Dye-sensitized solar cells (DSCs) are low-cost alternatives to conventional silicon technologies for solar energy conversion. A typical DSC is composed of a chromophore that is anchored to a mesostructured anode of anatase titania (TiO₂). Upon absorption of photons, electrons are injected from the excited state of the dye into the TiO₂ conduction band. The electrons injected into the semiconductor flow towards the counter electrode where the redox mediator is in electrolyte. The electrons injected into the semiconductor flow towards the counter electrode where the redox mediator is in turn reduced.[2] Under simulated AM 1.5 G illumination, the power conversion efficiency of a cell (η) is defined as the product of the generated photocurrent density (J_SC), the open-circuit photovoltage (V_OC), and the fill factor (FF), as follows: η = J_SC V_OC FF.[4]

In addition to their long-term stability, sensitizers of the [Ru(2,2'-bipyridine)₃(NCS)₂] type have attained power conversion efficiencies of up to 12% with iodine electrolytes.[5-9] The recent surge of organic dyes to this level of performance can be largely explained by the development of alternative redox mediators, in particular cobalt(II/III) complexes.[10] In contrast to the iodide/tribromide couple (I⁻/I₃⁻), the electrochemical potential of these species can be adjusted through substitution and/or the modification of the ligand skeleton.[11-15] This tuning minimizes energy losses in the device by optimizing the driving force for regeneration, which allows for considerable improvement of the open-circuit voltage relative to iodine electrolytes.

Current ruthenium(II) sensitizers are not designed to perform with cobalt electrolytes. Among the few examples reported in the literature,[11,16-20] only limited performances have been achieved. The highest performing dye (Z907) yields efficiencies of up to 6.5% with cobalt[16] vs. 8.5% with iodine,[21] unless the adsorbent is specifically engineered.[22] Molecular dynamic simulations suggest close contact interactions between the cobalt(III) species and the anchored sensitizer(s), which causes undesired recombination of the electrons injected into the TiO₂ to the redox mediator.[23] Similar issues have been addressed for organic dyes through the addition of peripheral bulky substituents. This strategy prolongs the electron lifetime in the semiconductor by preventing the electrolyte from accessing the surface.[12]

Implementation of a similar design principle could improve compatibility between ruthenium(II) sensitizers and cobalt electrolytes. Cyclometalated tris-heteroleptic complexes have the desirable photoelectrochemical properties,[24] to yield high-efficiency DSCs,[25] while presenting versatility towards NCS-free sensizers. Herein, we report a design that takes advantage of this multifunctional structure to insulate the surface from the electrolyte, tune the energy levels and the light-harvesting properties of the complex, and provide an anchor to the TiO₂. Owing to this rational design, DSCs exhibiting comparable efficiencies with both cobalt and iodine redox mediators were obtained.

To improve compatibility of ruthenium(II) sensitizers with cobalt redox mediators, one could design a tris-heteroleptic complex that maintains favorable highest occupied molecular orbital (HOMO) energetics while also enabling electronic coupling with the TiO₂ surface. However, this approach is not limited to cobalt electrolytes. We found that 2,6-dimethoxy-2,3-bipyridine to be convenient for tuning the HOMO energy level. The alkoxy substituents are also advantageous as a substitution point to insulate the TiO₂ surface by elongation of the chains. To validate this concept, both methoxy- and dodecylxoxy-derivatives were synthesized. The other two ligands used to complete the coordination sphere of the ruthenium center have two functions: 2,2'-bis(5-hexylthiophen-2-yl)-2,2'-bipyri...
idine enhances the absorptivity of the complex, compared to an unsubstituted 2,2’-bipyridine ligand, whereas 2,2’-bipyridine-4,4’-dicarboxylic acid serves as an electron-accepting ligand and anchor to the TiO₂.

Complexes 1–3 were prepared by following a straightforward procedure developed by Berlinguette et al. As shown in Scheme 1, with [Ru(C₆H₆)Cl₂]₂ as the ruthenium source, the cyclometalating ligand is introduced first to yield precursors 1a and 1b. The complex is subsequently reacted with stoichiometric amounts of the two different bipyridine ligands, in a one-pot procedure that gives the desired complexes, 2a or 2b, in yields close to the theoretical limit. Finally, sensitizers 3a and 3b are obtained as neutral complexes after saponification. Unlike most ruthenium(II) sensitizers, which are isolated using size-exclusion chromatography, complexes 1–3 can be purified using conventional chromatography over alumina or silica and by using precipitation techniques. Details on the synthesis and characterization of these compounds are given in the Supporting Information.

Owing to their tris-heteroleptic nature, complexes 2 and 3 can potentially adopt two conformations with cyclometalation either in trans to the dicarboxy-bipyridine or in trans to the dithiophenyl-bipyridine ligand. The NMR data indicate that a single isomer is produced. To confirm the arrangement of the ligands around the metal center, single crystals of 2a were grown by slow diffusion of hexane into a dichloromethane solution. The crystal structure is shown in Figure 1, with selected bond lengths and angles presented in the Supporting Information, Table S2. As expected, the complex adopts a distorted octahedral geometry around the ruthenium center. The dimethoxy ester bipyridine ligand, located trans to the cyclometalated ring, experiences the electron donating character of the C24–Ru bond, which manifests in an elongation of the Ru–N₁ bond. The NMR analysis from which we conclude that complexes 2 and 3 adopt this same conformation (Figures S7 and S8) is consistent with the observed trans effect, as detailed in the Supporting Information. The methoxy substituents of the cyclometalated ring are arranged within the plane of the ligand to avoid lone pair interactions with the pyridyl nitrogen. At the light-harvesting ligand, the thiophenes lie in the 2,2’-bipyridine plane (torsion angles < 1°), thus ensuring good electronic communication.

Figure 1. Crystal structure of 2a 2CH₂Cl₂. Thermal ellipsoids are drawn at the 50% probability level. The counter ion, hexyl chains, hydrogen atoms, and solvent molecules are omitted for clarity. Additional information can be found in Table S1. N blue, O red, S yellow, Ru turquoise.

Figure 2. a) Steady-state absorption and normalized emission spectra (λexc = 580 nm), and b) differential pulse voltammogram with a ferrocene internal standard in dichloromethane of 3b. Scan rate of 100 mVs⁻¹ with 10 mV pulses.
at 418 nm (23400 m cm\(^{-1}\)) and 580 nm (19600 m cm\(^{-1}\)), which are characteristic of metal-to-ligand charge-transfer transitions. These assignments are further supported by time-dependent density functional theory calculations for 3a (LR-TDDFT/M06; Figures S12–S21). Full details on the quantum chemical calculations can be found in the Supporting Information.

Furthermore, the energy levels of complexes 3a and 3b are adequately poised for use in DSCs. The differential pulse voltammogram of complex 3b exhibits quasi-reversible one-electron oxidation at +0.86 V (\(E_{\text{HOMO}} = -4.91\) eV) and one-electron reduction at −1.35 V vs. NHE.\(^{[28]}\) The anodic peak potential is ascribed to the oxidation of the metal center to ruthenium(III), whereas the cathodic peak is assigned to a ligand-centered reduction. According to (U)DFT/M06 calculations, the vertical ionization energy of 3a is calculated at 5.04 eV, whereas the adiabatic ionization energy lies at 4.96 eV. Both values are in good agreement with the estimated HOMO energy and corroborate the oxidation of the ruthenium center.\(^{[29]}\) As observed in Figure S13, the spin density of the geometry optimized 3a* appears only slightly delocalized over the cyclometalated pyridine.

These \(E_{\text{S}}\) values allow regeneration of 3a* and 3b* from iodine (\(E^0 = +0.35\) V vs. NHE), as well as a variety of cobalt-based electrolytes with more positive electrochemical potentials.\(^{[13]}\) In this study, a tris(1,10-phenanthroline) cobalt(ii) electro-lyte is chosen to maximize the driving force for regeneration. The excited state oxidation potential of the dyes \(E_{\text{S, NC}}\) is estimated using the zero- and normalized emission spectra. The \(E_{\text{S, NC}}\) values for 3a and 3b (ca. −0.90 V vs. NHE) provide a priori ample driving force for electron injection into the TiO\(_2\) conduction band (\(E_{\text{C}} = ca. −0.5\) V vs. NHE).\(^{[30]}\)

Provided that electron injection is not an issue, the efficiency of TiO\(_2\) films sensitized with 3a and 3b depends on two main charge-transfer reactions: 1) back-recombination, which corresponds to electron transfer from the electron in the TiO\(_2\) to the oxidized dye, and 2) dye-regeneration, which corresponds to reductive electron transfer from the electrolyte to the oxidized sensitizer. Their respective time constants \(\tau_{\text{rec}}\) and \(\tau_{\text{reg}}\) can be quantified using transient absorption (TA) decay measurements. The oxidized forms of the dyes have absorption spectra that differ sharply from their neutral counterparts (Figure 3a,b). Following excitation at 470 nm, the photoinduced absorption (PIA) signal that appears at 740 nm is characteristic of the formation of a ruthenium(III) species,\(^{[31]}\) whose TA decay is used to derive the corresponding time constants. The decays were fitted with a single exponential component

\[
\Phi_{\text{reg}} = k_{\text{reg}} \tau_{\text{reg}}
\]

\((k_{\text{rec}} + k_{\text{reg}}) = 96\%\) (where \(k_i = 1/\tau_i\)), which is paramount for efficient DSCs.

The incident photon-to-current efficiency (IPCE) spectra using a [Co\(^{III}(\text{phen})_3\)]\(^{2+}\) electrolyte are shown in Figure 4a. Complex 3b was also investigated using I\(_2\)/I\(_3\) for comparison purposes. The three IPCEs have a similar shape in the range of 380–770 nm, but with significantly different intensities. Similar to other ruthenium(II) sensitizers,\(^{[14,19,22]}\) the photocurrent action spectra is limited to ca. 50% with 3a. The presence of C\(_{12}\) alkoxy chains on the cyclometalated ligand results in an increase of up to 70%, as exemplified by 3b. Notably, this is lower than what can be obtained when iodine is used as redox mediator. The solar-to-electricity conversion efficiencies were evaluated by recording the \(J-V\) characteristics under simulated AM 1.5 G illumination (100 mW cm\(^{-2}\)). The \(J-V\) characteristics for devices employing 3a and 3b. Film thickness: (4.0+4.0) μm. Cobalt electrolyte: 0.25 m [Co(phen)]\(^{(2+)}\) (TFSI), 0.05 m [Co(phen)]\(^{(2+)}\) (TFSI), 0.25 m TBP, 0.1 m LiTFSI in acetonitrile; iodine electrolyte: 1.0 m PMII, 0.03 m I\(_2\), 0.5 m TBP, 0.1 m GuNCS, 0.05 m LiTFSI. 3a+cobalt (---), 3b+cobalt (-----), 3b+iodine (-----). GuNCS = guanidinium thiocyanate, phen = 1,10-phenanthroline, PMII = 1-propyl-3-methylimidazolium iodide, TBP = 4-tert-butylpyridine, TFSI = trifluoromethanesulfonimide.

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**Figure 3.** a,b) PIA spectra after 470 nm excitation, and (c,d) TA decay traces following excitation at 520 nm (probe at 750 nm) of 8.0 μm thick TiO\(_2\) films coated with 3a (a, c) and 3b (b, d), respectively. Decays in acetonitrile (-----) and in presence of [Co\(^{III}(\text{phen})_3\)]\(^{2+}\) electrolyte (----) were fitted with a single exponential component \(\Delta A(t) \times A_0 \exp(-t/\tau)\). 7 ns (fwhm) laser pulse of 50 μJ cm\(^{-2}\).

**Figure 4.** a) Photocurrent action spectra in mesoscopic solar cells, and b) \(J-V\) characteristics measured under simulated AM 1.5 G full sun illumination (100 mW cm\(^{-2}\)) for devices employing 3a and 3b. Film thickness: (4.0+4.0) μm. Cobalt electrolyte: 0.25 m [Co(phen)]\(^{(2+)}\) (TFSI), 0.05 m [Co(phen)]\(^{(2+)}\) (TFSI), 0.25 m TBP, 0.1 m LiTFSI in acetonitrile; iodine electrolyte: 1.0 m PMII, 0.03 m I\(_2\), 0.5 m TBP, 0.1 m GuNCS, 0.05 m LiTFSI. 3a+cobalt (---), 3b+cobalt (-----), 3b+iodine (-----). GuNCS = guanidinium thiocyanate, phen = 1,10-phenanthroline, PMII = 1-propyl-3-methylimidazolium iodide, TBP = 4-tert-butylpyridine, TFSI = trifluoromethanesulfonimide.
the trend observed in IPCE intensities. The measured $V_{OC}$ values show large differences between 3a and 3b. The lower $V_{OC}$ obtained with iodine in the case of 3b highlights the benefit of using a cobalt electrolyte.

Relative shifts in IPCE intensities and $J-V$ characteristics can be rationalized based on transient photovoltage decays and charge extraction measurements. While maintaining constant electrolyte variations in $V_{OC}$ can often be attributed to shifts in the conduction band edge of TiO$_2$.[33] In the presence of $[\text{Co II/III}(\text{phen})_3]^{2+/3+}$, we observe negligible variation in the conduction band edge (Figure 5a), which indicates improved in cobalt-based DSCs. Upon increasing the steric properties of the cyclometalating ring, notable improvements in photon-to-current conversion and $J-V$ characteristics are observed. Transient absorption decay measurements indicate that the kinetics of recombination and regeneration remain constant, despite the modifications of the sensitizers. However, through charge extraction measurements, the device efficiency is directly correlated to increased surface protection. Physical insulation of the TiO$_2$ surface prolongs the electron lifetime by preventing abnormal recombination of injected electrons into the cobalt(III) species. This approach demonstrates a general principle that leads to unprecedented efficiency for a ruthenium(II) sensitizer used in combination with a cobalt electrolyte.

Figure 5. a) Charge density of TiO$_2$ ($d_e$) and b) electron lifetime ($t_e$) against the open-circuit photovoltage ($V_{OC}$). 3a+cobalt (○). 3b+cobalt (●).

Table 1: Detailed photovoltaic parameters of devices employing 3a and 3b under simulated AM 1.5 G illumination (100 mWcm$^{-2}$).

<table>
<thead>
<tr>
<th>Dye</th>
<th>Electrolyte</th>
<th>$J_{SC}$ [mAcm$^{-2}$]</th>
<th>$V_{OC}$ [mV]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>cobalt</td>
<td>8.3</td>
<td>714</td>
<td>0.79</td>
<td>4.7</td>
</tr>
<tr>
<td>3b</td>
<td>cobalt</td>
<td>13.2</td>
<td>837</td>
<td>0.78</td>
<td>8.6</td>
</tr>
<tr>
<td>3b</td>
<td>iodine</td>
<td>16.3</td>
<td>715</td>
<td>0.75</td>
<td>8.7</td>
</tr>
</tbody>
</table>

In summary, we have shown that the efficiency of cyclometalated ruthenium(II) sensitizers can be greatly

Keywords: cobalt · dye-sensitized solar cells · energy conversion · ruthenium · sensitizers

Received: May 28, 2013
Published online: July 4, 2013

[3] The $V_{OC}$ is defined as the energy difference between the Fermi level ($E_F$) of the TiO$_2$ and the HOMO level of the redox mediator, as follows: $V_{OC} = (E_F - E_{\text{HOMO}}) / e$, where $e$ is the elementary charge.
[4] This equation is applicable under 100 mWcm$^{-2}$ irradiation with $J_{SC}$ in mAcm$^{-2}$ and $V_{OC}$ in V.
[29] The vertical ionization corresponds to the energy difference between the cationic and the neutral species at the molecular geometry of the neutral compound; the adiabatic ionization energy corresponds to the energy difference between the optimized cationic and optimized neutral species.