Impact of molecular packing rearrangement on solid-state fluorescence: polyhalogenated *N*-hetarylamines *vs* their co-crystals with 18-crown-6

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

Parameter	Code of the substance					
	2B·cr	**2C·cr**	**2D·cr**	**2E·cr**	**2F·cr**	**2G·cr**
Chemical formula	$2(C_5H_2ClF_3N_2)$, $C_{12}H_{24}O_6$	$2(C_5H_2Cl_2F_2N_2)$, $C_{12}H_{24}O_6$	$2(C_5H_3F_3N_2)$, $C_{12}H_{24}O_6$	$2(C_5H_2ClF_3N_2)$, $C_{12}H_{24}O_6$	$2(C_9H_6F_2N_2)$, $C_{12}H_{24}O_6$	$2(C_9H_4ClF_3N_2)$, $C_{12}H_{24}O_6$
Formula weight	629.38	662.28	560.50	629.38	624.63	729.50
Temperature (K)	296	296	296	296	296	296
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/c$	*C*2/*c*	$P2_1/n$	$P2_1/n$
a (Å)	19.1536(10)	19.2435(8)	8.722(2)	22.3524(11)	12.6301(5)	12.5421(5)
b (Å)	9.5830(5)	9.9058(4)	16.464(4)	8.0294(3)	8.1303(3)	9.4386(3)
c (Å)	17.3666(14)	17.6406(8)	9.500(2)	16.3762(8)	15.8162(6)	14.5435(6)
α (deg)	90	90	90	90	90	90
β (deg)	118.714(2)	119.630(2)	100.139(9)	109.214(2)	106.549(2)	106.472(2)
γ (deg)	90	90	90	90	90	90
Cell volume (Å^3)	2795.6(3)	2923.0(2)	1343.0(6)	2775.4(2)	1556.83(10)	1651.00(11)
Z	4	4	2	4	2	2
d_{calc} (g cm^{-3})	1.495	1.505	1.386	1.506	1.332	1.467
μ (mm^{-1})	0.316	0.474	0.127	0.318	0.109	0.279
Crystal dimensions (mm)	0.22×0.36×0.76	0.14×0.16×0.31	0.16×0.28×0.47	0.15×0.34×0.55	0.42×0.56×0.58	0.35×0.43×0.48
θ range (deg)	27.51	30.21	26.02	28.76	28.02	30.14
Reflections collected/ unique	22277/3208	30667/4345	18817/2649	35519/3584	27327/3766	36550/4872
R (int)	0.0307	0.0509	0.0524	0.0391	0.0422	0.0423
Reflections with $I > 2\sigma(I)$	2549	3147	1664	2659	2962	3681
Parameters	198	189	180	190	207	225
Final R_1 ($I > 2\sigma(I)$)	0.0505	0.0474	0.0521	0.0435	0.0404	0.0519
Final wR_2 (all data)	0.1513	0.1348	0.1626	0.1627	0.1224	0.1726
Goodness-of-fit on F^2	1.080	0.990	1.006	1.028	0.994	0.956
CCDC number	1911499	1911500	1911501	1911502	1911503	1911504

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

Parameter	Code of the substance					
	2H·cr	**B**	**C**	**D**	**E**	**H**
Chemical formula	$2(C_{20}H_{14}F_3N_3)$, $C_{12}H_{24}O_6$	$C_5H_2ClF_3N_2$	$C_5H_2Cl_2F_2N_2$	$C_5H_3F_3N_2$	$C_5H_2ClF_3N_2$	$C_{20}H_{14}F_3N_3$
Formula weight	971.00	182.54	198.99	148.09	182.54	353.34
Temperature (K)	296	200	296	200	296	296
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_1/c$	$P2_1/n$	P-1	P-1
a (Å)	15.8794(6)	9.2213(16)	15.0718(7)	3.6538(3)	5.0807(5)	8.5190(8)
b (Å)	13.2887(6)	13.783(2)	13.6626(5)	7.6296(8)	7.6319(7)	12.8724(13)
c (Å)	11.5020(4)	5.0802(8)	7.0649(3)	20.158(2)	8.5518(9)	15.6110(17)
α (deg)	90	90	90	90	77.722(4)	110.573(4)
β (deg)	98.930(2)	90	92.519(2)	91.323(4)	89.064(5)	98.064(4)
γ (deg)	90	90	90	90	87.753(4)	90.097(4)
Cell volume (Å^3)	2397.69(16)	645.70(19)	1453.40(11)	561.79(10)	323.75(6)	1584.5(3)
Z	2	4	8	4	2	4
d_{calc} (g cm^{-3})	1.345	1.878	1.819	1.751	1.872	1.481
μ (mm^{-1})	0.104	0.576	0.857	0.180	0.575	0.114
Crystal dimensions (mm)	0.37×0.48×0.58	0.05×0.36×0.42	0.25×0.36×0.60	0.08×0.13×0.48	0.28×0.37×0.57	0.21×0.29×0.46
θ range (deg)	27.89	26.11	28.00	30.55	26.03	25.12
Reflections collected/ unique	48173/5726	4219/1127	27163/3498	16065/1711	5129/1265	26270/5628
R (int)	0.0456	0.0419	0.0463	0.0382	0.0235	0.0379
Reflections with $I > 2\sigma(I)$	4296	954	2758	1386	1040	2580
Parameters	328	106	216	100	108	469
Final R_1 ($I > 2\sigma(I)$)	0.0445	0.0467	0.0424	0.0516	0.0303	0.0978
Final wR_2 (all data)	0.1398	0.1492	0.1338	0.1391	0.0758	0.2623
Goodness-of-fit on F^2	0.997	0.965	0.972	1.023	0.988	0.913
CCDC number	1911505	1911494	1911495	1911496	1911497	1911498

Table S2 Hydrogen bonding in the co-crystals

Associate	Interaction N–H…O	N–H (Å)	H…O (Å)	N…O (Å)	Angle N–H…O (deg)	Symmetry code for acceptor
2B·cr	N(2)-H(2A)...O(2)	0.86(3)	2.43(3)	3.217(3)	153(3)	
	N(2)-H(2A)...O(3)	0.86(3)	2.53(3)	3.170(3)	132(2)	
	N(2)-H(2B)...O(1)	0.84(2)	2.49(2)	3.042(3)	124(2)	1-x,-y,1-z
	N(2)-H(2B)...O(2)	0.84(2)	2.39(2)	3.169(3)	156(3)	1-x,-y,1-z
2C·cr	N(2)-H(2A)...O(2)	0.86(2)	2.52(2)	3.304(3)	152(2)	x,1-y,-1/2+z
	N(2)-H(2B)...O(2)	0.86(2)	2.45(2)	3.242(2)	153(2)	1-x,y,1/2-z
	N(2)-H(2B)...O(3)	0.86(2)	2.46(2)	3.047(2)	126(2)	1-x,y,1/2-z
2D·cr	N(2)-H(1N)...O(2)	0.88(2)	2.21(2)	3.084(3)	176(2)	
	N(2)-H(2N)...O(3)	0.87(2)	2.51(3)	3.196(3)	136(2)	2-x,-y,1-z
2E·cr	N(2)-H(2A)...O(3)	0.91(3)	2.22(3)	3.095(3)	162(3)	
	N(2)-H(2B)...O(1)	0.83(3)	2.28(3)	3.099(3)	170(3)	
2F·cr	N(2)-H(2A)...O(1)	0.85(1)	2.24(2)	3.052(2)	161(2)	
	N(2)-H(2B)...O(2)	0.85(1)	2.24(1)	3.079(2)	172(1)	-x,1-y,1-z
2G·cr	N(2)-H(2A)...O(2)	0.84(3)	2.27(3)	3.065(3)	158(2)	
	N(2)-H(2B)...O(1)	0.85(2)	2.41(2)	3.186(3)	153(2)	-x,1-y,-z
2H·cr	N(2)-H(2A)...O(2)	0.85(2)	2.20(2)	3.037(2)	171(2)	
	N(2)-H(2B)...O(3)	0.87(2)	2.26(2)	3.093(2)	160(2)	-x,1-y,2-z

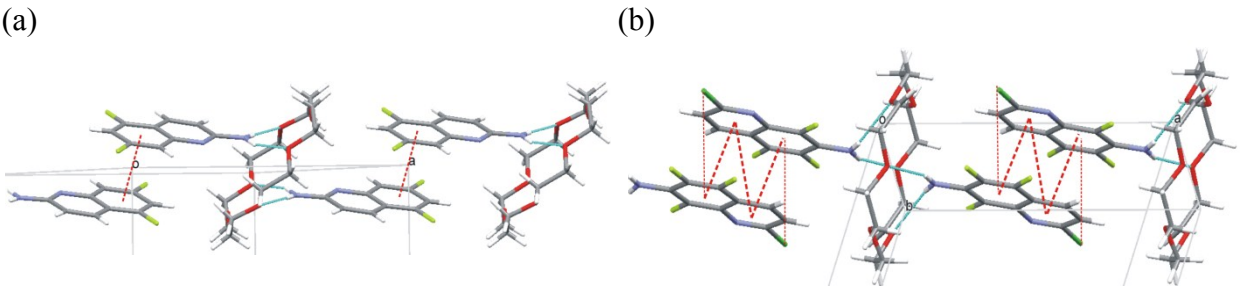

Fig. S1 Crystal packing in the co-crystals **2F·cr** (a) and **2G·cr** (b), top view on the rods

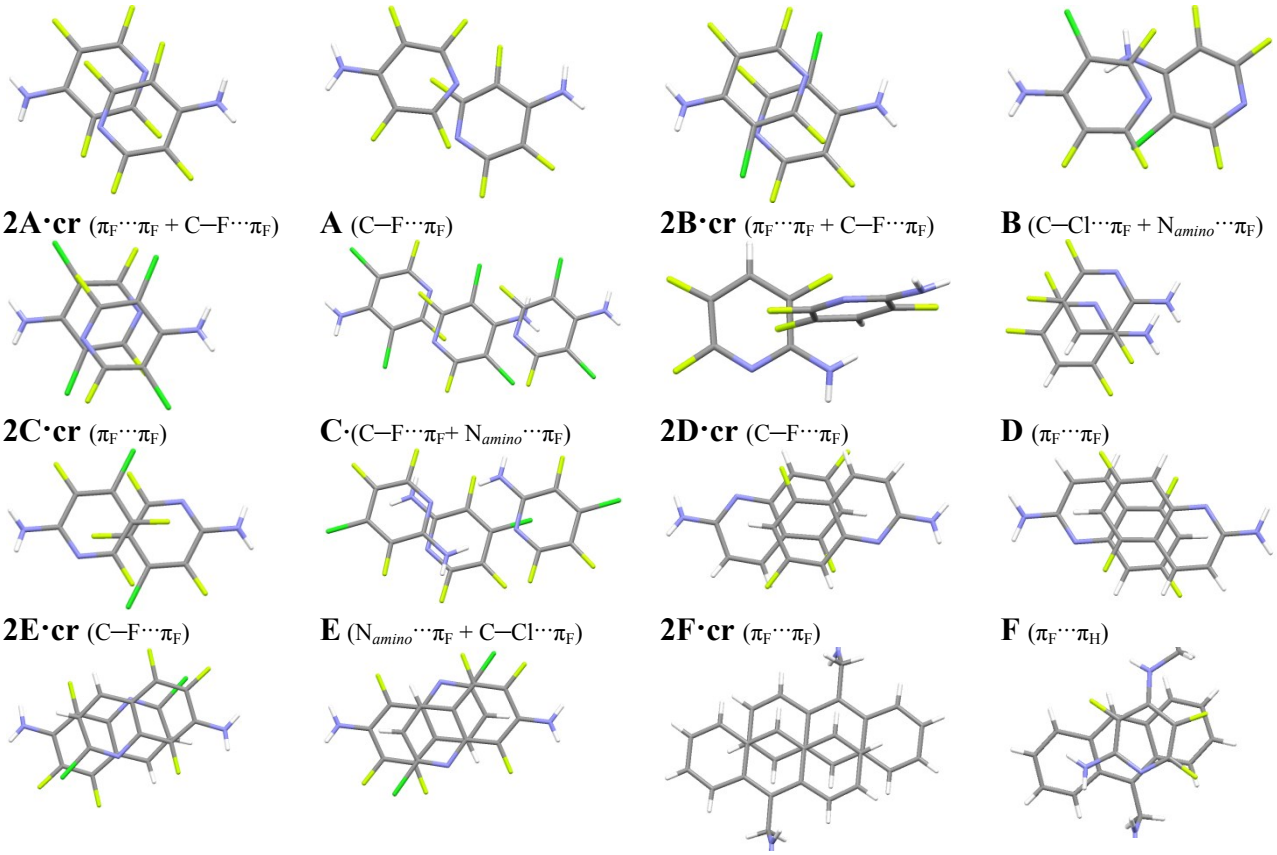

Fig. S2 Overlap of stacked molecules in the crystals; intermolecular interactions are shown in brackets

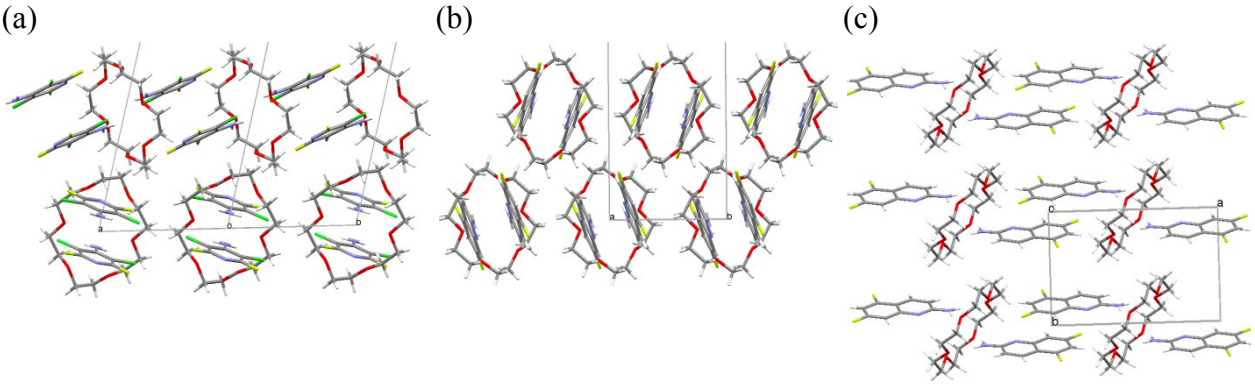

Fig. S3 Packing of the rods in co-crystals: **2C·cr**, crosswise deposition (a); **2F·cr**, parallel deposition (b) and "ledge-to-cavity" packing (c)

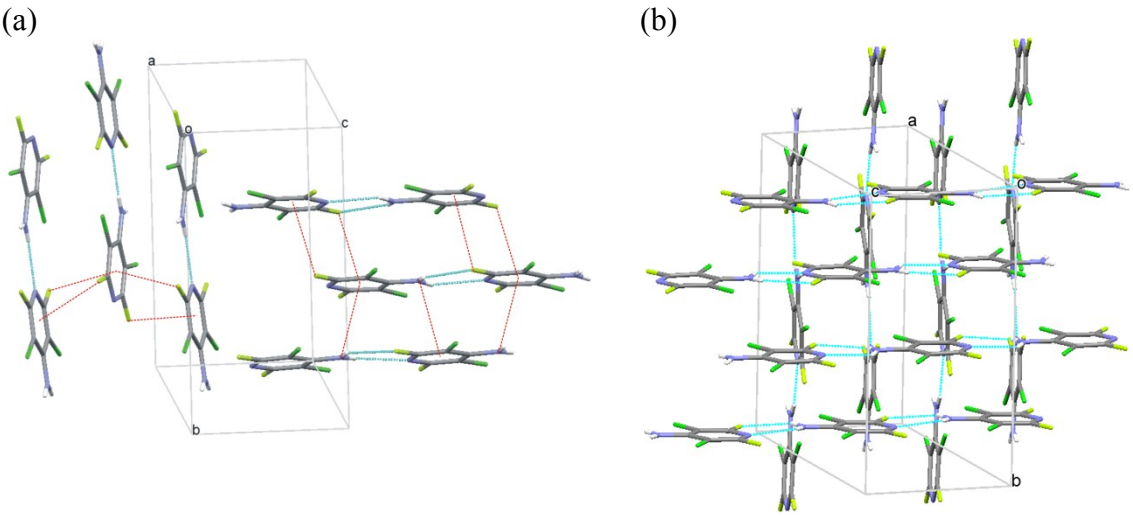

Fig. S4 Molecular packing in the single crystals of amine **C**: adjacent chains (a); grid (b)

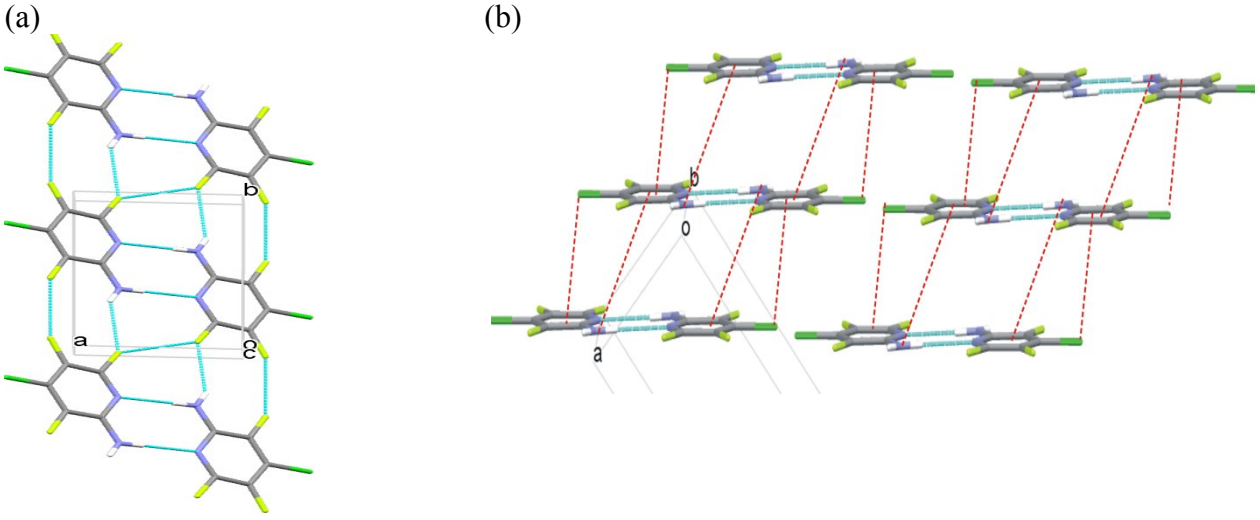

Fig. S5 Molecular packing in the single crystals of amine **E**: top view on the layer (a); adjacent layers (b).

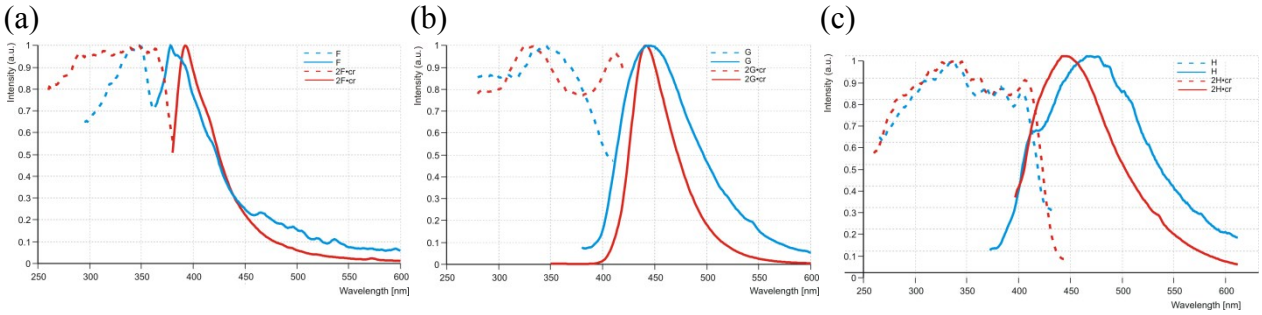

Fig. S6 Absorption (dashed lines) and fluorescence (solid lines) spectra of arylamines (blue lines) and their co-crystals with 18-crown-6 (red lines): (a) **F** and **2F·cr**, (b) **G** and **2G·cr**, (c) **H** and **2H·cr**.

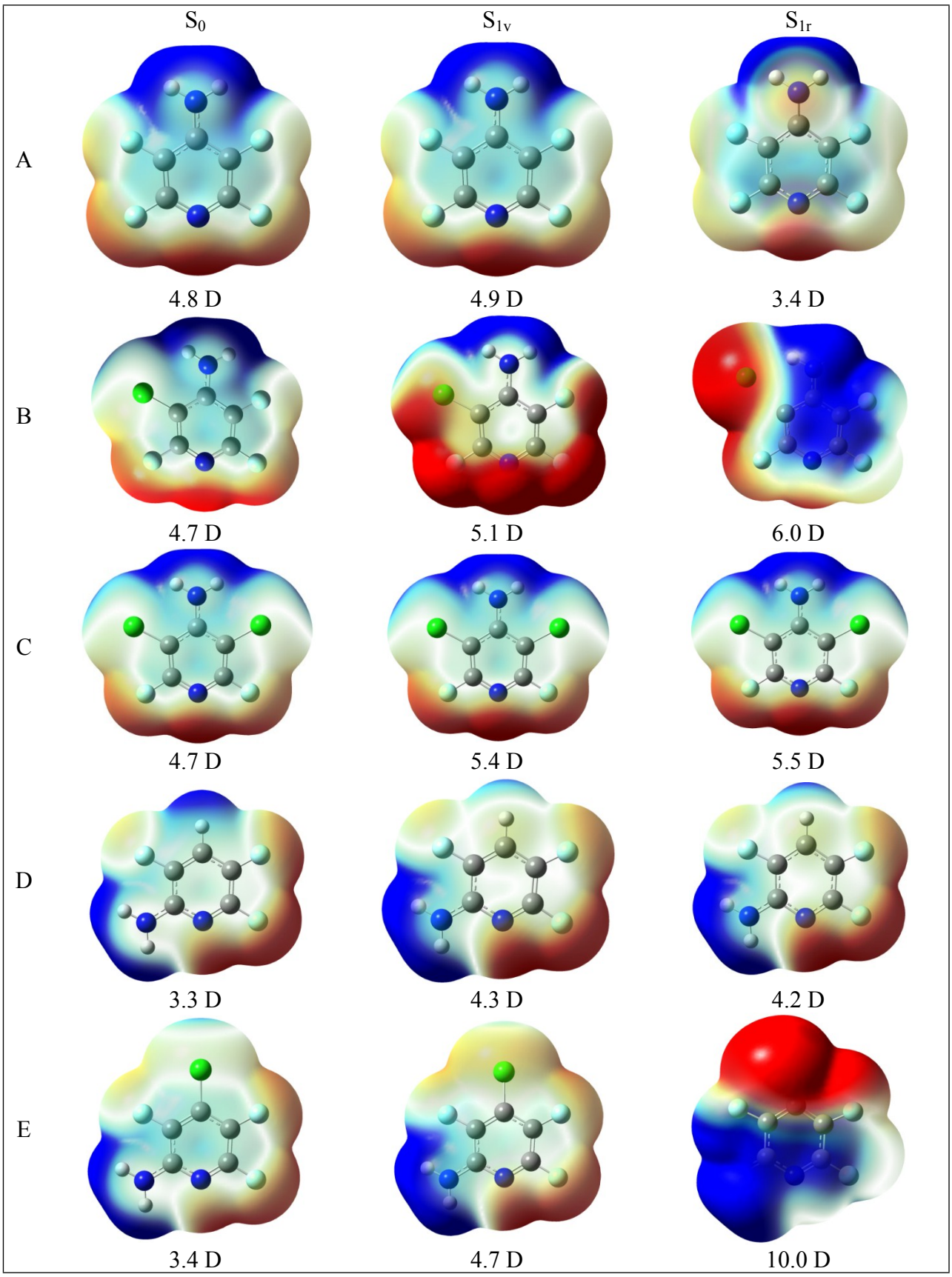

Fig. S7 Molecular Electrostatic Potential (MEP) maps for molecules **A** to **E**, in the ground state (S_0), Frank-Condon S_1 state (S_{1v}), and relaxed S_1 state (S_{1r}). MEP is mapped on the molecular density (| Isovalue | = 0.004 a.u.); the interval is [-0.025 ; 0.025] *e* (from red to blue). The value of the electric dipole moment is depicted underneath the figures

Table S3 Computed absorption and fluorescence wavelength and oscillator strength for isolated amines in the gas phase

Amine	λ_{abs} (nm)	f	λ_{fl} (nm)	f
A	290	0.2840	358	0.0489
B	284	0.3453	357	0.0581
C	351	0.4224	399	0.0612
D	335	0.1955	398	0.1180
E	339	0.1005	426	0.0000

Table S4 Energy differences between emissive singlet and triplet states of hetarylamines ($\Delta E_{S\text{-}T}$, eV).

Code	Isolated molecule	Homocrystal	Co-crystal
A	0.374	0.362	0.358
B	0.302	0.296	0.284

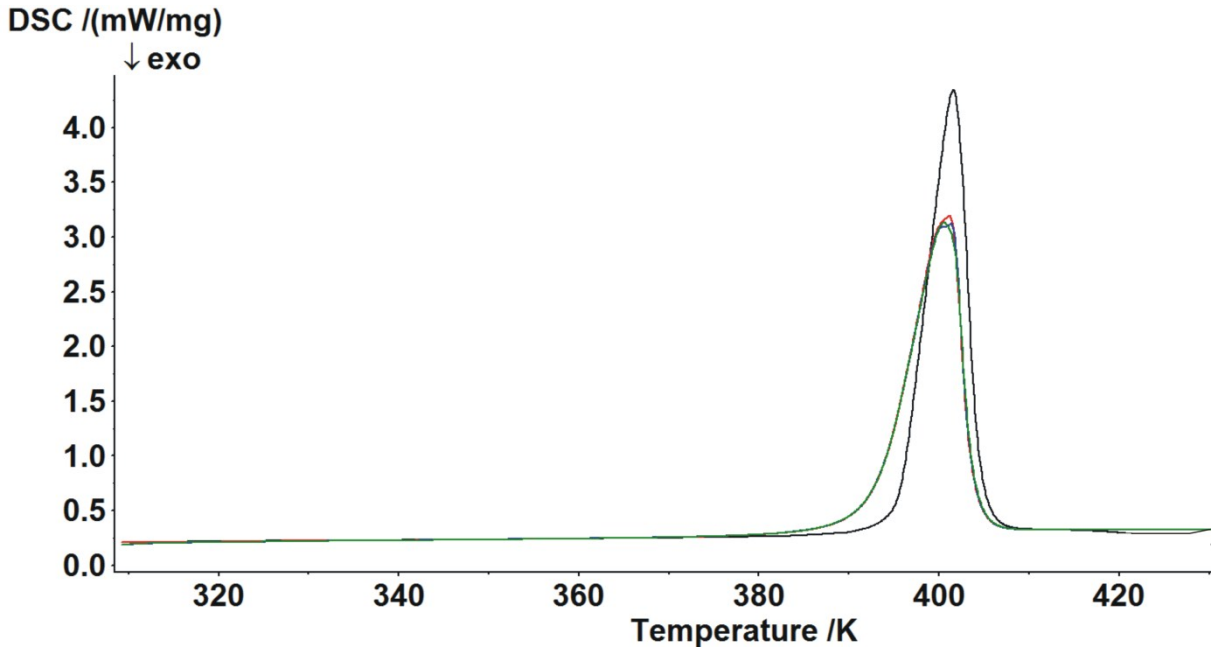

Fig. S8 DSC curves of the associate **2B·cr**: the first (black) and subsequent (red, blue, green) heating runs

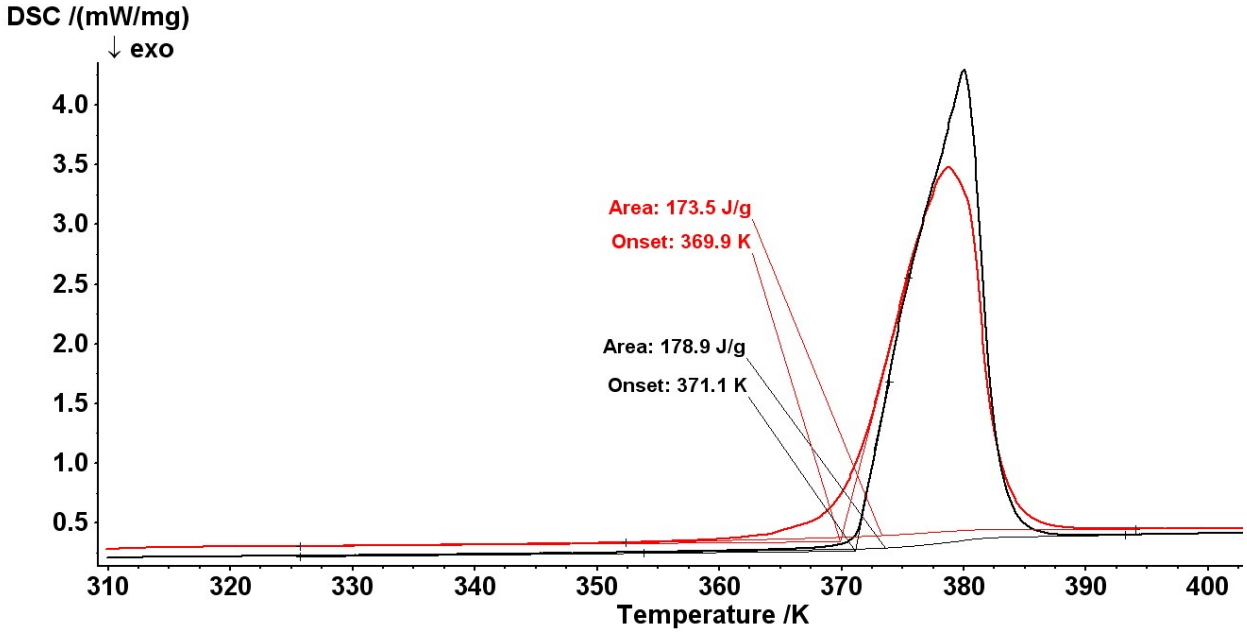

Fig. S9 DSC curves of the co-crystal **2C·cr**: the first (black) and second (red) heating runs

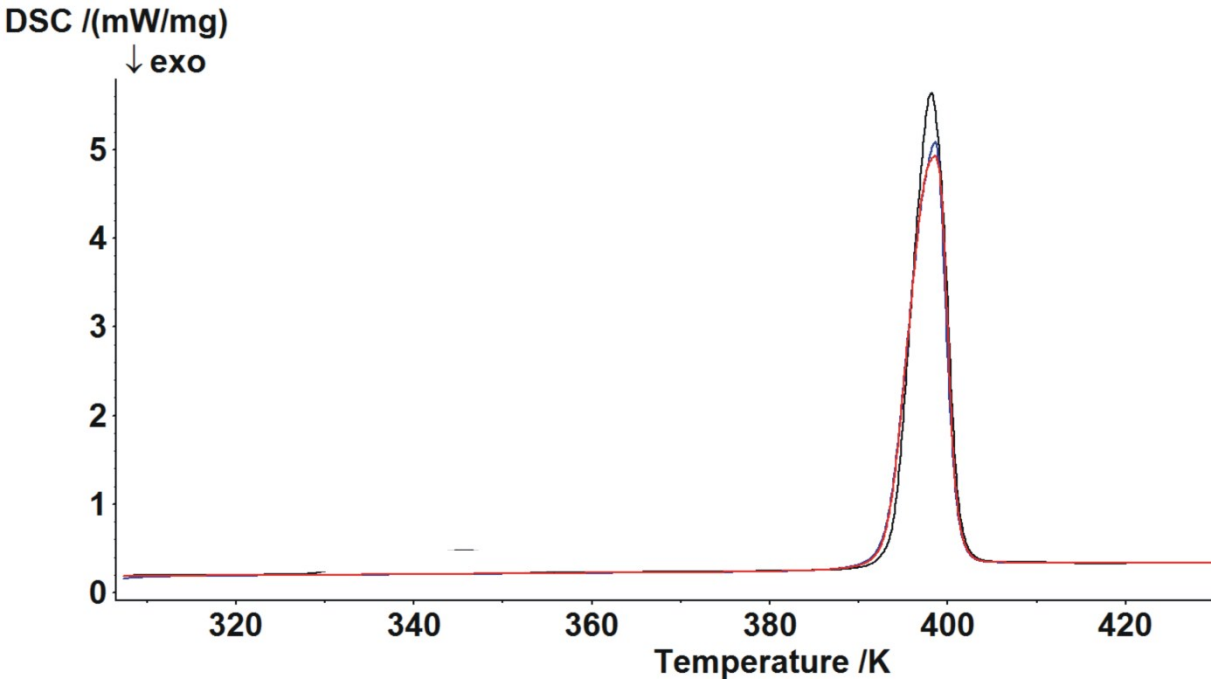

Fig. S10 DSC curves of the co-crystal **2E·cr**: the first (black) and subsequent (red, blue) heating runs

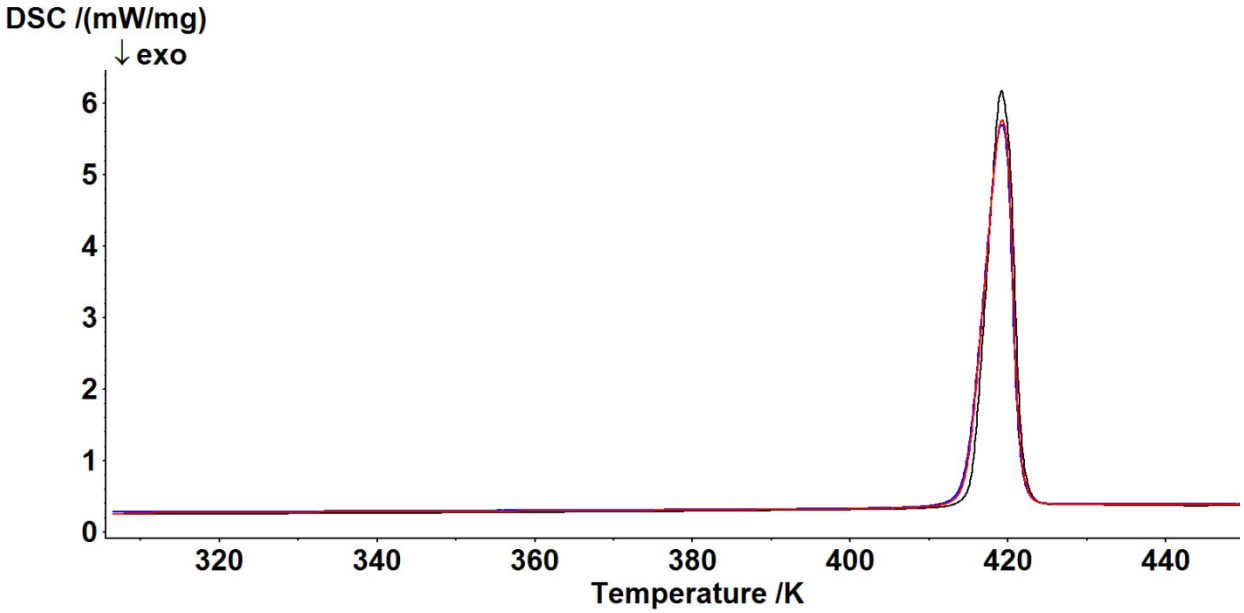

Fig. S11 DSC curves of the co-crystal **2G·cr**: the first (black) and subsequent (red, blue) heating runs

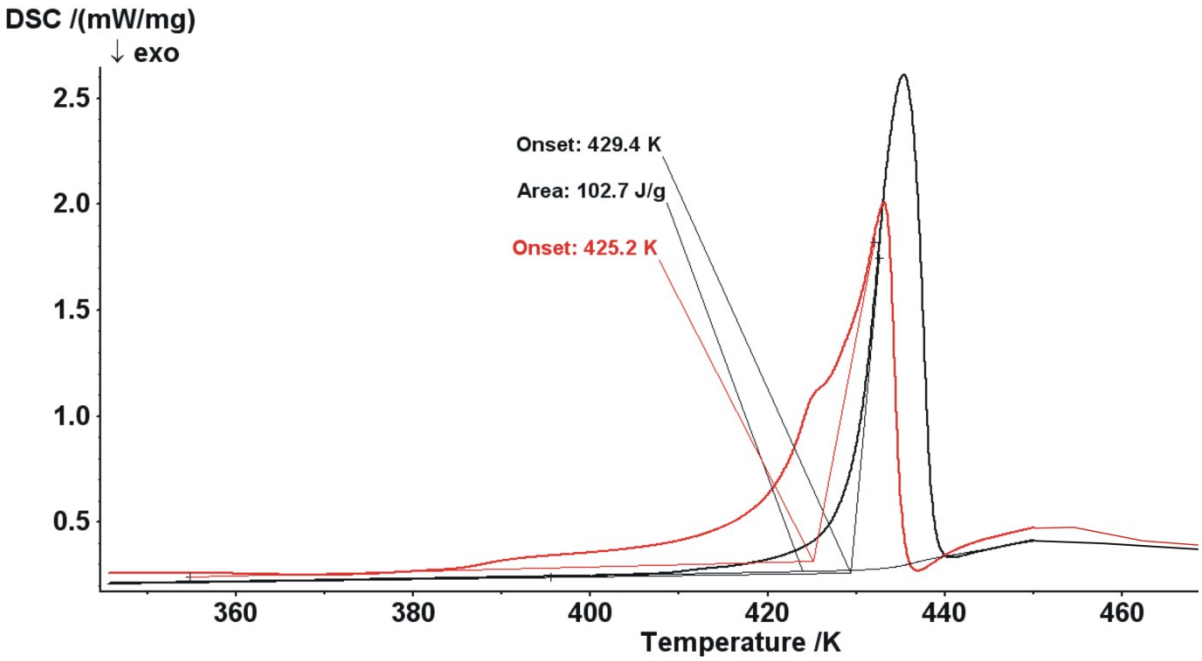

Fig. S12 DSC curves of the co-crystal **2H·cr**: the first (black) and second (red) heating runs