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(54) **FULLERENE DERIVATIVES**

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C07F 7/04 (2006.01)

C07F 7/08 (2006.01)

(52) **U.S. Cl.** **556/465; 556/489**

(58) **Field of Classification Search** None

See application file for complete search history.

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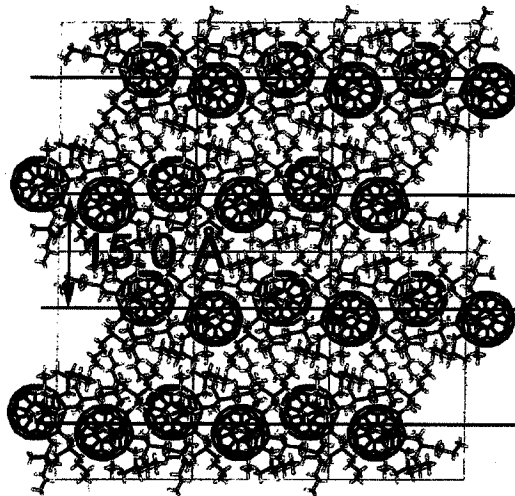
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(57) **ABSTRACT**

The present invention provides a fullerene derivative represented by the following formula (1):

wherein in formula (1), R¹ is a substituted or unsubstituted organic group or a hydrogen atom, and wherein in formulae (2) and (3): W is a single bond, C₁-C₁₁, alkylenyl, C₂-C₁₂ alkenyl, or C₂-C₁₂ alkynyl, wherein any —CH₂— in the alkylenyl, alkenyl or alkynyl can be substituted with —O—, —S—, —COO—, or —OCO—; Z is an element belonging to group IVB; and R²¹ to R²³ are each independently a substituted or unsubstituted C₁-C₂₀ alkyl group, a substituted or unsubstituted C₂-C₁₅ alkenyl group, or a substituted or unsubstituted C₂-C₁₅ alkynyl group.

9 Claims, 8 Drawing Sheets



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Fig. 1

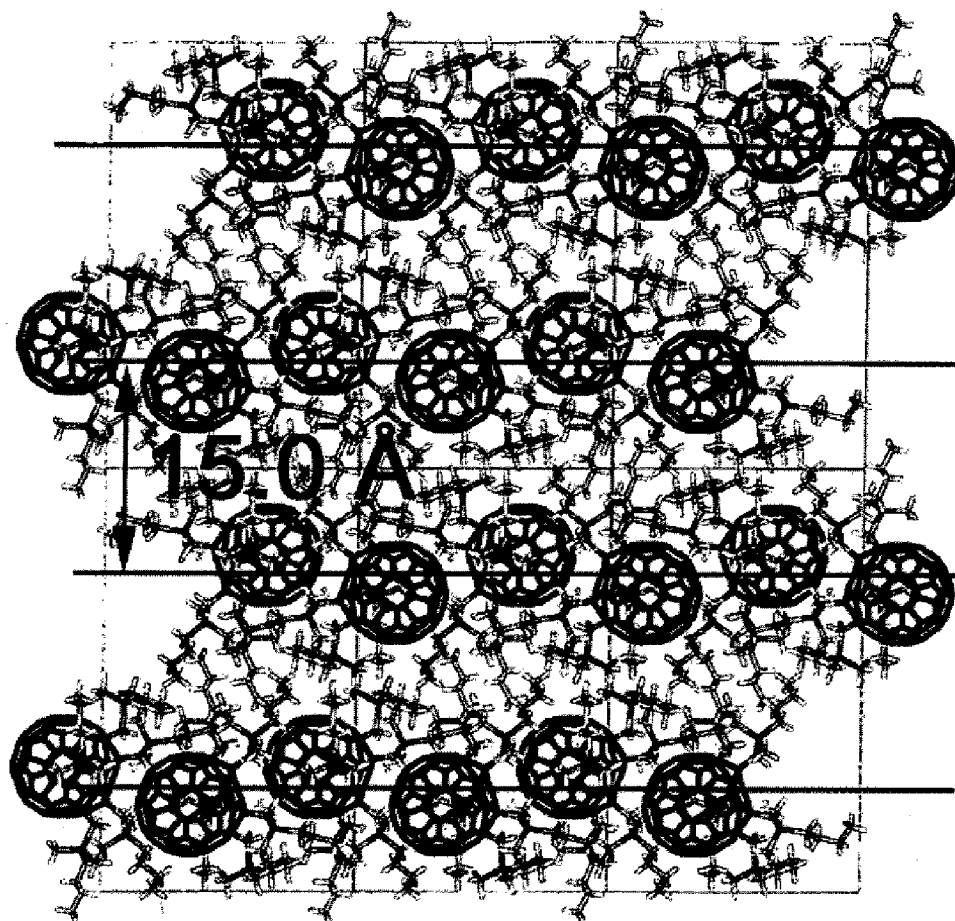


Fig. 2

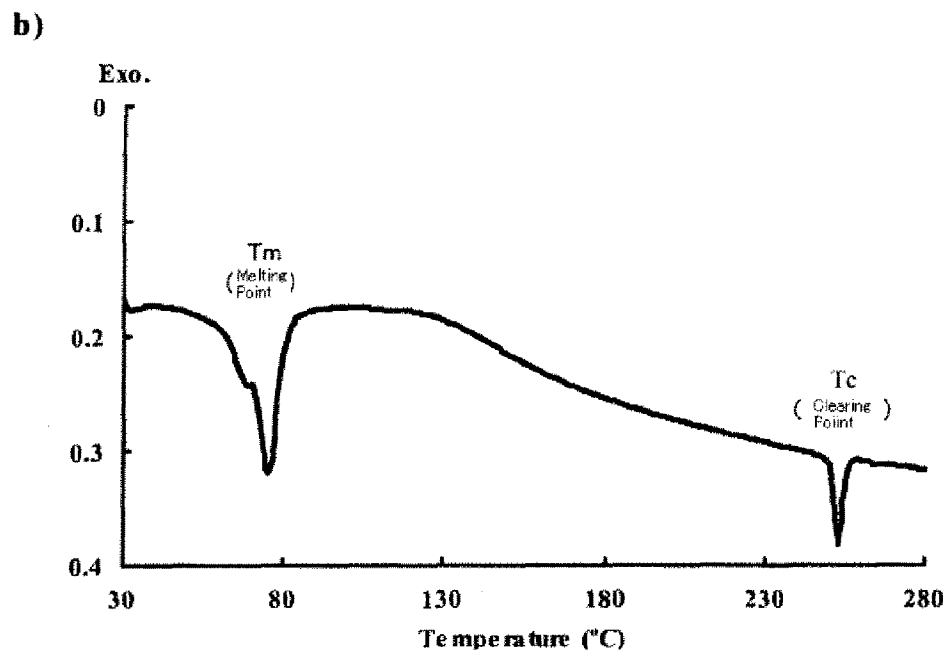


Fig. 3

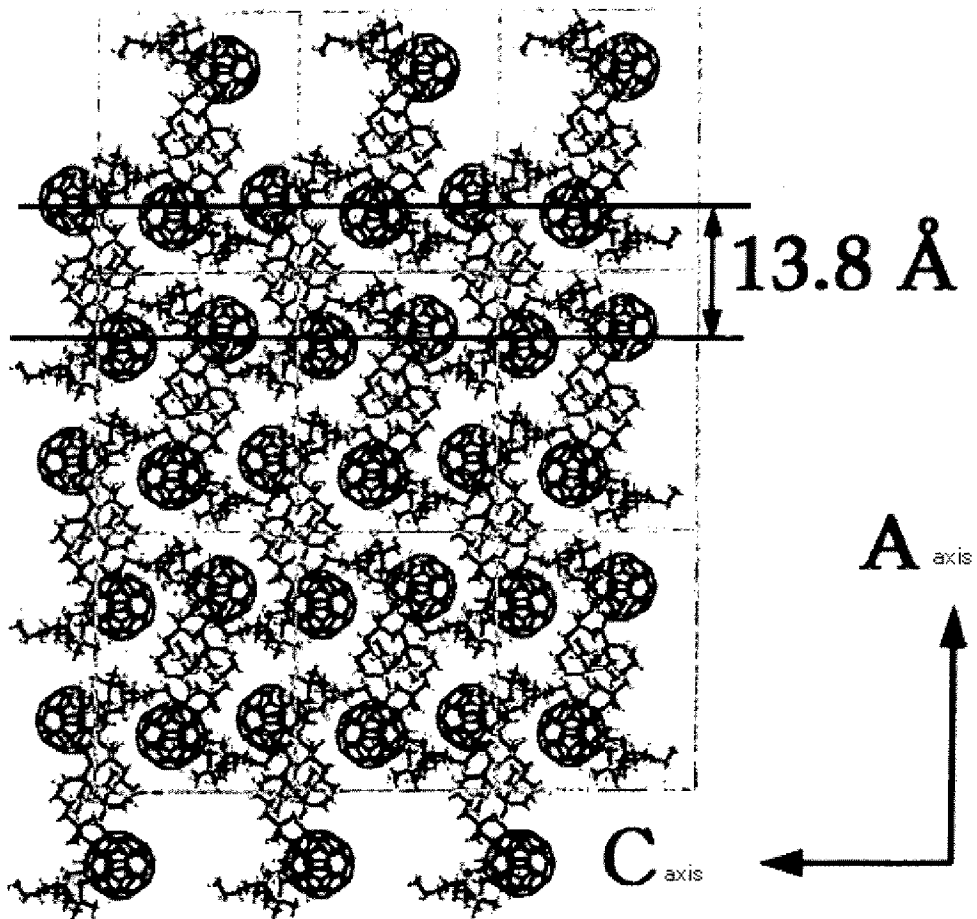


Fig. 4

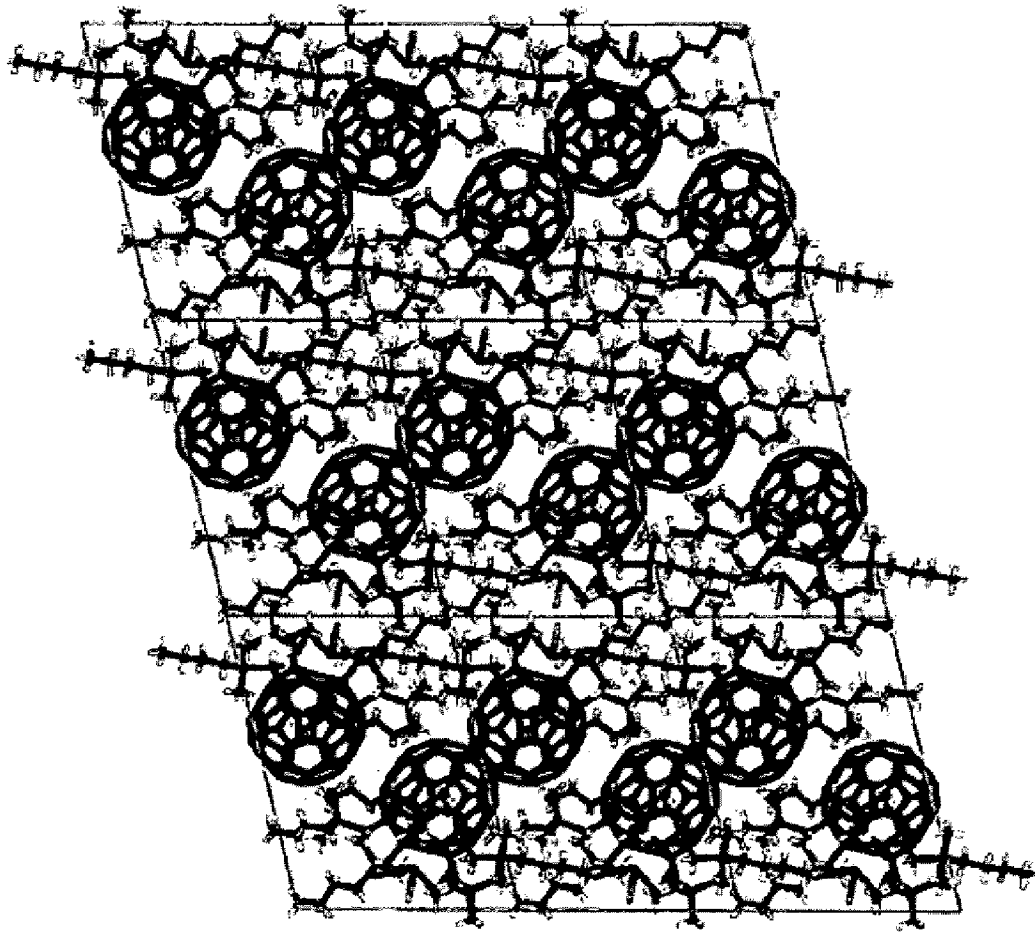


Fig. 5

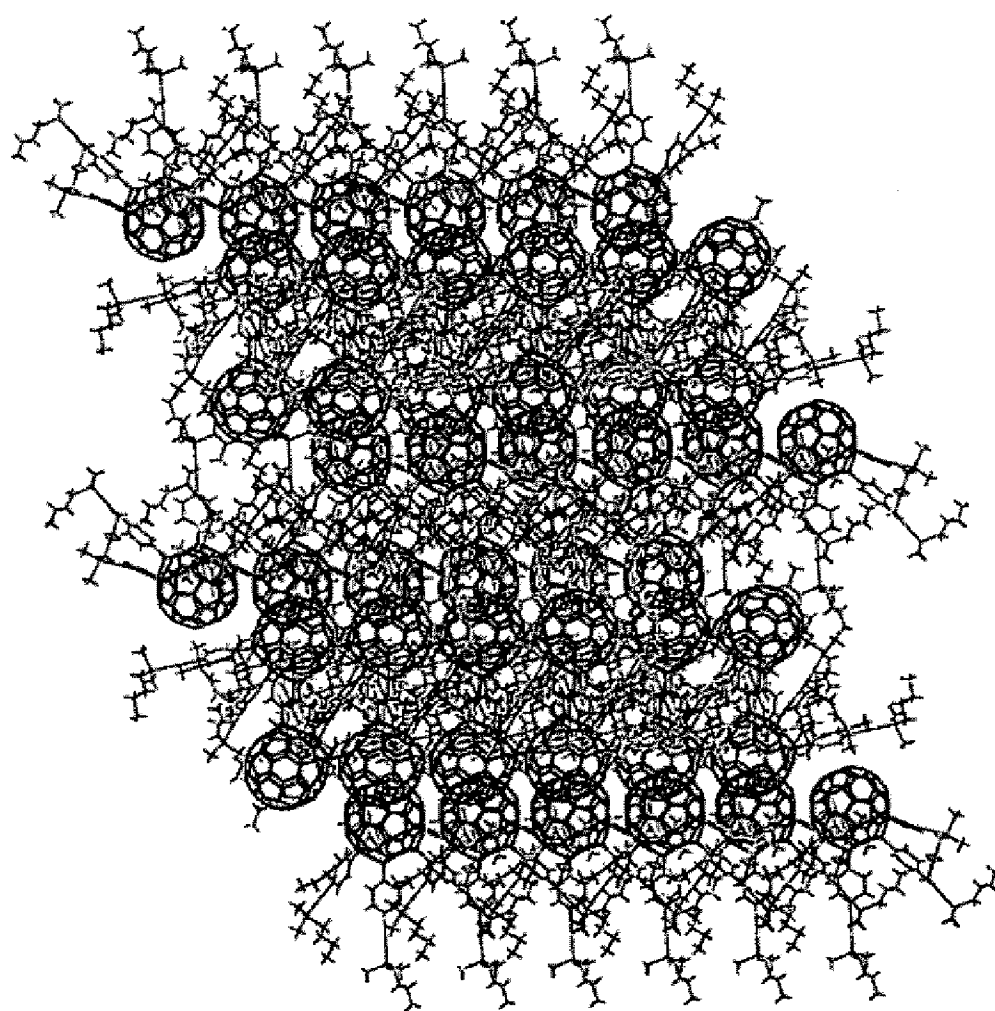


Fig. 6

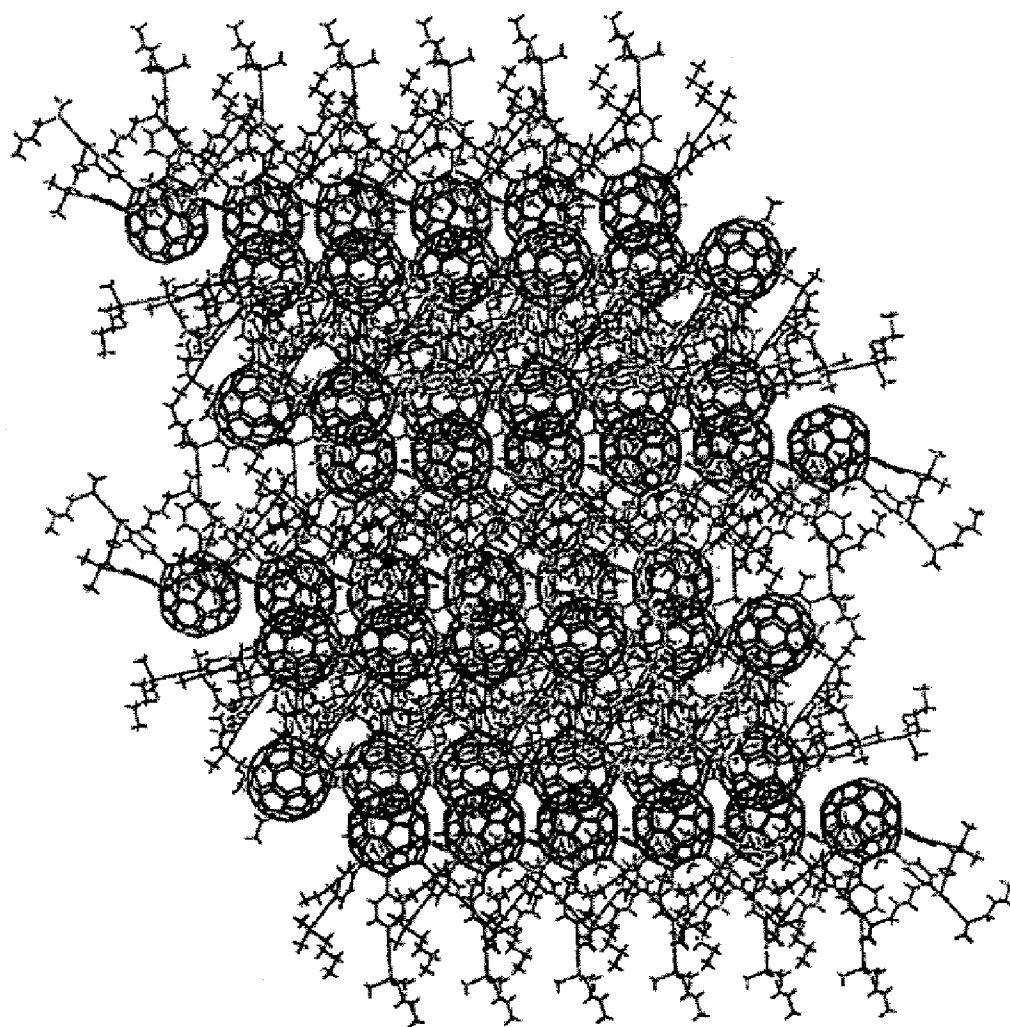


Fig. 7

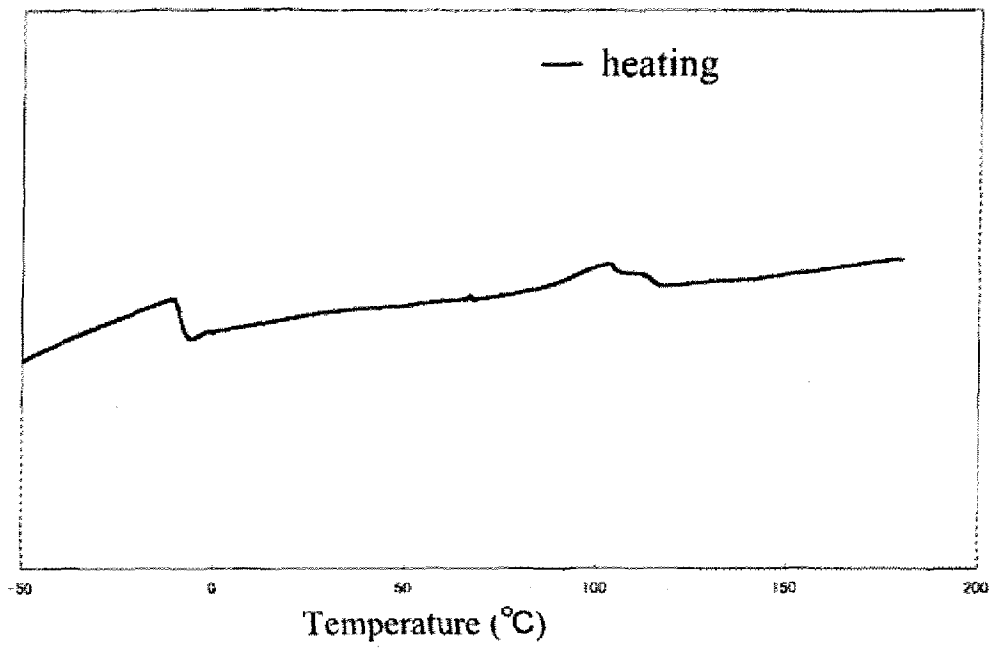
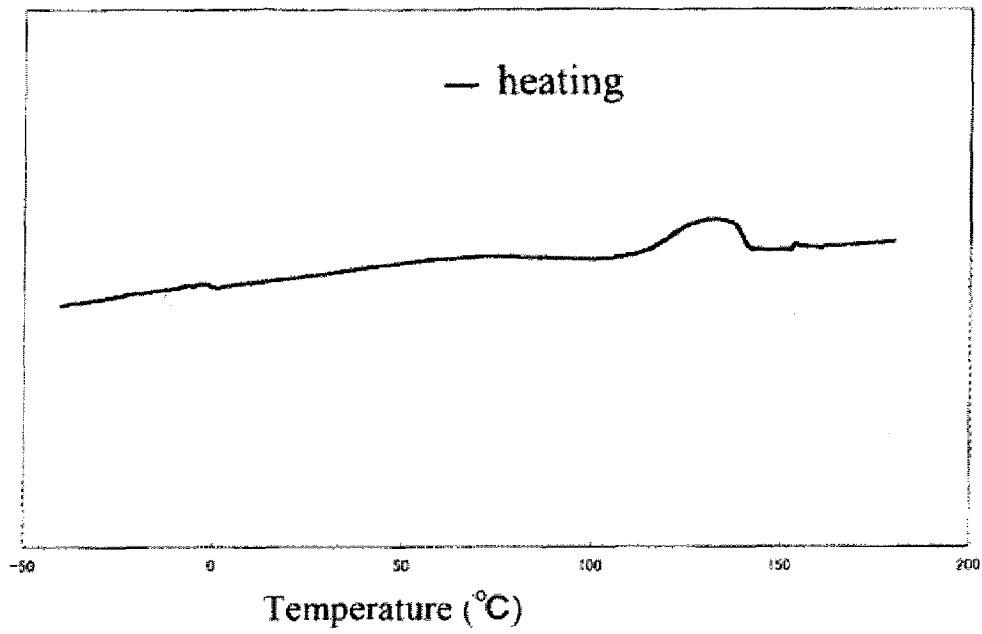


Fig. 8



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FULLERENE DERIVATIVES

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a U.S. National Phase Application of International Application PCT/JP2006/322409 filed Nov. 2, 2006, which claims the benefit of Japanese Patent Application No. 2006-061143, filed Mar. 7, 2006, each of which is incorporated by reference in its entirety.

TECHNICAL FIELD

The present invention relates to fullerene derivatives.

BACKGROUND ART

Since the method for synthesizing a carbon cluster (hereinafter also referred to as "fullerene"), in which carbon atoms are arranged to form a spherical shape or a rugby ball shape, was established, fullerene has been energetically studied. As a result, many fullerene derivatives have been synthesized.

With respect to specific examples of such fullerene derivatives, methods for synthesizing a fullerene derivative, in which 5 organic groups bind to a fullerene skeleton (hereinafter also just referred to as "penta(organo)fullerene derivative"), have been reported (e.g., Japanese Laid-Open Patent Publication No. Hei 10-167994; Japanese Laid-Open Patent Publication No. Hei 11-255509; J. Am. Chem. Soc., 118 12850 (1996); Org. Lett., 2, 1919 (2000); and Chem. Lett., 1098 (2000)).

Further, since a metal-containing fullerene derivative, in which a fullerene is a ligand, has electronic properties based on characteristics of the metal, it is expected that the fullerene derivative will be successfully applied to electrochemical devices. Cyclopentadienyl metal complex of fullerene, which is derived from a penta(aryl)fullerene derivative, etc., have been reported (Japanese Laid-Open Patent Publication No. Hei 11-255509).

In terms of easiness of production of a device, increase in area of a device, etc., materials having an intermediate phase (mesophase) between a solid and a liquid attract attention as functional materials, which are excellent in charge transport characteristics and physical property of photoelectron, and which can be used in electrochemical devices, and liquid crystal-blended materials comprising a fullerene derivative, etc. have been proposed (e.g., Japanese Laid-Open Patent Publication No. 2003-146915 and Japanese Laid-Open Patent Publication No. 2004-331848). Specifically, exhibition of liquid crystallinity of a carbon cluster derivative based on a fullerene derivative having a shuttlecock-like molecular shape has been reported (Japanese Laid-Open Patent Publication No. 2003-146915). Unlike general discotic-type fullerene derivatives, this shuttlecock-shaped fullerene derivative has a cup stack type lamination as a conical molecule (Nature, Vol. 4, 419, 681-(2002)). Therefore, the shuttlecock-shaped fullerene derivative has a column-shaped molecular arrangement which is stabler than discotic-type fullerene derivatives and its use as a liquid crystal material is expected.

However, since the shuttlecock-shaped fullerene derivative has a column-like structure, there are problems that temperature of transition to an isotropic phase is low and that it is difficult to perform rearrangement. Therefore, it is difficult to use the shuttlecock-shaped fullerene derivative as a liquid crystal material.

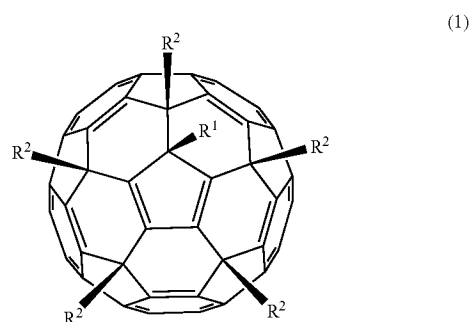
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Further, though it is known that liquid crystalline fullerene-ferrocene dyads and fullerene liquid crystalline dendrimers have a layer structure, it is necessary to add a bulky group to a fullerene skeleton, and therefore it is difficult to obtain a product of interest in good yield.

DISCLOSURE OF THE INVENTION

Under the above-described circumstances, a novel fullerene derivative is desired. Specifically, for example, a fullerene derivative, which has a layer structure in the crystal state or liquid crystalline state, is desired. Moreover, for example, a fullerene derivative, which can be used in a liquid crystal material, is desired.

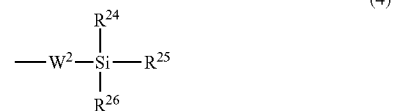
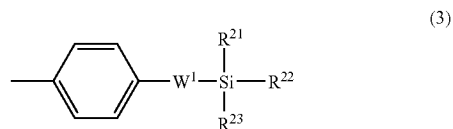
[1] A fullerene derivative represented by the following formula (1):



wherein:

R¹ is a substituted or unsubstituted organic group or a hydrogen atom; and

each R² is independently a group represented by the following formula (3) or (4),



wherein:

W¹ is C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(O)—

W² is a single bond, C₁-C₁₁ alkylene, C₂-C₁₂ alkenylene, or C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkylene, alkenylene or alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(O)—;

R²¹ to R²⁵ are each independently a substituted or unsubstituted C₁-C₂₀ alkyl group, a substituted or unsubstituted C₂-C₁₅ alkenyl group, or a substituted or unsubstituted C₂-C₁₅ alkynyl group; and

R²⁶ is a substituted or unsubstituted C₄-C₂₀ alkyl group, a substituted or unsubstituted C₄-C₁₅ alkenyl group, or a substituted or unsubstituted C₄-C₁₅ alkynyl group.

[2] The fullerene derivative according to item [1], wherein R¹ is a substituted or unsubstituted C₁-C₂₀ hydrocarbon group, a

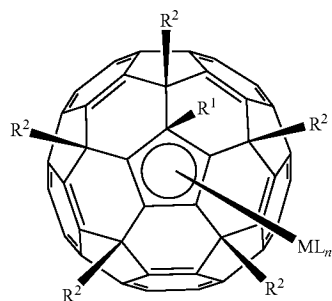
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substituted or unsubstituted C₁-C₂₀ alkoxy group, a substituted or unsubstituted C₆-C₂₀ aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (—SY¹: in the formula, Y¹ is a substituted or unsubstituted C₁-C₂₀ alkyl group), a substituted or unsubstituted arylthio group (—SY²: in the formula, Y² is a substituted or unsubstituted C₆-C₁₈ aryl group), a substituted or unsubstituted alkylsulfonyl group (—SO₂Y³: in the formula, Y³ is a substituted or unsubstituted C₁-C₂₀ alkyl group), or a substituted or unsubstituted arylsulfonyl group (—SO₂Y⁴: in the formula, Y⁴ is a substituted or unsubstituted C₆-C₁₈ aryl group).

[3] The fullerene derivative according to item [1], wherein R¹ is a substituted or unsubstituted C₁-C₁₀ alkyl group, a substituted or unsubstituted C₁-C₁₀(alkenyl group, or a substituted or unsubstituted C₁-C₁₀ alkynyl group.

[4] The fullerene derivative according to any one of items [1] to [3], wherein R¹ has one or more substituents selected from the group consisting of ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, aryl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group.

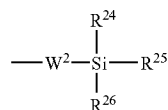
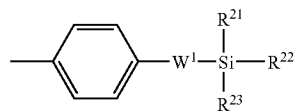
[5] A fullerene derivative represented by the following formula (2):



wherein:

R¹ is a substituted or unsubstituted organic group or a hydrogen atom; and

each R² is independently a group represented by the following formula (3) or (4),



wherein:

W¹ is C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(O)—;

W² is a single bond, C₁-C₁₁ alkenylene, C₂-C₁₂ alkenylene, or C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkenylene, alkenylene or alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(=O)—

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R²¹ to R²⁵ are each independently a substituted or unsubstituted C₁-C₂₀ alkyl group, a substituted or unsubstituted C₂-C₁₅ alkenyl group, or a substituted or unsubstituted C₂-C₅ alkynyl group; and

R²⁶ is a substituted or unsubstituted C₄-C₂₀ alkyl group, a substituted or unsubstituted C₄-C₁₅ alkenyl group, or a substituted or unsubstituted C₄-C₁₅ alkynyl group.

[6] The fullerene derivative according to item [5], wherein M is a transition metal.

[7] The fullerene derivative according to item [5], wherein M is a group 8-10 transition metal.

[8] The fullerene derivative according to item [5], wherein: M is Fe, Ru, or Os; n is an integer from 0 to 5; and L is a halogen atom, alkoxy group, alkyl group, alkine group or cyclopentadienyl group.

[9] The fullerene derivative according to any one of items [1] to [8], wherein W¹ is —C≡C—.

[10] The fullerene derivative according to any one of items [1] to [8], wherein W² is a single bond, C₁-C₄ alkenylene, C₂-C₄ alkenylene, or C₂-C₄ alkynylene.

[11] The fullerene derivative according to any one of items [1] to [10], wherein R²¹, R²², R²⁴ and R²⁵ are methyl groups,

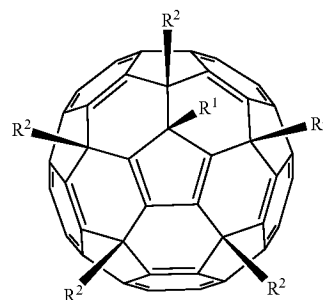
[12] The fullerene derivative according to any one of items [1] to [11], wherein the fullerene derivative in the crystal state has a layer structure.

[13] The fullerene derivative according to any one of items [1] to [11], wherein the fullerene derivative in the liquid crystalline state has a layer structure.

[14] The fullerene derivative according to any one of items [1] to [13], which has an intermediate phase.

[15] A composition, which comprises the fullerene derivative according to any one of items [1] to [14], and which has an intermediate phase.

[16] A fullerene derivative represented by the following formula (1):



wherein:

R¹ is a substituted or unsubstituted organic group or a hydrogen atom; and

each R² is independently a substituted or unsubstituted C₁-C₂₀ hydrocarbon group, a substituted or unsubstituted C₁-C₂₀ alkoxy group, a substituted or unsubstituted C₆-C₂₀ aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (—SY¹ in the formula, Y¹ is a substituted or unsubstituted C₁-C₂₀ alkyl group), a substituted or unsubstituted arylthio group (—SY²: in the formula, Y² is a substituted or unsubstituted C₆-C₁₈ aryl group), a substituted or unsubstituted alkylsulfonyl group (—SO₂Y³: in the formula, Y³ is a substituted or unsubstituted C₁-C₂₀ alkyl group), or a substituted or unsubstituted arylsulfonyl group (—SO₂Y⁴: in the formula, Y⁴ is a substituted or unsub-

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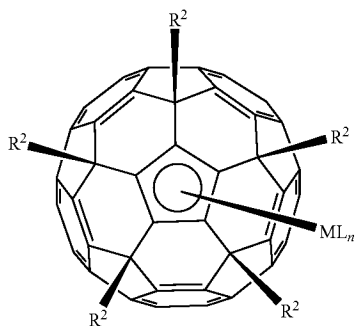
stituted C_6-C_{18} aryl group), and wherein the fullerene derivative in the crystal state or liquid crystalline state has a layer structure.

[17] The fullerene derivative according to item [16], wherein R^1 is a substituted or unsubstituted C_1-C_{20} hydrocarbon group, a substituted or unsubstituted C_1-C_{20} alkoxy group, a substituted or unsubstituted C_6-C_{20} aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ($-SY^1$: in the formula, Y^1 is a substituted or unsubstituted C_1-C_{20} alkyl group), a substituted or unsubstituted arylthio group ($-SY^2$: in the formula, Y^2 is a substituted or unsubstituted C_6-C_{20} aryl group), a substituted or unsubstituted alkylsulfonyl group ($-SO_2Y^3$: in the formula, Y^3 is a substituted or unsubstituted C_1-C_{20} alkyl group), or a substituted or unsubstituted arylsulfonyl group ($-SO_2Y^4$ in the formula, Y^4 is a substituted or unsubstituted C_6-C_{18} aryl group).

[18] The fullerene derivative according to item [16], wherein R^1 is a substituted or unsubstituted C_1-C_{10} alkyl group, a substituted or unsubstituted C_1-C_{10} alkenyl group, or a substituted or unsubstituted C_1-C_{10} alkynyl group.

[19] The fullerene derivative according to any one of items [16] to [18], wherein R^1 has one or more substituents selected from the group consisting of ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, aryl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group.

[20] A fullerene derivative represented by the following formula (2):



wherein:

each R^2 is independently a substituted or unsubstituted C_1-C_{20} hydrocarbon group, a substituted or unsubstituted C_1-C_{20} alkoxy group, a substituted or unsubstituted C_6-C_{20} aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ($-SY^1$: in the formula, Y^1 is a substituted or unsubstituted C_1-C_{20} alkyl group), a substituted or unsubstituted arylthio group ($-SY^2$: in the formula, Y^2 is a substituted or unsubstituted C_6-C_{18} aryl group), a substituted or unsubstituted alkylsulfonyl group ($-SO_2Y^3$: in the formula, Y^3 is a substituted or unsubstituted C_1-C_{20} alkyl group), or a substituted or unsubstituted arylsulfonyl group ($-SO_2Y^4$: in the formula, Y^4 is a substituted or unsubstituted C_6-C_{18} aryl group);

M is a metallic atom;

L is a ligand of M ; and

n is the number of L s, and wherein the fullerene derivative in the crystal state or liquid crystalline state has a layer structure.

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[21] The fullerene derivative according to item [20], wherein M is a transition metal.

[22] The fullerene derivative according to item [20], wherein M is a group 8-10 transition metal.

[23] The fullerene derivative according to item [20], wherein: M is Fe, Ru, or Os; n is an integer from 0 to 5; and L is a halogen atom, alkoxy group, alkyl group, alkyne group or cyclopentadienyl group.

[24] The fullerene derivative according to any one of items [16] to [23], wherein R^2 is a substituted or unsubstituted C_1-C_{10} alkyl group or a substituted or unsubstituted aryl group.

[25] The fullerene derivative according to any one of items [16] to [24], wherein R^2 has one or more substituents selected from the group consisting of ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, aryl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group.

[26] The fullerene derivative according to any one of items [16] to [24], wherein R^2 has one or more substituents selected from the group consisting of ester group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group and aryl group.

[27] The fullerene derivative according to any one of items [16] to [26], which has an intermediate phase.

[28] A composition, which comprises the fullerene derivative according to any one of items [16] to [27], and which has an intermediate phase.

According to the preferred embodiment of the present invention, crystal of a fullerene derivative having a layer structure can be obtained in good yield. Further, in the case of the fullerene derivative according to the preferred embodiment of the present invention, a temperature of transition to an isotropic phase is high, and it is easy to perform rearrangement.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the structure of Compound 10.

FIG. 2 shows DSC measurement result of crystal of Compound 10.

FIG. 3 shows X-ray structure analysis of Compound 10.

FIG. 4 shows the structure of Compound 10A.

FIG. 5 shows the structure of Compound 12.

FIG. 6 shows the structure of Compound 13.

FIG. 7 shows DSC measurement result of Compound 14.

FIG. 8 shows DSC measurement result of Compound 15.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the method of the present invention will be specifically described.

1. Fullerene Derivative

The fullerene derivative of the present invention is represented by the above-described formula (1) or (2). In this regard, "fullerene" is a general term for carbon clusters which are formed by arranging carbon atoms in a spherical shape or a rugby ball shape (see Gendai-Kagaku, June 2000, page 46; and Chemical Reviews 98, 2527 (1998)). Examples thereof include fullerene C_{60} (so-called buckminsterfullerene), fullerene C_{70} , fullerene C_{76} , fullerene C_{78} , fullerene C_{82} , fullerene C_{84} , fullerene C_{90} , fullerene C_{94} , and fullerene C_{96} .

1.1. Fullerene Derivatives Represented by Formula (1)

In formula (1), R^1 is each independently a substituted or unsubstituted organic group or a hydrogen atom.

Preferably, R^1 is a substituted or unsubstituted C_1 - C_{20} hydrocarbon group, a substituted or unsubstituted C_1 - C_{20} alkoxy group, a substituted or unsubstituted C_6 - C_{20} aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ($-\text{SY}^1-$ in the formula, Y^1 is a substituted or unsubstituted C_1 - C_{20} alkyl group), a substituted or unsubstituted arylthio group ($-\text{SY}^2-$ in the formula, Y^2 is a substituted or unsubstituted C_6 - C_{18} aryl group), a substituted or unsubstituted alkylsulfonyl group ($-\text{SO}_2\text{Y}^3-$ in the formula, Y^3 is a substituted or unsubstituted C_1 - C_{20} alkyl group), or a substituted or unsubstituted arylsulfonyl group ($-\text{SO}_2\text{Y}^4-$ in the formula, Y^4 is a substituted or unsubstituted C_6 - C_{18} aryl group). Among them, R^1 is preferably a substituted C_1 - C_{10} alkyl group or an unsubstituted aryl group.

Further, R^1 may have one or more substituents selected from the group consisting of ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, aryl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group. Among these substituents, one or more substituents selected from the group consisting of ester group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, and aryl group are preferable. Further, the number of substituents introduced into R^1 is preferably 0 or 1.

In formula (1), each R^2 is independently a substituted or unsubstituted C_1 - C_{20} hydrocarbon group, a substituted or unsubstituted C_1 - C_{20} alkoxy group, a substituted or unsubstituted C_6 - C_{20} aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group ($-\text{SY}^1-$ in the formula, Y^1 is a substituted or unsubstituted C_1 - C_{20} alkyl group), a substituted or unsubstituted arylthio group ($-\text{SY}^2-$ in the formula, Y^2 is a substituted or unsubstituted C_6 - C_{18} aryl group), a substituted or unsubstituted alkylsulfonyl group ($-\text{SO}_2\text{Y}^3-$ in the formula, Y^3 is a substituted or unsubstituted C_1 - C_{20} alkyl group), or a substituted or unsubstituted arylsulfonyl group ($-\text{SO}_2\text{Y}^4-$ in the formula, Y^4 is a substituted or unsubstituted C_6 - C_{18} aryl group). In formula (1), preferably, at least one R^2 is each independently a group represented by the above-described formula (3) or (4). Moreover, among five R^2 's in formula (1), it is preferred that as many R^2 's as possible (in the range of 1 to 5) are each independently a group represented by the above-described formula (3) or (4). That is, among five R^2 's in formula (1), it is preferred that as many R^2 's as possible are groups represented by the above-described formula (3) or (4), and it is particularly preferred that five R^2 's are groups represented by the above-described formula (3) or (4). It is most preferred that five R^2 's are all groups represented by the above-described formula (3) or are all groups represented by the above-described formula (4).

In formula (3), W^1 is C_2 - C_{12} alkynylene, wherein any $-\text{CH}_2-$ in the alkynylene can be substituted with $-\text{O}-$, $-\text{S}-$, $-\text{COO}-$ or $-\text{OCO}-$. W^1 is preferably $-\text{C}\equiv\text{C}-$, since a fullerene derivative in a preferred embodiment has a layer structure in this case.

In formula (4), R^{24} and R^{25} are each independently a substituted or unsubstituted C_1 - C_{20} alkyl group, a substituted or unsubstituted C_2 - C_{15} alkenyl group, or a substituted or unsubstituted C_2 - C_{15} alkynyl group. Further, R^{26} is preferably a substituted or unsubstituted C_4 - C_{20} alkyl group, a substituted or unsubstituted C_4 - C_{15} alkenyl group, or a substituted or unsubstituted C_4 - C_{15} alkynyl group, since a fullerene derivative in a preferred embodiment has a layer structure in this case.

The fullerene derivative represented by formula (1) preferably has a crystalline structure. More preferably, the crystalline structure is a layer structure.

When a composition only consists of the metal-containing fullerene derivative of the present invention or further comprises other substances, the metal-containing fullerene derivative represented by formula (1) may be an intermediate phase (mesophase). Herein, "intermediate phase" refers to a plastic crystal or liquid crystalline state.

In the case of carbon cluster derivatives exhibiting a thermotropic intermediate phase, an intermediate phase can be obtained by heating or cooling in a certain temperature range. In general, by heating to the state of intermediate phase and thereafter slowly cooling, a carbon cluster derivative, in which molecules are voluntarily oriented/accumulated, can be obtained. In the case of a fullerene derivative having a layer-type crystalline structure, there are advantages as follows: it is easy to perform rearrangement; an oriented state having high homogeneity can be obtained; and it is stabler than a columnar structure and the liquid crystal phase is maintained to a high temperature.

In the present specification, the hydrocarbon group of the " C_1 - C_{20} hydrocarbon group" may be a saturated or unsaturated acyclic group or a saturated or unsaturated cyclic group. When the C_1 - C_{20} hydrocarbon group is acyclic, it may be linear or branched. The " C_1 - C_{20} hydrocarbon group" includes C_1 - C_{20} alkyl group, C_2 - C_{20} alkenyl group, C_2 - C_{20} alkynyl group, C_4 - C_{20} alkyldienyl group, C_6 - C_{18} aryl group, C_7 - C_{20} alkylaryl group, C_7 - C_{20} arylalkyl group, C_4 - C_{20} cycloalkyl group, C_4 - C_{20} cycloalkenyl group, and (C_3 - C_{10} cycloalkyl) C_1 - C_{10} alkyl group.

In the present specification, the " C_1 - C_{20} alkyl group" is preferably C_1 - C_{10} alkyl group, and more preferably C_1 - C_6 alkyl group. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, and dodecanyl.

In the present specification, the " C_2 - C_{20} alkenyl group" is preferably C_2 - C_{10} alkenyl group, and more preferably C_2 - C_6 alkenyl group. Examples of alkenyl groups include, but are not limited to, vinyl, allyl, propenyl, isopropenyl, 2-methyl-1-propenyl, 2-methylallyl, and 2-butenyl.

In the present specification, the " C_2 - C_{20} alkynyl group" is preferably C_2 - C_{10} alkynyl group, and more preferably C_2 - C_6 alkynyl group. Examples of alkynyl groups include, but are not limited to, ethynyl, propynyl, and butynyl.

In the present specification, the " C_4 - C_{20} alkyldienyl group" is preferably C_4 - C_{10} alkyldienyl group, and more preferably C_4 - C_6 alkyldienyl group. Examples of alkyldienyl groups include, but are not limited to, 1,3-butadienyl.

In the present specification, the " C_6 - C_{18} aryl group" is preferably C_6 - C_{10} aryl group. Examples of aryl groups include, but are not limited to, phenyl, 1-naphthyl, 2-naphthyl, indenyl, biphenyl, anthryl, and phenanthryl.

In the present specification, the " C_7 - C_{20} alkylaryl group" is preferably C_7 - C_{12} alkylaryl group. Examples of alkylaryl groups include, but are not limited to, o-tolyl, m-tolyl, p-tolyl, 2,3-xylyl, 2,4-xylyl, 2,5-xylyl, o-cumenyl, m-cumenyl, p-cumenyl, and mesityl.

In the present specification, the " C_7 - C_{20} arylalkyl group" is preferably C_7 - C_{12} arylalkyl group. Examples of arylalkyl groups include, but are not limited to, benzyl, phenethyl, diphenylmethyl, triphenyl methyl, 1-naphthylmethyl, 2-naphthylmethyl, 2,2-diphenylethyl, 3-phenylpropyl, 4-phenylbutyl, and 5-phenylpentyl.

In the present specification, the " C_4 - C_{20} cycloalkyl group" is preferably C_4 - C_{10} cycloalkyl group. Examples of cycloalkyl

groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

In the present specification, the "C₄-C₂₀ cycloalkenyl group" is preferably C₄-C₁₀ cycloalkenyl group. Examples of cycloalkenyl groups include, but are not limited to, cyclopropenyl, cyclobutenyl, cyclopentenyl, and cyclohexenyl.

In the present specification, the "C₁-C₂₀ alkoxy group" is preferably C₁-C₁₀ alkoxy group, and more preferably C₁-C₆ alkoxy group. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy, butoxy, and pentyloxy

In the present specification, the "C₆-C₂₀ aryloxy group" is preferably C₆-C₁₀ aryloxy group. Examples of aryloxy groups include, but are not limited to, phenyloxy, naphthyloxy, and biphenyloxy.

In the present specification, in "alkylthio group (—SY¹: in the formula, Y¹ is a substituted or unsubstituted C₁-C₂₀ alkyl group)" and "alkylsulfonyl group (—SO₂Y³: in the formula, Y³ is a substituted or unsubstituted C₁-C₂₀ alkyl group)", Y¹ and Y³ are preferably C₁-C₁₀ alkyl group, and more preferably C₁-C₆ alkyl group. Examples of alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, and dodecanyl.

In the present specification, in "arylthio group (—SY²: in the formula, Y² is a substituted or unsubstituted C₆-C₁₈ aryl group)" and "arylsulfonyl group (—SO₂Y⁴: in the formula, Y⁴ is a substituted or unsubstituted C₆-C₁₈ aryl group)", Y² and Y⁴ are preferably C₆-C₁₀ aryl group. Examples of aryl groups include, but are not limited to, phenyl, 1-naphthyl, 2-naphthyl, indenyl, biphenyl, anthryl, and phenanthryl.

"C₁-C₂₀ hydrocarbon group," "C₁-C₂₀ alkoxy group," "C₆-C₂₀ aryloxy group," "amino group," "silyl group," "alkylthio group," "arylthio group," "alkylsulfonyl group," and "arylsulfonyl group" may be substituted. Examples of substituents in these cases include ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group. In these cases, one or more substituents may be introduced into replaceable positions, and preferably, 1 to 4 substituents are introduced. When the number of substituents is 2 or more, the substituents may be the same or different.

In the present specification, examples of "substituted or unsubstituted amino group" include, but are not limited to, amino, dimethylamino, methylamino, methylphenylamino, and phenylamino.

In the present specification, examples of "substituted or unsubstituted silyl group" include, but are not limited to, dimethylsilyl diethylsilyl, trimethylsilyl, triethylsilyl, trimethoxysilyl, triethoxysilyl, diphenylmethylsilyl, triphenylsilyl, triphenoxysilyl, dimethylmethoxysilyl, dimethylphenoxysilyl, and methylmethoxyphenyl.

The fullerene derivative represented by formula (1) preferably has a crystalline structure. More preferably, the crystalline structure is a layer structure. Further, the fullerene derivative represented by formula (1) may have a layer structure in liquid crystal.

1.2. Fullerene Derivatives Resented by Formula (2)

In formula (2), each R² is independently a substituted or unsubstituted organic group or a hydrogen atom; M is a metallic atom; L is a ligand of M; and n is the number of Ls.

M is not particularly limited as long as it is a metallic atom, and it may be a typical metal or transition metal. Specific examples of M include: typical metals such as Li, K, Na, Mg, and Al; and transition metals such as Ti, Zr, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Rh, Ir, Ni, Pd, Pt, Cu, and Zn. When using the obtained fullerene derivative in an electronic material, M is preferably a transition metal since an electronic nature based

on redox behavior peculiar to metal is provided to the fullerene skeleton. Among transition metals, group 8-10 transition metals such as Fe, Ru, Os, Rh, Ir, Ni, Pd and Pt are preferred, and group 8 transition metals such as Fe, Ru and Os are more preferred.

n is the number of Ls (ligands of M), and it is not particularly limited as long as it is less than or equal to an integer which can be the number of ligands of M and is more than 0. Preferably, n is an integer from 0 to 5. When the number of Ls is 2 or more, the ligands (Ls) may be the same or different.

Further, L is preferably a hydrogen atom; a halogen atom such as Cl, Br and I; an alkoxy group such as methoxy group and ethoxy group; an alkyl group such as methyl group and ethyl group; a carbonyl group; an alkyne group; or a cyclopentadienyl group.

Moreover, among five R²'s in formula (2) it is preferred that as many R²'s as possible (in the range of 1 to 5) are each independently a group represented by the above-described formula (3) or (4). That is, among five R²'s in formula (1), it is preferred that as many R²'s as possible are groups represented by the above-described formula (3) or (4).

Note that R¹ in formula (2) is as described above.

The fullerene derivative represented by formula (2) preferably has a crystalline structure. More preferably, the crystalline structure is a layer structure. Further, the fullerene derivative represented by formula (2) may have a layer structure in liquid crystal.

When a composition only consists of the metal-containing fullerene derivative of the present invention or further comprises other substances, the metal-containing fullerene derivative represented by formula (2) may be an intermediate phase.

In the case of carbon cluster derivatives exhibiting a thermotropic intermediate phase, an intermediate phase can be obtained by heating or cooling in a certain temperature range. In general, by heating to the state of intermediate phase and thereafter slowly cooling, a carbon cluster derivative, in which molecules are voluntarily oriented/accumulated, can be obtained. In the case of a fullerene derivative having a layer-type crystalline structure, there are advantages as follows: it is easy to perform rearrangement; an oriented state having high homogeneity can be obtained; and it is stabler than a columnar structure and the liquid crystal phase is maintained to a high temperature.

4.2. Method for Producing the Fullerene Derivative of the Present Invention

The fullerene derivative represented by formula (1) can be produced using, for example, the methods described in Japanese Laid-Open Patent Publication Nos. 10-167994, 11-255509 and 2002-241323 and methods according thereto.

For example, an organocopper reagent such as CuBr.S(CH₃)₂ is mixed with an inert solvent such as toluene, tetrahydrofuran, dichlorobenzene and a mixture thereof, an additive such as dimethylimidazolidinone and a Grignard reagent are added thereto, and the obtained mixture is stirred. After that, with the reaction system, fullerene dissolved in an organic solvent is mixed to produce the fullerene derivative of the present invention. A synthesis reaction of the fullerene derivative of the present invention can be terminated by adding an aqueous solution of ammonium chloride or the like to the reaction system.

The reaction is preferably performed under ordinary pressure at a temperature of -70° C. to 70° C., and more preferably at a temperature of -50° C. to 50° C.

Reaction time depends on a solvent used, temperature, etc. In general, the reaction is performed for about several minutes to 5 hours, and preferably for about 10 minutes to 4 hours.

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A method for isolating the fullerene derivative from the reaction system is not particularly limited. For example, isolation is performed by passing a reaction solution through a silica gel column to remove by-products such as inorganic substances. Depending on the necessity, isolated substances may be further purified by HPLC, general column chromatography or the like to improve purity of the fullerene derivative.

The fullerene derivative represented by formula (2) can be produced using, for example, the methods described in Japanese Laid-Open Patent Publication No. 10-167994, etc. or methods according thereto. Specifically, it can be obtained by reacting the fullerene derivative represented by formula (1) with metal alkoxide.

As metal alkoxide to be used in the production of the metal complex of the present invention, alkali metals such as Li and K; transition metals such as Ti, Cu and Ru; and metal alkoxide comprising lanthanoid metal such as Sm(III) can be used. Further, as an alkoxy group that constitutes metal alkoxide, for example, lower alkoxy groups such as C₁-C₆ alkoxy group can be used. Examples thereof include methoxy group, ethoxy group, n-propoxy group, isopropoxy group, n-butoxy group, sec-butoxy group, tert-butoxy group, and neopentoxy group. As metal alkoxide, for example, lithium tert-butoxide, potassium tert-butoxide, thallium ethoxide, copper tert-butoxide and the like can be used.

For example, a reaction between the fullerene derivative represented by formula (1) and metal alkoxide can be generally performed in an inert solvent at a temperature of about -78° C. to room temperature using metal alkoxide in an amount of about 0.5 to 1.5 equivalent, preferably in an amount of about 1.0 equivalent of the carbon cluster derivative (III). The type of solvent is not particularly limited as long as it is inert at the time of reaction. Examples of solvents include tetrahydrofuran and toluene. When another ligand is coordinated to a metal atom, a reaction can be performed in the presence of a phosphorous compound or the like. For example, in the case of using Cu(I) tert-butoxide, if a phosphine compound such as triethyl phosphine is added, a metal complex, in which the phosphine compound is coordinated/bonded to a metal atom, can be obtained.

3. Uses of the Fullerene Derivative of the Present Invention

The fullerene derivative of the preferred embodiment of the present invention has various characteristics such as magnetic, electrical, optical, photochemical and electrochemical characteristics, and orientation/accumulation of molecules attributed to an intermediate phase and the like allow utilization of the fullerene derivative in various indicating devices, optical devices, photoelectric conversion devices, etc.

The fullerene derivative of the preferred embodiment of the present invention is very useful as a liquid crystal material since the temperature of transition to the intermediate phase is high and it is easy to perform rearrangement.

Moreover, when using the carbon cluster derivative of the preferred embodiment of the present invention in various devices, it can be used in a state in which molecular orientation attributed to the intermediate phase is utilized, and it can also be used in the solid state after molecular orientation attributed to the intermediate phase is given thereto.

The metal-containing fullerene derivative of the preferred embodiment of the present invention may have a metal atom, and natures peculiar to the metal atom are given thereto. As a result, for example, the metal-containing fullerene derivative can be utilized in devices of electronic materials and the like

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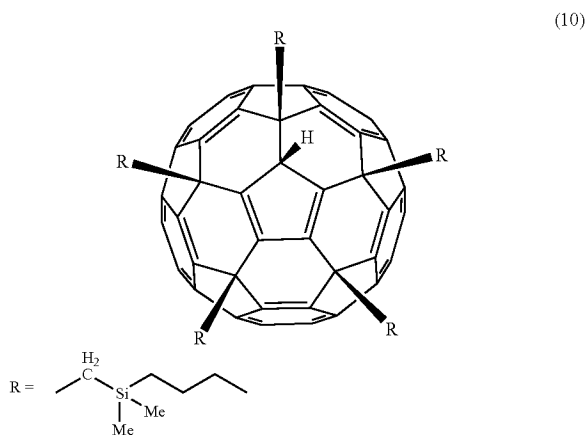
in which electrical behavior based on redox behavior of the metal atom in addition to redox behavior derived from the fullerene skeleton is utilized.

EXAMPLES

Hereinafter the present invention will be described in more detail based on Examples. However, the present invention is not limited thereby

Example 1

Compound Represented by the Following Formula (10)



Copper bromide-dimethylsulfide complex (1.03 g, 5.05 mmol) was suspended in 20 mL of tetrahydrofuran. The mixture was maintained at 0° C., and dimethylimidazolidinone (0.54 mL, 4.46 mmol) and BuMe₂SiCH₂MgCl (1.03M THF solution, 4.33 mL, 4.46 mmol) were added to the mixture, and the obtained mixture was stirred. After stirring for 5 minutes, 1,2-dichlorobenzene solution (25 mL) of C₆₀ (200 mg, 0.28 mmol) was added to the mixture and heated to 25° C. After stirring for 1 hour, 0.25 mL of saturated ammonium chloride solution was added to the mixture. The reaction mixture was diluted with 150 mL of toluene. Toluene was used as a developing solvent, and the mixture was passed through a short-pass silica gel column to remove by-products such as copper salt, etc. The solvent was distilled away until the amount of the remaining solvent became about 5 mL. 300 mL of methanol was added to the remaining solvent to perform reprecipitation, and a compound represented by formula (10) having the purity of about 95% (hereinafter referred to as "Compound 10", etc.) was obtained. Note that "Me" represents methyl in the present specification. The isolated yield was 87% (379 mg).

NMR and UV data of the obtained Compound 10 were as follows:

¹H NMR (500 Hz, CDCl₃): δ 0.04 (s, 6H), 0.09-0.11 (overlapping m, 24H), 0.58-0.64 (m, 10H), 0.80-0.84 (m, 15H), 1.25-1.30 (m, 20H), 1.84-2.14 (m, 10H), 4.64 (s, 1H); ¹³C NMR (CDCl₃): δ -1.20, -1.16, 13.68, 13.72, 16.23, 16.27, 25.95, 26.01, 26.04, 26.42, 26.45, 29.52, 29.95, 29.83, 52.86, 53.21, 54.79, 63.25, 142.34, 143.14, 143.22, 143.40, 143.64, 144.75, 144.98, 145.16, 145.49, 145.97, 146.24, 146.64, 146.87, 146.93, 147.50, 147.76, 147.78, 147.93, 148.05, 148.42, 148.45, 148.59, 149.80, 154.04, 154.30, 154.45, 157.59

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USV-vis (hexane), λ_{max} 395, 356, 348, 262, 241, 212.

Compound 10 was red powder at room temperature. The compound in the solid state was stable in air at room temperature.

By slowly diffusing methanol in chloroform solution of Compound 10, red single crystal suitable for X-ray crystal structure analysis was successfully obtained. Further, crystallographic data of crystal of Compound 10 were as follows:
Crystalline system: monoclinic, Space group: P21/c

a, Å	14.4090(7)
b, Å	17.2910(8)
c, Å	30.0080(12)
α , deg	90.00
β , deg	101.757(3)
γ , deg	90.00
Volume V, Å ³	7319.5(6)
Number of molecules in unit cell Z,	4
Temperature, K	153(2)
Crystal size, mm	0.3 × 0.3 × 0.3
Number of independent reflections	14605
Number of parameters	
R1, wR2 (all data)	0.082, 0.135
R, R _w (I > 2.0 σ (I))	0.058, 0.132
GOF on F ²	1.158

X-ray structure analysis of crystal of Compound 10 was performed, and the structure was as shown in FIG. 1. It was confirmed from FIG. 1 that Compound 10 has a layer structure in its crystalline state.

When a fullerene derivative has an intermediate phase, it is generally confirmed by observing transition from a crystal phase to the intermediate phase and transition from the intermediate phase to an isotropic phase (liquid phase) by measurement of DSC (differential scanning calorimetry). Therefore, crystal of Compound 10 was subjected to measurement of DSC, and measurement results were as shown in FIG. 2.

Regarding the derivative of Compound 10, it was confirmed from FIG. 2 that T_c (clearing point) is 254° C., T_m (melting point) is 75° C., and an intermediate phase is exhibited at a temperature of 75° C. to 254° C.

Further, when Compound 10 was subjected to X-ray diffraction measurement at 200° C., crystallographic data thereof were as follows:

a, Å	27.68
b, Å	21.00
c, Å	15.44
α , deg	90.00
β , deg	90.00
γ , deg	90.00
Temperature, K	473

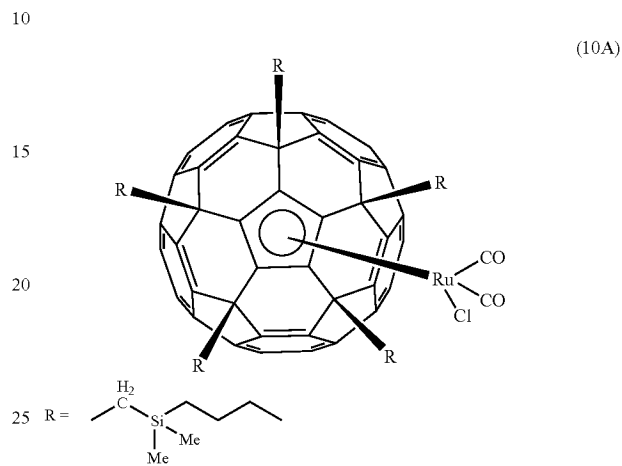
When Compound 10 was subjected to X-ray structure analysis at 200° C., the structure was as shown in FIG. 3. It

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was confirmed from the data and FIG. 3 that Compound 10 has a layer structure in its liquid crystalline state.

Example 2

Compound Represented by the Following Formula (10A)



Potassium t-butoxide/THF solution (1M, 0.26 mL, 0.26 mmol) was added to tetrahydrofuran (40 mL) solution of Compound 10 (200 mg) at 25° C. After stirring for 15 minutes, [RuCl₂(CO)₃]₂ was added to the mixture. The reaction mixture was diluted with toluene and passed through a short-pass silica gel column, and thereafter the solution was distilled away. The solid was dissolved in carbon disulfide, and silica gel column chromatography was performed using a mixed solvent of carbon disulfide and hexane to obtain red microcrystal of Compound 10A (55 mg, 0.032 mmol, Isolated yields 25%).

NMR and UV data of the obtained Compound 10A were as follows:

¹H NMR (500 Hz, CDCl₃): δ 0.04 (s, 30H), 0.58 (t, J=8.0 Hz, 10H), 0.80 (t, J=700 Hz, 15H), 1.24-1.26 (m, 20H), 2.17 (s, 10H); ¹³C NMR (CDCl₃): δ -1.33, 13.65, 16.03, 25.84, 26.31, 34.76, 52.99, 115.00, 143.07, 144.03, 147.24, 148.19, 148.66, 152.11, 196.93

UV-vis (hexane) λ_{max} 391, 356, 260, 213.

Compound 10A was red powder at room temperature. The compound in the solid state was stable in air at room temperature.

By slowly diffusing methanol in chloroform solution of Compound 10A, red single crystal suitable for X-ray crystal structure analysis was successfully obtained. Further, crystallographic data of crystal of Compound 10A were as follows:

Crystalline System: Triclinic, Space Group: P-1

a, Å	14.3750(7)
b, Å	14.5870(9)
c, Å	19.4600(12)
α , deg	96.350(3)
β , deg	101.761(3)
γ , deg	107.106(3)
Volume V, Å ³	3754.2(4)
Number of molecules in unit cell Z,	2
Temperature, K	153(2)

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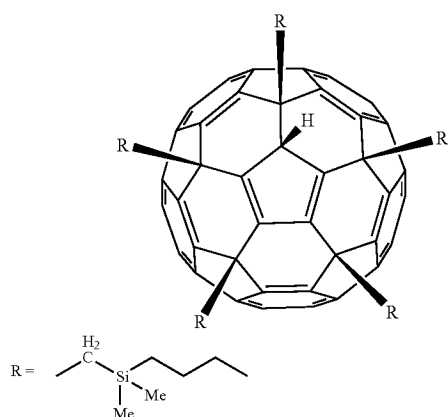
-continued

Crystal size, mm	0.3 × 0.3 × 0.3
Number of independent reflections	13385
Number of parameters	960
R1, wR2 (all data)	0.0827, 0.1916
R, R _w (I > 2.0σ(I))	0.0735, 0.02077
GOF on F ²	1.045

X-ray structure analysis of crystal of Compound 10A was performed, and the structure was as shown in FIG. 4. It was confirmed from FIG. 3 that Compound 10A has a layer structure in its crystalline state.

Example 3

Compound Represented by the Following Formula (11)



Copper bromide-dimethylsulfide complex (1.03 g, 5.05 mmol) was suspended in 20 mL of tetrahydrofuran. The mixture was maintained at 0° C., and dimethylimidazolidinone (0.54 mL, 4.46 mmol) and BuMe₂SiCH₂MgCl (0.82M THF solution, 5.4 n 4.46 mmol) were added to the mixture, and the obtained mixture was stirred. After stirring for 5 minutes, 1,2-dichlorobenzene solution (25 mL) of C₆₀ (200 mg, 0.28 mmol) was added to the mixture and heated to 25° C. After stirring for 1 hour, 0.25 mL of saturated ammonium chloride solution was added to the mixture. The reaction mixture was diluted with 150 mL of toluene. Toluene was used as a developing solvent, and the mixture was passed through a short-pass silica gel column to remove by-products such as copper salt, etc. The solvent was distilled away until the amount of the remaining solvent became about 5 mL. 300 mL of methanol was added to the remaining solvent to perform reprecipitation, and Compound 11 having the purity of about 95% was obtained. The isolated yield was 84% (350 mg).

NMR and UV data of the obtained Compound 11 were as follows:

¹H NMR (500 Hz, CDCl₃): δ 0.03 (s, 6H), 0.04-0.1 (overlapping m, 24H), 0.53-0.62 (m, 10H), 0.82-0.85 (m, 15H), 1.20-1.31 (m, 40H), 1.85-2.15 (m, 10H), 4.65 (s, 1H); TIC NMR (CDCl₃): δ -1.20, -1.15, 14.15, 16.57, 16.61, 22.61, 23.78, 23.81, 23.84, 29.55, 29.96, 31.49, 31.53, 31.55, 33.20, 33.24, 36.84, 52.87, 53.21, 54.79, 63.26, 142.36, 143.15, 143.23, 143.41, 143.65, 144.26, 144.99, 145.17, 145.49, 145.98, 146.25, 146.64, 146.88, 146.93, 147.49, 147.76,

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147.80, 147.94, 148.05, 148.42, 148.45, 148.59, 149.82, 154.03, 154.32, 154.47, 157.62

UV-vis (hexane) λ_{max} 395, 356, 348, 262, 241, 211.

Compound 11 was red fluid with high viscosity at room temperature. The compound in the solid state was stable in air at room temperature.

Moreover, optical texture was observed using a polarization microscope, and the presence of intermediate phase in Compound 11 was confirmed. The intermediate phase was maintained at temperatures of up to 180° C. When Compound 11 was annealed at 180° C. for 3 hours, batonnet texture, which is often found in a smectic phase, was observed by the polarization microscope.

Moreover, as in the case of Example 1, it was confirmed from data of X-ray structure analysis that Compound 11 has a layer structure in its crystalline state.

Example 4

Compound Represented by the Following Formula (11A)

(11)

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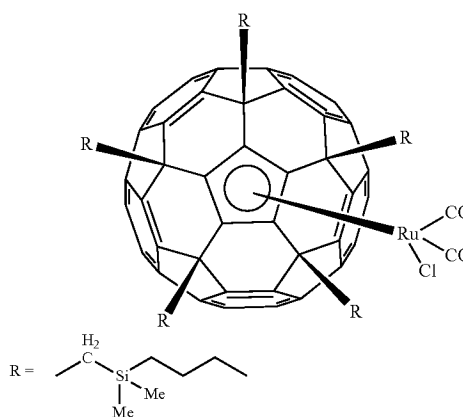
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Potassium t-butoxide/THF solution (1M, 0.26 mL, 0.26 mmol) was added to tetrahydrofuran (40 mL) solution of Compound 11 (200 mg) at 25° C. After stirring for 15 minutes, [RuCl₂(CO)₃]₂ (136 mg) was added to the mixture. The reaction mixture was diluted with toluene and passed through a short-pass silica gel column, and thereafter the solution was distilled away. The solid was dissolved in carbon disulfide, and silica gel column chromatography was performed using a mixed solvent of carbon disulfide and hexane to obtain Compound 11A (50.0 mg-0.0294 mmol, 23%).

NMR and UV data of the obtained Compound 11A were as follows:

¹H NMR (500 Hz, CDCl₃): δ 0.046 (s, 30H), 0.59 (t, J=8.0 Hz, 10H), 0.85 (t, J=7.0 Hz, 15H), 1.19-1.57 (m, 40H), 2.18 (s, 10H); ¹³C NMR (CDCl₃): δ -1.32, 14, 13, 16.37, 22.57, 23.65, 31.44, 33.10, 34, 77, 52.98, 114.99, 143.07, 144.03, 147.24, 148.18, 148.66, 152.11, 196.94

UV-vis (hexane) λ_{max} 393, 356, 260, 213.

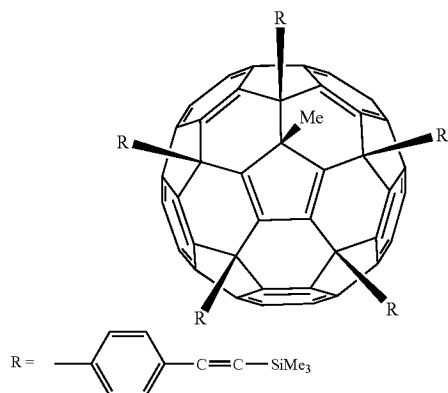
Compound 11A was fluid with high viscosity at room temperature. Optical texture, which indicates the presence of intermediate phase, was observed by a polarization microscope.

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Moreover, as in the case of Example 2, when X-ray structure analysis was performed, it was confirmed from data of the structure analysis that Compound 11A has a layer structure in its crystalline state.

Example 5

Compound Represented by the Following Formula
(12)



THF solution (8 mL) of (4-bromophenylethynyl)trimethylsilane (607 mg, 2.4 mmol) was added dropwise to THF suspension of magnesium turnings (60 mg, 2.5 mmol). After the mixture was stirred at room temperature for 3 hours, copper bromide-dimethylsulfide complex (512 mg, 2.5 mmol) was added to the mixture to prepare an organocopper reagent. 10 minutes later, 1,2-dichlorobenzene solution (10 mL) of C₆₀ (144 mg, 0.2 mmol) was added thereto at once. After stirring at room temperature for 2 hours, methyl iodide (1.24 mL, 20 mmol) was added to the mixture. After stirring at room temperature for 3 hours, the reaction was terminated by the addition of saturated ammonium chloride solution. The mixture was diluted with toluene, and copper salt was removed by means of a short-pass silica gel column. The obtained filtrate was concentrated to obtain Compound 12 by means of flash column chromatography. (290 mg isolated yield: 91).

NMR data of the obtained Compound 12 were as follows:
¹H NMR (CDCl₃): δ 0.21 (s, 9H, SiMe₃), 0.28 (s, 18H, SiMe₃), 0.30 (s, 18H, SiMe₃), 1.36 (s, 3H, C₆₀Me), 7.07 (d, J=8.00 Hz, 2H, ArH), 7.20 (d, J=8.00 Hz, 2H, ArH), 7.44 (d, J=8.00 Hz, 4H, ArH), 7.46 (d, J=8.00 Hz, 4H, ArH), 7.60 (d, J=8.00 Hz, 4H, ArH), 7.71 (d, J=8.00 Hz, 4H, ArH).
¹³C NMR (CDCl₃): δ -0.17 (3C, SiMe₃), -0.06 (6C, 2SiMe₃), -0.02 (6C, 2SiMe₃), 34.35 (C₆₀Me), 57.95 (2C, 2C₆₀(C_α)), 60.81 (2C, 2C₆₀(C_α)), 62.22 (1C, C₆₀(C_α)), 62.33 (1C, C₆₀(CMe)), 95.35 (1C, C=CSi), 95.45 (2C, 2C=CSi), 95.47 (2C, 2C=CSi), 104.07 (1C, C=CSi), 104.36 (2C, 2C=CSi), 104.51 (2C, 2C=CSi), 122.04 (1C, Ar), 122.79 (2C, Ar), 122.95 (2C, Ar), 127.92 (4C, Ar), 128.46 (4C, Ar), 129.54 (2C, Ar), 131.78 (2C, Ar), 132.34 (4C, Ar), 132.62 (4C, Ar), 137.93, 139.58, 142.44, 142.48, 143.50, 143.66, 143.92, 144.12, 144.30, 144.35, 144.45, 144.61, 145.25, 145.47, 147.10, 147.28, 147.30, 147.82, 148.19, 148.26, 148.37, 148.47, 148.71, 148.75, 148.82, 151.31, 152.37, 156.61, 160.64.

Compound 12 was orange powder at room temperature. The compound in the solid state was stable in air at room temperature.

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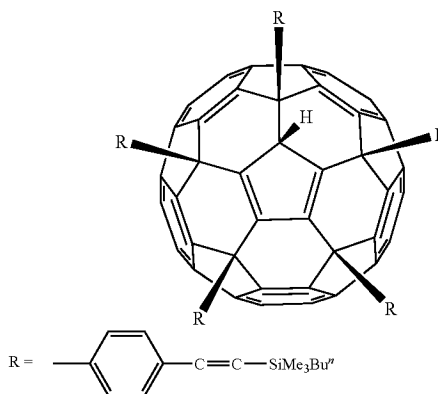
By slowly diffusing methanol in chloroform solution of Compound 12, red single crystal suitable for X-ray crystal structure analysis was successfully obtained. Further, crystallographic data of crystal of Compound 12 were as follows:
 5 Crystalline System: Triclinic, Space Group: P-1

	a, Å	14.449
	b, Å	17.506
10	c, Å	23.235
	α, deg	103.57
	β, deg	100.73
	γ, deg	105.18
	Volume V, Å ³	5318
	Number of molecules in unit cell Z,	2
15	Temperature, K	153(2)
	Crystal size, mm	0.68 × 0.32 × 0.12
	Number of independent reflections	16452
	Number of parameters	1135
	R1, wR2 (all data)	0.2962, 0.4836
	R, Rw (I > 2.0σ(I))	0.1777, 0.4183
20	GOF on P2	1.304

When Compound 12 was subjected to X-ray structure analysis, the structure was as shown in FIG. 5. It was confirmed from FIG. 5 that Compound 12 has a layer structure in its crystalline state.

Example 6

Compound Represented by the Following Formula
(13)



i-propylmagnesiumbromide (0.67 M/THF solution, 3.10 mL, 2.1 mmol) was added dropwise to THF solution (15 mL) of 1-bromo-4-ethynylbenzene (382 mg, 2.0 mmol) at 0° C. After the mixture was stirred for 20 minutes, an ice water bath was removed. After stirring at room temperature for 10 minutes, n-butyldimethylsilyl chloride (0.69 mL, 4.0 mmol) was added to the mixture. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (5 mL). The reaction mixture was extracted with ethyl acetate, and it was concentrated and thereafter purified by means of flash column chromatography to obtain (4-bromophenylethynyl)-n-butyldimethylsilane (530 mg, isolated yield: 90%).

THF solution (4 mL) of (4-bromophenylethynyl)-n-butyldimethylsilane obtained (295 mg, 1.0 mmol) was added dropwise to THF suspension (2 mL) of magnesium turnings (26 mg, 1.1 mmol). After the mixture was stirred at room tem-

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perature for 3 hours, copper (I) bromide-dimethylsulfide complex (225 mg, 1.1 mmol) was added to the mixture to prepare an organocopper reagent. After stirring for 10 minutes, 1,2-dichlorobenzene solution (10 mL) of C₆₀ (36 mL, 0.05 mmol) was added thereto at once. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (0.05 mL). The reaction mixture was diluted with toluene (10 mL), and copper salt was removed by a silica gel column. The obtained filtrate was concentrated and purified by preparative GPC to obtain Compound 13 (78 mg, isolated yield: 87%). Note that "Bu" represents butyl in the present specification.

NMR data of the obtained Compound 13 were as follows.

¹H NMR (CDCl₃) δ 0.21 (s, 6H, SiMe₂), 0.24 (s, 12H, 2SiMe₂), 0.6 (s, 12H, 2SiMe₂), 0.73 (m, 10H, 5SiCH₂), 0.93 (m, 15H, 5CH₂CH₃), 1.40 (m, 20H, 10CH₂), 5.22 (s, 1H, C₆₀H), 7.28 (s, 4H, ArH), 7.32 (d, J=8.55 Hz, 4H, ArH), 7.46 (d, J=8.55 Hz, 4H, ArH), 7.48 (d, J=8.55 Hz, 4H, ArH), 7.68 (d, J=8.55 Hz, 4H, ArH). ¹³C(CDCl₃): δ -1.73 (6C, 3SiMe₂), 1.01 (4C, 2SiMe₂), 13.84 (5C, 5SiCH₂), 15.84 (3C, 3CH₂CH₃), 15.86 (2C, 2CH₂CH₃), 26.02 (5C, 5CH₂), 26.25 (3C, 3CH₂), 26.27 (2C, 2CH₂), 58.60 (2C, 2C₆₀(C_α)), 58.72 (1C, C₆₀(C_α)), 60.73 (2C, 2C₆₀(C_α)), 62.87 (1C, C₆₀(CH)), 94.74 (2C, 2C≡CSi), 94.77 (1C, C≡CSi), 94.94 (2C, 2C≡CSi), 104.56 (1C, C≡CSi), 104.78 (2C, 2C≡CSi), 104.86 (2C, 2C≡CSi), 122.45 (1C, Ar), 122.70 (2C, Ar), 122.97 (2C, Ar), 127.34 (2C, Ar), 127.64 (4C, Ar), 127.66 (4C, Ar), 132.42 (4C, Ar), 132.55 (2C, Ar), 132.65 (4C, Ar), 139.55, 139.57, 143.24, 143.43, 144.11, 144.23, 144.30, 144.41, 145.13, 145.38, 145.47, 145.61, 145.67, 146.89, 147.07, 147.16, 147.27, 147.74, 148.10, 148.14, 148.25, 148.38, 148.67, 148.77, 148.80, 150.90, 151.81, 152.46, 155.54.

Compound 13 was orange powder at room temperature. The compound in the solid state was stable in air at room temperature.

By slowly diffusing ethanol in toluene solution of Compound 13, orange single crystal suitable for X-ray crystal structure analysis was obtained. Crystallographic data of crystal of Compound 13 were as follows:

Crystalline System: Monoclinic, Space Group: P 2₁/n

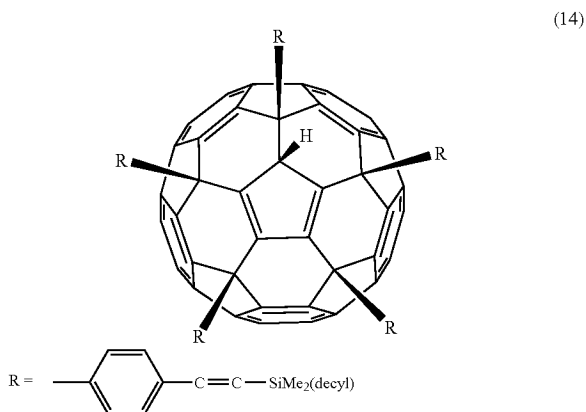
a, Å	18.564
b, Å	17.636
c, Å	32.451
α, deg	90.000
β, deg	99.671
γ, deg	90.000
Volume V, Å ³	10473(4)
Number of molecules in unit cell Z,	4
Temperature, K	153(2)
Crystal size, mm	0.75 × 0.45 × 0.20
Number of independent reflections	17181
Number of parameters	1107
R1, wR2 (all data)	0.2769, 0.5134
R, Rw (I > 2.0σ(I))	0.1877, 0.4567
GOF on F ²	1.701

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When crystal of Compound 13 was subjected to X-ray structure analysis, the structure was as shown in FIG. 6.

Example 7

Compound Represented by the Following Formula (14)



i-propylmagnesiumbromide (0.67 M/THF solution, 3.10 mL, 2.1 mmol) was added dropwise to THF solution (15 mL) of 1-bromo-4-ethynylbenzene (382 mg, 2.0 mmol) at 0° C. After the mixture was stirred for 20 minutes, an ice water bath was removed. After stirring at room temperature for 10 minutes, *n*-decyldimethylsilyl chloride (1.5 mL, 4.0 mmol) was added to the mixture. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (5 mL). The reaction mixture was extracted with ethyl acetate, and it was concentrated and thereafter purified by means of flash column chromatography to obtain colorless liquid, (4-decylphenylethynyl)-*n*-butyldimethylsilane (646 mg, isolated yield: 85%).

THF solution (4 mL) of (4-decylphenylethynyl)-*n*-butyldimethylsilane obtained (529 mg, 1.3 mmol) was added dropwise to THF suspension (2 mL) of magnesium turnings (32 mg, 1.3 mmol). After the mixture was stirred at room temperature for 3 hours, copper (I) bromide-dimethylsulfide complex (287 mg, 1.4 mmol) was added to the mixture to prepare an organocopper reagent. After stirring for 10 minutes, 1,2-dichlorobenzene solution (10 mL) of C₆₀ (50 mL, 0.07 mmol) was added thereto at once. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (0.05 mL). The reaction mixture was diluted with toluene (10 mL), and copper salt was removed by a silica gel column. The obtained filtrate was concentrated and purified by preparative GPC to obtain Compound 14 (153 mg, isolated yield: 93%).

NMR data of the obtained Compound 14 were as follows:

¹H NMR (CDCl₃): δ 0.21 (s, 6H, SiMe₂), 0.24 (s, 12H, 2SiMe₂), 0.26 (s, 12H, 2SiMe₂), 0.73 (m, 10H, 5SiCH₂), 0.86 (m, 15H, 5CH₂CH₃), 1.20-1.50 (m, 100H, 50CH₂), 5.22 (s, 1H, C₆₀H), 7.29 (s, 4H, ArH), 7.31 (d, J=8.00 Hz, 4H, ArH), 7.45 (d, J=8.00 Hz, 4H, ArH), 7.49 (d, J=8.00 Hz, 4H, ArH), 7.68 (d, J=8.00 Hz, 4H, ArH). ¹³C NMR (CDCl₃): δ -1.72 (10C, 5SiMe₂), 14.13 (5C, 5SiCH₂), 16.09 (5C, 5CH₂CH₃),

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22.69 (5C, 5CH₂), 23.78 (5C, 5CH₂), 29.32 (m, 10C, 10CH₂), 29.66 (m, 20C, 20CH₂), 31.91 (5C, 5CH₂), 33.29 (5C, 5CH₂), 58.60 (2C, 2C₆₀(C₆₀)), 58.72 (1C, C₆₀), 60.73 (2C, temperature for 3 hours, copper (I) bromide-dimethylsulfide complex (287 mg, 1.4 mmol) was added to the mixture to prepare an organocopper reagent. After stirring for 10 minutes, 1,2-dichlorobenzene solution (10 mL) of C₆₀ (50 ml, 0.07 mmol) was added thereto at once. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (0.05 mL). The reaction mixture was diluted with toluene (10 mL), and copper salt was removed by a silica gel column. The obtained filtrate was concentrated and purified by preparative GPC to obtain Compound 15 (133 mg, isolated yield: 86%).

NMR data of the obtained Compound 15 were as follows:

¹H NMR (CDCl₃): δ 0.22 (s, 6H, SiMe₂), 0.25 (s, 12H, 2SiMe₂), 0.27 (s, 12H, 2SiMe₂), 0.73 (m, 10H1, 5SiCH₂), 0.85 (m, 15H, 5CH₂CH₃), 1.26-1.56 (m, 80H, 40CH₂), 5.22 (s, 1H, C₆₀H), 7.29 (s, 4H, ArH), 7.32 (d, J=8.00 Hz, 4H, ArH), 7.45 (d, J=8.00 Hz, 4H, ArH), 7.49 (d, J=8.00 Hz, 4H, ArH), 7.68 (d, J=8.00 Hz, 4H, ArH). ¹³C NMR (CDCl₃): δ -1.74 (4C, 2SiMe₂), -1.73 (4C, 2SiMe₂), -1.71 (2C, SiMe₂), 14.13 (5C, 5SiCH₂), 16.08 (1C, CH₂CH₃), 16.12 (4C, 4CH₂CH₃), 22.69 (5C, 5CH₂), 23.76 (3C, 3CH₂), 23.79 (2C, 2CH₂), 29.32 (m, 10C, 10CH₂), 29.66 (m, 1C, 10CH₂), 31.90 (5C, 5CH₂), 33.29 (5C, 5CH₂), 58.58 (2C, 2C₆₀(C₆₀)), 58.71 (1C, C₆₀(C₆₀)), 60.72 (2C, 2C₆₀(C₆₀)), 62.85 (1C, C₆₀(CH)), 94.75 (2C, 2C≡CSi), 94.77 (1C, C≡CSi), 94.96 (2C, 2C≡CSi), 104.55 (1C, C≡CSi), 104.76 (2C, 2C≡CSi), 104.84 (2C, 2C≡CSi), 122.45 (1C, Ar), 122.70 (2C, Ar), 122.97 (2C, Ar), 127.31 (2C, Ar), 127.60 (4C, Ar), 127.63 (4C, Ar), 132.42 (4C, Ar), 132.54 (2C, Ar), 132.65 (4C, Ar), 139.54, 139.56, 143.23, 143.42, 144.10, 144.22, 144.23, 144.30, 144.40, 145.12, 145.36, 145.47, 145.60, 145.67, 146.88, 147.07, 147.15, 147.26, 147.74, 148.09, 148.14, 148.24, 148.38, 148.66, 148.77, 148.80, 150.90, 151.81, 152.46, 155.52.

Compound 15 was orange solid with high viscosity at room temperature. Further, the compound in the solid state was stable in air at room temperature.

Compound 15 was subjected to DSC measurement, and measurement results were as shown in FIG. 8.

It was confirmed from FIG. 8 that the derivative of Compound 15 exhibits an intermediate phase at a temperature of 131° C. or lower.

INDUSTRIAL APPLICABILITY

The fullerene derivative obtained in the present invention has an ordered 2C₆₀(C₆₀), 62.86 (1C, C₆₀(CH)), 94.75 (2C, 2C≡CSi), 94.96 (3C, 3C≡CSi), 104.54 (1C, C≡CSi), 104.75 (2C, 2C≡CSi), 104.83 (2C, 2C≡CSi), 122.46 (1C, Ar), 122.71 (2C, Ar), 122.98 (2C, Ar), 127.32 (2C, Ar), 127.61 (4C, Ar), 127.63 (4C, Ar), 132.43 (4C, Ar), 132.54 (2C, Ar), 132.65 (4C, Ar), 139.56, 143.25, 143.43, 144.11, 144.22, 144.24, 144.30, 144.25, 144.30, 144.41, 145.13, 145.36, 145.47, 145.61, 145.69, 146.89, 147.09, 147.17, 147.28, 147.75, 148.11, 148.16, 148.26, 148.40, 148.68, 148.79, 148.82, 150.91, 151.83, 152.48, 155.54.

Compound 14 was orange solid with high viscosity at room temperature. The compound in the solid state was stable in air at room temperature.

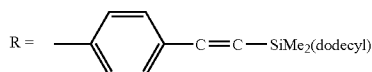
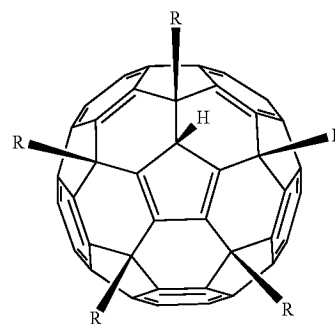
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Compound 14 was subjected to DSC measurement, and measurement results were as shown in FIG. 7.

It was confirmed from FIG. 7 that the derivative of Compound 14 has phase transition at 102° C. and 110° C. and exhibits an intermediate phase at a temperature of 110° C. or lower.

Example 8

Compound Represented by the Following Formula (15)



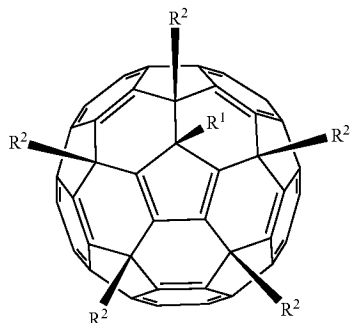
i-propylmagnesiumbromide (0.67 M/TH solution, 3.10 mL, 3.1 mmol) was added dropwise to THF solution (15 mL) of 1-bromo-4-ethynylbenzene (382 mg, 2.0 mmol) at 0° C. After the mixture was stirred for 20 minutes, an ice water bath was removed. After stirring at room temperature for 10 minutes, *n*-dodecyltrimethylsilyl chloride (1.5 mL, 4.0 mmol) was added to the mixture. After stirring for 2 hours, the reaction was terminated by the addition of saturated ammonium chloride solution (5 mL). The reaction mixture was extracted with ethyl acetate, and it was concentrated and thereafter purified by means of flash column chromatography to obtain colorless liquid, (4-dodecylphenylethynyl)-*n*-butyldimethylsilane (627 mg, isolated yield: 77%).

THF solution (4 mL) of (4-dodecyl phenylethynyl)-*n*-butyldimethylsilane obtained (492 mg, 1.3 mmol) was added dropwise to THF suspension (2 mL) of magnesium turnings (32 mg, 1.3 mmol). After the mixture was stirred at room structure with high regularity, in which, for example, the fullerene derivative has a layer crystalline structure in which no organic group is positioned between fullerene skeletons. Temperature of transition to an isotropic phase of the structure is higher and stabler compared to that of a columnar structure, and therefore the fullerene derivative of the present invention is useful as a liquid crystal material. Moreover, the fullerene derivative obtained in the present invention is stable, for example, in air, and therefore can be used as an electron-conductive material and an optical functional material.

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The invention claimed is:

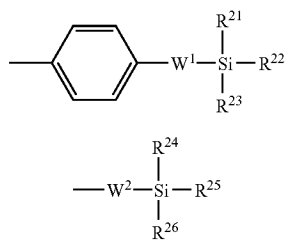
1. A fullerene derivative represented by the following formula (1):



wherein:

R¹ is a substituted or unsubstituted organic group or a hydrogen atom; and

each R² is independently a group represented by the following formula (3) or (4),



wherein:

W¹ is C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(=O)—;

W² is a single bond, C₁-C₁₁ alkylene, C₂-C₁₂ alkenylene, or C₂-C₁₂ alkynylene, wherein any —CH₂— in the alkylene, alkenylene or alkynylene is optionally substituted with —O—, —S—, —C(=O)O—, or —O—C(=O)—;

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R²¹ to R²⁵ are each independently a substituted or unsubstituted C₁-C₂₀ alkyl group, a substituted or unsubstituted C₂-C₁₅ alkenyl group, or a substituted or unsubstituted C₂-C₁₅ alkynyl group; and

R²⁶ is a substituted or unsubstituted C₄-C₂₀ alkyl group, a substituted or unsubstituted C₄-C₁₅ alkenyl group, or a substituted or unsubstituted C₄-C₁₅ alkynyl group, wherein the fullerene derivative in the crystal state or the liquid crystal state has a layer structure.

2. The fullerene derivative according to claim 1, wherein R¹ is a substituted or unsubstituted C₁-C₂₀ hydrocarbon group, a substituted or unsubstituted C₁-C₂₀ alkoxy group, a substituted or unsubstituted C₆-C₂₀ aryloxy group, a substituted or unsubstituted amino group, a substituted or unsubstituted silyl group, a substituted or unsubstituted alkylthio group (—SY¹: in the formula, Y¹ is a substituted or unsubstituted C₁-C₂₀ alkyl group), a substituted or unsubstituted arylthio group (—SY²: in the formula, Y² is a substituted or unsubstituted C₆-C₁₈ aryl group), a substituted or unsubstituted alkylsulfonyl group (—SO₂Y³: in the formula, Y³ is a substituted or unsubstituted C₁-C₂₀ alkyl group), or a substituted or unsubstituted arylsulfonyl group (—SO₂Y⁴: in the formula, Y⁴ is a substituted or unsubstituted C₆-C₁₈ aryl group).

3. The fullerene derivative according to claim 1, wherein R¹ is a substituted or unsubstituted C₁-C₁₀ alkyl group, a substituted or unsubstituted C₁-C₁₀ alkenyl group, or a substituted or unsubstituted C₁-C₁₀ alkynyl group.

4. The fullerene derivative according to claim 1, wherein R¹ has one or more substituents selected from the group consisting of ester group, carboxyl group, amide group, alkyne group, trimethylsilyl group, trimethylsilylethynyl group, aryl group, amino group, phosphonyl group, thio group, carbonyl group, nitro group, sulfo group, imino group, halogeno group, and alkoxy group.

5. The fullerene derivative according to claim 1, wherein W¹ is —C≡C—.

6. The fullerene derivative according to claim 1, wherein W² is a single bond, C₁-C₄ alkylene, C₂-C₄ alkenylene, or C₂-C₄ alkynylene.

7. The fullerene derivative according to claim 1, wherein R²¹, R²², R²⁴ and R²⁵ are methyl groups.

8. The fullerene derivative according to claim 1, which has an intermediate phase.

9. A composition, which comprises the fullerene derivative according to claim 1, and which has an intermediate phase.

* * * * *