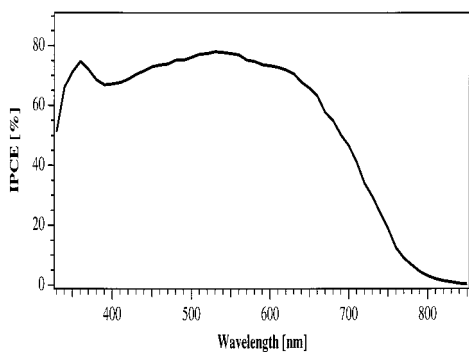


Figure 2. Photocurrent action spectrum obtained with complex **1** attached to nanocrystalline TiO₂ films. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light.

dark currents reducing significantly the charge-collection efficiency and thereby decreasing the total efficiency of the cell.¹⁷ The long chains of the sensitizer in all likelihood interact laterally to form an aliphatic network thereby probably impeding triiodide from reaching the TiO₂ surface. The increased open circuit potential of the cell containing hydrophobic sensitizers **1–3**, compared to the N3 sensitizer is attributed to the reduced number of protons adsorbed on the TiO₂ surface, which is known to have a Nernstian dependence on pH.^{12,18}

The effect of water in the electrolyte on the overall stability of a solar cell has been studied systematically. Stable cells have been prepared using the sensitizer **1** and N3 for comparison. The reported data are a mean value of 12 cells prepared at different times. The stability measurements were done at 0.015 mW/cm² by using HMII + 10 mM I₂ as an electrolyte. The data show that over a period of 50 days, all the cells are stable in an electrolyte that contains no added water (Figure 3). However, in the presence of an electrolyte that contains 5 and 10% added water, the performance of N3 cells decreased compared to the cells that contained sensitizer **1** (Figure 3). The stability of the cells containing amphiphilic heteroleptic ruthenium(II) sensitizers is due to their insolubility in water caused by the aliphatic chains.

Conclusion

We have designed new sensitizers that yield incident photon-to-current conversion efficiency values of about 80%. The performance of these novel hydrophobic com-

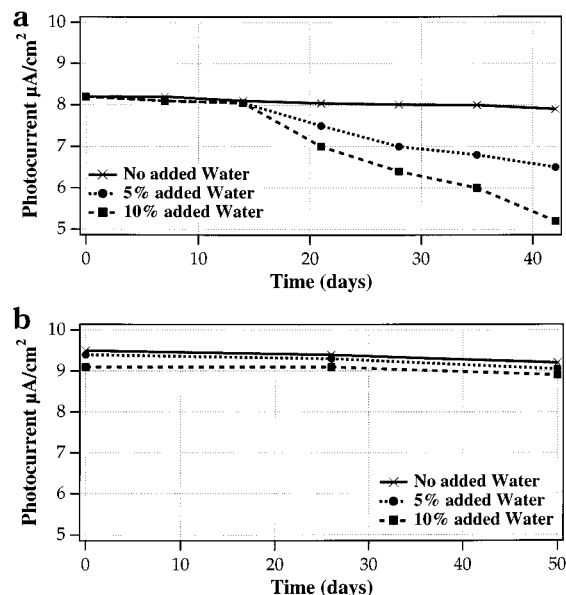


Figure 3. (a) Stability test with the N3 sensitizer. Measurements were taken at 0.015 mW/cm², showing the short circuit currents in dependence of the water amount in the electrolyte (HMII + 10 mM I₂). (b) Stability test with the sensitizer **1**. Measurements were taken at 0.015 mW/cm², showing the short circuit currents in dependence of the water amount in the electrolyte (HMII + 10 mM I₂).

plexes as charge-transfer photosensitizers in a nanocrystalline TiO₂ based solar cell show an excellent stability toward water-induced desorption. This class of sensitizers opens up a new avenue for the development of dye-sensitized solar cells that can operate in the presence of water-containing electrolytes.

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Supporting Information Available: Experimental procedures for the synthesis of mddbpy ligand and the ruthenium complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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