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Ligand Engineering for the Efficient Dye-Sensitized Solar Cells with Ruthenium Sensitizers and Cobalt Electrolytes

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Supporting Information

ABSTRACT: Over the past 20 years, ruthenium(II)-based dyes have played a pivotal role in turning dye-sensitized solar cells (DSCs) into a mature technology for the third generation of photovoltaics. However, the classic I_3^-/I^- redox couple limits the performance and application of this technique. Simply replacing the iodine-based redox couple by new types like cobalt(3+/2+) complexes was not successful because of the poor compatibility between the ruthenium(II) sensitizer and the cobalt redox species. To address this problem and achieve higher power conversion efficiencies (PCEs), we introduce here six new cyclometalated ruthenium(II)-based dyes developed through ligand engineering. We tested DSCs employing these ruthenium(II) complexes and achieved PCEs of up to 9.4% using cobalt(3+/2+)based electrolytes, which is the record efficiency to date featuring a



ruthenium-based dye. In view of the complicated liquid DSC system, the disagreement found between different characterizations enlightens us about the importance of the sensitizer loading on TiO_2 , which is a subtle but equally important factor in the electronic properties of the sensitizers.

INTRODUCTION

The global challenge to develop carbon-neutral renewable energy sources can be addressed by harnessing solar power using photovoltaics.¹ As an alternative to conventional solar cells, third-generation photovoltaic devices with dye-sensitized solar cells (DSCs) at the forefront have been extensively studied.² In standard DSCs, mesoporous TiO_2 is sensitized by a ruthenium(II) complex or an organic dye, and I_3^-/I^- is widely employed as the most effective redox couple.^{3,4} Congruence between the dye molecule chemisorbed on a mesoporous oxide and redox pair in the electrolyte in DSCs should be fine-tuned to obtain fast dye regeneration and ideally slow charge recombination. The present certified record power conversion efficiencies (PCEs) of up to 11.1% were achieved with I_3^{-}/I^{-} and heteroleptic ruthenium dyes.⁵⁻⁷ However, regeneration of a ruthenium(II) complex by electron donation from the I_3^{-}/I^{-} redox couple entails a loss of around 500 mV, with over 300 mV of that being directly related to the complicated sequence of reactions associated with the two-electron oxidation of iodide that do not involve the sensitizer molecule.⁸⁻¹⁰ The estimated lowest potential loss for the ruthenium metal

complex/iodide system is around 750 mV, which limits the maximum obtainable conversion efficiency to 13.4%.^{9,11}

To boost the efficiencies further, redox couples with a smaller loss in potential were introduced. Among the one-electron redox pairs, 12,13 cobalt(3+/2+) is the most promising for the following two reasons: (i) DSCs with organic dyes and cobalt electrolytes are more stable in comparison to the cells with other one-electron shuttles;¹⁴ (ii) it is possible to obtain cobalt complexes with various redox potentials just by ligand modification.^{15,16} It is worth noting that the recent advances with copper(2+/1+) phenantroline-based electrolytes may result in an improved performance.^{17,18} Contrary to the reduction of I₃, the unwanted recapture of the conductionband electrons by the cobalt(3+) complex is a simple oneelectron outer-sphere redox reaction, which can attain fast rates depending on the driving force, even though the cobalt(3+/2+)self-exchange reaction is slow due to spin change. This is prominent, in particular, for conventional ruthenium dyes such

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as N3, N719, and N749.¹⁹⁻²³ This caveat was ascribed to (i) the net negative charge on NCS-containing complexes causing columbic attraction between the positively charged cobalt complex and sensitizer, which results in adsorption of the cobalt complexes on the semiconductor surface²⁴ and (ii) the quenching of the triplet metal-to-lignad charge-transfer (³MLCT) state of ruthenium dyes by cobalt(3+) species, giving rise to a lower photocurrent.²⁵ To alleviate this problems, new ruthenium-free dye structures were accommodated with long alkyl or alkoxy chains to keep the redox pairs away from the surface.^{14,26,27} In this manner, PCEs of over 14% and open-circuit voltage higher than 1 V were achieved by employing bulky D- π -A dyes with a cobalt-based electrolyte.²⁸⁻³¹ A similar strategy was introduced for ruthenium dyes to improve their compatibility with the cobalt-based electrolvte.32

On the other hand, the bulky nature of the cobalt-based complexes compels one to use thinner mesoporous films in order to avoid mass-transport limitations of the photocurrent. This, in turn, requires the use of dyes with higher extinction coefficients. Ruthenium(II)-based sensitizers generally suffer from relatively low extinction coefficients, which motivated us to design and synthesize new cyclometalated tris-heteroleptic ruthenium(II) complexes. Through modification of the auxiliary ligands by attaching polyaromatic moieties, we can fine-tune the photophysical properties of the complexes, especially the extinction coefficient, and consequently the incident photon-to-current conversion efficiency (IPCE) in a device. It is known that the highest occupied molecular orbital (HOMO) in a cyclometalated ruthenium(II) complex involves the auxiliary ligand to a lesser degree than the cyclometalated ligand.^{23,32} This provides a wide window for modification of the auxiliary ligand without destabilization of the HOMO's energy.

Here, we introduce six new tris-heteroleptic cyclometalated ruthenium(II) dyes (SA22, SA25, SA246, SA282, SA284, and SA285; Figure 1). All of these complexes possess the same



Figure 1. Molecular structures of cyclometalated ruthenium(II) complexes.

anchoring ligand, 4,4'-dicarboxy-2,2'-bipyridine, and the same cyclometalated ligand as previously optimized.³² 2,2'-Bipyridines substituted in the 4 and 4' positions with polyaromatic rings were used as auxiliary ligands. With these sensitizers, we systematically investigated the influence of the auxiliary ligand by optical and electrochemical measurement, theoretical calculation, transient absorbance spectroscopy (TAS), and electrochemical impedance spectroscopy (EIS).

In the presence of cobalt(3+/2+) tris-phenantroline-based redox electrolytes, the highest PCE came from **SA246**, which possesses an insignificant absorption spectrum and the lowest electron lifetime. These contradictory results motivated us to unravel the critical parameters among the intricate effect of the kinds of factors. Through desorption experiments, we show that a proper substitution on the auxiliary ligands can dramatically increase the dye loading, which will play a decisive role in boosting the current density and quasi-Fermi level of TiO₂ and lead to an overtaking efficiency.

RESULTS AND DISCUSSION

Synthesis. We have previously reported³² 2,6-didodecyloxy-3,2'-bipyridine as a superior cyclometalating ligand over 2,6dimethoxy-3,2'-bipyridine because of its ability to keep the redox shuttle away from the semiconductor surface.³² The synthesis of the auxiliary ligands was carried out through palladium(0)-catalyzed cross-coupling of 4,4'-dibromo-2,2'bipyridine with corresponding adducts of polyaromatic substituents. For the synthesis of tris-heteroleptic cyclometalated ruthenium(II) complexes, we adopted the procedures developed by Bomben et al., which starts from reacting the cyclometalating ligand with $[Ru(C_6H_6)Cl_2]_2$ or [Ru(p $cymene)Cl_2]_2$ (Scheme 1).³⁶ After that, the intermediates were

Scheme 1. Synthesis of the Tris-heteroleptic Cyclometalated Ruthenium(II) Complexes



coordinated with the auxiliary and anchoring ligands in a onepot reaction, resulting in three products: two cyclometalated bis-heteroleptic complexes and one tris-heteroleptic complex.²³ It is worth mentioning that from the two possible isomers, where the cyclometalated ligand is in the trans position to the auxiliary or anchoring ligand pyridines, the former one is usually formed, as was shown from the single-crystal X-ray diffraction structures.^{23,32} Thus, the new ruthenium(II) complexes were separated and hydrolyzed to yield the final dye. All intermediates were characterized by ¹H NMR and the final complexes by ¹H NMR, ¹³C 135 DEPT NMR, and highresolution mass spectrometry. The results are provided in the Supporting Information.

Optical and Electrochemical Properties. Figure 2 shows the absorption spectra of the SA dyes in dichloromethane



Figure 2. UV-vis absorption spectra of SA22, SA25, SA246, SA282, SA284, and SA285 in DCM solution.

(DCM). All sensitizers have a set of $\pi - \pi^*$ transitions in the UV and near-UV regions. In the visible region, all dyes have characteristic metal-to-ligand charge-transfer (MLCT) bands. The extinction coefficient for the MLCT bands around 600 nm varies from 15×10^3 M⁻¹·cm⁻¹ (for SA22) to 24×10^3 M⁻¹· cm⁻¹ (for SA285). Except SA22 and SA284, all other dyes have more intense absorption bands than the sensitizer 3b reported in ref 28, which has hexylthiophene substitution on the auxiliary ligand. Moreover, except SA282, in the presented sensitizers, the low-energy MLCT band is red-shifted by 5-15 nm. SA22 and SA282 have similar shapes of absorption spectra. However, in the case of SA22 with the indenothiophene-substituted auxiliary ligand, the MLCT bands are red-shifted compared to that of SA282 with fluorene moieties on the auxiliary ligands. Despite the substantial MLCT band shift between SA22 and **SA282** (\approx 21 nm), the steeper drop of the MLCT band in long wavelengths in SA22 compared to SA282 results in a similar E_{0-0} value (1.77 eV; Table 1). SA246 and SA284 with thienothiophene and bithiophene moieties, respectively, also have shapes of absorption spectra similar with that of SA284,

Table 1.	. Photor	ohysical	and	Electrochemical	Pro	perties	of D	yes
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having more red-shifted bands in the near-UV region. SA25 and SA285 exhibit similar absorption spectra because of the same cyclopentadithiophenes. However, SA285, with longer alkyl chains on the cyclopentadithiophene moieties, has a higher extinction coefficient for the MLCT band than SA25.

Figure S3 presents the cyclic voltammograms of the SA dyes. From the intersection of normalized absorbance and emittance (Figure S1), E_{0-0} was calculated, and the excited-state oxidation potentials were calculated by subtracting E_{0-0} from the ground-state oxidation potentials. Table 1 and Figure 3 summarize the obtained optical and electrochemical data.



Figure 3. Energy diagram representing sensitizers' ground-state (GS) and excited-state (ES) oxidation potentials and redox couples' Nernst potentials with respect to the conduction band of TiO_2 . The sensitizer's GS oxidation potential was determined from cyclic voltammetry measurements, and the ES oxidation potential was obtained by subtracting E_{0-0} from the GS oxidation potential. Redox couple Nernst potentials are shown considering concentrations in a 2960⁴⁰ iodine-based electrolyte and in an optimized cobalt-based electrolyte.

All dyes have oxidation potentials between 0.88 and 0.92 V, which are higher than the Co(phen)₃^{3+/2+} standard oxidation potential (0.62 V) by at least 260 mV. This difference should create enough driving force for efficient dye regeneration. SA22 and SA282 have similar E_{0-0} values, which ideally should lead to identical MLCT band positions. The ground-state oxidation potential of SA285 (0.89 V) is surprisingly lower than that of SA25 (0.92 V) by 30 mV. Because of the same E_{0-0} values, the difference is maintained in the excited state. However, the error in cyclic voltammetry measurements up to 0.1 V has to be considered. All presented sensitizers have the excited-state oxidation potentials in the range of -0.79 to -0.89 V versus

dye	$\lambda_{\rm abs/max}$ nm ($\varepsilon \times 10^{-3} {\rm L \cdot mol^{-1} \cdot cm^{-1}}$) ^a	$E^{0}(S^{+}/S), V (vs NHE)^{b}$	$\lambda_{ m em/max}$ nm (in solution/on titania) a	$\tau_{1/2}, r_{ns}$	E_{0-0} , eV (in solution/on titania) ^d	$E^{0}(S^{+}/S^{*}), V (vs NHE)^{e}$
SA22	592 (15.2), 511 (12.5), 399 (39.2)	0.97	771/776	46	1.77/1.77	-0.80
SA25	593 (19.3), 448 (36.7)	0.92	808/811		1.71/1.71	-0.79
SA246	585 (21.5), 431sh (26.4), 382 (36)	0.88	798/814	38	1.72/1.71	-0.84
SA282	571 (22), 508sh (14.2), 411 (28.2)	0.88	775/798	48	1.77/1.74	-0.89
SA284	592 (16.3), 398 (30.4)	0.89	803/810	44	1.71/1.70	-0.82
SA285	595 (24.1), 456 (44)	0.89	804/822	82	1.71/1.67	-0.82
3b ³²	580 (19.6), 507 (14.1), 418 (23.4)	0.86	789/-		1.76/-	-0.90

^{*a*}Absorption and emission spectra were measured in DCM at room temperature. ^{*b*}Oxidation potentials were determined from cyclic voltammetry in 0.1 M NBu₄PF₆ in DCM. The working electrode was glassy carbon, the counter and reference electrodes were platinum wires and ferrocene (Fc) was used as an internal standard. To calculate the potentials versus NHE, 0.7 V was used as the Fc oxidation potential. ^{*c*}Excited-state lifetimes in a DCM solution were determined from fluorescence time-correlated single-photon-counting measurements. ^{*d*} E_{0-0} was determined from the intersection of normalized absorption and emission spectra. ^{*c*}Excited-state dye oxidation potentials were calculated by subtracting E_{0-0}/q (where *q* is a charge and is equal to one electron) from the ground-state oxidation potential.

NHE, which should guarantee an efficient charge injection into the titania conduction band.

One of the desired properties of a DSC sensitizer is its capability of sustaining numerous oxidation—reduction cycles under long-term operation, e.g., turnover numbers reaching 100 million for an outdoor lifetime of 20 years. *Isothiocyanate* ligands employed often for ruthenium(II) complexes cannot survive because of ligand exchange by electrolyte components such as *tert*-butylpyridine.⁴¹

In this regard, cyclometalated ruthenium(II) complexes were introduced as being potentially more stable, by ruling out the possibility of ligand exchange. However, on the basis of cyclic voltammetry measurements, our ruthenium(II) complexes are quasi-reversible because the obtained shifts between the peaks of the oxidative and reductive waves are usually around 120 mV.^{5,23,28,35–39}

To understand the origin of the electrochemical irreversibility in cyclometalated ruthenium dyes, we conducted spectroelectrochemical measurements in solution and in the complete device without a redox pair. We focused on the bands above 300 nm. Typical examples are represented in Figure S4. In solution (Figure S4A), none of these six complexes showed complete reversibility of both the $\pi - \pi^*$ and MLCT bands. Among them, SA22 and SA246 showed the best reversibility. However, these results should not be discouraging because dye features on titania may strongly change. In complete devices, SA22, SA282, and SA284 showed reversible behavior only for the $\pi - \pi^*$ transitions. Conversely, SA25, SA246, and SA285 have reversible MLCT bands in a device, but the $\pi - \pi^*$ transitions around 450 nm become extinct, indicating that the coordination core is more stable than the polyaromatic substituents (Figure S4C).

Computational Analysis. In Figure S5, the optimized geometries of studied SA dyes are shown. All of them have the typical geometry of ruthenium tris-bipyridine complexes. These optimizations were carried out for the isomers, which have a cyclometalated pyridine ring in the position trans to one of the anchoring carboxypyridine rings. It is worth noting that calculated molecular volumes meet expectations, and **SA246** and **SA284** with the least number of substituents have the lowest molecular volumes (Table S1).

Among the entire series of SA dyes, the lowest unoccupied molecular orbitals (LUMOs) have very close energies (Table S2) and are localized on the anchoring ligand, as can be observed from the isodensity plots in Figures S6 and S7. However, the HOMOs present variation in the energies mainly because of localization on the different substituents. In particular, SA25 and SA285 exhibit the highest HOMO energies with a consequent decrease of the HOMO-LUMO energy gap. As expected, the HOMOs not only are localized on the metal t_{2g} orbitals but also are partially delocalized through the auxiliary ligand, the degree of which depends on the different substituents. In SA25 and SA285, both cyclopentadithiophene moieties on the auxiliary ligands contribute to a major fraction of the HOMO. In SA22, SA246, and SA284, only one donating moiety on the auxiliary ligands, which is in the trans position to the anchoring carboxypyridine ring, owns a fraction of the HOMO. Fluorene moieties on the auxiliary ligand in SA282 do not possess any substantial fraction of the HOMO (Figure S7). These observations imply that, among all of these substituents on the auxiliary ligands, cyclopentadithiophene and fluorene own the strongest and weakest donating power, considering that dihedral angles

between the substituents and pyridine rings of the auxiliary ligand may also play a role (Table S1). Because the dihedral angles between the indenothiophene or fluorene moieties and pyridine planes are close values according to the density functional theory (DFT) calculations (36 and 38°, respectively; Table S1), the red-shifted spectrum of SA22 (or SA285) with respect to SA282 is more reasonably due to the higher donating power of indenothiophene than fluorene. Although the shapes of theoretical spectra do not perfectly follow the experimental results (Figure S8), the absorption maxima and the main calculated transitions (Table S4) are in perfect agreement with the experimental optical data.

TAS. To evaluate the influence of different substituents on the lifetimes of the photooxidized dyes in the environment of cobalt-based electrolytes, we performed TAS measurements on unbiased devices. Measurements were carried out on two different types of cells containing (a) redox-inactive pure acetonitrile and (b) a cobalt-based electrolyte. Dye molecules were excited with a low-intensity pulsed laser at 510 nm to ensure an average of less than one injected electron per nanoparticle, i.e., typically 40 μ J·cm⁻². The probe was monitored at 900 nm, following the oxidized dye signature, and transient absorbance decay was fitted with a mono-exponential function (Figure S9).

We find a regeneration yield of above 94% for all dyes, except SA282 and SA285. A low regeneration yield for SA282 and SA285 is reasonable considering the steric hindrance of their hexyl chains, which drastically affects the regeneration lifetime. We also observe that, for most of the dyes, regeneration does not seem complete and the dynamics reach a plateau, suggesting remaining oxidized species in the system. It is worth noting that, to estimate the regeneration efficiency, we consider that electron recombination with photooxidized dye and dye regeneration with the electrolyte rates follow first-order dynamics on the reductant concentration $\eta_{reg} = \tau_{rec} / (\tau_{rec} + \tau_{reg})$, where $\tau_{\rm rec}$ is the electron-oxidized dye recombination lifetime and au_{reg} the oxidized dye regeneration lifetime in the presence of an electrolyte; Table S6]. This procedure may not exactly represent the situation in a device under full sun illumination considering the following facts: (a) dye regeneration is not necessarily a first-order reaction⁴² and (b) the electron density in TiO₂ created by the laser pulse is not comparable to the electron density in the performing device at maximum power point.^{43,44} The second fact may bring an overestimated lifetime of photooxidized dyes in the devices with a redox-inactive electrolyte at a low-light regime. Although not exactly picturing devices in working conditions, we use these data as an approximation of the charge-transfer dynamics.⁴⁵

EIS. The $V_{\rm OC}$ trends of the devices with various dyes can be predicted by EIS analysis on complete devices in the dark. The Nyquist plots were fitted according to the transmission-line model developed by Bisquert et al., and the main parameters were extracted.^{46,47} They comprise the charge-transfer resistance, $R_{\rm cv}$ representing the charge recombination resistance for the electron in the TiO₂ conduction band with the oxidized form of the redox couple, the chemical capacitance, $C_{\mu\nu}$ representing the density of states (DOS) accessible to electrons in the TiO₂ nanocrystals, and the transport resistance, $R_{\rm trans}$, representing the resistance for the transport of the electrons through the mesoporous TiO₂ network. Using the obtained charge recombination ($R_{\rm ct}$) and transport ($R_{\rm trans}$) resistances along with the chemical capacitance ($C_{\rm chem}$) of the titania, one



Figure 4. Key parameters extracted from EIS analyses of the cobalt-based devices: recombination resistance (solid lines); transport resistance (dotted lines) and capacitance (dashed lines) over potential (left); electron recombination lifetime (solid lines) and transport lifetime (dotted lines) as a function of the capacitance (right). In all figures, lines with red, blue, green, black, yellow, and cyan colors refer to the devices with SA22, SA25, SA246, SA282, SA284, and SA285, respectively.

can calculate the electron lifetime (τ_n) and transport time (τ_{trans}) as $\tau_n = R_{ct}C_{chem}$ and $\tau_{trans} = R_{trans}C_{chem}$.

The main parameters from the EIS fitting of cobalt-based devices are shown in Figures 4 and S10. The cobalt-based devices showed pronounced changes in the conduction-band edge position. It is interesting to note that the highest chemical capacitance, and so the lowest conduction band, and the highest electron lifetimes were observed for SA22, followed by SA285, while the lowest values of the electron lifetime were obtained for SA246 and SA282.

The differences in $V_{\rm OC}$ due to the conduction-band shift and electron lifetime were estimated in reference to the values obtained with **SA22** and are presented in Table 2.

Table 2. Comparison of the V_{OC} Differences Estimated from EIS Analyses and Obtained from the *J*-*V* Measurements for the Cobalt-Based Electrolytes

dye	ΔE^{CB} , mV	$\tau_{n\nu}^{\ b}$ s (ΔV due to a change in τ_n with respect to SA22, mV)	estimated $\Delta V_{\text{OC}} = \Delta E^{\text{CB}} + \Delta V (\text{due} \text{to } \Delta \tau_{\text{n}})^{c}$	$\Delta V_{\rm OC}, \frac{d}{mV}$
SA22	0	0.180		0
SA25	24	0.052 (-32)	-8	-17
SA246	40	0.024 (-52)	-12	18
SA282	22	0.025 (-51)	-27	-33
SA284	23	0.035 (-43)	-20	-33
SA285	15	0.120 (-11)	4	-20

^{*a*}The shift in the conduction-band edge was estimated from EIS analyses. ^{*b*}The change in the voltage due to a change in the electron lifetime was calculated using the diode equation. ^{*c*}Total estimated change in $V_{\rm OC}$ due to the conduction-band edge difference and electron lifetime. ^{*d*}The difference in $V_{\rm OC}$ obtained from the J-V measurements. All values are brought in reference to the case with **SA22**. Positive values indicate the rise in $V_{\rm OC}$.

Photovoltaic Performance. Finally, to evaluate the influence of ligands on the photovoltaic performance, we put the complete devices with the cobalt-based electrolytes under photovoltaic characterization and present the results in Table 3. The iodine-based devices were also tested, and the results are shown in Figure S11B and Table S7. In the case of the DSCs with cobalt-based electrolytes, both J_{SC} and V_{OC} vary significantly between 9 and 14 mA·cm⁻² and 794 and 845 mV with the following trends: for J_{SC} , SA282 < SA25 < SA284 < SA285 < SA22 < SA246; for V_{OC} , SA282 = SA284 < SA285 < SA25 < SA22 < SA246 (Figure 5 and Table 3). The

sensitizer called **SA246** showed the best IPCE, which is in agreement with the measured J_{SC} value. Inconsistencies are found in both J_{SC} and V_{OC} , especially with **SA246**, which has relatively blue-shifted absorption spectrum and the lowest electron lifetime. An unexpected trend in the V_{OC} and J_{SC} values indicating some more vital parameters is controlling the photovoltaic performance.

Despite the indistinctive molar extinction coefficient and moderate absorption range with SA246, the high J_{SC} over other sensitizers is a baffling feature. To explain the highest J_{SC} provided by SA246, we analyzed the amount of dye adsorbed on the surface. One way to evaluate the absolute dye loading is the desorption experiment of sensitized titania films (Figure 6). The amount of SA246 adsorbed on titania is drastically higher compared to other dyes. It is worth noting that SA285 also provides high dye loading; however, because of inefficient dye regeneration (vide supra), SA285 fails to yield high PCE. The high dye loading of SA246 increased the absorbance (optical density) of the sensitized titania, which, in turn, boosted J_{SC} more than the other sensitizers with a higher molecular molar extinction coefficient and a wider absorption range. This effect has already been indicated by the IPCE spectra (Figure 5B).

At the same time, it is quite unexpected that the device with **SA246** gave the highest $V_{\rm OC}$ even though it possesses the lowest electron lifetime and therefore the highest recombination. It is known that the long electron lifetime is a necessary but not sufficient condition to lead to high $V_{\rm OC}$. We have to take the change in $J_{\rm SC}$ under light into consideration, which has been completely neglected in ESI analyses; e.g., the inversed correlation of the electron lifetime and $V_{\rm OC}$ in the case of **SA246** can be explained by the higher $J_{\rm SC}$ in the case of **SA246**. Higher $J_{\rm SC}$ will induce a higher steady-state electron density in titania in the performing device, which yields an upwardly shifted quasi-Fermi level $E^*_{\rm F,n}$ and, hence, $V_{\rm OC}$. In this case, the rise in $V_{\rm OC}$ compensates for the loss due to high electron recombination.

CONCLUSION

Six new cyclometalated tris-heteroleptic ruthenium complexes were synthesized and characterized in the course of ligand engineering compatible with cobalt-based electrolytes in DSCs. The substituents on the auxiliary ligand were the focus of this study. Various substituents result in different photophysical properties and different performances in the DSCs. With the cobalt-based devices, the record efficiency to date featuring

Table 3. Photovoltaic Performance of Iodine- and Cobalt-Based DSCs with SA Dyes

dye ^a	electrolyte	$J_{\rm SC}$, mA/cm ²	$V_{\rm OC}$ mV	FF, %	PCE(10%)	PCE(100%)
SA22	^b [Co(phen) ₃] ^{3+/2+}	12.25	827	75.5	8.4	7.9
SA25	b [Co(phen) ₃] ^{3+/2+}	10.68	810	77.9	7.4	6.9
SA246	b [Co(phen) ₃] ^{3+/2+}	14.55	845	74.7	9.4	9.4
SA282	^b [Co(phen) ₃] ^{3+/2+}	9.89	794	78.5	6.7	6.3
SA284	^b [Co(phen) ₃] ^{3+/2+}	11.28	794	76.9	7.2	7.0
SA285	$C_{\rm [Co(phen)_3]^{3+/2+}}$	11.85	807	73.6	6.1	7.2

[&]quot;All cells were measured under AM 1.5 simulated solar light irradiation with a power of 100 mW·cm⁻² at room temperature; ^bCobalt-based electrolyte: 0.25 M $[Co^{II}(phen)_3](TFSI)_2$, 0.05 M $[Co^{III}(phen)_3](TFSI)_3$, 0.25 M 4-(5-nonyl)pyridine, and 0.1 M LiTFSI; ^cCobalt-based electrolyte: 0.25 M $[Co^{II}(phen)_3](TFSI)_2$, 0.05 M $[Co^{III}(phen)_3](TFSI)_3$, 0.5 M 4-(5-nonyl)pyridine, and 0.1 M LiTFSI.



Figure 5. (A) *J*–*V* curves and (B) IPCE curves for DSCs based on cobalt electrolytes and cyclometalated ruthenium dyes SA22, SA25, SA246, SA282, SA284, and SA285.



Figure 6. Dye-loading values obtained by the desorption of SA dyes from the titania films.

ruthenium-based dyes was obtained for SA246 as 9.4%. The highest efficiency is explained by the higher dye loading, a factor that is normally neglected by the designers. The high absolute dye loading increases the optical density, which can lead to a higher photocurrent and voltage. This effect can even overwhelm the influence of the recombination rate. Provided in this work, different analyses indicate the complexity of the processes taking place and underline the compromise between various parameters to be considered from the sensitizer-design viewpoint. For the cobalt-based devices, the sensitizer molecule should have small enough size to maintain (i) efficient dye regeneration and (ii) high dye loading and, at the same time, (iii) a bulky periphery to keep the redox mediator away from the semiconductor surface. These results could be very instructive for further dye engineering to reach even higher PCEs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00842.

Synthetic procedures and characterization of all products, descriptive preparation of solar cells, photoluminescence spectra and excited-state decay for the final complexes, cyclic voltammograms for the final complexes, and DFT-time-dependent DFT calculation parameters and results (PDF)

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Notes

The authors declare no competing financial interest.

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