

1,3,5-Tris(functionalised-phenylethynyl)benzene–metal complexes: synthetic survey of mesoporous coordination polymers and investigation of their carbonisation

Norifumi Kobayashi and Masashi Kijima*

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A series of multicoordinate 1,3,5-tris(functionalised-phenylethynyl)benzenes (**1–9**) was synthesised, and coordination polymers were constructed from these organic linkers and copper ions in high yields. The carbonisation of the linkers **1–9** afforded a microporous carbon that shows type I adsorption–desorption isotherm. Although most of the coordination polymers prepared in this study turned out to be low porous materials, the coordination polymer **7e** prepared from the reaction of 1,3,5-tris(4-carboxyphenylethynyl)benzene tripotassium salt (**K₃7**) and copper (II) nitrate was a microporous material in addition to the mesoporous materials (**7c** and **7d**) prepared from the reaction of **K₃7** with copper (II) acetate and copper (II) chloride, respectively. The carbonisation of the coordination polymers unexceptionally brought about an increase of micropore volume. A stepwise analysis of **7c** pyrolysed at 350 °C, 600 °C, and 900 °C revealed that the mesoporosity hardly changed upon heat-treatment, which demonstrates, in other words, that microporosity could be successfully added to the mesoporous coordination polymer through the carbonisation process.

Introduction

Porous materials¹ are generally classified into three groups, that is, carbon materials,² inorganic materials,³ and coordination polymers.⁴ In particular, porous carbon materials have uniquely electrical conductivity in addition to thermal, hydrothermal, and mechanical stabilities compared to those uncarbonised, and they are used for a wide variety of application purposes not only in hydrogen fuel storage,⁵ gas separation,⁶ water purification,⁷ catalysis or catalyst supports,⁸ but also in energy storage devices such as lithium ion secondary battery⁹ and electric double layer capacitor.¹⁰

A surface activation procedure of the carbon or carbon precursor has conventionally been used to produce activated carbons,¹¹ but it is hard to eliminate their inherancy of inhomogeneous pore distribution. On the contrary to the activation method, the template synthesis is a promising method for constructing ordered nano-porous carbon materials.¹² In this case, the specific space of porous inorganic materials such as zeolite has been utilised in porous carbon synthesis, but inevitably the process is a reverse transcription of the template structure, and the template must be removed by post-cleaning using hydrofluoric acid or alkaline. After all, the pore structure of carbon is dependent on the template, and the mass production is difficult for the reason of the strict synthetic and removal processes.

On the other hand, the porous metal–organic frameworks

(MOFs) also attract a profound research interest because of their shape-selective, predictable, topological architectures together with their homogeneous metal dispersion.¹³ It is attractive to introduce these features to the porous carbon materials.

To our knowledge, despite many reports on synthesis of microporous MOFs (microMOFs) has been made,^{13e,14} mesoMOF with permanent porosity exhibiting type IV adsorption–desorption isotherm has been reported only once.¹⁵ Hence, the synthesis of novel mesoMOFs and transformation from the MOFs to porous carbon are a great challenge in the field of chemistry of coordination polymers and carbon materials.

We have recently reported that the pyrolytic carbonisation of conjugated polymers having an alternative structure of the phenylene and carbon–carbon triple bond portions could afford microporous carbons in high yields above 80% under an argon flow.¹⁶ More recent reports have successfully demonstrated that rigid networks of poly(aryleneethynylene) can construct microporous materials.¹⁷ It is also reported that large molecules having sixfold phenyleneethynylene bonds such as hexakis(4-functionalised-phenylethynyl)benzenes¹⁸ or hexakis[4-(4'-functionalised-phenylethynyl)phenyl]benzenes¹⁹ could serve as guest-inclusion organic crystals directed to organic zeolites because their rigid and starburst like structures tend to prevent network interpenetration.

For the reasons stated above, it is thought that multicoordinate π -conjugated molecules are appropriate as a scaffold to construct novel mesoMOFs which can be carbonised with retaining the framework in consequence of their rigid structures and the higher carbon content than the general MOFs. In this study, we initially investigate what kind of π -conjugated organic linker that would be appropriate as a

Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan. Fax: +81 29 853 4490; Tel: +81 29 853 6905; E-mail:

kijima@ims.tsukuba.ac.jp

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pre-carbon material to construct the carbonised MOFs. Next we synthesised some multicoordinate linkers, 1,3,5-tris(functionalised-phenylethynyl)benzene derivatives, and their coordination polymers with copper salts. Last they were pyrolysed to investigate behaviors of the transformation from coordination polymers to porous carbonised materials.

Experimental

General method and instrumentations

Synthetic manipulations shown in Scheme 1 were performed under an argon atmosphere using a Schlenk glassware. The disk-pellet sample ($\phi = 13$ mm, *ca.* 50 mg) was prepared under a pressure of 3 MPa using a press unit (Hitachi). The pellet sample on a quartz boat was carbonised in a quartz tube by heating up from room temperature to 900 °C at a rate of 5 °C min⁻¹ under flowing argon with a furnace EKRO-12K (Isuzu), then allowed to cool to room temperature and stored in a desiccator.

IR and NMR spectra were recorded on a JASCO FT/IR 550 spectrophotometer and a JEOL FT-NMR (270 MHz) spectrometer, respectively. Elemental analyses were carried out with a Perkin-Elmer type 2400. Inductively coupled plasma (ICP) atomic emission spectroscopy were done on an ICAP 757 (Jarrell-Ash) plasma spectrometer. Thermal analyses were carried out by an Extra 6000 TG/DTA (Seiko) thermogravimetric analyser at a rate of 10 °C min⁻¹ except for hexakis(phenylethynyl)benzene (from 210 °C to 370 °C, 2 °C min⁻¹) under an argon atmosphere. X-ray diffraction (XRD) patterns were performed with a Rint 2100 (Rigaku) with a Cu-K α (1.6418 Å) radiation. Scanning electron microscopy (SEM) images were acquired with a JSM-5610 (JEOL).

BET surface area was estimated from the results of N₂ adsorption isotherm at 77 K measured with a SA 3100 (Coulter). The pore characterisations were also carried out by the α_s -plots for micropores and the DH method for mesopores, respectively.¹⁹ The subtracting pore effect (SPE) analysis of the α_s -plots provides the total surface area (A_{total}) from the slope of the narrow linear region around $\alpha_s = 0.5$, the external surface area (A_{ext}) from the slope of the linear region between $\alpha_s = 0.7$ and 1.1, using the Eq. (1). The total micropore volume (V_{micro}) is also obtained from the intercept of the latter straight line. Further, the average micropore width (w_α) can be evaluated from the A_{total} , A_{ext} , and V_{micro} according to the Eq. (2), assuming that the pore shape is slit-like.

$$S_{\text{total}} = 2.14 \times (\text{slope}) [\text{m}^2 \text{g}^{-1}] \quad (1)$$

$$w_\alpha = 2V_{\text{micro}} / (A_{\text{total}} - A_{\text{ext}}) [\text{nm}] \quad (2)$$

Materials

Triethylamine and THF were distilled after drying with CaH₂ or sodium, respectively, under an argon atmosphere. The other solvents and reagents commercially available were used without further purification. Hexakis(phenylethynyl)benzene,²¹ hexakis(4-cyanophenyl)benzene,¹⁹ 1,3,5-triethynylbenzene,²² and 4-(*tert*-butyldimethylsilyloxy)iodobenzene²³ were prepared according to the established procedure. 1,3,5-Tris(4-cyanophenylethynyl)benzene (1),²⁴ 1,3,5-tris(4-

pyridylethynyl)benzene (2),²⁵ 1,3,5-tris[4-(ethoxycarbonyl)phenylethynyl]benzene (6), 1,3,5-tris(4-carboxyphenylethynyl)benzene (H₃7)²⁶ have been known in the literatures.

Synthesis

1,3,5-Tris(5-pyrimidinylethynyl)benzene (3). To a mixture of CuI (49.5 mg, 0.260 mmol), Pd(PPh₃)₄ (300 mg, 0.260 mmol), 1,3,5-triethynylbenzene (1.30 g, 8.66 mmol), 5-bromopyrimidine (6.19 g, 39.0 mmol) were added Et₃N (15 mL) and THF (70 mL), and the mixture was stirred at 55 °C for 12 h and then 70 °C for 14 h. The reaction mixture was concentrated and extracted with CHCl₃. The organic layer was washed with H₂O and brine, and dried over Na₂SO₄. Recrystallization from CHCl₃-EtOAc-hexane gave **3** (3.13 g, 94.0% yield) as a white solid. ¹H-NMR (CDCl₃) δ 9.17 (s, 3H), 8.86 (s, 6H), 7.75 ppm (s, 3H); ¹³C-NMR (CDCl₃) δ 158.6, 157.1, 135.0, 123.1, 119.1, 93.7, 84.2 ppm; IR (KBr) ν 3033 (m), 2220 (w), 1542 (s), 1426 (s), 1406 (s), 877 (m), 631(m) cm⁻¹; Anal. Calcd for C₂₄H₁₂N₆·0.2EtOAc: C, 74.09; H, 3.41; N, 20.90. Found: C, 74.01; H, 3.59; N, 20.74.

1,3,5-Tris[4-(*tert*-butyldimethylsilyloxy)phenylethynyl]benzene (4). A mixture of CuI (23.8 mg, 0.125 mmol), Pd(PPh₃)₄ (144 mg, 0.125 mmol), 1,3,5-triethynylbenzene (625 mg, 4.16 mmol), 4-(*tert*-butyldimethylsilyloxy)iodobenzene (5.97 g, 18.8 mmol), and THF (40 mL) in Et₃N (10 mL) was stirred at 45 °C for 18 h. Hexane was added to the reaction mixture, and the separated solid was filtered out. The filtrate was subjected to column chromatography on silica gel eluted with hexane-CH₂Cl₂ (4:1) to give **4** (2.75 g, 85.9% yield) as a light yellow solid. 1.89 g of the overloaded iodide was recovered. ¹H-NMR (CDCl₃) δ 7.58 (s, 3H), 7.42 (d, *J* = 8.7 Hz, 6H), 6.83 (d, *J* = 8.7 Hz, 6H), 1.00 (s, 27H), 0.23 ppm (s, 18H); ¹³C-NMR (CDCl₃) δ 156.1, 133.4, 133.0, 124.1, 120.2, 115.5, 90.4, 86.9, 25.7, 18.3, -4.2 ppm; IR (KBr): ν 2929 (m), 2211 (w), 1604 (m), 1579 (m), 1507 (s), 1256 (s), 912 (s), 837 (s), 781 (m), 680 (w) cm⁻¹; Anal. Calcd for C₄₈H₆₀O₃Si₃: C, 74.95; H, 7.86; N, 0.00. Found: C, 74.94; H, 7.55; N, 0.00.

1,3,5-Tris(4-hydroxyphenylethynyl)benzene (H₃5). A mixture of **4** (4.08 g, 5.30 mmol), THF (25 mL), MeOH (100 mL), and KOH (1.40 g, 21.2 mmol) in H₂O (5 mL) was stirred at room temperature for 12 h. The reaction mixture was diluted with H₂O, and the organic solvents were evaporated. The aqueous residue was acidified with 0.5 M HCl and extracted with EtOAc. The organic layer was washed with H₂O and brine and dried over Na₂SO₄ to give **5** (2.26 g, 99.9% yield) as a light yellow solid. ¹H-NMR (DMSO-*d*₆) δ 10.05 (s, 3H), 7.61 (s, 3H), 7.46 (d, *J* = 8.6 Hz, 6H), 6.87 ppm (d, *J* = 8.6 Hz, 6H); ¹³C-NMR (DMSO-*d*₆) δ 158.2, 133.1, 132.4, 124.0, 115.7, 111.8, 91.4, 85.7 ppm; IR (KBr) ν 3336 (m), 2209 (w), 1606 (m), 1578 (s), 1509 (s), 1262 (m), 1220 (m), 1170 (m), 830 (s), 680 (w) cm⁻¹; Anal. Calcd for C₃₀H₁₈O₃·0.2H₂O: C, 83.78; H, 4.31; N, 0.00. Found: C, 83.59; H, 4.46; N, 0.14.

1,3,5-Tris(4-hydroxyphenylethynyl)benzene tripotassium salt (K₃5). A mixture of H₃5 (206 mg, 0.483 mmol) and CH₃OK (102 mg, 1.45 mmol) in MeOH 8 mL was concentrated to give K₃5 (256 mg, 98.1% yield) as a yellow-brown solid. ¹H-NMR (DMSO-*d*₆) δ 7.11 (s, 3H), 6.98 (d, *J* =

195 8.6 Hz, 6H), 6.06 ppm (d, $J = 8.6$ Hz, 6H); ^{13}C -NMR (DMSO- d_6) δ 173.4, 133.0, 128.3, 125.5, 119.3, 97.3, 96.0, 84.8 ppm; IR (KBr): ν 3434 (s), 2200 (m), 1596 (m), 1575 (s), 1498 (s), 1296 (s), 1167 (m), 841 (m) cm^{-1} ; Anal. Calcd for $\text{C}_{30}\text{H}_{15}\text{O}_3\text{K}_3 \cdot 6.5\text{H}_2\text{O}$: C, 54.77; H, 4.29; N, 0.00. Found: C, 55.04; H, 4.33; N, 0.02.

1,3,5-Tris(4-carboxyphenylethynyl)benzene

tripotassium salt (**K₃7**). A mixture of **H₃7** (800 mg, 1.57 mmol) and CH_3OK (330 mg, 4.70 mmol) in MeOH 120 mL was concentrated to give **K₃7** (980 mg, 100% yield) as a white solid. ^1H -NMR (CD_3OD) δ 7.96 (d, $J = 8.1$ Hz, 6H), 7.68 (s, 3H), 7.55 ppm (d, $J = 8.1$ Hz, 6H); ^{13}C -NMR (CD_3OD) δ 174.1, 139.3, 134.8, 132.0, 130.2, 125.48, 125.46, 91.5, 89.3 ppm; IR (KBr): ν 3372 (s), 2214 (w), 1603 (s), 1584 (s), 1540 (s), 1385 (s), 1279 (w), 842 (w), 786 (m) cm^{-1} ; Anal. Calcd for $\text{C}_{33}\text{H}_{15}\text{O}_6\text{K}_3 \cdot 3.83\text{H}_2\text{O}$: C, 57.13; H, 3.29; N, 0.00. Found: C, 57.19; H, 3.46; N, 0.31.

1,3,5-Tris(4-bromophenylethynyl)benzene (**8**).

A mixture of CuI (56.2 mg, 0.295 mmol), $\text{Pd}(\text{PPh}_3)_4$ (340 mg, 0.295 mmol), 1,3,5-triethynylbenzene (1.47 g, 9.82 mmol), 1-bromo-4-iodobenzene (25.0 g, 88.4 mmol), and THF (75 mL) in Et_3N (22 mL) was stirred at room temperature for 40 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 . The organic layer was washed with H_2O and brine, and subjected to column chromatography on silica gel eluted with hexane- CH_2Cl_2 (7:1) to give **8** (5.92 g, 98.1% yield) as a white solid. 16.3 g of the overloaded iodide was recovered. ^1H -NMR (CDCl_3) δ = 7.63 (s, 3H), 7.50 (d, $J = 8.4$ Hz, 6H), 7.37 ppm (d, $J = 8.4$ Hz, 6H); ^{13}C -NMR (CDCl_3) δ 134.0, 133.0, 131.6, 123.7, 122.9, 121.5, 89.6, 88.7 ppm; IR (KBr) ν 2955 (w), 2922 (w), 2857 (w), 2210 (w), 1589 (s), 1486 (s), 1070 (s), 1011 (s), 875 (m), 820 (s), 752 (m) cm^{-1} ; Anal. Calcd for $\text{C}_{30}\text{H}_{15}\text{Br}_3$: C, 58.57; H, 2.46; N, 0.00; Br, 38.97. Found: C, 58.27; H, 2.78; N, 0.00; Br, 38.24.

1,3,5-Tris[4-(dihydroxyboryl)phenylethynyl]benzene (**9**).

To a solution of **8** (200 mg, 0.325 mmol) in THF (12 mL) was added dropwise a hexane solution of *n*-BuLi (2.60 M, 750 μL , 1.95 mmol) at -78 °C. After stirring at -78 °C for 1 h and then at -20 °C for 1.5 h, to the resulting solution was added $\text{B}(\text{OMe})_3$ (435 μL , 3.90 mmol) at -78 °C. The resulting mixture was warmed to room temperature for overnight with stirring, and then hydrolysed with 2 M HCl at 0 °C. After evaporation of THF, the residue was extracted with EtOAc. The organic layer was washed with 2 M HCl, H_2O , and brine, and dried over Na_2SO_4 . After evaporation of EtOAc, the residue was triturated with CH_2Cl_2 and filtered. The solid was recrystallised from benzene- CHCl_3 -MeOH to give **9** (125 mg, 75.5% yield) as a light yellow solid. ^1H -NMR (DMSO- d_6) δ 8.20 (s, 6H), 7.84 (d, $J = 8.1$ Hz, 6H), 7.76 (s, 3H), 7.55 ppm (d, $J = 8.1$ Hz, 6H); ^{13}C -NMR (DMSO- d_6) δ 135.2, 134.2, 133.7, 130.3, 123.6, 123.0, 91.1, 88.1 ppm; IR (KBr) ν 3400

(s), 3075 (w), 2208 (w), 1604 (s), 1341 (s), 1016 (w), 834 (w), 749 (w) cm^{-1} ; Anal. Calcd for $\text{C}_{30}\text{H}_{21}\text{B}_3\text{O}_6$: C, 70.66; H, 4.15; N, 0.00. Found: C, 70.62; H, 4.45; N, 0.00.

Preparation of 7c (7·2Cu·K·2CH₃CO₂·MeOH). To a solution of **K₃7** (120 mg, 0.192 mmol) in MeOH (40 mL) was added dropwise a solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (105 mg, 0.576 mmol) in MeOH (25 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A blue precipitate was collected by filtration and evacuated at 80 °C for 12 h (135 mg, 85.5% yield). This compound was insoluble in common organic solvents such as DMAc and DMSO. IR (KBr) ν 3389 (m), 1695 (w), 1604 (s), 1578 (s), 1533 (s), 1411 (s), 1177 (w), 1098 (w), 1016 (w), 860 (m), 779 (m) cm^{-1} ; Anal. Calcd for $(\text{C}_{38}\text{H}_{25}\text{Cu}_2\text{O}_{11}\text{K})_n$: C, 55.40; H, 3.06; N, 0.00; Cu, 15.4. Found: C, 55.29; H, 3.25; N, 0.20; Cu, 16.3. Metal concentration analyses were performed by ICP analysis for all coordination polymers.

Preparation of 7d (7·1.5Cu·0.25KCl·1.5MeOH). To a solution of **K₃7** (120 mg, 0.192 mmol) in MeOH (40 mL) was added dropwise a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (98.2 mg, 0.576 mmol) in MeOH (5 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A blue precipitate was collected by filtration and evacuated at 80 °C for 12 h (114 mg, 88.6% yield). This compound is insoluble in most of solvents. IR (KBr) ν 3045 (m), 1695 (m), 1604 (s), 1580 (s), 1535 (m), 1411 (s), 1281 (w), 1176 (w), 1099 (w), 1017 (w), 859 (w), 779 (m) cm^{-1} ; Anal. Calcd for $(\text{C}_{138}\text{H}_{84}\text{ClCu}_6\text{O}_{30}\text{K})_n$: C, 61.89; H, 3.16; N, 0.00; Cl, 1.32; Cu, 14.24. Found: C, 61.88; H, 3.42; N, 0.50; Cl, 2.82; Cu, 14.3.

Preparation of 7e (7·1.5Cu·6H₂O). A solution of **K₃7** (70 mg, 0.112 mmol) in DMF/MeOH (7:1 v/v, 80 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (54.1 mg, 0.224 mmol) in DMF/MeOH (1:1 v/v, 4 mL) was carefully layered on the top of the **K₃7** solution, followed by layering 1 mL of the mixed solvent DMF/MeOH (2:1 v/v) of intermediate density. The mixture was allowed to stand for 10 days at room temperature. The mixture was heated to a refluxing temperature for 5 h and then slowly cooled to room temperature. A blue precipitate was collected by filtration and evacuated at 80 °C for 12 h (76.0 mg, 95.4% yield). This compound was insoluble in water and common organic solvents. IR (KBr) ν 3421 (s), 1604 (s), 1581 (s), 1537 (m), 1409 (s), 1177 (w), 1099 (w), 1017 (w), 861 (w), 780 (m) cm^{-1} ; Anal. Calcd for $(\text{C}_{66}\text{H}_{54}\text{Cu}_3\text{O}_{24})_n$: C, 55.76; H, 3.83; N, 0.00; Cu, 13.41. Found: C, 56.02; H, 3.84; N, 0.32; Cu, 14.9.

Results and discussion

Thermal Analysis of Organic Linkers

To select a thermally stable organic linker, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of multicoordinate frameworks of hexakis(phenylethynyl)benzene, hexaphenylbenzene, and 1,3,5-tris(phenylethynyl)benzene were performed and the results are shown in Figure 1. These compounds are highly symmetrical (D_{6h} or D_{3h}), which can support radial coordination-bonding sites to form a predictable network with cavity based on the multipoint cooperative interactions, and can make an orthogonal arrangement of the interactive benzene-centered moieties in the network.²⁷ Judging from their TGA and DTA traces, hexakis(phenylethynyl)benzene is not appropriate for an organic linker because the Bergman-type cyclisation²⁸ occurs with an intensive exothermic peak at about 295 °C, although it showed the high carbonised residual ratio at 900 °C (78%). Therefore, the multiple bonds of the molecule must have distance from each other to prevent the Bergman-type cyclisations in the pyrolytic process. In the case of the hexakis(4-cyanophenyl)benzene, the exothermic peak was scarcely observed, but it is also inadequate for an organic linker because thermal cracking of the phenyl-phenyl bonds occurred at around 550 °C, which was reflected in its relatively low carbonisation yield (49% at 900 °C). From this standpoint, the star-shaped 1,3,5-tris(4-cyanophenylethynyl)benzene could have an optimal structure. As a consequence, it showed the mild pyrolysis process similar to hexakis(4-cyanophenyl)benzene in addition to the high carbonisation yield equivalent to hexakis(phenylethynyl)benzene.

Synthesis of functionalised 1,3,5-tris(substituted-

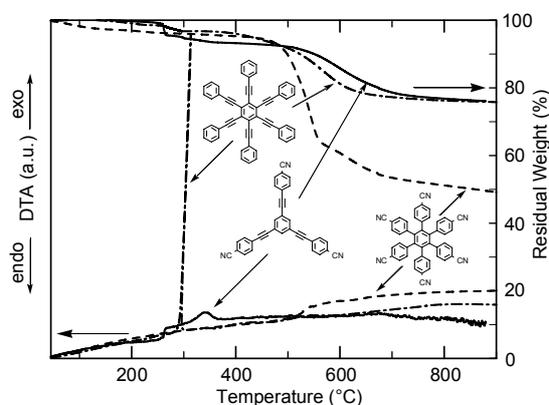
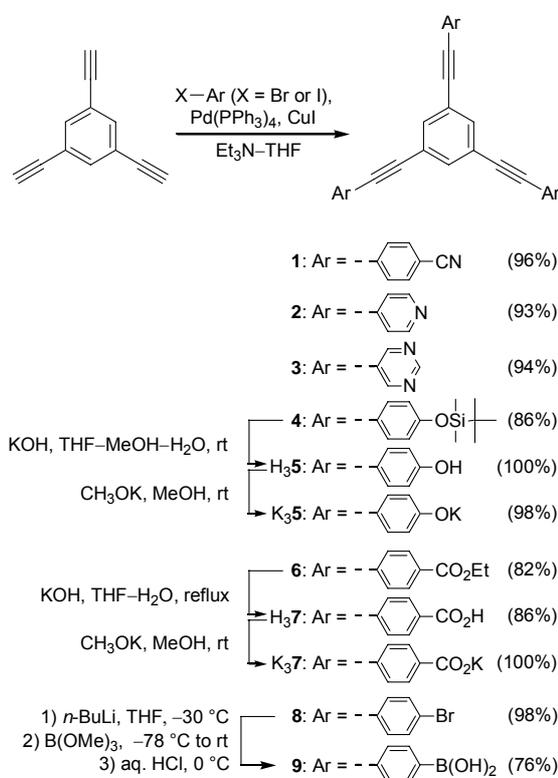


Fig. 1 TGA-DTA curves of hexakis(4-cyanophenyl)benzene, hexakis(phenylethynyl)benzene, and 1,3,5-tris(4-cyanophenylethynyl)benzene.

phenylethynyl)benzenes

Sonogashira coupling reaction is a powerful method for the synthesis of differentially functionalised 1,3,5-tris(phenylethynyl)benzenes because the reaction is tolerant of functional groups such as cyano and pyridyl groups.²⁹ 1,3,5-Triethynylbenzene was synthesised in 96% total yield by the reactions of 1,3,5-tribromobenzene with trimethylsilylacetylene and following desilylation. The Sonogashira coupling reaction of 1,3,5-triethynylbenzene with a functionalised phenylhalide in Et_3N -THF in the presence of

$\text{Pd}(\text{PPh}_3)_4$ and CuI was carried out to synthesise 1,3,5-tris(substituted-phenylethynyl)benzenes (Scheme 1). 4-Cyanophenyl (**1**), 4-pyridyl (**2**), 5-pyrimidinyl (**3**), 4-(*tert*-butyldimethylsilyloxy)phenyl (**4**), 4-(ethoxycarbonyl)phenyl (**6**), and 4-bromophenyl (**8**) groups were successfully introduced to 1,3,5-triethynylbenzene in high yields. The deprotection of the silyl ether of **4** and the ethyl ester of **6** with KOH gave 1,3,5-tris(4-hydroxyphenylethynyl)benzene (**H₃5**) and 1,3,5-tris(4-carboxyphenylethynyl)benzene (**H₃7**), respectively. Successively, **K₃5** and **K₃7** were produced quantitatively by treatment with potassium methoxide in methanol. The lithiation of **8** with *n*-BuLi followed by the reaction with $\text{B}(\text{OMe})_3$ gave 1,3,5-tris[4-(dihydroxyboryl)phenylethynyl]benzene (**9**). The linkers, **1**, **2**, **3**, **K₃5**, **H₃7**, **K₃7**, and **9**, synthesised in this section are subjected to reaction with metal ions to form 2- or 3-dimensional coordination polymers.



Scheme 1 Syntheses of functionalised 1,3,5-tris(substituted-phenylethynyl)benzenes.

Carbonisation of organic linkers

To investigate the carbonisation behavior of the organic linkers themselves, the compounds were carbonised by heating up from room temperature to 900 °C at a rate of 5 °C min^{-1} under flowing argon in a furnace, and then the surface analysis of the carbonised samples was carried out by N_2 adsorption method. The N_2 adsorption isotherms and the surface analysis data of the carbonised 1,3,5-tris(substituted-phenylethynyl)benzenes (**C-1-C-9**) are summarised in Figure 2 and Table 1. All isotherms of **C-1-C-9** show characteristic

of type I according to IUPAC classification.³⁰ The surface analysis data suggests that **C-1–C-9** are microporous materials with average pore widths (w_a) of ca. 0.7 nm estimated from the α_s plot by SPE method³¹ and have little meso- and macropores. The carbonisation yields of **1–9** were moderately high in the range of 53–83%. Brunauer–Emmett–Teller (BET) surface areas (A_{BET}) of **C-1–C-9** were scattering between 67 and 1040 m² g⁻¹. Since polymers have generally been used as starting substances of carbon materials, it is interesting that such small-molecules show the high carbonisation yields and lead to the carbonaceous materials with high surface areas. Annealing at 900 °C is effective to develop microporosity in

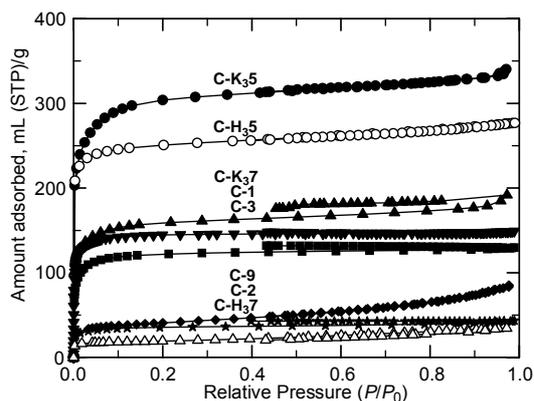


Fig. 2 Adsorption isotherms of nitrogen at 77 K for the carbonised (C-) 1,3,5-tris(substituted-phenylethynyl)benzenes (**1–9**).

Table 1 Surface parameters of C-1,3,5-tris(substituted-phenylethynyl)benzenes^a

sample	yield (%)	A_{BET}^b (m ² g ⁻¹)	V_{total}^c (mL g ⁻¹)	V_{micro}^d (mL g ⁻¹)	$V_{\text{meso}}/V_{\text{total}}^e$ (%)	w_a^f (nm)
1	82	495	0.23	0.22	1.2	0.72
2	84	113	0.068	0.040	0.9	0.85
3	70	459	0.20	0.19	0	0.74
H ₃ 5	59 ^g	840	0.43	0.37	7.0	0.64
K ₃ 5	56 ^g	1040	0.59	0.45	6.5	0.78
H ₃ 7	53 ^g	67	0.054	0.025	38	0.68
K ₃ 7	53 ^g	534	0.30	0.23	8.3	0.72
9	77	150	0.13	0.048	37	0.71

^a All the samples were carbonised by heating from r.t. to 900 °C at a heating rate of 5 °C min⁻¹. ^b The surface area was estimated by the Brunauer–Emmett–Teller (BET) method. ^c The total pore volume was estimated from the maximum adsorbed amount of N₂ in the adsorption isotherm. ^d The micropore volume was estimated by the α_s method. ^e The mesopore ratio was estimated by the Dollimore–Heal (DH) method. ^f The average micropore width was determined by the α_s plot and the SPE analysis. ^g Annealed at 900 °C for 3 h.

particular in the case of **C-5** and **C-7** but is accompanied with a considerable mass loss, which could be related to the degree of conversion from the amorphous carbon network material to the carbonised material that consists of the basic structure unit of carbonaceous layers.^{16a} **C-H₃7**, **C-2** and **C-9** showed low surface areas, which is probably due to an intermolecular filling of the carbon precursors with softening properties during the pyrolysis. On the contrary, the potassium salts, **C-K₃5** and **C-K₃7**, showed relatively high surface areas, because **K₃5** and **K₃7** were rigid solids with ionic interaction and, successively, K sublimed at around 760 °C after hardening of the carbonaceous precursors.

Synthesis and carbonisation of coordination polymers

In order to narrow down the specific conditions for obtaining permanent porous coordination polymers by solution reaction, in the beginning a variety of coordination polymers was prepared by a combinatorial reaction of the multicoordinated 1,3,5-tris(phenylethynyl)benzene derivatives with common transition metal salts such as Cu(CH₃CO₂)₂, CuCl₂·2H₂O, Cu(NO₃)₂·3H₂O, Ni(CH₃CO₂)₂·4H₂O, Ni(NO₃)₂·6H₂O, and AgOTf. All metal–organic coordination polymers were prepared from the slow intermixing method³² or rapid mixing method described in the experimental section. Chemically inert solvents such as 1,4-dioxane and THF were preferentially used in the preparations. All the coordination polymers were dried in vacuum at 80 °C for 12 hours, and their empirical formulas of the complexes were estimated from the results of the elemental, ICP, and thermogravimetric analyses. The preparation conditions and the synthetic yields of **2a–7e** are listed in the left quarter of Table 2.³³ Majority of the coordination polymers were obtained in good yields over 80%. Considering the total yields (ca. 60%) from the starting 1,3,5-tribromobenzene, it could be said that the synthetic procedure of these complexes are satisfactory for mass production of the coordination polymers.

In order to trace variation of the porosity through the pyrolysis, surface analysis of the coordination polymers **2a–7e**, as-heat-treated carbonised samples, and acid-washed carbonised **C-2a–C-7e** was carried out by N₂ adsorption method. The yields in each process and the extracted data on the surface analysis are summarised in the right three quarters of Table 2. Since the carbonised materials listed in Table 2 are basically microporous solids with mesoporosity in some degree, each adsorption volume such as V_{micro} and V_{meso} is roughly forecasted from the A_{BET} and the mesopore ratio ($V_{\text{meso}}/V_{\text{total}}$). Most of the coordination polymers were low porous materials showing small A_{BET} below 50 m² g⁻¹, which suggests that it is hard to keep the network structure on the occasion of solvate removal.^{14e,34} Generally, MOFs constructed from a larger ligand tend to be less stable.^{13c} Hence, utilisation of a strong metal–linker bond is desirable to form a variety of MOFs with a stable porous structure.³⁵ Actually, **7c–7e** prepared from the conjugated carboxylate linker **K₃7** with copper ions had considerable permanent total pore volumes (V_{total}), 0.261, 0.469, and 0.266 mL g⁻¹, respectively, which suggests that a large linker **7**, 1,3,5-tris[4-carboxyphenylethynyl]benzene, is notably adapted to construct stable MOFs.

Table 2 Preparations of coordination polymers, and surface parameters of the complexes, carbonised samples acid-washed carbons

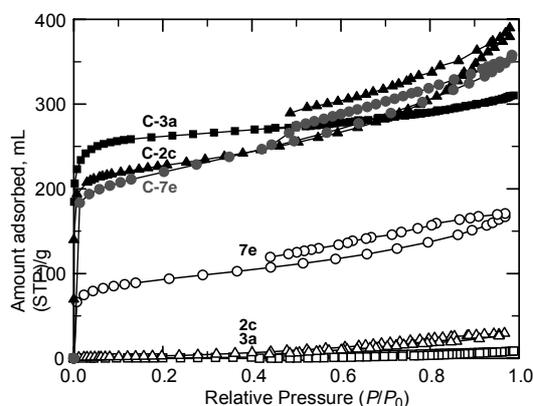
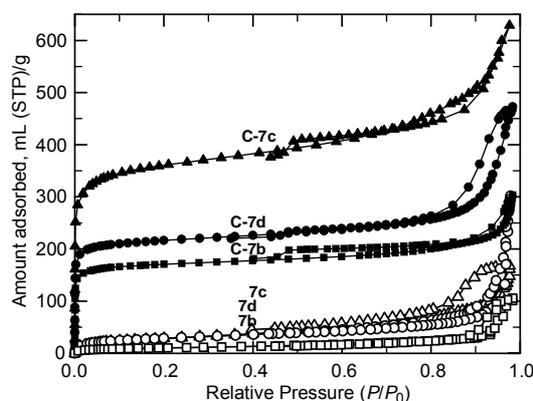
synthesis				complex (2a–7e)			as-prepared carbon ^c			acid-washed carbon (C-2a–C-7e)		
linker	metal salt	solvent ^a	yield (%)	complex	$A_{\text{BET}}/ \text{m}^2 \text{g}^{-1}$	$V_{\text{total}}^b/ \text{mL g}^{-1}$	carbonisation yield (%)	$A_{\text{BET}}/ \text{m}^2 \text{g}^{-1}$	$V_{\text{meso}}/V_{\text{total}}^d$ (%)	acid-washed yield (%)	$A_{\text{BET}}/ \text{m}^2 \text{g}^{-1}$	$V_{\text{meso}}/V_{\text{total}}^d$ (%)
2	Cu(CH ₃ CO ₂) ₂	diox	96	2a	2	0.012	51	434	3.2	74	453	17
2	CuCl ₂ ·2H ₂ O	diox	84	2b	7	0.037	65	568	14	68	624	9.4
2	Cu(NO ₃) ₂ ·3H ₂ O	diox–THF	60	2c	12	0.046	35	343	50	46	780	23
3	CuCl ₂ ·2H ₂ O	diox	85	3a	2	0.013	47 ^e			53	910	11
H ₃ 7	Cu(NO ₃) ₂ ·3H ₂ O	diox–THF	92	7a	15	0.052	69	552	9.4	78	584	30
H ₃ 7	Cu(CH ₃ CO ₂) ₂	diox	88	7b	37	0.164	60 ^e			78	584	30
K ₃ 7	Cu(CH ₃ CO ₂) ₂	MeOH	86	7c	105	0.261	68 ^e	724	38	67	1250	30
K ₃ 7	CuCl ₂ ·2H ₂ O	MeOH	89	7d	104	0.469	67 ^e	600	48	70	736	50
K ₃ 7	Cu(NO ₃) ₂ ·2H ₂ O	DMF–MeOH	95	7e	444	0.266	63	586	34	68	747	27

^a diox = 1,4-dioxane. ^b Estimated from the maximum adsorbed volume. ^c All the samples were treated at a heating rate of 5 °C min⁻¹ to 900 °C. ^d Estimated by the DH method. ^e Annealed at 900 °C for 3 h.

After the carbonisation of **2a–7e**, the as-heat-treated materials were washed with 8 M HNO₃ to remove the isolated copper that was sintered on the surface during pyrolysis, affording the acid-washed carbons, **C-2a–C-7e**. Removal of the sintering metal on the surface by the posttreatment was confirmed by disappearance of the XRD diffraction peaks of the metal. The difference between the A_{BET} of the acid-washed carbonised materials and those simply estimated from the A_{BET} of the as-heated samples and the yields of acid-washing (shown in Table 2) suggests the presence of a considerable amount of metal included in the materials.

For representative example, N₂ adsorption isotherms of the low-porous coordination polymers **2c**, **3a**, microporous MOF **7e**, and their acid-washed carbonised samples **C-2c**, **C-3a**, **C-**

7e are depicted in Figure 3. The A_{BET} of **C-2c**, **C-3a**, and **C-7e** (780, 910, and 747 m² g⁻¹) were considerably larger than those of **2c**, **3a**, and **7e** (12, 2, and 333 m² g⁻¹). The increase of A_{BET} is considered to be reasonable, because **2**, **3**, and K₃7 (the linkers of **2c**, **3a**, and **7e**, respectively) were pyrolysed to a microporous carbon as shown in Figure 2 and Table 1. Nevertheless, it should be noted that the A_{BET} of all the acid-washed carbonised samples **C-2a–C-7e** (Table 2) were larger than those of corresponding carbonised linkers (Table 1). Hence, constructing a coordination network in advance must be available to prepare a porous carbon with a high porosity, even if the coordination polymer is low-porous or nonporous. On the other hand, the mesopore volumes (V_{meso}) of **2c**, **3a**, and **7e** (0.036, 0.012, and 0.078 mL g⁻¹) were almost


Fig. 3 N₂ adsorption isotherms of the coordination polymers (low porous **2c**, **3a**, microporous **7e**), and their carbonised (C-) samples.

Fig. 4 N₂ adsorption/desorption isotherms of the mesoporous coordination polymers and their carbonised samples.

460 equivalent to the V_{meso} of their carbonised samples, **C-2c**, **C-3a**, and **C-7e** (0.14, 0.055, and 0.15 mL g⁻¹). In the P/P_0 range of 0.4–1, the shape of isotherms of all samples before and after carbonisation is similar to each other, which indicates that the coordination polymers retain the meso- and

465 macroporosity through the pyrolysis. Origin of the mesoporosity must be interspaces of aggregated nanoparticles as well as mesoporous polymer gels and carbonised ones.³⁶

In this work, three mesoporous coordination polymers, **7b**, **7c**, and **7d**, were obtained by the solution reaction of **7** with copper salts. The N₂ adsorption isotherms of **7b**, **7c**, and **7d** are shown in Figure 4 together with the acid-washed carbonised samples **C-7b**, **C-7d** and **C-7c**. In analogy with the low-porous coordination polymers, increases of V_{micro} and retainment of the mesoporous features were observed through the carbonisation with no exceptions. Exhibiting the steep N₂ uptakes at a high relative pressure (P/P_0) and the hysteresis loop extending from 0.8 to 1 in P/P_0 provides an evidence of existence of large mesopores. As a consequence, atypical porous carbons that have both of the mesoporosity of the coordination polymers and the microporosity of carbonised organic linkers were created. The V_{total} of **C-7b**, **C-7d** and **C-7c** came to 0.47, 0.98, 0.74 mL g⁻¹, respectively. These values are comparable to the porosity of carbon gels³⁶ which are a representative advanced mesoporous carbon.

485 Pyrolytic carbonisation behavior of mesoporous coordination polymer

In order to confirm that the mesoporosity of the carbonised coordination polymers **C-7b–d** were derived from those of pre-carbonised ones, a stepwise pyrolysis of **7c** that showed type IV adsorption–desorption isotherm was performed at 350 °C (**7c(350)**), 600 °C (**7c(600)**), and 900 °C (**7c(900)**). Their surface analyses by N₂ adsorption method, XRD, and SEM were carried out in this section.

The N₂ adsorption–desorption isotherms are shown in Figure 5, and the surface parameters are listed in Table 3. The specific surface areas monotonically increased in sequence of **7c** < **7c(350)** < **7c(600)** < **7c(900)** < **7c(900,3h)** as raising the heat treatment temperature. In the case of pyrolysis of conjugated polymers that have carbon–carbon triple bond, a

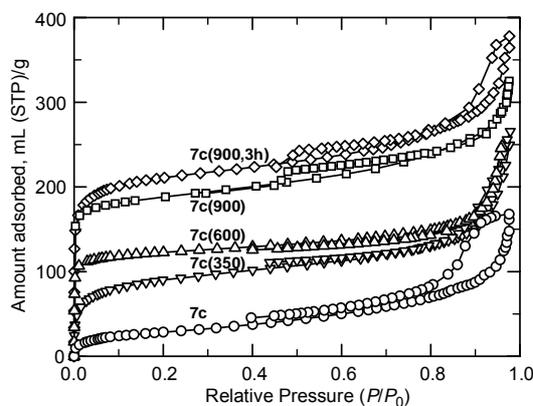


Fig. 5 N₂ adsorption/desorption isotherms of the mesoporous coordination polymer **7c** and the heat-treated samples at 350, 600, 900 °C, and 900 °C for 3 h.

Table 3 Surface parameters of **7c**, heat-treated samples, and acid-washed **C-7c**^a

temperature (°C)	$A_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{total}}/\text{mL g}^{-1}$	$V_{\text{micro}}/\text{mL g}^{-1}$	$V_{\text{meso}}/\text{mL g}^{-1}$	w_{α}/nm
900 ^b	1250	0.98	0.22	0.30	0.74
900 ^c	724	0.59	0.27	0.22	0.73
900	637	0.51	0.23	0.15	0.61
600	419	0.38	0.16	0.19	0.65
350	320	0.41	0.11	0.20	1.0
80 ^d	105	0.26	0.057	0.19	NA ^e

^a All the samples were treated at a heating rate of 5 °C min⁻¹. The V_{total} was estimated from the maximum adsorbed volume, and the V_{meso} was estimated by the DH method. The V_{micro} and w_{α} were determined by the α_s plots. ^b **C-7c**, the acid-washed carbon obtained from **7c(900,3h)**. ^c Annealed at 900 °C for 3 h. ^d **7c**, as-prepared complex. ^e Not applicable.

500 specific surface area begins to increase when the temperature is above 500 °C,³⁷ which is different from the tendency observed in **7c**. TG/DTA of **7c** (shown in ESI Figure S4) showed an exothermal peak accompanied by a mass loss at around 300 °C, which is due to decomposition or elimination

505 of the counter acetate anion. Therefore, the unexpected increase of the A_{BET} of **7c** when heat-treated at 350 °C (**7c(350)**) could be due to desorption of the acetate anion from the original building construction. On the contrary, the V_{meso} of **7c** (ca. 0.2 mL g⁻¹) remained unchanged during the heat-treatment from the starting temperature to 900 °C. These results mean that the mesoporosity of the mesoporous coordination polymer was kept during the process of transforming to a microporous carbon by heat-treatment.

The generation process of the microporosity and the 515 thermal behavior of the inclusion metal are traced by XRD analysis. The XRD patterns of the coordination polymer **7c**, the heat-treated samples at different temperatures, and the

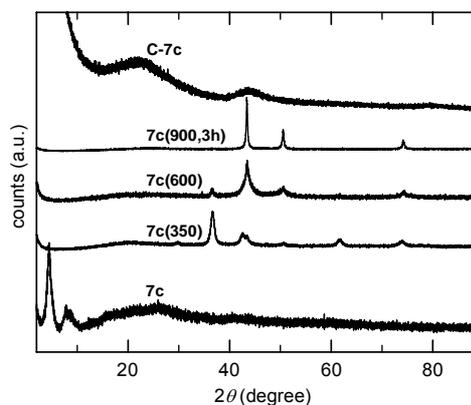


Fig. 6 XRD patterns of **7c**, heat-treated samples, and the acid-washed **C-7c**.

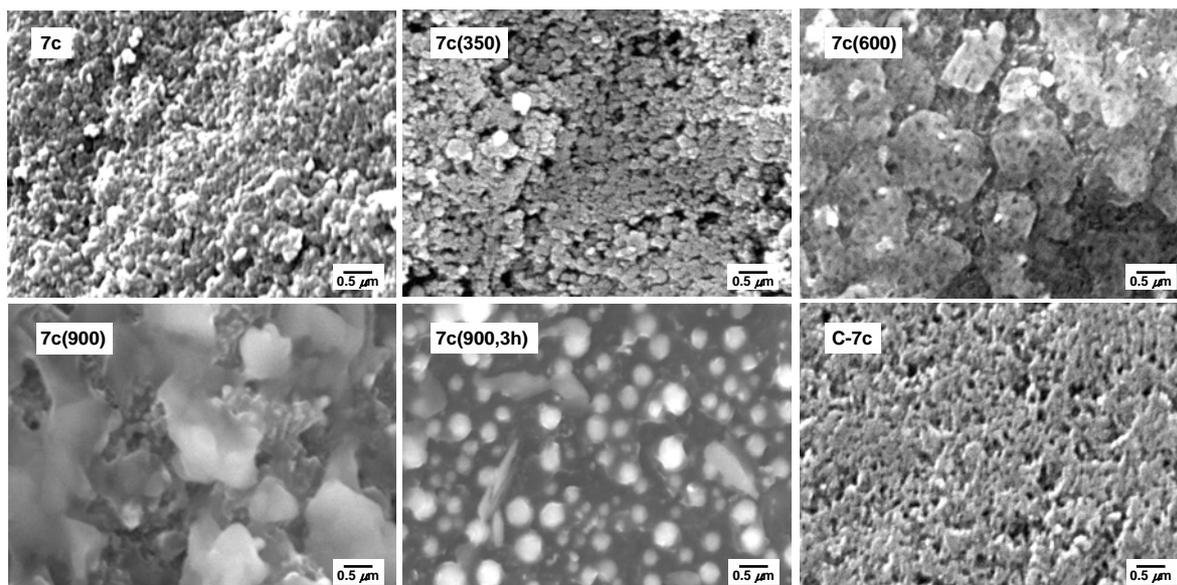


Fig. 7 SEM images of **7c**, the heat-treated samples, and the acid-washed **C-7c**.

acid-washed carbonised sample **C-7c** are shown in Figure 6. The coordination polymer **7c** has diffraction peaks at $2\theta = 4.5^\circ$ and 7.9° , which suggests that **7c** has a periodic structure with 2.0 and 1.0 nm distances as well as the microporous carbon synthesised by a template method.³⁸ The original diffraction peaks were completely lost under the heat treatment by 350 °C. At the same time, peaks of isolated copper (I) indexing Cu_2O newly appeared in **7c(350)**. The periodic microporous structure of **7c** could be disarranged by the increase of microporosity with the elimination of acetate during the pyrolysis. In the case of **7c(600)**, diffraction peaks of copper (0) appeared instead of the peaks of Cu_2O , which was attributed to reduction by carbon. The Cu peaks became sharper by the heat-treatment at 900 °C, which indicates that the particle size of the isolated metal grows larger. In the case of **C-7c**, the peaks of isolated copper observed in **7c(900,3h)** completely disappeared by leaching with nitric acid, and the broad peaks of carbon became apparent. Dimensions of the basic structure unit of carbon perpendicular and parallel to the basal plane and graphitic interlayer spacing were estimated from the (002) and (110) diffraction peaks by means of the Bragg formula and Scherrer equation³⁹ to be 1.6 nm (L_c), 2.5 nm (L_a), and 0.40 nm (d_i), respectively. The large d_i and small L values for **C-7c** are comparable to the hard carbon derived from the conjugated polymers^{16,34} and are different from graphitic materials such as carbon black.⁴⁰ Additionally, the acid-washed **C-7c** must include a highly dispersed copper, since the presence of copper (0.63 wt%) in **C-7c** was confirmed by ICP analysis despite XRD peaks of Cu were not observed.

At the last, the change of the surface morphology is checked by SEM. Figure 7 shows the SEM images of the coordination polymer **7c**, the heat-treated samples at different temperatures, and the acid-washed **C-7c**. The surface morphology of **7c** suggests presence of aggregates consisted

of particles having an average diameter of *ca.* 100 nm. The mesopores that should be interspaces between the aggregated particles are observed as countless black dots with a hole diameter smaller than 50 nm. The nano-particles seem to be gradually agglomerated as raising the heat-treated temperatures, and the size of the agglomerations observed in **7c(600)** came to the range of micron scales. The agglomeration is due to leaching out of the metal salt and following metalation on the surface, and the black dots can be observed unchanged. After the agglomeration, a thin layer metal covered the surface of **7c(900)**, and successively the sintering metal grew to about 250 nm-sized particles on the surface of **7c(900,3h)**. The surface of **C-7c** renovated by acid-washing using nitric acid showed a morphology similar to those observed in **7c** and **7c(350)**. This result supports that the mesoporosity of **7c** is hardly changed by the pyrolysis process which has already been observed in the N_2 adsorption analysis (Figure 5 and Table 3).

Conclusion

In this paper, we have demonstrated a novel strategy to prepare porous carbons from coordination polymers. For this purpose, we initially explored a thermally stable organic linker, and found that 1,3,5-tris(phenylethynyl)benzene derivatives could be carbonised in a high yield through a mild pyrolytic process without bringing about rapid and large structural changes. Then various types of 1,3,5-tris(functionalised-phenylethynyl)benzenes **1-9** were synthesised, and successively reacted with metal ions to construct coordination polymers. Although most of the coordination polymers synthesised by the solution reaction method are low porous materials, those synthesised from tricarboxy $\text{K}_3\text{7}$ as the linker exceptionally show either microporosity or mesoporosity.. Nevertheless, the

coordination polymers can be transformed to microporous carbons by pyrolysis without exception even if the pre-carbon materials are low-porous or nonporous, because the organic linkers **1–9** themselves can be converted to microporous carbons by pyrolysis. Consequently, the carbonised coordination polymers have higher porosity than the carbonised organic linkers. On the other hand, it was found that mesoporosity of the coordination polymers are hardly changed by the pyrolytic processes. Thus, it is realised that mesoporous coordination polymers can be converted to mesoporous carbons with microporosity.

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