

Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells

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Abstract: Dye-sensitized solar cells (DSCs) with cobalt-based mediators with efficiencies surpassing the record for DSCs with iodide-free electrolytes were developed by selecting a suitable combination of a cobalt polypyridine complex and an organic sensitizer. The effect of the steric properties of two triphenylamine-based organic sensitizers and a series of cobalt polypyridine redox mediators on the overall device performance in DSCs as well as on transport and recombination processes in these devices was compared. The recombination and mass-transport limitations that, previously, have been found to limit the performance of these mediators were avoided by matching the properties of the dye and the cobalt redox mediator. Organic dyes with higher extinction coefficients than the standard ruthenium sensitizers were employed in DSCs in combination with outer-sphere redox mediators, enabling thinner TiO₂ films to be used. Recombination was reduced further by introducing insulating butoxyl chains on the dye rather than on the cobalt redox mediator, enabling redox couples with higher diffusion coefficients and more suitable redox potential to be used, simultaneously improving the photocurrent and photovoltage of the device. Optimization of DSCs sensitized with a triphenylamine-based organic dye in combination with tris(2,2'-bipyridyl)cobalt(II/III) yielded solar cells with overall conversion efficiencies of 6.7% and open-circuit potentials of more than 0.9 V under 1000 W m⁻² AM1.5 G illumination. Excellent performance was also found under low light intensity indoor conditions.

Introduction

Dye-sensitized solar cells (DSCs) have received great interest as cost-effective alternatives to silicon-based photovoltaic devices. In the DSC, light is absorbed by a dye molecule, which is anchored to a mesoporous wide band gap semiconductor, normally TiO₂. Upon light absorption the photoexcited dye injects an electron into the conduction band of the semiconductor and its resulting oxidized state is regenerated by a redox mediator in the surrounding electrolyte.^{1–3} Thus far, the best conversion efficiencies in DSCs, about 11%,⁴ have been obtained with ruthenium-based dyes together with an iodide/triiodide redox couple.

For large-scale manufacturing of dye-sensitized solar cells (DSCs) it is, however, of interest to find an alternative redox mediator to the iodide/triiodide redox couple. The iodide/triiodide system is limited by its relatively high overpotential for dye regeneration⁵ and by competitive light absorption by the triiodide.^{2,6} Moreover, the scale up of DSCs and the module stability is hindered by the corrosiveness of the iodide/triiodide redox couple toward most metals and sealing materials. As a result, methods such as the use of current collecting metal grids over the substrate to reduce the high series resistance of the

transparent conductive oxide substrate, which limits the performance of large area DSCs and modules, is hindered. Several redox mediators have so far been examined as alternative redox couples in DSCs^{6–13} in order to avoid the problems associated with the iodide/triiodide system. The best alternative redox mediator to date is a recently reported disulfide/thiolate redox couple that yielded an efficiency of 6.4% under full sunlight.¹⁴

One-electron outer-sphere redox couples, such as cobalt complexes, are interesting alternative redox mediators since they show weak visible light absorption and are less aggressive

- (4) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiyama, R.; Koide, N.; Han, L. *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L638.
- (5) Boschloo, G.; Hagfeldt, A. *Acc. Chem. Res.* **2009**, *42*, 1819.
- (6) Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J.-E.; Grätzel, M. *Chem.—Eur. J.* **2003**, *9*, 3756.
- (7) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L. *J. Phys. Chem. B* **2001**, *105*, 1422.
- (8) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. *J. Phys. Chem. B* **2001**, *105*, 10461.
- (9) Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 11215.
- (10) Oskam, G.; Bergeron, B. V.; Meyer, G. J.; Searson, P. C. *J. Phys. Chem. B* **2001**, *105*, 6867.
- (11) Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 9648.
- (12) Zhang, Z.; Chen, P.; Murakami, T. N.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Funct. Mater.* **2008**, *18*, 341.
- (13) Teng, C.; Yang, X.; Yuan, C.; Li, C.; Chen, R.; Tian, H.; Li, S.; Hagfeldt, A.; Sun, L. *Org. Lett.* **2009**, *11*, 5542.

[†] Uppsala University.

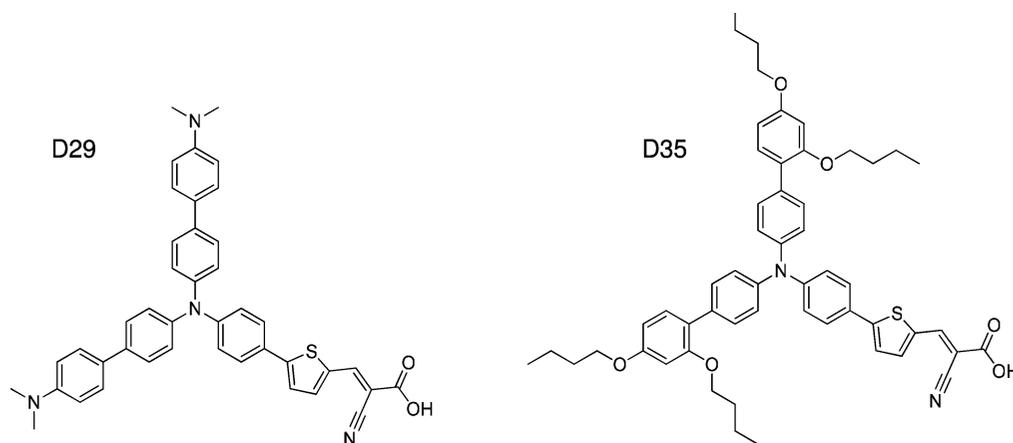
[‡] Royal Institute of Technology.

(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49.

(3) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269.

Chart 1. Chemical Structure of D29 and D35



toward metallic conductors than iodine.^{6,9,15} Unfortunately, recombination of electrons in the TiO₂ with one-electron redox mediators is much faster.^{7,16,17} It was, however, anticipated that recombination of cobalt(III) should be relatively slow due to a change in spin upon reduction to cobalt(II).¹⁸ Nevertheless, previous investigations have suggested that the performance of cobalt redox mediators in DSCs is limited by rapid recombination from electrons in the TiO₂ conduction band to the cobalt(III) species and furthermore by slow dye regeneration and mass transport problems in the mesoporous TiO₂ electrode.^{17,19} Much research has recently been focused on passivating the TiO₂ surface using, for example, atomic layer deposition (ALD) in order to diminish the fast recombination processes occurring when cobalt redox mediators are used.^{17,20,21}

Here, we will report on highly efficient DSCs based on TiO₂, organic dyes, and cobalt redox couples. A strategy of tuning the steric properties of both the sensitizer and the redox mediator and replacing standard ruthenium sensitizers with organic dyes with high extinction coefficients, to enable thinner mesoporous TiO₂ films to be used, has been employed to overcome mass transport and recombination limitations associated with cobalt polypyridine redox electrolytes. Triphenylamine (TPA)-based organic dyes have been widely reported as sensitizers in DSCs in recent years, due to the favorable electron-donating properties of the triphenylamine unit and their potential for low-cost production.^{22–24} Here, two TPA-based organic sensitizers, D29

and D35 (Chart 1),²⁵ were compared to investigate the effect of bulky alkoxy substituents on the sensitizer in devices employing cobalt polypyridine redox mediators. In the case of D29 the electron-donating substituent was *p*-*N,N*-dimethylanilino and for D35 *o,p*-dibutoxyphenyl. In a previous study it was shown that inclusion of bulky alkoxy electron-donating substituents efficiently suppresses recombination in iodide/triiodide-based DSCs.²⁶ These organic sensitizers have high extinction coefficients (about 30 000 M⁻¹ cm⁻¹ at their absorption maximum)²⁷ compared to ruthenium-based dyes (about 14 000 M⁻¹ cm⁻¹ for N719). Dyes with high extinction coefficients are advantageous in DSCs that use ionic liquids or solid-state hole conductors, since they allow for good light harvesting efficiencies using thinner TiO₂ films. A reduction in film thickness will decrease the charge recombination rate and the transport time, and can improve surface wetting and pore filling of the electrode by the electrolyte or hole conductor, thus improving the charge collection efficiency.^{28,29} In liquid DSCs incorporating an electrolyte with diffusion-limiting properties, it is of great importance to build thin-film DSCs in order to avoid mass transport problems of redox species through the mesoporous semiconductor structure.³⁰

The steric bulk of a selection of bipyridyl and phenanthroline cobalt redox shuttles was varied by introducing different alkyl substituents on the polypyridine ligands. An energy diagram of a DSC sensitized with D29 and D35, employing the different cobalt redox shuttles compared here, and the chemical structure of the complexes are shown in Figure 1a and 1b, respectively. The redox species were cobalt(III/II) tris(2,2'-bipyridine), [Co(bpy)₃]^{3+/2+}, cobalt(III/II) tris(4,4'-dimethyl-2,2'-bipyridine), [Co(dmb)₃]^{3+/2+}, cobalt(III/II) tris(4,4'-ditert-butyl-2,2'-bipyridine), [Co(dtbtb)₃]^{3+/2+}, and cobalt(III/II) tris(1,10-phenanthroline), [Co(phen)₃]^{3+/2+}.

- (14) Wang, M.; Chamberland, N.; Breaux, L.; Moser, J.-E.; Humphry-Baker, R.; Marsan, B.; Zakeeruddin, S. M.; Grätzel, M. *Nat. Chem.* **2010**, *2*, 385.
- (15) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. *J. Phys. Chem. C* **2001**, *105*, 10461.
- (16) Feldt, S. M.; Cappel, U. B.; Johansson, E. M. J.; Boschloo, G.; Hagfeldt, A. *J. Phys. Chem. C* **2010**, *114*, 10551.
- (17) Klahr, B. M.; Hamann, T. W. *J. Phys. Chem. C* **2009**, *113*, 14040.
- (18) Cameron, P. J.; Peter, L. M.; Zakeeruddin, S. M.; Grätzel, M. *Coord. Chem. Rev.* **2004**, *248*, 1447.
- (19) Nelson, J. J.; Amick, T. J.; Elliott, C. M. *J. Phys. Chem. C* **2008**, *112*, 18255.
- (20) Ondersma, J. W.; Hamann, T. W. *J. Phys. Chem. C* **2009**, *114*, 638.
- (21) DeVries, J. W.; Pellin, T. W.; Hupp, J. T. *Langmuir* **2010**, *26*, 9082.
- (22) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806.
- (23) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2006**, 2245.
- (24) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550.

- (25) Hagberg, D. P.; Jiang, X.; Gabrielsson, E.; Linder, M.; Marinado, T.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Mater. Chem.* **2009**, *19*, 7232.
- (26) Jiang, X.; Marinado, T.; Gabrielsson, E.; Hagberg, D. P.; Sun, L.; Hagfeldt, A. *J. Phys. Chem. C* **2010**, *114*, 2799.
- (27) In ethanol: D29: $\epsilon_{\text{max}}(485 \text{ nm}) = 27.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; D35: $\epsilon_{\text{max}}(463 \text{ nm}) = 28.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Note that erroneous values are reported in refs 25 and 26.
- (28) Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146.
- (29) Wang, M.; Liu, J.; Cevey-Ha, N.-L.; Moon, S.-J.; Liska, P.; Humphry-Baker, R.; Moser, J.-E.; Grätzel, C.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Nano Today* **2010**, *5*, 169.

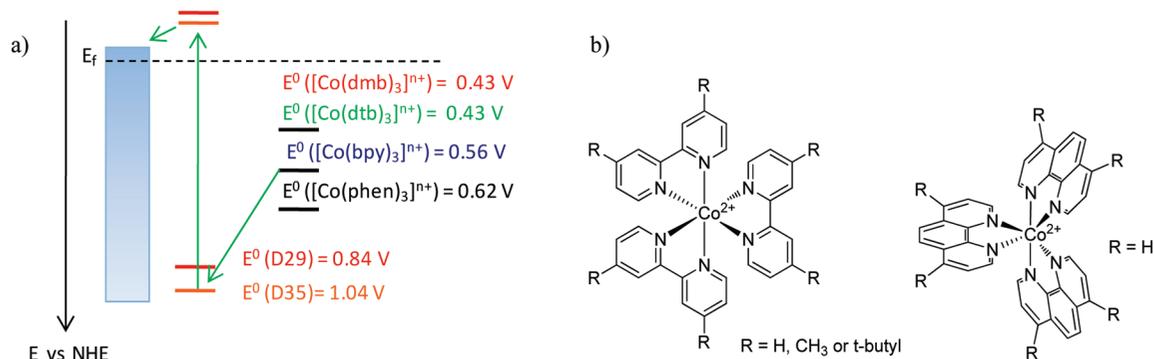


Figure 1. (a) Schematic energy diagram for a nanostructured TiO_2 electrode sensitized with D35 or D29 employing $[\text{Co}(\text{bpy})_3]^{2+/3+}$, $[\text{Co}(\text{dmb})_3]^{2+/3+}$, $[\text{Co}(\text{dtbb})_3]^{2+/3+}$, and $[\text{Co}(\text{phen})_3]^{2+/3+}$ -based electrolytes. Formal potentials indicated are vs NHE. (b) Chemical structure of the different cobalt polypyridyl redox couples employed herein.

By tuning the steric bulk of the dye and the redox mediator, the recombination and mass transport problems associated with the electrolyte were minimized and highly efficient DSCs were obtained. Solar cell efficiencies recorded in this study surpass the highest values reported so far for devices containing iodine-free electrolytes, reaching 6.7% overall conversion efficiency under 1000 W m^{-2} AM1.5G illumination and 7.8% at 100 W m^{-2} .

Experimental Section

All chemicals were purchased from Sigma Aldrich unless otherwise noted. D35 and D29 were prepared according to the published procedure.²⁵

Synthesis of Cobalt Complexes. The cobalt complexes $[\text{Co}(\text{bpy})_3(\text{PF}_6)_2]^{2+}$, $[\text{Co}(\text{dmb})_3(\text{PF}_6)_2]^{2+}$, $[\text{Co}(\text{dtbb})_3(\text{PF}_6)_2]^{2+}$, and $[\text{Co}(\text{phen})_3(\text{PF}_6)_2]^{2+}$ were synthesized as described elsewhere.^{9,17} Briefly, 1 equiv of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3.3 equiv of the polypyridine ligand were dissolved in a minimal amount of methanol (Merck), and the solution was stirred at reflux for 2 h. An excess of ammonium hexafluorophosphate was then added to the solution to precipitate the compound that was filtered, washed with methanol and ethanol, dried under vacuum, and used without further purification.

Oxidation of the cobalt(II) complexes was performed by adding a slight excess of NOBF_4 to an acetonitrile solution of the complex and then by removing the acetonitrile solution by rotary evaporation. The complex was then redissolved in acetonitrile, and a large amount of NH_4PF_6 was added to the solution. The final product was precipitated with diethyl ether, filtered, 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 overnight using (in order) ethanol, water, and ethanol. The conducting glass substrates were pretreated by immersion in a 40 mM aqueous TiCl_4 solution at 70°C for 30 min and then washed with water. Mesoporous TiO_2 films of different thicknesses were prepared with an area of 0.25 cm^2 by repeatedly screen printing colloidal TiO_2 paste (Dyesol DSL 30 NRD-T) and drying at 300°C between deposition steps. After sintering, the thickness of the films was measured with a profilometer (Veeco Dektak 3) and was $5.6 \mu\text{m}$, unless otherwise noted. Only in the optimization study for some cells a light-scattering TiO_2 layer (PST-400C, JGC Catalysts and Chemical Ltd., gratefully received from JGC Catalysts and Chemical Ltd.) was deposited on top of the mesoporous TiO_2 film. The electrodes were gradually heated in an oven (Nabertherm Controller P320) in an air atmosphere. The temperature gradient program had four levels at 180 (10 min), 320 (10 min), 390 (10 min), and 500°C (60 min). After sintering, the electrodes were, once again, immersed in aqueous TiCl_4 and rinsed as above. A second and final heating step, at 500°C for 60 min, was performed.

After the sintering, when the temperature cooled to about 90°C , the electrodes were immersed in a dye bath containing 0.2 mM D35 in ethanol or 0.2 mM D29 in acetonitrile and left overnight. The films were then rinsed in ethanol to remove excess dye. Solar cells were assembled, using a $30 \mu\text{m}$ thick thermoplastic Surlyn frame, with a platinized counter electrode (TEC8), which was prepared by depositing $10 \mu\text{L cm}^{-2}$, 4.8 mM H_2PtCl_6 solution in ethanol to the glass substrate followed by heating in air at 400°C for 30 min. An electrolyte solution was then introduced through two holes predrilled in the counter electrode, and the cell was sealed with thermoplastic Surlyn covers and a glass coverslip. Unless otherwise noted, the electrolyte consisted of 0.22 M $\text{Co}(\text{L})_3(\text{PF}_6)_2$, 0.033 M $\text{Co}(\text{L})_3(\text{PF}_6)_3$, 0.1 M LiClO_4 , and 0.2 M 4-*tert*-butylpyridine (TBP) in acetonitrile, where L ascribes the different polypyridine ligands. For comparison, DSCs were prepared using 0.6 M tetrabutylammonium iodide, 0.1 M LiI , 0.05 M I_2 , and 0.2 M TBP in acetonitrile.

Solar Cell Characterization. Current–voltage (I – V) characteristics were measured using a Keithley 2400 source/meter and a Newport solar simulator (model 91160) giving light with AM 1.5 G spectral distribution, which was calibrated using a certified reference solar cell (Fraunhofer ISE) to an intensity 1000 W m^{-2} or with the help of a neutral density filter to 100 W m^{-2} . A black mask with an aperture slightly larger ($0.6 \times 0.6 \text{ cm}^2$) than the active area of the solar cell ($0.5 \times 0.5 \text{ cm}^2$) was applied on top of the cell to avoid significant additional contribution from light falling on the device outside the active area. Photovoltaic measurements at low light intensities were performed using a compact fluorescent lamp (Osram Dulux Value 8W/827, warm white) as a light source at an illuminance of 250 lx. Incident photon to current conversion efficiency (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 potentiostat (EG&G PAR 273), 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 the 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.³¹ Extracted charge measurements were performed by illuminating the cell for 10 s under open-circuit conditions and then turning the lamp off to let the voltage to decay to a voltage V .

(30) Ito, S.; Zakeeruddin, S.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M.; Pěchy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202.

The cell was then short circuited, and the current was measured under 0.1 s and integrated to obtain Q_{oc} (V).

Photoinduced Absorption Spectroscopy (PIA). PIA measurements were performed using the same setup as described elsewhere.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.

Electrochemical Measurements. Cyclic voltammetry was performed on a CH Instruments 660 potentiostat using a three-electrode setup. For the diffusion measurements a $20 \mu\text{m}$ diameter platinum microelectrode was used as the working electrode, glassy carbon as the counter electrode, and a Ag/AgNO_3 (10 mM AgNO_3 , 0.1 M TBAPF₆ in acetonitrile) reference electrode. The reference electrode was calibrated versus ferrocene in the same supporting electrolyte. The redox electrolyte solution was 15 mM $\text{Co}(\text{L})_3(\text{PF}_6)_2$ and 0.1 M TBAPF₆ in acetonitrile. The scan rate was 10 mV s^{-1} . Charge-transfer resistances at the counter electrode were determined by impedance spectroscopy, using a two-electrode setup consisting of two platinized FTO electrodes (prepared as for the DSCs) in a sandwich device using a $30 \mu\text{m}$ thick thermoplastic frame (inner dimensions $7 \text{ mm} \times 7 \text{ mm}$), infiltrated with redox electrolyte as used in the DSCs. Measurements were performed on an Iviumstat XR potentiostat at a bias of 0 V and an ac frequency range between 100 kHz and 0.1 Hz.³³

Results and Discussion

Effect of the Steric Properties of the Dye and Redox Shuttle on the Photovoltaic Performance. Incident-photon-to-current conversion efficiency (IPCE) spectra were recorded for DSCs sensitized with the organic dyes D29 and D35, containing $[\text{Co}(\text{bpy})_3]^{3+/2+}$, $[\text{Co}(\text{dmb})_3]^{3+/2+}$, $[\text{Co}(\text{dtb})_3]^{3+/2+}$, or the iodide/triiodide redox shuttle, see Figure 2a and 2b. The IPCE for the D29-based DSCs increased with the steric bulk of the cobalt complexes, and a maximum IPCE of about 70% was found for DSCs employing $[\text{Co}(\text{dtb})_3]^{3+/2+}$. A similar trend was found by Hamann and co-workers for DSCs sensitized by the Ru complexes $\text{Ru}(\text{dcby})_2(\text{NCS})_2$ and $\text{Ru}(\text{dcbp})(\text{bpy})_2(\text{PF}_6)_2$ with the same series of redox mediators.^{17,20} The good performance of $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in the IPCE measurements is attributed to the bulky *tert*-butyl substituents that slow down the recombination rate.^{17,20} Although Nelson et al. showed that mass transport of $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in the pores of the TiO_2 film can be slow and limit the overall photovoltaic performance,¹⁹ this should not limit the photocurrent in IPCE measurements, because low monochromatic light intensities ($1\text{--}5 \text{ W m}^{-2}$) are used. The lower IPCE values obtained for the devices containing the less bulky cobalt complexes used in conjunction with D29 could be a result of the smaller 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 TiO_2 and the Co(III) complex in the electrolyte. The different aspects will be discussed in detail in the next sections.

The IPCE for DSCs sensitized with D35 was about 90% for each of the different redox mediators employed, regardless of

the steric bulk of the cobalt complex. As no antireflection coating was applied on these solar cells, about 10% of the incoming light is reflected. This implies that 100% of absorbed photons are converted into electrons. In the spectral range between 360 and 460 nm the IPCE was higher for DSCs employing cobalt redox mediators than for those employing iodide/triiodide. This is due to competitive light absorption by triiodide. This effect is even more marked when the cell is illuminated from the counter electrode side rather than through the working electrode (see Figure S1 in the Supporting Information).

The current–voltage curves for this series of DSCs are shown in Figure 2c and 2d. The photovoltaic performance of cobalt polypyridine redox mediators was superior to that of the iodide/triiodide redox shuttle for thin-film DSCs sensitized with triphenylamine-based organic sensitizers. The best efficiency at 1000 W m^{-2} illumination for the DSCs sensitized with D29 of 2.6% was obtained using a $[\text{Co}(\text{dmb})_3]^{3+/2+}$ -based electrolyte. At this intensity a lower efficiency was obtained when $[\text{Co}(\text{dtb})_3]^{3+/2+}$ was used, which is, most likely, a result of slow mass transport of this redox mediator. Despite the enhanced spectral response of D29 in the red region of the electromagnetic spectrum (see Figure S2 in the Supporting Information) the efficiency was higher for DSCs sensitized with D35. The higher efficiency obtained using D35 is due to the decreased recombination rate between electrons in TiO_2 and Co(III) species in the electrolyte, as follows from electron lifetime studies (see next section) and $I\text{--}V$ curves recorded in the dark (see Figure S3 in the Supporting Information). The bulky butoxyl groups on D35 molecules prevent close contact between the oxidized species in the electrolyte and the TiO_2 surface.

Among the different redox mediators employed, $[\text{Co}(\text{bpy})_3]^{3+/2+}$ in combination with D35 gave the highest efficiency of 4.9%. By comparison, a modest efficiency of 1.3% was obtained using $[\text{Co}(\text{bpy})_3]^{3+/2+}$ in combination with ruthenium-based dyes in Klahr and Hamann's study, which was explained by fast recombination, even though insulating alumina coatings were applied on the TiO_2 surface.¹⁷ The open-circuit voltage (V_{oc}) for DSCs sensitized with D35 is remarkably high as a result of the insulating effect of the alkoxy groups and the more positive potential of Co-based redox mediators. The high V_{oc} for the D35-based DSCs employing $[\text{Co}(\text{bpy})_3]^{3+/2+}$ (0.88 V) is in stark contrast to the results obtained by other groups, where the use of one-electron redox couples with a more positive redox potential than the iodide/triiodide redox shuttle was found to lead to high dark current densities and lower photovoltages.^{7,10,34} The lower photocurrent observed using the iodide/triiodide redox couple illustrates one of the advantages of using cobalt redox couples in DSCs and can partly be explained by the loss in photocurrent due to light adsorption by triiodide. In agreement with earlier reports, the fill factor was rather poor using $[\text{Co}(\text{dtb})_3]^{3+/2+}$, which has been attributed to the mass transport problems associated with these species that lead to increased series resistance in the device.^{17,19} The fill factor was better for DSCs based on D29 compared to D35. This could be a result of the lower resistive losses due to the lower current densities obtained with D29 or, possibly, due to the steric bulk of D35 that slightly hinders the mass transport of the cobalt bipyridyl complexes through the mesoporous TiO_2 film. The effect of mass transport limitations in cobalt mediator-based DSCs will be discussed in a later section.

(31) Boschloo, G.; Hagman, L.; Hagfeldt, A. *J. Phys. Chem. B* **2006**, *110*, 13144.

(32) Boschloo, G.; Hagfeldt, A. *Inorg. Chim. Acta* **2008**, *361*, 729.

(33) Hauch, A.; Georg, A. *Electrochim. Acta* **2001**, *46*, 3457.

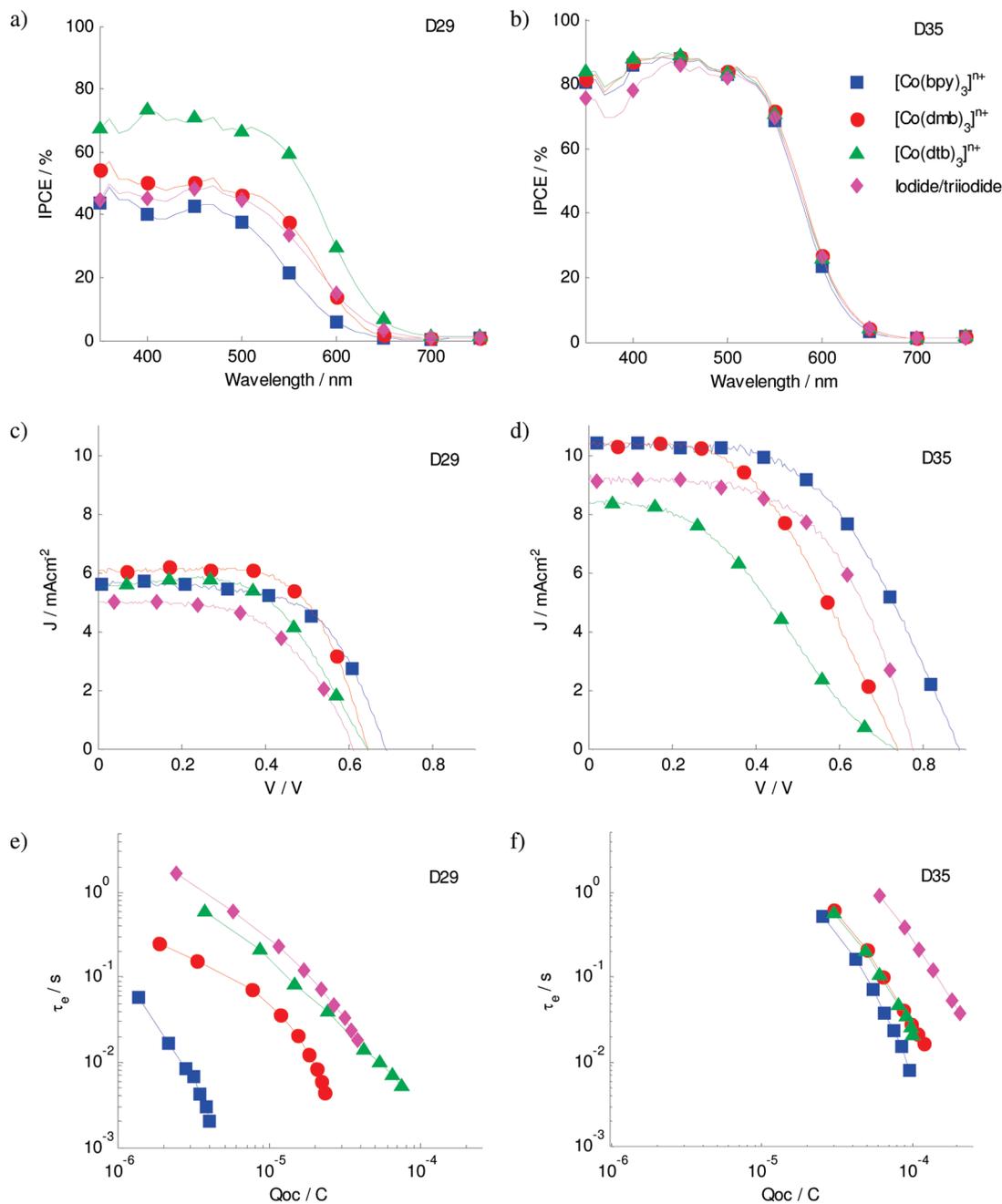


Figure 2. Spectra of incident photon to current efficiency (IPCE) for DSCs sensitized with (a) D29 and (b) D35. Current density versus applied potential curves under AM1.5G illumination for DSCs sensitized with (c) D29 and (d) D35. Electron lifetime as a function of extracted charge under open-circuit conditions for DSCs sensitized with (e) D29 and (f) D35. Every fifth data point is marked with a symbol in the IPCE spectra and every 20th data point in the $I-V$ plots.

Effect of the Steric Properties of the Dye and Redox Shuttle on the Charge Recombination Reaction. Losses due to charge recombination between the electrons in the semiconductor and the oxidized species in the redox electrolyte limit the DSC efficiency by lowering the charge-collection efficiency and, therefore, the photocurrent. In addition, fast recombination will lead to lower concentrations of electrons in the conduction band and correspondingly lower photovoltages. For many one-electron, outer-sphere redox couples, faster recombination and shorter electron lifetimes have been measured compared to devices incorporating iodide/triiodide, and this is thought to be the main limitation to these alternative redox systems^{7,11,12,16,34}. To avoid this problem, a number of groups have applied thin,

insulating blocking layers to the TiO_2 surface.^{20,21,35,36} While this had been shown to reduce the charge recombination and increase the photovoltage obtained, the electron injection kinetics may be affected, leading to a reduction in photocurrent.

The current–voltage curves for the DSCs sensitized with D35 employing $[\text{Co}(\text{bpy})_3]^{3+/2+}$, $[\text{Co}(\text{dmb})_3]^{3+/2+}$, or $[\text{Co}(\text{phen})_3]^{3+/2+}$ -based electrolytes are shown in Figure 3. The V_{oc} increased with the Nernst potential of the redox shuttles and the highest V_{oc} was obtained using $[\text{Co}(\text{phen})_3]^{3+/2+}$. DeVries et al.²¹ found that for

(34) Li, T. C.; Spokoyny, A. M.; She, C.; Farha, O. K.; Mirkin, C. A.; Marks, T. J.; Hupp, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 4580.

(35) Hamann, T. W.; Farha, O. K.; Hupp, J. T. *J. Phys. Chem. C* **2008**, *112*, 19756.

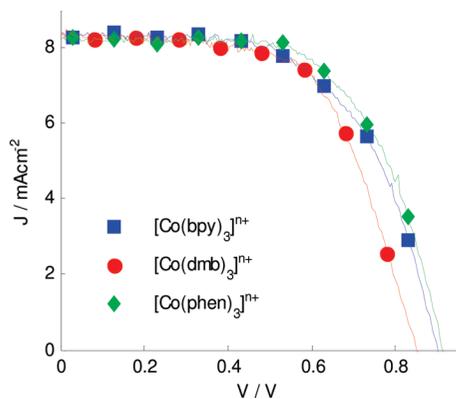


Figure 3. Current density versus applied potential curves under AM1.5G illumination for DSCs sensitized with D35. Every 20th data point is marked with a symbol.

a series of cobalt complexes with phenanthroline derivatives the V_{oc} increased as the formal potential of the redox couple became more positive. In contrast, the quasi-Fermi level in the TiO_2 at open circuit became less negative with more positive redox potential, because of faster interception of photoinjected electrons by Co(III) as the driving force for recombination increased, indicating Marcus normal-region behavior. Our results here are in agreement with this explanation; however, we propose that the recombination is not only dependent on the driving force for recombination but also on the steric properties of the redox mediator.

The recombination kinetics were investigated using a small amplitude light-modulation technique to study the effects of the steric properties of the dyes and the redox mediators on the electron lifetime. The electron lifetime as a function of extracted charge for the DSCs sensitized with D29 and D35, employing the three different cobalt bipyridyl redox mediators or iodide/triiodide, is shown in Figure 2e and 2f, respectively. As anticipated, for the devices incorporating D29 as the sensitizer, the electron lifetime was dependent on the substituents around the periphery of the cobalt complexes. According to the Marcus–Gerischer model, electron transfer rates are dependent on the rate of diffusion of the reactants (we will discuss this in a later section), the driving force for the reaction, the reorganization energy, and the electronic coupling. Cobalt complexes are known to have relatively slow electron transfer kinetics compared to other transition metal complexes such as iron(II/III) on account of the large internal reorganization energy when going from d^7 (high spin) to d^6 (low spin). Both iron(II) (d^6) and iron(III) (d^5) are low-spin, octahedral complexes and, therefore, fast redox shuttles which perform poorly as redox electrolytes in complete devices, in the absence of insulating layers on the TiO_2 surface, on account of the substantially shorter electron lifetime.^{16,35}

The redox potentials of the cobalt bipyridine complexes employed in this study are shown in Figure 1 and are 0.56 V vs NHE for $[Co(bpy)_3]^{3+/2+}$ and 0.43 V vs NHE for $[Co(dmb)_3]^{3+/2+}$ and $[Co(dtbb)_3]^{3+/2+}$.^{9,17} Assuming that recombination occurs between electrons in the conduction band of the TiO_2 and cobalt(III) species in the electrolyte, the driving force for recombination will be proportional to the potential difference between the electrons in the TiO_2 conduction band and the redox potential of the redox couple in solution. Therefore, in terms of driving force, the recombination is expected to be fastest for $[Co(bpy)_3]^{3+/2+}$; the electron lifetime data (Figure 2e) is in agreement with this. The redox potential of $[Co(dmb)_3]^{3+/2+}$ and $[Co(dtbb)_3]^{3+/2+}$ is similar, but the electron lifetimes for the two devices were very different. Solvent reorganization energy is

dependent on the radius of the ions, and therefore, $[Co(dtbb)_3]^{3+/2+}$ should have a smaller reorganization energy than $[Co(dmb)_3]^{3+/2+}$. However, the electronic coupling of the donor and acceptor has a larger effect on the rate of electron transfer. Since this is exponentially distance dependent, the rate of electron transfer (k) depends on the spatial separation of the donor and acceptor (R) according to eq 1³⁷

$$k = k_0 \exp[-\beta(R - R_0)] \quad (1)$$

where R_0 is the van der Waals separation and k_0 and β are constants. A possible (smaller) distance dependence of the reorganization energy is ignored in this equation.

The increased steric bulk of $[Co(dtbb)_3]^{3+/2+}$ decreases the electronic coupling compared to $[Co(dmb)_3]^{3+/2+}$ and reduces the rate of recombination accordingly. The trend of increasing electron lifetime as the steric bulk of the redox mediator was increased is consistent with the corresponding increase in IPCE. This is in agreement with previous results from Klahr and Hamann¹⁷ where the bulky groups on $[Co(dtbb)_3]^{3+/2+}$ were found to act as insulating spacers, hindering the recombination processes.

For D35, however, the insulating effect of the alkoxy chains on the dye itself efficiently hinders recombination and the electron lifetimes were increased significantly for all of the redox couples investigated. D35 blocks the dark current for each of the redox couples more efficiently than D29, consistent with the trend in electron lifetime for the dyes. The differences in electron lifetime between the cobalt complexes with different substituents were less pronounced with D35 than with D29. Since the electron transfer rate is exponentially dependent on the distance, at longer distances from the semiconductor surface the steric effects of the bipyridine substituents have less effect. It appears that D35 prevents the close approach of the cobalt complexes to the TiO_2 surface to such extent that there is little difference in the recombination rate between $[Co(dmb)_3]^{3+/2+}$ and $[Co(dtbb)_3]^{3+/2+}$. Instead, the driving force for recombination appears to be more important at this distance, and accordingly, the device containing $[Co(bpy)_3]^{3+/2+}$ has a shorter lifetime than the DSCs with the other redox couples. While the electron lifetime was slightly shorter when $[Co(bpy)_3]^{3+/2+}$ was employed, the photovoltaic performance was still good when used in combination with D35 and fast recombination kinetics did not appear to be limiting the efficiency.

When the electron lifetimes in DSCs with either the iodide/triiodide or the cobalt-based mediators were compared, it was found that the former gave the longest lifetimes, with one exception: for D29 lifetimes were very similar for I^-/I_3^- and $[Co(dtbb)_3]^{3+/2+}$. As was noted in our previous work, the electron lifetimes in I^-/I_3^- -based DSCs were shorter for D29 than for D35, which was mainly attributed to the blocking effect of the steric groups on D35.²⁸ On substituting D35 for D29, the electron lifetimes with the I^-/I_3^- mediator increased significantly more than with the $[Co(dtbb)_3]^{3+/2+}$ redox mediator (Figure 2e and 2f). Specific chemical interactions between triiodide (or iodide) with the dye molecules are likely³⁸ and probably play a role in the relatively short lifetime in D29-sensitized solar cells. Similar chemical interactions are not likely to occur between the Co complexes and the dye molecules. One potential disadvantage of the investigated cobalt-based mediators is their positive charge. Nelson et al.¹⁹ observed electrostatic

(36) Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. *J. Am. Chem. Soc.* **2002**, *125*, 475.

(37) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

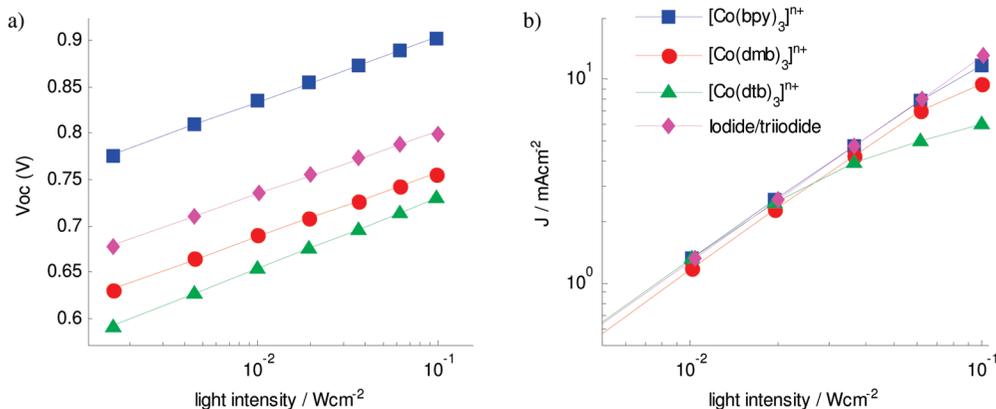


Figure 4. Light intensity dependence of (a) the open-circuit voltage and (b) the current density under short-circuit conditions for DSCs sensitized with D35.

adsorption of cationic complexes, including $[\text{Co}(\text{dtb})_3]^{3+/2+}$, on the surface of TiO_2 . Electrostatic interactions would likely speed up the interfacial charge transfer,³⁹ giving rise to the shorter lifetimes observed compared to the anionic triiodide/iodide redox electrolyte.

The best overall solar cell efficiency was obtained with the combination of D35 and $[\text{Co}(\text{bpy})_3]^{3+/2+}$, despite the fact that electron lifetimes were about 1 order of magnitude lower than that of the $\text{D35}-\text{I}^-/\text{I}_3^-$ combination at the same electron concentration in the TiO_2 electrode. This can be attributed to the ~ 0.2 V more positive redox potential of the cobalt mediator.

Nonlinearity of the Charge Recombination Kinetics. The light intensity dependence on the open-circuit potential for DSCs sensitized with D35 employing the three different cobalt bipyridyl redox mediators and iodide/triiodide is shown in Figure 4a. The slope in the V_{oc} versus light intensity plot was about 76 mV/decade for each of the redox mediators. If recombination occurs solely via the conduction band of the TiO_2 and the reaction is first order in the concentration of conduction band electrons, a linear increase of the conduction band electron concentration and the recombination rate with light intensity is predicted, resulting in a slope of 59 mV/decade at 298 K in the V_{oc} versus $\log(\text{light intensity})$ plot. The observed deviation, implying nonlinear recombination kinetics, can be due to electron transfer via surface states, effects of the transfer coefficient for the electron transfer process, and/or shifts in the conduction band under illumination.⁴⁰ A recombination reaction mediated by a distribution of surface states at the $\text{TiO}_2/\text{electrolyte}$ interface appears to be the most likely cause.⁴¹ Jennings and Wang showed recently for N719-sensitized DSCs with iodide/triiodide-based electrolyte that the “ideality” and the linearity of the semilogarithmic plots of the photovoltage versus incident photon flux increase with increasing Li^+ concentration.⁴² For the Co-mediator-based DSCs investigated here, the slope in the V_{oc} vs light intensity plots was also affected by the choice of cation in the supporting electrolyte. The slope for DSCs containing 0.1 M TBAPF_6 in the electrolyte was higher than for DSCs containing 0.1 M LiClO_4 and was found to depend on the substituents on the cobalt redox mediators (see

Figure S4 in the Supporting Information). The slope increased up to 131 mV/decade for DSCs with electrolyte containing $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and 0.1 M TBAPF_6 . The increase of the slope is correlated with the decrease of steric bulk of the cobalt complexes and the decrease of electron lifetime. This effect was not found when Li^+ ions were present in the electrolyte, possibly because charge compensation of the electrons in TiO_2 occurs mainly by Li^+ ions in this case. Nakade et al.⁴³ showed that recombination was slowed down by addition of Li^+ in DSCs employing a cobalt redox mediator, and they attributed the effect to a decrease in local concentration of $\text{Co}(\text{III})$ caused by electrostatic repulsion due to adsorbed Li^+ cations. When Li^+ ions are replaced by bulky TBA^+ ions, it is likely that the positively charged Co complexes are more involved in local charge compensation of electron in TiO_2 , which will affect the recombination kinetics.

Mass Transport Limitations in Cobalt-Based DSCs. The effect of slow mass transport in DSCs employing cobalt bipyridyl redox mediators was investigated by monitoring photocurrent transients using a large modulation (on/off) of the incident light.¹⁹ Using a white LED, with the output set to match the photocurrent obtained under 1000 W m^{-2} AM1.5G illumination, photocurrent transients were recorded for D29- and D35-sensitized DSCs with the different cobalt bipyridyl redox mediators, see Figure 5. A maximum in photocurrent was observed when the light is switched on, followed by a decrease in photocurrent, reaching a constant value after a few seconds, similar to the observations by Nelson et al.¹⁹ They found that the steady-state current increased with increasing concentration of $\text{Co}(\text{III})$ in the electrolyte and suggested that diffusion of $\text{Co}(\text{III})$ to the counter electrode limits the cell performance.¹⁹ We found that cell performance and, in particular, the fill factor increase with the increasing concentration of $\text{Co}(\text{III})$ (see Figure S5 in the Supporting Information), which agrees with the conclusion that slow mass transport of $\text{Co}(\text{III})$ to the counter electrode limits the cell performance. The ratio of initial peak current to steady state current in the photocurrent transients decreases in the order $[\text{Co}(\text{dtb})_3]^{3+/2+} > [\text{Co}(\text{dmb})_3]^{3+/2+} > [\text{Co}(\text{bpy})_3]^{3+/2+}$, indicating that mass transport is retarded by the steric bulk of the redox mediator. For the combination D35 and $[\text{Co}(\text{bpy})_3]^{3+/2+}$ the decrease in photocurrent was negligible ($<1.5\%$). At lower light intensities, mass transport is no longer a problem and no current spike is observed (data not shown). The initial peak current for DSCs sensitized with D29 increases with the steric bulk of the cobalt complexes but is about the

(38) O'Regan, B. C.; Wally, K.; Juozapavicius, M.; Anderson, A.; Matar, F.; Ghaddar, T.; Zakeeruddin, S. M.; Klein, C. d.; Durrant, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 3541.

(39) Gaal, D. A.; McGarrah, J. E.; Liu, F.; Cook, J. E.; Hupp, J. T. *Photochem. Photobiol. Sci.* **2004**, *3*, 240.

(40) Villanueva-Cab, J.; Wang, H.; Oskam, G.; Peter, L. M. *J. Phys. Chem. Lett.* **2010**, *1*, 748.

(41) Salvador, P.; Hidalgo, M. G.; Zaban, A.; Bisquert, J. *J. Phys. Chem. B* **2005**, *109*, 15915.

(42) Jennings, J. R.; Wang, Q. *J. Phys. Chem. C* **2009**, *114*, 1715.

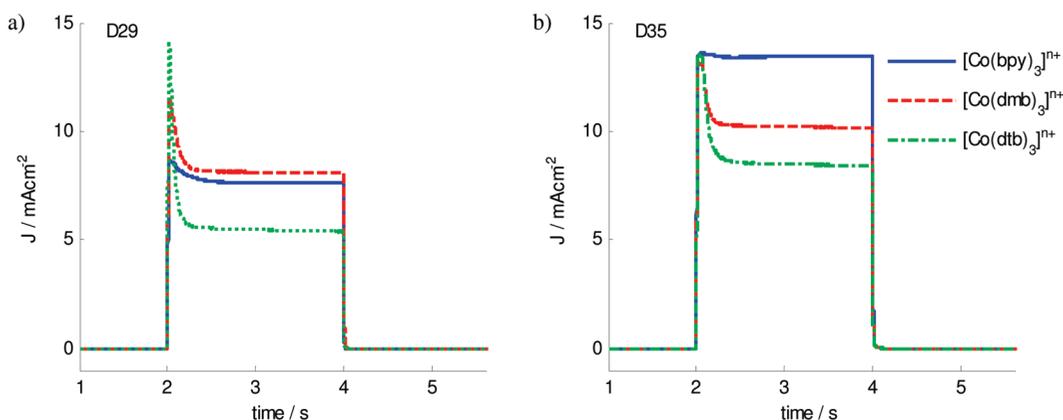


Figure 5. Plots of current transients measured at an illumination intensity of 1000 W m^{-2} for DSCs sensitized with (a) D29 and (b) D35.

same for DSCs sensitized with D35, suggesting that the current depends not only on the slower mass transport of the bulky redox species in the case of D29 but also on the recombination of photoinjected electrons with the oxidized form of the redox mediator, as discussed above.

The diffusion coefficients of the cobalt bipyridyl redox mediators were determined from the diffusion-limiting current measured by slow scan cyclic voltammetry to $5.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Co}(\text{dtb})_3]^{2+}$, $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Co}(\text{dmb})_3]^{2+}$, and $9.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Co}(\text{bpy})_3]^{2+}$ in acetonitrile. The diffusion-limiting current for $[\text{Co}(\text{bpy})_3]^{2+}$ is shown in Figure S6 in the Supporting Information. The diffusion is somewhat slower for the cobalt bipyridyl redox mediators than for triiodide, which has a diffusion coefficient of $18 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.¹⁹ The diffusion of $[\text{Co}(\text{bpy})_3]^{3+/2+}$ seems, however, to be fast enough in a $6 \mu\text{m}$ thick DSC, as the current spike in the photocurrent transient was negligible. The short-circuit current is also shown in Figure 4b to be linear with light intensity for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ but deviates from linearity at higher light intensity for $[\text{Co}(\text{dmb})_3]^{3+/2+}$ and $[\text{Co}(\text{dtb})_3]^{3+/2+}$ due to slower mass transport of the bigger cobalt complexes. The high efficiency for the DSCs sensitized with D35 and using $[\text{Co}(\text{bpy})_3]^{3+/2+}$ can, therefore, be explained by the efficient blocking of the recombination by the bulky alkoxy substituents on the dye. By adding steric bulk to the dye, rather than the cobalt complex, mass transport problems are avoided.

In the cyclic voltammetry experiments, the electrochemical reaction at the platinum electrode was increasingly less reversible for the cobalt complexes in the following order $[\text{Co}(\text{bpy})_3]^{3+/2+} < [\text{Co}(\text{dmb})_3]^{3+/2+} < [\text{Co}(\text{dtb})_3]^{3+/2+}$. Cobalt complexes containing alkyl substituents in the 4 and 4' or equivalent positions have been shown to be surface sensitive with respect to the roughness and material of the electrode, and quasi-irreversible behavior on platinized electrodes has been reported elsewhere.⁹ The charge-transfer resistance at the platinized counter electrode for the different cobalt bipyridyl complexes was compared using impedance spectroscopy (see Figure S7 in the Supporting Information). The lowest charge-transfer resistance at the counter electrode was measured for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and demonstrates the advantage of employing the less bulky redox mediator in DSCs. Initial results comparing alternative materials as counter electrodes are promising and suggest that alternative, cheap counter electrode materials will become available.

Effect of the Steric Properties of the Dye and Redox Shuttle on the Dye Regeneration Reaction. As for the recombination reaction, the rate of electron transfer between the dye and the redox couple is expected to depend on the structure of

the redox mediator and the dye, since the size of the electron donor and acceptor should affect the reorganization energy and the electronic coupling.⁴⁴ While no time constants for the regeneration were measured in this work, Nusbaumer et al. compared the regeneration of ruthenium-based sensitizers and a cobalt-based redox mediator, $[\text{Co}(\text{dbbip})_2](\text{ClO}_4)_2$.⁵ This redox couple was found to regenerate N719 and the hydrophobic dye Z907 on the microsecond time scale with high efficiency ($\varphi_{\text{reg}}(\text{N719}) = 0.98$ and $\varphi_{\text{reg}}(\text{Z907}) = 0.91$), suggesting that neutral, sterically hindered dyes are regenerated more slowly than smaller, negatively charged dyes. Cazzanti et al. reported the lifetime of Z907 in the presence of $[\text{Co}(\text{dtb})_3]^{3+/2+}$ to be about 390 ns.⁴⁴ This was substantially slower than regeneration of the same dye by ferrocene, which does not suffer from the large reorganization energy requirements that apply to cobalt redox couples. By comparison, triiodide/iodide regenerates N719 and Z907 in the microsecond range.^{45,46}

The regeneration of the dyes by the cobalt complexes was investigated with photoinduced absorption spectroscopy, performed under conditions similar to the operational conditions of DSCs (ca. 100 W m^{-2}). The PIA spectra of D29- and D35-sensitized TiO_2 in the presence and absence of the three different cobalt bipyridyl redox mediators or iodide/triiodide are shown in Figure 6a and 6b, respectively. In the absence of a redox mediator, a bleach was found at 520 nm for D35 and 540 nm for D29, respectively, and an increase in absorbance in the near infrared. The latter can be attributed to the presence of oxidized dye and to a lesser extent electrons in TiO_2 (in agreement with the results from measurements by spectroelectrochemistry shown in Figure S8 in the Supporting Information). The bleach is attributed to superposition of the bleach corresponding to the ground-state dye on the formation of the oxidized dye together with a Stark shift caused by the photoinjected electrons that give a local change in the electrical field across the dye molecules.^{47,48} When the electrolyte was added to the sensitized film, the features from the oxidized dye in the near infrared disappeared, indicating that the redox mediators had regenerated the dye, and a broad absorption due to accumulated electrons in the TiO_2 was seen. A bleach at about 520 nm persisted, caused by

(43) Nakade, S.; Makimoto, Y.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2005**, *109*, 3488.

(44) Cazzanti, S.; Caramori, S.; Argazzi, R.; Elliott, C. M.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2006**, *128*, 9996.

(45) Clifford, J. N.; Palomares, E.; Nazeeruddin, M. K.; Grätzel, M.; Durrant, J. R. *J. Phys. Chem. C* **2007**, *111*, 6561.

(46) Pelet, S.; Moser, J.-E.; Grätzel, M. *J. Phys. Chem. B* **2000**, *104*, 1791.

(47) Ardo, S.; Sun, Y.; Staniszewski, A.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **2010**, *132*, 6696.

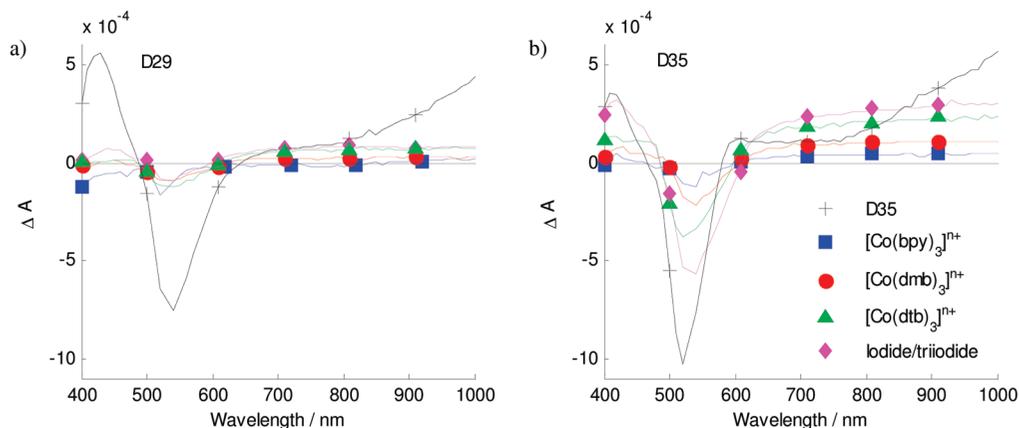


Figure 6. PIA spectra of TiO₂ sensitized with (a) D29 and (b) D35. The electrolyte was 0.1 M Co(L)₃(ClO₄)₂, 0.01 M Co(L)₃(ClO₄)₃, 0.1 M LiClO₄, and 0.2 M TBP in acetonitrile. Every 10th data point is marked with a symbol.

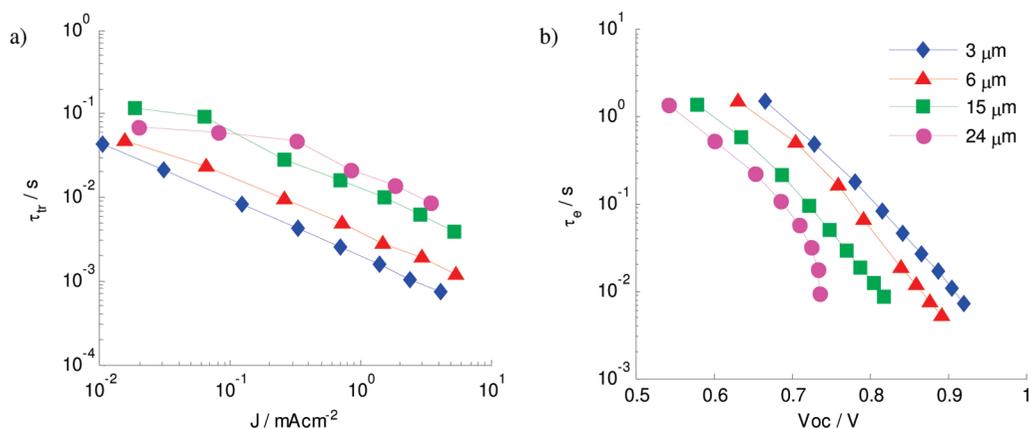


Figure 7. (a) Transport time as a function of short-circuit current density and (b) electron lifetime as a function of open-circuit voltage for [Co(bpy)₃]^{2+/3+}-based DSCs sensitized with D35 using a different thickness of TiO₂.

the Stark effect. The electroabsorption spectra of D35 and D29 have a shape similar to the first derivative of the dye absorption spectrum (shown in Figure S9 in the Supporting Information) and demonstrate that the observed bleaches are caused by a change in the absorbance spectra of the dye by a local electric field.^{47,48} The absence of any trace of oxidized dye in the steady-state spectra in the presence of electrolyte suggests that all the dye has been efficiently regenerated for all the redox couples investigated.

The results of the PIA measurements and the high IPCE values for the DSCs sensitized with D35 with each redox mediator, despite structural differences, suggest that the regeneration efficiency is high under the conditions used in the experiments. The photocurrent in our devices was, furthermore, not significantly affected by the redox potential of the cobalt complexes, in agreement with observations by DeVries et al.,²¹ suggesting that the driving force for regeneration is sufficient for the cobalt-mediator-based DSCs employed here. The lower IPCE value for DSCs sensitized with D29 was, therefore, not attributed to a lower driving force for regeneration but rather to fast recombination kinetics as discussed in the electron lifetime section above. However, in the PIA measurements we used thinner films (about 2 μm) than those applied in real devices. This means that we cannot rule out that dyes may be located deep in the pores in very thick films, which may not be accessible to larger redox species. Slow mass transport of the cobalt mediator can lead to depletion of Co(III) at the counter electrode but also to accumulation of Co(III) and a decrease of

Co(II) in the pores of TiO₂. This can inhibit efficient dye regeneration and increase undesirable recombination processes.

Effect of Film Thickness. The results discussed above refer to DSCs with a mesoporous TiO₂ film thickness of 5.6 μm. Figure 7 shows the effect of varying film thickness on the electron transport and lifetime in DSCs sensitized with D35 using a [Co(bpy)₃]^{3+/2+}-based electrolyte. The electron lifetime decreased and the transport time increased, i.e., the electron transport became slower, with increasing thickness of the TiO₂. Electron transport is suggested to be driven by diffusion and has been shown elsewhere to require a longer time in DSCs with thicker films.⁴⁹ The charge-collection efficiency of photoinjected electrons is higher in DSCs with thinner films since the distance required for electron diffusion to the charge collector is smaller, resulting in shorter transport times and lower electron densities in the film, which limits recombination losses. The decrease in electron lifetime, measured at open-circuit conditions, with film thickness may be explained as follows: At a given V_{OC}, the electron concentration in the TiO₂ is constant, even though the strong light absorption by the organic dyes leads to charge injection mostly close to the substrate. Regeneration of the dye leads to generation of Co(III) species close to the substrate, from where it diffuses toward the bulk electrolyte. Under steady-state conditions, the rather slow diffusion of the cobalt complexes in the pores of the TiO₂ leads to a local increase of

(48) Cappel, U. B.; Feldt, S. M.; Schöneboom, J.; Hagfeldt, A.; Boschloo, G. *J. Am. Chem. Soc.* **2010**, *132*, 9096.

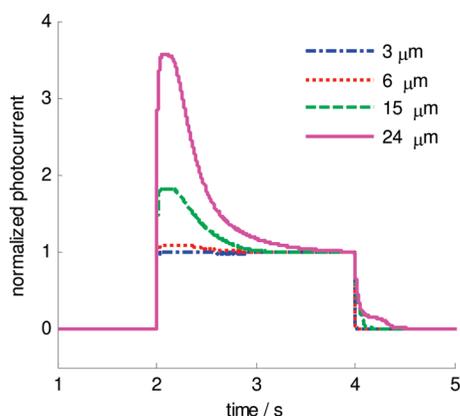


Figure 8. Plots of current transients measured at an illumination intensity of 1000 W m^{-2} for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ -based DSCs sensitized with D35 using a different thickness of TiO_2 .

their concentration, which will depend on the film thickness. The result will be a smaller electron lifetime for thicker TiO_2 films.

Figure 8 shows the effect of varying the TiO_2 film thickness on the photocurrent transients for the DSCs sensitized with D35, employing $[\text{Co}(\text{bpy})_3]^{3+/2+}$ in the electrolyte. The photocurrent transients were normalized with respect to the steady-state current in order to illustrate the increase in the current spike with increasing film thickness as the light is switched on. In DSCs with thicker TiO_2 films, the current is clearly limited by slow mass transport through the mesoporous TiO_2 film. The cell performance was not substantially affected by varying the thickness of the Surlyn spacer, suggesting that it is the diffusion through the mesoporous TiO_2 network rather than in the bulk electrolyte that limits the performance of DSCs employing cobalt polypyridine redox mediators. The diffusion of $[\text{Co}(\text{dbpy})_3]^{n+}$ through mesoporous titania films was determined by Nelson et al.¹⁹ to be about 1 order of magnitude slower than for I_3^- . Organic dyes with high extinction coefficients can, however, be used to build thin-film DSCs in order to overcome mass transport and recombination limitations related to cobalt-based redox mediators.

Optimized Photovoltaic Performance. The current–voltage characteristics were optimized for the DSCs sensitized with D35 employing the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ or the iodide/triiodide electrolyte, and the best efficiencies obtained are shown in Figure 9 and Table 1. Although the mass transport problems were shown to be avoided in the thin-film DSCs employing $[\text{Co}(\text{bpy})_3]^{3+/2+}$, the best efficiency was still obtained for thicker films because of the increased light-harvesting efficiency, i.e., two layers of TiO_2 and one light-scattering layer giving a total thickness of $15 \mu\text{m}$ ($12 + 3 \mu\text{m}$). The best efficiencies obtained in this study measured at 1000 W m^{-2} AM1.5G illumination are shown in Figure 9a and were 6.7% for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and 5.5% for iodide/triiodide. The efficiency reported above (and for all the devices mentioned so far) was measured using a $6 \text{ mm} \times 6 \text{ mm}$ mask, following the recommendation by Ito et al.⁵⁰ Since certified solar cell efficiencies for DSCs are quoted for a defined aperture size,⁵¹ we also measured the most efficient cells with a mask that was slightly smaller than the film area ($4 \text{ mm} \times 4 \text{ mm}$). In this case, the efficiency found was 6.3% for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and 5.4% for iodide/triiodide.

The efficiency of DSCs sensitized with D35 employing cobalt complexes is superior to that obtained by other groups working

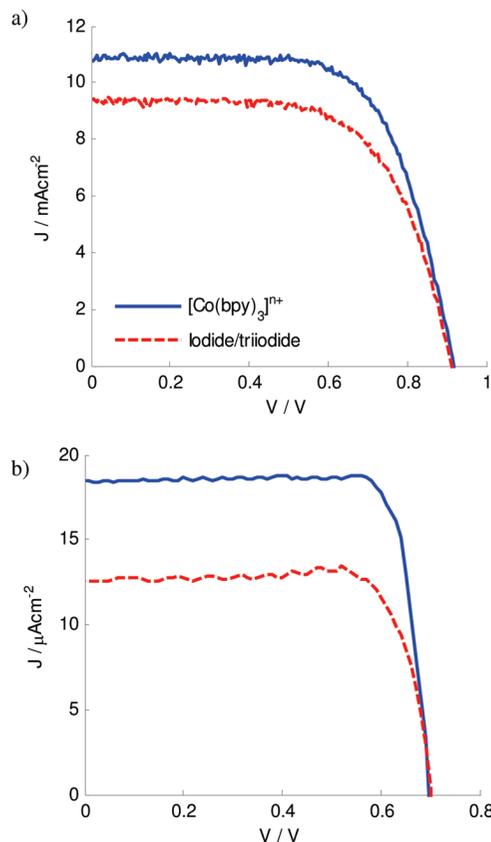


Figure 9. Current density versus applied potential curves under (a) 1000 W m^{-2} AM1.5G and (b) 250 Lux illumination for DSCs sensitized with D35. The electrolytes were 0.5 M $\text{Co}(\text{bpy})_3(\text{PF}_6)_2$, 0.1 M $\text{Co}(\text{bpy})_3(\text{PF}_6)_3$, 0.5 M TBP, and 0.1 M LiClO_4 in acetonitrile or 0.6 M 1-butyl-3-methylimidazoliumiodide, 0.03 M I_2 , 0.5 M TBP, and 0.1 M guanidinium thiocyanate in acetonitrile, respectively.

Table 1. Current–Voltage Characteristics of DSCs Sensitized with D35 Using $[\text{Co}(\text{bpy})_3]^{2+/3+}$ and Iodide/Triiodide-Based Electrolytes Measured Using a $6 \text{ mm} \times 6 \text{ mm}$ Mask under Different Illumination Conditions

light intensity	$V_{\text{oc}}(\text{V})$	$J_{\text{sc}}(\text{mA cm}^{-2})$	FF	η (%)	max power ($\mu\text{W cm}^{-2}$)
$[\text{Co}(\text{bpy})_3(\text{PF}_6)]^{2+/3+}$					
1000 W m^{-2a}	0.92	10.7	0.68	6.7	
100 W m^{-2a}	0.85	1.12	0.76	7.2	
250 lx^b	0.70	18.5×10^{-3}	0.80		10.7
iodide/triiodide					
1000 W m^{-2a}	0.91	9.38	0.65	5.5	
100 W m^{-2a}	0.86	0.89	0.75	5.7	
250 lx^b	0.70	12.6×10^{-3}	0.79		7.2

^a AM1.5G spectral distribution. ^b Fluorescent light (Osram Dulux Value 8W/827).

with cobalt-based DSCs using ruthenium-based sensitizers. Control devices with the ruthenium-based sensitizers Z907 and N719 were performed, see Figure S10 in the Supporting Information. The photovoltaic performance of Z907 in combination with the coadsorber 1-decylphosphonic acid (DPA) was much better than that of N719 and illustrates the importance of introducing alkoxy groups on the dye that prevents the TiO_2 surface from $\text{Co}(\text{III})$ species in the electrolyte in cobalt-based DSCs. The structural properties of D35 seem, however, to prevent recombination more efficiently than Z907 in cobalt-based DSCs and a higher efficiency and V_{oc} was obtained with this organic dye. It was further noted that the efficiency increased when the solar cells were warmed under the solar simulator

(49) Nissfolk, J.; Fredin, K.; Simiyu, J.; Häggman, L.; Hagfeldt, A.; Boschloo, G. *J. Electroanal. Chem.* **2010**, *646*, 91.

(50) Ito, S.; Nazeeruddin, M. K.; Liska, P.; Comte, P.; Charvet, R.; Péchy, P.; Jirousek, M.; Kay, A.; Zakeeruddin, S. M.; Grätzel, M. *Prog. Photovoltaics Res. Appl.* **2006**, *14*, 589.

since the diffusion of the cobalt complexes is faster at higher temperatures. Liberatore et al.⁵² found that the standard rate electron coefficient for $[\text{Co}(\text{dtb})_3]^{3+/2+}$ in methoxypropionitrile increased more than six times and the ionic diffusion coefficient more than three times at 80 °C.

The V_{oc} and electron lifetime are approximately the same for the optimized DSCs employing iodide/triiodide or cobalt-based redox mediators when a large amount of TBP is present in the electrolyte (see Figure S12 in the Supporting Information). The V_{oc} and solar cell efficiency increase much upon addition of TBP to both types of redox electrolyte. For iodide/triiodide-based electrolyte this has been explained by a negative shift in the conduction band as a result of a decreased amount of adsorbed Li cations at the TiO_2 surface as well as an increase of electron lifetime.^{43,53,51} A similar mechanism is expected for the cobalt-based redox mediators. In agreement with findings from Nakade et al.,^{43,53} we found that TBP increases the electron lifetime in cobalt mediator-based DSCs.

The DSCs employing cobalt redox mediators are also promising for indoor applications as the efficiency and the open-circuit voltage remain high even at low light intensities. The photovoltage for DSCs sensitized with D35 employing $[\text{Co}(\text{bpy})_3]^{3+/2+}$ at an indoor light illumination of 250 lx was about 700 mV, as shown in the current–voltage characteristics in Figure 9b. For comparison, Burnside et al.⁵⁴ reported 539 mV per cell at 250 lx for ruthenium-based sensitizer (N719) based DSC modules employing the iodide/triiodide redox couple, while a commercial amorphous silicon module gave 677 mV/element. At 100 W m^{-2} AM1.5G illumination we obtained 7.8% efficiency for DSCs with cobalt redox mediators using a TiO_2 film thickness of 22 μm and a lower concentration of cobalt mediator in the electrolyte (see Figure S11 in the Supporting Information).

Conclusion

Efficient dye-sensitized solar cells using cobalt-based mediators can be obtained by matching the steric bulk of triphenylamine-based organic sensitizers and cobalt polypyridine redox mediators. Careful tuning of their properties minimizes the recombination between electrons in TiO_2 and Co(III) species in the electrolyte solution and avoids the mass transport limitations of the redox mediator. The organic sensitizer D35, equipped with bulky alkoxyl groups, efficiently suppresses recombination, allowing the use of cobalt redox mediators with smaller steric bulk. By building thin-film DSCs sensitized with dyes with high extinction coefficients, previously encountered problems associated with cobalt redox mediators, such as fast recombination and mass transport limitations, can efficiently be avoided. The best efficiency for DSCs, sensitized with D35 and employing a $[\text{Co}(\text{bpy})_3]^{3+/2+}$ -based electrolyte of 6.7% at full sunlight (1000 W m^{-2} AM1.5G illumination) is superior to the highest efficiency obtained so far with iodide-free electrolytes. The best efficiency was, however, achieved for DSCs with a

thicker film of TiO_2 due to enhanced light-harvesting efficiency, and it is therefore a need of organic dyes with even higher extinction coefficients and more red-shifted absorption spectra. One advantage of using one-electron redox couples in DSCs is that the driving force for regeneration is expected to be lower than that for the iodide/triiodide redox shuttle, and the absorption of the dye can therefore be broadened by tuning the HOMO level of the dye. The current was, in addition, higher in the DSCs employing cobalt redox mediators since the cobalt complexes absorb less light than iodide/triiodide.

Cobalt polypyridine complexes are promising alternative redox mediators to the iodide/triiodide redox couple for large-scale manufacturing of DSCs, since they are less aggressive toward metal contacts and sealing materials. DSCs sensitized with organic dyes employing cobalt polypyridine redox mediators are promising for indoor applications since the voltage and efficiency remain high under low light intensities. Mass transport limitations are also efficiently avoided at lower light intensities, and the stability of the devices can be extended by using a more viscous electrolyte solvent. The V_{oc} of the devices is high (>900 mV) because of the more positive redox potential of the complexes and can easily be tuned, as the large amount of commercially available ligands makes it possible to adjust the redox potential by changing the coordination sphere of the complexes.

Most importantly, we demonstrated that one-electron outer-sphere complexes may be employed in n-type DSCs without the need for surface-insulating layers. By choosing an appropriate dye, the recombination, which is otherwise fast with organometallic complexes, can be prevented and the lifetime of the electrons can be increased to time scales comparable with the standard iodide/triiodide electrolyte. This in turn removes an extra step in the preparation of the working electrodes, which would increase the manufacturing cost if such devices were to be produced commercially.

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Supporting Information Available: IPCE spectra from CE illumination for D29 and D35; absorption spectra of D29 and D35; dark current–voltage characteristics of D29 and D35; light intensity dependence of the open-circuit voltage for D35-based DSCs using a supporting electrolyte of TBAPF_6 or LiClO_4 ; current–voltage characteristics of D35-based DSCs with a different amount of oxidized $[\text{Co}(\text{bpy})_3]^{3+}$ in the electrolyte; diffusion-limiting current for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ determined by cyclic voltammetry; impedance spectra of the different cobalt bipyridyl redox mediators employed herein; spectroelectrochemistry measurements of D29 and D35; electroabsorption spectra of D29 and D35; current–voltage characteristics comparing D35 and ruthenium sensitizers in cobalt-based DSCs; current–voltage characteristics for D35-based DSCs employing $[\text{Co}(\text{bpy})_3]^{2+/3+}$ at 100 W m^{-2} AM1.5G illumination; electron lifetime as a function of extracted charge plot for the optimized DSCs sensitized with D35 employing $[\text{Co}(\text{bpy})_3]^{2+/3+}$ - or iodide/triiodide-based electrolytes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (51) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. *Prog. Photovoltaics Res. Appl.* **2010**, *18*, 144.
- (52) Liberatore, M.; Petrocco, A.; Caprioli, F.; La Mesa, C.; Decker, F.; Bignozzi, C. A. *Electrochim. Acta* **2010**, *55*, 4025.
- (53) Nakade, S.; Kanzaki, T.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2005**, *109*, 3480.
- (54) Burnside, S.; Winkel, S.; Brooks, K.; Shklover, V.; Grätzel, M.; Hinsch, A.; Kinderman, R.; Bradbury, C.; Hagfeldt, A.; Pettersson, H. *J. Mater. Sci.-Mater. Electron.* **2000**, *11*, 355.