Supporting Information

Hydrogen Gas Storage in Fluorinated Ultramicroporous Tunnel Crystal

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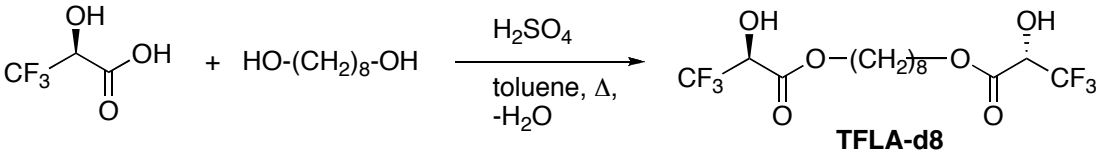
1 General

Reagents and solvents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich Chemical., Ltd. and used without further purification. Optically pure (*S*)-trifluorolactic acid was prepared by literature methods.[SI-1] IR spectra were measured on a Hitachi Model 270-30 Infrared Spectrophotometer. Elemental analyses were performed on a Perkin Elmer series II CHNS/O Analyzer 2400. GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A. Melting points were recorded by a Yanaco MP-S3 melting point measurement apparatus. ^{1}H (300 MHz) and ^{19}F (288 MHz) NMR spectra were recorded by a Varian MERCURY 300 instrument and the chemical shifts are reported in δ (ppm) values relative to TMS (δ 0 ppm for ^{1}H NMR in $CDCl_3$), C_6F_6 (δ 0 ppm for ^{19}F NMR in $CDCl_3$). ^{13}C (150 MHz) NMR spectra were recorded by a Varian UNITY INOVA 600 instrument and the chemical shifts are reported in δ (ppm) values relative to $CDCl_3$ or CD_3OD (δ 77 ppm or δ 49 ppm for ^{13}C NMR, respectively). Coupling constants are reported in hertz (Hz).

2 Preparation of TFLA-d8 crystals and/or solids



TFLA-d8

Typical procedure for preparation of **TFLA-d8** was described in our previous paper.[3]

Round-bottomed flask equipped with a Dean-Stark apparatus surmounted by reflux condenser was charged with 1,8-octanediol (0.91 g, 10 mmol), (*S*)-trifluorolactic acid (4.32 g, 30 mmol), and one drop of H_2SO_4 as a catalyst in toluene (10 ml). The reaction mixture was brought to reflux with the removal of water for 15 h. The resulting mixture was cooled to ambient temperature and water was added to the mixture then, extracted with diethyl ether. The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude distilled under reduced pressure (1 mmHg) at 150 ºC to give **TTFLA-d8**.

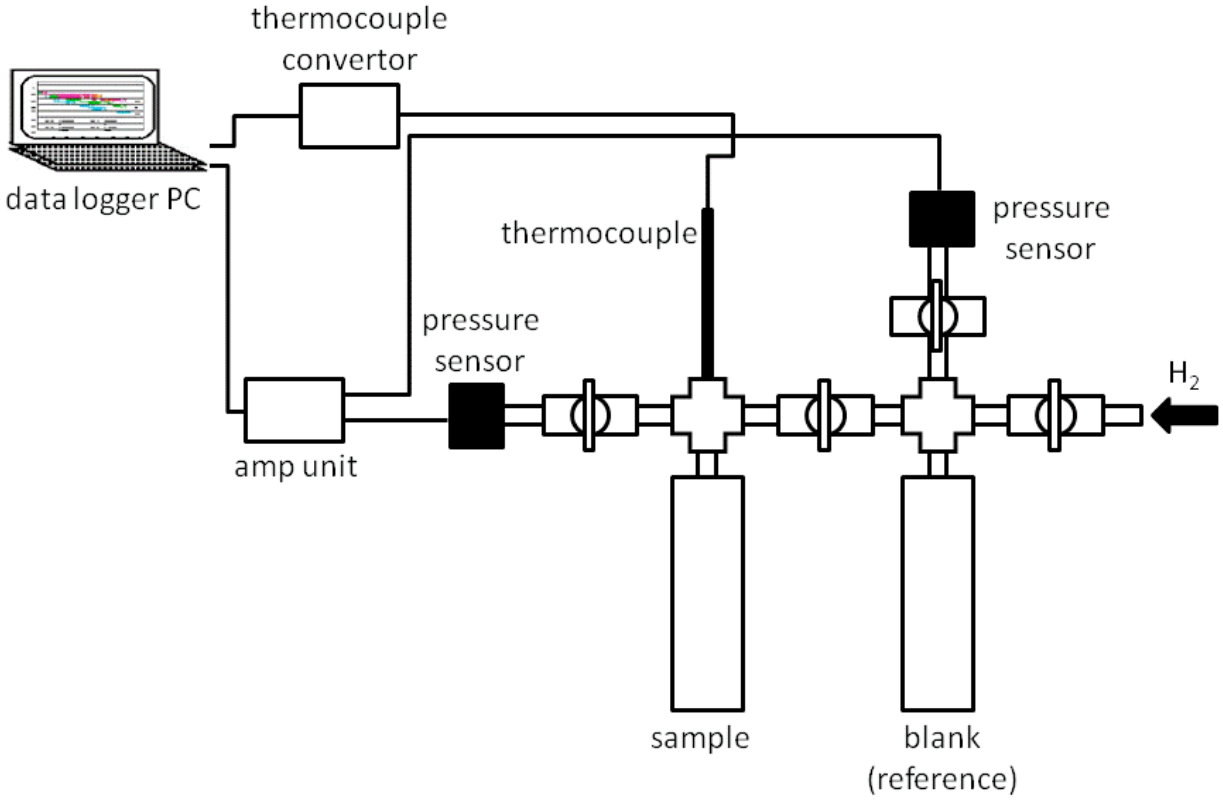
octamethylene-(*S*,*S*)-bis(3,3,3-trifluorolactate (**TFLA-d8**), 90% yield. Colourless crystal. Mp. 71-72 ºC. IR (KBr): 3452, 2948, 1750, 1734, 1224, 1198, 1134 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.47 (quintet, *J* = 7.2 Hz, 2H), 4.36 (dt, *J* = 10.5 Hz, *J* = 6.6 Hz, 2H), 4.30 (dt, *J* = 10.8 Hz, *J* = 6.6 Hz, 2H), 3.41 (d, *J* = 7.8 Hz, 2OH), 1.71 (quintet, *J* = 6.6 Hz, 4H), 1.35 (brs, 8H). ^{19}F NMR ($CDCl_3$): δ 85.0 (d, *J* = 6.9 Hz, 6F). ^{13}C NMR ($CDCl_3$ ^{1}H decoupled): δ 167.5, 122.2 (q, *J* = 284 Hz), 69.7 (q, *J* = 33.3 Hz), 67.6, 28.7, 28.1, 25.3. MS: m/z 145 (1), 129 (1), 111 (21), 110 (12), 98 (8), 95 (7), 83 (10), 82 (41), 81 (22), 69 (100), 68 (31), 67 (42), 56 (10), 55 (84), 54 (37), 43 (16), 42 (16), 41 (62); Anal. Calcd. for $C_{14}H_{20}F_6O_6$: C 42.22, H 5.06, Found: C 42.0, H 5.29. $[\alpha]^{25}_{D}$ –4.38 (*c* 1.1, acetone). The ee was

determined to be >99% ee by HPLC analysis of the dibenzoate ester (Daicel Chiralcel® OD-H, 100:1 hexane:*i*-PrOH, 1.0 mL / min, 254 nm, t_{SS}(major) = 13.3 min, t_{RS}(minor) = 15.6 min, t_{RR}(minor) = 19.1 min).

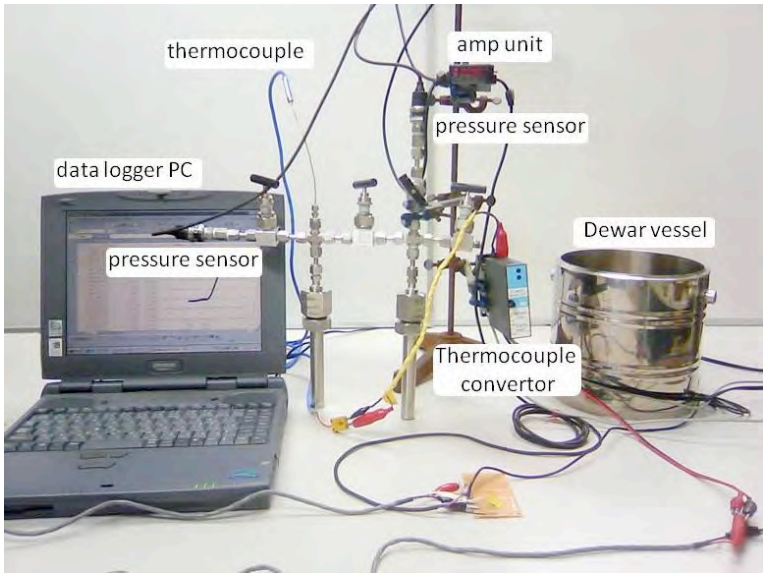
Single crystal of **TFLA-d8** was prepared by slow evaporation of the *n*-hexane/ether solutions. An amorphous solid of **TFLA-d8** was prepared by rapid evaporation of EtOH solution. Another amorphous solids were prepared by rapid addition of hexane into the concentrated ethereal solution of **TFLA-d8**.

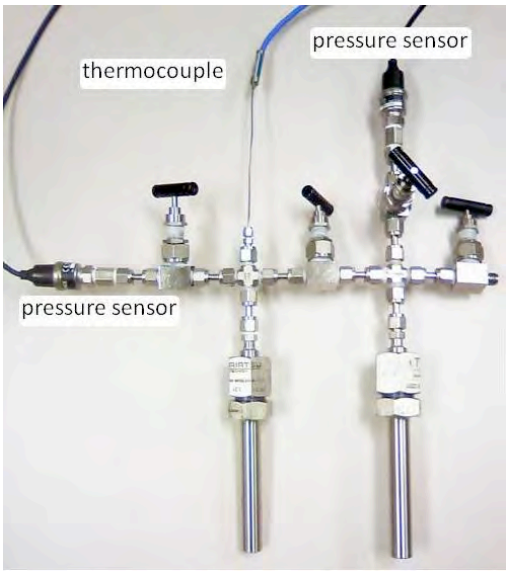
3 Pressure measurement apparatus

The amount of hydrogen-storage was measured by change of the pressure of the custom-made vessels as illustrated in Figure S1a, and showed its photo in Figure S1b and S1c.



(a)





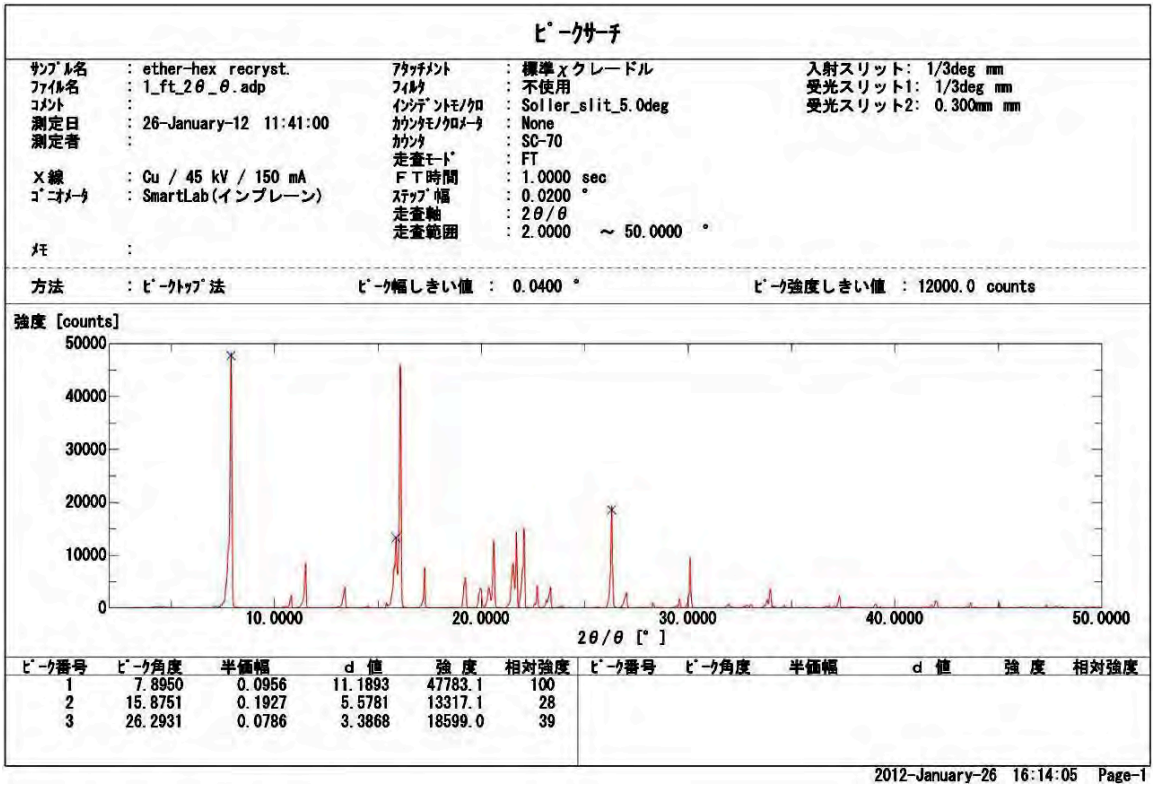
(b) (c)

Figure S1. Apparatus for hydrogen-storage measurements. (a) Schematic illustrates, (b) and (c) Photo.

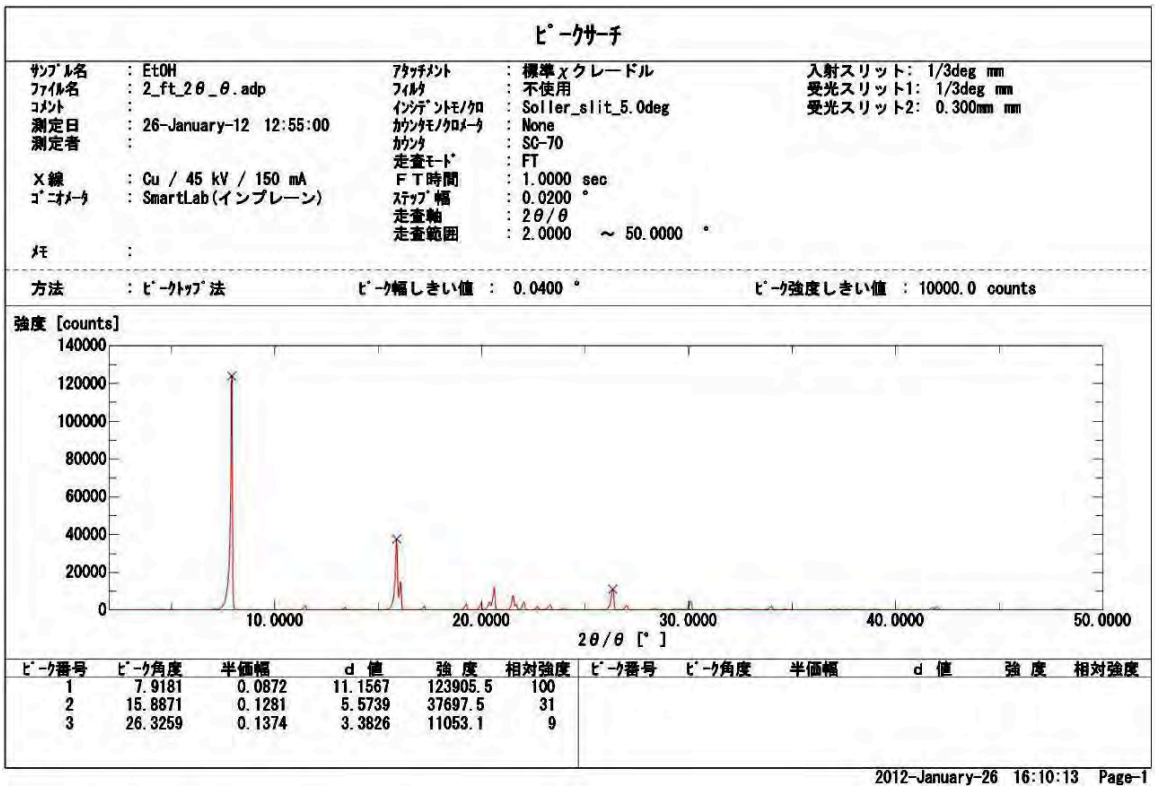
Vessels (SUS316) were purchased from Taiatsu Techno Corporation. Inner volume of each vessel is 10.5 ml that contains dead volumes of piping. Keyence type AP-15S gas pressure sensor and type AP-V80 amp unit were used for high pressure measurements, and type AP-13S sensor and type AP-V82 amp unit were used for ordinal pressure measurement. AS-ONE type 1-9930-11 K-type thermocouple was inserted into the sample vessel to measure the temperature of the atmosphere of the sample crystal. The pressure was registered with the temperature via MTT corporation type MS3701-A-K6 thermocouple converter and Keyence type NR-110 data logger with FLEX LOGGER /EX software (ver. 3.00) to PC (Dynabook Satellite 2510, with Windows 98 OS). The data were processed on Microsoft Excel 97.

XRD spectra

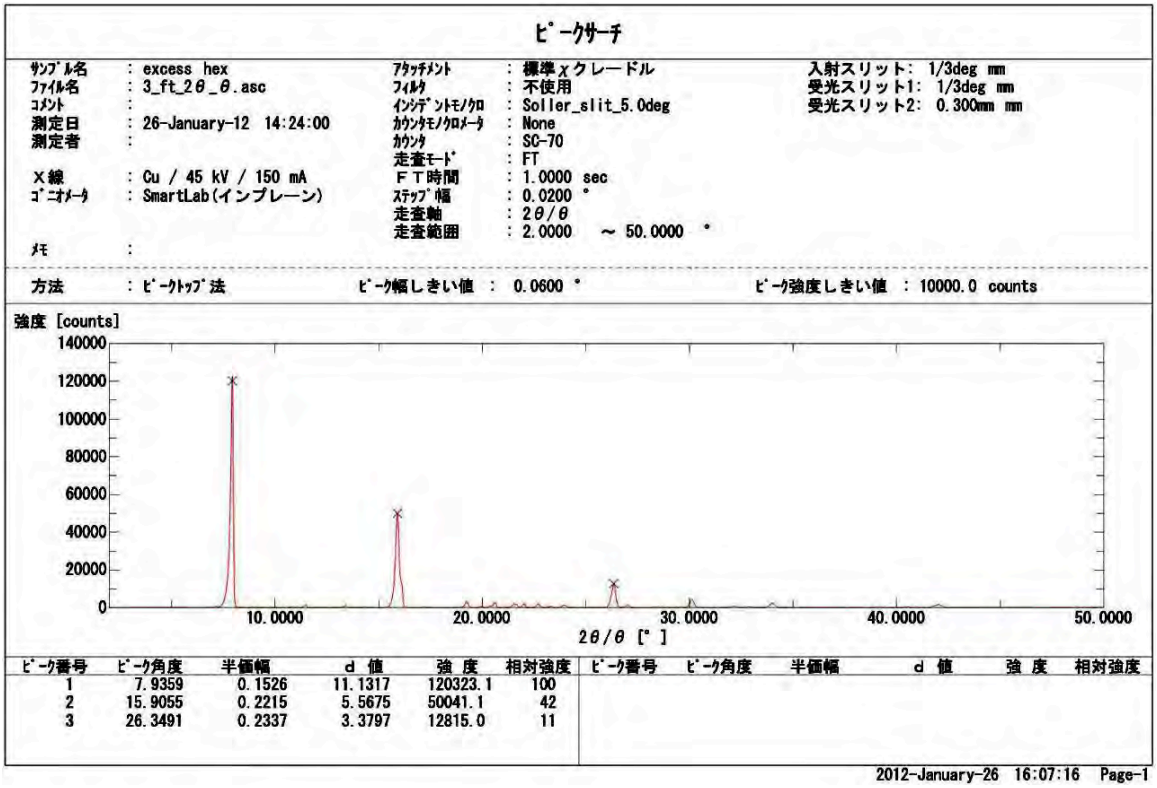
(a) Recrystallised from diethyl ether-hexane solution,



(b) crushed solid prepared by a rapid evaporation of EtOH solution,



(c) raw solid prepared by the addition of hexane to the diethyl ether solution.



Reference

[S-1] Katagiri, T.; Obara, F.; Toda, S.; Furuhashi, K. *Synlett*, **1994**, 507-508.