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Supporting Information (SI)

Customization of molecular structure to modulate the crystal packing style of energetic materials

Qi Huang[*, †], *Zhicheng Guo*[§], *Longyu Liao*[‡], *Shilong Hao*[‡], *Fude Nie*[‡] *and Hongzhen Li*[*, ‡]

†State Key Laboratory of Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, China

§Sichuan Co-Innovation Center for New Energetic Materials, Southwest University of Science and Technology, Mianyang, Sichuan, 621010, China

‡Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, China

Section S1. Crystal data and structure refinement for A1, A2 and A3

Table S1. Crystallographic data of A1, A2 and A3.

Compound	A1	A2	A3
CCDC number	1554917	1554918	1554915
Empirical formula	$C_6H_6N_8O_8$	$C_8H_8N_{10}O_{14}$	$C_6H_6N_8O_9$
Formula weight	318.19	468.24	334.19
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Tetragonal	Monoclinic
Space group	*Pbca*	*P* 4_32_12	*P*$2_1/c$
Unit cell dimensions	a = 11.0661(15) Å b = 13.9316(19) Å c = 15.839(2) Å α = 90° β = 90° γ = 90°	a = 7.0912(5) Å b = 7.0912(5) Å c = 34.097(4) Å α = 90° β = 90° γ = 90°	a = 7.6484(13) Å b = 16.154(3) Å c = 11.156(2) Å α = 90° β = 106.283(4)° γ = 90°
Volume	2441.8(6) $Å^3$	1714.6(3) $Å^3$	1323.0(4) $Å^3$
Z	8	4	4
Density	1.731 Mg/m^3	1.814 Mg/m^3	1.678 Mg/m^3
Absorption coefficient	0.160 mm^{-1}	0.175 mm^{-1}	0.158 mm^{-1}
F(000)	1296	952	680
Crystal size	0.22 x 0.17 x 0.12 mm^3	0.20 x 0.17 x 0.11 mm^3	0.22 x 0.18 x 0.10 mm^3
Theta range for data collection	2.572 to 26.000°	2.389 to 25.497°	2.282 to 25.494°
Index ranges	-13<=h<=13 -17<=k<=17 -19<=l<=15	-8<=h<=6 -8<=k<=8 -41<=l<=38	-9<=h<=9 -19<=k<=19 -13<=l<=10
Reflections collected	13736	9946	7408
Independent reflections	2401 [$R_{(int)}$ = 0.0475]	1603 [$R_{(int)}$ = 0.0375]	2459 [$R_{(int)}$ = 0.0414]
Completeness to theta = 25.242°	100.00%	100.00%	99.90%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6254	0.7456 and 0.6732	0.7456 and 0.6433
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data/ restraints / parameters	2401 / 0 / 202	1603 / 0 / 146	2459 / 0 / 210
Goodness-of-fit on F^2	1.089	1.083	1.068
Final R indices [I>2sigma(I)]	R_1 = 0.0464 wR_2 = 0.1049	R_1 = 0.0390 wR_2 = 0.0956	R_1 = 0.0499 wR_2 = 0.1207
R indices (all data)	R_1 = 0.0598 wR_2 = 0.1110	R_1 = 0.0427 wR_2 = 0.0978	R_1 = 0.0651 wR_2 = 0.1307
Largest diff. peak and hole	0.229 and -0.181 $e.Å^{-3}$	0.177 and -0.153 $e.Å^{-3}$	0.260 and -0.151 $e.Å^{-3}$

Section S2. 2D-fingerprint and the associated Hirshfeld surfaces of A1, A2 and A3

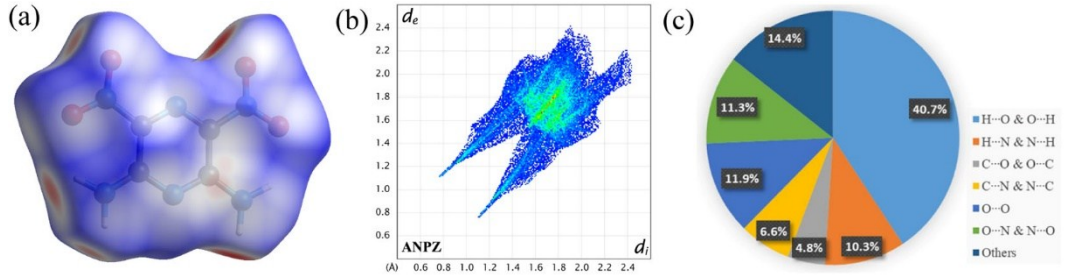

Figure S1. (a) The Hirshfeld surface; (b) The 2D-fingerprint plots; (c) The individual atomic percentage contribution to the Hirshfeld surface of ANPZ in crystal stacking.

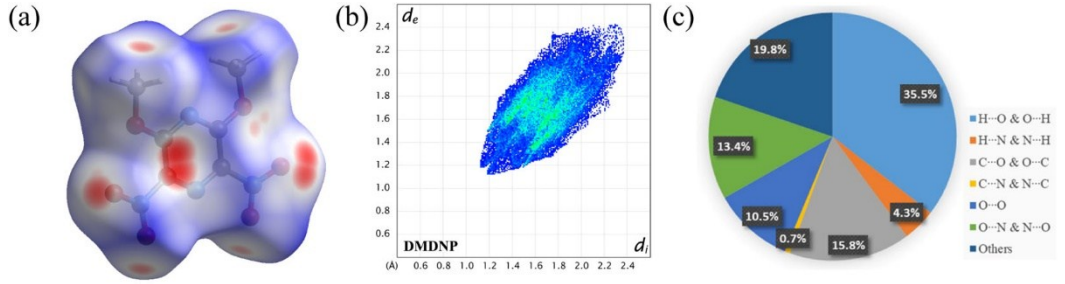

Figure S2. (a) The Hirshfeld surface; (b) The 2D-fingerprint plots; (c) The individual atomic percentage contribution to the Hirshfeld surface of DMDNP in crystal stacking.

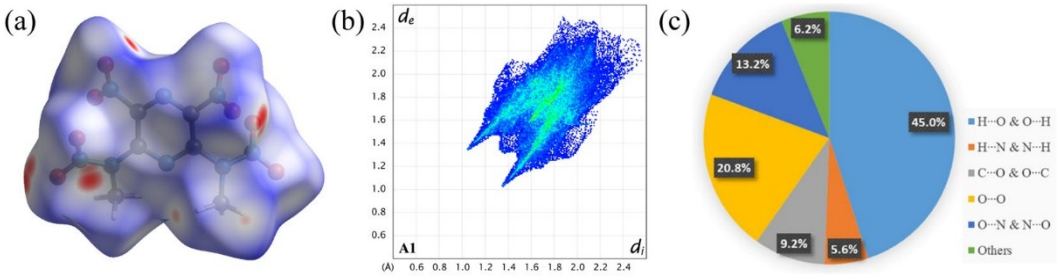

Figure S3. (a) The Hirshfeld surface; (b) The 2D-fingerprint plots; (c) The individual atomic percentage contribution to the Hirshfeld surface of A1 in crystal stacking.

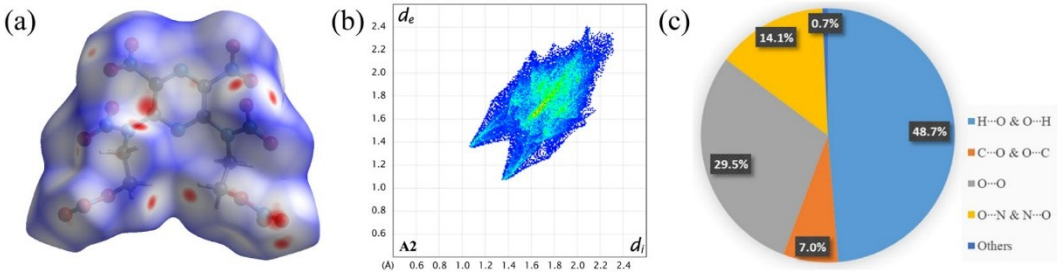

Figure S4. (a) The Hirshfeld surface; (b) The 2D-fingerprint plots; (c) The individual atomic percentage contribution to the Hirshfeld surface of A2 in crystal stacking.

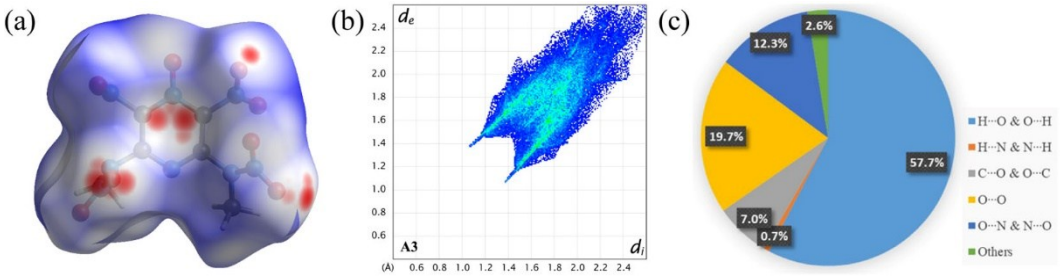

Figure S5. (a) The Hirshfeld surface; (b) The 2D-fingerprint plots; (c) The individual atomic percentage contribution to the Hirshfeld surface of A3 in crystal stacking.

Section S3. Metadata of heat of formation[1, 2]

Table S2. Total energies and heat of formation of A1, A2 and A3.

Molecule	E_0 (kJ/mol)	ZPE(kj/mol)	E_e (kJ/mol) [a]	H_{298} (kJ/mol) [b]	ΔH_f (298 K) (kJ/mol) [c]
A1	-3334605.646	441.1706751	-3335046.817	-3334550.679	271.0842917
A2	-5007796.486	621.2616103	-5008417.747	-5007718.411	90.60374911
A3	-3531669.262	447.2355806	-3532116.497	-3531610.865	349.1877387

[a]The E_e energies (in hartrees) of the atoms are H (-0.503351), C (-37.788532), N (-54.524842), O (-74.993634).

[b]H_{298} is the calculated enthalpy of the molecule at 298 K.

[c]Calculation by Eq. (1) from Reference 2.

Eq. (1):

$$\Delta_f H(A_xB_yC_z,298K) = \Delta_f H(A_xB_yC_z,0K) + [H(A_xB_yC_z,298K) - H(A_xB_yC_z,0K)] - x[H(A,298K) - H(A,0K)] - y[H(B,298K) - H(B,0K)] - z[H(C,298K) - H(C,0K)]$$

Reference

1. L. A. Curtiss, K. Raghavachari, P. W. Deutsch and J. A. Pople, *The Journal of Chemical Physics*, 1991, **95**, 2433-2444.
2. L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *The Journal of Chemical Physics*, 1997, **106**, 1063-1079.