Electronic Supplementary Information

3,5-Dinitro-1-(3,3,3-trifluoropropyl)-1*H*-pyrazol-4-amine as insensitive and thermostable energetic melt-castable material

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Table of contents

1. Experimental Section

Caution! Although we have encountered no difficulties in preparing these nitrogen-rich compounds in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided!

General. All reagents (analytical grade) were purchased from Macklin or Aladdin and were used as supplied, 3,5-dinitro-1*H*-pyrazol-4-amine (**1**) was synthesized according to the reported literature.[1] ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz nuclear magnetic resonance spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si or deuterated solvents. Melting and decomposition points were recorded on a differential scanning calorimeter (DSC, TA Discovery 25) at the scan rates of 5~20 °C·min^{-1}. Impact and friction sensitivity measurements were made using standard BAM fall hammer and BAM friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer.

Synthesis of TFDNPA: The 3,5-dinitro-1*H*-pyrazol-4-amine (1.00 g, 5.8mmol) was dissolved in N,N-Dimethylformamide and a aqueous solution (2mL) of potassium hydroxide (0.65 g, 11.6 mmol) was slowly

added to give the homogeneous solution. Then, the 1,1,1-trifluoro-2-iodoethane (1.50 g, 7.1 mmol) was added and the solution was heated to 90 ℃ for 24 hours. The solution was cooled down and filtered out, a pale yellow solid was obtained after drying (isolated yield: 94.3%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.43 (s), 4.93 (t), 2.80-2.81 (m). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.89, 131.66, 129.98, 126.03, 77.37, 77.16, 76.95, 48.50, 33.98. IR (KBr, cm^{-1}): 3498.87, 3387.00, 1656.85, 1481.33, 1303.87, 1136.07, 1033.84, 825.53, 773.46, 663.51, 553.57. ESI-HRMS: m/z calcd for $[TFDNPA]^-$: 268.0299, found: 268.0298. Elemental analysis calcd (%) for $C_6H_6F_3N_5O_4$ (269.14): C 26.78, H 2.25, N 26.02; found: C 27.08, H 2.53, N 25.65.

2. X-ray Crystallography

Table S1 Crystal data and structural refinement parameters of **TFDNPA**

Parameter	**TFDNPA**
CCDC number	2402298
Empirical formula	C6H6F3N5O4
Formula weight	269.16
Temperature/K	293
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	11.6467(3)
b/Å	5.65600(10)
c/Å	31.9545(12)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	2104.96(10)
Z	8
ρcalcg/cm^3	1.699
μ/mm-1	1.565
F(000)	1088
Crystal size/mm^3	0.02 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	11.076 to 155.006
Index ranges	-13 ≤ h ≤ 14, -7 ≤ k ≤ 5, -40 ≤ l ≤ 38
Reflections collected	8708
Independent reflections	3559 [Rint = 0.0507, Rsigma = 0.0680]
Data/restraints/parameters	3559/1/325
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R1 = 0.0664, wR2 = 0.1828
Final R indexes [all data]	R1 = 0.0785, wR2 = 0.1933
Largest diff. peak/hole / e Å^{-3}	0.35/-0.26
Flack parameter	0.5(3)

Table S2 Bond Length (Å) of **TFDNPA**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N001	N00D	1.321(7)	N00D	C00Q	1.346(9)
N001	C00U	1.460(10)	F00H	C4	1.303(14)
N001	C00W	1.380(9)	N00I	C00W	1.401(9)
O002	N00A	1.218(10)	C00K	C00N	1.397(9)
N003	N009	1.313(7)	N00L	C00O	1.345(10)
N003	C00K	1.372(9)	N00M	C00N	1.317(10)
N003	C00X	1.469(10)	C00N	C00P	1.409(9)
N005	O008	1.239(9)	C00O	C00Q	1.414(9)
N005	O00G	1.240(9)	C00O	C00W	1.390(9)
N005	C00K	1.397(8)	C00U	C00V	1.483(13)
O006	N00I	1.222(9)	C00V	C4	1.502(14)
O007	N00I	1.212(9)	C00X	C00Y	1.546(13)
N009	C00P	1.323(9)	C00Y	C0AA	1.445(19)
N00A	O00F	1.222(10)	C4	F0AA	1.306(18)
N00A	C00Q	1.409(9)	C4	F2	1.257(18)
O00B	N00C	1.227(10)	C0AA	F1	1.332(16)
N00C	O00J	1.228(11)	C0AA	F1AA	1.364(18)
N00C	C00P	1.422(8)	C0AA	F4	1.304(17)

Table S3 Bond Angles for **TFDNPA**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N00D	N001	C00U	118.3(5)	N00L	C00O	C00W	129.0(6)
N00D	N001	C00W	111.5(5)	C00W	C00O	C00Q	102.4(6)
C00W	N001	C00U	129.9(5)	N009	C00P	N00C	119.5(6)
N009	N003	C00K	110.4(5)	N009	C00P	C00N	113.9(5)

N009	N003	C00X	118.6(6)	C00N	C00P	N00C	126.6(6)
C00K	N003	C00X	130.7(5)	N00A	C00Q	C00O	126.9(6)
O008	N005	O00G	122.8(6)	N00D	C00Q	N00A	120.5(6)
O008	N005	C00K	120.2(6)	N00D	C00Q	C00O	112.6(5)
O00G	N005	C00K	116.9(7)	N001	C00U	C00V	114.9(6)
N003	N009	C00P	106.0(5)	C00U	C00V	C4	115.8(9)
O002	N00A	O00F	123.8(8)	N001	C00W	N00I	124.7(6)
O002	N00A	C00Q	117.0(7)	N001	C00W	C00O	108.0(6)
O00F	N00A	C00Q	119.0(7)	C00O	C00W	N00I	127.3(7)
O00B	N00C	O00J	124.6(7)	N003	C00X	C00Y	111.5(7)
O00B	N00C	C00P	119.3(7)	C0AA	C00Y	C00X	115.7(9)
O00J	N00C	C00P	116.1(7)	F00H	C4	C00V	114.6(9)
N001	N00D	C00Q	105.5(5)	F00H	C4	F0AA	103.7(13)
O006	N00I	C00W	119.8(6)	F0AA	C4	C00V	111.3(10)
O007	N00I	O006	124.3(6)	F2	C4	F00H	109.4(11)
O007	N00I	C00W	115.9(7)	F2	C4	C00V	112.1(13)
N003	C00K	N005	125.0(6)	F2	C4	F0AA	104.8(14)
N003	C00K	C00N	109.2(5)	F1	C0AA	C00Y	112.7(15)
C00N	C00K	N005	125.8(6)	F1	C0AA	F1AA	101.2(11)
C00K	C00N	C00P	100.5(6)	F1AA	C0AA	C00Y	113.9(10)
N00M	C00N	C00K	130.1(6)	F4	C0AA	C00Y	114.7(12)
N00M	C00N	C00P	129.5(6)	F4	C0AA	F1	104.5(10)
N00L	C00O	C00Q	128.6(6)	F4	C0AA	F1AA	108.7(17)

Table S4 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **TFDNPA**

Atom	x	y	z	U(eq)

H00A	4549.35	4999.13	7377.51	81
H00B	5323.01	2902.49	7385.39	81
H00G	7108.74	10012.69	2624.83	83
H00H	7870.69	7898.36	2614.01	83
H00C	2034.1	3755.62	5975.09	69
H00D	2757.3	1870.61	5732.19	69
H00E	3406.17	6601.51	5796.47	88
H00F	2723.61	5598.97	5414.28	88
H00I	5340.52	6859.04	4275.26	80
H00J	4590.68	8714.9	4033.27	80
H00K	6074.31	11618.23	4182.96	96
H00L	5351.34	10837.42	4571.52	96

3. Calculation Methods

3.1 Computational methods for heats of formation

The enthalpy (*H*) for compound at standard condition (298K, 1atm) were directly calculated by G4(MP2)-6x method with Gaussian 09 (Revision D.01) suite of program. G4(MP2)-6x method is a composite procedure with a lower cost but performance approaching that of G4.[2] In this method, geometries were optimized with the BMK functional using the 6-31+G(2df,p) basis set. Zero-point vibrational energies (ZPVEs) and thermal corrections to enthalpy (ΔH) at 298K, derived from scaled BMK/6-31+G(2df,p) frequencies, were incorporated into the total energies. Single-point energies were obtained at the HF/GFHFB3, HF/GFHFB4,

MP2(FrzG4)/GTMP2LargeXP, and CCSD(T,FrzG4)/GTBas1 levels with composite procedures.

After acquiring the enthalpy of compounds, their gas phase enthalpy of formation can be calculated by atomization method as following equation (1):

$$\Delta H_f(g) = H\left(C_l H_m O_n N_i(g)\right) - lH(C(g)) - \frac{m}{2}H\left(H_2(g)\right) - \frac{n}{2}H\left(O_2(g)\right) - \frac{i}{2}H\left(N_2(g)\right) + lH_{vap}(graphite) \quad (1)$$

For neutral compounds with calculated gas state heat of formation, the solid state heat of formation was calculated by the following equation (2). The heat of sublimation ΔH_{SUB} was estimated by the following equation (3). T is the melting point or decomposition point temperature in Kelvin.

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{SUB} \quad (2)$$

$$\Delta H_{SUB}(g) = 0.188 * T \quad (3)$$

3.2 Computational methods for Ab initio molecular dynamics (AIMD)

The computational simulations were carried out using the CP2K (version 9.1) program package.[3] The initial structures of the systems were constructed using Materials Studio (version 8.0). The structures were then optimized using CP2K to ensure that they were in their minimum energy configurations before further ab initio molecular dynamics (Sees Figure

S1). The Perdew-Burke-Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA) was employed to describe the exchange-correlation interactions.[4] A double-zeta valence plus polarization (DZVP-MOLOPT-SR-GTH) basis set was used for all atoms. Goedecker-Teter-Hutter (GTH) pseudopotentials were employed to represent the core electrons. A plane-wave cutoff energy of 400 Ry was chosen for the auxiliary plane wave basis set. The relative cutoff for the Gaussian basis set was set to 55 Ry. Geometry optimizations were performed until the forces on all atoms were less than $4.5E^{-4}$ hartree/bohr and the maximum displacement allowed for each optimization step was set to $3E^{-3}$ bohr. For ab initio molecular dynamics, NVT (constant number of particles, volume, and temperature) ensemble was used. The CSVR thermostat was applied to maintain the temperature at 4000 K with a time constant of 200 fs. A time step of 0.5 fs was used for integrating the equations of motion. Each simulation was run for a total duration of 5 ps (10000 steps in total).

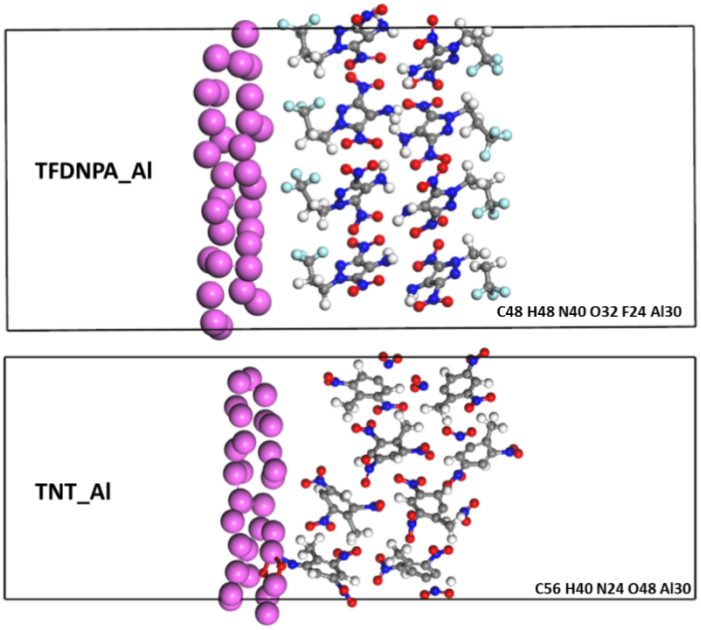

Figure S1. Structures after geometry optimization

4. Reference

[1] Y. Zhang, Y. Huang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem.*, 2011, **21**, 6891.

[2] B. Chan, J. Deng and L. Radom, *J. Chem. Theory Comput.*, 2011, **7**, 112-120.

[3] T. D. Kühn, M. Iannuzz, M. D. Be, V. V. Rybkin, P. Seewald, F. Stein, T. Lain, R. Z. Khaliulli, O. Schüt, F. Schiffman, D. Golze, J. Wilhel, S. Chulko, M. H. Bani-Hashemian, V. Webe, U. Borštni, M. Taillefumie, A. S. Jakobovits, A. Lazzaro, H. Pabs, T. Mülle, R. Schad, M. Guido, S. Andermat, N. Holmber, G. K. Schente, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacch, A. Glö, M. Las, I. Bethun, C. J. Mund, C. Pless,

M. Watkin, J. V. Vondel, M. Krac, J. Hutter, *J Chem Phys*, 2020, **152**, 19.

[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys Rev Lett*, 1996, **77**, 3865.

5. NMR, Mass and IR Spectra of TFDNPA

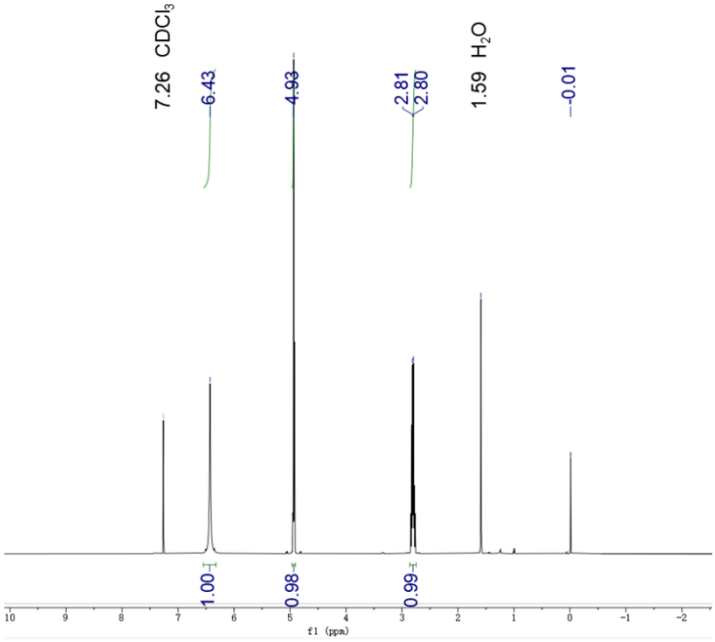

Figure S2 ^{1}H NMR spectrum of **TFDNPA**

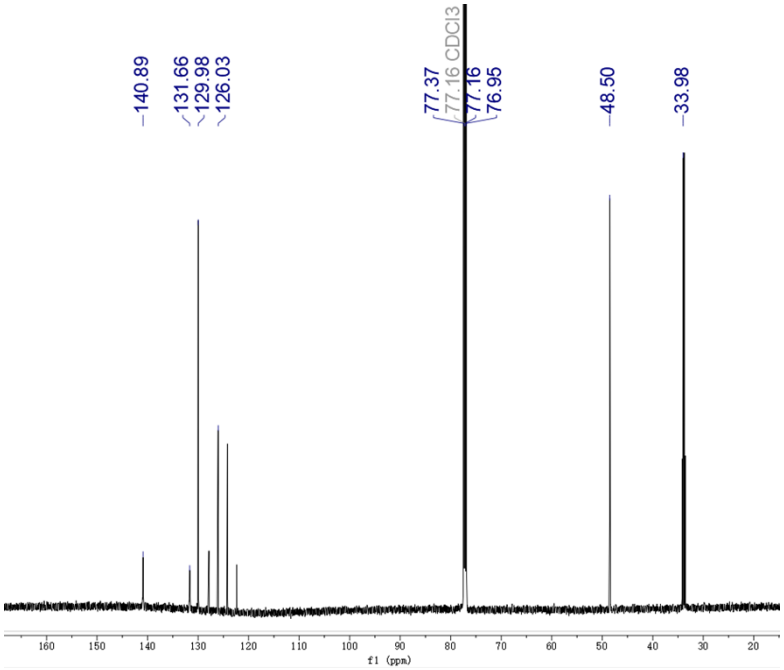

Figure S3 ^{13}C NMR spectrum of **TFDNPA**

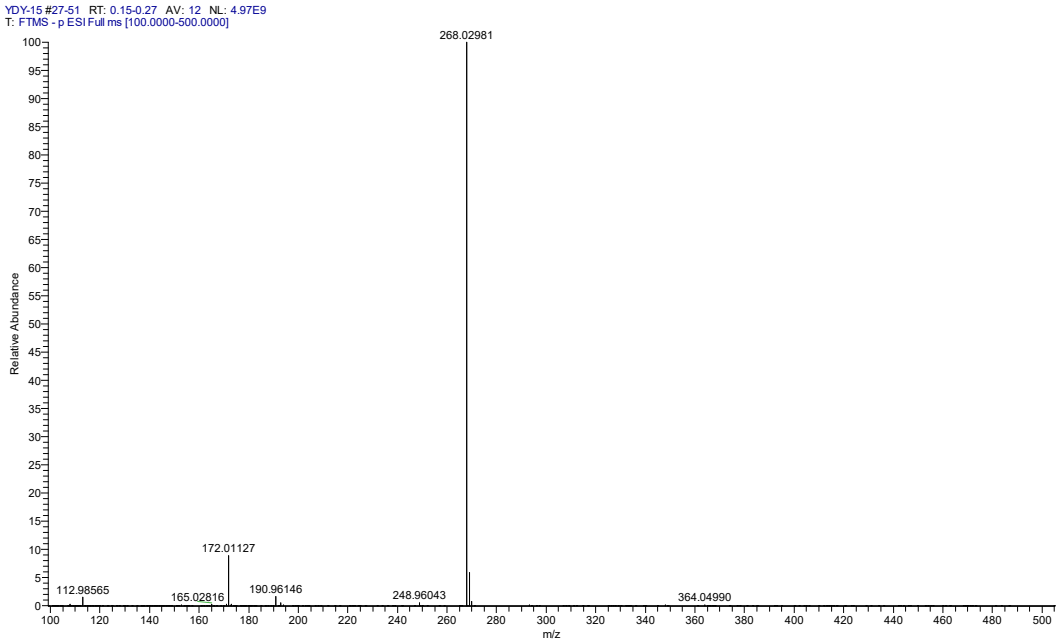

Figure S4 HRMS-Neg spectrum of **TFDNPA**

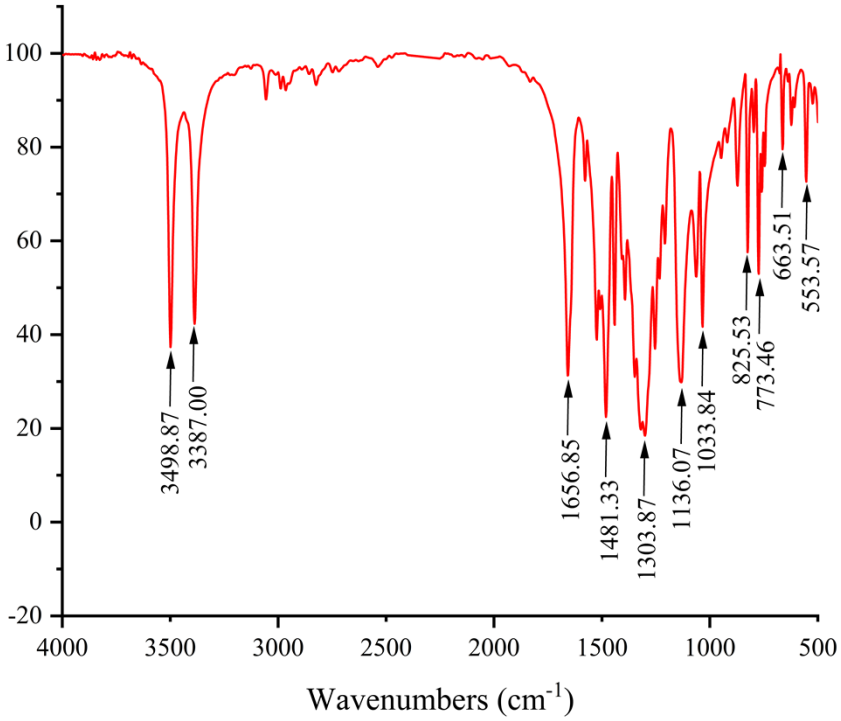

Figure S5 IR curve of compound **TFDNPA**