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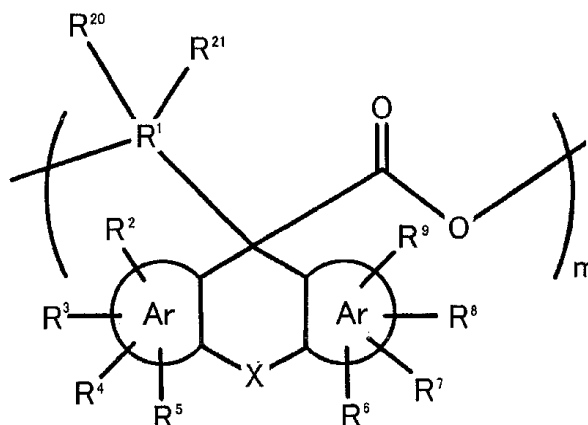
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(54) NOUVEAU POLYESTER COMPRENANT UN GROUPE A CONJUGAISON-PI. DANS LA CHAINE LATERALE ET UN MATERIAU DE TRANSPORT DE CHARGE UTILISANT CELUI-CI

(54) NOVEL POLYESTER HAVING PI-CONJUGATED GROUP IN SIDE CHAIN AND CHARGE TRANSPORTING MATERIAL USING THE SAME

(57)

A polyester, characterized in that it is represented by the structural formula (1): (1) wherein Ar represents an aromatic group including a hetero ring, R1 represents a carbon atom or nil (a direct bonding), R2 to R9 each represent a hydrogen atom, an electron donating group or an electron attracting group, R20 and R21 represent a hydrogen atom or an organic group, and X represents a hetero atom, a hetero atom containing group, an organic group or nil (a direct bonding), and m is an integer of 2 or greater; and a charge transporting material comprising the polyester and, incorporated therein, an electron accepting compound or an electron donating compound.

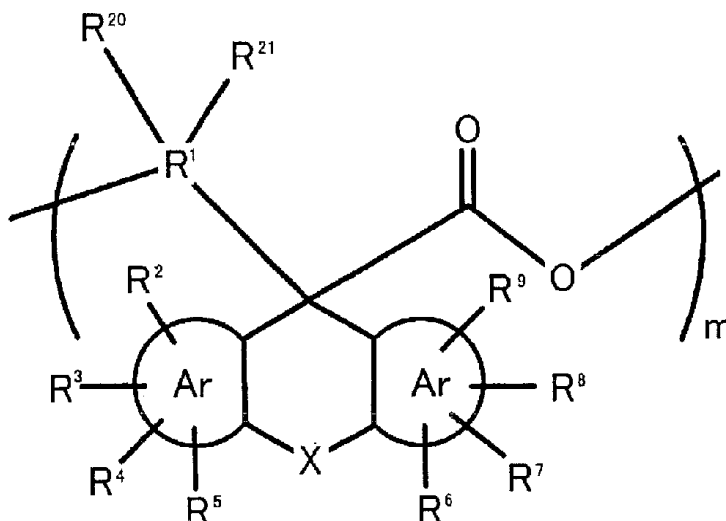




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 MATERIAL USING THE SAME



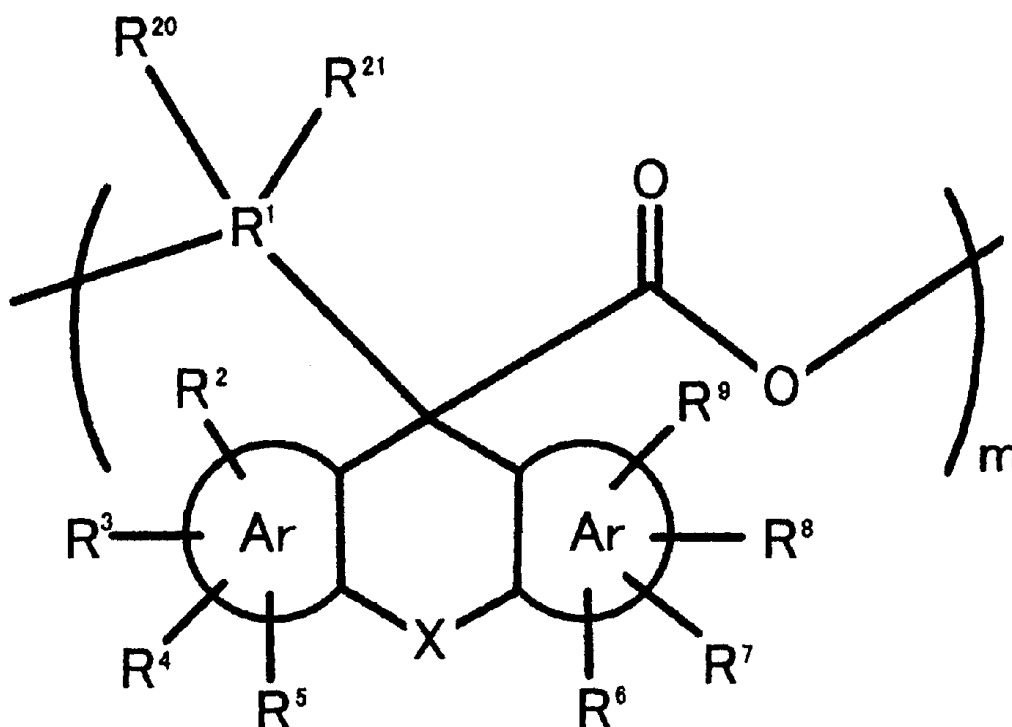
(57) **Abrégé/Abstract:**

A polyester, characterized in that it is represented by the structural formula (1): (1) wherein Ar represents an aromatic group including a hetero ring, R¹ represents a carbon atom or nil (a direct bonding), R² to R⁹ each represent a hydrogen atom, an electron donating group or an electron attracting group, R²⁰ and R²¹ represent a hydrogen atom or an organic group, and X represents a hetero atom, a hetero atom containing group, an organic group or nil (a direct bonding), and m is an integer of 2 or greater; and a charge transporting material comprising the polyester and, incorporated therein, an electron accepting compound or an electron donating compound.



ABSTRACT

A polyester expressed by the following structural formula 1, and a charge transport material obtained by adding an electron acceptor compound or an electron donor compound to this polyester.



In the aforesaid structural formula, Ar is an aromatic group and this aromatic group may contain a heterocyclic ring.

10 R^1 is a carbon atom or absent (direct bond), R^2 - R^9 are hydrogen atoms, electron donor groups or electron attracting groups, R^{20} , R^{21} are hydrogen atoms or organic groups, X is a hetero atom, hetero atom-containing group, organic group or absent (direct bond), and m is an integer equal to 2 or more.

Novel polyester having π -conjugated group in side chain, and charge transport material using this polyester

FIELD OF THE INVENTION

5 This invention relates to a novel polymer compound having a fluorene residue in a side chain. In particular, it relates to a novel polymer compound which can form a charge transfer complex with an electron acceptor compound or an electron donor compound, and a charge transfer complex formed
10 by addition of the electron acceptor compound or electron donor compound.

BACKGROUND OF THE INVENTION

As described in Tokkai 2000-319366, a polyester with a
15 fluorene residue is already known. This polyester has excellent heat-resistance and transparency, high refractive index, low birefringence and low water absorptivity, and is therefore suitable as an optical instrument material. However, as there was almost no overlap of fluorene residues, it was difficult to
20 make it express electrical characteristics using the properties of π -conjugated electrons.

It is also known that by adding an electron acceptor compound or an electron donor compound to a polymer material with a π -conjugated group such as polyacetylene or
25 polyfluorene, a material exhibiting charge transport qualities will be obtained. However, as such a material is degraded by water or oxygen, there was a problem as to its stability as a material exhibiting charge transport qualities.

SUMMARY OF THE INVENTION

The inventor made a detailed study of polymer compounds having special electrical qualities due to the properties of π -conjugated electrons. As a result, it was discovered that a polyester having a fluorene residue in a side chain had unique electrical qualities, and forms a charge transfer complex of excellent stability with a suitable electron acceptor compound or electron donor compound, which led to the present invention.

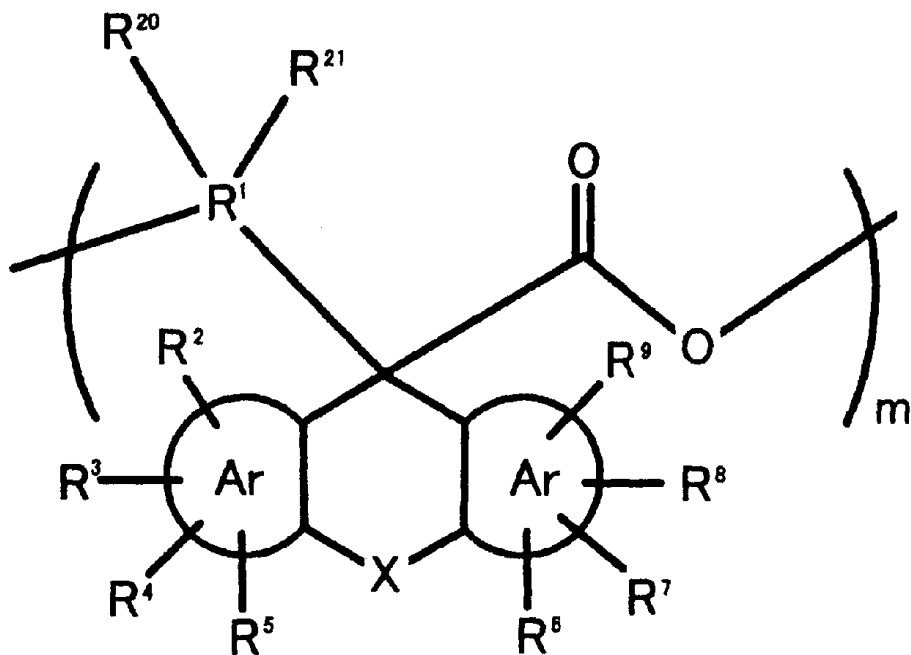
It is therefore a first object of this invention to provide a polyester having π -conjugated electrons, that is a polyester having unique electrical qualities due to the properties of π -conjugated electrons.

It is a second object of this invention to provide a composition which forms a stable charge transfer complex with an electron acceptor compound or an electron donor compound.

The aforesaid objects of this invention are attained by a polyester expressed by the following structural formula 1.

In the formula, m is an integer equal to 2 or more.

structural formula 1



In addition, in the aforesaid structural formula, Ar is an aromatic group and this aromatic group may contain a heterocyclic ring.

R^1 is a carbon atom or absent (direct bond), R^2 - R^9 are hydrogen atoms, electron donor groups or electron attracting groups, R^{20} , R^{21} are hydrogen atoms or organic groups, and X is a hetero atom, hetero atom-containing group, organic group or absent (direct bond).

In this invention, it is preferred that R^1 is absent, i.e., that it is the end of a polymerizing unit.

DETAILED DESCRIPTION OF THE INVENTION

The hetero atom X in the structural formula 1 is -O-, -NR- or -S-. The organic group is preferably $-(CH_2)-$ or an aromatic group.

The electron donor group in the aforesaid structural formula 1 of this invention is a functional group which, due to the introduction of a substituent, has an increased electron density in the fluorene residue and enhanced electron donor properties in the fluorene residue. This electron donor group may for example be -F, -Cl, -Br, -I, -OH, -OR, -O(C=O)R, -NR¹⁰R¹¹, -SR, -SH or an alkyl group, but among these, -C₅H₁₁, -t-C₄H₉ and -NR¹⁰R¹¹ are preferred. R, R¹⁰ and R¹¹ may be H or an organic group, but preferably an aromatic group or an alkyl group. R²⁰, R²¹ may be a hydrogen atom, alkyl group, aromatic group, -CN or ester group.

The electron attracting group is a functional group which, due to the introduction of a substituent, has a decreased electron density in the fluorene residue, and enhanced electron acceptor properties in the fluorene residue. This electron acceptor group may for example be -C≡N, -(C=O)R, -SO₂-, -NO₂, phenyl, -COOH or -COOR, but -C≡N and -NO₂ are preferred.

By introducing the aforesaid electron-attracting group and electron donor group into the polymer, a more stable charge-transfer complex is obtained when an electron donor compound and electron acceptor compound, described later, are added.

Preferred combinations of R²-R⁹ are:

- (1) all of R²-R⁹ are H;
- (2) R³, R⁸ are NR¹⁰R¹¹ (R¹⁰, R¹¹ are respectively H, an alkyl group or an aromatic group), and R², R⁴-R⁷, R⁹ are H;
- (3) R³, R⁸ are NH₂, and R², R⁴-R⁷, R⁹ are H;
- (4) R³, R⁸ are -N(C₆H₅)₂, and R², R⁴-R⁷, R⁹ are H;

(5) R³, R⁸, R⁶ are NO₂, and R², R⁴, R⁵, R⁷, R⁹ are H;

(6) R³, R⁸ are NO₂, and R², R⁴-R⁷, R⁹ are H;

(7) R³, R⁸, R⁶ are CN, and R², R⁴, R⁵, R⁷, R⁹ are H;

(8) R³, R⁸ are CN, R², R⁴-R⁷, R⁹ are H.

5 The electron acceptor compound described above is a compound having a stronger electron affinity than the polymer of structural formula 1. Examples are the following halogens, Lewis acids, proton acids and transition metal halogens etc.

Halogens: I₂, Br₂, Cl₂, ICl, ICl₃, IBr, IF

10 Lewis acids: BF₃, PF₅, AsF₅, SbF₅, SO₃, BBr₅, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, ClO₄⁻

Proton acids: HNO₃, H₂SO₄, HClO₄, HF, HCl, FSO₃H, CF₃SO₃H

Transition metal halides: FeCl₃, MoCl₅, WCl₅, SnCl₄, MoF₅, FeOCl, RuF₅, TaBr₅, SnI₄, LnCl₃ (Ln is La, Ce, Pr, Nd or Sm)

15 Others:(9-fluorenylidene)acetonitrile,

(9-fluorenylidene)malononitrile,

(2,4,7-trinitro-9-fluorenylidene)acetonitrile,

(2,4,7-trinitro-9-fluorenylidene)malononitrile,

o-dinitrobenzene, m-dinitrobenzene, p-dinitrobenzene,

20 2,4,7-trinitrobenzene, 2,4,7-trinitrotoluene, TCNQ, TCNE,

DDQ.

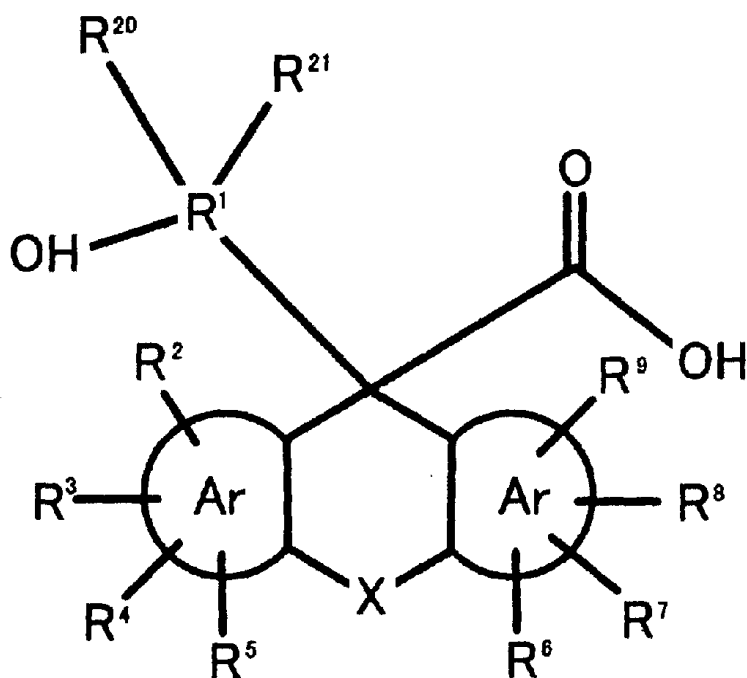
On the other hand, the electron donor compound is a compound having a smaller ionization potential than the polymer of structural formula 1. Examples are
25 hexamethylbenzene, alkali metals, ammonium ion and lanthanoids.

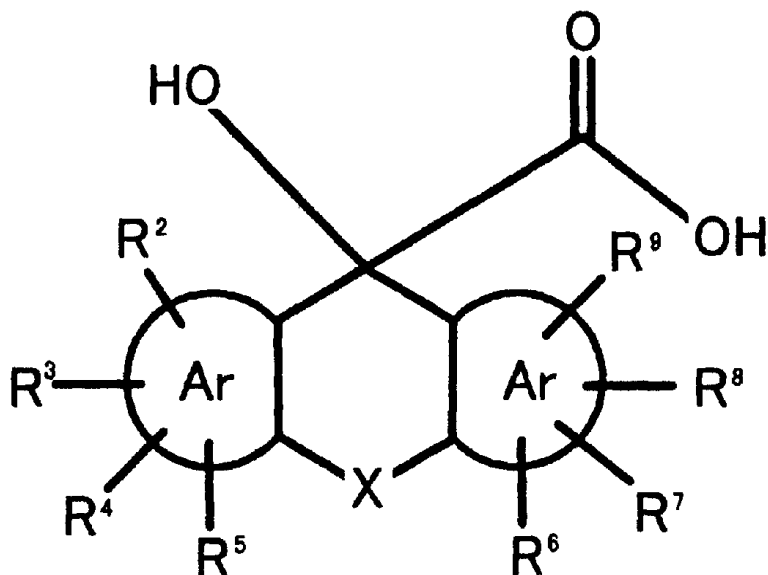
When an electron-attracting functional group is introduced into a fluorene residue, an electron donor compound

is preferably added, and when an electron donor functional group is introduced into a fluorene residue, an electron acceptor compound is preferably added. A stable charge-transfer type complex is thus obtained.

5 (Synthesis method)

To synthesize the polymer of this invention, for example, the following compounds may be polycondensed using the usual catalyst.





R^1 - R^9 , and R^{20} , R^{21} are respectively identical to R^1 - R^9 , and R^{20} , R^{21} in structural formula 1.

The molecular weight of the polymer is preferably 400-1 million but more preferably 800-100,000 in terms of number average molecular weight. If it is less than 400, it is rare for an electron acceptor compound or electron donor compound to enter between fluorene residues, and if it is more than 1 million, the solubility decreases.

The distance between fluorene residues is 4-20Å, but preferably 5-10Å. If it is less than 4Å, the electron acceptor compound or electron donor compound cannot enter between fluorene residues. If it is more than 20Å, the electron acceptor compound or electron donor compound which entered between fluorene residues cannot easily form an electron donor-acceptor complex.

Tg of the polymer is preferably 30-300°C, but more preferably 80-200°C. When Tg is less than 30°C, formation of the electron donor-acceptor complex is blocked by structural change of the polymer due to temperature change.

5 If the aforesaid conditions are satisfied, a stable electron donor-acceptor complex can be obtained. Such a stable electron donor-acceptor complex is suitable as a charge transport material, for example as a hole transport layer of an organic EL or a solar cell. Such a charge transport material can be easily
10 manufactured by a known method, such as spin coating.

EXAMPLES

Hereafter, this invention will be described in further detail referring to examples, but this invention is not to be
15 construed as being limited in any way thereby.

Example 1: (Polymer synthesis).

<Synthesis of 9-hydroxymethyl-9-fluorene carboxylic acid (monomer)>

20 9-fluorene carboxylic acid (4.98g, 23.7mmol) and anhydrous THF (300ml) were introduced into a flame-dried reaction vessel in which the atmosphere had been replaced by nitrogen, the reaction solution was cooled to -78°C, and n-butyl lithium (41.0ml of 1.6M hexane solution, 71.0mmol) was added.
25 After stirring the reaction solution at -78°C for 30 minutes, paraformaldehyde (2.30g, 75.0mmol) dissolved in anhydrous THF (100ml) was added at -78°C, and stirred at room temperature for 13 hours. Distilled water was added, the

solution was extracted with ether, and the pH of the aqueous layer was adjusted to 2 using 1N hydrochloric acid. It was then extracted again with chloroform, and the organic layer was dried by anhydrous magnesium sulfate. The low-boiling fraction was distilled under reduced pressure with the rotary evaporator, and 4.21g of crude product was thus obtained. The methylene chloride-insoluble fraction of this crude product was collected, and the target compound (4.60g, 19.3mmol, 80.5%) was thus obtained. ¹H-NMR (500MHz, CDCl₃) δ: 7.78 (d, J= 7.5, 2H), 7.67 (d, J= 7.5, 2H), 7.46 (dd, J= 7.0, 2H), 7.54 (dd, J= 8.0, 2H), 4.02(s, 4H).

<Synthesis of polymer using 9-hydroxymethyl-9-fluorene carboxylic acid as starting material>

9-hydroxymethyl-9-fluorene carboxylic acid (50.4mg, 0.21mmol) and 0.9mg of a catalyst (CF₃SO₃)₂Sn were introduced into a reaction vessel (9mm Φ × 50mm), and the mixture was shaken to render it uniform. Subsequently, it was heated at 180°C for 3 hours while blowing in nitrogen (a syringe needle was fixed over about 2mm of compound). After 3 hours, the obtained compound was separated by decantation into a THF soluble part (47.1mg) and a THF-insoluble part (2.20mg). The dried and weighed THF-soluble part was re-dissolved in THF (3ml), diazomethane (ether solution, 1ml) was slowly dripped in with stirring, and stirred at room temperature for 5 hours. After 5 hours, the solvent and volatile component were distilled off with the rotary evaporator, the obtained crude product was divided into a methanol-soluble part (8.10mg) and

methanol-insoluble part (34.9mg), and the methanol-insoluble part was divided into a THF-soluble part (14.19mg) and a THF-insoluble part (20.64mg). The part which was insoluble in methanol but soluble in THF had a molecular weight distribution of approx. 1,000 to 10^5 (SEC, polystyrene conversion).

Example 2: (Polymer synthesis)

Anhydrous methylene chloride (17ml) was added to 9-hydroxy-9-fluorene carboxylic acid (1.01g, 4.42mmol) in a flame-dried reaction vessel in which the atmosphere had been replaced by nitrogen, and stirred at room temperature for 5 minutes to give a uniform solution. Anhydrous triethylamine (0.62ml, 4.502mmol) was then dripped in. The reaction solution was stirred at room temperature for 30 minutes, and an anhydrous methylene chloride (3ml) solution of p-tosyl chloride (762mg, 4.42mmol) was dripped in. The reaction solution was stirred at room temperature for 15 hours and extracted with chloroform, and the organic layer was dried by anhydrous magnesium sulfate. The solvent was distilled off under reduced pressure with the rotary evaporator, and the obtained crude product was classified into a hexane-soluble part (111mg) and a hexane-insoluble part (777mg). The hexane-insoluble part was dissolved in THF (20ml), diazomethane (ether solution, 3ml) was gradually dripped in with stirring, and the solution stirred at room temperature for 5 hours. The reaction product was a mixture of polymers consisting of 2-10 monomers. This polymer mixture was classified by recycling liquid chromatography, and

the pure dimer, trimer and tetramer were thus obtained.

Example 3: (D-A complexing, spectrometry)

<Formation of D-A complex from
5 poly(9-hydroxymethyl-9-fluorene carboxylic acid) and
m-dinitrobenzene (DNB)>

1. Absorption spectrum measurement in solution

The polymer (2.98mg) and DNB (1.80mg, 0.01mmol) were
dissolved in THF for ultraviolet absorption spectra to give 10ml
10 of solution. This was diluted 100 times, and used for absorption
spectrum measurements (quartz cell; 10mm) at room
temperature. The absorption intensity of the polymer and DNB
mixture was smaller than the absorption intensity of the
polymer alone. The intensity which was 0.140 at 242nm changed
15 to 0.108 after adding DNB. This change depended on the
concentration, and when the DNB concentration was changed to
 $2.5 \times 10^{-5}M$ and $5.0 \times 10^{-5}M$, the absorption intensity at 242nm
changed to 0.077 and 0.059, respectively. This hypochromic
effect proved that the fluorene ring of the polymer and DNB
20 formed a stacked complex.

The absorption at long wavelength extended from 310nm
to 345nm.

2. D-A complexing in solid state

The polymer (100mg) and m-nitrobenzene (100mg) were
25 taken up as a CH_2Cl_2 solution, and the light red solid produced
while distilling off the solvent was collected. When this was
again dissolved in CH_2Cl_2 and the solvent was distilled off, thin
red acicular crystals were obtained.

Example 4:

<Formation of D-A complex using poly(9-hydroxy-9-fluorene
carboxylic acid) and 2,4,7-trinitro-9-fluorenylidene
5 malononitrile (TNFMN)>

1. Absorption spectrum measurement in solution

TNFMN (363.3mg, 1.0mmol) was dissolved in methylene
chloride solvent for ultraviolet absorption spectra to give 100ml
of solution. Next, a polymer (10.4mg of a mixture of polymer
10 consisting of 2-10 monomers, 0.05mmol in monomer units) was
dissolved using this solution. The absorption spectrum was
measured at room temperature on 1ml of solution (quartz cell;
0.1mm). As a result of this measurement, new peaks due to a
D-A complex, 386nm ($\lambda_{max} = 0.038$) and 488nm ($\lambda_{max} = 0.009$),
15 were observed.

2. D-A complexing in solid state

TNFMN (15.1mg, 0.04mmol) and a polymer (10.4mg,
0.05mmol in monomer units) were put into methylene chloride
solution, and the solvent was distilled off to dryness to give an
20 orange-red solid. A composition analysis by ^1H NMR of this solid
showed that the proportion of monomer units:TNFMN was 1:1.

Example 5:

<D-A complexing using trimer of 9-hydroxy-9-fluorene
25 carboxylic acid and TNFMN>

1. Absorption spectrum measurement in solution

TNFMN (363.3mg, 1.0mmol) was dissolved in methylene
chloride solvent for ultraviolet absorption spectra to give 100ml

of solution. Next, the trimer (10.4mg, 0.05mmol in monomer units) was dissolved using this solution, and the absorption spectrum was measured at room temperature on 1ml of solution (quartz cell; 0.1mm). As a result, new peaks due to the D-A complex, 388nm ($\lambda_{max} = 0.037$) and 489nm ($\lambda_{max} = 0.009$), were observed. These absorption intensities depended on concentration, and when the concentration of fluorene was changed to 0.03M and 0.04M, the absorption intensity at 388nm changed to 0.022 and 0.029, respectively.

10 2. D-A complexing in solid state

TNFMN (15.1mg, 0.04mmol) and a trimer (10.4mg, 0.05mmol in monomer units) were put into methylene chloride solution, and the solvent was distilled off to dryness to give an orange solid. A composition analysis by ^1H NMR of this solid showed the proportion of monomer units:TNFMN was 1:1.

Example 6: (Conductivity: Time of flight measurement)

A mixture having a polymerization degree of approx. 20 (principal components are dimer-tetramer) was taken in CH_2Cl_2 solution, 1% 2,4,7-trinitrofluorene malononitrile was added to this, and dissolved. The solution was then spread on an ITO glass substrate, and dried to produce a thin film (1 μm thickness). Aluminum was deposited on the obtained film (thickness 1000 \AA , area 5mm \times 5mm). A voltage of 5.0V was applied between the ITO and aluminum using TOF301 (Optel, Inc.), a 337nm pulse laser (nitrogen laser, pulse width, 1ns, 150 μJ) was simultaneously irradiated from the ITO side, and the time of flight was measured. From the test results at room

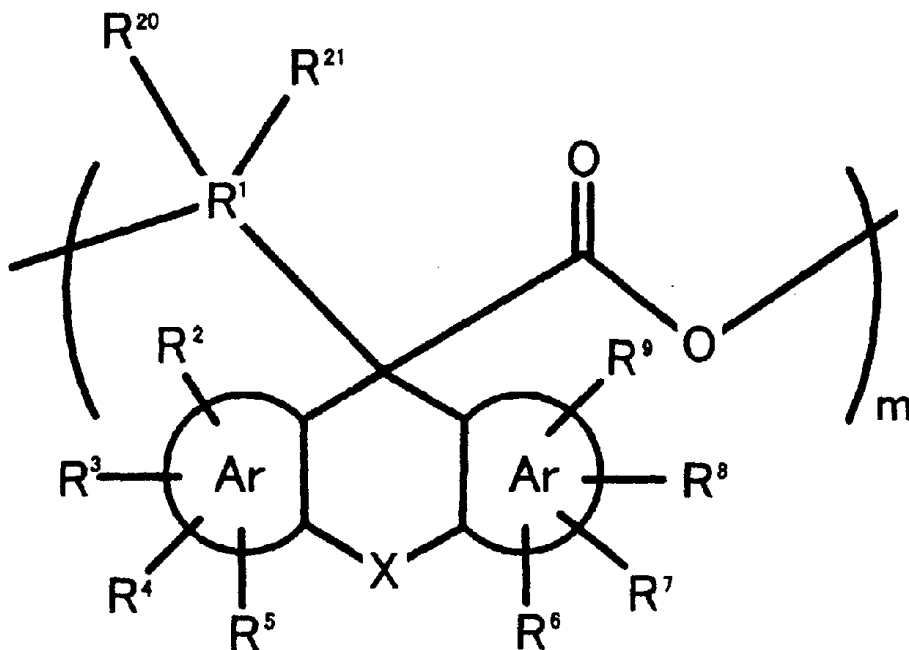
temperature, the hole mobility was determined as $1.20 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$.

Industrial Application

5 The polyester of this invention has a fluorene residue in a side chain, and it can form a charge transfer complex having excellent stability with an electron acceptor compound or electron donor compound. It is therefore suitable as a charge transport material such as an organic EL material, or the hole
10 transport layer of a solar cell.

WHAT IS CLAIMED IS:

1. A polyester expressed by the following structural formula 1:



5 wherein, R^1 is C_nH_{2n} , n is an integer equal to 0 or more, R^2 - R^9 are hydrogen atoms, electron donor groups or electron attracting groups, and m is an integer equal to 2 or more.

In the aforesaid structural formula, Ar is an aromatic group and this aromatic group may contain a heterocyclic ring.

10 R^1 is a carbon atom or absent (direct bond), R^2 - R^9 are hydrogen atoms, electron donor groups or electron attracting groups, R^{20} , R^{21} are hydrogen atoms or organic groups, and X is a hetero atom, hetero atom-containing group, organic group or absent (direct bond).

15

2. The polyester according to Claim 1, wherein the molecular weight of said polyester is 400-1 million in terms of number

average molecular weight.

3. The polyester according to Claim 2, wherein the distance between fluorene residues in said polyester is 4-20Å.

5

4. The polyester according to Claim 1, wherein Tg of said polyester is 30-300°C.

5. A composition obtained by adding an electron acceptor
10 compound or an electron donor compound to the polyester according to Claim 1.

6. The composition according to Claim 5, wherein said composition forms a charge transfer complex.

15

7. A charge transport material formed using the composition according to Claim 6.