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SUPPORTING INFORMATION

Uncovering the Origins of Supramolecular Similarity in a Series of Benzimidazole Structures

Tainára Orlando[1], Leandro C. Lopes[2], Darlon A. M. Neumann[2], Valquiria P. Andrade[2], Mateus Mittersteiner[2], Cláudia Q. Rocha[1], Nilo Zanatta[2], Helio G. Bonacorso[2], Marcos A. P. Martins[2], and Paulo R. S. Salbego[3*]

[1]Department of Chemistry, Federal University of Maranhão (UFMA), São Luís, MA, Brazil.

[2]Núcleo de Química de Heterociclos (NUQUIMHE), Department of Chemistry, Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil.

[3]Núcleo de Química de Heterociclos (NUQUIMHE), Department of Engineering and Environmental Technology (DETA), Federal University of Santa Maria (UFSM), Frederico Westphalen Campus, RS, Brazil.

**E-mail: paulosalbego@gmail.com*

1. Crystallographic data

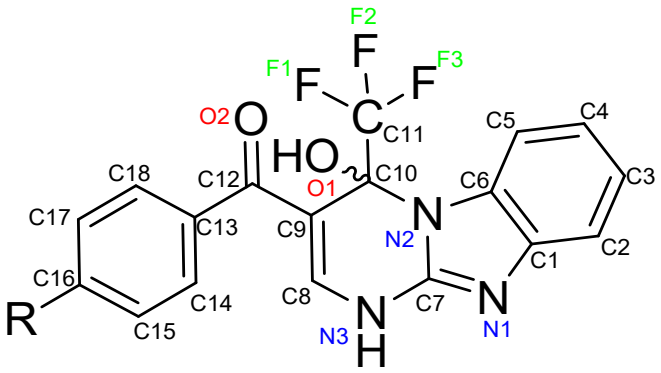

Figure S1. Numbering of atoms in crystalline structures of compounds **2** – **5**.

Table S1. Crystallographic data of compounds **2** - **5**.

Compound	**2**	**3**	**4**	**5**
Formula	$C_{19}H_{14}F_3N_3O_2$	$C_{19}H_{14}F_3N_3O_3$	$C_{18}H_{11}ClF_3N_3O_2$	$C_{18}H_{11}BrF_3N_3O_2$
Formula weight	373.337	389.337	393.755	438.206
Temperature (K)	100	110	293.15	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	6.0391(2)	6.0869(3)	6.0309(11)	5.9853(2)
b (Å)	15.7043(6)	15.3931(8)	15.898(2)	15.8708(5)
c (Å)	17.1155(6)	17.5350(9)	17.1914(16)	17.1004(6)
α (º)	90	90	90	90
β (º)	91.874(1)	92.951(2)	90.932(7)	90.897(1)
γ (º)	90	90	90	90
Cell volume (Å^3)	1622.36(10)	1640.79(14)	1648.1(4)	1624.19(9)
Z	4	4	4	4
Calculated density (g cm^{-3})	1.528	1.576	1.587	1.792
μ (mm^{-1})	0.125	0.131	2.545	2.584
F(000)	768.6	800.7	804.6	871.9
Crystal size (mm^3)	0.162 × 0.13 × 0.062	0.162 × 0.154 × 0.102	0.449 × 0.22 × 0.156	0.219 × 0.082 × 0.064
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)
2Θ range for data collection (°)	4.76 to 54.3	4.66 to 54.4	11.14 to 145.26	4.76 to 54.26
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21	-7 ≤ h ≤ 7, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22	-7 ≤ h ≤ 7, -19 ≤ k ≤ 19, -21 ≤ l ≤ 20	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -21 ≤ l ≤ 20
Reflections collected	47272	45928	24123	29911
Independent reflections	3589 [R_{int} = 0.0380, R_{sigma} = 0.0181]	3656 [R_{int} = 0.0863, R_{sigma} = 0.0340]	3209 [R_{int} = 0.0265, R_{sigma} = 0.0163]	3593 [R_{int} = 0.0323, R_{sigma} = 0.0193]
Data/ restraints/ parameters	3589/0/263	3656/0/255	3209/0/245	3593/0/245
Goodness-of-fit on F^2	1.056	1.068	1.047	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0950	R_1 = 0.0459, wR_2 = 0.1111	R_1 = 0.0388, wR_2 = 0.1071	R_1 = 0.0260, wR_2 = 0.0565
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1009	R_1 = 0.0593, wR_2 = 0.1199	R_1 = 0.0419, wR_2 = 0.1103	R_1 = 0.0335, wR_2 = 0.0594
$\Delta\rho_{máx.}$, $\Delta\rho_{min.}$ (e Å^{-3})	0.36, -0.31	0.61, -0.42	0.23, -0.35	0.51, -0.43

2. Supramolecular Cluster Data

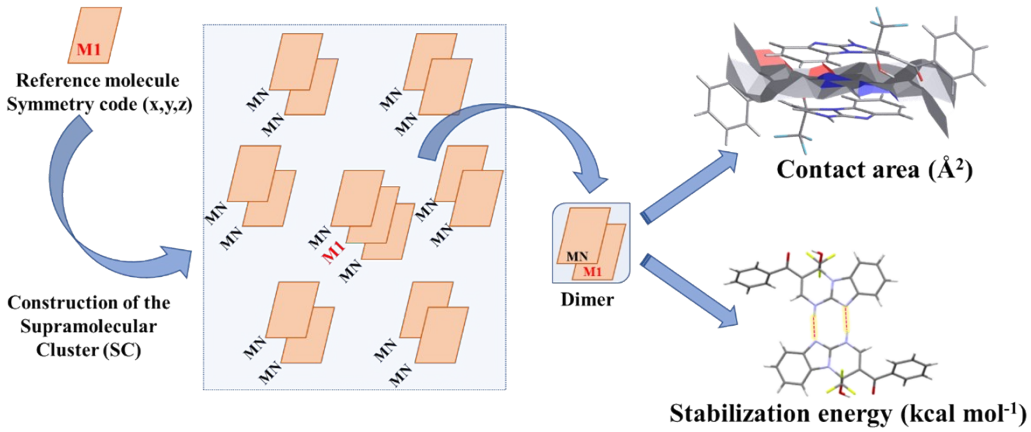

Figure S2. Construction of the supramolecular cluster (SC).

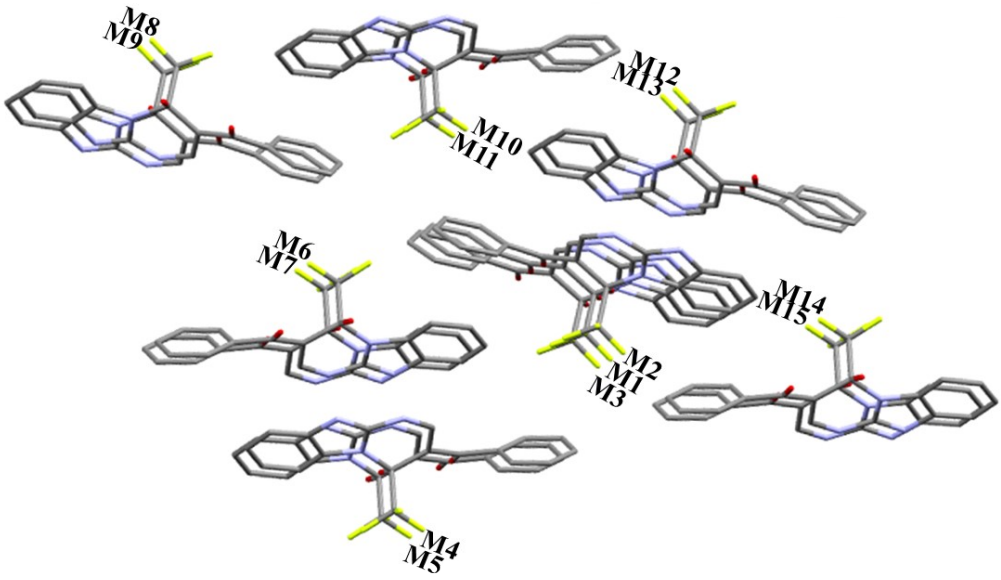

Figure S3. Supramolecular cluster of compound **1**.

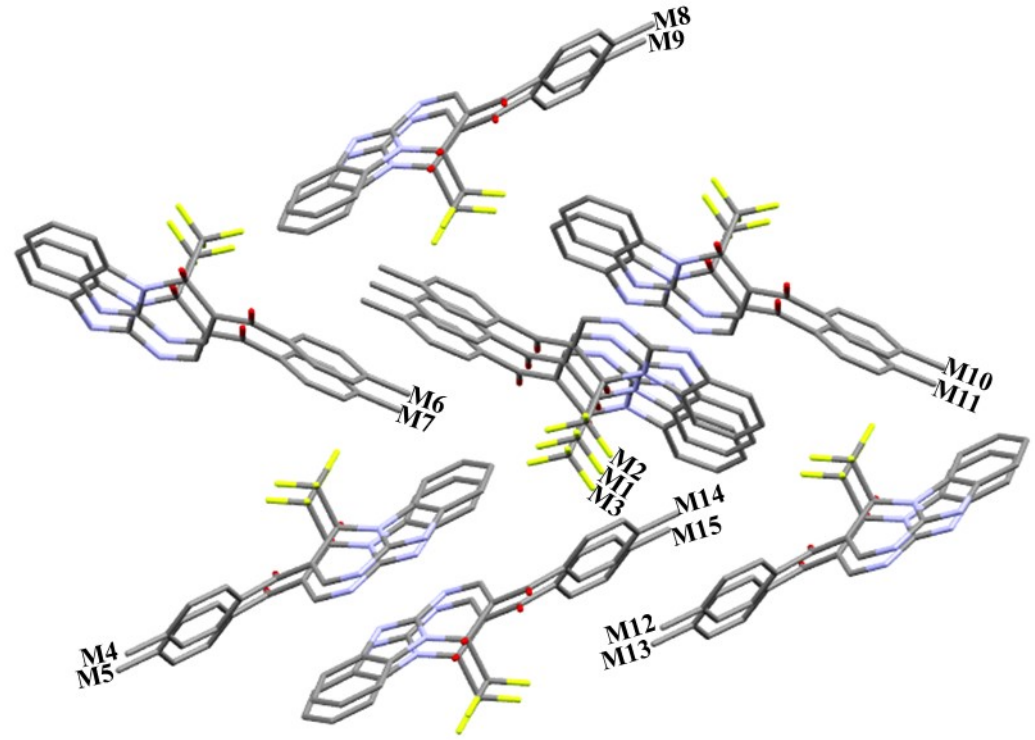

Figure S4. Supramolecular cluster of compound **2**.

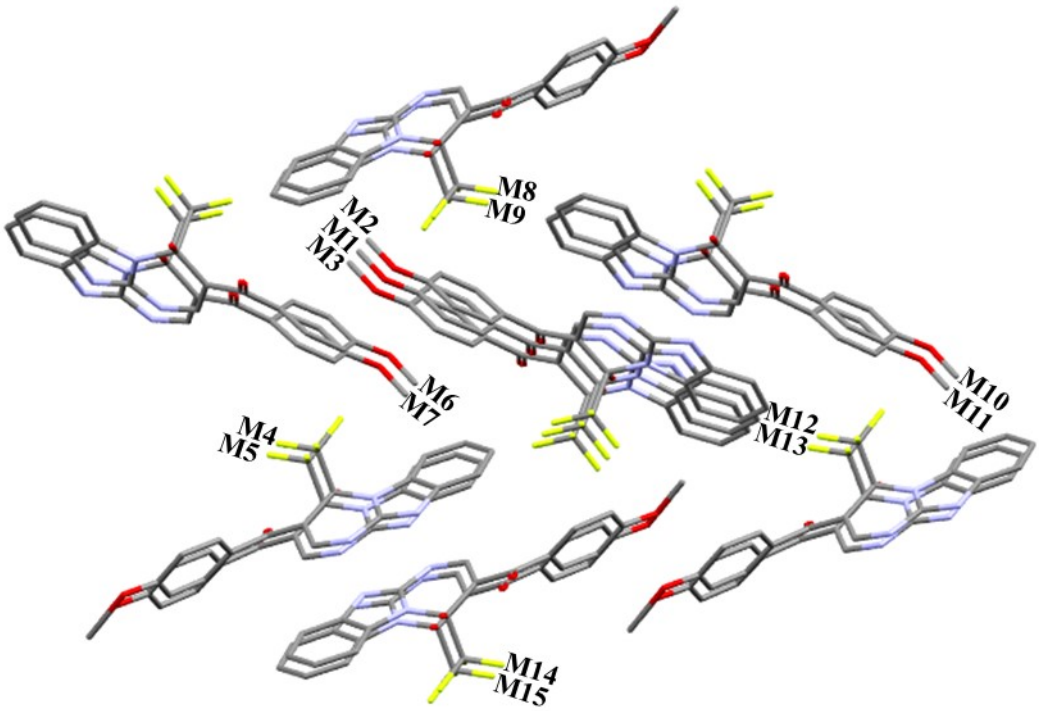

Figure S5. Supramolecular cluster of compound **3**.

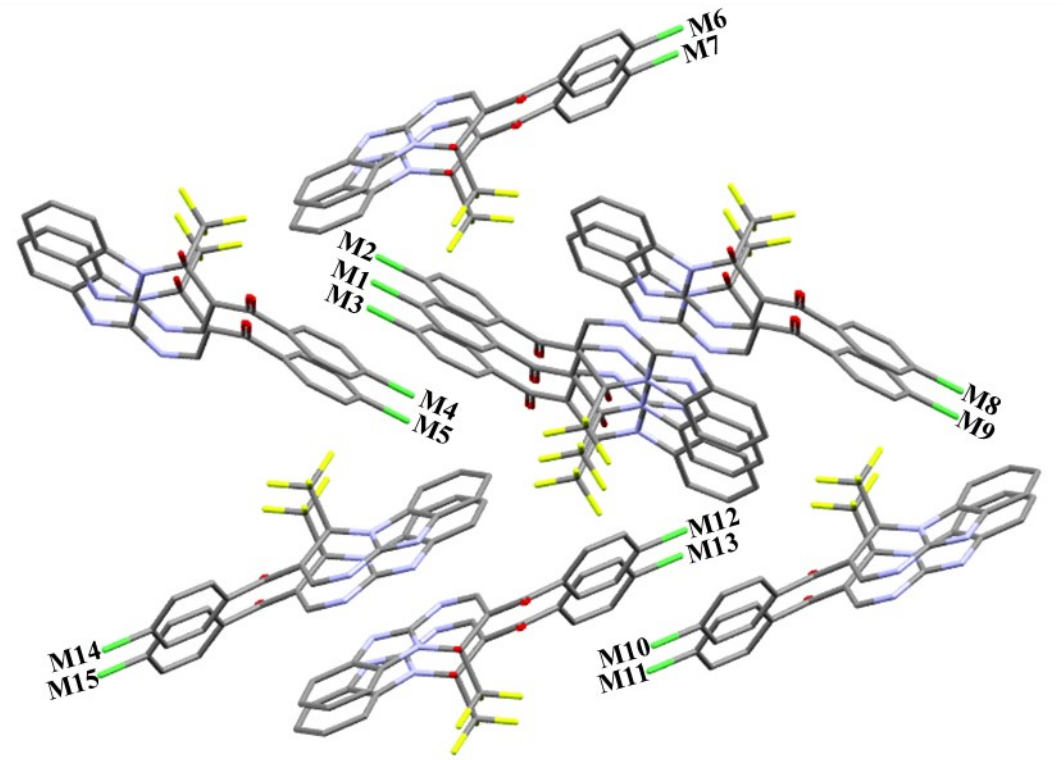

Figure S6. Supramolecular cluster of compound **4**.

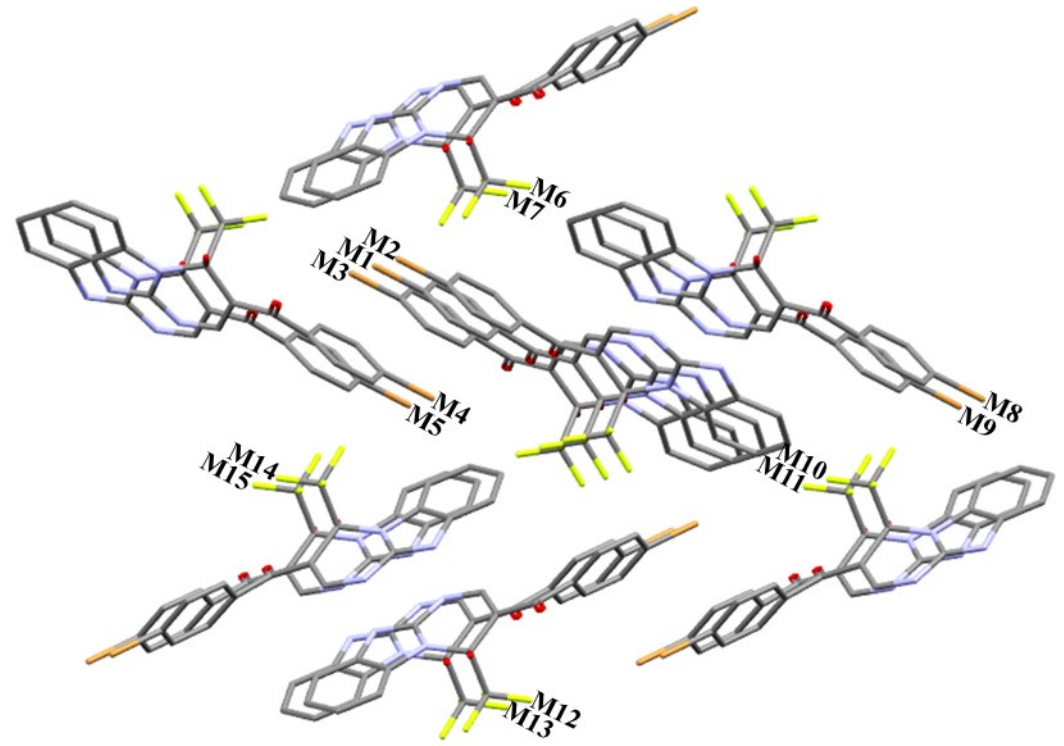

Figure S7. Supramolecular cluster of compound **5**.

Table S2. Symmetry codes for the molecules of the supramolecular cluster of compounds **1**-**3**.

MN	**1**	**2**	**3**
M1	x,y,z	x,y,z	x,y,z
M2	1+x,y,z	1+x,y,z	1+x,y,z
M3	-1+x,y,z	-1+x,y,z	-1+x,y,z
M4	1/2+x,1.5-y,1/2+z	1/2+x,1/2-y,1/2+z	1/2+x,1.5-y,1/2+z
M5	-1/2+x,1.5-y,1/2+z	-1/2+x,1/2-y,1/2+z	-1/2+x,1.5-y,1/2+z
M6	1.5-x,1/2+y,1.5-z	2-x,1-y,2-z	5-x,2-y,3-z
M7	1/2-x,1/2+y,1.5-z	1-x,1-y,2-z	4-x,2-y,3-z
M8	1-x,2-y,1-z	1.5-x,1/2+y,1.5-z	4.5-x,1/2+y,2.5-z
M9	-x,2-y,1-z	1/2-x,1/2+y,1.5-z	3.5-x,1/2+y,2.5-z
M10	1/2+x,1.5-y,-1/2+z	2-x,1-y,1-z	5-x,2-y,2-z
M11	-1/2+x,1.5-y,-1/2+z	1-x,1-y,1-z	4-x,2-y,2-z
M12	2-x,1-y,1-z	1/2+x,1/2-y,-1/2+z	1/2+x,1.5-y,-1/2+z
M13	1-x,1-y,1-z	-1/2+x,1/2-y,-1/2+z	-1/2+x,1.5-y,-1/2+z
M14	1.5-x,-1/2+y,1.5-z	1.5-x,-1/2+y,1.5-z	4.5-x,-1/2+y,2.5-z
M15	1/2-x,-1/2+y,1.5-z	1/2-x,-1/2+y,1.5-z	3.5-x,-1/2+y,2.5-z

Table S3. Symmetry codes for the molecules of the supramolecular cluster of compounds **4** and **5**.

MN	**4**	**5**
M1	x,y,z	x,y,z
M2	1+x,y,z	1+x,y,z
M3	-1+x,y,z	-1+x,y,z
M4	2-x,1-y,2-z	1-x,-y,1-z
M5	1-x,1-y,2-z	-x,-y,1-z
M6	1.5-x,1/2+y,1.5-z	1/2-x,1/2+y,1/2-z
M7	1/2-x,1/2+y,1.5-z	-1/2-x,1/2+y,1/2-z
M8	2-x,1-y,1-z	1-x,-y,-z
M9	1-x,1-y,1-z	-x,-y,-z
M10	1/2+x,1/2-y,-1/2+z	1/2+x,-1/2-y,-1/2+z
M11	-1/2+x,1/2-y,-1/2+z	-1/2+x,-1/2-y,-1/2+z
M12	1.5-x,-1/2+y,1.5-z	1/2-x,-1/2+y,1/2-z
M13	1/2-x,-1/2+y,1.5-z	-1/2-x,-1/2+y,1/2-z
M14	1/2+x,1/2-y,1/2+z	1/2+x,-1/2-y,1/2+z
M15	-1/2+x,1/2-y,1/2+z	-1/2+x,-1/2-y,1/2+z

Table S4. Contact area ($C_{M1\cdots MN}$) and stabilization energy ($G_{M1\cdots MN}$) data from the dimers of the supramolecular cluster for compounds **1-3**.

Dimer	**1**		**2**		**3**	
	$C_{M1\cdots MN}$	$G_{M1\cdots MN}$ [a]	$C_{M1\cdots MN}$	$G_{M1\cdots MN}$ [a]	$C_{M1\cdots MN}$	$G_{M1\cdots MN}$ [a]
M1···M2	49.60	-7,01	42.82	-6.82	39.81	-6.93
M1···M3	49.60	-7,01	42.82	-6.82	39.81	-6.93
M1···M4	11.41	-1,64	20.45	-2.25	21.90	-2.87
M1···M5	3.97	-1,44	14.04	-1.34	12.23	-1.44
M1···M6	36.70	-6,30	16.98	-1.28	20.55	-2.14
M1···M7	37.14	-4,75	31.77	-7.53	35.75	-9.01
M1···M8	16.43	-0,45	28.54	-5.16	31.59	-5.88
M1···M9	1.04	-0,10	24.83	-2.74	25.51	-3.41
M1···M10	3.97	-1,44	24.63	-17.54	24.42	-17.89
M1···M11	11.41	-1,64	68.01	-20.15	68.30	-20.02
M1···M12	23.57	-1,69	14.04	-1.34	12.23	-1.44
M1···M13	73.08	-2,18	20.45	-2.25	21.90	-2.87
M1···M14	36.70	-6,30	28.54	-5.16	31.59	-5.88
M1···M15	37.14	-4,75	24.83	-2.74	25.51	-3.41
Total	391.76	-80,73	402.75	-83.13	411.10	-90.13

[a] Obtained through the equation $G_{M1\cdots MN} = G_{M1+MN} - (G_{M1} + G_{MN})$.

Table S5. Contact area ($C_{M1\cdots MN}$) and stabilization energy ($G_{M1\cdots MN}$) data from the dimers of the supramolecular cluster for compounds **4** and **5**.

Dimer	**4**		**5**	
	$C_{M1\cdots MN}$	$G_{M1\cdots MN}$ [a]	$C_{M1\cdots MN}$	$G_{M1\cdots MN}$ [a]
M1···M2	46.65	-7.46	47.35	-7.99
M1···M3	46.65	-7.46	47.35	-7.99
M1···M4	15.59	-2.12	15.73	-2.62
M1···M5	27.61	-5.02	28.45	-6.31
M1···M6	22.91	-3.26	22.11	-3.85
M1···M7	24.53	-3.04	25.19	-3.27
M1···M8	25.73	-17.44	25.42	-17.78
M1···M9	65.92	-19.47	66.26	-19.78
M1···M10	14.22	-1.47	13.82	-1.38
M1···M11	22.54	-2.12	22.10	-1.96
M1···M12	22.91	-3.26	22.11	-3.85
M1···M13	24.53	-3.04	25.19	-3.27
M1···M14	22.54	-2.12	22.10	-1.96
M1···M15	14.22	-1.47	13.82	-1.38
Total	396.55	-78.75	397.00	-83.38

[a] Obtained through the equation $G_{M1\cdots MN} = G_{M1+MN} - (G_{M1} + G_{MN})$.

Table S6. Normalized contact area ($NC_{M1\cdots MN}$) and stabilization energy ($NG_{M1\cdots MN}$) data from the dimers of the supramolecular cluster for compounds **1**-**3**.

Dimer	**1**		**2**		**3**	
	$NC_{M1\cdots MN}$ [a]	$NG_{M1\cdots MN}$ [b]	$NC_{M1\cdots MN}$ [a]	$NG_{M1\cdots MN}$ [b]	$NC_{M1\cdots MN}$ [a]	$NG_{M1\cdots MN}$ [b]
M1···M2	1.77	1.22	1.49	1.15	1.36	1.08
M1···M3	1.77	1.22	1.49	1.15	1.36	1.08
M1···M4	0.41	0.29	0.71	0.38	0.75	0.45
M1···M5	0.14	0.25	0.49	0.23	0.42	0.22
M1···M6	1.31	1.09	0.59	0.22	0.70	0.33
M1···M7	1.33	0.82	1.10	1.27	1.22	1.40
M1···M8	0.59	0.08	0.99	0.87	1.08	0.91
M1···M9	0.04	0.02	0.86	0.46	0.87	0.53
M1···M10	0.14	0.25	0.86	2.95	0.83	2.78
M1···M11	0.41	0.29	2.36	3.39	2.33	3.11
M1···M12	0.84	3.07	0.49	0.23	0.42	0.22
M1···M13	2.61	3.50	0.71	0.38	0.75	0.45
M1···M14	1.31	1.09	0.99	0.87	1.08	0.91
M1···M15	1.33	0.82	0.86	0.46	0.87	0.53
Total	14.00	14.00	14.00	14.00	14.00	14.00

[a] Obtained through the equation $NC_{M1\cdots MN} = (C_{M1\cdots MN}/\sum C_{M1\cdots MN}) \times N$; [b] Obtained through the equation $NG_{M1\cdots MN} = (G_{M1\cdots MN}/\sum G_{M1\cdots MN}) \times N$.

Table S7. Normalized contact area ($NC_{M1\cdots MN}$) and stabilization energy ($NG_{M1\cdots MN}$) data from the dimers of the supramolecular cluster for compounds **4** and **5**.

Dimer	**4**		**5**	
	$NC_{M1\cdots MN}$ [a]	$NG_{M1\cdots MN}$ [b]	$NC_{M1\cdots MN}$ [a]	$NG_{M1\cdots MN}$ [b]
M1···M2	1.65	1.33	1.67	1.34
M1···M3	1.65	1.33	1.67	1.34
M1···M4	0.55	0.38	0.55	0.44
M1···M5	0.97	0.89	1.00	1.06
M1···M6	0.81	0.58	0.78	0.65
M1···M7	0.87	0.54	0.89	0.55
M1···M8	0.91	3.10	0.90	2.99
M1···M9	2.33	3.46	2.34	3.32
M1···M10	0.50	0.26	0.49	0.23
M1···M11	0.80	0.38	0.78	0.33
M1···M12	0.81	0.58	0.78	0.65
M1···M13	0.87	0.54	0.89	0.55
M1···M14	0.80	0.38	0.78	0.33
M1···M15	0.50	0.26	0.49	0.23
Total	14.00	14.00	14.00	14.00

[a] Obtained through the equation $NC_{M1\cdots MN} = (C_{M1\cdots MN}/\sum C_{M1\cdots MN}) \times N$; [b] Obtained through the equation $NG_{M1\cdots MN} = (G_{M1\cdots MN}/\sum G_{M1\cdots MN}) \times N$.

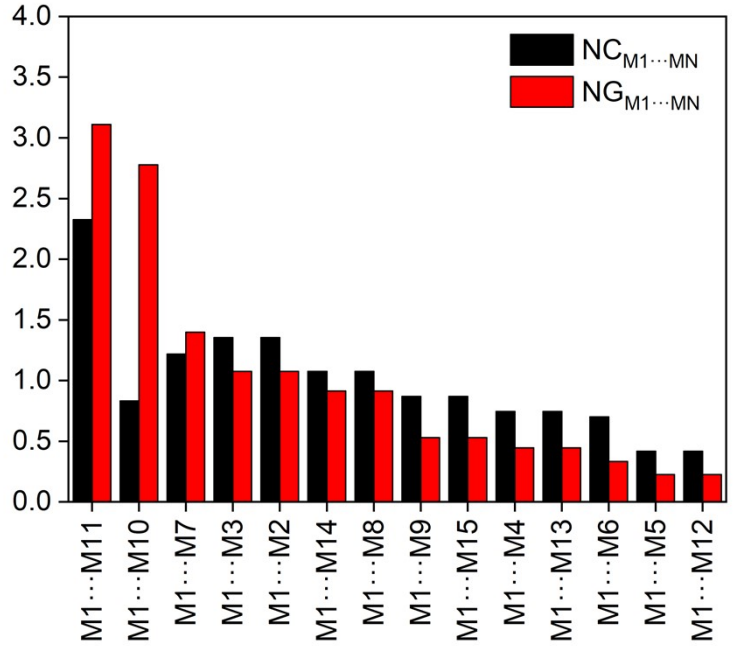

Figure S8. Normalized contact area and stabilization energy data ($NC_{M1\cdots MN}$ and $NG_{M1\cdots MN}$) for compound **3**.

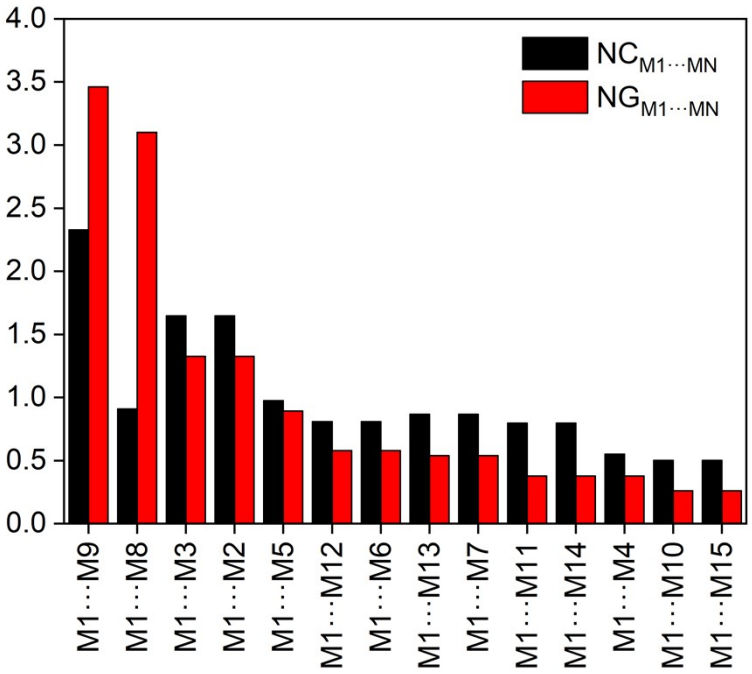

Figure S9. Normalized contact area and stabilization energy data ($NC_{M1\cdots MN}$ and $NG_{M1\cdots MN}$) for compound **4**.

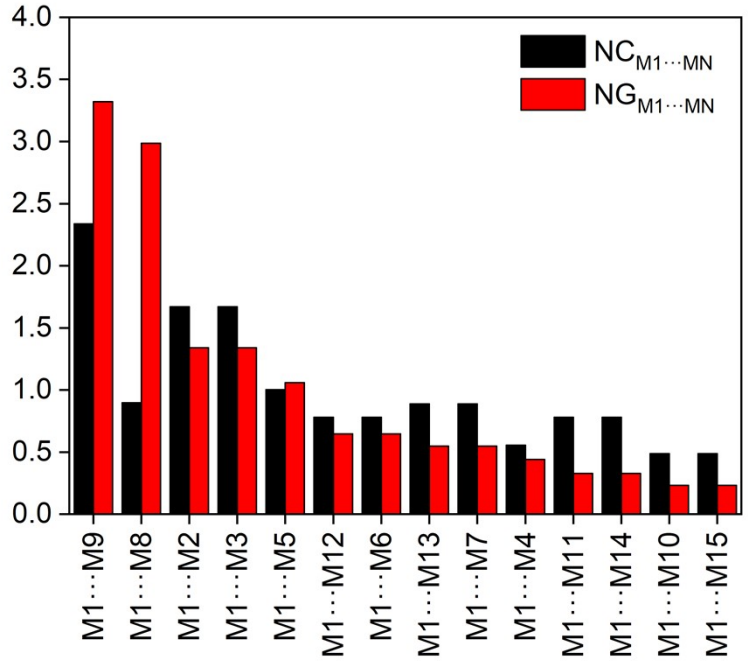

Figure S10. Normalized contact area and stabilization energy data ($NC_{M1\cdots MN}$ and $NG_{M1\cdots MN}$) for compound **5**.

3. Similarity Indices

Table S8. Similarity indices data (I^D, I^C, I^G, and I^{DCG}) for all comparisons between compound **1**-**5**.

Comparison	I^D	I^C	I^G	I^{DCG}
1 vs **2**	0.54	0.59	0.57	0.57
1 vs **3**	0.53	0.58	0.58	0.56
1 vs **4**	0.54	0.59	0.63	0.58
1 vs **5**	0.54	0.60	0.63	0.59
2 vs **3**	0.86	0.92	0.93	0.90
2 vs **4**	0.98	0.90	0.83	0.89
2 vs **5**	0.98	0.89	0.86	0.90
3 vs **4**	0.85	0.83	0.76	0.81
3 vs **5**	0.92	0.82	0.82	0.85
4 vs **5**	0.99	0.95	0.92	0.94

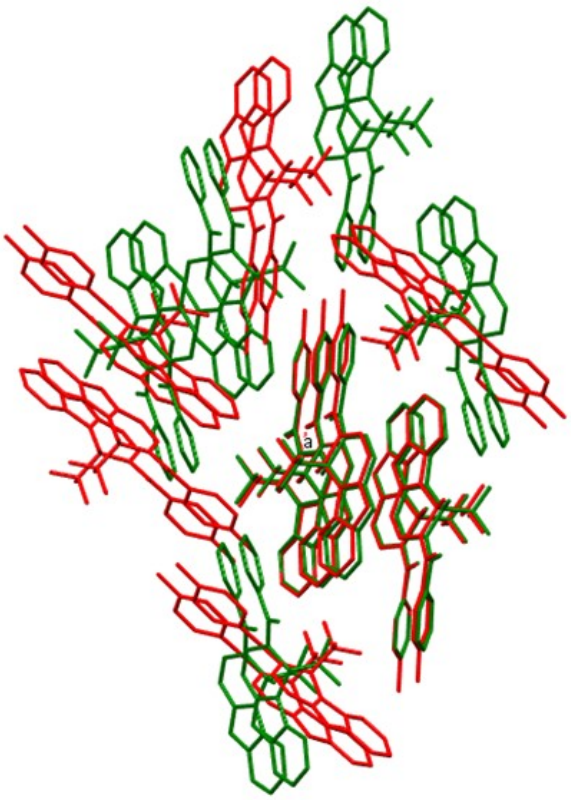

Figure S11. Supramolecular cluster overlay of **1** (green) vs. **2** (red).

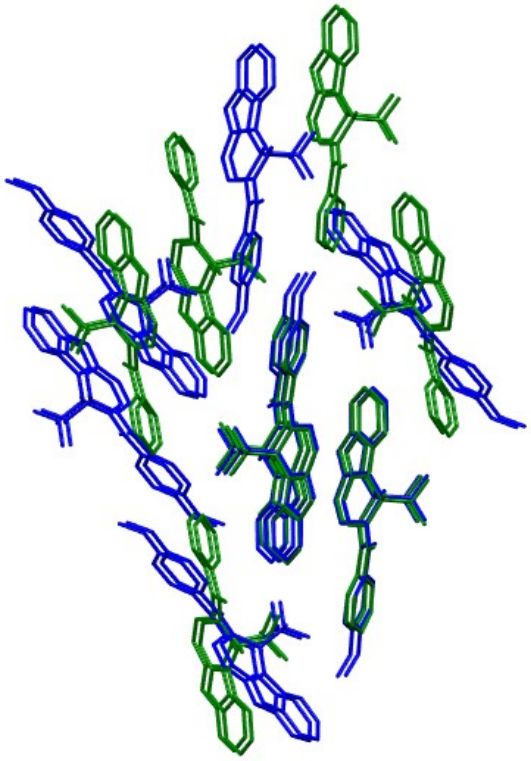

Figure S12. Supramolecular cluster overlay of **1** (green) vs. **3** (blue).

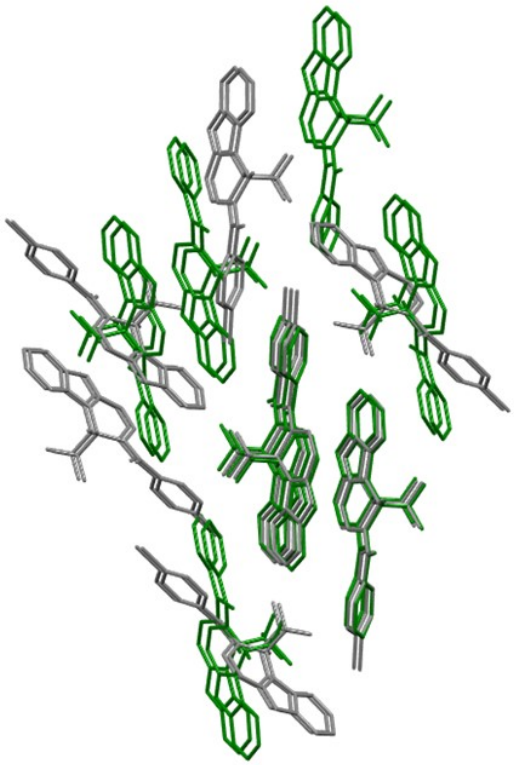

Figure S13. Supramolecular cluster overlay of **1** (green) vs. **4** (grey).

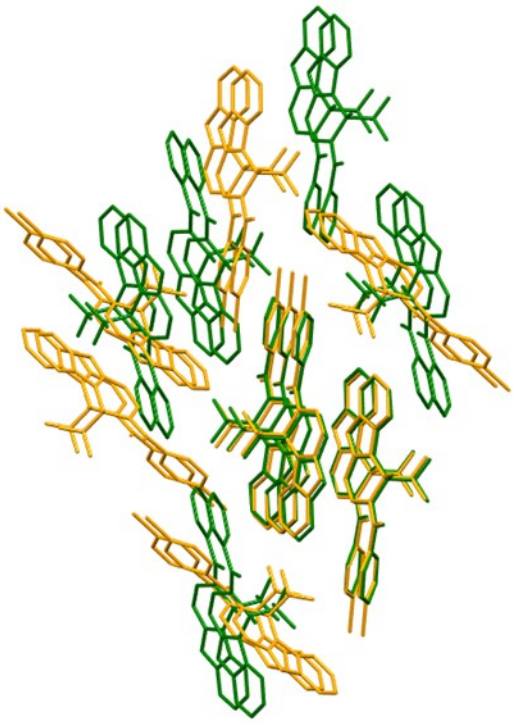

Figure S14. Supramolecular cluster overlay of **1** (green) vs. **5** (orange).

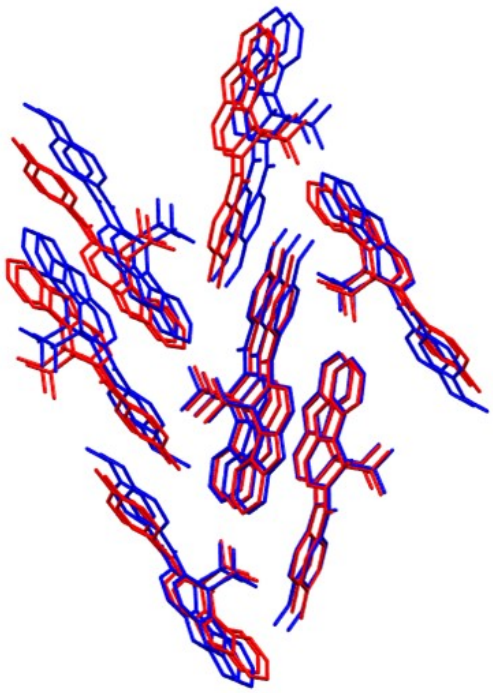

Figure S15. Supramolecular cluster overlay of **2** (red) vs. **3** (blue).

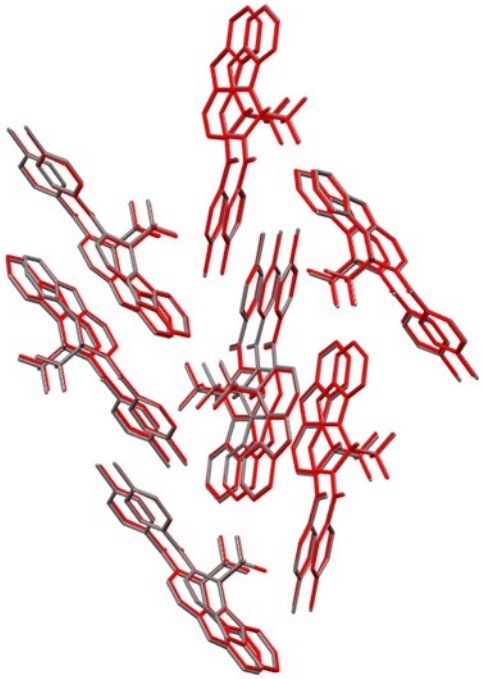

Figure S16. Supramolecular cluster overlay of **2** (red) vs. **4** (grey).

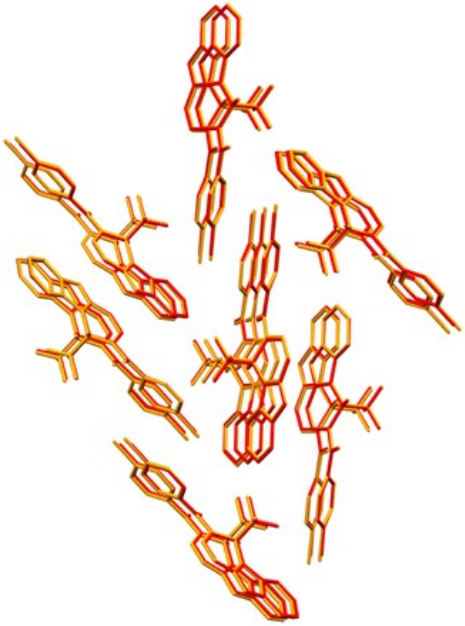

Figure S17. Supramolecular cluster overlay of **2** (red) vs. **5** (orange).

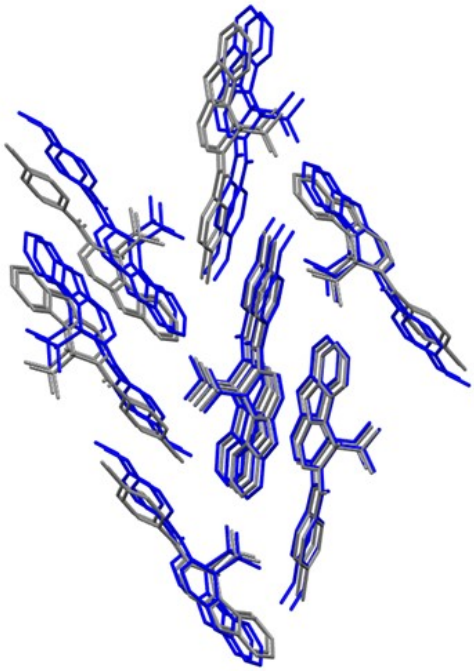

Figure S18. Supramolecular cluster overlay of **3** (blue) vs. **4** (grey).

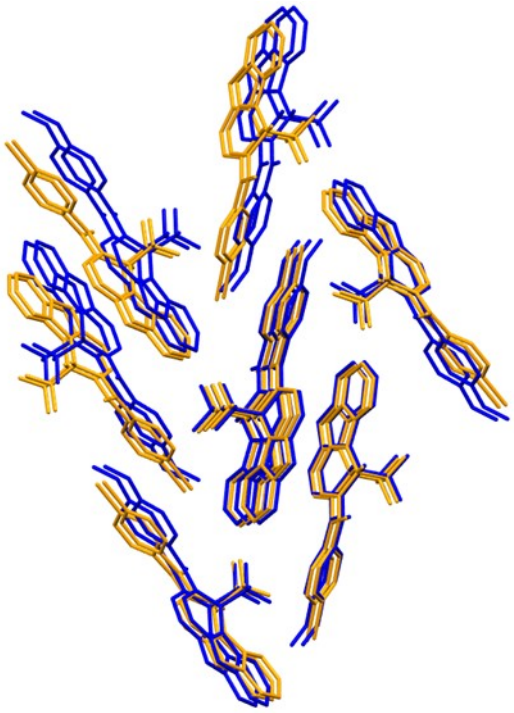

Figure S19. Supramolecular cluster overlay of **3** (blue) vs. **5** (yellow).

Figure S20. Supramolecular cluster overlay of **4** (grey) vs. **5** (yellow).

4. Crystallization mechanism proposals

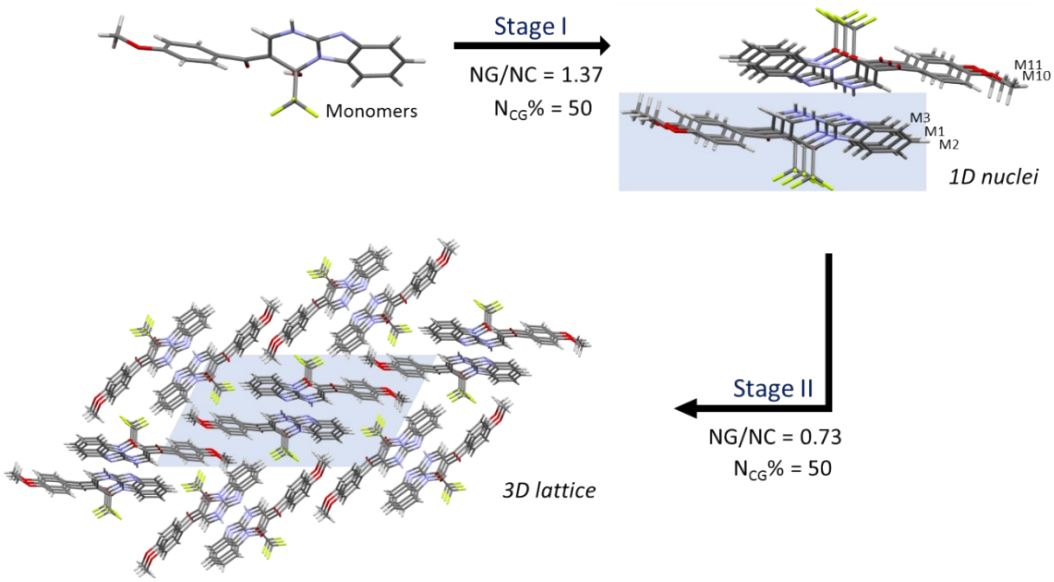

Figure S21. The proposed crystallization mechanism for compound **3**.

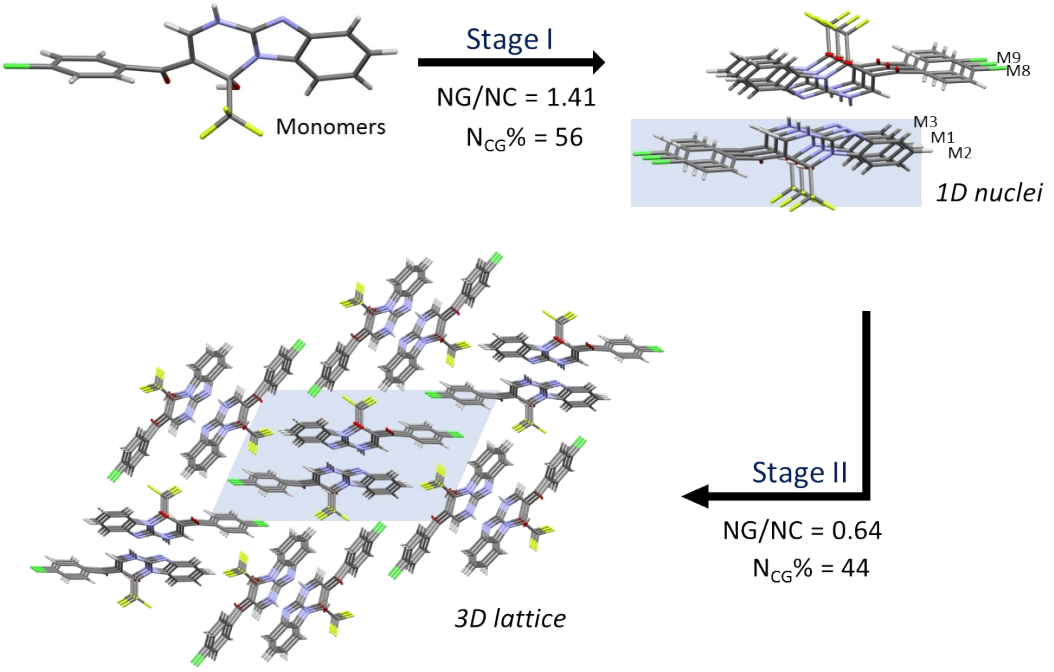

Figure S22. The proposed crystallization mechanism for compound **4**.

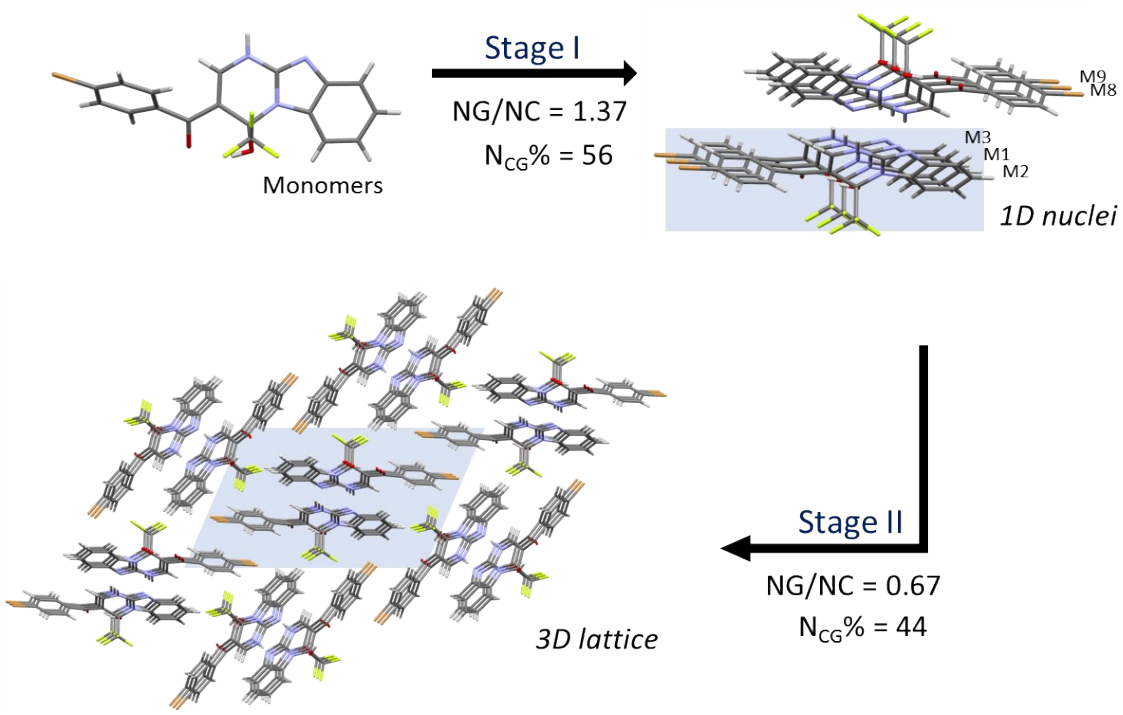

Figure S23. The proposed crystallization mechanism for compound **5**.

5. QTAIM data

Table S9. The QTAIM data of dimers M1···M12 and M1···M13 from the supramolecular cluster of compound **1**.

Dimer	Interaction	Atoms	ρ_{BCP}	$\nabla^2\rho$	ε	K	V	G	BPL	G_{AI}[a]
M1···M13	π···π	C10···C1	0.0063000	0.0162500	0.6179420	-0.0006430	-0.0027760	0.0034190	7.0427900	-3.58
	π···π	C10···C1	0.0063000	0.0162500	0.6179420	-0.0006430	-0.0027760	0.0034190	7.0427900	-3.58
	π···π	N13···C5	0.0050360	0.0149300	483.4944770	-0.0005670	-0.0025990	0.0031660	6.9665090	-2.86
	π···π	N13···C5	0.0050360	0.0149300	483.2179390	-0.0005670	-0.0025990	0.0031660	6.9665070	-2.86
	O···N	O3···N11	0.0029800	0.0120880	0.7384650	-0.0006060	-0.0018100	0.0024160	6.7725000	-1.69
	O···N	O3···N11	0.0029800	0.0120880	0.7384650	-0.0006060	-0.0018100	0.0024160	6.7725000	-1.69
	π···π	N4···C12	0.0034350	0.0120160	0.7663740	-0.0005250	-0.0019540	0.0024790	6.7636720	-1.95
	π···π	N4···C12	0.0034350	0.0120160	0.7663740	-0.0005250	-0.0019540	0.0024790	6.7636720	-1.95
M1···M12	N-H···N	N13H13···N11	0.02757400	0.09255800	0.07656100	-0.00228300	-0.01857300	0.02085600	3.88554100	-8.85
	N-H···N	N13H13···N11	0.02757400	0.09255800	0.07656100	-0.00228300	-0.01857300	0.02085600	3.88554200	-8.85

[a] Obtained by the equation $G_{AI\,(X\cdots Y)} = (\rho_{BCP}/\Sigma\rho_{BCP}) \times G_{M1\cdots MN}$.

6. Abbreviation List

Table S9. Abbreviations used for supramolecular cluster and similarity indices calculations.

Abbreviation	Definition
SC	Supramolecular Cluster
M1	Reference molecule of the Supramolecular Cluster
M*N*	Molecule that composes the Supramolecular Cluster
M1···M*N*	Dimer formed between the M1 and MN molecules
G	Stabilization Energy
C	Contact Area
G_{M1}	Stabilization Energy of the M1 molecule
G_{MN}	Stabilization Energy of the MN molecule
G_{M1+MN}	Total stabilization energy value of the considered dimer
$G_{M1\cdots MN}$	Intermolecular stabilization energy value of the considered dimer
$C_{M1\cdots MN}$	Contact area value of the considered dimer
N	Molecular Coordination Number
I^X	Similarity Index
I^D	Geometric Similarity Index
I^C	Contact Area Similarity Index
I^G	Stabilization Energy Similarity Index
I^{mp}	Multiparameter Similarity Index
I^{DCG}	Multiparameter Similarity Index considering Geometric, Contact Area, and Stabilization Energy Parameters
ND_i	Normalized geometric data
i	Value used to normalize the geometric parameter (i = m x *N*)
m	Number of atom-atom distances between the monomers of the considered dimer
NG	Normalized Stabilization Energy data
NC	Normalized Contact Area data
$NG_{predict}$	Predicted Normalized Stabilization Energy data
$NC_{predict}$	Predicted Normalized Contact Area data
N_{CG}%	Contribution of the considered crystallization mechanism stage in relation to the total crystallization process in terms of stabilization energy and contact area
NG/NC	Parameter that drives the considered crystallization mechanism stage