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(54) **METHOD FOR PRODUCING A THREE-DIMENSIONAL STRUCTURE**

VERFAHREN ZUR HERSTELLUNG EINER DREIDIMENSIONALEN STRUKTUR

PROCÉDÉ DE FABRICATION D'UNE STRUCTURE TRIDIMENSIONNELLE

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**Description**

TECHNICAL FIELD

5 **[0001]** The present invention relates to methods of producing three-dimensional structures.

BACKGROUND ART

10 **[0002]** Coordination polymers and organometallic complexes have been conventionally studied because they exhibit optically, magnetically and electrochemically interesting properties. For example, an organometallic complex structure and a coordination polymer structure have been proposed (for example, JP 2005-255651 A and JP 2007-63448 A). A method of fabricating a three-dimensional structure in a solution also has been proposed (Eun-Young Choi, et al., "Pillared Porphyrin Homologous Series: Intergrowth in Metal-Organic Frameworks", Inorganic Chemistry, Vol. 48, No. 2, Pages 426-428, 2009).

15 CITATION LIST

Patent Literature

20 **[0003]**

Patent Literature 1 JP 2005-255651 A

Patent Literature 2 JP 2007-63448 A

25 Non-Patent Literature

**[0004]** Non-Patent Literature 1 Eun-Young Choi, et al., "Pillared Porphyrin Homologous Series: Intergrowth in Metal-Organic Frameworks", Inorganic Chemistry, Vol. 48, No. 2, Pages 426-428, 2009

30 SUMMARY OF INVENTION

Technical Problem

35 **[0005]** In the above conventional art, however, the structures are each formed by mixing its component materials in a solution, which makes it difficult to control the size and position of the structure. For the application of such a structure to a device, it is important to form the structure on a substrate, but the structure is not formed on a substrate in the above conventional method.

40 **[0006]** Under these circumstances, one of the objects of the present **disclosure** is to provide a size- and shape-controlled three-dimensional structure formed on a base and the present invention relates to a method of producing the structure.

Solution to Problem

45 **[0007]** In order to achieve the above object, the present **disclosure** provides a three-dimensional structure formed on a base. This three-dimensional structure includes stacked two-dimensional structures. The two-dimensional structure contains a plurality of porphyrins, a plurality of first metal ions, and a plurality of specific organic molecules. The porphyrin contains two or more functional groups, the first metal ion is a metal ion for linking the functional group of one porphyrin to the functional group of another porphyrin, and the specific organic molecule is an organic molecule that forms a coordinate bond with a metal ion contained in the two-dimensional structure and that has only one site to coordinate to the metal ion.

50 **[0008]** The present invention also provides a method of producing a three-dimensional structure formed on a base, comprising stacked two-dimensional structures, as disclosed in claim 1. The two-dimensional structure contains a plurality of porphyrins, a plurality of first metal ions, and a plurality of specific organic molecules. The porphyrin contains two or more functional groups, the first metal ion is a metal ion for linking the functional group of one porphyrin to the functional group of another porphyrin, and the specific organic molecule is an organic molecule that forms a coordinate bond with a metal ion contained in the two-dimensional structure and that has only one site to coordinate to the metal ion.

## Advantageous Effects of Invention

5 [0009] According to the **method of the** present invention, a size- and shape-controlled three-dimensional structure formed on a base can be obtained. A crystalline three-dimensional structure also can be obtained by selecting appropriate materials.

## BRIEF DESCRIPTION OF DRAWINGS

## [0010]

10 Fig. 1A shows an example of the compound used in the present invention.

Fig. 1B shows another example of the compound used in the present invention.

Fig. 2 schematically shows the production method of the present invention.

15 Fig. 3 is a diagram showing the areas per porphyrin metal complex molecule in the presence and absence of cupric chloride.

Fig. 4A shows the relationship between the number of deposition cycles and the absorption spectrum.

Fig. 4B shows the relationship between the number of deposition cycles and the maximum absorbance.

20 Fig. 5 (a) and (b) show the absorption spectra of CoTCPP-pyridine solutions in the presence and absence of cupric chloride. Fig. 5 (c) and (d) show the absorption spectra of CoTCPP- and pyridine-containing films formed on the surface of a cupric chloride aqueous solution and the surface of pure water.

Fig. 6(a) to (c) show an example of the result of an X-ray diffraction measurement of a three-dimensional structure formed on a silicon substrate.

25 Fig. 7 (a) and (b) show actual measured values and calculated values in an X-ray diffraction measurement. Fig. 7 (c) to (e) show a model of a three-dimensional structure.

Fig. 8 (a) to (f) show another example of the result of an X-ray diffraction measurement of a three-dimensional structure formed on a silicon substrate.

Fig. 9 schematically shows a model of a three-dimensional structure.

## DESCRIPTION OF EMBODIMENTS

30 [0011] Hereinafter, embodiments of the present invention will be described with examples. The present invention is not limited to the following embodiments and examples. In the following description, specific numerical values or specific materials may be given by way of examples, but other numerical values or other materials may be used as long as the effects of the present invention can be obtained. In the following drawings, metal ions may be shown as atoms.

35 (Production method of three-dimensional structure)

40 [0012] The method of the present invention is a method of producing a three-dimensional structure **formed on a base, comprising stacked two-dimensional structures**. According to this production method, a three-dimensional structure formed on a base, **comprising stacked two-dimensional structures** can be obtained. This production method includes the following steps (i), (ii) and (iii).

45 [0013] In the step (i), a two-dimensional structure is formed on the surface of a liquid. The two-dimensional structure contains a plurality of porphyrins, a plurality of first metal ions, and a plurality of specific organic molecules. Hereinafter, the porphyrin contained in the two-dimensional structure is sometimes referred to as a "component (A)", and the specific organic molecule is sometimes referred to as a "pillar molecule". The component (A) contains two or more (for example, three or four) functional groups. The first metal ion is a metal ion for linking the functional group of one component (A) to the functional group of another component (A). Specifically, the first metal ion links the functional groups of the neighboring components (A) via the first metal ion itself. The pillar molecule is an organic molecule that forms a coordinate bond with a metal ion contained in the two-dimensional structure and that has only one site to coordinate to the metal ion. A typical example of the two-dimensional structure is composed of organometallic complexes, first metal ions, and pillar molecules.

50 [0014] In this description, examples of "porphyrin" include a porphyrin molecule that is not in the form of a metal complex and a porphyrin metal complex. When the porphyrin (component (A)) is a porphyrin metal complex, examples of the central metal ion that coordinates to the porphine ring (porphyrin ring) include transition metal ions (for example, cobalt ion and palladium ion). Examples of the functional group in the component (A) include carboxyl group, dithiocarboxyl group, and thioamide group.

55 [0015] Examples of the first metal ion include polyvalent metal ions (for example, divalent metal ions). Examples of the first metal ion include transition metal ions, for example, copper ion. The first metal ion may be divalent copper ion

or divalent nickel ion. Examples of the combination of the functional group in the component (A) and the first metal ion for linking (cross-linking) the functional groups include combinations of carboxyl group and copper ion, carboxyl group and cobalt ion, dithiocarboxyl group and nickel ion, dithiocarboxyl group and platinum ion, thioamide group and copper ion, thioamide group and iron ion, and carboxyl group and nickel ion.

5 [0016] When the component (A) does not contain a metal ion, the pillar molecule is a molecule that forms a coordinate bond with the first metal ion. When the component (A) contains a metal ion, the pillar molecule is a molecule that forms a coordinate bond with at least one metal ion selected from the metal ion in the component (A) and the first metal ion. For example, when the component (A) is a porphyrin metal complex, the pillar molecule is a molecule that forms a coordinate bond with at least one metal ion selected from a central metal ion (a second metal ion) of the porphyrin metal complex and the first metal ion. In one example, the pillar molecule coordinates to the central metal ion of the porphyrin metal complex. In another example, the pillar molecule coordinates to the first metal ion, which is a component of a dinuclear paddle wheel structure to be described later.

10 [0017] Examples of the pillar molecule include pyridine, methylpyridine, isoquinoline, and phenylpyridine. Examples of the combination of a pillar molecule and a metal ion to which the pillar molecule coordinates include combinations of pyridine and cobalt ion, pyridine and copper ion, phenylpyridine and cobalt ion, and phenylpyridine and copper ion. Preferably, the number of sites that are contained in the pillar molecule and that coordinate to the metal ion is one. Preferably, the pillar molecule is a molecule that is oriented in a direction perpendicular or approximately perpendicular to a direction in which the two-dimensional structure extends (hereinafter sometimes referred to as an "in-plane direction"). Examples of the pillar molecule do not include pyrazine or 4,4'-bipyridine having two or more sites to coordinate to metal ions. However, a molecule even having two or more atomic groups that can coordinate to metal ions falls within the pillar molecule if the structure of the molecule allows only one of the sites to coordinate to the metal ion of the two-dimensional structure.

15 [0018] In the step (ii), the two-dimensional structure formed in the step (i) is deposited on a base so that its in-plane direction is parallel to the surface of the base. The two-dimensional structure is placed on the base by the step (ii). Examples of the method for forming a two-dimensional structure on the surface of a liquid and depositing the structure on a base include the Langmuir-Blodgett method (LB method). That is, the step (i) and the step (ii) may be performed by the Langmuir-Blodgett method. The LB method is well known as a method for forming a monomolecular film on the surface of a liquid.

20 [0019] There is no particular limitation on the base as long as the two-dimensional structure is to be deposited thereon. Examples of the base include semiconductor substrates (for example, a silicon substrate), substrates made of inorganic materials such as quartz substrates, glass substrates and metal substrates (for example, a gold substrate), graphite substrates, and resin substrates.

25 [0020] In the step (iii), a cycle (hereinafter sometimes referred to as a "deposition cycle") including the step (i), the step (ii) **and the step (x)** is repeated once or more. The two-dimensional structures are stacked on the base by the step (iii). There is no particular limitation on the number of deposition cycles, and the number of cycles can be determined for the intended purpose. The thickness of the three-dimensional structure can be controlled by the number of deposition cycles. The number of deposition cycles performed in the step (iii) may be determined in the range of 1 to 100 (for example, 5 to 20). When the step (i) and the step (ii) are performed only once without performing the step (iii), a two-dimensional structure formed on the base is obtained.

30 [0021] The production method of the present invention includes, after the step (ii), a step (x) of immersing the base on which the two-dimensional structure is deposited into a solvent. The step (iii) is a step of repeating a cycle (a deposition cycle) including the step (i), the step (ii) and the step (x) once or more. It is desired that the solvent used in the step (x) be a solvent that dissolves the first metal ions and that does not break any of the bond between the component (A) and the first metal ion, the coordinate bond between the pillar molecule and the first metal ion, and the coordinate bond between the pillar molecule and the metal ion in the component (A). Examples of the solvent include pure water and ethanol.

35 [0022] In one example of the production method of the present invention, porphyrin (component (A)) may contain four carboxyl groups. Specifically, the porphyrin may be a porphyrin containing four carboxyl groups but not containing a central metal ion coordinated to a porphine ring, or may be a porphyrin metal complex containing four carboxyl groups and a central metal ion coordinated to a porphine ring. In one example, the component (A) is a porphyrin molecule (a porphyrin that is not in the form of a metal complex) containing four carboxyl groups, and the first metal ion is a transition metal ion. In another example, the component (A) is a porphyrin metal complex containing four carboxyl groups and a central metal ion coordinated to a porphine ring, and the first metal ion is a transition metal ion. The central metal ion in the porphyrin metal complex may be a transition metal ion. For example, it may be cobalt ion.

40 [0023] Fig. 1A shows a porphyrin metal complex containing four carboxyl groups and a cobalt ion. Hereinafter, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato-cobalt (II) in Fig. 1A is sometimes referred to as "CoTCPP". Examples of the pillar molecule containing a nitrogen-containing aromatic ring include pyridine (see Fig. 1B). Hereinafter, pyridine is sometimes referred to as "py".

[0024] In the production method of the present invention, the first metal ion may be divalent copper ion or divalent nickel ion, and the pillar molecule may be a molecule containing a nitrogen-containing aromatic ring. For example, the first metal ion may be divalent copper ion, and the pillar molecule may be a molecule containing a nitrogen-containing aromatic ring.

5 [0025] In the production method of the present invention, the pillar molecule may be pyridine.

[0026] The step (i) may be a step of forming a two-dimensional structure on the surface of a liquid by adding a second solution containing the components (A) and the pillar molecules to a first solution containing the first metal ions. In one example, the first solution is an aqueous solution, and a solvent in the second solution is an organic solvent.

10 [0027] The concentration of the first metal ions in the first solution may be in the range of 1 mmol/L to 100 mmol/L or in the range of 1 mmol/L to 5 mmol/L.

[0028] The step (ii) may be a step of bringing the base closer to (into contact with) the two-dimensional structure, with the surface of the base kept parallel to the surface of the liquid, and thereby depositing the two-dimensional structure on the base. Such a method is sometimes referred to as "horizontal dipping".

15 [0029] The pillar molecule may contain nitrogen. The pillar molecule may contain a  $\pi$  electron. In one example, neighboring two-dimensional structures are fixed together by interactions (for example,  $\pi$ - $\pi$  interactions) between the pillar molecules that are oriented in a direction perpendicular or approximately perpendicular to the in-plane direction. In this case, the two-dimensional structures can sometimes be moved to slide in the in-plane direction. It is expected that the use of such sliding will allow the three-dimensional structure to have various functions. For example, the size of pores in the three-dimensional structure can be changed by such sliding. More specifically, it is expected that the adsorption of gas molecules on the three-dimensional structure will change the size of the pores in the three-dimensional structure. Such a change allows selective adsorption of molecules or selective reaction control. It should be noted that this sliding of the two-dimensional structure is the effect that can be obtained only by the use of monodentate pillar molecules.

20 [0030] In the conventional method for building a three-dimensional structure in a solution, the three-dimensional structure is built by linking two-dimensional structures in the solution. Therefore, in the conventional method, monodentate pillar molecules cannot be used. On the other hand, the present inventors have found that a combination of specific materials and specific methods makes it possible to build a three-dimensional structure using monodentate pillar molecules. In the method of the present invention, a three-dimensional structure is formed by stacking two-dimensional structures formed on the surface of a liquid. Therefore, unlike the conventional method, the method of the present invention allows a three-dimensional structure to be formed using monodentate pillar molecules. In the method of the present invention, the number of two-dimensional structures to be stacked can be adjusted by the number of cycles, each including the step (i) and the step (ii), to be performed. That is, according to the method of the present invention, the thickness of the three-dimensional structure can be controlled easily. The thickness of the three-dimensional structure fabricated by the method of the present invention may be in the range of 10 nm to 100 nm.

35 (Three-dimensional structure)

[0031] The three-dimensional structure of the present **disclosure** can be produced by the above production method of the present invention. Since the details of the production method of the present invention that have been described can be applied to the three-dimensional structure of the present **disclosure**, the same description may be omitted. Furthermore, the details of the three-dimensional structure of the present **disclosure** that have been described can be applied to the production method of the present invention.

40 [0032] The three-dimensional structure of the present **disclosure** is formed on a base. The three-dimensional structure includes stacked two-dimensional structures. The two-dimensional structure contains a plurality of porphyrins (components (A)), a plurality of first metal ions, and a plurality of specific organic molecules (pillar molecules). The porphyrin contains two or more functional groups. The first metal ion is a metal ion for linking the functional group of one porphyrin to the functional group of another porphyrin. The pillar molecule is an organic molecule that forms a coordinate bond with a metal ion contained in the two-dimensional structure and that has only one site to coordinate to the metal ion. Since the porphyrin (component (A)), the first metal ion, and the pillar molecule have been described above, the same description may be omitted.

50 [0033] As described above, the porphyrin (component (A)) may contain four carboxyl groups. Specifically, the porphyrin may be a porphyrin containing four carboxyl groups but not containing a central metal ion coordinated to a porphine ring, or may be a porphyrin metal complex containing four carboxyl groups and a central metal ion coordinated to a porphine ring. In one example of this case, the carboxyl groups of neighboring porphyrins (components (A)) are cross-linked by the first metal ions (for example, transition metal ions). Such a cross-linked structure is sometimes referred to as a dinuclear paddle wheel structure.

## EXAMPLES

**[0034]** Examples in which the three-dimensional structures of the present disclosure were produced according to the method of the present invention are described below.

(Example 1)

**[0035]** In Example 1, CoTCPP (manufactured by Porphyrin Systems) was used as components (A). Cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) was used as a compound containing the first metal ion. Pyridine was used as the pillar molecule. For the X-ray diffraction measurement (XRD) and atomic force microscope (AFM) measurement, a silicon single crystal substrate ((100) plane) was used as a substrate. For the ultraviolet-visible absorption spectrum measurement, a quartz substrate was used as a substrate. These substrates were subjected to ultrasonic cleaning in chloroform, acetone, and ethanol, each for 30 minutes, before two-dimensional structures are stacked in layers thereon.

**[0036]** First, 8.5 mg of CoTCPP and 20  $\mu\text{L}$  of pyridine were dissolved in 50 mL of chloroform/methanol mixed solvent. The volume ratio of chloroform and methanol was 3:1. A PTFE trough (with dimensions of  $375 \times 75 \times 5$  mm and a capacity of 0.16 L) was filled with an aqueous solution of cupric chloride dihydrate (with a concentration of 0.1 M). A film formation apparatus including this trough is provided with two opposing barrier bars. The surface of the aqueous solution in the trough was cleaned by aspiration.

**[0037]** Next, 96  $\mu\text{L}$  of CoTCPP/pyridine solution was spread with a microsyringe between the two barrier bars on the surface of the cupric chloride solution. Next, the two barriers were moved closer to each other at a rate of 10 mm/min while measuring the surface pressure. A film (two-dimensional structure) was formed on the surface of the aqueous solution in this manner (Step (i)). Then, the film at a surface pressure of  $5 \text{ mNm}^{-1}$  was transferred to the substrate (Step (ii)). The film was transferred to the substrate by bringing the substrate into contact with the film with the surface of the substrate kept parallel to the surface of the aqueous solution (the surface of the film). Next, the substrate was rinsed with distilled water for 3 minutes, immersed in distilled water for 3 minutes (Step (x)), and dried by blowing nitrogen. A film (a two-dimensional structure) composed of CoTCPP, copper ion, and pyridine was formed on the substrate in this manner.

**[0038]** Next, a step including, as one cycle, the above step (i), step (ii), and rinsing/immersing Step (x)/drying was performed repeatedly. Thereby, a three-dimensional structure including stacked two-dimensional structures was formed on the substrate. Fig. 2 shows these steps schematically.

(Comparative Example 1)

**[0039]** In Comparative Example 1, the same processes were carried out as in Example 1, except that pure water was used instead of the aqueous solution of cupric chloride dihydrate. Specifically, pure water was placed in a trough, and 160  $\mu\text{L}$  of CoTCPP/pyridine solution was spread on the surface of the pure water. The other processes were carried out in the same manner as in Example 1.

**[0040]** Fig. 3 shows the relationship between the area per porphyrin metal complex and the surface pressure in each of the case using the aqueous solution of cupric chloride dihydrate and the case of using pure water. At the same surface pressure, the area per molecule was larger in Example 1 where the aqueous solution of cupric chloride was used. This suggests that CoTPPs are cross-linked by copper ions by the use of the aqueous solution of cupric chloride and that a two-dimensional structure is formed on the surface of the liquid.

(Ultraviolet-visible absorption spectrum measurement)

**[0041]** Fig. 4A shows a change in the absorption spectrum with a change in the number of stacked two-dimensional structures. Fig. 4B shows a change in the height of the absorption peak at about 440 nm (the Soret band). In these diagrams, the number of cycles being 1 (one cycle) means that only one two-dimensional structure layer is formed on the base.

**[0042]** The calculated value for the monolayer shown in Fig. 4B is a value obtained by considering the absorption coefficient of porphyrin and the orientation of the molecule. This value is in good agreement with the actual measured value for one cycle, that is, the actual measured value for only one two-dimensional structure layer formed on the substrate. This suggests that the surface of the substrate is sufficiently covered with a CoTCPP-py-Cu monolayer. Furthermore, as shown in Fig. 4B, the height of the absorption peak is proportional to the number of cycles. This suggests that the number of stacked two-dimensional structures increases one by one in each cycle.

**[0043]** For reference, Fig. 5 (a) and (b) show the absorption spectra in solutions. Fig. 5 (a) shows the absorption spectra of CoTCPP-pyridine (py) solutions in the presence and absence of  $\text{CuCl}_2$ . The solvent is a chloroform/methanol mixed solvent. Fig. 5 (b) is diagram showing a selected portion of Fig. 5 (a). In the presence of  $\text{CuCl}_2$ , the Soret band

at about 440 nm shifts toward shorter wavelengths. This shift indicates the coordination between the carboxyl groups of CoTCPP and  $\text{Cu}^{2+}$  ions.

[0044] Fig. 5 (c) shows the absorption spectra of CoTCPP- and pyridine (py)-containing films formed on the surface of a 0.1 M (mol/L)  $\text{CuCl}_2$  aqueous solution and the surface of pure water. The film formed on the surface of the aqueous solution was transferred to a quartz substrate and then its absorption spectrum was measured. Fig. 5 (d) is a diagram showing a selected portion of Fig. 5 (c). As shown in Fig. 5 (d), also in the LB film, the Soret band shifts in the same manner as in Fig. 5 (b) in the presence of  $\text{CuCl}_2$ . This suggests that constitutional units composed of CoTCPP and pyridine (py) react with  $\text{Cu}^{2+}$  to form a two-dimensional structure composed of CoTCPP, pyridine (py) and  $\text{Cu}^{2+}$ .

(Synchrotron X-ray diffraction measurement)

[0045] The synchrotron X-ray diffraction data was obtained at room temperature at beamline BL13XU (with a wavelength of 1.554 angstroms) in Spring-8. During the measurement, helium gas was supplied to a measurement cell.

[0046] Fig. 6 (a) to (c), Fig. 7 (a), Fig. 7 (b), and Fig. 8 show the results of the X-ray diffraction measurements of the three-dimensional structure formed on the silicon substrate. The three-dimensional structure was formed by repeating the above-mentioned cycle 20 times.

[0047] Fig. 6 (a) to (c) show the results of out-of-plane X-ray diffraction (XRD). In the diagram, filled circles represent measured values, and solid lines plotted along the filled circles represent fitting curves. Solid lines below the fitting curves represent differences between the measured values and the fitting curves. The spacing between neighboring two-dimensional structures was calculated from the

[0048] (001) Bragg reflection at  $2\theta = 9.50^\circ$ , and was 0.938 nm. The total thickness of the three-dimensional structure was calculated from the full width at half maximum (FWHM) of the peaks, and was 20 nm. This value is in good agreement with the value ( $0.938 \text{ nm} \times 20 \approx 19 \text{ nm}$ ) obtained when 20 two-dimensional structures are stacked in layers.

[0049] Fig. 7 (a) shows the results of in-plane synchrotron X-ray diffraction. Fig. 7(b) is a diagram showing a selected portion of Fig. 7 (a). Fig. 7 (a) also shows the values calculated on the assumption that there is  $\pi$ - $\pi$  stacking and the values calculated on the assumption that there is no  $\pi$ - $\pi$  stacking.

[0050] Fig. 8 (a) to (f) show the results of high-statistics fine scans of in-plane grazing incidence X-ray diffraction (GIXRD). In Fig. 8 (a) to (f), filled circles represent measured values, and solid lines plotted along the filled circles represent fitting curves. Solid lines below the fitting curves represent differences between the measured values and the fitting curves.

[0051] In the in-plane X-ray diffraction, only the (hk0) peaks were observed. On the other hand, in the out-of-plane X-ray diffraction, only the (hkl) ( $l \neq 0$ ) peaks were observed.

[0052] The average domain size of the crystal was calculated to be about 18 nm from the X-ray diffraction results. On the other hand, the image of the atomic force microscope shows that the domain size is about 20 nm, which means that the X-ray diffraction results and the results of observation with the atomic force microscope were in good agreement.

[0053] Fig. 7 (c), Fig. 7 (d), Fig. 7 (e), and Fig. 9 show one example of the predicted structural model of the three-dimensional structure. Fig. 7 (c) shows the structure viewed in a direction parallel to the a-b axis direction. Fig. 7 (d) shows the structure viewed in a direction parallel to the b-c axis direction. Fig. 7 (e) shows the structure viewed in a direction parallel to the a-c axis direction. Fig. 9 shows a perspective view thereof. It should be noted that the values calculated on the assumption that there is  $\pi$ - $\pi$  stacking shown in Fig. 7 (a) and (b) are the calculated values for this model.

[0054] In the illustrated model, the CoTCPP units are linked by dinuclear  $\text{Cu}_2(\text{COO})_4$  paddle wheels. In this model, each side of each CoTCPP is coordinated with one pyridine (a monodentate ligand). Each side of each dinuclear copper block is also coordinated with one pyridine. The heterocycles of the pyridines are oriented in a direction approximately perpendicular to the direction in which the two-dimensional structure extends. In the illustrated model, the two-dimensional structures are linked by  $\pi$ - $\pi$  interactions between the pyridines coordinated to the dinuclear paddle wheels (Fig. 7 (c) to (e)).

[0055] As shown in Fig. 7 (a), the calculated values for this model (the values calculated on the assumption that there is  $\pi$ - $\pi$  stacking) include only the (ht0) peaks, and are in good agreement with the measured values. The spacing between the two-dimensional structures in this model also is in good agreement with the measured spacing thereof (0.938 nm).

[0056] The details of the mechanism for the  $\pi$ - $\pi$  interactions between pyridines are not known. In one hypothesis, the  $\pi$ - $\pi$  interactions may not occur in the two-dimensional structure immediately after the transfer to the base. Instead, the  $\pi$ - $\pi$  interactions may occur in the step (Step (x)) of immersing the two-dimensional structure in a solvent sometime after the transfer.

(Study of Step (i))

[0057] The first solution used in the step (i), i.e., a solution in which a metal salt is dissolved, was studied. Specifically, two-dimensional structures were formed by dissolving various types of metal salts with various concentrations in the first solution. The first metal ions are supplied by dissolving a metal salt in the first solution.

**[0058]** As the metal salt, cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), nickel (II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), or nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was used. That is, as the first metal ion, divalent copper ion or divalent nickel ion was used. As the second solution to be spread (the solution to be spread) on the first solution, the same solution as in Example 1, i.e., a solution containing a porphyrin metal complex and pyridine was used. As the porphyrin metal complex, CoTCPP or PdTCPP obtained by replacing the central metal ion of CoTCPP by a palladium ion was used.

**[0059]** The second solution was spread on the first solution by the same method as in Example 1. Next, two barriers were moved in the same manner as in Example 1, and thus a film (a two-dimensional structure) was formed on the surface of the first solution. Then, the area of the film at a surface pressure of 5 mN/m was measured, and the area per porphyrin metal complex molecule was calculated from this measured area and the amount of the porphyrin metal complex in the second solution. Next, the film formed on the surface of the first solution was transferred to a substrate by the same method as in Example 1. Then, it was examined by X-ray diffraction whether or not the first metal ions were deposited on the film transferred to the substrate in the form of the original metal salt which has not reacted with the second solution. Only some of the films were subjected to this examination. Table 1 shows the experimental results and measurement results.

[Table 1]

	Type of porphyrin metal complex	Type of metal salt	Concentration of metal salt (mmol/L)	Area per porphyrin metal complex molecule ( $\text{nm}^2$ )	Presence or absence of metal salt deposition
Experiment 1	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	1	1.4	Not deposited
Experiment 2	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	5	1.4	Not deposited
Experiment 3	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	10	1.4	Unexamined
Experiment 4	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	50	1.4	Unexamined
Experiment 5	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	100	1.4	Deposited
Experiment 6	CoTCPP	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	5	1.3	Unexamined
Experiment 7	CoTCPP	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10	1.3	Unexamined
Experiment 8	CoTCPP	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	100	1.3	Unexamined
Experiment 9	CoTCPP	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	100	1.2	Unexamined
Experiment 10	CoTCPP	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.1	0.6	Unexamined
Experiment 11	CoTCPP	Not used (pure water)	0	0.6	Not deposited
Experiment 12	PdTCPP	Not used (pure water)	0	0.6	Not deposited

**[0060]** In Table 1, "not deposited" means that no X-ray diffraction peak corresponding to a metal salt used as a source material for the first metal ion solution was observed, and "deposited" means that the X-ray diffraction peak was observed.

**[0061]** In Experiments 1 to 9, the areas per porphyrin metal complex molecule at a surface pressure of 5 mN/m fell within the range of 1.2 to 1.4  $\text{nm}^2$ . On the other hand, when the concentration of the metal salt in the first solution was 0.1 mmol/L or less, the areas occupied by the porphyrin metal complex decreased significantly. This seems to suggest that the two-dimensional structure was not properly formed in some portions. Furthermore, no deposition of the metal

salt was observed when the concentrations of the metal salt were in the range of 1 mmol/L to 5 mmol/L. The deposition of the metal salt as a source material may cause a decrease in the surface coverage of the intended three-dimensional structure on the substrate, resulting in a decrease in the properties thereof. These results suggest that the concentration of metal ions in the first solution is preferably in the range of 1 mmol/L to 100 mmol/L, and particularly preferably in the range of 1 mmol/L to 5 mmol/L.

#### INDUSTRIAL APPLICABILITY

**[0062]** The three-dimensional structure obtained by the method of the present invention can be used for organic devices, catalysts, electrodes, etc.

#### Claims

1. A method of producing a three-dimensional structure structure formed on a base, comprising stacked two-dimensional structures, comprising the steps of:

- (i) forming a two-dimensional structure on the surface of a liquid;
- (ii) depositing the two-dimensional structure on a base so that its in-plane direction is parallel to the surface of the base;
- (x) immersing the base on which the two-dimensional structure is deposited into a solvent; and
- (iii) repeating a cycle including the step (i)\_the step (ii) and the step (x) once or more, wherein

the two-dimensional structure contains a plurality of porphyrins, a plurality of first metal ions, and a plurality of specific organic molecules,  
 the porphyrin contains two or more carboxyl groups,  
 the first metal ion is a metal ion for linking the carboxyl group of one porphyrin to the carboxyl group of another porphyrin,  
 the specific organic molecule is an organic molecule that forms a coordinate bond with a metal ion contained in the two-dimensional structure and that has only one site to coordinate to the metal ion.

2. The production method according to claim 1, wherein the porphyrin is a porphyrin containing four carboxyl groups but not containing a central metal ion coordinated to a porphine ring, or is a porphyrin metal complex containing four carboxyl groups and a central metal ion coordinated to a porphine ring.

3. The production method according to claim 1, wherein the first metal ion is divalent copper ion or divalent nickel ion, and the specific organic molecule is a molecule containing a nitrogen-containing aromatic ring.

4. The production method according to claim 3, wherein the specific organic molecule is pyridine.

5. The production method according to claim 1, wherein the porphyrin is a porphyrin metal complex containing four carboxyl groups and a cobalt ion coordinated to a porphine ring.

6. The production method according to claim 1, wherein the porphyrins are cross-linked by dinuclear paddle wheel structures, each dinuclear paddle wheel structure being composed of four carboxyl groups and two first metal ions, each side of each of the dinuclear paddle wheel structures is coordinated with one specific organic molecule, the two-dimensional structures are linked by  $\pi$ - $\pi$  interactions between the specific organic molecules coordinated to the sides of each of the dinuclear paddle structures, and the specific organic molecule contains a  $\pi$  electron.

7. The production method according to claim 1, wherein the step (i) is a step of forming the two-dimensional structure on the surface of the liquid by adding a second solution containing the porphyrins and the specific organic molecules to a first solution containing the first metal ions.

8. The production method according to claim 1, wherein the step (ii) is a step of bringing the base closer to the two-dimensional structure, with the surface of the base kept parallel to the surface of the liquid, and thereby depositing the two-dimensional structure on the base.

**Patentansprüche**

1. Verfahren zum Herstellen einer dreidimensionalen Struktur, die auf einer Basis ausgebildet ist und die gestapelte zweidimensionale Strukturen umfasst, umfassend die Schritte des:

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- (i) Ausbildens einer zweidimensionalen Struktur auf der Oberfläche einer Flüssigkeit,
- (ii) Ablagerns der zweidimensionalen Struktur auf einer Basis, so dass ihre Ebenenrichtung parallel zur Oberfläche der Basis ist,
- (x) Eintauchens der Basis, auf der die zweidimensionale Struktur abgelagert ist, in ein Lösungsmittel und
- (iii) ein- oder mehrmaligen Wiederholens eines den Schritt (i), den Schritt (ii) und den Schritt (x) umfassenden Zyklus, wobei

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die zweidimensionale Struktur mehrere Porphyrine, mehrere erste Metallionen und mehrere spezifische organische Moleküle enthält,

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das Porphyrin zwei oder mehrere Carboxylgruppen enthält, das erste Metallion zum Verlinken der Carboxylgruppe von einem Porphyrin mit der Carboxylgruppe eines anderen Porphyrins ist,

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das spezifische organische Molekül ein organisches Molekül ist, das eine Koordinationsbindung mit einem in der zweidimensionalen Struktur enthaltenen Metallion ausbildet und das nur eine Stelle aufweist, um mit dem Metallion zu koordinieren.

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2. Herstellungsverfahren nach Anspruch 1, wobei das Porphyrin ein Porphyrin ist, das vier Carboxylgruppen enthält, aber das kein mit einem Porphyrinring koordiniertes Zentralmetallion enthält, oder das ein Porphyrinmetallkomplex ist, der vier Carboxylgruppen und ein mit einem Porphyrinring koordiniertes Zentralmetallion enthält.

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3. Herstellungsverfahren nach Anspruch 1, wobei das erste Metallion ein zweiwertiges Kupferion oder ein zweiwertiges Nickelion ist und das spezifische organische Molekül ein Molekül ist, das einen stickstoffhaltigen aromatischen Ring enthält.

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4. Herstellungsverfahren nach Anspruch 3, wobei das spezifische organische Molekül Pyridin ist.

5. Herstellungsverfahren nach Anspruch 1, wobei das Porphyrin ein Porphyrinmetallkomplex ist, der vier Carboxylgruppen und ein mit dem Porphyrinring koordiniertes Kobaltion enthält.

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6. Herstellungsverfahren nach Anspruch 1, wobei die Porphyrine über binukleare Schaufelradstrukturen quervernetzt sind, wobei jede binukleare Schaufelradstruktur aus vier Carboxylgruppen und zwei ersten Metallionen besteht, jede Seite von jeder der binuklearen Schaufelradstrukturen mit einem spezifischen organischen Molekül koordiniert ist,

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die zweidimensionalen Strukturen über  $\pi$ - $\pi$ -Wechselwirkungen zwischen den spezifischen organischen Molekülen verlinkt sind, die mit den Seiten von jedem der binuklearen Schaufelradstrukturen koordiniert sind, und das spezifische organische Molekül ein  $\pi$ -Elektron enthält.

7. Herstellungsverfahren nach Anspruch 1, wobei der Schritt (i) ein Schritt des Ausbildens der zweidimensionalen Struktur auf der Oberfläche der Flüssigkeit ist mittels Hinzufügens einer zweiten Lösung, die Porphyrine und die spezifischen organischen Moleküle enthält, zu einer ersten Lösung ist, die die ersten Metallionen enthält.

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8. Herstellungsverfahren nach Anspruch 1, wobei der Schritt (ii) ein Schritt des Näherbringens der Basis zur zweidimensionalen Struktur ist, wobei die Oberfläche der Basis parallel zur Oberfläche der Flüssigkeit gehalten wird, und wodurch die zweidimensionale Struktur auf der Basis abgelagert wird.

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**Revendications**

1. Procédé de production d'une structure tridimensionnelle formée sur une base, comprenant deux structures bidimensionnelles empilées, comprenant les étapes de :

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- (i) formation d'une structure bidimensionnelle sur la surface d'un liquide ;

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- (ii) déposition de la structure bidimensionnelle sur une base de façon que sa direction dans le plan soit parallèle à la surface de la base ;
- (x) immersion dans un solvant de la base sur laquelle la structure bidimensionnelle est déposée ; et
- (iii) répétition d'un cycle comprenant l'étape (i), l'étape (ii) et l'étape (x) une ou plusieurs fois,

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dans lequel

la structure bidimensionnelle contient une pluralité de porphyrines, une pluralité de premiers ions métalliques, et une pluralité de molécules organiques spécifiques,

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la porphyrine contient deux ou plus de deux groupes carboxyle,

le premier ion métallique est un ion métallique pour lier le groupe carboxyle d'une porphyrine au groupe carboxyle d'une autre porphyrine,

la molécule organique spécifique est une molécule organique qui forme une liaison de coordination avec un ion métallique contenu dans la structure bidimensionnelle et qui n'a qu'un seul site pour se coordonner à l'ion métallique.

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2. Procédé de production selon la revendication 1, dans lequel la porphyrine est une porphyrine contenant quatre groupes carboxyle mais ne contenant pas d'ion métallique central coordonné à un cycle porphine, ou est un complexe de porphyrine et de métal contenant quatre groupes carboxyle et un ion métallique central coordonné à un cycle porphine.

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3. Procédé de production selon la revendication 1, dans lequel le premier ion métallique est un ion cuivre divalent ou un ion nickel divalent, et la molécule organique spécifique est une molécule contenant un cycle aromatique azoté.

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4. Procédé de production selon la revendication 3, dans lequel la molécule organique spécifique est la pyridine.

5. Procédé de production selon la revendication 1, dans lequel la porphyrine est un complexe de porphyrine et de métal contenant quatre groupes carboxyle et un ion cobalt coordonné à un cycle porphine.

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6. Procédé de production selon la revendication 1, dans lequel les porphyrines sont réticulées par des structures en roue à aubes dinucléaire, chaque structure en roue à aubes dinucléaire étant composée de quatre groupes carboxyle et de deux premiers ions métalliques, chaque côté de chacune des structures en roue à aubes dinucléaire est coordonné à une molécule organique spécifique,

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les structures bidimensionnelles sont liées par des interactions  $\pi$ - $\pi$  entre les molécules organiques spécifiques coordonnées aux côtés de chacune des structures en roue à aubes dinucléaire, et la molécule organique spécifique contient un électron n.

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7. Procédé de production selon la revendication 1, dans lequel l'étape (i) est une étape de formation de la structure bidimensionnelle sur la surface du liquide par addition d'une deuxième solution contenant les porphyrines et les molécules organiques spécifiques à une première solution contenant les premiers ions métalliques.

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8. Procédé de production selon la revendication 1, dans lequel l'étape (ii) est une étape consistant à mettre la base plus proche de la structure bidimensionnelle, la surface de la base étant maintenue parallèle à la surface du liquide, et ainsi à déposer la structure bidimensionnelle sur la base.

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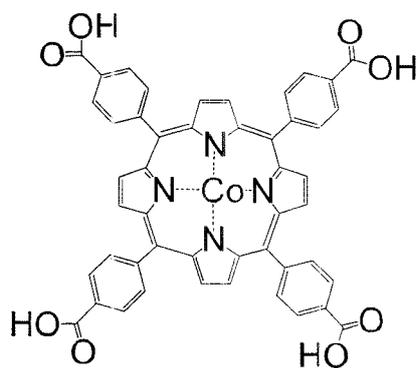


Fig. 1A

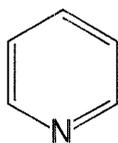


Fig. 1B

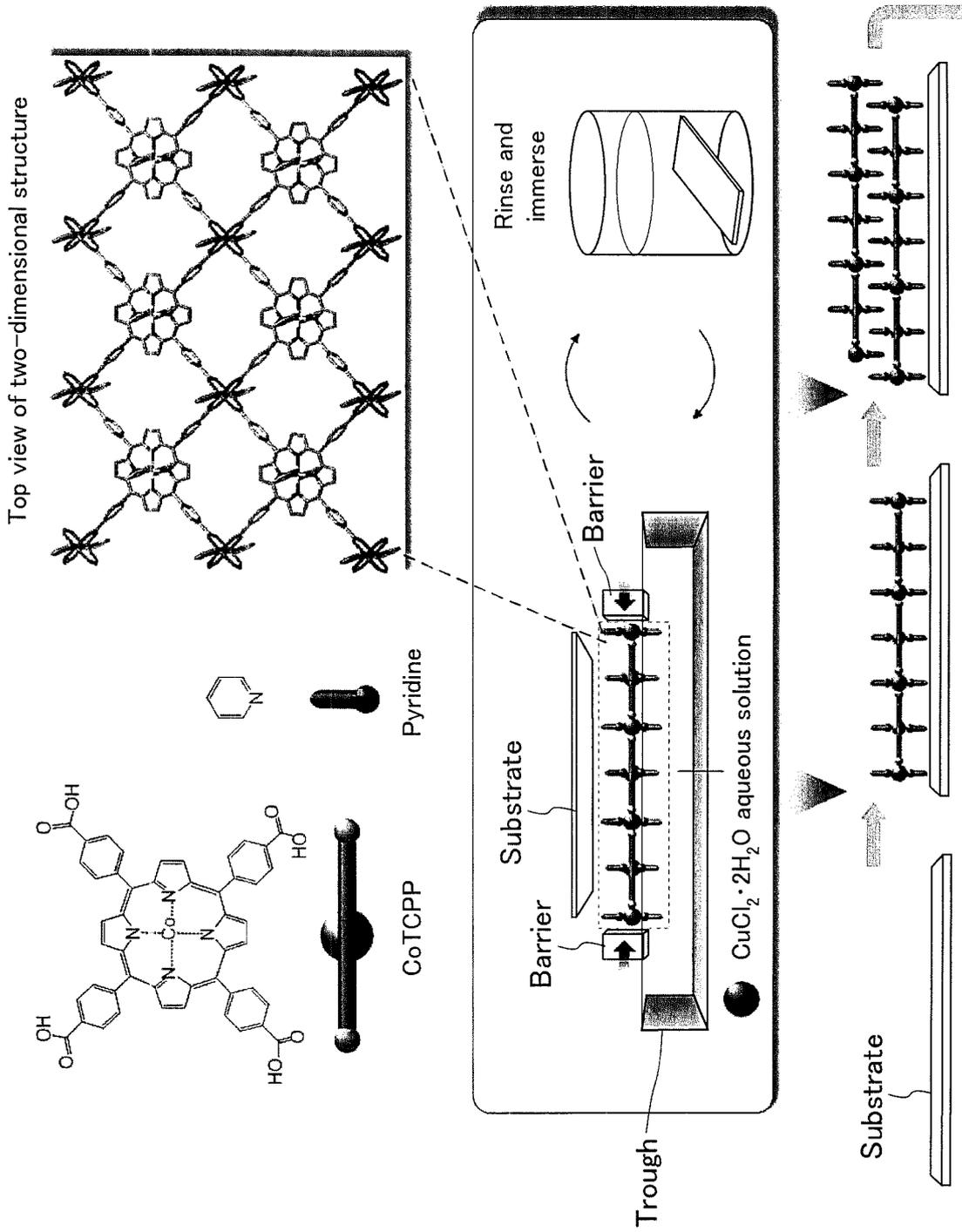


Fig. 2

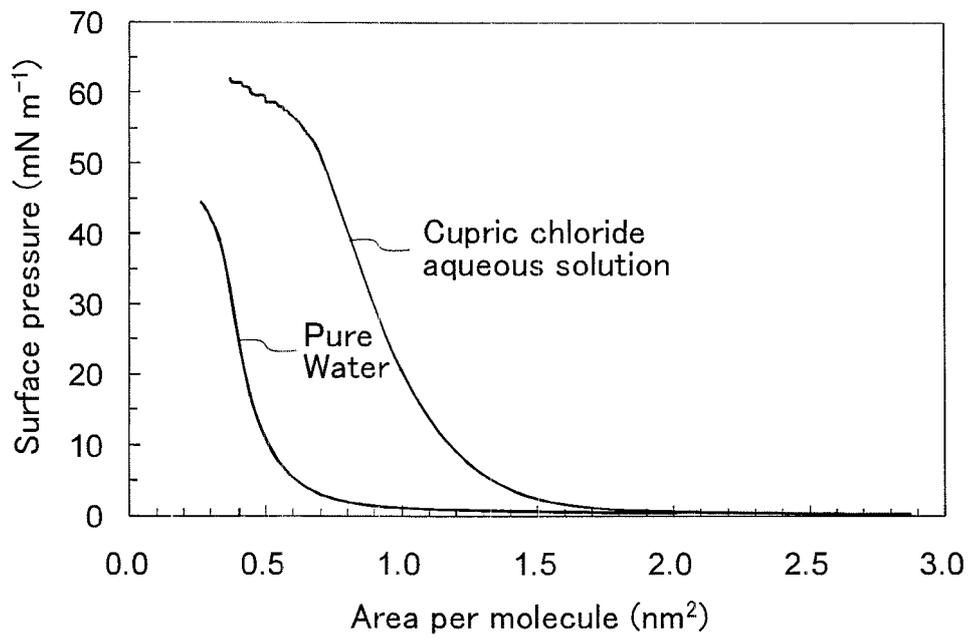


Fig. 3

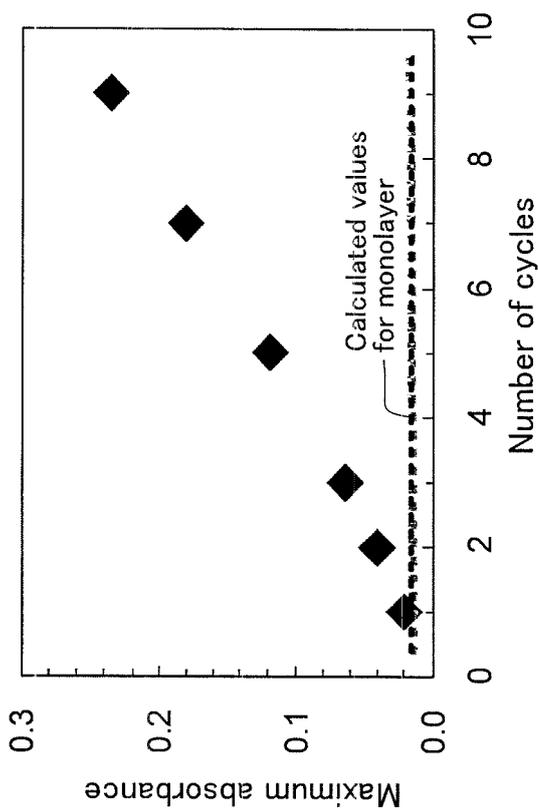


Fig. 4B

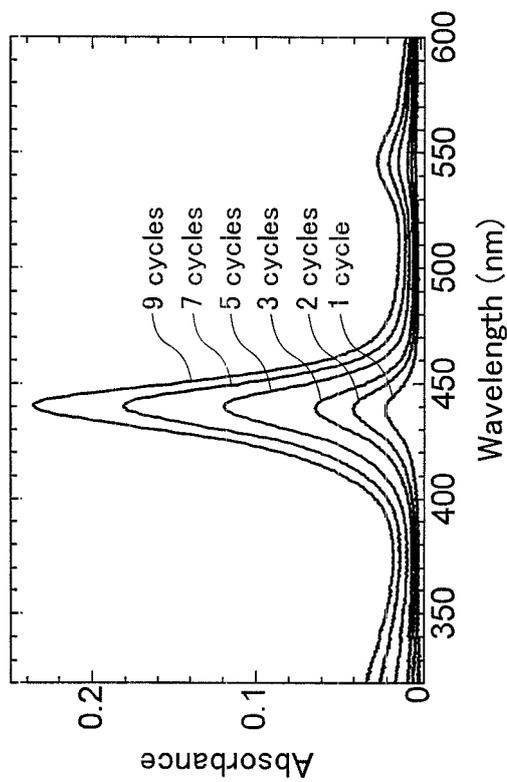


Fig. 4A

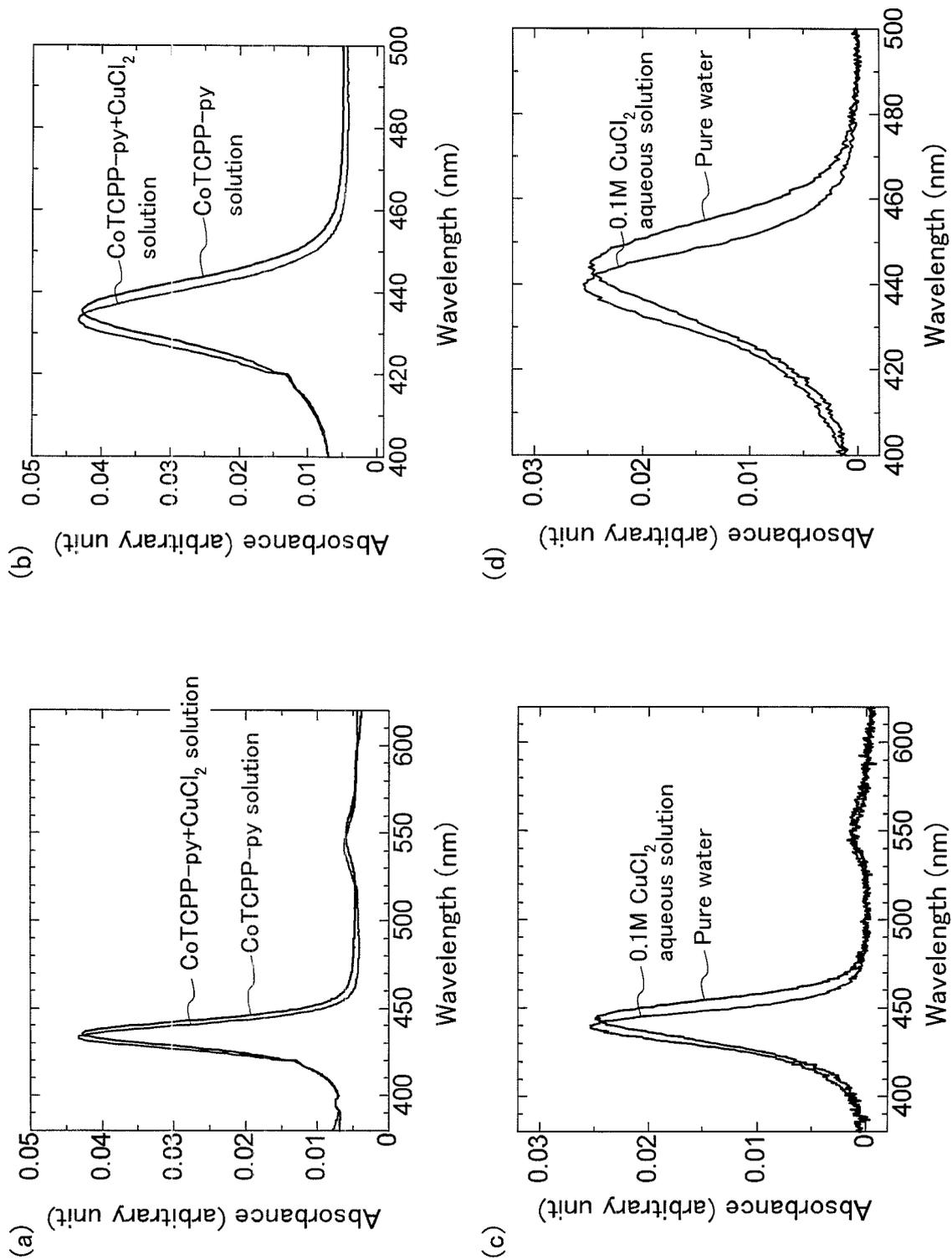


Fig. 5

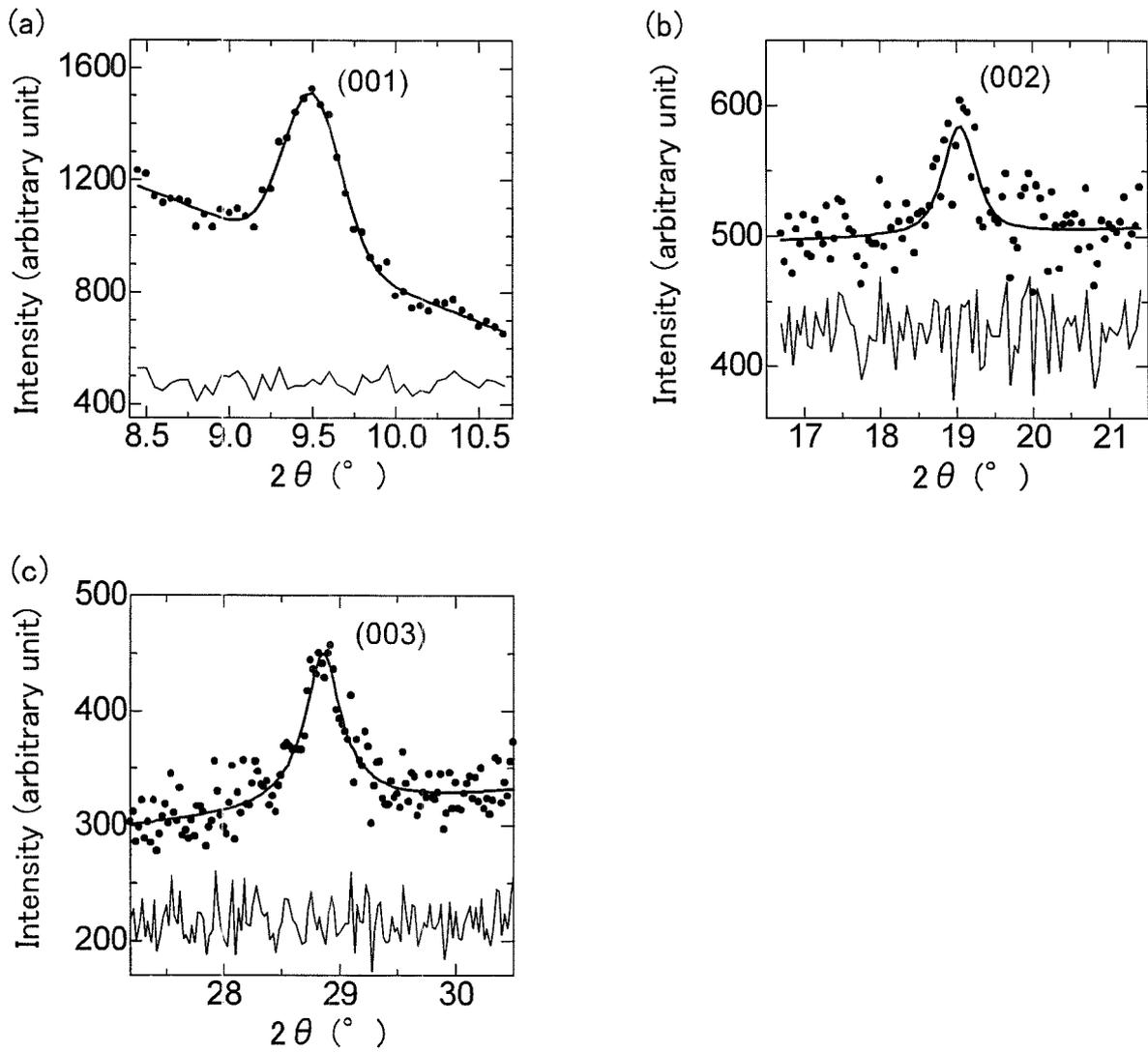


Fig. 6

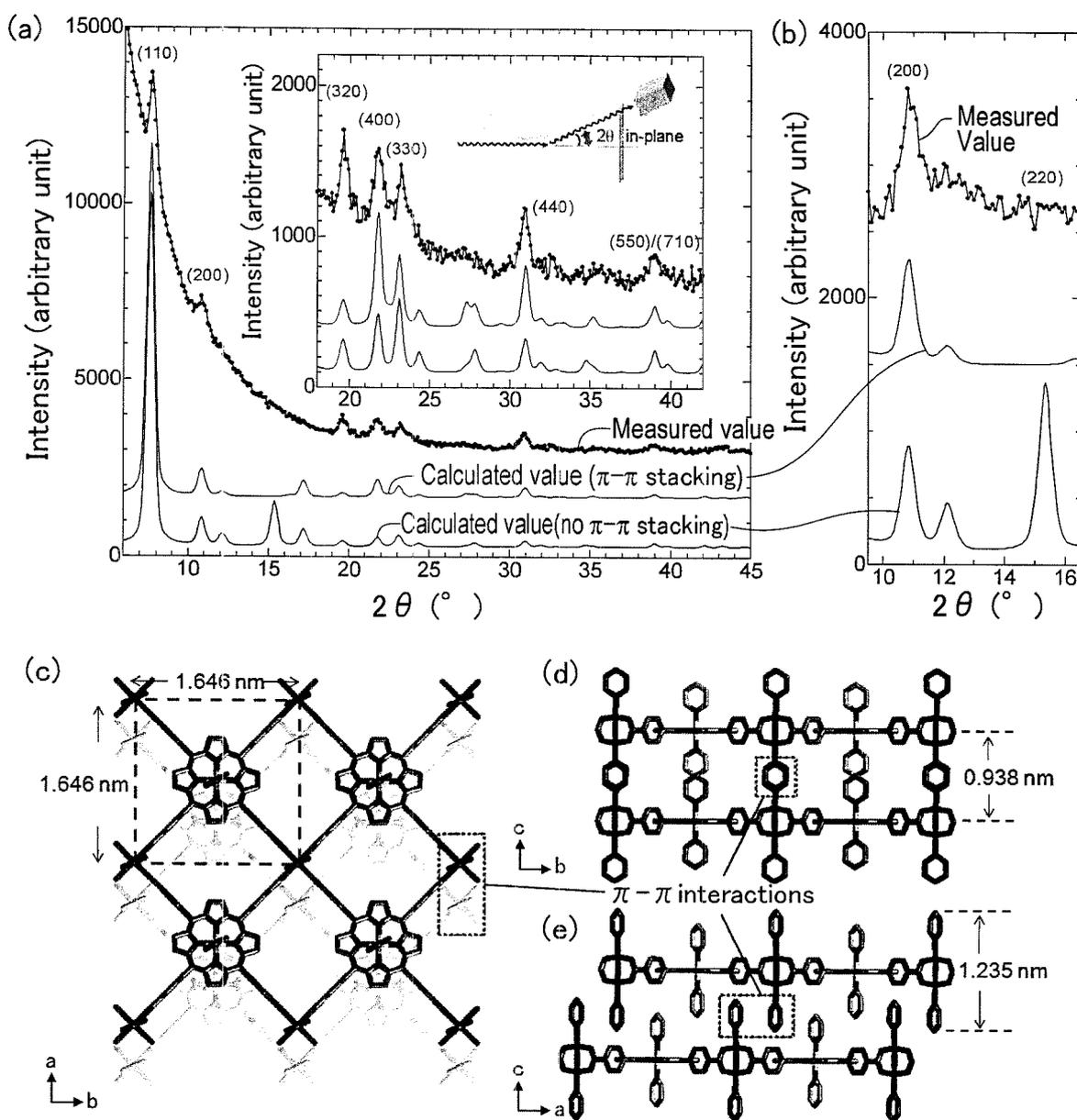


Fig. 7

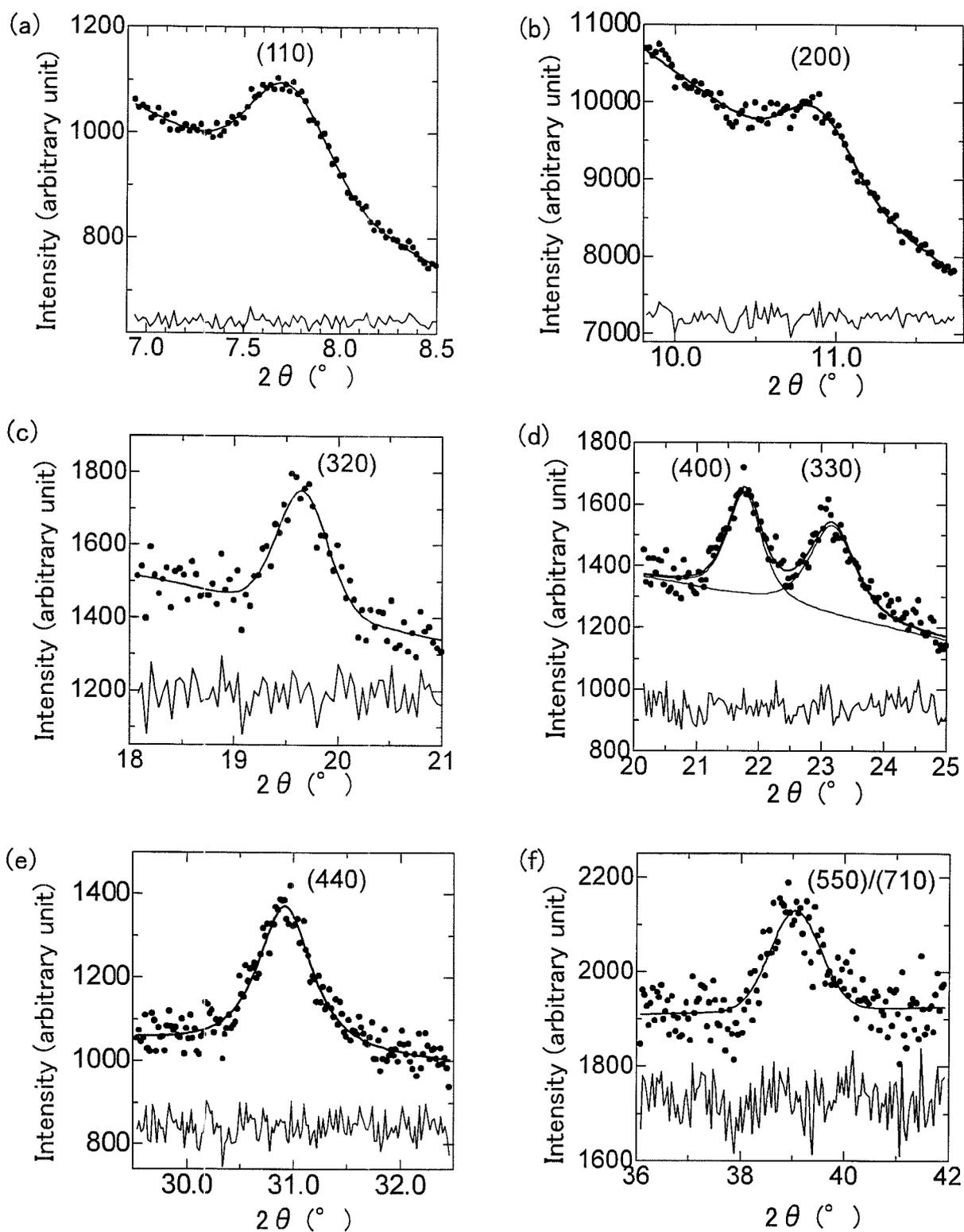


Fig. 8

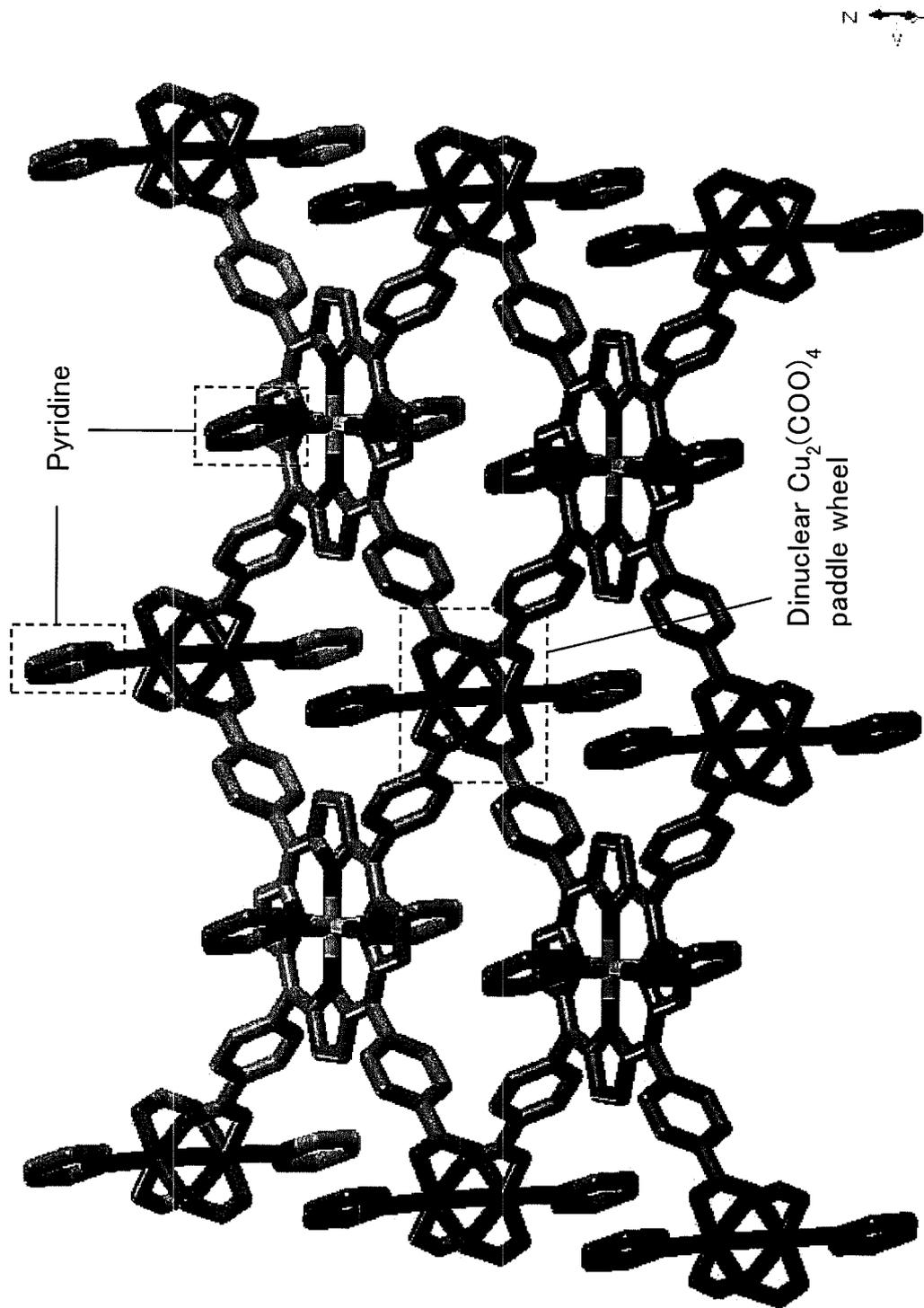


Fig. 9

**REFERENCES CITED IN THE DESCRIPTION**

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