Electronic Supplementary Information

Co-crystals of polyhalogenated diaminobenzonitriles with 18-crown-6: effect of fluorine on the stoichiometry and supramolecular structure

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Table S1 Crystallographic data and structure refinement parameters of the co-crystals and individual diamines

Parameter	Code of the substance			
	A_4·cr_3	**A_2·cr**	**B·cr**	**C·cr**
Chemical formula	$4C_7H_4F_3N_3·3C_{12}H_{24}O_6$	$2C_7H_4F_3N_3·C_{12}H_{24}O_6$	$C_7H_5F_2N_3·C_{12}H_{24}O_6$	$C_7H_5F_2N_3·C_{12}H_{24}O_6$
Formula weight	1541.46	638.57	433.45	433.45
Temperature (K)	295	293	296	200
Space Group	Triclinic, P-1	Monoclinic, $P2_1/c$	Triclinic, P-1	Monoclinic, C2/c
a (Å)	11.7416 (7)	9.295 (5)	7.664(6)	13.4328 (6)
b (Å)	12.0658 (10)	14.527 (5)	10.486(8)	16.8984 (8)
c (Å)	15.0919 (10)	11.722 (5)	15.090(9)	9.2577 (4)
α (deg)	113.393 (7)	90	74.09(2)	90
β (deg)	98.517 (5)	109.33 (6),	87.76(3)	96.591 (2)
γ (deg)	103.527 (6)	90	69.95(2)	90
Cell volume ($Å^3$)	1837.0 (2)	1493.6 (13)	1093.5(1)	2087.54 (16)
Z	1	2	2	4
μ (mm^{-1})	0.12	1.10	0.11	0.11
Crystal dimensions (mm)	0.30 × 0.30 × 0.25	0.40 × 0.05 × 0.03	0.56 × 0.51 × 0.03	0.56 × 0.33 × 0.04
θmax	25.35	67.79	25.2	27.5
Reflections collected, unique	10728, 6512	7158, 2541	6922, 3874	15279, 2384
R(int)	0.035	0.053	0.063	0.046
Reflections with I >2σ(I)	3576	923	2094	1842
Parameters	584	77	271	146
Final *w*R2, R (all data)	0.0894, 0.0829	0.773, 0.475 (low-resolution struct.)	0.4525, 0.1923	0.1138, 0.0499
Final R_I (I > 2σ(I))	0.0392	0.408 (low-resolution struct.)	0.1439	0.0348
Goodness-of-fit on F^2	0.836	2.388	1.071	0.987
CCDC number	2075033	2075034	2076049	2076050

Table S1 Crystallographic data and structure refinement parameters of the co-crystals and individual diamines (continue)

Parameter	Code of the substance			
	D·cr	**E·cr**	**A·0.5H$_2$O**[a]	**B**
Chemical formula	$C_7H_4ClF_2N_3 \cdot C_{12}H_{24}O_6$	$C_7H_5ClFN_3 \cdot C_{12}H_{24}O_6$	$C_7H_4F_3N_3 \cdot 0.5H_2O$	$C_7H_5F_2N_3$
Formula weight	467.89	449.9	196.13	169.14
Temperature (K)	200	299	296	296
Space Group	Triclinic, P-1	Monoclinic, C2/c	Orthorhombic, Pna21	Triclinic, P-1
a (Å)	7.3003 (11)	27.0089 (13)	13.9801(16)	7.1619(5)
b (Å)	9.7706 (14)	10.1240 (5)	15.5918(17)	7.5769(6)
c (Å)	16.622 (2)	17.2092 (7)	3.6651(4)	7.6716(5)
α (deg)	89.928 (5)	90	90	107.270(4)
β (deg)	89.964 (5)	97.123 (2)	90	100.818(3)
γ (deg)	75.875 (4)	90	90	107.844(3)
Cell volume (Å^3)	1149.8 (3)	4669.3 (4)	798.90(15)	360.19(5)
Z	2	8	4	2
μ (mm^{-1})	0.22	0.21	0.15	0.14
Crystal dimensions (mm)	0.43 × 0.24 × 0.12	0.62 × 0.31 × 0.09	0.67 × 0.13 × 0.07	0.62 × 0.36 × 0.09
θmax	27.3	25.1	28.3	29.9
Reflections collected, unique	27857, 5134	26879, 4146	17134, 1976	7318, 1963
R(int)	0.034	0.051	0.031	0.023
Reflections with I >2σ(I)	4394	2649	1609	1457
Parameters	297	282	126	126
Final *w*R2, R (all data)	0.0843, 0.0463	0.3001, 0.1181	0.1577, 0.0613	0.1506, 0.0609
Final R_I (I > 2σ(I))	0.0355	0.0815	0.0459	0.0448
Goodness-of-fit on F^2	0.972	0.956	1.014	1.090
CCDC number	2076051	2076052	2076053	2076054

[a] The Flack parameter is 0.0(2).

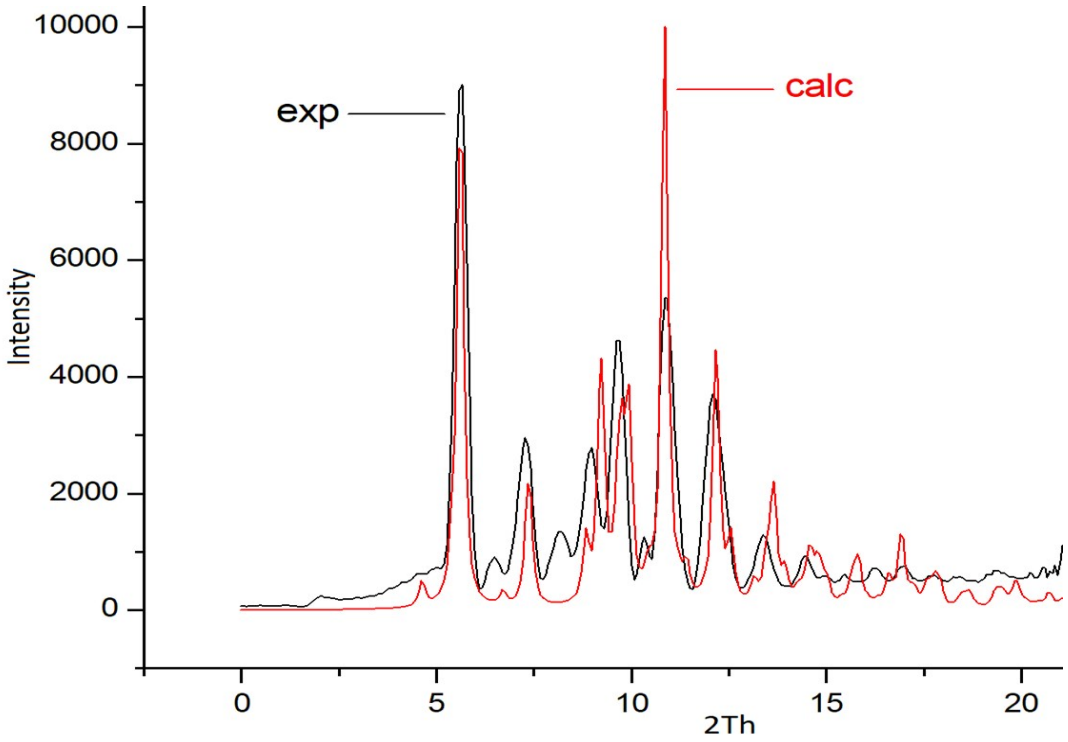

Fig. S1 PXRD patterns of **A_2·cr**: simulated from SC-XRD data using MERCURY software with peak shape 0.3 (calc) and bulky precipitate crystallized from CCl_4 (exp); the precipitate contains some crystalline impurity of a phase that could not be identified.

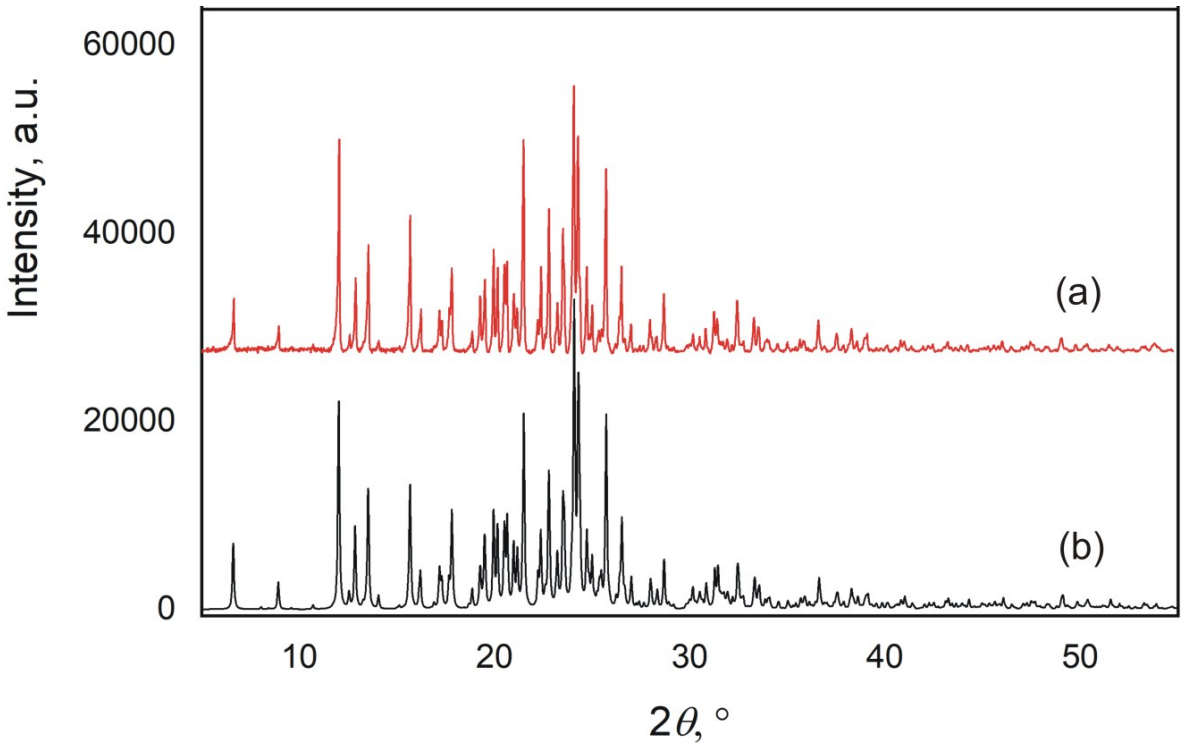

Fig. S2 PXRD patterns of **A_4·cr_3**: bulky precipitate crystallized from MeOH (experimental, a) and simulated from SC-XRD data (b).

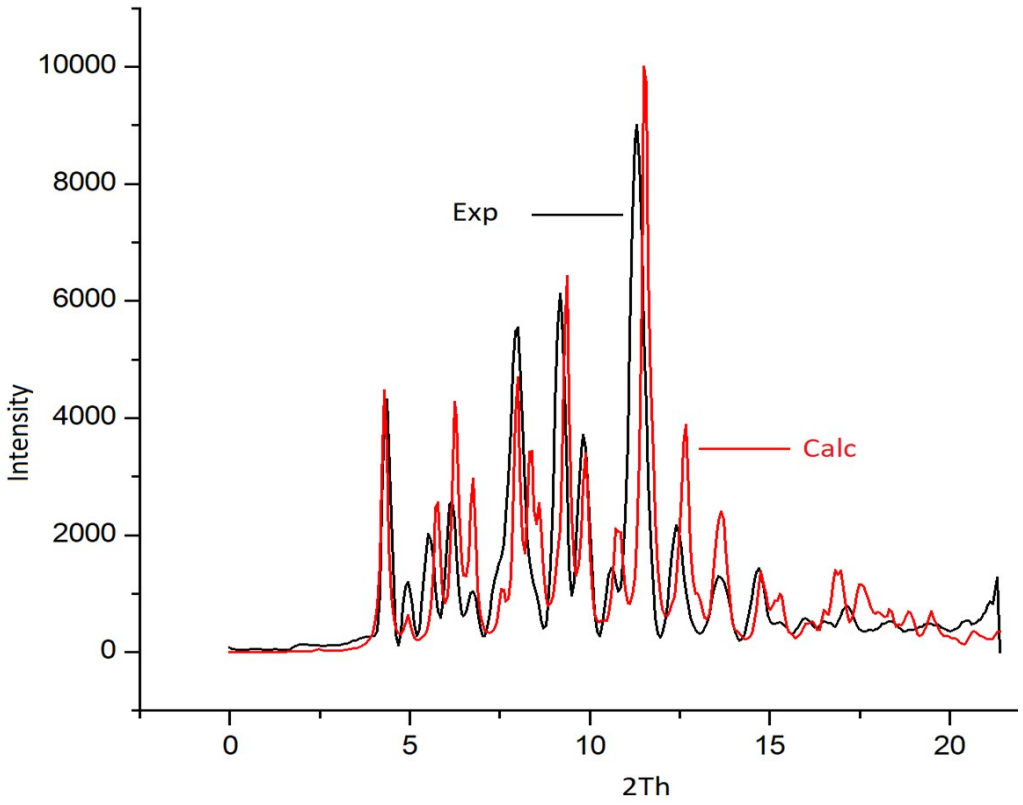

Fig. S3 PXRD patterns of **D·cr**: simulated from SC-XRD data using MERCURY software with peak shape 0.3 (calc) and bulky precipitate (exp).

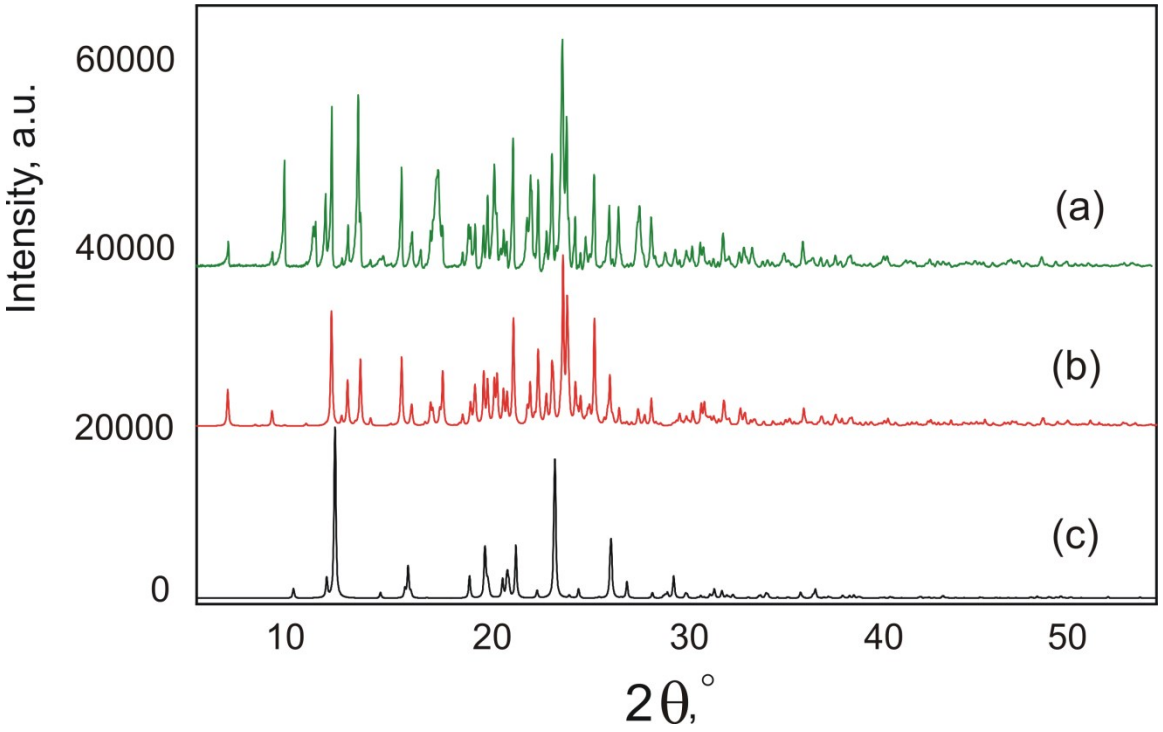

Fig. S4 PXRD patterns of (**A+cr**) composition crystallized from the melt (experimental, a), $\mathbf{A_4{\cdot}cr_3}$ (simulated from SC-XRD data, b) and $\mathbf{A_2{\cdot}cr}$ (simulated from SC-XRD data, c). The sample (a) corresponds to $\mathbf{A_4{\cdot}cr_3}$ co-crystal containing crystalline impurity of a phase(s) that could not be identified.

Table S2 Hydrogen bonding in the co-crystals and homocrystals

Sample code	Interaction D-H···A	$l_{D\text{-}H}$ (Å)	$l_{H\ldots A}$ (Å)	$l_{D\ldots A}$ (Å)	Angle D-H···A (deg)	Symmetry code for acceptor
A_4·cr$_3$	N(2)-H(2A)···N(4)	0.82(2)	2.31(2)	3.091(3)	161(2)	
	N(2)-H(2B)···O(8A)	0.82(2)	2.28(2)	3.041(11)	156(2)	
	N(3)-H(3A)···O(2)	0.86(2)	2.38(2)	3.123(2)	145(2)	1-x,1-y,1-z
	N(3)-H(3B)···O(6)	0.89(2)	2.25(2)	3.129(2)	168.0(18)	1-x,1-y,1-z
	N(5)-H(5A)···N(1)	0.85(2)	2.27(2)	3.109(3)	170.7(19)	1+x,y,z
	N(6)-H(6A)···O(5)	0.86(2)	2.34(2)	3.126(2)	153(2)	
	N(6)-H(6B)···O(1)	0.82(3)	2.28(3)	3.074(3)	166(2)	
A_2·cr[a]	N(3)-H(1)···O(1)	1.02	2.17	3.1601	163	
	N(3)-H(2)···O(5)	1.02	2.08	3.0879	169	
	N(9)-H(5)···O(2)	1.02	2.08	3.0879	169	x,y,1+z
	N(9)-H(6)···O(4)	1.02	2.15	3.1418	163	x,y,1+z
	N(6)-H(12)···O(11)	1.02	2.07	3.0831	169	x,1+y,z
	N(3)-H(2)···O(7)	1.02	2.16	3.1472	163	x,1+y,z
	N(12)-H(16)···O(8)	1.02	2.07	3.0805	169	
	N(12)-H(15)···O(10)	1.02	2.15	3.1458	163	
	N(2)-H(3)···N(10)	1.03	2.12	3.1222	165	x,y,-1+z
	N(8)-H(8)···N(4)	1.03	2.12	3.1219	166	x,y,1+z
	N(11)-H(14)···N(1)	1.03	2.12	3.1191	165	
	N(5)-H(10)···N(7)	1.03	2.12	3.1200	165	
B·cr	N(2)-H(2A)···O(3)	0.86	2.35	3.148(9)	154	1+x,y,z
	N(2)-H(2B)···O(3)	0.86	2.47	3.228(9)	147	1-x,-y,2-z
	N(3)-H(3A)···O(5)	0.86	2.55	3.302(13)	146	
	N(3)-H(3B)···O(5)	0.86	2.50	3.294(14)	153	1-x,1-y,1-z
C·cr	N(2)-H(2A)···O(2)	0.88(2)	2.30(2)	3.1669(17)	170.2(17)	3/2-x,1/2-y,-z
	N(2)-H(2B)···O(2)	0.883(19)	2.317(19)	3.1452(11)	156.3(15)	

D·cr	N(2)-H(2A)···O(2)	0.844(19)	2.341(19)	3.172(2)	168.3(17)	
	N(2)-H(2B)···O(2)	0.88(2)	2.42(2)	3.283(2)	166(2)	1-x,-1-y,-z
	N(3)-H(3B)···O(4)	0.848(17)	2.211(18)	3.084(2)	168(2)	x,y,-1+z
E·cr[b]	N(2)-H(2A)···O(1)	0.86	2.30	3.088(5)	153	
	N(3)-H(3A)···O(4)	0.86	2.46	3.290(6)	163	x,1-y,-1/2+z
	N(3)-H(3B)···O(2)	0.86	2.47	3.163(5)	139	x,1-y,-1/2+z
A_2·H_2O	N(2)-H(1)···O(1A)	0.86	2.27	3.03(3)	146	
	N(2)-H(1)···O(1B)	0.86	2.32	3.07(3)	146	
	N(3)-H(3A)···N(1)	0.86	2.33	3.172(4)	169	-1/2+x,1/2-y,1+z
	N(3)-H(3B)···N(1)	0.86	2.27	3.116(4)	170	1/2-x,1/2+y,1/2+z
B	N(2)-H(2A)···N(1)	0.94(2)	2.33(2)	3.199(2)	154(2)	1-x,2-y,2-z
	N(2)-H(2B)···F(2)	0.95(3)	2.44(3)	3.3669(18)	167(3)	x,1+y,z
	N(3)-H(3A)···F(1)	0.86(2)	2.36(2)	3.1987(17)	167(2)	-x,1-y,-z
	N(3)-H(3B)···N(1)	0.86(2)	2.60(3)	3.389(2)	154(3)	-1+x,-1+y,-1+z

[a] The H-bond parameters are obtained from the DFT optimized crystal structure A2cr_relax.cif, ESI.

[b] H-bonds are not specified for minor parts of crown ether and diamine.

A2cr_relax.cif

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# CRYSTAL DATA

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_cell_length_a                         9.29500
_cell_length_b                         14.52699
_cell_length_c                         11.72200
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_cell_angle_beta                       109.33002
_cell_angle_gamma                      90
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   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
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   _atom_site_type_symbol
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   C4         1.0     0.767624      0.487570      0.251141     Biso  1.000000 C
   C5         1.0     0.728747      0.511405      0.354716     Biso  1.000000 C
   C6         1.0     0.798547      0.471192      0.465215     Biso  1.000000 C
   C7         1.0     0.983142      0.361968      0.595551     Biso  1.000000 C
   F1         1.0     0.931417      0.400204      0.173911     Biso  1.000000 F
   F2         1.0     0.620263      0.578216      0.342999     Biso  1.000000 F
   F3         1.0     0.752826      0.495646      0.560569     Biso  1.000000 F
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   N2         1.0     1.077839      0.319192      0.393278     Biso  1.000000 N
   N3         1.0     0.699125      0.527331      0.142556     Biso  1.000000 N
   C8         1.0     0.148166      0.905465      0.037244     Biso  1.000000 C
   C9         1.0     0.102173      0.880587      0.138322     Biso  1.000000 C
   C10        1.0     0.176844      0.922833      0.248696     Biso  1.000000 C
   C11        1.0     0.294253      0.988029      0.269301     Biso  1.000000 C
   C12        1.0     0.333053      1.012358      0.165868     Biso  1.000000 C
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F5	1.0	0.440677	1.079764	0.177840	Biso	1.000000	F
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N4	1.0	0.020069	0.823382	-0.165936	Biso	1.000000	N
N5	1.0	-0.014298	0.818798	0.126684	Biso	1.000000	N
N6	1.0	0.362429	1.027802	0.377956	Biso	1.000000	N
C15	1.0	0.146601	0.594814	0.536752	Biso	1.000000	C
C16	1.0	0.101137	0.619603	0.638112	Biso	1.000000	C
C17	1.0	0.176576	0.577569	0.748486	Biso	1.000000	C
C18	1.0	0.294638	0.512822	0.768888	Biso	1.000000	C
C19	1.0	0.333002	0.488599	0.665215	Biso	1.000000	C
C20	1.0	0.262723	0.528458	0.554565	Biso	1.000000	C
C21	1.0	0.078624	0.637832	0.424176	Biso	1.000000	C
F7	1.0	0.130977	0.600361	0.846161	Biso	1.000000	F
F8	1.0	0.441472	0.421731	0.677144	Biso	1.000000	F
F9	1.0	0.307840	0.503646	0.459029	Biso	1.000000	F
N7	1.0	0.018199	0.677080	0.333725	Biso	1.000000	N
N8	1.0	-0.015605	0.681163	0.626828	Biso	1.000000	N
N9	1.0	0.363754	0.473306	0.877557	Biso	1.000000	N
C22	1.0	0.914631	0.094887	0.983001	Biso	1.000000	C
C23	1.0	0.960084	0.119315	0.881540	Biso	1.000000	C
C24	1.0	0.884422	0.077125	0.771333	Biso	1.000000	C
C25	1.0	0.766388	0.012379	0.751153	Biso	1.000000	C
C26	1.0	0.728091	-0.011538	0.854989	Biso	1.000000	C
C27	1.0	0.798441	0.028621	0.965435	Biso	1.000000	C
C28	1.0	0.982807	0.138048	1.095430	Biso	1.000000	C
F10	1.0	0.929736	0.099715	0.673436	Biso	1.000000	F
F11	1.0	0.619454	-0.078217	0.843587	Biso	1.000000	F
F12	1.0	0.753295	0.004177	1.061092	Biso	1.000000	F
N10	1.0	1.043561	0.177419	1.185749	Biso	1.000000	N
N11	1.0	1.077055	0.180661	0.892544	Biso	1.000000	N
N12	1.0	0.697273	-0.027289	0.642610	Biso	1.000000	N
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O2	1.0	0.627869	0.334544	-0.080125	Biso	1.000000	O
O3	1.0	0.458802	0.330655	0.090865	Biso	1.000000	O
C29	1.0	0.788005	0.420558	-0.168070	Biso	1.000000	C
C30	1.0	0.771880	0.333691	-0.101454	Biso	1.000000	C
C31	1.0	0.605435	0.253814	-0.016874	Biso	1.000000	C
C32	1.0	0.452749	0.260265	0.002440	Biso	1.000000	C
C33	1.0	0.318526	0.335327	0.117252	Biso	1.000000	C
C34	1.0	0.317998	0.418396	0.195050	Biso	1.000000	C
O4	1.0	0.301675	0.500814	0.123024	Biso	1.000000	O
O5	1.0	0.436366	0.667182	0.100041	Biso	1.000000	O
O6	1.0	0.605295	0.670259	-0.069762	Biso	1.000000	O

C35	1.0	0.274992	0.580721	0.186436	Biso	1.000000	C
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C37	1.0	0.459947	0.748246	0.037894	Biso	1.000000	C
C38	1.0	0.612436	0.741025	0.018411	Biso	1.000000	C
C39	1.0	0.744554	0.665532	-0.097626	Biso	1.000000	C
C40	1.0	0.743044	0.582834	-0.176534	Biso	1.000000	C
O7	1.0	0.301073	0.000446	0.624204	Biso	1.000000	O
O8	1.0	0.434655	-0.166346	0.601036	Biso	1.000000	O
O9	1.0	0.603100	-0.170632	0.430077	Biso	1.000000	O
C41	1.0	0.273833	-0.079362	0.687480	Biso	1.000000	C
C42	1.0	0.289781	-0.166318	0.620985	Biso	1.000000	C
C43	1.0	0.457042	-0.247388	0.538306	Biso	1.000000	C
C44	1.0	0.609460	-0.241087	0.518489	Biso	1.000000	C
C45	1.0	0.742964	-0.165928	0.403074	Biso	1.000000	C
C46	1.0	0.742626	-0.082967	0.324868	Biso	1.000000	C
O10	1.0	0.760559	-0.000590	0.397144	Biso	1.000000	O
O11	1.0	0.626824	0.166033	0.421040	Biso	1.000000	O
O12	1.0	0.457538	0.170463	0.591126	Biso	1.000000	O
C47	1.0	0.786524	0.079286	0.333356	Biso	1.000000	C
C48	1.0	0.771028	0.166272	0.400002	Biso	1.000000	C
C49	1.0	0.604216	0.247200	0.483453	Biso	1.000000	C
C50	1.0	0.451498	0.240889	0.502759	Biso	1.000000	C
C51	1.0	0.317487	0.165772	0.617832	Biso	1.000000	C
C52	1.0	0.317733	0.082912	0.696156	Biso	1.000000	C
H1	1.0	0.721516	0.504695	0.067543	Biso	1.000000	H
H2	1.0	0.603224	0.566328	0.129146	Biso	1.000000	H
H3	1.0	1.073778	0.282076	0.317846	Biso	1.000000	H
H4	1.0	1.109392	0.280612	0.470125	Biso	1.000000	H
H5	1.0	0.459678	0.434389	0.890702	Biso	1.000000	H
H6	1.0	0.341772	0.496115	0.952667	Biso	1.000000	H
H7	1.0	-0.048209	0.719043	0.549362	Biso	1.000000	H
H8	1.0	-0.010376	0.719074	0.701952	Biso	1.000000	H
H9	1.0	-0.046477	0.780757	0.049357	Biso	1.000000	H
H10	1.0	-0.010165	0.781271	0.201836	Biso	1.000000	H
H11	1.0	0.458232	1.066890	0.391399	Biso	1.000000	H
H12	1.0	0.339934	1.005120	0.452901	Biso	1.000000	H
H13	1.0	1.109660	0.219090	0.969547	Biso	1.000000	H
H14	1.0	1.072659	0.217729	0.817022	Biso	1.000000	H
H15	1.0	0.719193	-0.004752	0.567333	Biso	1.000000	H
H16	1.0	0.601478	-0.066277	0.629697	Biso	1.000000	H
H17	1.0	0.696938	0.254032	0.571194	Biso	1.000000	H
H18	1.0	0.604766	0.309041	0.428468	Biso	1.000000	H
H19	1.0	0.361657	0.224107	0.416326	Biso	1.000000	H
H20	1.0	0.424362	0.308149	0.533921	Biso	1.000000	H
H21	1.0	0.864346	0.171923	0.487005	Biso	1.000000	H
H22	1.0	0.776766	0.225923	0.343080	Biso	1.000000	H

H23	1.0	0.902518	0.076727	0.327019	Biso	1.000000 H
H24	1.0	0.704136	0.080079	0.241094	Biso	1.000000 H
H25	1.0	0.837910	-0.089330	0.289054	Biso	1.000000 H
H26	1.0	0.635224	-0.079610	0.247471	Biso	1.000000 H
H27	1.0	0.636191	-0.308366	0.487069	Biso	1.000000 H
H28	1.0	0.699734	-0.224416	0.604729	Biso	1.000000 H
H29	1.0	0.456653	-0.309319	0.593177	Biso	1.000000 H
H30	1.0	0.364044	-0.254102	0.450716	Biso	1.000000 H
H31	1.0	0.283022	-0.226008	0.677496	Biso	1.000000 H
H32	1.0	0.197177	-0.171706	0.533537	Biso	1.000000 H
H33	1.0	0.355246	-0.080312	0.780121	Biso	1.000000 H
H34	1.0	0.157382	-0.076619	0.692837	Biso	1.000000 H
H35	1.0	0.424630	0.079898	0.774078	Biso	1.000000 H
H36	1.0	0.221787	0.089071	0.731210	Biso	1.000000 H
H37	1.0	0.302234	0.229121	0.665007	Biso	1.000000 H
H38	1.0	0.219690	0.158647	0.532923	Biso	1.000000 H
H39	1.0	0.840948	-0.158951	0.487868	Biso	1.000000 H
H40	1.0	0.757887	-0.229228	0.355646	Biso	1.000000 H
H41	1.0	0.865330	0.327845	-0.014528	Biso	1.000000 H
H42	1.0	0.776908	0.273899	-0.158391	Biso	1.000000 H
H43	1.0	0.706029	0.419789	-0.260498	Biso	1.000000 H
H44	1.0	0.904210	0.422960	-0.173970	Biso	1.000000 H
H45	1.0	0.606164	0.191659	-0.071247	Biso	1.000000 H
H46	1.0	0.698213	0.247483	0.070914	Biso	1.000000 H
H47	1.0	0.425529	0.193000	0.033559	Biso	1.000000 H
H48	1.0	0.362911	0.277135	-0.083967	Biso	1.000000 H
H49	1.0	0.837298	0.589369	-0.213461	Biso	1.000000 H
H50	1.0	0.634825	0.579625	-0.253153	Biso	1.000000 H
H51	1.0	0.759243	0.729017	-0.144776	Biso	1.000000 H
H52	1.0	0.843044	0.658143	-0.013231	Biso	1.000000 H
H53	1.0	0.702243	0.724119	0.104805	Biso	1.000000 H
H54	1.0	0.640246	0.807965	-0.013147	Biso	1.000000 H
H55	1.0	0.367255	0.755578	-0.049781	Biso	1.000000 H
H56	1.0	0.460347	0.810111	0.093099	Biso	1.000000 H
H57	1.0	0.286136	0.727315	0.177452	Biso	1.000000 H
H58	1.0	0.198953	0.673850	0.033105	Biso	1.000000 H
H59	1.0	0.158489	0.578306	0.191737	Biso	1.000000 H
H60	1.0	0.356375	0.581368	0.279101	Biso	1.000000 H
H61	1.0	0.424483	0.421582	0.273328	Biso	1.000000 H
H62	1.0	0.221588	0.412222	0.229567	Biso	1.000000 H
H63	1.0	0.220907	0.341934	0.032141	Biso	1.000000 H
H64	1.0	0.303569	0.272126	0.164860	Biso	1.000000 H

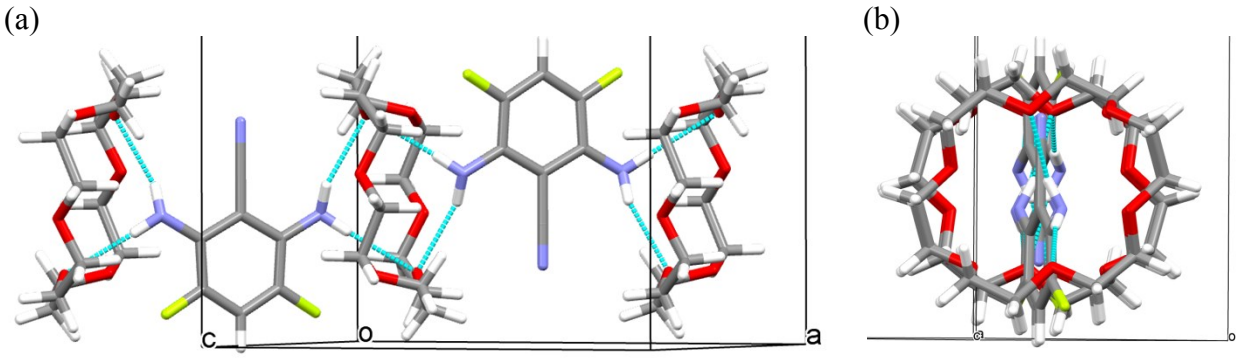


Fig S5. 1D assembly in the co-crystal **C·cr**: top (a) and cross-section (b) view.

Packing of the 1D assemblies in co-crystals. Rods in the co-crystals are disposed parallel to each other (Figs. 7, 8, S5-S7). In the co-crystals **B·cr** and **C·cr**, units in the neighbouring rods are arranged with a shift relative to each other (ledge-to-cavity packing, see Figs. 7b, S5b). In the co-crystal **D·cr**, rods are packed without mutual displacement of units (Fig. S6). The crystal packing in **E·cr** differs in that the layers are arranged in pairs (Fig. 8a); the pairs of layers are displaced relative to each other along the *b* axis by half the distance between the rods' axes. There is no mutual displacement of units in the layer (Fig. 8b), but in the pair of layers there is a mutual displacement of units by 50% of the unit length along the *c* axis (Fig. S7).

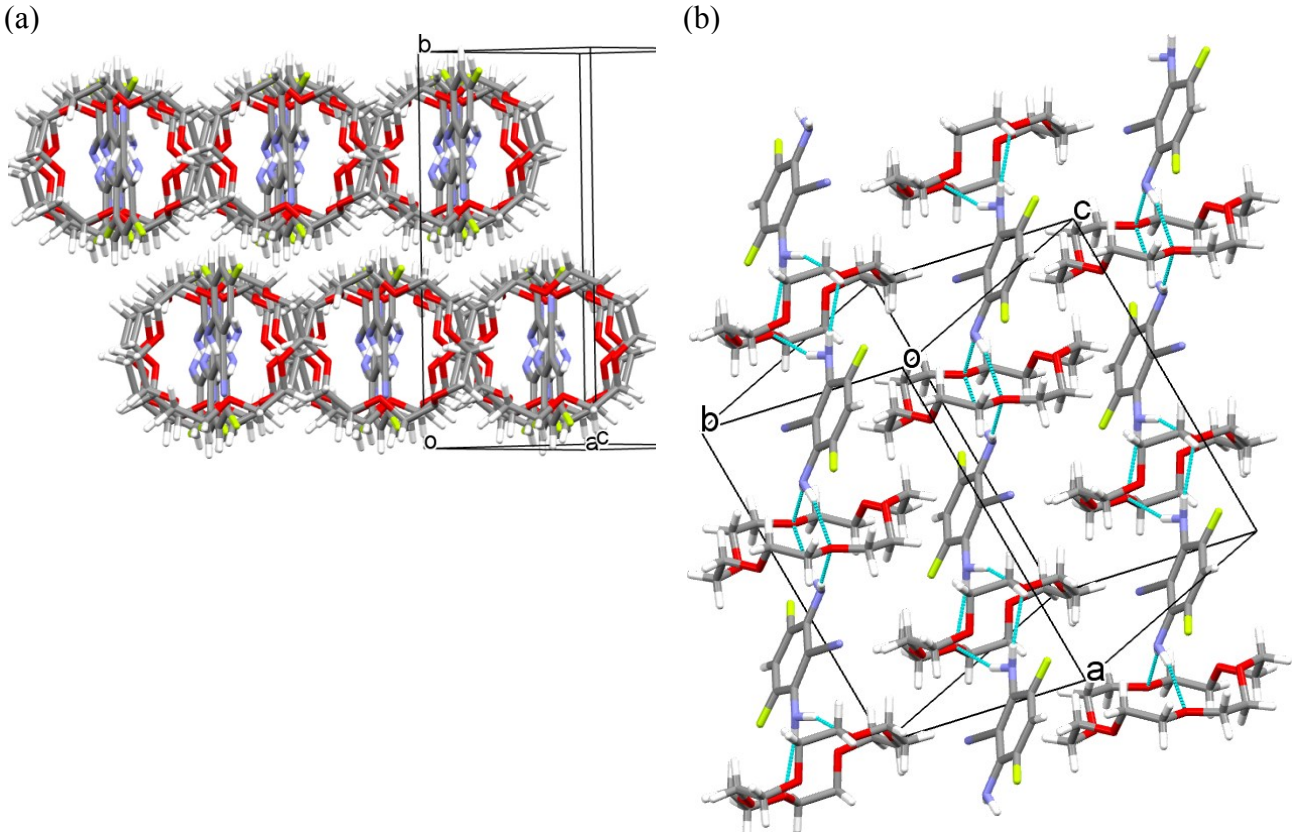


Fig. S6. Packing of the rods in **C·cr**: (a) cross-section view; (b) layer top view.

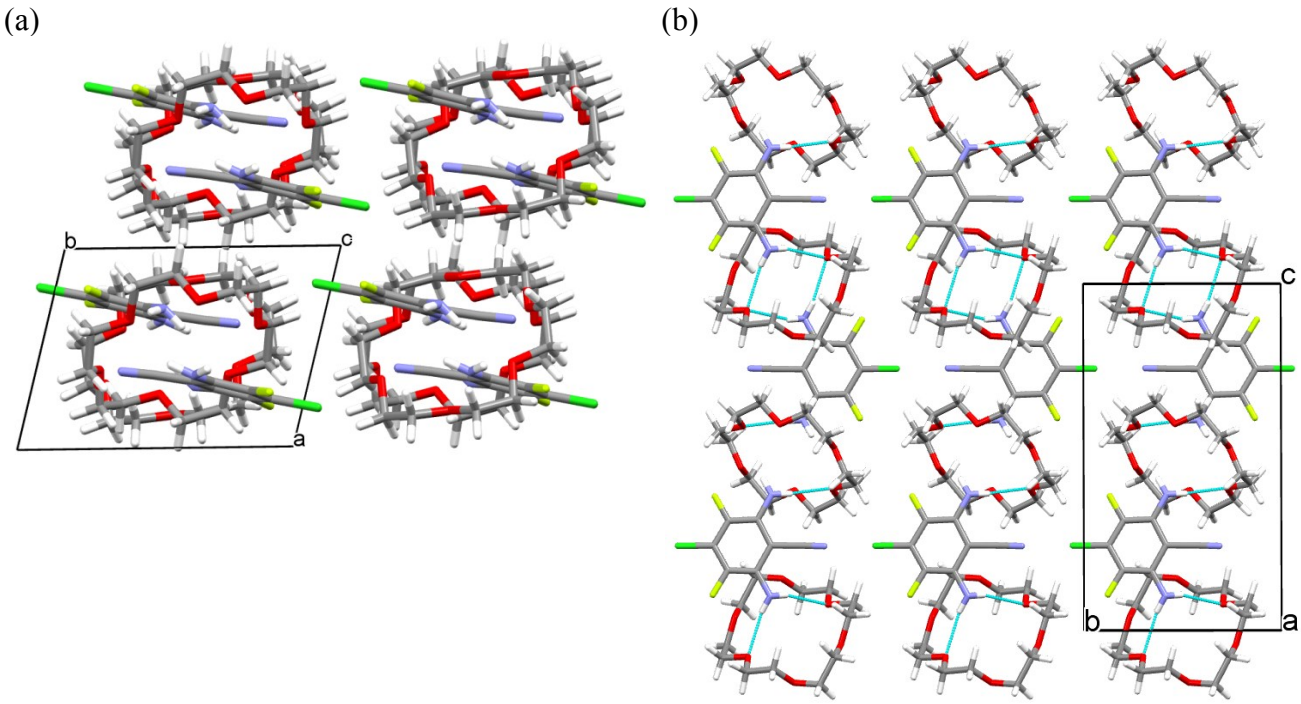


Fig. S7. Packing of the rods in **D·cr**: (a) cross-section view; (b) layer top view.

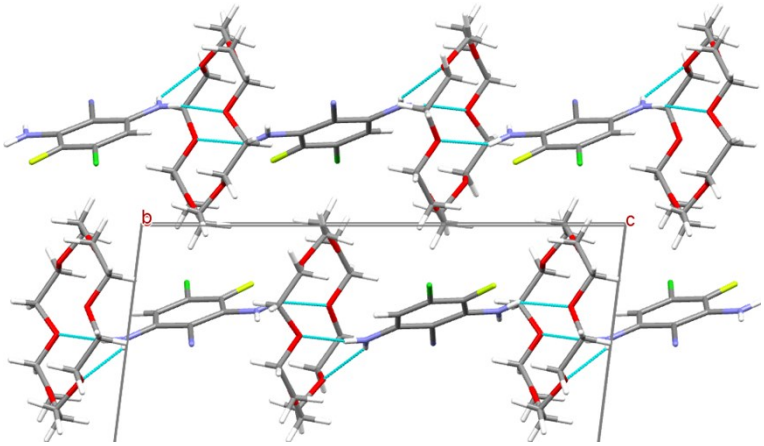


Fig. S8. Ledge-to-cavity packing in the pair of layers in **E·cr**.

Table S3 Calculated packing enthalpies of the experimental and DFT simulated (in the square brackets) co-crystal of **A** and **B** diamines, ΔH (kJ g-unit^{-1})[a, b]

Stoichiometry	Molar fraction of diamine, x	$\Delta H(B_x \cdot cr_{1-x})$	$\Delta H(A_x \cdot cr_{1-x})$
1:1	1/2	-156	[-157]
4:3	4/7	[-151]	-154
2:1	2/3	[-141]	-144

[a] To compare the enthalpies of co-crystals of different stoichiometries, ΔH values were normalized per unit $Y_x \cdot cr_{1-x}$, where Y – diamine **A** or **B**, x – molar fraction of the diamine in the co-crystal.
[b] Calculations were based on the equation S1 (cf. Ref.[18]).

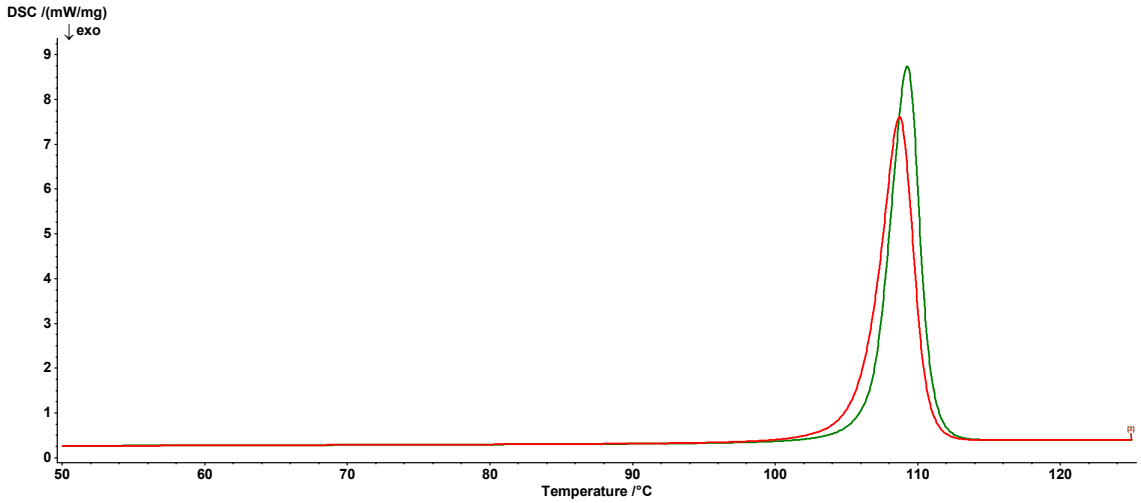
$$xY_{gas} + (1-x)cr_{gas} = [Y_x \cdot cr_{1-x}]_{solid} + \Delta H(Y_x \cdot cr_{1-x}) \quad \text{(S1)}$$

Approach to the assessment of the co-crystallization enthalpies taking into account the packing enthalpies of homocrystalline phases (similar to that described in Ref.[81]):

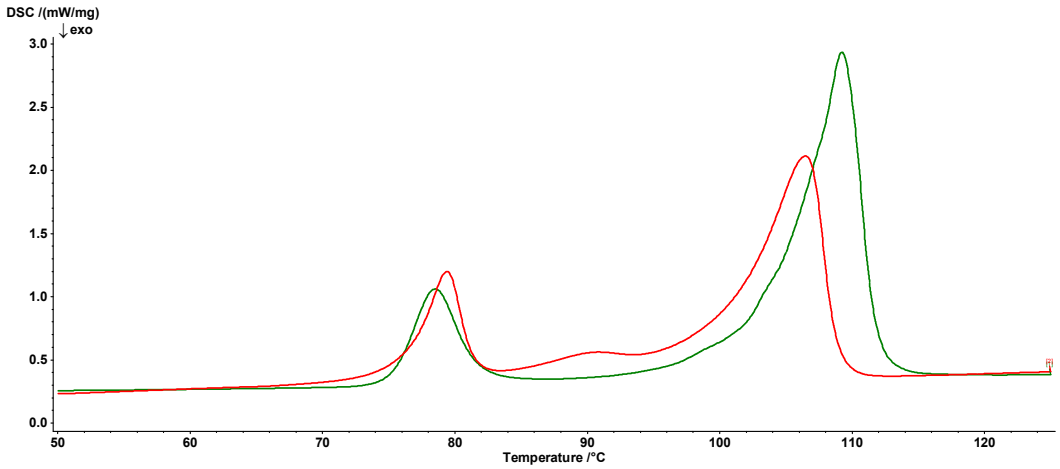
$$x \cdot \Delta H(Y) + (1-x) \cdot \Delta H(cr) = \Delta H(Y_x \cdot cr_{1-x}) + \Delta H_{cc} \quad \text{(S2)}$$

where ΔH – packing enthalpies of solids.

(a)



(b)



(c)

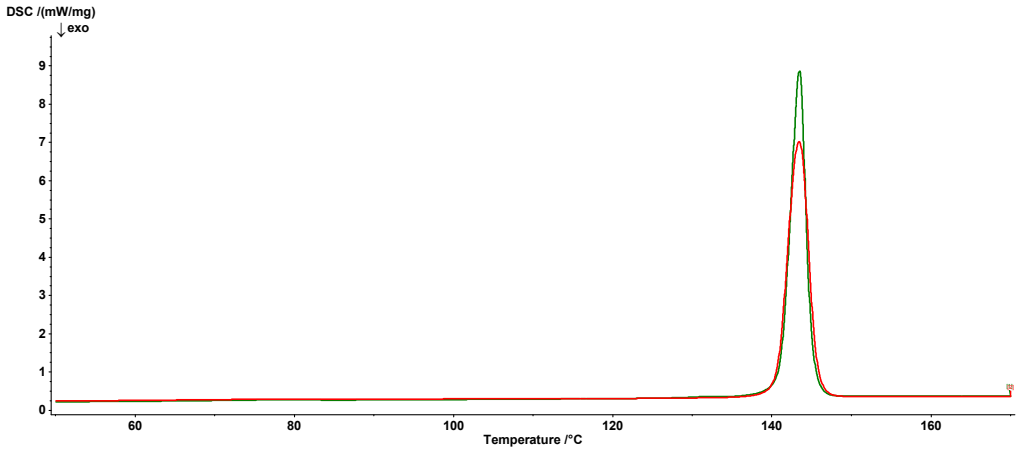


Fig. S9. DSC curves of the co-crystals, the first (green) and second (red) heating runs: **B·cr** (a), **D·cr** (b); **E·cr** (c).

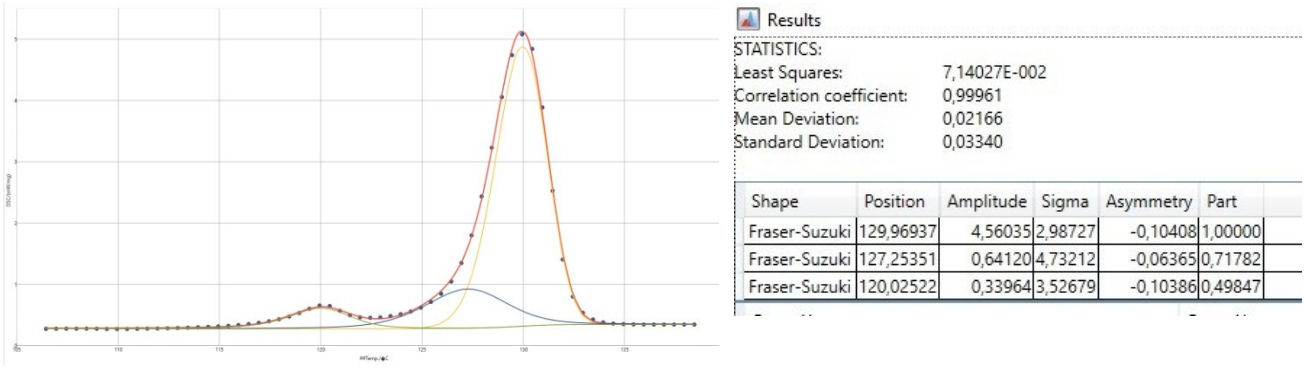


Fig. S10. DSC curves of **A_2·cr**, the second heating run, decomposing into 3 peaks.

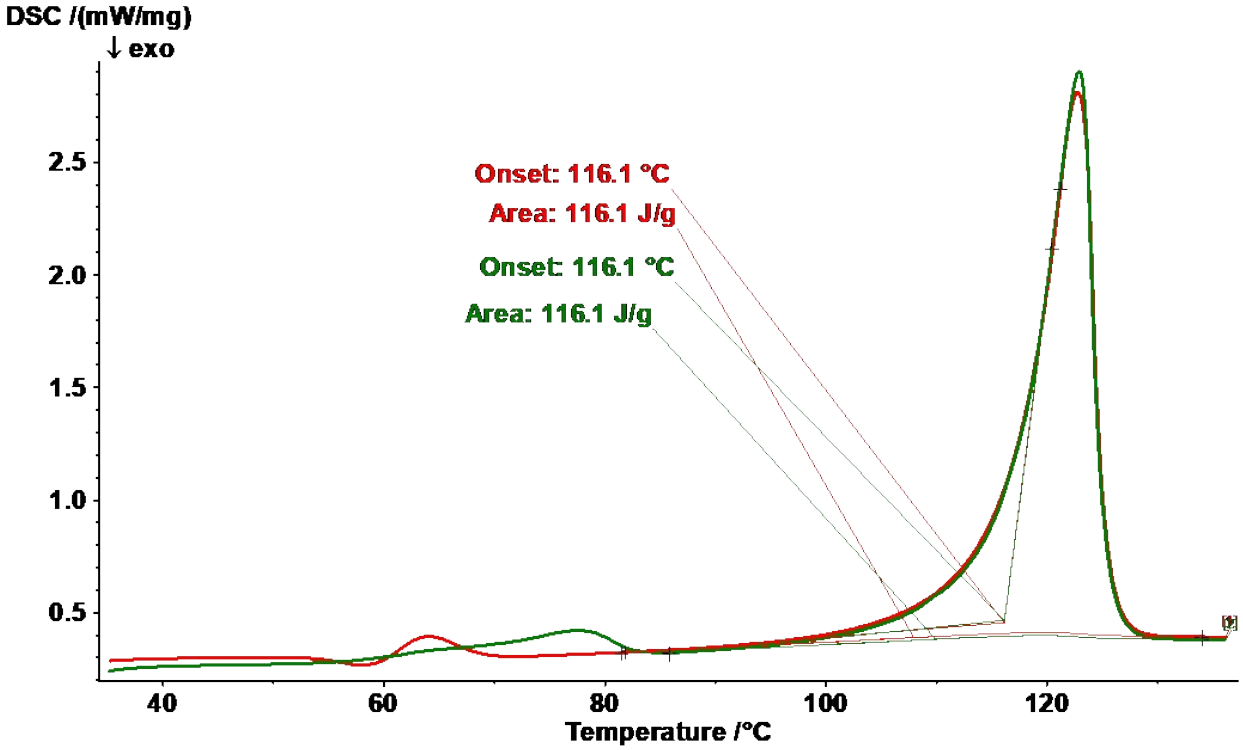


Fig. S11. DSC curves of the (**A+cr**) composition crystallized from the melt, the first (green) and second (red) heating runs.