Electronic Supplementary Material (ESI) for Energy Advances.

Poly(triazine-co-pyrrole) based Conjugated Microporous Polymers for Carbon dioxide Capture

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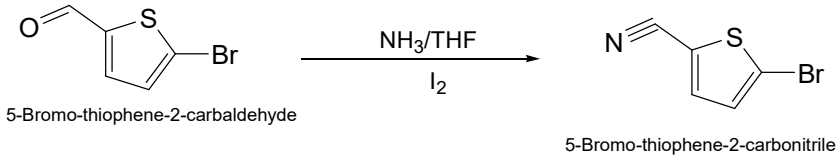
1. Synthesis of 5-bromothiophene-2-carbonitrile

The synthesis of 5-bromothiophene-2-carbonitrile (BTCN) (**Scheme S1**) has performed using 5-bromothiophene-2-carboxaldehyde (BTCHO) according to the method specified by Yasuda and coworkers (2011) with some modifications. The organic reactions have proceeded with dried solvents and reactants under N_2 environment. Tetrahydrofuran (THF) drying has done using benzophenone-sodium still method and distilled, while the BTCHO has dried using calcium hydride (CaH_2) followed by vacuum distillation. As the starting material, distilled BTCHO 9.55 g (50 mmol) was dissolved in 30 ml of dried THF in an oven dried round bottom flask while stirring at room temperature.[1] Aqueous NH_3 112 ml (1.65 mol) was added to the BTCHO followed by the slow addition of I_2 14 g (55 mmol). The reaction was continued for two hours and quenched by adding 80 ml of circa, 5 % aqueous $Na_2S_2O_3$ solution. Then the product separation has done using liquid-liquid extraction with $CHCl_3$ 25 ml and washed with 50 ml of deionized water. The separated organic layer first dried over anhydrous Na_2SO_4, filtered and removed the solvents using rotary evaporation (BUCHI R-210 Rotavapor). The purification of BTCN has done using a silica gel column with $CHCl_3$/Hexane (2:1 v:v) and 5 % of methanol from the total mobile phase. The thin layer chromatography with ^1H and ^{13}C nuclear magnetic resonance (NMR) was used to identify the sequence of each compound elution. Finally, the solvent has dried via rotary evaporation after combining the first yellow color band collected to vials, obtaining brown-yellow oil like BTCN.

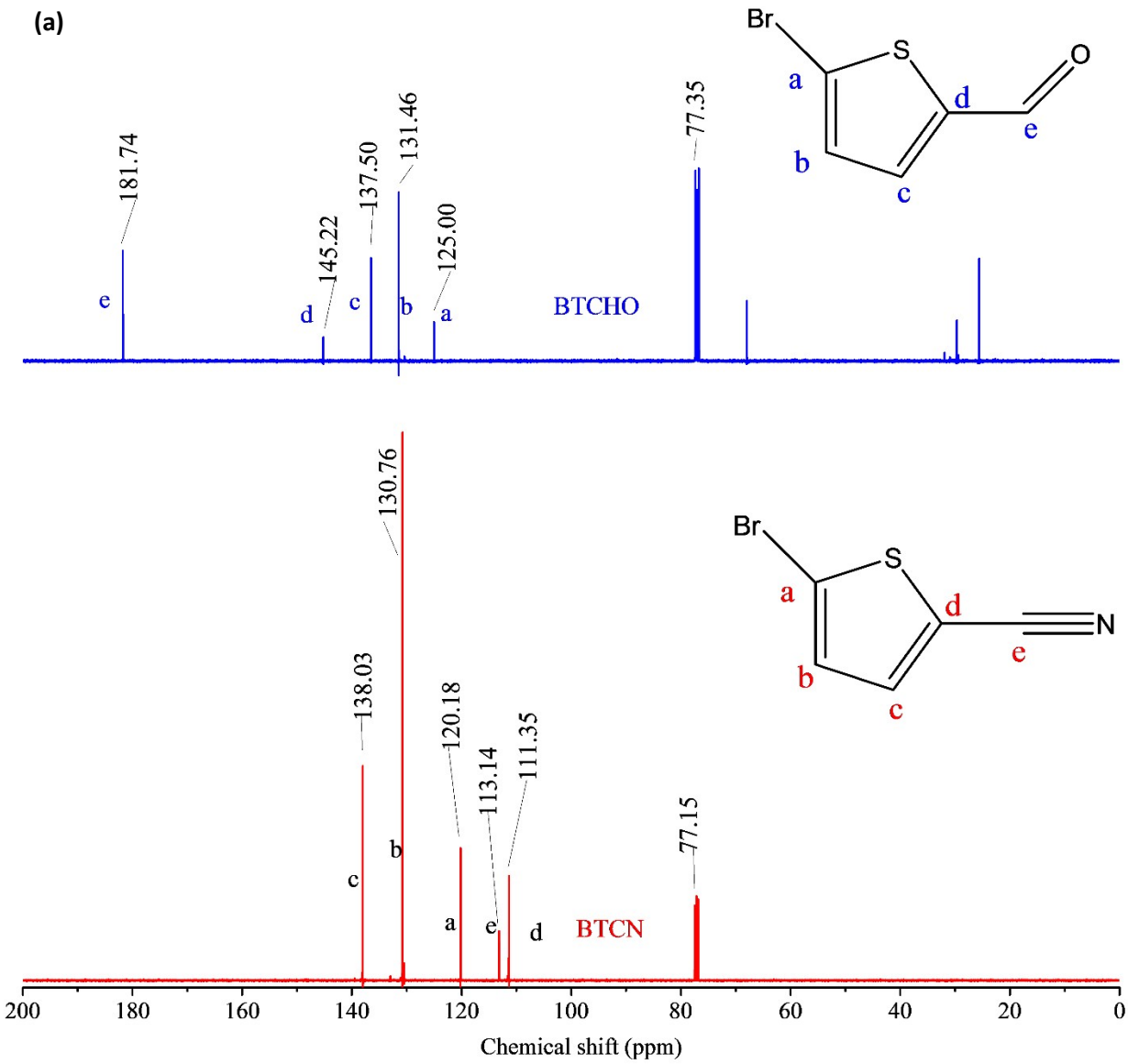


5-Bromo-thiophene-2-carbaldehyde

5-Bromo-thiophene-2-carbonitrile

Scheme S1: Synthesis of 5-bromothiophene-2-carbonitrile

Further, the analysis of C atoms and protons in the compound establishing more accurate chemical structure has been carried out using liquid ^{13}C and ^1H NMR spectroscopy (**Figure S1**).


(a)
Br
S
O
a
b
c
d
e
181.74
145.22
137.50
131.46
125.00
77.35
BTCHO
130.76
138.03
120.18
113.14
111.35
77.15
BTCN
N
200
180
160
140
120
100
80
60
40
20
0
Chemical shift (ppm)

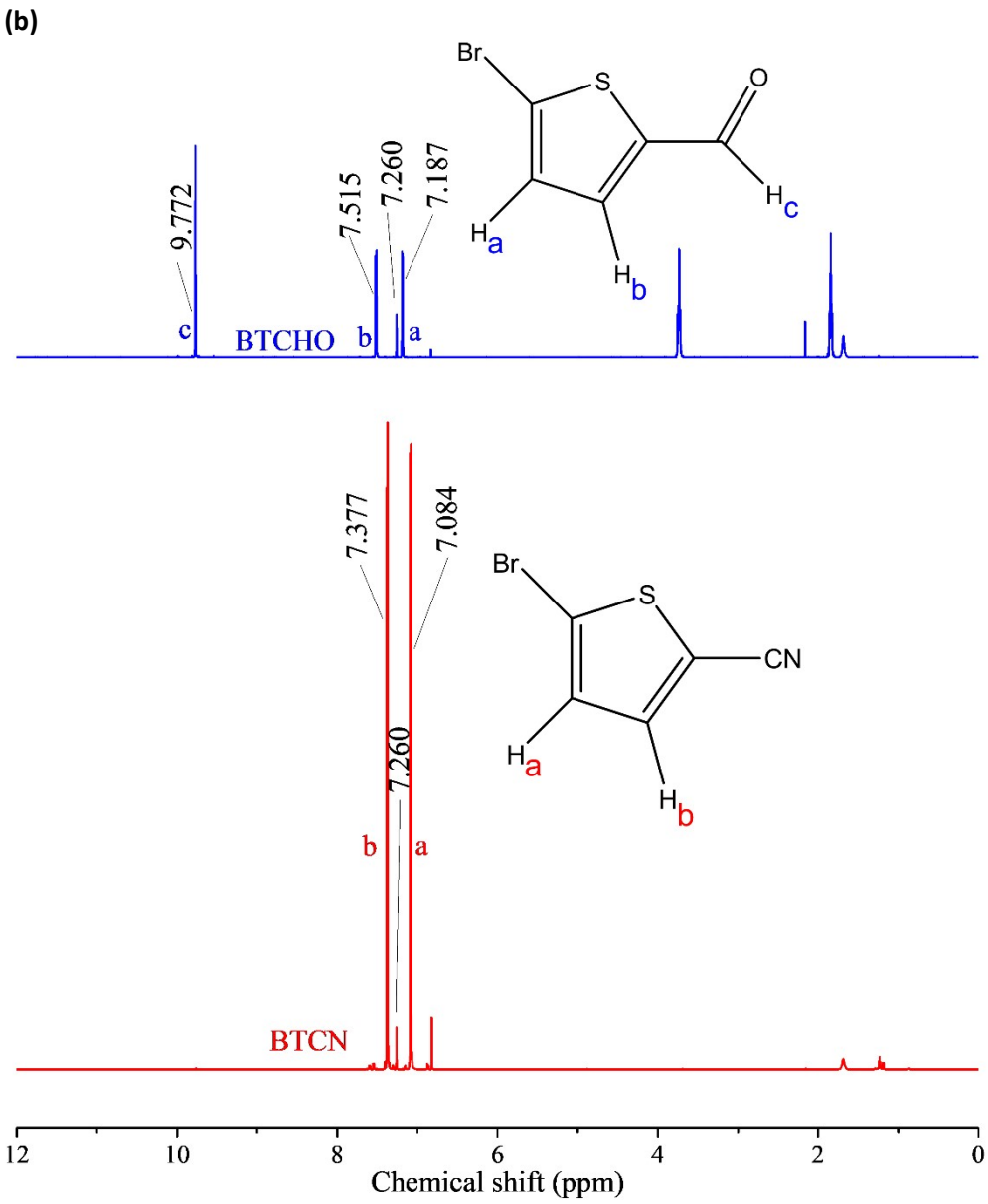
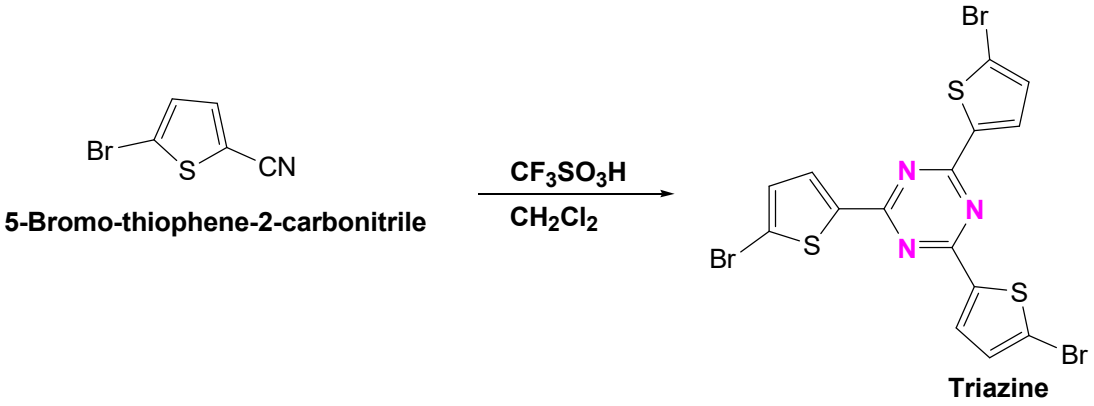


Figure S1: BTCHO and BTCN NMR spectra **(a)** ^{13}C NMR, **(b)** ^{1}H NMR

2. Synthesis of 2,4,6-tris(5-bromothiophene-2-yl)-1,3,5-triazine (triazine) monomer

7.20 g (48 mmol) of trifluoromethanesulfonic acid was added to a stirred solution of 9.03 g (48 mmol) 5-bromothiophene-2-carbonitrile in 120 mL of dry CH_2Cl_2 at 0 °C. The mixture was then stirred at room temperature for 36 h. The solvent was then removed under reduced pressure and the residue was neutralized with an aqueous $NaHCO_3$[2] The precipitate was then filtered, washed with water, methanol, acetone, and hexane in this order, and then dried under vacuum to afford 2,4,6-tris-(5-bromo-thiophen-2-yl)-[1,3,5]triazine as an off-white solid (**Scheme S2**).



Scheme S2: Synthesis of 2,4,6-tris-(5-bromo-thiophen-2-yl)-[1,3,5]triazine

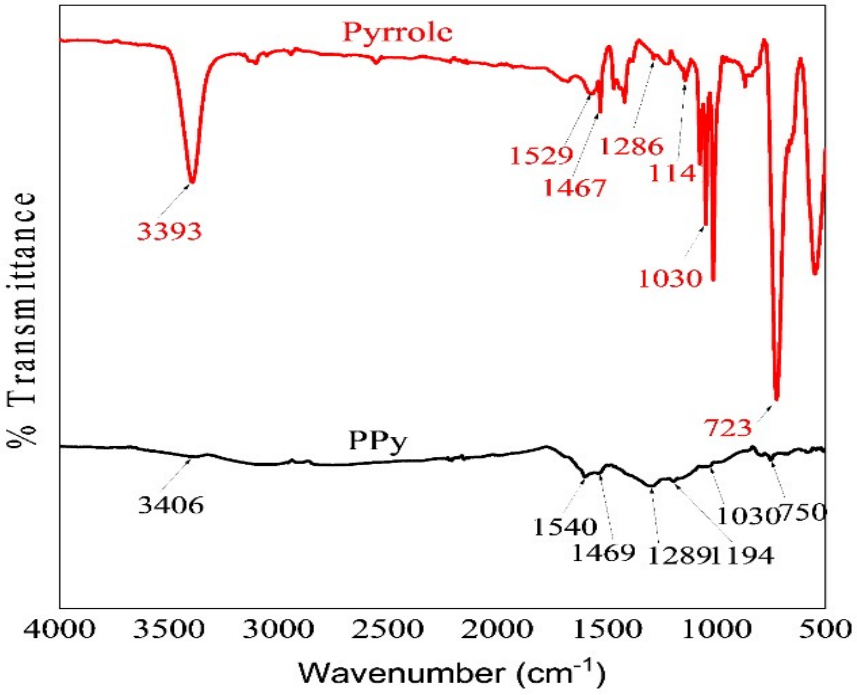


Figure S2: FTIR spectrum of pyrrole and polypyrrole (PPy)

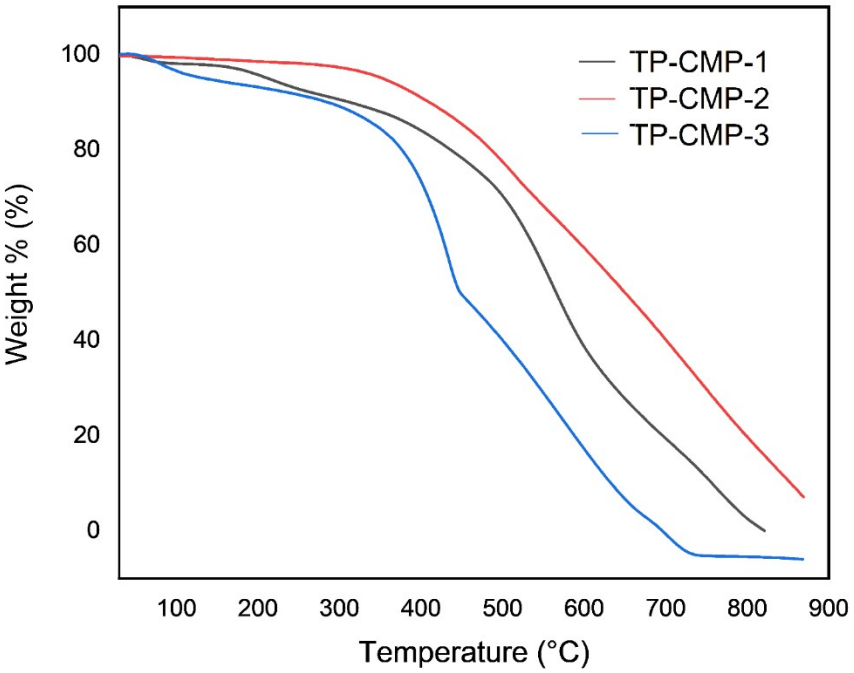


Figure S3: TGA curves for the synthesized TP-CMPs

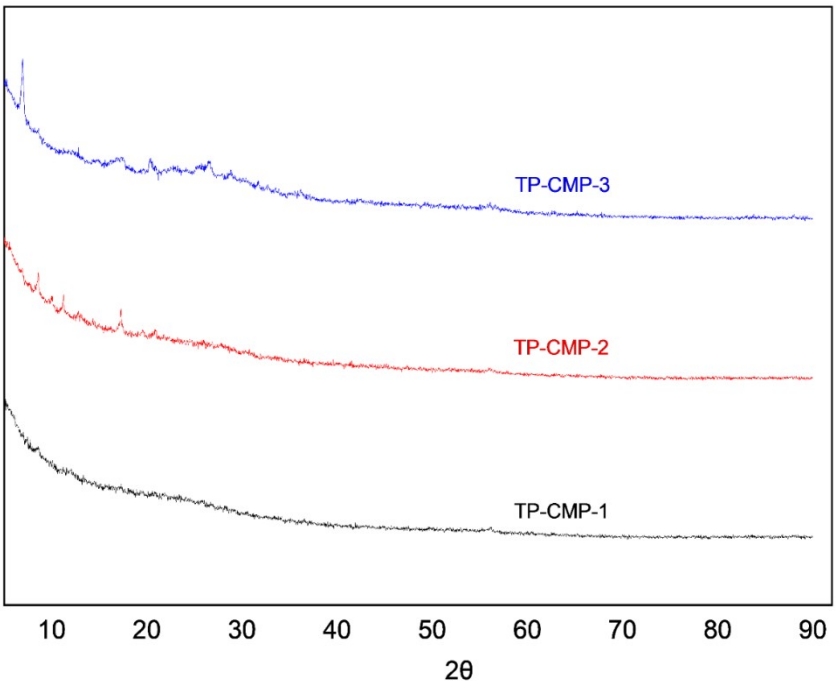


Figure S4: PXRD pattern of the synthesized TP-CMPs

Reference

1. T. Yasuda, T. Shimizu, F. Liu, G. Ungar and T. Kato, *Journal of the American Chemical Society*, 2011, **133**, 13437-13444.
2. A. R. Katritzky, C. A. Ramsden, J. A. Joule and V. V. Zhdankin, in *Handbook of Heterocyclic Chemistry (Third Edition)*, eds. A. R. Katritzky, C. A. Ramsden, J. A. Joule and V. V. Zhdankin, Elsevier, Amsterdam, 2010, DOI: https://doi.org/10.1016/B978-0-08-095843-9.00009-4, pp. 383-472.