Supplementary Information

Size-Matched Hydrogen Bonded Hydroxylammonium Frameworks for Regulation of Energetic Materials

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I. ORTEP Drawings of the Crystal Structures .......................... S2
II. NMR Spectra Data ................................................................. S19
III. DSC Plots ............................................................................. S25
IV. Computation and Properties.................................................. S28
V. Application expansion of size matching strategy...................... S39
VI. Supplementary References.................................................... S52
I. ORTEP Drawings of the Crystal Structure

1. Crystal data of compound NT

**Supplementary Fig. 1.** Asymmetric unit of js417c. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2102199

**Supplementary Tab.1.** Crystal data and structure refinement for NT.

| Property                          | Value          |
|-----------------------------------|----------------|
| Identification code               | js417c         |
| Empirical formula                 | C$_2$H$_3$N$_7$O$_4$ |
| Formula weight                    | 189.11         |
| Temperature/K                     | 173            |
| Space group                       | P21/n          |
| a/Å                               | 6.4149(3)      |
| b/Å                               | 10.3449(5)     |
| c/Å                               | 10.7002(5)     |
| α/°                               | 90             |
| β/°                               | 98.909(4)      |
| γ/°                               | 90             |
| Volume/Å$^3$                      | 701.51(6)      |
| Z                                 | 4              |
| ρcalcg/cm$^3$                     | 1.791          |
| μ/mm$^{-1}$                       | 1.487          |
| F(000)                            | 384.0          |
2. Crystal data of HHF-T

![Crystal Structure Diagram](image)

**Supplementary Fig. 2.** Asymmetric unit of twin4. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2102200

**Supplementary Tab. 2.** Crystal data and structure refinement for HHF-T.

| Property                  | Value                      |
|---------------------------|-----------------------------|
| Identification code       | twin4                       |
| Empirical formula         | C₂H₂N₇O₄, H₄NO              |
| Formula weight            | 222.15                      |
| Temperature/K             | 173                         |
| Space group               | P-1                         |
| a/Å                       | 7.640(2)                    |
| b/Å                       | 7.719(2)                    |
| c/Å                       | 8.094(2)                    |
| α/°                       | 78.312(3)                   |
| β/°                       | 65.723(4)                   |
| γ/°                       | 69.745(3)                   |
| Volume/Å³                 | 407.20(2)                   |
| Z                         | 2                           |
| ρ calcg/cm³               | 1.812                       |
| μ/mm⁻¹                    | 0.170                       |
| F(000)                    | 228.0                       |
3. Crystal data of compound NF

![Crystal structure of NF](image)

**Supplementary Fig. 3.** Asymmetric unit of yyy_tw. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2094882

**Supplementary Tab. 3.** Crystal data and structure refinement for NF.

| Property                  | Value                          |
|---------------------------|--------------------------------|
| Identification code       | yyy_tw                         |
| Empirical formula         | C$_2$H$_3$N$_5$O$_3$            |
| Formula weight            | 145.09                         |
| Temperature/K             | 296                            |
| Space group               | P21/c                          |
| a/Å                       | 8.483(12)                      |
| b/Å                       | 6.177(8)                       |
| c/Å                       | 11.249(13)                     |
| $\alpha$/°                | 90                             |
| $\beta$/°                 | 109.716(9)                     |
| $\gamma$/°                | 90                             |
| Volume/Å$^3$              | 555.0(12)                      |
| Z                         | 4                              |
| $\rho$ calc/g/cm$^3$      | 1.737                          |
| $\mu$/mm$^{-1}$           | 0.159                          |
| $F$(000)                  | 296.0                          |
4. Crystal data of compound HHF-F

Supplementary Fig. 4. Asymmetric unit of mo_210606(QL)_20210529_298K_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2094484

Supplementary Tab. 4. Crystal data and structure refinement for HHF-F.

| Identification code          | mo_210606(QL)_20210529_298K_0m |
|------------------------------|---------------------------------|
| Empirical formula            | C₂H₂N₅O₃, H₄NO                  |
| Formula weight               | 178.13                          |
| Temperature/K                | 298                             |
| Space group                  | P2₁/n                           |
| a/Å                          | 6.589(10)                       |
| b/Å                          | 12.545(18)                      |
| c/Å                          | 8.200(13)                       |
| α/°                          | 90                              |
| β/°                          | 106.280(1)                      |
| γ/°                          | 90                              |
| Volume/Å³                    | 650.6(17)                       |
| Z                            | 4                               |
| ρcalc g/cm³                  | 1.819                           |
| μ/mm⁻¹                       | 0.169                           |
| F(000)                       | 368.0                           |
5. Crystal data of compound HHF-N14

Supplementary Fig. 5. Asymmetric unit of 1-a. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201536

Supplementary Tab. 5. Crystal data and structure refinement for HHF-N14.

| Identification code | 1-a          |
|---------------------|--------------|
| Empirical formula   | C₃H₇N₇O₄    |
| Formula weight      | 205.16       |
| Temperature/K       | 296          |
| Space group         | P21/n        |
| a/Å                 | 5.1960(6)    |
| b/Å                 | 4.8598(5)    |
| c/Å                 | 29.794(3)    |
| α/°                 | 90           |
| β/°                 | 93.102(3)    |
| γ/°                 | 90           |
| Volume/Å³           | 751.24(14)   |
| Z                   | 4            |
| ρ calc/g/cm³        | 1.814        |
| μ/mm⁻¹              | 0.163        |
| F(000)              | 424.0        |
6. Crystal data of compound HHF-N4

**Supplementary Fig. 6.** Asymmetric unit of mo_2022565_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201537

**Supplementary Tab. 6.** Crystal data and structure refinement for HHF-N4.

| Identification code          | mo_2022565_0m |
|------------------------------|---------------|
| Empirical formula            | C₃H₇N₅O₄     |
| Formula weight               | 145.09        |
| Temperature/K                | 170           |
| Space group                  | P-1           |
| a/Å                          | 10.320(3)     |
| b/Å                          | 10.354(2)     |
| c/Å                          | 13.616(3)     |
| α/°                          | 92.100(8)     |
| β/°                          | 91.385(8)     |
| γ/°                          | 94.516(8)     |
| Volume/Å³                    | 1448.9(6)     |
| Z                            | 8             |
| ρ calc g/cm³                 | 1.624         |
| μ/mm⁻¹                       | 0.147         |
| F(000)                       | 736.0         |
7. Crystal data of compound HHF-H4

**Supplementary Fig. 7.** Asymmetric unit of cu_220501(QL)_20220428_6. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201538

**Supplementary Tab. 7.** Crystal data and structure refinement for HHF-H4.

| Property                  | Value          |
|---------------------------|----------------|
| Identification code       | cu_220501(QL)_20220428_6 |
| Empirical formula         | C_2H_8N_6O_4   |
| Formula weight            | 180.14         |
| Temperature/K             | 170            |
| Space group               | Pna2_1         |
| a/Å                       | 24.7340(12)    |
| b/Å                       | 3.5707(2)      |
| c/Å                       | 3.5707(2)      |
| α/°                       | 90             |
| β/°                       | 90             |
| γ/°                       | 90             |
| Volume/Å³                 | 3.5707(2)      |
| Z                         | 8              |
| ρ_calcd g/cm³             | 1.645          |
| µ/mm⁻¹                    | 1.341          |
| F(000)                    | 752.0          |

S 8
8. Crystal data of compound HHF-H11

**Supplementary Fig. 8.** Asymmetric unit of mo_2022458_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201539

**Supplementary Tab. 8.** Crystal data and structure refinement for HHF-H11.

| Property                        | Value                  |
|---------------------------------|------------------------|
| Identification code             | mo_2022458_0m          |
| Empirical formula               | C₃H₅N₅O₅             |
| Formula weight                  | 191.12                 |
| Temperature/K                   | 170                    |
| Space group                     | P 21/c                 |
| a/Å                             | 3.801(6)               |
| b/Å                             | 24.39(5)               |
| c/Å                             | 9.309(14)              |
| α/°                             | 90                     |
| β/°                             | 91.038(3)              |
| γ/°                             | 90                     |
| Volume/Å³                       | 1422.41(9)             |
| Z                               | 8                      |
| ρcalcg/cm³                      | 1.785                  |
| μ/mm⁻¹                          | 0.168                  |
| F(000)                          | 784.0                  |
9. Crystal data of compound HHF-H17

**Supplementary Fig. 9.** Asymmetric unit of pl_sq. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201540

**Supplementary Tab. 9.** Crystal data and structure refinement for HHF-H17.

| Property                          | Value                     |
|----------------------------------|---------------------------|
| Identification code              | pl_sq                     |
| Empirical formula                | C$_3$H$_6$N$_6$O$_5$      |
| Formula weight                   | 206.14                    |
| Temperature/K                    | 296                       |
| Space group                      | P 21/c                    |
| a/Å                              | 3.801(6)                  |
| b/Å                              | 24.39(5)                  |
| c/Å                              | 9.309(14)                 |
| α/°                              | 90                        |
| β/°                              | 96.726(15)                |
| γ/°                              | 90                        |
| Volume/Å$^3$                     | 857(2)                    |
| Z                                | 4                         |
| $\rho_{\text{calc}}$/g/cm$^3$    | 1.598                     |
| μ/mm$^{-1}$                      | 0.149                     |
| F(000)                           | 424.0                     |
10. Crystal data of N-1

**Supplementary Fig. 10.** Asymmetric unit of mo_2022792_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203242

**Supplementary Tab. 10.** Crystal data and structure refinement for N-1.

| Parameter                  | Value               |
|----------------------------|---------------------|
| Identification code        | mo_2022792_0m       |
| Empirical formula          | C$_3$H$_7$N$_7$O$_4$ |
| Formula weight             | 205.16              |
| Temperature/K              | 170                 |
| Space group                | P-1                 |
| a/Å                        | 6.695(4)            |
| b/Å                        | 7.286(6)            |
| c/Å                        | 8.487(7)            |
| α/°                        | 99.79(2)            |
| β/°                        | 102.865(1)          |
| γ/°                        | 99.038(18)          |
| Volume/Å$^3$               | 298.85(2)           |
| Z                          | 2                   |
| ρ$_{calc}$/cm$^3$           | 1.748               |
| μ/mm$^{-1}$                | 0.157               |
| F(000)                     | 212.0               |
11. Crystal data of N-2

**Supplementary Fig. 11.** Asymmetric unit of mo_2022486_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203236

**Supplementary Tab. 11.** Crystal data and structure refinement for N-2.

| Identification code   | mo_2022486_0m   |
|-----------------------|-----------------|
| **Empirical formula** | C₂H₄N₄O₂        |
| **Formula weight**    | 114.08          |
| **Temperature/K**     | 170             |
| **Space group**       | P2₁/c           |
| **a/Å**               | 8.8973(6)       |
| **b/Å**               | 10.0597(6)      |
| **c/Å**               | 9.9665(6)       |
| **α/°**               | 90              |
| **β/°**               | 106.828(2)      |
| **γ/°**               | 90              |
| **Volume/Å³**         | 853.84(9)       |
| **Z**                 | 8               |
| **ρcalc/g/cm³**       | 1.775           |
| **μ/mm⁻¹**            | 0.157           |
| **F(000)**            | 464.0           |
12. Crystal data of N-3

**Supplementary Fig. 12.** Asymmetric unit of mo_2022559_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203237

**Supplementary Tab. 12.** Crystal data and structure refinement for N-3.

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Identification code        | mo_2022559_0m          |
| Empirical formula          | C<sub>2</sub>H<sub>5</sub>N<sub>5</sub> |
| Formula weight             | 99.11                  |
| Temperature/K              | 150                    |
| Space group                | P21/c                  |
| a/Å                        | 10.6320(12)            |
| b/Å                        | 4.2922(6)              |
| c/Å                        | 10.8180(6)             |
| α/°                        | 90                     |
| β/°                        | 118.755(4)             |
| γ/°                        | 90                     |
| Volume/Å³                  | 432.80(9)              |
| Z                          | 4                      |
| ρ<sub>calc</sub>/g/cm³     | 1.521                  |
| μ/mm⁻¹                     | 0.115                  |
| F(000)                     | 208.0                  |
13. Crystal data of N-4

**Supplementary Fig. 13.** Asymmetric unit of cu_220503_cjx_s9_3no2_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2201541

**Supplementary Tab. 13.** Crystal data and structure refinement for N-4.

| Identification code          | cu_220503_cjx_s9_3no2_0m |
|-----------------------------|---------------------------|
| Empirical formula           | C₄H₇N₅O                  |
| Formula weight              | 141.15                    |
| Temperature/K               | 170                       |
| Space group                 | P21                       |
| a/Å                         | 4.8345(2)                 |
| b/Å                         | 8.9774(4)                 |
| c/Å                         | 7.0631(3)                 |
| α/°                         | 90                        |
| β/°                         | 102.865(1)                |
| γ/°                         | 90                        |
| Volume/Å³                   | 298.85(2)                 |
| Z                           | 2                         |
| ρ(calc) g/cm³               | 1.569                     |
| μ/mm⁻¹                      | 1.026                     |
| F(000)                      | 148.0                     |
Supplementary Fig. 14. Asymmetric unit of PL20220801Cl_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203240

Supplementary Tab. 14. Crystal data and structure refinement for N-5.

| Identification code            | mo_2022792_0m       |
| Empirical formula             | 2(C₃ClN₄O₄), 2(H₂O), H₄N |
| Formula weight                | 437.11              |
| Temperature/K                 | 296                 |
| Space group                   | P-1                 |
| a/Å                           | 7.668(7)            |
| b/Å                           | 8.115(8)            |
| c/Å                           | 14.459(14)          |
| α/°                           | 91.573(14)          |
| β/°                           | 102.948(15)         |
| γ/°                           | 108.177(13)         |
| Volume/Å³                     | 298.85(2)           |
| Z                              | 2                   |
| ρcalc/g/cm³                   | 1.748               |
| μ/mm⁻¹                         | 0.466               |
| F(000)                        | 442.0               |
15. Crystal data of N-6

**Supplementary Fig. 15.** Asymmetric unit of 226_0m_a. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203238

**Supplementary Tab. 15.** Crystal data and structure refinement for NT-6.

| Property                     | Value                      |
|------------------------------|----------------------------|
| Identification code          | 226_0m_a                   |
| Empirical formula            | C₃H₂N₂Br₂                  |
| Formula weight               | 225.87                     |
| Temperature/K                | 296                        |
| Space group                  | I41/a                      |
| a/Å                          | 15.730(6)                  |
| b/Å                          | 15.730(6)                  |
| c/Å                          | 9.663(4)                   |
| α/°                          | 90                         |
| β/°                          | 90                         |
| γ/°                          | 90                         |
| Volume/Å³                    | 2391(2)                    |
| Z                            | 16                         |
| ρcalc/g/cm³                  | 2.510                      |
| μ/mm⁻¹                       | 13.434                     |
| F(000)                       | 1664.0                     |
16. Crystal data of N-7

**Supplementary Fig. 16.** Asymmetric unit of 2_tw. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203239

**Supplementary Tab. 16.** Crystal data and structure refinement for NT-7.

| Identification code | 2_tw |
|---------------------|------|
| Empirical formula   | C₃H₂N₂Br₂ |
| Formula weight      | 225.87 |
| Temperature/K       | 296 |
| Space group         | P-1 |
| a/Å                 | 7.9127(14) |
| b/Å                 | 10.4942(15) |
| c/Å                 | 11.8451(14) |
| α°                  | 112.250(11) |
| β°                  | 104.401(11) |
| γ°                  | 101.103(15) |
| Volume/Å³           | 835.4(3) |
| Z                   | 16 |
| ρcalc/g/cm³         | 2.510 |
| μ/mm⁻¹              | 14.423 |
| F(000)              | 618.0 |
17. Crystal data of N-8

Supplementary Fig. 17. Asymmetric unit of 3I_0m. Anisotropic displacement parameters are drawn at 50% probability. CCDC: 2203241

Supplementary Tab. 17. Crystal data and structure refinement for NT-8.

| Identification code   | 3I_0m   |
|-----------------------|---------|
| Empirical formula     | 2(C_3H_N_3I_3), CH_4O |
| Formula weight        | 923.56  |
| Temperature/K         | 296     |
| Space group           | P21/c   |
| a/Å                   | 11.354(15) |
| b/Å                   | 9.119(12)  |
| c/Å                   | 18.042   |
| α/°                   | 90      |
| β/°                   | 94.910(18) |
| γ/°                   | 90      |
| Volume/Å³             | 1861(4)  |
| Z                      | 4       |
| ρ calc/g/cm³          | 3.296   |
| μ/mm⁻¹                | 10.011  |
| F(000)                | 1608.0  |
II. NMR Spectra Data

Supplementary Fig. 18. $^1$H NMR of compound NT

Supplementary Fig. 19. $^{13}$C NMR of compound NT
Supplementary Fig. 20. $^1$H NMR of compound HHF-T

Supplementary Fig. 21. $^{13}$C NMR of compound HHF-T

Supplementary Fig. 22. $^1$H NMR of compound NF
Supplementary Fig. 23. $^{13}$C NMR of compound NF

Supplementary Fig. 24. $^1$H NMR of compound HHF-F
Supplementary Fig. 25. $^{13}$C NMR of compound HHF-F

Supplementary Fig. 26. $^1$H NMR of compound HHF-N4
Supplementary Fig. 27. $^{13}$C NMR of compound HHF-N4

Supplementary Fig. 28. $^1$H NMR of compound HHF-N14
Supplementary Fig.29 $^{13}$C NMR of compound HHF-N14
III. DSC Data

Supplementary Fig. 30. DSC of compound NT

Supplementary Fig. 31. DSC of compound HHF-T
Supplementary Fig. 32. DSC of compound NF

Supplementary Fig. 33. DSC of compound HHF-F
**Supplementary Fig. 34.** DSC of compound HHF-N4

**Supplementary Fig. 35.** DSC of compound HHF-N14
IV. Computation and properties

Packing Coefficient Calculations

Packing coefficients were calculated by using equation (1), where \( V_m \) and \( V_c \) are the molecular and crystal volumes, respectively. A volume enclosed through a surface with an assigned electronic density was considered as \( V_m \). In this work, the electronic density was calculated at the theory level of M062X/6-311+G (d, p) and the density of 0.003 au was adopted for \( V_m \) calculations.

\[
PC = \frac{\sum V_{mol}}{V_{cell}} \quad \text{(1)}
\]

2D fingerprint plot for intermolecular contact

Hirshfeld surfaces in a crystal are constructed in terms of the electron distribution, calculated as the sum of spherical atom electron densities.\(^1^,\)\(^2\) The normalized contact distance (\( d_{\text{norm}} \)) is determined by \( d_i \) and \( d_e \), the distances from the surface to the nearest atom interior and exterior to the surface, respectively, and the van der Waals radii of the atoms. \( d_{\text{norm}} \) enables the identification of the regions of particular significance to intermolecular interactions. That is to say, a Hirshfeld surface is composed of lots of points, and each point parametrized as (\( d_i \), \( d_e \)) can provide information about related contact distances from it. The smaller \( d_i + d_e \) implies closer atom–atom contact. Both \( d_i \) and \( d_e \) were constrained in a range of 0-3.0 Å. Mapping these (\( d_i \), \( d_e \)) points and considering their relative frequencies, we can get a two-dimensional (2D) fingerprint plot. For any symmetrically dependent molecule in any crystal, the fingerprint is unique. This is the basis for identifying a crystal environment of a given molecule. The color mapping distinguishes the intensity of points, and the red and the blue represent the high and low intensities, respectively. Therefore, through the locations of (\( d_i \), \( d_e \)) points and their relative frequencies discernible on the surface and the 2D fingerprint plot, we can ascertain the distances and intensities of these contacts. All the fingerprint plots were created using CrystalExplorer 17.5\(^3\) in this work, and the surfaces were mapped over a \( d_{\text{norm}} \) range of -0.4 to 1.4 Å.

Theoretical study of heat of formation

The geometric optimization and frequency analyses of the structures were calculated using M062X/6-31+G** level.\(^4\)\(^,\)\(^5\) The heats of formation for N-(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)nitramide, (5-amino-3-nitro-1H-1,2,4-triazol-1-yl)(nitro)amide ion, N-(4-amino-1,2,5-oxadiazol-3-yl)nitramide, (4-amino-1,2,5-oxadiazol-3-yl)(nitro)amide ion, hydroxylammonium ion were obtained by atomization approach using G2 composite method\(^6\) (Supplementary Tab. 18). The gas-phase enthalpies of the molecules were obtained by using the atomization method with the G2 ab initio calculations.

Methods for estimating the diameter of guest molecules

A method\(^7\) for estimating the molecular kinetic diameter based on the iso-electronic density surfaces. The Gaussian 09 program (Revision D.01) was used to calculate the geometric optimization and frequency analyses of the guest structure, and the PBE0/def2-TZVP level is used. subsequently, the coordinates of the iso-electronic density surfaces vertices are calculated.
using Multiwfn, and finally the distance between the surface vertices is measured by VMD to derive the dimensions of the guest structure.

**Supplementary Tab. 18. Enthalpies of the gas-phase species M (G2 method).**

| M                                      | ΔH\textsubscript{f} (kJ mol\textsuperscript{-1}) |
|----------------------------------------|-----------------------------------------------|
| N-(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)nitramide | 320.697817                                   |
| (5-amino-3-nitro-1H-1,2,4-triazol-1-yl)(nitro)amide   | 75.59139622                                   |
| N-(4-amino-1,2,5-oxadiazol-3-yl)nitramide           | 232.5717802                                   |
| (4-amino-1,2,5-oxadiazol-3-yl)(nitro)amide          | 51.92925468                                   |
| hydroxylammonium                          | 669.5240231                                   |

Based on the literature, the heat of sublimation is estimated with Trouton’s rule.\textsuperscript{8} The solid phase heat of formation of 1 was calculated with equation 1, in which T\textsubscript{d} represents the decomposition temperature.\textsuperscript{8}

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

(1)

According to empirical formula (2)\textsuperscript{9} the heat of sublimation can be computed from the temperature of melting (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).

\[ \Delta H_{sub} = 188 \times (T+273.15)/1000 \]  

(2)

The solid phase heats of formation of 1 and 4 were calculated with eq 3.

\[ \Delta H_{f, solid} = \Delta H_{f, gas} - \Delta H_{sub} \]  

(3)

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (**Supplementary Fig. 36.**).\textsuperscript{9} The number is simplified by equation 4:

\[ \Delta H_f^0 (\text{salt, 298 K}) = \Delta H_f^0 (\text{cation, 298K}) + \Delta H_f^0 (\text{anion, 298K}) - \Delta H_f (\text{4}) \]
in which $\Delta H_L$ can be predicted by using the formula suggested by Jenkins, et al.\(^9\) (equation 5):

$$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (5)$$

In this equation, $n_M$ and $n_X$ depend on the nature of the ions $M^+$ and $X^{-}$, respectively. The equation for lattice potential energy $U_{pot}$ (equation 6) has the form:\(^9\)

$$U_{POT} [kJ \text{ mol}^{-1}] = \gamma(\rho/M_m)^{1/3} + \delta \quad (6)$$

where $\rho_m [g \text{ cm}^{-3}]$ is the density of the salt, $M_m$ is the chemical formula mass of the ionic material, and values for $\gamma$ and the coefficients $\gamma$ (kJ mol$^{-1}$ cm) and $\delta$ (kJ mol$^{-1}$) are assigned literature values.\(^9\) By using the measured room temperature densities, all the newly prepared compounds are listed in Supplementary Tab. 19.

**Supplementary Tab. 19.** The density, calculated lattice energy and calculated heat of formation.

| compound | $d^[a] \text{[g cm}^{-3}]$ | $\Delta H_L^[b]$ | $\Delta H_r^[c] \text{[kJ mol}^{-1}]$ |
|----------|--------------------------|-----------------|----------------------------------|
| NT       | 1.791 (173K)             | -               | 243.97                           |
| HHF-T    | 1.812 (173K)             | 500.2           | 239.95                           |
| NF       | 1.737                    | -               | 157.53                           |
| HHF-F    | 1.819                    | 533.6           | 182.85                           |

[a] Density was calculated based on a single crystal at room temperature. [b] Calculated lattice energy. [c] Calculated heat of formation.

**Supplementary Tab. 20.** Physical and detonation properties of energetic materials (NT, HHF-T, NF, and HHF-F).

| Energetic compounds | Chemical Formula | $T_d^[a] \text{[°C]}$ | $d^[b] \text{[g cm}^{-3}]$ | $\Delta H_r^[d] \text{[kJ mol}^{-1}]$ | $D^[e] \text{[m s}^{-1}]$ | $P^[f] \text{[GPa]}$ | $OB(CO_2)^[g]$ | $IS^[h]$ | $FS^[i]$ |
|---------------------|-----------------|-----------------------|--------------------------|-----------------------------------|--------------------------|----------------|----------------|--------|--------|
| NT                  | $C_2H_3NO_4$    | 135                   | 1.758$^c$                | 243.97                            | 8769                     | 32.7                  | -12.7             | 2      | 60     |
| HHF-T               | $C_2H_6NO_5$    | 160                   | 1.779$^c$                | 239.95                            | 9099                     | 34.95                  | -14.4             | 10     | 160    |
| NF                  | $C_2H_3NO_3$    | 126                   | 1.737                    | 157.53                            | 8433                     | 29.17                  | -27.57            | 10     | 160    |
| HHF-F               | $C_2H_6NO_4$    | 181                   | 1.819                    | 182.85                            | 9286                     | 35.85                  | -29.65            | 50     | 360    |

[$^a$ Decomposition temperature (onset). $^b$ Density ((calculated based on a single crystal at room temperature). $^c$ Single crystal density calculated at 170 °C. $^d$ Heat of formation (calculated). $^e$ Detonation velocity (calculated). $^f$ Detonation pressure (calculated). $^g$ Oxygen balance (based on CO$_2$) for CaHbOcNd, 1600 (c–2a–0.5b)/MW, MW = molecular weight. $^h$ Impact sensitivity. $^i$ Friction sensitivity.]

The enthalpy of formation ($\Delta H^o$) is a significant parameter to evaluate the energy performance of EMs. The constant-volume combustion heat ($\Delta U^o$) measurement of the HHF-F was carried out by oxygen bomb calorimetry (Parr 6200 Oxygen bomb calorimeter (NLFRM-45)), and the test value of $\Delta U^o$ is 9.23 MJ kg$^{-1}$. The standard molar enthalpy of combustion ($\Delta_h^o$) can be obtained according to the formula (Eq. 7).\(^10\) The ideal combustion reaction equation of HHF-F is given in Eq. 8. The standard
enthalpy of formation ($\Delta_f H^\circ$) of HHF-F was calculated from $\Delta_f H^\circ$ (Eq. 9, Hess’s Law) to be $-4.59 \text{ kJ mol}^{-1}$ [$\Delta_f H^\circ(\text{CO}_2, \text{ g}) = -393.51 \text{ kJ mol}^{-1}$; $\Delta_f H^\circ(\text{H}_2\text{O}, \text{ l}) = -285.83 \text{ kJ mol}^{-1}$].

\[
\Delta_f H^\circ = \Delta_c U^\circ + \Delta nRT \tag{7}
\]

$\Delta n = n_{\text{product}} - n_{\text{reactant}}$ ($n_g$ is the total molar amount of gases in the products or reactants, $R = 8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$, $T = 298.15 \text{ K}$).

\[
\begin{align*}
\text{C}_2\text{H}_6\text{O}_4\text{N}_6 + 7/2\text{O}_2 &\rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 3\text{N}_2 \tag{8} \\
\Delta_f H_m(\text{C}_2\text{H}_6\text{N}_4\text{O}_6, \text{ s}) &\equiv [2\Delta_f H^\circ(\text{CO}_2, \text{ g}) + 3 \Delta_f H^\circ(\text{H}_2\text{O}, \text{ l})] - \Delta_c H^\circ(\text{C}_2\text{H}_6\text{N}_4\text{O}_6, \text{ s}) \tag{9}
\end{align*}
\]
Computational analysis of internal stress

Any external mechanical force acting on an energetic material can lead to a certain shape change to produce strain and store mechanical energy.\textsuperscript{11} When this mechanical energy exceeds the limit of the energetic material, decomposition will be activated and trigger a series of explosions.\textsuperscript{12} In order to explore the different performance of HHF-F and NF on safety issues, a force field was established for both unit cells and their abilities to handle external stimuli were probed. To simplify the simulation, only vertical compression and horizontal sliding of the crystal unit cell were investigated since all direction stimuli can be split into these two types.\textsuperscript{13,14} Therefore, the deformation potential (P) can be expressed by the energy difference before and after deformation for energetic materials. For convenient comparison, the value is converted from mol units into volume units by dividing by the unit cell volume (eq 10).

\[ P = \frac{(E_{\text{after def}} - E_{\text{before def}})}{V_{\text{unit cell}}} \]  \hspace{1cm} (10)

In this part of the calculations, single point energies were obtained from optimized structures using BLYP-D3 def2-SVP method\textsuperscript{14} using ORCA 4.0.1\textsuperscript{15}

\[ V_{\text{unit cell}} = 0.001 \times M \times Z / d \]

M: molar mass; Z: Number of molecules in a cell; d: calculated density of single crystal.

**Supplementary Tab. 21.** Absolute energy and internal stress (P) of HHF-F.

| Distance (Å) | SPE1\textsuperscript{a} (hartrees) | \( P_{\text{ob}} \) kJmol\textsuperscript{-1}/MJm\textsuperscript{-3} | SPE2\textsuperscript{b} (hartrees) | \( P_{\text{oc}} \) kJmol\textsuperscript{-1}/MJm\textsuperscript{-3} |
|-------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|
| 0           | -2832.1999                     | 0/0                            | -2832.1999                    | 0/0                            |
| 0.1         | -2832.1991                     | 2.100/5.364                    | -2832.1994                    | 1.313/3.353                    |
| 0.2         | -2832.1980                     | 4.988/12.740                   | -2832.1989                    | 2.626/6.707                    |
| 0.3         | -2832.1961                     | 9.977/25.482                   | -2832.1977                    | 7.776/14.753                   |
| 0.4         | -2832.1938                     | 16.016/40.907                  | -2832.1962                    | 9.714/24.810                   |
| 0.5         | -2832.1913                     | 22.579/57.670                  | -2832.1946                    | 13.915/35.54                   |
| 0.6         | -2832.1886                     | 29.668/75.776                  | -2832.1927                    | 18.903/48.281                  |
| 0.7         | -2832.1857                     | 37.282/95.224                  | -2832.1905                    | 24.680/63.036                  |
| 0.8         | -2832.1837                     | 42.533/108.636                 | -2832.1890                    | 28.617/73.092                  |

[a] Single point energy of HHF-F after sliding along ob axis. [b] Internal stress for HHF-F after sliding along oc axis.

**Supplementary Tab. 22.** Absolute energy and internal stress (P) of NF.

| Distance (Å) | SPE1\textsuperscript{a} (hartrees) | \( P_{\text{ob}} \) kJmol\textsuperscript{-1}/MJm\textsuperscript{-3} | SPE2\textsuperscript{b} (hartrees) | \( P_{\text{oc}} \) kJmol\textsuperscript{-1}/MJm\textsuperscript{-3} |
|-------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|
| 0           | -2306.3457                     | 0/0                            | -2306.3457                    | 0/0                            |
| 0.1         | -2306.3447                     | 2.626/7.859                    | -2306.3455                    | 0.526/1.574                    |
Supplementary Statistic works of Monocyclic N-rich azole hydroxylammonium salts

Based on the CCDC database, almost all monocyclic N-rich azole hydroxylammonium salts (a-w) were found in the literature.\textsuperscript{16-32} They are listed in Supplementary Fig. 37., and their decomposition temperatures are listed in Supplementary Table 23.

From Supplementary Table 23, it is obvious that except for compounds d, h, k, l, and q, the decomposition temperatures of all monocyclic N-rich azole hydroxylammonium salts are lower than 170 °C.

| Compound | Single point energy of NF | Internal stress for NF | Decomposition temperature |
|----------|---------------------------|------------------------|---------------------------|
|          | after sliding along ob axi | after sliding along oc axis |                           |
| 0.2      | -2306.3435                | 5.776/17.289           | -2306.3452                | 1.312/3.929               |
| 0.3      | -2306.3416                | 10.76/32.220           | -2306.3447                | 2.625/7.859               |
| 0.4      | -2306.3390                | 17.590/52.653          | -2306.3440                | 4.463/13.360              |
| 0.5      | -2306.3354                | 27.042/80.944          | -2306.3432                | 6.564/19.647              |
| 0.6      | -2306.3303                | 40.433/121.02          | -2306.3421                | 9.452/28.291              |
| 0.7      | -2306.3234                | 58.549/175.248         | -2306.3407                | 13.128/39.293             |
| 0.8      | -2306.3143                | 82.440/246.762         | -2306.3390                | 24.607/73.653             |

[a] Single point energy of NF after sliding along ob axi. [b] Internal stress for NF after sliding along oc axis.

Supplementary Fig. 37. Structural formulas of reported monocyclic N-rich azole hydroxylammonium salts. According to the types of azole rings, the above structures can be...
divided into substituted triazole (c, f, i, t, u-w); oxadiazole (n, r); tetrazole (a, b, d, e, g, h, j, k, l, m, o, q, s) and pyrazole (p).
Supplementary Fig. 38. The diameter (d) of azole anions based on Hirshfeld surfaces of reported monocyclic N-rich azole hydroxylammonium salts. According to the size of the anion diameter, they can be summarized as follows: 7 < d ≤ 8 Å (a-c); 8 < d ≤ 9 Å (d-h); 9 < d ≤ 10 Å (i-p); 10 < d ≤ 11 Å (q-s); 11 < d ≤ 12 Å (t-v); 12 < d ≤ 13 Å (w).

Supplementary Fig. 39. The crystal structure of reported monocyclic N-rich azole hydroxylammonium salts. To facilitate the observation of crystal packing, hydroxylammonium cations are blue, and azole anions are red. Examples of hydroxylammonium cations in layers
are marked with green boxes. The comparative analysis about crystal packing mode shows that most of them are sandwich-like (b, c, i, k-m, q-r, u, v), and the crystal structures of a, j, n, o, p, s, t, w show mixed packing mode, only five cases are layer-by-layer packing of the hydroxyammonium cation within the layer (d-h).

**Supplementary Tab. 23.** Decomposition temperatures and density of reported monocyclic N-rich azole hydroxyammonium salts

| Compound | Decomposition (°C) | Density (g cm\(^{-3}\))\(^{a}\) | IS(J) | D (m s\(^{-1}\)) | Note |
|----------|-------------------|-------------------------------|-------|----------------|------|
| a        | 138               | 1.634                         | >40   | 9034           | Ref 16 |
| b        | 155               | 1.664                         | 10    | 9056           | Ref 17 |
| c        | 138               | 1.75(127k)                    | >40   | 8779           | Ref 18 |
| d        | 173               | 1.660                         | 40    | 8180           | Ref 19 |
| e        | 96                | 1.649                         | <1    | 8959           | Ref 20 |
| f        | 146(Melting point)| 1.74(103k)                    | 17    | 8876           | Ref 21 |
| g        | 157               | 1.85                          | 4     | 9499           | Ref 22 |
| h        | 185               | 1.627                         | 8     | 8651           | Ref 23 |
| i        | -                 | 1.891(293k)                   | -     | -              | Ref 24 |
| j        | 166               | 1.771                         | 10    | 9214           | Ref 23 |
| k        | 172               | 1.785                         | 2     | 9236           | Ref 23 |
| l        | 171               | 1.639(100k)                   | 10    | 8614           | Ref 25 |
| m        | -                 | 1.848                         | -     | -              | Ref 26 |
| n        | 140               | 1.875                         | 10    | 9589           | Ref 27 |
| o        | 130               | 1.813(298k)                   | 1.5   | 9807           | Ref 26 |
| p        | 141               | 1.772                         | -     | -              | Ref 28 |
| q        | 178               | 1.614                         | 15    | 8298           | Ref 29 |
| r        | 138               | 1.82(296k)                    | 8     | 9087           | Ref 30 |
| s        | 164               | 1.704(100k)                   | >40   | 8934           | Ref 25 |
| t        | 149               | 1.804                         | 1     | 9426           | Ref 31 |
| u        | 145               | 1.881\(^{b}\)                | 3     | 9313           | Ref 32 |
| v        | 165               | 1.848\(^{b}\)                | 10    | 9690           | Ref 32 |
| w        | 147               | 1.836\(^{b}\)                | 4     | 9297           | Ref 32 |

a. Density was calculated based on a single crystal at 173 K. b. Measured densities: gas pycnometer at room temperature.

The impact sensitivity of compounds a, c, d, and s in the above example is insensitive (is greater than or equal to 40 J), because none of these N-rich azole anions contain energetic substituents such as nitro or nitramine groups.
Supplementary Fig. 40. a) Crystal structure of hydroxylammonium 2-amino-5-nitramino-1,3,4-oxadiazolate (r); b) The part of the Hirshfeld surface attributed to the oxygen interaction; c) Highlight O⋯O contacts of 2D fingerprint plots in crystal stacking for hydroxylammonium 2-amino-5-nitramino-1,3,4-oxadiazolate (r).

Supplementary Fig. 41. Crystal density (g cm\(^{-3}\)) and packing coefficient (NT, HHF-T, and HHF-F: 173 K; NF: 296 K).
Supplementary Fig. 42. The 2D fingerprint plots in crystal stacking for NT(a) and NF(c); Pie graphs for NT (b) and NF (d) show the percentage contributions of the individual atomic contacts to the Hirshfeld surface, Hirshfeld surfaces (inside).
V Application expansion of size matching strategy

For N-rich azole anions, the combination of different skeletons and substituents can get various structures of different sizes. In general, for the monocyclic systems studied in this work, their dimensions are mostly in the range of 7-15 Å.

According to the source classification of acid hydrogen in N-rich azoles for energetic hydroxylammonium salts in the CSD database, the most abundant ones are nitroamino- and nitro-substituted heterocycles, respectively. The acidic hydrogen of HHF-F and HHF-T reported in this work is derived from nitroamine-based structures.

In order to expand the application of this strategy, we construct the nitroamine unit based on the monocyclic N-rich azoles as the skeleton and introduce the nitro group, amino group, alkyl group, amide group, and carboxylic acid in other positions to adjust the guest anion size. Thus, a candidate library of guest anions is established.

Supplementary Fig. 43. Guest-Nitramidate (GN), according to the types of azole rings, the above structures can be divided into substituted triazole (GN-14, 16); oxadiazole (GN-1-6, 13, 15, 17) and pyrazole (GN-7-12, 18).

Then, theoretical calculation and prediction of the size of the above structure are carried out, and the predicted size is shown in the figure below:
Supplementary Fig. 44. The predicted diameter of guest azole anions based on theoretical calculations. According to the size of the anion diameter, they can be summarized as follows: $8 < d \leq 9$ Å (GN-1-4); $9 < d \leq 10$ Å (GN-5-11, 13, 15); $10 < d \leq 11$ Å (GN-12, 14, 16-18).

According to the results of theoretical calculation, the diameter of the anionic guest GN1-4 is between 8-9 Å. Due to the large volume of the hydroxylamine structure itself, there is no...
structure whose predicted diameter is less than 8 Å. The GN-3 (8.8 Å) is the guest structure of HHF-F which is mainly discussed in this paper, and its predicted diameter is very close to the actual Hershfield surface diameter (8.5 Å) measured by the crystal structure.

We attempted to synthesize the above structures to verify the correlation between the predicted size and the actual crystal packing. For the above synthesis of hydroxylammonium salts containing nitramine groups, we used the following general steps:

Supplementary Fig. 45. The general synthesis steps for HHF

With reference to the size prediction results, we prepared the crystals of hydroxylammonium salts corresponding to GN-1, GN-2, GN-3 and GN-4 with the guest anion size in the range of 8-9 Å. Also to verify the feasibility of the strategy, some hydroxylammonium salts with guest anion sizes larger than 10 Å were selected for synthesis. The crystal data of the following two compounds HHF-N4 (hydroxylammonium (4-methyl-1,2,5-oxadiazol-3-yl)(nitro)amide) and HHF-N14 (hydroxylammonium 4-carbamoyl-5-nitramino-2H-1,2,3-triazole) were obtained. In addition, we obtained ammonium salt crystals of GN-16 (ammonium (5-carbamoyl-2-methyl-2H-1,2,3-triazol-4-yl)(nitro)amide, crystal-N-1) during the incubation of the hydroxymonium salt crystals of GN-16 (Supplementary Fig. S46).

Supplementary Fig. 46. a) GN-4 as guest to form HHF-N4 (hydroxylammonium (4-methyl-1,2,5-oxadiazol-3-yl)(nitro)amide) b) GN-14 as guest to form HHF-N14 (hydroxylammonium 4-carbamoyl-5-nitramino-2H-1,2,3-triazole) c) GN-16 as guest to form ammonium (5-carbamoyl-2-methyl-2H-1,2,3-triazol-4-yl)(nitro)amide(N-1).
Supplementary Fig. 47. a) and e) Molecular structure and crystal packing of HHF-N4 and HHF-N14. b) and f) Molecular structure of HHF-N4 and HHF-N14. c) and g) Planar molecular geometry of HHF-N4 and HHF-N14. d) and h) Crystal stacking structures of HHF-N4 and HHF-N14.

Supplementary Fig. 48. a) Layer assembly mode of HHF-N4 and its crystal packing diagram. b) Layer assembly mode of HHF-N14 and its crystal packing diagram.
From the above supplementary figure 47 and 48, the guest molecules in HHF-N4 are successfully embedded in the hydrogen bond framework composed of ammonium hydroxide, displaying face-to-face stacking. Analysis of the above two compounds, HHF-N4 and HHF-N14 by two-dimensional fingerprints and Hirshfeld surfaces revealed that HHF-N4 (8.8 Å), which has guest anion sizes of 8-9 Å, also has more O...H interactions in the crystal structure than HHF-N14 (10.1 Å). This means that for the nitro group, more hydrogen bonds can be made to stabilize it.

Supplementary Fig. 49. The 2D fingerprint plots in crystal stacking for HHF-N4 (a) and HHF-N14 (d); Pie graphs for HHF-N4 (b) and HHF-N14 (e) show the percentage contributions of the individual atomic contacts to the Hirshfeld surface, Hirshfeld surfaces (inside). Short contact for HHF-N4 (c) and HHF-N14 (f).

In this part, the Hirshfeld surface diameter of the guest anion is in good agreement with the predicted value, and their crystal packing mode is consistent with the conclusion that for a guest with size in the range of 8 to 9 Å, a more orderly crystal packing can be obtained. This indicates that the size-match strategy can be applied in this above series of N-rich azole anion guests. In addition, we extended our size-matching strategy to structure prediction of hydroxylamine hydrogen bond framework using a series of anions guest formed by N-rich heterocyclic azoles with acid hydrogen.

In addition, we extended our size-matching strategy to structure prediction of hydroxylamine hydrogen bond framework using a series of anions guest formed by N-rich heterocyclic azoles with acid hydrogen.
Supplementary Fig. 50. Guest-Heterocycle (GH), according to the types of azole rings, the above structures can be divided into substituted triazole (GH-1, 2, 4, 6, 12, 15, 21, 22, 24, 25, 27, 29); imidazole (GH-3, 11, 14, 16, 19, 20, 30); tetrazole (GH-23) and pyrazole (GH-5, 7-10, 13, 17, 18, 26, 28).

Theoretical calculation and prediction of the size for the above structure are carried out, and the predicted size is shown in the figure below:
Supplementary Fig. 51. The predicted diameter of guest azole anions based on theoretical calculations. According to the size of the anion diameter, they can be summarized as follows: 7 < d ≤ 8 Å (GH-2, 4, 21, 23, 27); 8 < d ≤ 9 Å (GH-1, 3, 5-12, 19, 22, 25); 9 < d ≤ 10 Å (GH-13-18, 24, 26, 28, 29); 10 < d ≤ 11 Å (GH-20, 30).

From the above predictions, some of the smaller sized structures (GH-2, 4, 21, 23, 27) give ionic diameters less than 8 Å when the structures do not contain nitramine groups. Also, the predicted diameters of the guest GH-5-12,19, 22, and 25 are in the range of 8-9 Å. The other guest structures have diameters greater than 9 Å. To verify the correlation between the predicted size and the actual crystal packing, we try to synthesis those hydroxylammonium salts via the following general steps:
**Supplementary Fig. 52.** The general synthesis steps for HHF that N-rich heterocyclic azoles with acid hydrogen as the raw reagent.

With reference to the size prediction results, we try to prepare the crystals of hydroxylammonium salts corresponding to GH-5-12, 19, 22, and 25 with the guest anion size in the range of 8-9 Å. Also to verify the feasibility of the strategy, some hydroxylammonium salts with guest anion sizes less than 8 Å and larger than 10 Å were selected for synthesis. The crystal data were successfully obtained for the following three compounds. They are HHF-H4 (hydroxylammonium 4-nitro-1,2,3-triazole-2-ide, hydroxylamine), HHF-H11 (hydroxylammonium 4,5-dinitroimidazol-1-ide) and HHF-H17 (hydroxylammonium 4-amino-3,5-dinitropyrazol-1-ide) (Supplementary Fig. 54. a, e, i).

In addition, we obtained ammonium salt crystals of GH-18 (ammonium 4-chloro-3,5-dinitropyrazol-1-ide, crystal-N5) during the incubation of the hydroxymonium salt crystals of GH-18 (Supplementary Fig. 53. g). During the preparation of such compounds, we observe that cyano-group turn into amino oximes (Supplementary Fig. 53. d). This may be one of the reasons why there are few hydroxylammonium salts containing cyano-zoles in the current CSD database. Also some of the structures (Supplementary Fig. 53. a, b, h, i, j) may lack sufficient acidity to obtain hydroxylammonium salt crystals, and the corresponding neutral compounds are directly precipitated from the system. The above-mentioned problems also reflect the difficulty of preparing energetic hydroxylammonium crystals.
Supplementary Fig. 53. a) GH-1 as guest to form crystal N-2 (3-nitro-1H-1,2,4-triazole); b) GH-2 as guest to form crystal N-3 (1H-1,2,4-triazole-3,5-diamine); c) GH-4 as guest to form ammonium (hydroxylammonium 4-nitro-1,2,3-triazole-2-ide, hydroxylamine (HHF-H4); d) GH-9 as guest to form crystal N-4 (4-(amino(hydroxyamino)methyl)-1H-pyrazol-3-amine) e) GH-11 as guest to form crystal HHF-H11 (hydroxylammonium 4,5-dinitroimidazol-1-ide) f) GH-17 as guest to form ammonium (hydroxylammonium 4-amino-3,5-dinitropyrazol-1-ide (HHF-H17); g) GH-18 as guest to form crystal N-5 (ammonium 4-chloro-3,5-dinitropyrazol-1-ide); h) GH-26 as guest to form crystal N-6 (3,5-dibromo-1H-pyrazole) i) GH-27 as guest to form crystal N-7 (ammonium (4,5-dibromo-1H-1,2,3-triazole); j) GH-30 as guest to form crystal N-8 (2,4,5-triiodo-1H-imidazole).
Supplementary Fig. 54. a), e) and i) Molecular structure of HHF-H4, HHF-H11 and HHF-H17. b), f) and k) Crystal structure of HHF-H4, HHF-H11 and HHF-H17. c), g) and j) Planar molecular geometry of HHF-H4, HHF-H11 and HHF-H17; d), h) and l) Crystal stacking structures of HHF-H4, HHF-H11 and HHF-H17.
Supplementary Fig. 55. c) Layer assembly mode of HHF-H4 and its crystal packing diagram; d) Layer assembly mode of HHF-H11 and its crystal packing diagram; e) Layer assembly mode of HHF-H17 and its crystal packing diagram.

Using their crystal data, the Hershfeld surface diameters of the three guest anions were measured as GH-4 (7.6 Å), GH-11 (8.6 Å) and GH-17 (10.9 Å), which are very close to the diameters predicted by their theoretical calculations (GH-4 (7.8 Å), GH-11 (8.7 Å) and GH-17 (9.9 Å)).

To verify the relationship between the above types of anion guest size and crystal stacking, we analyzed their stacking mode, as shown in the figure above HHF-H4 not only does not possess a layer-by-layer stacking structure with hydroxylammonium units due to its small size, but also forms co-crystals with neutral hydroxylamine molecules. In contrast, HHF-H11 with a guest size of 8.6 Å shows an ordered crystal structure with the energetic guest wrapped by the hydroxylammonium hydrogen bonding framework, which possesses good layer-by-layer stacking in the three-dimensional structure, while HHF-H17 with a guest anion size of 11.0 Å does not enter the layers formed by the hydroxylammonium structure due to its larger size, which is consistent with our size matching strategy.
Supplementary Fig. 56. The 2D fingerprint plots in crystal stacking for HHF-H4 (a), HHF-H11 (c) and HHF-H17 (e); Pie graphs for HHF-H4 (b), HHF-H11 (d) and HHF-H17 (f) show the percentage contributions of the individual atomic contacts to the Hirshfeld surface, Hirshfeld surfaces (inside).

In summary, for the two guest systems mentioned above, by analyzing the relationship between the guest molecule size and the crystal stacking structure of seven examples obtained in this work, it can be concluded that the guest molecules of HHF-F (8.5 Å), HHF-N4 (7.6 Å), and HHF-H11 (8.6 Å), which have guest molecule sizes of 8-9 Å, are embedded in the hydroxylammonium composed of a hydrogen-bonded frameworks and exhibit layer-by-layer stacking, while the other over- or undersized guest molecules of HHF-N14 (10.1 Å), HHF-H17 (8.8 Å), HHF-T (11.1 Å), and HHF-H4 (7.6 Å) display a more disordered crystal structure. We believe the simple method to design energetic materials based on the size matched strategy could promote an ordered hydrogen bonded assembly between energetic molecules, thus displaying layer by layer packing in a solid state and forming a hydrogen bonded framework. And the above additional work also confirms this strategy can be applied more broadly.
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