Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Single-crystal-to-single-crystal Transformation of Tetrathiafulvalene-Based Hydrogen-bonded organic frameworks

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Experimental Section

Unless otherwise mentioned, all reagents and solvents were purchased from commercial sources and used as received without further purification. Tetrathiafulvalene tetracarboxylic acid (H_4TTFTB) was supplied by Shanghai Tensus Biotech. The material is an amorphous powdery substance. It was characterized by ^{1}HNMR to verify its purity and the result is shown as Fig. S10.

1.1 Synthesis of PFC-77

Weigh 30 mg of H_4TTFTB into a vial, add 5 mL each of water and THF to dissolve H_4TTFTB. Without tightening the cap, put the vial in an oven at 60°C to allow the THF to gradually volatilize. After 72 h, dark brown-red crystals were obtained.

1.2 Synthesis of PFC-78

Immerse PFC-77 in acetone, PFC-78 can be obtained after 8 h.

1.3 Synthesis of PFC-78

Immerse PFC-77 or PFC-78 in CH_2Cl_2, and PFC-79 can be obtained within 10 minutes.

1.4 Analysis of studied structures

1H-NMR spectra were recorded on Bruker AVANCE III 400MHz spectrometers. Single crystal X-ray diffraction data was collected at 150K on an Bruker D8 Venture diffractometer equipped with Cu-Kα radiation (λ = 0.71073 Å). PXRD was performed on Rikagu Miniflex 600 Benchtop X-ray diffraction instrument. TGA was performed on a Seiko S-II instrument, and the dried crystalline samples were heated at a rate of 5 °C/min up to 800 °C and then cooled to room temperature under N_2 atmosphere. The N_2 gas isotherms of the samples were measured using ASAP 2460 from Micromeritics Co. Ltd.

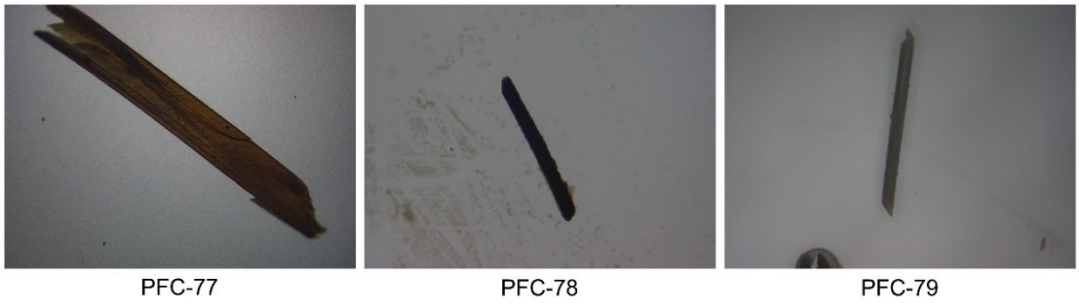

Fig. S1. Microscope image of PFC-77, PFC-78 and PFC-79.

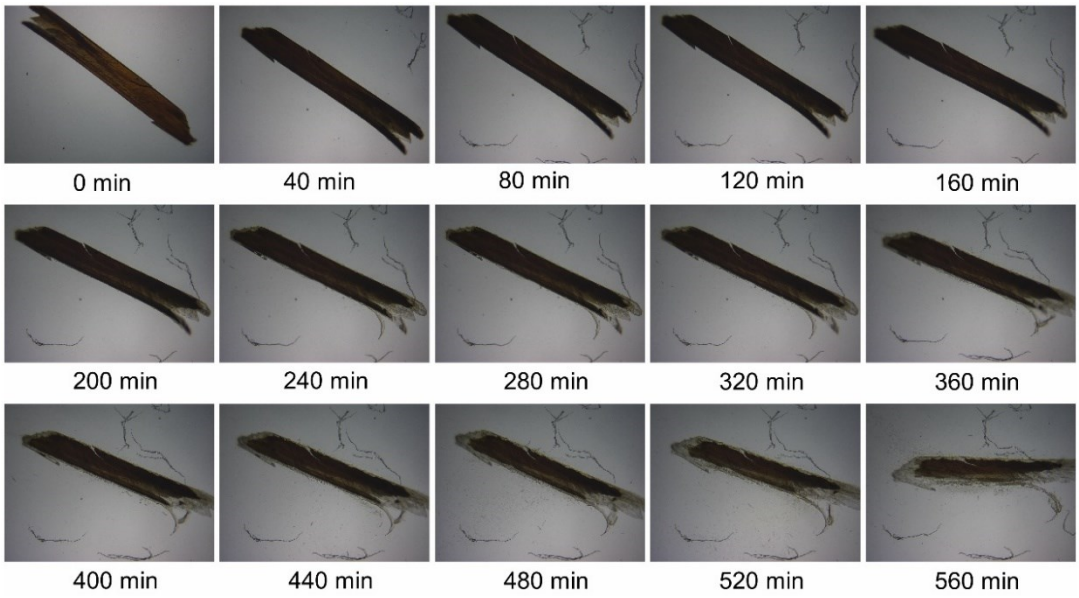

Fig. S2. The transformation process from PFC-77 to PFC-78.

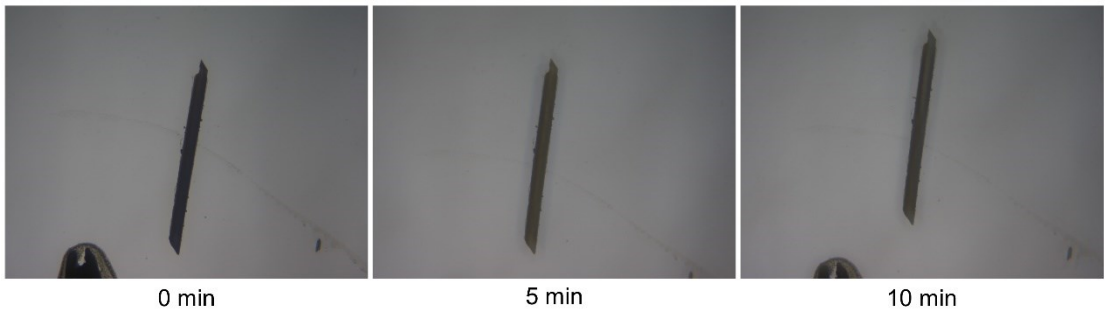

Fig. S3. The transformation process from PFC-78 to PFC-79.

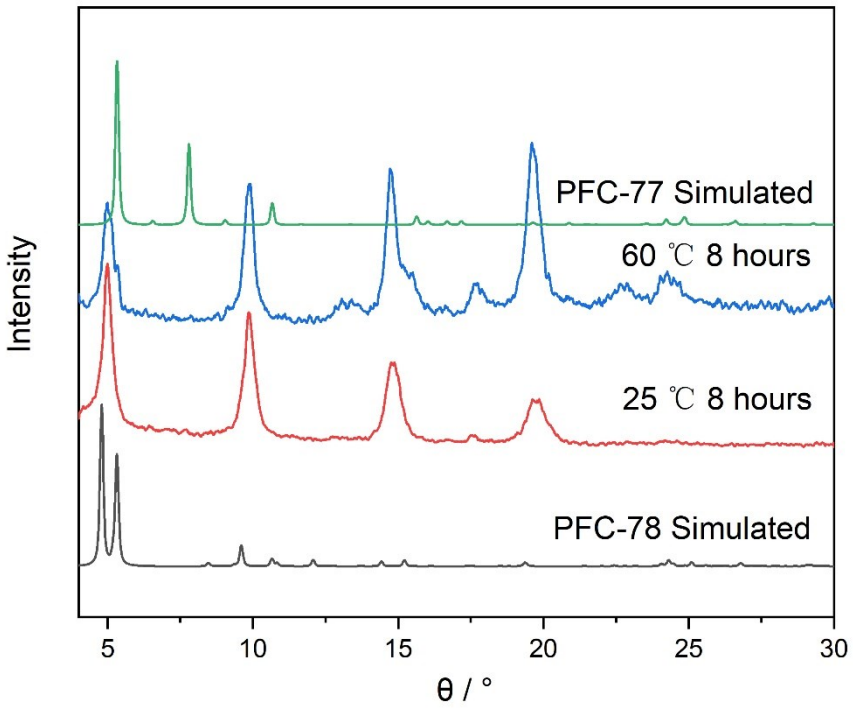

Fig. S4. PXRD pattern of PFC-78 immersed in mother liquid of PFC-77 for 8 hours at 25 ℃ and 60 ℃.

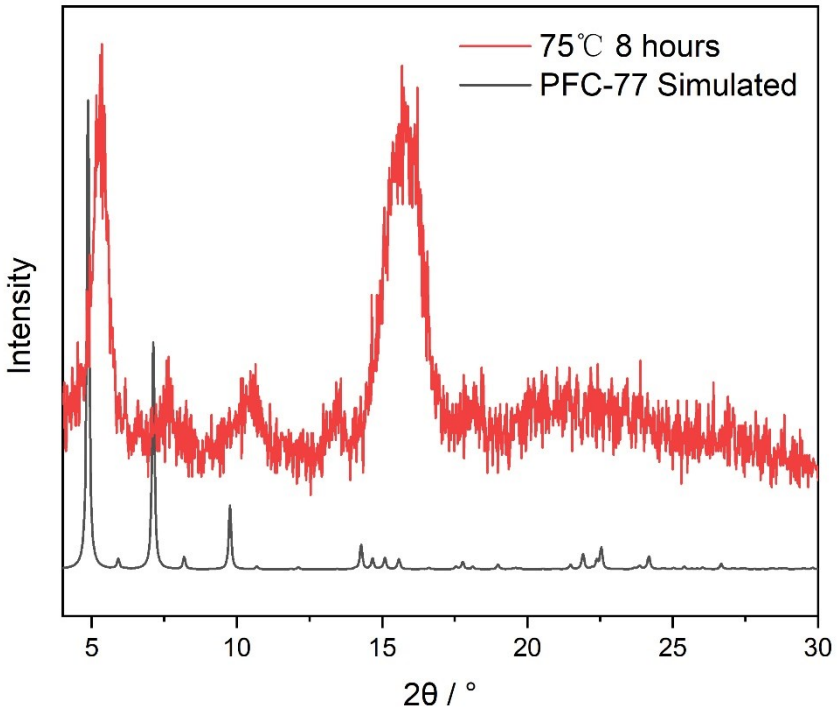

Fig. S5. PXRD pattern of PFC-77 heated at 75 ℃ under vacuum for 8 hours.

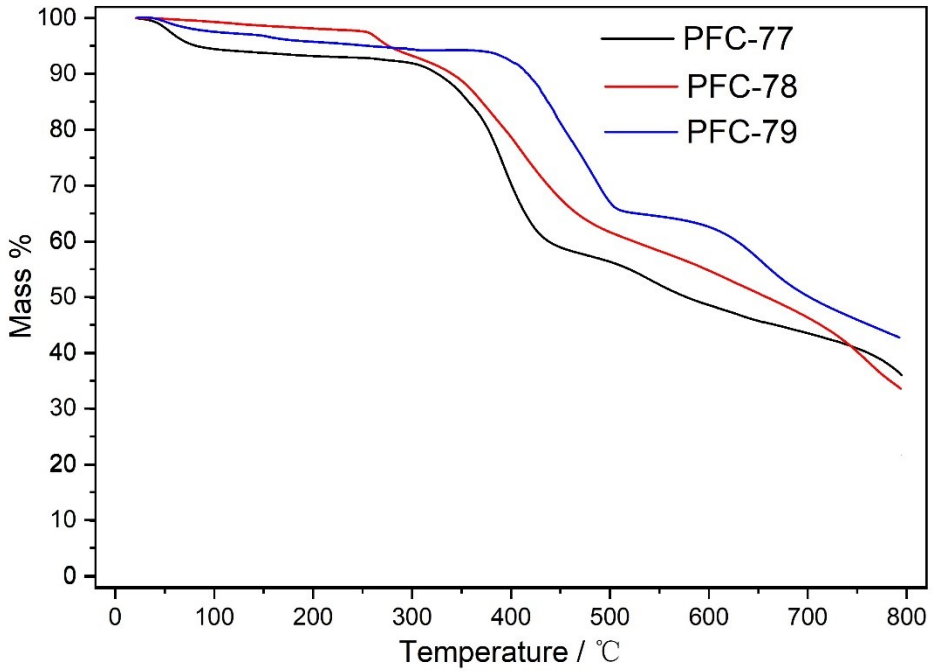

Fig. S6. TGA curves of PFC-77, activated PFC-78 and PFC-79.

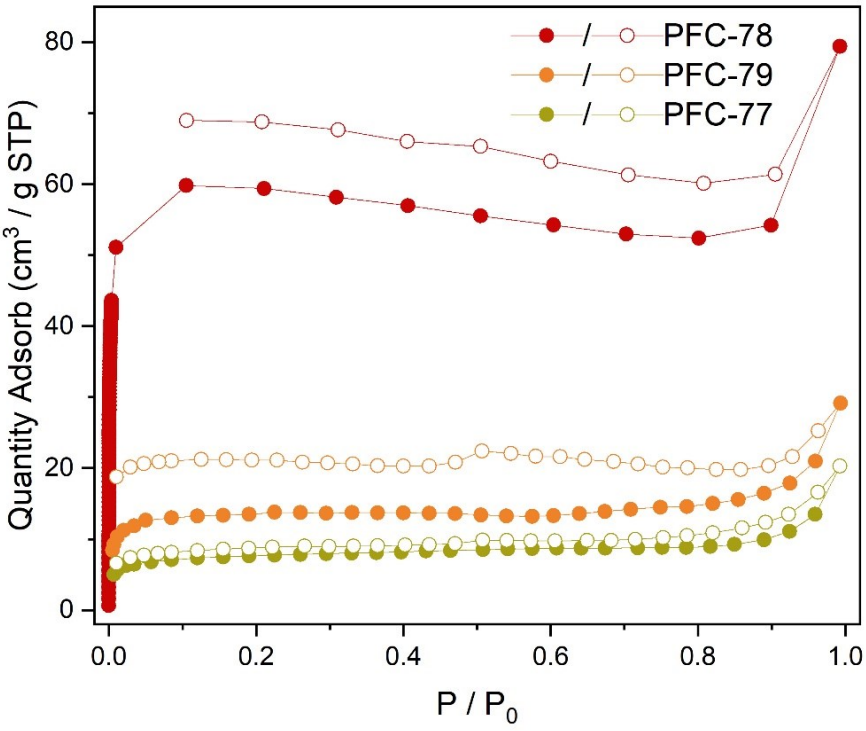

Fig. S7 N_2 isotherm of MTV PFC-77, PFC-78 and PFC-79 at 77 K.

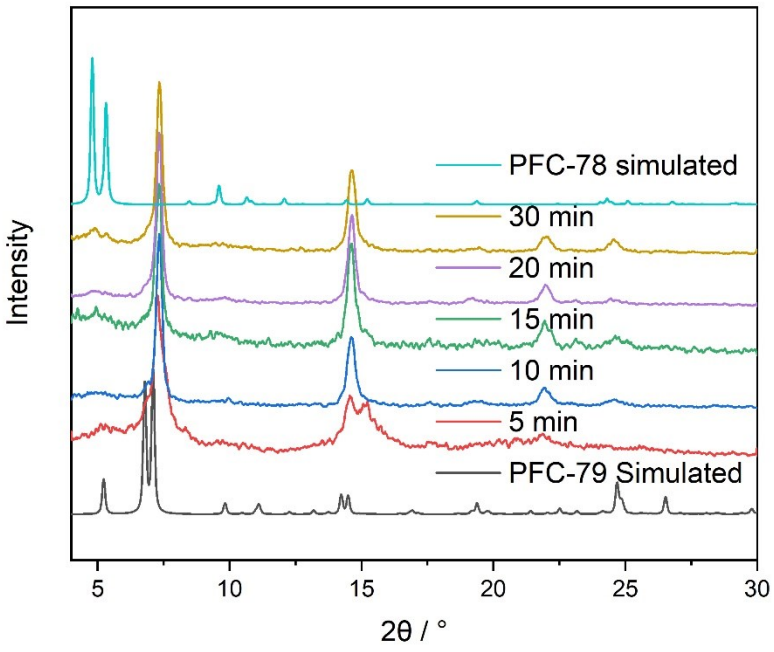

Fig. S8 PXRD patterns of PFC-78 immersed in CH_2Cl_2 after increasing minutes.

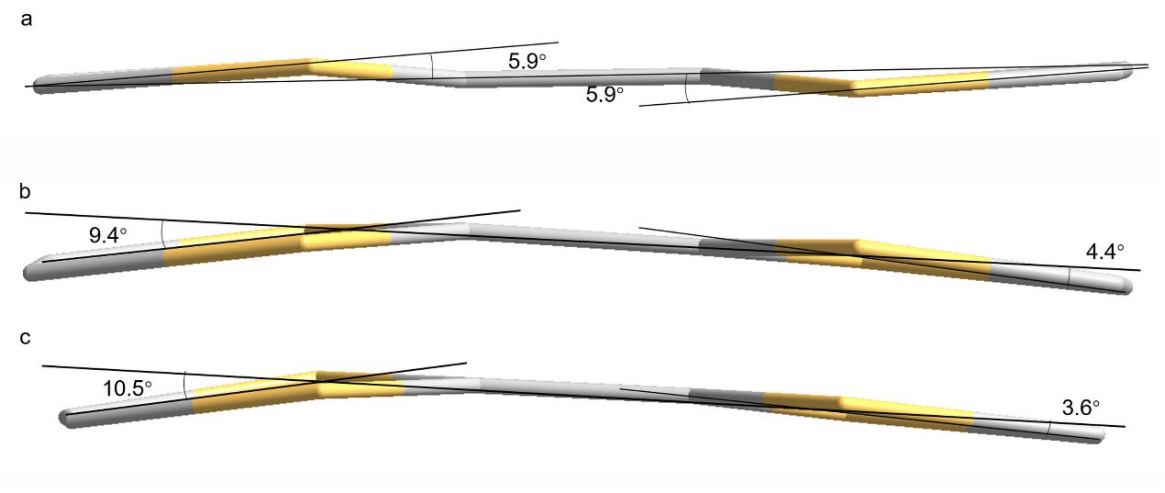

Fig. S9 Torsion angle of a) PFC-77 b) PFC-78 c) PFC-79.

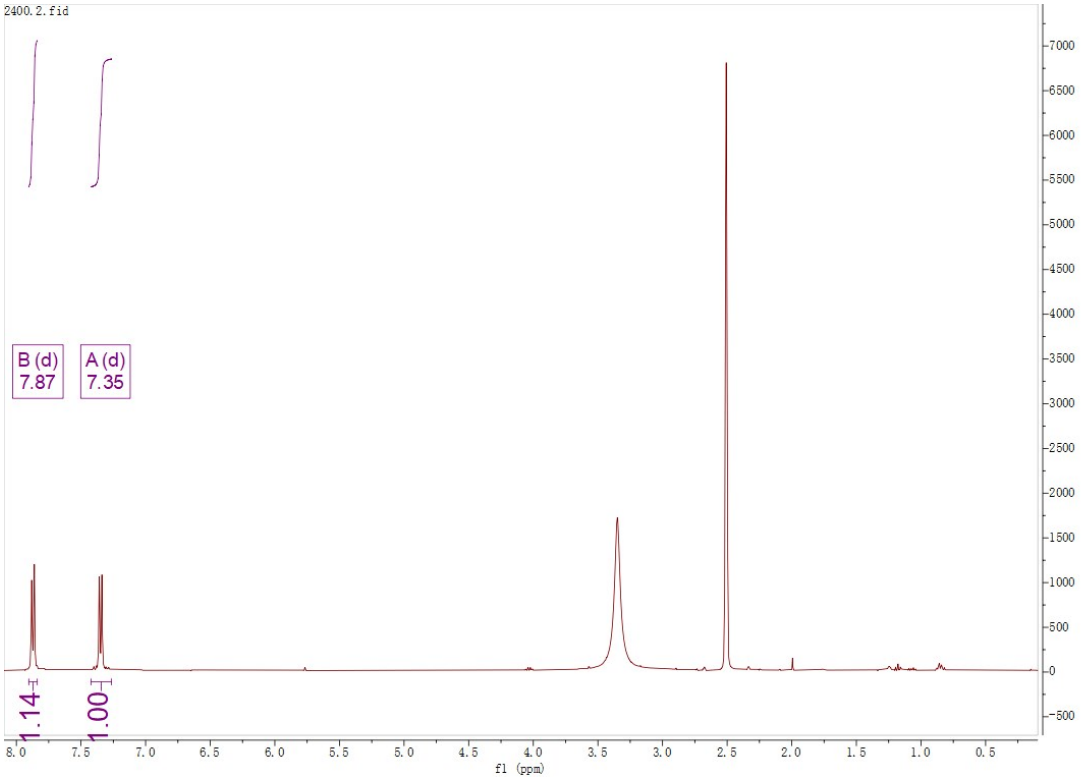

Fig. S10. ^{1}HNMR of H_4TTFTB

Single-Crystal X-ray Crystallography

Single-crystal X-ray diffraction data was collected at 150 K on an Bruker D8 Venture diffractometer equipped with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct method and refined using SHELXL-2014 software package. In addition, the "SQUEEZE" command was employed because of the seriously disordered solvent molecules (H_2O, CH_2Cl_2 and acetone) in pores. Additional crystallographic data with CCDC reference numbers 2077900, 2077917 and 2077923 for PFC-77, PFC-78 and PFC-79 have been deposited within the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/deposit. Crystal data are summarized in Table S1.

Table S1 Crystal data of the PFC-77, PFC-78 and PFC-79

Identification code	PFC-77	PFC-78	PFC-79
Empirical formula	$C_{17}H_{10}O_4S_2$	$C_{34}H_{20}O_8S_4$	$C_{34}H_{20}O_8S_4$
Formula weight	342.37	684.74	684.74
Temperature/K	140.15	149.99	149.99
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	5.778(3)	8.301(7)	8.4537(17)
b/Å	13.713(7)	18.954(18)	14.128(3)
c/Å	16.811(8)	20.558(15)	18.021(4)
α/°	81.532(19)	114.88(5)	106.291(9)
β/°	81.28(2)	96.22(6)	97.991(9)
γ/°	86.70(2)	95.19(7)	103.267(10)
Volume/Å^3	1301.4(11)	2884(4)	1962.5(7)
Z	2	2	2
ρ_{calc}g/cm^3	0.874	0.789	1.159
μ/mm^{-1}	0.214	0.194	0.284
F(000)	352	704	704
Crystal size/mm^3	0.3 × 0.2 × 0.1	1.0 × 0.2 × 0.1	1 × 0.6 × 0.6
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.012 to 45.446	4.318 to 37.918	4.826 to 41.632
Index ranges	-6 ≤ h ≤ 6, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-7 ≤ h ≤ 7, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-8 ≤ h ≤ 8, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	8974	13491	12077
Independent reflections	3487 [R_{int} = 0.0772, R_{sigma} = 0.1183]	4544 [R_{int} = 0.1408, R_{sigma} = 0.1413]	4074 [R_{int} = 0.1757, R_{sigma} = 0.1751]
Data/restraints/parameters	3487/1/113	4544/55/200	4074/50/418
Goodness-of-fit on F^2	1.395	1.882	1.442
Final R indexes [I>=2σ (I)]	R_1 = 0.1420, wR_2 = 0.4046	R_1 = 0.1960, wR_2 = 0.4930	R_1 = 0.1693, wR_2 = 0.4086
Final R indexes [all data]	R_1 = 0.1810, wR_2 = 0.4283	R_1 = 0.2800, wR_2 = 0.5540	R_1 = 0.2913, wR_2 = 0.4897
Largest diff. peak/hole / e Å^{-3}	0.72/-0.51	1.61/-0.84	0.71/-0.74

Cyclic voltammetry curve (CV)

The cyclic voltammetry (CV) test is done on the rotating ring disk electrode system. 5 mg of the sample to be tested was soaked in 1 mL of acetone and sonicated for 30 min for dispersion. Then 100 μL of naphthol solution was added to the mixed solution. Leave a space of 1 cm^2 at both ends on the 1 cm wide conductive glass, and brush nail polish on the remaining area to isolate the conductive glass from contacting the electrolyte. 20 μL pipette was used to drop the dispersed sample mixture evenly on a blank area of the conductive glass and wait for it to dry. Repeat five times. The electrolyte used are 250 mL each of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution for PFC-77 and PFC-78 or 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) trichloromethane solution for PFC-79.