Dye-sensitized solar cells (DSCs)\[1\] 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 (TiO\(_2\)). Upon absorption of photons, electrons are injected from the excited state of the dye into the TiO\(_2\) conduction band. Subsequently, the ground state form of the sensitizer is regenerated by reductive electron transfer from the 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 (100 mW cm\(^{-2}\)), the power conversion efficiency of a cell (\(\eta\)) is defined as the product of the generated photocurrent density (\(J_{\text{SC}}\)), the open-circuit photovoltage (\(V_{\text{OC}}\)),\[3\] and the fill factor (FF), as follows: \(\eta = J_{\text{SC}}V_{\text{OC}}\text{FF}\).\[4\]

In addition to their long-term stability, sensitizers of the \([\text{Ru(2,2'-bipyridine)}_2(\text{NCS})_2]\) 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.\[10\]

The excitation of the dye(s), which causes undesired recombination of the electrons injected into the TiO\(_2\) to the redox mediator.\[23\] 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 TiO\(_2\) 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 sensitizers. 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 TiO\(_2\). 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 interfacial control at the TiO\(_2\) surface. However, thus far the literature does not contain a ligand that fulfills both of these criteria.\[26–27\] We found 2,6-dimethoxy-2,3’-bipyridine to be convenient for tuning the HOMO energy level. The alkoxyl substituents are also advantageous as a substitution point to improve compatibility of ruthenium(II) sensitizers with cobalt redox mediators.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304608.
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 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.

The optical and electrochemical properties of 3a and 3b were determined in dichloromethane solution (Figure 2; see also Figures S10 and S11). Both complexes show virtually identical properties, as summarized in Table S3. The UV/Vis spectrum of 3b shows broad and intense absorptions below 350 nm that are dominated by p–p* transitions. At longer wavelengths, the spectrum reveals two strong bands centered...
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 \((E_{\text{HOMO}} = -4.91 \text{ eV})\) and one-electron reduction at −1.35 V vs. NHE.\[^{[28]}\] The anodic peak potential is ascribed to 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 \(E_{\text{GSE}}\) values allow regeneration of 3a\(^+\) and 3b\(^+\) from iodine (\(E^\text{\text{I}}\text{2} = +0.35 \text{ V vs. NHE}\)), as well as a variety of cobalt-based electrolytes with more positive redox chemical potentials.\[^{[13]}\] In this study, a tris(1,10-phenanthroline) cobalt(II/III) ([Co\(^{\text{III}}\)(phen)\(_3\)]\(^2/3\))\(^{[21]}\), \(E^\text{\text{I}}\text{2} = +0.62 \text{ V vs. NHE}\) electrolyte is chosen to maximize the \(V_\text{OC}\) while maintaining sufficient driving force for regeneration. The excited state oxidation potential of the dyes \((E_{\text{GSE}})\) is estimated using the zero-zero transition energy \((E_{\text{00}})\) measured at the intersection of the absorption and normalized emission spectra. The \(E_{\text{GSE}}\) values obtained 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 \((E_\text{C} = ca. −0.5 \text{ V vs. NHE})\).\[^{[30]}\]

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 \(A(t) = A_0 \exp(-t/\tau)\), where \(A_0\) is the pre-exponential factor and \(\tau\) is the characteristic time constant.\[^{[21]}\] The fits are represented as solid lines on Figure 3c,d. With an inert electrolyte, \(\tau_{\text{rec}}\) was estimated at 280 and 373 ms for 3a and 3b, respectively. In contrast, the presence of [Co\(^{\text{III}}\)(phen)]\(^{2+}\) gives rise to accelerated TA decays, with \(\tau_{\text{reg}}\) values of 9.7 μs and 17 μs for 3a and 3b, respectively. These \(\tau_{\text{rec}}\) and \(\tau_{\text{reg}}\) constants indicate nearly quantitative regeneration quantum yields, \(\Phi_{\text{reg}} = k_{\text{reg}}/k_{\text{rec}}\).

\[^{[21]}\] The incident photon-to-current efficiency (IPCE) spectra using a [Co\(^{\text{III}}\)(phen)]\(^{2+}\) electrolyte are shown in Figure 4a. Complex 3b was also investigated using I\(^{-}/I_2\) 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,\[^{[16,19,22]}\] 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\(^{-2}\)) for devices employing 3a and 3b. Film thickness: (4.0 ± 0.05) μm. Cobalt electrolyte: 0.25 M [Co(phen)]\(^{3+}\)(TFSI)\(_2\), 0.05 M [Co(phen)]\(^{2+}\)(TFSI)\(_2\), 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 guanidinium thiocyanate, phen = 1,10-phenanthroline, TFSI = trifluoromethanesulfonimide.
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} [mA cm^{-2}]</th>
<th>V_{OC} [mV]</th>
<th>FF</th>
<th>η [%]</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>

Table 1: 

![Figure 5](image_url)

Figure 5. a) Charge density of TiO2 (d_{n}) and b) electron lifetime (τ_{n}) against the open-circuit photovoltage (V_{OC}). 3a+cobalt (○). 3b+cobalt (●).

that the TiO2 experiences a similar dipole shift with 3a and 3b. Therefore, differences in V_{OC} can be attributed to the relative electron lifetimes in TiO2 (τ_{n}); the electron lifetime of 3b is prolonged by ca. 1.5 orders of magnitude relative to 3a (Figure 5b). The recombination of electrons injected into the semiconductor can occur by reductive electron transfer to the electrolyte and/or to the oxidized form of the sensitizer. Given that the time constants for recombination of injected electrons with 3a+ and 3b+ are similar, the presence of C_{12} alkoxy chains clearly insulates the TiO2 surface by preventing close proximity with the redox mediator. This effect has a major impact on both the J_{SC} and V_{OC} photovoltaic parameters, as shown in Table 1. Overall, the J_{SC} and V_{OC} obtained for 3a (8.3 mA cm^{-2} and 714 mV, respectively) contribute to a power conversion efficiency of 4.7%. As a result of the increased electron lifetime, the values measured for 3b rise to 13.2 mA cm^{-2} and 837 mV, respectively; DSCs with this sensitizer reach efficiencies of up to 8.6% in the presence of a cobalt electrolyte. Notably, this result closely matches those obtained with iodine (8.7%), which has been shown to achieve similar efficiencies for ruthenium(II) sensitizers.

In summary, we have shown that the efficiency of cyclometalated ruthenium(II) sensitizers can be greatly 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 sensitzers. However, through charge extraction measurements, the device efficiency is directly correlated to increased surface protection. Physical insulation of the TiO2 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.

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

[3] The V_{OC} is defined as the energy difference between the Fermi level (E_{F}) of the TiO2 and the HOMO level of the redox mediator, as follows: V_{OC}=(E_{F}−E_{HOMO})/e, where e is the elementary charge.
[4] This equation is applicable under 100 mW cm^{-2} irradiation with J_{SC} in mA cm^{-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.