Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Can heavy trinitromethyl group always result in a higher density?

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1. General Methods

All reagents were purchased from Energy Chemical of analytical grade and were used as supplied, if not stated otherwise. The melting points and decomposition temperatures were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 mL min^{-1}.

2. Safety Precautions

All the new pyrazole compounds in this manuscript are powerful explosives, and should be handled with extreme care using the best safety practices.

3. Experimental procedures

1-trinitromethyl-4-amino-3,5-dinitropyrazole (**TN-116**): A solution of AT-116[1] (0.4 g, 1.75 mmol) in 100% H_2SO_4 (4 mL) was stirred at 0–5 °C and treated by dropwise addition of 90% HNO_3 (3 ml) and the mixture was stirred for 2 days at room temperature. Separated crude product was filtered off, washed with CF_3CO_2H (3 ml), dried over P_2O_5. TN-116 (0.28 g, 50%) was isolated as light-yellow crystals by recrystallization from CH_3CN. T_d(onset): 113 ºC. ^1H NMR (DMSO-d_6): 7.11 ppm. ^{13}C NMR (DMSO-d_6): 150.41, 137.26, 133.26, 124.00 ppm. IR (KBr): =(delete) 3250, 1635, 1591, 1536, 1435, 1394, 1353, 1318, 1271, 1175, 1169, 1119, 815 796 cm^{-1}. Elemental analysis for $C_4H_2N_8O_{10}$. Calcd: C 14.92; H 0.63 N 34.79 %. Found: C 15.16; H 0.88; N 34.22 %.

4. Spectrum Analysis

4.1 NMR spectra.

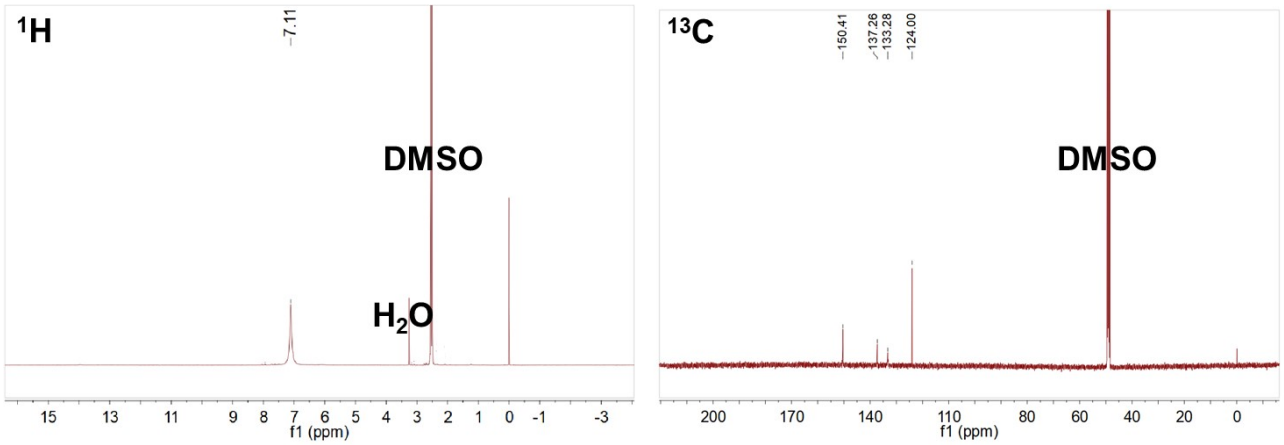


Figure S1. ^{1}H NMR and $1^{3}C$ NMR of TN-116 in DMSO-d_6.

4.2 IR Spectrum.

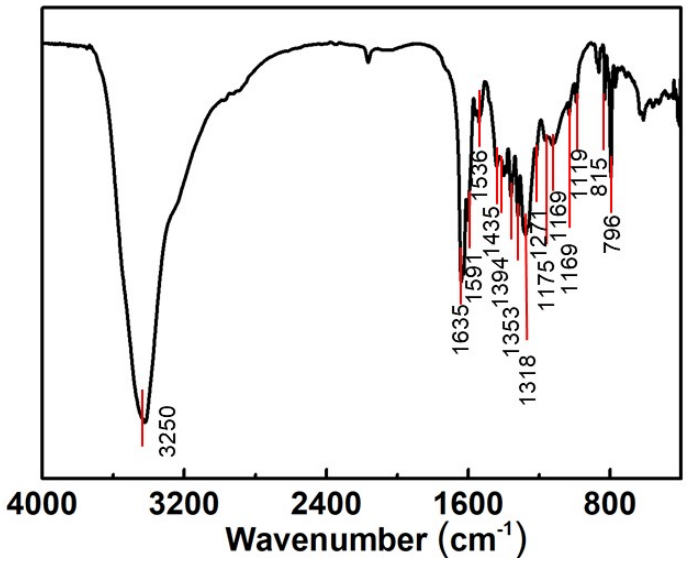


Figure S2. IR spectrum of TN-116.

5. Crystal Structures

5.1 X-ray crystallography details

A colorless block crystal (**TN-116**) of dimensions 0.20×0.20×0.20 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 296 K. Corrections for Lorentz and polarization effects and for absorption (ψ scan) were applied. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares calculation on F2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they were attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

Table S1. Crystallographic data for **TN-116** and **LLM-116**.

Compound	**TN-116**	**LLM-116**
Formula	$C_4H_2N_8O_{10}$	$C_3H_3N_5O_4$
M_w	322.14	173.10
Crystal system	orthorhombic	Orthorhombic
Space group	P 21 21 21	P 21 21 21
a [Å]	8.033 (3)	4.7257(5)
b [Å]	11.591 (5)	4.7312(6)
c [Å]	12.100 (5)	27.063(4)
α[°]	90	90
β[°]	90	90
γ[°]	90	90
V [$Å^3$]	1126.6 (8)	605.07(13)
Z	4	4
T [K]	296	294
λ [Å]	0.71073	1.54178
P_{calcd}[g cm^{-3}]	1.899	1.900
μ [mm^{-1}]	0.188	1.555
F(000)	648.0	352
θ range[°]	2.433-25.025	13.45-36.33
Index ranges	-9 ≤ h ≤ 8	-5 ≤ h ≤ 5
	-13 ≤ k ≤ 12	0 ≤ k ≤ 5
	-14 ≤ l ≤ 14	0 ≤ l ≤ 29
Data/restraints/parameters	1972/0/199	851/0/111
GOF on F2	1.071	1.101
R[F^2> 2σ(F^2)]	0.0439	0.0329
wR(F^2)	0.1017	0.0880

5.2 Bond lengths and angles

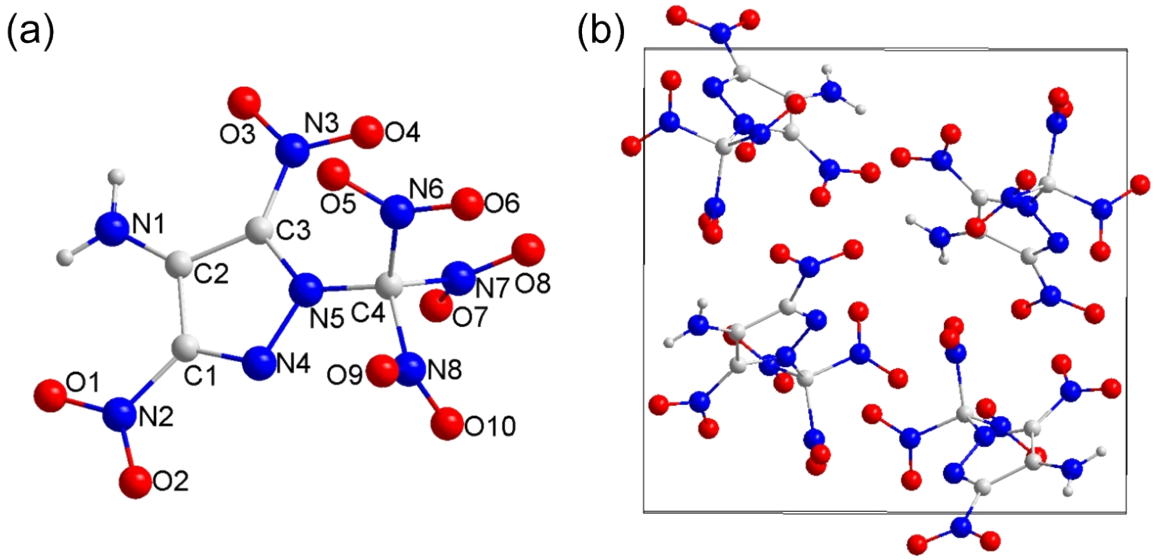


Figure S3. (a) Crystal structure of **TN-116**; (b) Packing diagram of **TN-116.**

Table S2. Bond lengths (Å) and bond angles (°) for **TN-116**.

Bond lengths		
C1 N4 1.317(5)	C4 N8 1.536(6)	N3 O4 1.232(5)
C1 C2 1.422(6)	C4 N6 1.545(6)	N4 N5 1.358(5)
C1 N2 1.449(6)	C4 N7 1.551(6)	N6 O5 1.184(5)
C2 N1 1.332(5)	N1 H1A 0.8600	N6 O6 1.206(5)
C2 C3 1.375(6)	N1 H1B 0.8600	N7 O7 1.196(5)
C3 N5 1.388(5)	N2 O2 1.203(5)	N7 O8 1.208(5)
C3 N3 1.398(6)	N2 O1 1.225(5)	N8 O10 1.191(6)
C4 N5 1.400(5)	N3 O3 1.225(5)	N8 O9 1.205(6)
Bond angles		
N4 C1 C2 114.6(4)	N8 C4 N7 106.6(4) .	N4 N5 C3 110.6(3)
N4 C1 N2 118.1(4) .	N6 C4 N7 111.8(4)	N4 N5 C4 118.1(3)
C2 C1 N2 127.2(4) .	C2 N1 H1A 120.0	C3 N5 C4 131.3(4)
N1 C2 C3 129.1(4)	C2 N1 H1B 120.0	O5 N6 O6 126.7(5)
N1 C2 C1 129.0(4)	H1A N1 H1B 120.0	O5 N6 C4 117.2(4)
C3 C2 C1 101.8(4)	O2 N2 O1 125.1(4) .	O6 N6 C4 115.8(4)
C2 C3 N5 108.6(4)	O2 N2 C1 119.1(4)	O7 N7 O8 128.5(5)

C2 C3 N3 128.3(4) .	O1 N2 C1 115.7(4)	O7 N7 C4 114.6(4)
N5 C3 N3 123.1(4) .	O3 N3 O4 124.6(4)	O8 N7 C4 116.9(5)
N5 C4 N8 110.0(3)	O3 N3 C3 117.0(4)	O10 N8 O9 128.6(5)
N5 C4 N6 112.2(4)	O4 N3 C3 118.4(4)	O10 N8 C4 116.2(5)
N8 C4 N6 105.3(4)	C1 N4 N5 104.3(3)	O9 N8 C4 115.2(4)
N5 C4 N7 110.7(4)		

6. Calculation of packing coefficient

Packing coefficient were calculated using traditional method by using the equation $PC=\sum V_m/V_c$, where V_m is the volume enclosed by a surface with an electronic density of 0.003 a.u., and V_c is the unit cell volume. However, single-crystal X-ray data of many trinitromethyl compounds and precursors were collected at different temperatures, the direct comparison using existing method would cause large errors, and even the single-crystal data of some compounds were missing, so it is impossible to calculate and compare the packing coefficient. In order to realize the comparison of packing coefficient at the same level, the calculation method of packing coefficient was optimized in this study. The key to optimization lies in how to replace the unknown cell volume (V_m) by other known parameters, for which we further derive the existing calculation equations. As the derivation process shown in Figure S1 we found that the packing coefficient can be replaced by $PC = \rho_c/\rho_M$, where ρ_c is the crystal density (this density can be the room temperature crystal density, the density converted from the low temperature crystal density, and the room temperature measured density) and ρ_M is calculated single molecular density.

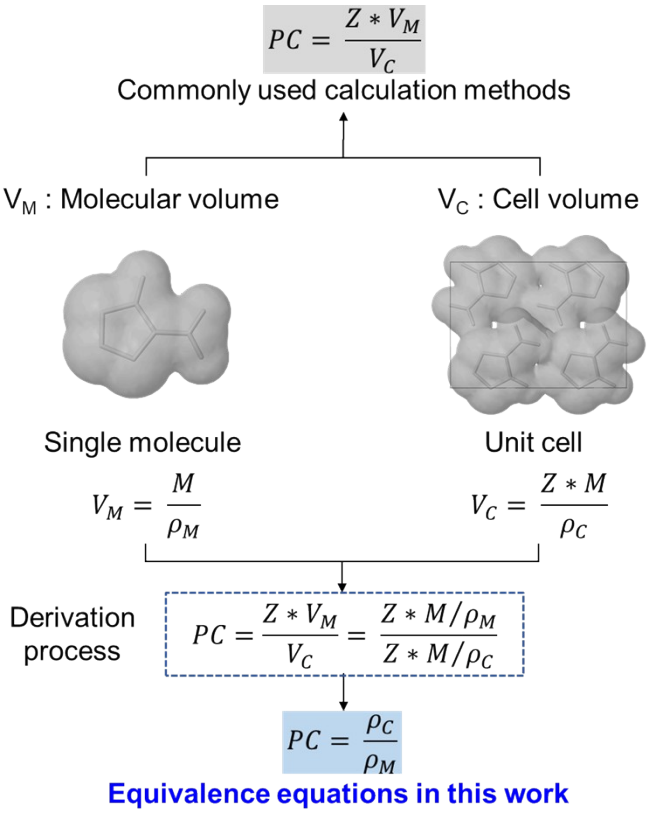
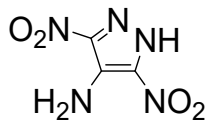
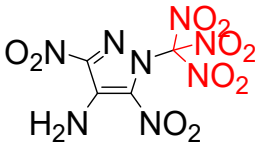
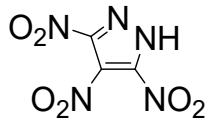
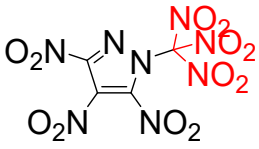
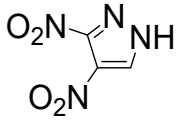
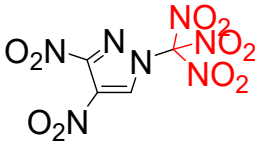
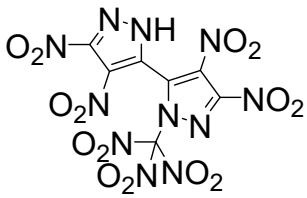
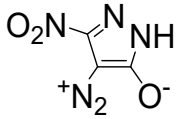
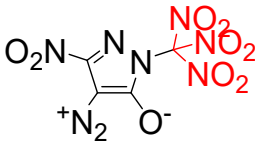
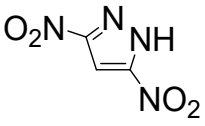
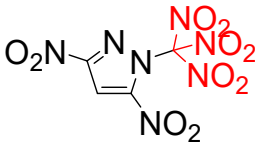
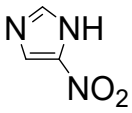
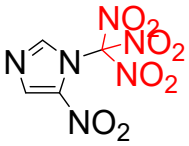
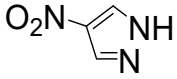
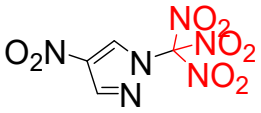
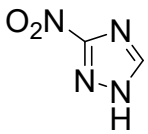
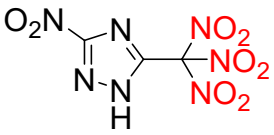
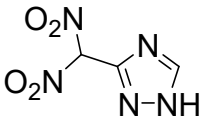
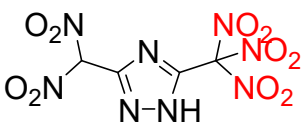
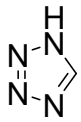
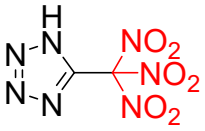


Figure S4. The optimized method on calculating packing coefficient.

Table S3. Density and packing coefficient of the compounds before and after the introduction of trinitromethyl group.

Structure	ρ_c (298 K)	ρ_M	PC(%)	ref
	1.900	2.334	81.41	[2]
	1.899	2.520	75.37	**This work**
	1.867	2.488	75.03	[3]
	1.964	2.615	76.33	[4]
	1.780	2.354	76.13	[5]
	1.917	2.545	76.96	[6]
	1.881	2.545	73.94	[7]
	2.021	2.582	78.26	[8]
	1.770	2.386	74.20	[9]

	1.917	2.483	77.19	[1]
	1.787	2.347	76.13	[5]
	1.937	2.486	77.92	[6]
	1.661	2.151	76.36	[10]
	1.882	2.437	77.23	[11]
	1.499	2.178	68.83	[10]
	1.793	2.403	74.62	[6]
	1.720	2.267	75.88	[12]
	1.940	2.537	76.48	[13]
	1.750	2.306	75.91	[12]
	1.970	2.5081	78.55	[14]

	1.529	2.022	75.63	[15]
	1.920	2.492	77.04	[16]
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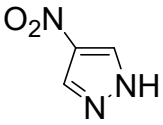
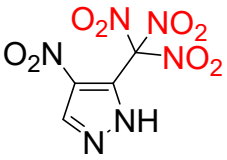
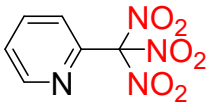
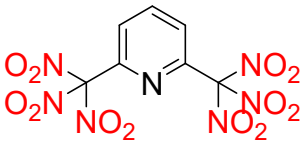
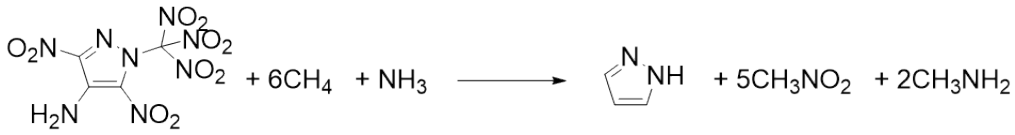
	1.640	-	-	[18]
	1.499	-	-	[10]
	1.750	-	-	[18]
	0.978	-	-	[19]
	1.692	-	-	[20]
	1.832	-	-	[20]

7. Heat of formation

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (H_{corr}), and other thermal factors. The heats of formation of other compounds in Scheme S2 were obtained from the NIST WebBook. The solid state heats of formation were calculated with Trouton's rule according to the following equation (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).

$$\Delta H_{sub}=188/Jmol^{-1}K^{-1}\bullet T$$



Scheme S1. Isodesmic reactions for calculating heats of formation for **DNTP**, respectively.

Table S4. Calculated Total Energy (E_0), Zero Point Energy (ZPE), values of Thermal Correction (H_{corr}) and gas phase heat of formation of the compounds.

Compound	ZPE/a.u.	H_{corr}/a.u.	E_0/a.u.	ΔHf(gas) (kJ mol^{-1})
TN-116	0.125906	0.145892	-1340.512307	216.0926565
CH_4	0.044793	0.048605	-40.3796224	-74.6
NH_3	0.034372	0.03819	-56.4154644	-45.9
Pyrazole	0.064026	0.068877	-408.7261129	177.4
CH_3NH_2	0.064026	0.068401	-95.5938452	-22.9
CH_3NO_2	0.049856	0.055129	-244.4784875	-74.3

Table S5. Data of gas phase heat of formation and heat of sublimation for TN-116

Compound	ΔHf(gas) (kJ mol^{-1})	ΔH_{sub} (kJ mol^{-1})	ΔHf(solid) (kJ mol^{-1})
TN-116	216.0926565	72.5962	143.4964565

8. Noncovalent interaction

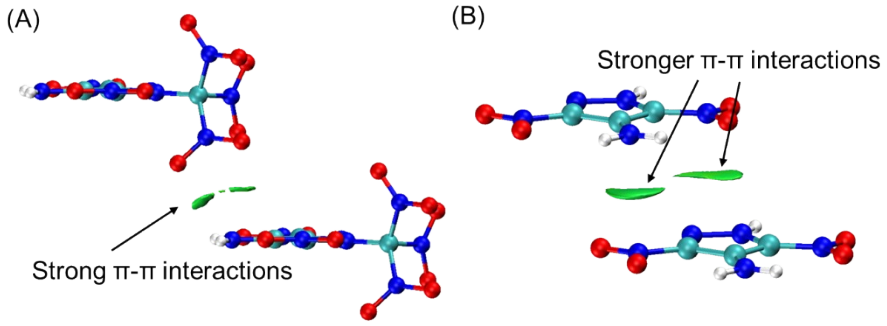


Figure S5. Noncovalent interaction of LLM-116 and TN-116.

9. Thermal stability

Differential scanning calorimetry (DSC/TG) showed that the decomposition temperature of **TN-116** is 112 °C.

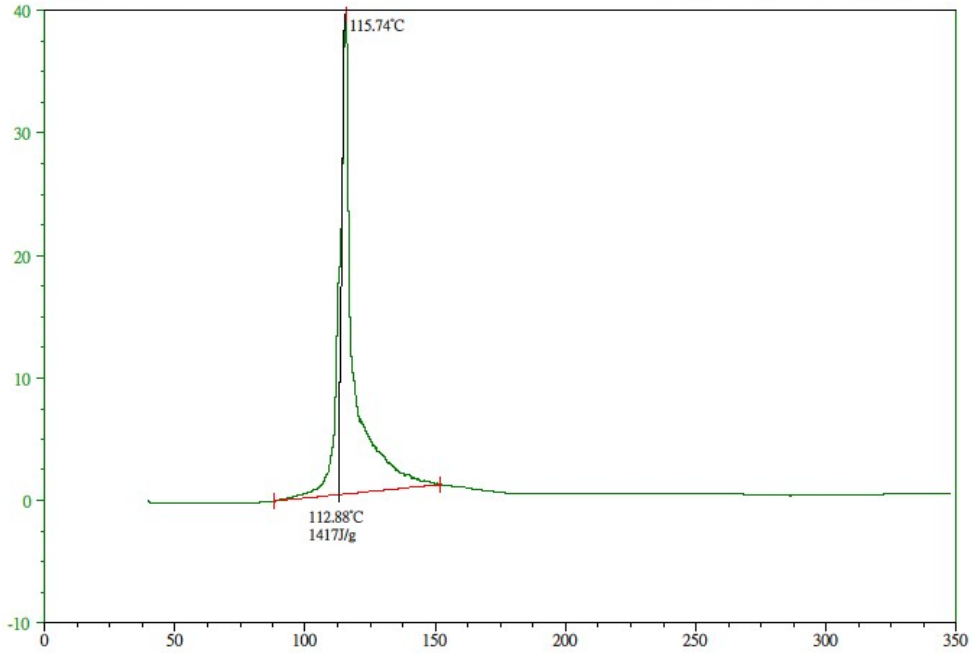


Figure S6. DSC plot for TN-116.

REFERENCE

1. N. Ding, Q. Sun, C. Zhao, W. Zhang, S. Li and S, Pang, *Mater. Chem. Front.* 2022, **6**, 2670.

2. P. Yin, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2016, **55**, 14409.

3. G. Herve, C. Roussel and H. Graindorge, *Angew. Chem., Int. Ed.*, 2010, **49**, 3177.

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