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Selective Synthesis of Co_8S_{15} Cluster in Bowl-Shaped Template of the Pentaaryl[60]fullerene Ligand

Masashi Maruyama,[†] Kenta Imoto,[†] Matthias König,[‡] Dirk M. Guldi,*[,‡] Shin-ichi Ohkoshi,[†,§] Eiichi Nakamura,[†] and Yutaka Matsuo*[,†]

[†]Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[‡]Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, Erlangen 91058, Germany

[§]CREST, JST, K's Gobancho, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

S *Supporting Information*

ABSTRACT: A cobalt–sulfur cluster Co_8S_{15} with molecular formula $(C_{60}Ar_5)$-$Co_8S_{15}{}^nBu_2$-$(C_{60}Ar_5)$ (Ar = 4-^{t}BuC_6H_4) was selectively synthesized from a pentaaryl[60]fullerene cobalt trisulfide complex, $(\eta^5$-$C_{60}Ar_5)CoS_3$. The bowl-shaped steric templating fullerene ligand, as well as the metastable cobalt trisulfide moiety, played important roles in the exclusive cluster formation. X-ray crystallography, as well as electrochemical, time-resolved photophysical, and magnetic, measurements revealed a mixed-valence cluster with six cobalt(III) and two high-spin cobalt(II) centers showing reversible redox behavior and photoinduced charge separation.

Controlling the reactivity of metals and chalcogens is a long-standing challenge in preparing metal chalcogenide cluster complexes.[1] Metal chalcogenide clusters are structural motifs utilized, for example, in enzymatic active sites,[2] catalysts,[3] and optical/optoelectronic materials.[4] However, methods for the precise synthesis of these clusters are still underdeveloped and this area of research remains largely unexplored.[5,6] For metal chalcogenide cluster synthesis, three types of reactants are generally necessary (metal and chalcogen sources, and terminal ligands), making the systems complicated. Synthetic methods for iron–sulfur cluster complexes have progressed as a result of research on enzymatic models with developing useful iron–sulfur precursors and efficient terminal ligands.[7,8] However, much less is known about the synthesis of nonbiomimetic metal–sulfur clusters.[1,9]

Among nonbiomimetic cluster complexes, those consisting of cobalt and sulfur are particularly attractive[10] due to their potential as catalysts,[3a] electrocatalysts,[3b] semiconducting materials,[10c] and so forth. Moreover, intriguing properties have been reported for cobalt sulfide nanoparticles,[11] giving rise to interest in cobalt–sulfur cluster complexes. However, synthetic routes to cobalt–sulfur cluster complexes are quite limited and their structural diversity is very low.[10d,12] Thus, development of facile cobalt–sulfur sources and terminal ligands is strongly desired. Against this background, we focused on a cobalt trisulfide complex[13] with a pentaaryl[60]fullerene ligand (Figure 1). Pentaaryl[60]fullerene derivatives are crowded, bowl-shaped molecules,[14] which can be utilized for molecular stacking control,[15] surface modification,[16] and steric protection/restriction.[13,17,18] Bearing a metastable cobalt sulfide moiety, complex **1** is a promising cobalt–sulfur source, and the bowl-shaped ligand has sufficient bulkiness to act as a terminal ligand. Taking advantages of the features of complex **1**, we synthesized a well-defined cobalt–sulfur cluster inside the bowl-shaped restricted space. We consider such unprecedented cluster formation will provide new methodology for precise synthesis of well-defined clusters.

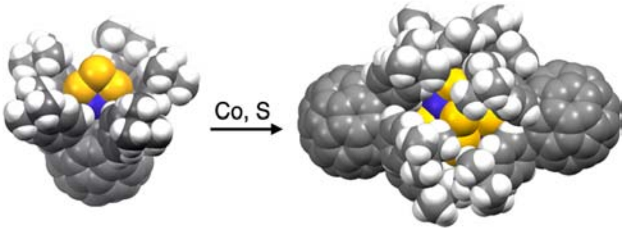

Figure 1. Structures of cobalt trisulfide complex **1** (left) and obtained Co_8S_{15} cluster complex **2** (right).

In the presence of 10 equiv of *n*-butanethiol, cobalt trisulfide complex, $(\eta^5$-$C_{60}Ar_5)CoS_3$ (**1**; Ar = 4-^{t}BuC_6H_4) underwent a slow disproportionation reaction to give a Co_8S_{15} cluster complex $(C_{60}Ar_5)$-$Co_8S_{15}{}^nBu_2$-$(C_{60}Ar_5)$ (**2**) selectively in 54% yield as to the cobalt atoms (Scheme 1). The reaction proceeded without addition of any external cobalt source but gave the demetalated ligand $C_{60}Ar_5H$ (**3**) as a major byproduct.[19] This observation clearly suggests that the stepwise growth of **2** involves degradation of cobalt trisulfide **1** and cluster growth through addition of the resulting cobalt–sulfur species. Cobalt trisulfide complex **1** served as the terminal cap of clusters as well as a cobalt–sulfur source in this cluster formation reaction. It is noteworthy that other cluster sizes were not observed in the product mixture at all, indicating the strong steric templating effect of the $C_{60}Ar_5$ ligand. Furthermore, the stability of the resulting cluster complex **2** was quite high due to the bowl-shaped steric environment of $C_{60}Ar_5$, allowing for purification by silica gel column chromatography.

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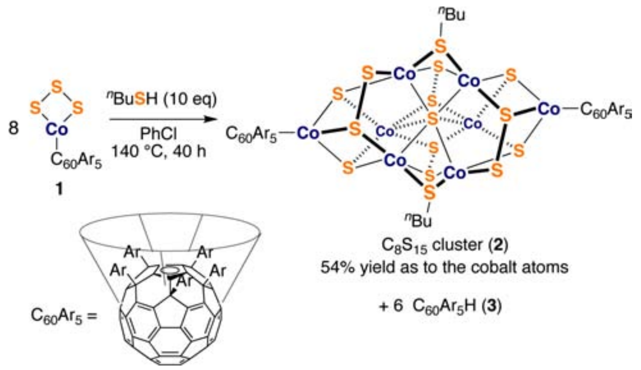
Scheme 1



X-ray crystallographic analysis revealed unambiguous structure of the central part in **2** (Figure 2).[20] The Co_8S_{15} cluster moiety possesses a corner-sharing double-cubane-like core structure, in which two Co_4S_5 units[21] are fused at a central sulfur atom and coordinated by μ_4-S_2 and μ_2-S^nBu ligands (Figure 2b,c). To the best of our knowledge, cobalt−sulfur clusters with double-cubane-type structures related to FeMo-cofactor are quite rare.[22] The importance of the bowl-shaped $C_{60}Ar_5$ ligands is evident in the crystal structure of **2**; the inner space between two $C_{60}Ar_5$ ligands is almost completely filled by the ellipsoidal Co_8S_{15} cluster unit (Figures 2d,e, and S1). This suggests that this novel Co_8S_{15} structure originates from steric templating by the bowl-shaped terminal ligands.[23] Note that bulkier thiols such as cyclohexanethiol and benzenethiol did not give cluster compounds, likely because of strong steric repulsion.

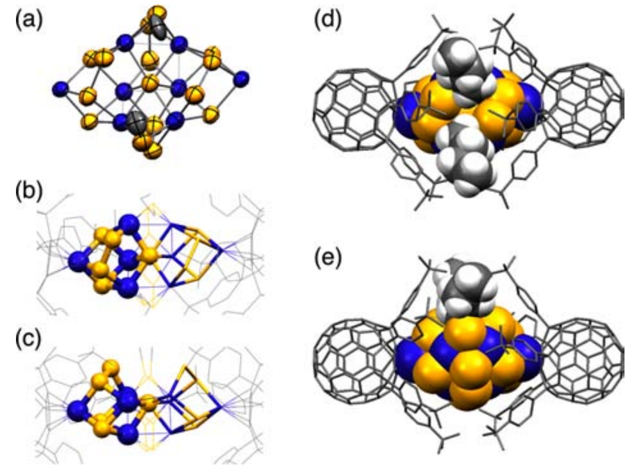


Figure 2. Crystal structures of **2**. (a) ORTEP drawing of the central Co_8S_{15} moiety (top view). (b) Top view and (c) side view of the Co_8S_9 substructure; one of the cubane-like Co_4S_5 units is emphasized. (d) Top view and (e) side view of the whole molecule. The central Co_8S_{15} cluster moiety is shown as a space-filling model. Disordered moieties and hydrogen atoms in $C_{60}Ar_5$ ligands are omitted for clarity.

A closer investigation of the bond lengths revealed a zigzag Co−Co bonding arrangement in the central cluster part of **2** (Figure 3). The Co−Co distances in the central Co_6 structure can be divided into two types: weak Co−Co bonds with lengths around 2.57 Å[24] (Co2−Co3, Co3−Co4, Co4−Co5, Co5−Co6, and Co6−Co7; blue lines in Figure 3) and nonbonding Co−Co distances of around 2.94 Å (Co2−Co5 and Co4−Co7; green lines in Figure 3).[25] There have been many reports on Co−Co bonds in multinuclear cobalt complexes,[26] but the present bonding mode is the first example among various bonding modes. Regarding the 15 sulfur atoms, four S−S single bonds were found in the structure of **2**. We consider that four $(S-S)^{2-}$, five S^{2-}, two $^nBuS^-$, and two $C_{60}Ar_5^-$ formally have 22-valent negative charges $[(4 \times 2) + (5 \times 2) + (2 \times 1) + (2 \times 1) = 22]$; and eight cobalt atoms formally consist of two cobalt(II) and six cobalt(III) centers to balance the charge $[(2 \times 2) + (6 \times 3) = 22]$. This consideration is in good agreement with the result of a magnetic measurement (vide infra). It was hard to determine which two cobalt atoms are cobalt(II) from the bond length analysis.

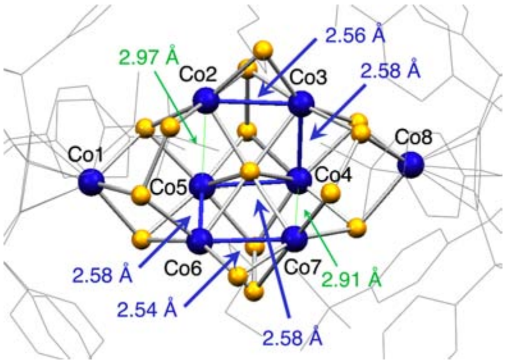


Figure 3. Bonding mode of the central cluster (X-ray measurements at −50 °C). Blue indicates distances for weak Co−Co bonds and green indicates distances between nonbonding Co atoms.

We performed electrochemical, photophysical, and magnetic measurements for deeper understanding of the properties of **2**. Cyclic voltammetry of **2** revealed several reversible redox processes (Figure 4a). The oxidation wave at $E_{1/2}$ = +0.22 V is attributed to one-electron oxidation of cobalt(II) to cobalt(III), and the reduction wave at $E_{1/2}$ = −0.70 V, to one-electron reduction of cobalt(III) to cobalt(II). These results are consistent with a mixed valence cluster. Notably, complex **2**

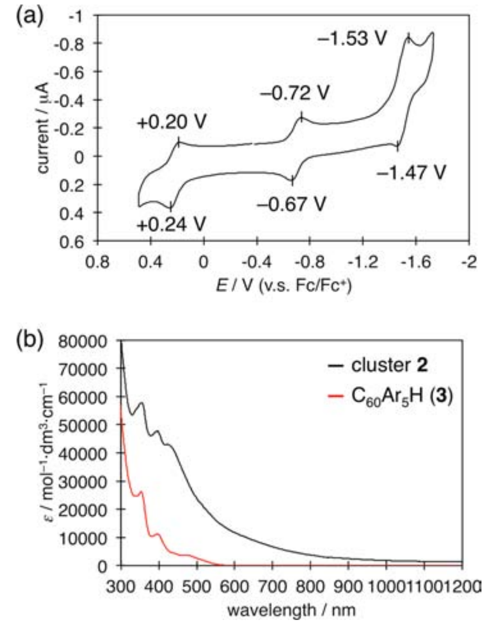


Figure 4. (a) Cyclic voltammogram of cluster **2** in CH_2Cl_2 ($TBAPF_6$ as supporting electrolyte). (b) UV/vis/near-IR absorption spectra of cluster **2** and $C_{60}Ar_5H$ in CH_2Cl_2.

exhibited a weak but broad vis/near-IR absorption peak, implying intervalence transitions (Figure 4b). Another reduction wave was observed at $E_{1/2} = -1.50$ V, for which deconvolution analysis suggested the overlap of a one-electron process centered on the cluster moiety and a simultaneous two-electron process centered on the C_{60} moieties (Figure S2).

Investigation of the excited state properties of **2** revealed photoinduced charge separation and charge shift (Figure 5).

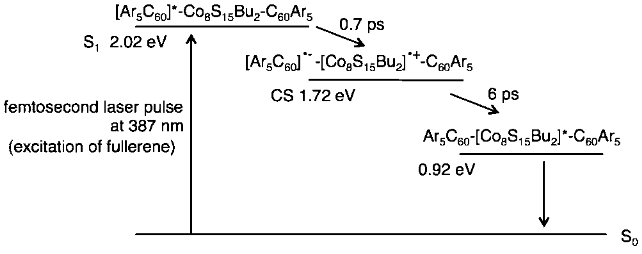


Figure 5. A diagram for the excited state dynamics of cluster **2**.

When photoexciting **2** at 387 nm with femtosecond laser pulses, the immediate formation of the fullerene singlet excited state (~2.02 eV, Figure S3)[27] evolved with an absorption maximum at 915 nm. Next is a fast decay (~0.7 ps) of the fullerene singlet excited state, which converts the latter into an energetically high lying radical ion pair state (1.72 eV), which features maxima at 480 and 580 nm and a minimum at 430 nm. Implicit is here the oxidation of one of the two divalent cobalt centers and the reduction of the fullerene. Subsequently, the decay of this radical ion pair state occurred (~6 ps) to afford a lower lying central excitonic state (0.92 eV) of **2**, which implies a charge shift from the reduced fullerene to a trivalent cobalt center, whose distribution differs from the initial ground state. The final deactivation of this state to reinstate the ground state with its initial distribution of divalent and trivalent cobalt centers, was found to be very fast.

Measurement for the magnetic susceptibility of **2** elucidated its spin state. At room temperature, the product of molar magnetic susceptibility χ_M and temperature T ($\chi_M T$ value) was 5.30 K cm^3 mol^{-1}, which corresponds to the calculated $\chi_M T$ value of 5.4 K cm^3 mol^{-1} for two high-spin Co^{II} ($S = 3/2$, $g = 2.4$).[28] The higher $\chi_M T$ value than the spin-only value of two $Co^{II}(S = 3/2)$ ions (3.76 K cm^3 mol^{-1}) is due to the mixing between the ground state ($^4A_2$) and the excited state (^4E) through spin−orbit coupling, which is consistent with the reported value in a five-coordinate square pyramidal Co(II) complex.[29]

In summary, we have demonstrated the selective synthesis of a well-defined Co_8S_{15} cluster complex **2** from a cobalt trisulfide complex **1**. Precursor complex **1** served as a cobalt−sulfur source as well as a powerful sterically templating terminal ligand. The Co_8S_{15} core had a double-cubane-like geometry and represented the first example of a cobalt−sulfur analogue to biological iron−sulfur clusters,[7,8] making its catalytic activity an interesting area for further study. Crystallographic, electrochemical, photophysical, and magnetic measurements revealed a mixed-valence cluster with two high-spin cobalt(II) centers. This study also points toward new opportunities for developing artificial functional metal−sulfur cluster complexes as photo-electro-magnetically active materials end-capped by penta(organo)[60]fullerenes as terminal ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, electrochemical data, and crystallographic data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

guldi@chemie.uni-erlangen.de; matsuo@chem.s.u-tokyo.ac.jp

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For example (a) Varhenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322–329. (b) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed.* **1991**, *30*, 769–788. (c) Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 14–26. (d) Schmid, G. *Nanoparticles—From Theory to Application*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004.

(2) For example (a) Peters, J. W.; Stonewell, M. H. B.; Soltis, S. M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C. *Biochemistry* **1997**, *36*, 1181–1187. (b) Vassiliev, I. R.; Antonkine, M. L.; Golbeck, J. H. *Biochim. Biophys. Acta* **2001**, *1507*, 139–160. (c) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696–1700. (d) Pandy, A. S.; Harris, T. V.; Giles, L. J.; Peters, J. W.; Szilagyi, R. K. *J. Am. Chem. Soc.* **2008**, *130*, 4533–4540. (e) Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, *473*, 55–60.

(3) (a) Riaz, U.; Curnow, O. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 4357–4363. (b) Kushi, Y.; Nagao, H.; Nishioka, T.; Isobe, K.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1223–1224. (c) Yuhas, B. D.; Prasittichai, C.; Hupp, J. T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 15854–15847. (d) Yuhas, B. D.; Smeigh, A. L.; Douvalis, A. P.; Wasieleski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2012**, *134*, 10353–10356.

(4) (a) Shi, S.; Ji, W.; Xin, X. Q. *J. Phys. Chem.* **1995**, *99*, 894–898. (b) Bag, S.; Trikalitis, P. N.; Chupas, P. J.; Armatas, G. S.; Kanatzidis, M. G. *Science* **2007**, *317*, 490–493. (c) Zhang, Q.; Chung, I.; Jang, J. I.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 9896–9897. (d) Li, J.; Zhang, J.; Humphrey, M. G.; Zhang, C. *Eur. J. Inorg. Chem.* **2013**, 328–346.

(5) Precise controls of metal clusters such as gold clusters are also of great interest and intense studies are carried out (see ref 6).

(6) For example (a) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885. (b) Maity, P.; Xie, S.; Yamauchi, M.; Tsukuda, T. *Nanoscale* **2012**, *4*, 4027–4037.

(7) (a) Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2484–2494. (b) Zhang, Y.; Holm, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 3910–3920. (c) Rao, P. V.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527–559. (d) Lee, S. C.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1135–1157. (e) Groysman, S.; Holm, R. H. *Biochemistry* **2009**, *48*, 2310–2320.

(8) (a) Ohki, Y.; Sunada, Y.; Honda, M.; Katada, M.; Tatsumi, K. *J. Am. Chem. Soc.* **2003**, *125*, 4052–4053. (b) Ohki, Y.; Ikagawa, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2007**, *129*, 10457–10465. (c) Ohki, Y.; Tanifuji, K.; Yamada, N.; Imada, M.; Tajima, T.; Tatsumi, K. *Proc. Natl. Acad. Sci. U,S,A,* **2011**, *108*, 126395–12640.

(9) For example (a) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093–2121. (b) Koutmos, M.; Kalyvas, H.; Sanakis, Y.; Simopoulos, A.; Coucouvanis, D. *J. Am. Chem. Soc.* **2005**, *127*, 3706–

3707. (c) Kure, B.; Ogo, S.; Inoki, D.; Nakai, H.; Isobe, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 14366−14374.

(10) (a) Pulliam, C. R.; Thoden, J. B.; Stacy, A. M.; Spencer, B.; Englert, M. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 7398−7410. (b) Deng, L.; Bill, E.; Wieghardt, K.; Holm, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 11213−11221. (c) Bordman, B. M.; Widawsky, J. R.; Park, Y. S.; Schenk, C. L.; Venkataraman, L.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2011**, *133*, 8455−8457.

(11) (a) Shafaei-Fallah, M.; He, J.; Rothenberger, A.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 1200−1202. (b) Wang, H.; Liang, Y.; Li, Y.; Dai, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 10969−10972.

(12) (a) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164−2174. (b) Christou, G.; Hagen, K. S.; Bashkin, J. K.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1010−1018. (c) Bencini, A.; Ghilardi, C. A.; Orlandini, A.; Midollini, S.; Zanchini, C. *J. Am. Chem. Soc.* **1992**, *114*, 9898−9908.

(13) (a) Maruyama, M.; Guo, J.-D.; Nagase, S.; Nakamura, E.; Matsuo, Y. *J. Am. Chem. Soc.* **2011**, *133*, 6890−6893. (b) Maruyama, M.; Matsuo, Y. *Chem. Commun.* **2012**, *48*, 9334−9342.

(14) (a) Matsuo, Y.; Muramatsu, A.; Tahara, K.; Koide, M.; Nakamura, E. *Org. Synth.* **2006**, *83*, 80−87. (b) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016−3028.

(15) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702−705. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432−433. (c) Matsuo, Y.; Morita, K.; Nakamura, E. *Chem. Asian J.* **2008**, *8*, 1350−1357. (d) Kennedy, R. D.; Ayzner, A. L.; Wanger, D. D.; Day, C. T.; Halim, M.; Khan, S. I.; Tolbert, S. H.; Schwartz, B. J.; Rubin, Y. *J. Am. Chem. Soc.* **2008**, *130*, 17290−17292.

(16) (a) Matsuo, Y.; Kanaizuka, K.; Matsuo, K.; Zhong, Y.-W.; Nakae, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5016−5017. (b) Matsuo, Y.; Ichiki, T.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 9932−9937. (c) Matsuo, Y.; Maruyama, M. *J. Nanosci. Nanotechnol.* **2012**, *12*, 6869−6871.

(17) (a) Matsuo, Y.; Maruyama, M.; Gayathri, S. S.; Uchida, T.; Guldi, D. M.; Kishida, H.; Nakamura, A.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 12643−12649. (b) Maruyama, M.; König, M.; Guldi, D. M.; Nakamura, E.; Matsuo, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 3015−3018.

(18) (a) Kuninobu, Y.; Matsuo, Y.; Toganoh, M.; Sawamura, M.; Nakamura, E. *Organometallics* **2004**, *23*, 3259−3266. (b) Matsuo, Y.; Mitani, Y.; Zhong, Y.-W.; Nakamura, E. *Organometallics* **2006**, *25*, 2826−2832. (c) Halim, M.; Kennedy, R. D.; Suzuki, M.; Khan, S. I.; Diaconescu, P. L.; Rubin, Y. *J. Am. Chem. Soc.* **2011**, *133*, 6841−6851.

(19) A small amount of cobalt trithioperoxobutylate complex (a C−H functionalized product) formed as a byproduct under these conditions (see also ref 17b).

(20) Crystal data for **2**: monoclinic space group $P2_1/n$ (No. 14), a = 19.5786(4), b = 32.8041(6), c = 31.8927(6) Å, β = 98.9220(7)°, Z = 4, V = 20235.5(7) Å^3, T = 223(2) K, total reflections = 225 535, total unique reflections = 35 983, number of parameters = 2359, R = 0.1147, wR = 0.2168, and GOF = 1.097.

(21) Adams, R. D.; Miao, S. *Inorg. Chim. Acta* **2005**, *358*, 1401−1406.

(22) Cubane-type cobalt−sulfur clusters can be found in some literatures, such as refs 9c and 10d.

(23) The $C_{60}Ar_5$ moieties also play dominant roles in the crystal packing structure of cluster **2**, in which the dumbbell-shaped molecules gather through strong π−π interactions at the C_{60} moieties to give a porous network (see also Figure S1).

(24) The Co−Co distance of 2.57 Å corresponds to a weak single bond (cf. conventional Co−Co single bonds are around 2.47 Å; see also ref 25).

(25) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 4290−4293.

(26) For example (a) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082−5084. (b) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164−2174. (c) Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Inorg. Chem.* **1984**, *23*, 2073−2079. (d) Brunner, H.; Cattey, H.; Meier, W.; Mugnier, Y.; Stückl, A. C.; Wachter, J.; Wanninger, R.; Zabel, M. *Chem.—Eur. J.* **2003**, *9*, 3796−3802.

(27) Guldi, D. M.; Rahman, G. M. A.; Marczak, R.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9420−9427.

(28) Diamagnetic correction of 1.898×10^{-3} cm^3·mol^{-1} from Pascal's constants was applied.

(29) (a) Gerloch, M.; Kohl, J.; Lewis, J.; Urland, W. *J. Chem. Soc. A* **1970**, 3283−3296. (b) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343−402.