Electronic Supplementary Material (ESI) for ChemComm.


# Supplementary Information for

## "Mechanochemical Synthesis of Two-Dimensional Aromatic Polyamides"

*Yang Yang,[a] Fanxing Bu,[a] Jingjing Liu,[a] Imran Shakir,[b] and Yuxi Xu*,[a]*

[a] State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200438, China

[b] Sustainable Energy Technologies Center, College of Engineering, King Saud University, Riyadh 11421, Kingdom of Saudi Arabia

**Materials and Reagents**

1, 3, 5-benzenetricarbonyl chloride, 1, 4-phenylenediamine, 4, 4'-diaminobiphenyl and NMP were all commercially available and used as received.

**Instrumentation and Characterization**

TEM images were obtained on a JEOL JEM-2100F (acceleration voltage: 200 kV). For TEM observations, all samples were dispersed in DMF via sonication and then dropped onto carbon mesh grids. The carbon mesh grids were heated mildly (at 80 $^{o}$C in *vacuo* overnight) to remove the residual solvent. SEM images were obtained on a Zeiss Ultra 55. For SEM observations, the carbon mesh grids with samples were attached to an aluminum sample holder and then directly placed into the instrument without gold coating. Elemental analysis was obtained on a Carlo-Erba1106 for C, H, and N and a Metrohm 905 Titrando for Cl. FT-IR spectra were obtained on a Nicolet 6700 in transmission mode. $^{13}$C CP-MAS solid-state NMR spectra were obtained on a Bruker 400WB AVANCE III. TGA curves were obtained on a PerkinElmer Pyris 1 TGA under $N_2$ atmosphere at a heating rate of 10 $^{o}$C/min from 40-800 $^{o}$C. PXRD patterns were obtained on a PANalytical X'pert PRO. AFM images were obtained on a Bruker Multimode 8. For AFM measurements, samples were dispersed in DMF via sonication and then dropped onto freshly cleaved mica. The residual solvent was removed via mild heating.

**Synthesis of 2DAPAs**

1, 3, 5-benzenetricarbonyl chloride (532.0 mg, 2.00 mmol) and corresponding diamine [1, 4- phenylenediamine (for 2DAPA-1, 325.0 mg, 3.00 mmol) or 4, 4'-diaminobiphenyl (for 2DAPA-2, 553.0 mg, 3.00 mmol ) were added into a 50 mL agate jar, with eight 10 mm diameter agate balls and fifty 6 mm diameter agate balls. The mixture was milled at room temperature in a planetary ball mill (QM-3SP04, Nanjing University Instrument Co. Ltd) at 500 rpm for 15 min. After this procedure, 15 mL of 5 % NaOH aqueous solution was added into the jar and the mixture was milled at 500 rpm for another 10 min. Then, the suspension was filtered through a 0.22 μm membrane. The filter cake was washed with deionized water and ethanol alternately, and finally dried in *vacuo* at 80 $^{o}$C overnight to afford a light yellow powder in ~75% isolated yield.

**Synthesis of RS-1**

1, 4- phenylenediamine (69.5 mg, 0.64 mmol) and 10 mL of NMP were first added into a 50 mL flask under argon atmosphere with stirring. Then the solution of 1, 3, 5-benzenetricarbonyl chloride (113.8 mg, 0.43 mmol in 5 m L of NMP) was added into the flask slowly. The reaction mixture was stirred at room temperature. After 2 h, the reaction mixture was diluted in 50 mL of deionized water filtered through a 0.22 μm membrane. The filter cake was washed with deionized water and ethanol alternately, and finally dried in *vacuo* at 80 $^{o}$C overnight to afford a brown powder in 87% isolated yield.

**Synthesis of RS-2**

1, 3, 5-benzenetricarbonyl chloride (532.0 mg, 2.00 mmol), 1, 4- phenylenediamine (325.0 mg, 3.00 mmol) and 0.4 mL of NMP were first added into the agate jar. All other experimental procedures and parameters were the same as the synthesis of 2DAPAs. Finally, an olive powder was obtained in ~65% isolated yield.

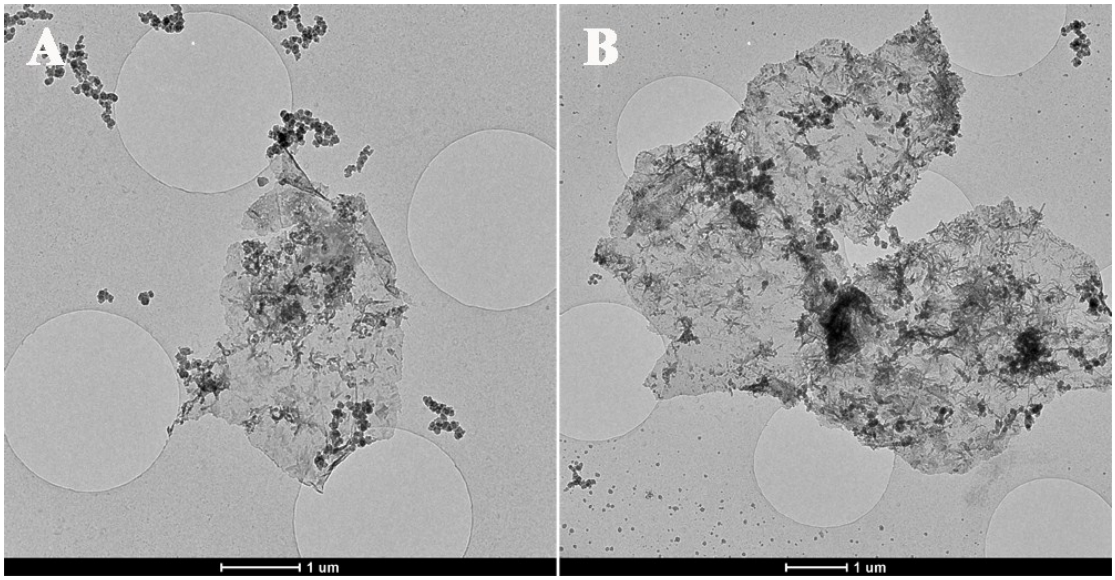


**Figure S1.** TEM images of the rude products of 2DAPA-1 (A) and 2DAPA-2 (B).

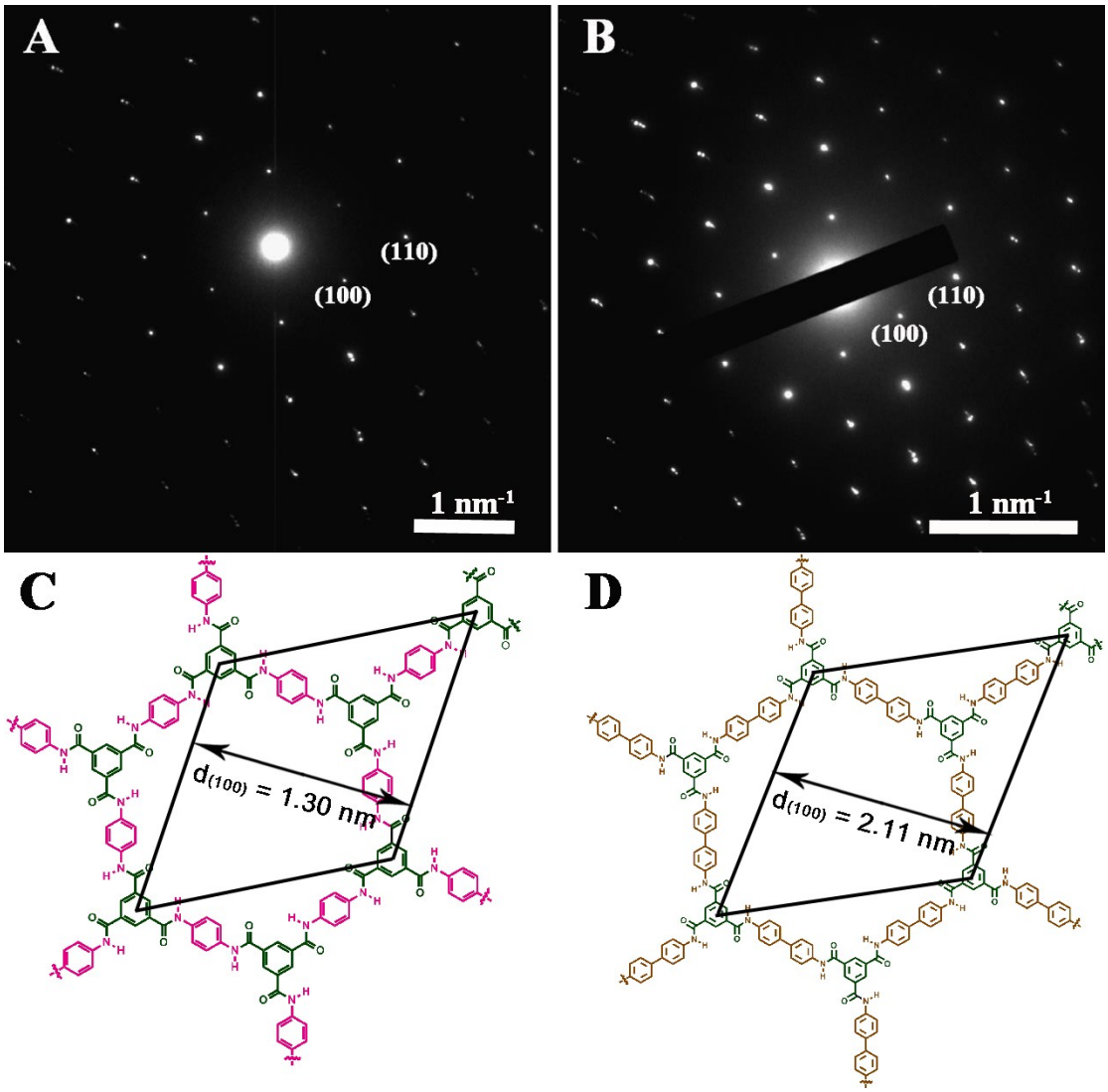


**Figure S2.** Indexing of SAED patterns of 2DAPA-1 (A) and 2DAPA-2 (B) and corresponding crystal structures of 2DAPA-1 (C) and 2DAPA-2 (D)

**Table S1.** Elemental analysis of 2DAPAs.

| sample | C (wt %) | N (wt %) | H (wt %) | Cl (wt %) | C/N ratio (mol) |
|---|---|---|---|---|---|
| 2DAPA-1 | 62.42 | 12.32 | 4.35 | < 0.5 | 5.91 |
| 2DAPA-2 | 71.12 | 9.42 | 4.57 | < 0.5 | 8.81 |

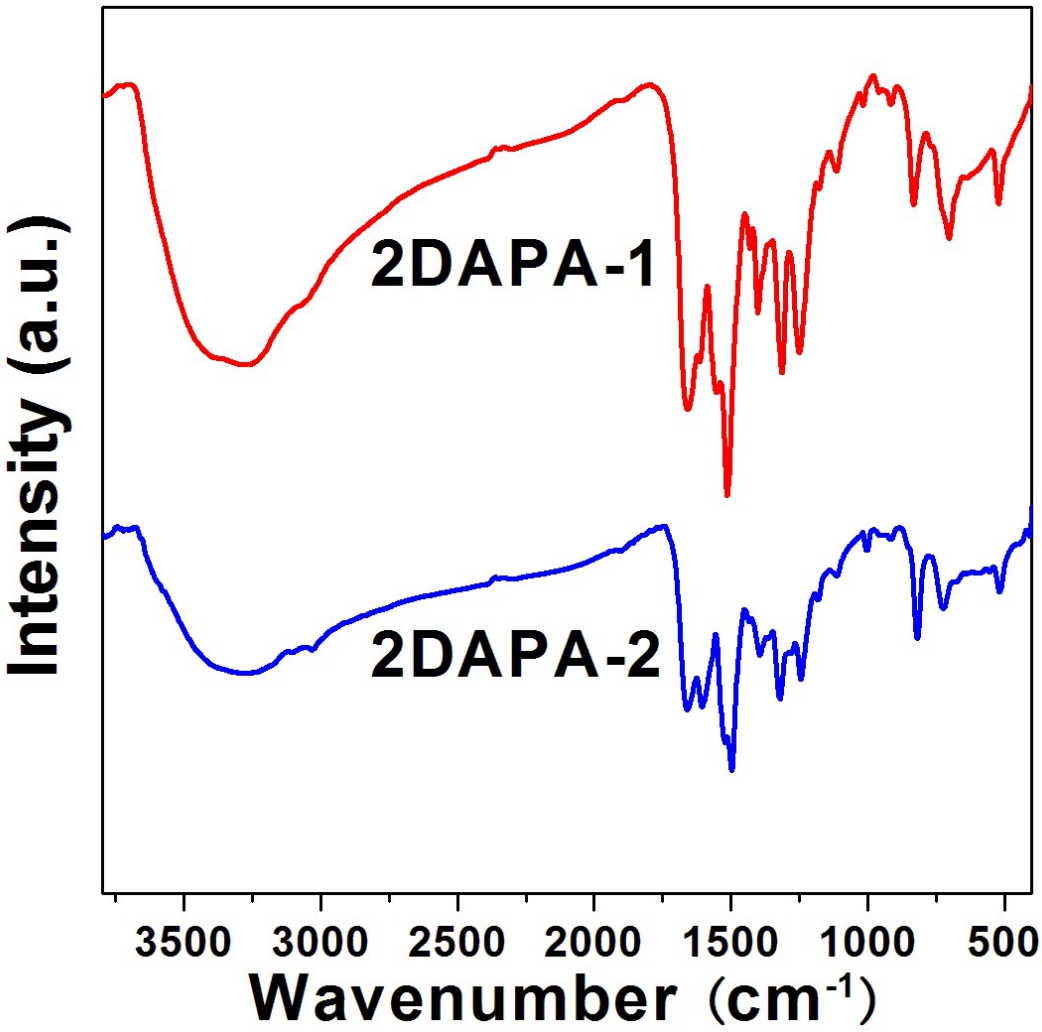


**Figure S3.** FT-IR spectra of 2DAPA-1 and 2DAPA-2.

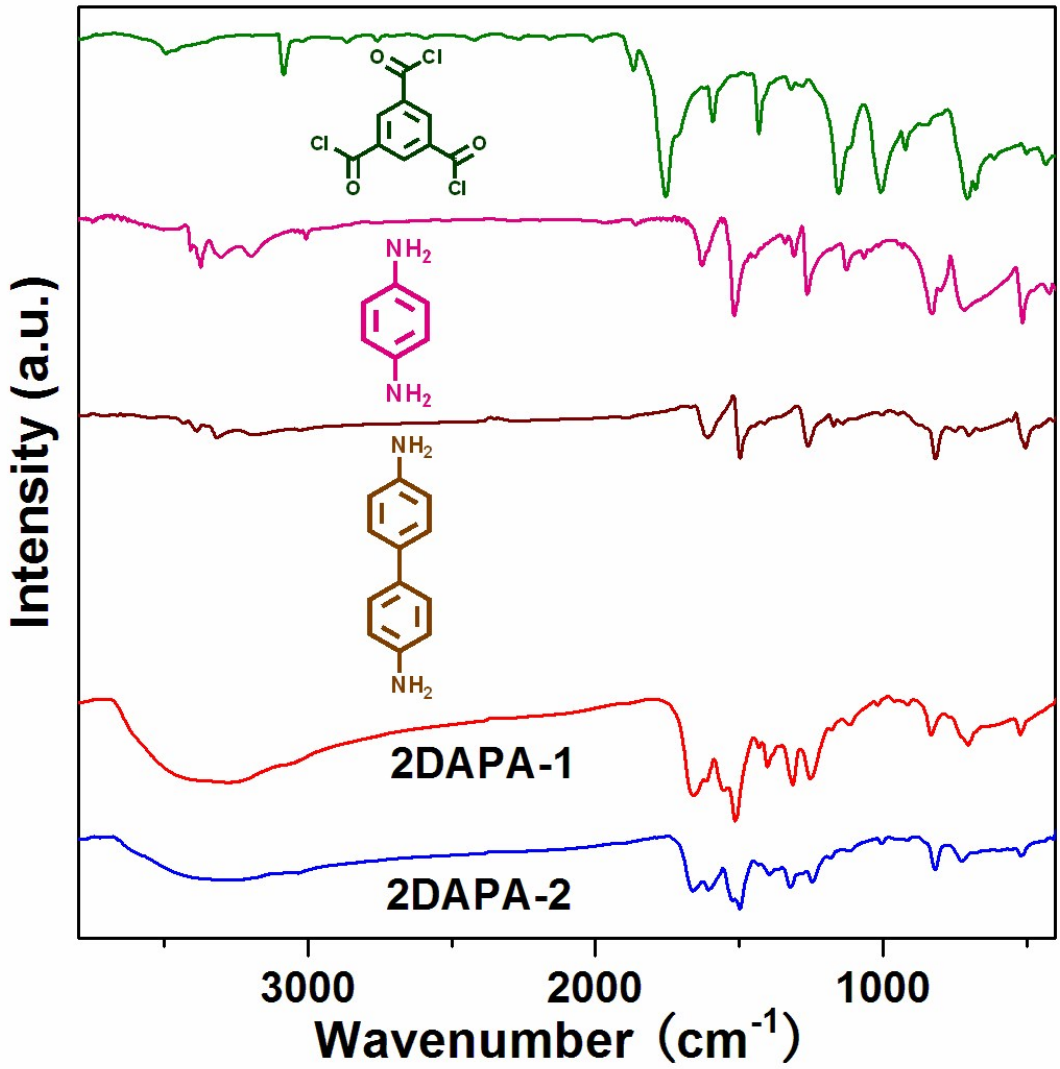


**Figure S4.** FT-IR spectra of 1, 3, 5-benzenetricarbonyl chloride, 1, 4-phenylenediamine, 4, 4'-diaminobiphenyl, 2DAPA-1 and 2DAPA-2.

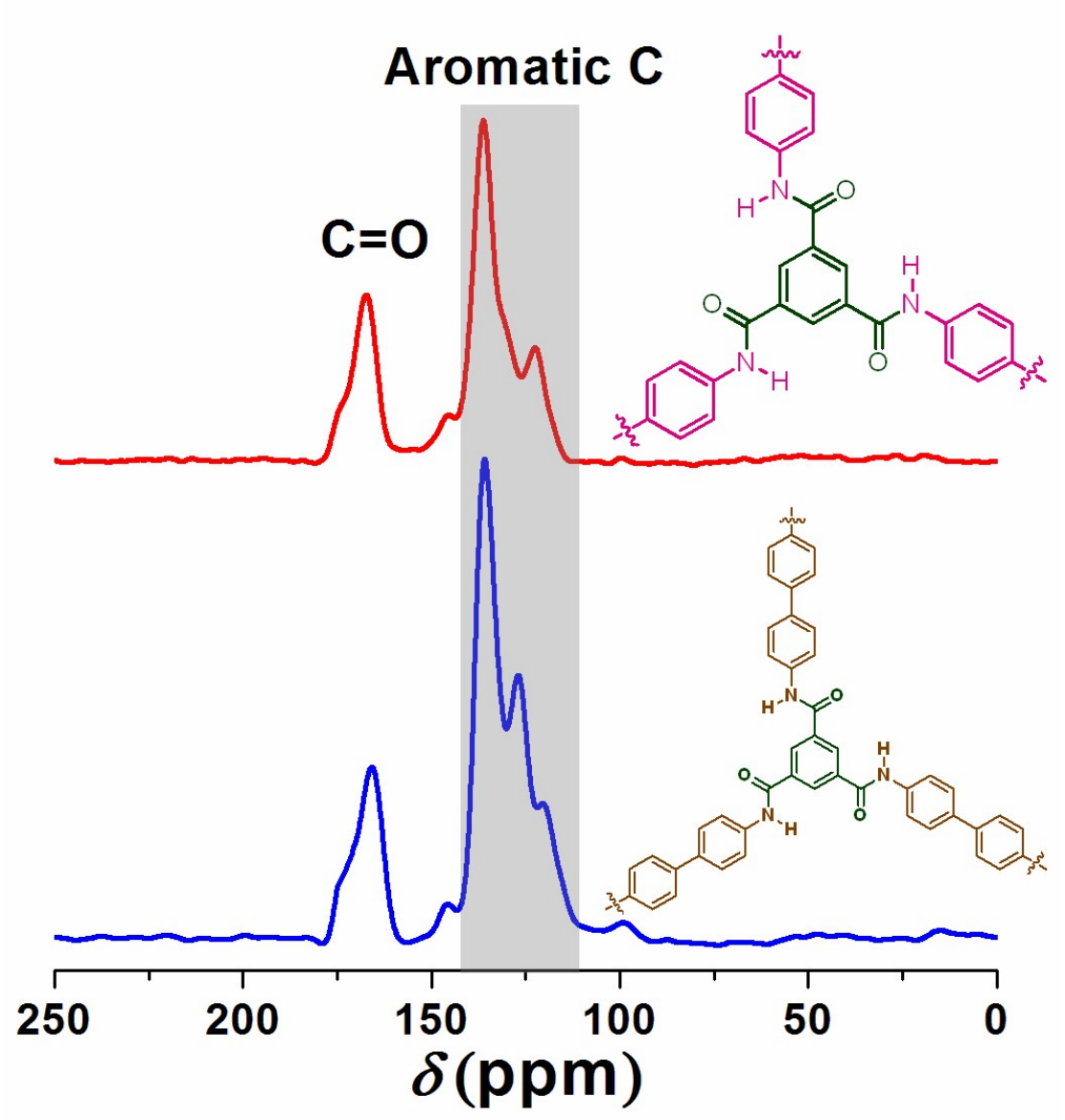


**Figure S5.** $^{13}C$ CP-MAS solid-state NMR spectra of 2DAPA-1 and 2DAPA-2.

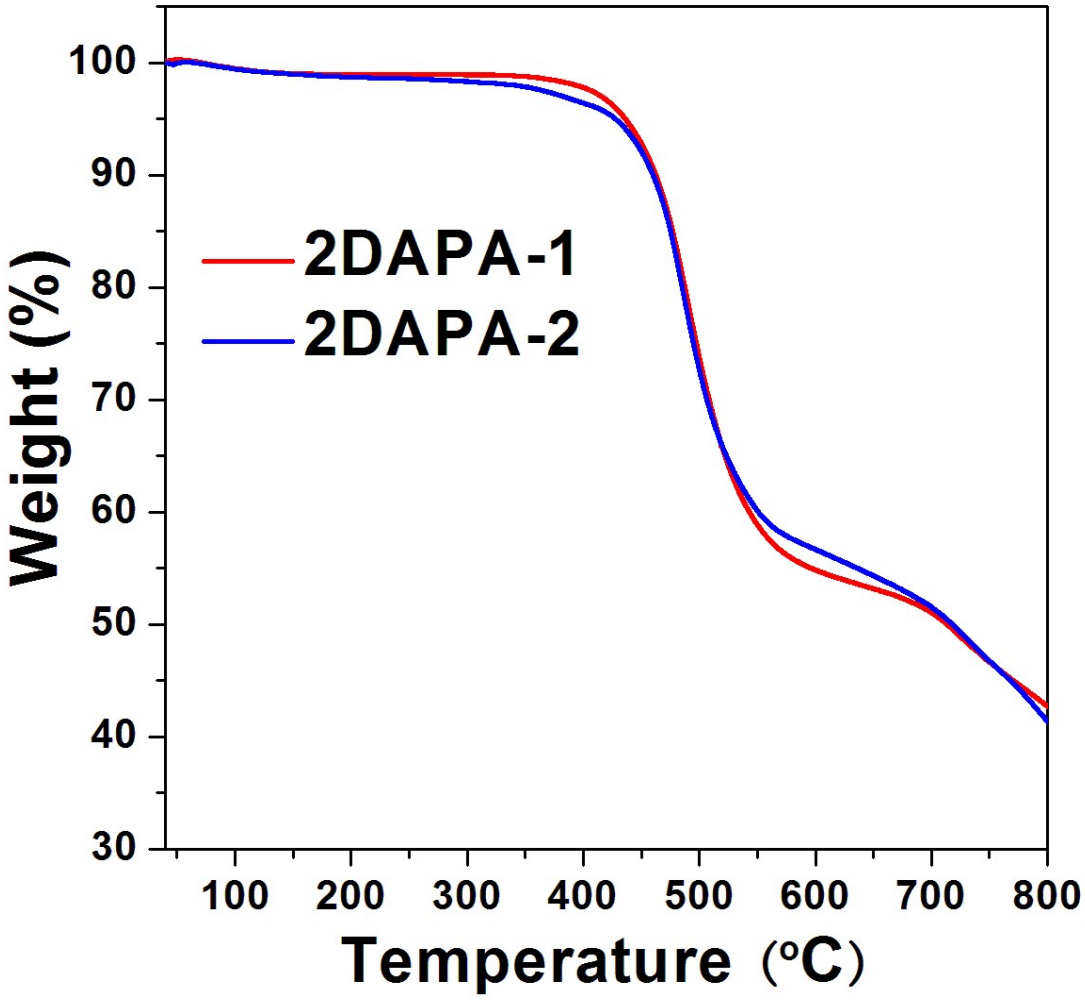


**Figure S6.** TGA curves of 2DAPA-1 and 2DAPA-2.

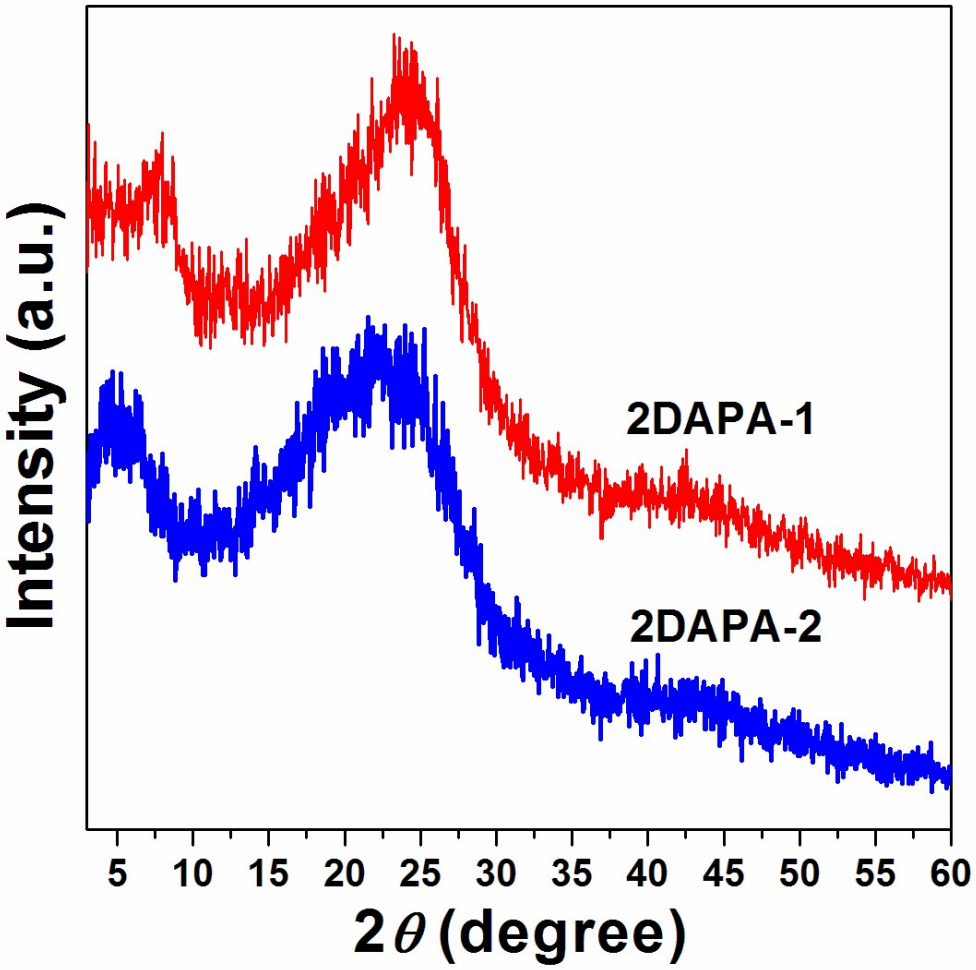


**Figure S7.** PXRD patterns of 2DAPA-1 and 2DAPA-2.