

Electronic Supplementary Information

Furazan-based Bisnitramide-bridging Energetic Materials

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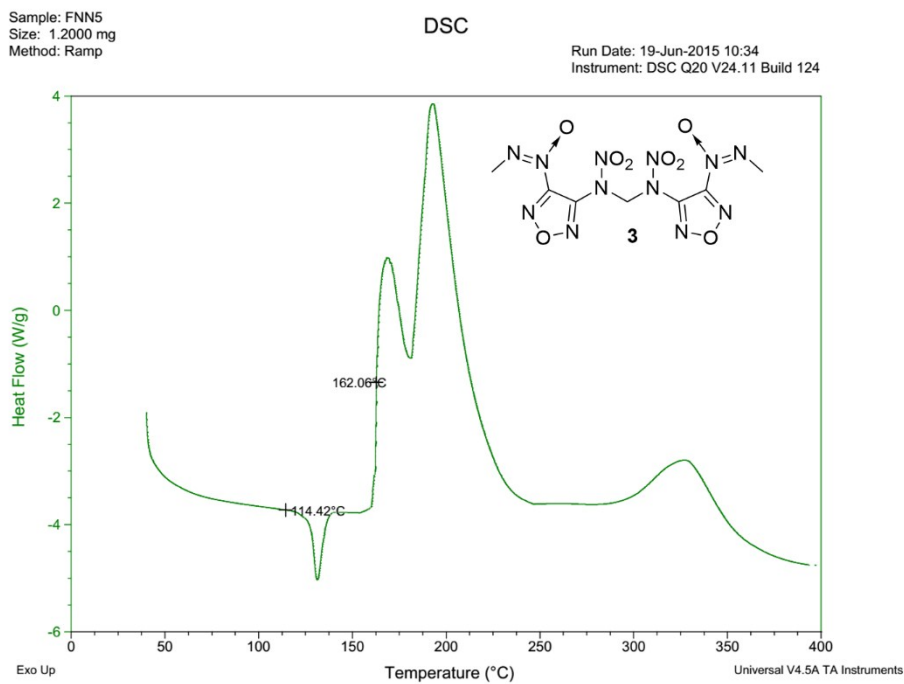


Figure S1. DSC plot of compound 3.

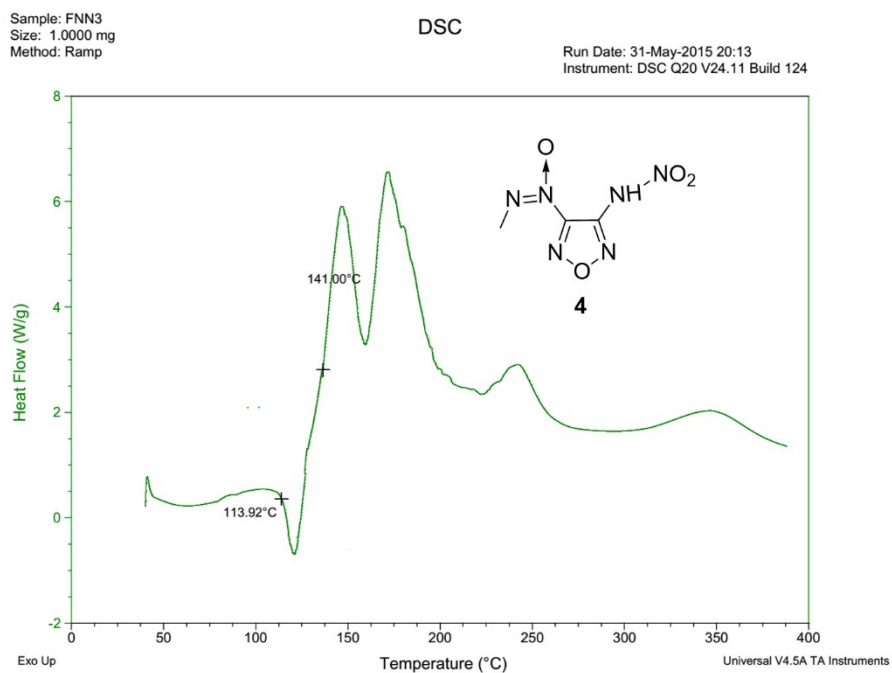


Figure S2. DSC plot of compound 4.

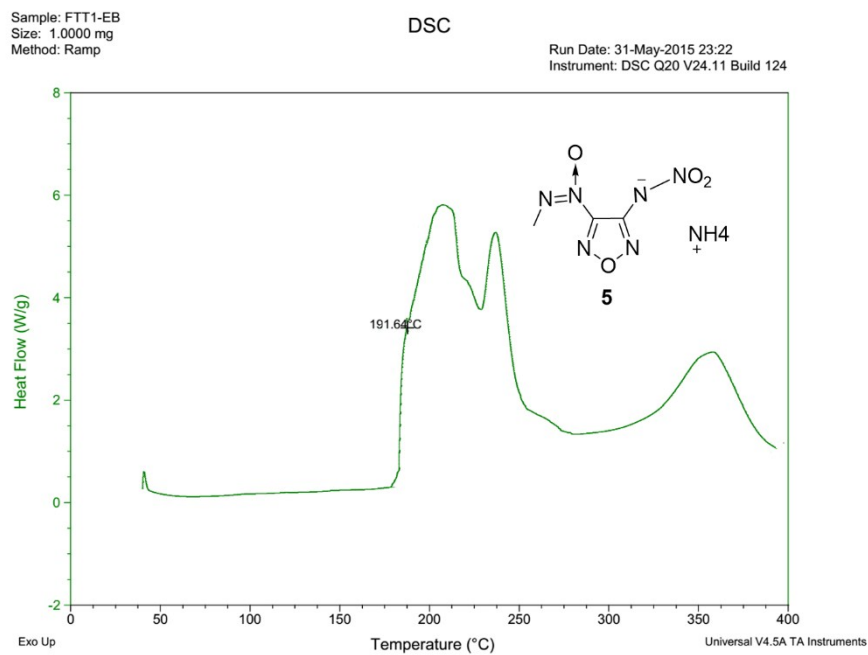


Figure S3. DSC plot of compound **5**.

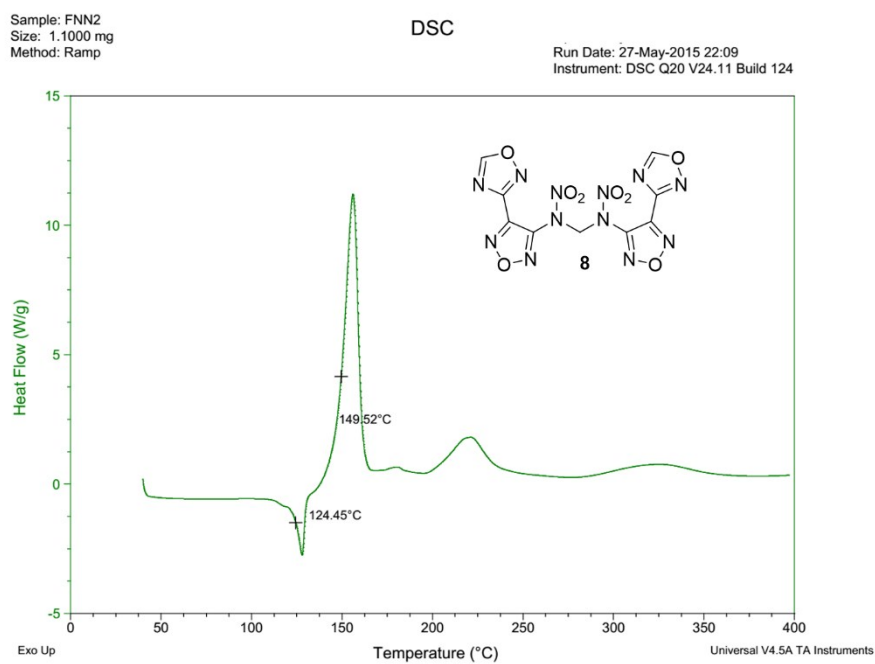


Figure S4. DSC plot of compound **8**.

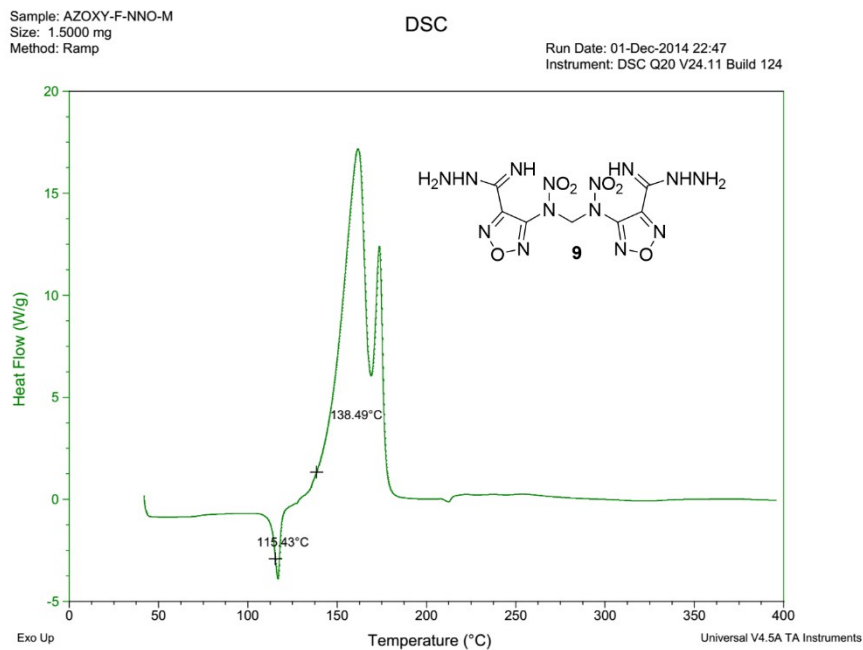


Figure S5. DSC plot of compound **9**.

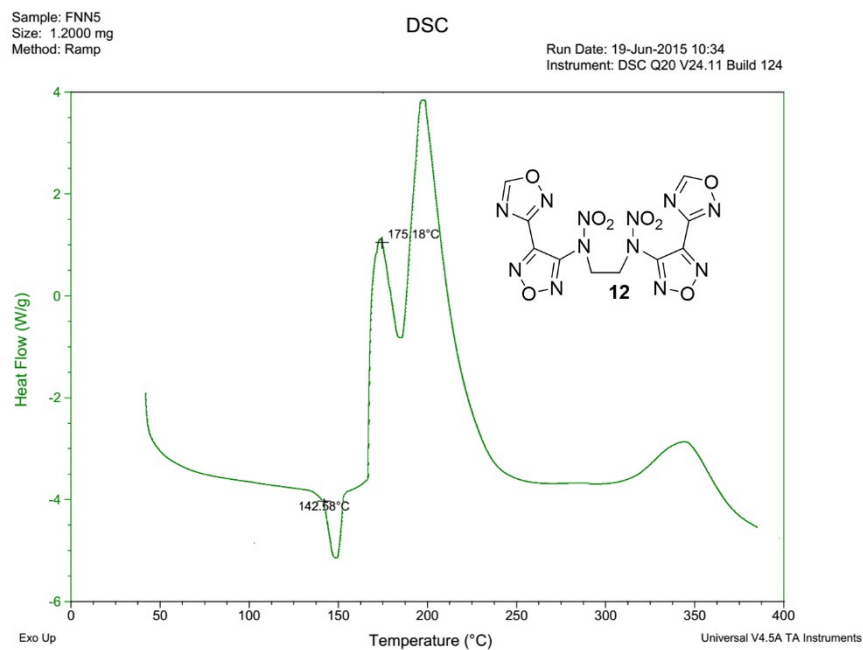


Figure S6. DSC plot of compound **12**.

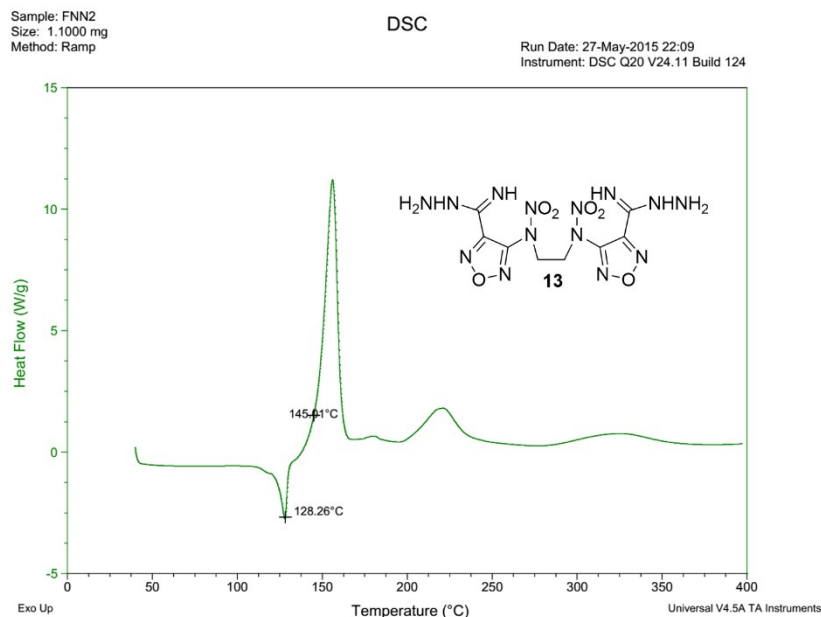


Figure S7. DSC plot of compound **13**.

X-ray Crystallography. A colorless prism of dimensions 0.187 x 0.091 x 0.087 mm³ for **3** and a colorless plate crystal of dimensions 0.217 x 0.108 x 0.010 mm³ for **12** was separately mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil for the X-ray crystallographic analysis. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK α radiation ($\lambda = 0.71073$). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K for **3** during data collection.

Table 1. Selected crystal parameters of **3** and **12**.

Empirical formula	C ₇ H ₈ N ₁₂ O ₈ (3)	C ₁₀ H ₆ N ₁₂ O ₈ (12)
Formula weight	388.21	422.27
Temperature/K	150	296
Crystal system	orthorhombic	monoclinic
Space group	Pna2 ₁	P2 ₁ /n
a/Å	14.3822(16)	9.2994(8)
b/Å	9.5669(11)	8.8927(8)
c/Å	11.2707(13)	9.8472(9)
α /°	90	90
β /°	90	100.317(3)
γ /°	90	90
Volume/Å ³	1550.8(3)	801.17(1)
Z	4	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.663	1.750
μ/mm^{-1}	0.150	0.153
F(000)	792	428
CCDC number	1474579	1504349

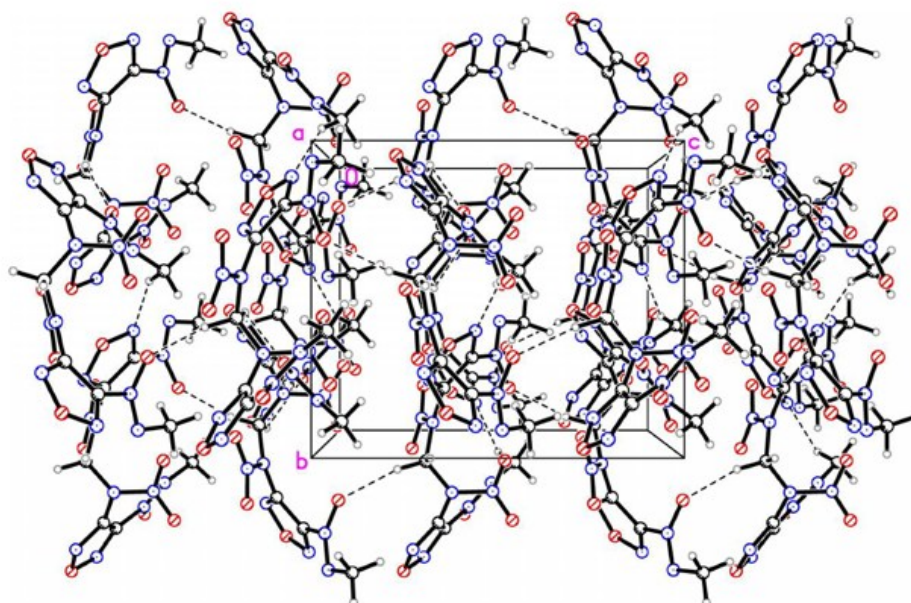


Figure S8. Unit cell view for **3** along *a* axis, hydrogen bonds are marked as dotted lines.

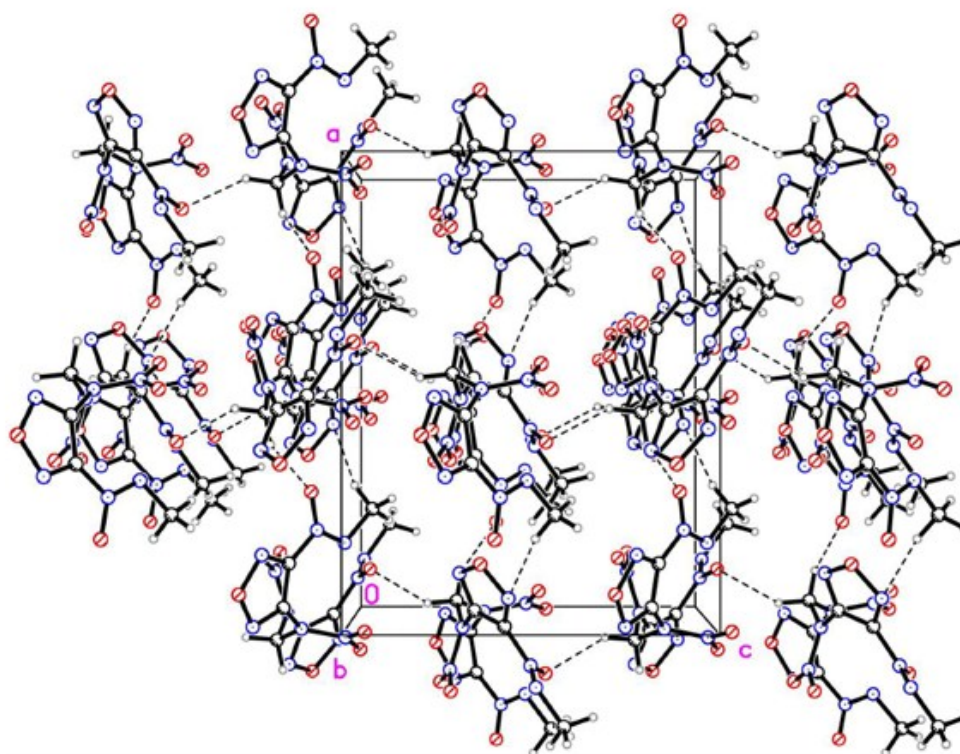


Figure S9. Unit cell view for **3** along *b* axis, hydrogen bonds are marked as dotted lines.

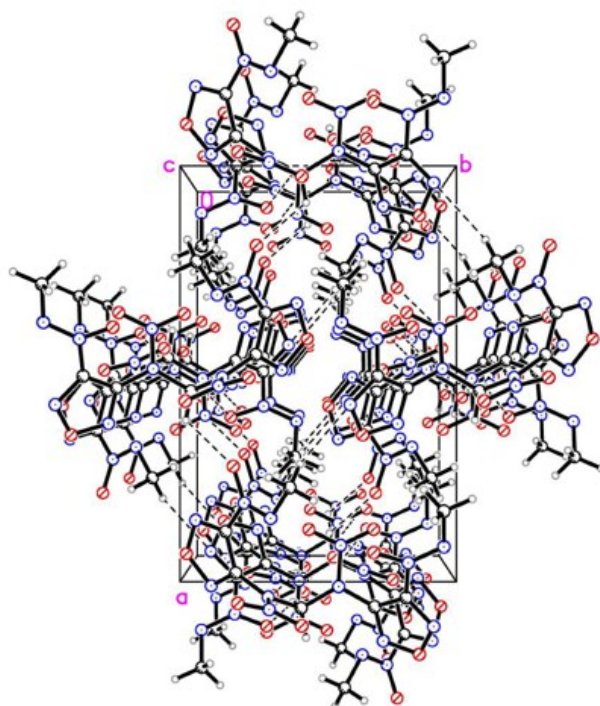


Figure S10. Unit cell view for **3** along *c* axis, hydrogen bonds are marked as dotted lines.

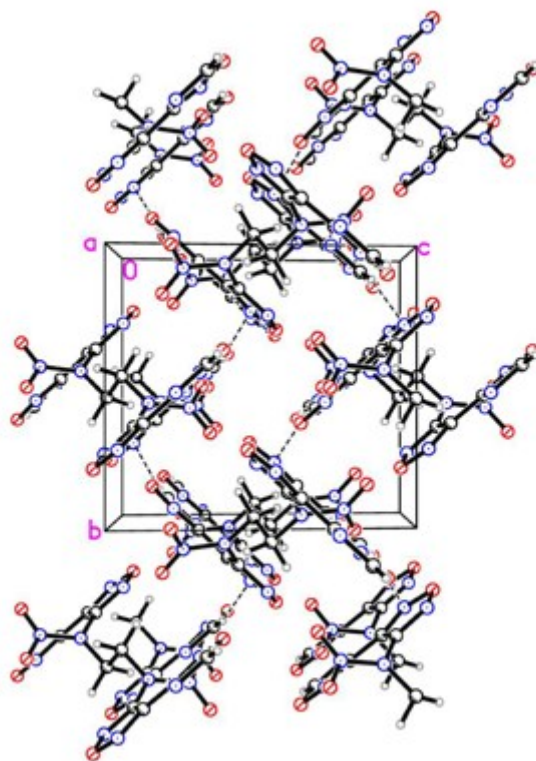


Figure S11. Unit cell view for **12** along *a* axis, hydrogen bonds are marked as dotted lines.

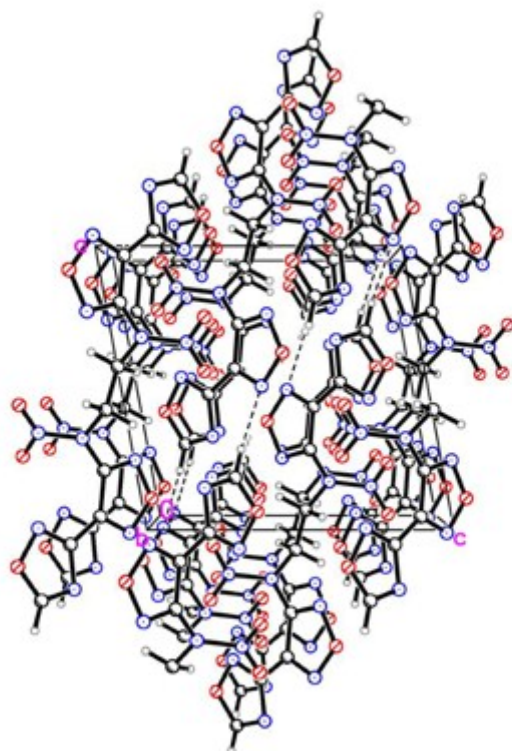


Figure S12. Unit cell view for **12** along *b* axis, hydrogen bonds are marked as dotted lines.

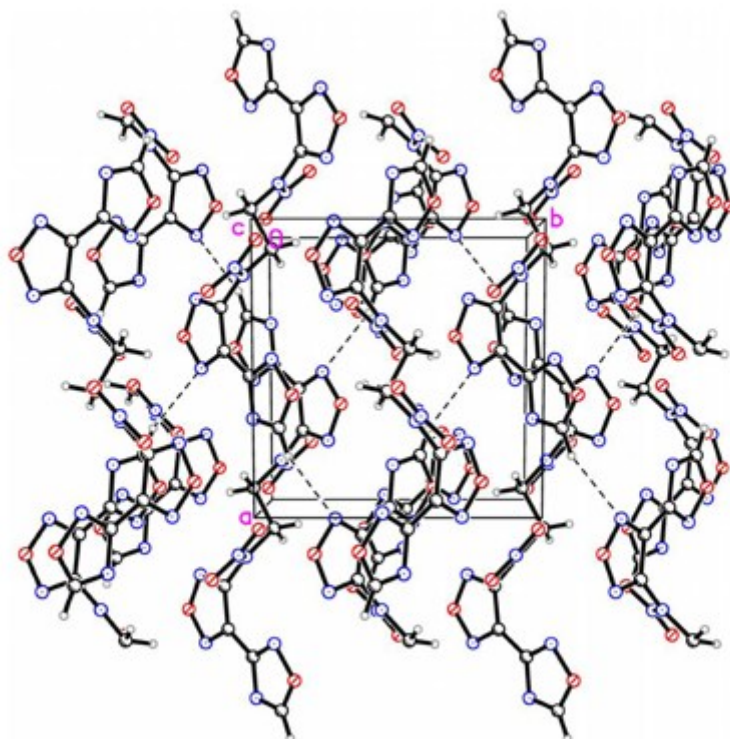
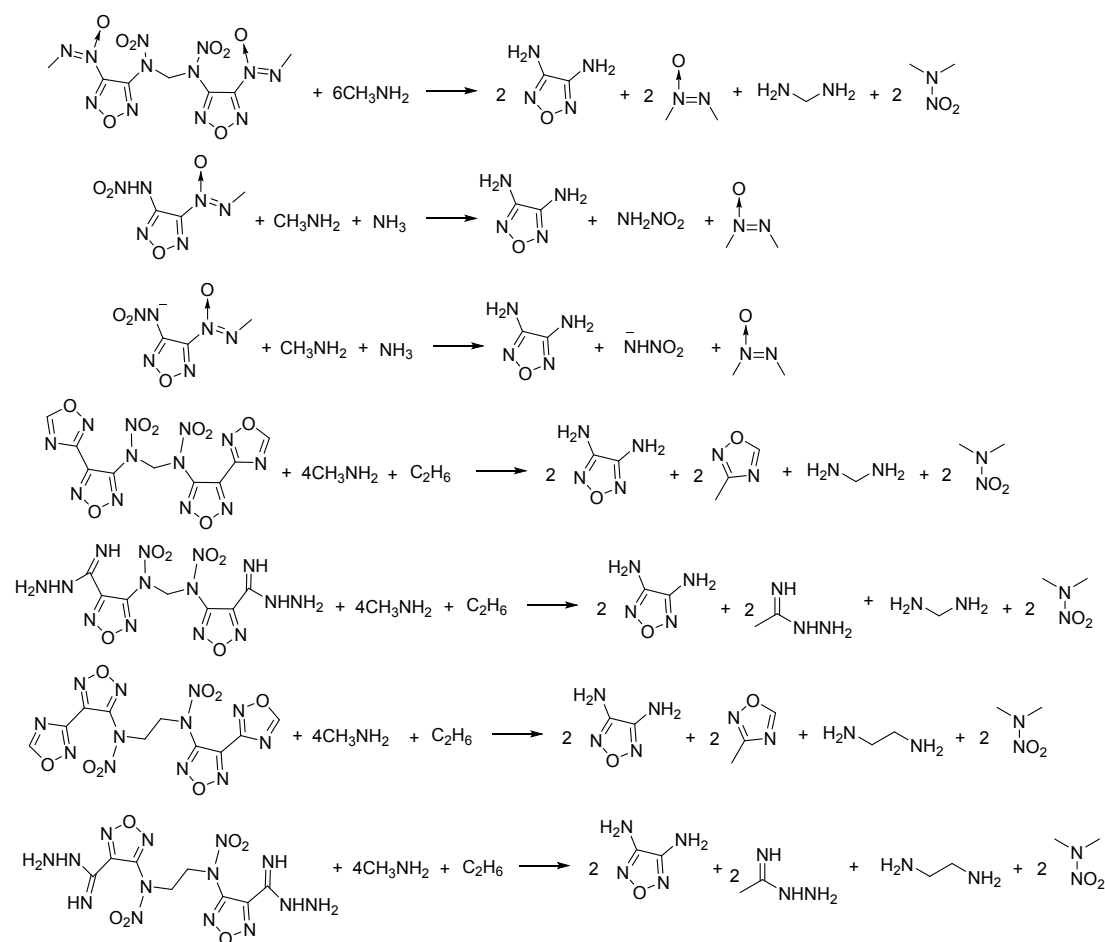


Figure S13. Unit cell view for **12** along *c* axis, hydrogen bonds are marked as dotted lines.

Theoretical calculations

As mentioned in the manuscript, the gas phase heats of formation for all newly prepared neutral compounds and the 4-(methyl-azoxy)-3-nitraminofurazanate anion were obtained using isodesmic reactions (Scheme S1). The geometric optimization and frequency analysis of the structures were calculated using B3LYP function with 6-31+G** basis set.¹ All of the optimized structures were checked to be true local energy minima on the potential energy surface without imaginary frequencies. Single-point energies based on the optimized structures were calculated at the MP2/6-311++G** set.² Atomization energies for frame molecules or ions were obtained by employing the G2 *ab initio* method.³ The conversion of gas phase enthalpies to solid phase values for neutral compounds was done by subtracting the empirical heat of sublimation obtained based on Trouton's rule. For the ionic derivative **5**, the solid phase heat of formation was calculated on the basis of a Born-Haber energy cycle. The heats of formation of other compounds in Scheme S1 were determined from the NIST WebBook.⁴



Scheme S1. Isodesmic reactions for calculating heats of formation for **3**, **5** and the 4-(methyl-azoxy)-3-nitraminofurazanate anion.

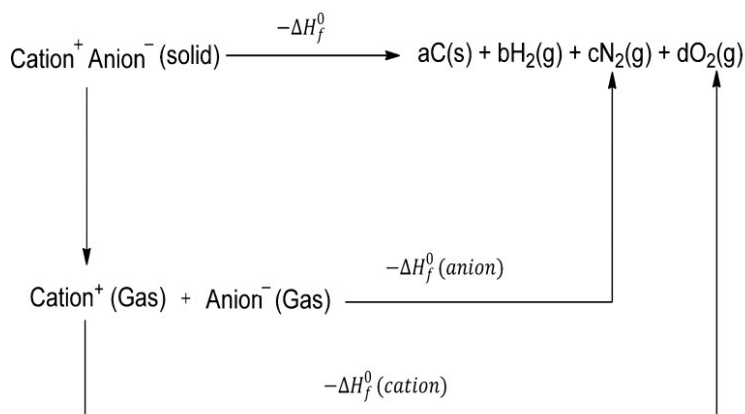
Table S2. Enthalpies of the gas-phase species (NIST value and G2 method).^{3,4}

M	ΔH_f° (kJ mol ⁻¹)
Methylamine	-23.5
Ammonia	-45.9
3,4-Diamino-furazan	198.9
Nitramide	17.2
1,2-Dimethyldiazene 1-oxide	62.3
Nitramide anion	-84.0
Methanediamine	-4.5
N,N-Dimethylnitramide	-19.6
Ammonium ion	626.4
Ethane	-84.0
3-Methyl-1,2,4-oxadiazole	36.9
Acetimidohydrazide	119.7
Ethane-1,2-diamine	-13.6

Based on the literature, the heat of sublimation is estimated with Trouton's rule.⁵ The solid phase heats of formation of neutral compounds were calculated with equation 1, in which T_d represents the decomposition temperature.

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{\text{sub}} = \Delta H_f(g) - 188[\text{J mol}^{-1} \text{K}^{-1}] \times T_d \quad (1)$$

For energetic salt **5**, the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S2).⁶ The number is simplified by equation 2:

**Scheme S2.** Born–Haber Cycle for the formation of energetic salt **4**.

$$\Delta H_f^\circ(\text{salt}, 298 \text{ K}) = \Delta H_f^\circ(\text{cation}, 298\text{K}) + \Delta H_f^\circ(\text{anion}, 298\text{K}) - \Delta H_L \quad (2)$$

in which ΔH_L can be predicted by using the formula suggested by Jenkins, et al.⁶(equation 3):

$$\Delta H_L = U_{\text{pot}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (3)$$

In this equation, n_M and n_X depend on the nature of the ions Mp^+ and Xq^- , respectively. The equation for lattice potential energy U_{pot} (equation 4) has the form:

$$U_{\text{POT}} [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (4)$$

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for γ ($\text{kJmol}^{-1}\text{cm}$) and δ (kJmol^{-1}) are assigned literature values.⁶ By using the measured room temperature densities, the $\Delta_f H_{\text{Lat}}$ of **5** was calculated to be $505.7 \text{ kJ mol}^{-1}$ and the solid phase heat of formation of **5** was obtained as $346.0 \text{ kJ mol}^{-1}$.

References

1. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
2. Head-Gordon, M; Pople, J. A. MP2 Energy Evaluation by Direct Methods, *Chem. Phys. Lett.* 1988, **153**, 503-506.
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5. a) Trouton, F. *Philos. Mag.* 1884, **18**, 54-57; b) Westwell, M. S.; Searle, M. S.; Wales, D. J.; Williams, D. H. *J. Am. Chem. Soc.* 1995, **117**, 5013-5015.
6. Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* 2002, **41**, 2364-2367.