Packing and Conformational Polymorphism in 1,2-Bis(amino carbonyl-(1-*tert*-butyl-1*H*-pyrazole-(3)5-yl))-ethanes. Illuminating Examples of Highly Flexible Molecules

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Table of Contents

1. Crystallographic Data of Compounds 1-2

Table S1. X-ray data for compounds **1a-b**

Compound	**1aI**	**1aII**	**1b**
CCDC	2063650	2063637	1453941
Empirical formula	$C_{20}H_{32}N_6O_2$	$C_{20}H_{32}N_6O_2$	$C_{30}H_{34}F_2N_6O_2.2H_2O$
Mw	388.52	388.52	584.66
T [K]	100	100	293
Crystal system	Monoclinic	Triclinc	Triclinc
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
λ (Å)	Mo / 0.71073	Mo / 0.71073	Mo / 0.71073
a [Å]	6.207 (3)	6.3362 (2)	8.0475 (3)
b [Å]	11.186 (6)	7.9693 (3)	9.0924 (5)
c [Å]	15.526 (8)	10.7737 (4)	11.3156 (5)
α [°]	90	87.1720 (10)	108.716 (3)
β [°]	92.969 (13)	83.2190 (10)	95.044 (2)
γ [°]	90	87.6340 (10)	95.755 (2)
V [Å^3]	1076.4 (10)	539.21 (3)	773.88 (6)
Z	4 (0.5)	1 (0.5)	2 (0.5)
$D_{calcd.}$ [g cm^{-3}]	1.199	1.196	1.255
μ [mm^{-1}]	0.080	0.080	0.093
F(000)	420	210	310
Crystal size (mm)	0.40×0.20×0.19	0.30×0.25×0.20	0.62×0.56× 0.37
θ range for data	3.87 to 30.09	3.24 to 27.14	1.92 to 27.27
Collection (deg) *h. k. l* range	-8≤ h ≤ 8 -15≤ k ≤ 15 -21≤ l ≤ 21	-8≤ h ≤ 8 -10≤ k ≤ 10 -13≤ l ≤ 10	-10≤ h ≤ 10 -11≤ k ≤ 11 -14≤ l ≤ 14
Reflections collected/unique	14140 / 3121 [R(int) =0.0245]	17455 / 2357 [R(int) =0.0268]	22264 / 3466 [R(int) = 0.0252]
Data/restraints/parameters	3121 / 0/ 127	2357 / 18/ 131	3466 / 4 / 189
Absoption correction	Multi-scan	Multi-scan	Gaussian
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices	R1 = 0.0713. wR2 = 0.2025	R1 = 0.0930. wR2 = 0.2450	R1 = 0.0517. wR2 = 0.1332
R all data	R1 = 0.0959. wR2 = 0.2219	R1 = 0.1027. wR2 = 0.2537	R1 = 0.0669. wR2 = 0.1466
Goodness of fit on F^2	1.043	1.053	1.039
Largest diff. peak and hole (e Å^3)	0.817 and -0.299	1.012 and -0.488	0.509 and -0.405

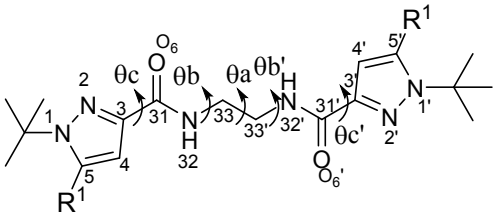
Table S2. X-ray data for compounds **1c-d** and **2a**

Compound	**1c**	**1d**	**2aI**	**2aII**
CCDC	2063652	2063657	2063664	2063665
Empirical formula	$C_{30}H_{34}Cl_2N_6O_2$	$C_{30}H_{34}Br_2N_6O_2$. $2(C_2H_3CN)$	$C_{20}H_{32}N_6O_2$	$C_{20}H_{32}N_6O_2$. $2(H_2O)$
Mw	581.53	752.56	388.51	424.55
T [K]	100	296 (2)	100	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	C $2/c$	$P2_1/c$	$P2_1/c$
λ (Å)	Mo / 0.71073	Cu / 1.54178	Mo / 0.71073	Cu / 1.54178
a [Å]	6.2058 (6)	18.2905 (13)	9.6598(5)	9.4612(2)
b [Å]	7.4087 (8)	8.4837 (5)	26.0820(15)	18.6670(4)
c [Å]	31.068 (3)	24.6711 (15)	9.6981(5)	14.2833(3)
α [°]	90.000(3)	90	90	90
β [°]	89.033 (3)	110.526 (6)	117.691	101.4630(10)
γ [°]	90.000(3)	90	90	90
V [Å^3]	1428.3 (3)	3585.2 (4)	2163.6 (2)	2472.29(9)
Z	2 (0.5)	4 (0.5)	4 (1)	4(1)
$D_{calcd.}$ [g cm^{-3}]	1.352	1.394	1.193	1.141
μ [mm^{-1}]	0.267	3.199	0.080	0.659
F(000)	612	1544	840	920
Crystal size (mm)	0.31×0.05×0.05	0.16×0.14×0.06	0.28×0.15×0.09	0.44×0.26×0.18
θ range for data	2.623 to 27.15	3.826 to 68.634	2.381 to 27.145	4.769 to 68.261
Collection (deg) *h. k. l* range	-7≤ *h* ≤ 7 -9≤ *k* ≤ 9 -39≤ *l* ≤ 39	-17≤ *h* ≤ 21 -10≤ *k* ≤ 10 -29≤ *l* ≤ 29	-12 ≤ *h* ≤ 12 -33 ≤ *k* ≤ 33 -12 ≤ *l* ≤ 12	-11 ≤ *h* ≤ 11 -22 ≤ *k* ≤ 22 -17 ≤ *l* ≤ 17
Reflections collected/unique	37699 / 3150 [R(int) = 0.198]	26365 / 3232 [R(int) = 0.098]	31440 / 4782 [R(int) = 0.065]	29580 / 4434 [R(int) = 0.027]
Data/restraints/para-meters	3150 / 0 / 181	3232 / 0/ 209	4782 / 0 / 289	4434 / 0 / 295
Absoption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final *R* indices	R1 = 0.0849. wR2 = 0.1634	R1 = 0.0602. wR2 = 0.1501	R1 = 0.0595. wR2 = 0.1112	R1 = 0.0506. wR2 = 0.1384
R all data	R1 = 0.1528. wR2 = 0.1814	R1 = 0.0917. wR2 = 0.1637	R1 = 0.0970. wR2 = 0.1230	R1 = 0.0600. wR2 = 0.1469
Goodness of fit on F^2	1.165	1.063	1.060	1.045
Largest diff. peak and hole (*e* Å^3)	0.502 and -0.397	0.338 and -0.551	0.361 and -0.228	0.352 and -0.178

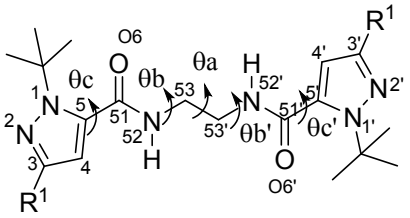
Table S3. X-ray data for compounds **2b-d**.

Compound	**2b**	**2c**	**2dI**	**2dII**
CCDC	1453942	1498649	1498643	2063666
Empirical formula	$C_{30}H_{34}F_2N_6O_2$	$C_{30}H_{34}Cl_2N_6O_2$	$C_{30}H_{34}Br_2N_6O_2$	$C_{30}H_{34}Br_2N_6O_2$
Mw	548.63	581.53	670.45	670.45
T [K]	293(2)	293	293	296
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$C2/c$	$C2/c$	$C2/c$	$P4_2/n$
λ (Å)	Mo / 0.71073	Mo / 0.71073	Mo / 0.71073	Cu / 1.54178
a [Å]	25.2656(6)	26.6417 (8)	27.6305(9)	18.7994(4)
b [Å]	11.4447(2)	11.3041 (3)	11.0991(3)	18.7994(4)
c [Å]	9.7315(2)	9.7939 (2)	9.8477(2)	18.8804(6)
α [°]	90	90	90	90
β [°]	94.7990(10)	91.318 (2)	90.520(2)	90
γ [°]	90	90	90	90
V [Å^3]	2804.07(10)	2948.76 (13)	3019.91(14)	6672.7
Z	4(0.5)	8 (0.5)	4(0.5)	8(0.5)
$D_{calcd.}$ [g cm^{-3}]	1.300	1.310	1.475	1.335
μ [mm^{-1}]	0.093	0.258	2.722	3.353
F(000)	1160	1224	1368	2736
Crystal size (mm)	0.44×0.38×0.20	0.77×0.54× 0.44	0.45×0.367×0.27	0.30×0.21×0.13
θ range for data	1.62 to 27.18	1.96 to 27.57	1.47 to 28.36	3.317 to 68.38
Collection (deg) *h. k. l* range	-32 ≤ h ≤ 32 -14 ≤ k ≤ 14 -12 ≤ l ≤ 12	-34 ≤ h ≤ 34 -14 ≤ k ≤ 14 -12 ≤ l ≤ 12	-36 ≤ h ≤ 36 -14 ≤ k ≤ 14 -13 ≤ l ≤ 13	-22 ≤ h ≤ 22 -22 ≤ k ≤ 22 -22 ≤ l ≤ 22
Reflections collected/unique	38626 / 3119 [R(int)= 0.043]	40005/3402 [R(int) = 0.0275]	34371/ 3758 [R(int) = 0.0297]	102040 / 6111 [R(int) = 0.050]
Data/restraints/parameters	3119 / 0/ 194	3402/ 0 / 181	3758 / 0 / 182	6111/ 0 /361
Absoption correction	Gaussian	Gaussian	Gaussian	Multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices	R1 = 0.0399, wR2 = 0.0990	R1 = 0.0387, wR2= 0.1026	R1 = 0.0340, wR2 = 0.0967	R1 = 0.0553, wR2 = 0.1679
R all data	R1 = 0.0649, wR2 = 0.1133	R1= 0.0484 wR2= 0.1097	R1 = 0.0571, wR2 = 0.1138	R1 = 0.0727, wR2 = 0.1831
Goodness of fit on F^2	1.039	1.052	1.111	1.044
Largest diff. peak and hole (e Å^3)	0.177 and -0.130	0.185 and -0.254	0.471 and -0.262	0.560 and -0.568

Table S4. Characterization of dihedral angles for compounds **1-2**.[a]



1,3-pyrazole regioisomer



1,5-pyrazole regioisomer

R^1 = Me (**a**), 4-F-Ph (**b**), 4-Cl-Ph (**c**), 4-Br-Ph (**d**)

Cpd	dihedral angles (°)					Cpd	dihedral angles (°)				
	θa[b]	θb[c]	θb′[d]	θc[e]	θc′[f]		θa[g]	θb[h]	θb′[i]	θc[j]	θc′[k]
1aI	-180	86	-86	-159	159	**2aI** [l]	180	-143	143	-75	76
							-180	-119	119	-75	76
1aII	180	89	-89	-162	162	**2aII**	-180	103	-80	-54	-57
1b	180	90	-90	-176	176	**2b**	-59	110	110	-30	-30
1c	180	78	-78	-170	170	**2c**	-59	110	110	-30	-30
1d	-171	93	93	177	177	**2dI**	-59	111	111	-29	-29
						2dII [l]	-172	-107	-107	-48	-48
							-178	-99	-99	61	61

[a]The negative sign refers to the definition of the dihedral angle counterclockwise and positive clockwise. [b]N32-C33-C33′-N32′; [c]C31-N32-C33-C33′; [d]C31′-N32′-C33′-C33; [e]C4-C3-C31-N32; [f]C4′-C3′-C31′-N32′; [g]N52-C53-C53′-N52′; [h]C51-N52-C53-C53′; [i]C51′-N52′-C53′-C53; [j]C4-C5-C51-N52; [k]C4-C5-C51-N52; [l] Z′ = 1 (two half molecules).

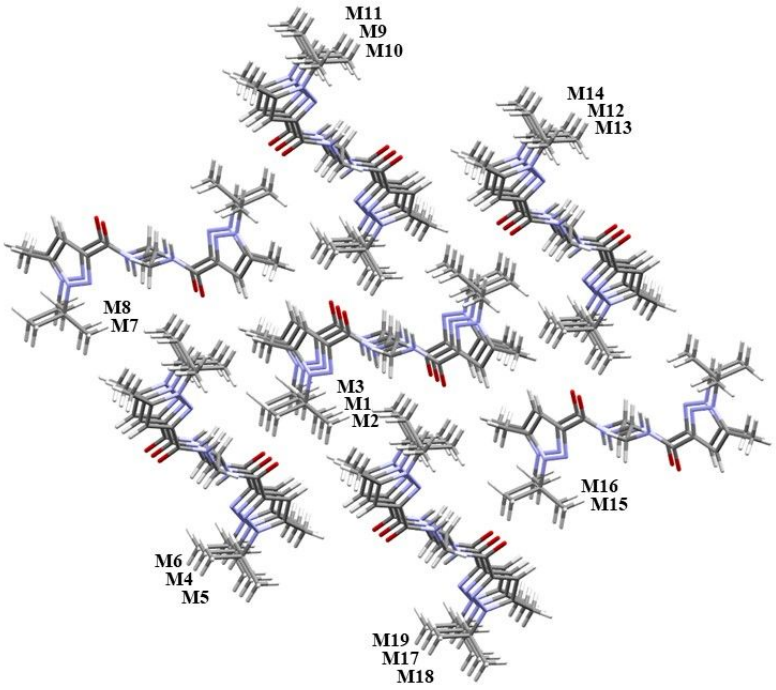
2. Supramolecular Cluster

2.1 Molecular Coordination Number and Supramolecular Cluster

Table S5**.** Molecular Coordination Number (MCN) of compounds **1-2**.

Compound	MCN	Compound	MCN
1aI	18	**2aI**	14
1aII	16	**2aII**	22 (14:8 H_2O)
1b	24 (14:10)	**2b**	16
1c	16	**2c**	16
1d	14	**2dI**	16
		2dII	20

Table S6. Supramolecular clusters and molecules labels of compounds **1**-**2**.



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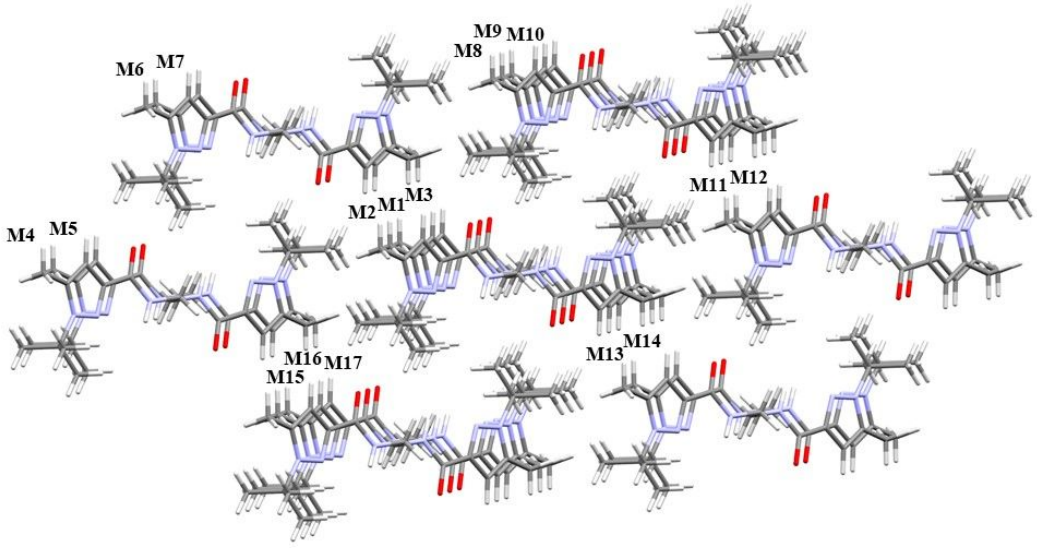

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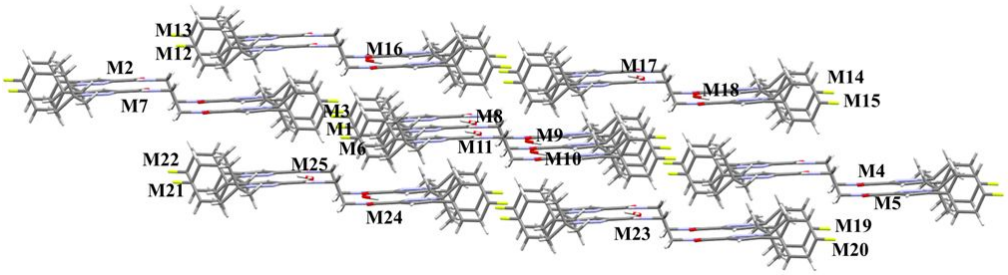
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M4
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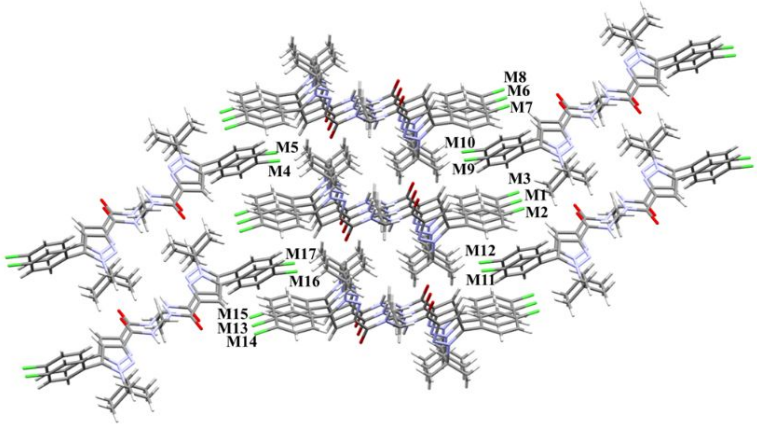
M23
M19
M20

1b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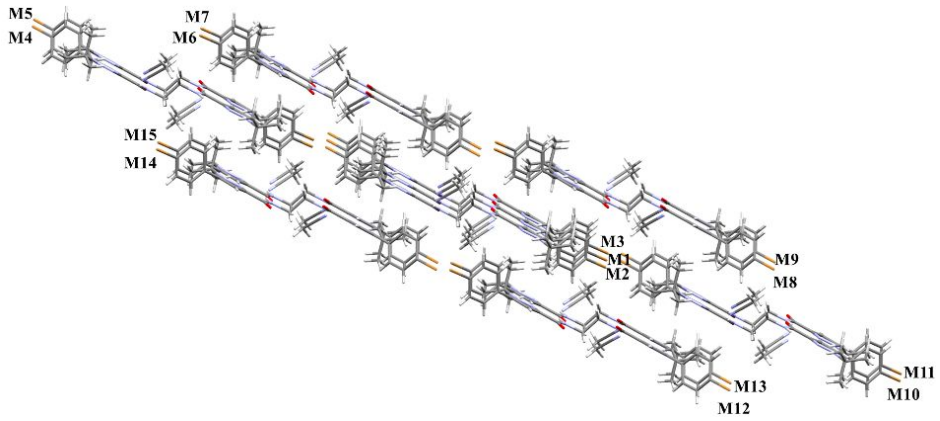
1c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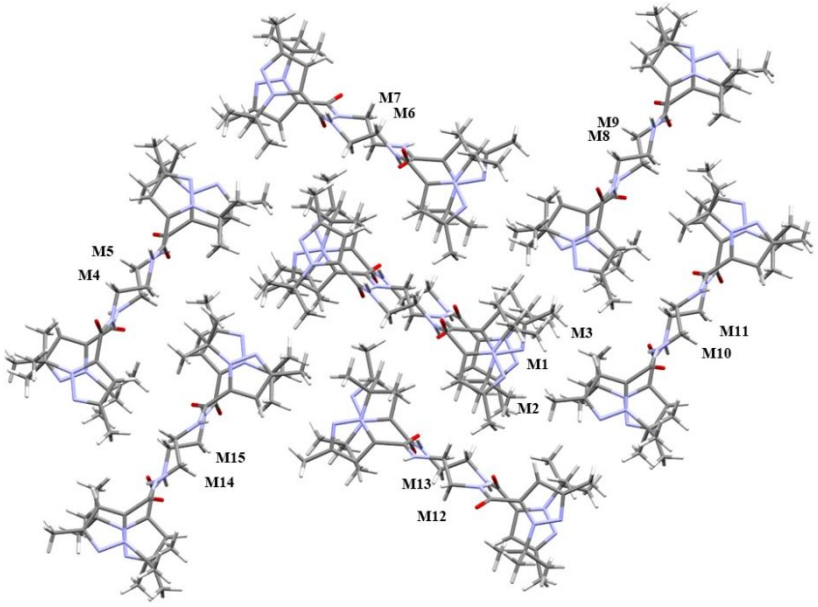
1d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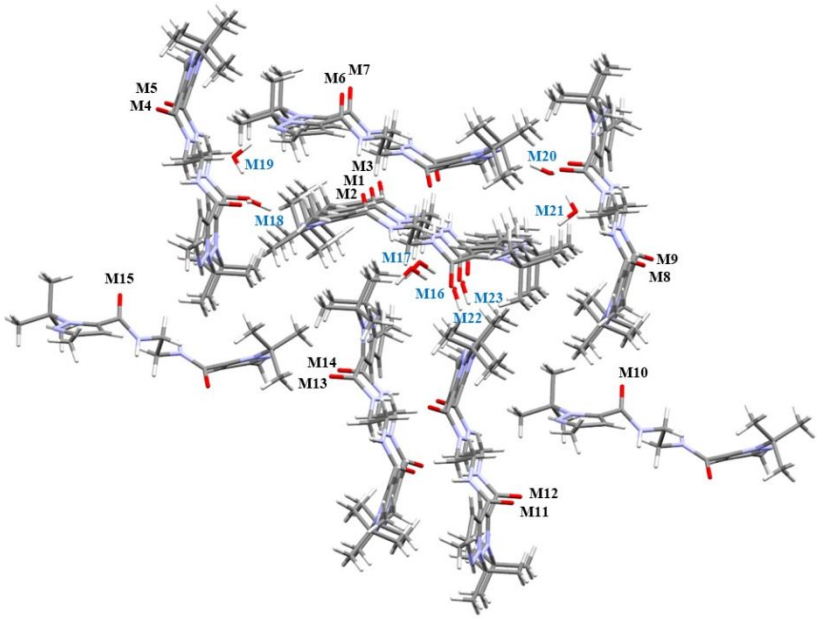
2aI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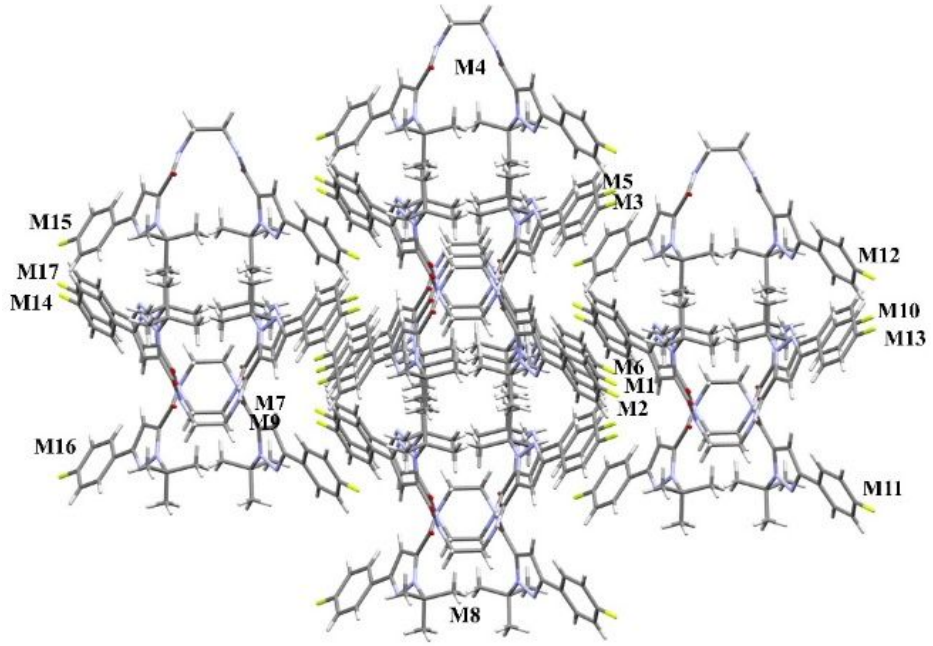
2aII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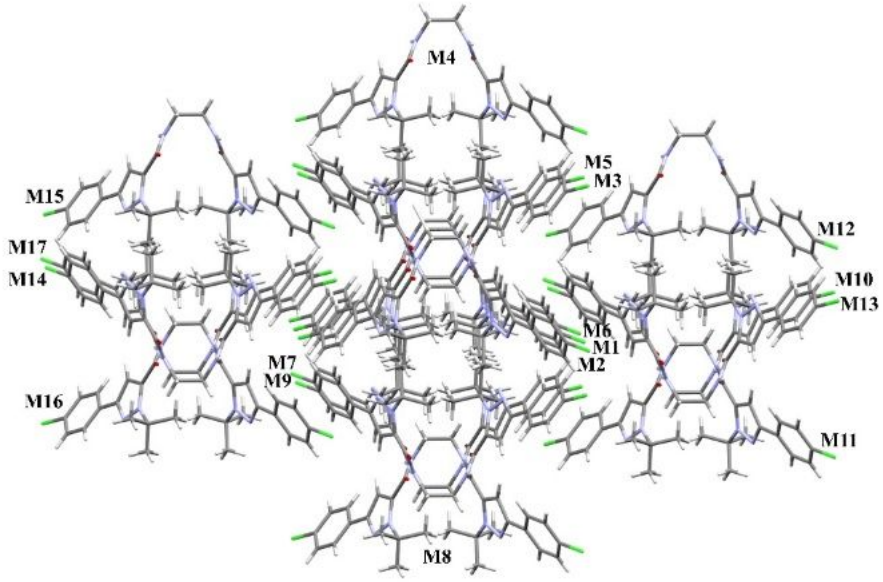
2b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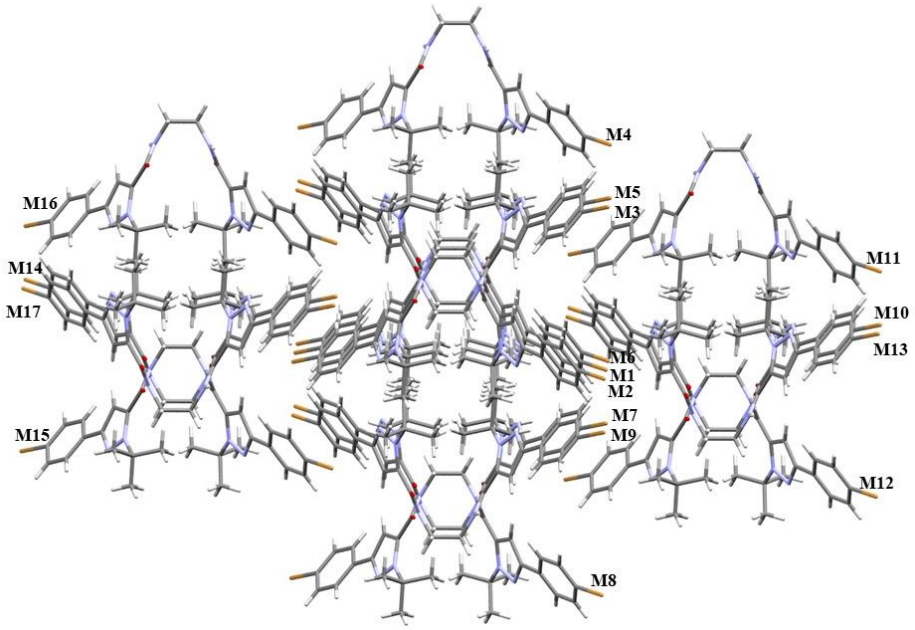
2c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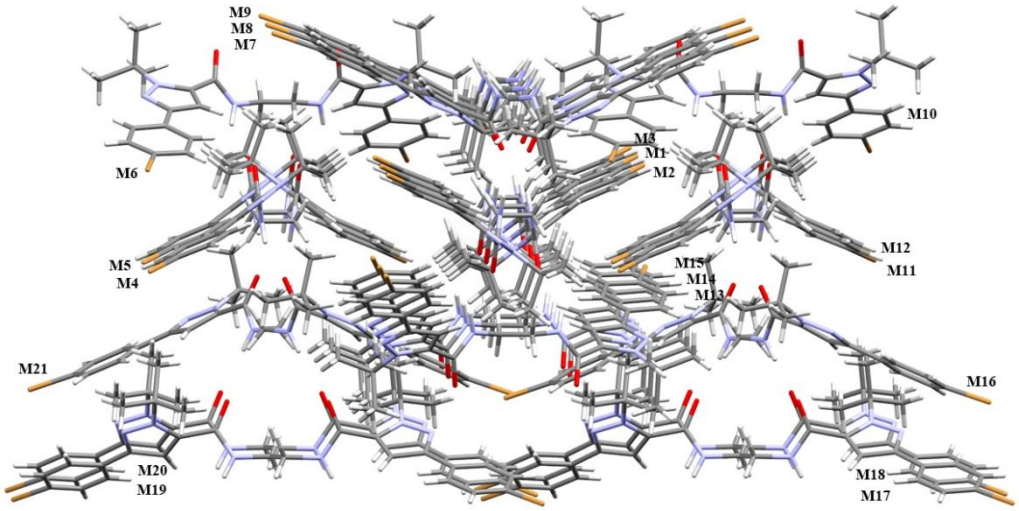
2b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M16
M20
M18
M19
M17

2dII

2.2 Topological and energetic data of compounds 1-2

Table S7. Topological and energetic data of each dimer from the supramolecular cluster of compound **1aI**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	1+x, y, z	89.12	-15.92	3.07	2.93
M1···M3	-1+x, y, z	89.12	-15.92	3.07	2.93
M1···M4	1-x,1/2+y,1.5-z	35.67	-7.18	1.23	1.32
M1···M5	2-x,1/2+y,1.5-z	16.94	-3.18	0.58	0.59
M1···M6	-x,1/2+y,1.5-z	17.80	-2.11	0.61	0.39
M1···M7	-1+x,1+y, z	20.54	-6.49	0.71	1.20
M1···M8	-2+x,1+y, z	11.17	-1.51	0.38	0.28
M1···M9	1+x,1.5-y, -1/2+z	35.67	-7.18	1.23	1.32
M1···M10	2+x,1.5-y, -1/2+z	17.80	-2.11	0.61	0.39
M1···M11	x,1.5-y, -1/2+z	16.94	-3.18	0.58	0.59
M1···M12	1+x,1/2-y, -1/2+z	35.67	-7.18	1.23	1.32
M1···M13	2+x,1/2-y, -1/2+z	17.80	-2.11	0.61	0.39
M1···M14	x,1/2-y, -1/2+z	16.94	-3.18	0.58	0.59
M1···M15	2+x, -1+y, z	11.17	-1.51	0.38	0.28
M1···M16	1+x, -1+y, z	20.54	-6.49	0.71	1.20
M1···M17	-1+x,1/2-y,1/2+z	35.67	-7.18	1.23	1.32
M1···M18	x,1/2-y,1/2+z	16.94	-3.18	0.58	0.59
M1···M19	-2+x,1/2-y,1/2+z	17.80	-2.11	0.61	0.39
Total		523.30	-97.71	18	18

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S8. Topological and energetic data of each dimer from the supramolecular cluster of compound **1aII**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	1+x, y, z	88.53	-16.77	2.70	2.74
M1···M3	-1+x, y, z	88.53	-16.77	2.70	2.74
M1···M4	-1+x,1+y, -1+z	21.48	-2.40	0.65	0.39
M1···M5	-2+x,1+y, -1+z	28.16	-4.87	0.86	0.80
M1···M6	-1+x, y, -1+z	7.78	-1.11	0.69	0.18
M1···M7	-2+x, y, -1+z	22.55	-6.35	0.24	1.04
M1···M8	2+x, -1+y, z	29,76	-4.50	0.34	0.74
M1···M9	1+x, -1+y, z	52.98	-10.56	1.62	1.73
M1···M10	x, -1+y, z	11,14	-2.33	0.91	0.38
M1···M11	2+x, -1+y,1+z	28.16	-4.87	0.86	0.80
M1···M12	1+x, -1+y,1+z	21.48	-2.58	0.65	0.42
M1···M13	2+x, y,1+z	22.55	-6.41	0.24	1.05
M1···M14	1+x, y,1+z	7.78	-1.17	0.69	0.19

M1···M15	x,1+y, z	11.14	-2.33	0.91	0.38
M1···M16	-1+x,1+y, z	52.98	-10.33	1.62	1.69
M1···M17	-2+x,1+y, z	29.76	-4.50	0.34	0.74
Total		524.76	-97.84	16	16

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S9. Topological and energetic data of each dimer from the supramolecular cluster of compound **1b**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	1+x,1+y,2+z	42.20	-4.84	1.49	0.95
M1···M3	-1+x,y,z	64.46	-8.52	2.27	1.67
M1···M4	-2+x,-1+y,-2+z	2.15	-0.45	0.08	0.09
M1···M5	-1+x,-1+y,-2+z	42.20	-5.08	1.49	1.00
M1···M6	1+x,y,z	64.46	-8.52	2.27	1.67
M1···M7	2+x,1+y,2+z	2.15	-0.01	0.08	0.00
M1···M8	x,y,1+z	18.30	-1.11	0.65	0.22
M1···M9	-x,1-y,1-z	10.37	-5.36	0.37	1.05
M1···M10	1-x,1-y,1-z	18.30	-1.11	0.65	0.22
M1···M11	1+x,y,1+z	10.37	-5.36	0.37	1.05
M1···M12	1+x,1+y,1+z	40.05	-9.95	1.41	1.96
M1···M13	x,1+y,1+z	39.31	-7.44	1.39	1.46
M1···M14	-1+x,y,-1+z	35.66	-9.71	1.26	1.91
M1···M15	x,y,-1+z	63.19	-12.02	2.23	2.36
M1···M16	1-x,2-y,2-z	9.18	-0.47	0.32	0.09
M1···M17	x,y,z	10.23	-0.67	0.36	0.13
M1···M18	-x,1-y,-z	5.16	-0.62	0.18	0.12
M1···M19	-1+x,-1+y,-1+z	40.05	-9.95	1.41	1.96
M1···M20	x,-1+y,-1+z	39.31	-7.44	1.39	1.46
M1···M21	1+x,y,1+z	35.66	-9.71	1.26	1.91
M1···M22	x,y,1+z	63.19	-12.02	2.23	2.36
M1···M23	x,-1+y,z	9.18	-0.47	0.32	0.09
M1···M24	1-x,1-y,2-z	10.23	-0.67	0.36	0.13
M1···M25	1+x,y,2+z	5.16	-0.62	0.18	0.12
Total		680.52	-122.09	24	24

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S10. Topological and energetic data of each dimer from the supramolecular cluster of compound **1c**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	-1+x,y,z	128.07	-23.17	2.98	3.01
M1···M3	1+x,y,z	128.07	-23.17	2.98	3.01
M1···M4	1.5+x,1/2-y,-1/2+z	23.29	-3.61	0.54	0.47
M1···M5	2.5+x,1/2-y,-1/2+z	34.10	-5.46	0.79	0.71
M1···M6	1+x,1+y,z	57.58	-11.79	1.34	1.53
M1···M7	x,1+y,z	8.22	-1.62	0.19	0.21
M1···M8	2+x,1+y,z	34.75	-6.92	0.81	0.90
M1···M9	-2.5+x,1/2-y,1/2+z	34.10	-5.46	0.79	0.71
M1···M10	-1.5+x,1/2-y,1/2+z	23.29	-3.61	0.54	0.47
M1···M11	-2.5+x,-1/2-y,1/2+z	34.10	-5.46	0.79	0.71
M1···M12	-1.5+x,-1/2-y,1/2+z	23.29	-3.61	0.54	0.47
M1···M13	-1+x,-1+y,z	57.58	-11.79	1.34	1.53
M1···M14	-2+x,-1+y,z	34.75	-6.92	0.81	0.90
M1···M15	x,-1+y,z	8.22	-1.62	0.19	0.21
M1···M16	1.5+x,-1/2-y,-1/2+z	23.29	-3.61	0.54	0.47
M1···M17	2.5+x,-1/2-y,-1/2+z	34.10	-5.46	0.79	0.71
Total		686.80	-123.29	16	16

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S11. Topological and energetic data of each dimer from the supramolecular cluster of compound **1d**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x,-1+y,z	95.35	-23.42	1.65	1.99
M1···M3	x,1+y,z	95.35	-23.42	1.65	1.99
M1···M4	-1/2+x,-1/2+y,-1+z	10.29	-1.85	0.18	0.16
M1···M5	-1/2+x,1/2+y,-1+z	10.29	-1.86	0.18	0.16
M1···M6	1/2-x,1/2-y,1-z	59.79	-6.39	1.03	0.54
M1···M7	1/2-x,1.5-y,1-z	87.39	-20.95	1.51	1.78
M1···M8	1-x,1-y,2-z	105.31	-19.09	1.82	1.62
M1···M9	1-x,2-y,2-z	31.68	-8.88	0.55	0.75
M1···M10	1/2+x,-1/2+y,1+z	10.29	-1.84	0.18	0.16
M1···M11	1/2+x,1/2+y,1+z	10.29	-1.84	0.18	0.16
M1···M12	1.5-x,1/2-y,2-z	59.79	-6.37	1.03	0.54
M1···M13	1.5-x,1.5-y,2-z	98.24	-20.92	1.70	1.78
M1···M14	1-x,1-y,1-z	105.31	-19.09	1.82	1.62
M1···M15	1-x,2-y,1-z	31.68	-8.90	0.55	0.76
Total		811.05	-164.81	14	14

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S12. Topological and energetic data of each dimer from the supramolecular cluster of compound **2aI**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x, y, z	96.94	-26.61	2.56	3.70
M1···M3	1+x,y,z	96.94	-26.61	2.56	3.70
M1···M4	-x,-1/2+y,-1/2-z	19.56	-2.87	0.52	0.40
M1···M5	1-x,-1/2+y,-1/2-z	19.90	-3.12	0.52	0.43
M1···M6	x,y,-1+z	30.71	-5.98	0.81	0.83
M1···M7	x,y,-1+z	58.56	-6.21	1.54	0.86
M1···M8	-x,1/2+y,-1/2-z	19.56	-2.87	0.52	0.40
M1···M9	1-x,1/2+y,-1/2-z	20.29	-2.76	0.53	0.38
M1···M10	1-x,1/2+y,1/2-z	19.90	-2.87	0.52	0.40
M1···M11	1-x,1/2+y,1/2-z	19.56	-2.87	0.52	0.40
M1···M12	x,y,1+z	58.56	-6.21	1.54	0.86
M1···M13	1+x,y,1+z	30.71	-5.98	0.81	0.83
M1···M14	1-x,-1/2+y,1/2-z	20.29	-2.76	0.53	0.38
M1···M15	1-x,-1/2+y,1/2-z	19.56	-2.87	0.52	0.40
Total		531.04	-100.59	14	14

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S13. Topological and energetic data of each dimer from the supramolecular cluster of compound **2aII**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	1+x,y,z	32.43	-3.10	1.44	0.69
M1···M3	-1+x,y,z	32.43	-3.10	1.44	0.69
M1···M4	2-x,1/2+y,1.5-z	7.51	-1.48	0.33	0.33
M1···M5	1-x,1/2+y,1.5-z	32.60	-5.26	1.45	1.18
M1···M6	2-x,1-y,1-z	42.19	-6.19	1.87	1.39
M1···M7	1-x,1-y,1-z	92.40	-23.92	4.11	5.36
M1···M8	x,1/2-y,-1/2+z	32.92	-4.30	1.46	0.96
M1···M9	-1+x,1/2-y,-1/2+z	31.04	-3.93	1.38	0.88
M1···M10	1-x,-y,1-z	8.54	-1.08	0.38	0.24
M1···M11	2-x,-1/2+y,1.5-z	7.51	-1.48	0.33	0.33
M1···M12	1-x,-1/2+y,1.5-z	33.00	-5.26	1.47	1.18
M1···M13	1+x,1/2-y,1/2+z	23.52	-3.93	1.04	0.88
M1···M14	x,1/2-y,1/2+z	32.92	-4.30	1.46	0.96
M1···M15	2-x,1-y,2-z	6.61	-1.49	0.29	0.33
M1···M16	x,y,z	13.81	-5.12	0.61	1.15
M1···M17	-1+x,y,z	7.39	-1.53	0.33	0.34
M1···M18	2-x,1/2+y,1.5-z	11.23	-5.04	0.50	1.13
M1···M19	2-x,1/2+y,1.5-z	5.57	-1.49	0.25	0.33
M1···M20	x,1/2-y,-1/2+z	0.27	-0.03	0.01	0.01
M1···M21	-1+x,1/2-y,-1/2+z	19.51	-5.36	0.87	1.20
M1···M22	x,y,z	17.45	-9.58	0.78	2.15
M1···M23	-1+x,y,z	4.31	-1.18	0.19	0.26
Total		495.16	-98.15	22	22

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S14. Topological and energetic data of each dimer from the supramolecular cluster of compound **2b**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x,y,1+z	20.53	-3.75	0.53	0.55
M1···M3	-x,1-y,1-z	82.95	-21.91	2.16	3.22
M1···M4	x,1+y,z	6.54	-1.25	0.17	0.18
M1···M5	-x,1-y,-z	82.95	-22.05	2.16	3.25
M1···M6	x,y,-1+z	20.53	-3.75	0.53	0.55
M1···M7	-x,-y,-z	101.44	-13.52	2.64	1.99
M1···M8	x,-1+y,z	6.54	-1.25	0.17	0.18
M1···M9	-x,-y,1-z	101.44	-13.35	2.64	1.96
M1···M10	1/2-x,1/2-y,1-z	57.66	-9.07	1.50	1.33
M1···M11	1/2+x,-1/2+y,1+z	14.84	-1.61	0.39	0.24
M1···M12	1/2+x,1/2+y,1+z	14.84	-1.61	0.39	0.24
M1···M13	1/2-x,1/2-y,2-z	8.87	-1.65	0.23	0.24
M1···M14	-1/2-x,1/2-y,-z	57.66	-9.07	1.50	1.33
M1···M15	-1/2+x,1/2+y,-1+z	14.84	-1.61	0.39	0.24
M1···M16	-1/2+x,-1/2+y,-1+z	14.84	-1.61	0.39	0.24
M1···M17	-1/2-x,1/2-y,-1-z	8.87	-1.65	0.23	0.24
Total		615.34	-108.73	16	16

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S15. Topological and energetic data of each dimer from the supramolecular cluster of compound **2c**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x,y,1+z	23.59	-4.19	0.59	0.59
M1···M3	-x,2-y,1-z	87.14	-23.21	2.17	3.27
M1···M4	x,1+y,z	8.22	-1.32	0.21	0.19
M1···M5	-x,2-y,-z	87.14	-23.22	2.17	3.27
M1···M6	x,y,-1+z	23.59	-4.19	0.59	0.59
M1···M7	-x,1-y,-z	106.06	-13.70	2.65	1.93
M1···M8	x,-1+y,z	8.22	-1.32	0.21	0.19
M1···M9	-x,1-y,1-z	106.06	-13.70	2.65	1.93
M1···M10	1/2-x,1.5-y,1-z	59.18	-9.68	1.48	1.36
M1···M11	1/2+x,-1/2+y,1+z	13.80	-1.53	0.34	0.22
M1···M12	1/2+x,1/2+y,1+z	13.80	-1.53	0.34	0.22
M1···M13	1/2-x,1.5-y,2-z	8.55	-1.60	0.21	0.23
M1···M14	-1/2-x,1.5-y,-z	59.80	-9.68	1.48	1.36
M1···M15	-1/2+x,1/2+y,-1+z	13.80	-1.53	0.34	0.22
M1···M16	-1/2+x,-1/2+y,-1+z	13.80	-1.53	0.34	0.22
M1···M17	-1/2-x,1.5-y,-1-z	8.55	-1.60	0.21	0.23
Total		641.30	-113.52	16	16

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

Table S16. Topological and energetic data of each dimer from the supramolecular cluster of compound **2dI**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x,y,1+z	23.64	-4.32	0.58	0.60
M1···M3	-x,2-y,1-z	88.49	-22.86	2.17	3.15
M1···M4	x,1+y,z	9.86	-1.51	0.24	0.21
M1···M5	-x,2-y,-z	88.49	-22.86	2.17	3.15
M1···M6	x,y,-1+z	23.64	-4.32	0.58	0.60
M1···M7	-x,1-y,-z	109.30	-14.08	2.68	1.94
M1···M8	x,-1+y,z	9.86	-1.51	0.24	0.21
M1···M9	-x,1-y,1-z	109.30	-14.08	2.68	1.94
M1···M10	1/2-x,1.5-y,1-z	58.30	-9.99	1.43	1.38
M1···M11	1/2+x,1/2+y,1+z	13.69	-1.85	0.34	0.26
M1···M12	1/2+x,-1/2+y,1+z	13.69	-1.85	0.34	0.26
M1···M13	1/2-x,1.5-y,2-z	8.76	-1.55	0.22	0.21
M1···M14	-1/2-x,1.5-y,-1-z	8.76	-1.55	0.22	0.21
M1···M15	-1/2+x,-1/2+y,-1+z	13.69	-1.85	0.34	0.26
M1···M16	-1/2+x,1/2+y,-1+z	13.69	-1.85	0.34	0.26
M1···M17	-1/2-x,1.5-y,-z	58.30	-9.99	1.43	1.38
Total		651.46	-116.02	16	16

[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

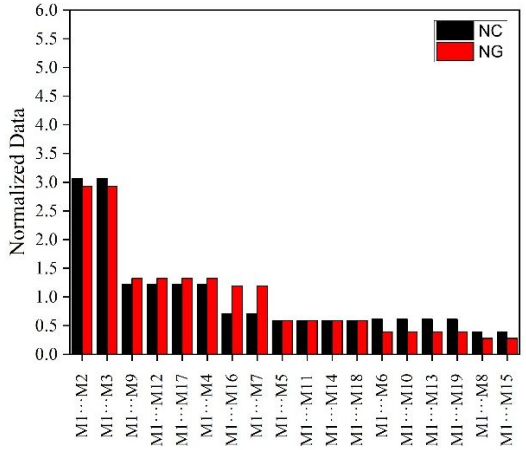
Table S17. Topological and energetic data of each dimer from the supramolecular cluster of compound **2dII**.

Dimer	Symmetry code [a]	$C_{M1\cdots MN}$ [b]	$G_{M1\cdots MN}$ [c]	$NC_{M1\cdots MN}$	$NG_{M1\cdots MN}$
M1···M2	x,-1+y,z	31.76	-2.95	0.83	0.48
M1···M3	x,1+y,z	31.76	-2.85	0.83	0.48
M1···M4	-x,1-y,1-z	64.62	-9.42	1.70	1.54
M1···M5	-x,2-y,1-z	5.11	-0.12	0.13	0.02
M1···M6	-x,1-y,1-z	61.55	-11.73	1.62	1.91
M1···M7	1-y,-1/2+x,1/2+z	20.81	-2.50	0.55	0.41
M1···M8	1-y,1/2+x,1/2+z	110.82	-24.46	2.91	3.99
M1···M9	1-y,1.5+x,1/2+z	20.81	-2.50	0.55	0.41
M1···M10	1-x,2-y,1-z	61.55	-11.73	1.62	1.91
M1···M11	1/2+x,-1/2+y,1-z	5.11	-0.12	0.13	0.02
M1···M12	1-x,2-y,1-z	64.62	-9.42	1.70	1.54
M1···M13	x,-1+y,z	13.72	-1.04	0.36	0.17
M1···M14	x,y,z	149.08	-29.86	3.92	4.87
M1···M15	1/2-x,2.5-y,z	13.72	-1.04	0.36	0.17
M1···M16	y,1/2-x,1/2-z	44.12	-4.69	1.16	0.76
M1···M17	y,1/2-x,1/2-z	4.41	-0.89	0.12	0.14
M1···M18	y,1.5-x,1/2-z	4.41	-0.89	0.12	0.14
M1···M19	-1+y,1/2-x,1/2-z	4.41	-0.89	0.12	0.14
M1···M20	-1+y,1.5-x,1/2-z	4.41	-0.89	0.12	0.14
M1···M21	-1+y,1.5-x,1/2-z	44.12	-4.69	1.16	0.76
Cluster		760.92	-122.66	20	20

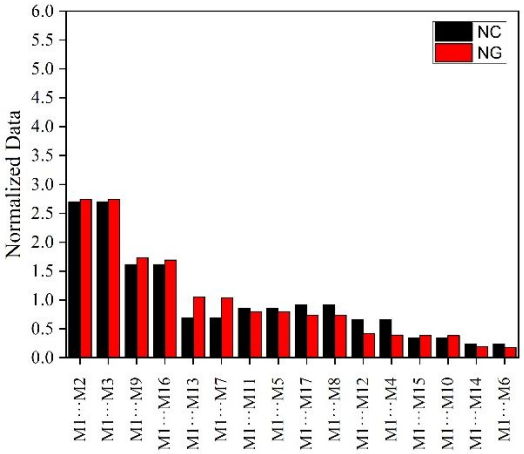
[a] Symmetry code obtained by the Mercury software. [b] $Å^2$, contact surface obtained by ToposPro. [c] kcal mol^{-1}, interaction energy obtained using ωB97X-D/cc-pVDZ theory level.

2.3 Normalized Contact Area and Energy

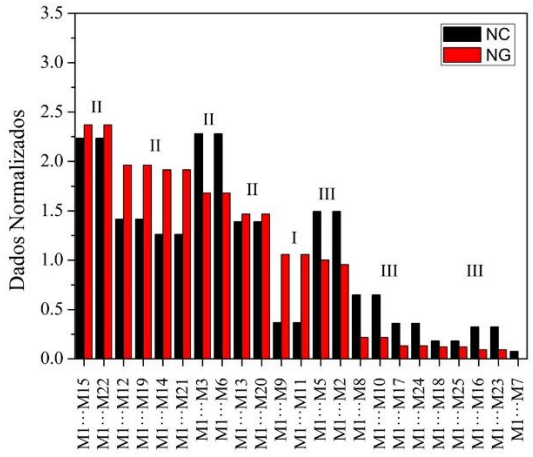
Table S18. Normalized contact area and energy of compounds **1-2**.



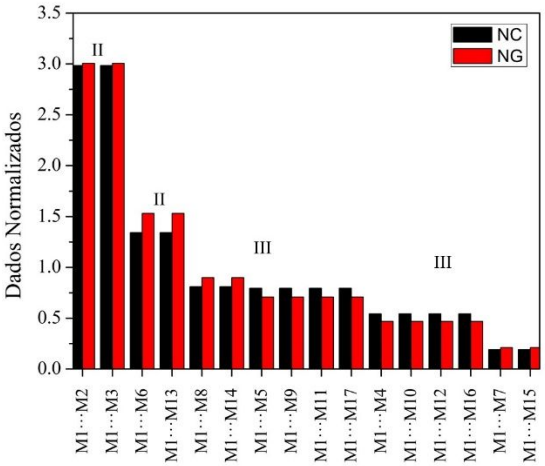
1aI



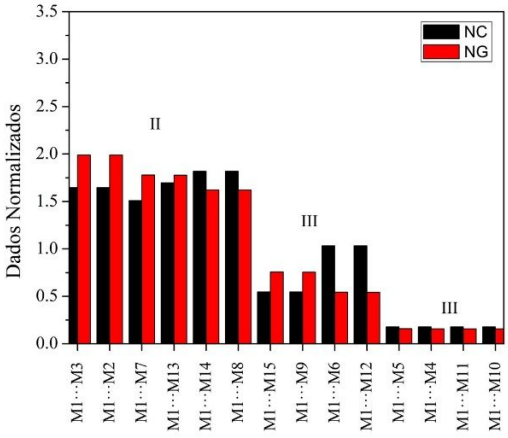
1aII



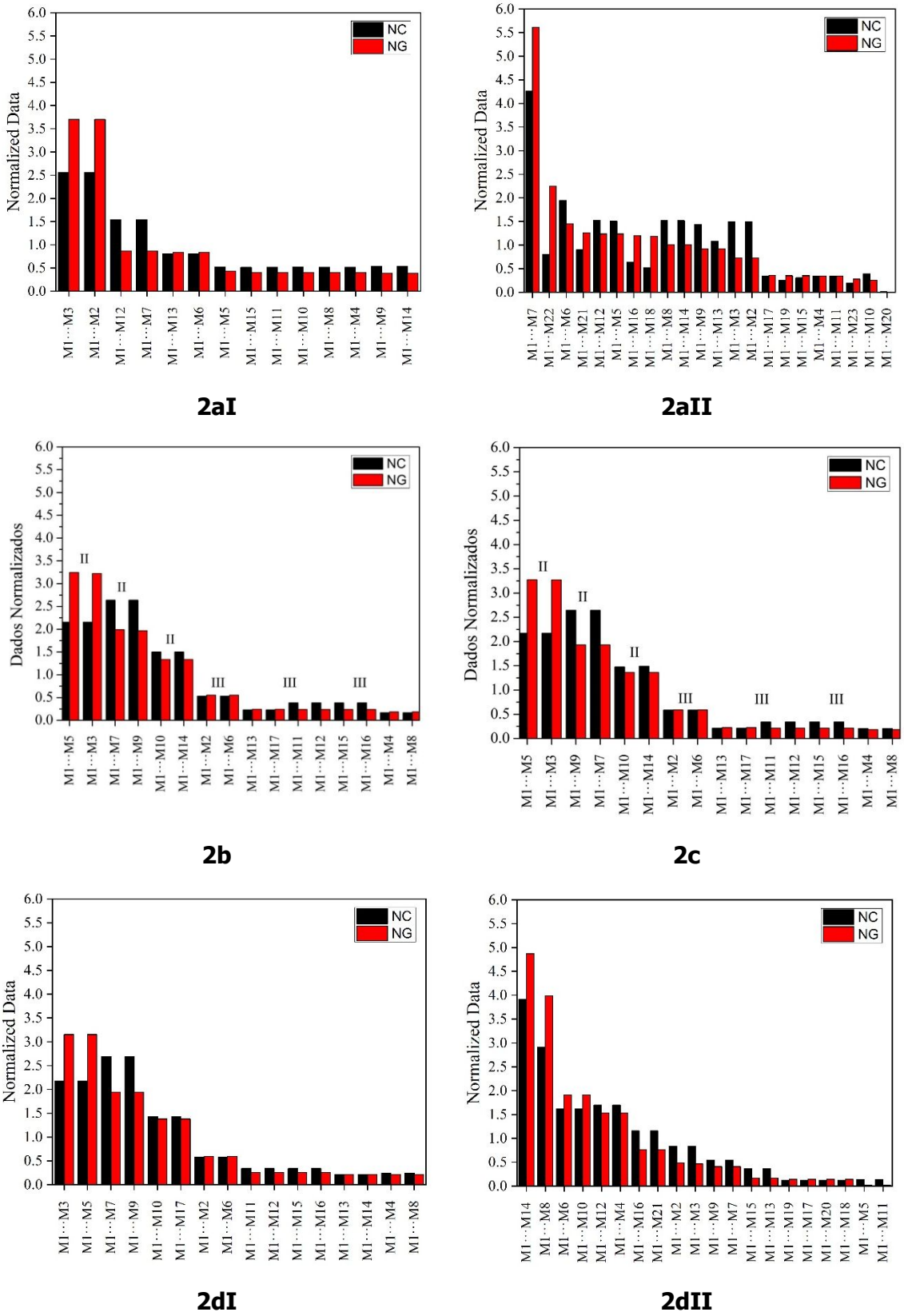
1b



1c



1d



2aI **2aII**

2b **2c**

2dI **2dII**

Figure S1. Topological and energetic normalized data of each dimer from the supramolecular cluster of compounds **1a-d** and **2a-d**.

3. Proposed Crystallization Mechanisms

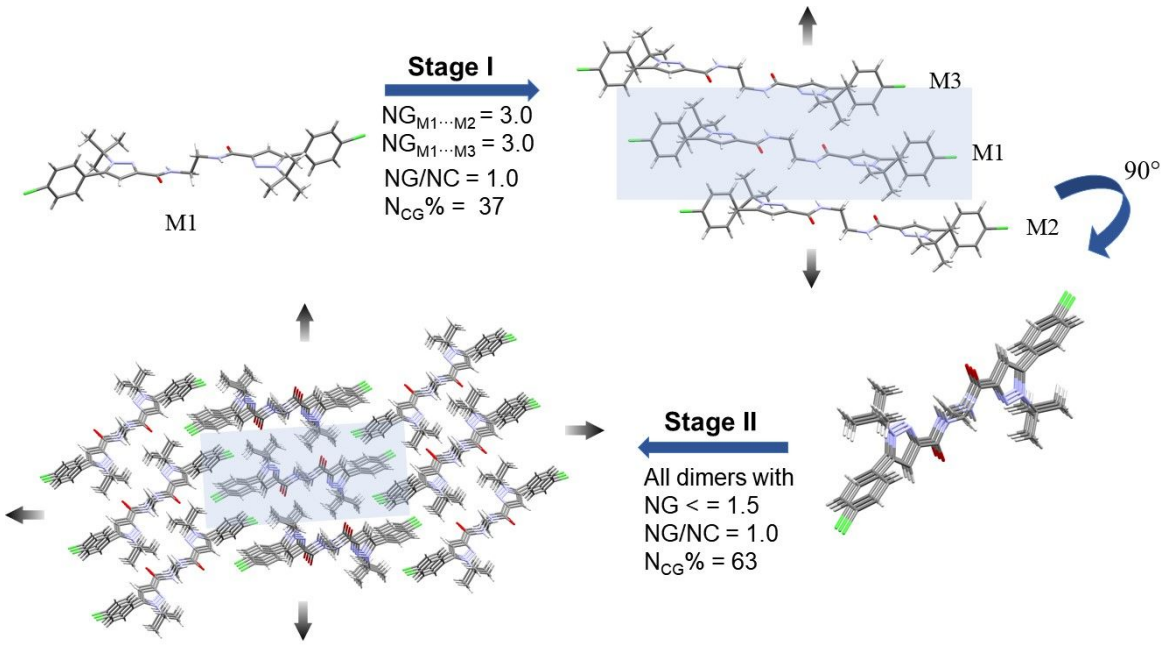


Figure S2. Proposed crystallization mechanism for polymorphs **1c**. The shaded area represents the portion in the previous stage. The arrows in each stage indicate the direction of growth.

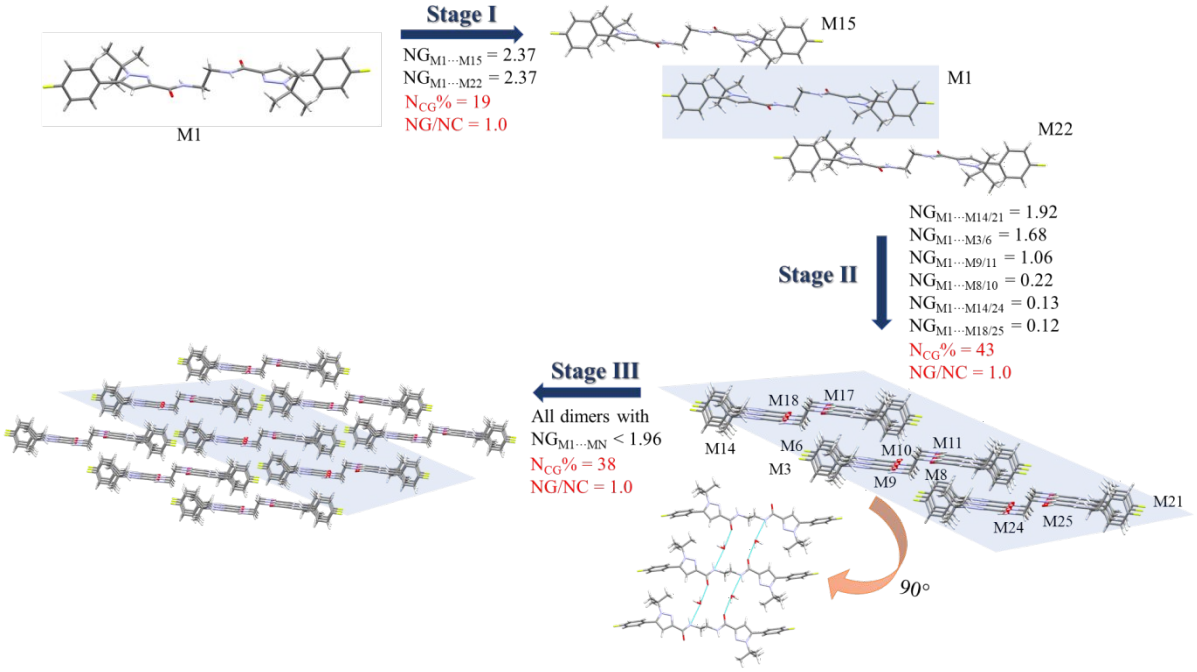


Figure S3. Proposed crystallization mechanism for polymorphs **1b**. The shaded area represents the portion in the previous stage. The arrows in each stage indicate the direction of growth.

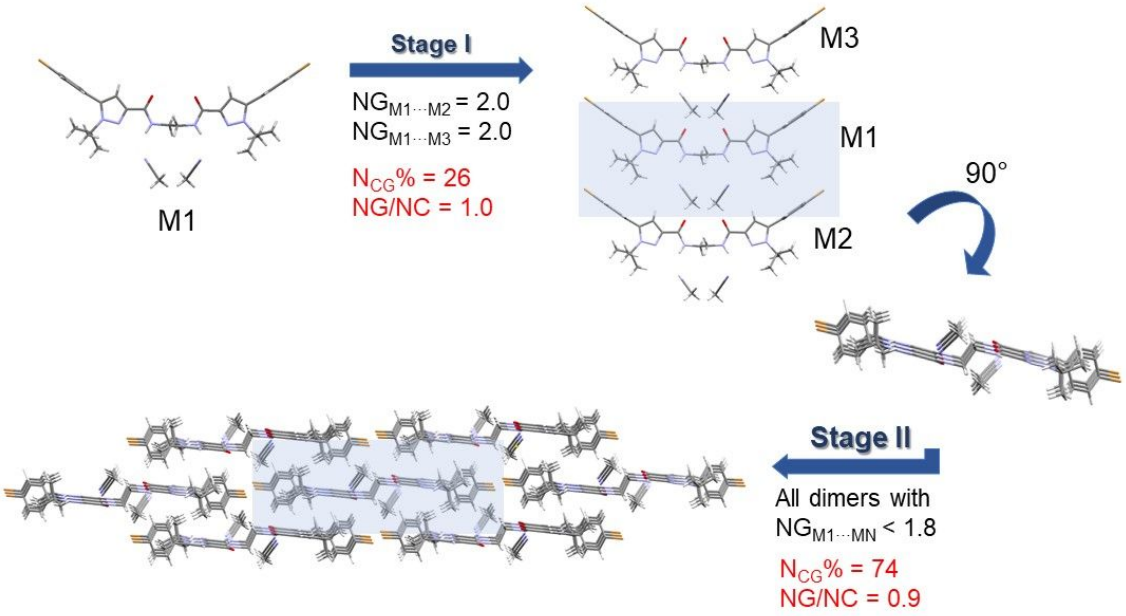


Figure S4. Proposed crystallization mechanism for polymorphs **1d**. The shaded area represents the portion in the previous stage. The arrows in each stage indicate the direction of growth.

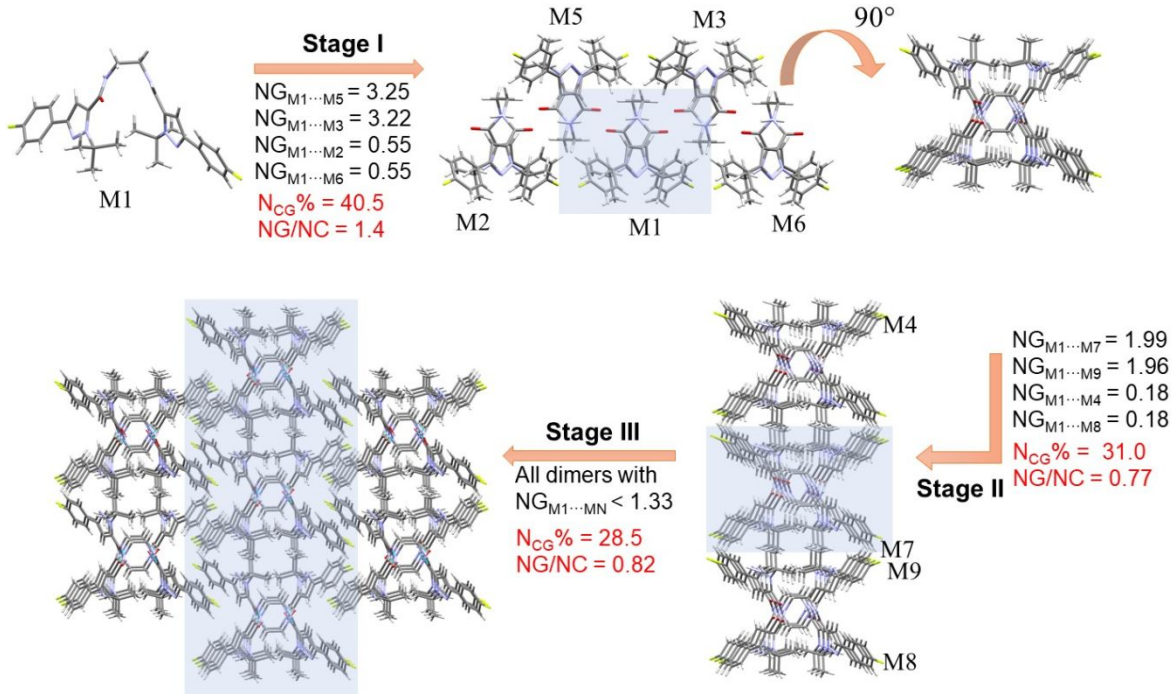


Figure S5. Proposed crystallization mechanism for polymorphs **2b**. The shaded area represents the portion in the previous stage. The arrows in each stage indicate the direction of growth.

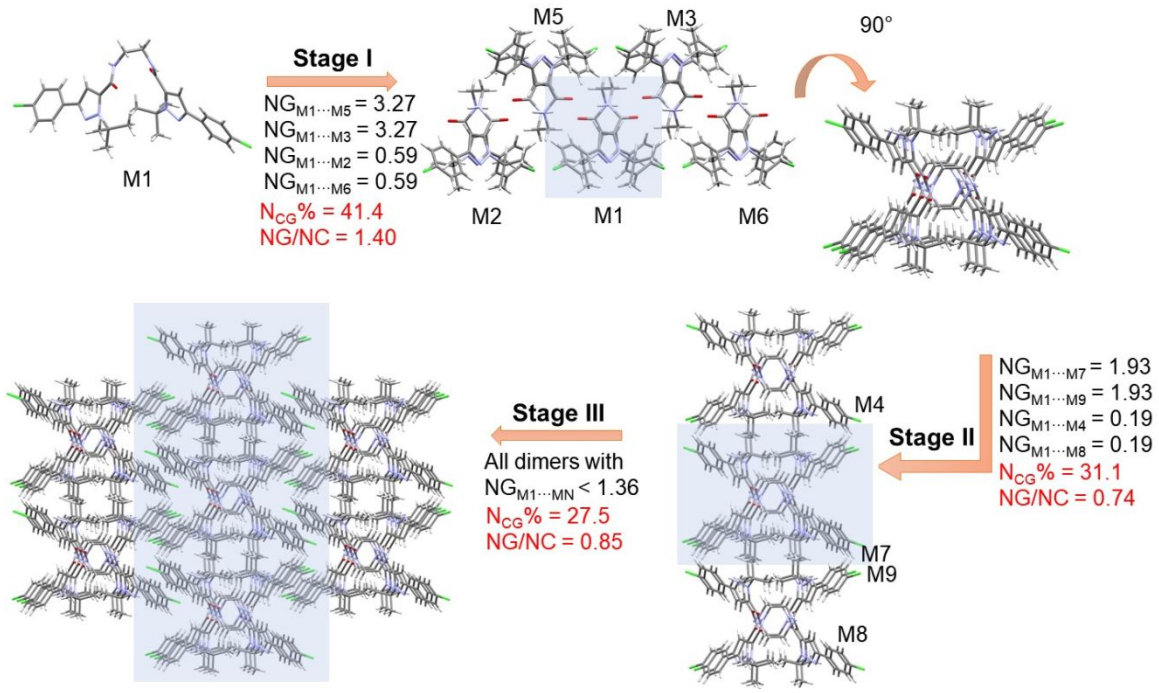


Figure S6. Proposed crystallization mechanism for polymorphs **2c**. The shaded area represents the portion in the previous stage. The arrows in each stage indicate the direction of growth.

4. QTAIM Analysis Data

Table S19. QTAIM data and G_{AI} of dimers of compound **2dI** and **2dII**

Dimer	Interaction	ρ_{INT}	$\nabla^2\rho$	ε	K	V	G	BPL	H	G_{AI}
	O-O	0.00108	0.00620	3.1685	-0.00053	-0.00049	0.00102	7.3805	0.000532	-0.40
2dI	CH···N	0.00177	0.00696	0.3894	-0.00043	-0.00087	0.00131	6.4455	0.000433	-0.65
M1···M3	CH···N	0.00177	0.00696	0.3895	-0.00043	-0.00087	0.00131	6.4455	0.000433	-0.65
M1···M5	CH···HC	0.00193	0.00842	1.0146	-0.00067	-0.00077	0.00144	5.8491	0.000669	-0.71
	CH···HC	0.00193	0.00842	1.0145	-0.00067	-0.00077	0.00144	5.8491	0.000669	-0.71
	CH···HC	0.00304	0.01340	0.0379	-0.00090	-0.00156	0.00245	5.0305	0.000898	-1.12
	CH···HC	0.00304	0.01341	0.0379	-0.00090	-0.00156	0.00245	5.0305	0.000898	-1.12
	CH···O	0.00783	0.02921	0.0783	-0.00089	-0.00553	0.00641	4.9174	0.000888	-2.88
	CH···O	0.00783	0.02921	0.0782	-0.00089	-0.00553	0.00642	4.9173	0.000888	-2.88
	NH···O	0.01593	0.06153	0.0483	-0.00137	-0.01264	0.01401	4.1072	0.001373	-5.86
	NH···O	0.01593	0.06153	0.0483	-0.00137	-0.01264	0.01401	4.1072	0.001373	-5.86
Total		0.06209								-22.86
	CH···HC	0.00262	0.01050	0.03634	-0.00071	-0.00122	0.00192	5.1251	0.00071	-0.99
	CH···HC	0.00262	0.01050	0.03634	-0.00071	-0.00122	0.00192	5.1251	0.00071	-0.99
	CH···O	0.00352	0.01571	0.62192	-0.00100	-0.00194	0.00293	5.8170	0.00100	-1.33
	CH···O	0.00352	0.01571	0.62192	-0.00100	-0.00194	0.00293	5.8170	0.00100	-1.33
	CH···HC	0.00405	0.01548	0.07514	-0.00080	-0.00226	0.00307	4.6925	0.00080	-1.53
2dII	CH···HC	0.00405	0.01548	0.07514	-0.00080	-0.00226	0.00307	4.6925	0.00080	-1.53
M1···M14	CH···π	0.00443	0.01533	3.10517	-0.00094	-0.00195	0.00289	6.2337	0.00094	-1.67
	CH···π	0.00443	0.01533	3.10517	-0.00094	-0.00195	0.00289	6.2337	0.00094	-1.67
	Br···π	0.00502	0.01301	0.85883	-0.00046	-0.00234	0.00279	7.1493	0.00046	-1.89
	Br···π	0.00502	0.01301	0.85883	-0.00046	-0.00234	0.00279	7.1493	0.00046	-1.89
	CH···O	0.00552	0.02218	0.10554	-0.00088	-0.00379	0.00467	5.1674	0.00088	-2.08
	CH···O	0.00552	0.02218	0.10554	-0.00088	-0.00379	0.00467	5.1674	0.00088	-2.08
	NH···O	0.01445	0.05547	0.03876	-0.00102	-0.01182	0.01284	4.2166	0.00102	-5.45
	NH···O	0.01445	0.05547	0.03876	-0.00102	-0.01182	0.01284	4.2166	0.00102	-5.45
Total		0.07922								-29.86

2dII M1···M8	CH···π	0.002423	0.008403	2.182752	-0.0005	-0.00111	0.001605	6.38494	0.000497	-1.01
	CH···π	0.002423	0.008403	2.182752	-0.0005	-0.00111	0.001605	6.38494	0.000497	-1.01
	CH···HC	0.002726	0.011354	0.031061	-0.00079	-0.00127	0.002054	5.17894	0.000785	-1.13
	CH···HC	0.002726	0.011354	0.031061	-0.00079	-0.00127	0.002054	5.17894	0.000785	-1.13
	CH···HC	0.003189	0.013739	0.715006	-0.00099	-0.00146	0.002447	5.47027	0.000987	-1.33
	CH···HC	0.003189	0.013739	0.715006	-0.00099	-0.00146	0.002447	5.47027	0.000987	-1.33
	CH···N	0.006462	0.020306	0.244956	-0.00061	-0.00386	0.004469	5.27269	0.000608	-2.69
	CH···N	0.006462	0.020306	0.244956	-0.00061	-0.00386	0.004469	5.27269	0.000608	-2.69
	NH···O	0.014583	0.056035	0.030919	-0.00113	-0.01174	0.012875	4.19162	0.001134	-6.07
	NH···O	0.014583	0.056035	0.030919	-0.00113	-0.01174	0.012875	4.19162	0.001134	-6.07
Total		0.058766								-24.46