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Divergent Synthesis and Tuning of the Electronic Structures of Cobalt–Dithiolene–Fullerene Complexes for Organic Solar Cells

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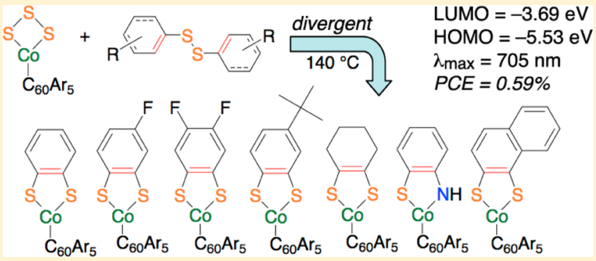
Supporting Information

ABSTRACT: A pentakis(aryl)[60]fullerene cobalt trisulfide complex (**1a**) was obtained from the reaction of a pentakis(aryl)[60]fullerene cobalt dicarbonyl complex (**2a**) with triphenylmethanethiol. This reaction proceeded smoothly even at ambient temperature to produce **1a** in moderate to high yield. The series of pentakis(aryl)[60]fullerene cobalt dithiolene complexes **3**–**9** were also synthesized by the reaction of **1a** with a variety of readily available disulfide compounds. The HOMO and LUMO levels of the complexes could be tuned by making changes to the substituents on the dithiolene ligands, with changes to the electronic structure of the compounds influencing their photovoltaic performance, especially in terms of their open-circuit voltage. Small-molecule organic solar cells constructed from the naphthalene dithiolene complex **9** and tetrabenzoporphyrin showed a power conversion efficiency of 0.59%.



1. INTRODUCTION

Transition-metal fullerene complexes[1] have attracted considerable attention because of their rich electrochemical and photophysical properties[2] and their potential applications in organometallic transformation[3] and photofunctional materials.[4] Cobalt trisulfide pentakis(aryl)[60]fullerene complexes of the general formula $(\eta^5\text{-}C_{60}Ar_5)CoS_3$ (Ar = 4-^{n}BuC$_6$H$_4$ (**1a**), 4-^{t}BuC$_6$H$_4$ (**1b**)), in particular, have recently attracted special attention because of their unique structure and properties.[5] Complexes of this particular type possess an organometallic four-membered-ring structure, which represents a rare four-membered aromatic system.[6] Furthermore, this compound exhibits remarkable reactivity, with the most notable examples including the simultaneous activation of the three C–H bonds of the methyl group of *p*-xylene[7] and the selective formation of the Co_8S_{15} cluster.[8] These examples suggest that complex **1** is a useful starting material for the formation of various thiolate cobalt fullerene complexes.

Cobalt dithiolene complexes have been studied since the 1960s. Cobalt dithiolene complexes are functional molecules,[9] and their functional properties are based on (1) their long-wavelength light absorption characteristics resulting from ligand-to-metal charge transitions from the organic pπ orbital to the metal dπ* orbital,[10] (2) their high electron affinity resulting from the coordinatively unsaturated 16-electron metal center,[11] and (3) their high level of stability resulting from their metallacyclic 6π aromaticity. We previously reported the reactivity of the cobalt trisulfide **1b** to give two cobalt dithiolene complexes (benzene-1,2-dithiolene and cyclohexene-1,2-dithiolate complexes) as part of a study pertaining to multiple C–H bond activation by **1b**.[7] In the current study, we have divergently synthesized a variety of different pentakis(aryl)[60]fullerene cobalt dithiolene complexes bearing electron-donating and electron-withdrawing substituents and a π-expanding moiety on the dithiolene ligands to tune the electronic properties of these functional molecules. The pentakis(*n*-butylphenyl)[60]fullerene ligand (i.e., complex **1a**) has been used in the current study to synthesize dithiolene complexes with improved solubility that could be employed in photovoltaic devices.[12,13] In addition, we report an improved synthetic route for the preparation of the starting material **1a** using triphenylmethanethiol as a sulfur source. This study provides a rare example of the use of light-absorbing organometallic fullerene electron acceptors in organic thin-film solar cells.

2. RESULTS AND DISCUSSION

2.1. Improved Synthesis of the Cobalt Trisulfide Complex using Triphenylmethanethiol.

In this section, we describe our improved synthesis of the cobalt trisulfide complexes **1a**,**b** as starting materials in excellent yield under mild conditions. The cobalt dicarbonyl complex of pentakis(aryl)[60]fullerene, $(\eta^5\text{-}C_{60}Ar_5)Co(CO)_2$ (**2b**; Ar = 4-^{t}BuC$_6$H$_4$), successfully reacted with 3 equiv of triphenylmethanethiol in chlorobenzene at 140 °C to give the cobalt trisulfide complex **1b** in only 30 min (Scheme 1). This reaction proceeded cleanly and quantitatively to give **1** in 96% HPLC area ratio on reaction monitoring with the HPLC analysis, affording the pure product in 83% isolated yield (Table 1, entry 1). The chemical yield for this reaction was greater than that achieved in the previously reported method, which relied on

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Scheme 1. Improved (a) and Previously Reported (b) Procedures for the Synthesis of 1a,b

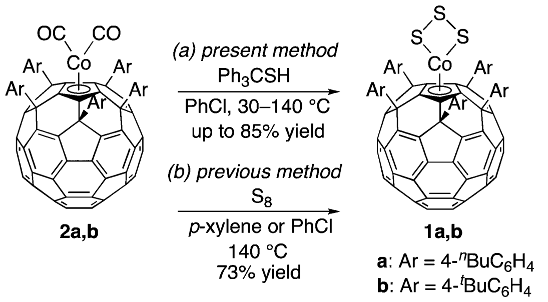


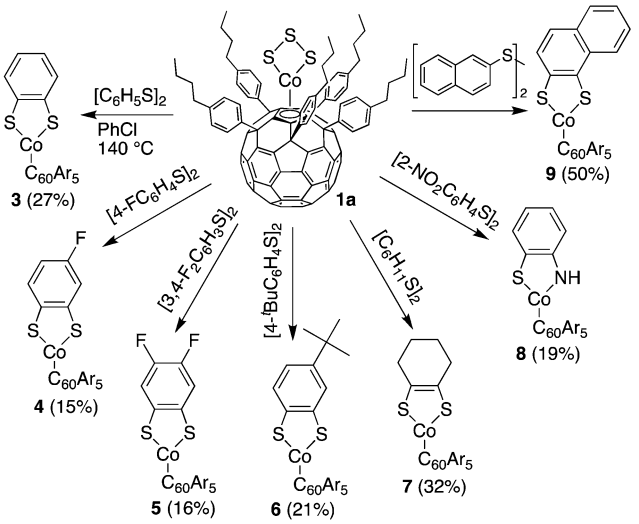
Table 1. Reaction Conditions and Yields for the Improved Synthesis of 1b

entry	amt of Ph_3CSH (equiv)	temp (°C)	reaction time (h)	HPLC area ratio (%)	isolated yield (%)
1	3	140	0.5	96	83
2	8	60	12	92	84
3	8	40	96	45	35
4	8	30	120	28	24

the use of elemental sulfur (73%).[5] In addition, the present reaction proceeded under much milder conditions with a reaction temperature in the range of 30−60 °C, whereas the previously reported procedure required a much higher temperature of 140 °C. The reaction of **2b** with Ph_3CSH (8 equiv) for 12 h at 60 °C gave **1b** in 92% HPLC area ratio and 84% isolated yield (Table 1, entry 2). When the reaction was conducted at 30 or 40 °C, it proceeded at a much slower rate to give a lower yield of **1b** (Table 1, entries 3 and 4). It is noteworthy, however, that the previously reported method involving elemental sulfur failed to provide any of the desired product when it was conducted at these lower temperatures. These reactions afforded 3 equiv of triphenylmethane to the product **1b** formed. The protonated pentakis(aryl)[60]fullerene ligand $C_{60}Ar_5H$ was found to be the only fullerene-based side product formed from this reaction. These results indicated that no more than three sulfur atoms add to the starting material. A similar reaction of $(\eta^5\text{-}C_{60}Ar_5)Co(CO)_2$ (**2a**; Ar = $4\text{-}{}^nBuC_6H_4$) with triphenylmethanethiol in chlorobenzene at 140 °C for 30 min gave **1a** in 85% isolated yield on a large scale. The products **1a,b** were readily purified by silica gel column chromatography under ambient conditions.

2.2. Synthesis of Cobalt Dithiolene Complexes from the Cobalt(III) Trisulfide Complex. Having successfully developed a new procedure for the synthesis of **1a**, we proceeded to synthesize a series of pentakis(aryl)[60]fullerene cobalt dithiolene complexes (**3**−**9**) using complex **1a** as a starting material. The reaction of **1a** with variety of readily available organic disulfide compounds in chlorobenzene at 140 °C for 12 h gave the corresponding dithiolenes **3**−**9** in 15−50% isolated yield (Scheme 2). This scheme illustrates the scope of this divergent reaction. The reaction proceeded smoothly with diphenyl disulfides bearing electron-withdrawing groups (for **4** and **5**) or electron-donating groups (for **6**), a dicyclohexyl disulfide (for **7**), and disulfides with a nitro group (**8**) or a π-conjugated group (for **9**). During the course of the reaction, the aromatic and aliphatic C−H bonds were activated by an unidentified reactive species derived from cobalt trisulfide **1a**. In case of compound **8**, unexpectedly the nitro group took part in the reaction to produce the aminobenzenethiolate complex **8**, whose electrochemical and photophysical characteristics were in good agreement with those of the reported *tert*-butylphenyl analogue.[7] We propose that thermal homolysis of the disulfides leads to the formation of sulfur radicals that react with **1a** to generate the reactive species. Compounds **3**−**9** were soluble in a variety of common organic solvents, including toluene, chloroform, and THF, and were also stable in air, which allowed them to be purified by silica gel column chromatography. Products **3**−**9** were characterized on the basis of ^1H and ^{13}C NMR spectra and elemental analyses. The ^1H and ^{13}C NMR spectra of **3**−**9** contained signals characteristic of C_{5v}-symmetric patterns. These observations indicated that the rotation rates of the cobalt dithiolene moieties along with the Co−$C_{60}Ar_5$ axis were greater than the relaxation time of the NMR measurements.

Scheme 2. Synthesis of the Pentakis(aryl)[60]fullerene Cobalt Dithiolene Complexes 3−9 from 1a



The combination of the pentakis(aryl)[60]fullerene ligand with a variety of different cobalt disulfide complexes provided some unique electrochemical and photophysical properties. Cyclic voltammetry measurements for **3**−**9** revealed cobalt(III)-centered reversible reduction in the range of −0.89 to −1.38 V vs Fc/Fc$^+$ (Figure 1, Table 2). The LUMO levels were subsequently estimated from the first reduction potentials[14] to be in the range of −3.42 to −3.91 eV (Figure 2) and were therefore comparable to those of the fullerene-based electron acceptors, including [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), which is used in organic solar cells.[15] The UV−vis spectra of these complexes exhibited ligand to metal charge-

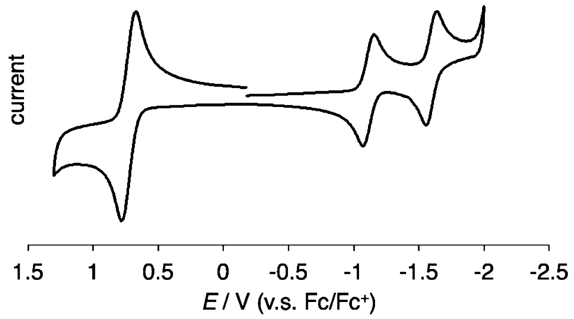


Figure 1. Cyclic voltammogram of **9**.

Table 2. Electrochemical Properties of 3−9[a]

compound	E^{ox} (V)	$E_{1/2}^{red}$ (V)	HOMO[d] (eV)	LUMO[d] (eV)	ΔE (eV)
3	0.72[b]	−1.03, −1.60	−5.52	−3.77	1.75
4	0.76[b]	−0.99, −1.59	−5.56	−3.81	1.75
5	0.83[b]	−0.89, −1.58	−5.63	−3.91	1.72
6	0.68[c]	−1.09, −1.60	−5.48	−3.71	1.77
7	0.63[c]	−1.41, −1.62	−5.41	−3.39	2.02
8	0.57[c]	−1.42, −1.63	−5.37	−3.38	1.99
9	0.73[c]	−1.11, −1.60	−5.53	−3.69	1.84

[a] Potentials in volts vs the ferrocene/ferrocenium (Fc/Fc^+) measured in CH_2Cl_2 solution containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 100 mV/s. Glassy-carbon, platinum-wire, and Ag/$AgClO_4$ electrodes were used as working, counter, and reference electrodes,respectively. [b] Determined by oxidation potentials in differential pulse voltammetry. [c] Determined by $E_{1/2}^{ox}$ in cyclic voltammetry. [d] Values from the vacuum level were estimated using the following equations: HOMO level = E^{ox} + 4.8, LUMO level = $E_{1/2}^{red}$ + 4.8, $\Delta E = E_1^{ox} - E_{1/2}^{red}$.

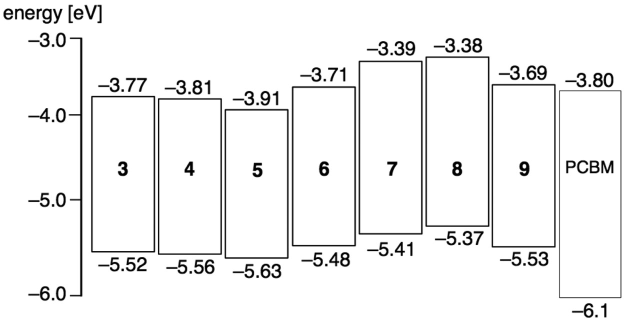


Figure 2. HOMO−LUMO levels of **3**−**9**, with PCBM included as a reference.

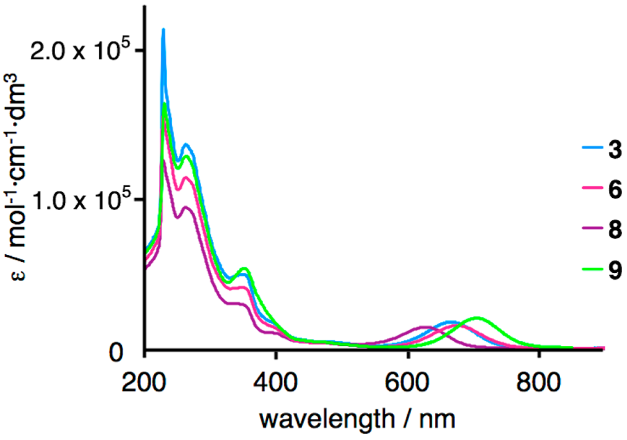


Figure 3. UV−vis absorption spectra of **3**, **6**, **8**, and **9** in CH_2Cl_2.

Table 3. Photophysical Data for 3−9

compound	λ_{max} (nm) (log ε)
3	263 (5.11), 349 (4.70), 666 (4.27)
4	263 (5.09), 352 (4.66), 670 (4.21)
5	261 (5.06), 352 (4.63), 672 (4.22)
6	262 (5.06), 348 (4.62), 674 (4.21)
7	261 (5.06), 349 (4.63), 640 (4.03)
8	263 (4.98), 339 (4.49), 628 (4.18)
9	263 (4.98), 352 (4.73), 705 (4.33)

transfer (LMCT) absorptions from the dithiolene ligands to the cobalt(III) center (Figure 3, Table 3). The absorption maxima of the LMCT bands were red-shifted in comparison to those of the corresponding Cp and Cp* compounds.[16] These changes in the absorption maxima were attributed to the effect of π conjugation to the pentakis(aryl)[60]fullerene ligand. The absorption maximum of the naphthalene dithiolate **9** was the most red-shifted of all of the complexes tested because of the expansion of the π-conjugation system.[4c] In comparison with the benchmark compound **3**, compound **6** bearing an electron-donating *tert*-butyl group exhibited a red-shifted absorption, whereas the cyclohexene dithiolene **7** and the amino-benzenethiolate complex **8** showed a blue-shifted absorption. These results suggested that the band gap could be tuned by making changes to the substituents on the dithiolene moieties.

2.3. Photovoltaic Performances of the Cobalt Dithiolene Complexes. The performances of organic solar cells containing the pentakis(aryl)[60]fullerene cobalt dithiolene complexes as electron acceptors were evaluated. We employed solution-processed small-molecule organic solar cells using tetarabenzoporphyrin (BP) as an electron donor.[17] The device was set up with a p−n heterojunction configuration as follows: ITO/PEDOT:PSS/BP/metal fullerene acceptor/Ca/Al. After optimization, the best performance was obtained using naphthalenedithiolate **9**, which gave a 0.59% power conversion efficiency (PCE) under 1 sun simulated AM1.5G solar illumination with a short-circuit current density (J_{SC}) of 2.5 mA/cm^2, an open-circuit voltage (V_{OC}) of 0.60 V, and a fill factor (FF) of 0.39 (Table 4). In comparison with compounds **3**−**5**, the V_{OC} value decreased in that order as the number of electron-withdrawing fluorine substituents increased. This result was attributed to a decrease in the energy difference between the HOMO level of the donor and the LUMO level of the acceptor.[18] These data therefore supported the notion that the fullerene cobalt dithiolene complexes were behaving as electron acceptors in these organic solar cell devices.

Table 4. Photovoltaic Performances of the Organic Solar Cells using BP and Penta(aryl)[60]fullerene Cobalt Dithiolene Complexes

compound	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
3	1.63	0.62	0.19	0.19
4	1.50	0.40	0.27	0.16
5	1.36	0.39	0.26	0.14
9	2.53	0.60	0.39	0.59

3. CONCLUSION

We have described an improved procedure for the synthesis of the key starting material pentakis(aryl)[60]fullerene cobalt trisulfide complex **1a** using pentakis(aryl)[60]fullerene cobalt dicarbonyl complex **2** and triphenylmethanethiol, with the reaction even proceeding at ambient temperature. With improved access to the starting material, we divergently synthesized a series of pentakis(aryl)[60]fullerene cobalt dithiolene complexes (**3**−**9**) using readily available various organic disulfide compounds through a process of S−S bond cleavage and C−H bond activation. The HOMO and LUMO levels of these materials could be tuned by making changes to the substituents on the dithiolene ligands. We fabricated organic solar cells using fullerene cobalt dithiolene complexes as electron acceptors and BP as an electron donor, and the resulting material gave a respectable PCE of 0.59% for the p−n heterojunction device. This study provides a platform for the development of new electron acceptors constructed from light-absorbing organometallic fullerene complexes in organic solar cells.

4. EXPERIMENTAL SECTION

4.1. General Procedure. Syntheses were carried out under a nitrogen or argon atmosphere with standard Schlenk techniques. The water contents of the solvents were determined, using a Karl Fischer moisture titration (MK-210, Kyoto Electronics Co.), to be less than 30 ppm. All of the reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6 × 250 mm, Nacalai Tesque; flow rate, 2.0 mL/min; eluent, toluene/isopropyl alcohol; detector, Shimadzu SPD-M10Avp). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene/isopropyl alcohol as the eluent (detected at 350 nm with a UV spectrophotometric detector, Shimadzu SPD-6A). Flash column chromatography was performed on silica gel (Kanto Kagaku, silica gel 60N, 40−100 mm). The isolated yields were calculated on the basis of the starting fullerene compounds. The NMR spectra were recorded on a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from the internal tetramethylsilane at δ 0.00 ppm or residual protons of the deuterated solvent for ^{1}H NMR. Mass spectra were measured on a JEOL JMS-T100LC APCI/ESI-TOF mass spectrometer. UV−vis absorption spectra were recorded on a JASCO V-570 spectrometer. Photoluminescence spectra were recorded on a Hitachi F-4500 spectrometer. Cyclic voltammetry was performed using a Hokuto Denko HZ-5000 voltammetric analyzer.

4.2. Syntheses and Characterization. *4.2.1. Materials.* Compound **2** was prepared according to our previous paper.[5] Disulfide compounds were readily synthesized by oxidative coupling of the corresponding organic thiols by using potassium carbonate in acetonitrile under air. A THF solution of KO^{t}Bu was purchased from Sigma-Aldrich Co. ^{n}Bu$_4$NPF$_6$, for electrochemical measurements, was purchased from Kanto Chemicals and used after recrystallization from ethanol.

*4.2.2. Preparation of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) Trisulfide (**1a**).* A mixture of cobalt dicarbonyl complex **2a** (776 mg, 0.51 mmol) and triphenylmethanethiol (1.1 g, 4.1 mmol) in chlorobenzene (10 mL) was heated to 140 °C. The reaction was complete within 30 min to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give the dark green solid **1a** (667 mg, 0.43 mmol, 85%).

*4.2.3. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) Benzene-1,2-dithiolate (**3**).* A mixture of cobalt trisulfide complex **1a** (213 mg, 138 μmol) and diphenyl disulfide (1.5 g, 6.9 mmol) in chlorobenzene (10 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give a dark green solid of the title compound (66 mg, 42 μmol, 27%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.83 (t, J = 7.5 Hz, 15H), 1.16−1.23 (m, 10H), 1.34−1.46 (m, 10H), 2.40 (t, J = 7.5 Hz, 10H), 6.98 (d, J = 8.0 Hz, 10H), 7.05−7.07 (m, 2H), 7.88−7.89 (m, 2H), 8.01 (d, J = 8.0 Hz, 10H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.2, 22.5, 33.9, 35.5, 58.7, 101.1, 122.8, 128.4, 128.7, 130.1, 131.7, 136.9, 142.9, 144.2, 144.5, 148.0, 148.9, 149.1, 151.9, 163.8; UV−vis (solution in CH_2Cl_2) $\lambda_{\max}$ (ε) 682 (1.1×10^4). Anal. Calcd for $C_{116}H_{69}S_2Co$: C, 87.85; H, 4.39. Found: C, 87.39; H, 4.39.

*4.2.4. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) 4-Fluorobenzene-1,2-dithiolate (**4**).* A mixture of cobalt trisulfide complex **1a** (120 mg, 78 μmol) and bis(4-fluorophenyl) disulfide (988 mg, 3.9 mmol) in chlorobenzene (6 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give a dark green solid of the title compound (18 mg, 16 μmol, 15%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.82 (t, J = 7.5 Hz, 15H), 1.15−1.20 (m, 10H), 1.39−1.43 (m, 10H), 2.39 (t, J = 7.5 Hz, 10H), 6.82 (dt, J = 2.5 Hz, J = 8.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 10H), 7.55 (dd, J = 9.0 Hz, 1H), 7.62 (dd, J = 2.5 Hz, J = 9.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 10H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 22.4, 33.8, 35.5, 58.6, 97.4, 101.0, 111.7, 116.1, 128.7, 128.8, 130.0, 130.1, 132.4, 136.7, 143.0, 144.1, 144.2, 144.3, 148.0, 148.9, 149.1, 151.7, 159.3; UV−vis (solution in CH_2Cl_2) $\lambda_{\max}$ (ε) 670 (1.1×10^4). Anal. Calcd for $C_{116}H_{68}S_2FCo$: C, 86.87; H, 4.27. Found: C, 86.66; H, 4.54.

*4.2.5. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) 4,5-Difluorobenzene-1,2-dithiolate (**5**).* A mixture of cobalt trisulfide complex **1a** (134 mg, 87 μmol) and bis(3,4-difluorophenyl) disulfide (1.3 g, 4.3 mmol) in chlorobenzene (8 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give a dark green solid of the title compound (22 mg, 14 μmol, 16%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.82 (t, J = 7.5 Hz, 15H), 1.16−1.20 (m, 10H), 1.40−1.46 (t, J = 7.5 Hz, 10H), 7.03 (d, J = 8.0 Hz, 10H), 7.39 (t, J = 9.0 Hz, 2H), 7.99 (d, J = 8.5 Hz, 10H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.0, 22.4, 33.6, 33.8, 35.5, 58.7, 58.8, 97.5, 97.8, 128.8, 128.9, 129.8, 129.9, 136.7, 136.8, 143.1, 143.2, 144.1, 144.2, 144.3, 147.8, 148.8, 149.0, 151.6, 151.8; UV−vis (solution in CH_2Cl_2) $\lambda_{\max}$ (ε) 672 (1.1×10^4). Anal. Calcd for $C_{116}H_{67}S_2F_2Co$: C, 85.91; H, 4.16. Found: C, 85.91; H, 4.40.

*4.2.6. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) 4-tert-Butylbenzene-1,2-dithiolate (**6**).* A mixture of cobalt trisulfide complex **1a** (231 mg, 150 μmol) and bis(4-*tert*-butylphenyl) disulfide (2.5 g, 7.5 mmol) in chlorobenzene (10 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give the dark green solid **6** (51 mg, 31 μmol, 21%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.83 (t, J = 6.5 Hz, 15H), 1.07 (s, 9H), 1.16−1.24 (m, 10H), 1.39−1.45 (m, 10H), 2.39 (t, J = 7.5 Hz, 10H), 6.98 (d, J = 8.0 Hz, 10H), 7.27−7.29 (m, 1H), 7.86 (d, J = 10.0 Hz, 1H), 7.91 (s, 1H), 8.03 (d, J = 8.0 Hz, 10H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 22.5, 30.7, 33.7, 34.6, 35.5, 58.7, 100.9, 121.6, 128.3, 128.7, 130.1, 142.8, 144.2 144.8, 145.9, 147.9, 148.8, 149.0, 151.9; UV−vis (solution in CH_2Cl_2) $\lambda_{\max}$ (ε) 675 (1.1×10^4). Anal. Calcd for $C_{120}H_{77}S_2Co$: C, 87.78; H, 4.73. Found: C, 87.63; H, 5.01.

*4.2.7. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) Cyclohexene-1,2-dithiolate (**7**).* A mixture of cobalt trisulfide complex **1a** (120 mg, 80 μmol) and dicyclohexyl disulfide (1.1 g, 4.8 mmol) in chlorobenzene (6 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give a dark green solid of the title compound (41 mg, 26 μmol, 32%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.84 (t, J = 7.5 Hz, 15H), 1.18−1.25 (m, 14H), 1.43−1.50 (m, 10H), 2.12 (br, 4H), 2.45 (t, J = 7.5 Hz, 10H), 7.04 (d, J = 8.0 Hz, 10H), 8.00 (d, J = 8.0 Hz, 10H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.2, 22.5, 22.8, 33.9, 35.6, 36.1, 58.6, 100.2, 128.5, 130.1, 137.7, 142.5, 144.2, 144.8, 147.9, 148.9, 149.1, 152.4, 172.2; UV−vis (solution in CH_2Cl_2) λ_{max} (ε) 640 (1.1 × 10^4). Anal. Calcd for $C_{116}H_{73}S_2Co$: C, 87.63; H, 4.63. Found: C, 87.37; H, 4.81.

*4.2.8. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) Benzene-1-aminate-2-thiolate (**8**).* A mixture of cobalt trisulfide complex **1a** (154 mg, 100 μmol) and bis(2-nitrophenyl) disulfide (1.5 g, 5.0 mmol) in chlorobenzene (7 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give the dark blue solid **5** (31 mg, 19 μmol, 19%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.82 (t, J = 7.5 Hz, 15H), 1.14−1.21 (m, 10H), 1.38−1.46 (m, 10H), 2.40 (t, J = 7.5 Hz, 10H), 6.80 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 10H), 7.37 (t, J = 8.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 10H), 10.53 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 22.5, 33.7, 35.4, 58.4, 98.2, 119.2, 119.9, 125.6, 128.8, 129.6, 131.9, 137.0, 142.8, 144.1, 144.8, 147.8, 148.7, 149.1, 152.5, 154.2, 165.0; UV−vis (solution in CH_2Cl_2) λ_{max} (ε) 628 (1.1 × 10^4). Anal. Calcd for $C_{116}H_{70}NSCo$: C, 88.81; H, 4.50; N, 0.89. Found: C, 87.96; H, 4.79; N, 0.88.

*4.2.9. Synthesis of Pentakis(4-n-butylphenyl)[60]fullerenyl Cobalt(III) Naphthalene-1,2-dithiolate (**9**).* A mixture of cobalt trisulfide complex **1a** (57.0 mg, 37 μmol) and dinaphthyl disulfide (589 mg, 1.85 mmol) in chlorobenzene (2.5 mL) was heated to 140 °C. The reaction was complete within 12 h to give a dark green solution, which could be monitored with HPLC (Buckyprep, toluene/^{i}PrOH 6/4). The resulting reaction mixture was filtered through a pad of silica gel, and the filtrate was reprecipitated with MeOH. The crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH 5.5/4.5) and reprecipitated with MeOH to give a dark green solid of the title compound (30 mg, 19 μmol, 50%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.80 (t, J = 7.5 Hz, 15H), 1.14−1.18 (m, 10H), 1.37−1.43 (m, 10H), 2.38 (t, J = 7.5 Hz, 10H), 6.97 (d, J = 8.5 Hz, 10H), 7.39−7.48 (m, 4H), 7.75 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 8.5 Hz, 10H), 8.79 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 14.1, 22.5, 33.7, 35.4, 58.6, 101.1, 124.0, 125.3, 126.9, 127.3, 128.3, 128.6, 129.9, 130.1, 130.2, 135.2, 137.0, 142.9, 144.2, 144.6, 147.9, 148.8, 149.1, 152.0, 164.1, 165.2; UV−vis (solution in CH_2Cl_2) λ_{max} (ε) 705 (1.1 × 10^4). Anal. Calcd for $C_{120}H_{71}S_2Co$: C, 88.10; H, 4.39. Found: C, 87.65; H, 4.45.

4.3. Electrochemical Measurements. Electrochemical measurements were performed using a BAS CV-50W voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and the reference electrode was a Ag/Ag$^+$ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half-wave potentials $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc$^+$.

4.4. Device Fabrications and Evaluation. Organic solar cells having a p−n structure were fabricated as follows. An ITO-coated glass substrate was exposed to UV ozone prior to usage and was then coated with PEDOT:PSS (CLEVIOS P VP AI4083). The substrate was first heated to 120 °C for 10 min in air. A 0.5 wt % solution of 1,4:8,11:15,18:22,25-tetraethano-29H,31H-tetrabenzo[b,g,l,q]-porphyrin (CP; a precursor of tetrabenzoporphyrin (BP)) in chlorobenzene/chloroform (2/1 w/w) was spin-coated on the PEDOT:PSS layer. The resulting film was heated to 180 °C for 20 min, converting the soluble CP to insoluble crystalline BP, which serves as a p layer. The thickness of the crystallized BP p layer was ~30 nm. On top of the BP layer, a 0.5 wt % solution of the pentakis(aryl)[60]fullerene cobalt ditholene complex in toluene was spin-coated (1000 rpm) as an n layer. The thickness of the n layer using **8** was ~30 nm. After thermal annealing of the p−n film, a Ca/Al electrode (Ca, 20 nm; Al, 80 nm) was deposited onto the film by thermal evaporation through a shadow mask, resulting in a device with an active area of 0.04 cm^2. The current density−voltage characteristics under AM 1.5G solar illumination (100 mW cm^{-2}) was recorded using a Keithley 2400 source measurement unit.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving UV−vis spectra for **4**, **5**, and **7**, J−V characteristics for **9**, and ^{1}H and ^{13}C NMR spectra for **3**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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