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# Molecularly Engineered Ru(II) Sensitizers Compatible with Cobalt(II/ III) Redox Mediators for Dye-Sensitized Solar Cells

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#### **S** Supporting Information

ABSTRACT: Thiocyanate-free isoquinazolylpyrazolate Ru-(II) complexes were synthesized and applied as sensitizers in dye-sensitized solar cells (DSCs). Unlike most other successful Ru sensitizers, Co-based electrolytes were used, and resulting record efficiency of 9.53% was obtained under simulated sunlight with an intensity of 100 mW cm<sup>-2</sup>. Specifically, dye 51-57dht.1 and an electrolyte based on Co(phen), led to measurement of a  $J_{SC}$  of 13.89 mA cm<sup>-2</sup>,  $V_{OC}$  of 900 mV, and FF of 0.762 to yield 9.53% efficiency. The improved device performances were achieved by the inclusion of 2-hexylthiophene units onto the isoquinoline subunits, in addition to lengthening the perfluoroalkyl chain on the pyrazolate



chelating group, which worked to increase light absorption and decrease recombination effects when using the Co-based electrolyte. As this study shows, Ru(II) sensitizers bearing sterically demanding ligands can allow successful utilization of important Co electrolytes and high performance.

# INTRODUCTION

In a matter of hours, the sun bombards our planet with enough energy to meet annual human consumption. Thus, photovoltaic technology could prove a much-needed answer to the world's energy needs. Specifically, advances in dye-sensitized solar cells (DSCs) have seen top all-organic, organometallic, and quantum dot sensitizer efficiencies leap from  $7.9\%^1$  in 1991 to >13.0% currently.<sup>2-6</sup> If perovskite materials are also included as inorganic sensitizers, efficiencies have skyrocketed to 20.2% and are poised to leap higher.

While Ru sensitizers were the first to be employed in DSCs and several sensitizers have yielded devices with >10% efficiency, in general the champion dyes have suffered from comparatively low short-circuit current  $(J_{SC})$  values. Even though these sensitizers absorb strongly from 400 to 800 nm, charge recombination from the semiconductor to the sensitizer or redox shuttle means the overall current is diminished. Some high (>20 mA/cm<sup>2</sup>)  $J_{SC}$  sensitizers have been reported; however, in general they suffer from low voltage at open circuit  $(V_{OC})$  compared to other sensitizer classes.<sup>8,9</sup> The DSC  $V_{\rm OC}$  corresponds to the difference of the quasi-Fermi level of electrons in the TiO2 under illumination and the Nernst potential of the redox couple in the electrolyte. A redox shuttle with a larger positive magnitude (more stabilized) redox potential provides higher  $V_{\rm OC}$  in devices. Upon stabilization of the redox shuttle oxidation potential, though, the driving force for dye regeneration  $(\Delta E_{regen})$  is diminished. This leads to slower dye regeneration, which diminishes both  $V_{\rm OC}$  and  $J_{\rm SC}$ through recombination pathways as well.<sup>10</sup> Thus, fine-tuning of the electrolyte composition is a critical issue for increasing the performance of DSCs.<sup>11,12</sup>

Even though thiocyanate-ligated Ru sensitizers yield stable devices utilizing the iodide/triiodide redox couple system, performance is limited by the relatively high overpotential for dye regeneration associated with this couple.<sup>13</sup> Furthermore, the inclusion of thiocyanate ligands results in destabilization of oxidized sensitizers through the monodentate SCN ligand as well as tedious isomer separation of N- and S-bound linkage isomers.<sup>14,15</sup> Thus, the replacement of singly bound thiocyanate

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Scheme 1. Structures of Ru Sensitizers Used in This Study, with Important Structural Differences Marked in Red, Blue, or Green

with higher chelation number ligands, which are better able to reduce recombinative and other nonproductive electrontransfer pathways, is advantageous in designing high efficiency sensitizers.<sup>16–18</sup> In assessing whether to aim for Co<sup>III</sup>- or  $I^-/I_3^-$ based electrolyte systems, there is another important issue to consider: The large mismatch between its oxidation potential and the dye oxidation potential limits the open-circuit voltage  $(V_{\rm OC})$  to 0.7–0.8 V. Furthermore, the reduction of I<sub>2</sub> and I<sub>3</sub><sup>-</sup> is a complex multistep reaction, each with a performance-diminishing overpotential.<sup>19,20</sup> Boschloo et al. reported that the regeneration of oxidized dye with iodide leads to the formation of the diiodide radical  $(I_2^{\bullet-})$  and then  $I_2^{\bullet-}$ disproportionates to I<sup>-</sup> and I<sub>3</sub><sup>-</sup> ( $E^{\circ}$  (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) = ca. 0.29 V and  $E^{\circ}(I_2^{\bullet-}/I^-) < 0.93$  V vs NHE in acetonitrile), giving a large loss in potential energy.<sup>13</sup> Therefore, the development of stable, alternative redox couples with more positive (stabilized) oxidation potentials can avoid the problems associated with the aforementioned  $I^{-}/I_{3}^{-}$  system.<sup>21,2</sup>

Because of low molar extinction coefficients and tunable redox potentials controlled by their substituents, cobalt complexes are interesting alternative redox mediators for dyesensitized solar cells. Furthermore, because the redox shuttle involves outer sphere single electron transfer  $(Co^{(II)/(III)})$ , the kinetics of dye regeneration are simplified greatly. However, there are several drawbacks, such as slower diffusion through the mesoporous TiO<sub>2</sub> film to the counter electrode due to the larger ionic radius, effective mass, and diffusion coefficient compared to the  $I^{-}/I_{3}^{-}$  electrolyte. This limitation enhances the electron recombination from the semiconductor to the oxidized Co(III) species and restricts achievable photocurrent densities at full sun intensity.<sup>23</sup> Lastly, unlike the negatively charged  $I^{-}/I_{3}^{-}$  redox shuttle, both Co(III) and Co(II) species are strongly attracted to the n-type TiO<sub>2</sub> surface (approximately -0.5 V vs normal hydrogen electrode, (NHE)), which also exacerbates recombination problems.

In 2001, the cobalt-based mediator, bis[2,6-bis(1'-butylbenzimidazol-2'-yl)pyridine] cobalt(II) complex, was found to rival the  $I^-/I_3^-$  system in terms of dye regeneration. However, serious diffusion problems limited performance under full sunlight (1 sun).<sup>24</sup> Later it was reported that cobalt polypyridine complexes formed from structurally simple ligands functioned as efficient electron-transfer mediators in DSCs and concluded that added Li<sup>+</sup> resulted in reduced recombination between the electrons in the TiO<sub>2</sub> conduction band and the Co(III) species. This result contrasts with the observations made with  $I^-/I_3^-$  cells.<sup>25</sup> A classic study in organic sensitizers examining the steric properties of triphenylamine-based organic dyes in the presence of cobalt redox mediators showed a decrease in interfacial charge recombination between TiO<sub>2</sub> and electrolytes with increasing donor sterics.<sup>21</sup> In 2011, a power conversion efficiency (PCE) of 9.6% was achieved with organic sensitizer **Y123** and Co<sup>(II/III)</sup>(bipyridine)<sub>3</sub>,<sup>22</sup> and then Yella et al. boosted the PCE to 12.3% by using a Co<sup>(II/III)</sup>(bipyridine)<sub>3</sub>-based electrolyte in conjunction with a zinc porphyrin sensitizer (**YD2-o-C8**).<sup>26</sup> The gain in the device performance was largely due to the molecular design of **YD2-o-C8**, which included many nonconjugated substituents meant to block the semiconductor surface from the redox shuttle and led to an increase in V<sub>OC</sub>.

Using Ru(II) sensitizers N719 and Z907, and the  $Co^{(II/III)}(bpy)_3$  (bpy = bipyridine) redox shuttle, lower PCE and  $J_{SC}$  values were observed due to decreased charge collection and increased charge recombination. Despite this drawback, a PCE of up to 6.5% was achieved using **Z907** with cobalt redox mediators,<sup>25</sup> while, with other sensitizer classes, one way to improve the PCEs is to increase the bulkiness of the Ru(II) sensitizer for blocking the approach of redox electrolyte to the TiO<sub>2</sub> surface.<sup>27–29</sup> Here, three thiocyanate-free Ru(II) sensitizers, **S1-5ht**, **S1-57dht**, and **S1-57dht.1** (Scheme 1), are compared to investigate the effect of steric hindrance, recombination driving force, and dye regeneration kinetics on performance in devices employing cobalt-based electrolytes.

# EXPERIMENTAL SECTION

General Procedures. All reactions were performed under argon atmosphere, and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. [Ru(dcbpy)(p-cymene)-Cl]Cl was obtained from treatment of  $[Ru(p-cymene)Cl_2]_2$  with dcbpy (4,4'-bis(ethoxycarbonyl)-2,2'-bipyridine) in refluxing methanol solution. 2-(5-Hexylthiophen-2-yl)-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane was prepared from 2-hexylthiophene and 2-isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane as documented in the literature.<sup>3</sup> Bromoisoquinoline was prepared by monobromination of isoquinoline in concentrated  $H_2SO_4$  using N-bromosuccinimide (NBS),<sup>31</sup> while 5,7-dichloroisoquinoline was synthesized from the respective halogenated benzalaminoacetal reagents according to the Pomeranz-Fritsch reaction.<sup>32,33</sup> Acetylation of all isoquinolines was then conducted using para-acetaldehyde, *t*-BuO<sub>2</sub>H, trifluoroacetic acid, and  $FeSO_4$ ·7H<sub>2</sub>O.<sup>34</sup> Next, all halogen substituents on isoquinoline framework were replaced by a 2-hexylthienyl group (ht) using dioxaborolane reagent with Suzuki coupling. Finally, conversions to the isoquinolinyl pyrazoles were achieved using standard Claisen condensation with ethyl trifluoroacetate or ethyl heptafluorobutanoate,

followed by hydrazine cyclization in refluxing ethanol solution (yield >50%).<sup>35</sup> The detail ligand synthetic procedures are reported in Supporting Information. The syntheses of **51-5ht**, **51-57dht**, and **51-57dht.1** sensitizers are similar, using similar experimental procedures.<sup>28,36,37</sup> All reactions were monitored using precoated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury-400 instrument. Elemental analysis of the Ru(II) sensitizers was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

**Synthesis of 51-5ht Sensitizer.** A mixture of [Ru(dcbpy)(*p*-cymene)Cl]Cl (65 mg, 0.14 mmol), (L5ht)H (91 mg, 0.21 mmol, see Scheme 2), and potassium acetate (50 mg, 0.51 mmol) in 30 mL of

Scheme 2. Structures of Ligands Used To Synthesize Ru Sensitizers



xylene was refluxed for 5 h. After the solvent was removed, the residue was extracted with  $CH_2Cl_2$  (3 × 25 mL), washed with water, and concentrated to dryness. The mixture of products was purified by silica gel column chromatography (ethyl acetate/hexane = 1:3) to afford black solid (42 mg, 20%).

Next, the above-mentioned solid (42 mg, 0.043 mmol) was dissolved in a mixture of acetone (20 mL) and 1 M NaOH solution (0.2 mL). The solution was heated to 60  $^{\circ}$ C under nitrogen for 3 h. After then, the solvent was removed under vacuum, and the residue was dissolved in H<sub>2</sub>O solution (10 mL), followed by acidification with 2 M HCl to pH 3 for inducing a dark brown precipitate. The collected precipitate was rinsed with deionized water, acetone, and diethyl ether in sequence, giving a dark brown solid (30 mg, 78%).

Other Ru(II) sensitizers, namely, **51-57dht** and **51-57dht.1**, were prepared from Ru(II) source complex [Ru(dcbpy)(p-cymene)Cl]Cl and respective free ligand, i.e., (L57dht)H and (L57dht.1)H, using similar experimental procedures.

Spectral data of **51-5ht** follow. MS (FAB, <sup>102</sup>Ru): m/z 1202 (M + 1)<sup>+</sup>. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO, 298 K):  $\delta$  8.90 (s, 4H), 8.10 (d, J = 6.0 Hz, 2H), 7.82–7.78 (m, 6H), 7.70–7.67 (m, 4H), 7.12 (d, J = 6.8 Hz, 2H), 7.06 (d, J = 3.2 Hz, 2H), 6.84 (d, J = 3.6 Hz, 2H), 2.76–2.68 (m, 4H), 1.50–1.47 (m, 4H), 1.21–1.14 (m, 12H), 0.79 (t, J = 6.7 Hz, 6H). <sup>19</sup>F NMR (376 MHz,  $d_6$ -DMSO, 298 K):  $\delta$  –58.16 (s, 6F). Anal. Calcd for C<sub>58</sub>H<sub>50</sub>F<sub>6</sub>N<sub>8</sub>O<sub>4</sub>S<sub>2</sub>Ru·H<sub>2</sub>O: C, 57.9; N, 9.34; H, 4.30. Found: C, 57.94; N, 9.32; H, 4.19.

Spectral data of **51-57dht** follow. MS (FAB, <sup>102</sup>Ru): m/z 1534 (M + 1)<sup>+</sup>. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO, 298 K):  $\delta$  8.94 (s, 2H), 8.73 (s, 2H), 8.16 (d, J = 5.6 Hz, 2H), 7.92 (s, 2H), 7.72 (d, J = 5.6 Hz, 2H), 7.61 (d, J = 6.4 Hz, 2H), 7.52–7.49 (m, 4H), 7.15 (d, J = 6.0 Hz, 2H), 7.01 (s, 2H), 6.85 (d, J = 13.6 Hz, 4H), 2.82–2.74 (m, 8H), 1.64–1.55 (m, 8H), 1.36–1.20 (m, 24H), 0.85–0.80 (m, 12H). <sup>19</sup>F NMR (376 MHz,  $d_6$ -DMSO, 298 K):  $\delta$  –58.71 (s, 6F). Anal. Calcd for C<sub>78</sub>H<sub>78</sub>F<sub>6</sub>N<sub>8</sub>O<sub>4</sub>S<sub>4</sub>Ru·H<sub>2</sub>O: C, 60.33; N, 7.22; H, 5.19. Found: C, 60.15; N, 7.13; H, 4.97.

Spectral data of **51-57dht.1** follow. MS (FAB, 102Ru): m/z 1735 (M + 1)<sup>+</sup>. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO, 298 K): 8.82 (s, 2H), 8.66 (s, 2H), 8.00 (d, J = 4.4 Hz, 2H), 7.81 (s, 2H), 7.62 (d, J = 6.0 Hz, 2H), 7.47–7.44 (m, 4H), 7.37 (s, 2H), 7.13 (d, J = 6.0 Hz, 2H), 6.95 (s, 2H), 6.74 (d, J = 6.8 Hz, 4H), 2.74–2.69 (m, 8H), 1.56–1.53 (m, 8H), 1.28–1.07 (m, 24H), 0.78–0.69 (m, 12H). <sup>19</sup>F NMR (376 MHz,  $d_8$ -THF, 298 K): –79.86 (t, J = 8.3 Hz, 6 F), –107.20 (s, 4F), –126.78

(s, 4F). Anal. Calcd for  $C_{82}H_{78}F_{14}N_8O_4S_4Ru\cdot 2H_2O$ : C, 55.61; N, 6.33 H, 4.67. Found: C, 55.24; N, 6.49; H, 4.89.

Device Fabrication and Photovoltaic Characterization. The cells consisted of a mesoscopic TiO<sub>2</sub> film composed of a 4.1  $\mu$ m thick transparent layer of 20 nm sized TiO<sub>2</sub> anatase nanoparticles (Ti-2105, ETERDSC, 15–40 nm) onto which a second 4.5  $\mu$ m thick scattering layer of 400 nm sized TiO<sub>2</sub> (CCIC) was superimposed. The doublelayer film was heated to 520 °C and sintered for 30 min, then cooled to 80 °C and immersed into the dve solution (0.3 mM) containing the 20% DMSO in ethanol for 12 h. The iodine electrolyte (W95) contains 0.45 M 1-methyl-3-propylimidazolium iodide (PMII), 0.15 M I<sub>2</sub>, 0.15 M LiI, and 0.8 M tert-butylpyridine (TBP) in acetonitrile; the cobalt electrolyte (W187) contains 0.6 M [Coll(bpy)<sub>3</sub>][bis-(trifluoromethane)sulfonimide]<sub>2</sub>, 0.15 M  $[Co^{II}(bpy)_3][TFSI]_3$ , 0.15 M LiTFSI, and 0.8 M TBP in acetonitrile [TFSI = bis-(trifluoromethane)sulfonimide], and the cobalt electrolyte (W178) contains 0.6 M  $[Co^{II}(phenanthroline)_3][TFSI]_2$  (phen = phenanthroline), 0.15 M [CoIII(bpy)<sub>3</sub>][TFSI]<sub>3</sub>, 0.15 M LiTFSI, and 0.8 M TBP in acetonitrile. The cell was sealed with 15  $\mu$ m thick transparent Surlyn ring at 130 °C for 15 s to the counter electrode (fluorine-doped tin oxide (FTO) glass, 7  $\Omega$  per square, thermal deposited carbon at 450 °C for 15 min). The cells were filled with an electrolyte solution through a predrilled hole in the counter electrode. The hole was then sealed with a Bynel disk and a thin glass to avoid leakage of the electrolyte. The current-voltage characteristics, incident photon to current efficiency, and transient photocurrent/photovoltage measurements were performed as reported in our previous publications.<sup>28,3</sup>

Basic Characterization. Photophysical and Electrochemical Properties. Figure 1 shows absorption properties of Ru-pyrazolate



**Figure 1.** UV–vis absorption spectra of Ru sensitizers  $(1 \times 10^{-5} \text{ M})$  in DMF.

sensitizers **51-5ht**, **51-57dht**, and **51-57dht.1** measured in dimethylformamide (DMF), and the spectral data are summarized in Table 1. The absorption spectrum of the parent complex **51-5ht** exhibits two peak maxima in the UV region at 306 and 354 nm, which are assigned to  $\pi - \pi^*$  transitions, and the absorption peak at 510 nm is due to metal-to-ligand charge-transfer bands (MLCT) mixed with small amount of ligand-to-ligand charge-transfer contribution (*vide infra*). Upon introduction of 4-hexylthiophene substituents to **51-5ht** in the 7-position to form **51-57dht**, the lower energy MLCT absorption undergoes a slight red shift to 521 nm with increased molar absorptivity ( $\varepsilon$ ). Also, the higher energy band exhibited a red shift to 310 and 378 nm with a significantly enhanced molar extinction coefficient due to extended conjugation of ligands. In addition, the introduction of a heptafluoropropyl group did not alter the absorption spectrum for **51-57dht.1**.

Cyclic voltammetry was used to measure the oxidation potential of the sensitizers  $(E_{S+/S})$ , to see compatibility with the redox potential of

 Table 1. Photophysical and Electrochemical Data of the

 Studied Sensitizers in DMF

dye	$\lambda_{\rm abs} \ [\rm nm] \ (\varepsilon \times 10^{-3} \ [\rm L \ mol^{-1} \ cm^{-1}])^a$	$E^{\circ\prime}{}^{b}_{ox}$	$E_{0-0}^{c}$	$E^{\circ'*d}$
51-5ht	306 (44), 354 (39), 510 (23)	0.90	1.92	-1.02
51-57dht	310(65), 378 (44), 521 (28)	0.95	1.86	-0.91
51-57dht.1	309 (64), 379 (43), 518 (27)	0.93	1.86	-0.93

<sup>*a*</sup>Molar extinction coefficients data were measured in DMF solution. <sup>*b*</sup>Oxidation potentials of sensitizers were measured in DMF with 0.1 M [TBA][PF<sub>6</sub>] supporting electrolyte. The scan rate was 50 mV s<sup>-1</sup>, and the potentials were calibrated using Fc/Fc<sup>+</sup> as internal reference. The values were converted to NHE by addition of 0.63 V. <sup>*c*</sup>E<sub>0-0</sub> was determined from the intersection of the absorption and the tangent of emission peak in DMF. <sup>*d*</sup>E<sup>o</sup>'\* was calculated as  $E^{o'}_{ox} - E_{0-0}$ .

the cobalt electrolyte. The redox potential data of sensitizers are summarized in Table 1, which are more positive (more stabilized HOMO) compared to the redox potential of  $[Co(bpy)_3]^{2+/3+}$  (ca. 0.56 V vs NHE) and  $[Co(phen)_3]^{2+/3+}$  (ca. 0.63 V vs NHE), warranting enough ( $\Delta E_{regen} > 150$  mV) driving force for dye regeneration. The 0–0 transition energy ( $E_{0-0}$ ) was determined from the intersection of the absorption and the tangent of the emission peak in DMF, for which their energy gaps are identical due to the similar core structure. The excited-state oxidation potential ( $E_{S+/S^*}$ ) values were estimated from the difference in the  $E_{S+/S}$  and  $E_{0-0}$  of **51-Sht**, **51-57dht**, and **51-57dht.1** and are -1.02, -0.91, and -0.93 V, respectively, which are more negative than the conduction band edge of the TiO<sub>2</sub> electrode (ca. -0.5 V vs NHE), confirming that the  $E_{S+/S^*}$  was well-matched with the conduction band value of TiO<sub>2</sub>.

**Device Performance.** Several cobalt-specific device-engineering techniques are required to suppress the mass transport limitations present in those electrolyte systems, for example, using low viscosity solvent, controlling the  $TiO_2$  film pore size, and minimizing the space between  $TiO_2$  electrode and counter electrode. These are expected to improve the mass transport and overall efficiency.

Although platinum counter electrodes are generally employed for the  $I^{-}/I_{3}^{-}$  electrolyte, charge-transfer resistance in these devices is high, which can lead to losses in the fill factor. In 2002, Sapp et al. observed that gold and carbon are superior cathode materials to platinum by cyclic voltammetry, especially for Ru sensitizers with sterically demanding ligands.<sup>25</sup> Here, we evaluate the performance of devices modified by using either traditional thermally deposited platinum or carbon counter electrodes. Electron impedance spectroscopy (EIS) was used to investigate the properties and quality of the DSC device. The EIS spectrum of devices with Pt and carbon counter electrodes is presented as a Nyquist plot (Figure 2). The spectrum exhibits a first semicircle corresponding to the charge-transfer resistance  $(R_{CE})$  at the counter electrode/electrolyte interface. The R<sub>CE</sub> is the resistance of regenerating Co(II) from Co(III) at the counter electrode. The charge-transfer resistance was found to be 6.44  $\Omega$  (12.88  $\Omega$  cm<sup>-2</sup>) for Pt and 1.46  $\Omega$  (2.92  $\Omega$  cm<sup>-2</sup>) for the carbon counter electrode, meaning that the resistance at the carbon counter electrode is significantly lower than that of the Pt counter electrode.

**Optimization of Co(II) and t-Butylpyridine (TBP) Concentrations in Electrolyte.** The electron-transfer dynamics of a DSC dictates that, after electron injection, the photo-oxidized dye should be predominantly reduced by the Co(II) redox mediator (eq 1).

$$S^{+}(\text{on TiO}_{2}) + Co(II) \rightarrow S(\text{on TiO}_{2}) + Co(III)$$
 (1)

Thus, the concentration of the Co(II) complex affects the dye regeneration rate. Optimization of this key electrolyte component was undertaken (Figure 3, left), and the best results were observed when using the Co(II)/Co(III) ratio of 4:1 (i.e., 0.6 M Co(II)) with 0.1 M LiTFSI and 1.6 M TBP as additives. Another additive, *t*-butylpyridine (TBP), absorbs onto the TiO<sub>2</sub> surface and decreases the charge recombination in the TiO<sub>2</sub>/Co(III) interface. Thus, we also optimized the concentration of TBP in the electrolyte. The best device





**Figure 2.** Electrochemical impedance spectra measured under dark conditions at a forward bias of 0.85 V for the cells employing different counter electrodes.

performance was observed with a TBP concentration of 0.8 M (Figure 3, right).

Optimization of TiCl<sub>4</sub> Concentration and TiO<sub>2</sub> Film Thick**ness.** By tuning the pore size and porosity of  $TiO_2$  films, mass transport limitations can be addressed in devices using cobalt-based electrolytes. Post-treatment of TiO2 with TiCl4 not only enhances the connections between TiO<sub>2</sub> nanoparticles but also increases pore size and porosity in the iodine/triiodide electrolyte system. Here, we tried to control the pore size and porosity by simply optimizing the TiCl<sub>4</sub> post-treatment.<sup>38</sup> Device performances were obtained with the thin  $(4.1 + 4.5 \ \mu m)$  double-layered TiO<sub>2</sub> film consisting of an average particle size of 15-40 nm. After film fabrication, different TiCl<sub>4</sub> treatments of 15, 25, and 40 mM at 70 °C were administered for 30 min. The best device performance was observed at a concentration of 15 mM (Figure 4, left). Even though the performance of the devices treated with 25 and 40 mM were similar, the mass transport limitations were increased in the 40 mM case, as shown by the low  $V_{\rm OC}$  and FF. The diffusion limitation problems in cobalt-based electrolyte can be further investigated by recording photocurrent transients under different light intensities (Figure 4, right). The experiment shows an immediate rise of the photocurrent when the device is exposed to light, with the magnitude of the current density directly proportional to the light intensity. As illustrated by the two graphs in Figure 4, increasing the TiCl<sub>4</sub> concentration more than 15 mM lowered both the porosity and pore size of the TiO<sub>2</sub> photoanode, which suppressed Co(III) diffusion and resulted in poor  $J_{SC}$  and current-density profiles.

It is well-known that increasing the TiO<sub>2</sub> film thickness can enhance the photocurrent due to enhanced light absorption, but decrease the  $V_{\rm OC}$  due to enhanced recombination and charge transport distance. Because each sensitizer exhibits a different molar absorptivity profile, film thickness should be optimized in each case. We attempted to optimize film thickness, and the photocurrent transients with the different thicknesses are shown in Figure 5. Unfortunately, serious diffusion problems were observed even under low light intensity with a thicker (7.9  $\mu$ m) film. The photovoltaic performance of devices with different light intensity is also described in Table 2. Due to diffusion limitation problems accompanied by thicker TiO<sub>2</sub> films, the photocurrent dropped significantly after light exposure.

#### RESULTS AND DISCUSSION

Effect of Sensitizer Sterics and Driving Force for Recombination on Photovoltaic Performance. We examined the ruthenium sensitizers using  $Co(bpy)_3$  and  $Co(phen)_3$  complexes as redox mediators to investigate the influence of redox mediator energy levels on power conversion



Figure 3. Left: Optimization of Co(II) in the electrolyte. Right: Optimization of TBP in the electrolyte.



Figure 4. Left: Optimization of the concentration of  $TiCl_4$  during post-treatment. Right: Photocurrent transients of devices during  $TiCl_4$  optimization. The devices were measured using different incident light intensities, and the maximum intensity used was 100 mW cm<sup>-2</sup>.



**Figure 5.** Optimization of  $\text{TiO}_2$  film thickness by comparison of photocurrent transient of devices sensitized with **51-57dht.1** employing  $[\text{Co}(\text{phen})_3]^{+2/+3}$  electrolyte. The devices were probed at various incident light intensities up to 100 mW cm<sup>-2</sup>.

efficiency of the dye-sensitized solar cells. The device current–voltage characteristics demonstrate the  $V_{\rm OC}$  increased with increasing (more stabilized) Nernst potential of the redox

Table 2. Performance of 7.9 + 4.5  $\mu$ m Thick TiO<sub>2</sub> Film DSC Sensitized with 51-57dht.1 Employing  $[Co(phen)_3]^{+2/+3}$ Electrolyte<sup>*a*</sup>

dye	light intensity [%]	$J_{\rm SC}  [{ m mA}  { m cm}^{-2}]$	$V_{\rm OC}  [{ m mV}]$	FF	η [%]
51- 57dht.1	10	1.46	799	0.802	9.37
	50	6.73	863	0.810	9.41
	60	6.96	870	0.883	8.92
	100	8.89	884	0.870	6.85

<sup>*a*</sup>Devices were probed at various incident light intensities up to AM1.5 100 mW cm<sup>-2</sup>. All of the devices were fabricated using a 7.9 + 4.5  $\mu$ m TiO<sub>2</sub> anode with an electrolyte that consists of 0.6 M Co electrolyte (Co(II)/Co(III) ratio of 4:1), 0.1 M LiTFSI, and 0.8 M TBP in acetonitrile.

couple (see Table 3 for redox potential). Triphenylamine-based donor-acceptor organic sensitizer, D35, has been shown to minimize the recombination between electrons in the TiO<sub>2</sub> and the oxidized redox mediator in the electrolyte Co(III) due to increasing number of substituents on the donor moiety. Under full sunlight irradiation (AM1.5G, 100 mW cm<sup>-2</sup>), a device sensitized with **51-57dht.1** and incorporating a [Co-(phen)<sub>3</sub>]<sup>2+/3+</sup> redox mediator exhibited the best performance with the short-circuit photocurrent density ( $J_{SC}$ ) of 13.89 mA

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dye	redox mediator	$J_{\rm SC}  [{ m mA}  { m cm}^{-2}]$	$V_{\rm OC} \ [{\rm mV}]$	FF	$\eta$ [%]	dye loading <sup>d</sup> [×10 <sup>-8</sup> mol cm <sup>-2</sup> ]
51-5ht	$Co(bpy)_{3}^{2+/3+b}$	12.78	840	0.764	8.22	6.4
	$Co(phen)_3^{2+/3+b}$	12.17	842	0.750	7.69	
	$I^{-}/I_{3}^{-c}$	15.31	718	0.746	8.20	
51-57dht	$Co(bpy)_3^{2+/3+b}$	13.56	844	0.742	8.49	4.3
	$Co(phen)_3^{2+/3+b}$	12.32	898	0.754	8.34	
	$I^{-}/I_{3}^{-c}$	14.17	727	0.743	7.66	
51-57dht.1	$Co(bpy)_3^{2+/3+b}$	13.36	853	0.750	8.55	3.7
	$\operatorname{Co}(\operatorname{phen})_3^{2+/3+b}$	13.89	900	0.762	9.53	
	$I^{-}/I_{3}^{-c}$	13.53	740	0.749	7.50	

<sup>*a*</sup>All of the devices were fabricated using a 4.1 + 4.5  $\mu$ m TiO<sub>2</sub> anode. <sup>*b*</sup>Devices fabricated using an electrolyte that consists of 0.6 M Co electrolyte (Co(II)/Co(III) ratio of 4:1), 0.15 M LiTFSI, and 0.8 M TBP in acetonitrile. <sup>*c*</sup>Devices fabricated using an electrolyte that consists of 0.45 M PMII, 0.15 M I<sub>2</sub>, 0.15 M LiI, and 0.8 M TBP in acetonitrile. <sup>*d*</sup>The dye loading on 4.1 + 4.5  $\mu$ m TiO<sub>2</sub> films was determined by desorbing the dye into a 0.5 M TBAOH solution in 1:1 (v/v) MeOH/H<sub>2</sub>O and then performing the UV–vis spectral analysis.

cm<sup>-2</sup>, open-circuit voltage ( $V_{\rm OC}$ ) of 900 mV, and fill factor (FF) of 0.762, corresponding to a power conversion efficiency (PCE,  $\eta$ ) of 9.53%. Cells using the phenanthroline electrolyte exhibited better  $V_{\rm OC}$  than iodine/triiodide (160 mV) and  $[\rm Co(bpy)_3]^{2+/3+}$  (46 mV)-based cells. The analogues **51-5ht** and **51-57dht** provide lower device efficiencies of 7.69% and 8.34%, largely due to poor diffusion of cobalt complexes, which induces losses in  $J_{\rm SC}$ . Thus, careful tuning of the dye structure is very important.

The current-voltage curves of the champion cell measured under different light intensity are shown in Figure 6, and the



Figure 6. Current-voltage characteristics of a 51-57dht.1-sensitized dye-sensitized solar cell device measured under various light intensities.

photovoltaic performance data are listed in Table 4. The cell efficiency reached the higher value of 10.03% at 50% sun intensity due to less mass transport limitations at low light intensity.

Transient photocurrent and photovoltage decay measurements were carried out in order to detail the rates of interfacial recombination of electrons from the TiO<sub>2</sub> conduction band to the electrolyte. It is worth noting that  $V_{\rm OC}$  decays are dependent on the accumulated charge in the TiO<sub>2</sub> conduction band, and so to obtain a fair comparison of the TiO<sub>2</sub>/ electrolyte<sup>+</sup> recombination dynamics between different dyes, the charge density on both dyes must be equal. As presented in Figure 7a, the chemical capacitance  $C_{\mu}$  of devices rises

Table 4. Current–Voltage Characteristics of the Device Sensitized with 51-57dht.1 at Various Simulated Intensities up to AM1.5G  $(100 \text{ mW cm}^{-2})^a$ 

dye	intensity [mW cm <sup>-2</sup> ]	$\begin{bmatrix} J_{\rm SC} \\ [\rm mA~cm^{-2}] \end{bmatrix}$	$V_{\rm OC}  [{\rm mV}]$	FF	η [%]
51-57dht.1	10	1.41	813	0.806	9.21
	50	7.29	877	0.784	10.03
	100	13.89	900	0.762	9.53

<sup>*a*</sup>All of the devices were fabricated using a  $4.1 + 4.5 \ \mu m \ TiO_2$  anode. Devices fabricated using an electrolyte that consists of 0.6 M Co(phen)<sub>3</sub> electrolyte (Co(II)/Co(III) ratio of 4:1), 0.1 M LiTFSI, and 0.8 M TBP in acetonitrile.

exponentially with increased  $V_{\rm OC}$ . The  $C_{\mu}$  is directly proportional to the density of state (DOS) ( $C_{\mu} = q(e)$ DOS, where q(e) is electron charge).<sup>39,40</sup> It is clear that very similar electron densities are measured for sensitizers with Co(bpy)<sub>3</sub><sup>2+/3+</sup> and Co(phen)<sub>3</sub><sup>2+/3+</sup> redox mediators. The quasi-Fermi level of TiO<sub>2</sub> with different sensitizers are revealed in the negative shift: **51**-**57dht** > **51-57dht.1** > **51-5ht**. However, devices constructed with the **51-57dht.1** sensitizer with Co(phen)<sub>3</sub><sup>2+/3+</sup> electrolyte show longer electron lifetimes (Figure 7b) due to the longer fluoroalkyl chain efficiently suppressing the back-electron-transfer rate (i.e., recombination); however, the quasi-Fermi level of TiO<sub>2</sub> is deeper than **51-57dht**.

Influence of Sensitizer Driving Force on Regeneration Kinetics. The influence of driving force between sensitizer oxidation potential and the redox mediators oxidation potential for dye regeneration using a cobalt redox mediator was investigated by transient absorption spectroscopy (TAS), since the regeneration is a clearer estimation of these devices to monitor the kinetics of ground-state quenching because there is no overlapping signal from TiO<sub>2</sub> injected electron absorption in the visible region. Figure 8 demonstrates the ground-state quenching of the sensitizer at 550 nm without and with the redox mediator. The decrease in negative absorbance signal with redox mediator and inert electrolyte shows the recombination of conduction band electrons with the oxidized dye molecules. With the redox mediator, the enhanced signal is strongly accelerated suggesting rapid dye regeneration. The 51-**5ht** sensitizer shows a similar regeneration rate using  $I^{-}/I_{3}^{-}$  and cobalt redox mediator, while 51-57dht and 51-57dht.1 sensitizers both show a lower regeneration rate using the cobalt redox mediator. Therefore, the dye regeneration rate is not greatly affected by the increased steric bulk substituents of dye structure. In addition, regenerations of the oxidized dye



Figure 7. Electron (a) capacitance and (b) lifetime determined with photocurrent and photovoltage decay measurements of devices sensitized with 51-5ht, 51-57dht, and 51-57dht.1 dyes.



Figure 8. Transient absorption kinetics of (a) 51-5ht-, (b) 51-5dht-1, and (c) 51-5dht-1-sensitized  $TiO_2$  electrodes in the absence (black) and presence of redox mediator. The transient optical signal was observed at 550 nm after the laser pulse excitation at 500 nm with high intensity probe light.

with  $[Co(bpy)_3]^{2+/3+}$  and  $[Co(phen)_3]^{2+/3+}$  are similar and not affected by the different driving force (60 mV difference) with increasing (more stabilized) redox potential of cobalt redox mediators.

# CONCLUSIONS

We have designed and synthesized a series of new isoquinolinyl functionalized ancillary ligands and incorporated them into Ru(II) sensitizers to use in a cobalt-based electrolyte DSC device. The increase in  $\pi$  conjugation in the heterocyclic ancillary ligands of sensitizers significantly improves the light-harvesting capabilities resulting short-circuit current ( $J_{\rm SC}$ ) and power conversion efficiency. Additionally, the sterically demanding substituents on the ligands, with optimized TiO<sub>2</sub> film, and electrolyte composition, yielded in a power conversion efficiency of 9.5%, which is the highest reported to date for the ruthenium sensitizer and a cobalt-based electrolyte.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00427.

Full experimental details and characterization of compounds described (PDF)

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## **Author Contributions**

All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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