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1,3,5-Tris(functionalised-phenylethynyl)benzene–Metal Complexes: Synthetic Survey of Mesoporous Coordination Polymers and Investigation of Their Carbonisation

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Electronic Supplementary Information

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Materials

1,3,5-Tris(trimethylsilylethynyl)benzene. A mixture of CuI (182 mg, 0.954 mmol), $PdCl_2(PPh_3)_2$ (670 mg, 0.954 mmol), 1,3,5-tribromobenzene (10.0 g, 31.8 mmol), and trimethylsilylacetylene (12.5 mL, 127 mmol) in Et_3N (175 mL) was stirred at 65 °C for 16 h. Hexane was added to the reaction mixture, and subjected to short path column chromatography on silica gel. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane to give 1,3,5-tris(trimethylsilylethynyl)benzene (11.2 g, 96.4% yield) as a light yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.49 (s, 3H), 0.23 (s, 27H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ134.8, 123.6, 103.1, 95.6, −0.0.

1,3,5-Triethynylbenzene. A mixture of 1,3,5-tris(trimethylsilylethynyl)benzene (10.3 g, 27.8 mmol), THF (120 mL), MeOH (35 mL), and K_2CO_3 (461 mg, 3.34 mmol) in H_2O (7 mL) was stirred at room temperature for 6 h and then H_2O was added to the reaction mixture. After evaporation of organic solvents, the aqueous residue was extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine and dried over Na_2SO_4 to give 1,3,5-triethynylbenzene (4.18 g, 99.5% yield) as a white solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ135.4, 122.7, 81.5, 78.5.

1,3,5-Tris(4-cyanophenylethynyl)benzene (1). A mixture of CuI (38.0 mg, 0.200 mmol), $Pd(PPh_3)_4$ (231 mg, 0.200 mmol), 1,3,5-trietynylbenzene (1.00 g, 6.66 mmol), 4-bromobenzonitrile (5.45 g, 30.0 mmol), and THF (50 mL) in Et_3N (15 mL) was stirred at 50 °C for 6 h. The reaction mixture was concentrated and extracted with CH_2Cl_2. The organic layer was washed with H_2O and subjected to column chromatography on silica gel eluted with CH_2Cl_2 to give **1** (2.90 g, 96.0% yield) as a white solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71 (s, 3H), 7.68 (d, J = 8.2 Hz, 6H), 7.61 (d, J = 8.2 Hz,

6H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ134.7, 132.0, 127.1, 123.3, 118.1, 112.0, 91.2, 89.1; IR (KBr) 2227, 1603, 1499, 835 cm^{-1}.

1,3,5-tris(4-pyridylethynyl)benzene (2). A mixture of CuI (49.5 mg, 0.260 mmol), $Pd(PPh_3)_4$ (300 mg, 0.260 mmol), 1,3,5-trietynylbenzene (1.30 g, 8.66 mmol), 4-bromopyridine hydrochloride (7.58 g, 39.0 mmol), and THF (70 mL) in Et_3N (15 mL) was stirred at room temperature for 12 h and then 50 °C for 12 h. The reaction mixture was concentrated and extracted with CH_2Cl_2. The organic layer was washed with H_2O and subjected to column chromatography on silica gel eluted with CH_2Cl_2–EtOAc (1:3) to give **2** (3.08 g, 93.1% yield) as a white solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.64 (d, J = 6.1 Hz, 6H), 7.75 (s, 3H), 7.39 (d, J = 6.1 Hz, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ149.7, 135.0, 130.4, 125.3, 123.2, 91.3, 88.1.

1,3,5-tris[4-(ethoxycarbonyl)phenylethynyl]benzene (6). A mixture of CuI (49.5 mg, 0.260 mmol), $Pd(PPh_3)_4$ (300 mg, 0.260 mmol), 1,3,5-trietynylbenzene (1.30 g, 8.66 mmol), Et_3N (15 mL), and ethyl 4-bromobenzoate (8.93 g, 39.0 mmol) in THF (70 mL) was stirred at 50 °C for 20 h. The reaction mixture was concentrated and extracted with $CHCl_3$. The organic layer was washed with H_2O and brine and subjected to column chromatography on silica gel eluted with hexane–CH_2Cl_2 (1:4) to give **6** (4.22 g, 82.0% yield) as a white solid. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 6H), 7.67 (s, 3H), 7.56 (d, J = 8.6 Hz, 6H), 4.37 (q, J = 7.1 Hz, 6H), 1.39 (t, J = 7.1 Hz, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ165.8, 134.4, 131.5, 130.2, 129.4, 127.0, 123.7, 90.2, 90.0, 61.2, 14.4.

1,3,5-tris(4-carboxyphenylethynyl)benzene ($H_3$7). A mixture of **6** (3.50 g, 5.89 mmol), KOH (11.5 g, 177 mmol) in H_2O (100 mL), and THF (240 mL) was stirred at refluxing temperature for 15 h. After evaporation of THF, the aqueous residue was acidified with 2 M HCl and extracted with EtOAc. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of EtOAc, the solid was triturated with MeOH and filtered to give H_3**7** (2.60 g, 86.4% yield) as a white solid. ^{1}H NMR (270 MHz, DMSO-d_6) δ13.1 (brs, 3H), 7.98(d, J = 8.0 Hz, 6H), 7.85 (s, 3H), 7.70 (d, J = 8.0 Hz,

6H); ^{13}C NMR (67.5 MHz, DMSO-d_6) δ166.4, 134.3, 131.6, 130.8, 129.4, 125.8, 123.2, 90.1, 89.7; IR (KBr) ν3004, 2210, 1687, 1605, 1418, 1277, 1174, 856, 769 cm^{-1}.

Preparation of 1·AgOTf·0.3PhH (1a). A solution of **1** (170 mg, 0.375 mmol) in benzene (40 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of AgOTf (96.3 mg, 0.375 mmol) in benzene (10 mL) was carefully layered on top of the **1** solution, followed by layering benzene (20 mL). The mixture was allowed to stand for 5 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A white precipitate was collected by filtration and evacuated at 80 °C for 12 h (236 mg, 85.8% yield).

Preparation of 2·2Cu(CH$_3$CO$_2$)$_2$·2.5H$_2$O (2a). A solution of Cu(CH$_3$COO)$_2$ (125 mg, 0.688 mmol) in 1,4-dioxane (20 mL) was added dropwise to a solution of **2** (350 mg, 0.918 mmol) in 1,4-dioxane (10 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (260 mg, 96.3% yield).

Preparation of 2·1.25CuCl$_2$·1.75H$_2$O (2b). A solution of CuCl$_2$·2H$_2$O (98.2 mg, 0.576 mmol) in H$_2$O/1,4-dioxane (1:40 v/v, 20 mL) was added dropwise to a solution of **2** (250 mg, 0.655 mmol) in 1,4-dioxane (40 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A pale blue precipitate was collected by filtration and evacuated at 80 °C for 12 h (333 mg, 84.0% yield).

Preparation of 2·2Cu(NO$_3$)$_2$·3diox H$_2$O (2c). A solution of **2** (90.0 mg, 0.236 mmol) in 1,4-dioxane (12 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of Cu(NO$_3$)$_2$·3H$_2$O (114 mg, 0.472 mmol) in 1,4-dioxane/THF (1:1 v/v, 8 mL) was carefully layered on top of the **2** solution, followed by layering 1,4-dioxane/THF (5:3 v/v, 8 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (146 mg, 59.7% yield).

Preparation of 2·1.75$NiCl_2$·0.5EtOH·1.5H_2O (2d). A solution of **2** (70 mg, 0.184 mmol) in EtOH (50 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $NiCl_2·6H_2O$ (87.2 mg, 0.367 mmol) in EtOH (5 mL) was carefully layered on top of the **2** solution, followed by layering EtOH (30 mL). The mixture was allowed to stand for 5 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A yellow precipitate was collected by filtration and evacuated at 80 °C for 12 h (99.2 mg, 94.9% yield).

Preparation of 2·1.67$Ni(NO_3)_2$·2.67THF (2e). A solution of **2** (90.0 mg, 0.236 mmol) in 1,4-dioxane (15 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $Ni(NO_3)_2·6H_2O$ (137 mg, 0.472 mmol) in THF (3 mL) was carefully layered on top of the **2** solution, followed by layering 1,4-dioxane/THF (3:2 v/v, 5 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (140 mg, 67.5% yield).

Preparation of 2·1.33AgOTf·2.67H_2O (2f). A solution of **2** (180 mg, 0.472 mmol) in benzene (20 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of AgOTf (121 mg, 0.472 mmol) in benzene (10 mL) was carefully layered on top of the **2** solution, followed by layering benzene (30 mL). The mixture was allowed to stand for 5 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A white precipitate was collected by filtration and evacuated at 80 °C for 12 h (276 mg, 100% yield).

Preparation of 2·1.5AcOAg (2g). A solution of CH_3COOAg (109 mg, 0.655 mmol) in acetic acid (5 mL) was added dropwise to a solution of **2** (250 mg, 0.655 mmol) in acetic acid (80 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A white precipitate was collected by filtration and washed by MeOH and then evacuated at 80 °C for 12 h (188 mg, 77.3% yield).

Preparation of 3·1.67$CuCl_2$·0.33diox·3.67H_2O (3a). A solution of $CuCl_2·2H_2O$ (444 mg, 2.60 mmol) in H_2O/1,4-dioxane (1:40 v/v, 20 mL) was added dropwise to a solution of **3** (250 mg, 0.650 mmol) in 1,4-dioxane (80 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (388 mg, 84.8% yield).

Preparation of 3·1.5Cu(CH_3CO_2)$_2$·H_2O (3b). A solution of $Cu(CH_3COO)_2$ (213 mg, 1.17 mmol) in 1,4-dioxane (20 mL) was added dropwise to a solution of **3** (300 mg, 0.780 mmol) in 1,4-dioxane (40 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature for 2 days. A green precipitate was collected by filtration and then evacuated at 80 °C for 12 h (221 mg, 41.9% yield).

Preparation of 3·1.5$CuCl_2$·diox·1.5H_2O (3c). A conc. HCl (1.54 mL, 18.5 mmol) and a solution of **3** (300 mg, 0.780 mmol) in 1,4-dioxane (80 mL) was added dropwise to a solution of $Cu(CH_3COO)_2$ (213 mg, 1.17 mmol) in 1,4-dioxane (120 mL) at refluxing temperature for 2 h and then slowly cooled to room temperature. A pale green precipitate was collected by filtration and then evacuated at 80 °C for 12 h (455 mg, 88.7% yield).

Preparation of 3·2.67Ni(NO_3)$_2$·2THF·1.33H_2O (3d). A solution of **3** (90.0 mg, 0.234 mmol) in 1,4-dioxane (25 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $Ni(NO_3)_2·6H_2O$ (272 mg, 0.937 mmol) in THF (3 mL) was carefully layered on top of the **2** solution, followed by layering 1,4-dioxane/THF (3:2 v/v, 5 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (188 mg, 77.1% yield).

Preparation of 3·2.67AgOTf·0.67diox (3e). A solution of **3** (100 mg, 0.260 mmol) in 1,4-dioxane/benzene (3:10 v/v, 65 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of AgOTf (272 mg, 0.937 mmol) in benzene (15 mL) was carefully layered on top of the **2**

solution, followed by layering 1,4-dioxane/benzene (1:10 v/v, 65 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A green precipitate was collected by filtration and evacuated at 80 °C for 12 h (234 mg, 83.2% yield).

Preparation of 5·3Ag·2AgOTf·MeOH (5a). A solution of K_3**5** (90.0 mg, 0.166 mmol) in MeOH/EtOH (1:1 v/v, 20 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of AgOTf (85.5 mg, 0.333 mmol) in EtOH (5 mL) was carefully layered on top of the **2** solution, followed by layering EtOH (5 mL). The mixture was allowed to stand for 3 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A dark green precipitate was collected by filtration and evacuated at 80 °C for 12 h (62.3 mg, 72.4% yield).

Preparation of 7·1.33Cu·0.67H·0.33NO_3·0.33diox·3H_2O (7a). A solution of H_3**7** (70.0 mg, 0.137 mmol) in 1,4-dioxane (14 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $Cu(NO_3)_2·3H_2O$ (663 mg, 0.274 mmol) in 1,4-dioxane/THF (5:1 v/v, 3 mL) was carefully layered on top of the **2** solution, followed by layering 1,4-dioxane/THF (10:1 v/v, 3 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to 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 (87.9 mg, 92.0% yield).

Preparation of 7·2Cu·CH_3CO_2·diox·0.5H_2O (7b). A solution of $Cu(CH_3COO)_2$ (160 mg, 0.882 mmol) in 1,4-dioxane (15 mL) was added dropwise to a solution of H_3**7** (150 mg, 0.294 mmol) in 1,4-dioxane (60 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 (204 mg, 87.6% yield).

Preparation of 7·2Ni·CH_3OO·5H_2 (7f). A solution of H_3**7** (80 mg, 0.157 mmol) in EtOH (20 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $Ni(CH_3COO)_2·4H_2O$ (78.0 mg, 0.313 mmol) in EtOH (5 mL) was carefully layered on top of the H_3**7**

solution, followed by layering EtOH (5 mL). The mixture was allowed to stand for 10 d at room temperature. The mixture was heated to 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 (98.1 mg, 80.9% yield).

Preparation of 7·2Ni·CH_3OO·5H_2O (7g). A solution of K_3**7** (70 mg, 0.112 mmol) in MeOH (30 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of $Ni(CH_3COO)_2·4H_2O$ (55.8 mg, 0.224 mmol) in MeOH (4 mL) was carefully layered on top of the K_3**7** solution, followed by layering MeOH (3 mL). The mixture was allowed to stand for 5 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A pale green precipitate was collected by filtration and evacuated at 80 °C for 12 h (78.0 mg, 80.9% yield).

Preparation of 7·2.5Ag·K·2H_2O (7h). A solution of K_3**7** (80 mg, 0.128 mmol) in MeOH (23 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of AgOTf (65.8 mg, 0.256 mmol) in MeOH (5 mL) was carefully layered on top of the K_3**7** solution, followed by layering MeOH (5 mL). The mixture was allowed to stand for 3 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A pale brown precipitate was collected by filtration and evacuated at 80 °C for 12 h (80.4 mg, 94.3% yield).

Preparation of 7·2Ag·1.5K·0.5CH_3OO·H_2O (7i). A solution of K_3**7** (120 mg, 0.192 mmol) in H_2O (20 mL) was placed in a long Pyrex tube with a 15 mm internal diameter. A solution of CH_3COOAg (96.1 mg, 0.576 mmol) in H_2O (20 mL) was carefully layered on top of the K_3**7** solution, followed by layering H_2O (5 mL). The mixture was allowed to stand for 3 d at room temperature. The mixture was heated to refluxing temperature for 5 h and then slowly cooled to room temperature. A pale brown precipitate was collected by filtration and evacuated at 80 °C for 12 h (155 mg, 97.0% yield).

Table S1. Preparations and Elemental Analysis Data of Metal−1,3,5-Tris(substituted-phenylethynyl)benzene Coordination Polymers.

synthesis					elemental analysis (%), found (calcd)				
linker	metal salt	solvent	chemical formula[b]	yield	C	H	N	Cl	M[a]
2	$Cu(CH_3CO_2)_2$	dioxane	**2**·2$Cu(CH_3CO_2)_2$·2.5H_2O (**2a**)	96.3	53.26 (53.23)	4.16 (4.08)	5.29 (5.32)		15.6 (16.1)
2	$CuCl_2·2H_2O$	dioxane	**2**·1.25$CuCl_2$·1.75H_2O (**2b**)	84.0	56.05 (55.81)	3.58 (3.21)	6.99 (7.23)	16.17 (15.25)	13.9 (13.7)
2	$Cu(NO_3)_2·3H_2O$	dioxane−THF	**2**·2$Cu(NO_3)_2$·3diox H_2O (**2c**)	59.7	44.86 (45.09)	3.62 (3.98)	9.18 (9.44)		13.2 (12.2)
3	$CuCl_2·2H_2O$	dioxane	**3**·1.67$CuCl_2$·0.33diox·3.67H_2O (**3a**)	84.8	43.25 (43.23)	2.99 (3.15)	11.64 (11.94)	19.79 (16.79)	15.5 (15.1)
3	$Cu(CH_3CO_2)_2$	dioxane	**3**·1.5$Cu(CH_3CO_2)_2$·H_2O (**3b**)	41.9	53.65 (53.39)	3.53 (3.44)	12.78 (12.45)		13.6 (14.1)
3	$Cu(CH_3CO_2)_2$	dioxane−HCl aq.	**3**·1.5$CuCl_2$·diox·1.5H_2O (**3c**)	88.7	47.26 (47.52)	2.92 (2.91)	13.01 (12.79)	16.81 (16.18)	14.2 (14.5)
H_3**7**	$Cu(NO_3)_2·3H_2O$	dioxane−THF	**7**·1.33Cu·0.67H·0.33NO_3·0.33diox·3H_2O (**7a**)	92.0	59.12 (59.17)	3.79 (3.52)	0.53 (0.67)		12.5 (12.2)
H_3**7**	$Cu(CH_3CO_2)_2$	dioxane	**7**·2Cu·CH_3CO_2·diox·0.5H_2O (**7b**)	87.6	59.31 (59.24)	3.54 (3.44)	0.08 (0.00)		15.3 (16.1)
K_3**7**	$Cu(CH_3CO_2)_2$	MeOH	**7**·2Cu·K·2CH_3CO_2·MeOH (**7c**)	85.5	55.29 (55.40)	3.25 (3.06)	0.20 (0.00)		16.3 (15.4)
K_3**7**	$CuCl_2·2H_2O$	MeOH	**7**·1.5Cu·0.25KCl·1.5MeOH (**7d**)	88.6	61.88 (61.89)	3.42 (3.16)	0.50 (0.00)	2.82 (1.32)	14.3 (14.2)
K_3**7**	$Cu(NO_3)_2·3H_2O$	DMF−MeOH	**7**·1.5Cu·6H_2O (**7e**)	95.4	56.02 (55.76)	3.84 (3.83)	0.32 (0.00)		14.9 (13.4)
2	$NiCl_2·6H_2O$	EtOH	**2**·1.75$NiCl_2$·0.5EtOH·1.5H_2O (**2d**)	94.9	51.18 (51.09)	3.47 (3.22)	6.62 (6.38)	18.87 (18.85)	15.6 (15.6)
2	$Ni(NO_3)_2·6H_2O$	dioxane−THF	**2**·1.67$Ni(NO_3)_2$·2.67THF (**2e**)	67.5	51.54 (51.51)	4.03 (4.17)	9.86 (10.10)		11.9 (11.1)
3	$Ni(NO_3)_2·6H_2O$	dioxane−THF	**3**·2.67$Ni(NO_3)_2$·2THF·1.33H_2O (**3d**)	77.1	36.68 (36.96)	2.86 (2.86)	15.06 (15.06)		15.7 (15.1)

H_3**7**	$Ni(CH_3CO_2)_2{\cdot}4H_2O$	EtOH	**7**·2Ni·CH_3OO·$5H_2O$ (**7f**)	80.9	54.04 (54.31)	4.05 (3.65)	0.28 (0.00)	16.1 (15.2)
K_3**7**	$Ni(CH_3CO_2)_2{\cdot}4H_2O$	MeOH	**7**·2Ni·CH_3OO·$5H_2O$ (**7g**)	78.0	54.02 (54.31)	3.97 (3.65)	0.11 (0.00)	15.2 (15.2)
1	AgOTf	PhH	**1**·AgOTf·0.3PhH (**1a**)	85.8	58.61 (58.59)	2.52 (2.31)	5.75 (5.73)	15.6 (14.7)
2	AgOTf	PhH	**2**·1.33AgOTf·2.67H_2O (**2f**)	100	44.01 (44.08)	2.72 (2.65)	5.08 (5.44)	19.2 (18.6)
2	AgOAc	AcOH	**2**·1.5AcOAg (**2g**)	77.3	56.57 (57.03)	3.15 (3.15)	6.91 (6.91)	25.5 (25.6)
3	AgOTf	dioxane–PhH	**3**·2.67AgOTf·0.67diox (**3e**)	83.2	31.15 (31.23)	1.68 (1.55)	7.72 (7.45)	25.1 (25.5)
K_3**5**	AgOTf	EtOH–MeOH	**5**·3Ag·2AgOTf·MeOH (**5a**)	72.4	30.68 (30.65)	1.74 (1.48)	0.08 (0.00)	45.7 (41.7)
K_3**7**	AgOTf	MeOH	**7**·2.5Ag·K·$2H_2O$ (**7h**)	94.3	47.42 (47.60)	2.18 (2.30)	0.13 (0.00)	32.6 (32.4)
K_3**7**	AgOAc	H_2O	**7**·2Ag·1.5K·0.5CH_3OO·H_2O (**7i**)	97.0	48.99 (49.24)	2.33 (2.25)	0.00 (0.00)	26.3 (26.0)

[a] Metal concentration analyses were performed by inductively coupled plasma (ICP). [b] diox = 1,4-dioxane.

Table S2. Surface Parameters of the Complexes, Carbonised Samples and Acid-Washed Carbons.

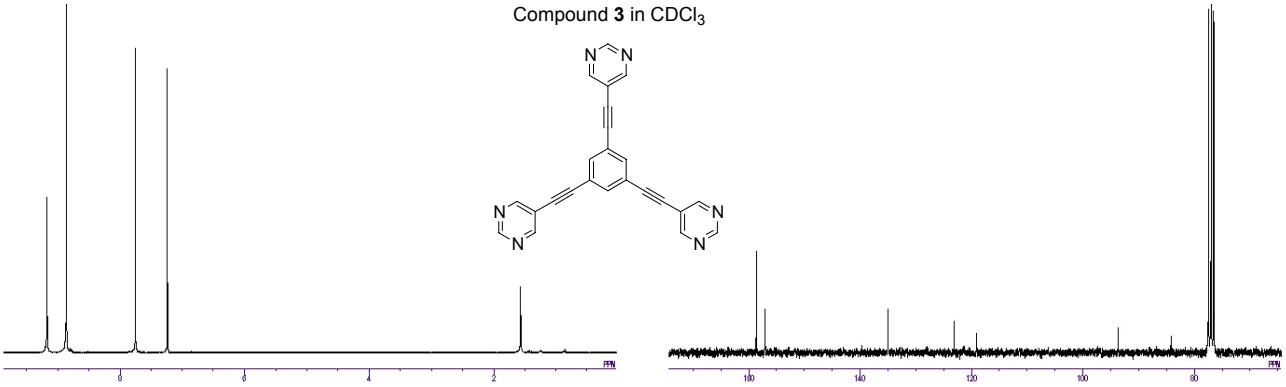
	complex			as-prepared carbon[a]			acid-washed carbon (**C-2a**–**C-7g**)	
complex	A_{BET} (m^2/g)	V_{total} (mL/g)[b]	carbonisation yield	A_{BET} (m^2/g)	V_{meso}/V_{total} (%)[c]	acid-washed yield	A_{BET} (m^2/g)	V_{meso}/V_{total} (%)[c]
2a	2	0.012	51	434	3.2	74	453	17
2b	7	0.037	65	568	14	68	624	9.4

2c	12	0.046	35	343	50	46	780	23
3a	2	0.013	47[d]			53	910	11
3c	20	0.079	49	536	3.3			
7a	15	0.052	69	552	9.4	78	584	30
7b	37	0.164	60[d]			78	584	30
7c	105	0.261	68[d]	724	38	67	1254	30
7d	104	0.469	67[d]	600	48	70	736	50
7e	333	0.266	63	586	34	68	747	27
2d	70	0.119	57	530	11	75	663	14
2e	15	0.042	42	483	35	85	423	19
3d	1	0.016	25	355	50	51	712	41
7f	30	0.041	58	555	27	68	730	25
7g	30	0.043	61	585	27	71	766	14
1a	8	0.040	76	10				
2f	6	0.022	65	382	14			
2g	2	0.015	82	308	116			
3e	28	0.070	54	351	7.9			
7h	54	0.113	73	388	34			
7i	4	0.032	74	443	12			

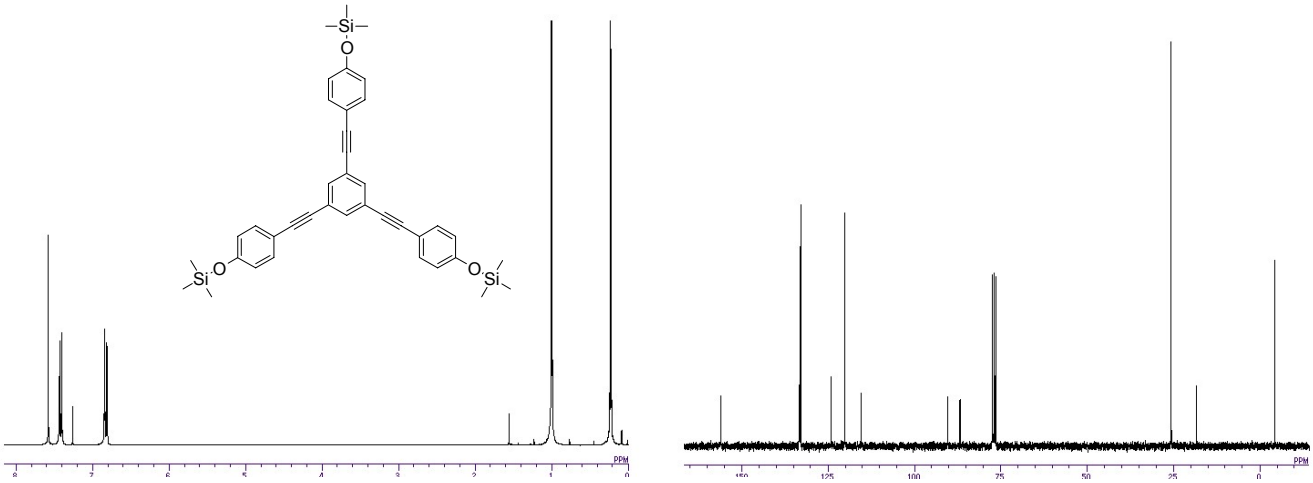
[a] All the samples were treated at a heating rate of 5 °C min^{-1} to 900 °C. [b] Estimated from the maximum adsorbed volume. [c] Estimated by the DH method. [d] Annealed at 900 °C for 3 h.

^{1}H NMR, ^{13}C NMR Spectra.

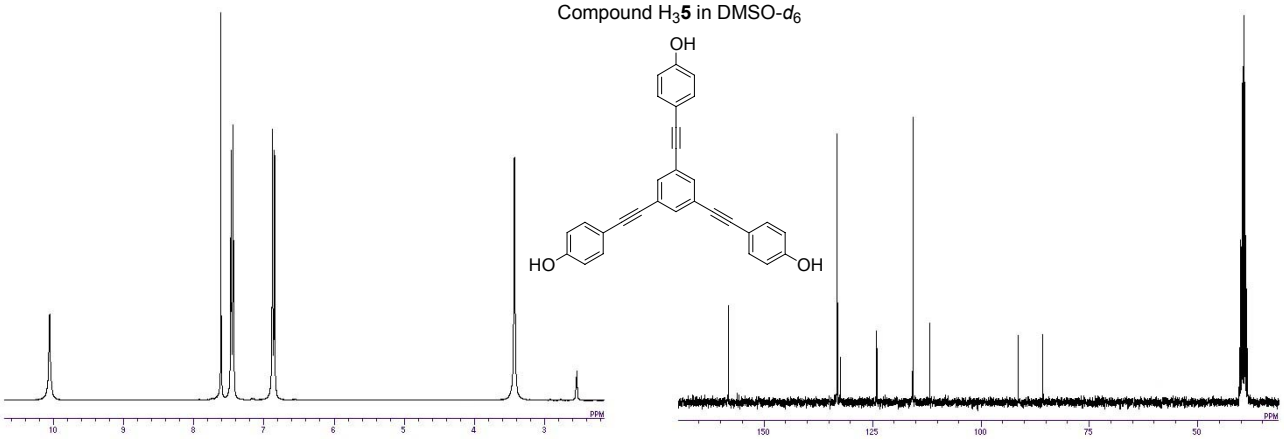
Compound **3** in $CDCl_3$



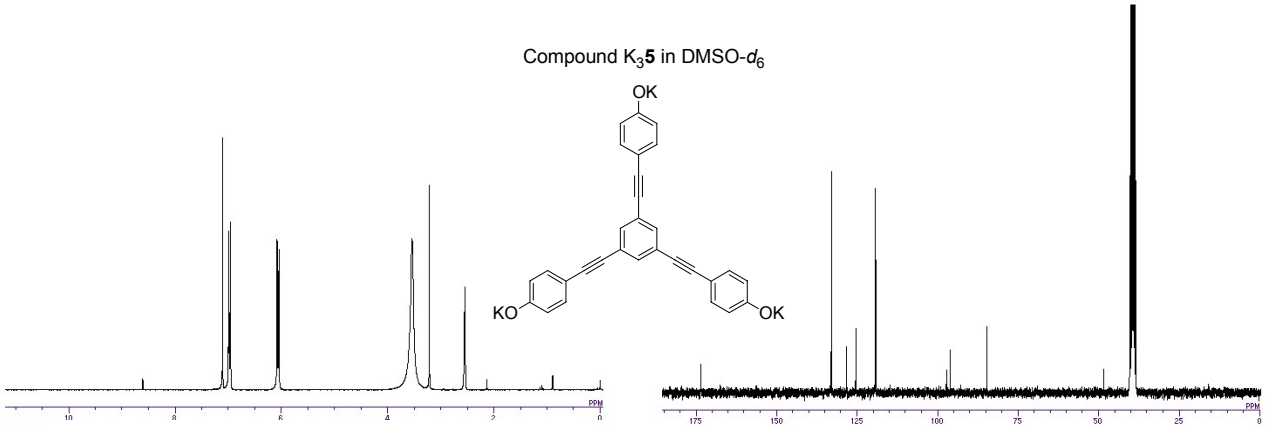
Compound **4** in $CDCl_3$



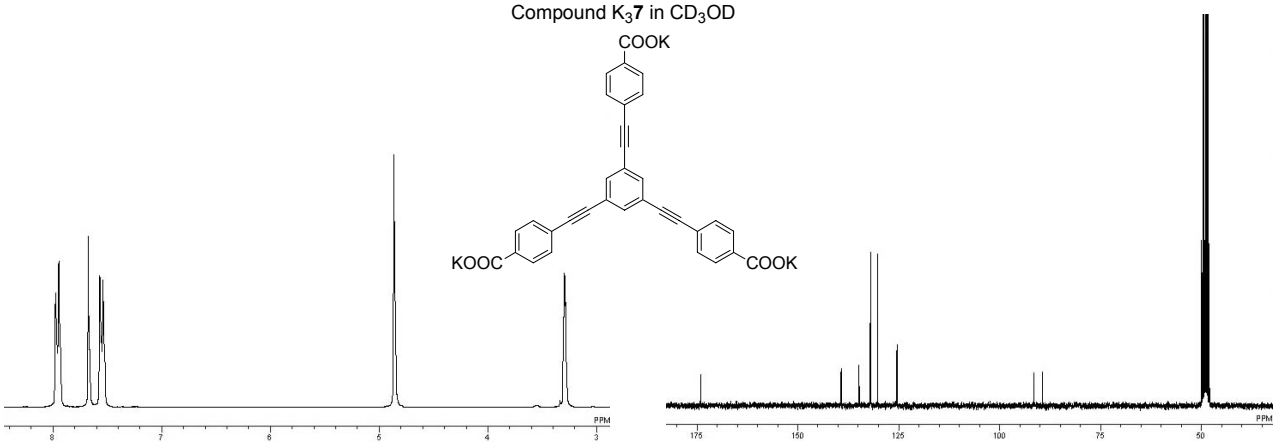
Compound H_3**5** in DMSO-d_6



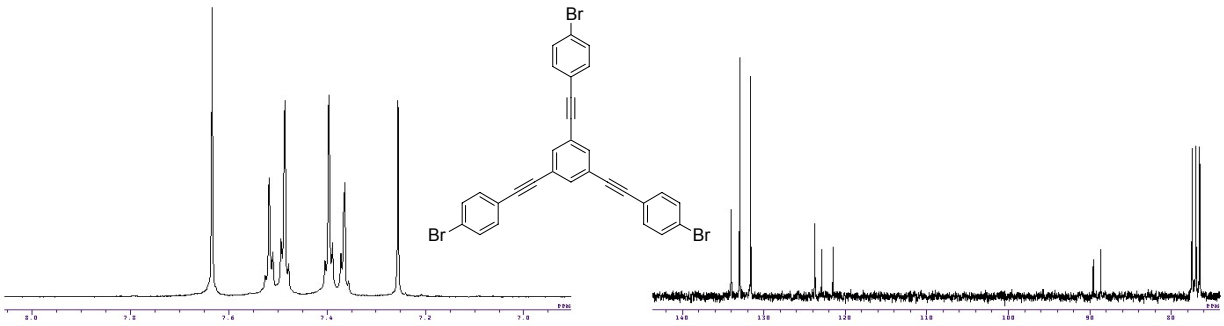
Compound K_3**5** in DMSO-d_6



Compound K_3**7** in CD_3OD



Compound **8** in $CDCl_3$



Compound **9** in DMSO-d_6

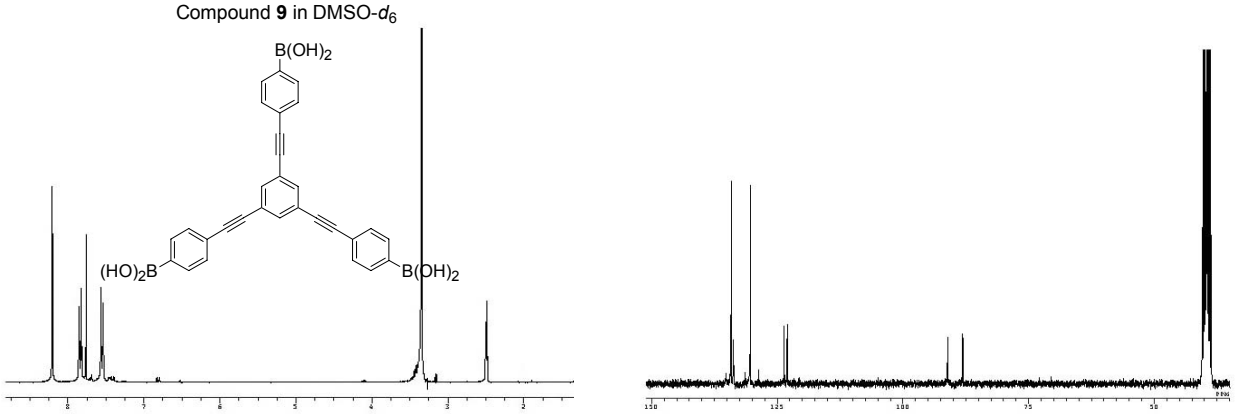
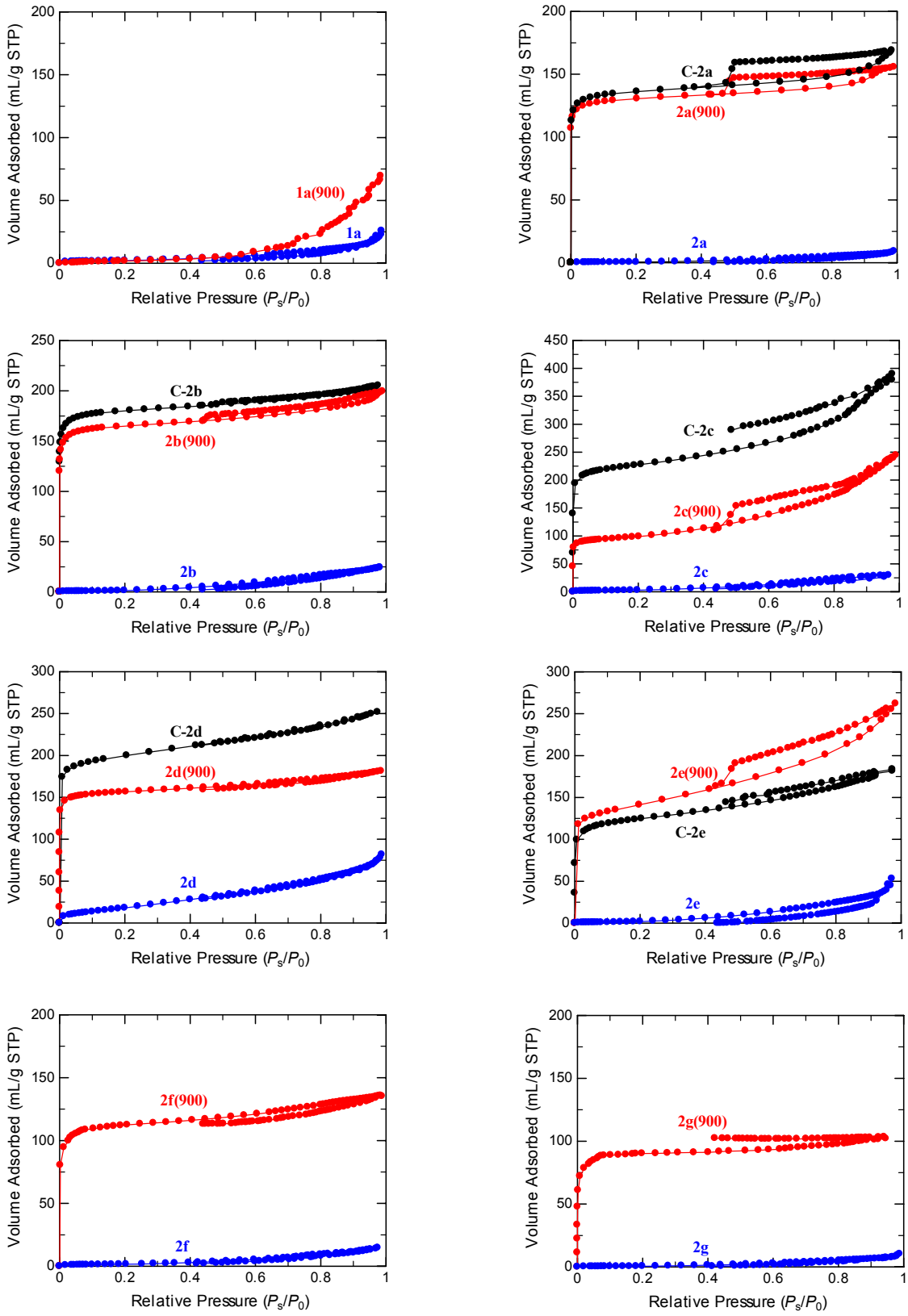
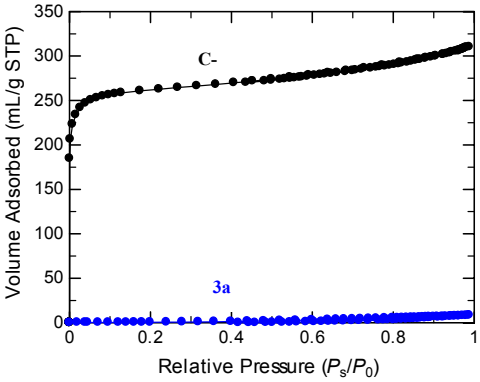
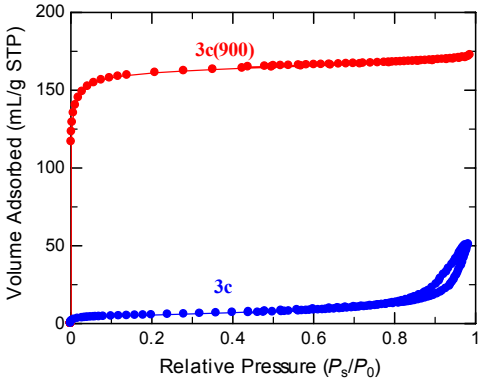
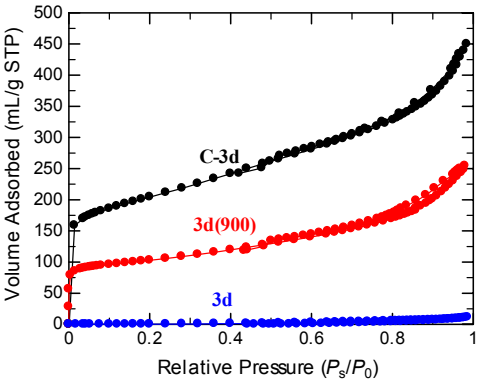


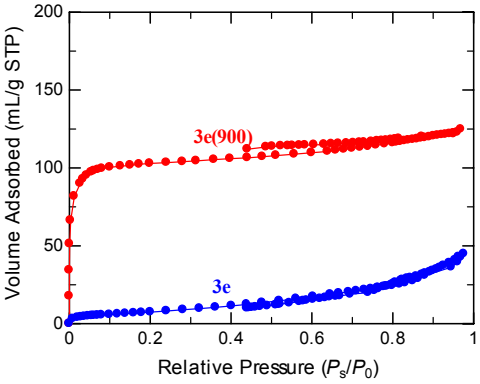
Figure S1. ^{1}H, ^{13}C NMR spectra of **3**, **4**, H_3**5**, K_3**5**, K_3**7**, **8**, **9**.

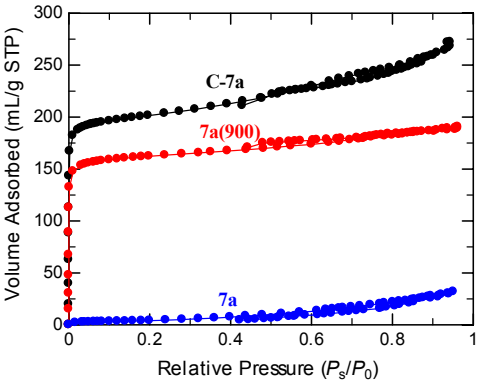


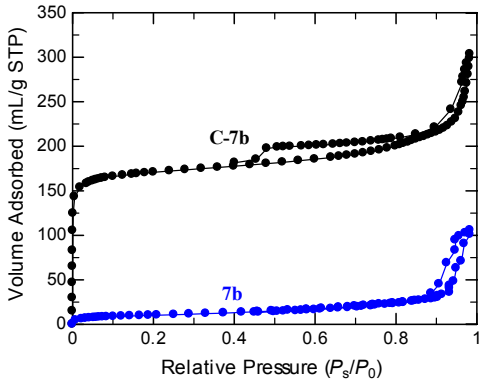


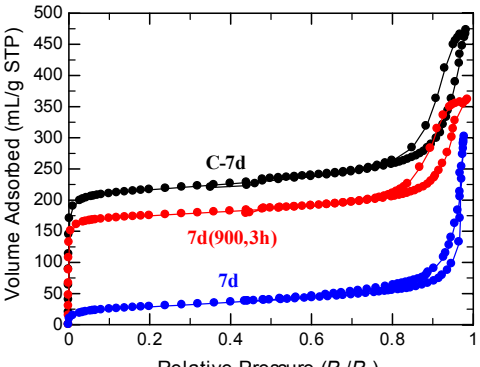


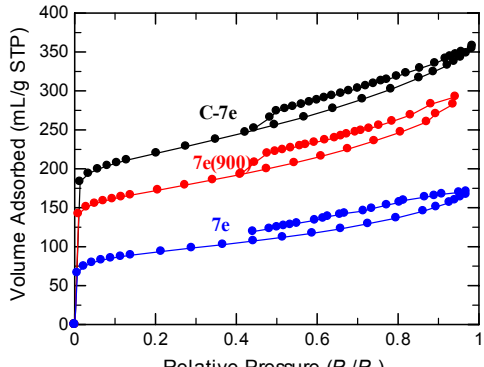












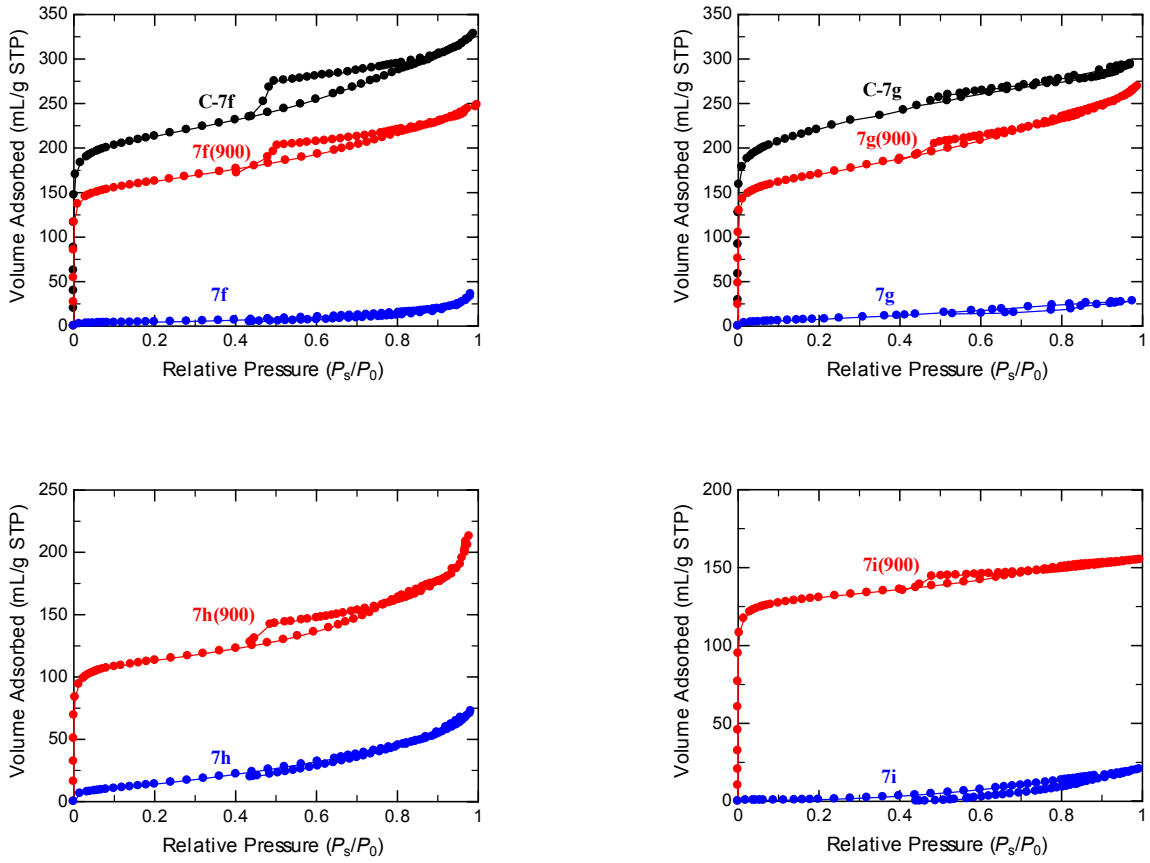
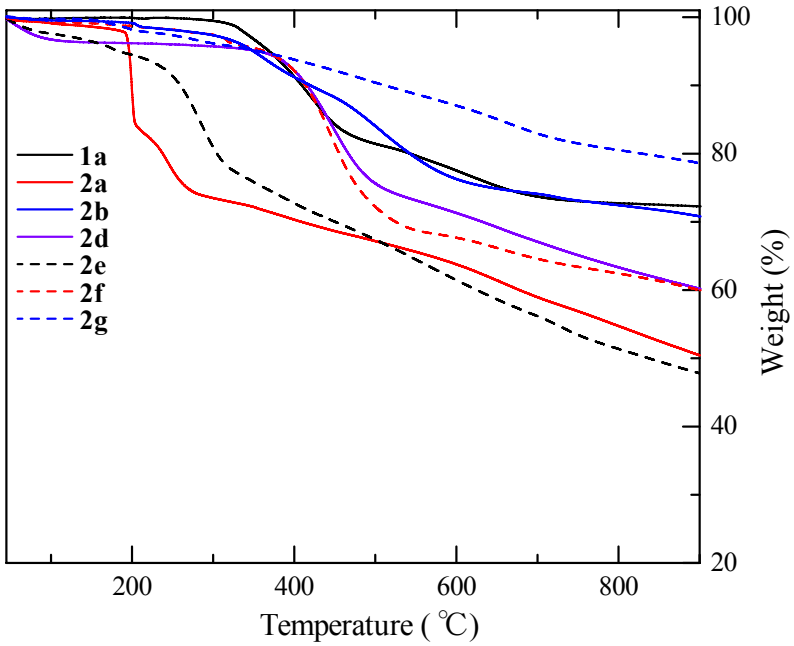
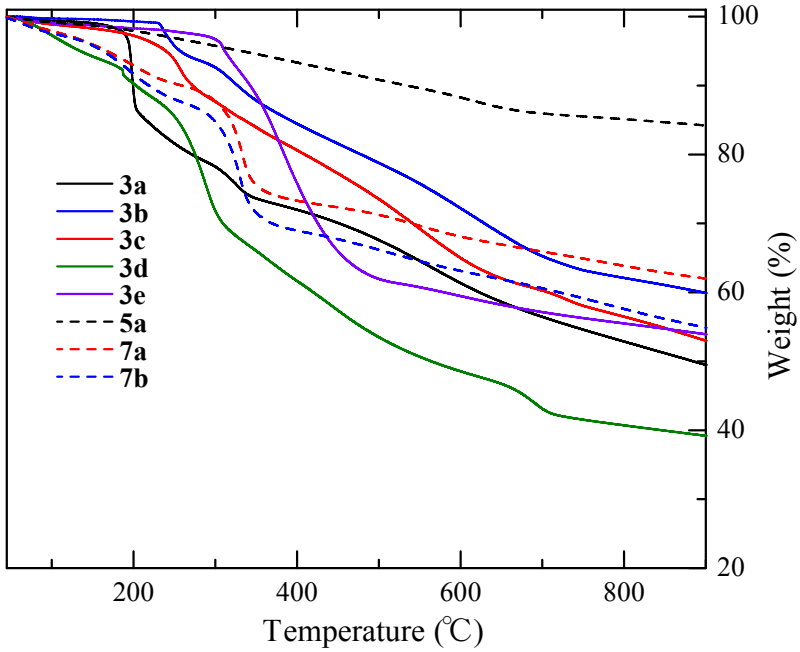


Figure S2. N_2 adsorption isotherms of **1a**, **2a**–**2g**, **3a**, **3c**–**3e**, **7a**–**7b**, **7d**–**7i**, and their carbonised samples.





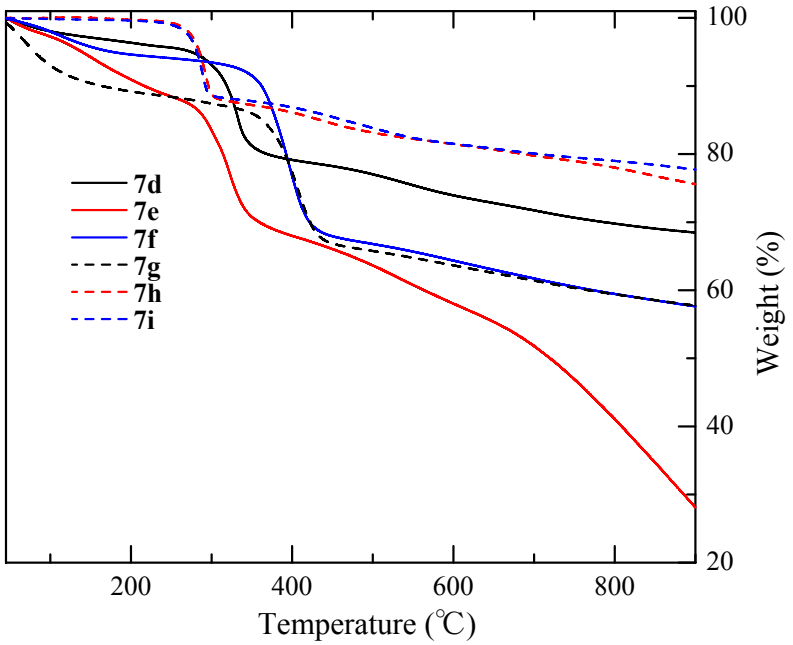


Figure S3. TGA plots of **1a**, **2a–2b**, **2d–2g**,**3a–3e**, **5a**, **7a–7b**, **7d–7i**.

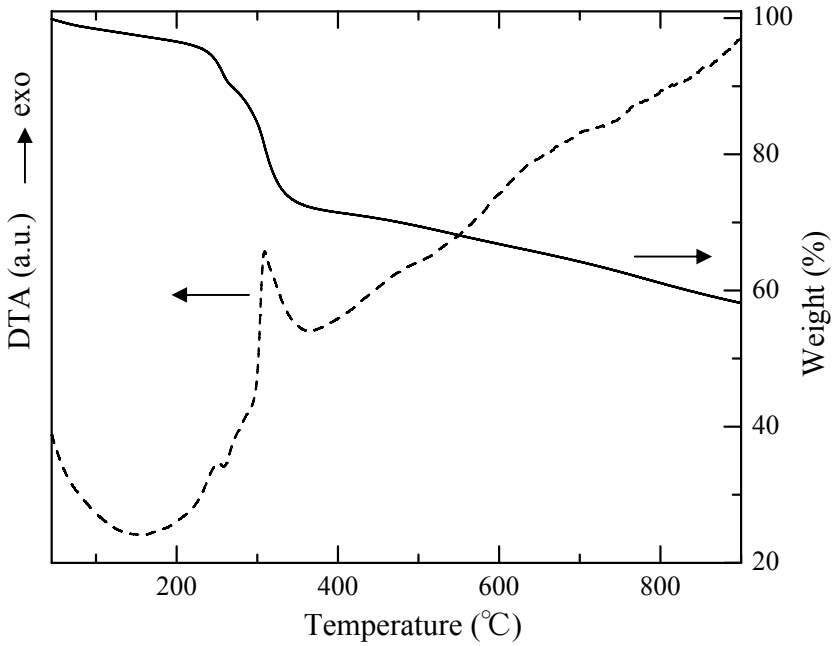


Figure S4. TGA/DTA plots of **7c**.