

## Supporting information

# **Boosting performance of energetic materials through thermal-induced conformational transition**

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## **Experimental section**

### **Caution**

Caution: These compounds are dangerous materials, explosions of which may occur in certain conditions. Although we had no difficulties on synthesizing and handling the compounds, proper safety precautions such as safety glasses, plastic spatulas and face shields must be used, especially when the experiments on a large scale.

### **Materials and General Methods**

DTAZF was synthesized according to a previously reported method<sup>1</sup>. Other commercially available reagents were used without further purification. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (DSC, Mettler Toledo DSC823e) at a scan rate of 5 °C min<sup>-1</sup> in closed Al containers with a nitrogen flow of 50 mL min<sup>-1</sup>. In addition, thermogravimetric analysis (TGA) was carried out at a heating rate of 5 °C min<sup>-1</sup> on a Mettler Toledo TGA/SDTA851e instrument.

**Synthesis of S-DTAZF.** DTAZF (0.0151g, 0.05mmol) was dissolved in 6ml ions-free water and kept it in a 10 ml sealed glass vial at the room temperature. Yellow particle-shaped crystals (0.01117 g, 0.037 mmol) were obtained after 24 hours (yield: 74%).

**Synthesis of U-DTAZF.** Kept S-DTAZF crystals in its mother solution and put it in a closed container. Then heated to 100°C within 100 mins and kept it at the same temperature for 3 days. Cooled to the room temperature, pale yellow needle-shaped crystals (0.00949 g, 0.031 mmol) were obtained (yield: 85%, based on S-DTAZF).

### X-ray crystallographic study

The crystal of S-DTAZF of dimensions 0.250×0.220×0.180 mm<sup>3</sup>, the crystal of U-DTAZF of dimensions 0.170×0.130×0.110 mm<sup>3</sup> were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å) at 123 K and 296 K, respectively. Integration and scaling of intensity data were accomplished using the SAINT program<sup>2</sup>. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full-matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and OH hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS4 Relevant crystal data and refinement results are summarized in Table S1.

Table S1 Crystal data and structure refinement for S-DTAZF and U-DTAZF

Compound	S-DTAZF	U-DTAZF
CCDC	1829898	1829902
Empirical formula	C <sub>6</sub> H <sub>2</sub> N <sub>14</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>2</sub> N <sub>14</sub> O <sub>2</sub>
Formula weight	302.22	302.22
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a	6.1954(13)	5.7955(12)
b	9.278(2)	9.7961(19)
c	9.776(2)	19.767(4)
$\alpha$	90	90
$\beta$	91.993(6)	92.904(7)
$\gamma$	90	90
V	561.6(2)	1120.8(4)
Z	2	4
Dc(g/cm <sup>3</sup> )	1.787	1.791
T(K)	123	296
$\mu$ (mm <sup>-1</sup> )	0.146	0.146
F(000)	304	608
GOF on F	1.188	1.046
R1[I>2 $\sigma$ (I)]	0.0622	0.0507
wR2(I>2 $\sigma$ (I))	0.1858	0.1296
R1[all data]	0.0652	0.0653
wR2(all data)	0.1884	0.1381

Table S2 Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for compound S-DTAZF

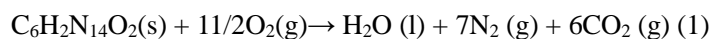
C1–N1	1.316(5)	N1–C1–N4	109.2(3)
C1–N4	1.330(4)	N1–C1–C2	127.5(3)
C1–C2	1.468(5)	N4–C1–C2	123.2(3)
C2–N5	1.302(5)	N5–C2–C3	109.6(3)
C2–C3	1.427(5)	N5–C2–C1	119.5(3)
C3–N6	1.311(5)	C3–C2–C1	130.9(3)
C3–N7	1.421(5)	N6–C3–N7	126.2(3)
N1–N2	1.370(4)	N6–C3–C2	108.2(3)
N2–N3	1.295(4)	N7–C3–C2	125.6(3)
N3–N4	1.347(4)	C1–N1–N2	105.7(3)
N4–H4A	0.9596	N3–N2–N1	109.8(3)
N5–O1	1.387(4)	N2–N3–N4	107.2(3)
N6–O1	1.365(4)	C1–N4–N3	108.0(3)
N7–N7	1.263(6)	C1–N4–H4A	129.9
		N3–N4–H4A	121.8
		C2–N5–O1	104.9(3)
		C3–N6–O1	105.9(3)
		N7–N7–C3	111.7(4)
		N6–O1–N5	111.4(2)

Table S3 Bond lengths [Å] and angles [°] for U-DTAZF

C1—N4	1.328(2)	N4—C1—N1	108.32(15)
C1—N1	1.338(2)	N4—C1—C2	121.62(15)
C1—C2	1.455(2)	N1—C1—C2	130.04(15)
C2—N5	1.309(2)	N5—C2—C3	107.83(15)
C2—C3	1.440(2)	N5—C2—C1	116.29(15)
C3—N6	1.313(2)	C3—C2—C1	135.88(15)
C3—N7	1.405(2)	N6—C3—N7	115.06(15)
C4—N11	1.319(2)	N6—C3—C2	108.81(14)
C4—N14	1.335(2)	N7—C3—C2	136.13(16)
C4—C5	1.454(2)	N11—C4—N14	109.16(15)
C5—N10	1.303(2)	N11—C4—C5	124.69(15)
C5—C6	1.424(2)	N14—C4—C5	126.14(15)
C6—N9	1.310(2)	N10—C5—C6	109.23(15)
C6—N8	1.418(2)	N10—C5—C4	121.89(15)
N1—N2	1.346(2)	C6—C5—C4	128.88(15)
N1—H1	0.9348	N9—C6—N8	125.49(15)
N2—N3	1.301(2)	N9—C6—C5	109.05(14)
N3—N4	1.355(2)	N8—C6—C5	125.44(15)
N5—O1	1.3759(19)	C1—N1—N2	108.53(14)
N6—O1	1.3632(18)	C1—N1—H1	132.2
N7—N8	1.252(2)	N2—N1—H1	118.6
N9—O2	1.3722(18)	N3—N2—N1	106.60(14)
N10—O2	1.3797(19)	N2—N3—N4	110.52(13)
N11—N12	1.357(2)	C1—N4—N3	106.03(14)
N12—N13	1.304(2)	C2—N5—O1	106.17(13)
N13—N14	1.342(2)	C3—N6—O1	105.71(14)
N14—H14	0.8699	N8—N7—C3	113.30(14)
		N7—N8—C6	111.92(14)
		C6—N9—O2	104.91(14)
		C5—N10—O2	104.89(13)
		C4—N11—N12	105.60(14)
		N13—N12—N11	110.45(13)
		N12—N13—N14	106.64(14)
		C4—N14—N13	108.14(14)
		C4—N14—H14	132.6
		N13—N14—H14	119.0
		N6—O1—N5	111.47(12)
		N9—O2—N10	111.92(12)

## Computational Methods

The experimental result for the constant volume combustion energy ( $\Delta_c U$ ) of S-DTAZF and U-DTAZF are  $-12496.147 \text{ J g}^{-1}$  and  $-12847.356 \text{ J g}^{-1}$ , respectively. According to the formula  $\Delta_c H_m^\theta = \Delta_c U_m^\theta + \Delta nRT$ ,  $\Delta n = n_g(\text{products}) - n_g(\text{reactants})$ , ( $n_g$  is the total molar amount of gases in the products or reactants,  $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $T=298.15\text{K}$ ), the enthalpy of combustion ( $\Delta_c H_m^\theta$ ) can be derived to be  $-3757.50 \text{ kJ mol}^{-1}$  and  $-3863.62 \text{ kJ mol}^{-1}$ . The combustion reaction equation is listed as follows:

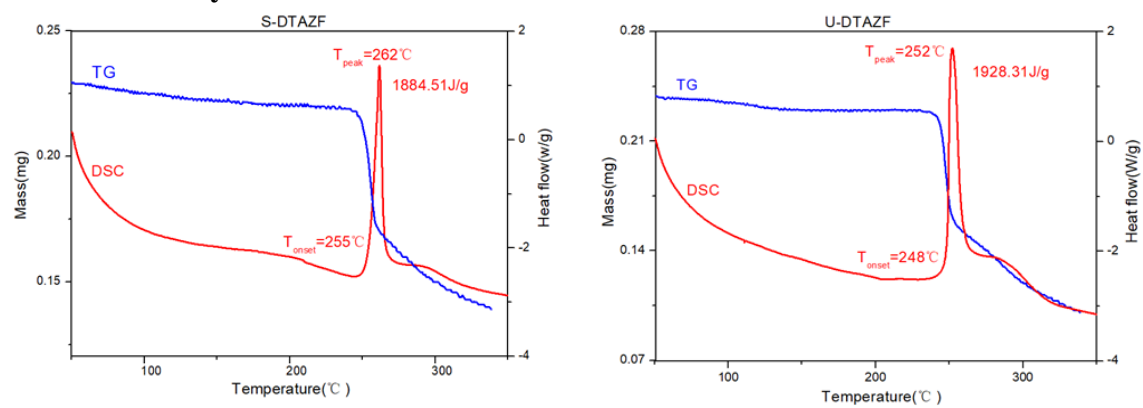


$$\Delta_f H_m^\theta(\text{S-DTAZF}, \text{s}) = \Delta_f H_m^\theta(\text{H}_2\text{O}, \text{l}) + 6\Delta_f H_m^\theta(\text{CO}_2, \text{g}) - \Delta_c H_m^\theta(\text{S-DTAZF}, \text{s}) \quad (2)$$

$$\Delta_f H_m^\theta(\text{U-DTAZF}, \text{s}) = \Delta_f H_m^\theta(\text{H}_2\text{O}, \text{l}) + 6\Delta_f H_m^\theta(\text{CO}_2, \text{g}) - \Delta_c H_m^\theta(\text{U-DTAZF}, \text{s}) \quad (3)$$

Based on the calculated standard molar enthalpy of combustion and the known enthalpy of formation of the combustion products determined experimentally,  $\Delta_f H_m^\theta(\text{H}_2\text{O}, \text{l}) = -285.830 \text{ kJ mol}^{-1}$ ,  $\Delta_f H_m^\theta(\text{CO}_2, \text{g}) = -393.51 \text{ kJ mol}^{-1}$ , the standard enthalpy of formation of S-DTAZF and U-DTAZF were back-calculated from the combustion equation. On the basis of Hess's law in thermochemical eqn (2) and (3), the standard enthalpy of formation of S-DTAZF and U-DTAZF are  $1110.61 \text{ kJ mol}^{-1}$  and  $1216.73 \text{ kJ mol}^{-1}$ , respectively.

## Thermal analysis



**Figure S1.** The TG-DSC curves of S- and U-DTAZF.

## The proposed transition

To comprehensively study the transition mechanism, the S-DTAZF crystal (25mg) was suspended in 1mL water and heated to 100°C. It is distinctly that the samples dissolved in hot water, as shown in Figure S2.

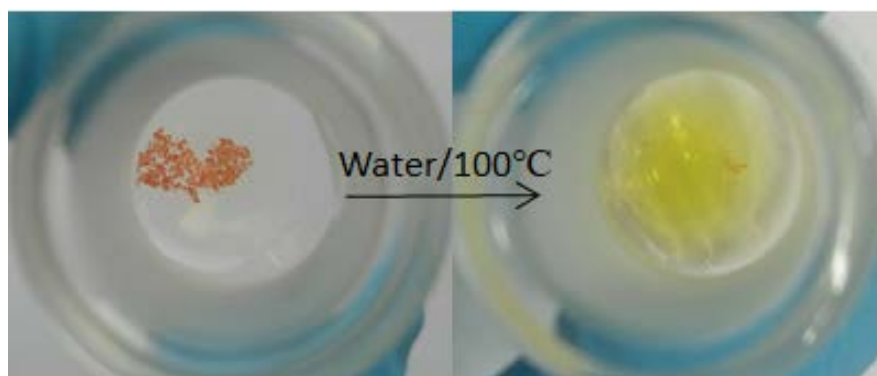


Figure S2. The solubility of S-DTAZF crystals in water and nitrobenzene.

The proposed transition may be described as: the S-DTAZF crystals dissolved in water at high temperature. Then C-N and C-C single bonds of DTAZF molecules rotated in assistance of thermal energy. When  $C2-C3-N7-N7 = -2.6^\circ$  and  $C3-C2-C1-N1 = -175.6^\circ$ , intramolecular hydrogen bonds (N1-H1  $\cdots$  N11) formed and “locked” corresponding conformational isomer, thus the U-DTAZF crystals formed (Fig. S3).

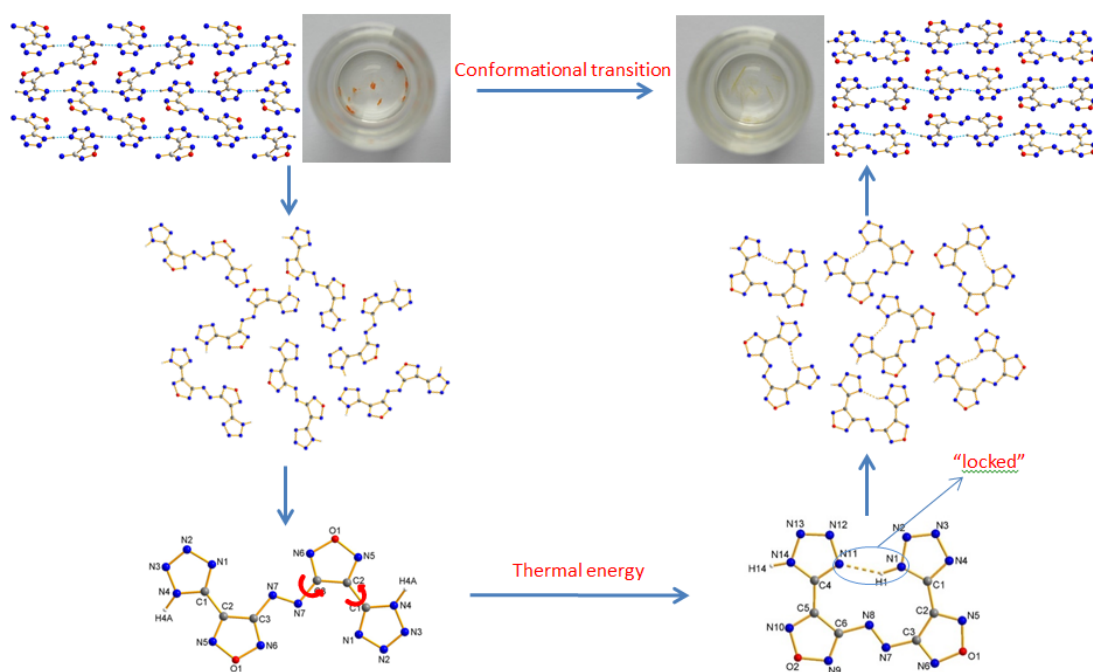


Figure S3. The proposed transition of from S-DTAZF to U-DTAZF



## Reference

- 1 Y. Qu, Q. Zeng, J. Wang, Qing. Ma, H. Li, H. Li and G. Yang, *Chem. Eur. J.* 2016, **22**, 12527– 12532.