Electronic Supplementary Material (ESI) for CrystEngComm.

Polymorphism and cocrystal salt formation of 2-((2,6-dichlorophenyl)amino)benzoic acid, harvest of a second form of 2-((2,6-dimethylphenyl)amino)benzoic acid, and isomorphism between the two systems

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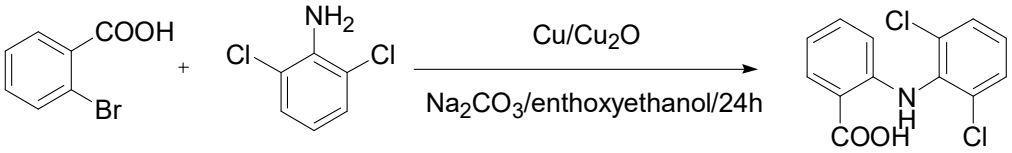
Synthesis and characterization



2-Bromobenzoic acid (2.0 g, 9.9 mmol), 2,6-dichloroaniline (1.7 g, 10.5 mmol), Cu (90.0 mg, 1.4 mmol), Cu_2O (0.1 g, 0.7 mmol) and Na_2CO_3 (2.1 g, 19.8 mmol) were added to a round-bottom flask, followed by addition of 2-ethoxyethanol (3.0 mL). The resulted system was reacted at 130℃ for 24 hours under nitrogen atmosphere. Then water (30.0 mL) was added, and the mixture was stirred for six minutes. After removing the unwanted solids by filtration, concentrated HCl was added dropwise to acidify the solution to pH ~2 and brown powder precipitated. The crude product was recovered by filtration and purified by column chromatography (using eluent PE/EA/acetic acid = 500/1/4). Pure product was obtained as light yellow solid (160.0 mg, yield%: 5.7).

^{1}H NMR (500 MHz, DMSO-d_6) δppm 13.16 (s, 1H), 9.51 (s, 1H), 7.93 – 7.88 (m, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.34 (dt, J = 16.8, 8.4 Hz, 2H), 6.78 (t, J = 7.5 Hz, 1H), 6.22 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δppm 170.1, 147.1, 134.8, 134.2, 133.5, 131.6, 129.2, 128.4, 117.5, 113.0, 111.9; IR (KBr, cm^{-1}) 3332 (s), 3007 (m), 1662 (s), 1582 (s), 1507 (s), 1447 (s), 1430 (s), 1405 (s), 1332 (s), 1319 (s), 1260 (s), 1201 (s), 1164 (s), 1086 (s), 1047 (s), 913 (s), 837 (s), 780(s), 771(s), 751 (s), 728 (s), 663 (s), 559 (s), 494 (s); MS (M+1): 280.39; mp: 215.7℃.

Note: the melting points were measured with DSC, and the onset temperature is recorded.

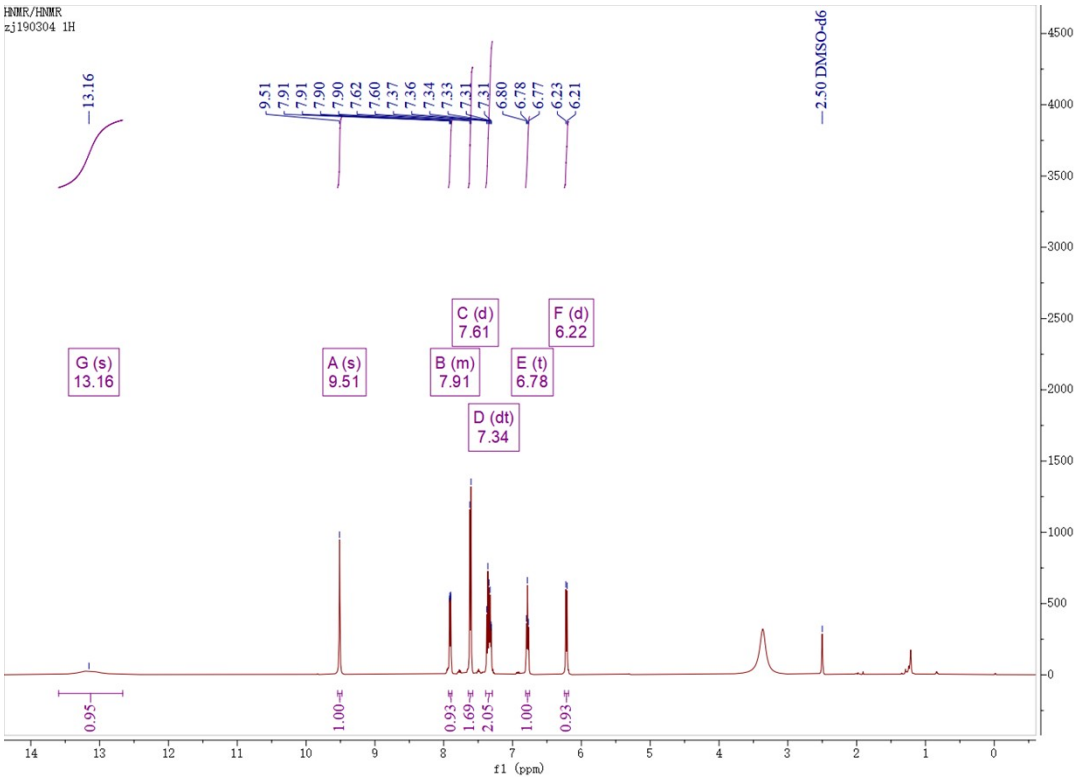


Figure S1 ^{1}H NMR spectrum of 2-DCABA

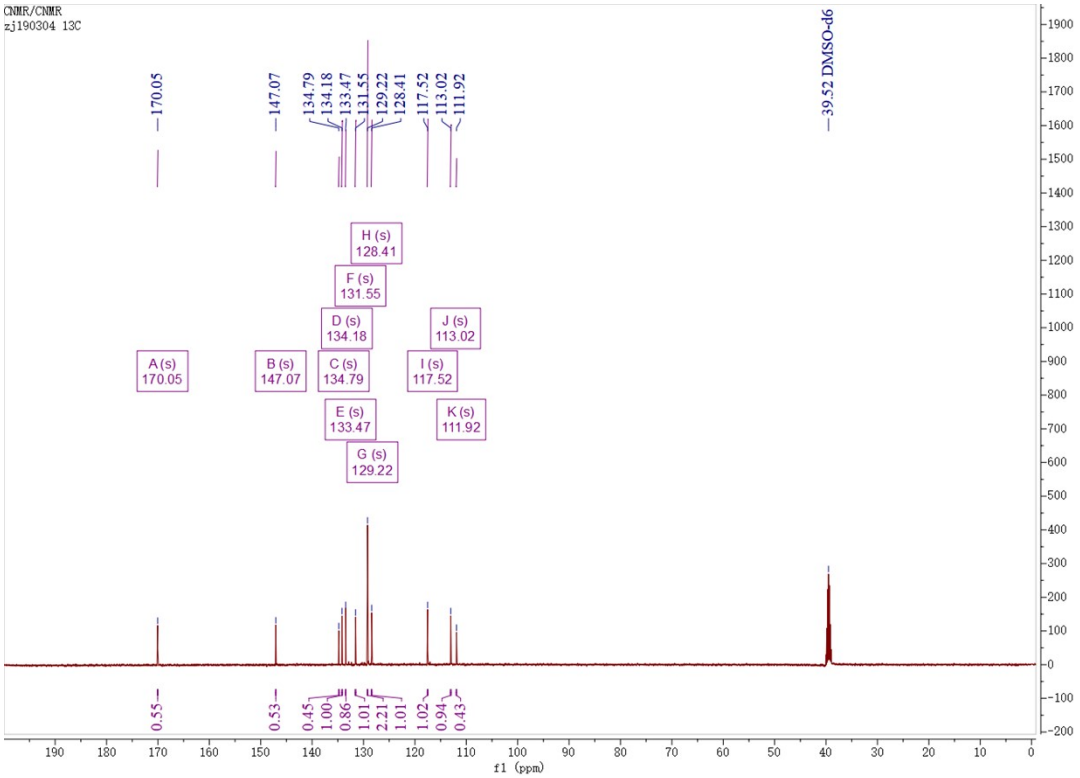


Figure S2 ^{13}C NMR spectrum of 2-DCABA

Crystal Growth

For slow evaporation, the pure compound was dissolved in different solvents, forming saturated solutions at room temperature (~25 °C). The solutions were set for slow evaporation in a vibration-free place until single crystals were harvested. For example, 30 mg of DCABA was added to 10 mL HPLC grade methanol. The mixture was stirred overnight and the remaining solid was removed by pipette filtration. A vial containing the clear solution was covered with perforated parafilm. Slow evaporation led to single crystals in about a week.

For melt crystallization, the ground sample of HDMPA-**I** was placed on a glass slide under ambient pressure, and heated to 215℃ at a heating rate of 50 K/min at first and 10 K/min between 190-215℃, and then cooled to room temperature. The melting and re-crystallization process was recorded by a hot-stage microscope (AxioScope.A1&LTS420).

DSC

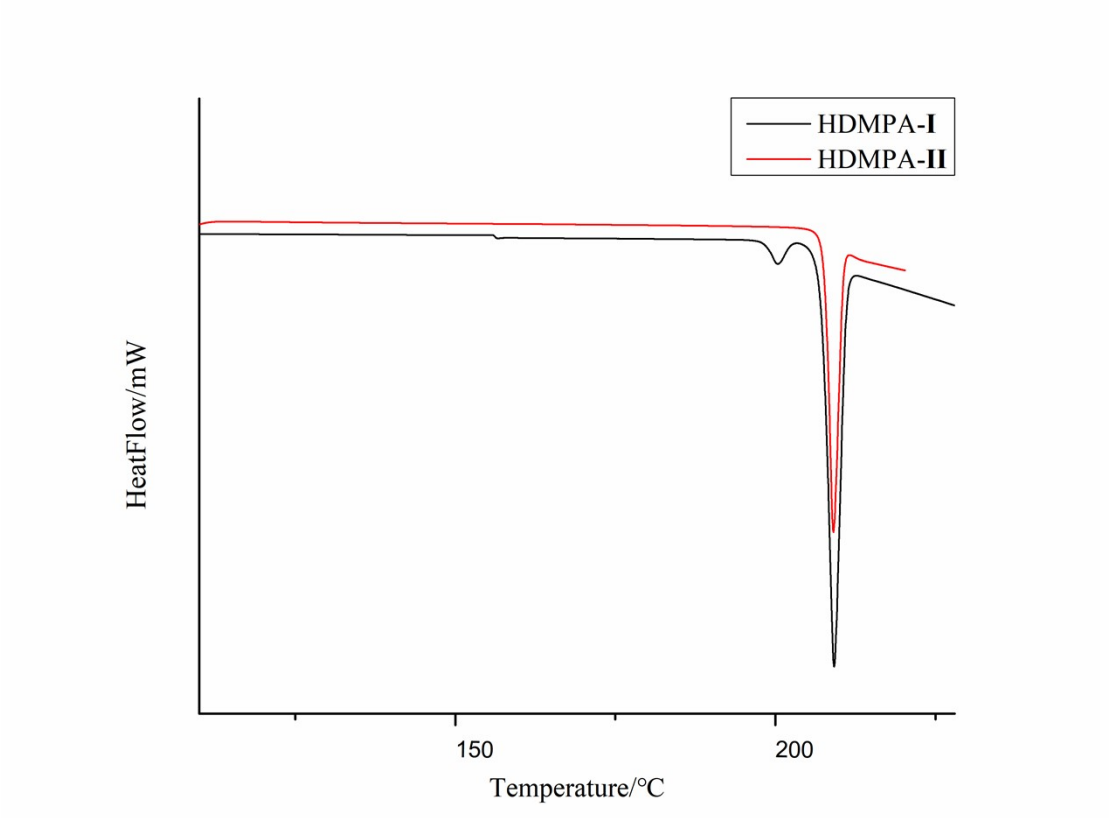


Figure S3. DSC thermograms of the two forms of HDMPA.

IR

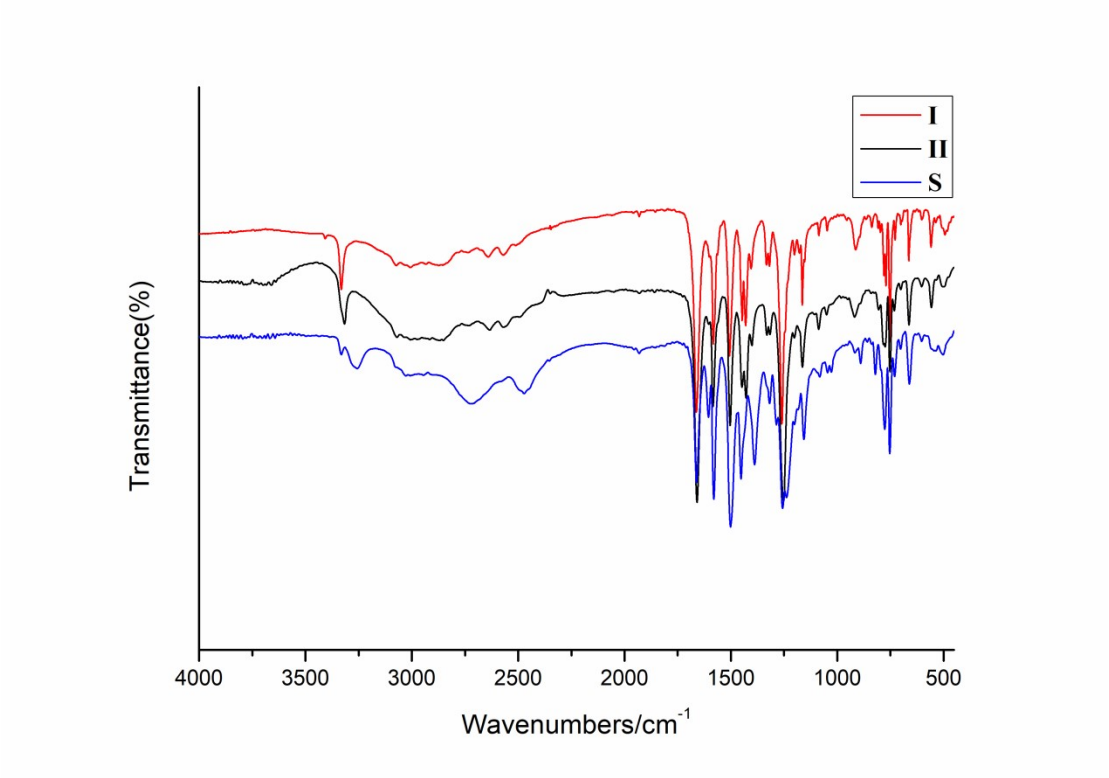


Figure S4. IR spectra of the three forms of **DCABA**.