

Supporting Information for

**Two Stacking Types of Three-Dimensional Structure
Cocrystals Based on Multiple Hydrogen Bonds**

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Supporting Information (SI)

Methods

Chemicals

All starting materials and solvents, unless otherwise specified, were purchased from Aladdin and used without prior purification.

Syntheses of Phpm

TTCA (0.177 g, 1 mmol) was dispersed in 20 mL of ethanol and HMTA (0.140 g, 1 mmol) was dispersed in 20 mL of deionised water. The two solutions then mix and instantly turn white and cloudy. After 1 min, the white product was centrifuged, collected, washed three times with ethanol–water (v/v=1:1) and then dried in an oven at 338 K. The sample was named Phpm.

For comparison, there is no crystals through the similar synthetic procedure of Phpm using 0.129 g of cyanuric acid (CA) instead of the TTCA precursor.

Syntheses of Phpm-o

TTCA (0.177 g, 1 mmol) was dispersed in 10 mL of deionised water, dissolved by adding $\text{NH}_3 \cdot \text{H}_2\text{O}$ (wt ~ 25%, 500 μL) and then stirred for 5 min with magnetic stirring. Then formaldehyde (wt ~ 37 - 40%, 2 mL) was added to the above solution. After 1 min, the white product was centrifuged, collected, washed three times with ethanol–water (v/v=1:1) and then dried in an oven at 338 K. The sample was named Phpm-o.

For comparison, there is no crystals through the similar synthetic procedure of Phpm-o using 0.129 g of cyanuric acid (CA) instead of the TTCA precursor.

Syntheses of Phpm-p

TTCA (0.177 g, 1 mmol) was completely dissolved in 10 mL of deionised water, then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (wt ~ 25%, 500 μL) was added and well mixed by sonication. The clear solution is then passed through a 0.22 μm pillow filter membrane. Then sodium formate solution (5.3 M, 500 μL) was added to the above solution. Then formaldehyde (wt ~ 37 - 40%, 200 μL) was added and placed in an oven at 358 K Celsius for static incubation, and the resulting large size crystals were named Phpm-p.

Syntheses of Phpm-h

TTCA (0.177 g, 1 mmol) was dispersed in 30 mL of deionised water, dissolved by adding $\text{NH}_3 \cdot \text{H}_2\text{O}$ (wt ~ 25%, 1500 μL) and then stirred for 5 min with magnetic stirring. Then formaldehyde (wt ~ 37 - 40%, 2 mL) was added to the above solution. After 5 min, the white product was centrifuged, collected, washed three times with ethanol–water (v/v=1:1) and then dried in an oven at 338 K. The sample was named Phpm-h.

Syntheses of Phpm-o-s

TTCA (0.177 g, 1 mmol) was dispersed in 20 mL of methanol, dissolved by adding $\text{NH}_3 \cdot \text{H}_2\text{O}$ (wt ~ 25%, 500 μL) and then stirred for 5 min with magnetic stirring. Then formaldehyde (wt ~ 37 - 40%, 2 mL) was added to the above solution. After 1 min, the white product was centrifuged, collected, washed three times with ethanol–water (v/v=1:1) and then dried in an oven at 338 K. The sample was named Phpm-o.

Syntheses of Phpm-h-p

TTCA (0.177 g, 1 mmol) was completely dissolved in 20 mL of deionised water, then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (wt ~ 25%, 500 μL) was added and well mixed by sonication. Then sodium formate solution (5.3 M, 3, 5, 7 mL) was added to the above solution. Then formaldehyde (wt ~ 37 - 40%, 2 mL) was added

and placed in an oven at 358 K Celsius for static incubation, and the resulting large size crystals were named Phpm-h-p.

Single Crystal XRD Studies

The crystals of suitable dimension and good quality were chosen for viewing under a microscope equipped. A suitable crystal was selected and placed on the goniometer of a 'Bruker APEX-II CCD' diffractometer equipped with a microfocus Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The X-ray intensity data were collected at 120.0 K, and the process was smooth in all cases. No additional precautions were necessitated, as the crystals were quite stable. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Powder X-ray diffraction

PXRD measurements were performed on a Bruker D8 ADVANCE Powder X-ray Diffractometer using Cu K α radiation (40 kV, 40 mA) at room temperature, from $2\theta = 5^\circ$ to 70° (2θ , the angle between the transmitted beam and reflected beam) with a 0.01° increment.

Structural modelling of Phpm-o

The cell parameters of Phpm-o, tested by the PXRD many times, refinement fitting by the INDEXING method of DIFFRAC.TOPAS software to obtain the crystal structure. Then the theoretical structural modelling of Phpm-o was carried out using the software package Materials Studio (v.20.1, Accelrys Software).

Density functional theory calculations

First-principles density functional theory calculations were performed using the Castep software (Materials Studio, v.18.1, Accelrys Software). A semi-empirical addition of dispersive forces to conventional density functional theory (TS) was included in the calculation to account for van der Waals interactions. The generalized gradient approximation with Perdew-Burke-Ernzerhof exchange correlation were used. A cut-off energy of 517 eV and a $1 \times 1 \times 1$ k -point mesh were found to be enough for the total energy to converge within 0.01 meV per atom. The specific parameter settings and convergence conditions are shown in Fig. S5 and Fig. S6.

Hirshfeld Surface Analysis

Hirshfeld surfaces with d_{norm} plots and their associated two-dimensional fingerprint plots were generated using Crystal Explorer 21.3 software¹. The normalized contact distance (d_{norm}) is a symmetric function of distances to the surface from nuclei inside and outside of the Hirshfeld surface (d_i and d_e , respectively) relative to their respective van der Waals radii. The 2D fingerprint plots provide information about the relative contributions in the Hirshfeld surfaces of the different intermolecular interactions present in the crystal structure. A color scale represents to visualize the strength of the interactions; red, strong acceptor donor interactions ($<$ sum of van der Waals radii); white, van der Waals interaction ($=$ sum of the van der Waals radii); blue, longer than the sum of the van der Waals radii.

Computation of Morphologies (BFDH Method)

Using the morphology prediction modules available within Materials Studio software, Bravais-Friedel-Donnay-Harker (BFDH) morphologies are computed for all structures.

Fourier transform infrared spectroscopy

FT-IR spectra were recorded on a Thermo Fisher Nicolet iN10 Fourier Transform Microscopic infrared spectrometer using KBr pellets.

Solid-state NMR spectroscopy

Solid-state ^{13}C CP/MAS NMR spectra were measured on an Agilent DD2–500 MHz system (125.7 MHz, with a spinning rate of 10 kHz, 1000 scans, a 4 s pulse delay, and a contact time of 4 ms).

Field-emission scanning electron microscopy

Field-emission scanning electron microscopy images were taken on a Nova Nano-SEM 450 operating at an accelerating voltage of 3.0 kV. The samples were prepared by drop-casting ethanol suspension onto a silica wafer and were coated with gold.

Transmission electron microscopy

The images for transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and element distribution mapping were analyzed and photographed using a HT7700 EXALENS and a JEOL Model JEM-F200 Fe-SEM system (200 kV), respectively.

Elemental analysis

The elemental content of all tested samples was analyzed by Vario EL cube element analyzer.

X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) analysis was determined by using the ESCALAB Xi+ equipment

TGA-DSC

The thermal gravimetric analyses-Differential Scanning Calorimetry (TGA-DSC) analysis was determined by using the STA449F3-QMS 403 equipment, and the heating rate was $10\text{ }^{\circ}\text{C min}^{-1}$ ($20\text{ }^{\circ}\text{C}$ - $700\text{ }^{\circ}\text{C}$).

Nitrogen sorption isotherms

The isotherm of nitrogen adsorption and desorption (77 K) and porosity information were measured by Beishide apparatus.

Supporting Figures and Tables

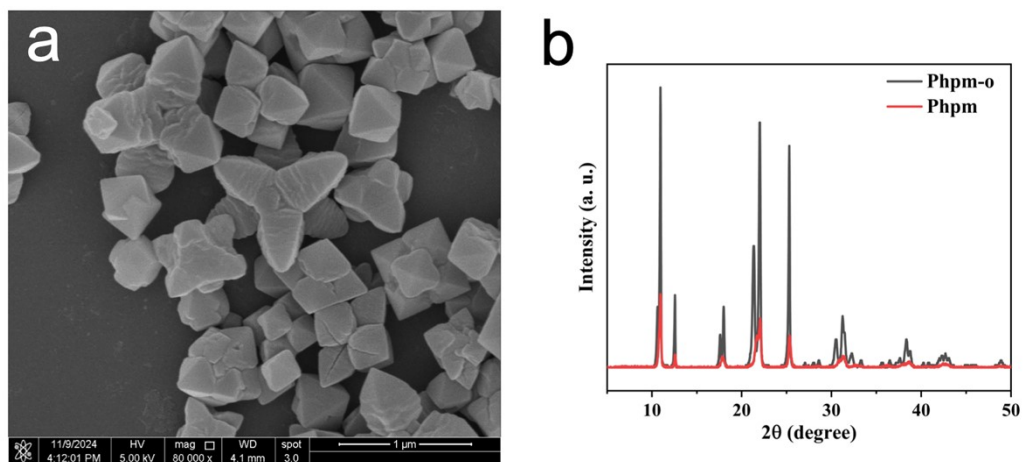


Fig. S1 (a) The SEM of Phpm, (b) The PXRD of Phpm and phpm-o

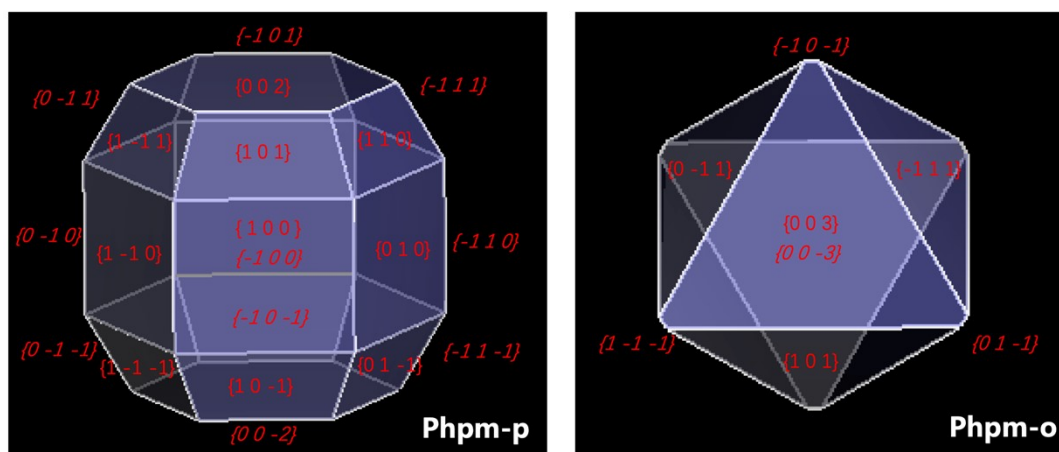


Fig. S2 The computed BDFH morphologies in the crystal structure of Phpm-o and Phpm-p

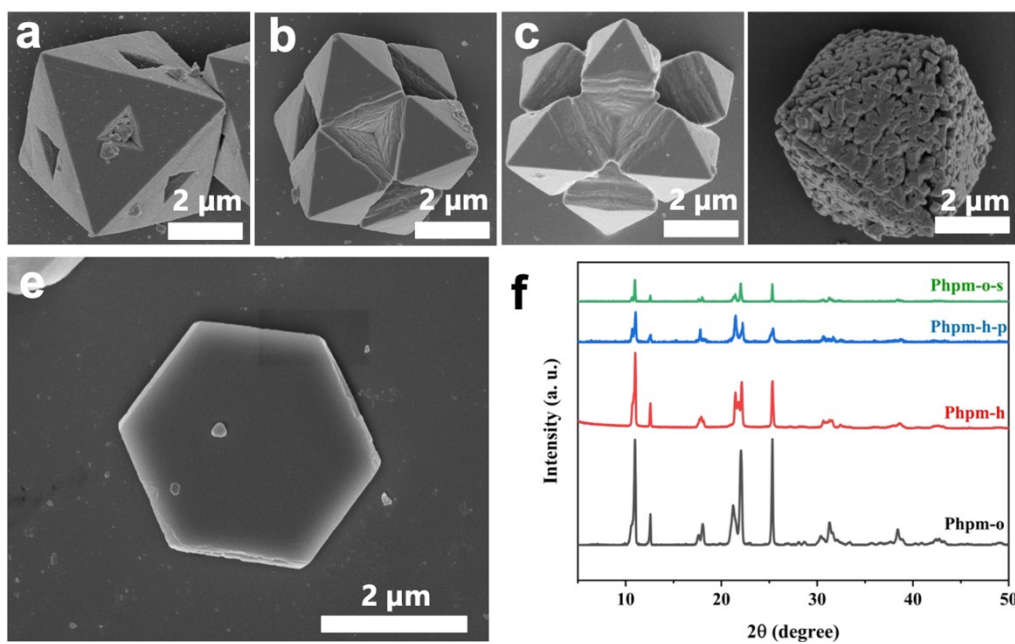


Fig. S3 The SEM of (a, b, c) Phpm-h-p, (d) Phpm-o-s and (e) Phpm-h, (f) The PXRD of Phpm-o, Phpm-h, Phpm-h-p and Phpm-o-s.

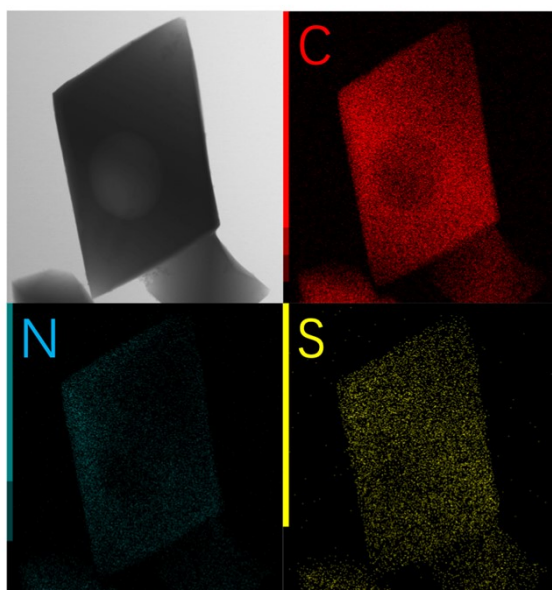


Fig. S4 The element distribution mapping corresponding to Phpm-o.

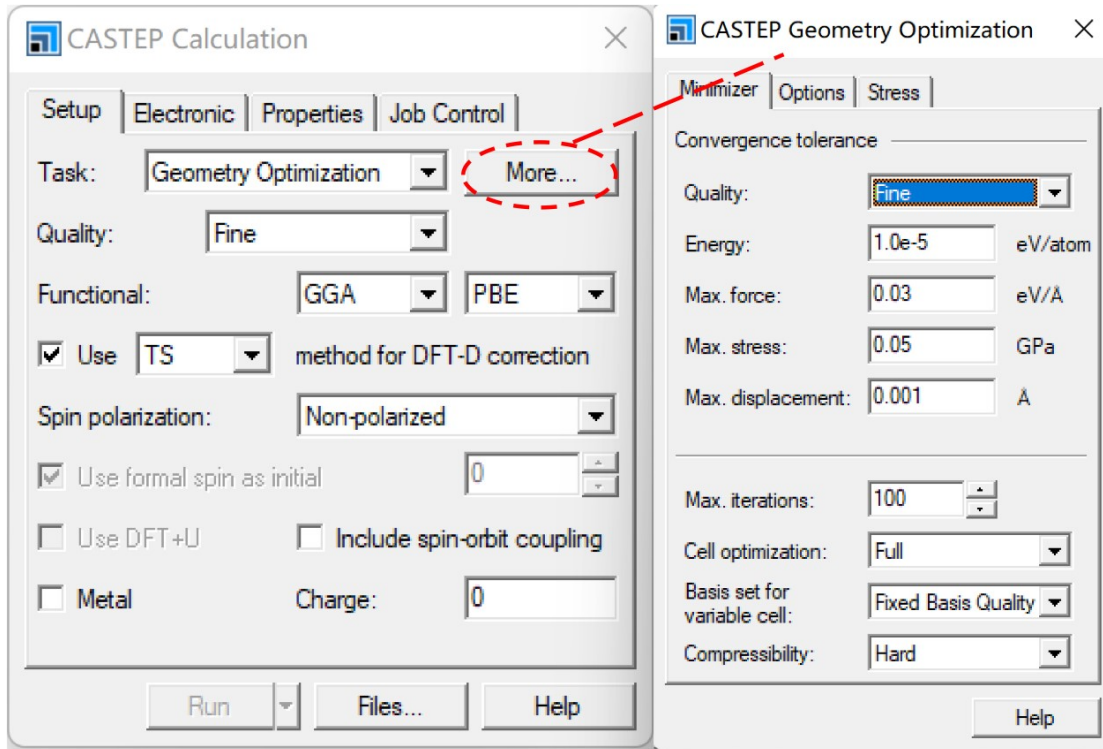


Fig. S5 The element distribution mapping corresponding to Phpm-o.

Parameter	value	tolerance	units	OK?	<-- LBFGS
dE/ion	9.705237E-007	1.000000E-005	eV	Yes	<-- LBFGS
F max	1.188148E-002	3.000000E-002	eV/A	Yes	<-- LBFGS
dR max	6.161717E-004	1.000000E-003	A	Yes	<-- LBFGS
Smax	1.621179E-002	5.000000E-002	GPa	Yes	<-- LBFGS

LBFGS: Geometry optimization completed successfully.

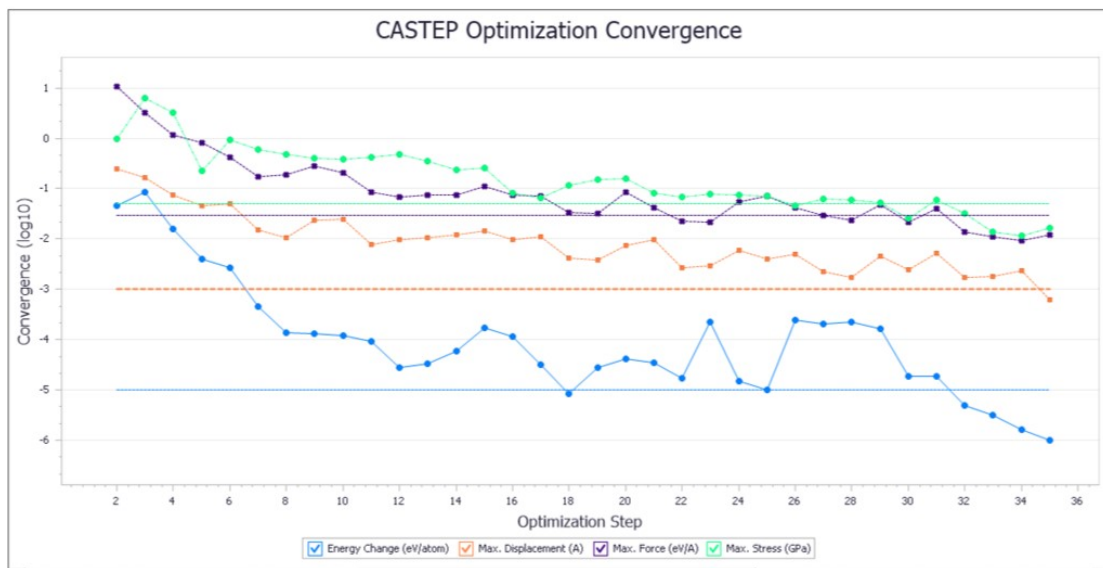


Fig. S6 The element distribution mapping corresponding to Phpm-o.

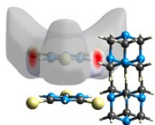
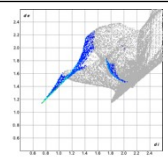
Table S1 Elemental Analysis of the Phpm-o

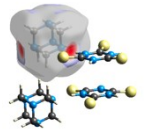
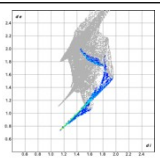
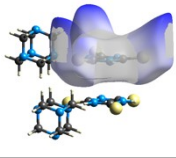
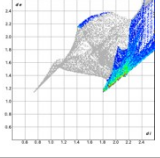
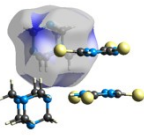
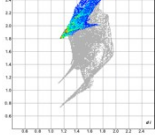
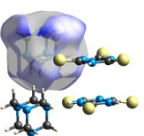
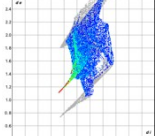
Elements	C	N	S	H
Contents (%)	33.54	29.85	31.69	4.92
Molar ratio	C : N : S : H = 1: 0.76: 0.36: 1.76			

Table S2 Crystallographic Information

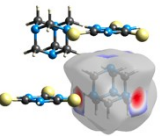
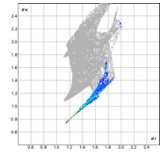
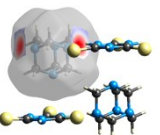
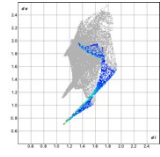
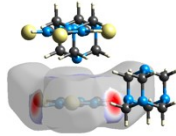
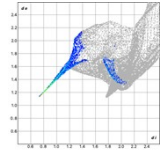
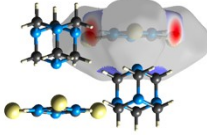
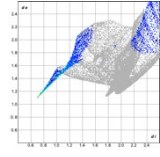
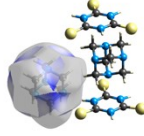
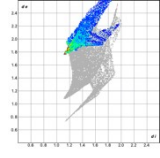
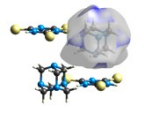
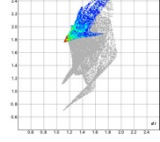
	Phpm-p	Phpm-o
Formula	$C_{18}H_{30}N_{14}S_6$	$C_9H_{15}N_7S_3$
Molecular weight	634.92	
T/K	120	273
Crystal system	hexagonal	trigonal
Space group	$P 63 mc$	R3
a/Å	9.6534(18)	9.7700
b/Å	9.6534(18)	9.7700
c/Å	16.438(5)	25.7744
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	120	120
Volume/Å ³	1326.6(6)	2130.6
Z	2	
D _{calc} /(g·cm ⁻³)	1.589	1.484
F(ooo)	664	
R	0.0455	
wR ²	0.1140	
CCDC Number	2368641	

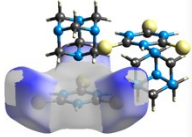
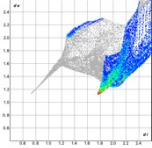
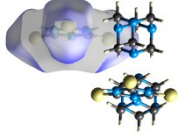
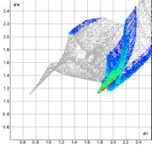
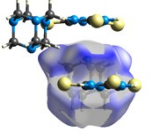
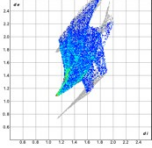
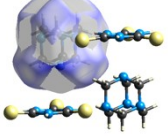
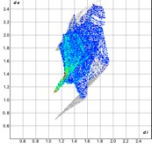
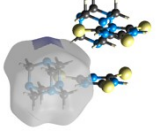
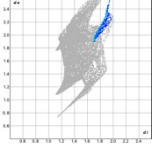
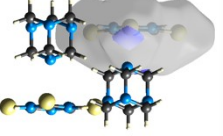
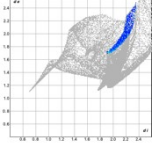
Finger print plots of Phpm-o.

	molecular	Hirshfeld surfaces	
N-H...N	TTCA		

	HMTA		
C-H...S	TTCA		
	HMTA		
C-H...H-C	HMTA		

Finger print plots of Phpm-p.

Cocrystal		Hirshfeld surfaces	
N-H...N	HMTA-layer-1		
	HMTA-layer-2		
	TTCA-layer-1		
	TTCA-layer-2		
C-H...S	HMTA-layer-1		
	HMTA-layer-2		

	TTCA-layer-1		
	TTCA-layer-2		
C-H...H-C	HMTA-layer-1		
	HMTA-layer-2		
S...N	HMTA-layer-1		
	TTCA-layer-2		

1. P. R. Spackman, M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, D. Jayatilaka and M. A. Spackman, *J Appl Crystallogr*, 2021, **54**, 1006-1011.