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(54) Title: METHOD FOR PRODUCING POLY-(PARA-PHENYLENE)

(57) Abstract: The present invention relates to a method for producing *poly-(para-phenylene)*, to a *poly-(para-phenylene)* compound obtained by said method, and to the use of said *poly-(para-phenylene)* compound in various applications. The *poly-(para-phenylene)* compound obtained by the method according to the present invention is unsubstituted, structurally defect-free as well as of sufficient chain length.



WO 2018/091605 A1

5 **Method for producing poly-(*para*-phenylene)**

The present invention relates to a method for producing poly-(*para*-phenylene), to a poly-(*para*-phenylene) compound obtained by said method, and to the use of said
10 poly-(*para*-phenylene) compound in various applications. The poly-(*para*-phenylene) compound obtained by the method according to the present invention is unsubstituted, structurally defect-free as well as of sufficient chain length.

Unsubstituted and structurally defect-free poly-(*para*-phenylene) having a sufficient
15 chain length may be regarded as the prototype of a conjugated polymer and has been the quest of various synthetic approaches. In neutral form, poly-(*para*-phenylene) (hereinafter also referred to as "PPP") is an insulator, whereas its conductivity increases up to $500 \Omega^{-1} \cdot \text{cm}^{-1}$ upon doping. Its high compressive strength, its low density as well as its high stability towards temperature, oxygen and moisture
20 render PPP a promising candidate for various applications, in particular in organic electronics.

Up to now, several routes towards the synthesis of PPP have been developed, such as the direct aryl-aryl coupling via *para*-dihalobenzenes. Due to the low solubility of
25 PPP in common organic solvents, only very short *para*-phenylene oligomers of about 10 phenylene moieties could be obtained by such direct aryl-aryl coupling.

Another approach to be mentioned in this respect is the oxidative coupling of benzene moieties. This so-called Kovacic method results, however, in a significant
30 amount of *ortho*-connected phenylene moieties, and thus, can only produce structurally defective poly-(*para*-phenylene).

Longer PPP with about 30 phenylene moieties can be obtained by the introduction of solubilizing side-chains such as alkyl and/or alkoxy groups in *ortho/meta*-position.
35 However, such an approach results in a low charge carrier mobility as well as in an

undesired blue-shift of the emission bands due to the deplanarization of the PPP backbone.

Besides, several approaches directed to a surface-assisted synthesis of PPP are known in the art. However, said approaches require a high experimental effort such as metal surfaces with a high Miller index, and result in low quality PPP in connection with a lack of follow-up processability.

Another strategy towards the synthesis of poly-(*para*-phenylene) is the so-called precursor route of Grubbs *et al.*, which addresses the problem of regioselectivity. Although precursor polymers for subsequent *syn*-elimination reactions can be obtained thereby, structurally perfect and unsubstituted PPP without impurities (e.g. acid residues) has not been achieved so far.

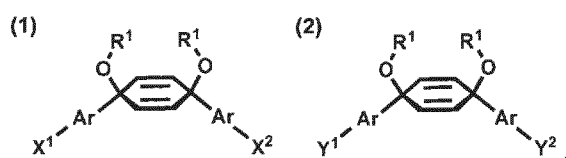
Accordingly, none of the synthetic approaches known in the art allows to produce unsubstituted and structurally defect-free poly-(*para*-phenylene) of sufficient chain length so as to be used in applications such as organic electronics.

Therefore, the technical problem underlying the present invention is to provide a method for producing unsubstituted and structurally defect-free poly-(*para*-phenylene) of sufficient chain length.

This problem is solved by providing the embodiments characterized in the claims.

In particular, according to a first aspect of the present invention, there is provided a method for producing poly-(*para*-phenylene), comprising the steps of:

(a) providing a compound represented by the following formula (1) and a compound represented by the following formula (2) as starting materials:

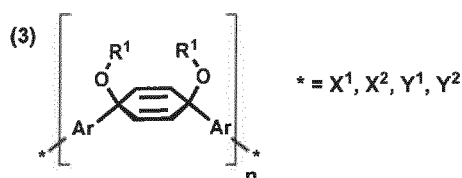


wherein each of the moieties Ar independently represents 1,4-phenylene or 4,4'-bisphenylene, respectively,

wherein each of the moieties R¹ independently represents a substituted or unsubstituted hydrocarbon group, respectively, and

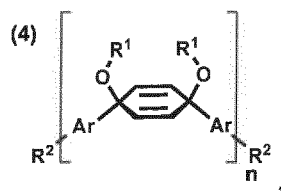
wherein each of the substituents X¹, X², Y¹ and Y² independently represents a halogen atom or a boronic ester residue, respectively, provided that two of the above-defined substituents X¹, X², Y¹ and Y² independently represent a halogen atom and the remaining two of the above-defined substituents X¹, X², Y¹ and Y² independently represent a boronic ester residue,

(b) reacting the above-defined compounds (1) and (2) in the presence of a transition metal catalyst to obtain a polymeric compound represented by the following formula (3):



wherein n is the number of repeating units,

(c) end-capping the above-defined polymeric compound (3) to obtain a poly-(*para*-phenylene) precursor compound represented by the following formula (4):

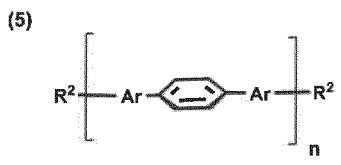


wherein each of the moieties R² independently represents a substituted or unsubstituted hydrocarbon group, respectively,

(d) optionally isolating the above-defined poly-(*para*-phenylene) precursor compound (4),

(e) optionally processing the above-defined poly-(*para*-phenylene) precursor compound (4), and

- (f) aromatizing the above-defined poly-(*para*-phenylene) precursor compound (4) by thermal treatment or by irradiation to obtain a poly-(*para*-phenylene) compound represented by the following formula (5):

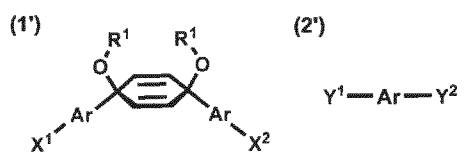


wherein Ar, R² and n are as defined above.

The above-defined method according to the first aspect of the present invention is also referred to as "first method" hereinafter.

According to a second aspect of the present invention, there is provided a method for producing poly-(*para*-phenylene), comprising the steps of:

- (a') providing a compound represented by the following formula (1') and a compound represented by the following formula (2') as starting materials:

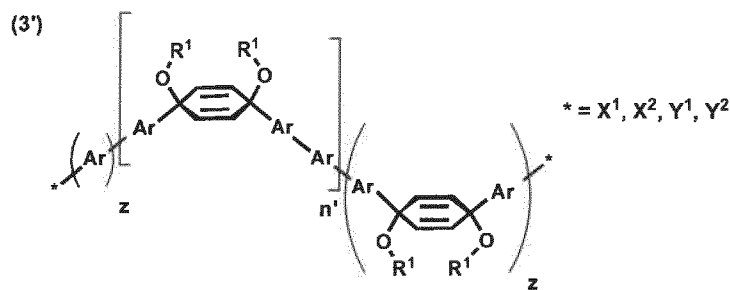


wherein each of the moieties Ar independently represents 1,4-phenylene or 4,4'-bisphenylene, respectively,

wherein each of the moieties R¹ independently represents a substituted or unsubstituted hydrocarbon group, respectively, and

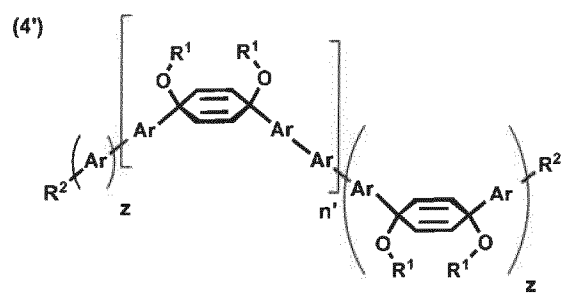
wherein each of the substituents X¹ and X² independently represents a halogen atom and each of the substituents Y¹ and Y² independently represents a boronic ester residue, respectively, or *vice versa*,

- (b') reacting the above-defined compounds (1') and (2') in the presence of a transition metal catalyst to obtain a polymeric compound represented by the following formula (3'):



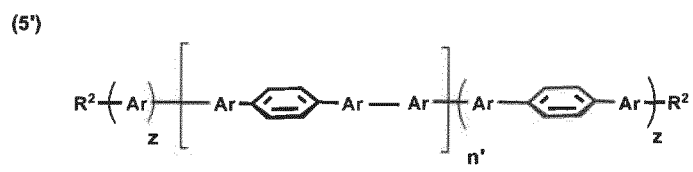
wherein n' is the number of repeating units and z is 0 or 1,

- (c') end-capping the above-defined polymeric compound (3') to obtain a poly-(*para*-phenylene) precursor compound represented by the following formula (4'):



wherein each of the moieties R² independently represents a substituted or unsubstituted hydrocarbon group, respectively,

- (d') optionally isolating the above-defined poly-(*para*-phenylene) precursor compound (4'),
- (e') optionally processing the above-defined poly-(*para*-phenylene) precursor compound (4'), and
- (f') aromatizing the above-defined poly-(*para*-phenylene) precursor compound (4') by thermal treatment or by irradiation to obtain a poly-(*para*-phenylene) compound represented by the following formula (5'):



wherein Ar, R², n' and z are as defined above.

The above-defined method according to the second aspect of the present invention is also referred to as "second method" hereinafter.

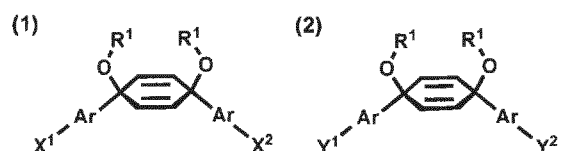
The first and second methods for producing poly-(*para*-phenylene) according to the present invention are based on a novel precursor route, making use of a well-soluble poly-(*para*-phenylene) precursor compound which is built up from at least one kinked monomer, respectively. According to the present invention, the poly-(*para*-phenylene) precursor compound is aromatized by thermal treatment or by irradiation without the need of any reducing agents. After aromatizing said PPP precursor compound, an unsubstituted and structurally defect-free poly-(*para*-phenylene) compound of sufficient chain length is obtained, which can be used in various applications, in particular in organic electronics.

According to the present invention, the term "unsubstituted" means that the obtained poly-(*para*-phenylene) compound has no substituents in *ortho*- or *meta*-position. In line with this, the term "structurally defect-free" means that all phenylene moieties of the obtained PPP compound are connected in *para*-position.

Moreover, the term "sufficient chain length" means a number of at least 25 phenylene moieties in the poly-(*para*-phenylene) compound obtained by the first or second method according to the present invention.

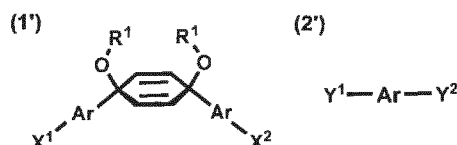
Hereinafter, the above-defined first method and the above-defined second method for producing poly-(*para*-phenylene) are described in more detail. Unless stated otherwise, all definitions given below apply both to the first method and to the second method for producing poly-(*para*-phenylene) according to the present invention.

In step (a) of the above-defined first method for producing PPP, a compound represented by the following formula (1) and a compound represented by the following formula (2) are provided as starting materials:



In the same way, in step (a') of the above-defined second method for producing PPP, a compound represented by the following formula (1') and a compound represented by the following formula (2') are provided as starting materials:

5



In the above formulae (1), (2), (1') and (2'), each of the moieties Ar independently represents 1,4-phenylene or 4,4'-bisphenylene, respectively. In this context, it is clear to a person skilled in the art that extending the moieties Ar by a further phenylene moiety in *para*-position should be principally possible. Herein, the moieties Ar are, however, limited to 1,4-phenylene and to 4,4'-bisphenylene, since any longer *para*-connected oligophenylene group such as terphenylene etc. may have a detrimental effect on the solubility of the PPP precursor compound due to its enlarged planar portion. According to the present invention, it is thus preferable that each of the moieties Ar represents 1,4-phenylene.

Furthermore, each of the moieties R¹ in the above formulae (1), (2), (1') and (2') independently represents a substituted or unsubstituted hydrocarbon group, respectively. Herein, the term "substituted or unsubstituted hydrocarbon group" is not specifically limited according to the present invention. In particular, the term "substituted or unsubstituted hydrocarbon group" as used herein comprises alkyl, alkenyl, alkynyl, aryl groups, as well as any combinations thereof, without being limited to a specific constitution, either. The above-defined hydrocarbon groups may be substituted with any heteroatom as long as the first and second methods for producing poly-(*para*-phenylene) as defined above are not affected adversely. Heteroatoms to be mentioned in this respect are silicon, oxygen, sulfur and nitrogen, while the present invention is not limited thereto.

In one embodiment of the present invention, each of the moieties R¹ independently represents a substituted or unsubstituted hydrocarbon group derived from benzene, naphthalene, anthracene, thiophene, pyridine, triaryl amine, pyrrole, phenazine, mor-

pholine, pyrroline, tetrahydrofuran, dioxane or piperidine, respectively, without being limited thereto.

In another embodiment of the present invention, each of the moieties R^1 independently represents an alkyl group, respectively, which may be linear, branched, or cyclic, or a combination thereof. For example, the alkyl group may be a linear, cyclic or branched C_1 - C_{35} alkyl group, C_1 - C_{25} alkyl group, C_1 - C_{15} alkyl group, C_1 - C_{10} alkyl group, C_1 - C_5 alkyl group, or C_1 - C_2 alkyl group. Examples of the above-defined alkyl group include methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *sec*-butyl, *tert*-butyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl, while the present invention is not limited thereto. In a preferred embodiment of the present invention, each of the moieties R^1 represents methyl, since the corresponding methoxy residues can be easily removed in step (f)/(f'), as described below.

Referring to the first method as defined above, in formulae (1) and (2), each of the substituents X^1 , X^2 , Y^1 and Y^2 independently represents a halogen atom or a boronic ester residue, respectively, provided that two of the above-defined substituents X^1 , X^2 , Y^1 and Y^2 independently represent a halogen atom and the remaining two of the above-defined substituents X^1 , X^2 , Y^1 and Y^2 independently represent a boronic ester residue. Accordingly, in the above-defined first method, the substituents X^1 and X^2 may both represent a halogen atom and the substituents Y^1 and Y^2 may both represent a boronic ester residue, or *vice versa*. In this case, compounds (1) and (2) undergo a cross coupling reaction of type a^1a^2/b^1b^2 in step (b). Apart therefrom, only one of the substituents X^1 and X^2 may represent a halogen atom, with the remaining one of the substituents X^1 and X^2 representing a boronic ester residue. The same applies to the substituents Y^1 and Y^2 . In this case, compounds (1) and (2) undergo a homo coupling reaction of type a^1b^1/a^2b^2 in step (b). In case the substituents X^1 , X^2 , Y^1 and Y^2 represent only one specific halogen atom and only one specific boronic ester residue, respectively, the coupling reaction in step (b) is either a cross coupling reaction of type aa/bb or a homo coupling reaction of type ab/ab . In the latter case, compounds (1) and (2) are identical, and only specific compound is thus to be provided as the starting material in step (a) of the first method according to the present invention.

Referring to the second method as defined above, in formulae (1') and (2'), each of the substituents X^1 and X^2 independently represents a halogen atom and each of the substituents Y^1 and Y^2 independently represents a boronic ester residue, respectively, or *vice versa*. Accordingly, compounds (1') and (2') undergo a cross coupling reaction of type a^1a^2/b^1b^2 in step (b'). In case the substituents X^1 , X^2 , Y^1 and Y^2 represent only one specific halogen atom and only one specific boronic ester residue, respectively, the cross coupling reaction is of type aa/bb in step (b').

According to the present invention, the above-defined substituents X^1 , X^2 , Y^1 and Y^2 are neither limited to a specific halogen atom nor limited to a specific boronic ester residue. In one embodiment of the present invention, the halogen atom is selected from the group consisting of fluorine, chlorine, bromine and iodine. Preferably, the halogen atom is bromine.

Herein, the boronic ester residue is represented by the general formula $-B(OR)_2$, wherein each of the moieties R independently represents a substituted or unsubstituted hydrocarbon group, respectively. In this context, the term "substituted or unsubstituted hydrocarbon group" is as defined above. In a preferred embodiment of the above-defined first and second methods, the boronic ester residue is pinacol boronic ester.

In this context, it is clear to a person skilled in the art that substituents other than halogen atoms and boronic ester residues are principally suitable for coupling the compounds (1)/(1') and (2)/(2'). For example, substituents selected from the group consisting of silyl, stannyl, amino, nitro, diazonium, aryl, heteroaryl, carboxyl, alkoxycarbonyl, chlorocarbonyl, tosylate, mesylate and triflate also allow for a coupling of the compounds (1)/(1') and (2)/(2').

According to the present invention, the provision of the compounds (1) and (2) in the first method as defined above, and the provision of the compounds (1') and (2') in the second method as defined above are not specifically limited, i.e. any synthesis known to the skilled person, which is suitable for providing the above compounds may be applied.

In particular, the above-defined compounds (1)/(1') and (2)/(2') used as starting materials in step (a)/(a') are commercially available and/or can be easily synthesized from comparatively non-expensive educts.

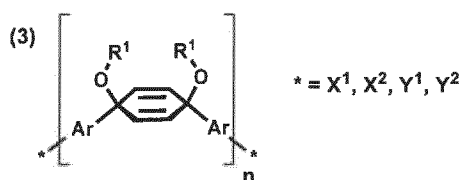
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For example, the kinked compounds, i.e. compounds (1), (2) and (1'), can be obtained by nucleophilic addition of two equivalents of a monolithiated halobenzene, e.g. obtained by *para*-dihalobenzene and *n*-butyllithium, to one equivalent of *para*-benzoquinone, followed by dialkylation using an alkylation agent, such as methyl iodide, and diborylation using a borylation agent, such as *iso*-propyl pinacol borate, as
 10 can be taken from the Example provided below.

Herein, the configuration of the above-defined compounds (1), (2) and (1') is not specifically limited. The -OR¹ residues thereof may be oriented in *syn*- and/or in *anti*-
 15 configuration with respect to each other. Accordingly, the same considerations also apply to the residues comprising the Ar moieties. Typically, the above-defined compounds (1), (2) and (1') are oriented in *syn*-configuration with respect to each other, as exemplarily depicted in formulae (1), (2) and (1') above.

20 Since the compounds (1) and (2) of the above-defined first method as well as the compounds (1') and (2') of the above-defined second method according to the present invention are bifunctional, said compounds can be readily subjected to the coupling reaction in step (b)/(b'), as described below.

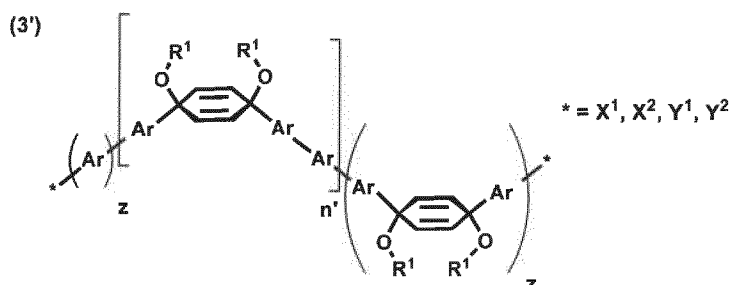
25 In step (b) of the first method for producing PPP according to the present invention, the above-defined compounds (1) and (2) are reacted in the presence of a transition metal catalyst, thereby obtaining a polymeric compound represented by the following formula (3):



30

In the same way, in step (b') of the second method for producing PPP according to the present invention, the above-defined compounds (1') and (2') are reacted in the presence of a transition metal catalyst, thereby obtaining a polymeric compound represented by the following formula (3'):

5



In the above formulae (3) and (3'), n and n' are the number of repeating units, respectively, and z is 0 or 1.

The specific reaction conditions of step (b)/(b') *inter alia* depend on the transition metal catalyst used for the coupling reaction. The transition metal catalyst usable in the reaction of step (b)/(b') is not particularly limited and may include any transition metal catalyst which is capable of coupling the above-defined compounds (1)/(1') and (2)/(2'). Typical examples of the transition metal catalyst are palladium catalysts, such as tetrakis(triphenylphosphine) palladium, and nickel catalysts, such as bis(cyclooctadiene) nickel.

In a specific embodiment of the present invention, the coupling of the above-defined compounds (1)/(1') and (2)/(2') follows the Suzuki coupling scheme. When using Pd(PPh₃)₄ as the transition metal catalyst, the reaction is typically carried out at a temperature of 20 to 65°C, such as about 60°C, using a solvent, such as THF:H₂O (10:1), and a base, such as cesium carbonate, as can be taken from the Example provided below. Depending on the specific reaction conditions and the reactants, the Suzuki coupling is accomplished after 6 to 48 h, e.g. after about 24 h, yielding the polymeric compound (3)/(3') as defined above.

In this context, a person skilled in the art readily knows that an oxidative reaction or an *in-situ* trans-metalation starting from suitable monomers also allows to obtain the polymeric compound (3)/(3') according to the present invention.

5 Furthermore, it may also be considered by a person skilled in the art to combine steps (b) and (b'), i.e. to conduct the coupling of the above-defined compounds (1), (2) and (2'). In this case, a polymeric compound is obtained which may have different repeating units.

10 The above-defined polymeric compound (3) of the first method according to the present invention comprises repeating units as depicted in formula (3) above. Herein, the number n of said repeating units is not specifically limited as long as it corresponds to at least 25 phenylene moieties. However, in order to be particularly usable in various applications, in particular in organic electronics, the above-defined poly-
15 meric compound (3) should comprise at least $n = 10$, preferably at least $n = 15$, more preferably at least $n = 20$, and particularly preferably at least $n = 25$ of said repeating units. As can be taken from formula (3) as depicted above, the polymeric compound (3) represents a homopolymer of $[A]_n$ type.

20 In the same way, the above-defined polymeric compound (3') of the second method according to the present invention comprises repeating units as depicted in formula (3') above. Herein, the number n' of said repeating units is not specifically limited as long as it corresponds to at least 25 phenylene moieties. However, in order to be particularly usable in various applications, in particular in organic electronics, the above-
25 defined polymeric compound (3') should comprise at least $n' = 8$, preferably at least $n' = 12$, more preferably at least $n' = 16$, and particularly preferably at least $n' = 20$ of said repeating units. As can be taken from formula (3') as depicted above, the polymeric compound (3') represents an alternating copolymer of $[AB]_{n'}$ type. In this context, it is clear to a skilled person that the polymeric compound (3') obtained in step
30 (b') may have a constitution such as $[AB]_{n'}$, $[AB]_{n'}A$, $B[AB]_{n'}$ and $B[AB]_{n'}A$, without being limited to only one of said specific constitutions. In order to include all of the aforementioned constitutions, formula (3') makes use of curved brackets labeled with the index z which is 0 or 1. The same applies to formula (4') and to formula (5'), respectively.

In this context, it is clear to a person skilled in the art that the chain length of the polymeric compound (3)/(3') can be controlled by the reaction time as well as by the concentrations of the compounds (1)/(1') and (2)/(2').

5

In order to avoid the occurrence of an intramolecular coupling, i.e. the formation of macrocycles, which principally competes with the linear polymerization, it is preferable to conduct the coupling in step (b)/(b') under kinetically-controlled conditions at comparatively high concentrations of the above-defined compounds (1)/(1') and (2)/(2'). For example, by applying monomer concentrations of at least 0.1 M, respectively, the tendency to form such macrocycles can be significantly reduced.

Due to the kinked shape of at least one of the starting materials, the above-defined polymeric compound (3)/(3') also exhibits a kinked structure. Thereby, the polymeric compound (3)/(3') is prevented from aggregating and is well-soluble in common organic solvents. In this respect, the polymeric compound (3)/(3') is different from planar PPP which is practically insoluble in common organic solvents due to aggregation.

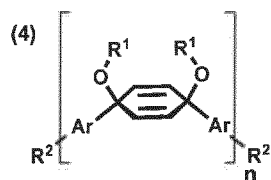
This enhanced solubility allows to carry out the chain propagation of the above-defined polymeric compound (3)/(3') until the compounds (1)/(1') and (2)/(2') have been mostly consumed. Consequently, a polymeric compound (3)/(3') of sufficient chain length is obtained in step (b)/(b') of the first and second methods according to the present invention.

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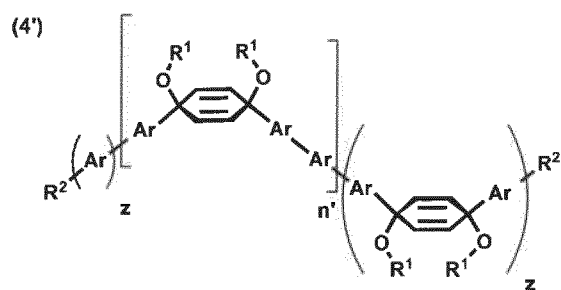
The above-defined polymeric compound (3)/(3') obtained by the coupling reaction of the compounds (1)/(1') and (2)/(2') carries reactive functional end groups represented by the substituents X¹, X², Y¹ and Y², i.e. halogen atoms, boronic ester residues, or a combination thereof, which can lead to the formation of undesired macrocyclic by-products.

30

Therefore, in step (c) of the first method for producing PPP, the above-defined polymeric compound (3) is end-capped, thereby obtaining a poly-(*para*-phenylene) precursor compound represented by the following formula (4):



In the same way, in step (c') of the second method for producing PPP, the above-defined polymeric compound (3') is end-capped, thereby obtaining a poly-(*para*-phenylene) precursor compound represented by the following formula (4'):



In the above formulae (4) and (4'), each of the moieties R^2 independently represents a substituted or unsubstituted hydrocarbon group, respectively. In this context, the term "substituted or unsubstituted hydrocarbon group" is as defined above.

Generally, end-capping of the polymeric compound (3)/(3') can be accomplished using a boron-substituted compound as well as a halo-substituted compound. In a preferred embodiment of the present invention, each of the moieties R^2 represents phenyl or 4-phenylphenyl. In this case, e.g. phenylboronic acid pinacol ester as well as bromobenzene can be used for end-capping. Thereby, a PPP precursor compound (4)/(4') is obtained which has no substituents in *para*-position. After aromatizing said PPP precursor compound (4)/(4') in step (f)/(f') of the above-defined first and second methods, respectively, perfect poly-(*para*-phenylene), i.e. poly-(*para*-phenylene) consisting of phenyl(ene) moieties only, is obtained.

In another example, when using 4-*tert*-butylphenylboronic acid pinacol ester and 1-bromo-4-*tert*-butylbenzene for end-capping, the above-defined poly-(*para*-phenylene) precursor compound (4)/(4') carries 4-*tert*-butylphenyl groups on both ends. Such 4-

tert-butylphenyl groups may be used as a spectroscopic probe, since they allow for an estimation of the chain length via ^1H -NMR spectroscopy.

Accordingly, when using a boron-substituted compound and a halo-substituted compound having the same substituent in *para*-position for end-capping in step (c)/(c'), identical moieties R^2 are obtained on both ends of the PPP precursor compound (4)/(4'), irrespective of how the above-defined polymeric compound (3)/(3') is terminated.

According to the present invention, the boron-substituted compound and the halo-substituted compound which are used for end-capping in step (c)/(c') can be reacted with the above-defined polymeric compound (3)/(3') simultaneously or consecutively.

As already mentioned above, the polymeric compound (3)/(3') has a good solubility in common organic solvents due to its kinked structure. The same applies to the above-defined poly-(*para*-phenylene) precursor compound (4)/(4') obtained in step (c)/(c'). Therefore, the latter can be easily isolated and processed before being aromatized to the target compound, i.e. to the poly-(*para*-phenylene) compound (5)/(5'), as described below.

Besides the poly-(*para*-phenylene) precursor compound (4)/(4'), oligomeric and macrocyclic byproducts as well as the unreacted boron-substituted compound and the unreacted halo-substituted compound used for end-capping are contained in the crude product obtained in step (c)/(c').

Accordingly, in step (d)/(d') of the first and second methods for producing poly-(*para*-phenylene) according to the present invention, respectively, the above-defined PPP precursor compound (4)/(4') is optionally isolated from the other constituents contained in the crude product, as required.

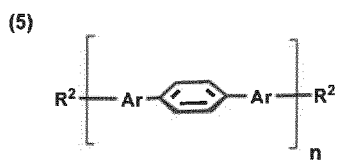
The procedures for isolating the poly-(*para*-phenylene) precursor compound (4)/(4') in step (d)/(d') of the above-defined first and second methods are not specifically limited, respectively. In one embodiment of the present invention, the isolation in step (d)/(d') is conducted by fractionated precipitation. For example, the crude product

may be subjected to several dissolution and precipitation cycles, using chloroform for the dissolution steps and solvents such as petroleum ether, diethyl ether and toluene for the precipitation steps. One example of such an isolation procedure is depicted in Fig. 2. However, the fractionated precipitation when conducted in step (d)/(d') for isolating the above-defined poly-(*para*-phenylene) precursor compound (4)/(4') is not limited to the above solvents used for dissolution and precipitation.

Furthermore, in step (e)/(e') of the first and second methods for producing poly-(*para*-phenylene) according to the present invention, respectively, the above-defined PPP precursor compound (4)/(4') is optionally further processed, as required. In this case, the above-defined poly-(*para*-phenylene) precursor compound (4)/(4'), e.g. in isolated form, may be dissolved in an appropriate solvent such as chloroform. According to the present invention, step (e)/(e') of the above-defined first and second methods is not limited to any specific processing procedure, respectively.

In one embodiment of the present invention, the processing in step (e)/(e') is a film formation procedure conducted by spin-coating. Thereby, nanometer-sized thin films of the above-defined poly-(*para*-phenylene) precursor compound (4)/(4') can be obtained. Herein, the term "nanometer-sized" typically means a film thickness in the range of 1 to 1000 nm, such as 10 to 500 nm, or 20 to 300 nm. Said nanometer-sized thin films may be regarded as PPP precursor films. After aromatizing said PPP precursor films to PPP films by thermal treatment or by irradiation, the aromatized PPP films can be used in various applications, in particular in organic electronics. According to the present invention, the processing procedures in step (e)/(e') of the above-defined first and second methods are not limited to spin-coating and to the formation of nanometer-sized thin films, respectively. Depending on the application purpose, other forms of processing may be applied in step (e)/(e'), such as dip-coating, casting molding or printing.

In step (f) of the first method according to the present invention, the above-defined poly-(*para*-phenylene) precursor compound (4) which has been optionally isolated and optionally processed in steps (d) and (e), respectively, is aromatized by thermal treatment or by irradiation, thereby obtaining a poly-(*para*-phenylene) compound represented by the following formula (5):

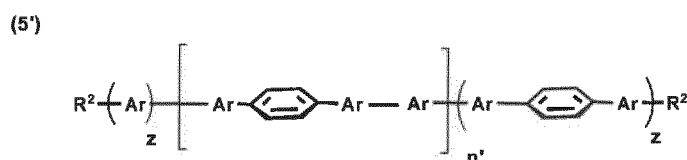


In the above formula (5), Ar, R² and n are as defined above.

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In the same way, in step (f') of the second method according to the present invention, the above-defined poly-(*para*-phenylene) precursor compound (4') which has been optionally isolated and optionally processed in steps (d') and (e'), respectively, is aromatized by thermal treatment or by irradiation, thereby obtaining a poly-(*para*-phenylene) compound represented by the following formula (5'):

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In the above formula (5'), Ar, R², n' and z are as defined above.

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According to the present invention, the aromatization in step (f)/(f') is conducted by thermal treatment or by irradiation. In one embodiment of the present invention, the aromatization is conducted by thermal treatment in a temperature range of 100 to 500°C, e.g. 125 to 400°C, or 150 to 300°C. In another embodiment of the present invention, the aromatization is conducted by irradiation in the wavelength range of 100 to 1500 nm.

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Irrespective of the specific aromatization procedure applied in step (f)/(f') as described above, the substituted cyclohexadienylene moieties of the poly-(*para*-phenylene) precursor compound (4)/(4') are reduced to phenylene moieties. Thereby, the kinked structure of the above-defined poly-(*para*-phenylene) precursor compound (4)/(4') is planarized. Advantageously, conducting the aromatization by thermal treatment or by irradiation allows for a complete aromatization of the PPP precursor compound.

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On the other hand, as found by the present inventors, when carrying out the aromatization in solution using a reducing agent, the resulting poly-(*para*-phenylene) compound (5)/(5') precipitates due to its reduced solubility as a result of aggregation with increasing polymer chain length. As a consequence, the aromatization of the PPP precursor compound (4)/(4') remains incomplete.

In a preferred embodiment of the present invention, the aromatization in step (f)/(f') is conducted by thermal treatment, preferably in a temperature range of 150 to 300°C. Such an aromatization procedure is particularly suitable when having processed the poly-(*para*-phenylene) precursor compound (4)/(4') into nanometer-sized thin films by spin-coating in step (e)/(e').

In contrast to oligomeric and macrocyclic *para*-phenylenes with their low molecular weight, thermal treatment in the above-defined temperature range does not lead to an evaporation of the poly-(*para*-phenylene) precursor compound, which would otherwise make the aromatization by thermal treatment impossible.

According to a further aspect, the present invention relates to a poly-(*para*-phenylene) compound obtained by the first or second method as defined above. Due to the novel precursor route on which the above-defined first and second methods are based, respectively, said poly-(*para*-phenylene) compound is unsubstituted, structurally defect-free and of sufficient chain length so as to be used in various applications, in particular in organic electronics.

If applicable and not stated otherwise, the definitions provided in the context of the first and second methods as defined above also apply to the poly-(*para*-phenylene) compound of the present invention.

As such, the poly-(*para*-phenylene) compound according to the present invention is characterized by a total number of at least 25 phenylene moieties. Accordingly, the poly-(*para*-phenylene) compound according to the present invention has a sufficient chain length. The total number of phenylene moieties is preferably at least 50, and more preferably at least 75. In this context, it is clear to a person skilled in the art that

the respective chain length of the poly-(*para*-phenylene) compound depends on the specific application purpose.

Another aspect of the present invention relates to the use of the above-defined poly-(*para*-phenylene) compound as a nanometer-sized thin film in organic electronics. As
5 already defined above, the term "nanometer-sized" typically means a film thickness in the range of 1 to 1000 nm, for example 10 to 500 nm, or 20 to 300 nm. The present invention further relates to the use of the above-defined poly-(*para*-phenylene) compound as a model compound and a precursor for graphene, as an insulator, as a
10 conducting material when doped, or as a material for thermoelectric devices.

The figures show:

Fig. 1 shows photographs of solutions/suspensions of the crude product **4** in different
15 solvents (Fig. 1a) and the dissolution of the crude product **4** in different volumes of chloroform (Fig. 1b).

Fig. 2 shows the procedure of fractionated precipitation for purification of the PPP
precursor compound.

20 Fig. 3 shows GPC chromatograms of the fractions **FP1**, **FP2F** and **FP2** (* = injection peak).

Fig. 4 shows GPC chromatograms of the fractions **FP2**, **FP3F** and **FP3** (* = injection
25 peak).

Fig. 5 shows the comparison of ¹H-NMR spectra of the fractions **FP1**, **FP2F**, **FP2**, **FP3F**, and **FP3** in chloroform-d₁.

30 Fig. 6 shows ¹H-NMR spectra of the fractions **FP1** and **FP3** in chloroform-d₁.

Fig. 7 shows the ¹³C-NMR spectrum of the fraction **FP3** in chloroform-d₁.

Fig. 8 shows the TGA trace of the fraction **FP3**.

Fig. 9 shows photographic images of the blank quartz substrate (left), the quartz substrate with the PPP precursor film (middle), and the quartz substrate with the PPP film under UV irradiation at 254 nm (Fig. 9a) and 365 nm (Fig. 9b).

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Fig. 10 shows IR spectra of the PPP precursor compound as a bulk and the PPP film, including a zoom of the region around 3000 cm⁻¹.

Fig. 11 shows absorption and emission spectra of the PPP precursor compound (top) and the PPP film (bottom), * = $\lambda_{\text{exc}}/2$ (500 nm).

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Fig. 12 shows normalized fluorescence spectra ($\lambda_{\text{exc}} = 250$ nm) of the PPP precursor compound and the PPP film, * = $\lambda_{\text{exc}}/2$ (500 nm), including an inset which shows the relative intensities of the emission spectra.

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Fig. 13 shows the ¹H-NMR spectrum of compound **2** in d₂-dichloromethane (250 MHz, 298 K).

Fig. 14 shows the ¹³C-NMR spectrum of compound **2** in d₂-dichloromethane (63 MHz, 298 K).

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Fig. 15 shows the ¹H-NMR spectrum of compound **3** in d₂-dichloromethane (250 MHz, 298 K).

Fig. 16 shows the ¹³C-NMR spectrum of compound **3** in d₂-dichloromethane (63 MHz, 298 K).

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The present invention provides two methods for producing poly-(*para*-phenylene), which are based on a novel precursor route, respectively.

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Advantageously, said novel precursor route makes use of a well-soluble poly-(*para*-phenylene) precursor compound which is built up from at least one kind of kinked monomers, thus preventing the PPP precursor compound from being aggregated.

Surprisingly, due to its enhanced solubility in common organic solvents, the poly-(*para*-phenylene) precursor compound can be readily isolated and processed depending on the application purpose.

- 5 After aromatizing the PPP precursor compound by thermal treatment or by irradiation, an unsubstituted and structurally defect-free poly-(*para*-phenylene) compound of sufficient chain length is obtained, which can be used in various applications, in particular in organic electronics.
- 10 Particularly, the present invention allows to obtain a poly-(*para*-phenylene) compound with a total number of at least 25 phenylene moieties, wherein said phenylene moieties are exclusively connected in *para*-position, and wherein said phenylene moieties are free of any side chains. Thereby, the poly-(*para*-phenylene) compound according to the present invention is not subject to any undesired deplanarization in
- 15 the polymer backbone.

Example

The following Example is intended to further illustrate the present invention. The

20 claims are not to be construed as being limited thereto.

General remarks

All commercially available chemicals were used without further purification unless

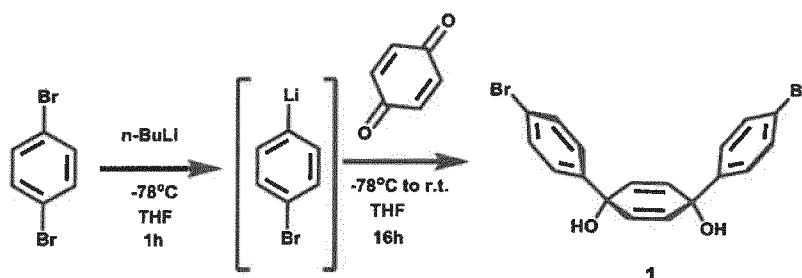
25 otherwise noted. The reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification of all compounds were performed under air and with reagent-grade solvents. Melting points were determined on a Büchi B-545 hot stage apparatus. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AVANCE 250, Bruker AVANCE 300, Bruker AVANCE 500 and Bruker

30 AVANCE 700 spectrometer in the listed deuterated solvents. Trimethylsilane (δ 0.00 ppm) or the deuterated solvent was used as an internal standard. Raman spectra were taken with a confocal Raman microscopy, Bruker (785 nm). Thin films were made via spin-coating with a Spin Coater SCV-10 on glass, quartz-glass, Si-wafer or gold substrate, which was vacuum-decomposed on Si-wafer (50-90 nm). Layer thick-

nesses of thin films were determined using a profilometer (DektakXT, Bruker). Solid-State UV/Vis absorption and emission spectra were recorded at room temperature on a Jasco V660 and FP6500 spectrophotometer of thin films on a quartz substrate. Field desorption (FD) mass spectra were obtained on a VG Instruments ZAB 2 SE-FPD. Solvent-free MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF spectrometer using a 337 nm nitrogen laser with TCNQ as a matrix.

Synthetic procedures

10 Synthesis of 1,4-dihydroxy-1,4-di(4-bromophenyl)cyclohexadiene (compound 1)



To a cooled (-78°C) solution of *para*-dibromobenzene (67.1 g, 285 mmol, 2.05 eq) in 1.50 L dry THF, *n*-butyllithium (2.50 M in hexane, 117 mL, 2.10 eq, 291 mmol) was added and stirred for 1 h at this temperature (salt formation). To this mixture, neat *para*-benzoquinone (15.0 g, 139 mmol, 1.00 eq) was added portion-wise (ca. 3.00 g each). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction was quenched with water (800 mL) and diluted with diethyl ether (800 mL). After layer separation, the aqueous layer was extracted with diethyl ether three times. The combined organic layers were washed with brine and dried over magnesium sulfate. The organic solvents were removed under reduced pressure. The crude product was precipitated from dichloromethane in petroleum ether three times and the precipitate was re-crystallized from diethyl ether and *n*-hexane several times to yield compound **1** as a colorless crystalline solid (8.80 g, 20.8 mmol, 15%). Principally, it is not required to isolate, e.g. crystallize, compound **1** before it is reacted to compound **2**.

FD-MS (*m/z*): calculated for C₁₈H₁₄Br₂O₂ 412.9, found 421.4.

Melting point: 150-152°C.

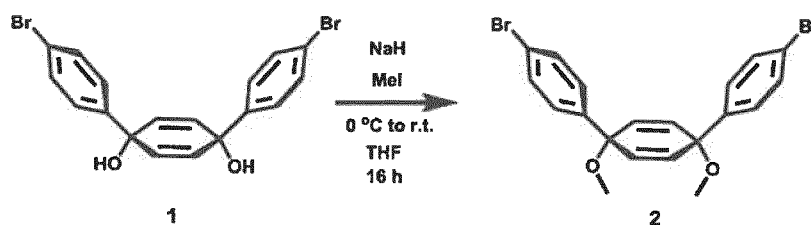
¹H-NMR (250 MHz, d₂-dichloromethane) δ [ppm] = 7.26-7.53 (m, 8H, H_{arom.}); 6.02 (s, 4H, H_{olefin.}); 2.64 (s, 2H, -OH).

¹³C-NMR (63 MHz, d₂-dichloromethane) δ [ppm] = 143.5; 132.5; 132.1; 127.9; 122.9; 69.4.

UV/Vis (THF) λ_{max} [nm] ([cm⁻¹]) = 259 (38610).

FT-IR = 3085; 3070; 3028; 2969; 2944; 2921; 2820; 1491; 1448; 1396; 1228; 1189; 1174; 1088; 1065; 1020; 943; 918; 900.

10 Synthesis of 1,4-dimethoxy-1,4-di(4-bromophenyl)cyclohexadiene (compound 2)



NaH (3.80 g, 60% mineral oil, 94.8 mmol, 4.00 eq) was suspended in 1.00 L dry THF and cooled to 0°C. The isolated compound 1 (10.0 g, 23.7 mmol, 1.00 eq) was put into the cooled suspension portion-wise (ca. 2 g each) and allowed to warm to room temperature. After stirring for 1 h, the mixture was re-cooled to 0°C and neat MeI (6.10 mL, 97.1 mmol, 4.10 eq) was added drop-wise. The mixture was warmed to room temperature and stirred for 16 h. The reaction was quenched with water (500 mL) and diluted with diethyl ether (200 mL). After layer separation, the aqueous layer was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over magnesium sulfate and the organic solvents were removed under reduced pressure. The crude product was first precipitated from dichloromethane into methanol. The precipitate was then collected and further crystallized from diethyl ether and methanol to yield compound 2 as colorless needles (10.5 g, 23.2 mmol, 98%).

FD-MS (*m/z*): calculated for C₂₀H₁₈Br₂O₂ 450.0, found 450.1.

Melting point: 134.0-135.7°C.

^1H -NMR (250 MHz, d_2 -dichloromethane) δ [ppm]: 7.20-7.49 (m, 8H, $\text{H}_{\text{arom.}}$); 6.07 (s, 4H, $\text{H}_{\text{olefin.}}$); 3.40 (s, 6H, -OMe).

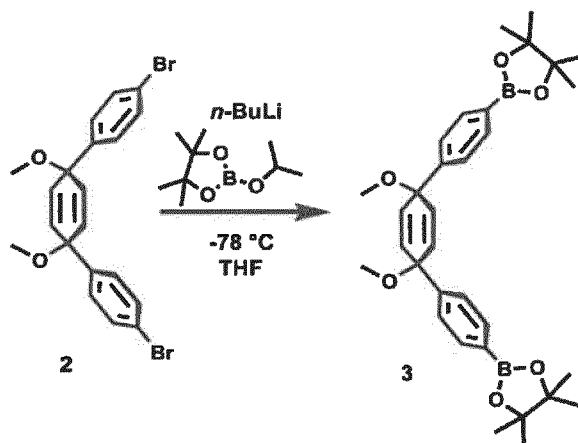
^{13}C -NMR (63 MHz, d_2 -dichloromethane) δ [ppm]: 143.1; 133.8; 131.7; 128.3; 121.8; 74.7; 52.3.

5 UV/Vis (THF) λ_{max} [nm] ($[\text{cm}^{-1}]$) = 260 (39462).

FT-IR = 3085; 3070; 3028; 2982; 2945; 2899; 2820; 1506; 1480; 1451; 1398; 1175; 1025; 1007; 948; 822; 756.

10 ^1H - and ^{13}C -NMR spectra of compound **2** can be taken from Figs. 13 and 14, respectively.

Synthesis of 1,4-dimethoxy-1,4-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclohexadiene (compound **3**)



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Compound **2** (5.00 g, 11.1 mmol, 1.00 eq) was dissolved in 300 mL dry THF and cooled to -78°C . At that temperature, *n*-butyllithium (9.80 mL, 24.4 mmol, 2.20 eq, 2.5 M in hexane) was added drop-wise. *iso*-propyl pinacol borate (9.10 mL, 44.4 mmol, 4.00 eq) was added via syringe. After stirring at -78°C for 30 min, the reaction was quenched with 100 mL water, allowed to warm to room temperature and was then diluted with 400 mL diethyl ether. After layer separation, the aqueous phase was extracted with diethyl ether three times. The collected organic layers were washed with brine, dried over magnesium sulfate and the organic solvents were removed under reduced pressure. The crude product was first precipitated from dichloromethane into methanol. The precipitate was then collected and re-crystallized from dichloro-

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methane and methanol to yield compound **3** as colorless plate crystals (4.60 g, 8.44 mmol, 76%).

FD-MS (m/z): calculated for $C_{32}H_{42}B_2O_6$ 544.3, found 545.6.

5 Melting point: 250.5°C.

1H -NMR (250 MHz, d_2 -dichloromethane) δ [ppm]: 7.32-7.74 (m, 8H, $H_{arom.}$); 6.08 (s, 4H, $H_{olefin.}$); 3.41 (s, 6H, -OMe); 1.32 (s, 24H, $H_{BPin.}$).

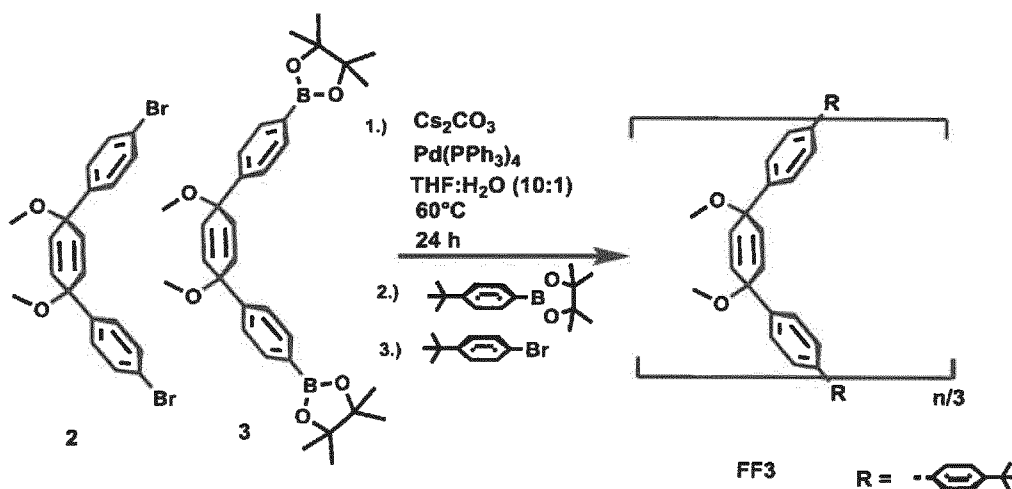
^{13}C -NMR (63 MHz, d_2 -dichloromethane) δ [ppm] 146.9; 135.1; 133.7; 125.8; 84.2; 75.3; 52.3; 25.0 (C-B signal was not visible due to isochronism).

10 UV/Vis (THF) λ_{max} [nm] ($[cm^{-1}]$) = 260 (39462).

FT-IR = 3085; 3070; 3028; 2988; 2974; 2938; 2820; 1610; 1361; 1324; 1272; 1141; 1090; 1080; 1066; 1016; 950; 857; 835; 741.

1H - and ^{13}C -NMR spectra of compound **3** can be taken from Figs. 15 and 16, respectively.

Suzuki coupling of compound **2** and compound **3**, followed by end-capping



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Compound **2** (2.00 mg, 4.44 mmol, 1.00 eq), compound **3** (2.42 g, 4.44 mmol, 1.00 eq), cesium carbonate (7.24 g, 22.2 mmol, 5.00 eq), and tetrakis(triphenylphosphine) palladium (513 mg, 444 μ mol, 10 mol%) were dissolved in 22 mL ($c = 50.0$ mM) of degassed 10:1 THF/water. The solution was heated to 60°C for 23 h. For end-capping, an excess of 4-*tert*-butylphenylboronic acid pinacol ester (301 mg, 1.16 mmol, 0.26 eq) in dry THF (10 mL) was added. After stirring for 2 h at the same tem-

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perature, an excess of 1-bromo-4-*tert*-butylbenzene (390 μ L, 2.22 mmol, 0.50 eq) was added and stirred at 60°C for additional 3 h. After cooling to room temperature, the aqueous layer was separated and the crude product was collected *via* precipitation of the organic layer into methanol. The crude product **4** (ca. 2.00 g) was purified by fractionated precipitation.

$^1\text{H-NMR}$ (300 MHz, d_2 -dichloromethane) δ [ppm] = 7.35-7.78 (m, $\text{H}_{\text{arom.}}$); 6.10 (s, $\text{H}_{\text{olefin.}}$); 3.50 (s, -OMe); 1.22-1.37 (m, 18H, $\text{H}_{t\text{-Bu}}$).

$^{13}\text{C-NMR}$ (75 MHz, d_2 -dichloromethane) δ [ppm] = 142.7; 140.1; 133.5; 127.2; 126.6; 74.8; 52.1; 31.5; 29.9.

UV/Vis (THF) λ_{max} [nm] ($[\text{cm}^{-1}]$) = 268 (37313).

FT-IR = 3030; 2980; 2937; 2899; 2822; 1608; 1557; 1491; 1464; 1450; 1391; 1176; 1272; 1176; 1085; 1085; 1024; 1004; 952; 822.

Fractionated precipitation

The crude product **4** was poorly soluble in THF which was the solvent for the Suzuki coupling. Further studies of the solubility in different solvents were carried out, as summarized in Fig. 1a. All solutions/suspensions were put in an ultrasonic bath for 1 h with the same concentration of 10 mg/mL. Toluene, dichloroethane and chlorobenzene showed similar solubility issues as THF, whereas chloroform turned out to be an excellent solvent. Addition of increasing volumes of chloroform to the crude product **4** resulted in complete solubility, as summarized in Fig. 1b.

The crude product **4** of the Suzuki coupling contained a variety of byproducts including polymers of small chain lengths, i.e. oligomers, and different macrocycles. Since with all polycondensation reactions, polymerization and macrocyclization competed. Fractionated precipitation was chosen as the separation method. Thereby, the varying solubilities could be exploited to separate the longest polymer fraction from all low molecular weight oligomers and macrocyclic byproducts.

The crude product **4** (ca. 2.0 g) was completely dissolved in chloroform and precipitated into petroleum ether to remove all small molecules (e.g. end-cappers) as well as traces of enclosed methanol. The fractionated precipitate **FP1** was separated via

filtration from the filtrate **FP1F** and re-dissolved in chloroform. Precipitation into diethyl ether led to the fractionated precipitate **FP2** and the corresponding filtrate **FP2F**. In this step, all small well-soluble macrocycles and their open-chained counterparts could be removed. The filtration residue **FP2** was re-dissolved in chloroform and finally precipitated into toluene. After 2 h at room temperature, no precipitation could be observed. Storage at -20°C for 2 h led to the formation of a dark grey precipitate **FP3** which was collected via filtration (0.192 g). The yellowish filtrate **FP3F** was concentrated under reduced pressure to yield a yellow solid **FP3F** (0.940 g), as can be taken from Fig. 2.

Analysis of the fractions via gel permeation chromatography (GPC)

As can be taken from Fig. 3, the GPC chromatogram of the filtration residue **FP1** exhibited a broad signal with at least four sharp peaks which protruded to higher elution volumes. Two of those peaks could be removed by precipitation into diethyl ether. Further peaks and shoulders remained in the filtration residue **FP2**. As expected, the filtrate **FP2F** had a higher elution volume compared to the filtration residue **FP2**, thus exhibiting a lower molecular mass. The sharpness of the peak also indicated the presence of small molecules and the absence of polymeric structures.

As can be taken from Fig. 4, the GPC chromatogram of the separation of the filtration residue **FP2** into the filtrate **FP3F** and the filtration residue **FP3** showed a further shift of the peak towards lower elution volumes. This observation was in excellent accordance with the expected solubility behavior of high molecular weight polymers and macrocyclic byproducts.

The values of the GPC analyses are summarized in Table A.

Table A – Different fractions of the fractionated precipitation vs. polystyrene.

	FP1	FP2F	FP2	FP3F	FP3
Mn/(g · mol ⁻¹)	2270	1126	2925	3390	5306
Mw/(g · mol ⁻¹)	5780	2364	7040	7716	11128
PDI	2.55	2.10	2.41	2.28	2.10

¹H-NMR analysis

All fractions were analyzed by ^1H -NMR spectroscopy. All spectra exhibited the same number of signals. The aromatic proton resonances appeared as multiplets at around 7.4-7.7 ppm, the signals of the olefinic protons as a singlet at around 6.1 ppm, those of the methoxy protons as singlets at around 3.5 ppm, and the *tert*-butyl protons at 0.6 ppm as multiplets. The observation of *tert*-butyl end groups in the ^1H -NMR spectra was a proof for the existence of linear macromolecules. At the same time, sharp overlapped singlets at around 3.5 and 6.1 ppm indicated the presence of discrete small molecules with the same structural motif in the spectra of fractions **FP1** to **FP3F**, as can be taken from Fig. 5. It is known in the art that cyclic products are formed under similar conditions. The absence of these sharp overlapped singlets in the fraction **FP3** proved the successful purification of the PPP precursor compound, as can be also taken from Fig. 5.

The relative intensities of the signals of the *tert*-butyl protons and the other signals in the fractions **FP1** and **FP3** were changed towards smaller ratios, as can be taken from Fig. 6.

In both spectra (fractions **FP1** and **FP3**), the integrals of the *tert*-butyl protons were set to 18 as a reference, since the end groups had 18 protons. Open-chained macromolecules could be distinguished from cyclic phenylenes by the presence or absence of the resonances of the *tert*-butyl end groups. Since the fraction **FP1** was a mixture of linear polymers as well as cyclic byproducts, the relative intensities of the signals of fraction **FP1** vs. the end groups were higher than those calculated for the NMR of the fraction **FP3** (38 vs. 25).

In the proton NMR, the isolated fraction **FP3** showed very broad peaks with the same number of resonances and multiplicities as the monomers, except for the end groups. This broadening was generally expected for all polymers. The chain length could be determined from the relative intensities of ^1H -NMR signals of the aromatic and olefinic resonances with respect to the *tert*-butyl end group resonances, resulting in an estimated degree of polymerization of $n_{\text{NMR}} = 25$, which means 75 phenylene moieties after aromatization, as can be taken from Fig. 6.

Further characterization via ^{13}C -NMR spectroscopy verified the open-chain nature of this macromolecule, as can be taken from Fig. 7. Two signals around 30 ppm (31.5 and 29.9 ppm) could be assigned to the two carbon atoms of the end groups.

5 Aromatization by thermal treatment

For the aromatization step, a thermal solid-state protocol was applied. The aromatization process was studied by thermal gravimetric analysis (TGA) of the bulk polymer, as can be taken from Fig. 8. The TGA trace showed a loss in mass of the PPP precursor compound at about 225-300°C. This mass loss was attributed to the demethoxylation, thereby yielding the corresponding phenylene moieties.

Film-forming process: spin-coating

The PPP precursor compound was dissolved in chloroform ($c = 5 \text{ mg/mL}$) and spin-coated (3000 rpm for 30 sec, and 4000 rpm for 60 sec) on a quartz substrate to yield 60 nm thick layers. Under the same conditions, a solution with a concentration of 1 mg/mL resulted in approximately 20 nm thick layers, whereas spin-coating on gold-substrates with a concentration of 5 mg/mL led to films of approximately 15-20 nm thickness.

The coated substrate was put onto a heat plate at 300°C under inert gas (N_2 , atmospheric pressure). The reaction could be easily monitored by irradiation with a UV lamp (365 nm), leading to a fluorescent film. Reactions were completed after ca. 2 h.

Photographic images of these films under UV irradiation at 254 nm and 365 nm are illustrated in Fig. 9. As can be taken therefrom, irradiation at 365 nm led to an emission of the aromatized film of such brightness so that the background became illuminated.

Analysis of the poly-(*para*-phenylene) compound

IR spectroscopy

IR spectroscopy is the tool most often used to account for PPP / oligo-(*para*-phenylene) (OPP) formation. In order to prove the quantitative aromatization in thin films, IR spectroscopy was conducted, showing bands typical for exclusive PPP formation, as can be taken from Fig. 10.

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The most obvious proof for the demethoxylation was the absence of the band at around 2820 cm⁻¹ after thermal aromatization, which is characteristic of the methoxy group of the PPP precursor compound. Furthermore sp²-hybridized C-H stretching modes appeared generally above 3000 cm⁻¹ (3030 cm⁻¹) which was expected for a polymer exclusively constructed from sp²-hybridized carbon atoms.

10

The most evident band for PPP is the "out-of-plane" C-H stretching mode of the *para*-disubstituted phenylene moiety at 810 cm⁻¹. This value may vary for different *para*-disubstituted phenylene compounds from 830 to 800 cm⁻¹, as known in the art. The other bands were comparable to reported *para*-connected phenylenes, as can be taken from Table B, below.

15

Table B – Comparison of IR bands of different *para*-phenylenes known in the art.

normal mode	Example of pres. invention	sexi-phenylene ^[1]	sexi-phenylene ^[2]	Grubbs PPP ^[3]	Yama-moto PPP ^[4]	Electro-pol. PPP ^[5]
C-H stretching	3030	3033	-	3033	>3000	-
C=C stretching	1601	-	-	1601	~1600	-
C=C-C bending	1480	1480	1479	1482	~1480	1482
	1399	1404	1402	1256	~1220	1398
C-H in-plane deformation	1001	1003	1001	~1000	~1000	1001
C-H out-of-plane deformation (<i>para</i> -substituted phenylene)	810	838	815	807	805	812

All values given in cm⁻¹.

20

Comparative data taken from:

^[1] Park *et al.*, Bulletin of the Korean Chemical Society 2014, 35, 531-538.

[2] Louarn *et al.*, Synthetic Metals 1993, 57, 4762-4767.

[3] Gin *et al.*, Synthetic Metals 1994, 66, 169-175.

[4] Yamamoto *et al.*, Polymer Journal 1990, 22, 187-190.

[5] Descroix *et al.*, Electrochimica Acta 2013, 106, 172-180.

5

Absorption- and fluorescence spectroscopy

In the UV/Vis spectroscopy, a broad absorption maximum at 268 nm was detected, whereas the fluorescence spectrum of the fraction **FP3** showed a slightly broader emission band at 381 nm with a mirror symmetry, as can be taken from Fig. 11. After aromatizing the film of the PPP precursor compound, the absorption maximum underwent a bathochromic shift of ca. 80 nm to 350 nm. Furthermore, the film of the aromatized PPP compound showed a bright green-blueish emission ranging from 400 to 600 nm, and exhibiting structured bands as well as a lack of mirror symmetry between the absorption and emission spectra. Besides PPP, for π -conjugated polymers such as poly-(*para*-phenylene vinylene) (PPV), polythiophene (PTh), and even *para*-sexiphenyl films, this observation is typical. It can be ascribed to the larger torsional mobility in the electronic ground state in comparison to the first excited singlet state. PPP exists in a nonplanar benzenoid form with an interplanar dihedral angle of 23 to 40°. Upon electronic excitation, this ring torsion lessens due to the contribution of the quinoidal canonical form. The obtained fine structured fluorescence spectrum exhibited four emission bands at 423, 447, 480, 515 nm (one shoulder at 550 nm) in comparison to many spectra reported in the prior art, which only show one very broad and unstructured band.

25

In the prior art, it has been reported on the fluorescence spectra of ordered OPP films on quartz which were prepared via vacuum-deposition of PPP (up to 13 phenylene moieties) prepared according to the Kovacic method. Depending on the chain length, three maxima at 434, 462 and 484 nm were observed, comparable to the four main peaks of the Example of the present invention, which slightly differ in the emission maxima (422, 450, 480 and 517 nm). This shift was caused by the different lengths of the polymer chain. Oriented *para*-sexiphenyl films (prepared via vacuum-deposition) exhibit similarly structured fluorescence spectra with four maxima (412, 440, 466, 496 nm). The fluorescence spectrum of the Example according to the pre-

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sent invention was not only in excellent agreement with those of oriented *para*-sexiphenyl films but also with those of oriented OPP films known in the prior art.

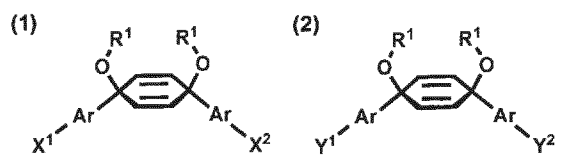
For further verification of the complete aromatization of the PPP precursor compound,
5 a fluorescence spectrum of the PPP film was analyzed at an excitation energy of 250 nm. No emission bands assignable to cyclohexadienylene moieties of the PPP precursor compound were detected in the PPP film, as can be taken from Fig. 12. The emission intensity of PPP itself is of low intensity and located around the peak of twice the excitation wavelength.

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Claims

1. A method for producing poly-(*para*-phenylene), comprising the steps of:
- (a) providing a compound represented by the following formula (1) and a compound represented by the following formula (2) as starting materials:

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wherein each of the moieties Ar independently represents 1,4-phenylene or 4,4'-bisphenylene, respectively,

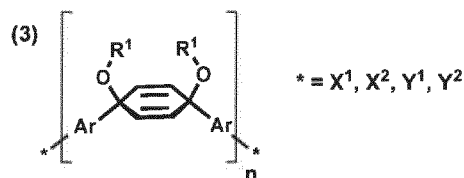
15 wherein each of the moieties R^1 independently represents a substituted or unsubstituted hydrocarbon group, respectively, and

wherein each of the substituents X^1 , X^2 , Y^1 and Y^2 independently represents a halogen atom or a boronic ester residue, respectively, provided that two of the above-defined substituents X^1 , X^2 , Y^1 and Y^2 independently represent a halogen atom and the remaining two of the above-defined substituents X^1 , X^2 , Y^1 and Y^2 independently represent a boronic ester residue,

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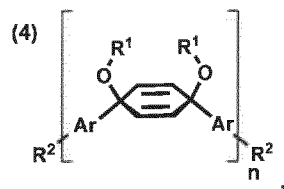
- (b) reacting the above-defined compounds (1) and (2) in the presence of a transition metal catalyst to obtain a polymeric compound represented by the following formula (3):

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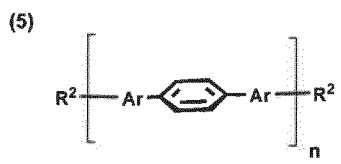
wherein n is the number of repeating units,

- (c) end-capping the above-defined polymeric compound (3) to obtain a poly-(*para*-phenylene) precursor compound represented by the following formula (4):



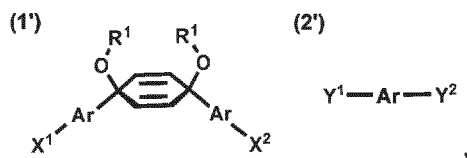
wherein each of the moieties R^2 independently represents a substituted or unsubstituted hydrocarbon group, respectively,

- (d) optionally isolating the above-defined poly-(*para*-phenylene) precursor compound (4),
- (e) optionally processing the above-defined poly-(*para*-phenylene) precursor compound (4), and
- (f) aromatizing the above-defined poly-(*para*-phenylene) precursor compound (4) by thermal treatment or by irradiation to obtain a poly-(*para*-phenylene) compound represented by the following formula (5):



wherein Ar, R^2 and n are as defined above.

2. The method according to claim 1, wherein the compounds (1) and (2) are identical.
3. A method for producing poly-(*para*-phenylene), comprising the steps of:
 - (a') providing a compound represented by the following formula (1') and a compound represented by the following formula (2') as starting materials:

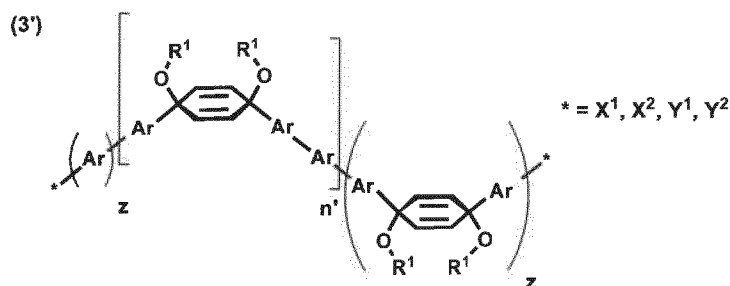


wherein each of the moieties Ar independently represents 1,4-phenylene or 4,4'-bisphenylene, respectively,

wherein each of the moieties R^1 independently represents a substituted or unsubstituted hydrocarbon group, respectively, and

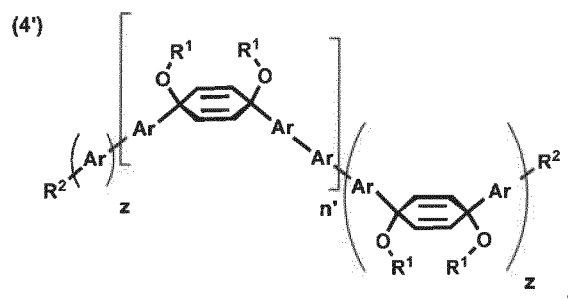
wherein each of the substituents X^1 and X^2 independently represents a halogen atom and each of the substituents Y^1 and Y^2 independently represents a boronic ester residue, respectively, or *vice versa*,

(b') reacting the above-defined compounds (1') and (2') in the presence of a transition metal catalyst to obtain a polymeric compound represented by the following formula (3'):



wherein n' is the number of repeating units and z is 0 or 1,

(c') end-capping the above-defined polymeric compound (3') to obtain a poly-(*para*-phenylene) precursor compound represented by the following formula (4'):



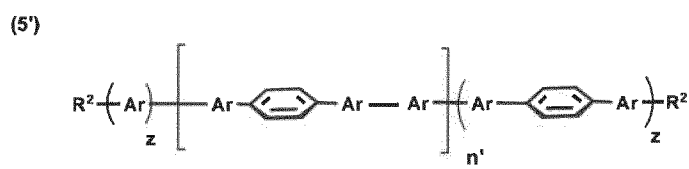
wherein each of the moieties R^2 independently represents a substituted or unsubstituted hydrocarbon group, respectively,

(d') optionally isolating the above-defined poly-(*para*-phenylene) precursor compound (4'),

5 (e') optionally processing the above-defined poly-(*para*-phenylene) precursor compound (4'), and

(f') aromatizing the above-defined poly-(*para*-phenylene) precursor compound (4') by thermal treatment or by irradiation to obtain a poly-(*para*-phenylene) compound represented by the following formula (5'):

10



wherein Ar, R^2 , n' and z are as defined above.

15 4. The method according to any one of claims 1 to 3, wherein the halogen atom is bromine.

5. The method according to any one of claims 1 to 4, wherein the boronic ester residue is pinacol boronic ester.

20

6. The method according to any one of claims 1 to 5, wherein each of the moieties Ar represents 1,4-phenylene.

7. The method according to any one of claims 1 to 6, wherein each of the moieties R^1 represents methyl.

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8. The method according to any one of claims 1 to 7, wherein each of the moieties R^2 represents phenyl or 4-phenylphenyl.

30 9. The method according to any one of claims 1 to 8, wherein the transition metal catalyst is selected from the group consisting of tetrakis(triphenylphosphine) palladium and bis(cyclooctadiene) nickel.

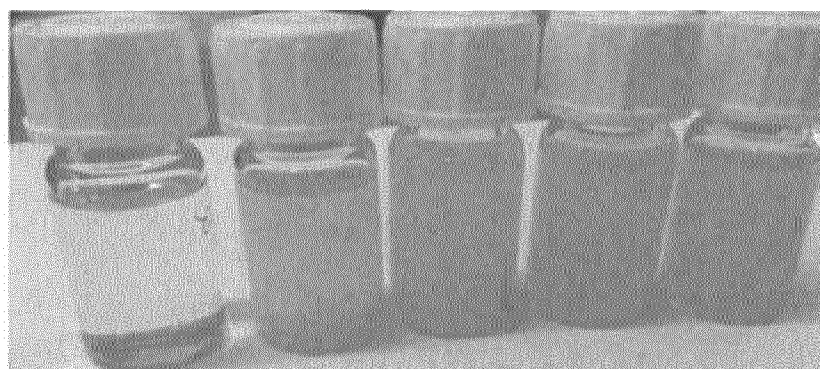
10. The method according to any one of claims 1 to 9, wherein the optional isolation is conducted by fractionated precipitation.
- 5 11. The method according to any one of claims 1 to 10, wherein the optional processing is a film formation conducted by spin-coating.
12. The method according to any one of claims 1 to 11, wherein the aromatization is conducted by thermal treatment in a temperature range of 150 to 300°C.
- 10 13. The method according to any one of claims 1 to 11, wherein the aromatization is conducted by irradiation in the wavelength range of 100 to 1500 nm.
14. A poly-(*para*-phenylene) compound obtained by the method according to any
15 one of claims 1 to 13, wherein the total number of phenylene moieties is at least 25.
15. Use of the poly-(*para*-phenylene) compound according to claim 14 as a nanometer-sized thin film in organic electronics, as a model compound and a precursor for graphene, as an insulator, as a conducting material when doped, or
20 as a material for thermoelectric devices.

Figures

Fig. 1

a)

chloroform chlorobenzene dichloroethane THF toluene

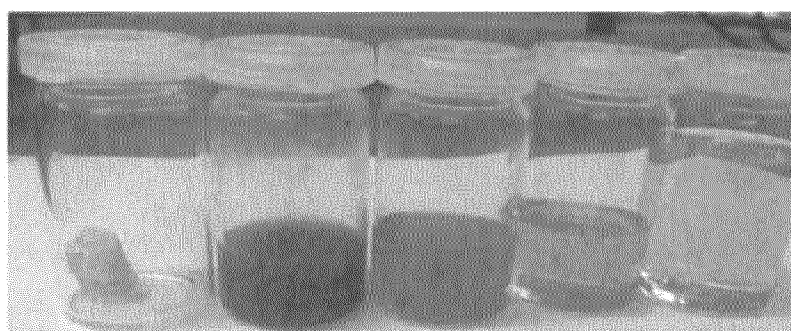


← solubility

1 h ultrasonic bath; $c \sim 10 \text{ mg/mL}$

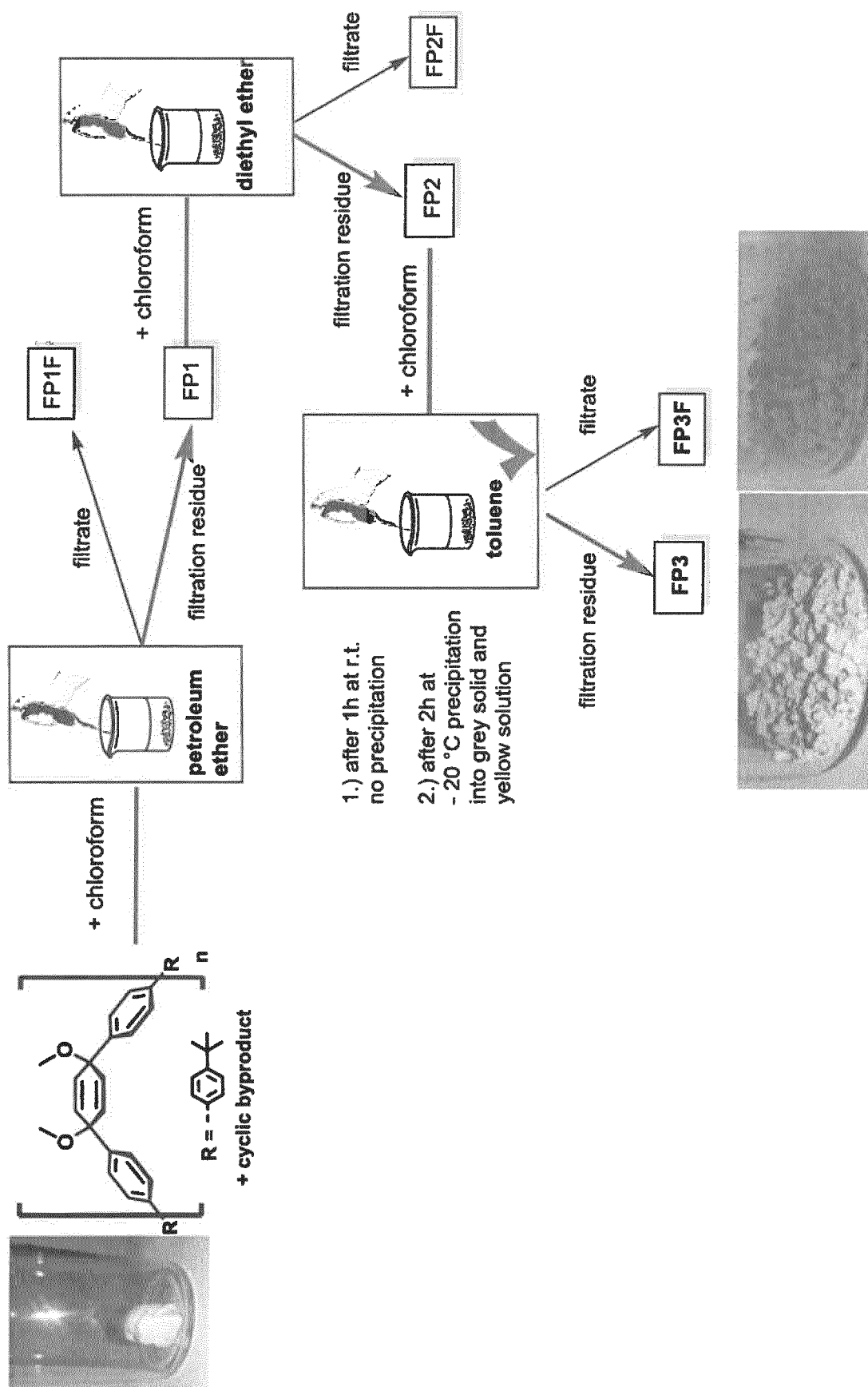
b)

dilution in chloroform



← concentration

Fig. 2



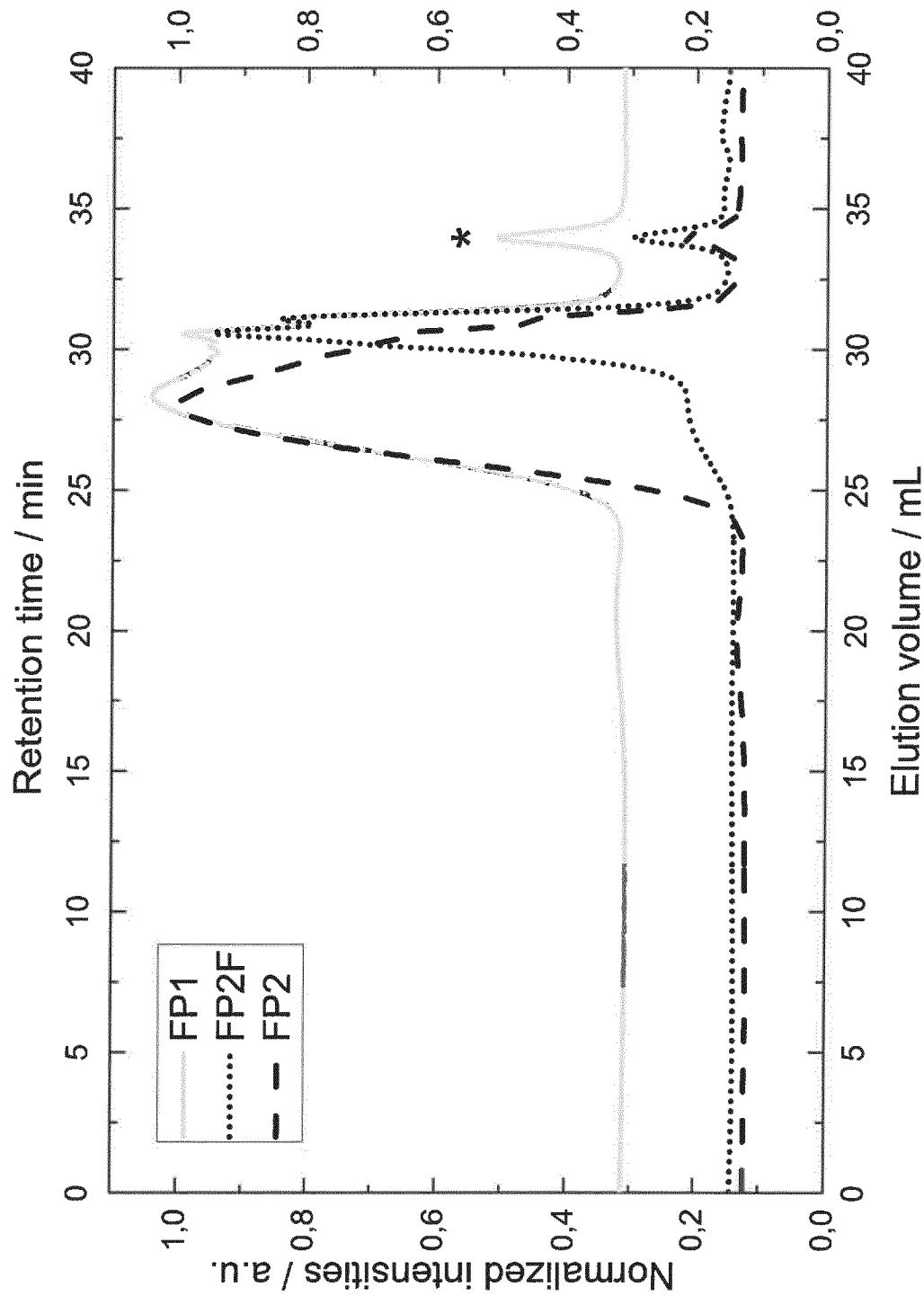


Fig. 3

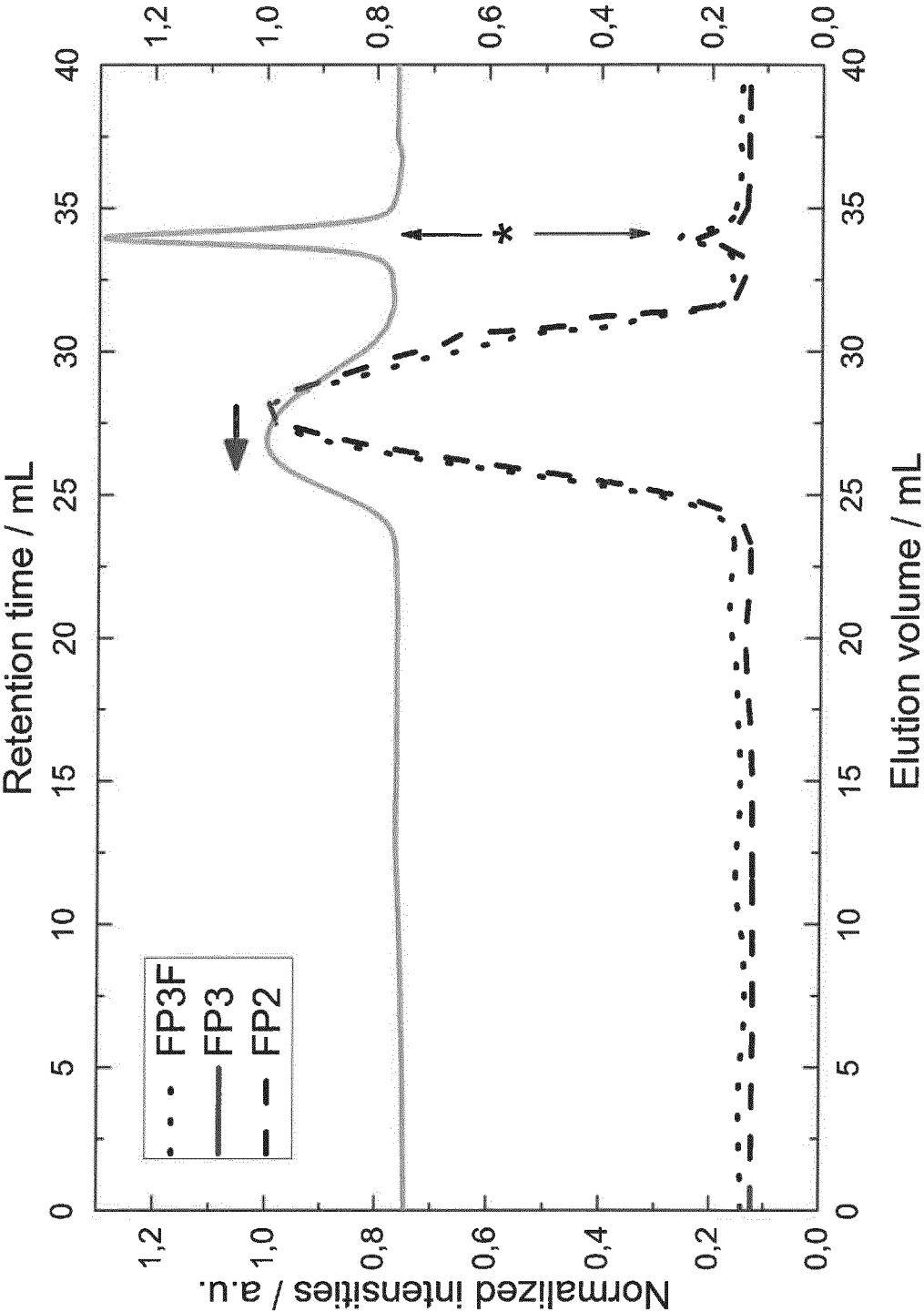


Fig. 4

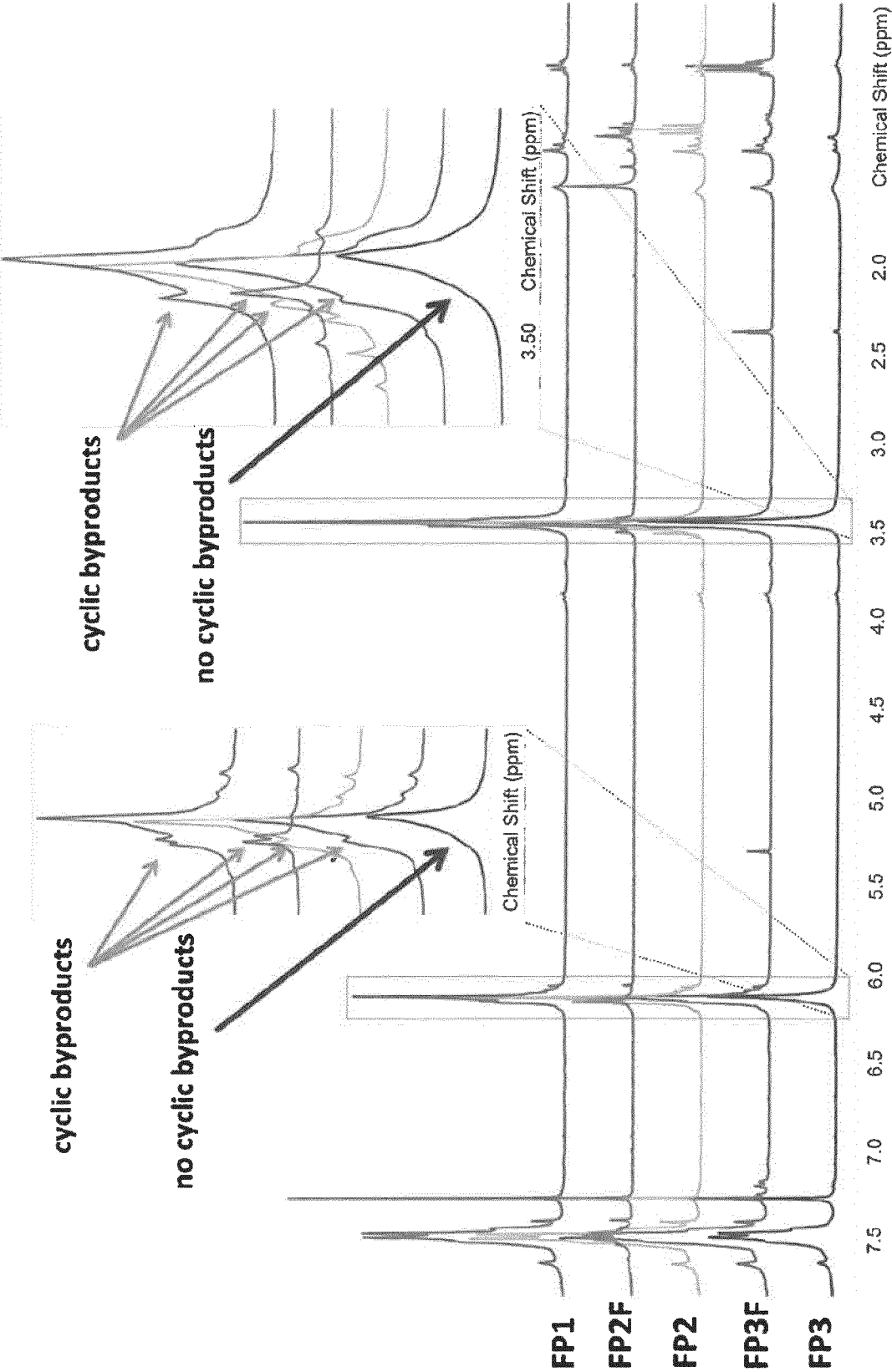
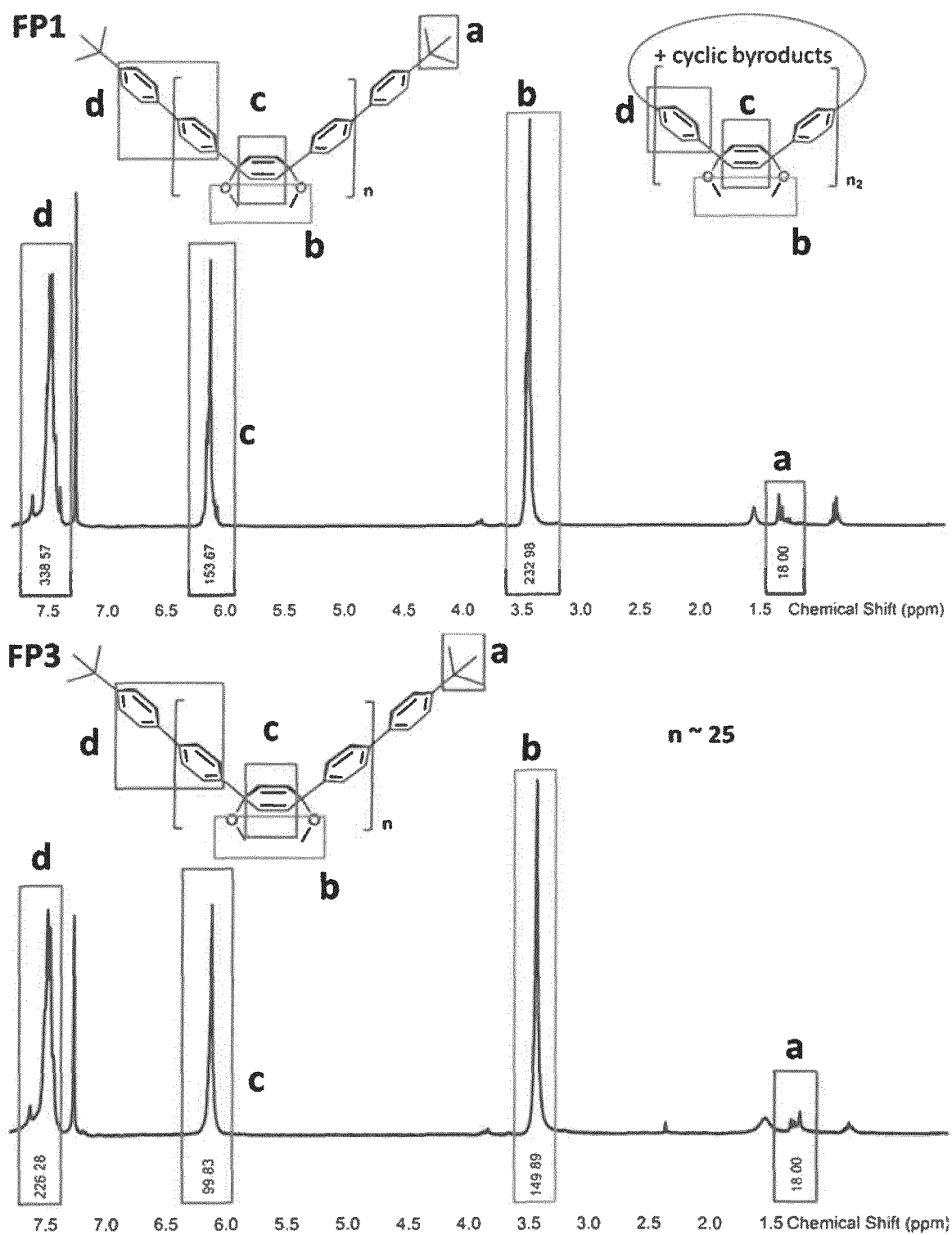


Fig. 5

Fig. 6



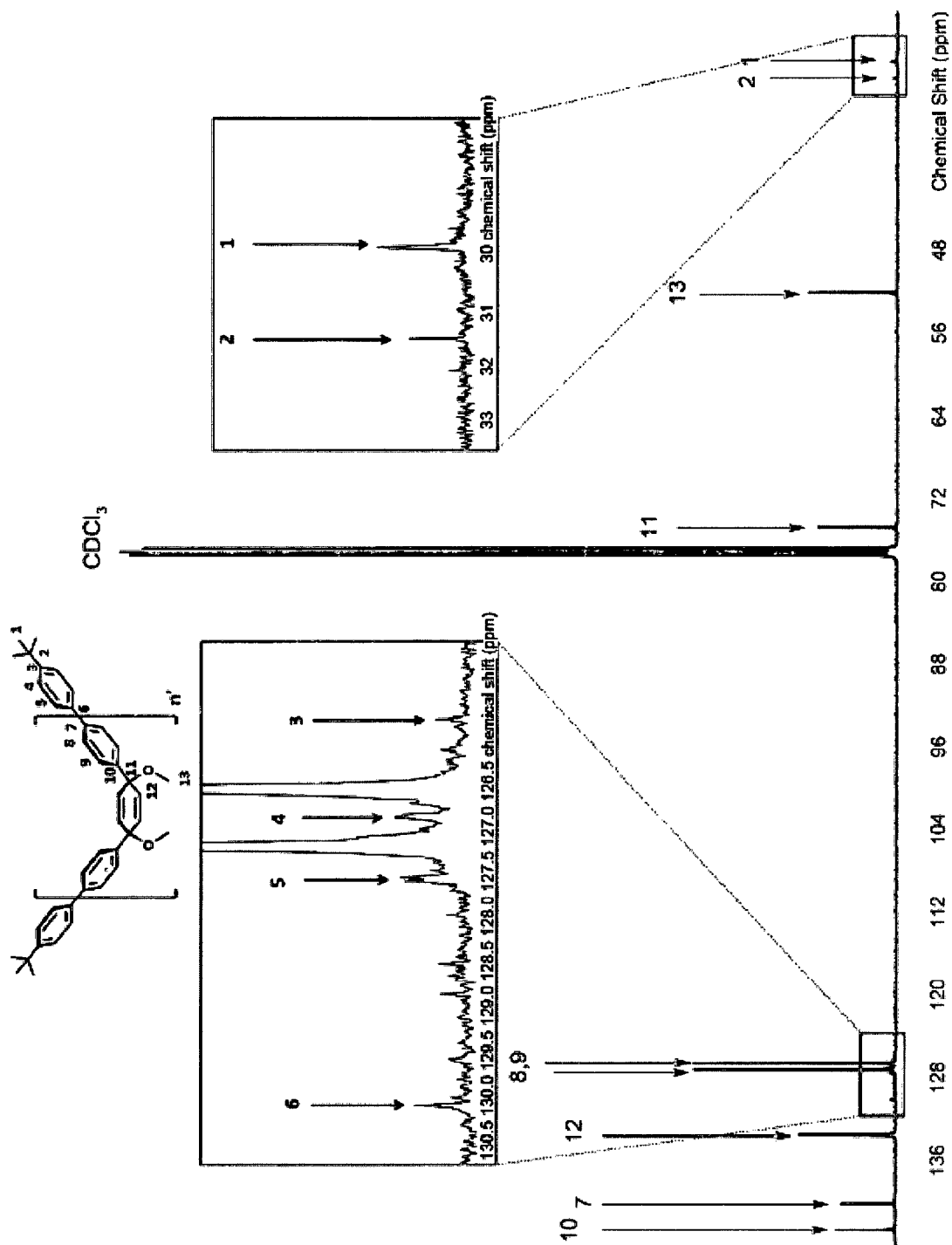


Fig. 7

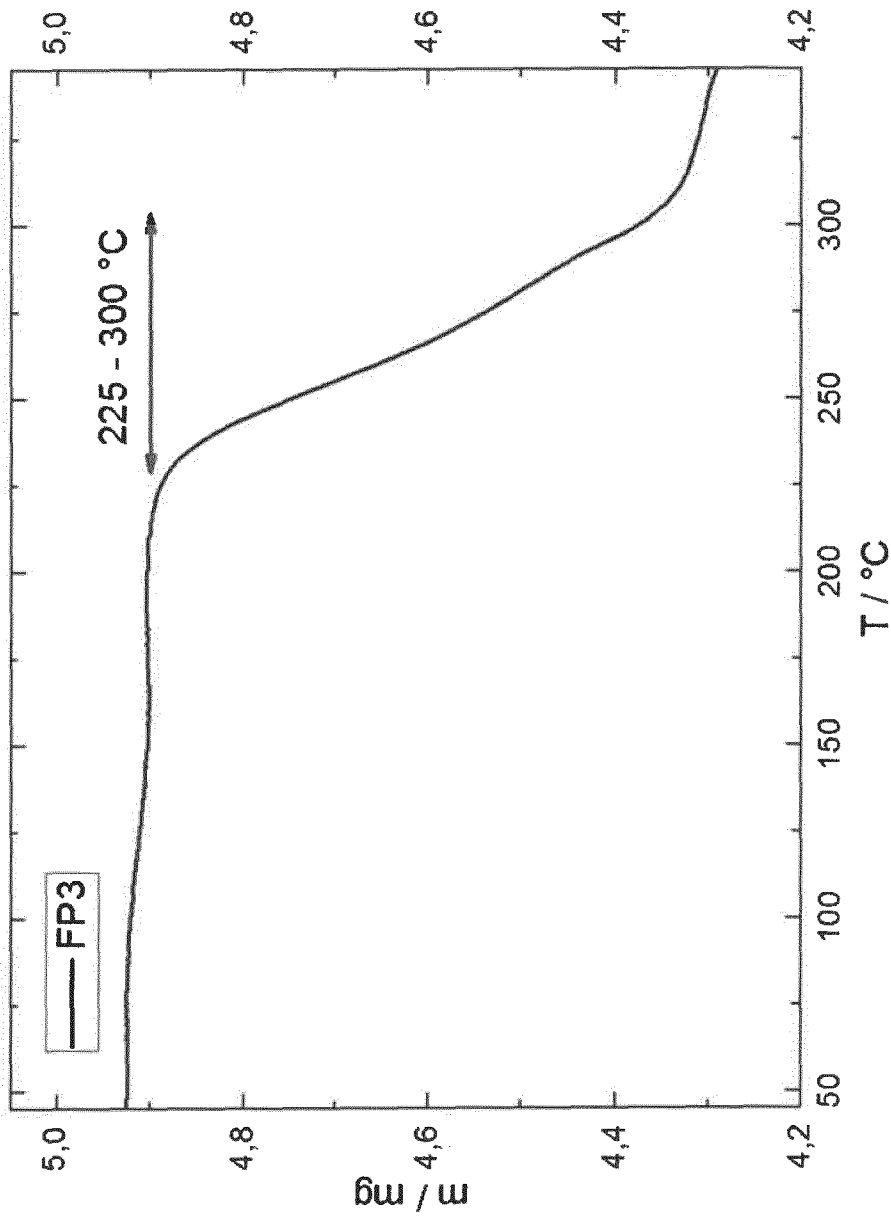


Fig. 8

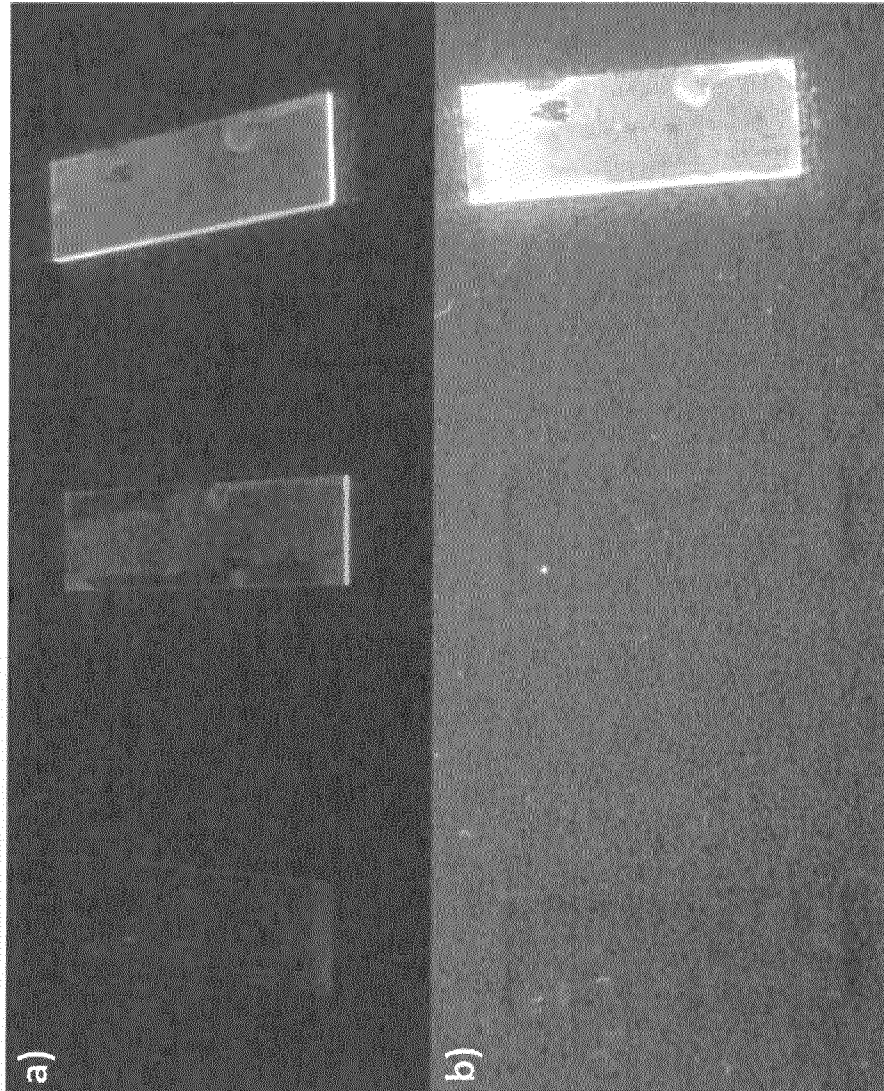


Fig. 9

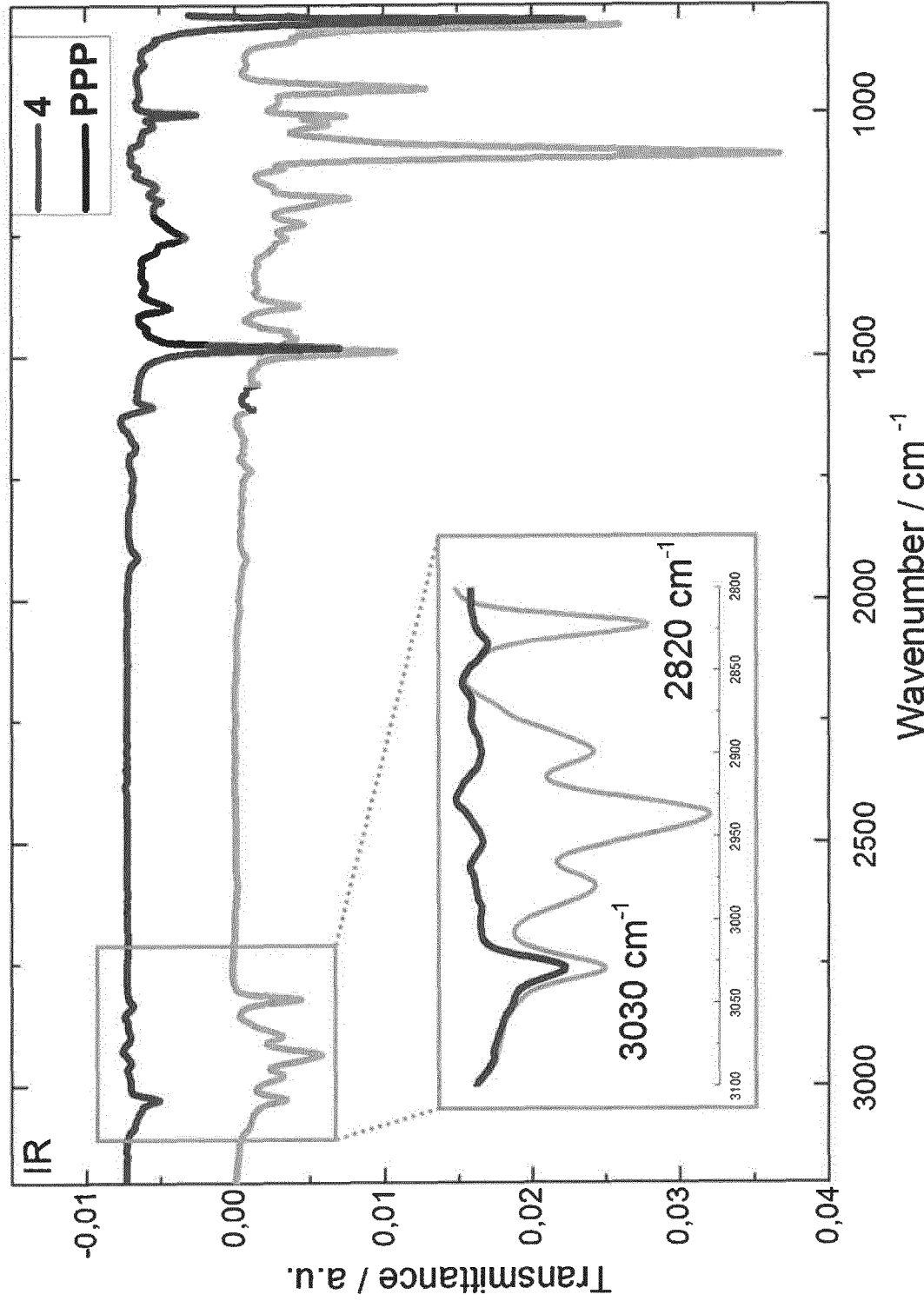
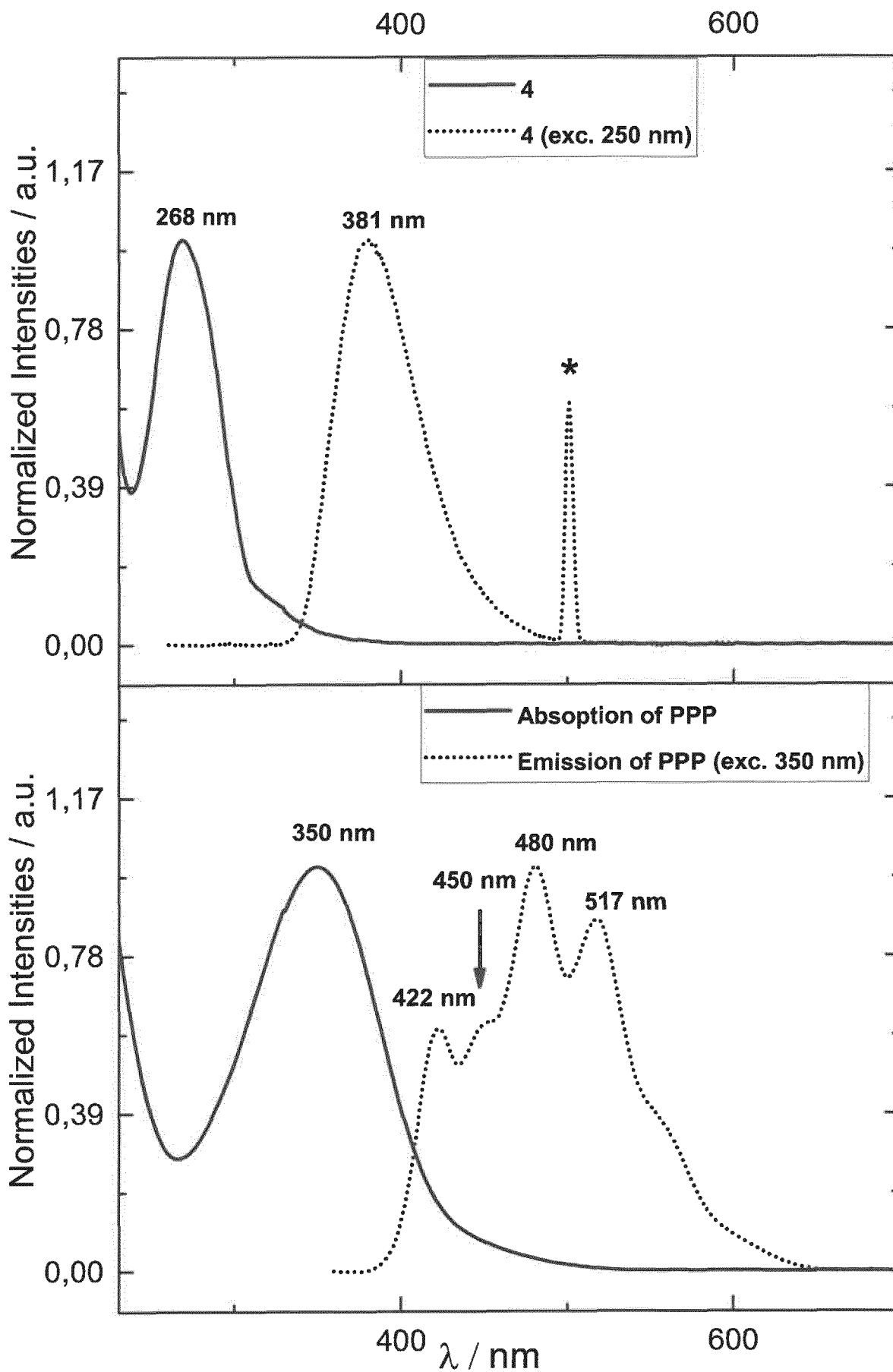


Fig. 10

Fig. 11



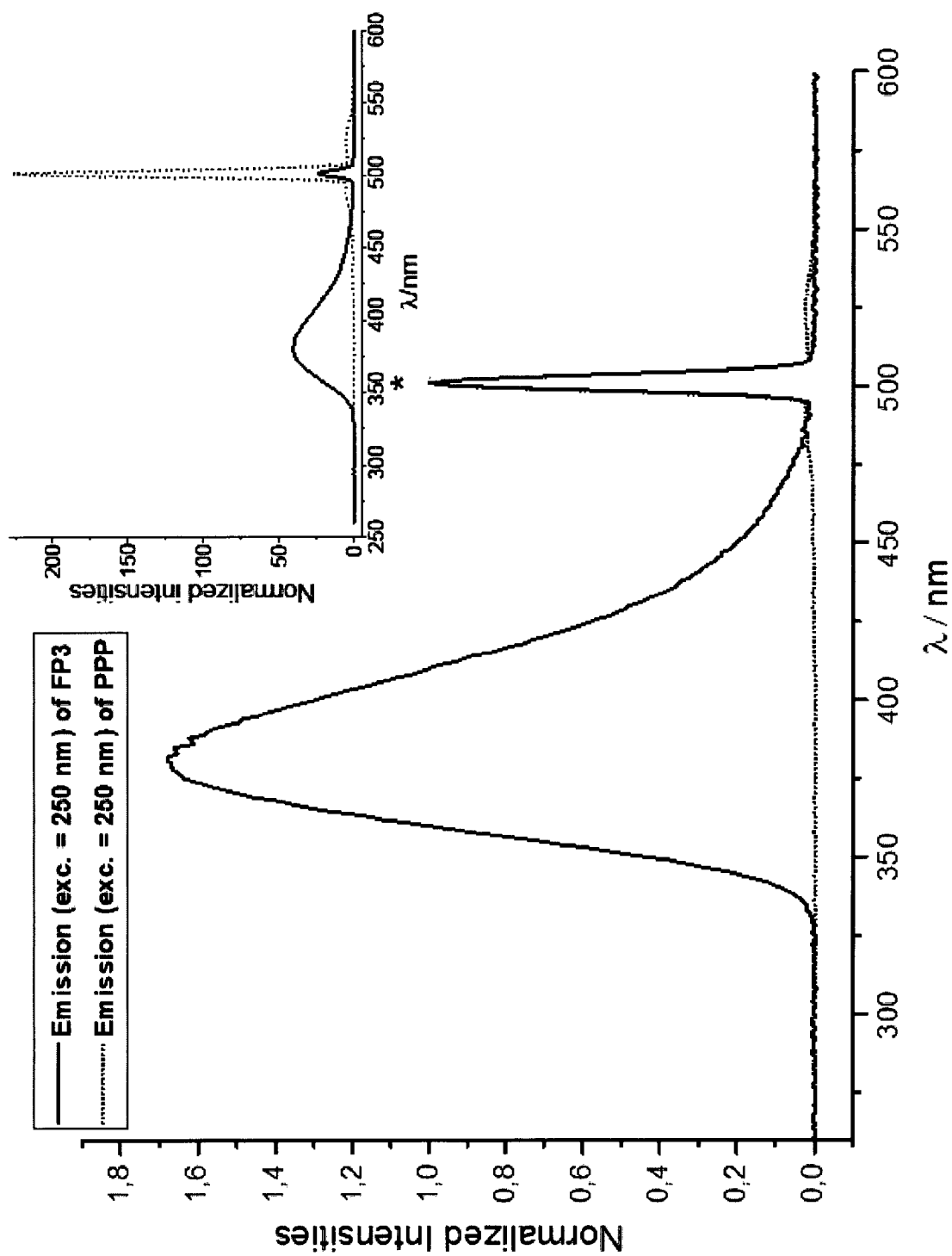


Fig. 12

Fig. 13

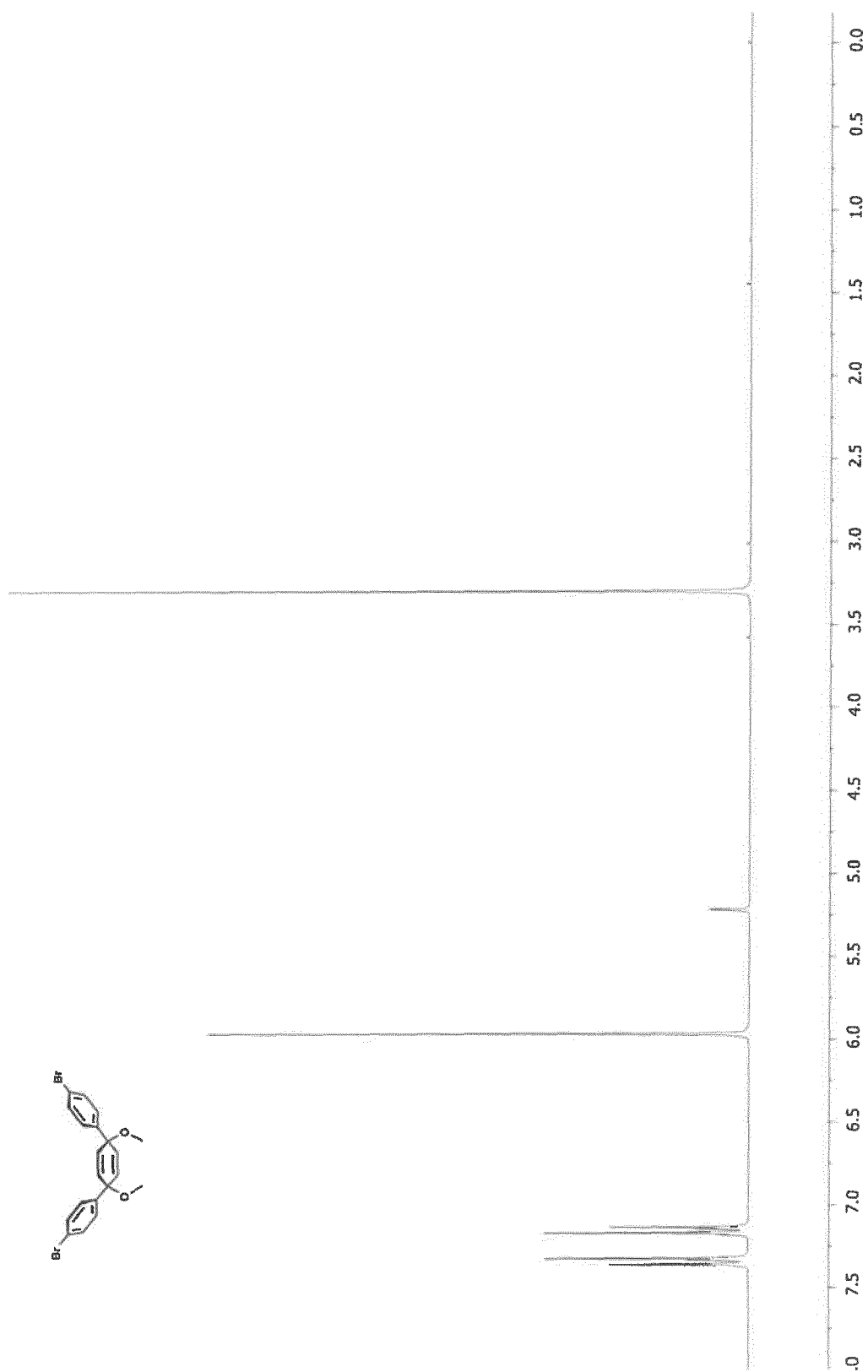


Fig. 14

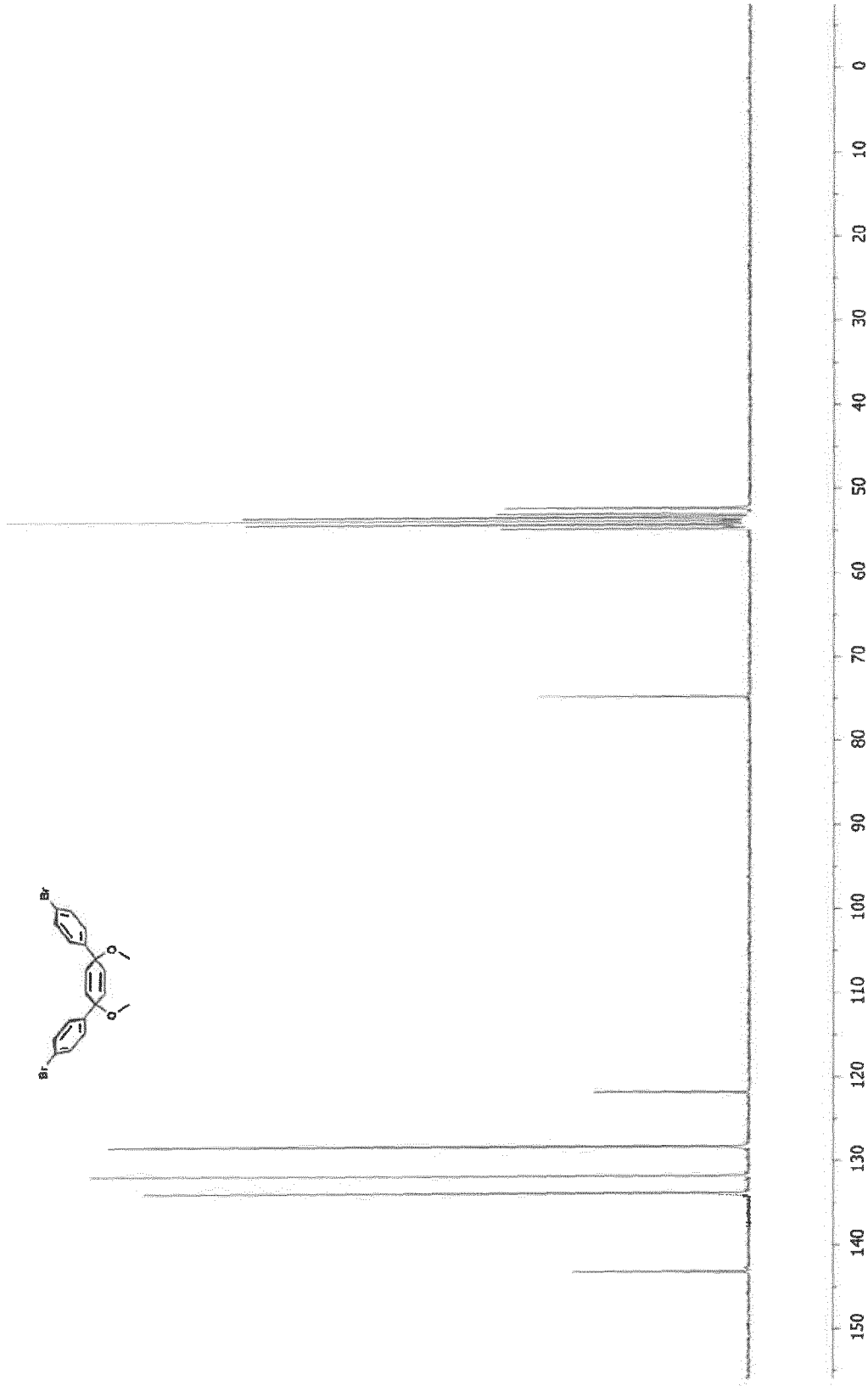


Fig. 15

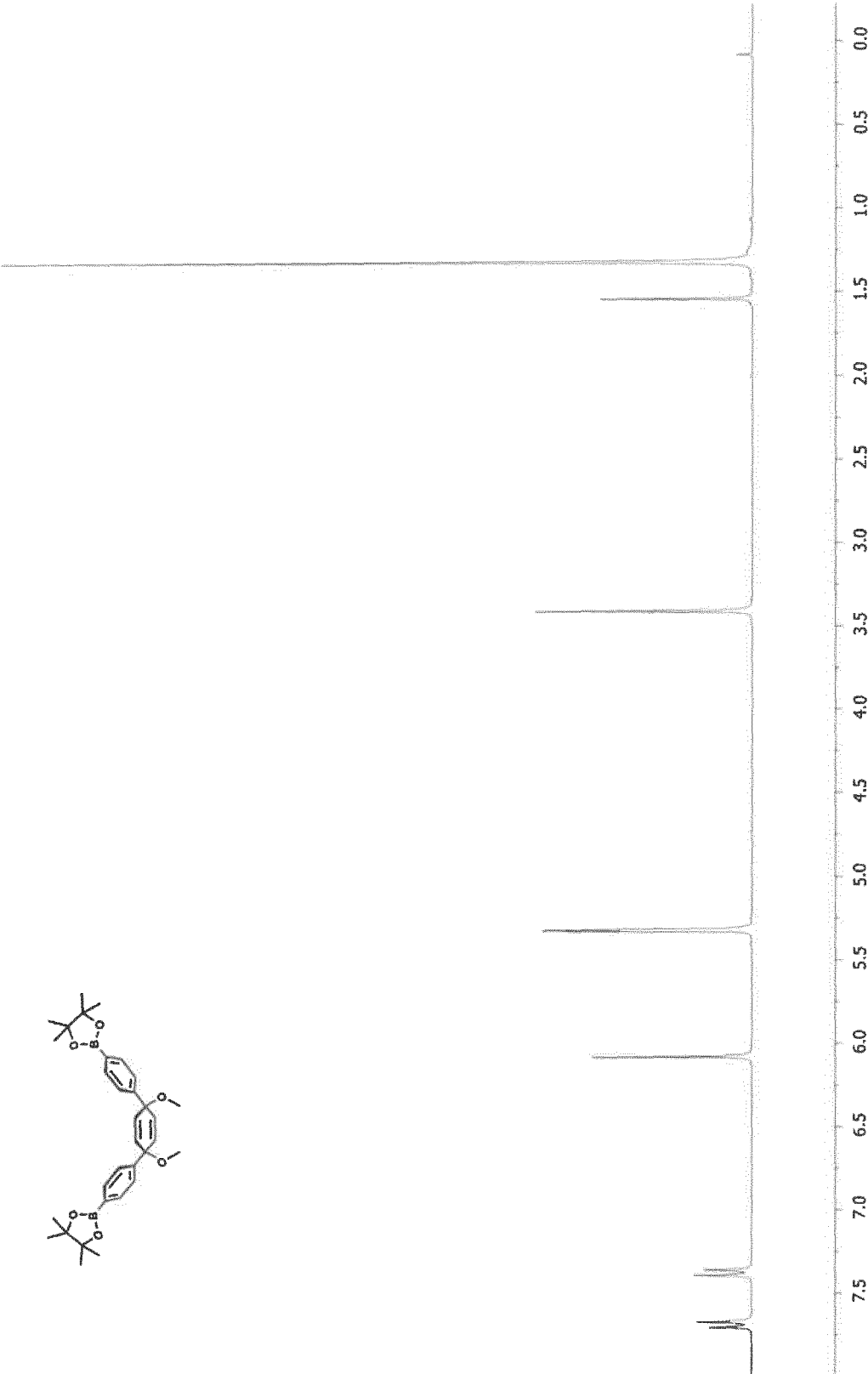
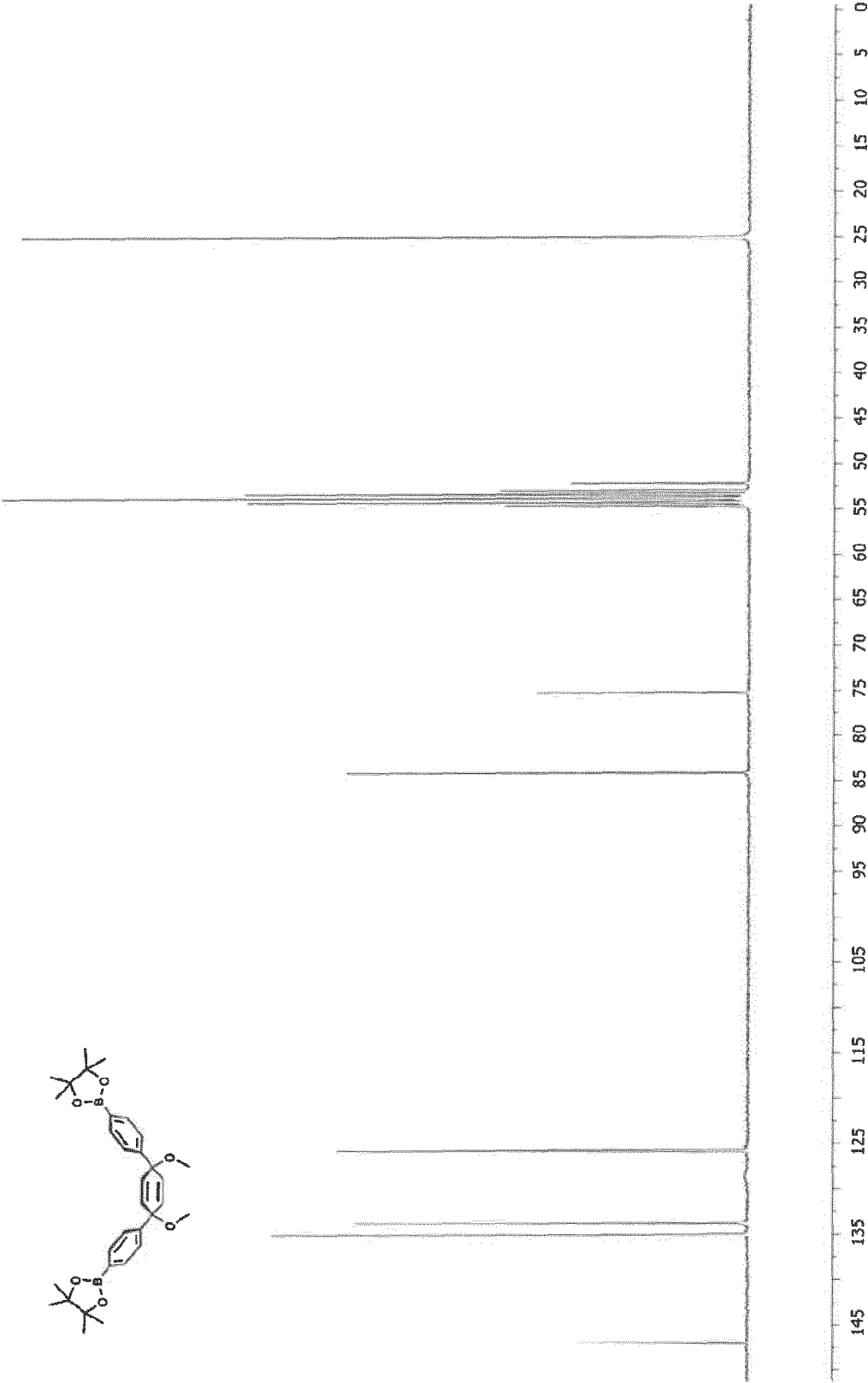


Fig. 16



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/079505A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G61/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GIN D L ET AL: "Synthesis and processing of poly(p-phenylene) via the phosphoric acid-catalyzed pyrolysis of a stereoregular precursor polymer: a characterization study", SYNTHETIC METALS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 66, no. 2, 30 September 1994 (1994-09-30), pages 169-175, XP024171997, ISSN: 0379-6779, DOI: 10.1016/0379-6779(94)90095-7 [retrieved on 1994-09-30] the whole document ----- -/--	14,15



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

31 January 2018

Date of mailing of the international search report

09/02/2018

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Authorized officer

Bernhardt, Max

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/079505

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YAMAMOTO T ET AL: "NEW METHOD FOR THE PREPARATION OF POLY(2,5-THIENYLENE), POLY(P-PHENYLENE), AND RELATED POLYMERS", POLYMER JOURNAL, SOCIETY OF POLYMER SCIENCE, TOKYO, JP, vol. 22, no. 2, 15 February 1990 (1990-02-15), pages 187-190, XP000151052, ISSN: 0032-3896, DOI: 10.1295/POLYMJ.22.187 the whole document	14,15
X	US 2011/166390 A1 (JASTI RAMESH [US] ET AL) 7 July 2011 (2011-07-07) the whole document	1-13
X	EVAN R. DARZI ET AL: "Selective Syntheses of [7]-[12]Cycloparaphenylenes Using Orthogonal Suzuki-Miyaura Cross-Coupling Reactions", THE JOURNAL OF ORGANIC CHEMISTRY, vol. 77, no. 15, 3 August 2012 (2012-08-03), pages 6624-6628, XP055214806, ISSN: 0022-3263, DOI: 10.1021/jo3011667 the whole document	1-13
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/079505

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