Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

S1. Methods for the selection of dimer configurations

The Genmer module in Molclus[1] is developed to produce any proportion of molecules in a multimer configuration. Based on the consideration of oxygen balance calculation and computational time consumption, the dimer configurations of NTO and AP are selected for the investigation. The principle of the Genmer module is to insert molecules into the center of a sphere in space from random radial directions. This model-building method can simulate almost all possible orientations (stable or unstable) between two molecules while a large number of configurations are generated.

Initial configurations are submitted to xtb for preliminary optimization using gfn2-xtb[2], which can quickly exclude those unstable structures, and the remaining 16 configurations were subjected to more accurate quantum chemistry calculations and subsequently classified into five configurations. If the configuration and energy are regarded as a function, then these five configurations are the five local minima of this function, representing the configurations that may occur when NTO interacts with AP.

Table S1 The Oxygen balance of NTO and AP composite with different ratios.

Ratio (NTO:AP)	Oxygen balance
4:1	-12.88
3:1	-9.95
2:1	-5.06
1:1	4.71
1:2	14.49
1:3	19.38
1:4	22.31

Fig. S1 The selection process of the dimer configurations of NTO and AP.

S2. Methods for the selection of co-crystal structure

The energy calculation method of Polymorph module uses classical force fields, so its accuracy in generating structures needs to be verified and the generated structures need to be optimized. First, the reliability of PBE-D3(BJ)/TZVP-GTH[3, 4] in optimizing NTO and AP unit cells is verified, the experimental cell parameters data are obtained from CCDC[5, 6]. As shown in Table S2, the optimized unit cell parameters were consistent with the experimental values, which proves that PBE-D3(BJ)/TZVP-GTH level is able to obtain reasonable unit cells. To verify the reliability of Polymorph module, 6 of the lowest energy co-crystal structures are selected for optimization and energy calculation at the PBE-D3(BJ)/TZVP-GTH level. The co-crystal structure with the lowest energy was used for further properties predictions.

Fig. S2 The selection process of the NTO/AP co-crystal structures

Table S2 Comparison of cell parameters of NTO and AP crystals from experiment and calculation.

		a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ (°)
NTO	Experiment	5.134	10.338	18.023	106.58	97.61	90.30
	Calculation	5.157	10.489	18.740	106.31	95.01	90.27
	Error (%)	0.448	1.461	3.978	-0.253	-2.664	-0.033
AP	Experiment	9.220	7.458	5.814	90	90	90
	Calculation	9.276	7.483	5.795	89.88	89.67	89.81
	Error (%)	0.607	0.335	-0.327	-0.133	-0.367	-0.211

S3. Statistical methods for thermal decomposition products

The statistics of decomposition products are done by applying a Tool Command Language (TCL) script of the vmd program, which contains defined bonding criteria. Since the statistical object is an instantaneous frame of the NTO/AP co-crystal system in AIMD simulation, at which time the chemical bond in the product may be in the state of being formed, the bonding criteria are set to be a little larger than the bond length in the product molecule under normal conditions, and the specific bonding criteria is as follows.

Table S3 Bonding criteria for defining decomposition products.

Atom pairs	Bond length (Å)
O-H	1.2
N-H	1.3
C-O	1.3
N-N	1.2
N-O	1.5

Even so, there are statistical fluctuations in the number of products in the statistics, which are not caused by the actual generation or disappearance of the product. Therefore, the data are smoothed to show the changing trend of the product more clearly.

S4. Hugoniot temperature

As shown below, the Hugoniot temperature of each specific volume of NTO/AP co-crystal is determined by the intersection point of the linear fitting line and the parallel line with Hg equal to 0. The equation of the fitting line and the R^2 values are marked in the figure, and the R^2 value close to 1 indicates the reliability of the line fitting.

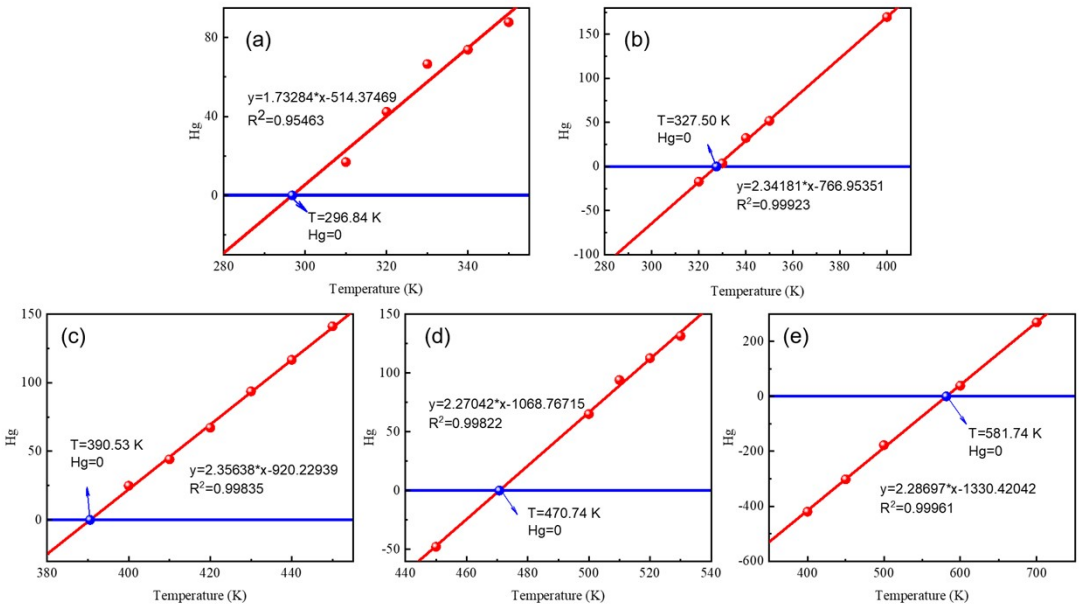

Fig. S3 Hugoniot temperatures of NTO/AP co-crystals with different volumes obtained by line fitting.

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