

Supporting info for:

Control of supramolecular chirality in co-crystals of achiral molecules via stacking interactions and hydrogen bonding.

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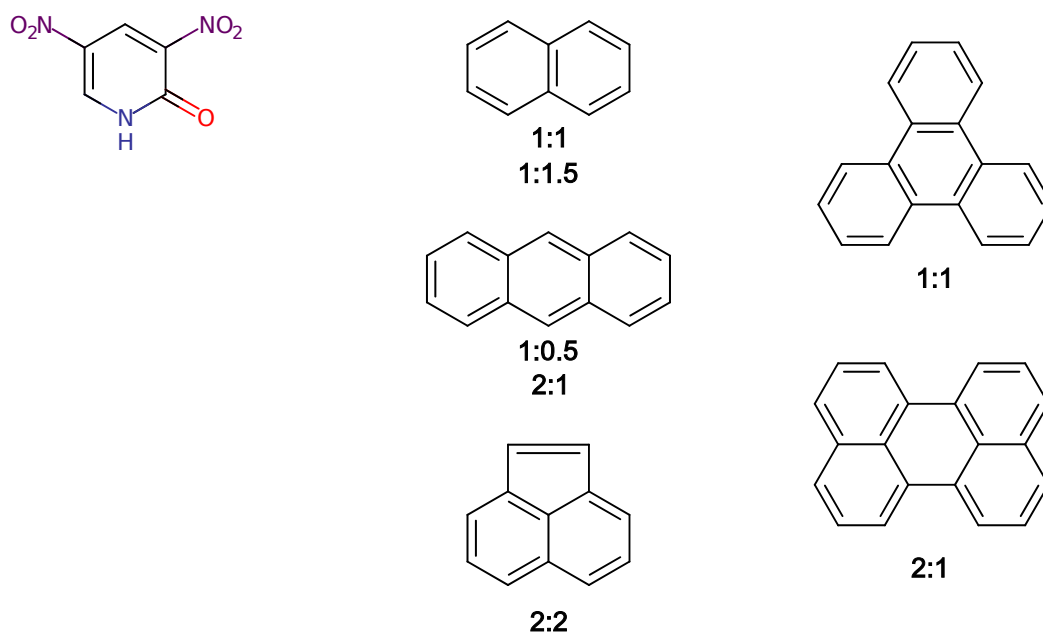
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1. Co-formers used for crystallization



Scheme S1. Molecules used for co-crystallization. The numbers denote the composition of the resulting structure.

2. Crystallographic data for co-crystals

Table TS1: Experimental crystallographic data and refinement parameters for co-crystals.

	NFT-I^(a)	NFT-II^(a)	ANT-I^(b)	ANT-II^(b)	ACNFT	TPH	PRL
Composition: DNP2O:PAH ^(c)	1:1	1:1.5	1:0.5	2:1	2:2	1:1	2:1
CCDC	2123841	2123844	2123846	2123842	2123845	2123843	2123847s
Formula	C ₁₅ H ₁₁ N ₃ O ₅	C ₂₀ H ₁₅ N ₃ O ₅	C ₂₄ H ₁₆ N ₆ O ₁₀	C ₂₄ H ₁₆ N ₆ O ₁₀	C ₁₇ H ₁₁ N ₃ O ₅	C ₂₃ H ₁₅ N ₃ O ₅	C ₃₀ H ₁₈ N ₆ O ₁₀
Formula weight	313.27	377.35	548.43	548.43	337.29	413.38	622.50
T, K				120			
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
Z / Z'	2 / 1	2 / 0.5	2 / 0.5	4 / 1	4 / 2	4 / 1	4 / 1
a, Å	7.1368(3)	6.9648(2)	11.3941(2)	20.2772(5)	7.9898(3)	7.6442(3)	13.6099(8)
b, Å	7.7530(3)	8.0641(2)	8.2165(2)	6.5794(2)	7.0018(3)	8.6092(3)	8.6026(5)
c, Å	12.3724(5)	30.4792(7)	12.7470(2)	17.0425(4)	25.9225(11)	27.0462(9)	21.6767(13)
β, °	99.282(2)	91.7020(10)	107.6050(10)	92.2871(16)	91.907(2)		90.440(3)
V, Å ³	675.62(5)	1711.10(8)	1137.48(4)	2271.86(10)	1449.38(10)	1779.92(11)	2537.8(3)
d _{calc} , g cm ⁻³	1.540	1.465	1.601	1.603	1.546	1.543	1.629
Radiation type	MoKα	CuKα	CuKα	CuKα	CuKα	MoKα	CuKα
Flack parameter	0.11(15)				0.00(7)	0.3(2)	
μ, cm ⁻¹	1.19	8.99	10.98	11.00	9.86	1.11	10.70
2θ _{max} , °	87	146	145	136	145	70	146
Reflns. collected	37496	42289	21350	24792	36677	44112	57378
Reflns. independent	10091	42289	2197	4037	5376	7853	5019
Observed reflections [I > 2σ(I)]	8667	39193	2126	3159	5351	6771	4734
No. of parameters	212	258	186	369	460	284	423
R ₁	0.0431	0.0383	0.0338	0.0375	0.0318	0.0416	0.0546
wR ₂	0.1088	0.1103	0.0844	0.0949	0.0886	0.1023	0.1398
GOF	1.015	1.049	1.005	1.048	1.001	0.996	1.075
Residual density, e Å ⁻³ (d _{max} /d _{min})	0.694/-0.233	0.198/-0.257	0.319/-0.209	0.195/-0.239	0.198/-0.246	0.408/-0.211	0.564/-0.310
Twin law(d)		1 0 0 0 1 0 0 -0.29 1			1 0 0 0 -1 0 -0.22 0 -1		
BASF		0.39			0.49		

(a) Two NFT co-crystals with different composition.

(b) Two polymorphic ANT co-crystals.

(c) Number of crystallographically independent molecules is used.

(d) Twin laws, as refined by SAINT, rounded to the 2nd decimal place.

3. Details of DFT calculations

The density functional theory (DFT) calculations of crystal structures were performed with CRYSTAL17 software suite. The PBE0 functional with the third version of dispersion correction and Becke-Johnson damping, PBE0-D3(BJ), was used in combination with POB-TZVP basis set specially designed for solid state calculations. Atomic coordinates were optimized using experimental unit cell parameters and symmetry (CSD refcodes for known structures: JERVUY01 for **DNP2O**, TRIPHE15 for **TPH**; NAPHTA15 for **NFT**). Shrinking factor 4 4 4 was used for Monkhorst–Pack grid, yielding 30 k -points in the irreducible Brillouin zone for **NFT** and its co-crystals and 27 k -points for **TPH**, its co-crystal and **DNP2O** crystal. For calculation of the lattice energy the wave functions of the isolated molecules in crystal geometry were computed. The energy of 1D periodic systems was calculated using $P112_1$ (for H-bonded chains) and $P1$ (for stacks) groups, with atomic coordinates from the crystals structure optimization.

The correction for basis set superposition error (BSSE) was applied by means of the counterpoise technique. A molecular calculations were performed, with a basis set including the basis functions of the selected molecule and of some of the neighbouring atoms. Then, the correction was calculated as:

$$E_{\text{BSSE}} = (E_{\text{isol}} - E_{\text{isol,disp}}) - E_{\text{ghosts}} \quad ,$$

where E_{BSSE} is the BSSE correction, E_{isol} is the energy of the selected isolated molecule, E_{ghosts} is the energy of the isolated molecule with the additional basis functions. Note that the empirical dispersion correction energy $E_{\text{isol,disp}}$ is not calculated by CRYSTAL17 in the presence of additional basis functions, so its value has to be subtracted from E_{isol} .

For crystals, E_{ghosts} was calculated in an automated fashion using the MOLEBSSE keyword; basis functions of all atoms within the radius of 9.5 Å were included in the calculations. For 1D synthons additional basis functions were placed in the atomic positions of four neighbouring molecules in the chain or stack (two from each side) with the GHOSTS keyword.

The lattice energy was calculated as

$$E_{\text{latt}} = E_{\text{cry}} - E_{\text{isol}} + E_{\text{BSSE}} \quad ,$$

where E_{cry} is the total energy of the optimized crystal structure, E_{isol} is the energy of the isolated molecule with the geometry obtained from the optimized crystal structure. The binding energy of the 1D synthons was calculated in the same fashion by using E_{synton} instead of E_{cry} .

The cohesion energy was calculated as

$$E_{\text{coh}} = E_{\text{cry}} - E_{\text{opt}} + E_{\text{BSSE}} \quad ,$$

where E_{opt} is the total energy of the optimized isolated molecule. The deformation energy $E_{\text{def}} = E_{\text{opt}} - E_{\text{isol}}$ corresponds to the energy difference between the optimized isolated molecule and the isolated molecule in the crystal geometry.

Table TS2. Cohesion energies, lattice energies of crystal structures and interaction energies in supramolecular synthons (kcal/mol), calculated at PBE0-D3/POB-TZVP level.

Structure	DNP2O	NFT	TPH	DNP2O·NFT-I	DNP2O·NFT-II	DNP2O·TPH
Lattice energy (E_{latt})	38.7	17.1	24.9	55.0	62.3	64.6
Cohesion energy (E_{coh})	36.2	16.8	24.2	52.6	59.6	62.1
Binding energy (chain)				19.9	19.6	18.6
Binding energy (stack)				18.5	18.2	21.2

4. Diagrams of the possible arrangement of molecules in co-crystals in some space groups.

The following figures are intended to illustrate possible arrangement of molecules in a co-crystal in six selected space groups. The schematic representation of molecules is drawn together with the space group diagrams. In all figures acceptor molecules are schematically drawn in red, and donor molecules are drawn in blue. Molecules below the drawing plane are shown with faded colours. Pseudo-3D elements are used to encode the tilt of the molecules relative to the drawing plane.

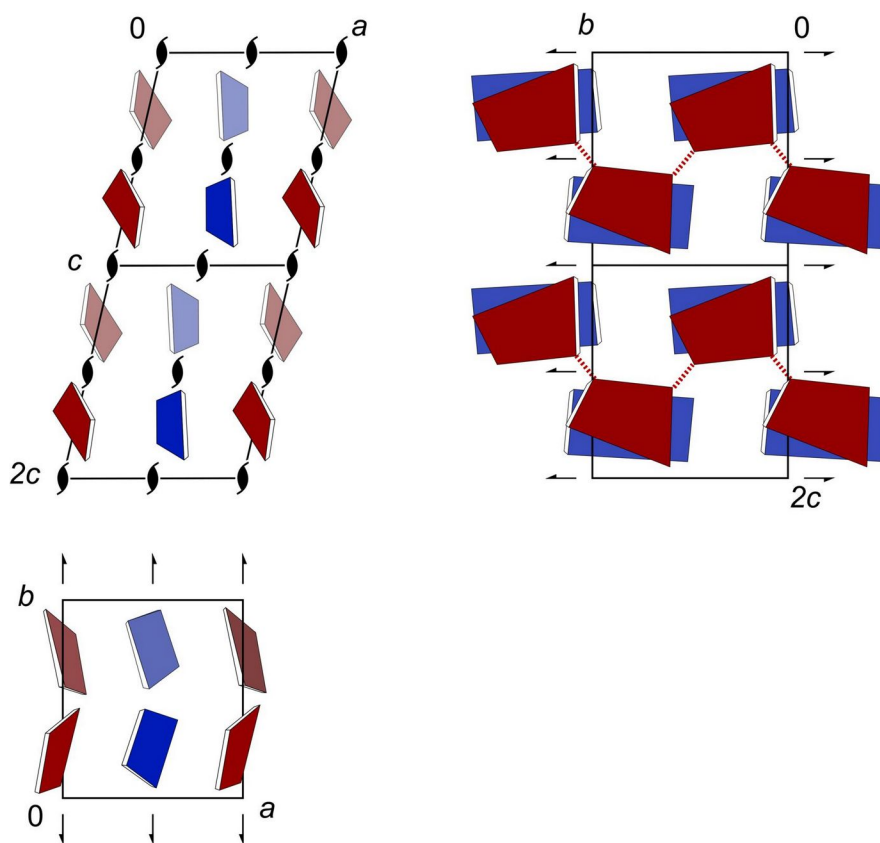


Fig. S1. Arrangement of the co-crystals components in space group $P2_1$ in three projections. The unit cell is doubled in c direction for comparison with all other groups.

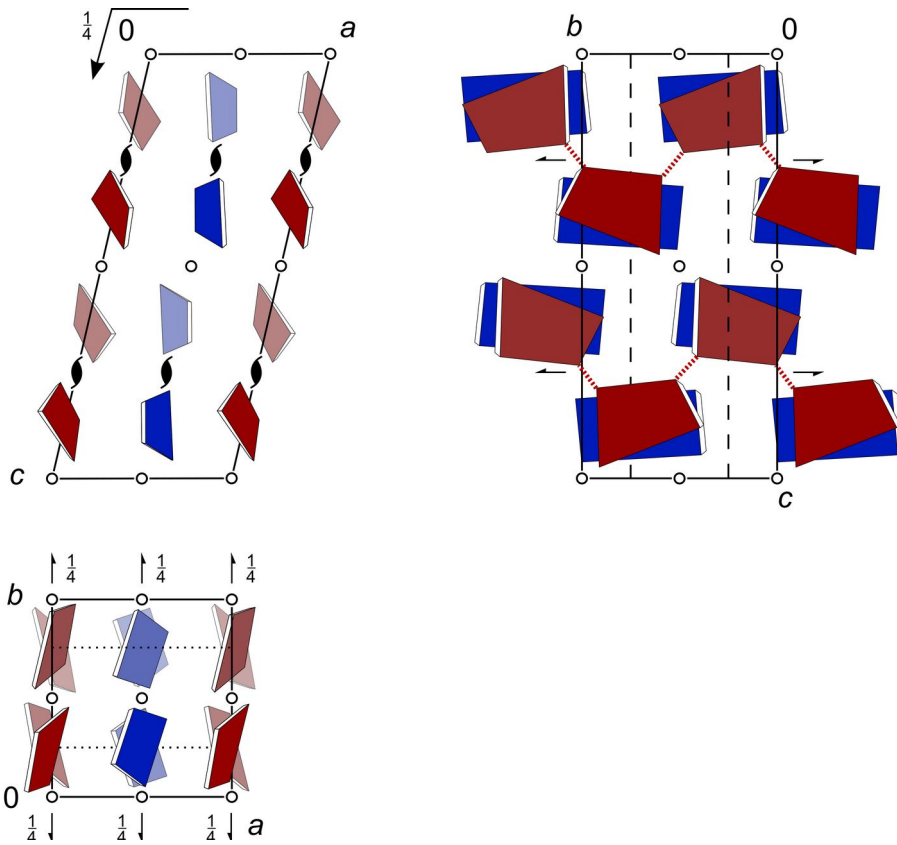


Fig. S2. Arrangement of the co-crystals components in space group $P2_1/c$ in three projections.

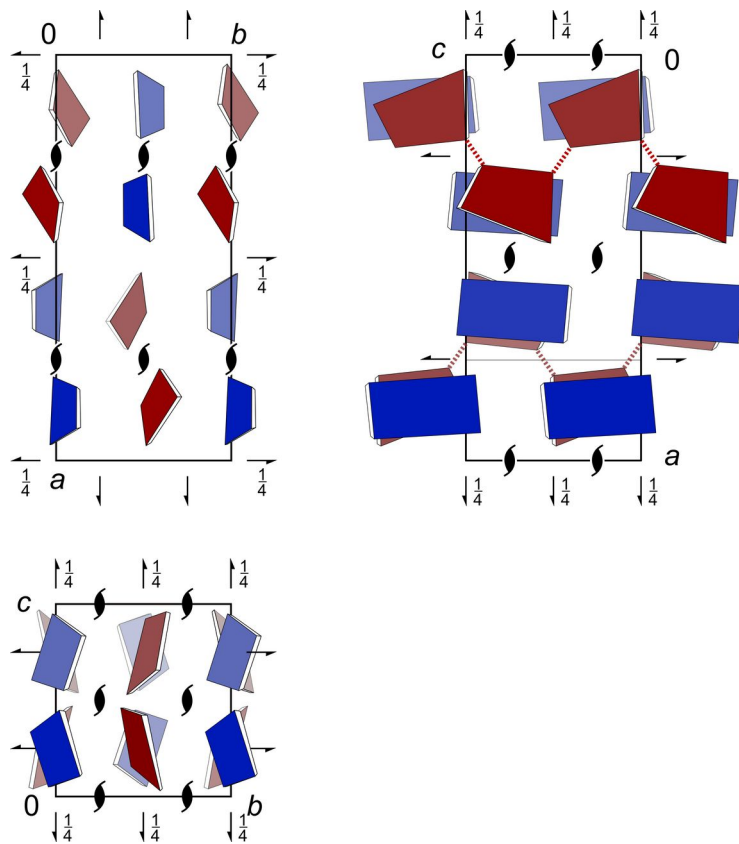


Fig. S3. Arrangement of the co-crystals components in space group $P2_12_12_1$ in three projections.

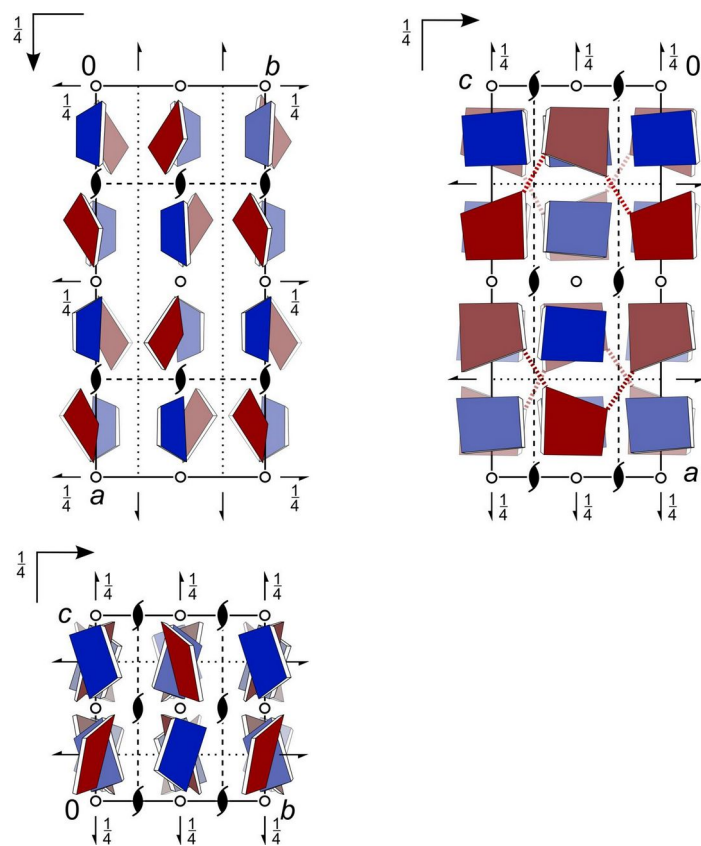


Fig. S4. Arrangement of the co-crystals components in space group $Pbca$ in three projections.

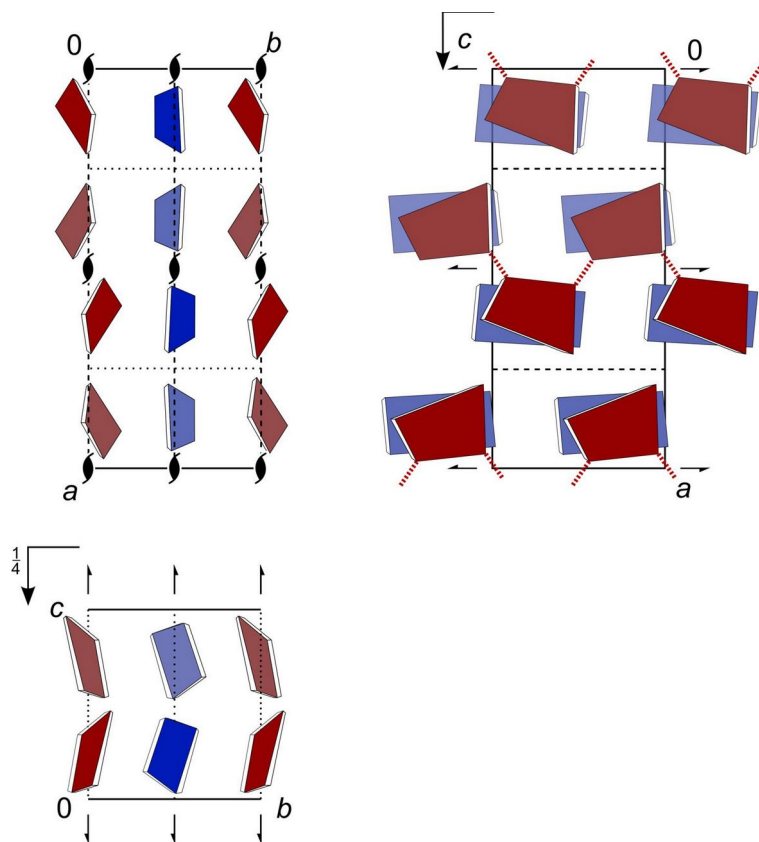


Fig. S5. Arrangement of the co-crystals components in space group $Pca2_1$ in three projections.

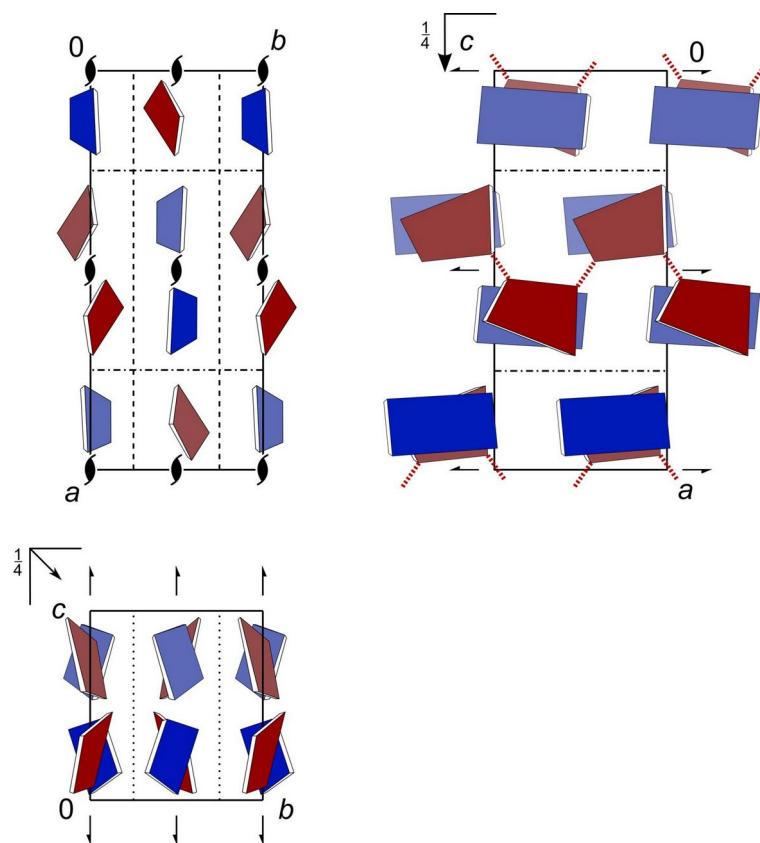


Fig. S6. Arrangement of the co-crystals components in space group $Pna2_1$ in three projections.

5. Comparison of the anisotropic displacement parameters of two NFT molecules in DNP2O·NFT-I co-crystal.

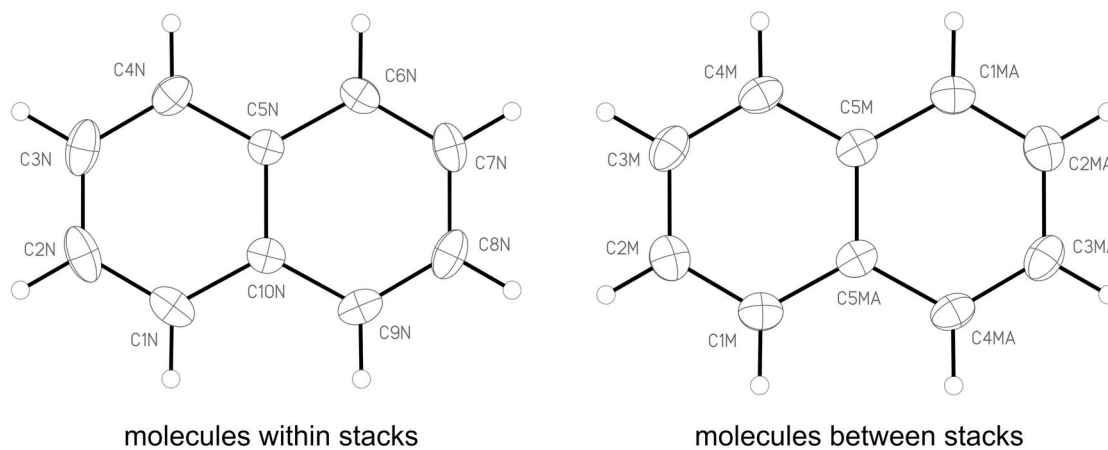


Fig. S7. Projection of the **NFT** molecules in **DNP2O·NFT-II** (1:1.5) co-crystal to their mean plane. Anisotropic displacement parameters are drawn at 50 % probability. Average U_{iso} values for both molecules are equal to 0.027 \AA^2 .

6. Additional figure of the crystal packing for DNP2O·NFT-I co-crystal.

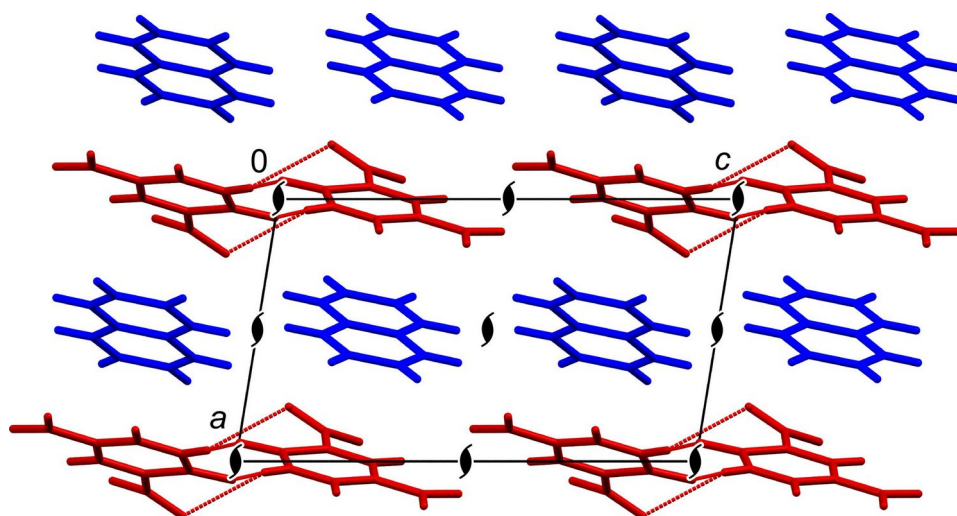


Fig. S8. A fragment of crystal packing of **DNP2O·NFT-I** co-crystal, view along the *b* axis. **DNP2O** molecules are drawn in red and **NFT** molecules are drawn in blue.

7. Additional figure of the crystal packing for DNP2O·NFT-II co-crystal.

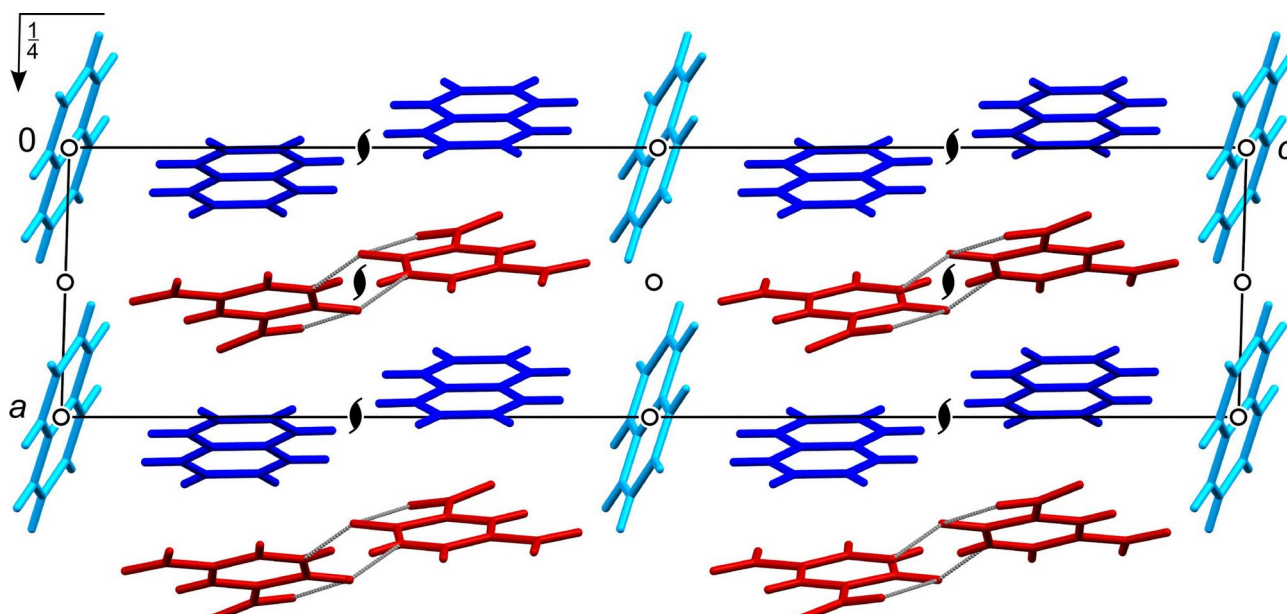


Fig. S9. A fragment of crystal packing of **DNP2O·NFT-II** co-crystal, view along the *b* axis. **DNP2O** molecules are drawn in red and **NFT** molecules are drawn in dark and light blue.

8. Additional figure of the crystal packing for DNP2O·ANT-II co-crystal.

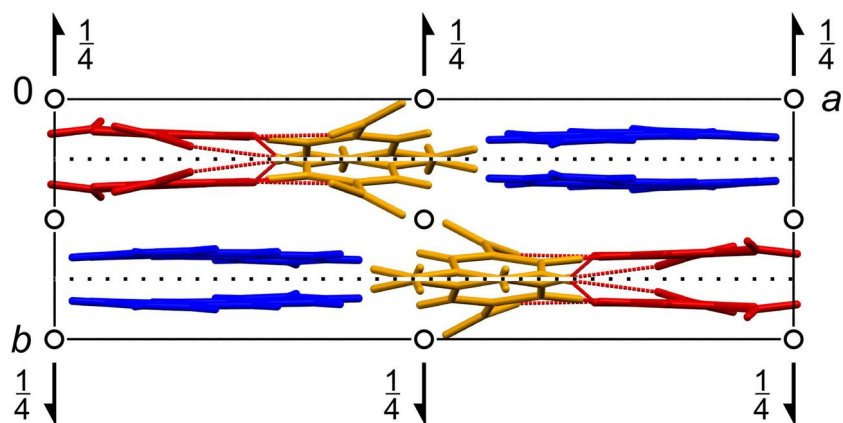


Fig. S10. A fragment of crystal packing of **DNP2O·ANT-II** co-crystal, view along the *c* axis. **DNP2O** molecules are drawn in red and orange and **NFT** molecules are drawn in dark and light blue.

9. Additional figures of the crystal packing for DNP2O·ACNFT co-crystal.

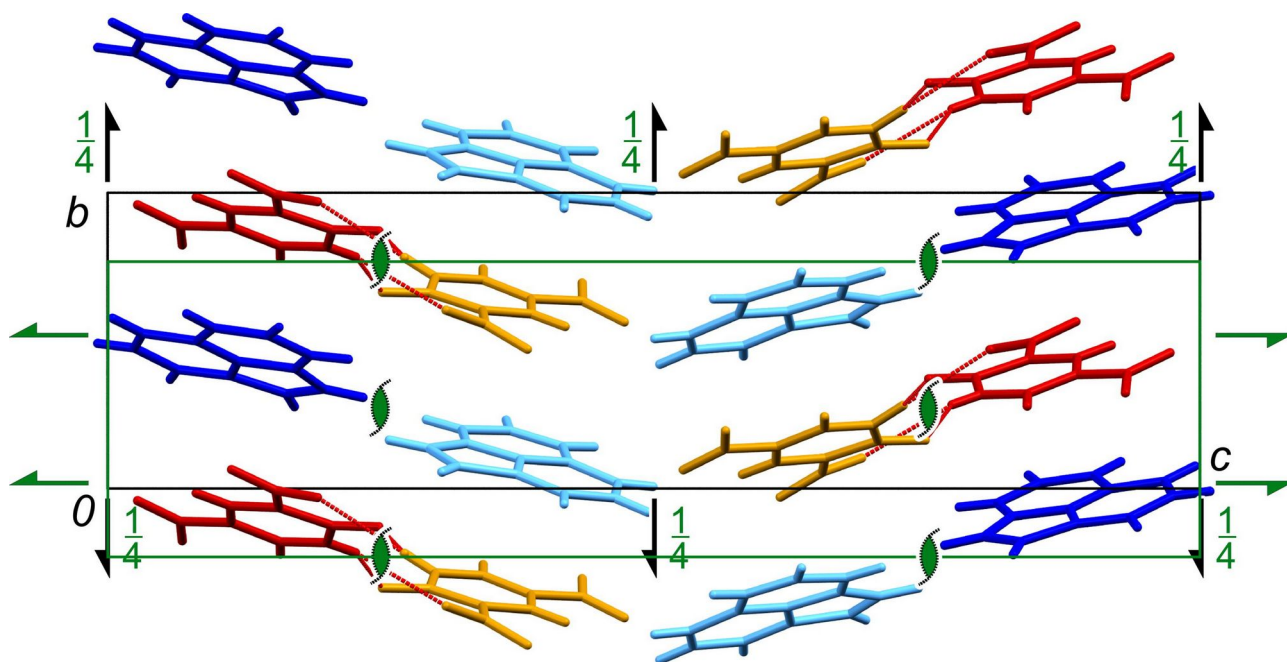


Fig. S11. A fragment of crystal packing of **DNP2O·ACNFT** co-crystal, view along the *a* axis. **DNP2O** molecules are drawn in red and orange and **NFT** molecules are drawn in dark and light blue. Pseudo-symmetry elements for the $P2_12_1$ are drawn with green colour, the cell origin is shifted by $\frac{1}{4}$ translation along the *b* axis relative to the $P2_1$ space group.

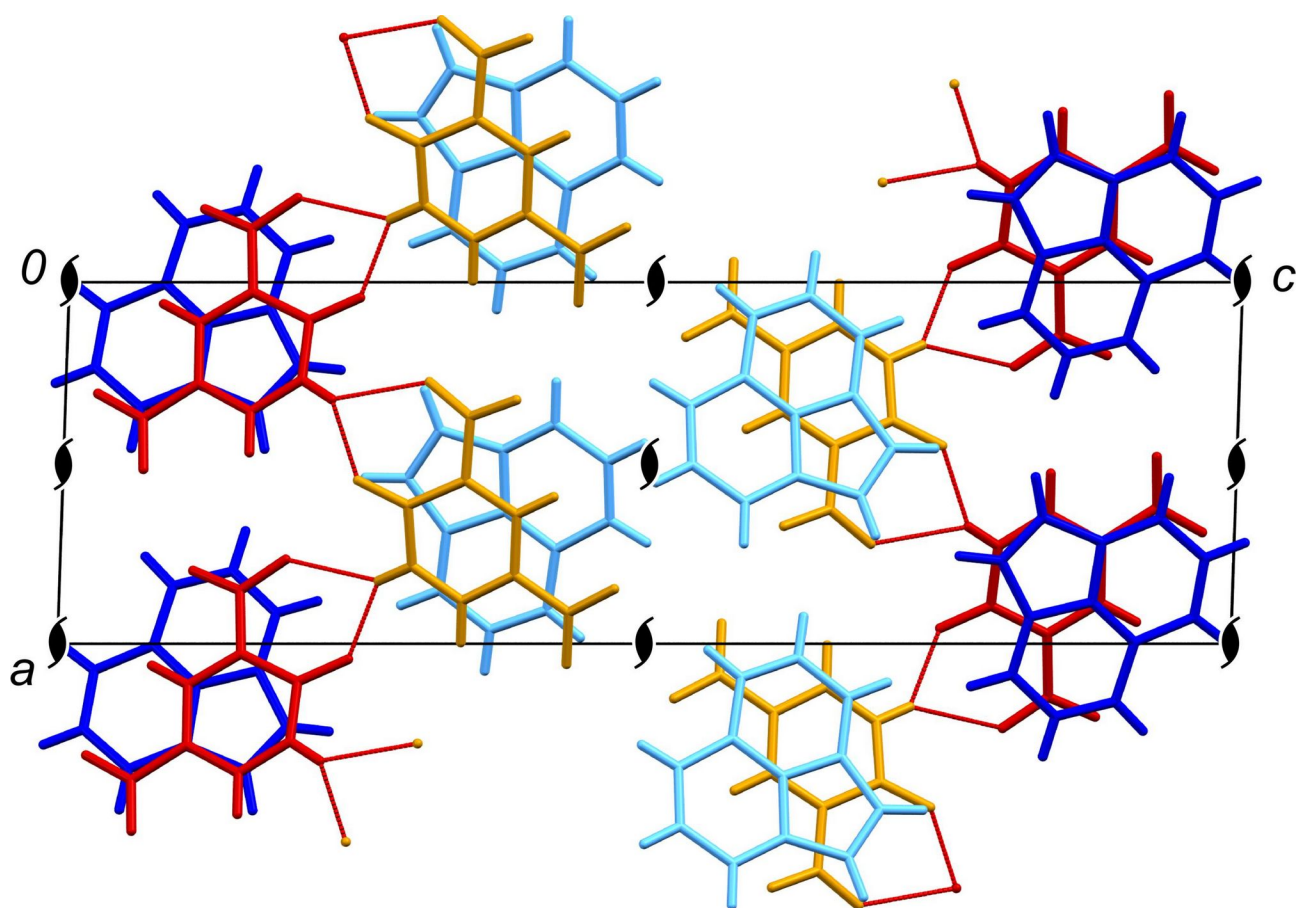


Fig. S12. A fragment of crystal packing of **DNP2O·ACNFT** co-crystal, view along the *b* axis. **DNP2O** molecules are drawn in red and orange and **NFT** molecules are drawn in dark and light blue.