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Supramolecular Hemicage Cobalt Mediators for Efficient and Stable Dye-Sensitized Solar Cells

Marina Freitag^{†,§,*}, Wenxing Yang[†], Lisa A. Fredin[§], Luca D'Amaro[†], K. Martin Karlsson[‡], Anders Hagfeldt^{†,§}, and Gerrit Boschloo[†]

[†]Department of Chemistry – Ångström Laboratory, Uppsala University, Box 523, SE-751 20 Uppsala, Sweden

[‡]Center of Molecular Devices, Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden

[§]Chemical Informatics Research Group, Chemical Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8320, Gaithersburg, Maryland, 20899-8320, USA

Abstract

A new class of dye-sensitized solar cells (DSCs) using the hemicage cobalt based mediator $[\text{Co}(\text{ttb})]^{2+/3+}$ with the highly preorganized hexadentate ligand 5,5'',5'''-((2,4,6-triethyl benzene-1,3,5-triyl)tris(ethane-2,1-diyl))tri-2,2'-bipyridine (ttb) have been fully characterized. The performance of DSCs sensitized with organic D- π -A dyes utilizing either $[\text{Co}(\text{ttb})]^{2+/3+}$ or the conventional $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (bpy = 2,2'-bipyridine) redox mediator have comparable efficiency under 1000 W m^{-2} AM 1.5G illumination. However, the hemicage complexes exhibit exceptional stability under thermal and light stress. In particular, a 120 hour continuous light illumination stability test for DSCs using $[\text{Co}(\text{ttb})]^{2+/3+}$ resulted in a 10% increase in performance, whereas 40% decrease in performance was found for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ electrolyte based DSCs under the same conditions. The improved stability at high solar cell efficiencies demonstrates the great promise of $[\text{Co}(\text{ttb})]^{2+/3+}$ complexes as redox mediators for efficient, cost-effective, large-scale DSC devices.

INTRODUCTION

Mesoscopic dye-sensitized solar cells (DSCs), developed in 1991 by O'Regan and Grätzel, are based on dye molecules attached to a nanostructured semiconductor (photoanode).^[1] They became a potential low-cost alternative for large-scale solar energy conversion,^[2] with an efficiency as high as those obtained from amorphous silicon solar cells

Corresponding Author: marina.freitag@epfl.ch.

[§]Current address: Laboratory for Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland.

SUPPORTING INFORMATION

Experimental section; electrochemical data for the redox couples diffusion coefficient and Co^{3+} thermal stress study; synthetic procedure, UV-Vis spectra and ¹H NMR spectra for the hemicage cobalt complexes; electron lifetime, electron transport time and extracted charge measurements; chemical structures of the presented dyes (MKA253, C218 and LEG4); calculated spin densities of each optimized minimum.

($\eta \sim 13\%$).^[3,4] Using low cost materials provides a large performance to price ratio.^[5] In addition DSCs do not require elaborate manufacturing apparatuses and they show excellent performance in low or diffuse light conditions.^[6,7]

In order to be commercially viable and compete with silicon-based solar cells, DSCs have to not only be cheap and efficient but also work over a long period of time (> 20 years) without significant performance loss. Dye-sensitized solar cells consist of various components where the performance and stability of the whole cell are a function of all the components and their interactions.^[8] While a lot of effort has focused on dye development, one of the key-components for the photovoltaic performance of the DSC is the redox electrolyte. The redox couple assumes the tasks of dye regeneration and charge transport between the two electrodes,^[9] which is crucial for determining the photovoltaic performance of DSCs.^[10] Finding an efficient, non-corrosive, electron-transfer mediator is an important step towards higher efficiency, longevity, and thus, the practical application of DSCs.^[11–15] The solvent for the electrolyte should have low viscosity and a high boiling point.

Cobalt complexes are especially interesting redox mediator candidates due to their favorable photoelectrochemical and kinetic behavior compared to the earlier used I^-/I_3^- couple, which for a long time has been the standard electrolyte.^[16–18] Their straightforward synthesis increases the promise of cobalt shuttles as it can give a library of accessible and adjustable complexes, allowing for optimization of the redox shuttle together with the sensitizer.^[19] The reduction potential of the redox shuttle can be matched to the dye ground state potential in order to minimize overpotential losses in the regeneration process. Another advantage is the low absorption profile of cobalt-complexes, which enables more incoming light to be used exclusively by the dye. Following the early work by Nusbaumer *et al.* regarding the use of the bis[2,6-bis(1-butylbenzimidazol-2'-yl) pyridine]cobalt (II/III) as an efficient redox mediator,^[20] cobalt polypyridine-complexes have been used successfully as redox mediators in a DSCs with suitable organic dyes.^[21–23] Feldt *et al.* reported efficient DSCs with cobalt complexes exceeding 7%,^{[16],[24]} This was accomplished by functionalizing the dye with alkoxy groups that block electron recombination from the TiO_2 to the electrolyte. By using this concept cobalt bipyridine complexes were employed by Grätzel in record efficiency cells, reaching up to 13 %.^[25] and recently a 14.3% efficiency DSC was reported by Kakiage *et al.*^[26]

A pressing problem for the cobalt-based redox mediator systems available at present is the limited stability of the cobalt complexes under prolonged irradiation conditions. This problem strongly diminishes the long-term stability and viability of the resulting DSCs.^[27,28] There are several reasons this lack of stability arises: dissociation of the complexes and exchange of ligands, long-term cobalt complex adsorption on the TiO_2 , or slow reduction of Co(III) by dissolved oxygen.^[29]

Here we investigate a new class of DSCs using a supramolecular cobalt-based mediator with desirable low visible light extinction coefficient, good diffusion coefficients, high stability, longevity, and efficiency. We combined all six nitrogen-donors in one multi-dentate ligand and used the well-known 1,3,5-tri-ethylphenyl-cap for attachment of three bipyridine-ligands in the 2, 4, and 6-position.^[30,31] This substitution pattern directs attachment of all three

bipyridine ligands to the same site because of steric repulsion with the three ethyl substituents.^[32,33] Therefore, this ligand 5,5'',5'''-((2,4,6-triethylbenzene-1,3,5-triyl)tris(ethane-2,1-diyl))tri-2,2'-bipyridine (ttb, Figure 1, right) exhibits a high degree of geometrical preorganization leading to exceptionally stable complexes, which are important to achieve long term stable DSCs. Additionally, the cage-like structure shields the cobalt metal from irreversible oxidation processes by preventing the reaction of the cobalt metal with dioxygen.^[34–36]

Here we characterize DSCs integrating the novel Co(ttb) as redox mediator and compare it to the commonly used Co(bpy)₃ (bpy = 2,2'-bipyridine). The complete device were characterized by current–voltage (I–V) measurements, incident photon to current conversion efficiency (IPCE) and various toolbox techniques. The DSCs components were further investigated by photoinduced absorption spectroscopy (PIA), transient absorption spectra (TAS), and the mediators were characterized by quantum chemical calculations.

RESULTS AND DISCUSSION

Photovoltaic Performance and Stability of the Hemicaged Cobalt Redox Mediators

The I–V curves for this series of DSCs are shown in Figure 2. The photovoltaic performance of [Co(ttb)]^{2+/3+} was comparable to the conventionally used [Co(bpy)₃]^{2+/3+} redox shuttle for thin-film DSCs sensitized with triphenylamine-based organic sensitizers. The best efficiency with the [Co(ttb)]^{2+/3+} based electrolyte of 6.6% at 1000 W m⁻² illumination was obtained for the DSCs with the cosensitized photoanode of C218 and MKA253 (4:1). Notably, the open-circuit potentials for the devices with [Co(ttb)]^{2+/3+} are comparable to those with [Co(bpy)₃]^{2+/3+}, which is remarkable considering that the Co(ttb) redox potential is 90 mV more negative. Its efficiency was insignificantly lower than was obtained with [Co(bpy)₃]^{2+/3+}, see Table 1, most likely as a result of slow mass transport of this redox mediator. The fill factor for the [Co(bpy)₃]^{2+/3+} is about 10% higher due to better diffusion (see below) and possibly less steric hindrance for the reduction reaction at the counter electrode.

The IPCE for the cosensitized DSCs with the cobalt complexes reached a similar maximum IPCE of about 78% in case of the [Co(ttb)]^{2+/3+} redox couple and slightly lower performance of 73% for [Co(bpy)₃]^{2+/3+}. The better performance of the hemicaged cobalt redox couple in the IPCE measurements is attributed to the bulkier ligand system that slows down the recombination rate and due to the higher electrochemical driving force for dye regeneration in comparison to [Co(ttb)]^{2+/3+}. The lower IPCE values (Figure 3) obtained for the devices containing the less bulky cobalt complexes used in conjugation with the cosensitized system could be a result of the lower driving force for the regeneration process, i.e., the reduction of oxidized dye by the Co(II) complex, and/or faster recombination kinetics between injected electrons in TiO₂ and the Co(III) complex in the electrolyte.

The highly preorganized [Co(ttb)]^{2+/3+} complexes exhibited exceptionally high stability under continuous simulated full sun irradiation at room temperature as compared to the [Co(bpy)₃]^{2+/3+} redox mediators. DSCs based on hemicaged cobalt complexes electrolyte outperformed those assembled with the reference mediator [Co(bpy)₃]^{2+/3+}, already in early

stages of the stability test. Within the first 24h of performance, the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ system dropped by 10%, while the performance of the $[\text{Co}(\text{ttb})]^{2+/3+}$ system increased by 30% due to an initial light soaking effect (Figure 4). DSCs with $[\text{Co}(\text{bpy})_3]^{2+/3+}$ based electrolyte showed poor device performance after a 120h performance test with a total efficiency drop of 40%, while the new $[\text{Co}(\text{ttb})]^{2+/3+}$ based electrolyte remained 10% above the initial efficiency (Figure 4).

Thermal stress of solar cell stability and performance plays a major role for potential application on industrial scale (Figure 5). The thermal stability of the cobalt complexes was assessed using differential pulse voltammetry (DPV). In separate work, we found that the peak current^[37], which is proportional to the active species concentration, decreased strongly in the case of $\text{Co}(\text{bpy})_3^{3+}$ in methoxypropionitrile (MPN) based electrolyte following a heat treatment, at 70° C for 7 days. Here, $\text{Co}(\text{ttb})_3^{3+}$ and $\text{Co}(\text{bpy})_3^{3+}$ in MPN are compared, see Figure 5. For the new hemicage based Co^{3+} complex, the peak current remained stable demonstrating a greatly improved thermal stability of $[\text{Co}(\text{ttb})]^{3+}$ compared with the $[\text{Co}(\text{bpy})_3]^{3+}$. The Co^{2+} species for both complexes showed almost no change in peak current after the thermal treatment independent of the ligand, indicating overall stability of these species.

Influence of the Hemicage Ligand-Cobalt Complex on Dye Regeneration

The regeneration of the dyes by the cobalt complexes was investigated with photoinduced absorption spectroscopy (PIA). The PIA spectra of LEG4 and C218/MKA253 photo anodes in the presence and absence of the different hemicaged cobalt redox mediators or cobalt bipyridine are shown in Figure 6.

In the absence of a redox mediator, for LEG4 a bleach of the main absorption band is found at 540 nm, and absorption peaks of oxidized dye at 680 nm and 780 nm. The bleach occurs in the presence of the oxidized dye and is due to some extent of electrons in TiO_2 . The bleach corresponds to the conversion of the ground-state dye to the oxidized form with a Stark shift caused by the photoinjected electrons that give a local change in the electrical field across the dye molecules.^[38] When a $[\text{Co}(\text{ttb})]^{2+/3+}$ or $[\text{Co}(\text{bpy})_3]^{2+/3+}$ based electrolyte is added, the bleach of ground-state dye and the absorption peak of oxidized dye disappear because the ground state is rapidly regenerated from the oxidized dye by the redox mediator. A bleach in the region between 560 nm to 600 nm persists, caused by the Stark effect. It also indicates that the difference in driving forces between the redox couples do not affect the regeneration yield (and the IPCE).

The kinetics of dye regeneration using the hemicage cobalt based electrolyte was further investigated by transient absorption spectroscopy (TAS), Figure 7. The decay of the absorbance signal in the presence of inert electrolyte (0.1 M LiTFSI, 0.2 M TBP in acetonitrile) shows the recombination of TiO_2 conduction band electrons with the oxidized dye molecules. In presence of the cobalt electrolyte, the decay of the signal accelerates, indicating that the cobalt redox couples regenerate the dye molecules. The longer regeneration half time ($t_{1/2}$) of 15.3 μs for the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ redox couple implies that the hemicage cobalt complexes ($t_{1/2} = 5.1 \mu\text{s}$) have more effective regeneration, Table 2. The kinetics of dye regeneration is typically modeled with a stretched exponential decay. The

dye regeneration rate constant, k_{reg} , recovery rate constant, k_{rec} , and regeneration efficiency, Φ_{ref} , can be calculated using Equation 1.

$$\Phi_{\text{reg}} = \frac{k_{\text{reg}}}{k_{\text{reg}} + k_{\text{rec}}} = 1 - \frac{t_{1/2, \text{reg}}}{t_{1/2, \text{rec}}} \quad \text{Equation 1}$$

Hemicage Ligand Influence on Energetics of the Co-complex

Co(ttb) and Co(bpy)₃ were fully relaxed to their singlet, triplet, and quintet, as well as reduced doublet and quartet states at the PBE0/6-311G(d,p)/PCM(MeCN) level of theory in Gaussian G09.^[39] Their relative energies (relative to their Co(III) singlets) and structural parameters that describe the binding around the Co-center are summarized in Table 3. The charge/spin state is indicated by the notation ^mCo(Q) where m is the multiplicity and Q is the charge of the Co. Structurally, R characterizes the average Co-ligand bond distances, and O measures the octahedrality of the binding around Co, measured as the root mean square of the Co-ligand angles from a perfect octahedron (O ~ 0° is a perfect octahedron).

The energetics of the two systems are very similar (Table 3). The lowest energy Co(III) state is the singlet ground state and it has the smallest energy difference to the Co(II) doublet, indicating that the 2+/3+ mediator can be driven at low spin, reducing the opportunity for losing mediator to excited decay pathways. Co(ttb) is slightly more octahedral than Co(bpy)₃; however the connecting ring does not seem to affect the Co-ligand bond distances indicating that while it constrains the bpy groups to each other, it does not dominate the Co binding. In both complexes, adding additional unpaired electrons to the Co has the predicted effect of expanding the Co-ligand bonds, increasing R. It also leads to twisting of the ligands around the Co and thus less octahedral geometries (larger O's). While the structural changes in Co(bpy)₃ and Co(ttb) are similar in each of the Co(III) and Co(II) redox states, these calculations do not capture the dynamics of ligand loss. The increased twisting in higher spin and the Co(II) reduced state is known to lead to ligand loss in the Co(bpy)₃ complex. In contrast, the ttb ties the bpy's to each other, constraining the twisting somewhat as seen in the slightly lower O-values, leading to a much more stable structure.

Hemicage Ligand Influence on the Mass Transport of Cobalt Complexes as Redox Mediators

The redox potential for the [Co(ttb)]^{2+/3+} redox couple in acetonitrile was determined to be 0.47 V vs. NHE using cyclic voltammetry (see SI). This is more negative by approximately 100 mV in comparison to the cobalt trisbipyridine complex. The shift in potential can be attributed to the change in the ligand system. The connecting methyl group to the top benzyl ring of ttb will have an electron donating effect shifting the overall complex potential more negative.

The transport of the electroactive ions is expected to have a great influence on the overall performance of DSCs. From a geometric point of view, cobalt trisbipyridine is slightly less bulky than the hemicage system and is expected to diffuse more efficient in the electrolyte and the TiO₂ nanostructure.

The diffusion coefficients of the compounds in acetonitrile were determined using cyclic voltammetry at different scan rates and calculated according to the equation^[40]:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} C_0^* v^{1/2} \quad \text{Equation 2}$$

The i_p is peak current, n is the number of electrons, D is the diffusion coefficient of the species, A is the area of the electrode surface, C_0^* is the concentration of the oxidized species in the bulk solution and v is the potential scan rate.

The diffusion coefficients for Co(ttb)(TFSI)₂ and Co(ttb)(TFSI)₃ were determined to be 2.4×10^{-6} and $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively, somewhat lower than reported values of $D = 6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for Co(bpy)₃^{2+/3+} under similar conditions.^[41] The slightly lower diffusion coefficients could have arisen as a result of the bulkier hemicage.^[16,21]

CONCLUSIONS

Cobalt complexes with a highly preorganized hemicage hexadentate ligand (ttb) were prepared and tested as redox mediators in DSCs. Favorable solar cell performance was found, with photocurrent densities of 13.0 mA/cm^2 , open-circuit voltage of 805 mV, and power conversion efficiency (PCE) of 6.3% under simulated AM 1.5G one sun illumination. Electrochemical studies showed that the diffusion coefficient of [Co(ttb)]^{2+/3+} is slightly lower than that of [Co(bpy)₃]^{2+/3+}. However, the improved thermal stability of Co(ttb)³⁺ over [Co(bpy)₃]³⁺ led to vastly more stable high performing cells under full sun irradiation conditions. These results prove that stability does not need to be compromised in order to achieve high efficiency performance required for commercial applications.

EXPERIMENTAL

All chemicals were purchased from Sigma Aldrich unless otherwise noted. C218 was received from Merck.^[42] LEG4 and MKA253 were purchased from Dyenamo AB (Sweden).^a

Synthesis of Cobalt Complexes

The hemicage ligand was synthesized in a single step from commercially available starting materials with high yield, using the procedure described by Beeston *et al.* The cobalt complexes Co(ttb)^{2+/3+} were synthesized according to previously published procedures.^[31,32]

Briefly, 1 equiv of CoCl₂·6H₂O and 1 equiv of the new polypyridine ligand 5,5'',5''' - ((2,4,6-triethylbenzene-1,3,5-triyl)tris(ethane-2,1-diyl))tri-2,2'-bipyridine (ttb) were dissolved in a minimal amount of methanol, and the solution was stirred at reflux overnight under nitrogen atmosphere. An excess of lithium bistrifluoromethanesulfonimide (LiTFSI)

^aCertain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

was then added to the solution to precipitate the compound; that was filtered, washed with methanol and ether, and dried under vacuum. The cobalt complex was dissolved in minimal amount of acetonitrile and further purified by a sephadex column. The collected fraction was dried under vacuum and used without further purification.

Oxidation of the cobalt(II) complexes was performed by adding H₂O₂ (30%, 30 equiv.) and HCl (until pH=1) and removing the solvent by rotary evaporation. The cobalt complex was dissolved in minimal amount of acetonitrile and further purified by a sephadex column. The collected fraction was dried under vacuum and used without further purification.

Solar Cell Preparation

Fluorine-doped tin oxide (FTO) glass substrates (Pilkington, TEC15) were cleaned in an ultrasonic bath for 1h in following order of solvents water, ethanol, and acetone. The conducting glass substrates were pretreated by immersion in a 40 mM aqueous TiCl₄ solution at 70 °C for 90 min and then washed with water.

To prepare 0.25 cm² mesoporous TiO₂ films, colloidal TiO₂ paste (Dyesol DSL 30 NRD-T) was screen printed and dried at 120°C for 6 min between each deposition. Subsequently, a light-scattering TiO₂ layer was deposited on top of the mesoporous TiO₂ film. A profilometer (Veeco Dektak 3) measured the thickness of the active TiO₂ films at 6 µm and the thickness of the scattering layer at 3 µm. An oven (Nabertherm Controller P320) gradually heated the electrodes in an air atmosphere, applying a four level program: 180°C (10 min), 320°C (10 min), 390°C (10 min), and 450°C (30 min). After the sintering, the electrodes were treated in aqueous TiCl₄ at 70°C for 30 min and afterwards washed with water. A final heating step at 500°C (60 min) was performed followed by overnight immersion of the electrodes in the dye bath solution. The dye bath contained 0.2 mM LEG4 or 0.2 mM C218/0.05mM MKA253 (1:4) in tertbutanol and acetonitrile (1:1). The films were then rinsed in acetonitrile to remove excess dye. Solar cells were assembled, using a 25 µm thick thermoplastic Surlyn frame, with a PEDOT counter electrode (TEC8). The PEDOT electrodes were prepared by electropolymerization of EDOT from a micellar aqueous solution of 0.1 M SDS and 0.01 M EDOT. In the next step, electrolyte solution was introduced through a hole predrilled in the counter electrode under vacuum. The cells were sealed with thermoplastic Surlyn covers and a glass coverslip. Unless otherwise noted, the electrolyte consisted of 0.22 M Co(ttb)(TFSI)₂, 0.05 M Co(ttb)(TFSI)₃, 0.1 M LiTFSI, and 0.2 M 4-*tert*-butylpyridine (TBP) in acetonitrile. For comparison, DSCs were prepared using 0.22 M Co(bpy)₃(TFSI)₂, 0.05 M Co(bpy)₃(TFSI)₃, 0.1 M LiTFSI, and 0.2 M TBP in acetonitrile.

Solar Cell Characterization

Current-voltage (I–V) characteristics were measured with a Keithley 2400 source and a Newport solar simulator (model 91160). The simulator gave light with an AM 1.5 G spectral distribution and was calibrated using a certified reference solar cell (Fraunhofer ISE). The intensity was calibrated to 1000 W m⁻² and using a neutral density filter to 100 W m⁻². A black mask with a 0.5×0.5 cm² aperture as active area was used.

Incident photon to current conversion efficiency (IPCE)

IPCE spectra were recorded using a computer-controlled setup consisting of a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110), and a multimeter (Keithley 2700), which was calibrated using a certified reference solar cell (Fraunhofer ISE).

Electron lifetime, transport times, and extracted charge measurements were performed using a white LED (Luxeon Star 1W) as a light source. Voltage and current traces were recorded with a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic switches. Transport and lifetimes were determined by monitoring photocurrent and photovoltage transients at different light intensities upon applying a small square wave modulation to the base light intensity. The photocurrent and photovoltaic responses were fitted using first-order kinetics to obtain time constants.

Photoinduced Absorption Spectroscopy (PIA)

PIA measurements were performed using the setup as previously described.³² A square wave modulated blue LED (Luxeon Star 1 W, Royal Blue, 460 nm) used for excitation was superimposed on a white probe light provided by a 20 W tungsten-halogen lamp. The transmitted probe light was focused onto a monochromator (Acton Research Corp. SP-150) and detected using a UV-enhanced Si photodiode, connected to a lock-in amplifier (Stanford Research Systems model SR830) via a current amplifier (Stanford Research Systems model SR570). The intensity of the probe light was approximately 100 W m^{-2} , and the intensity of the excitation LED was approximately 80 W m^{-2} . The modulation frequency of the LED was 9.33 Hz.

Transient absorption spectra (TAS)

TAS and kinetics were recorded by a frequency tripled Q-switched Nd:YAG laser coupled with a MOPO (master optical parametric oscillator, Spectra-Physics S12 Quanta-Ray system) to obtain the desired wavelength for the pump light of 520 nm (~13 ns pulse at 10 Hz). The energy of the pump pulse was kept around 1 mJ. The cross-section area was estimated at 0.35 cm^2 , from a pump beam diameter of ca 0.5 cm and 45° positioning of the film vs. the incoming pump. A detection system (Edinburgh Instrument, L920) was used, equipped with a Xe arc lamp (continuous wave), a monochromator, and a CCD camera (Andor DH720) for transient absorption or a R928-type PMT read by an 500MHz oscilloscope (Tektronix TDS 3052B) for kinetics.

Electrochemical Measurements

Cyclic voltammetry was completed on a IVIUMSTAT.XR potentiostat with a three-electrode setup with a gold working electrode. Reversible waves were found for all the measurements. The redox potential of $\text{Co}(\text{ttb})^{2+/3+}$ was estimated to be 0.47 V vs. NHE (normal hydrogen electrode). The negative shift of the redox potential in comparison to the cobalt trisbipyridine complex (0.56 V vs NHE^[16]) by approximately 100 mV can be attributed to electron donating effect of the connecting methyl group to the top benzyl ring of ttb.

Differential pulse voltammetry (DPV) were performed in order to examine the stability of $\text{Co}(\text{ttb})^{2+/3+}$ and compared to $\text{Co}(\text{bpy})_3^{2+/3+}$ in 3-methoxypropionitrile (MPN). The experiments were conducted on an Autolab potentiostat (PGSTAT10) using a three-electrode setup. In all measurements, a 3 mm diameter glassy carbon disk voltammetry electrode, well-polished before use, was used as the working electrode, a 3 mm diameter graphite rod as the counter electrode, and a CHI 111, Ag/AgCl (LiCl in ethanol,). Two solutions containing 1mM Co^{2+} and 0.1 M TBA PF_6 in MPN or 1mM Co^{3+} and 0.1 M TBA PF_6 in MPN were measured before and after the heat treatment at 70°C for 168 hours.

For diffusion coefficient measurements, a platinum microelectrode was used as the working electrode. The counter and reference electrode (two electrode system) was graphite. The electrolyte composition was 5 mM complex, 0.1 M TBA PF_6 and 0.5 M TBP in acetonitrile.

A stability test lasting 120 hours under light-soaking conditions was conducted for the DSCs assembled with the previously described electrolytes and the performance of the DSCs was compared through current-voltage characteristics at various time points. Stability measurements were performed using a white LED as a light source with an intensity of one sun.

DFT calculations

Quantum chemical calculations can provide an accurate description of multiple spin states for a wide range of large molecular systems.^[43–45] In particular, geometrically relaxed density functional theory (DFT) calculations beyond the Franck-Condon region provide a more comprehensive theoretical understanding of the structural evolution accompanying reduction and oxidation of a metal-centered complex.^[46] Recently, such calculations have been used to predict the photoinduced cascade of model Ru-Co systems, accurately reproducing the excited state landscape which results in a final reduced $\text{Co}(\text{II})$.^[47] The $\text{Co}(\text{III})$ singlet, triplet, and quintet as well as the $\text{Co}(\text{II})$ doublet and quartet geometries of each complex were freely optimized using PBE0, which is known to give good agreement to experimental structures,^[48–50] and a triple- ζ 6-311G(d,p) basis set with a complete acetonitrile polarizable continuum model (PCM) in Gaussian G09.^[39] Each minimum is characterized by spin, energy, and the selected structural parameters, R , which characterizes the average Co-ligand bond distances, and O or octahedrality factor which is the root mean squared error of the Co-ligand angles (a perfect octahedron is $O \sim 0^\circ$).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. O'Regan B, Gratzel M. Nature. 1991; 353:737.

2. Asim N, Sopian K, Ahmadi S, Saeedfar K, Alghoul MA, Saadatian O, Zaidi SH. *Renew Sustain Energy Rev.* 2012; 16:5834.
3. Green MA, Emery K, Hishikawa Y, Warta W, Dunlop ED. *Prog Photovoltaics Res Appl.* 2012; 20:12.
4. Yang J, Banerjee A, Guha S. *Appl Phys Lett.* 1997; 70
5. Gong J, Liang J, Sumathy K. *Renew Sustain Energy Rev.* 2012; 16:5848.
6. Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. *Chem Rev.* 2010; 110:6595. [PubMed: 20831177]
7. Hagfeldt A, Grätzel M. *Acc Chem Res.* 2000; 33:269. [PubMed: 10813871]
8. Ardo S, Meyer GJ. *Chem Soc Rev.* 2009; 38:115. [PubMed: 19088971]
9. Green ANM, Palomares E, Haque SA, Kroon JM, Durrant JR. *J Phys Chem B.* 2005; 109:12525. [PubMed: 16852549]
10. Boschloo G, Hagfeldt A. *Acc Chem Res.* 2009; 42:1819. [PubMed: 19845388]
11. Tian H, Sun L. *J Mater Chem.* 2011; 21:10592.
12. Cong J, Yang X, Kloo L, Sun L. *Energy Environ Sci.* 2012; 5:9180.
13. Ahmad S, Guillen E, Kavan L, Gratzel M, Nazeeruddin MK. *Energy Environ Sci.* 2013; 6:3439.
14. Bai Y, Yu Q, Cai N, Wang Y, Zhang M, Wang P. *Chem Commun.* 2011; 47:4376.
15. Wang P, Zakeeruddin SM, Exnar I, Gratzel M. *Chem Commun.* 2002; 2972
16. Feldt SM, Gibson EA, Gabrielson E, Sun L, Boschloo G, Hagfeldt A. *J Am Chem Soc.* 2010; 132:16714. [PubMed: 21047080]
17. Sapp SA, Elliott CM, Contado C, Caramori S, Bignozzi CA. *J Am Chem Soc.* 2002; 124:11215. [PubMed: 12224970]
18. Wang M, Gratzel C, Zakeeruddin SM, Gratzel M. *Energy Environ Sci.* 2012; 5:9394.
19. Kumara GRA, Kaneko S, Konno A, Okuya M, Murakami K, Onwona-agyeman B, Tennakone K. *Prog Photovoltaics Res Appl.* 2006; 14:643.
20. Nusbaumer H, Zakeeruddin SM, Moser J-E, Grätzel M. *Chem – A Eur J.* 2003; 9:3756.
21. Feldt SM, Wang G, Boschloo G, Hagfeldt A. *J Phys Chem C.* 2011; 115:21500.
22. Yella A, Humphry-Baker R, Curchod BFE, Ashari Astani N, Teuscher J, Polander LE, Mathew S, Moser J-E, Tavernelli I, Rothlisberger U, Grätzel M, Nazeeruddin MK, Frey J. *Chem Mater.* 2013; 25:2733.
23. Li R, Liu J, Cai N, Zhang M, Wang P. *J Phys Chem B.* 2010; 114:4461. [PubMed: 20235566]
24. Feldt SM, Lohse PW, Kessler F, Nazeeruddin MK, Gratzel M, Boschloo G, Hagfeldt A. *Phys Chem Chem Phys.* 2013; 15:7087. [PubMed: 23552732]
25. Mathew S, Yella A, Gao P, Humphry-Baker R, E CF, Ashari-Astani N, Tavernelli I, Rothlisberger U, Khaja N, Grätzel M. *Nat Chem.* 2014; 6:242. [PubMed: 24557140]
26. Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa J, Hanaya M. *Chem Commun.* 2015; 51:15894.
27. Cameron PJ, Peter LM, Zakeeruddin SM, Grätzel M. *Coord Chem Rev.* 2004; 248:1447.
28. Jiang R, Anderson A, Barnes PRF, Xiaoe L, Law C, O'Regan BC. *J Mater Chem A.* 2014; 2:4751.
29. Gao J, Bhagavathi Achari M, Kloo L. *Chem Commun.* 2014; 50:6249.
30. Sohna Sohna J-E, Carrier V, Fages F, Amouyal E. *Inorg Chem.* 2001; 40:6061. [PubMed: 11681927]
31. Oyler KD, Coughlin FJ, Bernhard S. *J Am Chem Soc.* 2006; 129:210.
32. Beeston RF, Larson SL, Fitzgerald MC. *Inorg Chem.* 1989; 28:4187.
33. Williams AL, Bhuiyan AA, Turner MO, Millett F, Durham B. *J Coord Chem.* 2010; 64:48.
34. Murray JW, Dillard JG. *Geochim Cosmochim Acta.* 1979; 43:781.
35. Chen D, Martell AE. *Inorg Chem.* 1987; 26:1026.
36. Mase K, Ohkubo K, Fukuzumi S. *J Am Chem Soc.* 2013; 135:2800. [PubMed: 23343346]
37. Yang W, Hao Y, Ghamgosar P, Boschloo G. *Electrochem acta*, Submitt under Rev. 2016
38. Cappel UB, Feldt SM, Schöneboom J, Hagfeldt A, Boschloo G. *J Am Chem Soc.* 2010; 132:9096. [PubMed: 20552960]

39. GS Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng. Gaussian. 2009
40. Bard, Allen J., Faulkner, LR. *Electrochemical Methods: Fundamentals and Applications*. Wiley Subscription Services, Inc., A Wiley Company; 2001.
41. Kavan L, Yum J-H, Grätzel M. *Nano Lett.* 2011; 11:5501. [PubMed: 22103554]
42. Zhou D, Yu Q, Cai N, Bai Y, Wang Y, Wang P. *Energy Environ Sci.* 2011; 4:2030.
43. Cramer CJ, Truhlar DG. *Phys Chem Chem Phys.* 2009; 11:10757. [PubMed: 19924312]
44. Fantacci S, De Angelis F. *Coord Chem Rev.* 2011; 255:2704.
45. Garino C, Salassa L. *Philos Trans R Soc London A Math Phys Eng Sci.* 2013; 371
46. Kuhar K, Fredin LA, Persson P. *J Phys Chem B.* 2015; 119:7378. [PubMed: 25719556]
47. Smolentsev G, Canton SE, Lockard JV, Sundstrom V, Chen LX. *J Electron Spectrosc Relat Phenomena.* 2011; 184:125.
48. Fredin LA, Pápai M, Rozsályi E, Vankó G, Wärnmark K, Sundström V, Persson P. *J Phys Chem Lett.* 2014; 5:2066. [PubMed: 26270494]
49. Parada GA, Fredin LA, Santoni M-P, Jäger M, Lomoth R, Hammarström L, Johansson O, Persson P, Ott S. *Inorg Chem.* 2013; 52:5128. [PubMed: 23597274]
50. Liu Y, Kjær KS, Fredin LA, Chábera P, Harlang T, Canton SE, Lidin S, Zhang J, Lomoth R, Bergquist K-E, Persson P, Wärnmark K, Sundström V. *Chem – A Eur J.* 2015; 21:3628.

Figure 1. Molecular structure of the complex $\text{Co}(\text{ttb})^{2+/3+}$ (left), the cobalt redox mediator studied and the ligand ttb (right) in this work. The counter ion is bis(trifluoromethylsulfonyl)amine (TFSI).

Figure 2.

Current density (J) vs applied potential (V) curves for DSCs sensitized with LEG4 (dashed line) or C218/MKA253 (solid line) with $[\text{Co}(\text{ttbb})]^{2+/3+}$ (black) or $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (red) based electrolyte. Illumination conditions: 1000 W m^{-2} , AM 1.5G.

Figure 3.

IPCE spectra for DSCs employing C218/MKA253 (left) and LEG4 (right) as sensitizer and [Co(ttbb)]^{2+/3+} (black square) or [Co(bpy)₃]^{2+/3+} (red circle) based electrolyte.

Figure 4. Normalized efficiencies of the devices under continuous, simulated full sun irradiation stability experiment for DSCs based on the co-sensitized C218/MKA253 or LEG4 as sensitizer with [Co(ttb)]^{2+/3+} or [Co(bpy)₃]^{2+/3+} based electrolytes in acetonitrile.

Figure 5. Differential pulse voltammetry of (a) $[\text{Co}(\text{ttb})]^{3+}$ (left) and (b) $[\text{Co}(\text{bpy})_3]^{3+}$ (right) in 0.1 M TBAPF_6 in MPN solution before and after heat treatment, at 70°C for 7 days. The scan was conducted from 0.75 V to 0 V.

Figure 6.
PIA spectra of DSCs employing LEG4 as sensitizer and [Co(ttb)]^{2+/3+} or [Co(bpy)₃]^{2+/3+} based electrolyte.

Figure 7. Transient absorption spectroscopy measurements of LEG4 with inert electrolyte (red), $[Co(ttb)]^{2+/3+}$ (red line), or $[Co(bpy)_3]^{2+/3+}$ (black line) based electrolyte.

Figure 8.
Optimized ground state of $^1\text{Co(III)(ttb)}$.

Table 1

Current-Voltage characteristics of DSCs sensitized with LEG4 or C218/MKA253 with $[\text{Co}(\text{ttb})]^{2+/3+}$ or $[\text{Co}(\text{bpy})_3]^{2+/3+}$ based electrolyte. V_{oc} is voltage at open circuit conditions, J_{SC} is current at short circuit conditions, FF is the fill factor and η is the solar cell efficiency.

Dye/electrolyte	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF	η [%]
LEG 4/ $[\text{Co}(\text{ttb})]^{2+/3+}$	810	11.6	0.57	5.4
C218+MKA253/ $[\text{Co}(\text{ttb})]^{2+/3+}$	805	13.0	0.60	6.3
LEG4/ $[\text{Co}(\text{bpy})_3]^{2+/3+}$	805	12.1	0.68	6.6
C218+MKA253/ $[\text{Co}(\text{bpy})_3]^{2+/3+}$	810	12.2	0.69	6.9

Table 2

Calculated regeneration efficiencies of LEG4 with inert electrolyte, $[\text{Co}(\text{ttb})]^{2+/3+}$, or $[\text{Co}(\text{bpy})_3]^{2+/3+}$ based electrolyte.

Dye/electrolyte	$t_{1/2}$ [μs]	Φ_{reg} [%]
LEG4/inert	71.6	–
LEG4/ $[\text{Co}(\text{ttb})]^{2+/3+}$	5.1	99.3
LEG4/ $[\text{Co}(\text{bpy})_3]^{2+/3+}$	15.3	78.6

Table 3Geometry of possible spin/charge states using PBE0/6-311G(d,p)/PCM(MeCN).^[a]

		E	R ^[b]	Q ^[c]
Co(ttb)	¹ Co(III)	0.00	1.94 ± 0.001	4.45
	³ Co(III)	1.20	2.02 ± 0.3	5.68
	⁵ Co(III)	1.78	2.08 ± 0.006	6.19
	² Co(II)	-4.72	2.04 ± 0.04	5.48
	⁴ Co(II)	-5.07	2.14 ± 0.0002	7.28
Co(bpy) ₃	Co(III)	0.00	1.94 ± 0.001	4.70
	³ Co(III)	1.19	2.02 ± 0.03	5.94
	⁵ Co(III)	1.75	2.71 ± 0.007	6.09
	² Co(II)	-4.82	2.05 ± 0.04	5.97
	⁴ Co(II)	-5.14	2.14 ± 0.001	8.12

^[a] Energies, E, are in eV with respect to the lowest energy ground state, distances in Å, and angles in degrees. Deviations are calculated as σ_n -values;

^[b] R is the average of all metal coordinating atom bond distances;

^[c] average deviation = $(\sum |\text{ideal angle} - \text{measured angle}|)/n$