

Supplementary information for

Symmetrical *cyclo*-N₅⁻ hydrogen bonds: stabilization mechanism of four non-metallic cyclo-pentazolate energetic salts

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Calculation details for Integrate real space functions within RDG and IGM isosurface

Calculation details for SCHBs

Table. S1 Bond, angel of *cyclo-N₅⁻* corresponding to Fig. 2.

| | Bond Length (Å) | | | | | Angel (°) | | | | |
|--|-----------------|-------------|-------------|-------------|-------------|----------------|----------------|----------------|----------------|----------------|
| | l_{N1-N2} | l_{N1-N4} | l_{N2-N3} | l_{N4-N5} | l_{N3-N5} | $a_{N2-N1-N4}$ | $a_{N1-N2-N3}$ | $a_{N1-N4-N5}$ | $a_{N2-N3-N5}$ | $a_{N3-N5-N4}$ |
| PHAC | 1.310 | 1.310 | 1.324 | 1.324 | 1.309 | 107.81 | 108.31 | 108.30 | 107.79 | 107.80 |
| N ₂ H ₅ N ₅ | 1.322 | 1.321 | 1.310 | 1.322 | 1.326 | 107.87 | 108.25 | 108.08 | 108.07 | 107.79 |
| NH ₃ OHN ₅ | 1.320 | 1.314 | 1.322 | 1.321 | 1.318 | 107.91 | 108.23 | 108.24 | 107.92 | 108.11 |
| NH ₄ N ₅ | 1.313 | 1.314 | 1.319 | 1.319 | 1.317 | 108.05 | 108.14 | 108.14 | 107.84 | 107.83 |

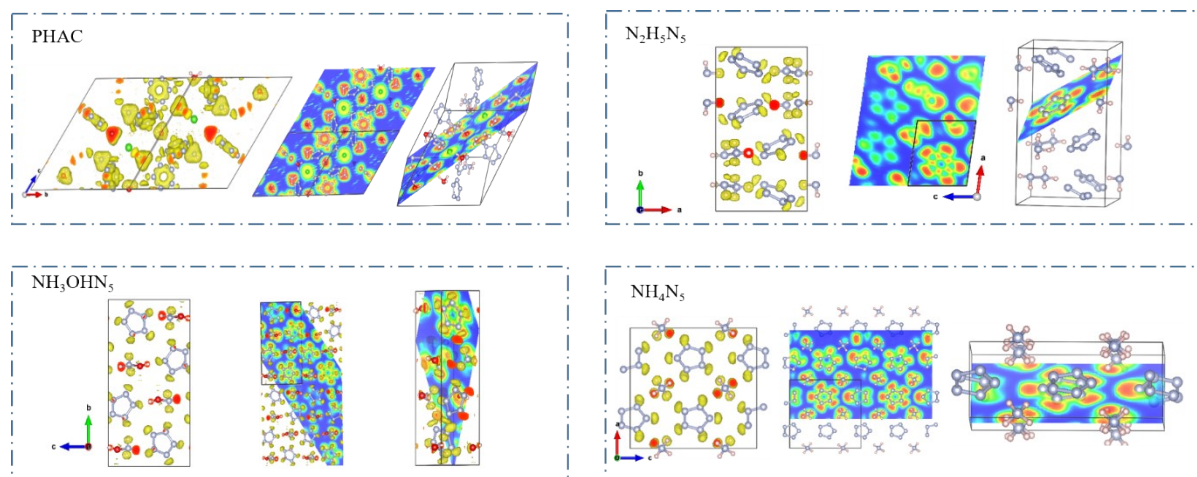


Fig. S1 Electron localization function (ELF) of four cyclo-pentazolate salts. *Cyclo-N₅⁻* rings are selected to make two-dimensional electron distribution plans.

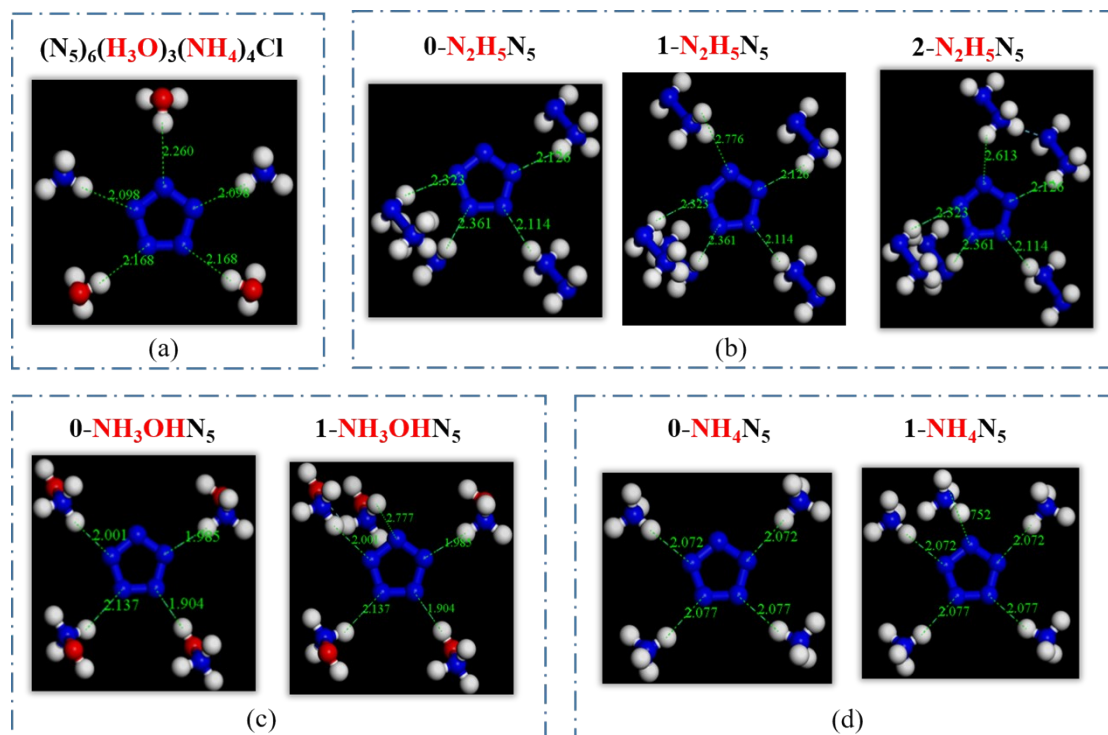
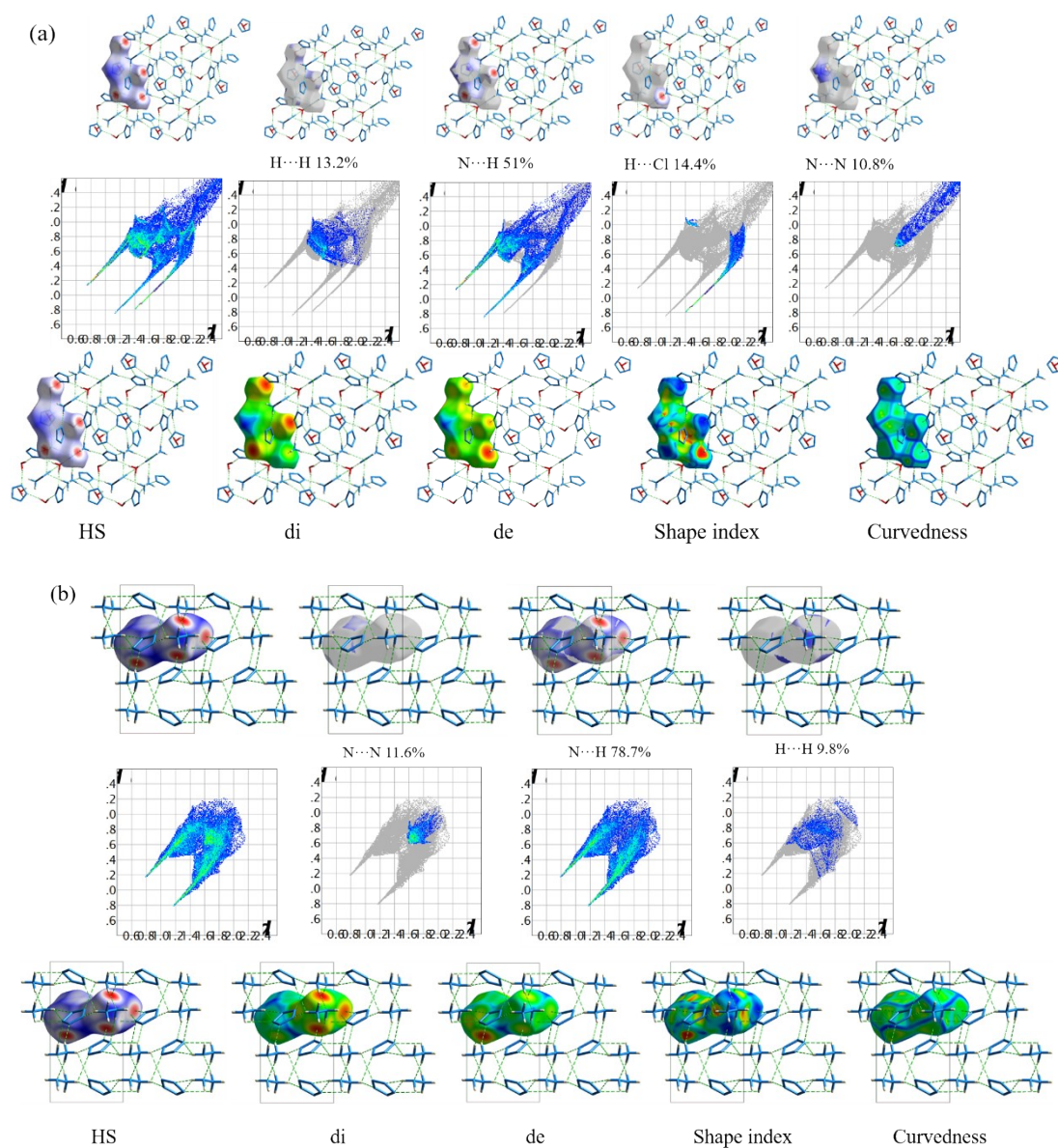


Fig. S2 The models of NICS calculations for PHAC, N₂H₅N₅, NH₃OHN₅ and NH₄N₅, respectively. '0-' indicates

the original models (with four hydrogen bonds around *cyclo-N₅⁻*), '1-' or '2-' both indicate a model obtained by adding the nearest group.

Table. S2 The NICS calculations corresponding to Fig. S2.

| | NICS _{zz} (0)_total | NICS _{zz} (1)_total | NICS(0.6)_total | NICS _{zz} (0.6)_total |
|--|------------------------------|------------------------------|-----------------|--------------------------------|
| PHAC | -36.24 | -43.44 | -20.08 | -49.22 |
| 0-N ₂ H ₅ N ₅ | -37.67 | -43.98 | -19.43 | -50.22 |
| 1-N ₂ H ₅ N ₅ | -36.82 | -43.98 | -19.54 | -50.12 |
| 2-N ₂ H ₅ N ₅ | -36.59 | -43.56 | -19.36 | -49.46 |
| 0-NH ₃ OHN ₅ | -35.21 | -43.09 | -19.52 | -48.67 |
| 1-NH ₃ OHN ₅ | -35.48 | -43.00 | -19.40 | -48.42 |
| 0-NH ₄ N ₅ | -35.91 | -43.44 | -19.58 | -49.03 |
| 1-NH ₄ N ₅ | -35.83 | -43.17 | -19.42 | -48.53 |



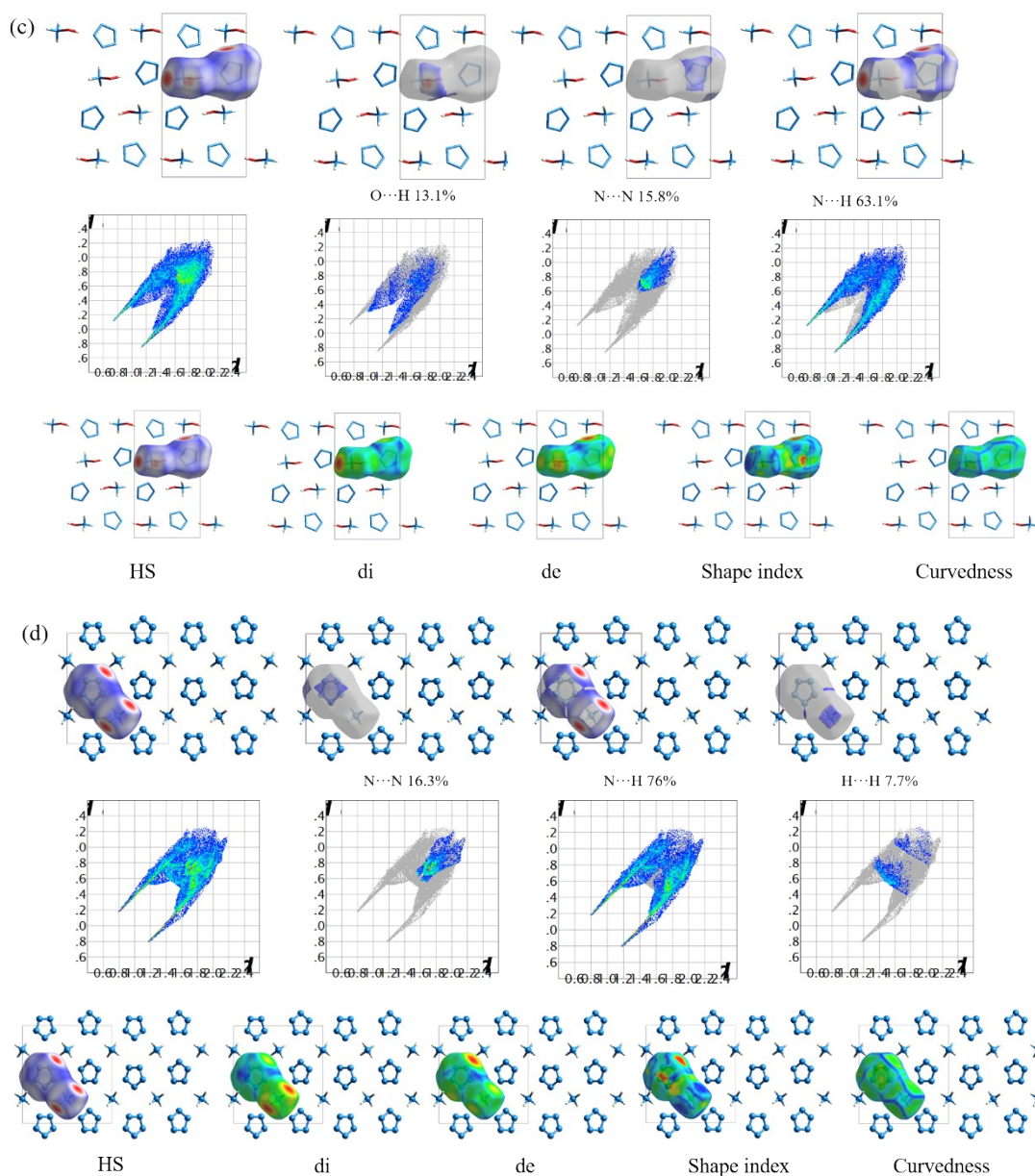


Fig. S3 The Hirshfeld surfaces (d_i surfaces, d_e surfaces, shape index surfaces and curvedness surfaces) of four cyclopentazolate salts. (a) to (d) are the 2D fingerprint plots of PHAC, $N_2H_5N_5$, NH_3OHN_5 and NH_4N_5 , respectively.

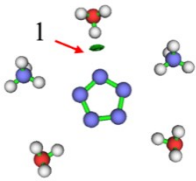
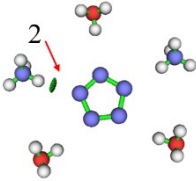
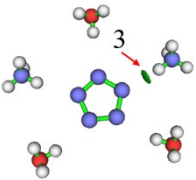
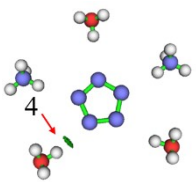
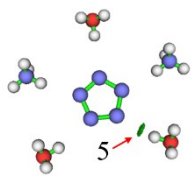
Calculation details for Integrate real space functions within RDG and IGM isosurface:

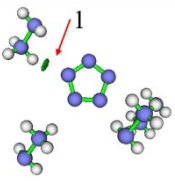
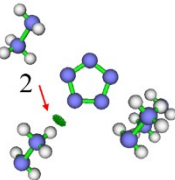
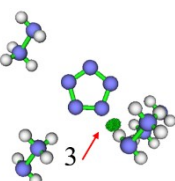
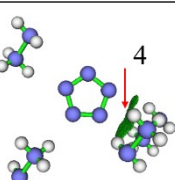
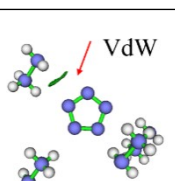
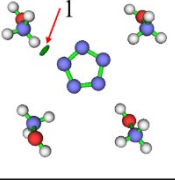
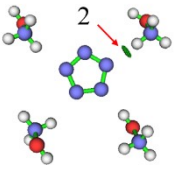
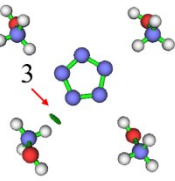
In Multiwfn, it is shown that the possibility of characterizing weak interaction by integrating domains enclosed by RDG isosurfaces. RDG domains defined as regions enclosed by isosurface of $RDG=0.5$, in other words, these domains composed of grid points where $RDG < 0.5$. The RDG isosurfaces, in Fig.6, can help us more accurately grasp the local region of weak interaction, so as to obtain the real space domains of integration. Such calculation results can be adopted to

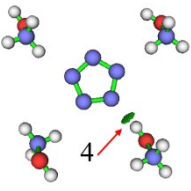
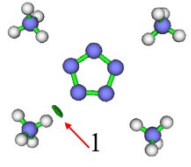
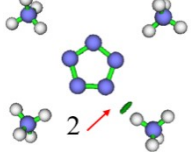
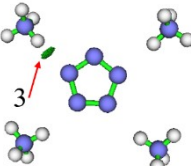
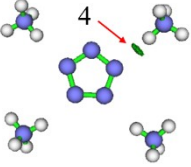
characterize the strength of weak interaction.

From the data in Table S3, we know the number of electrons involved in the weak-interaction domains corresponding to PHAC, $N_2H_5N_5$, NH_3OHN_5 , NH_4N_5 , respectively. They can be interpreted as overlapping electrons and are closely related to strength of same type of interactions (see discussion of DORI original paper *J. Chem. Theory Comput.*, 10, 3745 (2014)). As discussed in Fig. 6, the main interaction mode between *cyclo-N₅⁻* and surrounding cations is hydrogen bond, so the results of integration can reflect the strength of hydrogen bonds in the four samples.

Table S3. The Integrate real space functions within RDG isosurface corresponding to Fig. 6.

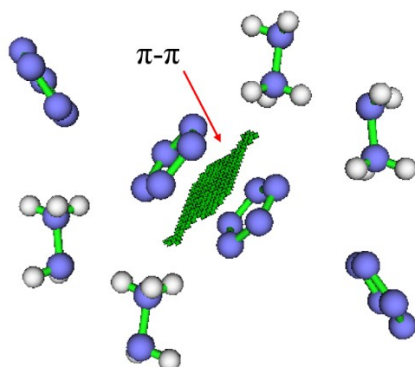
| PHAC | |
|---|--|
|  | Integration result: 0.1295596921E-01 a.u. Volume: 0.318000 Bohr ³ (0.047123 Angstrom ³) Average: 0.4074204886E-01 Maximum: 0.4849435328E-01 Minimum: 0.2994640300E-01 |
|  | Integration result: 0.1469330388E-01 a.u. Volume: 0.320000 Bohr ³ (0.047419 Angstrom ³) Average: 0.4591667246E-01 Maximum: 0.5396869259E-01 Minimum: 0.3886677127E-01 |
|  | Integration result: 0.1467705776E-01 a.u. Volume:0.333000 Bohr ³ (0.049346 Angstrom ³) Average: 0.4407524637E-01 Maximum: 0.5798579916E-01 Minimum: 0.3150220566E-01 |
|  | Integration result: 0.1666905709E-01 a.u. Volume:0.307000 Bohr ³ (0.045493 Angstrom ³) Average: 0.5429660338E-01 Maximum: 0.5996556287E-01 Minimum: 0.4527387071E-01 |
|  | Integration result: 0.1657608903E-01 a.u. Volume: 0.319000 Bohr ³ (0.047271 Angstrom ³) Average: 0.5196266159E-01 Maximum: 0.5999138590E-01 Minimum: 0.4473826720E-01 |
| $N_2H_5N_5$ | |

| | |
|---|--|
|  | <p>Integration result: 0.1427865750E-01 a.u.</p> <p>Volume: 0.342000 Bohr³ (0.050679 Angstrom³)</p> <p>Average: 0.4175045926E-01</p> <p>Maximum: 0.5495345440E-01</p> <p>Minimum: 0.2719047339E-01</p> |
|  | <p>Integration result: 0.1475673743E-01 a.u.</p> <p>Volume: 0.380000 Bohr³ (0.056310 Angstrom³)</p> <p>Average: 0.38833518810E-01</p> <p>Maximum: 0.4699168416E-01</p> <p>Minimum: 0.2583886038E-01</p> |
|  | <p>Integration result: 0.1324281723E-01 a.u.</p> <p>Volume: 0.315000 Bohr³ (0.046678 Angstrom³)</p> <p>Average: 0.4204068898E-01</p> <p>Maximum: 0.4895833122E-01</p> <p>Minimum: 0.2278352612E-01</p> |
|  | <p>Integration result: 0.4248503783E-01 a.u.</p> <p>Volume: 1.497000 Bohr³ (0.221833 Angstrom³)</p> <p>Average: 0.2838011852E-01</p> <p>Maximum: 0.3989898735E-01</p> <p>Minimum: 0.1189547303E-01</p> |
|  | <p>Integration result: 0.1089905582E-01 a.u.</p> <p>Volume: 0.448000 Bohr³ (0.066387 Angstrom³)</p> <p>Average: 0.2432824766E-01</p> <p>Maximum: 0.2996859296E-01</p> <p>Minimum: 0.1647621405E-01</p> |
| NH₃OHN₅ | |
|  | <p>Integration result: 0.1666905723E-01 a.u.</p> <p>Volume: 0.350000 Bohr³ (0.051865 Angstrom³)</p> <p>Average: 0.4762587726E-01</p> <p>Maximum: 0.5498940476E-01</p> <p>Minimum: 0.3727422316E-01</p> |
|  | <p>Integration result: 0.1783238533E-01 a.u.</p> <p>Volume: 0.362000 Bohr³ (0.053643 Angstrom³)</p> <p>Average: 0.4926073210E-01</p> <p>Maximum: 0.5698721184E-01</p> <p>Minimum: 0.2561168482E-01</p> |
|  | <p>Integration result: 0.1407148982E-01 a.u.</p> <p>Volume: 0.343000 Bohr³ (0.050827 Angstrom³)</p> <p>Average: 0.4102474978E-01</p> <p>Maximum: 0.5895624722E-01</p> <p>Minimum: 0.3273103983E-01</p> |

| | |
|---|--|
|  | Integration result: 0.1525075323E-01 a.u. Volume: 0.378000 Bohr ³ (0.056014 Angstrom ³) Average: 0.4034590727E-01 Maximum: 0.4996742261E-01 Minimum: 0.3308902836E-01 |
| NH ₄ N ₅ | |
|  | Integration result: 0.1829452973E-01 a.u. Volume: 0.342000 Bohr ³ (0.050679 Angstrom ³) Average: 0.5318177126E-01 Maximum: 0.5992439528E-01 Minimum: 0.4795236811E-01 |
|  | Integration result: 0.1797580975E-01 a.u. Volume: 0.380000 Bohr ³ (0.056310 Angstrom ³) Average: 0.5092297212E-01 Maximum: 0.5998570272E-01 Minimum: 0.4571100818E-01 |
|  | Integration result: 0.1770489723E-01 a.u. Volume: 0.315000 Bohr ³ (0.046678 Angstrom ³) Average: 0.5269314633E-01 Maximum: 0.5893369746E-01 Minimum: 0.4278352382E-01 |
|  | Integration result: 0.1786425763E-01 a.u. Volume: 1.497000 Bohr ³ (0.221833 Angstrom ³) Average: 0.5316743246E-01 Maximum: 0.5989748932E-01 Minimum: 0.4389649625E-01 |

In the terms of the strength of π - π stacking interaction, we have calculated the electron integral of IGM isosurface, as shown in Fig. S4. From the output we know the number of electrons involved in the domains corresponding to hydrogen bond and π - π stacking interactions are 0.0125~0.0183 a.u. and 0.0802 a.u., respectively. However, since these two domains correspond to different type of weak interactions, the magnitude of overlapping electrons is not perfect positively correlated to their strengths, namely we are unable thus to say that the π - π stacking interaction is stronger than the hydrogen bond. The “Volume” in the output denotes volume of the domain, we can find that π - π stacking interaction involves much wider spatial region than hydrogen bond. “Average” correspond to average value of real space function in the domain, from this quantity one can easily infer that the strength of interaction per contact region of hydrogen bond must be significantly higher than that of π - π stacking interaction, since as shown above, their average values are 0.0407~0.0532 a.u.

and 0.00999 a.u., respectively, the former is much larger than the latter.



Integration result: 0.802250854E-01 a.u.
Volume: 8.030000 Bohr³ (1.189923 Angstrom³)
Average: 0.9990670700E-02
Maximum: 0.1899327362E-01
Minimum: 0.7684506125E-02

Fig. S4 Face-to-face π - π stacking interaction between *cyclo*-N₅⁻ rings in N₂H₅N₅.

Calculation details for SCHBs:

For the calculation of hydrogen bond strength, the method discussed in the Ref.55 was adopted: “*Emamian, S. et al. J. Comput. Chem. 40, 2868-2881 (2019)*”. This work explored the underlying nature of H-bonds (HBs) of different types and strengths and tries to predict binding energies (BEs) based on the properties derived from wave function analysis. A total of 42 HB complexes constructed from 28 neutral and 14 charged monomers were considered. Among various explored correlations between BEs and wave function-based HB descriptors, a fairly satisfactory correlation was found for the electron density at the bond critical point (BCP; ρ_{BCP}) of HBs. The fitted equation for neutral complexes is $BE/\text{kcal/mol} = -223.08 \times \rho_{BCP}/\text{a. u.} + 0.7423$, while that for charged complexes is $BE/\text{kcal/mol} = -332.34 \times \rho_{BCP}/\text{a. u.} - 1.0661$. In this way, ρ_{BCP} can be adopted to estimate the strength of hydrogen bond. The hydrogen bonds in this paper belong to charged hydrogen bonds, thereby, the second formula was adopted. The cluster structures were optimized at B3LYP-D3(BJ)/def-TZVP level, in which the *cyclo*-N₅⁻ and the H atoms in SCHBs were frozen. The single point energy of the optimized structures were calculated at B3LYP-D3(BJ)/ma-TZVP level. The detailed data are seen in Table S4.

Table S4. Calculation Details of SCHBs strength.

| SCHBs | ρ_{BCP} (a.u.) | Strength (kcal/mol) |
|-------|---------------------|---------------------|
|-------|---------------------|---------------------|

| | | | |
|--|---|---------|-------|
| N ₂ H ₅ N ₅ | 1 | -0.0395 | 12.06 |
| | 2 | -0.0404 | 12.36 |
| | 3 | -0.0375 | 11.41 |
| | 4 | -0.0309 | 9.23 |
| NH ₃ OHN ₅ | 1 | -0.0440 | 13.56 |
| | 2 | -0.0462 | 14.29 |
| | 3 | -0.0391 | 11.93 |
| | 4 | -0.0413 | 12.67 |
| NH ₄ N ₅ | 1 | -0.0470 | 14.58 |
| | 2 | -0.0470 | 14.58 |
| | 3 | -0.0463 | 14.31 |
| | 4 | -0.0463 | 14.31 |

To verify the reliability of the calculation results, we calculated the hydrogen bond strength of PHAC by the same method (Table S5), with an error of - 5% to -2% compared with that reported in article *b*. The small discrepancy there by confirmed the reliability of the current calculation. In article *b*, the highest hydrogen bond strength of PHAC is 13.26 kcal/mol. Because the electrostatic interaction strength of charged hydrogen bonds is higher than that of uncharged hydrogen bonds, the hydrogen bond strength obtained in this paper will be higher. The results are reasonable.

Table S5. Calculation Details of SCHBs in PHAC.

| | SCHBs | ρ_{BCP} (a.u.) ^a | Strength (kcal/mol) ^a | Strength (kcal/mol) ^b | Error (%) |
|------|-------|----------------------------------|----------------------------------|----------------------------------|-----------|
| PHAC | 1 | -0.0370 | 11.23 | 11.81 | -5.16 |
| | 2/3 | -0.0402 | 12.31 | 12.06 | 2.03 |
| | 4/5 | -0.0440 | 13.56 | 13.26 | 2.21 |

^a Results in this paper. ^b The results in paper “Jiang, C. *et al*, *Science* 359, 6381 (2018).”