Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Synthesis of microporous polymers with exposed C_{60} surface by polyesterification of fullerenol

Hirotomo Nishihara*[a, b] Akio Harigaya,[b] Alberto Castro-Muñiz,[c] Mao Ohwada,[a] Takashi Kyotani,[b] and Yuta Nishina*[d]

[a] Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.

[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.

[c] Instituto del Ciencia y tecnología del Carbon, INCAR-CSIC, C/Francisco Pintado Fe 26, 33011 Oviedo, Spain.

[d] Research Core for Interdisciplinary Sciences, Okayama University, Tsushimanaka,Kita-ku, Okayama 700-8530, Japan.

Email: hirotomo.nishihara.b1@tohoku.ac.jp; nisina-y@cc.okayama-u.ac.jp

Experimental Section

Materials

Fullerenol ($C_{60}(OH)_n \cdot mH_2O$) was purchased from Frontier Carbon Co., Ltd. (nanom spectra D100). Other reagents and solvents (the best grade available) were purchased from commercial suppliers and were used without further purification.

Analysis of fullerenol

The composition of $C_{60}(OH)_n \cdot mH_2O$ was analysed by conventional organic elemental analysis (Yanaco JM10 analyser) and thermogravimetry coupled with differential thermal analysis (TG/DTA; Shimadzu DTG-0H) under air flow. TG measurement was carried out with a heating rate of 10 °C min^{-1} up to 700 °C under air flow. Also, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was carried out using 9-nitroanthracene as a matrix.

Sample preparation

Typically, ca. 50 mg of commercial fullerenol powder ($C_{60}(OH)_{8.5} \cdot 6.1H_2O$) was put into a closed vessel together with crosslinker (terephthaloyl chloride (TC) or 1,3,5-benzenetricarbonyl trichloride (BT)) and solvent (pyridine, 5 mL). To neutralise HCl formed by the esterification from the reaction system, pyridine was used as a solvent. The ratio of crosslinker to fullerenol is shown in Table 1. The mixture was treated at 180 °C for 1 h with a microwave reactor (Anton Paar, Monowave 300). When reaction temperature was decreased to 100 °C, much longer time (for example 24 h) was necessary. The fullerene-based polymers were obtained as dark-brown powder. The wet powder was thoroughly washed with water, ethanol, and then acetone to fully remove unreacted reactant and pyridine. After roughly evaporated the remaining acetone, the sample was dried at 100 °C for 3 h under vacuum. We have confirmed that there is no unreacted fullerenol in the resulting sample by MALDI-TOF-MS.

As for Pt-loading, a simple physical mixing method was used. F-BT was mixed with aqueous solution of Pt nanocolloid (the concentration of Pt is 200 ppm), and then the mixture was dried to obtain Pt/F-BT containing 1 wt% of Pt.[1] The Pt nanocolloid solution was purchased from Nippon Sheet Glass Co. Ltd. As a reference, we selected ketjenblack (KB; EC600JD, Lion) which is typical porous carbon popularly used for Pt support.

Characterization

FT-IR spectra of samples were measured on Shimadzu FTIR-8900. A KBr pellet containing ca. 0.5 wt% of sample was prepared, and the FT-IR spectrum was obtained with a transmission method. ^1H NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts of NMR spectra are reported as δ values in ppm relative to tetramethylsilane (TMS). Dimethyl sulfoxide-d6

(DMSO-d6) was used as a solvent for fullerenol and terephthaloyl chloride (TC). For the F-TC polymer, the mixture of the polymer and DMSO-d6 was kept at 100 °C for 3 h, and the supernatant was analysed by ^1H NMR. X-ray photoelectron spectroscopy (XPS) was performed on fullerene-based polymer using JEOL JPS-9200. The C 1s spectrum was deconvoluted into three portions, considering the presence of three chemical species: C=C/C–C, C–O (hydroxy), and O–C=O (ester). The order of their binding energies is the same as the above, considering the oxidation state of these species. The measured spectrum was calibrated by the position of the C=C/C–C peak (284.6 eV). From their peak areas, the molar ratios of these three species were estimated. When the number of remaining hydroxy groups in the polymer is assumed to N_{OH}, and the number of crosslinkers attached to one fullerenol molecule is assumed to N_{CL}, the number of carbon as a C=C/C–C form included in a unit structure of polymer becomes $60 - N_{\mathrm{OH}} + 3N_{\mathrm{CL}}$. From these relation and the XPS results, the ratios of the three species were obtained. N_2 adsorption-desorption isotherms of samples were measured on MicrotracBEL BELSORP-mini II at –196 °C. Prior to the measurement, the polymer was degassed at 150 °C for 3 h. Note that we have confirmed that the fullerene-based polymer is not thermally decomposed at 150 °C by TG coupled with mass spectroscopy as shown in Fig. S4. Note that evacuation of 150 °C is popularly used to eliminate physisorbed water from porous carbon materials without decomposition of oxygen-functional groups such as hydroxy and carboxy groups.[2] Specific surface area of a sample (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) method applied to the pressure range P/P_0 = 0.05–0.35. For microporous materials, lower pressure range P/P_0 = 0.01–0.05 was used to avoid overestimation.[3] Pore-size distribution was calculated by using the non-local density functional theory (NLDFT).[4] The structures of the fullerene-based polymers were observed by a scanning electron microscope (Hitachi, S-4800) and a transmission electron microscope (JEOL, JEM-2010). H_2 adsorption-desorption isotherms were measured with a static volumetric technique (using MicrotracBEL, BELSORP-max). We have previously developed a protocol by which reliable data can be obtained for H_2 adsorption-desorption isotherms up to 103 kPa.[1] Briefly, a large amount of sample, ca. 250−300 mg, was degassed at 150 °C for 6 h, by using the BELSORP-max instrument, and after the degassing step, measurement was immediately performed without exposure of the sample to any gas or air.

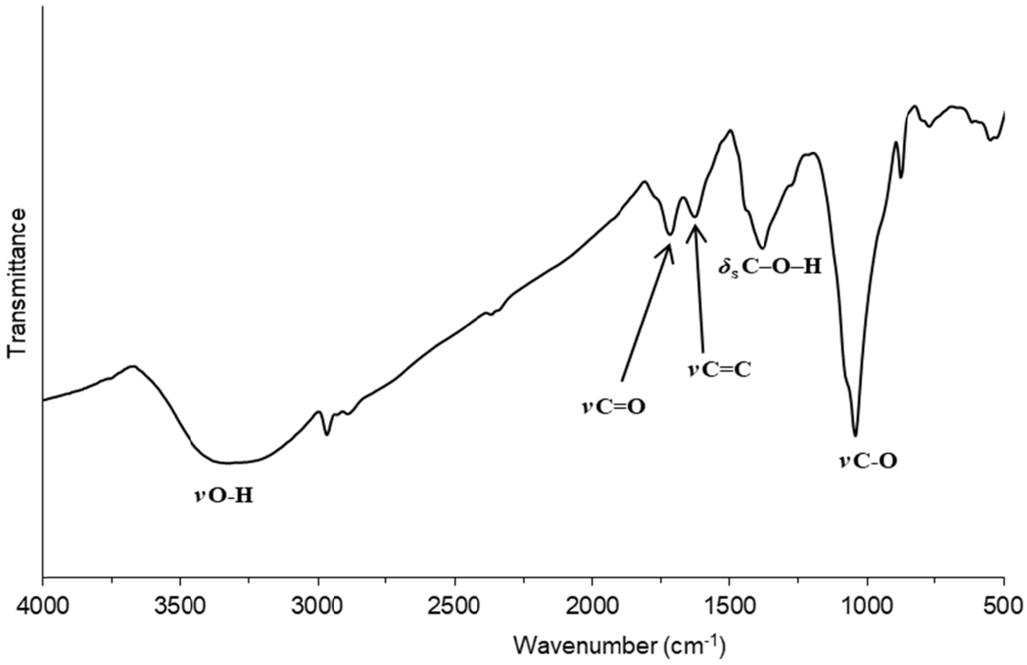

Figure S1 FT-IR spectrum of commercial $C_{60}(OH)_n \cdot mH_2O$.

Table S1 Elemental analysis results of $C_{60}(OH)_n \cdot mH_2O$.

C (wt%)	H (wt%)	O (wt%) [a]
73.9	2.1	24.0

[a] Calculated as a difference: (O content [wt%]) = 100 – (C content [wt%]) – (H content [wt%]). Note that the sample does not contain any ash, which is also revealed by TG (Fig. S2).

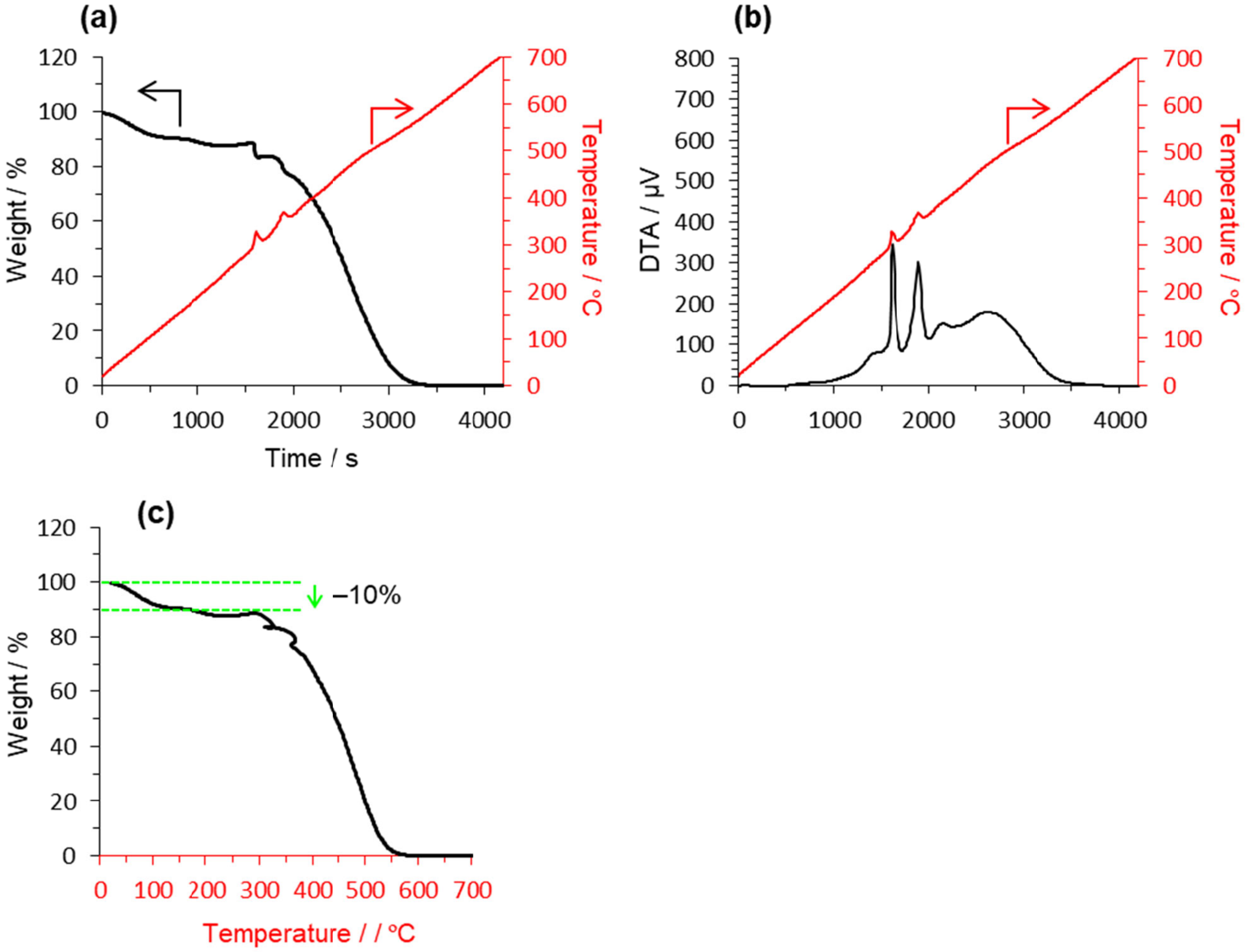

Figure S2 TG/DTA results of commercial $C_{60}(OH)_n{\cdot}mH_2O$. (a) TG curve (weight change) and temperature plotted against time elapsed. (b) DTA curve and temperature plotted against time elapsed. (c) Weight change plotted against temperature. In Fig. S2a, the sample weight is suddenly dropped at 314 °C and 359 °C because of temperature increase caused by exothermic processes at these two temperatures shown in Fig. S2b. In Fig. S2c, the sample shows weight decrease of −10 wt% below 150 °C, which is ascribed to the desorption of hydrated water.

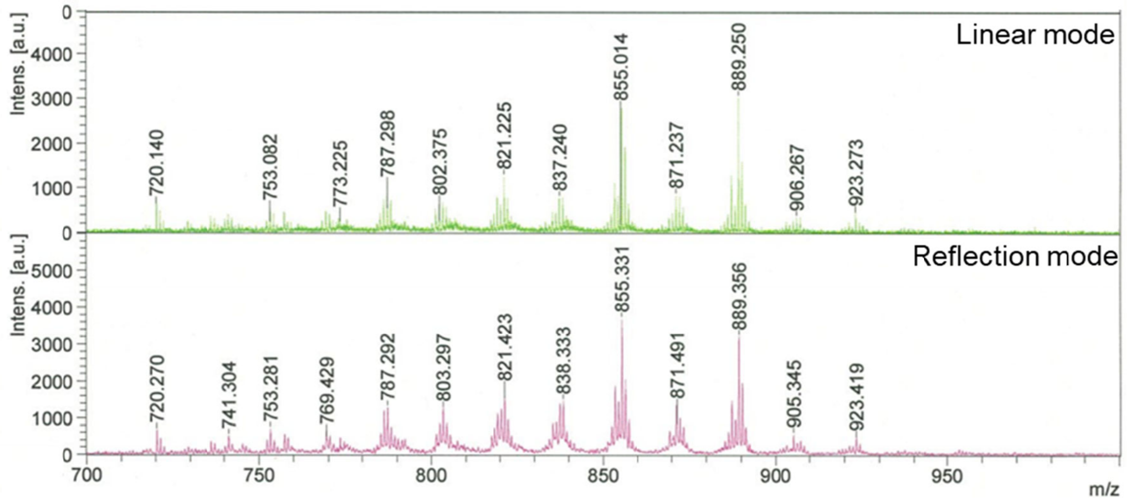

Figure S3 The results of MALDI-TOF-MS of $C_{60}(OH)_n \cdot mH_2O$. A linear mode (top) and a reflection mode (bottom) were applied. The most intense peaks almost accord to the estimated m/z values of $C_{60}(OH)_8$ (856) and $C_{60}(OH)_{10}$ (890). The results of MALDI-TOF-MS are reasonable compared with the average composition ($C_{60}(OH)_{8.5}$) estimated from the elemental analysis.

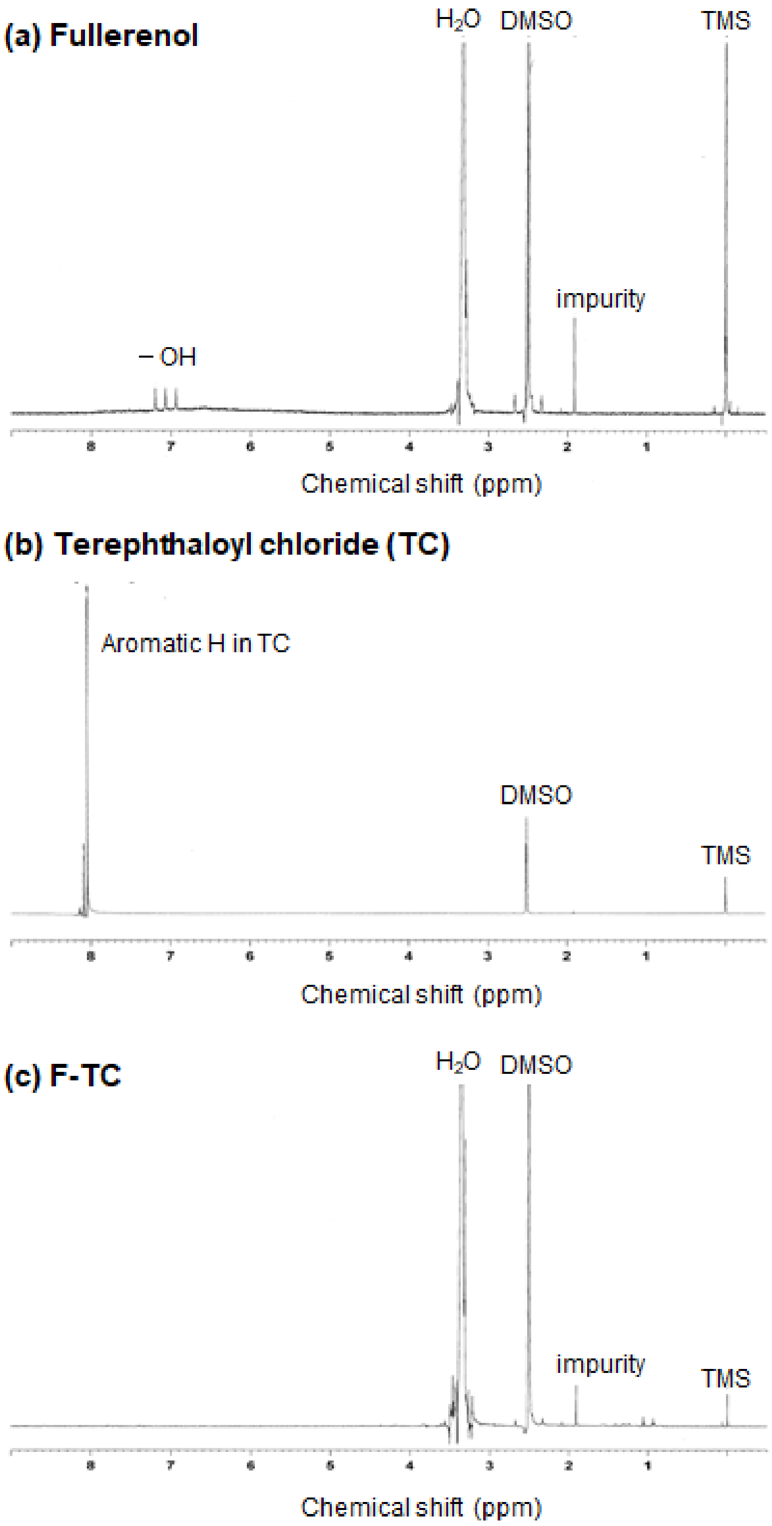

Figure S4 ^{1}H NMR (400 MHz) spectra of (a) fullerenol, (b) terephthaloyl chloride (TC), and (c) supernatant of the mixture of F-TC and DMSO-d6 after the mixture was heat treated at 100 °C for 3 h. The supernatant of F-TC (c) shows no signal of its building blocks (fullerenol and TC), indicating that the F-TC polymer is stable enough and is not decomposed at 100 °C.

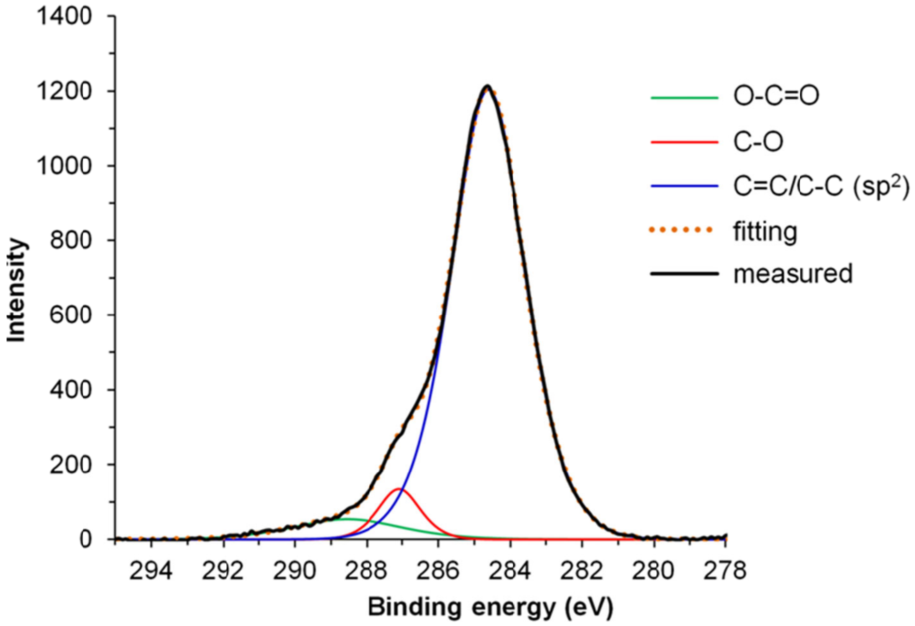

Figure S5 C 1s XPS results of F-TC polymer (crosslinker/fullerenol ratio is 2.5).

Table S2 Ratios of chemical forms of carbon in the fullerene-based polymer, calculated from XPS results.

Sample	C=C/C–C (%)	C–O (%)	O–C=O (%)
F-TC	88.5	5.7	5.8

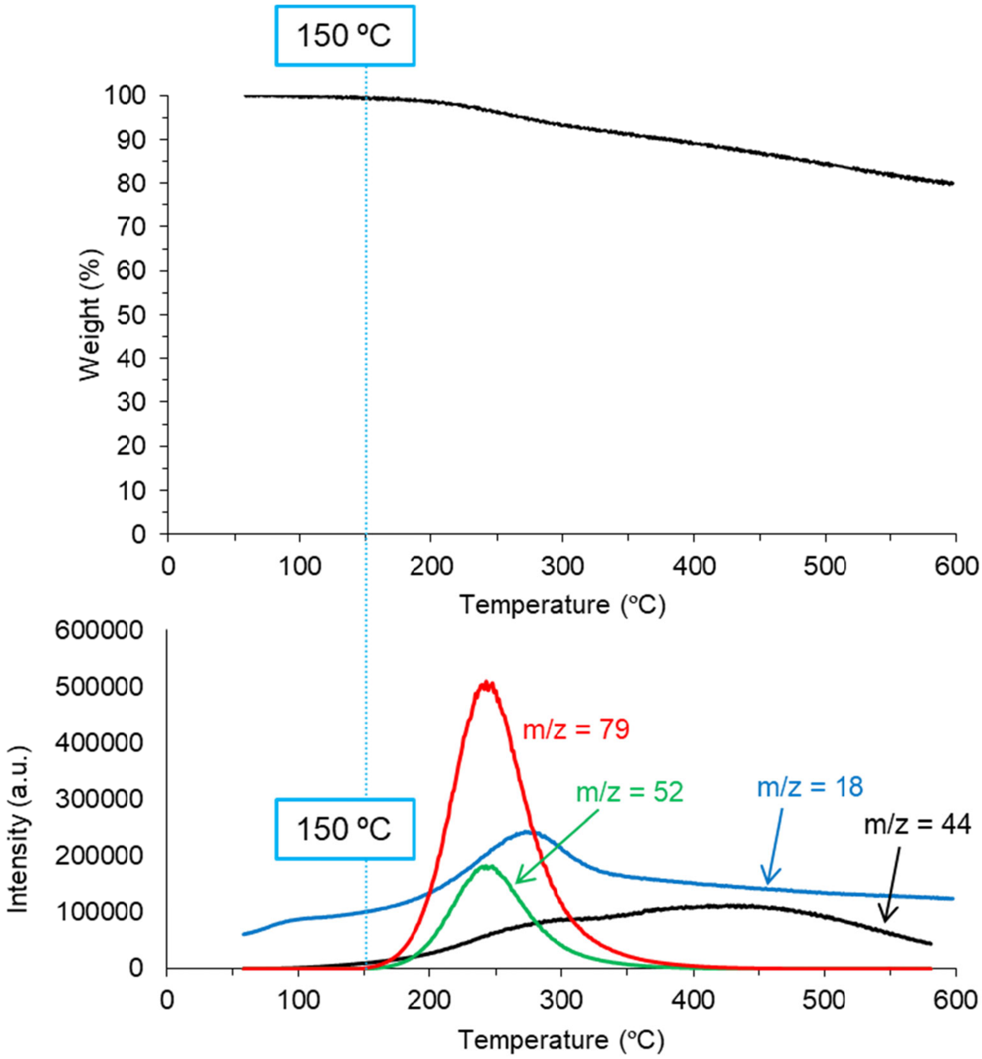

Figure S6 The results of TG (STA 449 Jupiter, Netzsch) coupled with a quadrupole mass spectrometer (JMS-G1500GC, JEOL) for F-TC. The sample was heated up to 600 °C with a heating rate of 10 °C min^{-1} under a He flow. The released gases having m/z up to 100 were monitored during the TG measurement, and the major species are shown here. Other species were negligible. While m/z = 18 and 44 are ascribed to H_2O and CO_2, m/z = 52 and 79 are ascribed to fragments generated by thermal decomposition of polymer.

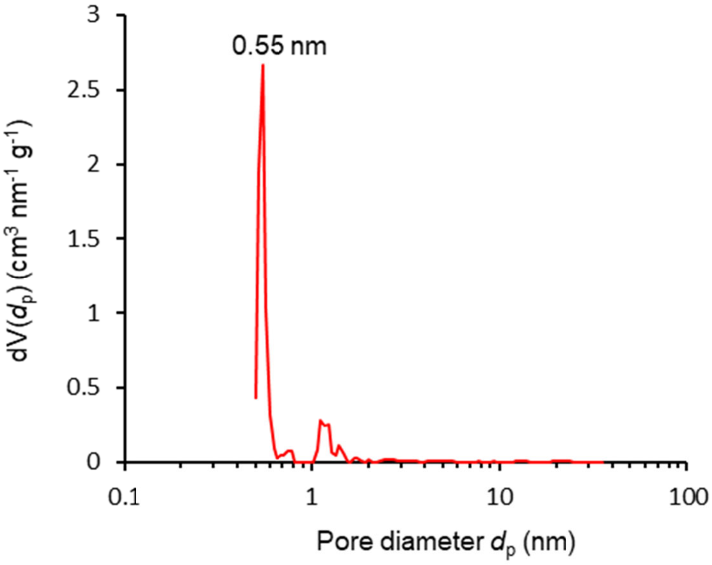

Figure S7 Pore-size distribution of fullerene-based polymer (F-TC), calculated by the NLDFT method.

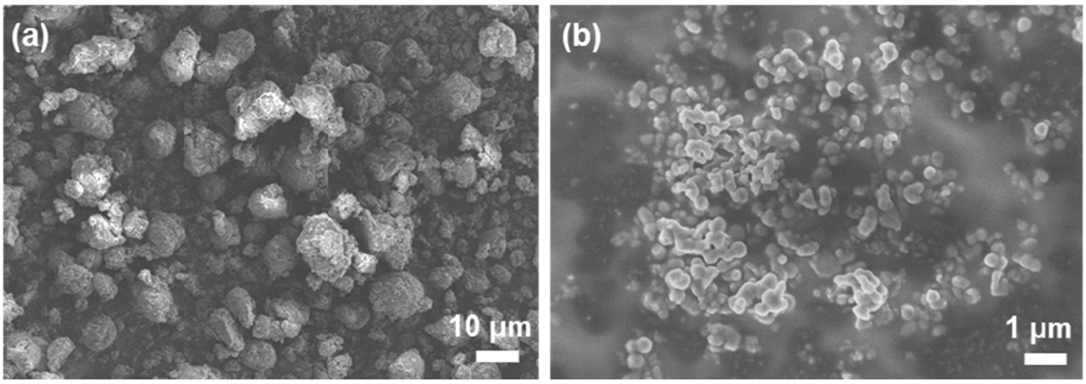

Figure S8 SEM images of (a) fullerenol and (b) F-BT.

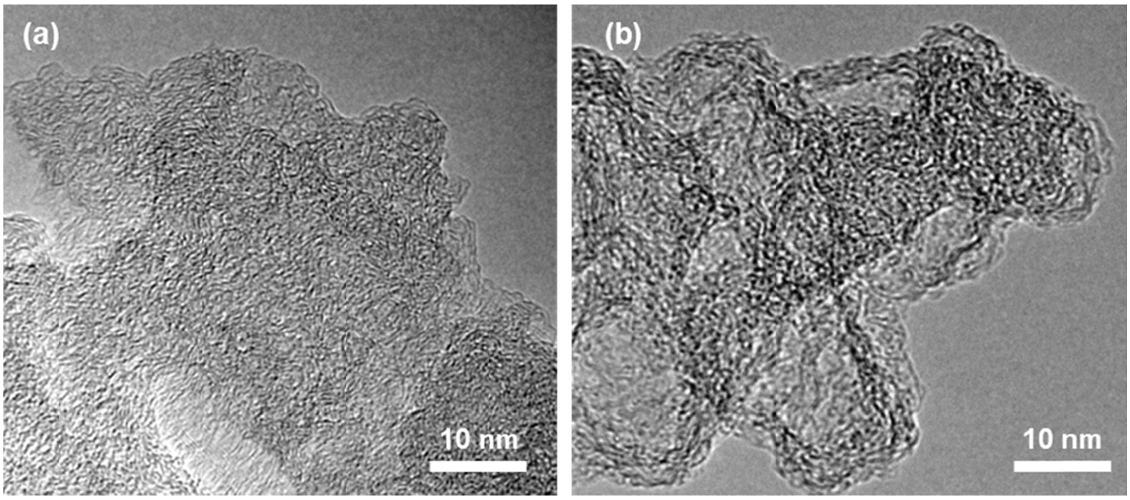

Figure S9 TEM images of (a) activated carbon fiber (A20, Unitika) and (b) Ketjenblack (EC600JD, Lion). These conventional porous carbons consist of graphene sheets, and slit-shaped micropores exist between the graphene sheets. In both samples, bent and stacked graphene sheets are seen. Ketjenblack is porous carbon black with hollow spherical structure. The diameter of the hollow spheres is about 30–50 nm, and the shell consists of stacked graphene sheets containing micropores.

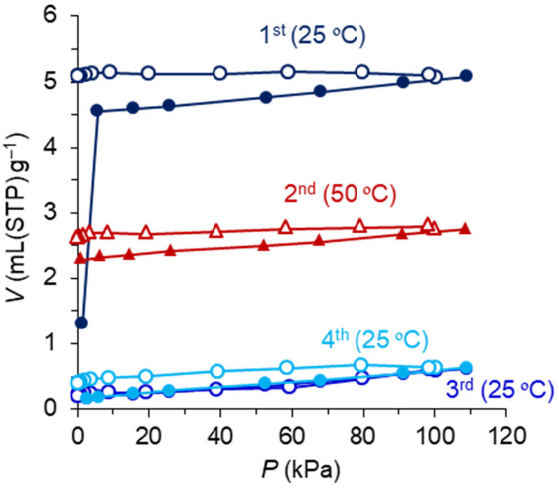

Figure S10 H_2 adsorption-desorption isotherms of Pt/F-BT measured at different temperatures. The first measurement was performed at 25 °C, and then the same measurement protocol was repeated at 50 °C (2nd run) and 25 °C (3rd and 4th runs). Before every measurement, the sample was evacuated at 150 °C for 6 h. We have previously demonstrated that such degassing step can fully remove hydrogen physically attached to the sample, and an adsorption isotherm after the degassing well overlaps the isotherm before the degassing treatment.[1] Thus, the irreversible behaviour until the 3rd run indicates that hydrogenation involving the formation of chemical bonding takes place.

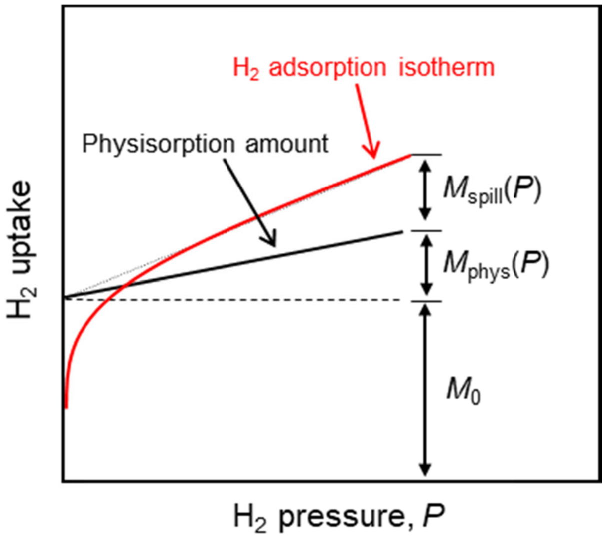

Figure S11 Illustration for the calculation of the pressure-dependent spillover storage amount, $M_{spill}(P)$ from the H_2 adsorption isotherm data.

Table S3 BET surface areas of F-BT, Pt/F-BT, KB, and Pt/KB.

Sample	S_{BET} ($m^2\ g^{-1}$)
F-BT	559
Pt/F-BT	576
KB	1348
Pt/KB	1258

Table S4 Comparison of the net hydrogen spillover amount at 25 °C reported so far.

Sample	Type	M_{spill}(100 kPa) (μmol-H_2 g^{-1})	Reference
F-BT	Fullerene-based polymer	7.9	This work
ZTC	Curved graphene	14.1	[1]
C_{60}/KB	C_{60}	12.3	[5]
KB	Conventional porous carbon	3.3	[5]

References

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