JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

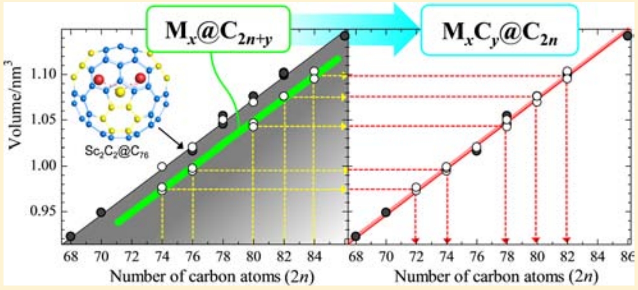
A Structural Diagnostics Diagram for Metallofullerenes Encapsulating Metal Carbides and Nitrides

Sachiko Maki,[†] Eiji Nishibori,*[,†] Ikuya Terauchi,[‡] Masayuki Ishihara,[‡] Shinobu Aoyagi,[§] Makoto Sakata,[∥] Masaki Takata,[†] Hisashi Umemoto,[⊥] Takashi Inoue,[⊥] and Hisanori Shinohara*[,⊥]

[†]RIKEN SPring-8 Center, RIKEN, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan
[‡]Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan
[§]Department of Information and Biological Sciences, Nagoya City University, Nagoya 467-8501, Japan
[∥]Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan
[⊥]Department of Chemistry and Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan

Supporting Information

ABSTRACT: Systematic structural studies of 24 different kinds of endohedral metallofullerenes, M_xC_{2n} (M = La, Y, Sc, Lu, Ti, Eu, Er, Hf, Sc_3N; $34 \leq n \leq 43$), as 1:1 cocrystals with solvent toluene molecules have been carried out using synchrotron radiation powder diffraction. Thirteen of the 24 molecular structures, including five metal carbides, one metal nitride endohedral fullerene, and one hollow fullerene, have been determined by a combination of the maximum entropy method and Rietveld refinement of the X-ray diffraction data obtained. We have found that the volume for one fullerene and one toluene molecule depends linearly on the number of carbon atoms in the fullerene cage. Fifteen different kinds of metal carbide endohedral fullerenes have been identified, which can be structurally characterized from the obtained lattice constants using only this linear dependence. The linear dependence found in the present study provides a metallofullerene diagnostics diagram that may have universal importance for structural characterization of the so-called cluster endohedral fullerenes.



INTRODUCTION

During the past couple of decades, endohedral metallofullerenes have attracted much interest because of their unique structural, electronic, and transport properties.[1] To date, more than 200 different kinds of endohedral metallofullerenes have been successfully produced and isolated, including monometal,[2] dimetal,[3] metal nitride,[4] metal carbide,[5] metal hydrocarbon,[6] metal oxide,[7] metal sulfide,[8] and metal carbonitride[9] endohedral fullerenes.

Among the various metal-cluster-encapsulating fullerenes, the structural characterization of metal carbide encapsulation has been a very intriguing topic of study since its discovery.[5] One of the main reasons for this is that metal carbide fullerenes ($M_xC_y@C_{2n}$) and pure metallofullerenes ($M_x@C_{2n+y}$) cannot be distinguished from each other (and thus cannot be identified) by means of commonly used mass spectroscopic techniques such as laser-desorption time-of-flight mass spectrometry (LD-TOF-MS).[10] After the discovery of metal carbide fullerenes,[5] several metallofullerenes that had previously been reported, such as Sc_3C_{82},[11,12] Y_2C_{84},[13,14] Sc_2C_{84},[15−18] and Ti_2C_{80},[19] were recharacterized as metal−C_2 cluster-encapsulating metallofullerenes. The experimental results of ion mobility,[20] UV−vis−NIR absorption,[13] and ^{13}C NMR[13] measurements have indicated that many di- and trimetallofullerenes may have $M_2C_2@C_{2n}$ and $M_3C_2@C_{2n}$ carbide structures, respectively, which should be distinguished from the corresponding pure metallofullerenes $M_2@C_{2n+2}$ and $M_3@C_{2n+2}$. The initial identification of newly synthesized di- and trimetallofullerenes therefore requires techniques other than mass spectrometry.

X-ray structural analyses have to date provided crucial and definitive information on the structure of endohedral metallofullerenes. In fact, the first metal carbide endohedral fullerene was found and identified by synchrotron radiation powder X-ray diffraction (SR-PXRD) analysis in 2001.[5] Several kinds of metallofullerenes have been structurally characterized to date by single-crystal[7,11,16−18,21−24] and powder[5,12,14,15,25−27] X-ray structural analyses. The structure determinations by single-crystal XRD are, however, limited to the relatively high yield metallofullerenes such as $M_3N@C_{80}$[21,22] and chemically functionalized metallofullerenes[23,24] because of the requirement of high-quality single crystals. Because of this tight restriction, the structures of only six metal carbide fullerenes, $(Sc_2C_2)@C_{80}$,[18,28,29] $(Sc_3C_2)@C_{80}$,[11,12] $(Sc_2C_2)@C_{82}$,[15−18] $(Sc_2C_2)@$

Received: November 10, 2012
Published: December 21, 2012

Table 1. Structural Parameters[a]

composition formula	lattice constants				V (nm^3)	label
	a (Å)	b (Å)	c (Å)	β (deg)		
La_2C_{78}	11.07998(1)	34.1330(4)	11.15338(2)	90	1.05453(3)	ST
Y_2C_{82}(II)	11.1537(2)	34.5587(6)	11.1629(2)	90	1.0757(2)	LA
Y_2C_{82}(III)					1.0992(1)	Ref
Y_2C_{84}(I)	11.2588(6)	34.883(3)	11.237(1)	90	1.1034(2)	LA
Y_2C_{84}(II)	11.22571(1)	34.9054(5)	11.24691(1)	90	1.10174(3)	ST
Y_2C_{84}(III)					1.1020(1)	Ref
Sc_2C_{74}	10.8112(2)	33.3443(7)	10.7941(2)	90	0.9728(1)	LA
Sc_2C_{76}	10.8894(5)	33.621(3)	10.8643(7)	90	0.9944(1)	LA
Sc_2C_{78}	10.97291(2)	33.9276(6)	10.95120(2)	94.1948(2)	1.01651(3)	ST
Sc_2C_{84}(III)					1.1007(3)	Ref
Sc_3C_{82}					1.07599(1)	Ref
Sc_3NC_{68}	10.6484(2)	32.7593(8)	10.6160(2)	94.827(3)	0.92252(4)	ST
Lu_2C_{74}	10.830(2)	33.3718(9)	10.8072(3)	90	0.9765(3)	LA
Lu_2C_{76}(I)	10.9038(5)	33.584(2)	10.8954(5)	90	0.9975(4)	LA
Lu_2C_{76}(II)	10.97291(2)	33.9276(6)	10.95120(2)	94.1948(2)	1.01651(4)	ST
Lu_2C_{78}	11.17825(2)	33.9342(7)	11.06126(2)	94.705(2)	1.04541(4)	ST
Lu_2C_{80}	11.1322(3)	34.5056(1)	11.1355(3)	90	1.0694(2)	LA
Lu_2C_{82}(II)	11.156(1)	34.557(5)	11.163(1)	90	1.0759(2)	LA
Lu_2C_{82}(III)	11.24506(8)	34.8280(3)	11.23053(9)	90	1.09960(2)	ST
Lu_2C_{84}(III)	11.23592(1)	34.8395(6)	11.23180(2)	90	1.09920(3)	ST
Lu_2C_{86}	22.0815(3)	18.3128(3)	11.4179(2)	98.2971(2)	1.14219(4)	ST
Ti_2C_{80}	11.0248(2)	33.9569(6)	11.1798(2)	90	1.0463(2)	LA
Ti_2C_{84}(II)	11.2333(6)	34.753(2)	11.2196(7)	90	1.0950(1)	LA
Ti_2C_{84}(III)	11.24628(2)	34.8106(5)	11.22890(2)	90	1.09900(4)	ST
EuC_{74}	10.917(9)	33.645(3)	10.8813(8)	90	0.9990(9)	LA
EuC_{82}(I)					1.0996(1)	Ref
EuC_{82}(III)					1.1019(1)	Ref
Er_2C_{82}(III)	11.25122(1)	34.8171(5)	11.23733(1)	90	1.10051(3)	ST
Er_2C_{84}(III)	11.24625(2)	34.8589(6)	11.24395(2)	90	1.10120(4)	ST
Hf_2C_{80}	11.008(1)	33.938(3)	11.159(1)	90	1.0422(15)	LA
C_{70}	21.02725(1)	33.09181(2)	10.90951(8)	90	0.94889(1)	ST
C_{76}	17.6624(5)	11.0612(3)	10.9980(2)	108.254(4)	1.02030(5)	LA
C_{78}	11.1430(4)	34.125(1)	11.0539(5)	90	1.0508(1)	LA

[a] Composition formulas, lattice constants, and effective volumes of one fullerene and one toluene molecule (V) were determined by SR-PXRD at 300 K. Definition of labels: ST, determination of molecular structure; LA, determination of lattice constants; Ref, reported in the previous study.

C_{84},[5,18] and $(Gd_2C_2)@C_{92}$,[30] have been determined by single-crystal XRD.

The powder diffraction technique can widely be applied to many kinds of metallofullerenes because it needs a relatively small amount of sample in comparison with single-crystal diffraction.[25] However, determination of the detailed structure, including carbon encapsulation, from powder diffraction data is normally difficult, since powder data in the d-spacing range $d >$ 1.7 Å are required for a reliable analysis of C_2 encapsulation, as reported in the previous studies.[12,14,15]

We previously carried out a series of structural studies of powder crystals of pure metallofullerenes in 1:1 cocrystals with a toluene molecule, $(M_x@C_{2n})(C_6H_5CH_3)$ (M = metal; x = 0, 1, 2, 3; n = 40−42).[12,14,15,25,27] We have successfully measured powder data for approximately 40 different kinds of monometallic, dimetallic, trimetallic, metal carbide, and metal nitride fullerenes on the BL02B2 beamline at SPring-8[31] and analyzed the data for structural characterizations.

Here we report the systematic structural characterization of endohedral metallofullerenes based on SR-PXRD. We have found that pure and metal carbide metallofullerenes (i.e., $M_x@C_{2n+y}$ and $M_xC_y@C_{2n}$) can be structurally characterized and identified from the experimentally obtained lattice constants simply by using the linear dependence of the volume on the number of carbon atoms in the fullerene cage, the so-called metallofullerene diagnostics diagram.

■ METHODS

Synthesis and Isolation of Metallofullerenes. Metallofullerenes were produced by the reported DC arc-discharge method.[1] Metallofullerenes for powder diffraction experiments were separated and isolated from various empty fullerenes and other metallofullerenes by multistage high-performance liquid chromatography (HPLC). Details of the production and isolation of metallofullerenes are described in the Supporting Information. The isolated metallofullerenes are listed in Table 1. The purities of the isolated metallofullerenes were checked by both positive- and negative-ion LD-TOF-MS as well as HPLC analyses.

SR-PXRD Experiments. The powder samples grown from toluene solvent were sealed in a glass capillary with an inside diameter of 0.4 mm. The powder diffraction data were measured on the BL02B2 beamline at SPring-8. An imaging plate (IP) with a pixel size of 50 μm was used as a detector. The measurements for all the samples were carried out at room temperature to avoid crushing of the powder crystal by lowering the temperature. Data for some materials were measured at low temperatures. The data measured at 300 K in the present study are shown in the Supporting Information.

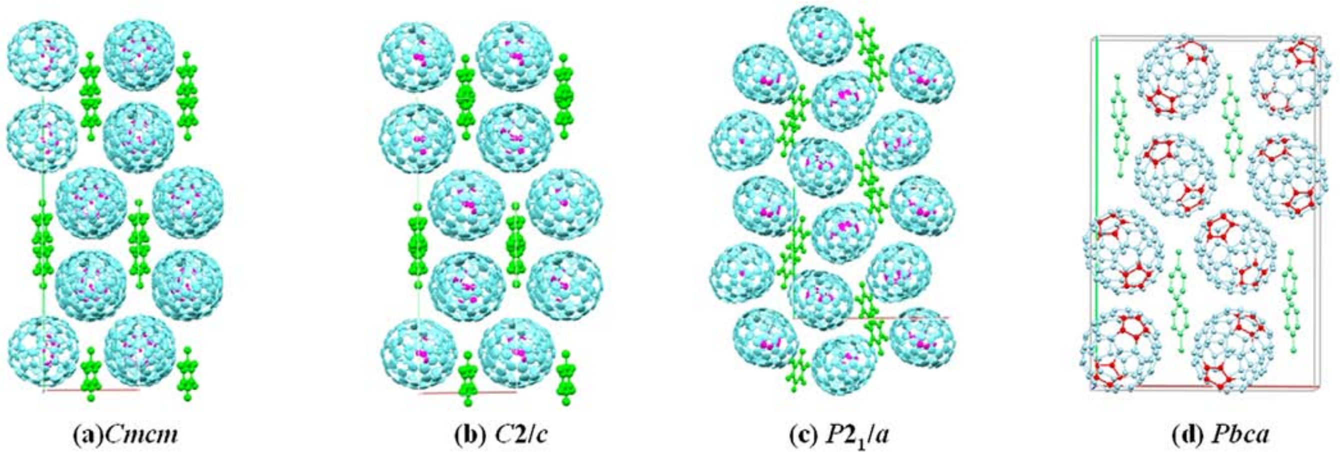


Figure 1. Crystal structures of fullerene 1:1 cocrystals with toluene molecules. Four kinds of space groups were found in the present study: (a) *Cmcm*, (b) *C*2/*c*, (c) *P*2$_1$/*a*, and (d) *Pbca*. Arrangements of fullerene and toluene molecules in the crystal are almost identical among these structures.

■ RESULTS AND DISCUSSION

On the basis of our previous works, the determination of the detailed structure (e.g., the cage structure, C_2 encapsulation, and metal atom disorder) from powder diffraction data requires data with $d > 1.7$ Å resolution.[12,14,15] In this study, species for which data in the $d > 1.7$ Å d-spacing range were available (labeled as "ST" in Table 1) were analyzed by a combination of the maximum entropy method and Rietveld refinement for determination of the the structure of the metallofullerene molecules. Those for which data in the $d > 1.7$ Å d-spacing rage were unavailable (labeled as "LA" in Table 1) were analyzed by the Rietveld method for determination of the lattice constants.

Figure 1 shows four kinds of crystal structures that were determined in the present study: (a) $Lu_2@C_{76}$, (b) $Lu_2@C_{78}$, (c) $Lu_2@C_{86}$, and (d) C_{70}. We determined 13 crystal structures, including that of hollow C_{70} fullerene. The details of each determined molecular structure are shown in the Supporting Information. Each crystal was a 1:1 cocrystal of a fullerene with a toluene molecule. The toluene molecules are located in the void space between fullerene molecules. There are four kinds of space groups in the present determined structures: (a) *Cmcm*, (b) *C*2/*c*, (c) *P*2$_1$/*a*, and (d) *Pbca*. It should be noted that the arrangements of the toluene and fullerene molecules in crystals with same space group are identical. The molecular arrangements in *C*2/*c* and *Pbca* are almost identical to that in *Cmcm*, as shown in Figure 1. The molecular arrangement in *P*2$_1$/*a* (i.e., $Lu_2@C_{86}$) seems to be slightly different from the others. The results suggest that all of the $(M_x@C_y)(C_7H_8)$ crystals have similar molecular arrangements, based on the so-called sphere packing model first reported by Kawada et al.[32] The details of the arrangements, such as the molecular orientation and the space group of the crystal, are different because of the shapes and structures of the fullerene molecules. In other words, the arrangements and orientations of fullerene and toluene molecules vary slightly depending on the molecular size of the metallofullerene to minimize the intermolecular void space present in the crystal.

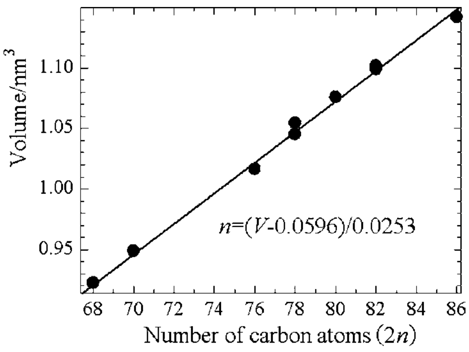


Figure 2. Plot of the effective volume (V) for one fullerene and one toluene molecule vs the number of carbon atoms in the fullerene cage ($2n$) for the present determined structures.

One can calculate the volume occupied by one fullerene and one toluene molecule (hereafter called the effective volume, V) from the determined crystal structures. Table 1 shows the lattice constants and the corresponding effective volumes. The volumes obtained from our previous results on $(M_x@C_y)(C_7H_8)$ (labeled as "Ref") are also listed in Table 1. Figure 2 shows a plot of V versus the number of carbon atoms ($2n$) in the fullerene cage for the samples labeled as ST and Ref. The smallest molecule represented is $Sc_3N@C_{68}$, and the largest molecule is $Lu_2@C_{86}$. The results for the hollow fullerenes C_{70}, C_{76}, and C_{78} are also plotted for reference. The plot of black circles indicates a good linear dependence of the effective volume on the number of carbon atoms, which can be fitted by the linear function

$$n = \frac{V - 0.0596}{0.0253} \tag{1}$$

where n is half of the number of carbon atoms in the cage. The effective volume depends linearly on the number of carbon atoms in the fullerene cage irrespective of the structural isomer. In the case of C_{78}, for example, the cage symmetry of $La_2@C_{78}$ is D_{3h}, which is different from those of $Lu_2@C_{78}$ (C_{2v}) and hollow C_{78} (C_{2v}), but the volume of $La_2@C_{78}$ is almost identical to that of $Lu_2@C_{78}$. These facts indicate that *the crystal lattice constant determines the number of carbon atoms in the fullerene cage in the 1:1 cocrystal of a metallofullerene with a toluene molecule.*

The linear relationship between the effective volume and the number of carbon atoms can be elucidated by considering the geometry of fullerene cages. Schematic pictures representing the geometry of fullerenes are shown in Figure 3. The number of five-membered rings in the fullerene cage is always 12 for fullerenes satisfying the so-called isolated pentagon rule (IPR).[33] The number of six-membered rings, in contrast, increases by one when two carbon atoms are added to the fullerene cage. The surface areas of isomeric fullerene cages are always identical if the areas of five- and six-memebered rings are assumed to be constant. The addition of two carbons to the fullerene cage can be regarded as an addition of one six-sided pyramid, as shown in Figure 3. We can calculate the volume of a six-sided pyramid using the structures of C_{60} and C_{80}-I_h molecules.

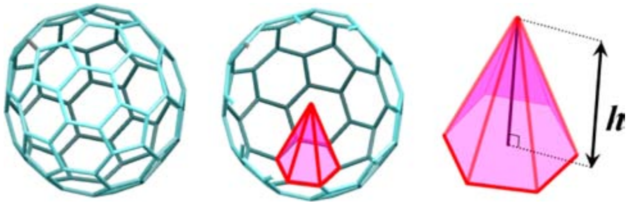


Figure 3. Schematic structure models of fullerene cages. The six-sided pyramid shows the volume that is added to the volume of the fullerene cage when two carbon atoms are added to the cage.

The volume of the six-sided pyramid is approximately 25 Å^3, which actually is identical to the volume difference between C_{2n} and $C_{2(n+1)}$ fullerene molecules. In fact, the radius of the fullerene molecule, which is the height of the pyramid, h, increases as the number of carbon atoms increases. For example, the average radius of C_{60} (3.55 Å) is approximately 10% shorter than that of C_{80}-I_h (3.875 Å). One can calculate the effective volume considering the van der Waals radius (1.7–2.0 Å) of a carbon atom for the radius of fullerene cage. The difference in the heights of the six-sided pyramids for C_{60} and C_{80}-I_h is less than 6%. Therefore, we can estimate the increment of the volume by using the linear relationship between the effective volume and the number of the carbon atoms in the range of C_{60} and C_{80}. This is a central reason for the linear relationship found in the present study.

The molecular structures labeled as LA in Table 1 could not be determined because of very weak signals in the higher-angle region, as described above. However, we successfully determined the lattice constants by Rietveld analysis and thus can calculate the corresponding effective volumes. The volumes of the LA-labeled samples are plotted as white circles in Figure 4. The x axis for the white circles in the left panel is the number of carbon atoms obtained from LD-TOF-MS. The black circles are the same as shown in Figure 2. Some of the white circles are located beneath the line formed by the black circles. We calculated values of $2n$ for all of the materials from eq 1, and the results are shown in Table 2. Some of the LA materials may be regarded as C_2-encapsulating metallofullerenes. The structural formulas based on the values of $2n$ are also listed in Table 2. The effective volumes are plotted versus the numbers of carbon atoms in the fullerene cage in the structural formulas in the

Table 2. Structural Formulas[a]

composition formula	$2n$	label	structural formula
La_2C_{78}	78.7	ST	$La_2@C_{78}$
Y_2C_{82}(II)	80.3	LA	$(Y_2C_2)@C_{80}$(II)
Y_2C_{84}(I)	82.5	LA	$(Y_2C_2)@C_{82}$(I)
Y_2C_{84}(II)	82.4	ST	$(Y_2C_2)@C_{82}$(II)
Sc_2C_{74}	72.2	LA	$(Sc_2C_2)@C_{72}$
Sc_2C_{76}	73.9	LA	$(Sc_2C_2)@C_{74}$
Sc_2C_{78}	75.6	ST	$(Sc_2C_2)@C_{76}$
Sc_3NC_{68}	68.2	ST	$(Sc_3N)@C_{68}$
Lu_2C_{74}	72.5	LA	$(Lu_2C_2)@C_{72}$
Lu_2C_{76}(I)	74.1	LA	$(Lu_2C_2)@C_{74}$(I)
Lu_2C_{76}(II)	75.6	ST	$Lu_2@C_{76}$(II)
Lu_2C_{78}	77.9	ST	$Lu_2@C_{78}$
Lu_2C_{80}	79.8	LA	$Lu_2@C_{80}$
Lu_2C_{82}	80.3	LA	$(Lu_2C_2)@C_{80}$
Lu_2C_{82}(III)	82.2	ST	$Lu_2@C_{82}$(III)
Lu_2C_{84}(III)	82.2	ST	$(Lu_2C_2)@C_{82}$(III)
Lu_2C_{86}	85.6	ST	$Lu_2@C_{86}$
Ti_2C_{80}	78.0	LA	$(Ti_2C_2)@C_{78}$
Ti_2C_{84}(II)	81.9	LA	$(Ti_2C_2)@C_{82}$(II)
Ti_2C_{84}(III)	82.2	ST	$(Ti_2C_2)@C_{82}$(III)
EuC_{74}	74.3	LA	$Eu@C_{74}$
Er_2C_{82}(III)	82.3	ST	$Er_2@C_{82}$(III)
Er_2C_{84}(III)	82.3	ST	$(Er_2C_2)@C_{82}$(III)
Hf_2C_{80}	77.7	LA	$(Hf_2C_2)@C_{78}$

[a] Composition formulas, values of $2n$ calculated from eq 1, labels (see Table 1 for definitions), and structural formula determined by the present study are shown.

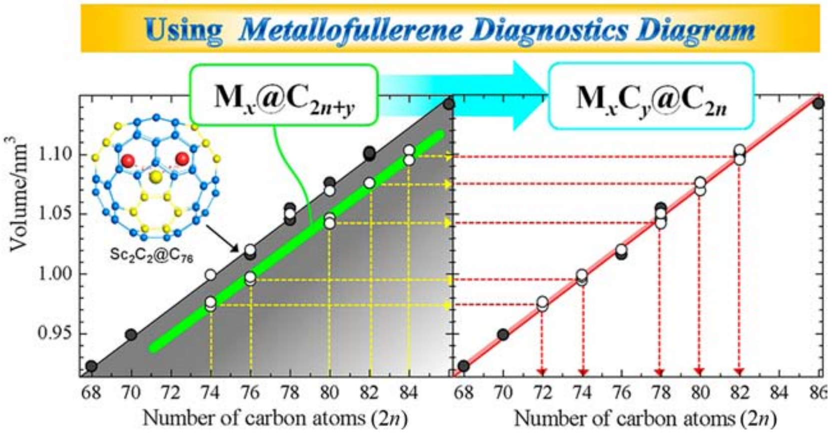


Figure 4. Metallofullerene diagnostics diagram. The x axis for the white circles in the left panel is the number of carbon atoms in fullerene cage as determined by LD-TOF-MS. The x axis for the white circles in the right panel is the $2n$ value as determined from eq 1.

right panel of Figure 4. Very importantly, all of the white circles exactly fit with the line obtained from eq 1, suggesting that the number of carbon atoms in the fullerene cage can be determined and predicted from this plot. For example, Lu_2C_{76} is a C_2-encapsulating metal carbide fullerene, $(Lu_2C_2)@C_{74}$, not the pure metallofullerene $Lu_2@C_{76}$. In this way, we have determined structural formulas of 24 different kinds of endohedral metallofullerenes from SR-PXRD.

The present plot includes one non-IPR metallofullerene, $Sc_3N@C_{68}$. The C_{68} cage of $Sc_3N@C_{68}$ has 12 five-membered rings and 24 six-membered rings. The effective volume of $Sc_3N@C_{68}$ lies on the line. This fact indicates that the linear relationship found in the present study can also be applied to non-IPR fullerenes having only 12 five-membered rings and various numbers of six-membered rings. Recently, the non-IPR metallofullerenes $Sc_2@C_{66}$,[26] $La@C_{72}$,[34] and $Gd_3N@C_{78}$[35] have been synthesized and structurally characterized. The fullerene cages of these materials have only 12 five-membered rings and various numbers of six-membered rings. Very importantly, the linear relationship can also be applied to these non-IPR metallofullerenes.

The lengths of the two short axes of the lattice constants for C_{74}-, C_{80}-, and C_{82}-based metallofullerenes are almost the same as each other, whereas the lengths of C_{78}-, and C_{86}-based metallofullerenes are different (0.15 Å for C_{78} and 0.4 Å for C_{86}). The shapes of C_{74}, C_{80} and C_{82} fullerene molecules are almost spherical, and the lengths of their long and short molecular axes differ by less than 0.13 Å. In contrast, C_{78} and C_{86} fullerene molecules possess rather ellipsoidal shape, and the lengths of their long and short molecular axes are 0.56 Å for C_{78}-$C_{2v}(3)$, 0.27 Å for C_{78}-$D_{3h}(5)$, and 1.7 Å for C_{86}-$C_{2v}(9)$. These facts suggest that powder structural studies of 1:1 cocrystals of metallofullerenes with toluene molecules can predict not only the number of carbon atoms in the fullerene cage but also probable candidates of structural isomers from only the difference in the experimental lattice constants.

■ CONCLUSION

We found a linear relationship between the effective volume and the number of carbon atoms for endohedral metallofullerenes, what we call the "metallofullerene diagnostics diagram", from SR-PXRD data. This diagram will be commonly used for fast and easy structural characterization/identification of metallofullerenes because it provides detailed structural information such as the C_2 encapsulation and probable candidates of cage structures. The novel type of metallofullerene, such as the pure trimetallofullerene $Y_3@C_{80}$,[36] can be structurally characterized even from very small amounts of powder sample by using the metallofullerene diagnostics diagram. The number of metallofullerene molecules that have been investigated is 33 at present. It should increase from now on by applying the relationships found in the present study to predict the structures of metallofullerenes accurately.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Separation and isolation of metallofullerenes, powder diffraction patterns of 1:1 cocrystals of fullerenes and toluene, results of crystal structure analysis, and crystallographic data for 13 kinds of materials. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

eiji.nishibori@riken.jp; noris@nagoya-u.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by Grants-in-Aid for Young Scientists (A) (17686003) and Scientific Research (B) (20360006) from MEXT, Japan. We also thank Dr. K. Kato and Dr. J. E. Kim for experimental help. The synchrotron radiation experiments were performed at SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI).

■ REFERENCES

(1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.

(2) Chai, Y.; Guo, T.; Jin, C.; Haufer, R. E.; Chibante, L. P. F.; Wang, J. F. L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564−7568.

(3) Alvarez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 10561−10563.

(4) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55−57.

(5) Wang, C.-R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew., Chem. Int. Ed.* **2001**, *40*, 397−399.

(6) Krause, M.; Ziegs, F.; Popov, A. A.; Dunsch, L. *ChemPhysChem* **2007**, *8*, 537−540.

(7) Stevenson, S.; Mackey, M. A.; Stuart, M. A.; Phillips, J. P.; Easterling, M. L.; Chancellor, C. J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 11844−11845.

(8) Dunsch, L.; Yang, S. F.; Zhang, L.; Svitova, A.; Oswald, S.; Popov, A. A. *J. Am. Chem. Soc.* **2010**, *132*, 5413−5421.

(9) Wang, T. S.; Feng, L.; Wu, J.-Y.; Xu, W.; Xiang, J.-F.; Tan, K.; Ma, Y.-H.; Zheng, J.-P.; Jiang, L.; Lu, X.; Shu, C.-Y.; Wang, C.-R. *J. Am. Chem. Soc.* **2010**, *132*, 16362−16364.

(10) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163.

(11) Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; Liu, M. T.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 12500−12501.

(12) Nishibori, E.; Terauchi, I.; Sakata, M.; Takata, M.; Ito, Y.; Sugai, T.; Shinohara, H. *J. Phys. Chem. B* **2006**, *110*, 19215−19219.

(13) Inoue, T.; Tomiyama, T.; Sugai, T.; Okazaki, T.; Suematsu, T.; Fujii, N.; Utsumi, H.; Nojima, K.; Shinohara, H. *J. Phys. Chem. B* **2004**, *108*, 7573−7579.

(14) Nishibori, E.; Narioka, S.; Takata, M.; Sakata, M.; Inoue, T.; Shinohara, H. *ChemPhysChem* **2006**, *7*, 345−348.

(15) Nishibori, E.; Ishihara, M.; Takata, M.; Sakata, M.; Ito, Y.; Inoue, T.; Shinohara, H. *Chem. Phys. Lett.* **2006**, *433*, 120−124.

(16) Iiduka, Y.; Wakahara, T.; Nakajima, K.; Nakahodo, T.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Liu, M. T. H.; Mizorogi, N.; Nagase, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5562−5564.

(17) Lu, X.; Nakajima, K.; Iiduka, Y.; Nikawa, H.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *J. Am. Chem. Soc.* **2011**, *133*, 19553−19558.

(18) Kurihara, H.; Lu, X.; Iiduka, Y.; Nikawa, H.; Hachiya, M.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *Inorg. Chem.* **2012**, *51*, 746−750.

(19) Sato, Y.; Yumura, T.; Suenaga, K.; Moribe, H.; Nishide, D.; Ishida, M.; Shinohara, H.; Iijima, S. *Phys. Rev. B* **2006**, *73*, No. 193401.

(20) Sugai, T.; Inakuma, M.; Hudgins, R.; Dugourd, P.; Fye, J. L.; Jarrold, M. F.; Shinohara, H. *J. Am. Chem. Soc.* **2001**, *123*, 6427−6428.

(21) Olmstead, M. M.; Dias, A. B.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1223−1225.

(22) Yang, S.; Troyanov, S. I.; Popov, A. A.; Krause, M.; Dunsch, L. *J. Am. Chem. Soc.* **2006**, *128*, 16733−16739.

(23) Maeda, Y.; Matsunaga, Y.; Wakahara, T.; Takahashi, S.; Tsuchiya, T.; Ishitsuka, M. O.; Hasegawa, T.; Akasaka, T.; Liu, M. T. H.; Kokura, K.; Horn, E.; Yoza, K.; Kato, T.; Okubo, S.; Kobayashi, K.; Nagase, S.; Yamamoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 6858−6859.

(24) Nikawa, H.; Kikuchi, T.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Rahman, G. M. A.; Akasaka, T.; Maeda, Y.; Yoza, K.; Horn, E.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 9684−9685.

(25) Takata, M.; Umede, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46−49.

(26) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Nature* **2000**, *408*, 426−427.

(27) Nishibori, E.; Takata, M.; Sakata, M.; Taninaka, A.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2998−2999.

(28) Kurihara, H.; Lu, X.; Iiduka, Y.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Akasaka, T.; Nagase, S. *J. Am. Chem. Soc.* **2011**, *133*, 2382−2385.

(29) Kurihara, H.; Lu, X.; Iiduka, Y.; Nikawa, H.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *J. Am. Chem. Soc.* **2012**, *134*, 3139−3144.

(30) Yang, H.; Lu, C. X.; Liu, Z. Y.; Jin, H. X.; Che, Y. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 17296−17300.

(31) Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y.; Yamakata, M.; Ikeda, N. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2001**, *467−468*, 1045.

(32) Kawada, H.; Fujii, Y.; Nakao, H.; Murakami, Y.; Watanuki, T.; Suematsu, H.; Kikuchi, K.; Achiba, Y.; Ikemoto, I. *Phys. Rev. B* **1995**, *51*, 8723−8730.

(33) Fowler, P. W.; Manolopoulos, D. E. *An Atlas of Fullerenes*; Dover Publications: Mineola, NY, 2006.

(34) Wakahara, T.; Nikawa, H.; Kikuchi, T.; Nakahodo, T.; Rahman, G. M. A.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Yamamoto, K.; Mizorogi, N.; Slanina, Z.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 14228−14229.

(35) Beavers, C. M.; Chaur, M. N.; Olmstead, M. M.; Echegoyen, L.; Balch, A. L. *J. Am. Chem. Soc.* **2009**, *131*, 11519−11524.

(36) Popov, A.; Zhang, L.; Dunsch, L. *ACS Nano* **2010**, *4*, 795−802.