Electronic Supplementary Information

Competition of intermolecular interactions in the self-assembly of co-crystals of trifluoro-*meta*-arylenediamines (benzene, nitrobenzene, pyridine) with 12-, 15-, 18-membered crown ethers

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Table S1 Crystallographic data and structure refinement parameters

Experiments were carried out at 296 K with Mo *K*α radiation using a Bruker APEX-II CCD.

	A•15cr5	**B•15cr5**	**2C•15cr5**
Crystal data			
Chemical formula	$C_6H_5N_2F_3 \cdot C_{10}H_{20}O_5$	$C_5H_4F_3N_3 \cdot C_{10}H_{20}O_5$	$2(C_6H_4F_3N_3O_2) \cdot C_{10}H_{20}O_5$
M_r	382.38	383.37	634.50
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Triclinic, $P^{-}1$
a, *b*, *c* (Å)	24.457 (5), 8.6861 (17), 18.097 (3)	24.7949 (15), 8.4611 (4), 17.9811 (10)	11.5203 (14), 11.5359 (15), 11.8617 (17)
α, β, γ (°)	90, 90.435 (9), 90	90, 91.929 (3), 90	106.975 (5), 108.550 (4), 90.001 (5)
V (Å^3)	3844.3 (13)	3770.2 (4)	1421.9 (3)
Z	8	8	2
μ (mm^{-1})	0.12	0.12	0.14
Crystal size (mm)	0.67 × 0.17 × 0.06	0.62 × 0.38 × 0.02	0.67 × 0.11 × 0.07
Data collection			
Absorption correction	Multi-scan *SADABS2016*/2	Multi-scan *SADABS2008*/1	Multi-scan *SADABS2016*/2
T_{min}, T_{max}	0.815, 0.971	0.951, 0.991	0.915, 0.971
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13107, 3382, 2440	32775, 3496, 2349	14729, 5290, 3401
R_{int}	0.055	0.054	0.047
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.597	0.605	0.608
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.095, 0.250, 1.07	0.075, 0.217, 1.08	0.064, 0.201, 1.03
No. of reflections	3382	3496	5290
No. of parameters	262	259	398
No. of restraints	56	30	4
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.33, -0.23	0.73, -0.46	0.49, -0.37

Table S1 Crystallographic data and structure refinement parameters (continued)

	2B•12cr4	**2C•12cr4**
Crystal data		
Chemical formula	$2(C_5H_4F_3N_3)\cdot C_8H_{16}O_4$	$2(C_6H_4F_3N_3O_2)\cdot C_8H_{16}O_4$
M_r	502.43	590.45
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	5.7104 (2), 9.5020 (4), 10.2481 (5)	15.4617 (18), 21.673 (3), 7.3234 (8)
α, β, γ (°)	88.963 (2), 87.032 (2), 81.176 (2)	90, 90.584 (5), 90
V (Å^3)	548.72 (4)	2454.0 (5)
Z	1	4
μ (mm^{-1})	0.14	0.15
Crystal size (mm)	0.41 × 0.25 × 0.21	0.65 × 0.18 × 0.08
Data collection		
Absorption correction	Multi-scan *SADABS2008*/1	Multi-scan *SADABS2016*/2
T_{min}, T_{max}	0.932, 0.970	0.803, 0.958
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19664, 2944, 2344	43266, 4876, 2325
R_{int}	0.034	0.056
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.686	0.622
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.108, 1.06	0.140, 0.447, 1.36
No. of reflections	2944	4876
No. of parameters	171	361
No. of restraints	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.24, -0.20	0.91, -0.45

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXS97* (Sheldrick 2008), *SHELXL2018*/3 (Sheldrick, 2018), Bruker *SHELXTL*.

Table S2 Hydrogen bonding in the co-crystals

Crystal	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·15cr5 [a]	N(1)-H(1A)...O(2A)	0.86	2.30	3.131(7)	164	
	N(1)-H(1B)...O(5)	0.86	2.26	3.033(7)	149	
	N(2)-H(2A)...O(1)	0.86	2.27	2.976(8)	140	x,-y,-1/2+z
	N(2)-H(2B)...O(4)	0.86	2.15	2.982(7)	163	x,-y,-1/2+z
	C(13)-H(13A)...F(2A)	0.97	2.43	3.276(11)	145	x,-1+y,z
B·15cr5 [a]	N(2)-H(2A)...O(4)	0.86	2.20	3.035(4)	162	x,y,1+z
	N(2)-H(2B)...O(1)	0.86	2.32	3.046(4)	142	x,y,1+z
	N(3)-H(3A)...O(5)	0.86	2.22	2.987(4)	148	x,1-y,1/2+z
	N(3)-H(3B)...O(2)	0.86	2.12	2.964(4)	167	x,1-y,1/2+z
C_2·15cr5 [a]	N(2)-H(2A)...O(3)	0.86	2.52	3.375(5)	173	1+x,y,z
	N(2)-H(2A)...O(4)	0.86	2.50	3.187(4)	137	1+x,y,z
	N(3)-H(3A)...O(9)	0.86	2.17	2.977(4)	156	2-x,1-y,1-z
	N(3)-H(3B)...O(6)	0.86	2.16	2.953(4)	154	2-x,1-y,1-z
	N(5)-H(5A)...O(2)	0.86	2.58	3.443(5)	178	x, y, z
	N(6)-H(6A)...O(7)	0.86	2.20	2.976(5)	150	x, y, z
	N(6)-H(6A)...O(8)	0.86	2.47	3.108(8)	132	x, y, z
	N(6)-H(6B)...O(5)	0.86	2.11	2.900(4)	153	x, y, z
	C(22)-H(22A)...O(2)	0.97	2.59	3.550(5)	153	x, 1+y, z
B_2·12cr4	N(2)-H(1)...N(1)	0.905(17)	2.206(17)	3.1112(16)	179.2(19)	-x,-y,2-z
	N(2)-H(2)...O(2)	0.812(17)	2.280(17)	3.0602(15)	161.3(16)	x,y,1+z
	N(3)-H(3)...F(1)	0.847(17)	2.342(17)	3.1324(14)	155.4(16)	1-x,1-y,2-z
	N(3)-H(4)...O(1)	0.854(17)	2.194(17)	3.0389(15)	170.1(14)	1+x,y,z
C_2·12cr4	N(2)-H(2A)...O(6)	0.86	2.08	2.912(9)	163	1-x,1-y,1-z
	N(3)-H(3A)...O(8)	0.86	2.15	2.983(9)	164	1+x,3/2-y,-1/2+z
	N(3)-H(3B)...O(3)	0.86	2.47	3.063(11)	127	1+x,y,z
	N(5)-H(5A)...O(7)	0.86	2.12	2.930(9)	156	-x,2-y,1-z
	N(6)-H(6A)...O(5)	0.86	2.26	3.063(9)	155	x,3/2-y,1/2+z
	N(6)-H(6B)...O(1)	0.86	2.49	3.088(10)	128	x, y, z
	C(14)-H(14A)...O(2)	0.97	2.38	3.345(12)	171	1-x,-1/2+y,1/2-z
	C(14)-H(14B)...F(4)	0.97	2.48	3.452(11)	177	x,3/2-y,-1/2+z

[a] H-bonds are specified for major parts of co-formers.

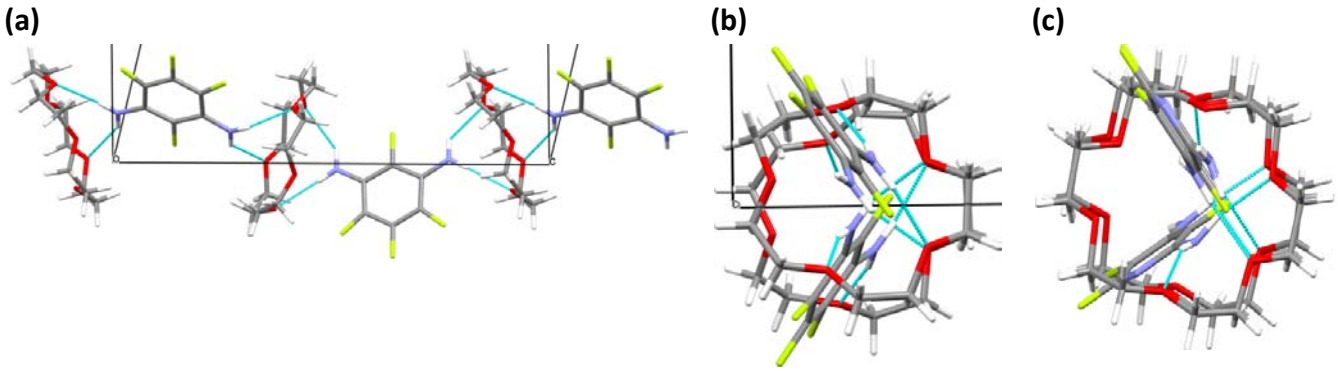


Fig. S1 1D assembly in the co-crystals: **A·15cr5**, top and cross-section view (a, b), **B·18cr6** (c).

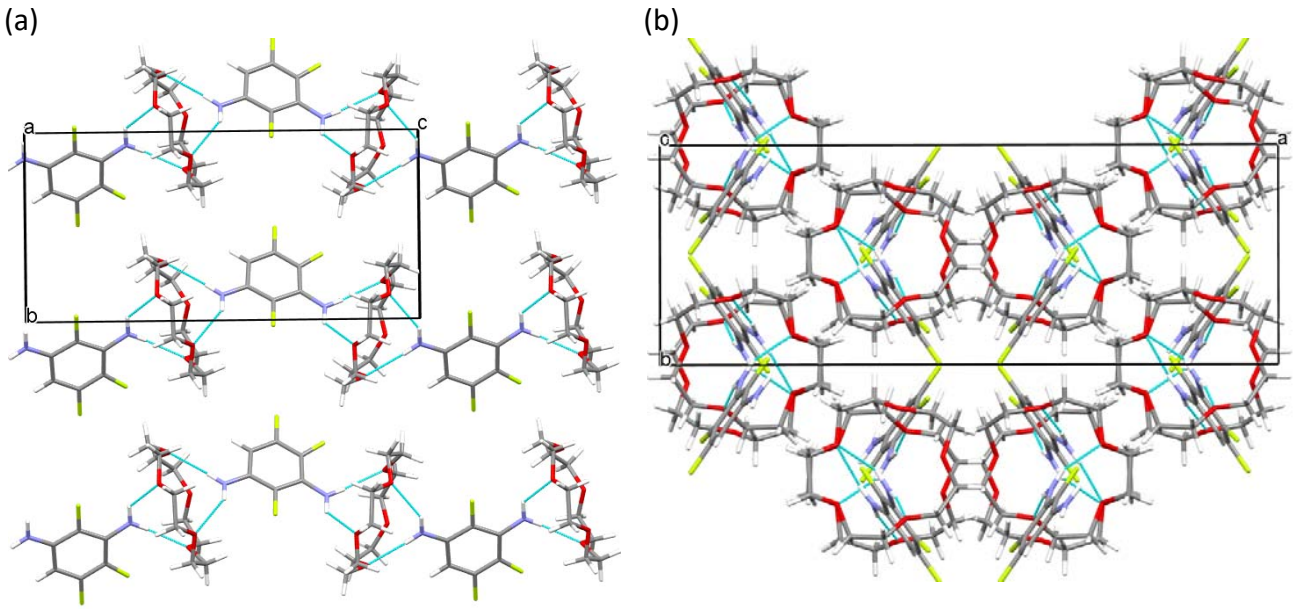


Fig. S2 Packing of the rods in **A·15cr5**, top view on the layer (a) and cross-section view (b).

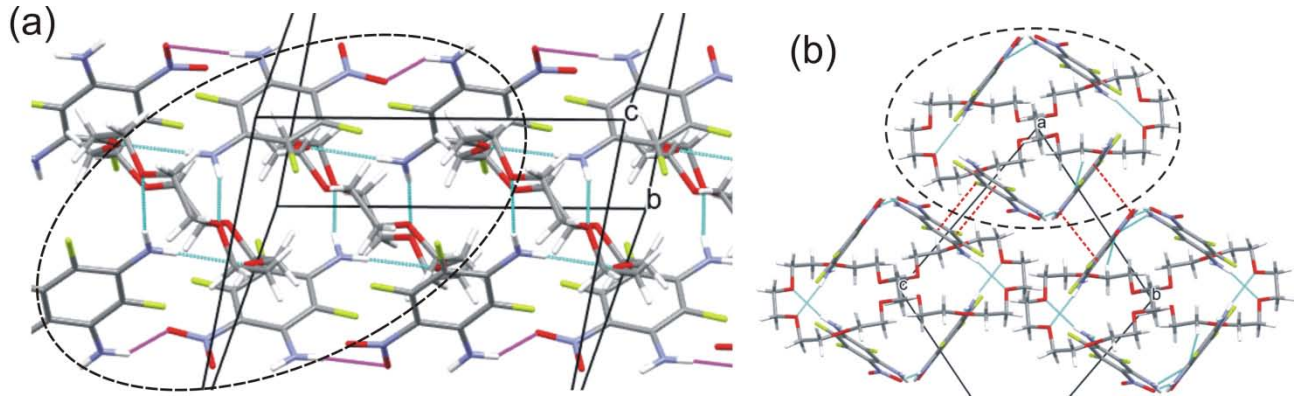
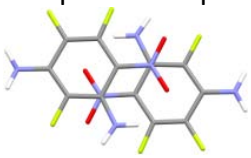


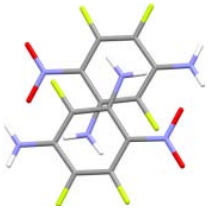
Fig. S3 Molecular packing in **C_2·18cr6**: H-bonded 1D assembly (a), N–H···O_{cr} (turquoise), N–H···O_{nitro} (magenta), unit (6 molecules) is framed; p···π interactions between assemblies (b).

anti-parallel displaced geometry

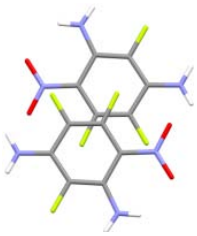


C_2·18cr6 (N-O···π)

C_2·18cr6 (C-F···π)

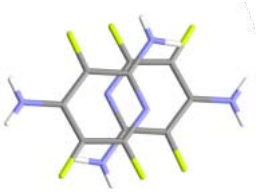


C_2·15cr5 (H-N···π)



C_2·15cr5(C-F···π)

anti-parallel displaced geometry



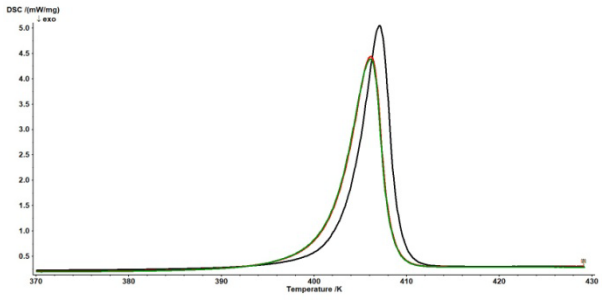
B_2·12cr4(π···π)

rotated geometry

C_2·12cr4 (π···π+ C-F···π)

Fig. S4 Overlap of stacked molecules in the co-crystals; intermolecular interactions are shown in brackets.

(a)



(b)

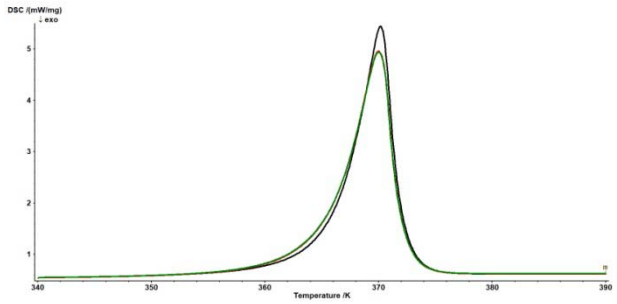


Fig. S5 DSC curves of the co-crystals, the first (black) second (red) and third (green) heating runs: **C_2·12cr4** (a); **B·15cr5** (b).

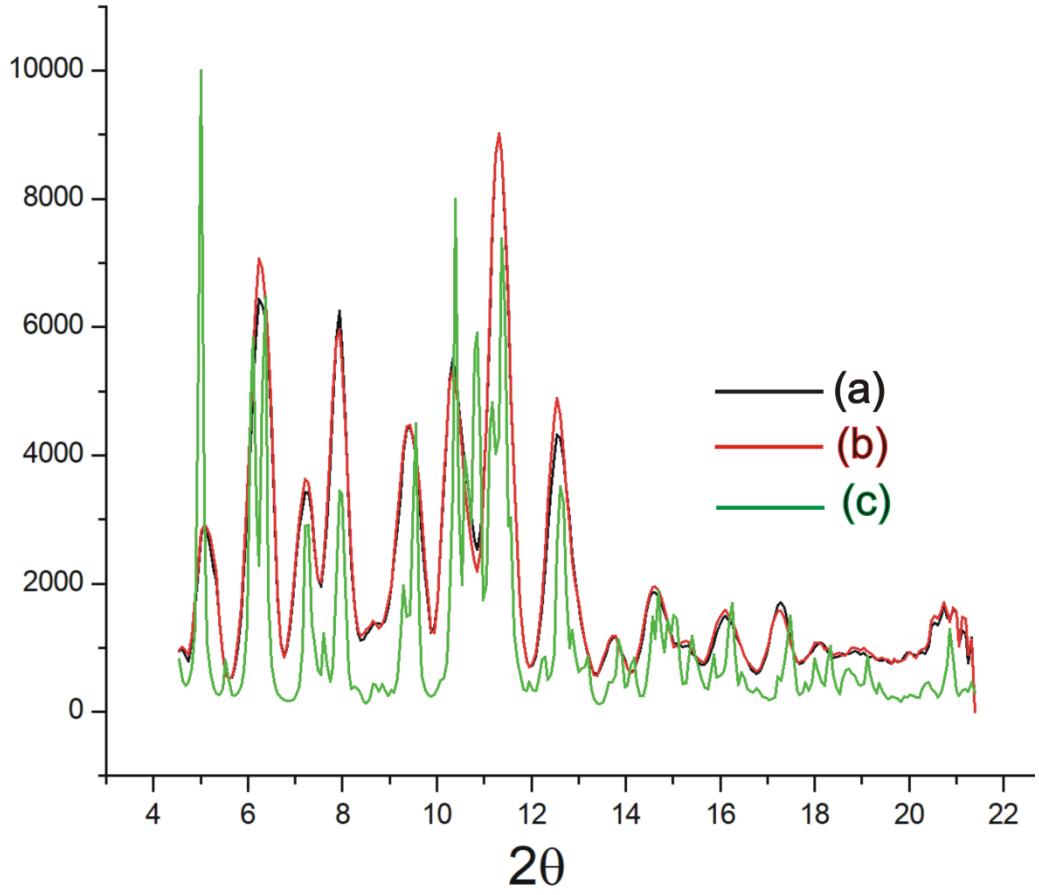


Fig. S6 PXRD patterns of **C_2·15cr5**: bulky precipitate crystallized from CCl_4+EtOAc (experimental, a), crystallized from the melt (experimental, b), simulated from SC-XRD data using MERCURY software with peak shape 0.1 (calculated, c).

Table S3 Enthalpies of co-crystals and isolated molecules. Level of theory: DFT/GGA-PBE/ USPP in QUANTUM ESPRESSO

Code	Final enthalpy (Ry)	Z	H/Z (Ry)[a]	$H(Y_x \cdot cr_{1-x})$[b](Ry)
1:1 co-crystals				
A·18cr6	-4965,43964502	8	-620,67995563	-310,33997782
A·15cr5	-4485,73906150	6	-560,71738269	-280,35869134
B·18cr6	-2512,69165561	4	-628,17291390	-314,08645695
B·15cr5	-4545,68850232	8	-568,21106279	-284,10553139
C·18cr6	-1407,99039845	2	-703,99519922	-351,99759961
2:1 co-crystals				
B_2·12cr4	-1553,31183037	2	-776,65591518	-258,88530506
C_2·18cr6	-2096,52758610	2	-1048,26379305	-349,42126435
C_2·15cr5	-1976,58304405	2	-988,29152202	-329,43050734
C_2·12cr4	-3713,32172365	4	-928,33043091	-309,44347697
Isolated molecules				
A	-260,89699642			
B	-268,38552210			
C	-344,21390406			
18cr6	-359,73061909			
15cr5	-299,76689594			
12cr4	-239,80588767			

[a] Z is the number of molecules in a cell.

[b] $H(Y_x \cdot cr_{1-x})$ is the enthalpy of a co-crystal normalized per unit, where Y – diamine, x – molar fraction of the diamine in the co-crystal (1/2 in 1:1 co-crystals and 2/3 in 2:1 co-crystals).

Table S4 Energies of individual molecules, H-bonded and p/π-dimers in co-crystals.[a] Level of theory: DFT/B3LYP/ M6-31G (TM)+*

Crystal	Molecule/dimer	*E* (Ha)	*E* (kJ mol^{-1})
1:1 co-crystals			
A·18cr6	A	-640,5123432	-1681216,798
	cr	-922,6781681	-2421845,656
	A···cr (*ortho*-N-H···Ocr)	-1563,2047691	-4103099,878
	A···cr (*para*-N-H···O_{cr})	-1563,2037276	-4103097,144
A·15cr5	A	-640,6850241	-1681670,051
	cr	-769,1717646	-2018922,048
	A···cr (*ortho*-N-H···O_{cr})	-1409,8719318	-3700631,847
	A···cr (*para*-N-H···O_{cr})	-1409,8702896	-3700627,536
B·18cr6	B	-656,7396075	-1723810,122
	cr	-923,0121607	-2422722,319
	B···cr (*ortho*-N-H···O_{cr})	-1579,7690408	-4146577,778
	B···cr (*para*-N-H···O_{cr})	-1579,7698471	-4146579,895
B·15cr5	B	-656,7396832	-1723810,320
	cr	-769,1722317	-2018923,274
	B···cr (*ortho*-N-H···O_{cr})	-1425,9267614	-3742772,563
	B···cr (*para*-N-H···O_{cr})	-1425,9282050	-3742776,352
2:1 co-crystals			
B_2·12cr4	B	-656,7390695	-1723808,710
	cr	-615,3344728	-1615129,924
	B···cr (*ortho*-N-H···O_{cr})	-1272,0786491	-3338952,038
	B···cr (*para*-N-H···O_{cr})	-1272,0826359	-3338962,503
	B…B (*ortho*-N-H···N_{het})	-1313,4959830	-3447664,256
	B…B (*para*-N-H···F)	-1313,4804502	-3447623,486
	B…B (π···π)	-1313,4787514	-3447622,027
C_2·15cr5	C1	-845,1848614	-2218441,224
	C2	-845,1851088	-2218441,874
	cr	-769,1711753	-2018920,501
	C1···cr (*para*-N-H···O_{cr})	-1614,3766912	-4237415,939
	C2···cr (*para*-N-H···O_{cr})	-1614,3746599	-4237410,607
	C1…C2 (*ortho*-N-H···O_{nitro})	-1690,3765745	-4436900,433
	C2…C1 (*ortho*-N-H···O_{nitro})	-1690,3761675	-4436899,364
	C1…C1 (H-N···π)	-1690,3710327	-4436885,887
	C2…C2 (C-F···π)	-1690,3746415	-4436895,359
C_2·12cr4	C1	-845,1844941	-2218440,260
	C2	-845,1845671	-2218440,452
	cr1	-615,3343722	-1615129,660
	cr2	-615,3351076	-1615131,590
	C1···cr2 (*ortho*-N-H···O_{cr})	-1460,5272960	-3833592,046
	C1···cr1 (*para*-N-H···O_{cr})	-1460,5280302	-3833593,974
	C2···cr1 (*ortho*-N-H···O_{cr})	-1460,5270929	-3833591,513

	C2⋯cr2 (*para*-N-H⋯O_{cr})	-1460,5269036	-3833591,017
	C1…C2 (*para*-N-H⋯O_{nitro})	-1690,3805087	-4436910,759
	C2…C1 (*para*-N-H⋯O_{nitro})	-1690,3806095	-4436911,024
	C1…C1 (π⋯π)	-1690,3708164	-4436885,319
	C2…C2 (π⋯π)	-1690,3712521	-4436886,463

[a] Intermolecular interaction energies Δ*E* (Table 6) were calculated by subtracting the energy of the two molecules from the dimer energy.

Table S5 ESP atomic charges for atoms of polyfluorinated arylenediamines in the gas phase (*q*, in units of elementary charge). The structures show the atom numbering scheme. Level of theory: DFT/B3LYP/ M6-31G (TM)+*.

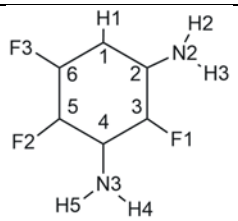
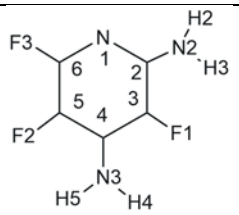
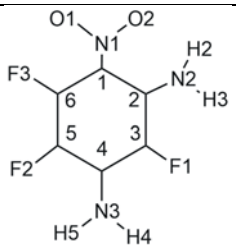
Code	**A**	**B**	**C**
Numbering scheme			
q(C1)	-0,411		-0,216
q(C2)	0,207	0,443	0,127
q(C3)	0,080	-0,076	0,101
q(C4)	0,077	0,216	0,101
q(C5)	0,097	-0,061	0,113
q(C6)	0,169	0,429	0,105
q(N1)		-0,529	0,776
q(N2)	-0,720	-0,734	-0,677
q(N3)	-0,686	-0,688	-0,682
q(O1)			-0,398
q(O2)			-0,479
q(F1)	-0,119	-0,103	-0,117
q(F2)	-0,127	-0,113	-0,123
q(F3)	-0,132	-0,162	-0,080
q(H1)	0,223		
q(H2)	0,342	0,355	0,397
q(H3)	0,326	0,330	0,340
q(H4)	0,332	0,342	0,350
q(H5)	0,343	0,351	0,361

Table S6. Comparison of QTAIM topological parameters at BCPs at intermolecular bonds for dimers in diaminopyridine A co-crystals: electron density (ρ), Laplacian of the electron density ($\nabla^2\rho$), G(r) - kinetic energy, V(r) –potential energy, E- total energy (in a.u).

System	ρ	$\nabla^2\rho$	G(r)	V(r)	E	$\lvert V(r)\rvert/G(r)$	E/ρ
B_2·12cr4_*ortho*-N-H···O_{cr}							
O(cr4)…H2(NH2)	0,024	0,079	0,019	-0,018	0,001	0,960	0,031
B_2·12cr4_*para*-N-H···O_{cr}							
O(cr4)…H(NH2)	0,022	0,075	0,017	-0,016	0,001	0,915	0,068
F1(C)…H1(cr)	0,006	0,031	0,006	-0,004	0,002	0,672	0,280
F1(C1)…H2(cr)	0,006	0,025	0,005	-0,003	0,002	0,664	0,280
B·15cr5_*ortho*-N-H···O_{cr}							
N…H(crCH2)	0,004	0,014	0,003	-0,002	0,001	0,672	0,209
N(NH2)…H(C1H2 cr)	0,005	0,019	0,004	-0,005	0,001	1,295	0,213
H(NH2)…O1(cr5)	0,015	0,060	0,013	-0,011	0,002	0,825	0,144
H(NH2)…O2(cr5)	0,021	0,074	0,017	-0,015	0,002	0,904	0,078
N(NH2)…H(C2H2 cr)	0,005	0,021	0,004	-0,003	0,001	0,677	0,238
H(NH2)…O3(cr5)	0,007	0,026	0,005	-0,003	0,002	0,698	0,229
B·15cr5_*para*-N-H···O_{cr}							
N(NH2)…H(C1H2 cr)	0,007	0,022	0,004	-0,003	0,001	0,752	0,155
H(NH2)…O1(cr5)	0,028	0,094	0,023	-0,023	0,001	0,986	0,012
H(NH2)…O2(cr5)	0,024	0,083	0,019	-0,018	0,001	0,926	0,061
F…H(C2H2 cr)	0,003	0,013	0,002	-0,001	0,001	0,630	0,267
B·18cr6_*ortho*-N-H···O_{cr}							
N…H(crC1)	0,006	0,021	0,004	-0,003	0,001	0,730	0,173
N…H(crC2)	0,007	0,022	0,004	-0,003	0,001	0,736	0,172
F…H(C1 cr)	0,002	0,010	0,002	-0,001	0,001	0,605	0,293
F…H(C2 cr)	0,005	0,021	0,004	-0,003	0,001	0,661	0,263
N(N1H2)…H(C1H2 cr)	0,004	0,018	0,003	-0,002	0,001	0,656	0,260
N(N1H2)…H(C2H2 cr)	0,004	0,017	0,003	-0,002	0,001	0,645	0,271
H1(N1H2)…O1(cr6)	0,019	0,070	0,016	-0,014	0,002	0,871	0,106
N1(N1H2)…O2cr6)	0,005	0,024	0,004	-0,003	0,001	0,659	0,282
H2(N1H2)…O3(cr6)	0,016	0,062	0,013	-0,011	0,002	0,839	0,131
B·18cr6_*para*-N-H···O_{cr}							
F1…H(C1 cr)	0,005	0,022	0,004	-0,003	0,001	0,660	0,272
F1…H(C2 cr)	0,008	0,036	0,007	-0,005	0,002	0,690	0,275
F2…H(C1 cr)	0,005	0,020	0,004	-0,002	0,002	0,648	0,281
F2…H(C2 cr)	0,005	0,019	0,004	-0,002	0,002	0,660	0,257
N(N1H2)…O1(cr6)	0,003	0,010	0,002	-0,001	0,001	0,634	0,236
N(N1H2)…O2(cr6)	0,004	0,016	0,003	-0,002	0,001	0,661	0,237
N(N1H2)…O3(cr6)	0,006	0,024	0,005	-0,003	0,002	0,683	0,244
H1(N1H2)…O4(cr6)	0,023	0,082	0,019	-0,018	0,001	0,929	0,058
H2(N1H2)…O5(cr6)	0,010	0,041	0,008	-0,006	0,002	0,754	0,197

B_2·12cr4_ *para*-N-H···F							
F1…H2	0,011	0,055	0,011	-0,008	0,003	0,727	0,261
F2…H1	0,011	0,055	0,011	-0,008	0,003	0,727	0,261
F1…F2	0,005	0,024	0,004	-0,003	0,002	0,637	0,329
B_2·12cr4_*ortho*-N-H···N_{het}							
N1…H2(NH2)	0,027	0,073	0,019	-0,020	-0,001	1,042	-0,030
H1(NH2)…N2	0,027	0,073	0,019	-0,020	-0,001	1,042	-0,030