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Effect of Ligand Structures of Copper Redox Shuttles on Photovoltaic Performance of Dye-Sensitized Solar Cells

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S Supporting Information

ABSTRACT: In recent years, copper(I/II) complexes have emerged as alternative redox shuttles in dye-sensitized solar cells (DSSCs), exhibiting more positive redox potential than iodine- and cobalt-based redox shuttles. In particular, copper(I/ II) complexes with 1,10-phenanthroline- or 2,2'-bipyridylbased ligands attained moderate to high power conversion efficiencies (6–11%) with a high open-circuit voltage (V_{OC}) over 1.0 V due to the positive potentials. Although copper(I/ II) complexes with 1,10-phenanthroline-based ligands with 2,9substituents have been developed, the effect of their ligand structures on the photovoltaic performance of DSSCs have not been fully addressed due to limited synthetic access to 1,10phenanthroline derivatives. In this study, we designed and



synthesized a series of copper (I/II) complexes with 1,10-phenanthroline ligands with different substituents at the 2,9-positions: $bis(2-n-butyl-1,10-phenanthroline)copper(I/II) ([Cu(bp)_2]^{1+/2+}), bis(2-ethyl-9-methyl-1,10-phenanthroline)copper(I/II)$ $([Cu(emp)_2]^{1+/2+})$, bis(2,9-diethyl-1,10-phenanthroline)copper(I/II) $([Cu(dep)_2]^{1+/2+})$, and bis(2,9-diphenyl-1,10-phenanthroline)copper(I/II) $([Cu(dpp)_2]^{1+/2+})$. The more positive redox potentials of $[Cu(emp)_2]^{1+/2+}$ and $[Cu(dep)_2]^{1+/2+}$, compared to that of bis(2,9-dimethyl-1,10-phenanthroline)copper(I/II) ([Cu(dmp)₂]^{1+/2+}), originate from the larger steric hindrance of the ethyl group instead of the methyl group, whereas the redox potential of $[Cu(bp)_2]^{1+/2+}$ is significantly shifted to the negative direction because of the lower steric hindrance of the 2-monosubstituted 1,10-phenanthroline ligands. The efficiency of the DSSC with $[Cu(bp)_2]^{1+/2+}$ (5.90%) is almost comparable to the DSSC with $[Cu(dmp)_2]^{1+/2+}$ (6.29%). In contrast, the DSSCs with $[Cu(emp)_2]^{1+/2+}$ (3.25%), $[Cu(dep)_2]^{1+/2+}$ (2.56%), and $[Cu(dpp)_2]^{1+/2+}$ (2.21%) exhibited lower efficiencies than those with $[Cu(dmp)_2]^{1+/2+}$ and $[Cu(bp)_2]^{1+/2+}$. The difference can be rationalized by the electron collection efficiencies. Considering the similar photovoltaic properties of the DSSCs with $[Cu(bp)_2]^{1+/2+}$ and $[Cu(dmp)_2]^{1+/2+}$, the use of copper(I/II) complexes with 2-monosubstituted 1,10-phenanthroline ligands as the redox shuttle may be useful to improve the short-circuit current density while retaining the rather high V_{OC} value when dyes with a smaller bandgap (i.e., better light harvesting) are developed.

INTRODUCTION

It is important to develop sustainable energy systems because of the increasing worldwide demand for energy. In this regard, organic photovoltaics have attracted great attention as promising technologies because of their potential advantages including low cost, ease of fabrication, transparency and color, and high performance under diffused illumination.^{1–15} Among them, dye-sensitized solar cells (DSSCs)¹⁻⁶ are particularly attractive candidates owing to their low cost and relative ease of high power conversion efficiency. $^{16-20}$ To achieve a high efficiency, it is a prerequisite to increase the open-circuit voltage $(V_{\rm OC})$. Although iodide and triiodide (I^-/I_3^-) have been the most commonly used redox shuttles for DSSCs, the high overpotential for efficient dye regeneration is a bottleneck to the V_{OC} value of DSSCs with I^-/I_3^{-21} In this context, transition-metal complexes are proposed as efficient redox

shuttles for DSSCs because their redox potentials can be tuned by a selection of metal and ligand combinations.²²⁻²⁴ The representative redox shuttle is tris(bipyridyl)Co(II/III) ([Co- $(bpy)_3]^{2+/3+}$, which can achieve a high V_{OC} with a resultant high efficiency as a consequence of its more positive redox potential (+0.57 V vs NHE) compared to that of I^{-}/I_{3}^{-} (+0.40 V vs NHE).²⁵ However, the large reorganization energy (λ) of $[Co(bpy)_3]^{2+/3+}$ is a disadvantage because $[Co(bpy)_3]^{2+/3+}$ still needs a large driving force for efficient dye regeneration (0.2– 0.4 eV), lowering the $V_{\rm OC}$ value.^{26–28} At the same time, rather fast charge recombination (CR) derived from the large λ value should be suppressed by the use of bulky substituents around

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Figure 1. Molecular structures of copper complexes $[Cu(dmp)_2]^{1+/2+}$, $[Cu(dep)_2]^{1+/2+}$, $[Cu(emp)_2]^{1+/2+}$, $[Cu(bp)_2]^{1+/2+}$, $[Cu(dpp)_2]^{1+/2+}$, and LEG4. The counterions for the copper complexes are trifluoromethanesulfonimide (TFSI⁻) for $[CuL_2]^{1+}$ and TFSI⁻ and chloride (Cl⁻) for $[CuL_2]^{2+}$.

dyes to prevent $[\text{Co}(\text{bpy})_3]^{2+/3+}$ from penetrating into the dye layer on TiO_2. $^{29-32}$

To overcome the issues, copper(I/II) complexes have emerged as alternative redox shuttles exhibiting more positive redox potential (0.8-1.1 V vs NHE) than [Co-(bpy)₃]^{2+/3+.33-40} In particular, copper(I/II) complexes with 1,10-phenanthroline- or 2,2'-bipyridyl-based ligands attained moderate to high efficiencies (6-11%) with a high V_{OC} value over 1.0 V. $^{35-40}$ These copper complexes have a distorted tetragonal geometry with a small λ value. In this context, the λ values of copper complexes have been estimated by DFT calculations and the λ values were found to be affected by the ligand structures.^{37,40–42} Importantly, bis(2,9-dimethyl-1,10phenanthroline)copper(I/II) ($[Cu(dmp)_2]^{1+/2+}$) can regenerate the oxidized dye efficiently in spite of the small driving force (ca. 0.1 eV),^{37,38} which indicates that copper redox shuttles can reduce the loss through overpotential. Namely, both high $V_{\rm OC}$ and efficiencies can be obtained by using copper redox shuttles. Nevertheless, the use of copper redox shuttles is limited to sensitizers with low HOMO levels due to the positive redox potentials. Along this line, several new copper(I/II) complexes with 1,10-phenanthroline-based ligands with 2,9-substituents have been developed.⁴¹⁻⁴⁴ However, the effect of their ligand structures on the photovoltaic performance of DSSCs has not been fully elucidated due to limited synthetic access to 1,10-phenanthroline derivatives.

In this study, we designed and synthesized a series of copper(I/II) complexes with 1,10-phenanthroline ligands with different substituents at the 2,9-positions: bis(2-*n*-butyl-1,10-phenanthroline)copper(I/II) ([Cu(bp)₂]^{1+/2+}), bis(2-ethyl-9-methyl-1,10-phenanthroline)copper(I/II) ([Cu(emp)₂]^{1+/2+}), bis(2,9-diethyl-1,10-phenanthroline)copper(I/II) ([Cu(dep)₂]^{1+/2+}), and bis(2,9-diphenyl-1,10-phenanthroline)-copper(I/II) ([Cu(dpp)₂]^{1+/2+}) (Figure 1). We examined the electrochemical properties of copper complexes together with the well-studied copper complex [Cu(dmp)₂]^{1+/2+}. To further evaluate the effect of the ligand structures, we investigated the

photovoltaic properties of the DSSCs using an organic donor– π –acceptor dye (LEG4)^{35,45} and the copper redox shuttles (Figure 1).

EXPERIMENTAL SECTION

Instrumentation and Materials. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography, thin-layer chromatography (TLC), and size-exclusion gel permeation chromatography (GPC) were performed according to our previous report.¹⁹ ¹H and ¹³C NMR spectra were recorded with a JEOL EX-400 spectrometer (operating at 400 MHz for ¹H and 100 MHz for ¹³C) by using the residual solvent as the internal reference for ¹H (CDCl₃ (δ = 7.26 ppm), acetone- d_6 (δ = 2.05 ppm), DMSO- d_6 (δ = 2.50 ppm)) and ¹³C (CDCl₃ (δ = 77.16 ppm), acetone- d_6 (δ = 29.84 ppm)). UV-vis/NIR absorption spectra, high-resolution mass spectra (HRMS), and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were measured according to our previous report.¹⁹ Redox potentials were measured by a cyclic voltammetry method on an ALS electrochemical analyzer model 660A with ferrocene (+0.642 V vs NHE) as an external standard.

Synthesis. $[Cu(dmp)_2](Cl)(TFSI)$,³⁵ $[Cu(dmp)_2](TFSI)$,³⁷ 2methyl-1,10-phenanthroline,⁴⁵ and LEG4⁴⁶ were prepared according to the literature. The details of syntheses of phenanthroline ligands are described in the Supporting Information.

 $[Cu(dep)_2](CI)(TFSI)$. CuCl₂ (27 mg, 0.20 mmol) was added to a solution of 2,9-diethyl-1,10-phenanthroline (189 mg, 0.80 mmol, 4.0 equiv) in ethanol (6 mL) under an argon atmosphere. After the solution was stirred for 9 h at room temperature, water (12 mL) and LiTFSI (287 mg, 1.0 mmol, 5.0 equiv) were added and the mixture was stirred for 1 h. The reaction mixture was extracted with CH₂Cl₂. The crude product was collected by filtration and washed with diethyl ether to give the target complex as an orange solid (76 mg, 0.089 mmol, 43%).

FT-IR (neat): ν (cm⁻¹) = 1590, 1500, 1460, 1340, 1179, 1131, 1057, 857, 783, 737, 649, 595, 568, 509. Mp: 192–193 °C.

 $[Cu(dep)_2](TFSI)$. A mixture of CuI (70 mg, 0.38 mmol, 1.0 equiv) and 2,9-diethyl-1,10-phenanthroline (354 mg, 1.5 mmol, 4.0 equiv) in ethanol (40 mL) was stirred for 2 h at room temperature under an argon atmosphere. Then, LiTFSI (546 mg, 1.9 mmol, 5.0 equiv) was added and the mixture was stirred for 1.5 h. The solvent was removed under reduced pressure, and the crude product was washed with diethyl ether to give the target complex as an orange solid (232 mg, 0.28 mmol, 74%).

¹H NMR (acetone- d_6 , 400 MHz, 25 °C): δ = 8.82 (d, J = 8.4 Hz, 4H), 8.53 (s, 4H), 8.04 (d, J = 8.4 Hz, 4H), 2.88–2.79 (m, 8H), 0.96 (t, J = 7.8 Hz, 12H). ESI-MS: m/z calcd for $C_{32}H_{32}CuN_4$ [M – TFSI]⁺: 535.1917; found 535.1911. Mp: 211 °C. FT-IR (neat): ν (cm⁻¹) = 1590, 1558, 1498, 1450, 1366, 1342, 1181, 1143, 1050, 978, 853, 687, 647, 597. Due to low solubility, we could not obtain the ¹³C NMR spectrum in a sufficient S/N ratio.

[Cu(emp)₂](Cl)(TFSI). CuCl₂ (32 mg, 0.24 mmol) was added to a solution of 2-ethyl-9-methyl-1,10-phenanthroline (210 mg, 0.94 mmol, 4.0 equiv) in ethanol (7.7 mL) under an argon atmosphere. After the solution was stirred for 2 h at room temperature, water (15 mL) and LiTFSI (345 mg, 1.2 mmol, 5.0 equiv) were added and the mixture was stirred for 5 h. The reaction mixture was extracted with CH₂Cl₂. The solvent was removed under reduced pressure, and the crude product was purified by GPC, using THF as the eluent, and reprecipitation (CH₂Cl₂/hexane) to give the target complex as a brown solid (39 mg, 0.047 mmol, 20%).

FT-IR (neat): ν (cm⁻¹) = 1713, 1628, 1509, 1347, 1176, 1131, 1053, 856, 737, 599. Mp: 160 °C.

 $[Cu(emp)_2](TFSI)$. CuI (11 mg, 0.058 mmol) was mixed with 2ethyl-9-methyl-1,10-phenanthroline (51 mg, 0.23 mmol, 4.0 equiv) in ethanol (2.7 mL) under an argon atmosphere. After the solution was stirred for 2 h at room temperature, LiTFSI (83 mg, 0.29 mmol, 5.0 equiv) was added and the mixture was stirred for 1.5 h. The reaction mixture was filtered and washed with diethyl ether to give the target complex as a red solid (18 mg, 0.023 mmol, 40%).

¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.87 (d, *J* = 8.4 Hz, 2H), 8.77 (d, *J* = 8.8 Hz, 2H), 8.23 (s, 4H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 2.69–2.65 (m, 4H), 2.41 (s, 6H), 0.82 (t, *J* = 7.6 Hz, 6H). ESI-MS: *m/z* calcd for C₃₀H₂₈CuN₄ [M – TFSI]⁺: 507.1604; found 507.1607. FT-IR (neat): ν (cm⁻¹) = 1559, 1496, 1349, 1186, 1052, 853, 739, 614, 570. Mp: 241 °C. Due to low solubility, we could not obtain the ¹³C NMR spectrum in a sufficient S/N ratio.

 $[Cu(bp)_2](CI)(TFSI)$. A mixture of CuCl₂ (40 mg, 0.30 mmol, 1.0 equiv) and 2-butyl-1,10-phenanthroline (284 mg, 1.2 mmol, 4.0 equiv) in ethanol (10 mL) was stirred for 2.5 h at room temperature under an argon atmosphere. Then, water (20 mL) and LiTFSI (431 mg, 1.5 mmol, 5 equiv) were added and the mixture was stirred for 2.5 h. The target complex was collected by filtration and washed with diethyl ether to give the target complex as a yellow solid (222 mg, 0.26 mmol, 87%).

FT-IR (neat): ν (cm⁻¹) = 2931, 2873, 1513, 1499, 1346, 1176, 1133, 1050, 857, 785, 739, 723, 648. Mp: 114–116 °C.

 $[Cu(bp)_2]$ (TFSI). A mixture of CuI (87 mg, 0.46 mmol, 1.0 equiv) and 2-butyl-1,10-phenanthroline (424 mg, 1.8 mmol, 4.0 equiv) in ethanol (50 mL) was stirred for 2 h at room temperature under an argon atmosphere. Then, LiTFSI (660 mg, 2.3 mmol, 5.0 equiv) was added and the mixture was stirred for 2 h. The solvent was removed under reduced pressure, and the crude product was dissolved in CH₂Cl₂. After removal of the solvent, diethyl ether was added to the residue to dissolve the unreacted ligand. The crude product was collected by filtration and purified by reprecipitation from CH₂Cl₂/*n*-hexane to give the target complex as an orange solid (239 mg, 0.29 mmol, 63%).

¹H NMR (acetone-*d*₆, 400 MHz, 25 °C): δ = 9.20 (d, *J* = 3.6 Hz, 2H), 8.87 (d, *J* = 8.0 Hz, 2H), 8.78 (d, *J* = 8.4 Hz, 2H), 8.28 (s, 4H), 8.08 (dd, *J* = 8.0 Hz, *J* = 4.8 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 2.80 (m, 18H). MALDI-MS: *m*/*z* calcd for C₃₂H₃₂CuN₄ [M - TFSI]⁺: 535.1917; found 535.1906. FT-IR (neat): ν (cm⁻¹) = 2952, 2866, 1508, 1492, 1348, 1328, 1192, 1134, 1062, 849, 828, 741. Mp: 164–166 °C. Due to low solubility, we could not obtain the ¹³C NMR spectrum in a sufficient S/N ratio.

 $[Cu(dpp)_2](CI)(TFSI)$. A mixture of CuCl₂ (26 mg, 0.2 mmol, 1.0 equiv) and 2,9-diphenyl-1,10-phenanthroline (266 mg, 0.8 mmol, 4.0 equiv) in ethanol (8 mL) was stirred for 1.5 h at room temperature under an argon atmosphere. Then, water (16 mL) and LiTFSI (574 mg, 2.0 mmol, 10 equiv) were added and the mixture was stirred for 3 h. The crude product was collected by filtration and purified by GPC

using THF as eluent. Reprecipitation from CH_2Cl_2/n -hexane gave the target complex as a brown solid (79.4 mg, 0.076 mmol, 38%).

FT-IR (neat): ν (cm⁻¹) = 1583, 1548, 1506, 1486, 1446, 1424, 1360, 1155, 866, 740, 699. Mp: 209–211 °C.

 $[Cu(dpp)_2](TFSI)$. A mixture of CuI (64.3 mg, 0.34 mmol, 1.0 equiv) and 2,9-diphenyl-1,10-phenanthroline (450 mg, 1.4 mmol, 4.0 equiv) in ethanol (40 mL) was stirred for 2 h at room temperature under an argon atmosphere. Then, LiTFSI (488 mg, 1.7 mmol, 5.0 equiv) was added and the mixture was stirred for 2 h. The solvent was removed under reduced pressure, and diethyl ether was added to the residue to dissolve the unreacted ligand. The crude product was collected by filtration and purified by GPC using THF as eluent. Reprecipitation from CH₂Cl₂/*n*-hexane gave the target complex as a brown solid (170 mg, 0.17 mol, 50%).

¹H NMR (acetone- d_6 , 400 MHz, 25 °C): $\delta = 8.75$ (d, J = 8.4 Hz, 4H), 8.22 (s, 4H), 8.07 (d, J = 8.0 Hz, 4H), 7.56 (d, J = 8.4 Hz, 8H), 6.83 (t, J = 7.6 Hz, 4H), 6.61 (t, J = 7.8 Hz, 8H). ¹³C NMR (acetone d_6 , 100 MHz, 25 °C): $\delta = 157.7$, 144.4, 140.1, 138.6, 129.5, 128.7, 128.0, 127.5, 125.7. ESI-MS: m/z calcd for C₄₈H₃₂CuN₄ [M – TFSI]⁺: 727.1917; found 727.1917. FT-IR (neat): ν (cm⁻¹) = 1582, 1486, 1418, 1354, 1181, 1134, 1053, 857, 737, 694. Mp: 120–121 °C.

Preparation of LEG4-Sensitized TiO₂ Electrode and Photovoltaic Measurements. The preparation of TiO₂ electrodes, and the counter Pt electrode, and the fabrication of the sealed cells for photovoltaic measurements were performed according to the literature.^{47,48} A 2 μ m nanocrystalline TiO₂ layer (20 nm, PST18NR-T, GreatCell Solar) was coated on the fluorine-doped tin oxide (FTO) glass plate by a screen-printing method as a transparent TiO₂ film. Then, a layer of the 2 μ m submicrocrystalline TiO₂ layer (400 nm, CCIC:PST400C, JGC-C&C) was further deposited as a light-scattering TiO₂ film on the transparent TiO₂ film. The TiO₂ electrode was immersed into an ethanol solution of LEG4 (0.20 mM) for 5 h at 25 °C.

A sandwich cell was prepared by using the dye-anchored TiO₂ film as a working electrode and a counter Pt electrode, which were assembled with a hot-melt ionomer film Surlyn polymer gasket (DuPont, 50 μ m). The electrolyte solution was composed of 0.20 M [CuL₂](TFSI), 0.05 M [CuL₂](Cl)(TFSI), 0.1 M LiTFSI, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. It is noted that all copper complexes were dried under a vacuum at 50 °C prior to use.

Incident photon-to-current efficiency (IPCE) and photocurrent– voltage (I-V) performance were measured with a simulated sunlight of AM1.5 (100 mW cm⁻²) according to our previous report.¹⁹ The convolution of the spectral response in the photocurrent action spectrum with the photon flux of the AM1.5G spectrum provided the estimated short-circuit current (J_{SC}), which is in good agreement with the J_{SC} value obtained from the I-V performance.

Microsecond Time-Resolved Transient Absorption Spectroscopy. The measurements were carried out with the laser system provided by UNISOKU according to our previous report.¹⁹ A sample was excited at $\lambda = 610$ nm, and the photodynamics were monitored by continuous exposure to a Xe lamp as a probe light. All the samples were made by the same method used for preparing the dye-anchored TiO₂ electrodes.

RESULTS AND DISCUSSION

Synthesis of Copper Complexes. The synthetic schemes of phenanthroline ligands and copper complexes are shown in Scheme 1. The reaction of 1,10-phenanthroline with various organolithium reagents afforded the corresponding 2-mono-substituted or 2,9-disubstituted 1,10-phenanthrolines (see the Supporting Information). Then, the reaction of the ligands with CuCl₂ and the subsequent counterion exchange with lithium trifluoromethanesulfonimide (LiTFSI) gave copper(II) complexes with chloride (Cl⁻) and trifluoromethanesulfonimide ions (TFSI⁻) as counterions ([Cu(L)₂](Cl)(TFSI)). The reaction with CuI in the presence of LiTFSI also provided copper(I) complexes with TFSI⁻ as a counterion ([Cu(L)₂]-

Scheme 1. Synthesis of 1,10-Phenanthroline Ligands and Copper Complexes



(TFSI)). These ligands and copper complexes were characterized by ¹H and ¹³C NMR, FT-IR spectroscopies, and highresolution mass spectrometry (Figures S1–S9). We conducted DOSY experiments for [Cu(dmp)₂](TFSI) and [Cu(bp)₂]-(TFSI) in CD₃CN, and the diffusion coefficients were determined to be 1.41 × 10⁻⁵ cm² s⁻¹, which is consistent with that determined by a rotating disk electrode measurement for [Cu(dmp)₂](TFSI) (1.26 × 10⁻⁵ cm² s⁻¹).³⁷ Thus, the ligand modification would have little impact on the mass transport limitation.

Electrochemical Properties of Copper Complexes. The electrochemical properties of the copper(I) complexes were examined by cyclic voltammetry (CV) techniques in acetonitrile versus NHE with LiTFSI as the electrolyte (Figure S10). We estimated the redox potentials (E_{redox}) of the copper redox shuttles from one electron oxidation potential of the copper(I) complexes because the oxidized dye on TiO₂ should be regenerated by the copper(I) complex. The copper(I)

complexes exhibit reversible or quasi-reversible oxidation peaks at 0.84-1.08 V vs NHE. The steric bulkiness of substituents at the 2,9-positions affects the redox potentials because copper(I)complexes prefer a tetrahedral geometry with a dihedral angle of ca. 90°, but copper(II) complexes prefer a distorted tetrahedral geometry. Upon oxidation of copper(I) to copper(II), the bulky substituents at the 2,9-positions hamper the conformational change. Consequently, the bulky substituents destabilize the copper(II) complex and the redox potential should be shifted to the positive direction. 49,50 In fact, the more positive E_{redox} values of $[Cu(emp)_2]^{1+/2+}$ and $[Cu(dep)_2]^{1+/2+}$ compared to that of $[Cu(dmp)_2]^{1+/2+}$ are consistent with the larger steric hindrance of the ethyl group than of the methyl group in the coordination sphere geometry (Figure 2). On the contrary, the E_{redox} value of $[Cu(bp)_2]^{1+/2+}$ is significantly shifted to the negative direction because of the lower steric hindrance of the 2-monosubstituted 1,10phenanthroline ligands. In contrast, the E_{redox} value of the phenyl-substituted $[Cu(dpp)_2]^{1+/2+}$ is comparable to that of $\left[Cu(dmp)_2 \right]^{1+/2+}$. Considering the oxidation potential (E_{ox}) of LEG4 on TiO₂ (1.07 V vs NHE),⁵¹ we calculated the driving forces for dye regeneration (ΔG_{reg}) (Figure 2). The ΔG_{reg} values for $[Cu(dmp)_2]^{1+/2+}$, $[Cu(bp)_2]^{1+/2+}$, and $[Cu-(dpp)_2]^{1+/2+}$ are more negative than -0.1 eV, ensuring that the dye-regeneration processes with these copper redox shuttles should occur smoothly. The less negative $\Delta G_{
m reg}$ values for $[Cu(emp)_2]^{1+/2+}$ (-0.05 eV) and $[Cu(dep)_2]^{1+/2+\circ}$ (+0.01 eV) may inhibit the efficient dye regeneration.

Photovoltaic Properties. We fabricated LEG4-sensitized DSSCs by using the copper redox shuttles and investigated their photovoltaic properties under standard AM1.5 illuminations to evaluate the effect of the ligand structures. The electrolyte solution was composed of 0.2 M [CuL₂](TFSI), 0.05 M [CuL₂](Cl)(TFSI), 0.1 M LiTFSI, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. The photocurrent–voltage characteristics are shown in Figure 3a, and the photovoltaic parameters are summarized in Table 1. The DSSC with [Cu(dmp)₂]^{1+/2+} exhibited the highest V_{OC} (1.03 V) and a high short-circuit current density ($J_{SC} = 10.0 \text{ mA cm}^{-2}$) and thus achieved the highest efficiency (6.29%). Although the DSSC with [Cu(bp)₂]^{1+/2+} exhibited the slightly higher J_{SC} value (10.6 mA cm⁻²) compared to that with [Cu(dmp)₂]^{1+/2+}, the former V_{OC} value (0.842 V) was smaller than the latter one because of the less positive redox potential of [Cu(bp)₂]^{1+/2+}.



Figure 2. Energy level diagrams for LEG4 and copper redox shuttles.



Figure 3. (a) Photocurrent–voltage characteristics and (b) photocurrent action spectra of the DSSCs based on LEG4 with the copper redox shuttles $[CuL_2]^{1+/2+}$: L = bp (red), dmp (blue), emp (green), dep (orange), and dpp (purple).

Table	e 1.	Photovo	ltaic	Perfor	mances	of t	the	DSSCs	Based	on	LEG4	with	Copper	Redox	Shuttl	esť
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$[CuL_2]^{1+/2+}$	$J_{\rm SC}/{\rm mA~cm^{-2}}$	$V_{\rm OC}/{ m V}$	ff	$\eta/\%$
$[Cu(bp)_2]^{1+/2+}$	$10.6 \ (10.4 \pm 0.6)$	$0.842 \ (0.836 \pm 0.007)$	$0.664 \ (0.634 \pm 0.037)$	$5.90 (5.53 \pm 0.23)$
$[Cu(dmp)_2]^{1+/2+}$	10.0 (10.1 ± 0.6)	$1.03 \ (1.03 \pm 0.01)$	$0.609 \ (0.592 \pm 0.034)$	$6.29~(6.12 \pm 0.11)$
$[Cu(emp)_2]^{1+/2+}$	$7.52 \ (7.82 \pm 0.75)$	$0.823~(0.794 \pm 0.002)$	$0.526 \ (0.505 \pm 0.064)$	$3.25 (3.09 \pm 0.11)$
$[Cu(dep)_2]^{1+/2+}$	$6.77 \ (6.45 \pm 0.23)$	$0.813 \ (0.803 \pm 0.006)$	$0.464 \ (0.449 \ \pm \ 0.021)$	$2.56 (2.33 \pm 0.17)$
$[Cu(dpp)_2]^{1+/2+}$	$4.18 \ (4.30 \pm 0.16)$	$0.848~(0.799\pm0.036)$	$0.624 \ (0.602 \ \pm \ 0.025)$	$2.21 \ (2.06 \pm 0.11)$

^aPhotovoltaic parameters are derived from the highest efficiency. The average values from four independent experiments are denoted in parentheses. Error bars represent a standard error of the mean.

Overall, the efficiency of the DSSC with $[Cu(bp)_2]^{1+/2+}$ (5.90%) is almost comparable to that with $[Cu(dmp)_2]^{1+/2+}$. Although the DSSCs with $[Cu(emp)_2]^{1+/2+}$, $[Cu(dep)_2]^{1+/2+}$, $[Cu(dpp)_2]^{1+/2+}$, and $[Cu(bp)_2]^{1+/2+}$ revealed rather similar V_{OC} values (0.813–0.848 V), the J_{SC} values of the DSSCs with $[Cu(emp)_2]^{1+/2+}$, $[Cu(dep)_2]^{1+/2+}$, and $[Cu(dpp)_2]^{1+/2+}$ are lower than those with $[Cu(bp)_2]^{1+/2+}$, leading to a decrease in the efficiencies of the DSSCs with $[Cu(emp)_2]^{1+/2+}$, $[Cu-(dep)_2]^{1+/2+}$, and $[Cu(dpp)_2]^{1+/2+}$. It is notable that the fill factors for $[Cu(emp)_2]^{1+/2+}$ (0.526) and $[Cu(dep)_2]^{1+/2+}$ (0.464) are very low, which can be ascribed to the insufficient ΔG_{reg} values.

The photocurrent action spectra are illustrated in Figure 3b. The integrated incident photon-to-current efficiency (IPCE) values are in good agreement with the J_{SC} values. The maximum IPCE value of the DSSC with $[Cu(bp)_2]^{1+/2+}$ is slightly higher than that with $[Cu(dmp)_2]^{1+/2+}$, whereas the maximum IPCE values of the DSSCs with [Cu(emp)₂]^{1+/2+} (ca. 50%), $[Cu(dep)_2]^{1+/2+}$ (ca. 40%), and $[Cu(dpp)_2]^{1+/2+}$ (ca. 30%) are lower than those with $[Cu(bp)_2]^{1+/2+}$ and $[Cu(dmp)_2]^{1+/2+}$ (ca. 70%). The IPCE value is calculated by the product of light-harvesting efficiency (LHE), electron injection efficiency (ϕ_{ini}), and charge collection efficiency (η_{col}) . Because all the DSSCs are fabricated with LEG4 in this study, the LHE and $\phi_{
m inj}$ values should be identical. Thus, the difference in the IPCE values is rationalized by the η_{col} values. The η_{col} value is associated with the dye-regeneration and CR processes between the electron in the CB of TiO₂ and the dye radical cation or the oxidized redox shuttle in the electrolyte solution.

To assess the dye-regeneration process, we performed microsecond time-resolved transient absorption (TA) experiments for the LEG4-sensitized TiO₂ films (Figures 4 and S11). We monitored the decay profiles at 715 nm because the LEG4 radical cation (LEG4^{•+}) possesses characteristic absorption at 670–800 nm (Figure S12). The lifetime (τ_1) of LEG4^{•+} in the absence of the copper redox shuttle was determined to be 68 μ s (Table S1). The lifetimes (τ_2) of LEG4^{•+} in the presence of



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Figure 4. Time absorption profiles of the LEG4-sensitized TiO₂ films in the absence (black) and presence of copper redox shuttles $[CuL_2]^{1+/2+}$ in acetonitrile: L = bp (red), dmp (blue), emp (green), dep (orange), and dpp (purple). The samples were excited at 610 nm, and the absorption profiles were monitored at 715 nm.

the copper redox shuttles were also determined to be 13 μ s for $[\mathrm{Cu}(\mathrm{bp})_2]^{1+/2+}$, 2.9 μ s for $[\mathrm{Cu}(\mathrm{dmp})_2]^{1+/2+}$, 3.9 μ s for $[\mathrm{Cu}(\mathrm{dmp})_2]^{1+/2+}$, 3.8 μ s for $[\mathrm{Cu}(\mathrm{dmp})_2]^{1+/2+}$, 5.8 μ s $[\mathrm{Cu}(\mathrm{dep})_2]^{1+/2+}$, and 5.8 μ s for $[\mathrm{Cu}(\mathrm{dpp})_2]^{1+/2+}$ (Table S1). From these results, the dye-regeneration efficiencies (φ_{reg}) were estimated to be 81–96%. However, the smaller φ_{reg} value for $[\mathrm{Cu}(\mathrm{bp})_2]^{1+/2+}$ (81%) than for $[\mathrm{Cu}(\mathrm{dmp})_2]^{1+/2+}$ (96%) is inconsistent with the larger driving force for $[\mathrm{Cu}(\mathrm{bp})_2]^{1+/2+}$ (0.23 V) than for $[\mathrm{Cu}(\mathrm{dmp})_2]^{1+/2+}$ (0.11 V) and similar high IPCE and J_{SC} values. Moreover, the high φ_{reg} values for $[\mathrm{Cu}(\mathrm{dep})_2]^{1+/2+}$ (91%) and $[\mathrm{Cu}(\mathrm{emp})_2]^{1+/2+}$ (94%) contradict the insufficient driving force for the dye regeneration and the low IPCE and J_{SC} values. To address these inconsistencies, we compared the initial intensities of the TA of LEG4^{•+} (Δ OD) in the presence of the copper redox shuttles. It increases in the following order: $[\mathrm{Cu}(\mathrm{dpp})_2]^{1+/2+}$ (0.005) < $[\mathrm{Cu}(\mathrm{dpp})_2]^{1+/2+}$ (0.007) < $[\mathrm{Cu}(\mathrm{bp})_2]^{1+/2+}$ (0.009). If the intensity (i.e., LEG4^{•+} concentration) corresponds to the η_{col} value, this trend is in good agreement with those on the IPCE and J_{SC} values. The reason

is not clear at this stage; this suggests at least the partial occurrence of a fast CR process between LEG4^{•+} and TiO₂ (<100 ns), involving the copper redox shuttles, which would lower the IPCE and J_{SC} values significantly in the cases of $[Cu(emp)_2]^{1+/2+}$, $[Cu(dep)_2]^{1+/2+}$, and $[Cu(dpp)_2]^{1+/2+}$ with the small driving forces. Considering rather similar high $\varphi_{\rm reg}$ values, the LEG4^{•+} remaining from the fast CR processes is quenched effectively by the redox shuttles, generating the photocurrent corresponding to the initial intensity of the TA of LEG4^{•+}. In particular, for $[Cu(bp)_2]^{1+/2+}$ the large initial intensity of the TA of LEG4^{•+} suggests that the fast CR process (<100 ns) would be suppressed significantly, probably due to the large driving force. Thus, the DSSC with $[Cu(bp)_2]^{1+/2+}$ exhibited the high IPCE and J_{SC} values in spite of the somewhat smaller $\varphi_{
m reg}$ value. Although our microsecond time-resolved TA experiments cannot fully evaluate the CR process, the η_{col} value and resultant IPCE and J_{SC} values are affected by both the fast CR process beyond the time resolution (<100 ns) and the slow regeneration process occurring in the microsecond region.

We also conducted electrical impedance spectroscopy (EIS) to evaluate the effect of the ligand structures on the CR processes. The EIS Nyquist plots under standard AM1.5 illumination and open-circuit conditions are shown in Figure S13. The electron transfer (ET) process at the interface of the $TiO_2/dye/electrolyte$ configuration is represented by R_p , which corresponds to a CR resistance between the electrolyte and TiO₂. The R_p values increase in the following order: $[Cu(bp)_2]^{1+/2+}$ (29 Ω) < $[Cu(dmp)_2]^{1+/2+}$ (73 Ω) < $[Cu(dpp)_2]^{1+/2+}$ (131 Ω) < $[Cu(emp)_2]^{1+/2+}$ (181 Ω) < $[Cu(dep)_2]^{1+/2+}$ (322 Ω). This tendency is consistent with the order of the redox potentials for the copper redox shuttles. This is reasonable considering that the CR process from the electron in the CB of $\rm TiO_2$ to the oxidized redox shuttle occurs in the Marcus inverted region, and thus the larger driving force leads to the slower CR. Although the larger R_p values for $[Cu(dmp)_2]^{1+/2+}$ than for $[Cu(bp)_2]^{1+/2+}$ match with the larger $V_{\rm OC}$ for $[Cu(dmp)_2]^{1+/2+}$ than for $[Cu(bp)_2]^{1+/2+}$, the large R_p values for $[Cu(dpp)_2]^{1+/2+}$, $[Cu(emp)_2]^{1+/2+}$, and $[Cu-p]^{1+/2+}$ $(dep)_2$ ^{1+/2+} contradict with the small V_{OC} values in comparison with those of $[Cu(dmp)_2]^{1+/2+}$. The contradiction may be explained by the plausible fast CR process between LEG4^{•+} and TiO₂ involving the redox shuttle, decreasing the $V_{\rm OC}$ values (vide supra). The DSSC with $[Cu(bp)_2]^{1+/2+}$ owns the slowest dye regeneration and lowest recombination resistance, then achieving the largest photocurrent and moderate photovoltage. Although the small recombination resistance indicates a fast CR of electrons in TiO₂ with copper(II) in the electrolyte, the further fast CR process involving the copper redox shuttle (<100 ns) would not be included in the recombination resistance. Accordingly, the photocurrent and voltage are influenced by the fast CR process (<100 ns) rather than the slow CR process. Consequently, the DSSC with $[Cu(bp)_2]^{1+/2+}$ attained the slightly higher J_{SC} value than the DSSC with $[Cu(dmp)_2]^{1+/2+}$, which is consistent with other copper redox shuttles with 2-monosubstituted phenanthroline ligands.⁴¹⁻⁴³ The use of [Cu- $(bp)_2$ ^{1+/2+} may be useful to improve the J_{SC} value by retaining the rather high V_{OC} value (>0.8 V) when dyes with a smaller bandgap (i.e., better light harvesting) are developed.

We designed and synthesized a series of copper(I/II) complexes with 1,10-phenanthroline ligands with different substituents at the 2,9-positions to examine the effect of the ligand structures on their electrochemical and photovoltaic properties. For the copper complexes with alkyl-substituted ligands, the redox potentials correlate with the steric hindrance of the ligands on the coordination sphere geometry. The redox potentials of $[Cu(emp)_2]^{1+/2+}$ and $[Cu(dep)_2]^{1+/2+}$ are shifted to the positive direction because of the larger steric hindrance of the ethyl than of the methyl groups, whereas that of $[Cu(bp)_2]^{1+/2+}$ is shifted to the negative direction because of the lower steric hindrance of the 2-monosubstituted 1,10phenanthroline ligands. In contrast, the redox potential of the phenyl-substituted $[Cu(dpp)_2]^{1+/2+}$ is comparable to that of $[Cu(dmp)_2]^{1+/2+}$. The driving force for the dye regeneration $[Cu(dmp)_2]^{1+/2+}$. The driving force for the dye regeneration increases in the order $[Cu(dep)_2]^{1+/2+}$ (+0.01 V) < $[Cu-(emp)_2]^{1+/2+}$ (-0.05 V) < $[Cu(dpp)_2]^{1+/2+}$ (-0.11 V) \approx $[Cu(dmp)_2]^{1+/2+}$ (-0.11 V) < $[Cu(bp)_2]^{1+/2+}$ (-0.23 V). The efficiency of the DSSC with $[Cu(bp)_2]^{1+/2+}$ (5.90%) is almost comparable to that with $[Cu(dmp)_2]^{1+/2+}$ (6.29%). In contrast, the DSSCs with $[Cu(emp)_2]^{1+/2+}$ (3.25%), $[Cu(dep)_2]^{1+/2+}$ (2.56%), and $[Cu(dpp)_2]^{1+/2+}$ (2.21%) exhibited lower efficiencies than those with $[Cu(dmp)_2]^{1+/2+}$ and $[Cu-(bn)_2]^{1+/2+}$. $(bp)_2$ ^{1+/2+}. The difference can be rationalized by the fact that the electron collection efficiencies associated with both the fast CR process (<100 ns) and slow regeneration process occur in the microsecond region. Considering the similar photovoltaic properties of the DSSCs with $[Cu(bp)_2]^{1+/2+}$ and $[Cu(dmp)_2]^{1+/2+}$, the use of copper(I/II) complexes with 2monosubstituted 1,10-phenanthroline ligands as the redox shuttle may be useful to improve the short-circuit current density while retaining the rather high $V_{\rm OC}$ value when dyes with a smaller bandgap (i.e., better light harvesting) are developed. Therefore, we believe that exploration of new ligands for copper(I/II) complexes would contribute to achieving a high photovoltaic performance of the DSSCs with copper-based redox shuttles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b02740.

Details of DSSC preparations and photovoltaic measurements, synthesis of phenanthroline ligands, highresolution mass spectra, NMR spectra, cyclic voltammograms, details of photovoltaic properties, figures of absorption profiles, UV–vis/NIR absorption spectrum of LEG4 radical cation, EIS Nyquist plots, and table of the lifetime of LEG4 radical cation and dye-regeneration efficiency (PDF)

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Notes

The authors declare no competing financial interest.

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