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Photogeneration of Microporous Amorphous Coordination Polymers from Organometallic Ionic Liquids

Takahiro Ueda,[a] Takumi Tominaga,[a] Tomoyuki Mochida,*[a] Kazuyuki Takahashi,[a] and Seiji Kimura[b]

Abstract: Ruthenium-containing organometallic ionic liquids with the $B(CN)_4$ anion were developed that generate microporous amorphous coordination polymers upon UV irradiation. UV light irradiation of $[Ru(C_5H_5)(C_6H_5R)][B(CN)_4]$ (R = butyl, ethyl, octyl) quantitatively generated a yellow powder of a coordination polymer with the formula $[Ru(C_5H_5)\{B(CN)_4\}]_n$. In this reaction, the arene ligand is eliminated by UV irradiation and coordination polymer is formed by coordination of the cyano groups of the anion to the Ru ion. The photogenerated solids exhibited gas absorption properties due to their microporous structure. This paper proposes a method to fabricate functional coordination polymers by photoirradiation of liquids.

Ionic liquids, salts with melting points below 100 °C, have attracted much attention because of their various functionalities.[1] Although most ionic liquids contain organic cations, a variety of functional ionic liquids containing cationic metal-complexes have been recently developed.[2] We have synthesized organometallic ionic liquids from cationic sandwich complexes.[3] In this paper, we report on organometallic ionic liquids that transform to microporous amorphous coordination polymers upon UV irradiation.

Coordination polymers, including metal-organic frameworks (MOFs), are solids consisting of polydentate bridging ligands and metal ions.[4] These polymers have attracted much attention in recent years owing to their functionality, such as magnetism and gas absorption properties. Previously, we reported on ionic liquids that undergo reversible transformation to coordination polymers by application of light and heat.[5] However, the resultant coordination polymers did not exhibit gas absorption properties because they were non-porous.

This paper reports on the photoreaction of room-temperature ionic liquids $[Ru(C_5H_5)(C_6H_5R)][B(CN)_4]$ (R = butyl (**1**), ethyl (**1′**), octyl (**1″**)), which contains a cationic ruthenium complex (Figure 1). The design of these ionic liquids is based on the photochemical reactivity of ruthenium sandwich complexes shown in Figure 2; UV light irradiation of $[Ru(C_5H_5)(arene)]^+$ in acetonitrile solution leads to the elimination of the arene ligand to produce an acetonitrile-coordinated cation $[Ru(C_5H_5)(CH_3CN)_3]^+$.[6] The above-mentioned reversible transformation between ionic liquids and coordination polymers is also based on this mechanism.[5] In the current study, we used $[B(CN)_4]^-$ as the counter anion, so that coordination of the polycyano anion, instead of acetonitrile, to the Ru ion occurs upon UV irradiation of the ionic liquid. It is worth mentioning that there are coordination polymers from an imidazolium $[B(CN)_4]$ salt.[7]

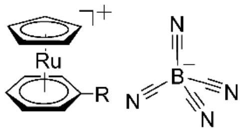

Figure 1. Structural formula of the ionic liquids $[Ru(C_5H_5)(C_6H_5R)][B(CN)_4]$ (R = ^{n}butyl (**1**), ethyl (**1′**), octyl (**1″**)).

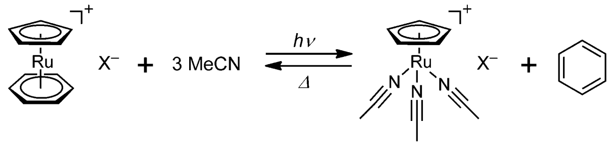

Figure 2. Photochemical reaction of arene-ruthenium sandwich complexes in an acetonitrile solution.[6]

Ionic liquid **1** was a pale yellow liquid that exhibited a glass transition at −66 °C.[3c] UV light irradiation of **1** on a quartz plate for 1h, followed by removal of butylbenzene, quantitatively generated a yellow powder of coordination polymer **2** with the formula $[Ru(C_5H_5)\{B(CN)_4\}]_n$ (Figure 3). The time course of the conversion rate is shown in Figure S1 (Supporting information), showing that the reaction was almost complete in 30 min. In this reaction, the arene ligand is eliminated by UV irradiation and coordination polymer **2** is formed due to coordination of the cyano groups of the anion coordinate to the Ru ion. The anion acts as a bridging ligand to form a 3-dimensional networked structure. The butylbenzene ligand released during the reaction was removed by vacuum drying at 80 °C or by washing with methanol. In the UV-vis spectra, a broad absorption peak appeared near 370 nm after the reaction (Figure 4), which is characteristic to a cyano coordinated complex.[6] In the IR spectra, the C=C arene stretching vibrations (1530 cm^{-1}) observed in **1** disappeared in **2** (Figure 4, inset), which is in agreement with the removal of the arene ligand. The CN stretching vibration in anion in **1** was observed as a very weak peak at 2220 cm^{-1} because of its tetrahedral symmetry, whereas that in **2** was observed as a strong peak at 2230 cm^{-1}. The blue shift is consistent with metal coordination to the cyano group[8] and the increase in peak strength results from breaking the symmetry of the anion; on an average, three of the four CN groups in the anion coordinate with the Ru ion because the metal center can accommodate only three CN groups. This rather broad peak likely also contains the

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Supporting information and the ORCID identification numbers for the authors of this article can be found under https://doi.org/10.1002/chem.201801365 absorption from the non-coordinated CN group. The Raman spectra of **1** and **2** were consistent with these (Figure S2, supporting information).

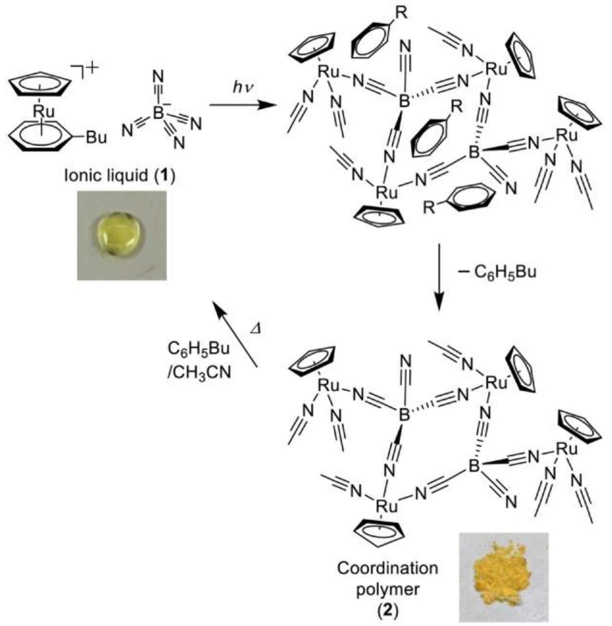

Figure 3. Transformation of ionic liquid **1** to amorphous coordination polymer **2** by photoirradiation (including photographs). The recycling reaction in solution is also shown.

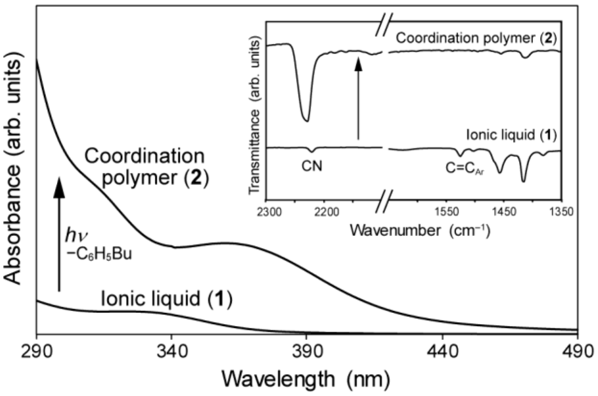

Figure 4. UV-vis and IR (inset) spectra of ionic liquid **1** and coordination polymer **2**.

Coordination polymer **2** was an amorphous solid as confirmed by powder X-ray diffraction. Upon heating, the coordination polymer decomposed at 203 °C as determined by themogravimetric analysis (at 3% weight loss, 10 °C min^{-1}; Figure S3, Supporting information). The coordination polymer did not exhibit melting, whereas some coordination polymers melt at high temperatures to give ionic liquids.[9] A scanning electron microscopy (SEM) image of **2**, showing a finely branched network structure, is shown in Figure 5a. Considering the reaction mechanism shown in Figure 3, removal of butylbenzene is expected to produce a microporous structure. Therefore, the porosity of coordination polymer **2** was evaluated by performing N_2 adsorption measurements at 77 K (Figure 6). The isotherms exhibit Type-I behavior according to IUPAC classifications. The increase in adsorbate volume in the low P/P_0 region indicates the presence of micropores and the strong increase in the N_2 adsorption at P/P_0 above 0.9 indicates the presence of macropores. The Brunauer–Emmett–Teller (BET) surface area and total pore volume of the sample were determined to be 202 m^2 g^{-1} and 0.27 cm^3 g^{-1}, respectively. Although the value of the BET surface area is one order of magnitude smaller than typical crystalline MOFs,[10] the gas absorption properties is still significant. Consistently, transmission electron microscopy (TEM) observation of the coordination polymer revealed the presence of nano-scale microstructures (Figure 5b). There was variation in the surface area among the samples (120–220 m^2 g^{-1}), as expected for amorphous materials. The ethyl derivative **1′** (T_m = 22.6 °C)[3c] exhibited almost identical photoreactivity in the liquid state. The BET surface area of the coordination polymer (**2′**) generated from **1′** was 80–170 m^2 g^{-1}. To further investigate the effect of the substituent size on porosity, the BET surface area of the coordination polymer (**2″**) generated from the octyl derivative **1″** (T_g = −65°C) was evaluated. The value was ~110 m^2 g^{-1}, which was comparable to those of **2** and **2′**. These results indicate that the alkyl chain length has no significant effect on porosity of the resultant coordination polymers.

The photogenerated amorphous coordination polymers (**2** and **2′**) exhibited a small hydrogen adsorption property (~30 cm^{-3} g^{-1} , at 100 kPa, at 77 K). The interaction of hydrogen with the cyano groups may contribute to the absorption properties.[11] In addition, they exhibited a small CO_2 adsorption property (~19 cm^{-3} g^{-1} at 100 kPa, at 273 K). The gas adsorption–desorption isotherms are shown in Figures S4–S6 (Supporting information).

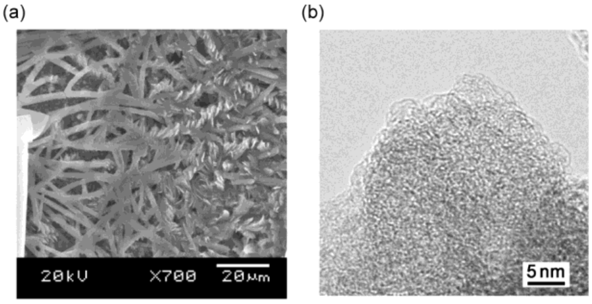

Figure 5. (a) SEM and (b) TEM images of coordination polymer **2**.

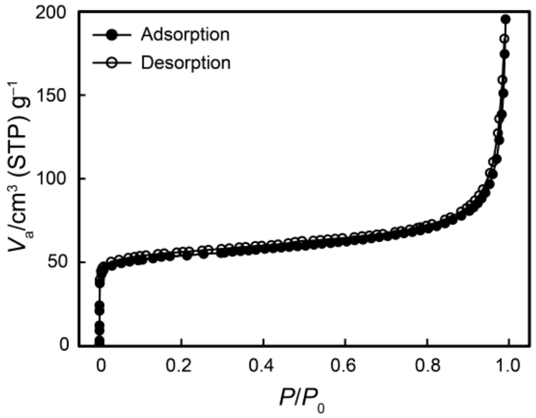

Figure 6. N_2 adsorption (closed symbol) and desorption (open symbol) isotherms of photogenerated coordination polymer **2** at 77 K.

The ionic liquids can be recovered from the coordination polymer through treatment with acetonitrile (Figure 3). Although the coordination polymers were insoluble in common organic solvents at room temperature, they dissolved in hot acetonitrile (80 °C), producing a yellow solution of $[Ru(C_5H_5)(NCCH_3)_3]^+$.[6] Addition of butylbenzene to this solution and overnight heating at 90 °C, followed by evaporation of the solvent, quantitatively regenerated ionic liquid **1**, as confirmed spectroscopically. The mechanism of the reaction is based on the thermally induced back reaction from $[Ru(C_5H_5)(NCCH_3)_3]^+$ to the sandwich complex, as depicted in Figure 2.

In conclusion, phototransformation from ionic liquids to porous coordination polymers was achieved based on a molecular design that combines a photoreactive cation and coordinating anion. $B(CN)_4^-$ acts as the anion and a bridging ligand to form the coordination polymer. The use of this anion is crucial because the corresponding ionic liquids with fluorinated anions such as $[Ru(C_5H_5)(C_6H_5Bu)][(SO_2F)_2N]$ exhibit no photoreactivity.[3b] There are several ionic liquids that exhibit solidification upon photoirradiation based on photoisomerization or photodimerization.[12] However, the transformation from ionic liquid to coordination polymer demonstrated here is accompanied by changes in intramolecular and intermolecular bonding, concomitant with drastic changes in the physical properties of the materials. Furthermore, the ionic liquid can be recovered from the coordination polymer via solvent treatment. Synthesis of porous materials by chemical reactions of ionic liquids has been reported,[13] demonstrating the advantage of using ionic liquids as a precursor. The photofabrication method presented in this study enables on-demand preparation of microporous coordination polymers from liquids, which may lead to various applications in the future. In addition, this study opens new avenues to functional amorphous coordination polymers. The amorphous coordination polymers may not be suitable for size selective gas separation, unlike crystalline porous coordination polymers. However, attempts to control porosity of the coordination polymer by using other ligands are underway in our laboratory.

Experimental Section

Thermogravimetric analyses were performed at a heating rate of 10 K min^{-1} under a nitrogen atmosphere using a Rigaku TG8120 thermal analyzer. Light irradiation was performed with a deep UV lamp (250 W) using USHIO SP-9 SPOT CURE. Gas adsorption-desorption properties of nitrogen, hydrogen, and carbon dioxide were measured using a BELSORP-max automatic gas adsorption apparatus (BEL Japan). Scanning electron microscopy (SEM) measurements were performed on a JEOL JSM-5510. Transmission electron microscopy (TEM) measurements were performed on a JEOL 2100F. TEM specimens were prepared by dropping an aqueous dispersion of a powdery sample on standard copper electron-microscope grids covered with carbon holey films. Ionic liquid 1″ (T_g = −65°C, determined by DSC) was prepared in 87% yield from the corresponding PF_6 salt by the method described in the literature.[3c] ^{1}H NMR (400 MHz, CD_3CN): δ = 0.85 (t, 3H, CH_3, J = 6.92 Hz), 1.25–1.53 (m, 12H,CH_2), 2.42 (t, 2H, J = 7.92 Hz, CH_2), 5.24 (s, 5H,Cp), 5.95–6.03 (m, 5H, Ar*H*); elemental analysis calcd (%) for $C_{23}H_{27}BN_4Ru$: C 58.61, H 5.77, N 11.89; found: C 58.57, H 5.54, N 12.06.

The amorphous coordination polymers were prepared as follows. The ionic liquids were sandwiched between two quartz plates and were irradiated with UV light for several hours. After the photoirradiation the powder samples that formed, were washed with methanol to remove the dissociated ligand. The rate of photoconversion was monitored by measuring ^{1}H NMR spectra of the samples dissolved in CD_3CN. Elemental analysis calcd (%) for $C_{36}H_{20}N_{16}B_4Ru_4$ (= $[C_9H_5BN_4Ru]_n$): C 38.46, H 1.79, N 19.94; found for **2**: C 38.36, H 1.34, N 18.74; found for **2′**: C 38.45, H 1.83, N 18.29; found for **2″**: C 39.20, H 1.86, N 18.85. The elemental analysis values are largely different from the values before photoirradiation (found for **1**: C 54.97, H 4.76, N 13.49; found for **1′**: C 52.57, H 4.03, N 14.54), which clearly indicates the dissociation of the arene ligands. The slightly smaller values of nitrogen might indicate slight decomposition of the cyano groups. Although **2** was amorphous, powder X-ray diffraction experiments showed that the solid contains a very slight crystalline component (Figure S7, supporting information). This was found to be a tetranuclear crystalline complex, formed at around the interface between the liquid and the air. The structure and properties of the complex, which does not exhibit nitrogen adsorption properties, will be reported elsewhere.

Acknowledgements

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Keywords: ruthenium • ionic liquids • coordination polymers • photochemical reaction • gas adsorption

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Entry for the Table of Contents

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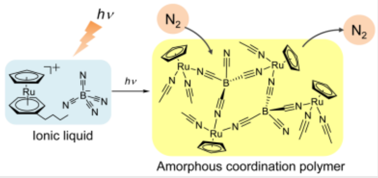
Ruthenium-containing organometallic ionic liquids with the $B(CN)_4$ anion were developed that generate amorphous coordination polymers upon UV irradiation. The photogenerated solids exhibited gas adsorption properties due to their microporous structure.



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Supporting Information

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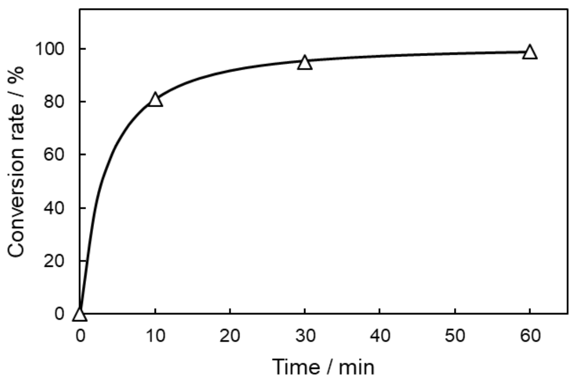

Figure S1. Time course of the conversion rate from ionic liquid **1** to coordination polymer **2**.

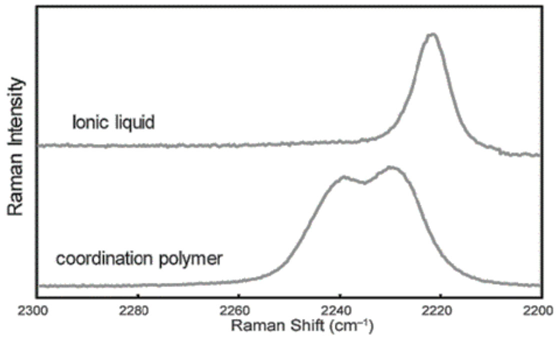

Figure S2. Raman spectra of ionic liquid **1** and coordination polymer **2** measured at room temperature (CN stretching vibration peaks, excitation wavelength: 532 nm).

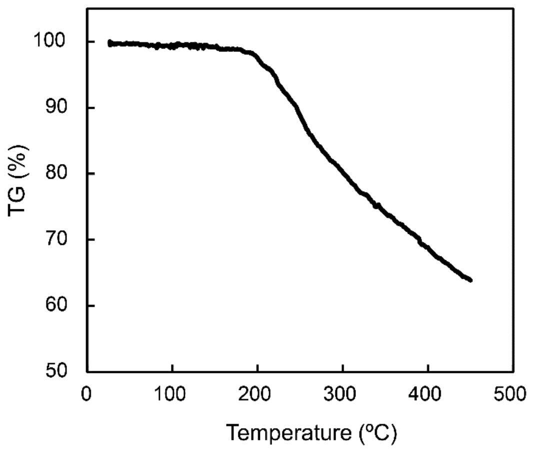

Figure S3. TG trace of **2** measured at 10 Kmin^{-1} under a nitrogen atmosphere.

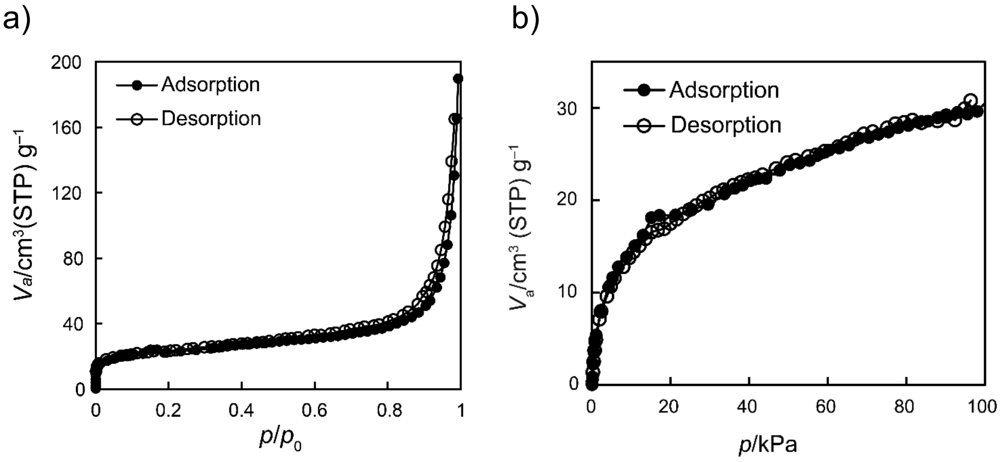

Figure S4. (a) N_2 and (b) H_2 adsorption–desorption isotherms of photogenerated coordination polymer **2′** at 77 K.

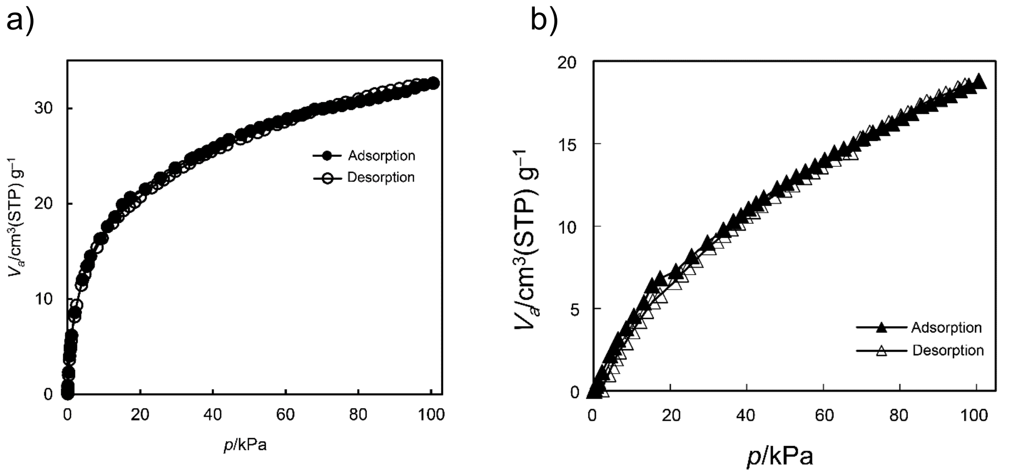

Figure S5. Gas adsorption–desorption isotherms of photogenerated coordination polymer **2**. (a) H_2 adsorption at 77 K and (b) CO_2 adsorption at 273 K.

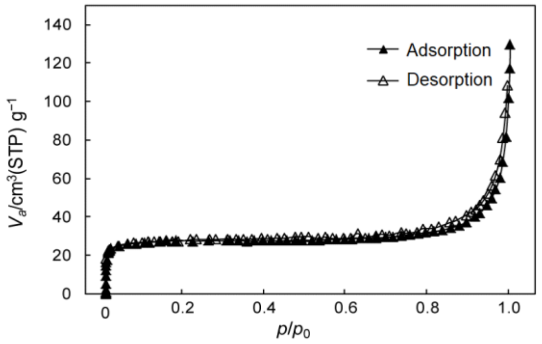

Figure S6. N_2 adsorption–desorption isotherms of photogenerated coordination polymer **2″** at 77 K.

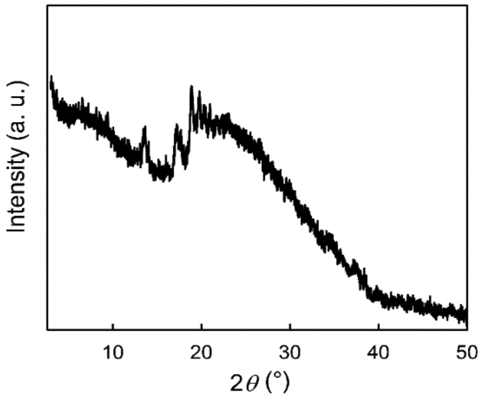

Figure S7. Powder X-ray diffraction pattern of **2** recorded at room temperature (magnified view).