**Supporting Information**

# Synthesis of Energetic Salts Containing Three Heterocyclic Anions by One-Pot Condensation Reaction

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## 1. Chemical and Materials.

**Synthesis of Ammonium 5-nitrotetrazole.** Firstly, 4.25 g (50 mmol) 5-aminotetrazole, 0.2 g (0.8 mmol) $Cu(SO_4)_2·5H_2O$ and 2.8 mL $H_2SO_4$ (98%) were added into 35 mL ice water, a blue transparent solution system A obtained after mixed and dissolved fully. Then, 35 g of crushed ice, 5.5 g (22 mmol) $Cu(SO_4)_2·5H_2O$, 10.4 g (150 mmol) $NaNO_2$ and 25 mL $H_2O$ (distilled water) were added into three flasks in turn, (ice salt bath) control temperature is below 3 °C and fully stirring obtained system B; then slowly adding A to B, control time is about 30 min, the whole process system temperature does not exceed 5 °C, fully stirring (color from dark green to blue and then to light green), after dripping, reaction at room temperature 1 h. Then 4.0 g (100 mmol) NaOH was dissolved in 10-15 mL disstilled water, which was added to the three flasks above, and the temperature was raised to 70 °C for 1 h. After the reaction, hot water filtration and wash 2-3 times, then 1.6 mL $H_2SO_4$ (98%) acidification filtrate and 4 g activated carbon was was added to filtrate for adsorbing 15 min. The filtrate was extracted and acidified again with 1.6 mL $H_2SO_4$ (98%). For acidified filtrate, the mixture of $CH_2Cl_2$ (130 mL) and laurylamine (20 mL) was used as extractant to extract for 3-5 times; the extracted solution was dried by adding appropriate amount of anhydrous $MgSO_4$ for 12 h, and then filtered; $NH_3$ was injected into the filtrate, resulting in a white precipitation of 5-nitrotetrazolium ammonium salt. Yield: 80%

(The density is 1.57 $g·cm^{-3}$, the melting point is 202 ℃, the impact sensitivity is 30/ 75 (12/ 12B/ cm), and the spark sensitivity is 2.66/ 7.58 (3/ 10/ -mil foil))

**Synthesis of Ammonium 3,5-dinitro-1,2,4-triazole.** 4 g (40.4 mmol) 3,5-diamino-1,2,4-triazole was dissolved in 292 mL $H_2SO_4$ (0.68 mol/L), and then clarified transparent solution A was obtained. In a three-port flask, 26.6 g (385.5 mmol) $NaNO_2$ was added to 30 mL distilled water, and the system B is obtained by stirring strongly at -7 °C. Then, A is slowly added to B (a large amount of $NO_2$ is produced), the reaction temperature is controlled between -10 ~ -5 °C, and the dripping time depends on the severity of the reaction (strictly controlling the reaction temperature and dripping acceleration to prevent the overflow or agglomeration of the solution), generally 2 ~ 3 h; After dropping, the reaction temperature rises to 60 °C for 1 h with the stirring rate 500 rpm, then cooling to 0-5 C, 13.25 mL $H_2SO_4$ (6 mol/L) are added to the reaction solution to acidification and 2 g urea to quenching, then 2 g activated carbon is added to absorb and decolorize for 30 min. Then the filtrate was extracted with mixed solvent of toluene (130 mL) and laurylamine (20 mL) for 3 ~

5 times; the extracted solution was dried with anhydrous $MgSO_4$ and stored in refrigerator at low temperature for 12 h, then $NH_3$ was injected into the filtrate at 0 ~ 5 °C to obtain the red-brown solid precipitation. $CH_2Cl_2$ (10 mL) washed the red-brown solid 2 ~ 3 times and then got the golden 5-dinitro-1,2,4-triazole ammonium salt solid, which was recrystallized with methanol/ethyl acetate mixed solvent. Yield: 75%

(The density is 1.632 g·cm$^{-3}$, the decomposition temperature is 170 ℃, the impact sensitivity is 59/ 80 (12/ 12B/ cm), and the critical temperature of thermal explosion is 222 ℃)

## 2. Experimental data and spectrum

**Product 1:** ((2E,2'E,2"E)-2,2',2"-(benzene-1,3,5-triyltris(methanylylidene))tris(hydrazin-1-yl-2-ylidene))tris(aminomethaniminium) 5-nitrotetrazolate

**Product 2:** ((2E,2'E,2"E)-2,2',2"-(benzene-1,3,5-triyltris(methanylylidene))tris(hydrazin-1-yl-2-ylidene))tris(aminomethaniminium) 3,5-dinitro-1,2,4-triazole

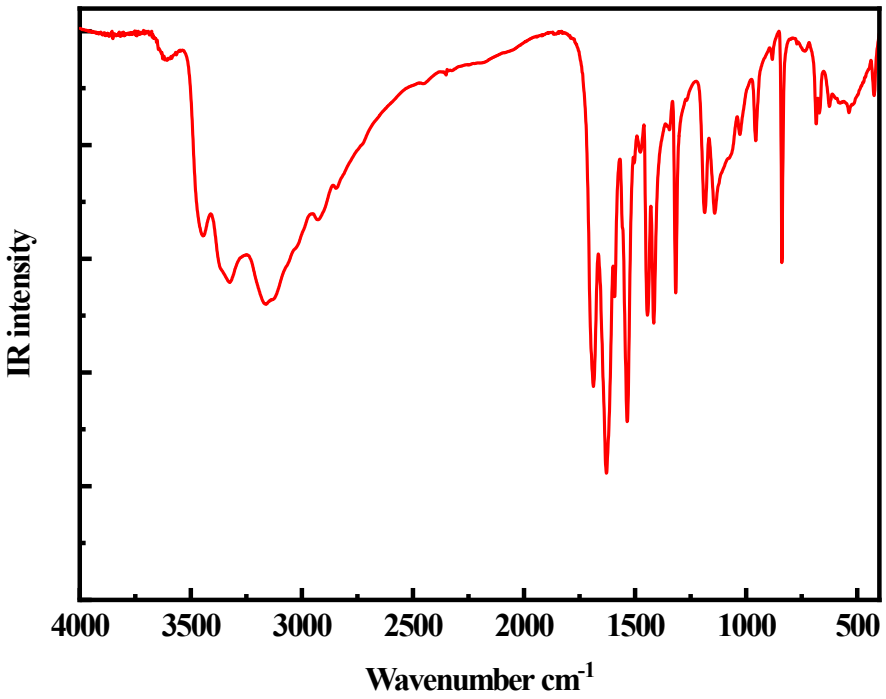


**Fig S1.** FT-IR spectrum of product **1**.

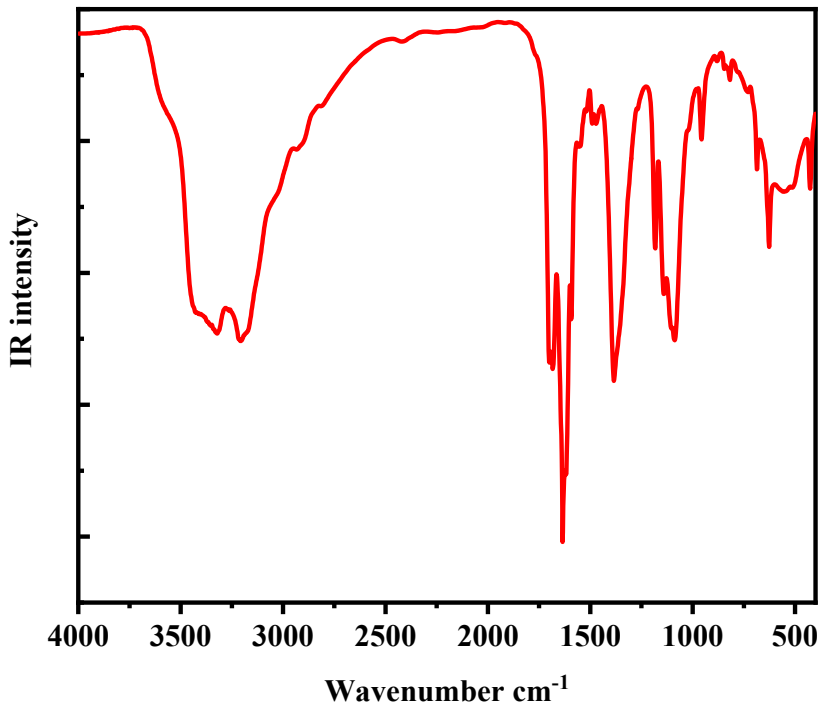


**Fig S2.** FT-IR spectrum of product **2**.

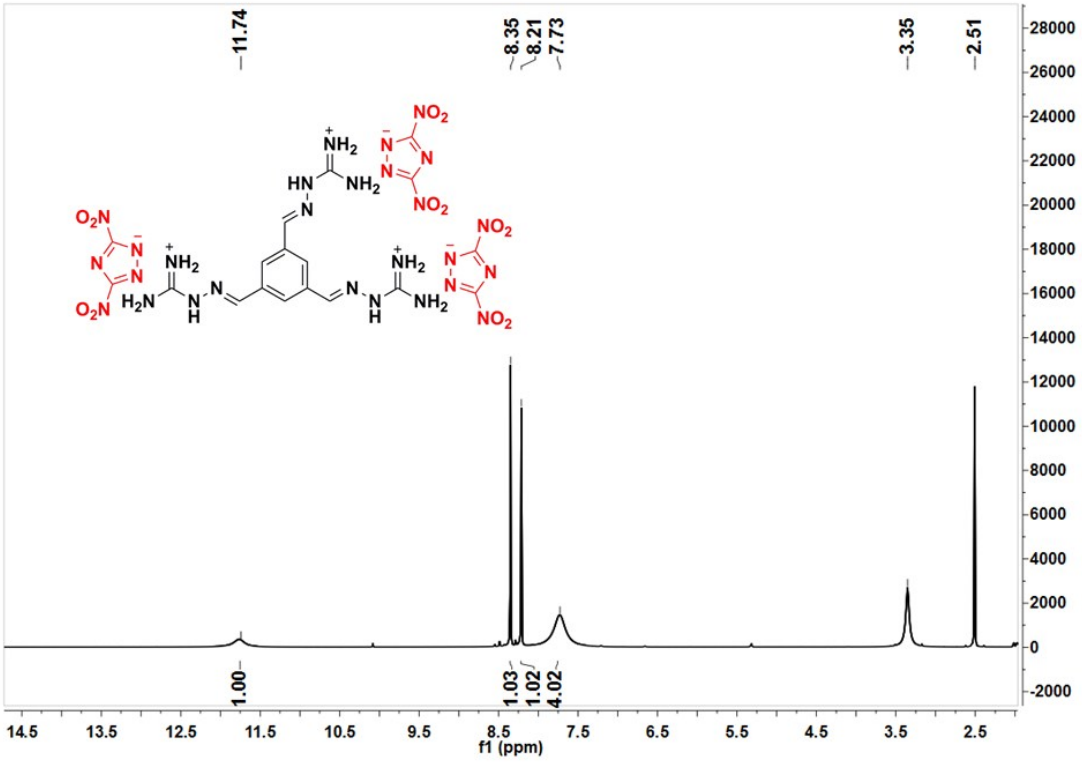


**Fig S3.** $^{1}$H NMR spectrum of product **2**.

**Product 3:** ((2E,2'E,2"E)-2,2',2"-(benzene-1,3,5-triyltris(methanylylidene))tris(hydrazin-1-yl-2-ylidene))tris(aminomethaniminium) 4-methylbenzenesulfonate

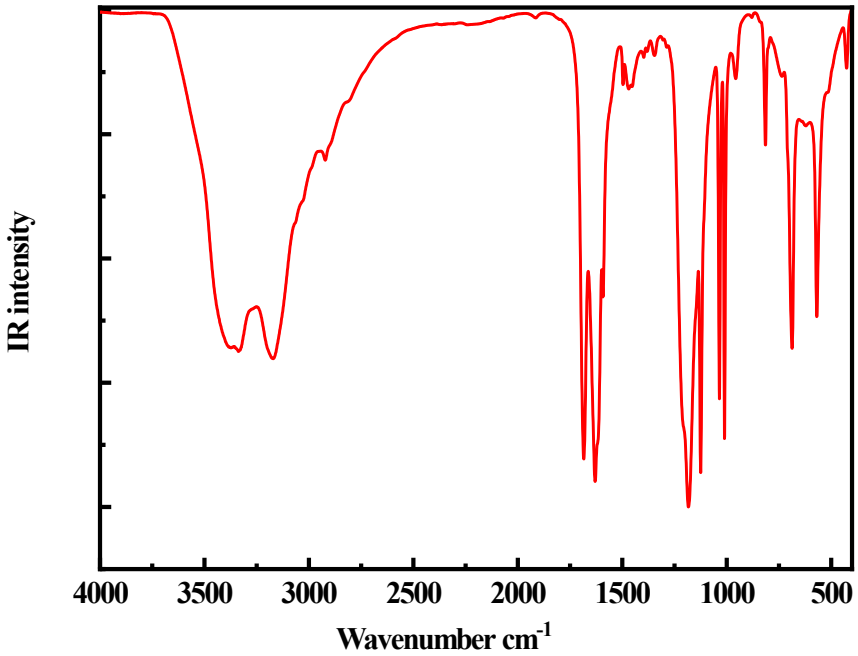


**Fig S4.** FT-IR spectrum of product **3**.

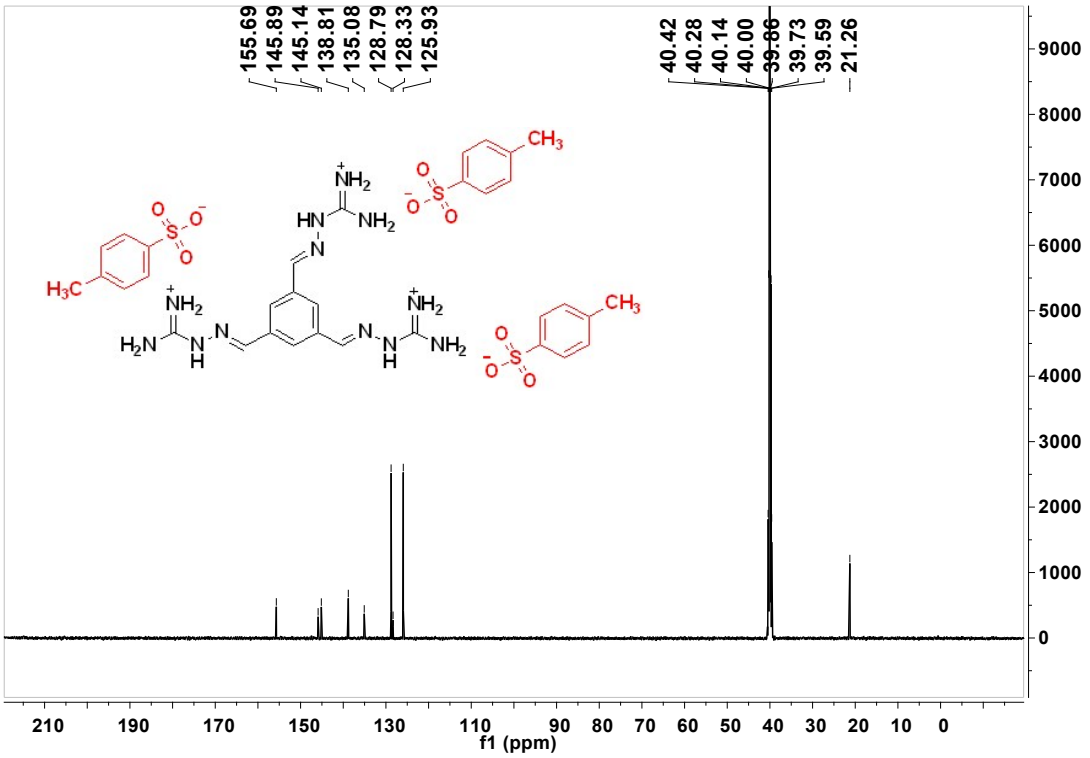


**Fig S5.** $^{13}C$ NMR spectrum of product **3**.

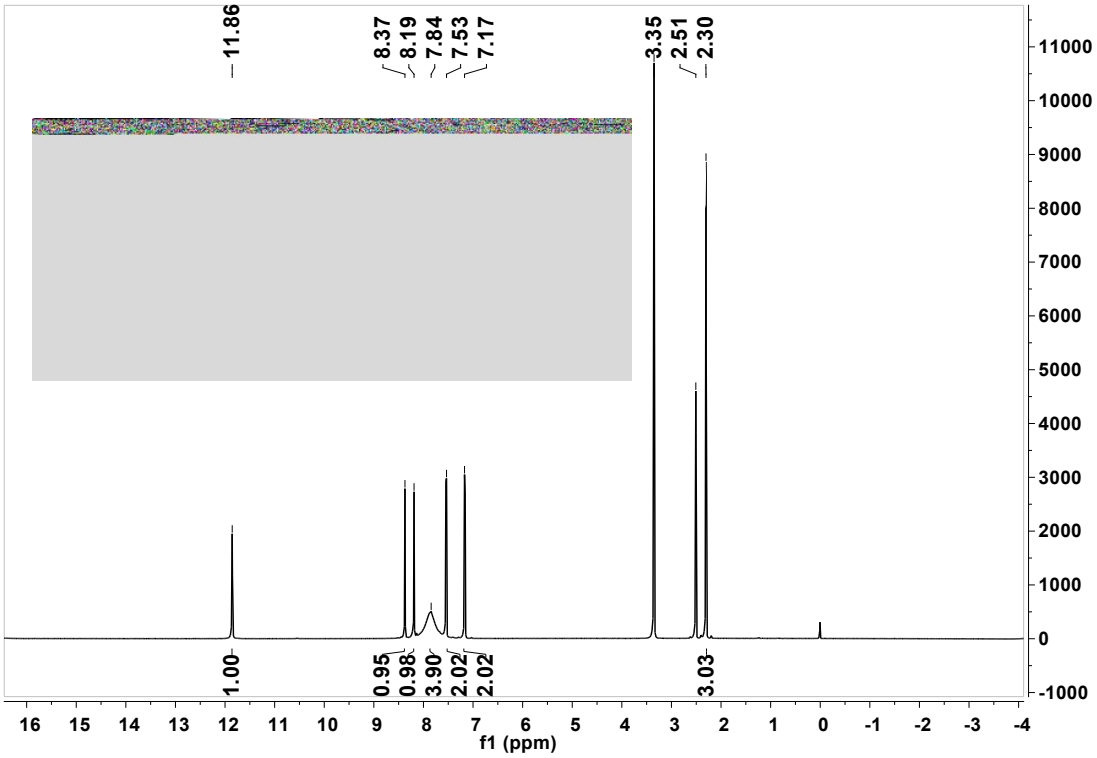


**Fig S6.** $^{1}$H NMR spectrum of product **3**.

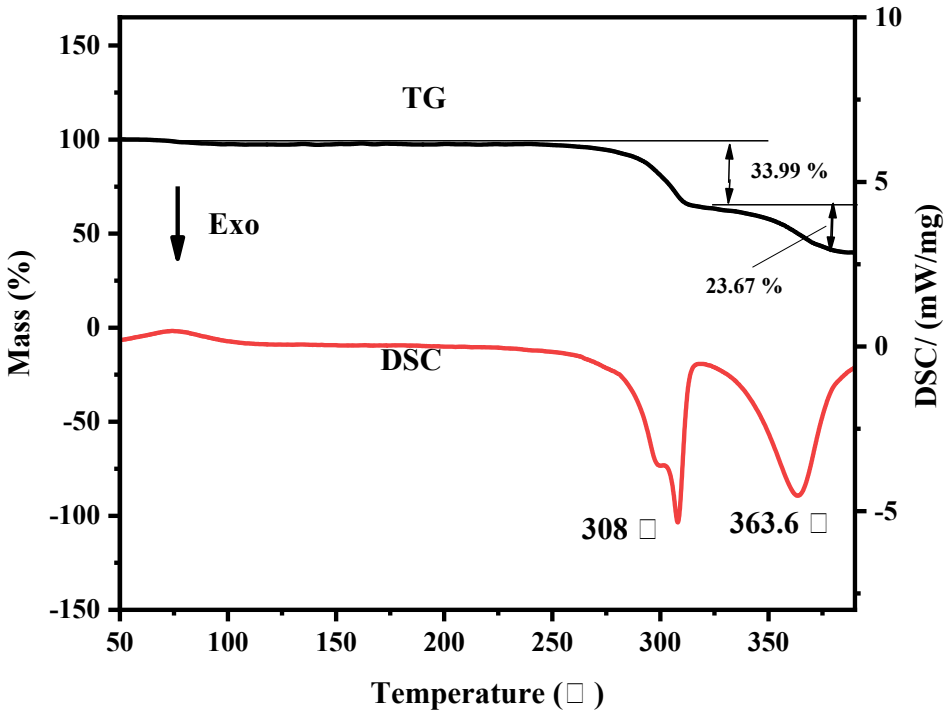


**Fig S7.** DSC-TG curves of product **2**.

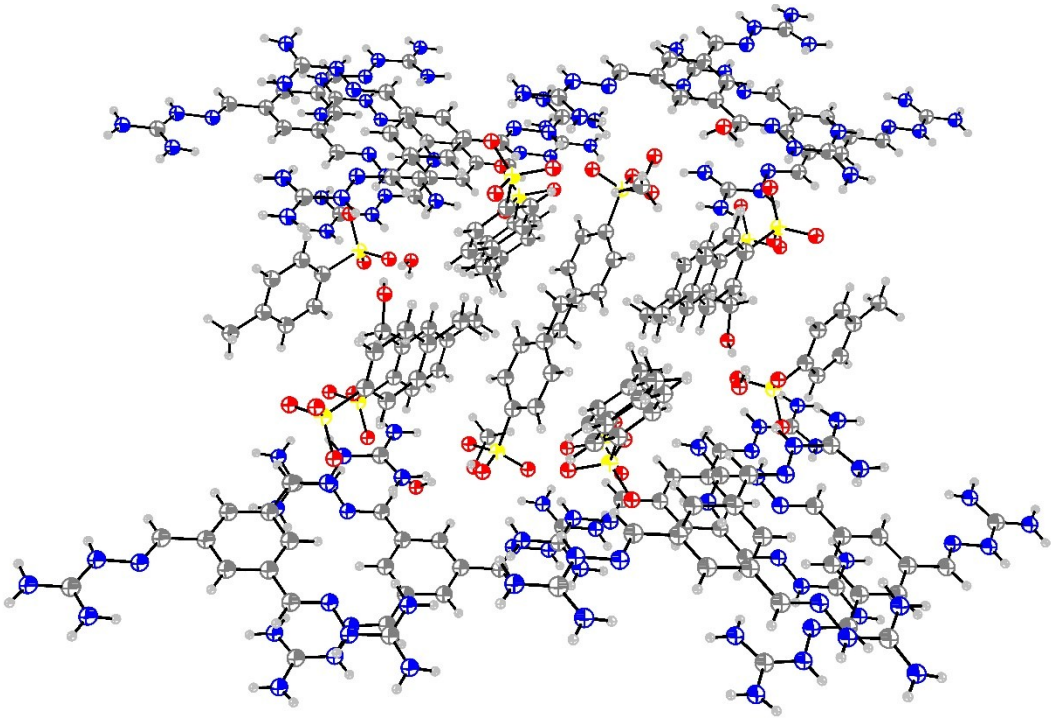

**Fig S8.** Cell stacking diagram of product **3**.