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(54) **CHALCOGEN-CONTAINING FUSED-RING POLYCYCLIC ORGANIC MATERIAL AND PROCESS FOR PRODUCING THE SAME**

(57) A diacetylene derivative was used as a starting material, and was subjected to dilithiation using an organolithium reagent. The resulting product was allowed to react with an excessive amount of chalcogen (S, Se). Accordingly, an intramolecular cyclization reaction proceeded simultaneously with formation of skeletons of three rings. As a result, a chalcogen-containing fused polycyclic organic material was found to be obtained which has the three rings and a dichalcogenid bond. Further, by subjecting the resulting compound to a dechal-

cogenation reaction, a heteroacene was found to be obtained in a satisfactory yield. These synthetic techniques have made it possible to synthesize a series of highly planar chalcogen-containing π -electron system materials. Therefore, it is possible to provide (i) a chalcogen-containing fused polycyclic organic material capable of exhibiting excellent charge-transporting properties and (ii) a method for producing the material.

Description

TECHNICAL FIELD

5 [0001] The present invention relates to: (i) a chalcogen-containing fused polycyclic organic material which can be applied to an organic thin-film transistor and an organic electroluminescence (hereinafter abbreviated as "EL") element and which has a highly efficient charge-transporting property; and (ii) a method for producing the chalcogen-containing fused polycyclic organic material.

10 BACKGROUND ART

[0002] In the field of organic electronics, it is a task of highest priority to develop a material which can be applied to an organic thin-film transistor (TFT) and an organic electroluminescence (EL) element and which exhibits excellent charge-transporting properties, regardless of whether the material is a p-type material or an n-type material. There has been fierce global-scale competition for the development of such a material.

15 [0003] A promising example of the molecular designing of the material is to build a highly planar π -conjugated skeleton, which will realize an effective intermolecular interaction. In fact, pentacene, which is an acenic compound having such a structure, is known to exhibit good charge-transporting properties, and has been studied in a wide range of researches.

20 [0004] The following materials are expected to serve as the material: (i) heteroacenes having a hetero atom introduced therein and (ii) fused polycyclic aromatic compounds having a dichalcogenide bond, which are similar to heteroacenes. (Patent Document 1)

Japanese Unexamined Patent Publication No. 261794/2001 (Tokukai 2001-261794; published on September 26, 2001) (Non-patent Document 1)

K. Oyaizu, T. Iwasaki, Y. Tsukahara, E. Tsuchida, *Macromolecules*, 2004, ASAP.

25 (Non-patent Document 2)

S. Naoki, Y. Mazaki, K. Kobayashi, T. Kobayashi, *J. Chem. Soc., Perkin Trans. 2*, 1992, pp. 765.

(Non-patent Document 3)

Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.* 1989, 30, pp. 3315.

(Non-patent Document 4)

30 K. Kobayashi, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1989, 43, pp. 187.

(Non-patent Document 5)

W. Schroth, E. Hintzsche, H. Viola, R. Winkler, H. Klose, R. Boese, R. Kempe, J. Sieler, *Chem. Ber.*, 1994, 127, pp. 401.

(Non-patent Document 6)

W. Schroth, E. Hintzsche, M. Felicetti, R. Spitzner, J. Sieler, R. Kempe, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, pp. 739.

35 (Non-patent Document 7) W. Schroth, D. Ströhl, I. Thondorf, W. Brandt, M. Felicetti, T. Gelbrich, *Tetrahedron*, 1995, 51, pp. 8853.

(Non-patent Document 8)

W. Schroth, E. Hintzsche, H. Jordan, T. Jende, R. Spitzner, I. Thondorf, *Tetrahedron*, 1997, 53, pp. 7509.

(Non-patent Document 9)

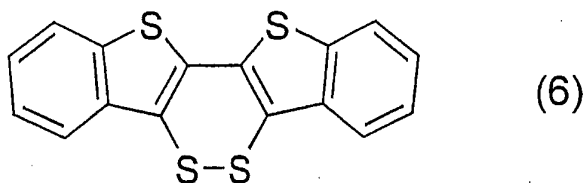
40 R. D. Adams, B. Captain, J. L. Smith Jr., *J. Organomet. Chem.*, 2004, 689, 65.

DISCLOSURE OF INVENTION

(Problem to be solved by the Invention)

45 [0005] However, because there is no effective and general method for synthesizing the fused polycyclic aromatic compound having a dichalcogenid bond, there have been only a few cases where the compound is applied to the field of organic electronics (Patent Document 1 and Non-patent Documents 1 to 4). Therefore, there has been a demand for an effective and general method for synthesizing the compound.

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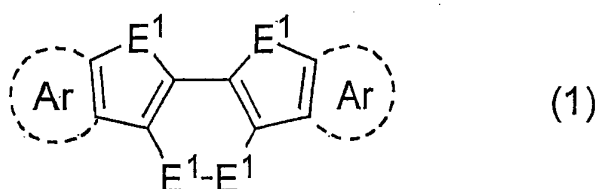
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[0006] Schroth et al. have reported on a synthesis and structure of an unsubstituted benzo fused-ring derivative (represented by formula (6)) (Non-patent Documents 5 to 8). This is the only research associated with the fused polycyclic aromatic compound having the dichalcogenid bond. However, the report neither discloses nor suggests the application of the structure to the field of organic electronics.

[0007] Further, Kobayashi and Tsuchida et al. have reported on the synthesis of the following heteroacenes: (i) an unsubstituted heteroacene compound represented by following formula (9) where R^1 , R^2 , R^3 , and R^4 are H; and (ii) a monomethyl substituted heteroacene compound represented by following formula (9) where R^1 is Me and R^2 , R^3 , and R^4 are H (Non-patent Documents 2 to 4 and Patent Document 1). Further, Tsuchida et al have reported on a synthesis of polymeric polythiacenes ((Patent Document 1 and Non-patent Document 2). However, a synthesis method by which a heteroacene having a substituent can be synthesized precisely as desired has not been attained, and therefore there has been a demand for such a method.

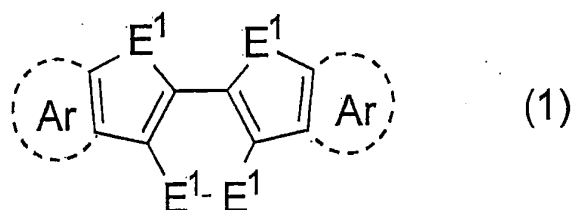
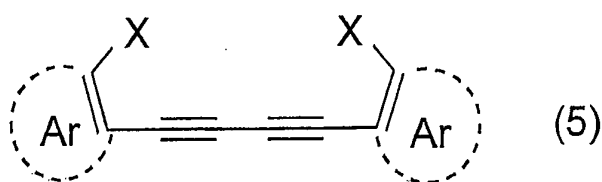
[0008] The present invention has been made in view of the foregoing problems. The inventors of the present invention made an effort to develop a conceptually novel synthetic method. As a result, the inventors has successfully developed an effective and general method for synthesizing the group of important compounds, i.e., the series of chalcogen-containing fused-ring polycyclic organic materials. It is an object of the present invention to provide the group of compounds and a producing method thereof.

[0009] In order to solve the foregoing problems, a chalcogen-containing fused polycyclic organic material according to the present invention has a structure represented by following formula (1):



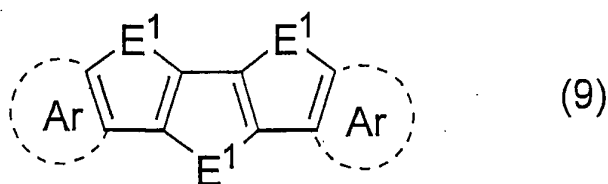
where E^1 is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at one double bond moiety, excluding that Ar is a benzene group when E^1 is S.

[0010] In order to solve the foregoing problems, a method according to the present invention for producing a chalcogen-containing fused polycyclic organic material includes the step of producing the foregoing chalcogen-containing fused polycyclic organic material by intramolecularly forming three rings in a diacetylene compound as expressed in following formula (5):



where X is I, Br, or Cl.

25 **[0011]** In order to solve the foregoing problems, another chalcogen-containing fused polycyclic organic material according to the present invention is a heteroacene compound represented by following formula (9):



where E¹ is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at its one double bond moiety, excluding that Ar is a benzene group when E¹ is S.

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(Effects of the Invention)

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[0012] As described above, the chalcogen-containing fused polycyclic organic material according to the present invention has the structure represented by formula (1) or (9). Accordingly, the material is expected to exhibit excellent charge-transporting properties. Therefore, the material can be applied to the field of organic electronics, e.g., to an organic thin-film transistor (TFT) and an organic electroluminescence (EL) element.

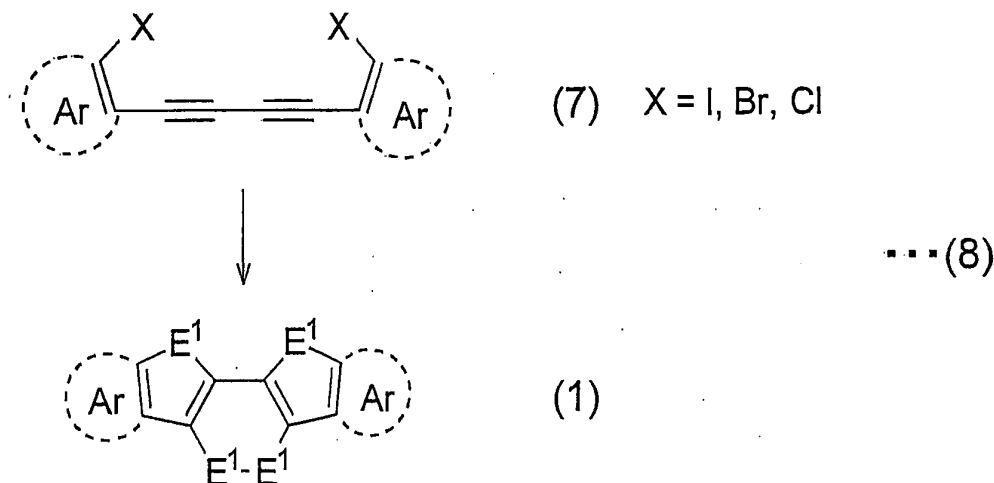
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[0013] As described above, the method according to the present invention for producing a chalcogen-containing fused polycyclic organic material makes it possible that a chalcogen-containing fused polycyclic organic material supposed to exhibit excellent charge-transporting properties is obtained by an intramolecular triple cyclization reaction. Therefore, the method can simplify and generalize the production of a chalcogen-containing fused polycyclic organic material suitable to the field of organic electronics, e.g., to an organic thin-film transistor (TFT) and an organic electroluminescence (EL) element.

55

BEST MODE FOR CARRYING OUT THE INVENTION

[0014] A first embodiment of the present invention will be described below. The following explains a method for synthesizing a compound represented by formula (1). See reaction formula (8) below. A diacetylene compound represented by following formula (7) is used as a starting material, and is dimetalated by a halogen-metal exchange reaction using an organic metallic base. Thereafter, the dimetalated product is allowed to react with a chalcogen element E¹. As a result, the compound (chalcogen-containing fused polycyclic organic material) represented by formula (1) can be synthesized by an intramolecular triple cyclization reaction.



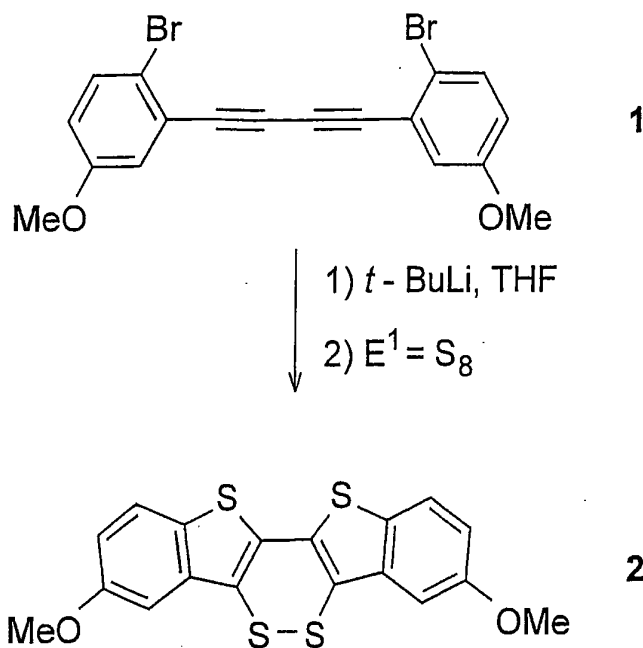
[0015] Examples of the organic metallic base used herein include: (i) an organolithium reagent such as n-BuLi, s-BuLi, or t-BuLi; and (ii) an organomagnesium reagent such as an alkyl Grignard reagent. Metalization in THF using t-BuLi gives the highest yield. Further, examples of the chalcogen element E¹ used herein include (i) a highly reactive chalcogen element, i.e., S₈, (b) a commercially available S (sulfur) or Se (selenium) crystal (S₈ or Se₈), and (c) a powder made of the crystal.

[0016] Further, a molar ratio of the chalcogen element E¹ to the diacetylene compound is preferably 2:1 to 10:1 and, more preferably, 4:1 to 6:1. The starting material is preferably a diacetylene compound having at least two halogenated ring compound groups. It is preferable that the 2-position of each of the ring compound groups be halogenated. The ring compound group may be, but are not limited to, (i) a phenyl group corresponding to benzene and (ii) a thiophene-derived group. Further, the ring compound group may have a substituent.

[0017] In the following, Examples will be described, by which the present invention will be described more specifically. It should be noted that the present invention is not limited to these Examples. The following shows synthetic schemes, actual operations, and results of identification of the compounds. Note that all the reactions described above and below is/was carried out under an atmosphere of argon gas.

(Synthesis of Compound 2)

[0018]



25 **[0019]** To a solution in which Compound 1 (2.3 g, 5.5 mmol) was mixed with THF (25 mL), *t*-BuLi (1.43 M heptane solution, 15.4 mL, 22 mmol) was added over a period of 5 minutes at -78°C. The reaction mixture was stirred for 90 minutes at the same temperature. Thereafter, to the reaction mixture, sulfur (crystal, S₈) (705 mg, 22 mmol) serving as the chalcogen element E¹ was added in the form of a solid. The reaction mixture so obtained was stirred for 10 minutes. Thereafter, the temperature was allowed to rise room temperature. Then, the reaction mixture was further stirred for 10 hours.

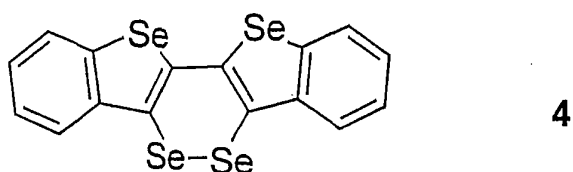
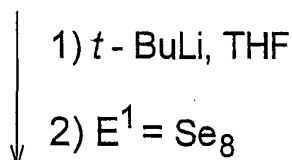
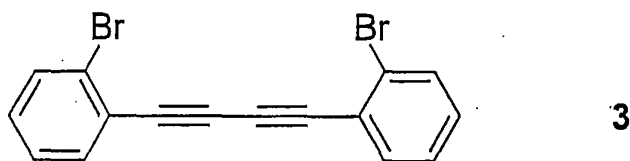
30 **[0020]** The reaction mixture was concentrated under reduced pressure. After a 10% aqueous solution of sodium hydroxide and then dichloromethane were added into the mixture so obtained, extraction was performed with shaking. Thereafter, an organic layer of the dichloromethane and an aqueous layer were separated. An aqueous solution of potassium ferricyanide was added to the separated aqueous layer. This precipitated a red solid. The red solid so obtained was extracted with dichloromethane.

35 **[0021]** The organic layer of the dichloromethane obtained by extraction of the red solid was washed with distilled water, and then was dried with magnesium sulfate. Thereafter, the solvent was distilled off from the organic layer. As a result, targeted Compound 2 was obtained in the form of a red powder. The properties of Compound 2 are as follows.

40 **[0022]** Compound 2: C₁₈H₁₂O₂S₄; red powder. ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, 2H, J = 8.5 Hz), 7.21 (d, 2H, J = 2.5 Hz), 7.04 (dd, 2H, J = 8.5 Hz, 2.5 Hz), 3.92 (s, 6H). ¹³C NMR (67.5 MHz, CDCl₃) δ 158.32, 138.02, 135.30, 130.65, 123.40, 120.09, 116.40, 104.93, 55.64.

(Synthesis of Compound 4)

45 **[0023]**



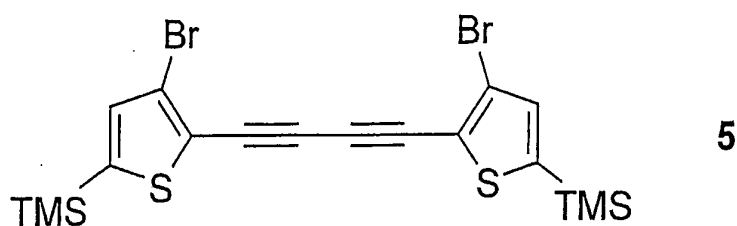
25 **[0024]** To a solution in which Compound 3 (360 mg, 1.0 mmol) was mixed with THF (10 mL), *t*-BuLi (1.45 M heptane solution, 2.8 mL, 4.0 mmol) was added over a period of five minutes at -78°C. The reaction mixture was stirred for 30 minutes at the same temperature. Thereafter, to the reaction mixture, selenium (powder, Se₈) (474 mg, 6.0 mmol) serving as the chalcogen element E¹ was added in the form of a solid. The reaction mixture so obtained was stirred for 10 minutes at -78°C. Thereafter, the temperature was allowed to rise to room temperature. Then, the reaction mixture was further stirred for 8 hours.

30 **[0025]** The reaction mixture was mixed with distilled water, and then was extracted with dichloromethane. As a result, an organic layer was obtained. The organic layer so obtained was washed with distilled water, and was dried using magnesium sulfate. Thereafter, the solvent was distilled off under reduced pressure. As a result, a purplish red mixture was obtained. The purplish red mixture so obtained was separated and purified by alumina column chromatography (developing solvent: dichloromethane). As a result, target Compound 4 (262 mg, 0.51 mmol, 51% yield) was obtained in the form of a purplish solid. The properties of Compound 4 are as follows.

35 **[0026]** Compound 4: C₁₆H₈Se₄; purple plates (recrystallized from dichloromethane-hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.89-7.86 (m, 4H), 7.49 (m, 2H), 7.33 (m, 2H). ¹³C NMR (67.5 MHz, CDCl₃) δ 140.97, 140.41, 127.00, 125.78, 125.67, 125.58, 116.15. MS (EI): 520 (M⁺).

40 (Synthesis of Compounds 6 and 7)

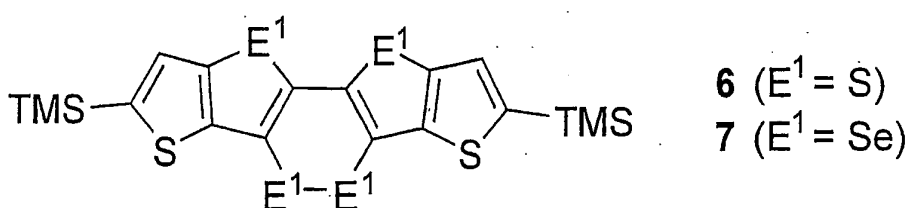
[0027]



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1) *t*-BuLi, THF
2) E¹ = S₈ or Se₈



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[0028] To a solution in which Compound 5 (200 mg, 0.39 mmol) having TMS (trimethylsilyl) groups was mixed with THF (5 mL), *t*-BuLi (1.48 M heptane solution, 1.05 mL, 1.55 mmol) was added dropwise over a period of 5 minutes at -78°C. The reaction mixture was stirred for 80 minutes at the same temperature. Thereafter, to the reaction mixture, sulfur (crystal) (50 mg, 1.55 mmol) was added in the form of a solid. The reaction mixture so obtained was stirred for 1 hour. Thereafter, the temperature was allowed to rise to room temperature. Then, the reaction mixture was further stirred for 3.5 hours.

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[0029] After a 10% aqueous solution of sodium hydroxide was added therein, the reaction mixture was treated with potassium ferricyanide. Thereafter, the resulting mixture was extracted with dichloromethane. As a result, an organic layer was obtained. The organic layer so obtained was washed with distilled water, and was dried using sodium sulfate. Thereafter, the solvent was distilled off under reduced pressure. As a result, a red mixture was obtained. The red mixture so obtained was allowed to pass through a short alumina column (developing solvent: dichloromethane), and then was separated and purified by using GPC (chloroform). As a result, target Compound 6 (78 mg, 0.16 mmol, 41% yield) was obtained in the form of a red solid. The properties of Compound 6 are as follows.

40

[0030] Compound 6: C₁₈H₂₀S₆Si₂; red plates (recrystallized from chloroform-ethanol). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (s, 2H), 0.39 (s, 18H). ¹³C NMR (67.5 MHz, CDCl₃) δ 145.38, 143.20, 136.86, 132.80, 125.54, 115.79, -0.25. MS (EI): 484 (M⁺).

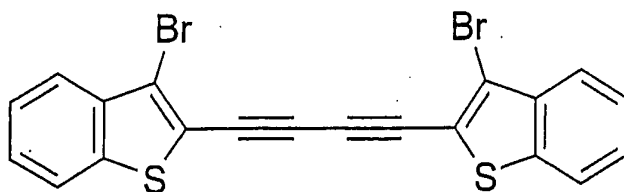
[0031] Compound 7 was synthesized in the same manner as Compound 6, except that selenium was used instead of sulfur. As a result, Compound 7 was obtained in a 56% yield. The properties of Compound 7 are as follows.

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[0032] Compound 7: C₁₈H₂₀S₂Se₄Si₂; purple plates (recrystallized from chloroform-ethanol). ¹H NMR (500 MHz, CDCl₃) δ 7.42 (s, 2H), 0.37 (s, 18H). ¹³C NMR (67.5 MHz, CDCl₃) δ 147.43, 144.62, 144.62, 142.03, 137.35, 129.52, 128.85, -0.23. MS (EI): 676 (M⁺).

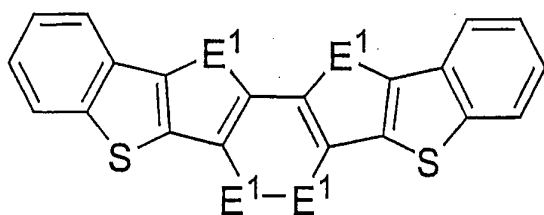
(Synthesis of Compounds 9 and 10)

50 **[0033]**



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1) *t*-BuLi, THF
2) E¹ = S₈ or Se₈

9 (E¹ = S)10 (E¹ = Se)

[0034] To a solution in which Compound 8 (1.42 g, 3.0 mmol) was mixed with THF (60 mL), *t*-BuLi (1.48 M heptane solution, 8.1 mL, 12.0 mmol) was added over a period of 5 minutes at -78°C. The reaction mixture was stirred for 100 minutes at the same temperature. Thereafter, to the reaction mixture, sulfur (crystal) (385 mg, 12.0 mmol) was added in the form of a solid.

[0035] The reaction mixture so obtained was stirred for 60 minutes. Thereafter, the temperature was allowed to rise to room temperature. Then, the reaction mixture was further stirred for 10 hours. The reaction mixture so obtained was mixed with a 10% aqueous solution of sodium hydroxide, and then was treated with potassium ferricyanide. As a result, a solid precipitate was obtained. Thereafter, the solid was filtered out. The solid so obtained was washed with distilled water and ethanol, and then was dried under reduced pressure in the presence of diphosphorus pentoxide. The solid so obtained was recrystallized in *o*-dichlorobenzene. As a result, Compound 9 (900 mg, 2.04 mmol, 68% yield) was obtained in the form of a red purple powder. The properties of Compound 9 are as follows.

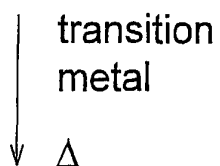
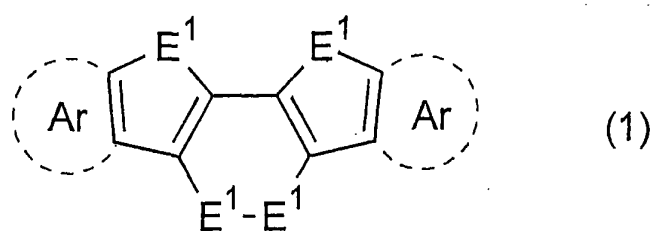
[0036] Compound 9: C₂₀H₈S₆; red purple powder. ¹H NMR (500 MHz, CDCl₃/CS₂ = 1/9) δ 7.86-7.80 (m, 4H), 7.47-7.38 (m, 4H). MS (EI): 440 (M⁺).

[0037] Compound 10 was synthesized in the same manner as Compound 9, except that selenium was used instead of sulfur. As a result, Compound 10 was obtained in a 24% yield. The properties of Compound 10 are as follows.

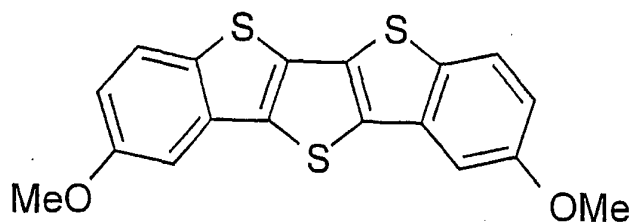
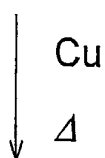
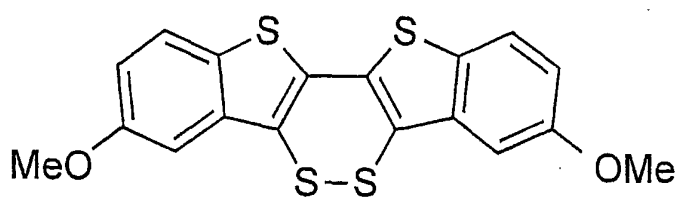
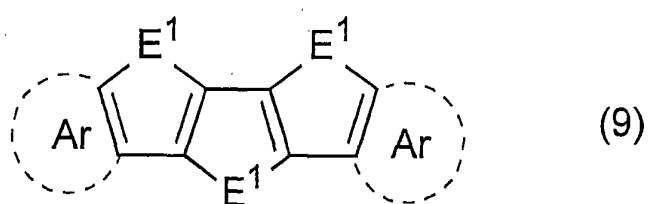
[0038] Compound 10: C₂₀H₈S₂Se₄; purple powder. MS (EI): 629 (M⁺).

[0039] Among these compounds thus successfully synthesized, Compound 4 was examined by X-ray crystallographic analysis. It was found that Compound 4 has a herringbone packing structure. This structure is very advantageous for good charge-transporting properties.

[0040] A heteroacene compound (chalcogen-containing fused polycyclic organic material) according to a second embodiment of the present invention will be described below. The following explains a method for synthesizing a compound represented by formula (9). By the dechalcogenation reaction described in Non-patent Documents 5 and 9 carried out with a compound represented by formula (1) as a starting material as illustrated in reaction formula (13) below, the compound represented by formula (9) can be synthesized as a heteroacene compound. Specifically, for example, the reaction may be carried out by heating the compound represented by formula (1) in the presence of a transition metal such as a platinum complex (Pt(COD)₂ or copper powder, where COD is 1,5-cyclooctadiene.



... (13)



[0041] An Example of the second embodiment of the present invention will be described below. Compound 2 (50 mg, 0.13 mmol) was heated by a heat gun (at approximately 200°C) for 15 minutes under an atmosphere of argon in the presence of copper (nanoscale powder) (32 mg, 0.50 mmol, 3.9 mol. amt.), and then was cooled down. Thereafter, Compound 2 was mixed with hot chloroform. After the insoluble was filtered out, the filtrate was concentrated. As a result, Compound 11 (32 mg, 70% yield) was obtained, which was a heteroacene compound in the form of a colorless solid. The properties of Compound 11 are as follows.

EP 1 724 272 A1

[0042] Compound 11: C₁₈H₁₂O₂S₃; colorless powders; ¹H NMR (270 MHz, CDCl₃) δ 7.74 (d, 2H, J = 8.9 Hz), 7.29 (d, 2H, J = 2.6 Hz), 7.01 (dd, 2H, J = 8.9 Hz, 2.6 Hz), 3.94 (s, 6H).

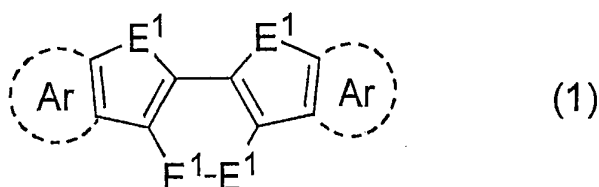
[0043] A chalcogen-containing fused polycyclic organic material according to the present invention is a novel compound that can be used as a charge-transporting material.

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(Means to solve the problem)

[0044] In order to solve the foregoing problems, a chalcogen-containing fused polycyclic organic material according to the present invention has a structure represented by following formula (1):

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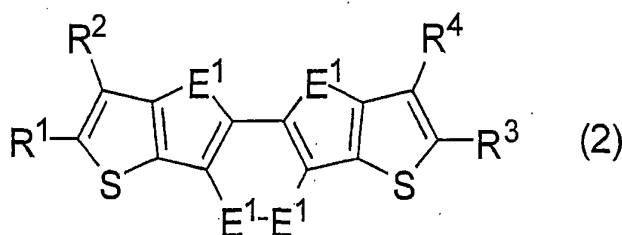
where E¹ is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at one double bond moiety, excluding that Ar is a benzene group when E¹ is S.

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[0045] The chalcogen-containing fused polycyclic organic material may have a structure represented by following formula (2):

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where R¹, R², R³, and R⁴ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxy carbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

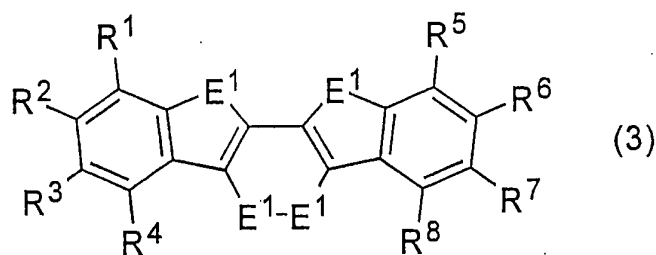
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[0046] The chalcogen-containing fused polycyclic organic material may have a structure represented by following formula (3):

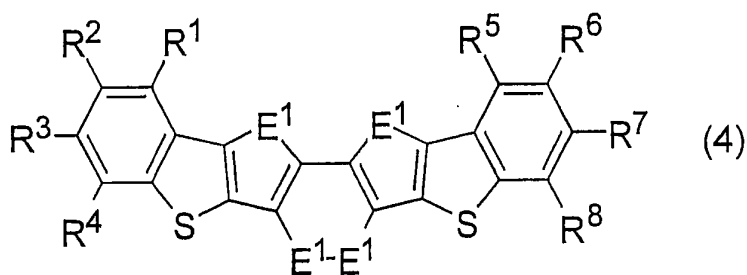
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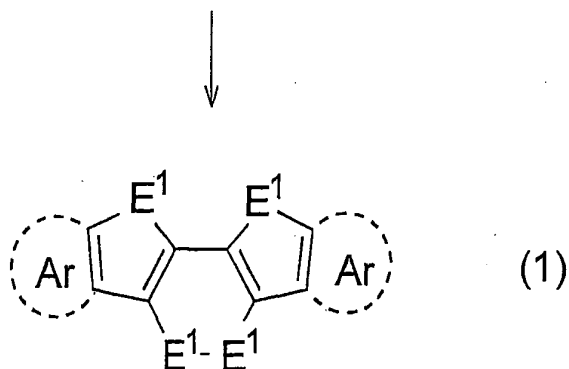
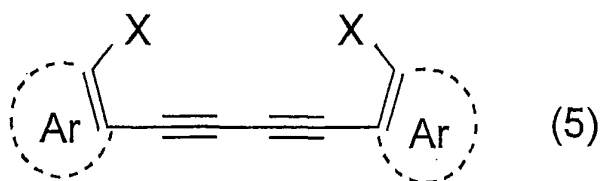
where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that R¹ = R² = R³ = R⁴ = R⁵ = R⁶ = R⁷ = R⁸ = a hydrogen atom when E¹ is S.

[0047] The chalcogen-containing fused polycyclic organic material may have a structure represented by following formula (4):



35 where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

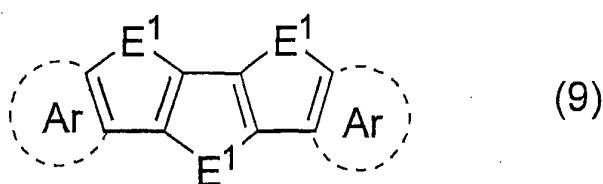
40 [0048] In order to solve the foregoing problem, a method according to the present invention for producing a chalcogen-containing fused polycyclic organic material includes the step of producing the foregoing chalcogen-containing fused polycyclic organic material by intramolecularly forming three rings in a diacetylene compound as expressed in following formula (5):



where X is I, Br, or Cl.

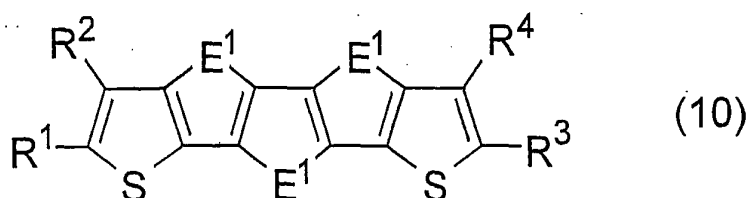
[0049] According to the foregoing producing method, the diacetylene compound is allowed to react with a chalcogen element E¹ after the diacetylene compound is dimetalated by a halogen-metal exchange reaction in which an organic metallic base is used.

[0050] In order to solve the foregoing problems, another chalcogen-containing fused polycyclic organic material according to the present invention is a heteroacene compound represented by following formula (9):



where E¹ is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at one double bond moiety, excluding that Ar is a benzene group when E¹ is S.

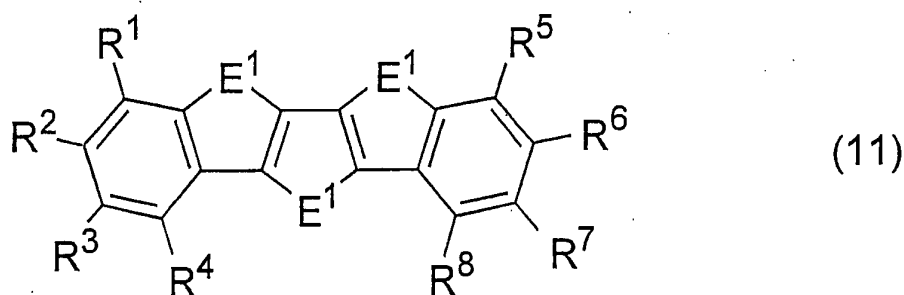
[0051] The chalcogen-containing fused polycyclic organic material may be a heteroacene compound having a structure represented by following formula (10):



where R¹, R², R³, and R⁴ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an

alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that $R^1 = R^2 = R^3 = R^4 =$ a hydrogen atom when E^1 is S, and that R^1 is a methyl group and $R^2 = R^3 = R^4 =$ a hydrogen atom when E^1 is S.

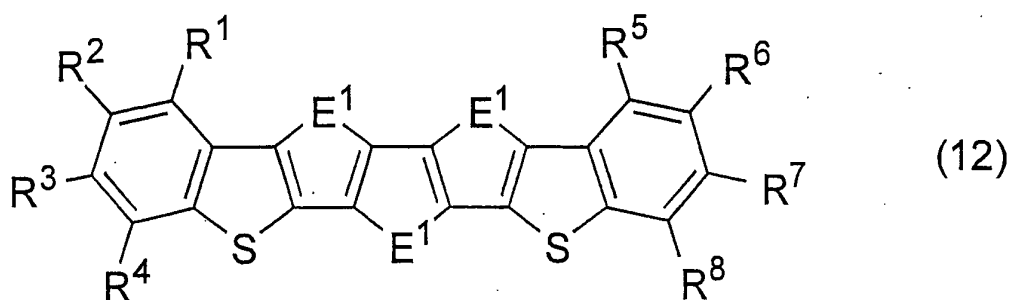
[0052] The foregoing chalcogen-containing fused polycyclic organic material may be a heteroacene compound having a structure represented by following formula (11):



where $R^1, R^2, R^3, R^4, R^5, R^6, R^7,$ and R^8 are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 =$ a hydrogen atom when E^1 is

S.

[0053] The foregoing chalcogen-containing fused polycyclic organic material may be a heteroacene compound having a structure represented by following formula (12):



where $R^1, R^2, R^3, R^4, R^5, R^6, R^7,$ and R^8 are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group; a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl

group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

INDUSTRIAL APPLICABILITY

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[0054] A chalcogen-containing fused polycyclic organic material according to the present invention is capable of exhibiting excellent charge-transporting properties. Therefore, the material can be applied to an organic thin-film transistor and an organic EL element, which are used for attaining thinner thickness or lighter weight in electronic devices such as a display device.

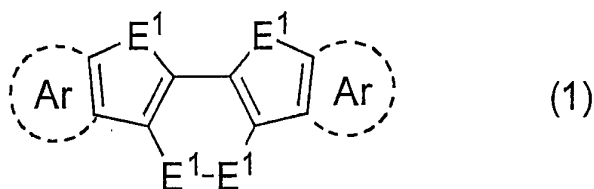
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[0055] A method according to the present invention for producing a chalcogen-containing fused polycyclic organic material makes it possible to easily and reliably obtain various chalcogen-containing fused polycyclic organic materials capable of exhibiting excellent charge-transporting properties.

15 Claims

1. A chalcogen-containing fused polycyclic organic material having a structure represented by following formula (1):

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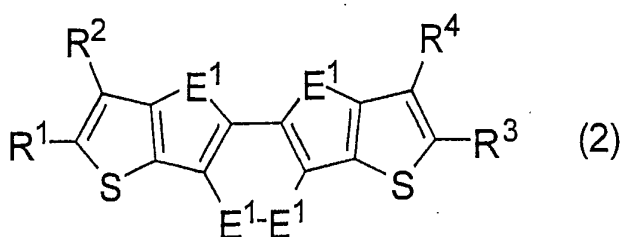
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where E¹ is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at one double bond moiety, excluding that Ar is a benzene group when E¹ is S.

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2. The chalcogen-containing fused polycyclic organic material as set forth in claim 1, wherein the structure is represented by following formula (2):

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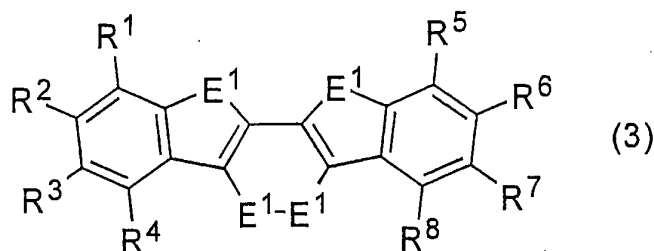


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where R¹, R², R³, and R⁴ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an aryl group, a substituted aryl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxy carbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

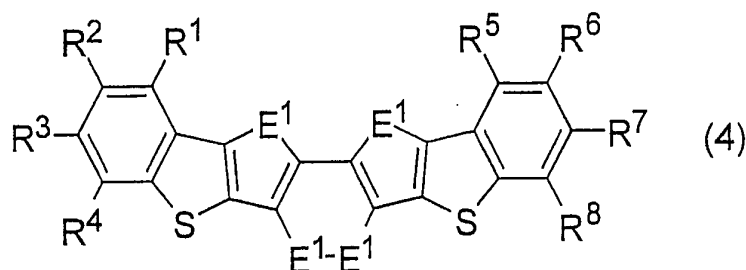
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3. The chalcogen-containing fused polycyclic organic material as set forth in claim 1, wherein the structure is represented by following formula (3):



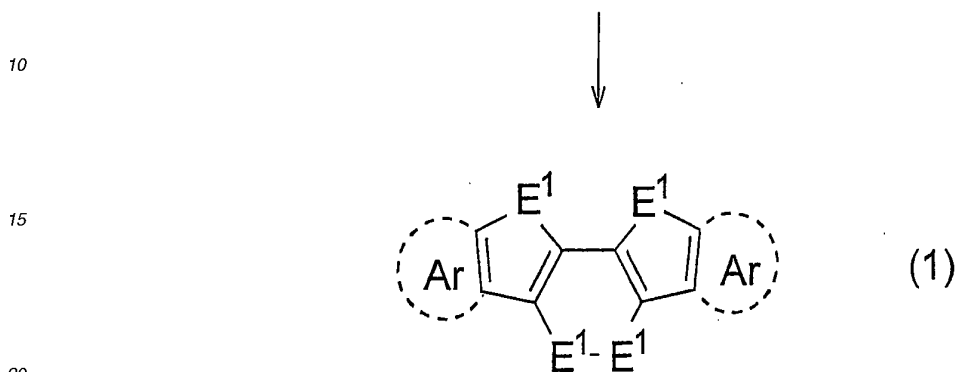
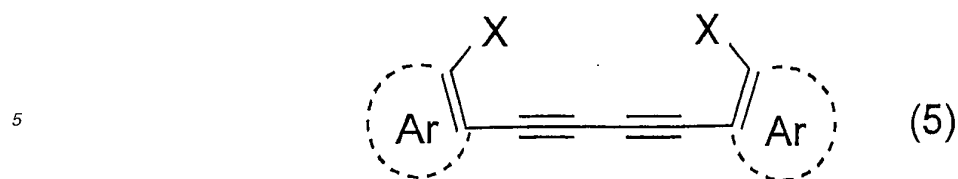
15 where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxy carbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group; a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that R¹ = R² = R³ = R⁴ = R⁵ = R⁶ = R⁷ = R⁸ = a hydrogen atom when E¹ is S.

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4. The chalcogen-containing fused polycyclic organic material as set forth in claim 1, wherein the structure is represented by following formula (4):



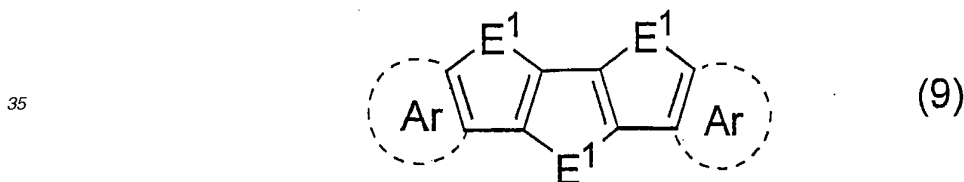
40 where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxy carbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

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5. A method for producing a chalcogen-containing fused polycyclic organic material, the method comprising the step of producing the foregoing chalcogen-containing fused polycyclic organic material as set forth in claim 1 by intramolecularly forming three rings in a diacetylene compound as expressed in following formula (5):



where X is I, Br, or Cl.

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6. The method as set forth in claim 5, wherein: the diacetylene compound is allowed to react with a chalcogen element E^1 after the diacetylene compound is dimetalated by a halogen-metal exchange reaction in which an organic metallic base is used.
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7. A chalcogen-containing fused polycyclic organic material, being a heteroacene compound represented by following formula (9):

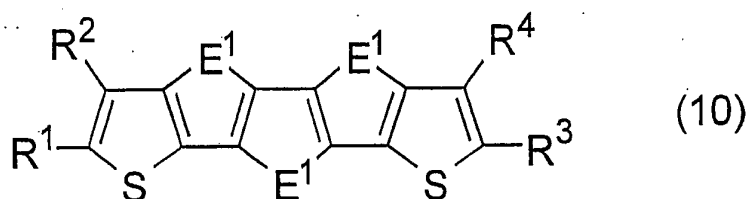


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where E^1 is S or Se, and Ar is one selected from the group consisting of a benzene group, a substituted benzene group, a naphthalene group, a substituted naphthalene group, an anthracene group, a substituted anthracene group, a thiophene group, a substituted thiophene group, a furan group, a substituted furan group, a pyrrole group, a substituted pyrrole group, a selenophene group, a substituted selenophene group, a pyridine group, a substituted pyridine group, a thiazole group, a substituted thiazole group, a benzothiophene group, a substituted benzothiophene group, a benzofuran group, a substituted benzofuran group, an indole group, and a substituted indole group, where Ar is fused thereto at one double bond moiety, excluding that Ar is a benzene group when E^1 is S.

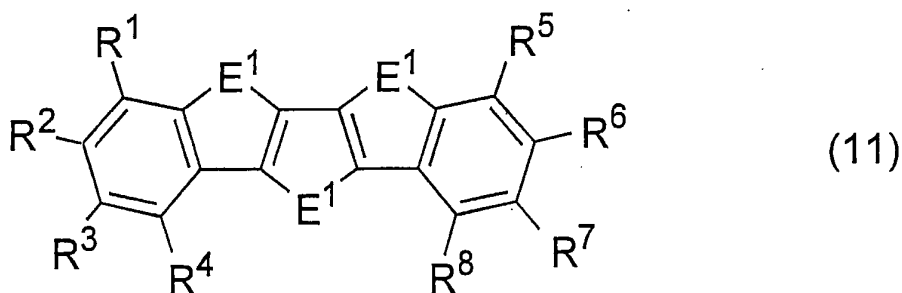
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8. The chalcogen-containing fused polycyclic organic material as set forth in claim 7, wherein the structure is represented by following formula (10):
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10 where R¹, R², R³, and R⁴ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that R¹ = R² = R³ = R⁴ = hydrogen when E¹ is S, and that R¹ is a methyl group and R² = R³ = R⁴ = a hydrogen atom when E¹ is S.

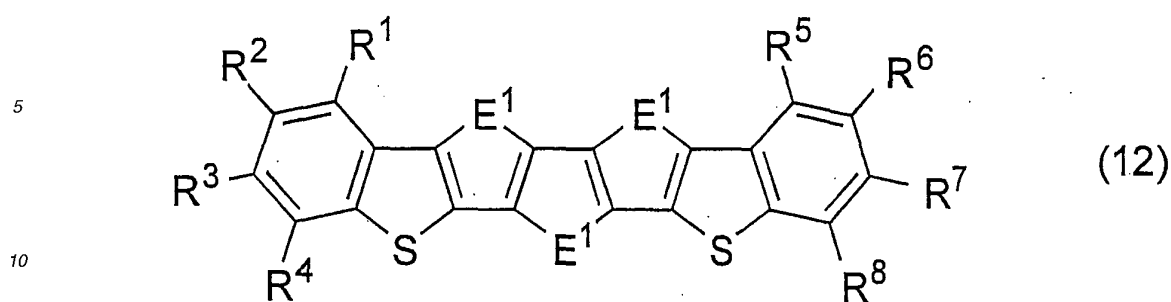
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- 25 9. The chalcogen-containing fused polycyclic organic material as set forth in claim 7, wherein the structure is represented by following formula (11):



40 where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxycarbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom, excluding that R¹ = R² = R³ = R⁴ = R⁵ = R⁶ = R⁷ = R⁸ = a hydrogen atom when E¹ is S.

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- 50 10. The chalcogen-containing fused polycyclic organic material as set forth in claim 7, wherein: the structure is represented by following formula (12):

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15 where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are independently an aryl group, a substituted aryl group, an oligoaryl group, a substituted oligoaryl group, a monovalent heterocyclic group, a monovalent substituted heterocyclic group, a monovalent oligoheterocyclic group, a monovalent substituted oligoheterocyclic group, a hydrogen atom, an alkyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group, an arylalkyl group, an arylalkoxy group, an arylalkylthio group, an alkenyl group, a substituted alkenyl group, an alkynyl group, a substituted alkynyl group, an allyl group, an amino group, a substituted amino group, an azo group, a carboxyl group, an acyl group, an alkoxy carbonyl group, a formyl group, a nitro group, a cyano group, a silyl group, a substituted silyl group, a stannyl group, a substituted stannyl group, a boryl group, a substituted boryl group, a phosphanyl group, a substituted phosphanyl group, a silyloxy group, a substituted silyloxy group, an arylsulfonyloxy group, an alkylsulfonyloxy group, or a halogen atom.

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EP 1 724 272 A1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/004006

<p>A. CLASSIFICATION OF SUBJECT MATTER Int.Cl⁷ C07D495/14, 495/22, 517/14, 517/22, C09K11/06, H05B33/14, 33/22</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>												
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) Int.Cl⁷ C07D495/14, 495/22, 517/14, 517/22, C09K11/06, H05B33/14, 33/22</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Caplus (STN), CASREACT (STN), REGISTRY (STN)</p>												
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X A</td> <td>Ken'ichi OYAIZU et al., Linear Ladder-Type π-Conjugated Polymers Composed of Fused Thiophene Ring Systems, Macromolecules, 24 February, 2004 (24.02.04), 37, pages 1257 to 1270, Scheme 1</td> <td>7, 8 1-6, 9, 10</td> </tr> <tr> <td>X A</td> <td>Xinnan ZHANG et al., Effect of Ring Fusion on the Electronic Absorption and Emission Properties of Oligothiophenes, J.Org.Chem., 2003, 68, pages 9813 to 9815, Fig. 2</td> <td>7, 8 1-6, 9, 10</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X A	Ken'ichi OYAIZU et al., Linear Ladder-Type π -Conjugated Polymers Composed of Fused Thiophene Ring Systems, Macromolecules, 24 February, 2004 (24.02.04), 37, pages 1257 to 1270, Scheme 1	7, 8 1-6, 9, 10	X A	Xinnan ZHANG et al., Effect of Ring Fusion on the Electronic Absorption and Emission Properties of Oligothiophenes, J.Org.Chem., 2003, 68, pages 9813 to 9815, Fig. 2	7, 8 1-6, 9, 10	
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X A	Xinnan ZHANG et al., Effect of Ring Fusion on the Electronic Absorption and Emission Properties of Oligothiophenes, J.Org.Chem., 2003, 68, pages 9813 to 9815, Fig. 2	7, 8 1-6, 9, 10										
<p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p>												
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
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<p>Date of the actual completion of the international search 06 June, 2005 (06.06.05)</p>		<p>Date of mailing of the international search report 21 June, 2005 (21.06.05)</p>										
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/004006

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	Naoki SATO et al., Linearly condensed Polythiophenes: Characteristic Molecular Aggregation of Thieno[2'',3'':4',5']thieno[2',3'-d]thieno[3,2-b]thiophene Crystals Revealed by Ultraviolet Photoelectron Spectroscopy, J.Chem.Soc.Perkin Trans., 2, 1992, pages 765 to 770, chemical compound 5	7,8 1-6,9,10
X A	Yasuhiro MAZAKI et al., Synthesis of Tetrathieno-Acene and Pentathieno-Acene: UV-spectral Trend in a Homologous Series of Thieno-Acenes, Tetrahedron Letters, 1989, 30, 25, pages 3315 to 3318, chemical compound 4	7,8 1-6,9,10
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