

## Supporting Information for

# **Poly(ethylene glycol)-Functionalized 3D Covalent Organic Framework as Solid-state Polyelectrolytes**

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## 1 Materials and general methods

### 1.1 Materials

All chemicals are used as received without further purification. All solvents were dried and distilled via normal approaches. 2,5-dibromobenzene-1,4-diol,  $K_2CO_3$ , NaOH, from energy chemical (Shanghai, China). 4-formylphenylboronic acid,  $Pd(PPh_3)_4$ , *p*-toluenesulfonyl chloride, triethylene glycol monomethyl ether, KOH, 2,2'-(ethane-1,2-diylobis(oxy))bis(ethan-1-ol), Bistrifluoromethanesulfonimide lithium salt (LiTFSI) was provided by Heowns Biochem Technologies LLC (Tianjin, China).

### 1.2 Characterization

PXRD patterns were collected on a Bruker D8 Advance diffractometer using Cu  $K\alpha$  radiation. Fourier Transform Infrared spectra were measured on a Thermo Fisher Scientific with Universal ATR accessory between the ranges of 4000 to 550  $cm^{-1}$ .  $N_2$  adsorption/desorption measurements were performed on a BELSORP II mini, samples were activated at 100 °C for 12 h with BELPREP VAC III before the measurement. TGA was performed using a TGA/SDTA851E under flowing  $N_2$  with 10  $K\ min^{-1}$  ramp rate from 50 °C-900 °C. SEM images were collected using a JSM-IT500HR system. Differential scanning calorimetry (DSC) was carried out with a Hitachi DSC7020 at the heating rate of 10  $K\ min^{-1}$ . The solid NMR of  $^7Li$  in the sample were recorded on AVANCE III WB 400 MHz of Bruker.

### 1.3 Ionic conduction measurements

The samples were pressed into pellets with a diameter of 5 mm, and then sandwiched between two stainless steel electrodes. AC impedance measurements were carried out by Biological SP-200 portable working station, and the frequency range was from 7 M to 0.1 Hz, the amplitude voltage was 20 mV, the temperature range was from

100 to 260 °C. The ionic conductivities of the materials were calculated by the equation (1):

$$\sigma = L / (S \times R) \quad (1)$$

where L (cm) is the thickness of electrolyte pellet, S is the area (cm<sup>2</sup>) of electrolyte pellet, and R is the impedance ( $\Omega$ ) which can be obtained directly from AC impedance measurement curves.

#### 1.4 Li<sup>+</sup> Transference number ( $t_{Li^+}$ ) measurements

The samples were pressed into pellets with a diameter of 5 mm, and then sandwiched between two lithium metal foils electrodes with a thickness of around 200  $\mu$ m to assemble into lithium symmetric coin cell. Li<sup>+</sup> transference number ( $t_{Li^+}$ ) measurements of 3D-COF-PEG6-Li were carried out by Biological SP-200 portable working station with a constant bias voltage of 50 mV at 100 °C. The  $t_{Li^+}$  of 3D-COF-PEG6-Li were calculated by the equation (2):

$$t_{Li^+} = \frac{I_s[\Delta V - I_0 R_0]}{I_0[\Delta V - I_s R_s]} \quad (2)$$

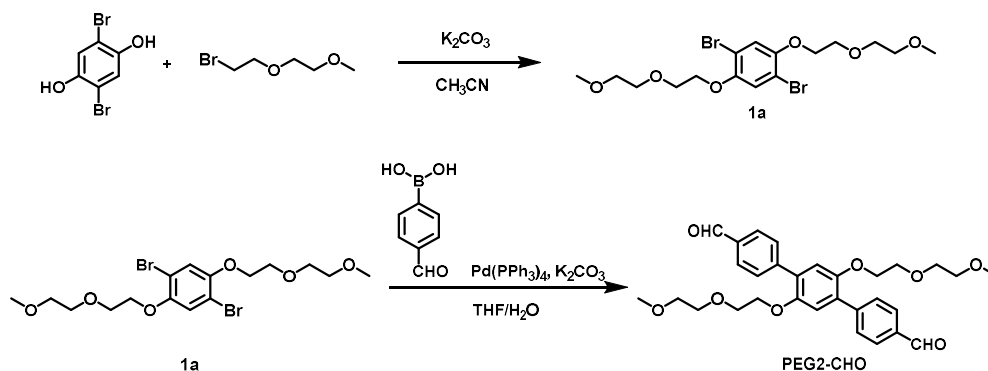
where  $\Delta V$  (mV) is polarization voltage,  $I_0$  ( $\mu$ A) and  $I_s$  ( $\mu$ A) are initial current and steady-state current obtained by constant voltage polarization method testing,  $R_0$  (k $\Omega$ ) and  $R_s$  (k $\Omega$ ) are the interface resistance before and after the test.

#### 1.5 Electrochemical stability window

The samples were pressed into pellets with a diameter of 5 mm, then were sandwiched between a stain steel and a lithium metal foil and assembled into coin cell. The electrochemical stability window of samples was obtained by a linear sweep voltammetry at the scanning rate of 1.0 mV/s from open circuit voltage to 6.0 V at 100 °C.

## 2. Synthesis

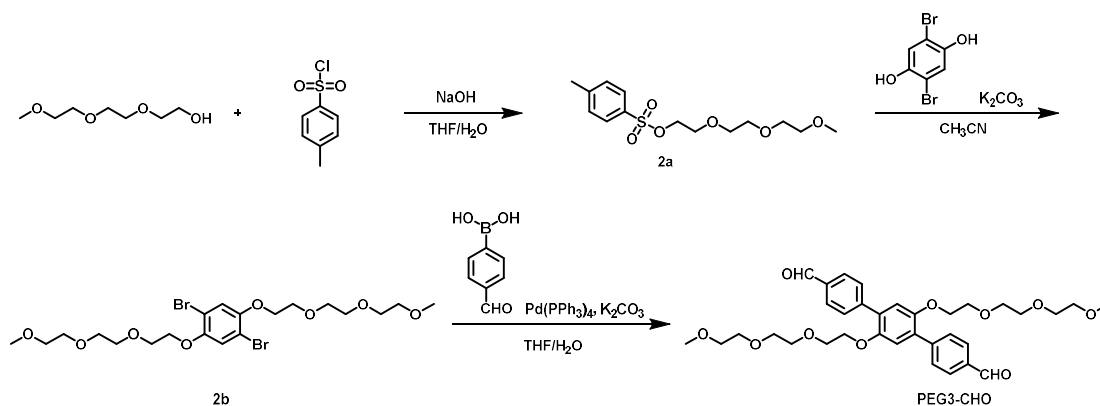
### 2.1 Synthesis of 2',5'-bis(2-(2-methoxyethoxy)ethoxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (PEG2-CHO)



*Synthesis of 1,4-dibromo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (1a):* To a 100 mL Schlenk, 2,5-dibromobenzene-1,4-diol (2.14 g, 8.0 mmol),  $K_2CO_3$  (5.52 g, 40.0 mmol) were added, then the flask was vacuumed for 30 minutes, during which argon gas was pumped three times. Under Ar atmosphere, dry acetonitrile (40 mL) and 1-bromo-2-(2-methoxyethoxy)ethane (2.4 mL, 17.5 mmol) were added, and the reaction was stirred at 90 °C for 12 h. The mixture was filtered and concentrated in vacuum. Silica gel column chromatography (hexane/ ethyl acetate; 1/1) was used to afford 1a as white powders (yield: 67%)

*Synthesis of PEG2-CHO:* To a 250 mL Schlenk, 1a (2.36 g, 5 mmol), 4-formylphenylboronic acid (2.26 g, 15 mmol),  $Pd(PPh_3)_4$  (340 mg) and  $K_2CO_3$  (2.07 g, 15 mmol) were dissolved in dry tetrahydrofuran (100 mL) and anaerobic water (20 mL) under Ar atmosphere. The reaction was stirred at 80 °C overnight. After cooling to room temperature, solvent was concentrated in vacuo and extracted with  $CH_2Cl_2$ , washed with  $H_2O$  (3×30mL), separated, dried over  $Na_2SO_4$ , filtered, and concentrated. The crude product was purified by column chromatography (hexane/ ethyl acetate; 1/1) to afford PEG2-CHO as off-white powders (yield: 56%)

## 2.2 Synthesis of 2',5'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (PEG3-CHO)



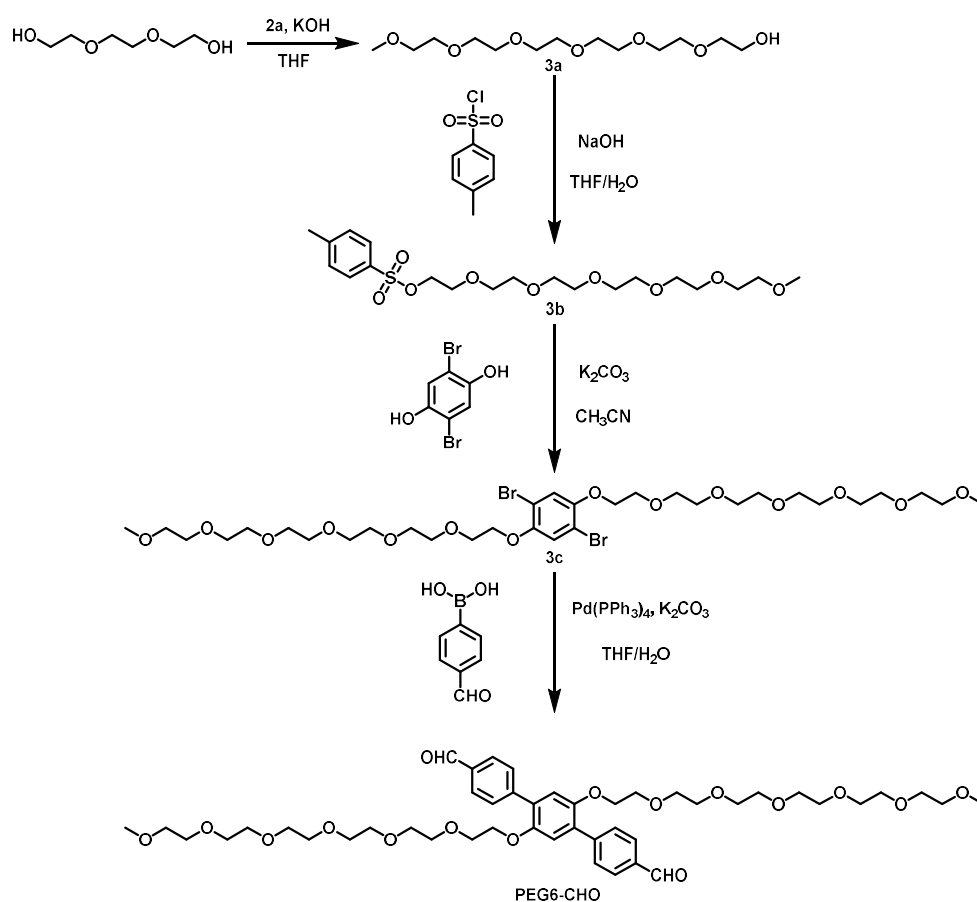
*Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (2a):* p-toluenesulfonyl chloride (5.72 g, 30.0 mmol) was dissolved in 8 mL tetrahydrofuran under Ar atmosphere, and cold to 0 °C. NaOH (1.20 g, 30 mmol) in 8 mL anaerobic water and triethylene glycol monomethyl ether (3.28g, 20 mmol) were added dropwise at 0 °C under Ar. The reaction was stirred at room temperature for 3 h. The organic layer was extracted with diethyl ether, washed with sat. aq. NaOH and H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was concentrated under vacuum to afford 5b as colorless oil (yield: 84%).

*Synthesis of 1,4-dibromo-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (2b):* 2,5-dibromobenzene-1,4-diol (1.07 g, 4 mmol) and potassium tert-butoxide (1.12 g, 10 mmol) were dissolved in 20 mL ethyl alcohol under Ar atmosphere. Then 2a (3.18 g, 10 mmol) was added to the above system at room temperature. The reaction was heated to reflux, and stirred for 48 h under Ar. After cooling to room temperature, H<sub>2</sub>O (20 mL) was added, and organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with sat. aq. NaOH and H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was concentrated under vacuum to afford crude product, which was used for next reaction without further purified.

*Synthesis of (PEG3-CHO):* To a 250 mL Schlenk, 2b (2.24 g, 4 mmol), 4-formylphenylboronic acid (1.81 g, 12 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (280 mg) and K<sub>2</sub>CO<sub>3</sub> (1.67 g, 12 mmol) were dissolved in dry tetrahydrofuran (100 mL) and anaerobic water (20 mL)

under Ar atmosphere. The reaction was stirred at 80 °C overnight. After cooling to room temperature, solvent was concentrated in vacuo and extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O (3×30mL), separated, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and methanol to afford PEG3-CHO as off-white powders (yield: 61%).

### 2.3 Synthesis of 2',5'-bis((2,5,8,11,14,17-hexaoxonadecan-19-yl)oxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (PEG6-CHO)<sup>[S1-S2]</sup>



*Synthesis of 2,5,8,11,14,17-hexaoxonadecan-19-ol (3a):* To a 100 mL Schlenk, KOH (1.85 g, 33 mmol), dry tetrahydrofuran (20 mL) and 2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-ol) (16 mL, 120 mmol) were added under Ar atmosphere, the mixture was reflux for 30 minutes. The reaction was cooled to room temperature, treated with 2a (9.55 g, 30 mmol), and kept reflux for 18 h. After cooling to room

temperature, solvent was concentrated in vacuum and extracted with  $\text{CHCl}_3$ , dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated to afford 3a as off-white oil (yield: 93%).

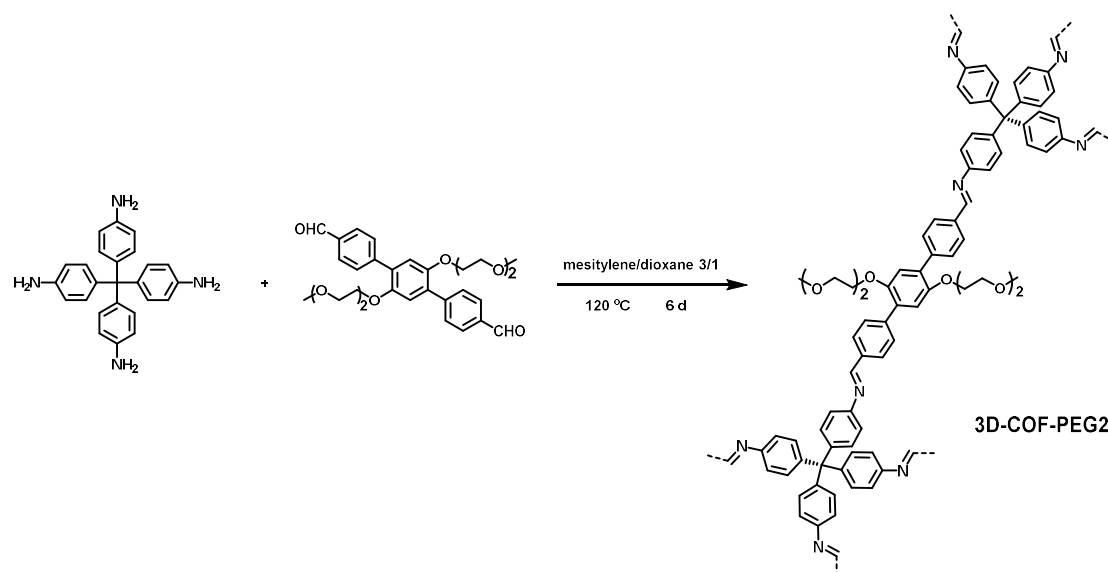
*Synthesis of 2,5,8,11,14,17-hexaoxonadecan-19-yl 4-methylbenzenesulfonate (3b):* p-toluenesulfonyl chloride (5.72 g, 30.0 mmol) was dissolved in 8 mL tetrahydrofuran under Ar atmosphere, and cold to 0 °C. NaOH (1.20 g, 30 mmol) in 8 mL anaerobic water and triethylene glycol monomethyl ether (5.93 g, 20 mmol) were added dropwise at 0 °C under Ar. The reaction was stirred at room temperature for 3 h. The organic layer was extracted with diethyl ether, washed with sat. aq. NaOH and  $\text{H}_2\text{O}$ , dried over  $\text{Na}_2\text{SO}_4$  and the solvent was concentrated under vacuum to afford 3b as colorless oil (yield: 91%).

*Synthesis of 19,19'-((2,5-dibromo-1,4-phenylene)bis(oxy))bis(2,5,8,11,14,17-hexaoxanona decane) (3c):* 2,5-dibromobenzene-1,4-diol (1.07 g, 4 mmol) and potassium tert-butoxide (1.12 g, 10 mmol) were dissolved in 20 mL ethyl alcohol under Ar atmosphere. Then 3b (4.5 g, 10 mmol) was added to the above system at room temperature. The reaction was heated to reflux, and stirred for 48 h under Ar. After cooling to room temperature,  $\text{H}_2\text{O}$  (20 mL) was added, and organic layer was extracted with  $\text{CH}_2\text{Cl}_2$ , washed with sat. aq. NaOH and  $\text{H}_2\text{O}$ , dried over  $\text{Na}_2\text{SO}_4$  and the solvent was concentrated under vacuum to afford crude product as off-white oil.

*Synthesis of PEG6-CHO:* To a 250 mL Schlenk, 3c (3.30 g, 4 mmol), 4-formylphenylboronic acid (1.81 g, 12 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (280 mg) and  $\text{K}_2\text{CO}_3$  (1.67 g, 12 mmol) were dissolved in dry tetrahydrofuran (100 mL) and anaerobic water (20 mL) under Ar atmosphere. The reaction was stirred at 80 °C overnight. After cooling to room temperature, solvent was concentrated in vacuum and extracted with  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{H}_2\text{O}$  (3×30mL), separated, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The crude product was purified by column chromatography to afford PEG6-CHO as faint yellow oil (yield: 48%).

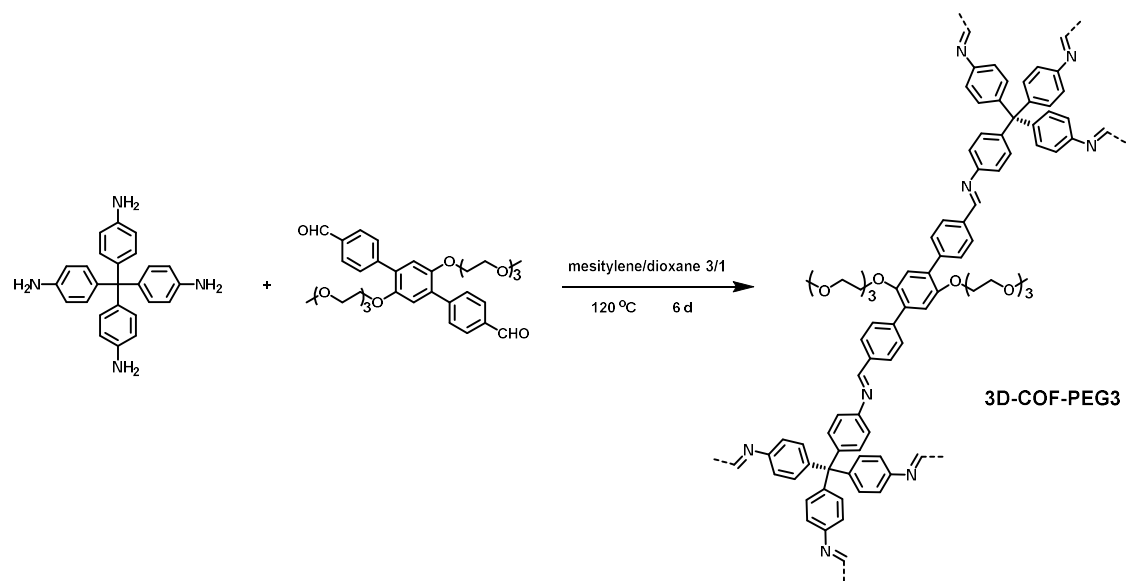


## 2.4 Synthesis of 3D-COF-PEG2



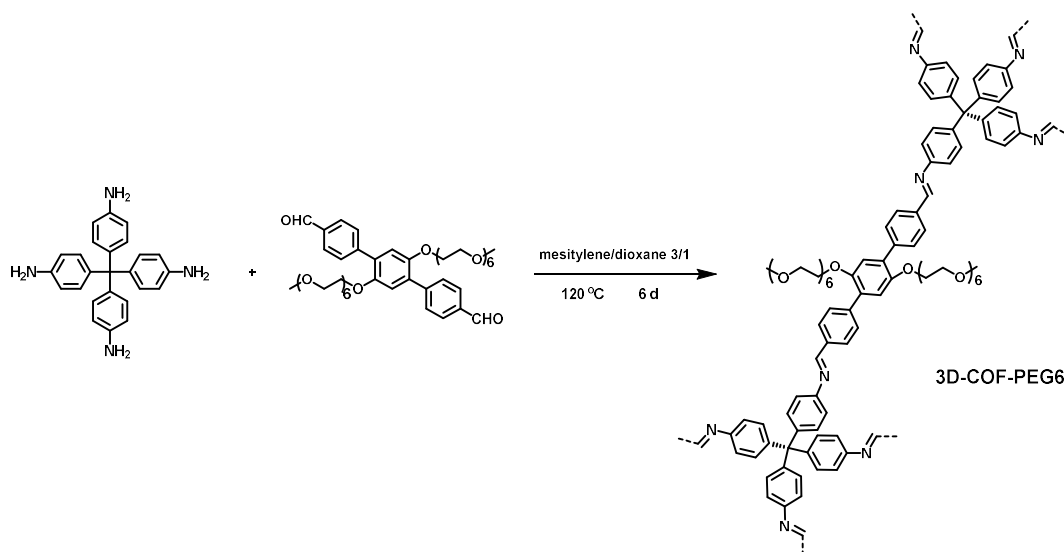
**PEG2-CHO** (52.2 mg, 0.10 mmol) and Tetrakis(4-aminophenyl)methane (**TAPM**, 19.0 mg, 0.05 mmol) were weighed into a Pyrex tube, then mesitylene (1.5 mL), dioxane (0.5 mL) were added. After ultrasound for 5 min, 6 M acetic acid (0.2 mL) was added as catalyst. The ampoule was degassed through freeze-pump-thaw cycles for three times and flame sealed. The reaction was kept at 120 °C for 6 days, then the solid was filtrated and washed with DMF and acetone, then the powders were carried out by soxhlet extraction from methanol and acetone for 48 h to give yellow powders. The sample was dried at 80 °C under vacuum for 24 h to yield **3D-COF-PEG2** (56 mg, 82.8%)

## 2.5 Synthesis of 3D-COF-PEG3



**PEG3-CHO** (61.0 mg, 0.10 mmol) and **TAPM** (19.0 mg, 0.05 mmol) were weighed into a Pyrex tube, then mesitylene (1.5 mL), dioxane (0.5 mL) were added. After ultrasound for 5 min, 6 M acetic acid (0.2 mL) was added as catalyst. The ampoule was degassed through freeze-pump-thaw cycles for three times and flame sealed. The reaction was kept at 120 °C for 6 days, then the solid was filtrated and washed with DMF and acetone, then the powders were carried out by soxhlet extraction from methanol and acetone for 48 h to give yellow powders. The sample was dried at 80 °C under vacuum for 24 h to yield **3D-COF-PEG3** (67 mg, 87.7%)

## 2.6 Synthesis of 3D-COF-PEG6



**PEG6-CHO** (87.5 mg, 0.10 mmol) and **TAPM** (19.0 mg, 0.05 mmol) were weighed into a Pyrex tube, then mesitylene (2 mL) were added. After ultrasound for 5 min, 6 M acetic acid (0.2 mL) was added as catalyst. The ampoule was degassed through freeze-pump-thaw cycles for three times and flame sealed. The reaction was kept at 120 °C for 6 days, then the solid was filtrated and washed with DMF and acetone, the powders were carried out by soxhlet extraction from methanol and acetone for 48 h to give yellow powders. The sample was dried at 80 °C under vacuum for 24 h to yield **3D-COF-PEG6** (52 mg, 50.5%).

## 2.7 Synthesis of 3D-COF-PEG<sub>x</sub>-Li (x = 2, 3, 6)

Lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) was dissolved in Tetrahydrofuran (THF) to obtain 1M LiTFSI/THF solution. **3D-COF-PEG<sub>x</sub>** (x = 2, 3, 6) powders (100 mg) were soaked in 30 mL 1M LiTFSI/THF solution at room temperature, after soaking for 12 h, the powders were collected by filtration. Repeat this operation for three times. Then, the samples were dried under vacuum at 100 °C overnight to obtain Lithium ion doped materials, denoted as **3D-COF-PEG<sub>x</sub>-Li** (x = 2, 3, 6).

### 3 Characterization

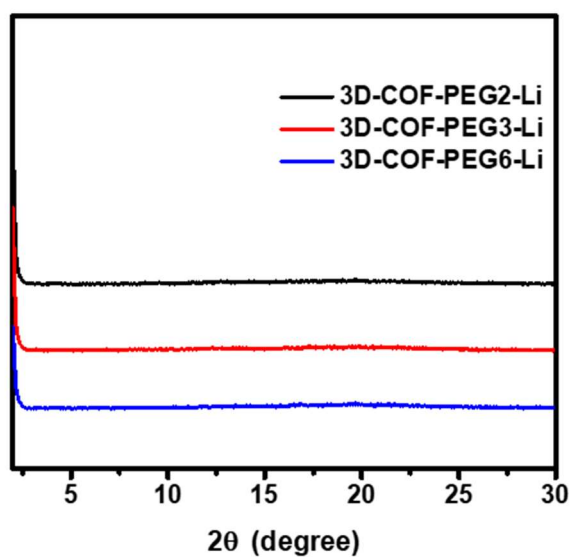


Figure S1. PXRD patterns of 3D-COF-PEG2-Li, 3D-COF-PEG3-Li and 3D-COF-PEG6-Li.

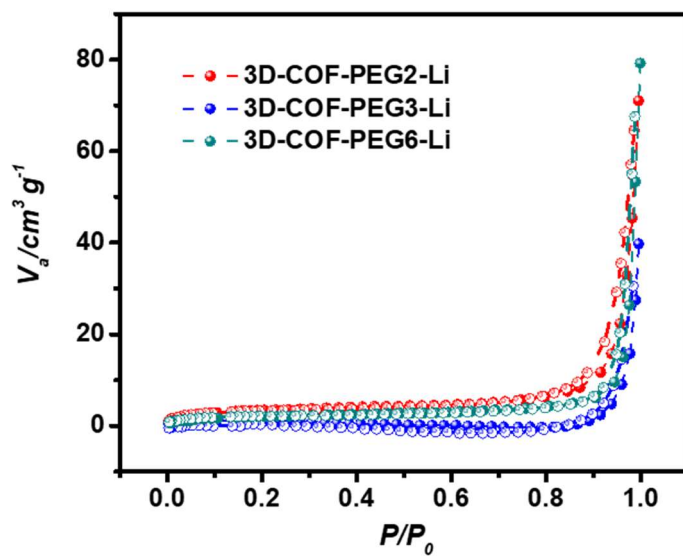


Figure S2. N<sub>2</sub> adsorption of 3D-COF-PEG2-Li, 3D-COF-PEG3-Li and 3D-COF-PEG6-Li.

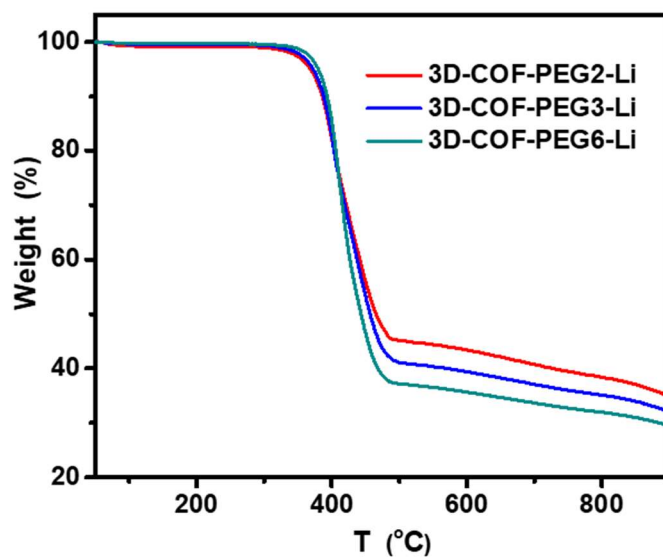


Figure S3. TG plots of 3D-COF-PEG2, 3D-COF-PEG3 and 3D-COF-PEG6.

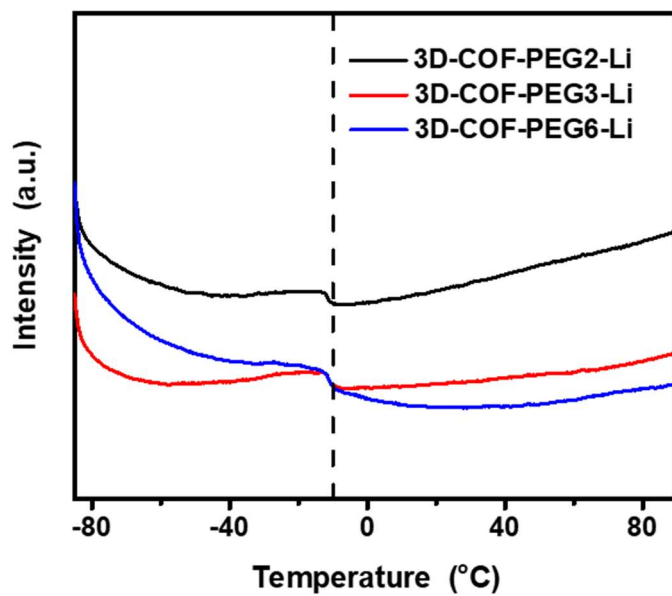
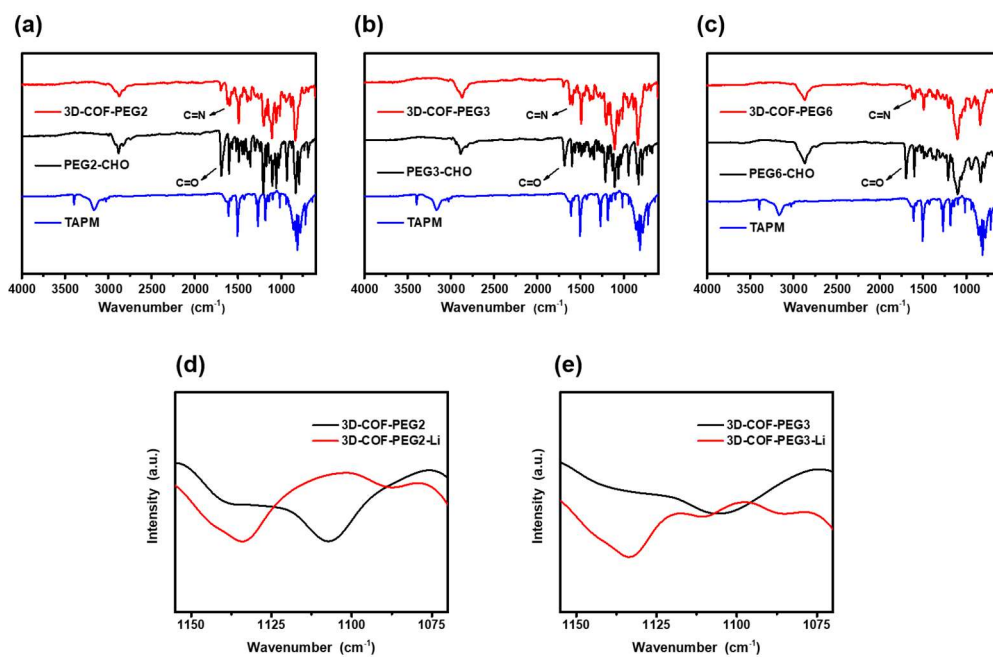
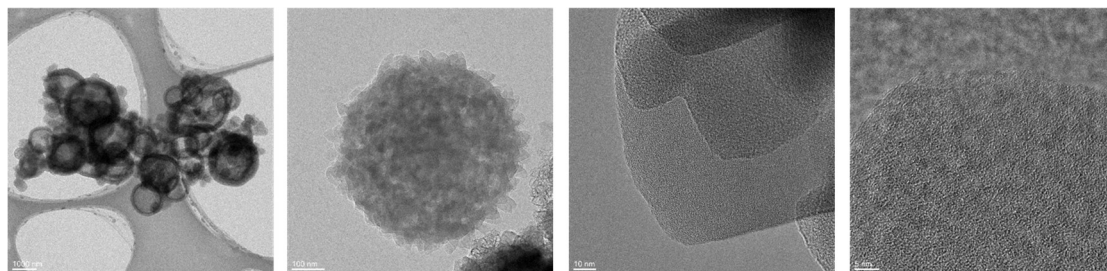


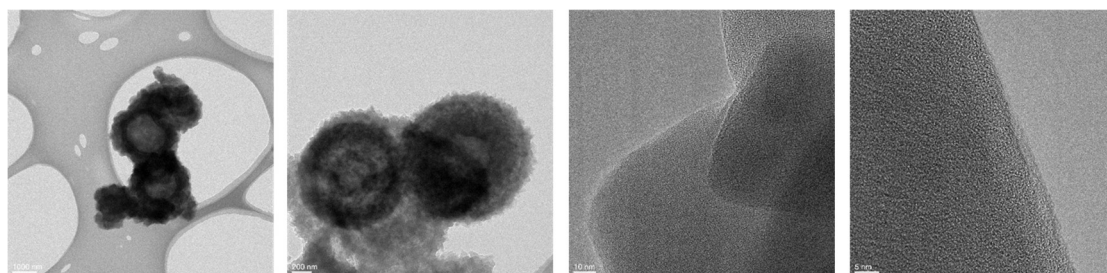
Figure S4. DSC curves of 3D-COF-PEG2-Li, 3D-COF-PEG3-Li and 3D-COF-PEG6-Li.



**Figure S5.** FT-IR plots of (a) 3D-COF-PEG2, PEG2-CHO and TAPM (b) 3D-COF-PEG3, PEG3-CHO and TAPM (c) 3D-COF-PEG6, PEG6-CHO and TAPM (d) 3D-COF-PEG2 and 3D-COF-PEG2-Li and (e) 3D-COF-PEG6 and 3D-COF-PEG6-Li.



**Figure S6.** TEM images of 3D-COF-PEG2.



**Figure S7.** TEM images of 3D-COF-PEG3.

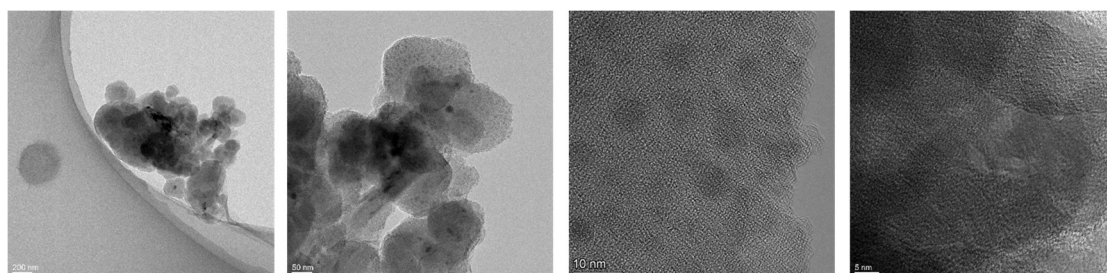


Figure S8. TEM images of 3D-COF-PEG6.

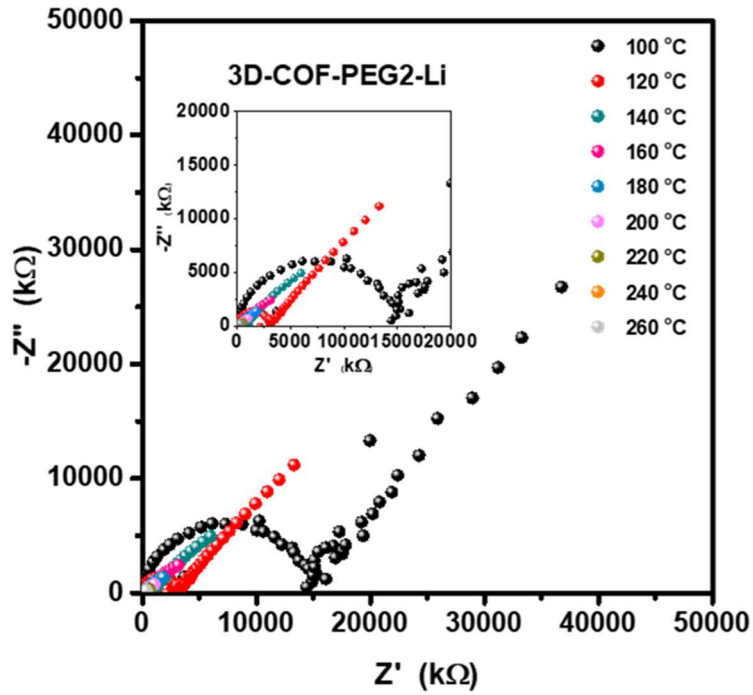


Figure S9. Nyquist plots at different temperatures of 3D-COF-PEG2-Li.

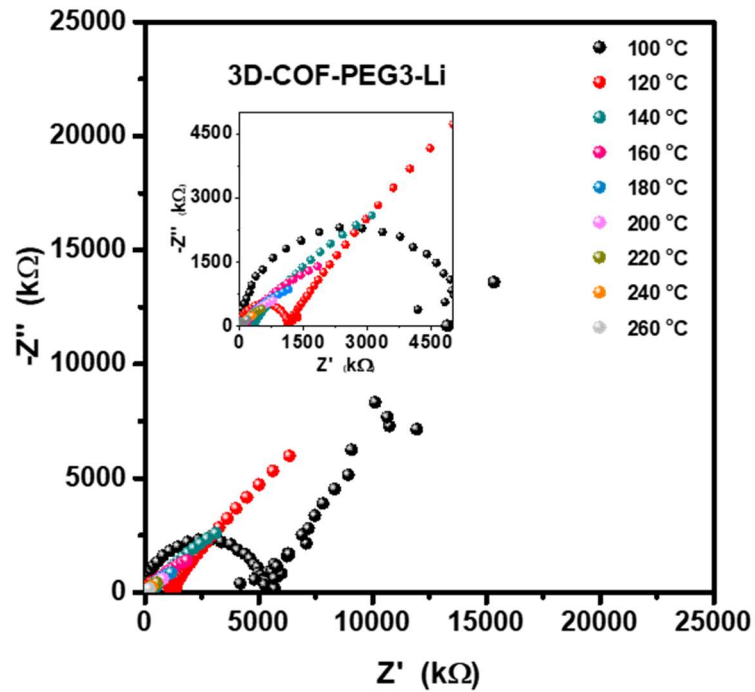


Figure S10. Nyquist plots at different temperatures of 3D-COF-PEG3-Li.

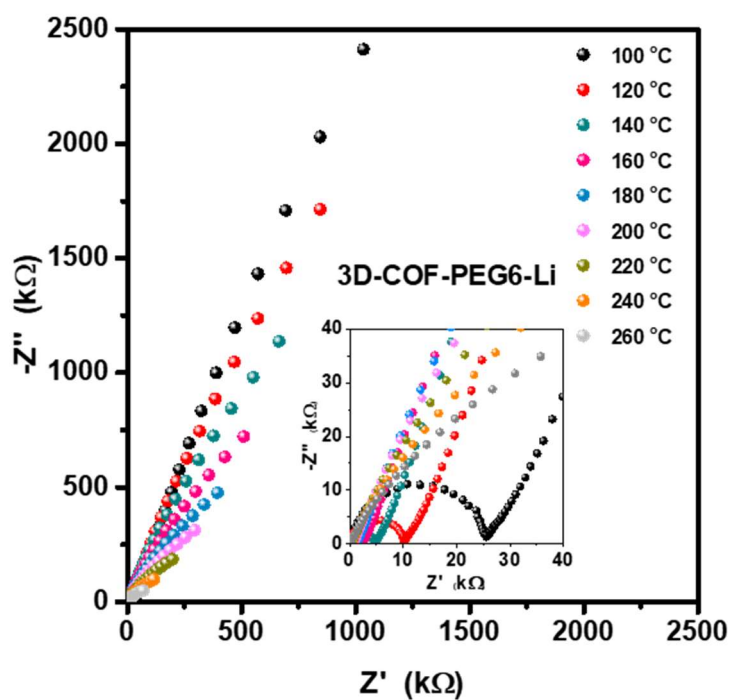


Figure S11. Nyquist plots at different temperatures of 3D-COF-PEG6-Li.

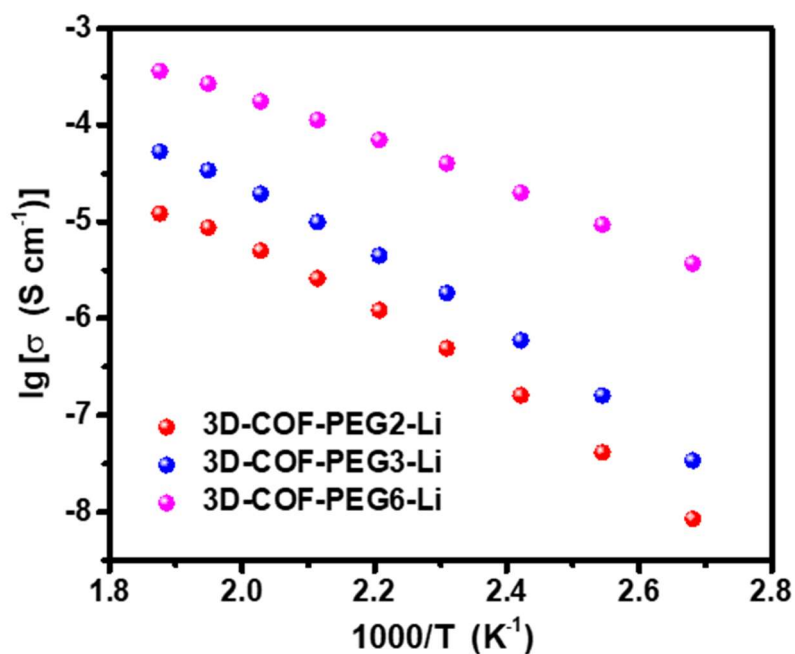
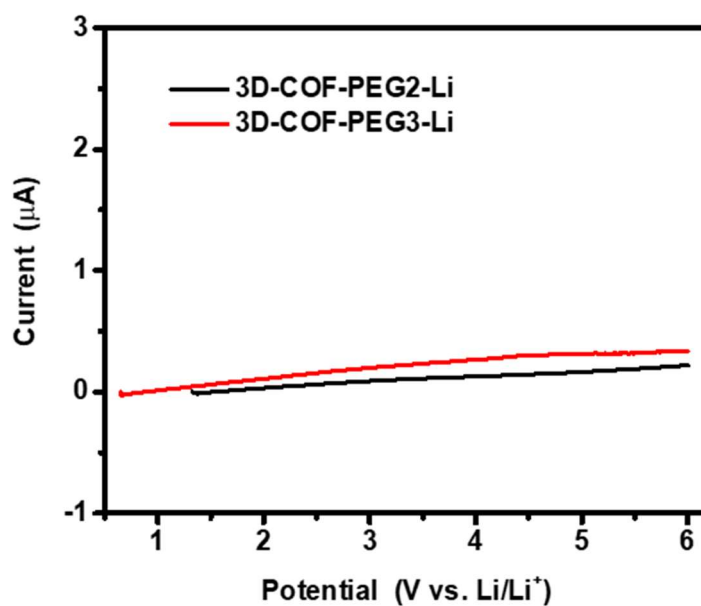


Figure S12. Temperature-dependent  $\text{Li}^+$  conductivities of 3D-COF-PEG2-Li, 3D-COF-PEG3-Li, 3D-COF-PEG6-Li.





**Figure S13.** Linear sweep voltammograms (LSV) of 3D-COF-PEG2-Li and 3D-COF-PEG3-Li at 100 °C.

**Table S1.** Li<sup>+</sup> conductivity comparison between this work and literatures.

	Materials	Temperature	Conductivity (mS cm <sup>-1</sup> )	Reference
1	3D-COF-PEG2-Li	200 °C	0.0026	This work
2	3D-COF-PEG3-Li	200 °C	0.010	
3	3D-COF-PEG6-Li	200 °C	0.11	
4	COF-PEO-3-Li	200 °C	0.097	<i>J. Am. Chem. Soc.</i> <b>2019</b> , <i>141</i> , 1227-1234.
5	COF-PEO-6-Li	200 °C	0.37	
6	COF-PEO-9-Li	200 °C	1.33	
7	Li <sup>+</sup> @TPB-DMTP-COF	80 °C	0.0054	<i>J. Am. Chem. Soc.</i> <b>2018</b> , <i>140</i> , 7429-7432.
8	COF-PEG-B6-Li	200 °C	1.5	<i>ACS Appl. Energy Mater.</i> <b>2021</b> , <i>4</i> , 11720-11725.
9	TpPa-SO <sub>3</sub> Li	RT	0.027	<i>J. Am. Chem. Soc.</i> <b>2019</b> , <i>141</i> , 5880-5885.

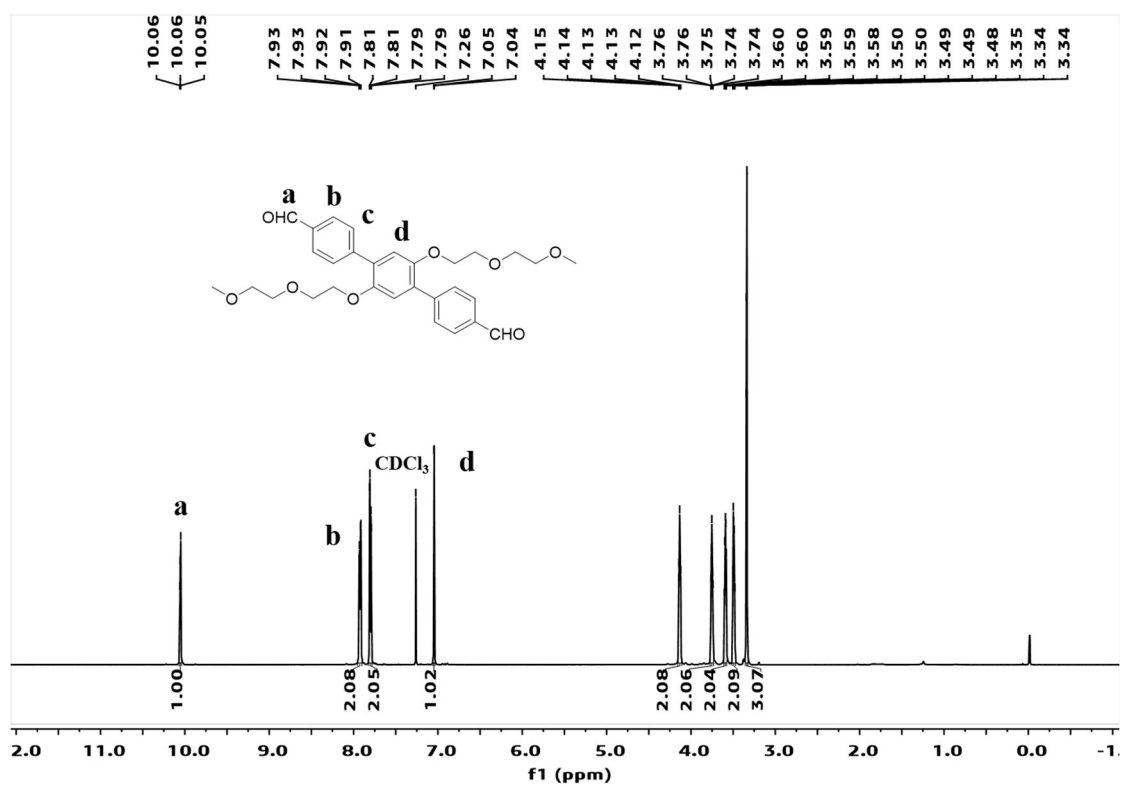


Figure S14. <sup>1</sup>H NMR of PEG2-CHO.

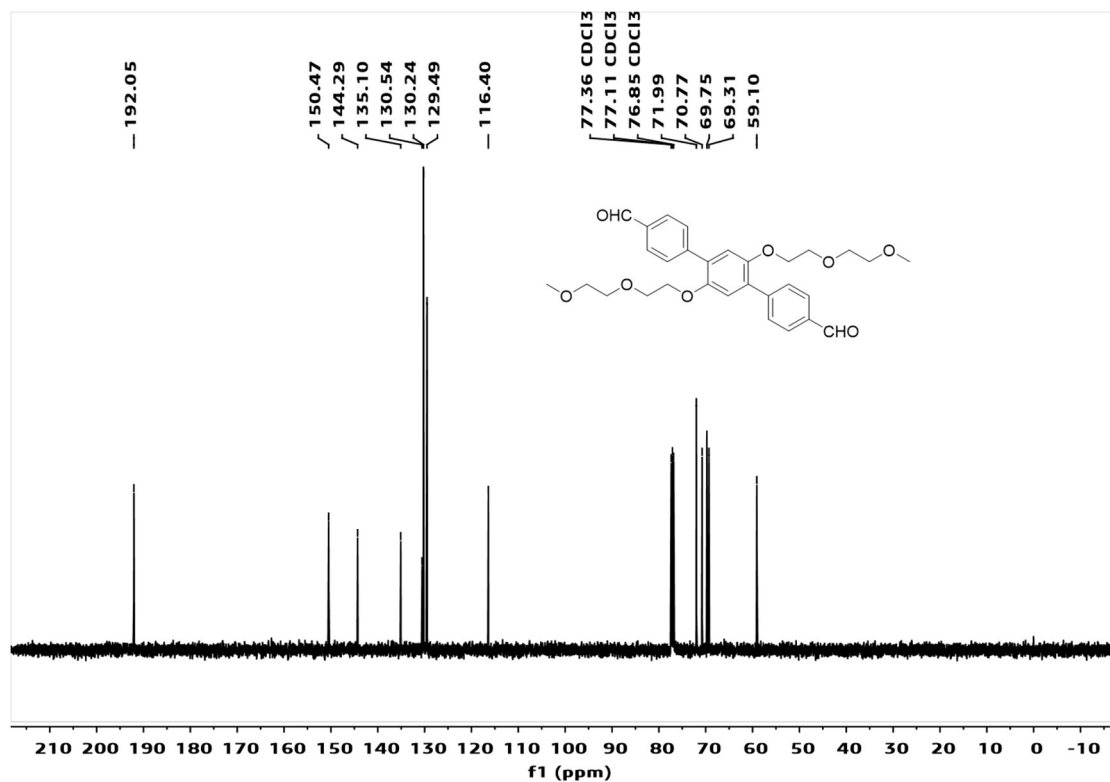


Figure S15. <sup>13</sup>C NMR of PEG2-CHO.

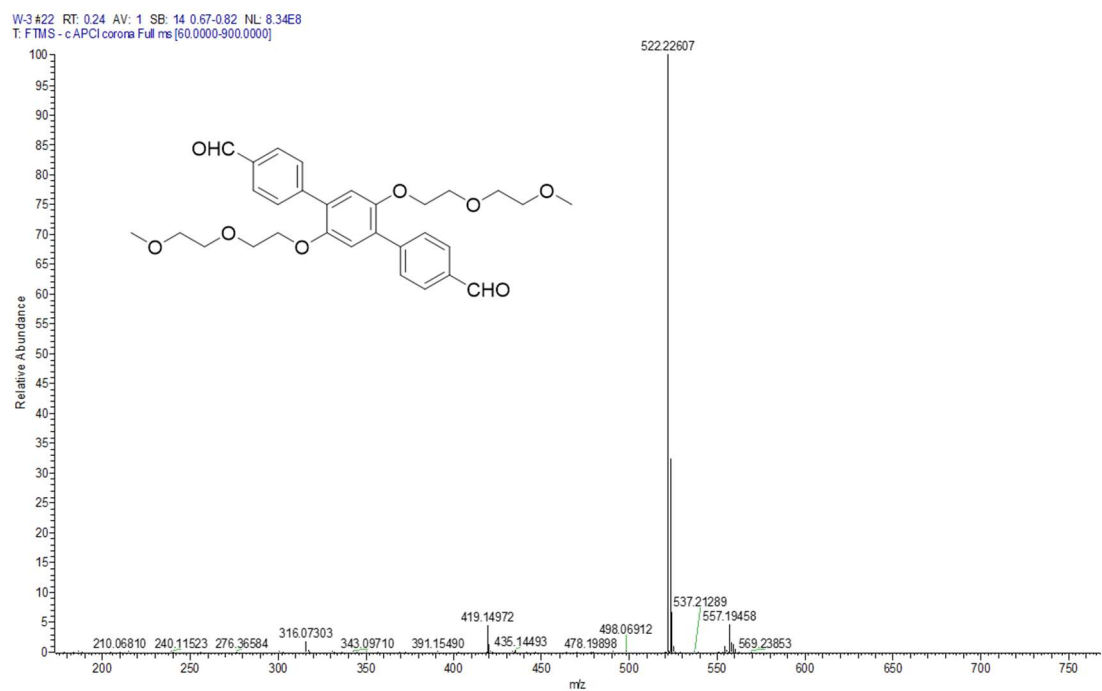


Figure S16. HRMS spectra of PEG2-CHO.

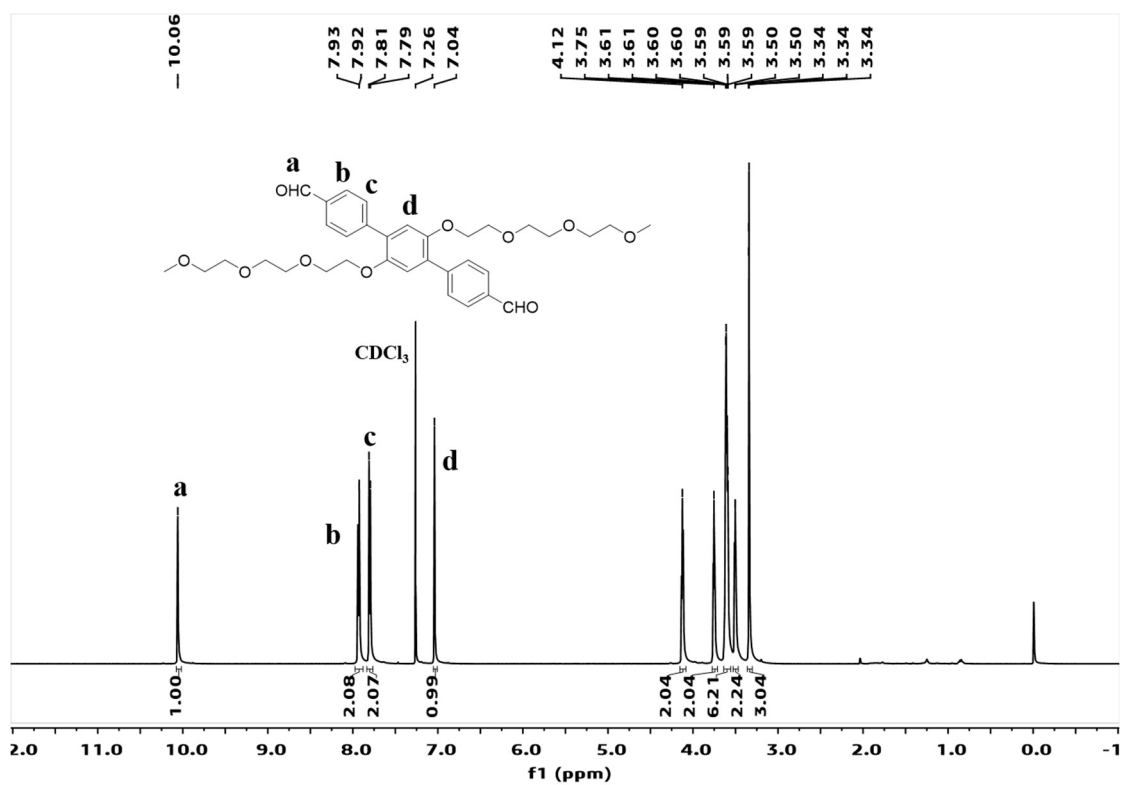
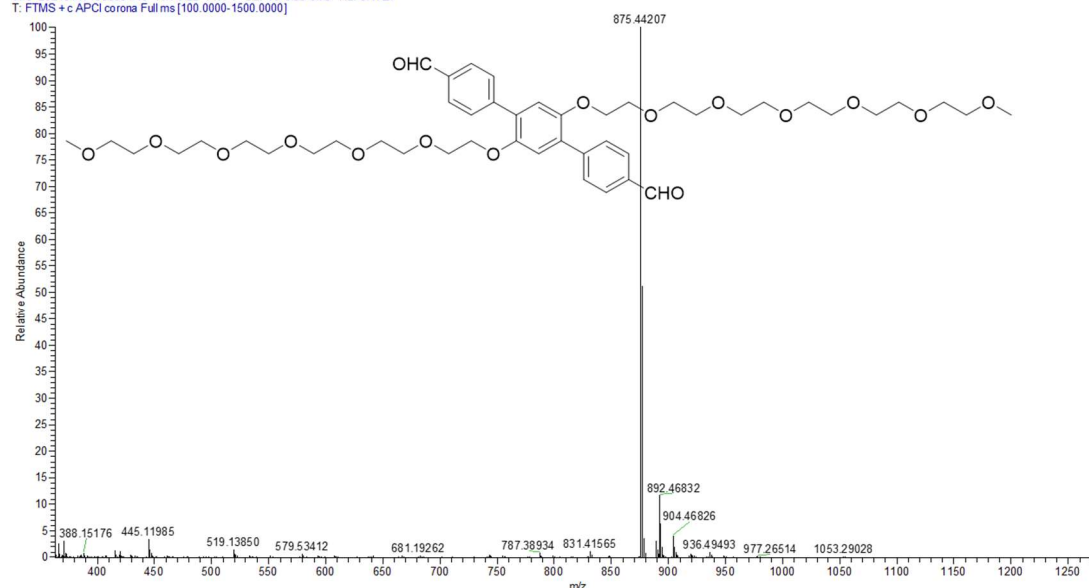


Figure S17. <sup>1</sup>H NMR of PEG3-CHO.





W-5 20210117153850 #19 RT: 0.22 AV: 1 SB: 18 0.55-0.75 NL: 3.17E7  
 T: FTMS + c APCI corona Full ms [100.0000-1500.0000]



**Figure S22.** HRMS spectra of PEG6-CHO.

**Table S2.** Fractional atomic coordinates for simulated 3D-COF-PEG2<sup>[S3]</sup>

Space group: <i>FDD</i>			
3D tetragonal; $a = 58.22 \text{ \AA}$ , $b = 57.87 \text{ \AA}$ , $c = 15.21 \text{ \AA}$ ; $\alpha = \beta = \gamma = 90^\circ$			
Atom	x	y	z
C1	0.31607	0.66706	0.61186
C2	0.30716	0.65308	0.67904
C3	0.32167	0.64208	0.73973
C4	0.34571	0.64465	0.73604
C5	0.3547	0.65861	0.66831
C6	0.34011	0.66959	0.60704
C7	0.36103	0.63396	0.80552
C8	0.29966	0.67909	0.55081
N9	0.30628	0.6916	0.48408
C10	0.29139	0.70436	0.42439
C11	0.35716	0.61138	0.83833
C12	0.37086	0.60304	0.90831
C13	0.44993	0.53836	0.40659
C14	0.46322	0.52477	0.46432
C15	0.48535	0.51673	0.44087
C16	0.49459	0.52578	0.36235
C17	0.4814	0.53947	0.30505
O18	0.34014	0.59766	0.79737
C19	0.33749	0.57371	0.8207
C20	0.35827	0.55909	0.79237
O21	0.36769	0.54803	0.8667

C22	0.38975	0.53903	0.84804
C23	0.09796	0.53499	0.56604
O24	0.07529	0.52732	0.58269
C25	0.06209	0.52931	0.50574
H26	0.28876	0.6507	0.68498
H27	0.31408	0.63163	0.79078
H28	0.37309	0.66096	0.66252
H29	0.34754	0.68018	0.5561
H30	0.28152	0.67678	0.56347
H31	0.36793	0.58606	0.93434
H32	0.43269	0.54338	0.42498
H33	0.45593	0.5203	0.52698
H34	0.51206	0.52164	0.34363
H35	0.48902	0.54465	0.24391
H36	0.32196	0.56697	0.7871
H37	0.33392	0.57174	0.89161
H38	0.37076	0.5708	0.75935
H39	0.35267	0.5459	0.74405
H40	0.40066	0.5511	0.80921
H41	0.38834	0.52231	0.81255
H42	0.10767	0.52182	0.52814
H43	0.09848	0.55168	0.52974
H44	0.04486	0.52172	0.51763
H45	0.0699	0.51971	0.44998
H46	0.05933	0.54773	0.48803
C47	0.25	0.75	0.25

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