Supplementary Information for

Densely fluorinated nanospace of a porous coordination polymer composed of perfluorobutyl-functionalized ligand

Hyung Joon Jeon,[a] Ryotaro Matsuda,*[a] Prakash Kanoo,[a] Hiroshi Kajiro,[b] Liangchun Li,[a] Hiroshi Sato,[a] Yongtai Zheng[a] and Susumu Kitagawa*[ac]

[a] Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

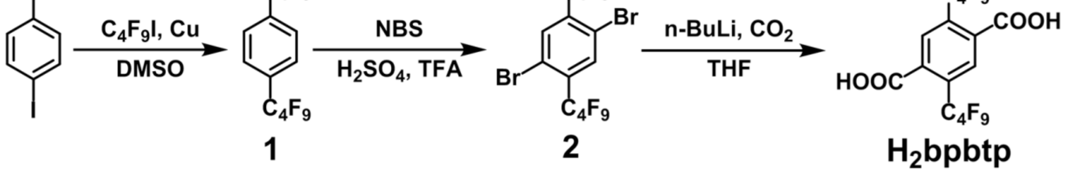
E-mail: rmatsuda@icems.kyoto-u.ac.jp; Fax: +81-75-383-2812; Tel: +81-75-383-2813

[b] Nippon Steel & Sumitomo Metal Corporation, Shintomo, Futtsu, Chiba 293-8511, Japan.

[c] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

General Methods

Commercially available reagents were used without further purification. The ^{1}H and ^{19}F NMR spectra were recorded with JEOL JNM-ECS400 (400 MHz) or JEOL-ECA600 (600 MHz) NMR spectrometer. The elemental analysis (EA) was performed on a Flash EA 1112 series, Thermo Finnigan instrument. The powder X-ray diffractions (PXRDs) were recorded with a RIGAKU UltimaIV with Cu $K\alpha$ radiation (λ = 1.54073 Å). Single crystal X-ray measurement was performed on Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å) and processed using the CrystalClear program (Rigaku). Crystal structure was solved by direct methods (SIR2004) and refined by full-matrix least-squares refinement using the SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement factors. The H atoms were refined geometrically, using a riding model. The void volume of crystal was estimated by the PLATON program. Thermogravimetric analyses (TGA) were carried out with a Rigaku Instruments TG-8120 up to 500 °C under a nitrogen atmosphere at a heating rate of 5 °C min^{-1}. The gas sorption isotherms were measured volumetrically using BELSORP-max (Bel Japan, Inc.). The as-synthesized sample was dried at 393 K in vacuum for over 10 hours in order to remove metal-coordinated and guest DMFs. Prior to measurement, the dried sample was evacuated again using the degas function of the analyzer for 2 h at 373 K. Highly pure gases (>99.999%) were used for the measurements.



Scheme S1. Synthesis of 2,5-bis(perfluorobutyl)terephthalic acid (H_2bpbtp).

Synthesis of 1,4-bis(perfluorobutyl)benzene (1)

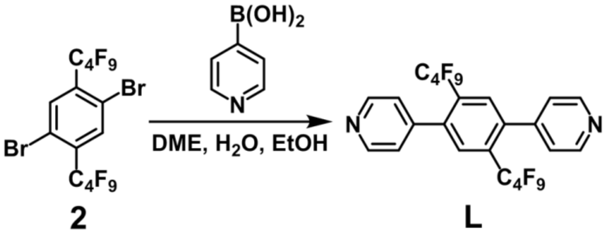
Nonafluoro-1-iodobutane (24.3 g, 70.4 mmol) was added to a mixture of 1,4-diiodobenzene (10.56 g, 32 mmol) and Cu powder (8.2 g, 128 mmol) in anhydrous DMSO (70 mL). The mixture was stirred for 70 h at 120 °C and was allowed to cool to room temperature. Water (50 mL) and diethyl ether (50 mL) were added to the mixture and stirred additional 30 min. The mixture was filtered, and the filtrate was extracted with diethyl ether (50 mL × 3). The extract was washed with brine (50 mL × 2), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was subjected to flash silica gel column chromatography eluting with hexane (13.58 g, 82.5%). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.76$ (s, 4H). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -128.56$ (4F), -125.61 (4F), -114.52 (4F), -83.97 (6F).

Synthesis of 1,4-dibromo-2,5-bis(perfluorobutyl)benzene (2)

1 (13.6 g, 26.4 mmol) was added to a mixture of trifluoroacetic acid (100 mL) and concentrated sulfuric acid (30 mL). The mixture was heated to 60 °C, and *N*-bromosuccinimide (14.3 g, 79.5 mmol) was added in portions (2.39 g h^{-1}) over 6 h. The stirring was continued for 48 h at 60 °C, and ice water (50 mL) was added to the reaction mixture. The precipitate was collected, washed with water, dissolved with dichloromethane, and dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was recrystallized from ethanol (13.63 g, 77%). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.93$ (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -128.68$ (4F), -123.18 (4F), -110.77 (4F), -83.75 (6F).

Synthesis of 2,5-bis(perfluorobutyl)terephthalic acid (H_2bpbtp)

n-Butyllithium solution (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise to a mixture of **2** (2 g, 2.5 mmol) in THF (100 mL) at −78 °C. The mixture was stirred for 1.5 h and was bubbled by CO_2 gas for 1 h while the temperature was held at −78 °C. 5N HCl solution was added to the mixture, and the resulting mixture was concentrated under low pressure. The residue was dissolved with an aqueous NaOH solution and washed with diethyl ether (30 mL × 2). The resulting aqueous layer was collected and acidified to pH 4 by the dropwise addition of HCl solution to precipitate a white solid of H_2bpbtp (1.52 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.11$ (s, 2H), 14.15 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -128.84$ (4F), -122.69 (4F), -108.40 (4F), -83.72 (6F).



Scheme S2. Synthesis of 2,5-bis(perfluorobutyl)-1,4-bis(4-pyridyl)benzene (L).

Synthesis of 2,5-bis(perfluorobutyl)-1,4-bis(4-pyridyl)benzene (L)

2 (672 mg, 1 mmol), 4-pyridineboronic acid (368 mg, 3 mmol), tetrakis(triphenylphosphine)palladium(0) (64 mg, 0.092 mmol), and Na_2CO_3 (636 mg, 6 mmol) were added to a mixture of 1,2-dimethoxyethane/EtOH/H_2O = 7:2:3 (14.4 mL). The 20 mL microwave vial containing the reaction mixture was sealed and heated for 1 hour at 160 °C in vacuum. After cooling to room temperature, the reaction mixture was concentrated and washed with brine (50 mL × 2). The resulting residue was purified by silica column chromatography (CH_2Cl_2 was used as the first eluent, and then CH_2Cl_2:THF = 95:5). (313 mg, 46.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (dd, 4H, J = 1.36 Hz, J = 4.56 Hz), 7.58 (s, 2H), 7.31 (d, 4H, J = 4.56 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = -128.40 (4F), -123.05 (4F), -106.71 (4F), -83.57 (6F).

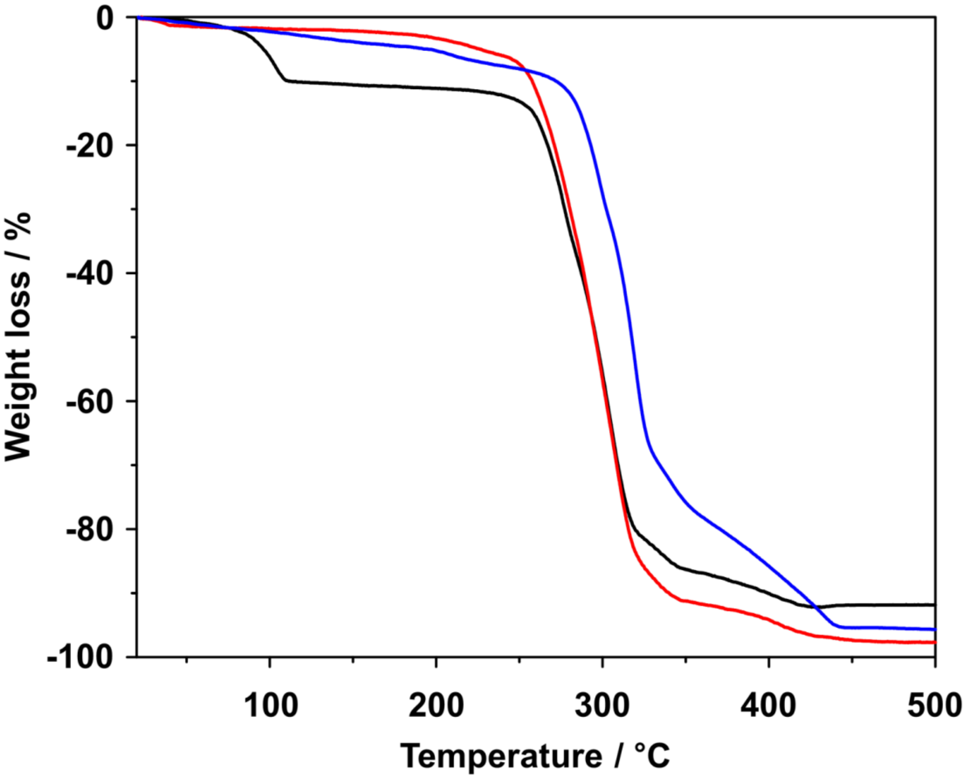


Fig. S1. TGA profiles with a heating rate of 5 K min^{-1}. As-synthesized, desolvated, and dichloromethane exchanged samples are colored in black, red, and blue, respectively. The desolvated sample was prepared by dry of as-synthesized PCP at 160 °C for 10 hours. The dichloromethane exchanged sample indicates that as-synthesized PCP which was immersed in CH_2Cl_2 for 2 days and dried at 40 °C for 10 hours.

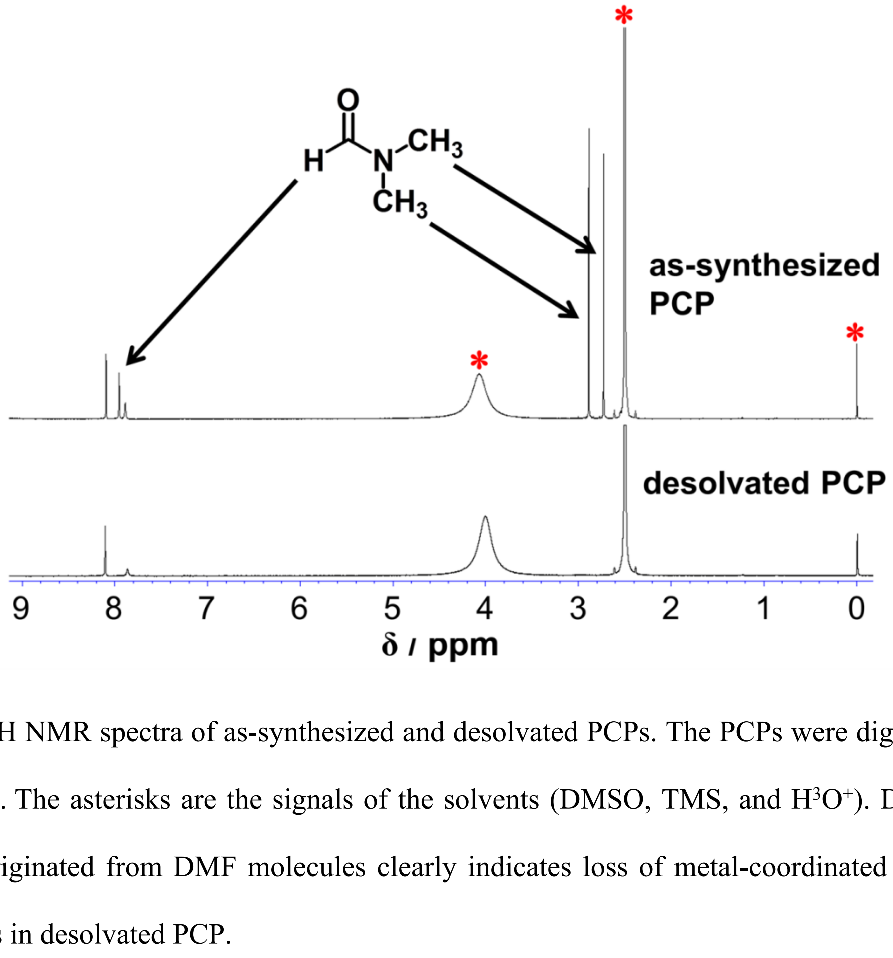


Fig. S2. ^{1}H NMR spectra of as-synthesized and desolvated PCPs. The PCPs were digested in DMSO-*d*$_6$/aq.HCl. The asterisks are the signals of the solvents (DMSO, TMS, and H^3O^+). Disappearance of signals originated from DMF molecules clearly indicates loss of metal-coordinated and guest DMF molecules in desolvated PCP.

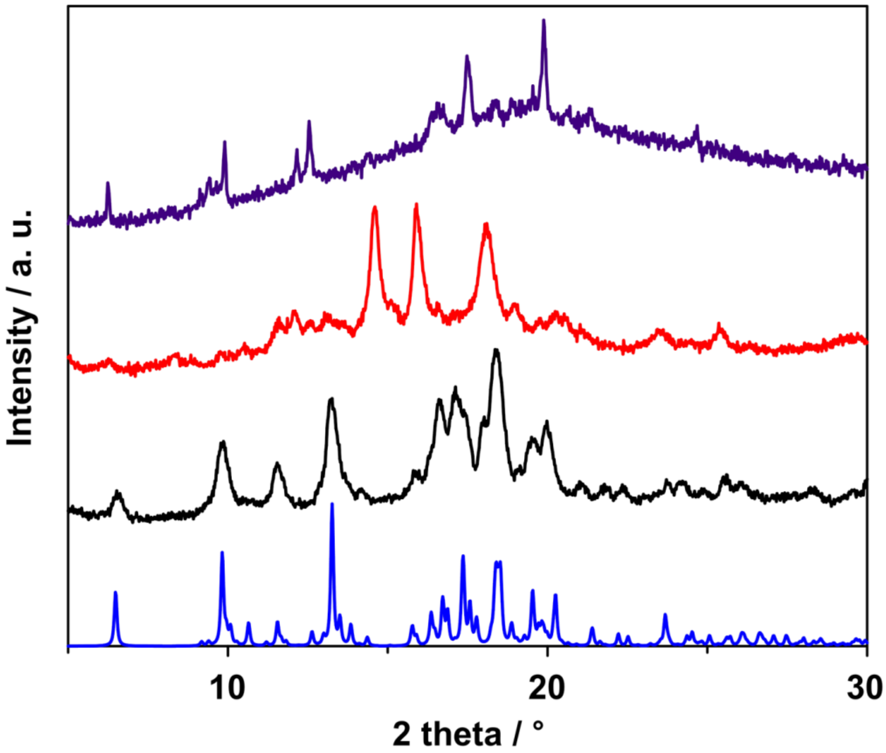


Fig. S3. PXRD patterns. Patterns of simulated, as-synthesized, and desolvated samples are colored in blue, black, and red, respectively. Purple shows the pattern of recovered sample, the desolvated sample was immersed in DMF for 2 hours.