

## Electronic Supplementary Information

### **Mechanochemistry-Driven Phase Transformation of Crystalline Covalent Triazine Frameworks Assisted by Alkaline Molten Salts**

Juntian Fan,<sup>a</sup> Xian Suo,<sup>a</sup> Tao Wang,<sup>b</sup> Zongyu Wang,<sup>b</sup> Chi-Linh Do-Thanh,<sup>a</sup> Shannon M. Mahurin,<sup>b</sup> Takeshi Kobayashi,<sup>c</sup> Zhenzhen Yang,<sup>\*,b</sup> and Sheng Dai<sup>\*,a,b</sup>

## Table of Contents

Table of Contents.....	2
1 Experimental Procedures .....	3
1.1 Materials.....	3
1.2 Characterization.....	3
1.3 Synthesis of CTF-1-AA and CTF-TCPM .....	3
2 Supplementary figures .....	5
Figure S1 Simulated and experimental PXRD patterns of CTF-1-AB based on DFT-D3 optimized structure and the corresponding top and side views of the structure. ....	5
Figure S2 Phase diagram of the KOH and LiOH mixture ( <a href="http://www.crct.polymtl.ca/fact/phase_diagram.php?file=KOH-LiOH.jpg&amp;dir=FTsalt">http://www.crct.polymtl.ca/fact/phase_diagram.php?file=KOH-LiOH.jpg&amp;dir=FTsalt</a> (accessed 26.04.16)). ....	5
Figure S3 Simulated and experimental PXRD patterns of CTF-1-AA based on DFT-D3 optimized structure and the corresponding top and side views of the structure. ....	5
Figure S4 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH during the ball milling procedure (3 h). ....	6
Figure S5 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 15 min. ....	6
Figure S6 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 2 h. ....	7
Figure S7 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 4 h. ....	7
Figure S8 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g LiOH and ball milling time of 30 min. ....	8
Figure S9 N <sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH and ball milling time of 30 min. ....	8
Figure S10 (A) XRD pattern and (B) N <sub>2</sub> isotherm of the as-afforded CTF product in the presence of water under the following condition: 0.2 g CTF-1-AB, 0.88 g LiOH/KOH, 20 µL H <sub>2</sub> O, ball milling 30 min.....	9
Figure S11 Representative unit cell structure of CTF-1-AA derived from the polymerization of terephthalonitrile. ...	9
Figure S12 TGA results of CTF-1-AA obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 30 min. ....	10
Figure S13 ESR of CTF-1-AA obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 30 min.....	10
Figure S14 BET plot of CTF-TCPM obtained from the ionothermal procedure catalyzed by CF <sub>3</sub> SO <sub>3</sub> H.....	11
Figure S15 BET plot of CTF-TCPM obtained after ball milling treatment of 30 min in the presence of KOH/LiOH.....	11
Figure S16 BET plot of CTF-TCPM obtained after ball milling treatment of 2 h in the presence of KOH/LiOH.....	12
Figure S17 XRD patterns of CTF-TCPM obtained before and after ball milling treatment in the presence of KOH/LiOH.. ....	12
Figure S18 FTIR spectrum of CTF-TCPM obtained after ball milling treatment of 1 h in the presence of KOH/LiOH. ....	13

## 1 Experimental Procedures

### 1.1 Materials

1,4-dicyanobenzene (DCB), Tetrakis(4-cyanophenyl)methane (TCPM), trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ), lithium hydroxide (LiOH), and potassium hydroxide (KOH) were purchased from commercial sources (Fisher Scientific and Millipore Sigma) and were used without further purification, unless indicated otherwise.

### 1.2 Characterization

The powder X-ray diffraction (PXRD) data were recorded with a PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step:  $0.026^\circ$  per step). The diffraction patterns were recorded in the range of  $5\text{--}60^\circ$ .  $\lambda = 0.1540598$  nm.

The nitrogen adsorption isotherms were measured at 77 K under a Gemini 2360 surface area analyzer. The samples were outgassed at  $150^\circ\text{C}$  for 16 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method.

FTIR spectra of the samples were collected on a TENSOR 27 FTIR instrument in the spectral range from  $4000$  to  $500\text{ cm}^{-1}$ . Each spectrum was recorded with 64 scans at a resolution of  $4\text{ cm}^{-1}$ .

Solid-state  $^{13}\text{C}$  NMR was performed using a Solid-State Varian INOVA 400 MHz spectrometer.

Electron paramagnetic resonance (EPR) was collected on an EPR spectrometer (Bruker ER 200D SRC) at room temperature, and the position was corrected using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as the standard. The Lande factor ( $g$ ) value was calculated by calculated by  $g = 0.07145 \times \nu(\text{MHz}) / H(\text{mT})$  ( $\nu$ : microwave frequency,  $H$ : magnetic field strength).

Field emission scanning electron microscopy (SEM) observations and elemental maps were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 15.0 kV. Transmission electron microscopy (TEM) were conducted on an aberration-corrected FEI Titan S 80-300.

Thermogravimetric analysis (TGA) measurements were taken under nitrogen atmosphere with a ramping rate of  $10^\circ\text{C min}^{-1}$  from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  by using TGA Q50 thermogravimetric analyzer.

### 1.3 Synthesis of CTF-1-AA and CTF-TCPM

#### Synthesis of CTF-1-AB precursor

A mixture of 1,4-dicyanobenzene (DCB) (2 mmol, 0.256 g) and  $\text{CF}_3\text{SO}_3\text{H}$  (1 mmol, 0.15 g) was added sequentially into a Pyrex tube, cooled down in liquid nitrogen, and flame-sealed under vacuum. After that, the tube was heated at  $250^\circ\text{C}$  for 12 h in a muffle furnace with a ramping rate of  $5^\circ\text{C min}^{-1}$ . After the reaction was complete, the Pyrex tube was cooled to room temperature and immersed in liquid nitrogen for 10 minutes before carefully opening in the fume hood. The solid was collected and denoted as CTF-1-AB without any washing procedure.

**Caution:**  $\text{CF}_3\text{SO}_3\text{H}$  used in this work is hygroscopic and corrosive. Fume hoods and protective gear should be used during the addition process. After the annealing process, Pyrex tubes contain some volatile compounds after the annealing process, thus it must be immersed in liquid nitrogen for at least 10 minutes and then opened carefully in a fume hood after cooling to room temperature.

#### Synthesis of CTF-1-AA by ball milling

In a typical synthesis, the CTF precursor and base additives were added to a commercially available 4.5 cm (diameter) by 5.5 cm (height) screw-capped stainless-steel reactor along with four stainless steel ball bearings ( $4 \times 1.2$  cm diameter). The reactor was placed in a high-speed vibrating ball mill (Retsch MM400 Mixer Mill, 25 Hz,  $1,200\text{ rounds min}^{-1}$ , 300 W motor power) and the mixtures were ball milled for a specified time. The ball milling treatment was conducted at ambient temperature.

In a typical ball milling process, 0.2 g CTF-A-AA was ball milled together with a molten salt composed of LiOH and KOH for a specified time

period. Molar ratio of LiOH to the total base (LiOH and KOH) used in this work was 0.314. To be specific, 0.22 g molten salt used in this work was composed of 1.5 mmol LiOH (0.036g) and 3.278 mmol KOH (0.184g). 0.44 g molten salt used in this work was composed of 3 mmol LiOH (0.072 g) and 6.555 mmol KOH (0.368 g). 0.88 g molten salt used in this work was composed of 6 mmol LiOH (0.144 g) and 13.11 mmol KOH (0.735 g). After the ball milling process, the solid was collected and washed thoroughly with water and ethanol to remove the remaining LiOH and KOH. Then, CTF-1-AA was obtained as greenish powder after 12 hours of vacuum drying at 60 °C.

#### **Synthesis of CTF-TCPM precursor**

A mixture of tetrakis(4-cyanophenyl)methane (TCPM) (2 mmol, 0.841 g) and  $\text{CF}_3\text{SO}_3\text{H}$  (1mmol, 0.15 g) was added sequentially into a Pyrex tube, cooled down in liquid nitrogen and flame-sealed under vacuum. After that, the tube was heated at 330 °C for 12 h in a muffle furnace with a ramping rate of 5 °C min<sup>-1</sup>. After the reaction was complete, the Pyrex tube was cooled to room temperature and immersed in liquid nitrogen for 10 minutes before opening in the fume hood carefully. The solid was collected and directly used for the subsequent step without further treatment.

Caution:  $\text{CF}_3\text{SO}_3\text{H}$  used in this work is hygroscopic and corrosive. Fume hoods and protective gear should be used during the addition process. After the annealing process, Pyrex tubes contain some volatile compounds after the annealing process, thus it must be immersed in liquid nitrogen for at least 10 minutes and then opened carefully in a fume hood after cooling to room temperature.

#### **Synthesis of CTF-TCPM by ball milling**

In a typical ball milling process, 0.2 g CTF-TCPM was ball milled together with molten salt composed of LiOH and KOH for certain time. Molar ratio of LiOH to the total base (LiOH and KOH) used in this work was 0.314. To be specific, 0.88 g molten salt used in this work was composed of 6 mmol LiOH (0.144 g) and 13.11 mmol KOH (0.735 g). After the ball milling process, the solid was collected and washed thoroughly with water and ethanol to remove the remaining LiOH and KOH. Then CTF-TCPM was obtained as greenish powder after 12 hours of vacuum drying at 60 °C.

## 2 Supplementary figures

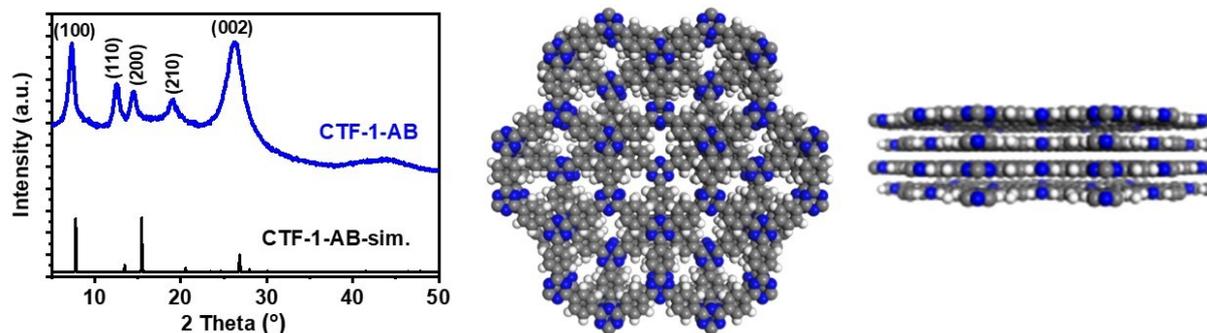


Figure S1 Simulated and experimental PXRD patterns of CTF-1-AB based on DFT-D3 optimized structure and the corresponding top and side views of the structure.

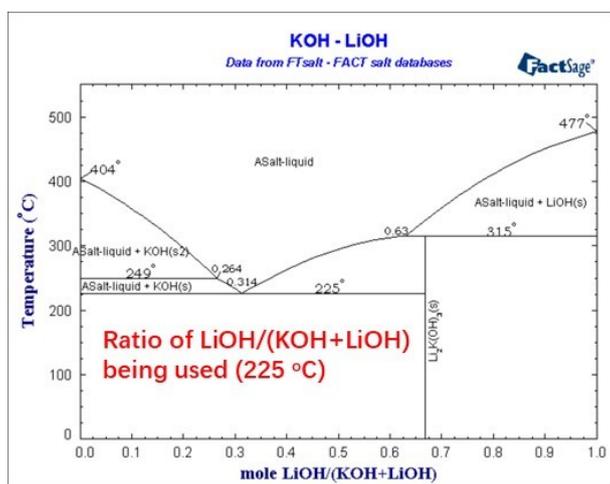


Figure S2 Phase diagram of the KOH and LiOH mixture ([http://www.crct.polymtl.ca/FACT/phase\\_diagram.php?file=KOH-LiOH.jpg&dir=FTsalt](http://www.crct.polymtl.ca/FACT/phase_diagram.php?file=KOH-LiOH.jpg&dir=FTsalt) (accessed 26.04.16)).

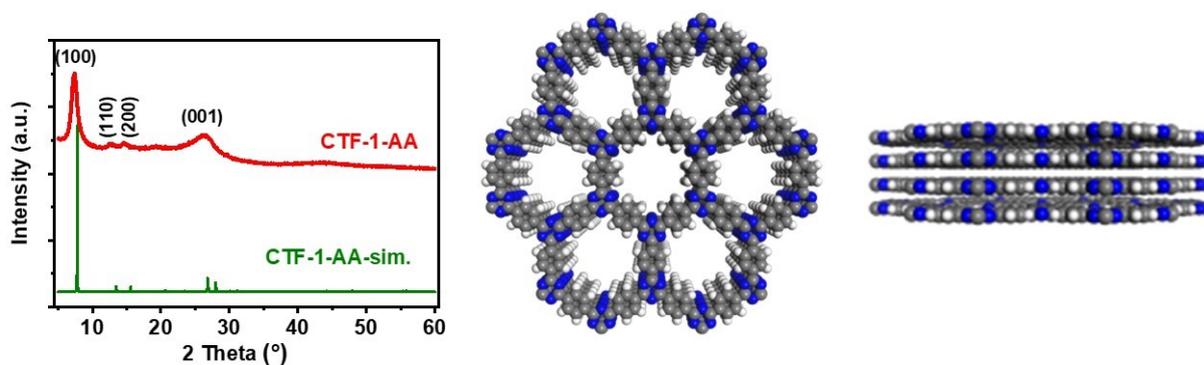


Figure S3 Simulated and experimental PXRD patterns of CTF-1-AA based on DFT-D3 optimized structure and the corresponding top and side views of the structure.

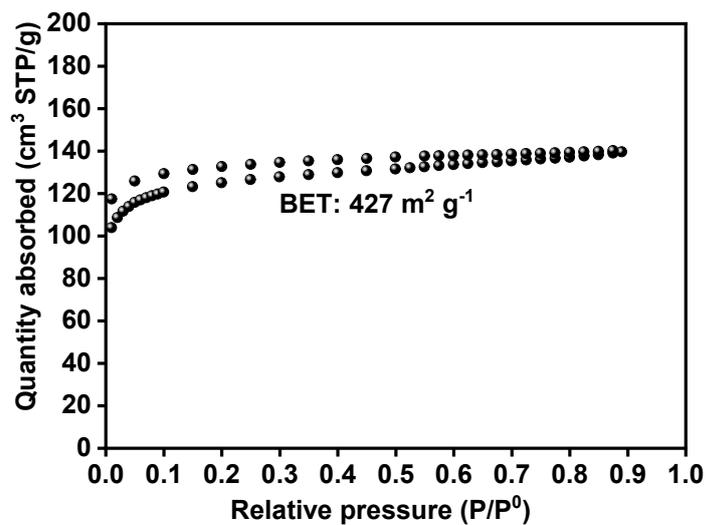


Figure S4 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH during the ball milling procedure (3 h).

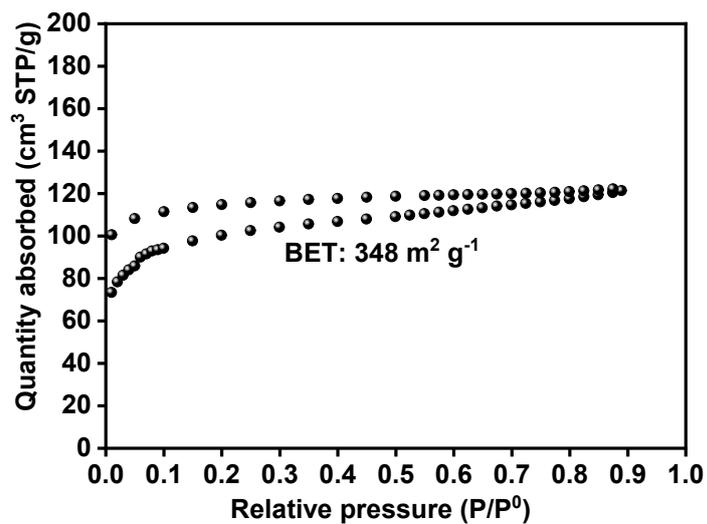


Figure S5 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 15 min.

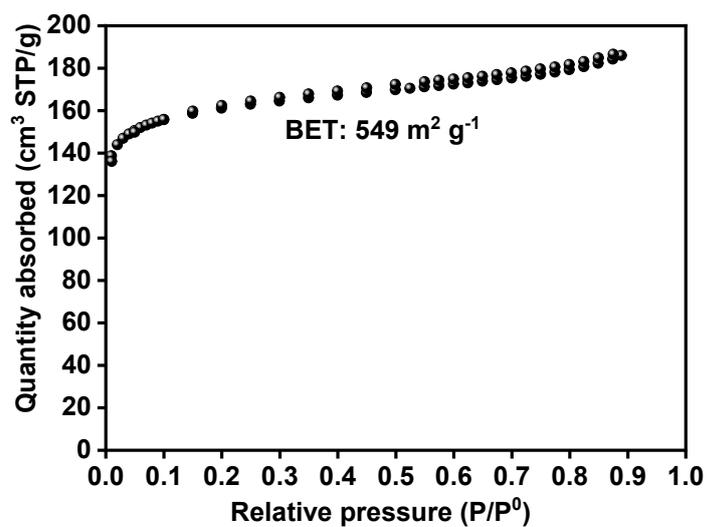


Figure S6 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 2 h.

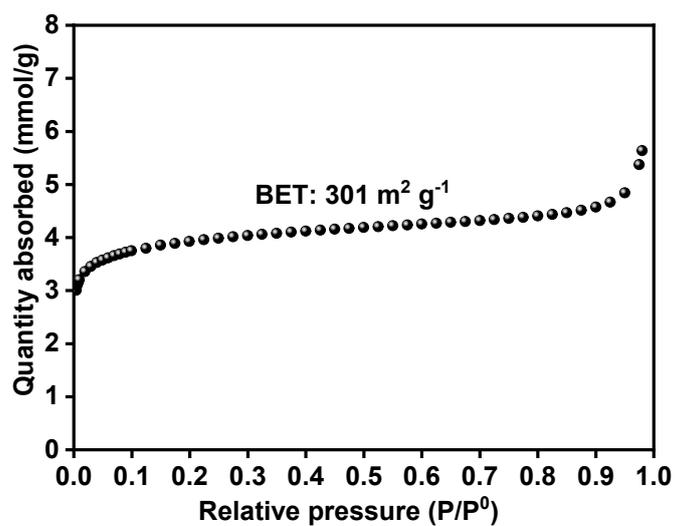


Figure S7 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 4 h.

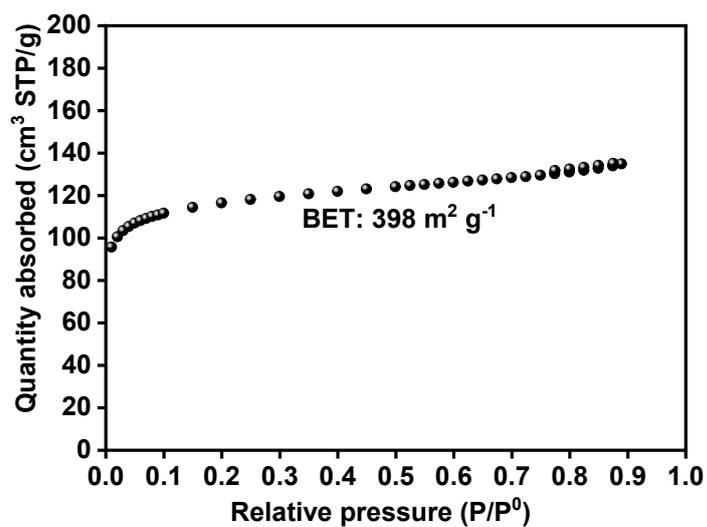


Figure S8 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g LiOH and ball milling time of 30 min.

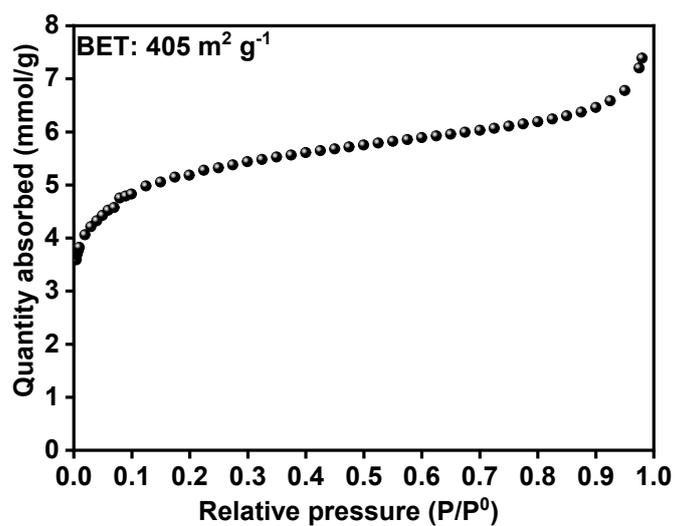


Figure S9 N<sub>2</sub> isotherm of CTF-1 obtained in the presence of 0.88 g KOH and ball milling time of 30 min.

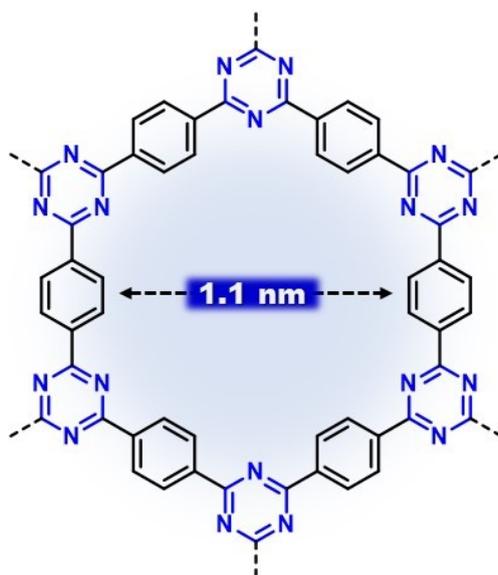
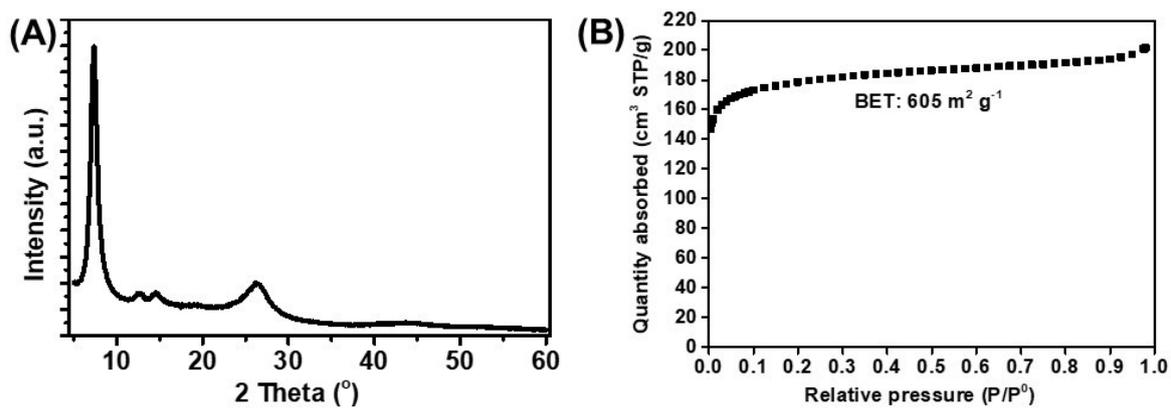


Figure S11 Representative unit cell structure of CTF-1-AA derived from the polymerization of terephthalonitrile.

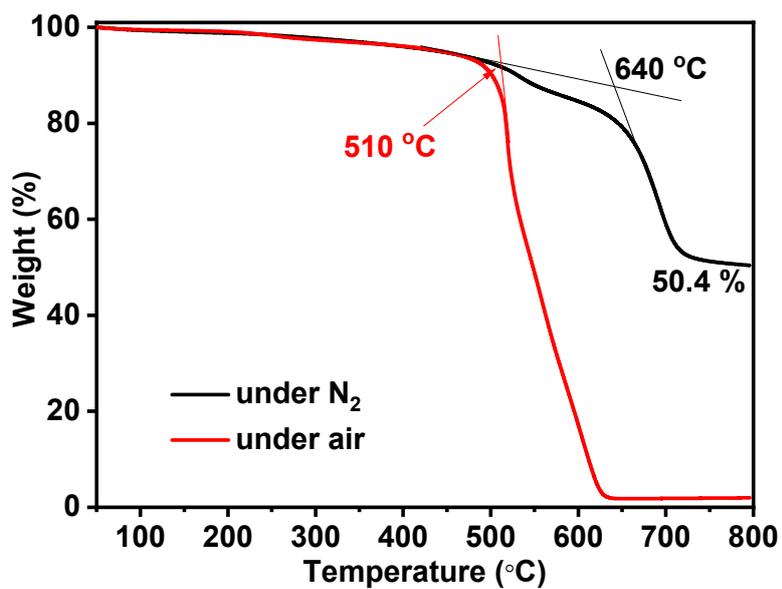


Figure S12 TGA results of CTF-1-AA obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 30 min.

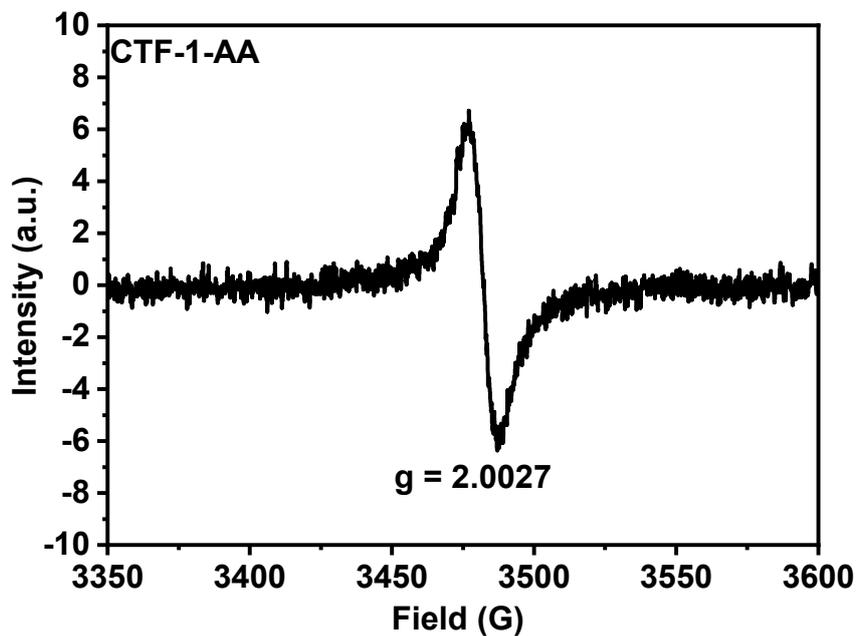


Figure S13 ESR of CTF-1-AA obtained in the presence of 0.88 g KOH/LiOH and ball milling time of 30 min.

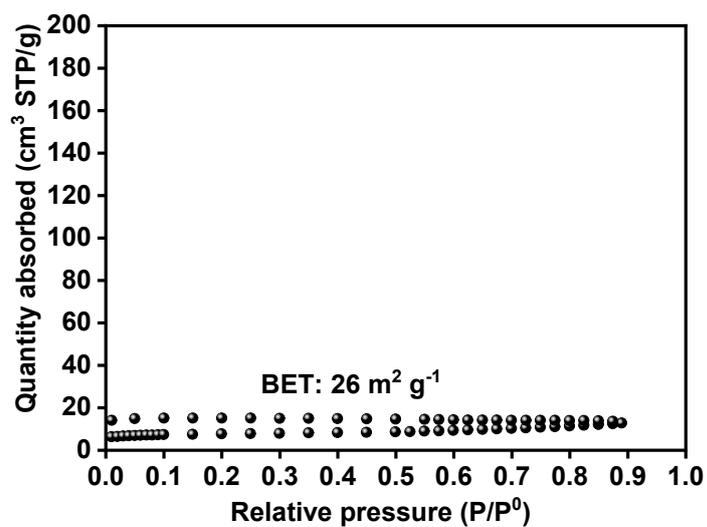


Figure S14 BET plot of CTF-TCPM obtained from the ionothermal procedure catalyzed by  $\text{CF}_3\text{SO}_3\text{H}$ .

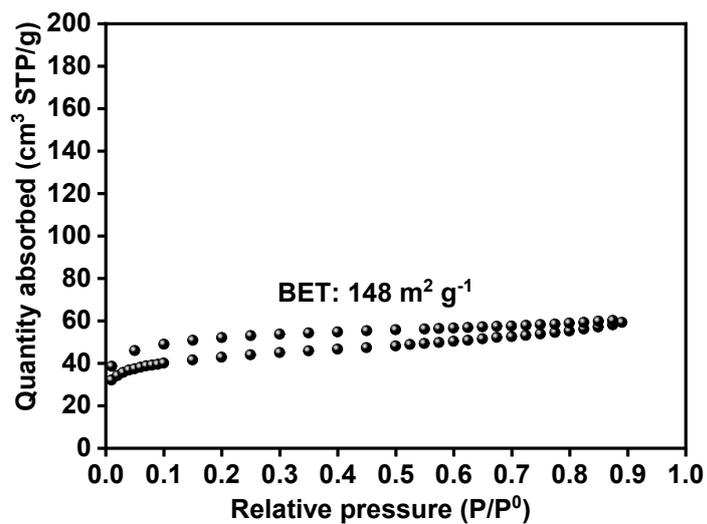


Figure S15 BET plot of CTF-TCPM obtained after ball milling treatment of 30 min in the presence of  $\text{KOH/LiOH}$ .

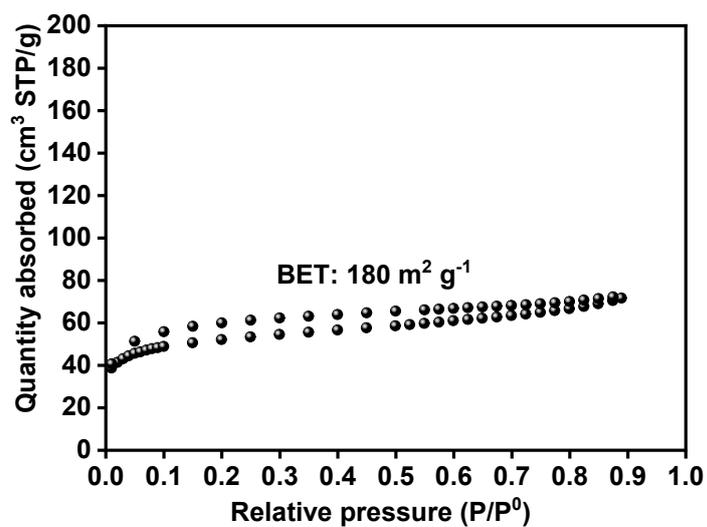


Figure S16 BET plot of CTF-TCPM obtained after ball milling treatment of 2 h in the presence of KOH/LiOH.

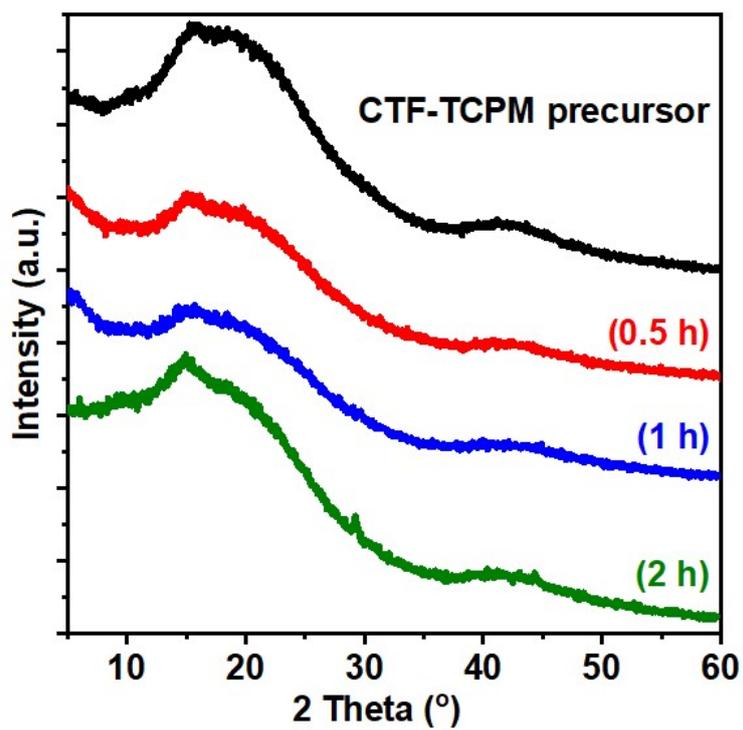


Figure S17 XRD patterns of CTF-TCPM obtained before and after ball milling treatment in the presence of KOH/LiOH..

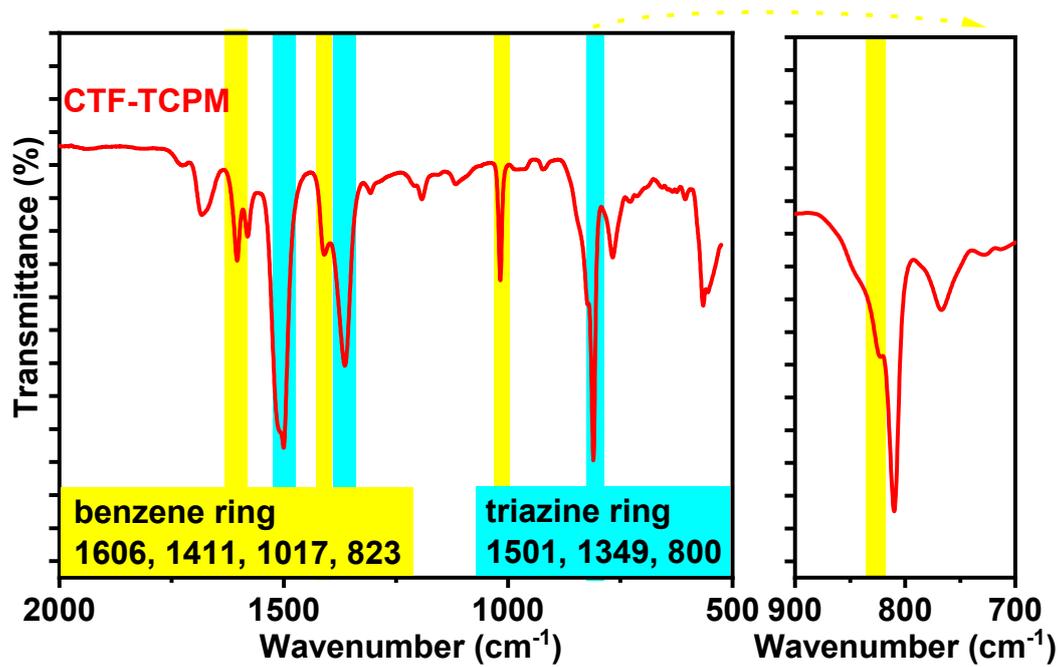


Figure S18 FTIR spectrum of CTF-TCPM obtained after ball milling treatment of 1 h in the presence of KOH/LiOH.