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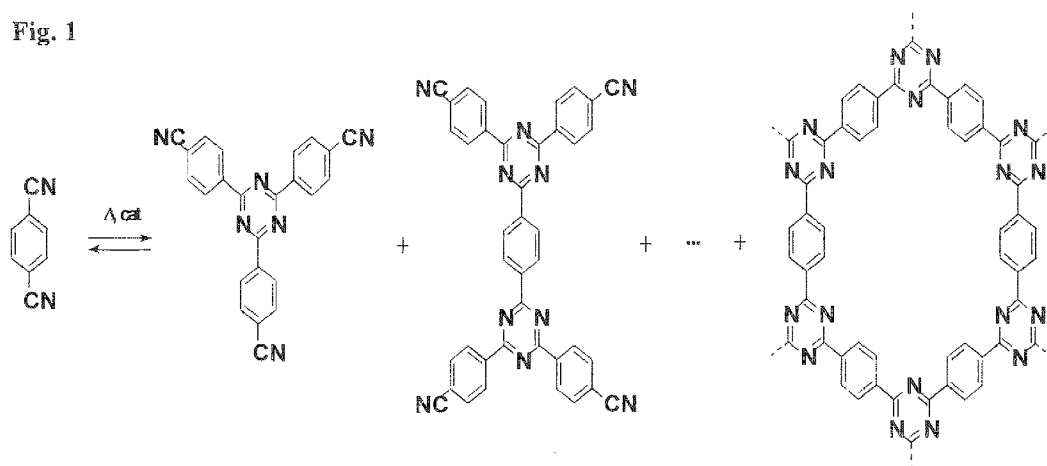
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(54) Title: METHOD OF PREPARING ORGANIC POROUS SOLIDS AND SOLIDS OBTAINABLE BY THIS METHOD

Fig. 1



(57) Abstract: The present invention relates to a method of preparing porous solids, which method comprises polymerizing, in a salt melt or a eutectic mixture of salt melt containing at least one Lewis acidic salt, cyano monomers having at least one or at least two cyano groups in their molecule, wherein the at least one or at least two cyano groups are bonded to a rigid linking group in the cyano monomer, as well as to the porous solids obtainable by that method. Owing to their porosity and the associated extremely high specific surface area, the porous solids are useful as sorbents, filtering and insulating materials, as well as catalyst carriers.

METHOD OF PREPARING ORGANIC POROUS SOLIDS AND SOLIDS
OBTAINABLE BY THIS METHOD

DESCRIPTION

FIELD OF THE INVENTION

The present invention relates to a method of preparing porous solids, as well as the porous solids obtainable by that method. Due to their porosity and large specific surface area, these solids proved useful e.g. as a catalyst carrier, as materials for separation and in chromatography, electrode materials and insulating materials, briefly in all fields of application where high specific surface areas are an asset.

BACKGROUND OF THE INVENTION

In the field of porous materials, apart from the high porosity and associated large surface area, an adjustable pore size was strongly desired.

There are many reports of inorganic materials having pores in the nanometer range in the literature. One example of microporous materials are zeolites. In the recent past, many mesoporous materials have been synthesized. The latest development in this field since the M41S family of materials was found by Mobil scientists is summarized by A. Vinu et al. in Science and Technology of Advanced Materials 2006, 7, pp. 753-771. In this review article, the synthesis of mesoporous carbonitride via replica synthesis by using, as a template, mesoporous silica SBA-15, with subsequent dissolution of the silica framework is described. More details on this type of hexagonal mesoporous carbonitride are given in Advanced Materials 2005, 17, pp. 1648-1652.

Different from inorganic materials, reports on organic materials having a regular ordered network are quite rare. Recently, the group of Yaghi prepared so called covalent organic frameworks (COFs). The condensation reaction of phenyl diboronic acid and hexahydroxytriphenylene is described in Science 2005, 310, pp. 1166-1170. The concept was extended to three-dimensional frameworks in Science 2007, 316, pp. 268-272.

Mesoporous poly(benzimidazole) with well-defined porosity and a pore diameter of 11 nm prepared by way of the hard templating approach using silica nanoparticles as a template is described in Macromolecules, 2007, 40, pp. 1299-1304. A. Fischer et al. in Advanced Materials 2007, 19, pp. 264-267 and F. Goettmann in Angewandte Chemie Int. Ed. 2006, 45, pp. 4467-4471) use nanometer size silica spheres and molten cyanamide to prepare mesoporous graphitic carbonitride. D.R. Miller et al., in J. Mater. Chem. 2002, 12, pp. 2463-2469 describe the synthesis of nitrogen-rich carbonitride powders. The structure features triazine rings connected by nitrogen atoms to form a two-dimensional polymer. A low surface area of 2 to 5 m²/g of the material is reported. This is due to macropores produced by gases evolving during the polymerization reaction.

US 3,164,555 relates to a method for producing heat resistant semi-conductor polymers comprising heating acetonitrile in an inert atmosphere in the presence of a catalyst. For instance, acetonitrile, benzonitrile or propionitrile are reacted in the presence of zinc chloride as a catalyst. D.R. Anderson et al., in J. Polymer Sci. A-1, 4 (1966), pp. 1689-1702 describe thermally resistant polymers containing the s-triazine ring. For instance, dicyanobiphenyl is reacted in the presence of chlorosulfonic acid. US 4,061,856 mentions polymeric or copolymeric products containing triaryl-s-triazine rings. In Example 4 of the patent, 1,4-dicyanobenzene (terephthalonitrile) is reacted in the presence of p-

toluenesulfonic acid monohydrate. However, the Brönsted acid-catalyzed polymerization of polynitriles will not yield porous polymers. This may be explained by the fact that the polymer formed is not sufficiently crosslinked allowing an efficient packing of the polymer chains without any formation of regular pores, or by the lack of any appropriate template.

US 3,775,380 pertains to the polymerization of aromatic nitriles having at least two cyano groups by heating to a temperature of from about 410 to about 550 °C in the presence of a catalyst, such as a metal chloride to form curable polymeric compositions. In the working examples of the patent, dicyanobenzenes are converted in the presence of a zinc chloride catalyst. However, due to the presence of merely catalytic amounts of zinc chloride, no porous material can be obtained. Like in the case of the acid-catalyzed polymerization, as addressed above, this may be due to the insufficient crosslinking of the framework, or by the lack of any appropriate template.

In view of the above, further organic materials exhibiting a porous network with an associated high specific surface area, which can moreover be prepared in a simple way, were in high demand.

SUMMARY OF THE INVENTION

The present inventors have unexpectedly found that porous organic materials solids can be prepared by a simple method which comprises polymerizing, in a salt melt or an eutectic mixture of salt melt containing at least one Lewis acidic salt, cyano monomers comprising a rigid linking group in the molecule. The cyano monomers for use in the method according to the present invention have at least two cyano groups in their molecule wherein the at least two cyano groups are bonded to the rigid linking group in the cyano monomer.

According to another embodiment, the cyano monomers can have one or more cyano groups in their molecule, which are bonded to the rigid linking group, and preferably they have one cyano group in their molecule, which is bonded to the rigid linking group.

The present invention has been completed based on the above finding. Specifically, the present invention relates to the above method, the porous solids obtainable by that method, and distinct uses of these solids. The porous solids of the invention exhibit high porosity and associated extremely high specific surface areas and total pore volumes. As such, these materials can be used in various fields where such high surface areas are advantageous, e.g. as a sorbent material, filtering material, insulating material, or as a catalyst carrier.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustrative drawing showing the schematic formation mechanism of a porous solid obtainable in accordance with the present invention, for 1,4-dicyanobenzene as a starting compound.

Fig. 2 shows the adsorption-desorption isotherm of the material obtained in Example 1.

Fig. 3 shows the pore size distribution of porous solids obtained by the polymerization of 1,4-dicyanobenzene at different temperatures in Example 11.

Fig. 4 is a graph showing the evolution of the C/N and C/H molar ratios of the porous solids obtained at different reaction temperatures in Example 11.

DETAILED DESCRIPTION OF THE INVENTION

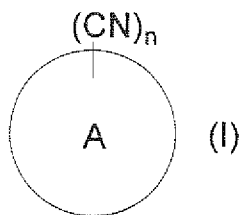
The preparation method in accordance with the invention involves the polymerization of cyano monomers having at least two cyano groups in their molecule, wherein the at least two cyano groups are bonded to a rigid linking group.

The term "rigid" characterizing the linking group in the cyano monomers is intended to indicate that the linking group when the cyano monomer containing the same is incorporated in the framework of the porous solid will prevent any substantial torsion or conformational change of the molecular framework. In other words, because the linking group, which will remain after the cyclotrimerization reaction to be described below, is rigid, the framework of the formed porous solid will be sufficiently stable and have a persistent pore structure.

During the polymerization yielding the porous solid free cyano groups, which all belong to different cyano monomers or oligomers, will undergo a cyclotrimerization to give the porous solid, which consequently comprises triazine rings, in particular 1,3,5-triazine rings. To undergo the above polymerization reaction (condensation reaction), the at least two cyano groups in the cyano monomer molecules are preferably freely accessible, i.e. not sterically hindered. An idealized polymerization mechanism is shown in Fig. 1 for 1,4-dicyanobenzene as a starting compound. As one of average skill in the art will be aware, there will always be side reactions, in particular condensations, other than the cyclotrimerization affording 1,3,5-triazine rings, e.g. Diels-Alder-type reactions. Nevertheless, the scheme of Fig. 1 gives a picture of the mechanism leading to the formation of the porous solids of the invention.

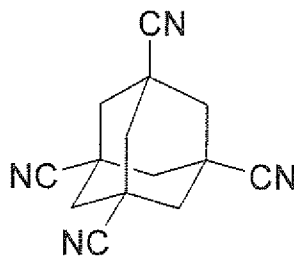
The cyano monomers for use in the method of the invention are not particularly limited in kind. In the broadest aspect of

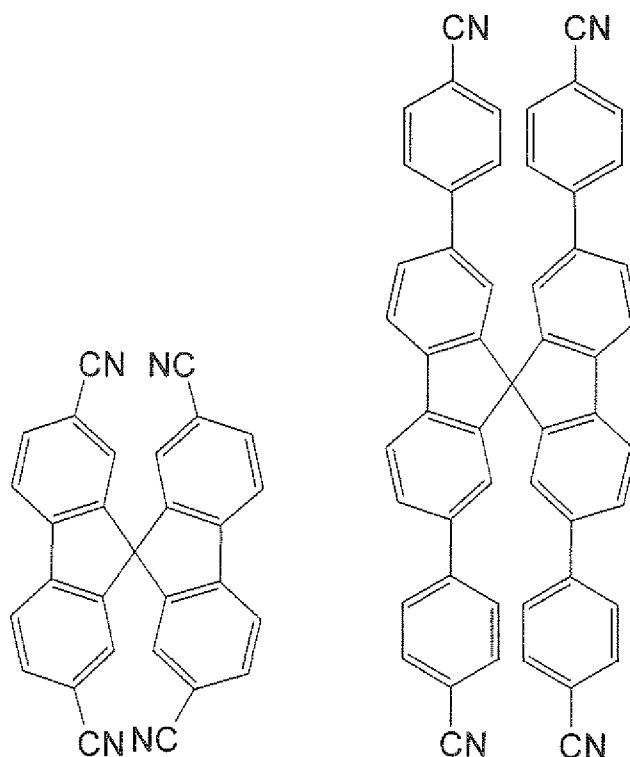
the method of the invention, they can be represented by the following general formula (I):



In formula (I), A means the rigid linking group. The index n indicating the number of cyano groups attached to the linking group A is ≥ 2 , preferably 2, 3 or 4, more preferably 2 or 3, and most preferably 2. Preferably, all of the n cyano groups are capable of undergoing the cyclotrimerization reaction as described above.

The linking group A may be a spiro moiety or an adamantane moiety. Examples of cyano monomers containing this type of rigid linking group are shown below. Needless to mention, the present invention is not limited to these examples.

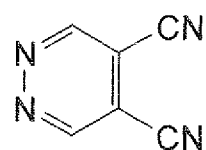
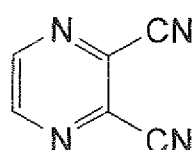
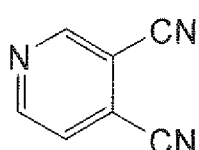
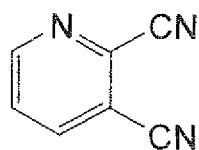
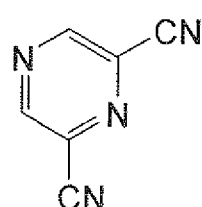
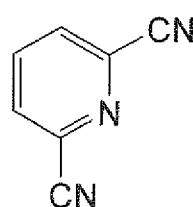
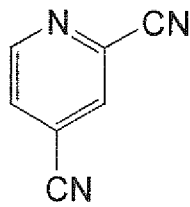
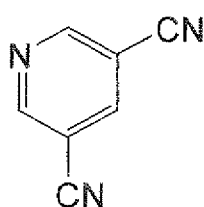
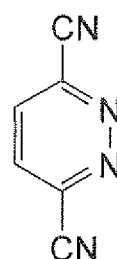
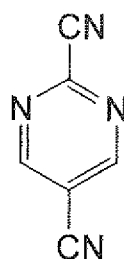
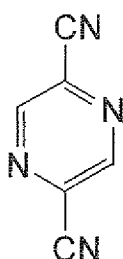
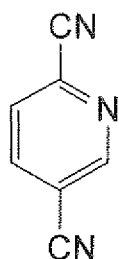
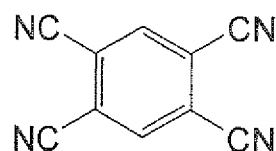
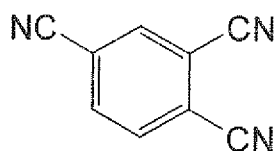
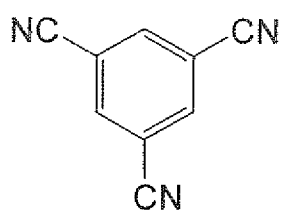
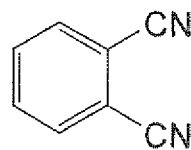
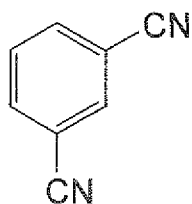
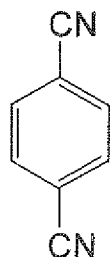


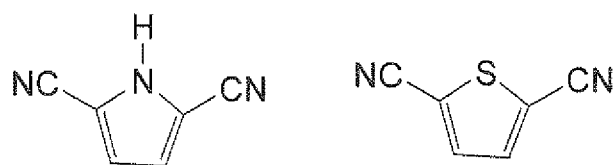


According to another embodiment, A represents an aromatic or heteroaromatic group, preferably having from 5 to 50, more preferably from 6 to 24, still more preferably from 6 to 18 ring atoms in total. The ring atoms may include, apart from carbon atoms, for instance, nitrogen, sulfur and oxygen atoms.

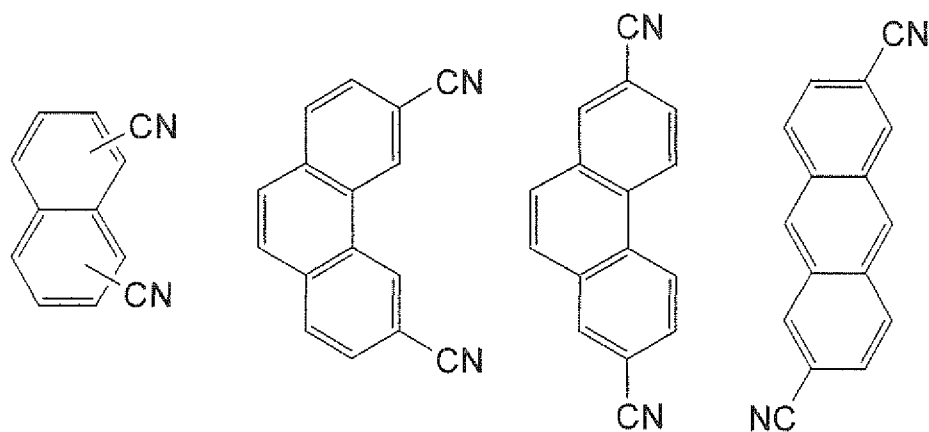
The aromatic or heteroaromatic linking group A may consist of an aromatic or heteroaromatic single ring. Preferably, the single ring is 5 or 6 membered, optionally containing hetero atoms such as N, S or O. For instance, the single ring linking group A may be benzene, pyridine, pyridazine, pyrimidine, pyrazine, thiophene, pyrrole and furane. In addition to the cyano groups, the single ring linking group A may be substituted, e.g. by one or more halogen atoms (F, Cl, Br and I), one or more aryl groups (preferably C₆-C₁₄-aryl groups) or one or more C₁₋₆ alkyl groups. The above alkyl substituents may optionally be substituted. For instance, they may be present in the form of perfluoroalkyl groups. Examples of

cyano monomers containing, as the rigid linking group, aromatic or heteroaromatic single rings are given below.

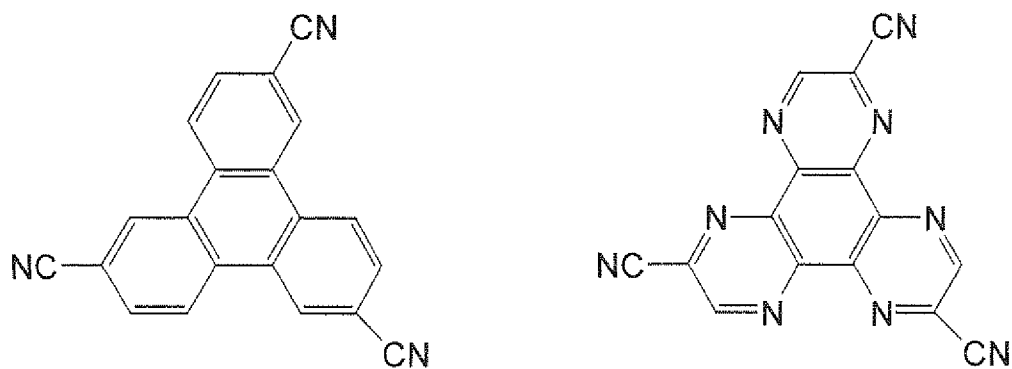


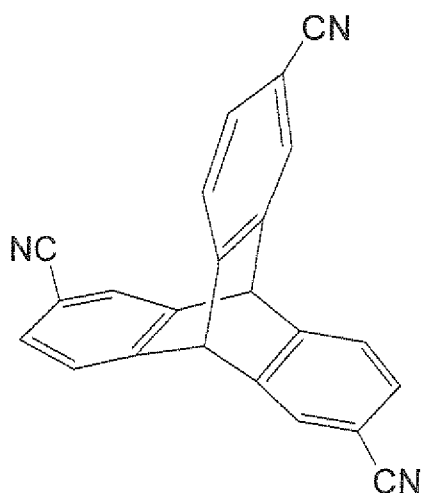


In the alternative, the (hetero)aromatic linking group A can be a fused ring system such as naphthalene, anthracene or phenanthrene. If desired, the fused ring systems can contain hetero atoms and have substituents such as exemplified above for the single ring. Examples of cyano monomers containing the fused ring system-type of rigid linking group are shown below.

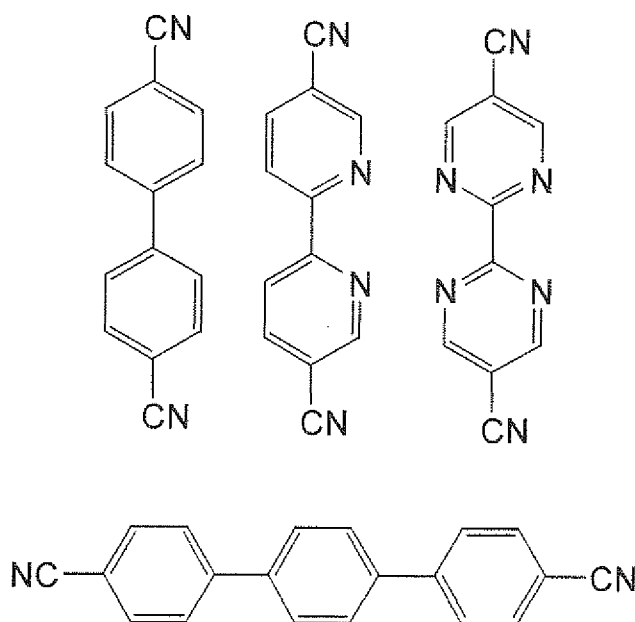


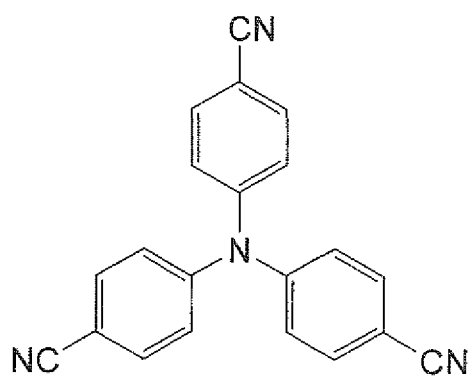
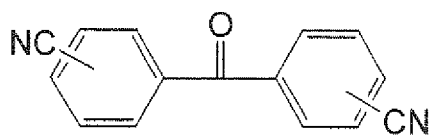
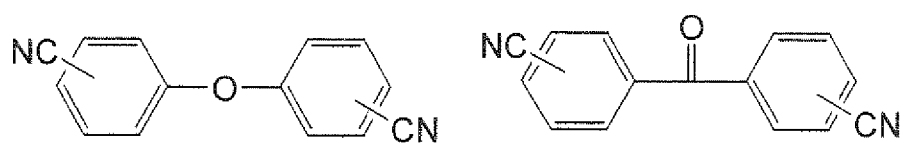
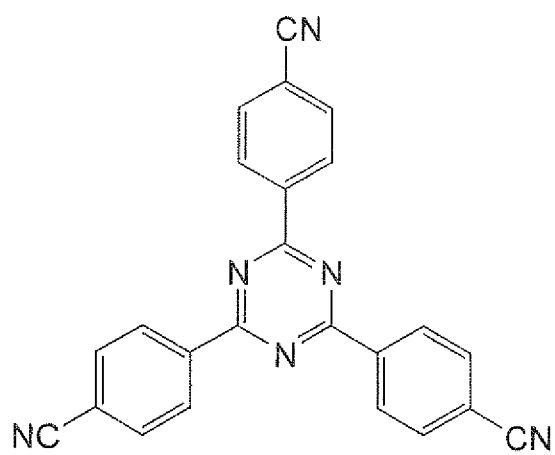
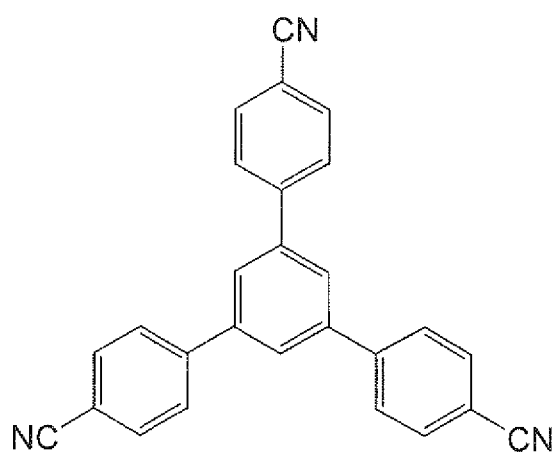
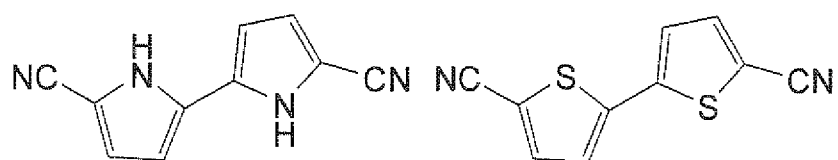
The above dicyanonaphthalene (see the left-hand formula) can for instance be substituted with the two cyano groups in 1,8-, 1,7-, 1,6-, 1,5-, 2,7- and 2,6-position. Further examples of this type of cyano monomers are the following:

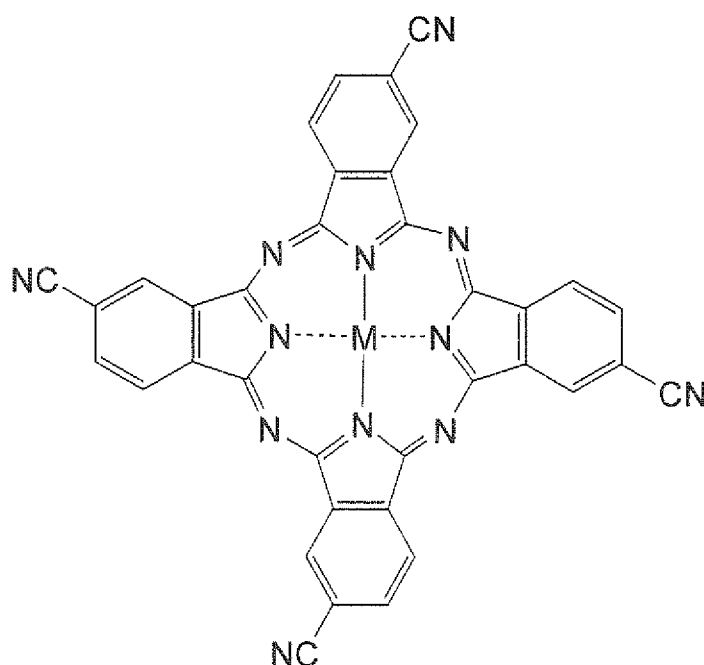




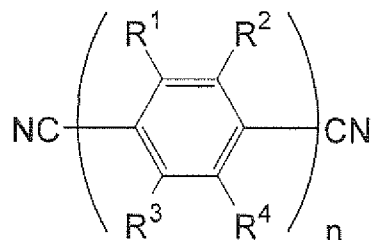
Finally, the rigid linking group A may comprise more than one rings (or fused ring systems) which are mutually connected e.g. by a single bond, a carbonyl group, an oxygen atom, or a nitrogen atom. Examples of corresponding cyano monomers are illustrated, hereinafter.







In the above formula, M may be $2 H^+$, $2 Li^+$, Cu^{2+} , Zn^{2+} or Ni^{2+} .



In the latter formula, R^1 , R^2 , R^3 and R^4 can be independently selected from hydrogen; halogen (F , Cl , Br , I); aryl, in particular C_6 - C_{14} -aryl; and C_{1-6} alkyl groups, in particular C_{1-6} -perfluoroalkyl groups.

In the method of the present invention, the cyano monomers shown above by way of their structural formula are used with preference, e.g. where the polymerization is carried out in a zinc chloride melt. More preferred are the cyano monomers employed in the working examples of this specification. The

cyano monomers used in the present working examples are preferably subjected to the polymerization in accordance with the method of the invention in a salt melt of ZnCl_2 . The most preferred cyano monomers are dicyanobenzenes, such as 1,3- and 1,4-dicyanobenzene. While mixtures of several types of cyano monomers can be used in the method of the invention, the use of a single kind of cyano monomer is preferred in view of the regularity of the obtained porous solid.

The solids which are obtainable by the preparation method of the invention are porous. The formation of the pores is illustrated in Fig. 1. The total pore volume of the materials may be in the range of $\geq 0.3 \text{ cm}^3/\text{g}$. Preferably, the total pore volume is in the range of 0.3 to $2.5 \text{ cm}^3/\text{g}$. More preferably, it is $\geq 1.5 \text{ cm}^3/\text{g}$, such as in the range of 1.5 and $2.5 \text{ cm}^3/\text{g}$. The porous solids of the invention may be microporous or mesoporous, and may additionally comprise macropores. As used herein, the pore sizes are defined in accordance with IUPAC Manual of Symbols and Terminology, Appendix 2, Part 1, Colloid and Surface Chemistry, Pure Appl. Chem. 1972, 31, pp. 587. That means, micropores have a width of less than 2 nm, mesopores of between 2 and 50 nm, and macropores of more than 50 nm.

Owing to their porosity, the BET specific surface area of the solids of the invention is $\geq 500 \text{ m}^2/\text{g}$, such as 500 to $2500 \text{ m}^2/\text{g}$, preferably it is $\geq 1000 \text{ m}^2/\text{g}$, for instance between 1000 and $2500 \text{ m}^2/\text{g}$. Most preferably, it is $> 2000 \text{ m}^2/\text{g}$.

In the solids of the invention, the porosity, specific surface area and functionality of the materials can be determined by selecting the cyano monomer, more specifically the rigid linking group in the cyano monomer that will remain in the final porous solid once the polymerization is completed. That means, by proper selection of the cyano monomer subjected to

the polymerization reaction, the properties of the resultant solids can be tailor-made.

In addition it was found that for a specific cyano monomer, the pore sizes can be tuned by variation of the molar ratio of the cyano monomers and the salt, *i.e.* the salt melt or eutectic mixture of salt melt. For example, and without limitation, it was shown that the above tuning of pore sizes is possible when cyano monomers comprising in the rigid linking group aromatic rings are used. More specifically, cyano monomers having a rigid linking group comprising more than one aromatic ring (such as benzene rings), which are connected by a linking group such as *e.g.* a single bond, a carbonyl group, an oxygen atom or a nitrogen atom, preferably a single bond, can be exemplified here. Without being bound to theory, it is speculated that the above tuning of pore sizes is due to phase separation during the reaction, *i.e.* polymerization reaction. In addition, it is assumed that Diels-Alder reactions are also occurring during the polymerization when using cyano monomers having rigid linking groups comprising aromatic rings as exemplified above. For tuning the pore sizes as detailed above, the high-temperature method of the invention (as explained below) is carried out with particular benefit, *e.g.* at a temperature of 600 °C, for instance using dicyanobiphenyls, such as 4,4'-dicyanobiphenyl, as the starting cyano monomer.

In the method of the invention, the polymerization of the cyano monomers is carried out in a salt melt or a eutectic mixture of salt melt containing, preferably consisting of, at least one Lewis acidic salt. Since the Lewis acidic salt (or mixture of more than one Lewis acidic salt) is used in the form of a salt melt, it can act as a solvent for the cyano monomers to be reacted, and at the same time catalyze the cyclotrimerization (*i.e.* polymerization) reaction. As such, the at least one Lewis acidic salt contained in or

constituting the salt melt or eutectic mixture of salt melt is not specifically limited in kind. For instance, AlCl_3 , FeCl_3 , GaCl_3 , TiCl_4 , BCl_3 , SnCl_4 , SbCl_5 , ZnCl_2 and ZnBr_2 can be used. Preferably, ZnCl_2 and/or ZnBr_2 , are used, and most preferably ZnCl_2 is used.

For the purpose of the present specification, the term of "eutectic mixture" is intended to mean, in the case of binary systems, a mixture of a specific ratio of two compounds, such as Lewis acidic salts, which are not miscible in the solid state but completely miscible in the liquid state.

As the polymerization in the method of the present invention is carried out in a salt melt, the reaction temperature is preferably above the melting point of the used Lewis acidic salt(s) constituting the salt melt.

The reaction temperature of the polymerization is not specifically limited provided a salt melt can be formed at that temperature.

According to a first embodiment, the reaction temperature is in the range of from 250 to 500 °C, preferably 400 to 500 °C. It is presumed that the trimerization of nitriles, e.g. the cyclotrimerization as explained above is dominant in that temperature range. This embodiment of the preparation method of the invention is occasionally referred to as the "low-temperature method", hereafter.

According to another embodiment, the reaction temperature is above 500 °C, preferably between 600 and 700 °C. This embodiment is also named "high-temperature method", hereinafter. Even where a salt melt of ZnCl_2 is used, a reaction temperature as high as 700 °C can be used as ZnCl_2 is boiling at about 730 °C. As the present inventors found, at the above high reaction temperatures, porous solids having

further enhanced porosities in comparison to materials obtained in the low-temperature method can be prepared. Without being bound by theory, it is presumed that the higher porosities, in the case of cyano monomers having rigid linking groups predominantly composed of carbon atoms, are due to carbonization reactions which will take place in addition to the trimerization of the nitriles. In the case of the rigid linking group comprising aromatic rings, C-C coupling reactions between the aromatic rings are presumed to occur. As the inventors found, the increase in porosity due to higher reaction temperatures (of preferably between 600 to 700 °C) are particularly pronounced when the rigid linking group comprises at least one aromatic ring, such as a benzene ring. Consequently, cyano monomers comprising at least one aromatic ring are preferred in the high-temperature preparation method of the invention. More preferred is a rigid linking group which is a single aromatic ring, such as a benzene ring. At the higher reaction temperatures according to this embodiment, specific surface areas of $> 2000 \text{ m}^2/\text{g}$ and even $\geq 2500 \text{ m}^2/\text{g}$, and a total pore volume of more than $2.3 \text{ cm}^3/\text{g}$ could be obtained. The material was shown to comprise micropores, as well as mesopores, with the mesopores showing a narrow distribution of pores.

In a third embodiment, insofar as the reaction temperature is concerned, the method according to the present invention is carried out in two steps, referred to as the first and second reaction step, hereinafter. This embodiment of the present invention is occasionally referred to as "two-step method". The first reaction step is carried out at a temperature of 250 to 500 °C, preferably 400 to 500 °C, especially 400 °C. It is presumed that the trimerization of nitriles, e.g. the cyclotrimerization is predominant in that reaction step and will result in the formation of a microporous polytriazine network. Then, the reaction temperature is increased, and the second reaction step is carried out at a temperature of

> 500 °C, preferably of 600 to 700 °C. At that temperature, carbonization reactions as explained above will be predominant. As regards the preferred cyano monomers to be subjected to the two-step method, reference can be made to the high-temperature process as illustrated above. The two-step process will allow the preparation of porous solids having extremely high BET specific surface areas, such as > 3000 m²/g, and a total pore volume of > 2.0 cm³/g.

The reaction time, which depends on the reactivity of the cyano monomers, may be from 1 to 100 h, preferably 20 to 50 h, most preferably 25 to 40 h. In the case of the two-step method, the above reaction time corresponds to the total reaction time (i.e. comprising the first and second reaction step). The first and the second reaction step are preferably each carried out independently for 10 to 30 h, more preferably 15 to 25 h in the two-step method.

The reaction can be carried out at ambient pressure or under vacuum, the latter being preferred. If desired, the reaction mixture can be agitated by conventional means, but this is unnecessary. While the reaction can be carried out in an open vessel, it is preferably carried out in a sealed vessel, in particular in an inert gas atmosphere (e.g. nitrogen or argon). These reaction conditions are preferred in that the evaporation of volatile cyano monomers, and the formation of zinc oxide side products can be suppressed. One of average skill in the art will select a suitable vessel material, such as Pyrex glass, quartz glass, stainless steel, or ceramics, which material will not be attacked by the salt melt reaction mixture. However, the vessel material is of no further relevance to the polymerization reaction.

The course of the polymerization reaction can be monitored by way of FT-IR. As the cyclotrimerization proceeds, the peak typical for CN (at a wave number slightly above 2200 cm⁻¹)

shrinks, and bands in the range of 1350 to 1500 cm^{-1} , which are typical for 1,3,5-triazine, appear. This confirms the formation of a framework as illustrated in Fig. 1.

After the completion of the polymerization reaction has been confirmed, e.g. by way of FT-IR, the material can optionally be comminuted, e.g. ground in a mortar. Subsequently, the porous material can be washed, e.g. using water and/or acetone, and finally dried, for instance by heating, optionally under vacuum.

All in all, the method of the invention is simple and can give the desired porous materials in high yield.

For the purpose of the present application, the BET (Brunauer-Emmett and Teller) specific surface area and the total pore volume of the materials were determined by way of nitrogen absorption analysis. Fig. 2 shows the absorption/desorption curve for the material obtained in Example 1. The absorption and desorption curve is not closed which is due to the nitrogen pressure exerted during the measurement and is typical for soft materials.

As mentioned earlier, in the present invention, different from the prior art, the polymerization is carried out in a salt melt of preferably zinc chloride, whereas merely catalytic amounts of zinc chloride were used in the prior art. Preferably, the molar ratio of the at least one Lewis acidic salt, and the cyano compound (e.g. ZnCl_2 /cyano compound) is ≥ 0.5 . More preferably the molar ratio is ≥ 5 , even more preferably 5 to 35, and still more preferably 7 to 15. Under these conditions, porous materials in accordance with the invention can generally be obtained which are amorphous materials. In the present specification, the term "amorphous" means that there are no distinct reflections in the powder XRD pattern (WAXS pattern) of the material, when this recorded on

a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ (1.5405 Å) radiation. The acquisition time was 30 minutes for a 40° 2θ scan.

When the molar ratio of the Lewis acidic salt, in particular ZnCl_2 , and the cyano monomers is kept within a range of 0.8 to 1.2, preferably 0.9 to 1.1, still more preferably about 1 (i.e. the salts constituting the melt and the cyano monomers are present in equimolar amounts), crystalline porous solids could be obtained, e.g. using 1,4-dicyanobenzene as the cyano compound. The crystalline solids represent another embodiment of the porous solids of the invention. Different from the amorphous materials, the powder XRD pattern of the crystalline materials, if measured under the above conditions, feature a distinct reflection at a diffraction angle corresponding to the pore wall distance. Simulated XRD powder patterns revealed a stacking of $\text{C}_8\text{H}_4\text{N}_2$ sheets in eclipsed conformation.

The present invention also relates to a method of preparing porous solids as specified above, wherein the cyano monomers subjected to the polymerization have one or more cyano groups in their molecule, wherein the cyano groups are bonded to a rigid linking group in the cyano monomer. Accordingly, cyano monomers having a single cyano group bonded to a rigid linking group also turned out to be useful for preparing porous solids. As will be appreciated, where cyano monomers having a single cyano group in their molecule are reacted in the method of the invention, a polymeric material could not be formed if only trimerization reactions would occur. Presumably, the formation of porous solids from cyano monomers having a single cyano group in their molecule is due to phase separation during the course of the reaction. As the present inventors found, in the case of cyano monomers having a single cyano group, the rigid linking group preferably comprises more than one aromatic ring (such as benzene rings). These aromatic rings can be connected by a linking group. The linking group

is for instance a single bond, a carbonyl group, an oxygen atom or a nitrogen atom, and preferably it is a single bond. As regards the formation of porous solids from cyano monomers having a single cyano group bonded to a rigid linking group comprising at least one aromatic ring, it is presumed that Diels-Alder reactions are also involved. The polymeric material obtained in the method using cyano monomers having a single cyano group in their molecule shows lower porosities as evidenced by its lower BET specific surface area in comparison to the materials obtained when cyano monomers having two or more cyano groups in their molecules are used. At the same time, the average pore diameter is larger, and this is assumed to result from more pronounced phase separation. The cyano monomer having a single cyano group to be subjected to the preparation method of the invention preferably is a monocyanobiphenyl, more preferably it is 4-cyanobiphenyl.

As regards the reaction conditions and preferred modes of carrying out the preparation process of the invention with cyano monomers having a single cyano group in their molecule, reference can be made to the above description in connection with the embodiment of the invention in which cyano monomers having two or more cyano groups in their molecule are used.

EXAMPLES

The present invention is further illustrated by way of the following examples, which are however not to be construed as limiting the scope of the invention as defined in the appended claims.

The IR spectra were collected with a BIORAD FTS 6000 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. Thermogravimetric analysis has been carried out using a NETZSCH TG209. The heating rate was 20 K/min. Transmission electron microscopy (TEM) images of microtomed

samples were taken with a Zeiss EM 912Ω at an acceleration voltage of 120 kV. Nitrogen adsorption data were obtained with a Quantachrome Autosorb-1 at liquid nitrogen temperature after having degassed the samples at 150 °C under high vacuum over night.

Example 1: Polymerization of 1,4-Dicyanobenzene

A Pyrex ampoule (diameter: 3 cm, height: 12 cm) was charged with 1,4-diacyanobenzene (2.0 g, 15.6 mmol) and ZnCl_2 (15 g, 110.0 mmol) in a nitrogen atmosphere. The ampoule was evacuated (0.01 mbar) and subsequently sealed. The vial was then heated to 400 °C (10 °C/min) and maintained at this temperature for 40 h. After cooling to room temperature, the vial was opened, and the reaction mixture was discharged. The discharged reaction mixture was ground in a mortar and stirred in water (200 ml) for 4 h. The resulting powder was separated using a glass frit, washed with water (2 × 50 ml) and acetone (50 ml), and subsequently dried at 150 °C under vacuum for 15 h.

Yield: 1.8 g; 90 %.

Elemental analysis: C, 67.1; N, 17.45; H, 2.89 %; C/N (mol) = 4.48.

Calculated $\text{C}_8\text{H}_4\text{N}_2$: C, 75.0; N, 21.86; H, 3.15 %; C/N (mol) = 4.0.

TGA (O_2 , 20-1000 °C, 10 °C min⁻¹): residual mass: 2.38 assigned to ZnO ; corresponding to 3.99 % ZnCl_2 .

The adsorption-desorption isotherm of the material is shown in Fig. 2.

Example 2: Polymerization of 1,4-Dicyanobenzene

The reaction was carried out like in Example 1 except that the reaction vessel was a quartz ampoule, the reaction temperature was 500 °C, the reaction time was reduced to 25 h, and 1.0 g (7.8 mmol) 1,4-dicyanobenzene and 20.0 g ZnCl_2 (146.6 mmol) were used.

Yield: 0.86 g, 86 %.

Example 3: Polymerization of 1,4-Dicyanobenzene

The reaction was carried out as described in Example 2, and the amount of reactants was 1.0 g (7.8 mmol) 1,4-dicyanobenzene, and 30.0 g (220.0 mmol) ZnCl_2 .

Yield: 0.83 g, 83 %.

Example 4: Polymerization of 1,4-Dicyanobenzene

The reaction was carried out as described in Example 1, except that 1.0 g (7.8 mmol) 1,4-dicyanobenzene and 1.0 g (7.3 mmol) ZnCl_2 were used. By way of WAXS powder patterns, it was confirmed that the obtained material was a crystalline material.

Yield: 0.92 g, 92 %.

Elemental analysis: C, 72.8; N, 19.30; H, 3.19 %; C/N (mol) = 4.4.

Calculated $\text{C}_8\text{H}_4\text{N}_2$: C, 75.0; N, 21.86; H, 3.15 %; C/N (mol) = 4.0.

Example 5: Polymerization of 1,2-Dicyanobenzene

The reaction was carried out as described in Example 1, except that 1,2-dicyanobenzene (2.0 g, 15.6 mmol) and ZnCl_2 (15.0 g, 110 mmol) were used.

Yield: 1.9 g, 95 %.

Elemental analysis: C, 64.3; N, 12.97; H, 1.42 %; C/N (mol) = 5.78.

Calculated $C_8H_4N_2$: C, 75.0; N, 21.86; H, 3.15 %; C/N (mol) = 4.0.

Example 6: Polymerization of 1,3-Dicyanobenzene

The reaction was carried out as described in Example 1, except that 1,3-dicyanobenzene (2.0 g, 15.6 mmol) and $ZnCl_2$ (15.0 g, 110.0 mmol) were used.

Yield: 1.8 g, 90 %.

Elemental analysis: C, 74.3; N, 13.93; H, 2.39 %; C/N (mol) = 6.22.

Calculated $C_8H_4N_2$: C, 75.0; N, 21.86; H, 3.15 %; C/N (mol) = 4.0.

Example 7: Polymerization of 4,4'-Dicyanobiphenyl

Reaction was carried out as is described in Example 1, except that there was used 4,4'-dicyanobiphenyl (1.8 g, 8.8 mmol) and $ZnCl_2$ (15.0 g, 110.0 mmol).

Yield: 1.5 g, 83 %.

Elemental analysis: C, 84.2; N, 5.41; H, 2.18 %; C/N (mol) = 18.13.

Calculated $C_{14}H_8N_2$: C, 82.3; N, 13.72; H, 3.95 %; C/N (mol) = 7.0.

TGA (O_2 , 20 - 1000 °C, 10 °C min⁻¹): 480 °C (decomposition, 94.55 %); residual mass 2.89 %, assigned to ZnO; corresponding to 4.84 % ZnCl₂.

Example 8: Polymerization of Tris(4-cyanophenyl)amine

The reaction was carried out as is described in Example 1, except that tris(4-cyanophenyl)amine (0.52 g, 1.62 mmol) and ZnCl₂ (6.6 g, 49 mmol) were used.

Yield: 0.51 g, 98 %.

Elemental analysis: C, 71.6; N, 7.94; H, 2.47 %; C/N (mol) = 10.5.

Calculated: C₂₁H₁₂N₄: C, 78.73; H, 3.78; N, 17.49; C/N (mol) = 5.25.

Example 9: Polymerization of 1,3,5-Tris(4-cyanophenyl)benzene

The reaction was carried out as is described in Example 1, except that tris(4-cyanophenyl)benzene (0.2 g, 0.52 mmol) and ZnCl₂ (2.2 g, 15.6 mmol) were used.

Yield: 0.19 g, 95 %.

Elemental analysis: C, 71.7; N, 4.21; H, 3.34 %; C/N (mol) = 19.8.

Calculated: C₂₇H₁₅N₃: C, 85.02; H, 3.96; N, 11.02; C/N (mol) = 9.0.

Example 10: Polymerization of 1,3,5,7-tetra(4-cyanophenyl)adamantane

The reaction was carried out like in Example 1, using 1,3,5,7-tetra(4-cyanophenyl) adamantane (0.5 g, 0.92 mmol) and ZnCl₂ (1.26 g, 9.2 mmol) at 500 °C for 25 h.

Yield: 0.41 g, 81 %.

Elemental analysis: C, 92.5; H, 2.38; N, 3.10.

Calculated for $C_{38}H_{28}N_4$: C, 84.42; H, 5.22; N, 10.36 %.

By way of sorption analysis, it was confirmed that all the materials obtained in the above examples are porous solids. For instance, in the case of Example 1, the material was primarily microporous (cf. Fig. 2), whereas the material was primarily mesoporous in the case of the polymer obtained in Example 7.

The results of the above examples are summarized in Table 1, below.

Table 1

Exempl e No.	Monomer	Temp. (°C)	Reaction time (h)	Yield (%)	Specific surface area (m ² g ⁻¹)	Molar ratio ZnCl ₂ / cyano compound
1	1,4- dicyano benzene	400	40	90	1110	7.05
2	1,4- dicyano benzene	500	25	86	1670	18.80
3	1,4- dicyano benzene	500	25	83	1589	28.21
4	1,4- dicyano benzene	400	40	92	1220	0.94

5	1,2-dicyano Benzene	400	40	95	530	7.05
6	1,3-dicyano Benzene	400	40	90	1505	7.05
7	4,4'-dicyano biphenyl	400	40	83	2515	12.50
8	Tris(4-cyano phenyl) amine	400	40	98	827	30.25
9	1,3,5-tris(4-cyano phenyl) benzene	400	40	95	1235	30.00
10	1,3,5,7-tetra(4-cyano- phenyl) adamantane	500	25	81	1584	10.00

Comparative Example 1: Acidic Polymerization of 4,4'-Dicyanobiphenyl

This Comparative Example was carried out in line with D.R. Anderson et al., J. Polym. Sci. part A: Polym. Chem. 1966, 4(7), 1689-1702. To 1.24 g (0.01 mole) of 4,4'-dicyanobiphenyl at 0°C was slowly added 50 ml of chlorosulfonic acid. The mixture was allowed to stand at room temperature for 48 h and was then poured onto cracked ice, filtered, and washed several times. The dark-coloured polymer was obtained in essentially a 100% yield. Nitrogen sorption measurement showed no porosity.

Comparative Example 2: Polymerization of 1,4-Dicyanobenzene using catalytic amounts of ZnCl_2

This Comparative Example was carried out in line with US 3,775,380. 1,4-dicyanobenzene (1g, 7.8 mmol) and ZnCl_2 (0.1g, 0.73 mmol) were finely ground in a mortar under an inert atmosphere, and transferred in a pyrex ampoule. The ampoule was heated at 400°C for 40 h. The brownish product was ground, washed with water and dried. It was obtained in essentially a 100% yield. Nitrogen sorption measurement showed no porosity.

As shown in the above examples, the solids of the invention exhibit a high porosity as evidenced by their high BET specific surface area, and can be prepared by a simple method.

Example 11: Polymerization of 1,4-dicyanobenzene at different reaction temperatures

Similar to Example 1, 1,4-dicyanobenzene was reacted in a salt melt of 5 eq. ZnCl_2 for a reaction time and at reaction temperatures as specified in Table 2, below. There were obtained porous solids having very high specific surface area (S_{BET}) and total pore volume. The properties of the obtained products are also indicated in the below Table 2.

Table 2

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_{SAXS} ($\text{m}^2 \text{ g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{ g}^{-1}$) ^f	mesopore volume (%) ($\text{cm}^3 \text{ g}^{-1}$) ^g	Average pore diameter (nitrogen sorption) (nm)	Average pore diameter (SAXS) (nm)
400 ^a	920	1450	0.47	0.16 (34)	2.0	1.5
500 ^b	1600	1760	1.00	0.61 (61)	2.5	2.2
600 ^b	1750	1800	1.58	1.34 (82)	3.6	3.5
6004d ^c	1930	/	2.09	1.94 (93)	4.3	/
400/600 ^d	2660	2410	1.82	1.44 (79)	2.7	3.0
400/6004d ^e	3270	/	2.4	1.96 (82)	2.9	/
700 ^b	2530	2600	2.26	2.06 (91)	3.6	3.5

^a 400°C, 40h. ^b 500, 600 or 700°C, 20h. ^c 600°C, 96h. ^d 400°C, 20h then 600°C, 20h. ^e 400°C, 20h then 600°C, 96h. ^f determined at $P/P_0 = 0.99$. ^g determined by NL-DFT pore size distribution.

As can be seen, the samples denoted "400/600" and "400/6004d" are intended to illustrate the two-step method of the invention. In the case of the two-step method, the resulting materials showed extremely high surface areas of about 3300 m^2/g and a total pore volume of 2.4 cm^3/g . As can be seen from

Table 2, the results obtained using nitrogen sorption analysis were confirmed with Small Angle X-ray Scattering (SAXS).

By non-linear density functional theory, the pore size distribution of the materials obtained at 400 °C (Reaction time: 40 h), and at 500, 600 or 700 °C (Reaction time: 20 h) was determined. The results are shown in Fig. 3. As can be seen, the materials obtained in the high-temperature method, i.e. at 600 °C and 700 °C were not only microporous but also mesoporous, and a narrow distribution of pores is formed at around about 5 nm.

Moreover, the C/N and C/H molar ratios of the products listed in the above Table 2, as determined by combustion elemental analysis, are shown in Fig. 4. For reference, the figure also shows the calculated ratio based upon the starting compounds ("calc."). As can be seen from Fig. 4, there is a modification of the chemical composition with increasing temperature. Nitrogen loss is observed at high temperatures.

Example 12: Polymerization of 4,4'-dicyanobiphenyl with variation of the monomer/salt ratio

Similar to Example 1, 4,4'-dicyanobiphenyl (DCBP) was reacted at reaction conditions as specified in Table 3, below.

Table 3

Temp [°C]	ZnCl ₂ [mol. equiv .]	S _{BET} [m ² g ⁻¹]	S _{BET} ^e (micro) [m ² g ⁻¹]	Total pore volume ^f [cm ³ g ⁻¹]	Micro- porous volume ^e [cm ³ g ⁻¹]	average pore diameter [nm]
400 ^a	2	1150	840	0.57	0.4	2
400 ^a	5	1140	730	0.64	0.37	2.2
400 ^a	10	1710	705	1.2	0.42	2.8

400 ^a	20	710	490	0.4	0.24	2.2
400 ^a	10 ^d	2120	790	1.7	0.51	3.3
600 ^b	2	1170	600	0.65	0.31	2.2
600 ^b	5	1400	290	1.55	0.2	4.4
600 ^b	10	1240	235	2.25	0.14	7.2
600 ^b	15	1260	340	2.76	0.19	8.8
600 ^b	20	1510	340	4.5	0.2	12.1
400/600 ^c	5	1630	400	1.29	0.22	3.2
400/600 ^c	10	1625	200	2.42	0.15	6.3
400/600 ^c	20	1430	205	2.96	0.14	8.3

a: 25°C to 400°C in 1h then 400°C during 40h, b: 25°C to 600°C in 1h then 600°C during 20h, c: 25°C to 400°C in 1h then 400°C during 20h, 400°C to 600°C in 1h then 600°C during 1h; d : fast heating; e: determined by NL-DFT ; f: at P/Po = 0.99

As can be seen, the average pore diameter can be tuned by variation of the monomer/salt ratio.

Example 13 and Comparative Example 3: Polymerization of 4-cyanobiphenyl (MCBP) and biphenyl (BP).

Similar to Example 1, 4-cyanobiphenyl (MCBP) and biphenyl (BP) were heated in a melt of ZnCl₂ (10 eq) under the reaction conditions shown in the below Table 4.

Table 4

Temp [°C]	Monomer	S _{BET} [m ² g ⁻¹]	S _{BET} ^e (micro) [m ² g ⁻¹]	Total pore volume ^f [cm ³ g ⁻¹]	Microporous volume ^e [cm ³ g ⁻¹]	average pore diameter [nm]
400 ^a	MCBP	1130	420	1.5	0.24	5.3
600 ^b	MCBP	675	285	0.17	0.14	10.0

600 ^b	BP	0	/	0	/	/
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a: 25°C to 400°C in 1h then 400°C during 40h, b: 25°C to 600°C in 1h then 600°C during 20h, e: determined by NL-DFT;
f: at $P/P_o = 0.99$

The porosity of the obtained materials are also shown in the table. In comparison to the products obtained in Example 12, the material obtained from MCBP showed lower porosities and bigger pores. When carrying out the reaction with BP, a black, non-porous material was obtained.

CLAIMS

1. A method of preparing porous solids, which method comprises polymerizing, in a salt melt or an eutectic mixture of salt melt containing at least one Lewis acidic salt, cyano monomers having at least two cyano groups in their molecule, wherein the at least two cyano groups are bonded to a rigid linking group in the cyano monomer.
2. The method according to Claim 1, wherein the salt melt or eutectic mixture of salt melt consists of at least one Lewis acidic salt.
3. The method according to Claim 1 or 2, wherein the polymerization is carried out in a salt melt of ZnCl_2 .
4. The method according to any one of Claims 1 to 3, wherein the cyano monomers have two, three or four cyano groups, preferably two cyano groups in their molecule.
5. The method according to Claim 4, the rigid linking group in the cyano monomers is an aromatic group.
6. The method according to any one of the preceding claims, wherein the molar ratio of the at least one Lewis acidic salt, and the cyano monomers is ≥ 0.5 , preferably ≥ 5 .
7. The method according to Claim 6, wherein the molar ratio is in the range of 0.8 to 1.2, preferably 0.9 to 1.1.
8. The method according to any one of the preceding claims, wherein the polymerization is carried out at a temperature of 400 to 500 °C.

9. The method according to any one of Claims 1 to 7, wherein the polymerization is carried out at a temperature of $> 500\text{ }^{\circ}\text{C}$, preferably in the range of 600 to $700\text{ }^{\circ}\text{C}$.

10. The method according to any one of Claims 1 to 7, wherein the polymerization is carried out in two steps, a first step at a temperature in the range of 400 to $500\text{ }^{\circ}\text{C}$, and a second step, at a temperature of 600 to $700\text{ }^{\circ}\text{C}$.

11. A method of preparing porous solids, which method comprises polymerizing, in a salt melt or an eutectic mixture of salt melt containing at least one Lewis acidic salt, cyano monomers having one or more cyano groups in their molecule, wherein the cyano groups are bonded to a rigid linking group in the cyano monomer.

12. A porous solid obtainable by the method according to any one of Claims 1 to 11.

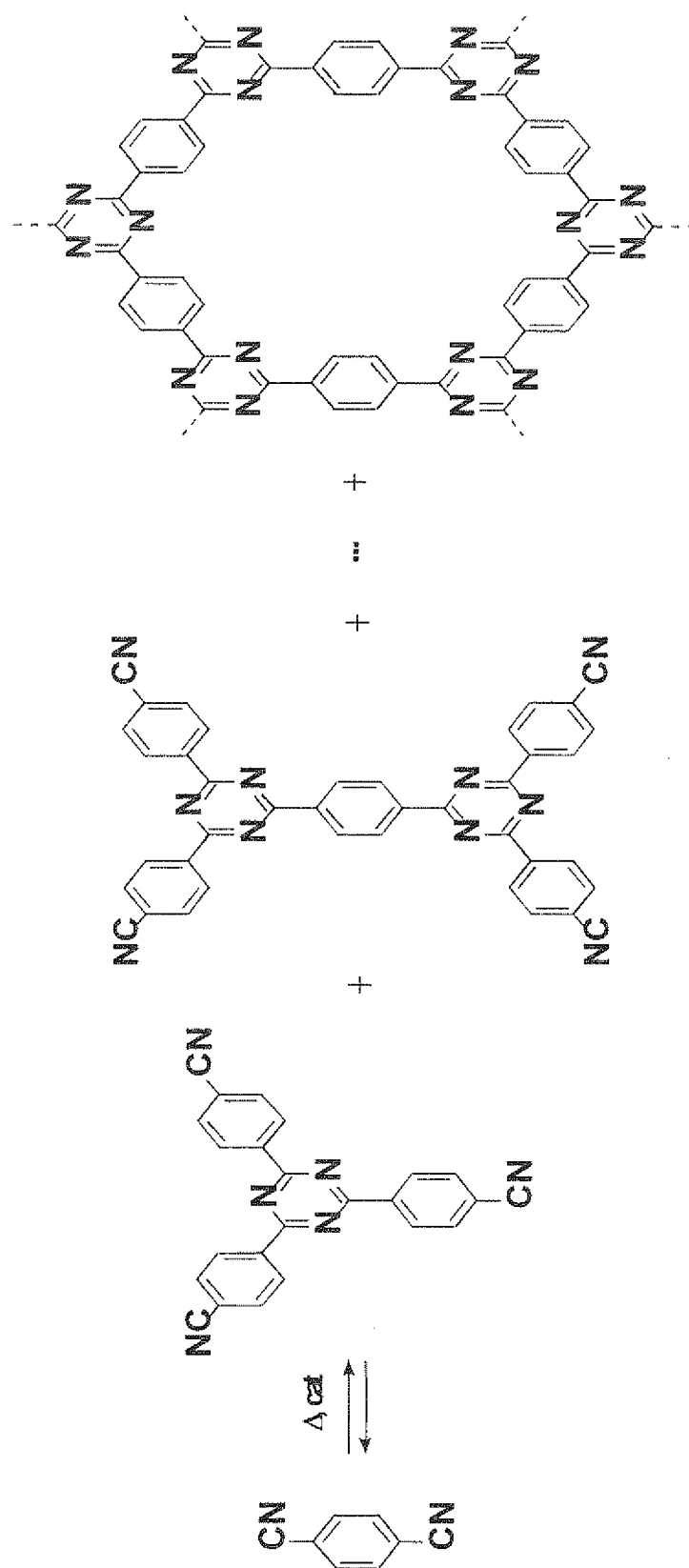
13. The porous solid according to Claim 12, which has a BET specific surface area of $\geq 500\text{ m}^2/\text{g}$, preferably $\geq 1000\text{ m}^2/\text{g}$, more preferably $\geq 2000\text{ m}^2/\text{g}$.

14. The porous solid according to Claim 12 or 13, which has a total pore volume of $\geq 0.3\text{ cm}^3/\text{g}$, preferably $\geq 1.0\text{ cm}^3/\text{g}$, more preferably $> 2\text{ cm}^3/\text{g}$.

15. A use of a porous solid as defined in any one of Claims 12 to 14, as a sorbent material, filtering material, insulating material, or as a catalyst carrier.

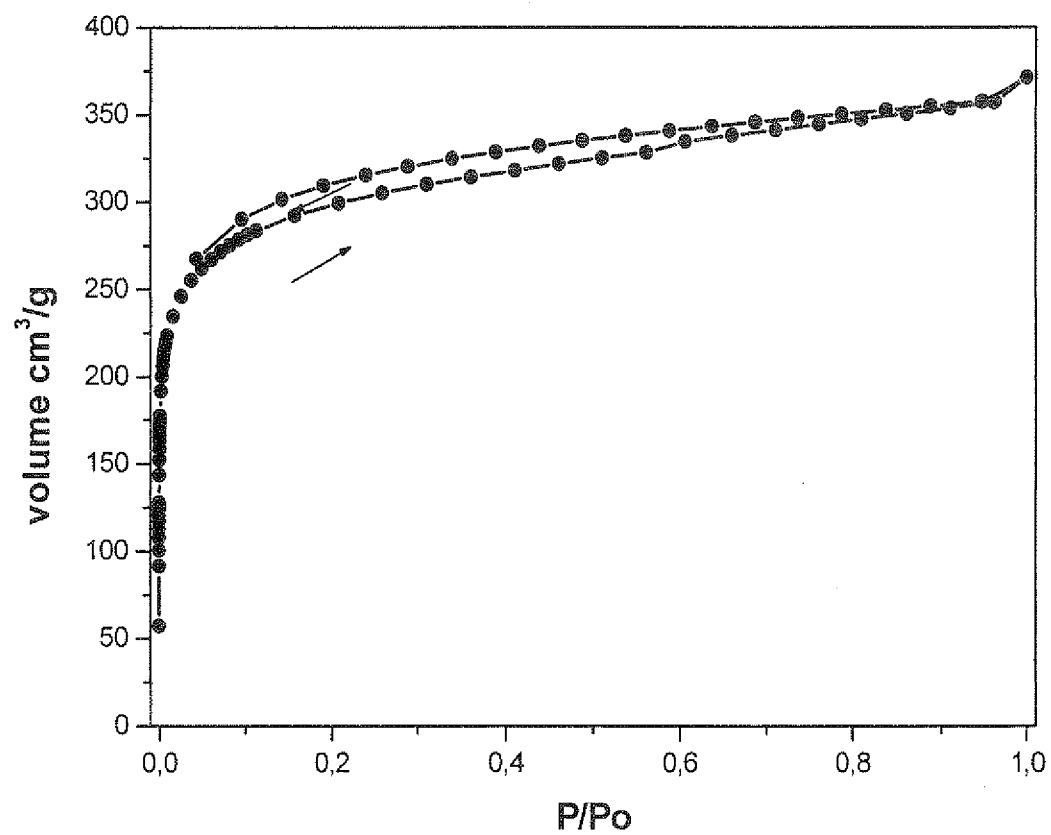
1/4

Fig. 1



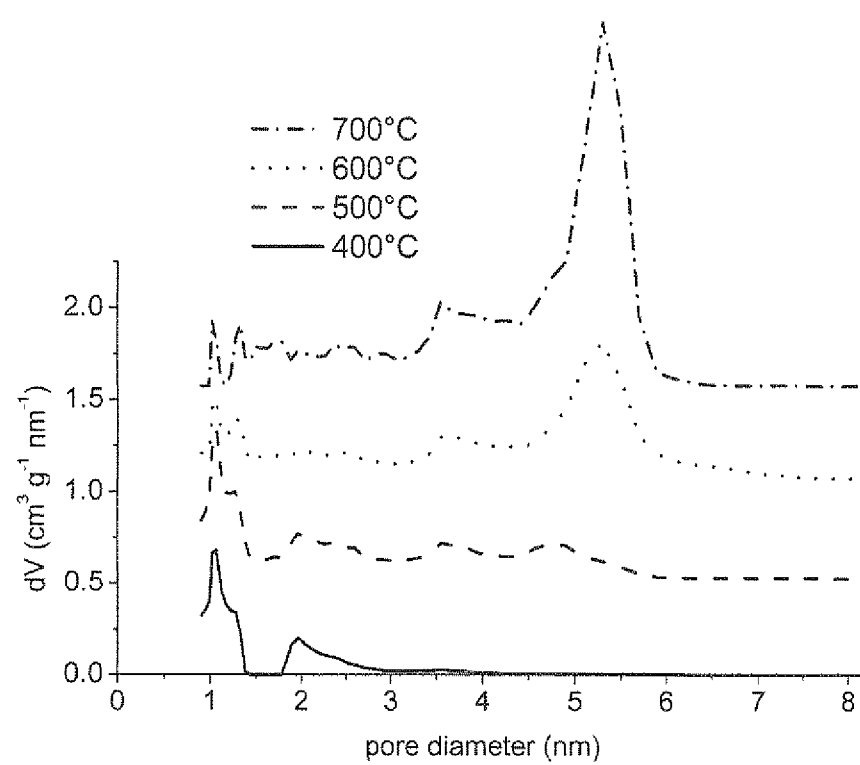
2/4

Fig. 2



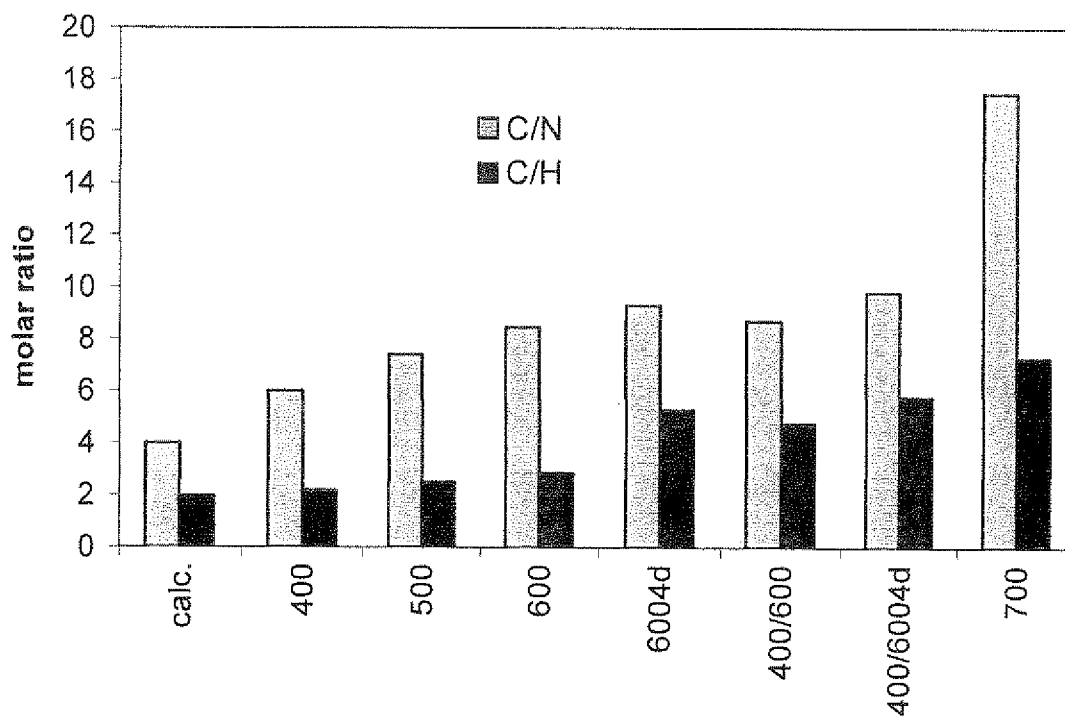
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Fig. 3



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Fig. 4



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/057542

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G73/06 C08J9/00

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 C08J

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 practical, 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.
A	US 3 775 380 A (MILLER G) 27 November 1973 (1973-11-27) cited in the application the whole document	1-13
A	US 3 654 192 A (VOGEL HERWARD A) 4 April 1972 (1972-04-04) the whole document	1-13
A	US 4 125 513 A (MILLER GORDON H) 14 November 1978 (1978-11-14) the whole document	1-13
A	WO 03/000774 A (UNIV MANCHESTER [GB]; MCKEOWN NEIL B [GB]; MAKHSEED SAAD [GB]) 3 January 2003 (2003-01-03) the whole document	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3775380	A	27-11-1973	NONE	
US 3654192	A	04-04-1972	NONE	
US 4125513	A	14-11-1978	US 4100147 A US 4133937 A	11-07-1978 09-01-1979
WO 03000774	A	03-01-2003	CA 2450786 A1 EP 1399500 A1 JP 2004532349 T US 2004198587 A1	03-01-2003 24-03-2004 21-10-2004 07-10-2004