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π-Conjugated Multidonor/Acceptor Arrays of Fullerene−Cobaltadithiolene−Tetrathiafulvalene: From Synthesis and Structure to Electronic Interactions

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Abstract: The synthesis, structure, photoelectrochemical behavior, and nonlinear optical (NLO) properties of a symmetric acceptor−acceptor−donor−acceptor−acceptor array, C_{60}-Co−TTF−Co-C_{60}, have been described. The precursors, namely, cobalt dicarbonyl complexes $Co(C_{60}Ar_5)(CO)_2$ were synthesized from the penta(organo)[60]fullerenes, $C_{60}Ar_5H$, as starting materials. In the next step, two cobalt−fullerene complexes were connected to a tetrathiafulvalene (TTF) tetrathiolate bridge to obtain the C_{60}-Co−TTF−Co-C_{60} array. In addition, the monomeric compounds, $Co(C_{60}Ar_5)(S_2C_2R_2)$ ($R = CO_2Me$ and CN) and $Co(C_{60}Ar_5)(S_2C_2S_2\,C{=}CS_2C_2R_2)$ were synthesized as references. The C_{60}-Co−TTF−Co-C_{60} array exhibits very strong transitions in the near-infrared region ($\lambda_{max} = 1{,}100$ nm, $\varepsilon = 30\,000\ M^{-1}\cdot cm^{-1}$) due to a ligand-to-metal-charge-transfer (LMCT) transition and six reversible electron transfer processes. In the crystal, a fullerene/TTF-layered packing structure is evident. Femtosecond flash photolysis revealed that photoexcitation of the array results in a charge separated state involving the strongly interacting cobaltadithiolene and TTF constituents which electronically relax via a resonance effect that extends all throughout the acceptor parts of the C_{60}-Co−TTF−Co-C_{60} array. The third-order NLO measurement of the array gave the magnitude of the third-order nonlinear susceptibility, $|\chi^{(3)}|$, values to be 9.28×10^{-12} esu, suggesting the π-conjugation of donors and acceptors in the array.

Introduction

Connecting and integrating several electron−donor and −acceptor moieties into π-conjugated donor/acceptor arrays have received tremendous attention owing to their unique applications in organic conductive materials,[1] nonlinear optical (NLO) materials,[2] near-infrared dyes,[3] molecular wires,[4] and so on. π-Conjugated donor/acceptor arrays differ from conventional donor−spacer−acceptor hybrids/conjugates by virtue of their high charge mobility. It is mainly the larger mobility rate that leads to faster response times when interacting with, for example, light. In comparison to ordinary π-electron conjugated systems such as π-conjugated wires and ribbons,[5] the π-conjugated donor/acceptor arrays may undergo charge separation under light or even in the dark via charge transfer from the donor to the acceptor. Such interactions impart unique physical features that range, for instance, from narrow HOMO−LUMO gaps to high polarizabilities. In particular, the former has recently attracted increased interests concerning photoelectric conversion.[6]

Attempts have been made to obtain a wide range of π-conjugated donor/acceptor molecules and polymers.[7] Alternatively, donors and acceptors are assembled in the crystal lattice through molecular association,[8] which is known as crystal

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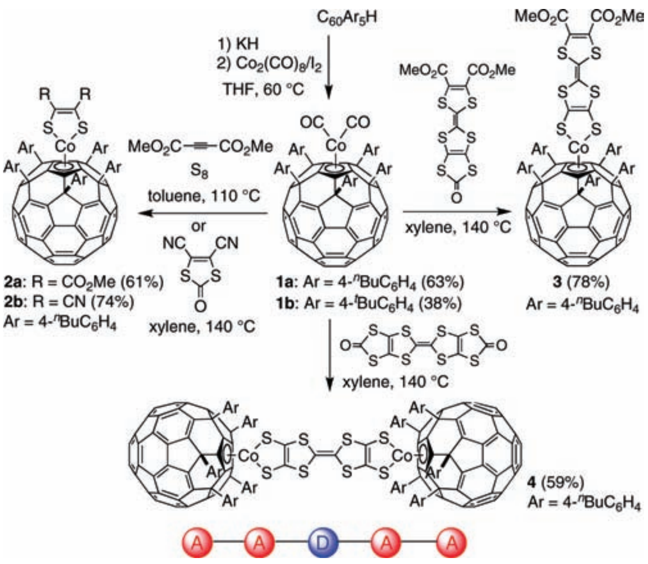
10.1021/ja902312q CCC: $40.75

Scheme 1



engineering.[9] Herein, we report the two-step synthesis, structure, and photophysical functions of a symmetric acceptor−acceptor−donor−donor−acceptor−acceptor array (Scheme 1), which combines two fullerenes, two cobaltadithiolenes, and one tetrathiafulvalene (TTF) to afford C_{60}-Co−TTF−Co-C_{60} (**4**).

The compound **4** represents a multiredox dπ-conjugated donor−acceptor array, which differs from previously reported donor−fullerene dyads for its compact and rigid one-dimensional structure.[10−12] Electrochemical and time-resolved photophysical investigations revealed its multielectron redox behavior, near-infrared light absorption, and resonant electronic interaction within the symmetric molecule. In addition, NLO studies were performed, since the one-dimensional confinement of the electron is of general interest in the area of optical devices. In fact, our results corroborate the π-conjugation between the donors and acceptors in the array. Given the growing interest in the design of molecules that are applicable as photoelectronically active materials, in both organic electronic device[13] and molecular functional device[14] areas, the present motif with multiple electron donor−acceptor arrays will open myriad opportunities in these fields.

Result and Discussion

Synthesis and Structural Characterization of the Fullerene−Cobaltadithiolene−TTF Arrays. The synthesis was started with preparing a new cobalt dicarbonyl complexes of penta(aryl)[60]fullerenes (Scheme 1). Treatment of $C_{60}Ar_5H$[15] with KH in THF generated a potassium complex K(thf)$_n$($C_{60}Ar_5$),[16] which was reacted with a cobalt iodide complex[17] derived from $Co_2(CO)_8$ and I_2 in THF to afford the dicarbonyl complexes, Co($C_{60}Ar_5$)(CO)$_2$ (**1a**, Ar = 4-^{n}BuC$_6$H$_4$; **1b**, Ar = 4-^{n}BuC$_6$H$_4$) in 61% and 38% yield, respectively. Structural characterization of this starting material was done by single crystal X-ray analysis of **1b**.[18] We next synthesized the cobaltadithiolene complexes, since the cobaltadithiolenes generally represent a light-absorbing, redox-active organometallic π-system. The reaction of **1a** with excess amounts of electron-deficient alkyne and S_8 in toluene at 110 °C produced the cobaltadithiolene fullerene complex **2a** in 61% yield. Alternatively, **1a** was reacted with 4,5-dicyano-1,3-dithiol-2-one (10 equiv) in xylene at 140 °C to obtain **2b** in 74% yield. Then, we selected TTF as a photophysically and electrochemically active organic bridge to expand the π-conjugated molecular array. Carbonyldithio-bis(methoxyl carbonyl)tetrathiafulvalene (1.2 equiv) was treated with **1a** under the same conditions to produce C_{60}-Co−TTF complex **3** in 78% yield. Finally, C_{60}-Co−TTF−Co-C_{60} complex **4** was obtained in 59% yield by the reaction of **1a** with bis(carbonyldithio)tetrathiafulvalene (2 equiv) under similar conditions.

All the cobalt compounds (**1**−**4**) were stable in air, and were either purified by silica gel column chromatography or by HPLC (i.e., equipped with a Buckyprep column). It is likely that the stability of **4** originates from protecting effects of the penta(aryl)[60]fullerenes,[19] while the core structure TTF tetrathiolato bismetal complexes are known to be air-sensitive in general.[20]

The molecular structure of C_{60}-Co−TTF−Co-C_{60} (**4**) was unambiguously determined by X-ray crystallographic analyses (Figure 1a). We obtained two polymorphic crystals from different solvent systems. Dark green single crystals of **4**·(CS_2)·(C_6H_6) and **4**·(PhCl) were successfully obtained by slow diffusion of diethyl ether or ethanol into benzene/CS_2 (1/1) or chlorobenzene solution of **4**. Molecular length of a long axis with van der Waals radii was 22.8 Å. A crystal packing view of **4**·(CS_2)·(C_6H_6) (Figure 1b) revealed a lamellar struc-

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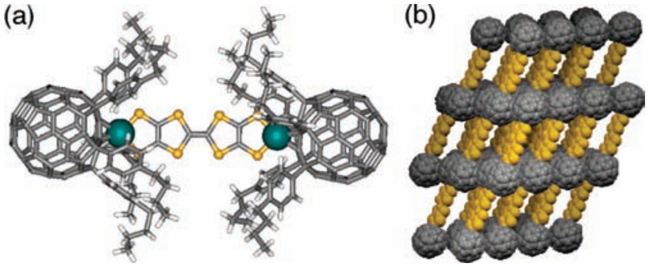

Figure 1. X-ray crystal structure of $4\cdot(CS_2)\cdot(C_6H_6)$. Solvent molecules are omitted for clarity. (a) Ball and stick drawing. Location of the carbon atoms in the butyl chains were optimized with geometrical restraints on the SHELX97 program.[23] (b) CPK drawing of the crystal packing. The butyl phenyl groups are omitted for clarity.

ture[21] containing fullerene and TTF in alternative layer, where fullerene parts are closely packed through van der Waals interactions within the same layer.[22] The interlayer distance was 19.4 Å.

Ground and Excited State Features. First, the ground state features of **2b**, **3**, and **4** are considered. They are all dominated by broad absorptions centering at 684 nm (1.81 eV) for **2b** (Figure 2b), 934 nm (1.33 eV) for **3** (Figure S6), and 1100 nm (1.13 eV) for **4** (Figure 2a) with extinction coefficients in the range of 10 000, 15 000, and 30 000 M^{-1} cm^{-1}, respectively.[24] Notable is the red-shift of the absorption maximum when contrasting **2b**, **3**, and **4** with the corresponding cyclopentadienyl cobaltadithiolene, $CpCoS_2C_2(CN)_2$ ($\lambda_{max} = 559$ nm).[25] Implicit are strong electronic interactions between the different constituents (i.e., C_{60},[26] cobaltadithiolene, and TTF), that is, partial redistribution of charge density between the electron donating (i.e., TTF) and electron accepting (i.e., cobaltadithiolene) constituents. There is no ground state charge separation as suggested by the fact that **4** is NMR active. This is corroborated by the lack of appreciable fluorescence due to the two penta(organo)[60]fullerene moieties ($\ll 10^{-5}$), which are expected to show stronger fluorescence (quantum yield of 2.2×10^{-3}). The long-wavelength absorptions are assigned to LMCT bands that are centered at the cobaltadithiolene part, whose absorption bands are known to shift in the presence of extended π-systems.[25]

Further support for this notion came from the cyclic voltammetric measurements. In the anodic range, array **4** gives rise to two reversible one-electron oxidation processes that are centered at TTF (0.12 and 0.42 V) and that correspond to the formation of the radical cation and dication, respectively. In the cathodic range, two reversible one-electron reduction processes are associated with the step-by-step reduction of the two cobaltadithiolenes (−1.07 and −1.30 V), while a reversible two-electron reduction process relates to the simultaneously occurring reduction of the two C_{60} (−1.68 V) (Figure 2c,d).[27] Relative to penta(organo)[60]fullerenes that show reduction potentials at ca. −1.4 V,[28] the reduction of the fullerene moiety in **4** is negatively shifted by ca. 0.3 V due to electronic interactions with the anion of the cobaltadithiolene moieties.

Overall, a remarkably small energy gap of 1.19 eV evolves, when considering the lowest oxidation (0.12 V) and lowest reduction (−1.07 V) potentials of the TTF and cobaltadithiolene, respectively. Such a value is in excellent agreement with the optically determined band gap of 1.13 eV.[29] These LMCT features are solvent independent, that is, no appreciable shifts evolve when the solvent polarity is increased gradually from toluene to benzonitrile. The presence of the butyl phenyl groups is likely to be responsible for this trend, since they shield the TTF/cobaltadithiolene couple from the surrounding solvent. A similar picture evolves for **2b** (*vide infra*) and **3** (see Supporting Information). For **2b**, oxidation is limited to a dithiolene centered process (1.05 V), while sequential reduction of cobaltadithiolene and C_{60} transpire at −0.61 and −1.49 V. Again, considering the lowest oxidation (1.05 V) and lowest reduction (−0.61 V) potentials, we derive an energy gap of 1.67 eV, which matches the optical band gap of 1.82 eV. An independent proof for the LMCT character came from the selective reduction of the metal by means of radiolytical and spectroelectrochemical means. To this end, differential absorption spectra reveal bleach at 1110 (**4**), 934 (**3**), and 680 nm (**2b**), which mirror images the ground state absorption. Implicit is that the reduced metal lacks the susceptibility to accept electrons from TTF in the ground state.

In the next stage, transient absorption measurements[30] were performed for **2b**, **3**, and **4** to examine the electronic interactions between the redox- and the photoactive components.[31,32] In **4**, commencing with the 388 nm laser excitation, where the fullerene moiety contributes more than 95% to the overall absorption, the instantaneous formation of a new transient (i.e., 1.5 ps) is registered (Figure 3, upper panel). In the visible range of the transient spectrum, fine structured features are seen with a minimum at 610 nm and maxima at 460 and 540 nm. In the near-infrared range, the new features include a broad transient bleach at around 1060 nm and a broad transient maximum at 1315 nm. Considering the perfect match with the spectroelectrochemically generated spectra (see Figures S11 and S12), we infer the prompt formation of a charge separated state involving the strongly interacting cobaltadithiolene and TTF constituents.[33,34]

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(31) In compound **2b**, the cobaltadithiolene moiety acts as an electron donor. Oxidation occurs at the cobaltadithiolene, while reduction can occur at both cobaltadithiolene and penta(organo)[60] fullerene moieties; see Supporting Information.

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(33) Excitation with 388 and 1100 nm light led to the same observation.

(34) Notable are, however, the differences seen relative to the separate constituents, that is, one-electron oxidized TTF and one-electron reduced cobaltadithiolene with marked features limited to the visible range.

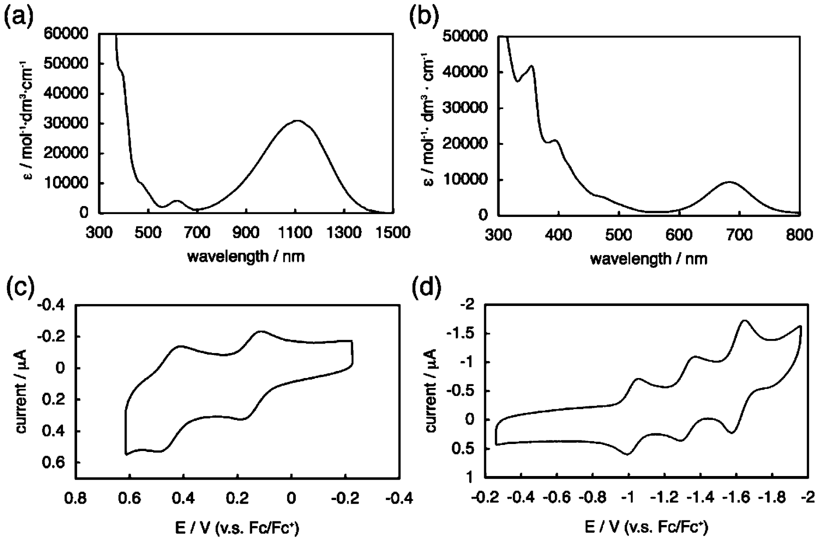

Figure 2. Photophysical and electrochemical properties of **2b** and **4**. (a) UV−vis-NIR spectrum of **4** in toluene. (b) UV−vis-NIR spectrum of **2b** in toluene. (c) Oxidation waves on the cyclic voltammogram of **4** in CH_2Cl_2 containing $^{n}Bu_4NClO_4$ as supporting electrolyte. (d) Reduction waves on the cyclic voltammogram of **4** in THF containing the same supporting electrolyte.

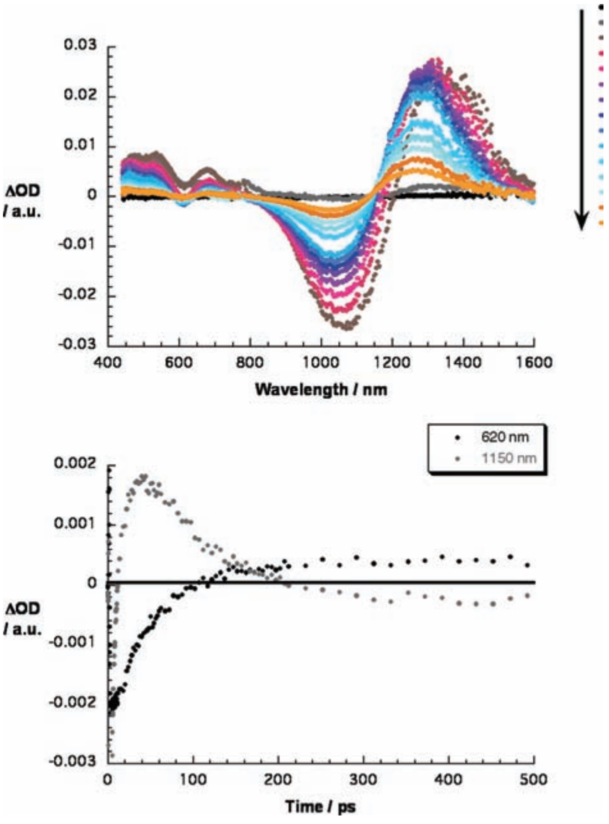

Figure 3. Time-resolved photophysical data for **4**. (Upper panel) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (388 nm - 200 nJ) of **4** (10^{-6} M) in THF with several time delays between 0 and 200 ps at room temperature; see legend for details about the time progression. (Lower panel) Time-absorption profiles of the spectra at 620 and 1150 nm.

Interestingly, with time, the near-infrared features shift to the blue, that is, to 1020 and 1260 nm, respectively. Less obvious are the changes in the visible part, that is, a blue-shift from 540 to 525 nm. The time absorption profiles taken at 620 and 1150 nm (see Figure 3) further corroborate this step. A likely rationale implies electronic relaxation of the charge separated state with a resonance effect that extends all throughout the acceptor parts of the array on a time scale of up to 40 ps in THF (Figure 3, lower panel). For example, the electrons may undergo equilibration between the two acceptor terminal, namely, cobaltadithiolene/$C_{60}Ar_5$.[35] Such a mechanism has been proposed in the past, although it has never been confirmed spectroscopically.[36] Although there is no doubt about the primary electron acceptors, namely, the cobaltadithiolenes, the C_{60} part acts only as secondary electron acceptors (*vide infra*), charge equilibration may as well be anticipated to occur between the primary and secondary electron acceptors.

On a time scale of up to 300 ps, we observed the decay of the relaxed/equilibrated charge separated state. The latter decay is accompanied by a long-lived state, a triplet excited state that is located predominantly on the fullerene part.[37] Characteristics include a transient maximum at 640 nm and an excited state lifetime of about 3 to 4 μs (see Figure S13). The mechanism by which the triplet excited state is formed remains unclear at present; possible pathways include charge recombination or intersystem crossing from a localized singlet excited state.

In **3**, the presence of just one acceptor terminal impacts the dominating LMCT absorptions, which are now shifted to 925 nm in THF. Still, upon excitation, the differential absorption changes reveal strong changes in the visible and near-infrared regions. Prevailing is the minimum at 925 and the maximum at 1230 nm (Figure 4, upper panel). These features are formed instantaneously (i.e., <2 ps). In other words, **3** and **4** give rise to a similar spectral pattern, which prompts to the unique combination of C_{60} and cobaltadithiolene as well as TTF. Unlike to what has been seen for **4**, the excited state of **3** lacks any notable shifts during the relaxation step. Kinetic confirmation

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(35) Note that the penta(organo)[60]fullerene radical anion exhibits absorption maximum at 1,100 nm. See. ref. 15a The value is smaller than absorption maximum for the TTF cation of **4** (1260 nm). This is the origin of the blue-shift in the relaxation process.

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(37) When this triplet state of **4** is compared with those of the references ($C_{60}Ph_5H$ and $Ru(C_{60}Ph_5)Cp$), the absorption maximum (660 nm) is identical. Lifetime (3∼4 ms in toluene) is shorter than that of $C_{60}Ph_5H$ (14 ms in benzonitrile), but longer than $Ru(C_{60}Ph_5)Cp$ (1.5 ms in benzonitrile). See ref 30a.

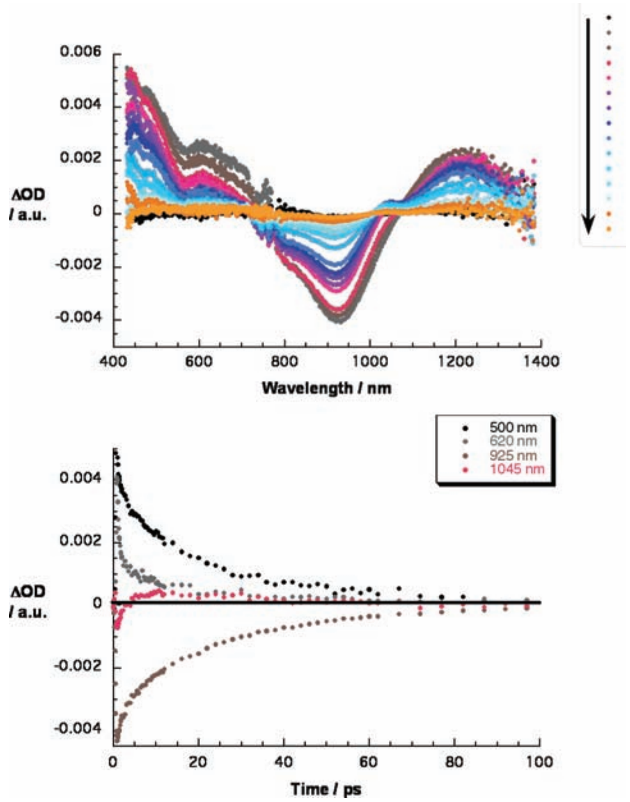

Figure 4. Time-resolved photophysical data for **3**. (Upper panel) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (388 nm - 200 nJ) of **3** (10^{-6} M) in THF with several time delays between 0 and 50 ps at room temperature; see legend for details about the time progression. (Lower panel) Time-absorption profiles of the spectra shown above at 500, 620, 925, and 1045 nm.

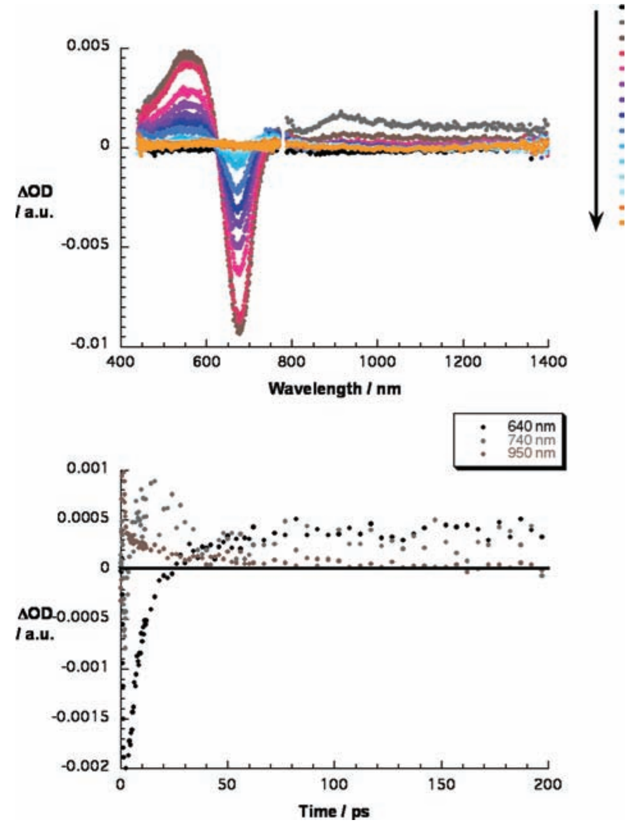

Figure 5. Time-resolved photophysical data for **2b**. (Upper panel) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (388 nm - 200 nJ) of **2b** (10^{-6} M) in THF with several time delays between 0 and 50 ps at room temperature; see legend for details about the time progression. (Lower panel) Time-absorption profiles of the spectra shown above at 640, 740, and 950 nm.

for the relaxation came from the time absorption profiles at 500, 620, 925, and 1045 nm. Important is that the relaxation is much faster (i.e., ~10 ps; Figure 4, lower panel) than what has been detected for **4**. Considering the lack of two acceptor terminals in **3**, this leaves the resonance between the primary and secondary electron acceptor as the only viable mechanism. Commencing with this relaxation, we note the decay of the relaxed/equilibrated charge separated state, which depends strongly on the solvent polarity: toluene − 43 ps; THF − 36 ps; benzonitrile − 65 ps. Beyond this time, a 640 nm maximum was detected in the femtosecond and complementary nanosecond experiments. In **3**, like in **4**, the lifetime of this triplet excited state is affected by the presence of molecular oxygen to generate correspondingly singlet oxygen.

Finally, changes associated with **2b** shall be discussed, which lacks TTF. The differential absorption changes are mainly limited to the visible region, where a maximum at 550 nm and a minimum at 680 nm (Figure 5, upper panel) are formed within 2.0 ps following the excitation. The minimum correlates with the maximum of the LMCT ground state absorption at 680 nm. On the other hand, much weaker are the characteristics in the near-infrared region with maxima at 960 and 1080 nm. Like what has been seen for **3**, no spectral shifts were noted to take place during the 10 ps relaxation. The relaxed excited state in **2b** decays quickly with solvent independent kinetics (i.e., 21 ps; Figure 5, lower panel).

Nonlinear Optical Properties of the Array. The third-order NLO properties of the array **4** and the reference **3** were investigated and the magnitudes of third-order nonlinear susceptibility, $|\chi^{(3)}|$, for cast films on SiO_2 substrates were evaluated by the third-harmonic generation (THG). The photon energy of the excitation laser was tuned as one-third of the absorption peak energy of each compound, where the three-photon resonance was expected. The obtained $|\chi^{(3)}|$ values are 9.28×10^{-12} esu for **4** at 0.376 eV (3300 nm) and 4.73×10^{-12} esu for **3** at 0.422 eV (2934 nm). The 2-fold enhancement of $|\chi^{(3)}|$ values observed in **4** can be ascribed to the symmetric charge-transfer (CT) excitation in the molecule.

The observed $|\chi^{(3)}|$ values were compared with three-photon resonant $|\chi^{(3)}|$ of other organic CT conjugated materials. Third-order optical nonlinearity of donor−acceptor type CT conjugated polymers has been reported.[2] Poly(thiophene-*alt*-quinoxaline) (PThQx), which is known to have strong CT character between donor and acceptor molecules,[1] showed enhanced optical nonlinearity.[2a] When comparing different systems, one should pay attention to the difference in the density of π-electrons. $|\chi^{(3)}|$ values are proportional to the density of π-electrons, defined as π-electron numbers on a molecule divided by the molecular volume, which depends on the molecular structures including nonconjugated side groups. To extract the optical nonlinearity inherent to π-conjugated systems, we adopted the figure of merit defined as $|\chi^{(3)}|/\alpha$ (α: absorption coefficient). Since both $|\chi^{(3)}|$ and α are proportional to the density of π-electrons, the difference in the density of π-electrons is canceled in $|\chi^{(3)}|/\alpha$. $|\chi^{(3)}|/\alpha$ of **4** and **3** is 3.29×10^{-16} and 1.66×10^{-16} esu cm, respectively, and that of PThQx evaluated by the three-photon resonant THG process reaches 4.26×10^{-16} esu cm, while that of homopolymer consisting of a single component with no CT character, regioregular poly(3-hexylthiophene) (RR-P3HT), is 2.41×10^{-16} esu cm. A comparison with these polymers reveals that the compound **4** has larger $|\chi^{(3)}|/\alpha$ than a non-CT polymer RR-P3HT, but a smaller value than a CT conjugated polymer PThQx. Considering that one-dimensional confinement enhances the optical nonlinearity in the polymer materials, the observed optical nonlinearity in **4** is quite large and the CT in the excited states largely enhances the optical nonlinearity.

Conclusion

Two fullerenes, two cobaltadithiolenes, and one TTF bridge were assembled into a compact and rigid one-dimensional donor/acceptor array **4** that shows reversible multielectron redox behavior, accepting and giving up a total of six electrons, and near-infrared light absorption at 1100 nm. Electronic interactions within the array were elucidated by femtosecond flash photolysis experiments and third-order NLO measurements. The former time-resolved studies indicated relaxation of the charge separated state, involving the strongly interacting cobaltadithiolene and TTF constituents, which is formed initially, via a resonance effect that extends all throughout the acceptor parts of the array. The latter optical studies revealed large optical nonlinearity of the array roughly being in the middle of CT polymers and conjugated polymers. One-dimensional structure as well as electrochemical, photophysical, optical properties of **4** will provide a unique wire motif for molecular electronics.[38−40] Crystal engineering that can make fullerene/TTF layered structures also suggests the use of **4** in organic thin-film devices[41] and crystalline organic electronic devices.[42] Potentially ambipolar nature and light absorption at long wavelength region with relatively large absorption coefficiency will be of immense interest in this field.

Experimental Section

General. All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Toluene and THF were used as dried over Na and distilled before use. *p*-Xylene was distilled over CaH_2 before use. All NMR spectra were recorded on JEOL ECA-500, and reported in parts per million (ppm, δ scale) form internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^1H NMR (δ 7.15 ppm for C_6D_6) and solvent carbon for ^{13}C NMR (δ 128 ppm for C_6D_6). Elemental analysis was performed at the University of Tokyo, Department of Chemistry, Organic Elemental Analysis Laboratory. UV−vis-NIR spectra were recorded on JASCO V-570.

$Co[C_{60}(4\text{-}^nBuC_6H_4)_5](CO)_2$ (1a). A suspension of $C_{60}(4\text{-}^nBuC_6H_4)_5H$ (0.300 g, 0.22 mmol) and excess amount of KH (dispersed in oil) in THF (2.0 mL) was warmed up to 60 °C and stirred for 30 min. To a solution of $Co_2(CO)_8$ (0.25 g, 0.73 mmol) in THF (1.5 mL) in another Schlenk tube was slowly added I_2 (0.15 g, 0.59 mmol) to turn green with gas evolution. To the green solution was added the solution of $KC_{60}(4\text{-}^nBuC_6H_4)_5$ slowly as unreacted KH residue remained, and then the reaction mixture was warmed up to 60 °C. After 15 min stirring, the mixture was diluted with toluene and filtered through a pad of silica gel. The filtrate was reprecipitated with MeOH. Obtained crude mixture was purified with preparative HPLC (Nacalai Tesque, Buckyprep, toluene/^{i}PrOH = 5/5) to afford **1a** (0.204 g, 0.136 mmol, 63%) as orange solid. ^1H NMR (500 MHz, C_6D_6) δ: 0.83 (t, J = 7.5 Hz, 15H, CH_3), 1.21 (m, 10 H, CH_2), 1.46 (m, 10H, CH_2), 2.46 (t, J = 7.5 Hz, 10H, CH_2), 7.09 (d, J = 8.6 Hz, 10H, Ar), 7.99 (d, J = 8.6 Hz, 10H, Ar); ^{13}C NMR (125 MHz, C_6D_6) δ: 14.0 (5C, CH_3), 22.5 (5C, CH_2), 33.7 (5C, CH_2), 35.5 (5C, CH_2), 58.2 (5C, $C_{60}(sp^3)$), 109.4 (5C, C_{60}(Cp)), 128.8, 129.1, 139.2, 142.9, 144.2, 145.0, 147.7, 148.7, 149.2, 152.1, 210.8 (2C, CO); Anal. Calcd for $C_{112}H_{65}O_2Co$: C, 89.58; H, 4.36. Found: C, 89.35; H, 4.57.

$Co[C_{60}(4\text{-}^tBuC_6H_4)_5](CO)_2$ (1b). The procedure described for **1a** was performed to obtain orange solid **1b** (0.120 g, 0.083 mmol, 38%). ^1H NMR (500 MHz, C_6D_6) δ: 1.25 (s, 45H, ^{t}Bu), 7.34 (d, J = 8.6 Hz, 10H, Ar), 8.04 (d, J = 8.0 Hz, 10H, Ar); ^{13}C NMR (500 MHz, C_6D_6) δ: 31.3, 34.5, 58.1, 109.2, 125.6, 128.9, 138.7, 144.2, 145.1, 147.7, 148.7, 149.2, 151.1, 152.2, 201.3 (CO); Anal. Calcd for $C_{112}H_{65}O_2Co$: C, 89.58; H, 4.36. Found: C, 89.35; H, 4.60.

$Co[C_{60}(4\text{-}^nBuC_6H_4)_5][(S_2C_2)(CO_2Me)_2]$ (2a). A solution of **1a** (20.0 mg, 13.3 μmol), elemental sulfur (4.3 mg, 0.13 mmol) and dimethyl acetylenedicarboxylate (4.2 μL, 1.3 mmol) in toluene (5.0 mL) was heated at 110 °C for 2 days. The resulting dark green reaction mixture was filtered through a pad of silica gel, and then the filtrate was reprecipitated with MeOH. Obtained crude mixture was subjected to silica gel column chromatography (toluene as eluent). A green band was collected and reprecipitated with MeOH to afford **2a** (13.4 mg, 8.1 μmol, 61%) as green solid. ^1H NMR (500 MHz, C_6D_6) δ: 0.85 (t, J = 7.2 Hz, 15H, CH_3), 1.21 (m, 10 H, CH_2), 1.46 (m, 10H, CH_2), 2.42 (t, J = 7.7 Hz, 10H, CH_2), 3.45 (s, 6H, CH_3), 7.02 (d, J = 8.0 Hz, 10H, Ar), 7.87 (d, J = 8.0 Hz, 10H, Ar); ^{13}C NMR (125 MHz, C_6D_6) δ: 14.1 (5C, CH_3), 22.5 (5C, CH_2), 33.7 (5C, CH_2), 35.4 (5C, CH_2), 58.5 (5C, $C_{60}(sp^3)$), 102.0 (5C, C_{60}(Cp)), 128.8, 129.8, 136.6, 143.3, 144.2, 144.3, 147.9, 148.8, 149.1, 151.5, 165.1, 165.8; UV−vis (solution in CH_2Cl_2) λ_{max} (ε): 640 (0.98×10^4); Anal. Calcd for $C_{116}H_{71}O_4S_2Co$: C, 84.34; H, 4.33. Found: C, 84.17; H, 4.46.

$Co[C_{60}(4\text{-}^nBuC_6H_4)_5][S_2C_2(CN)_2]$ (2b). A solution of **1a** (20.0 mg, 13.3 μmol) and 4,5-dicyano-1,3-dithiol-2-one (22.4 mg, 0.133 mmol) in *p*-xylene (5.0 mL) was heated at 140 °C for 10 h. The resulting dark green reaction mixture was diluted with toluene (5 mL), and filtered through a pad of silica gel. The filtrate was reprecipitated with MeOH to give dark yellow-green solid. Obtained crude mixture was subjected to silica gel column chromatography (toluene/hexane = 2/1). A green band was collected and reprecipitated with MeOH to afford dark green solid **2b** (15.7 mg, 9.9 μmol, 74%). ^1H NMR (500 MHz, C_6D_6) δ: 0.90 (t, J = 7.3 Hz, 15H, CH_3), 1.23 (m, 10 H, CH_2), 1.49 (m, 10H, CH_2), 2.43 (t, J = 7.7 Hz, 10H, CH_2), 7.02 (d, J = 8.6 Hz, 10H, Ar), 7.75 (d, J = 8.6 Hz, 10H, Ar); ^{13}C NMR (125 MHz, C_6D_6) δ: 14.1 (5C, CH_3), 22.4 (5C, CH_2), 33.8 (5C, CH_2), 35.4 (5C, CH_2), 58.5 (5C, $C_{60}(sp^3)$), 100.3 (5C, C_{60}(Cp)), 103.2, 129.0, 129.8, 136.1, 143.8, 144.3, 144.3, 145.0, 147.9, 148.9, 149.1, 150.7, 166.6; UV−vis-NIR (solution in CH_2Cl_2) λ_{max} (ε): 683 (0.94×10^4); Anal. Calcd for $C_{114}H_{65}N_2S_2Co$: C, 86.34; H, 4.13; N, 1.77. Found: C, 86.07; H, 4.28; N, 1.54.

$Co[C_{60}(4\text{-}^nBuC_6H_4)_5][S_2C_2S_2C{=}CS_2C_2(CO_2Me)_2]$ (3). A solution of **1a** (20.0 mg, 13.3 μmol) and dimethyl 2-(5-oxo-[1,3]dithiolo[4,5-*d*][1,3]dithiol-2-ylidene)-1,3-dithiole-4,5-dicarboxylate[43] (6.5 mg, 15.8 μmol) in *p*-xylene (10 mL) was heated at 140 °C for 1 h. The resulting red reaction mixture was diluted with toluene (5 mL), and filtered through a pad of silica gel. The filtrate was reprecipitated with MeOH to give dark red solid, which was subjected to silica gel column chromatography (toluene as eluent). A dark red band was collected and reprecipitated by MeOH to afford

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3 (19.1 mg, 10.4 μmol, 78%) as dark orange solid. ^{1}H NMR (500 MHz, C_6D_6) δ: 0.87 (t, J = 7.5 Hz, 15H, CH_3), 1.22 (m, 10 H, CH_2), 1.48 (m, 10H, CH_2), 2.45 (t, J = 7.5 Hz, 10H, CH_2), 3.18 (s, 6H, CH_3), 7.10 (d, J = 8.0 Hz, 10H, Ar), 8.04 (d, J = 7.1 Hz, 10H, Ar); ^{13}C NMR (125 MHz, C_6D_6/CS_2) δ: 14.2 (5C, CH_3), 22.5 (5C, CH_2), 33.9 (5C, CH_2), 35.5 (5C, CH_2), 52.7 (2C, CH_3), 58.4 (5C, C_{60}(sp^3)), 99.5 (5C, C_{60}(Cp)), 128.8, 130.0, 132.0, 143.2, 144.2, 144.5, 147.8, 148.8, 149.1, 151.9, 159.6, 165.5; UV−vis-NIR (solution in CH_2Cl_2) λ_{max} (ε): 934 (1.5 × 10^4); Anal. Calcd for $C_{120}H_{71}O_4S_6Co$: C, 78.84; H, 3.91. Found: C, 79.06; H, 4.19.

[Co{C_{60}(4-^{n}BuC_6H_4)$_5$}($S_2C_2S_2C$)]$_2$ (4). A solution of **1a** (10 mg, 6.7 μmol) and bis(carbonyldithio)tetrathiafulvalene (5.1 mg, 13 μmol) in *p*-xylene (2.0 mL) was heated at 140 °C for 4 h. The resulting dark yellow reaction mixture was diluted with toluene (5 mL), and filtered through a pad of silica gel. The filtrate was reprecipitated with MeOH to give dark yellow-green solid, which was purified with preparative HPLC separation (Buckyprep, toluene/^{i}PrOH = 8/2) to afford **4** (6.3 mg, 2.0 μmol, 59%) as dark green solid. ^{1}H NMR (500 MHz, C_6D_6) δ: 0.93 (t, J = 7.5 Hz, 15H, CH_3), 1.29 (m, 10 H, CH_2), 1.54 (m, 10H, CH_2), 2.51 (t, J = 7.5 Hz, 10H, CH_2), 7.10 (d, J = 8.1 Hz, 10H, Ar), 8.05 (d, J = 8.0 Hz, 10H, Ar); ^{13}C NMR (125 MHz, C_6D_6/CS_2) δ: 14.5 (5C, CH_3), 22.9 (5C, CH_2), 34.0 (5C, CH_2), 35.7 (5C, CH_2), 58.1 (5C, C_{60}(sp^3)), 99.1 (5C, C_{60}(Cp)), 120.0 (2C, sp^2), 128.7, 129.8, 137.2, 142.8, 144.1, 144.4, 147.8, 148.7, 149.0, 151.6, 164.9 (4C, sp^2); UV−vis-NIR (solution in CH_2Cl_2) λ_{max} (ε): 1100 (3.1 × 10^4), 613 (4.5 × 10^3); Anal. Calcd for $C_{226}H_{130}S_8Co_2$: C, 84.08; H, 4.08. Found: C, 84.30; H, 4.07.

Flash Photolysis Experiments. Femtosecond transient absorption studies were performed using the 388 nm laser pulses of 150 fs pulse width and 200 nJ energy, generated by a beta-Barium borate crystal upon higher order non-linear processes from an amplified Ti:Sapphire laser system (CPA 2001 Laser, Clark-MXR, Inc.). Nanosecond laser flash photolysis experiments were performed with 337-nm laser pulses from a nitrogen laser (8-ns pulse width) in front face excitation geometry.

Third Harmonic Generation (THG). The evaluation of $|\chi^{(3)}|$ was performed with the standard Maker's fringe method,[44] where the reference sample was SiO_2.[45] The excitation light was generated by combining a femtosecond regenerative amplifier system, Spitfire Pro (SpectraPhysics), and an optical parametric amplifier, TOPAS (Light conversion). By difference frequency generation of signal and idler lights from TOPAS, we obtained the excitation light of 3300 and 2934 nm. To avoid the effect of THG from ambient air, we performed the measurements in a vacuum cell.

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Supporting Information Available: Crystallographic data for **1b** and **4** (CIF file), absorption spectra, electrochemical and photoelectrochemical measurement data. This material is available free of charge via the Internet at http://pubs.acs.org.

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