Supporting Information

Additive Controlled Packing Polymorphism in Series of Halogen Substituted Dithieno[3,2-*a*:2',3'-*c*]phenazines

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Table S1. Intermolecular contacts shorter than van der Waals interactions in the studied polymorphs

Number	Atom1…Atom2	Length, Å	Length-VdW, Å	Symmetry operation for the 2-nd atom
α H–DTPhz				
1	S2…C10	3.476	-0.024	x-1, y, z
2	C9…C16	3.345	-0.055	x-1, y, z
3	H1…C15	2.752	-0.148	1.5-x, 1-y, z-1/2
4	H8…N1	2.528	-0.222	1-x, y-1/2, 1/2-z
5	H8…H2	2.306	-0.094	1-x, y-1/2, 1/2-z
6	C8…H16	2.833	-0.067	2-x, y-1/2, 1/2-z
7	N2…H13	2.725	-0.025	x-1/2, 1/2-y, 1-z
β H–DTPhz				
1	H14A…N1B	2.615	-0.135	x-1, y-1, z
2	C13A…H1B	2.868	-0.032	x, y-1, z
3	S2A…N1B	3.296	-0.054	x, y, z
4	S2A…H2B	2.950	-0.050	x, y, z
5	S2A…H16B	2.962	-0.038	x, y, z
6	H7A…S2B	2.927	-0.073	1-x, 1-y, 1-z
7	S1B…S2B	3.486	-0.114	1-x, 2-y, 1-z
8	H13B…H14B	2.158	-0.242	3-x, 1-y, 1-z
α F–DTPhz				
1	S2A…S2A	3.513	-0.087	-x, -y, 1-z
2	F1A…H16A	2.412	-0.258	-x, 1-y, -z
3	C11A…C13F	3.257	-0.143	1-x, 1-y, 1-z
4	C13A…C15F	3.242	-0.158	1-x, 1-y, 1-z
5	C15A…F2F	3.102	-0.068	1-x, 1-y, 1-z
6	C15A…C14F	3.376	-0.024	1-x, 1-y, 1-z

7	C14A…C15F	3.392	-0.008	1-x, 1-y, 1-z
8	C14A…C14F	3.355	-0.045	1-x, 1-y, 1-z
9	H8A…F1E	2.446	-0.224	x, y-1, z
10	C5A…C16E	3.331	-0.069	-x, 1-y, 1-z
11	C13A…C4E	3.246	-0.154	-x, 1-y, 1-z
12	C14A…C5E	3.370	-0.030	-x, 1-y, 1-z
13	C1A…H13D	2.796	-0.104	x-1, y, z
14	H1A…N2D	2.519	-0.231	x-1, y, z
15	S1A…C10D	3.363	-0.137	1-x, 1-y, 1-z
16	H7A…C2C	2.876	-0.024	x, y-1, z
17	H7A…C1C	2.886	-0.014	x, y-1, z
18	N1A…H7C	2.739	-0.011	x, y, z
19	F2…N1C	2.874	-0.146	-x, 1-y, -z
20	F2…C9C	2.911	-0.259	-x, 1-y, -z
21	H1F…F2B	2.647	-0.023	x, 1+y, z
22	F1F…C8B	3.161	-0.009	x, 1+y, 1+z
23	F1F…H8B	2.579	-0.091	x, 1+y, 1+z
24	C6F…C12B	3.347	-0.053	1-x, 1-y, 1-z
25	C13F…C3B	3.321	-0.079	1-x, 1-y, 1-z
26	C11F…C6B	3.390	-0.010	1-x, 1-y, 1-z
27	C8F…C14B	3.354	-0.046	1-x, 1-y, 1-z
28	C14…S1B	3.476	-0.024	1-x, 1-y, 1-z
29	S2F…C5D	3.345	-0.155	x, y, z
30	S2F…C4D	3.313	-0.187	x, y, z
31	H1F…F1D	2.539	-0.131	2-x, 2-y, 1-z
32	F1F…C16C	3.146	-0.024	1+x, y, 1+z
33	S2B…S2B	3.204	-0.396	1-x, -y, -z
34	H2B…C1B	2.757	-0.143	1-x, 1-y, -z
35	H2B…H1B	2.240	-0.160	1-x, 1-y, -z
36	C13B…C11E	3.365	-0.035	1-x, 1-y, 1-z
37	C15B…C13E	3.209	-0.191	1-x, 1-y, 1-z
38	C14B…C14E	3.361	-0.039	1-x, 1-y, 1-z
39	F1B…F2D	2.744	-0.196	x-1, y, z
40	N2B…H1D	2.741	-0.009	x, y-1, z
41	H7B…S1D	2.904	-0.096	x, y-1, z
42	F1B…H8D	2.481	-0.189	x, y, z
43	N1B…H8C	2.652	-0.098	x, y, z
44	H8B…F1C	2.640	-0.030	1+x, y-1, z
45	F2E…C14D	3.117	-0.053	x-1, y, z
46	F1E…C16D	3.154	-0.016	x-1, y, z
47	N1E…C1D	3.195	-0.055	1-x, 2-y, 1-z
48	N1E…H1D	2.481	-0.269	1-x, 2-y, 1-z
49	H2E…C2D	2.790	-0.110	1-x, 2-y, 1-z
50	S2E…C5C	3.366	-0.134	x, y, 1+z
51	C2E…H2C	2.893	-0.007	-x, 2-y, 1-z
52	C4D…C16C	3.295	-0.105	1+x, y, z

53	C16D…C4C	3.292	-0.108	1+x, y, z
β F-DTPhz				
1	F2…S3	3.093	-0.177	1+x, y, z
2	C2…C23	3.387	-0.013	2-x, 1-y, 1-z
3	C1…H39	2.745	-0.155	x, y, z
4	H1…N6	2.558	-0.192	x, y, z
5	S1…H34	2.890	-0.110	1-x, -y, -z
6	C1…N5	3.227	-0.023	1-x, -y, -z
7	H1…N5	2.614	-0.136	1-x, -y, -z
8	N2…H40	2.646	-0.104	2-x, 1-y, 1-z
9	H8…C50	2.887	-0.013	x, y, 1+z
10	C18…H40	2.876	-0.024	x, y, z
11	H23…C33	2.883	-0.017	1+x, 1+y, 1+z
12	H18…C56	2.849	-0.051	x, y, z
13	C24…F7	3.149	-0.021	x, 1+y, 1+z
14	H24…F7	2.611	-0.059	x, 1+y, 1+z
15	C24…F8	3.063	-0.107	2-x, 1-y, 1-z
16	H24…F8	2.647	-0.023	2-x, 1-y, 1-z
17	C24…S8	3.429	-0.071	2-x, 2-y, 1-z
18	C48…C60	3.297	-0.103	x, y, z
γ F–DTPhz				
1	C7…C12	3.341	-0.059	x, y-1, z
2	F1…H3	2.634	-0.036	1-x, y-1, 1-z
3	S1…S1	3.488	-0.112	1/2-x, 1.5-y, 1-z
4	S1…S2	3.577	-0.023	1/2-x, 1.5-y, 1-z
α Cl–DTPhz				
1	C4…Cl2	3.365	-0.085	1/2-x, y-1/2, 1/2-z
2	Cl2…H1	2.909	-0.041	x-1.5, 1.5-y, z-1/2
3	N1…H8	2.677	-0.073	x-1/2, 1.5-y, 1/2+z
4	H2…C7	2.897	-0.003	x-1/2, 1.5-y, 1/2+z
β Cl–DTPhz				
1	C1B…N1B	3.202	-0.048	1-x, y-1/2, 1.5-z
2	H1B…N1B	2.538	-0.212	1-x, y-1/2, 1.5-z
3	S2B…C10	3.471	-0.029	x-1, y, z
4	C8B…C6A	3.330	-0.070	x-1, y, z
5	C16B…C4A	3.273	-0.127	x, y, z
6	C12B…C10	3.395	-0.005	x, y, z
7	C4B…C16A	3.284	-0.116	x, y, z
8	C11B…C3A	3.367	-0.033	x, y, z
9	C9B…N1A	3.245	-0.005	x, y, z
10	C6B…C12A	3.392	-0.008	x, y, z
11	C7B…C13A	3.368	-0.032	x, y, z
12	Cl2B…C13A	3.411	-0.039	x, 1+y, z
13	N2B…H8A	2.705	-0.045	x-1/2, 1.5-y, 1-z
14	H7B…C8A	2.813	-0.087	x-1/2, 1.5-y, 1-z
15	Cl2A…N2A	3.271	-0.029	x-1/2, 1/2-y, 1-z

Br–DTPhz				
1	Br2A…N2A	3.193	-0.207	x-1/2, 1/2-y, 1-z
2	C12A…Br2B	3.541	-0.009	x, y-1, z
3	C13A…Br2B	3.486	-0.064	x, y-1, z
4	N1A…C9B	3.227	-0.023	x, y, z
5	C3A…C11B	3.344	-0.056	x, y, z
6	C4A…C16B	3.394	-0.006	x, y, z
7	C10A…C12B	3.397	-0.003	x, y, z
8	C12A…C6B	3.377	-0.023	x, y, z
9	C13A…C7B	3.334	-0.066	x, y, z
10	C16A…C4B	3.288	-0.112	x, y, z
11	S2A…C7B	3.484	-0.016	1+x, y, z
12	C6A…C8B	3.311	-0.089	1+x, y, z
13	C10A…S2B	3.480	-0.020	1+x, y, z
14	H13A…Br2B	3.046	-0.004	x-1/2, 1.5-y, 1-z
15	Br2A…H8B	3.023	-0.027	1/2+x, 1/2-y, 1-z
16	C8A…H7B	2.793	-0.107	1/2+x, 1.5-y, 1-z
17	H8A…N2B	2.725	-0.025	1/2+x, 1.5-y, 1-z
18	H1B…N1B	2.612	-0.138	-x, y-1/2, 1/2-z

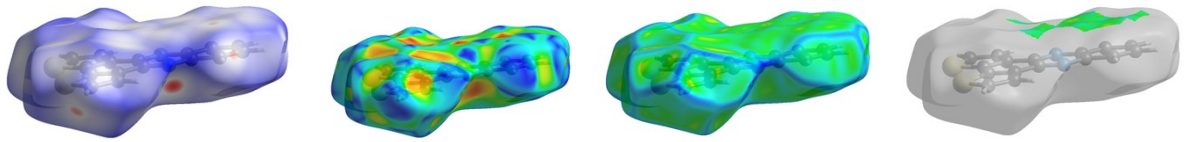

Figure S1. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle), and π-stacking area (right) for compound **α H–DTPhz**.

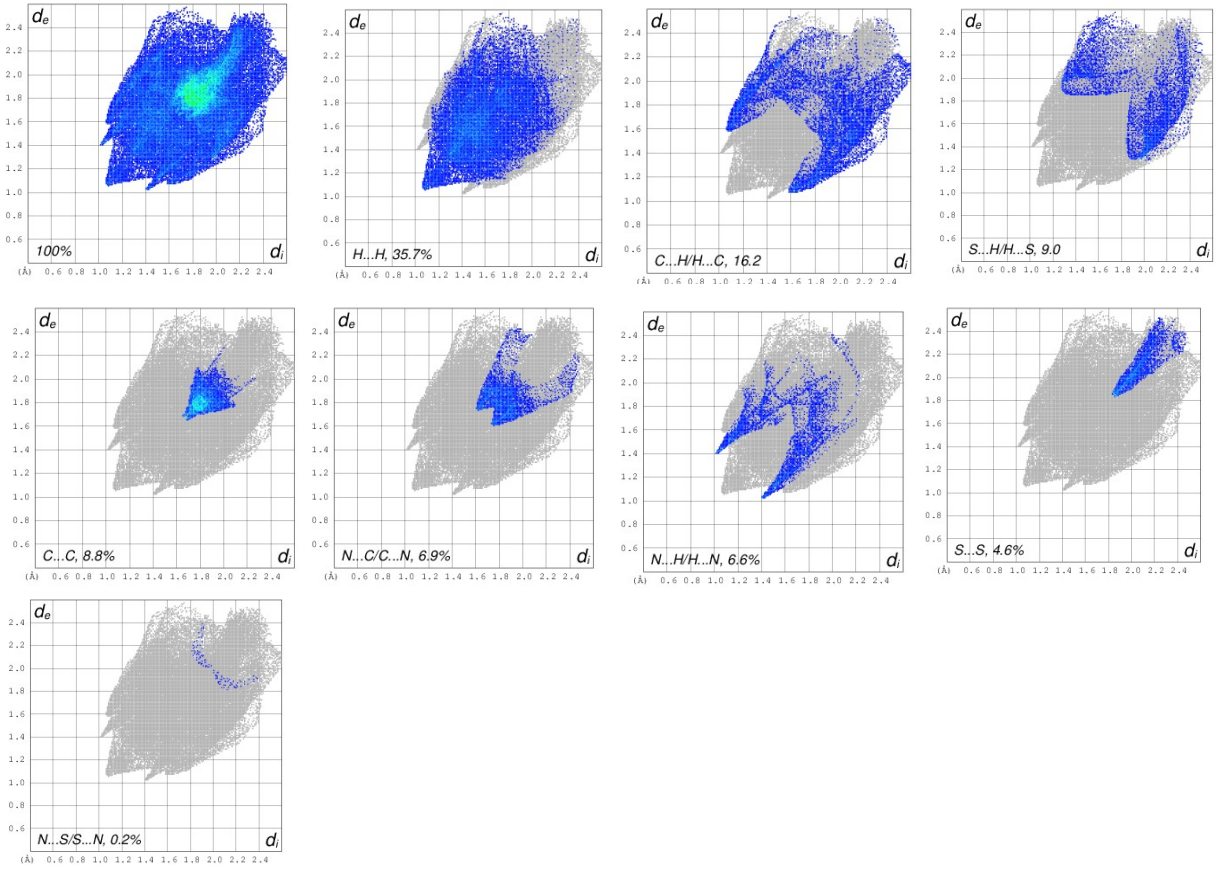

Figure S2. Fingerprint plots for compound **α H–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecule.

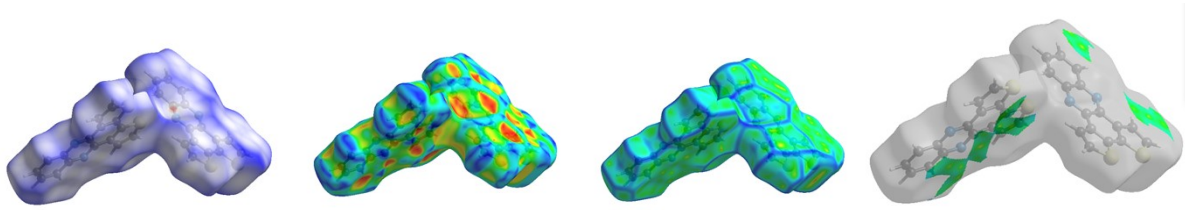

Figure S3. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle) and π-stacking area (right) for compound **β H–DTPhz**.

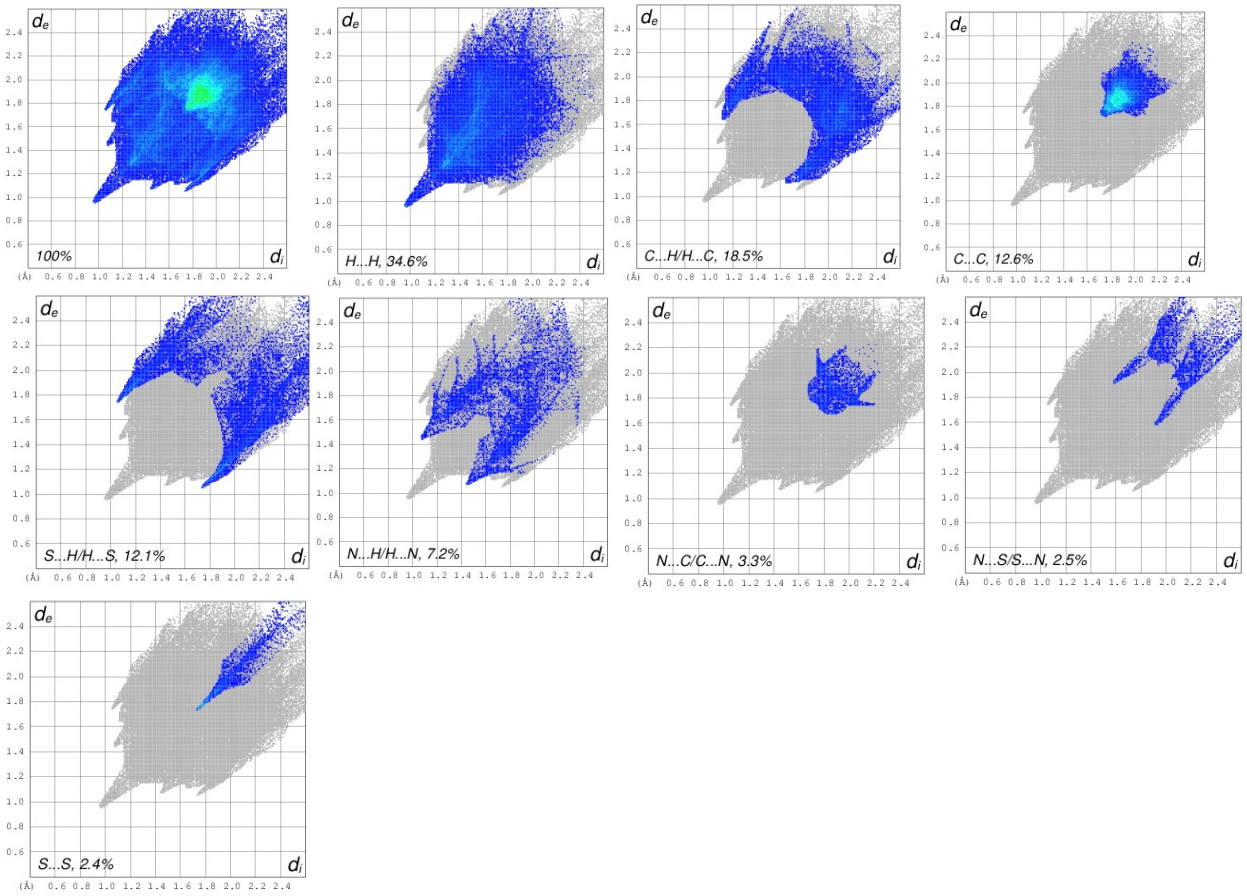

Figure S4. Fingerprint plots for compound **β H–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

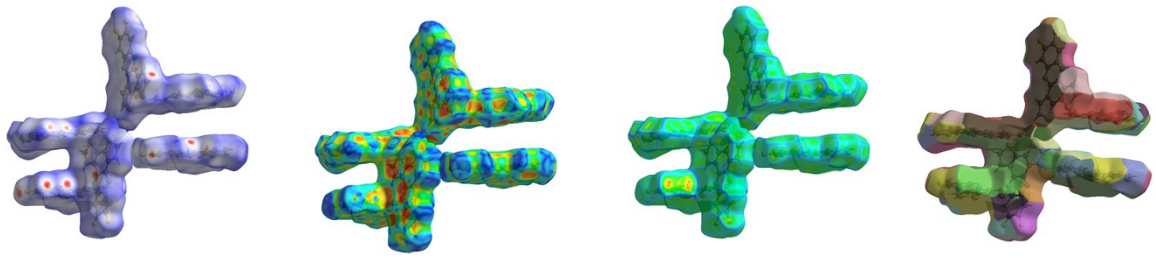

Figure S5. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle) and fragment patch (right) for compound **α F–DTPhz**.

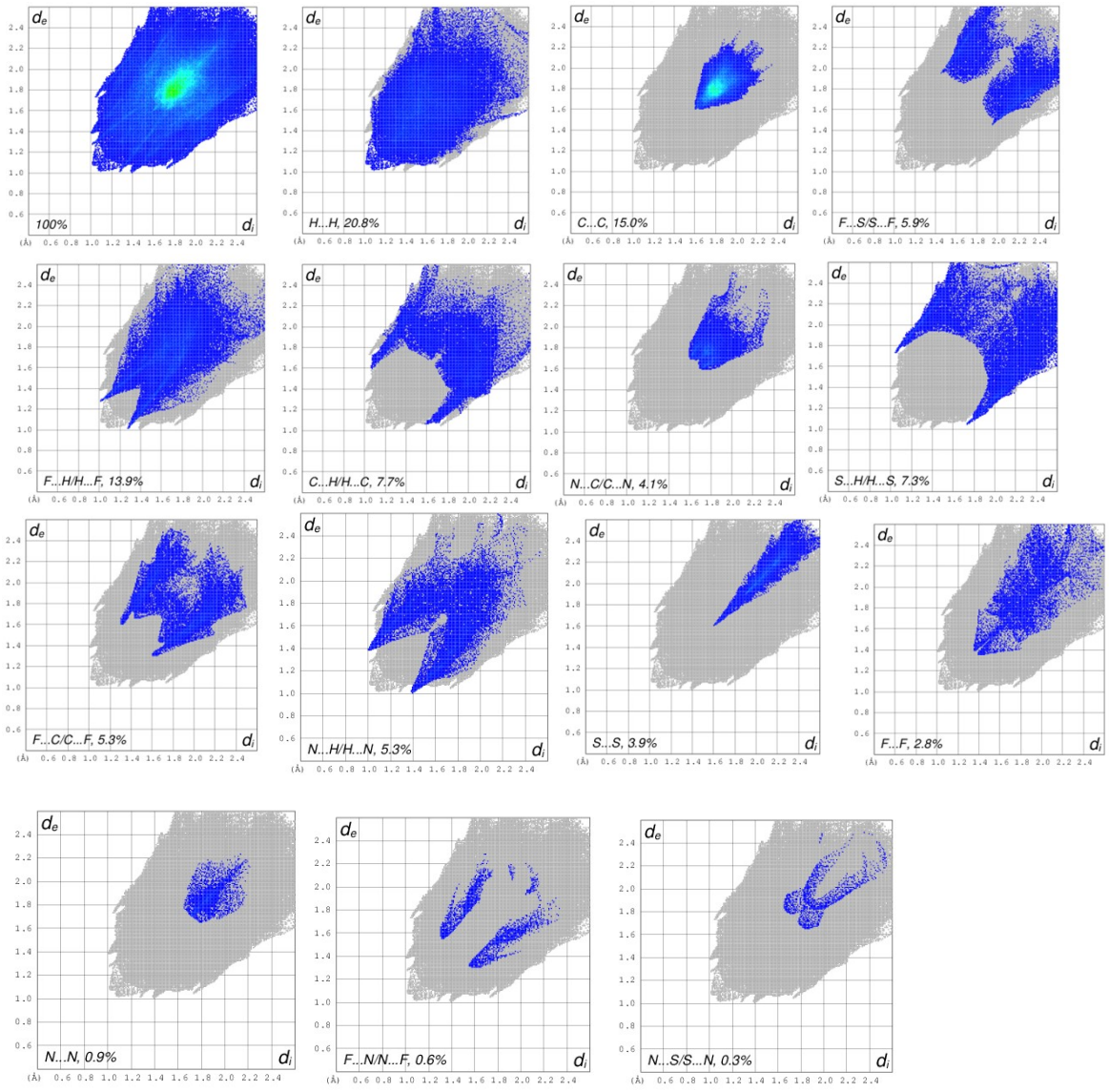

Figure S6. Fingerprint plots for **compound α F–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

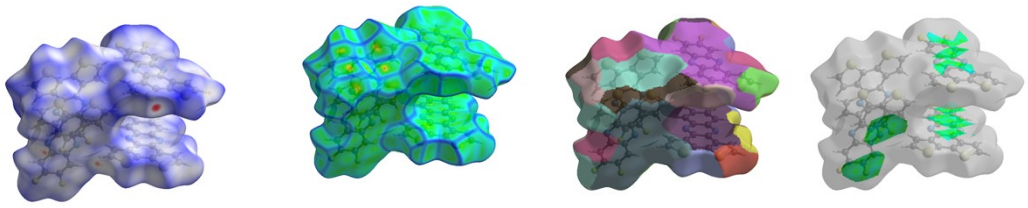

Figure S7. Hirshfeld surface mapped with d_{norm} (left), fragment patch (middle), curvedness (middle) and π-stacking area (right) for compound **β F–DTPhz.**

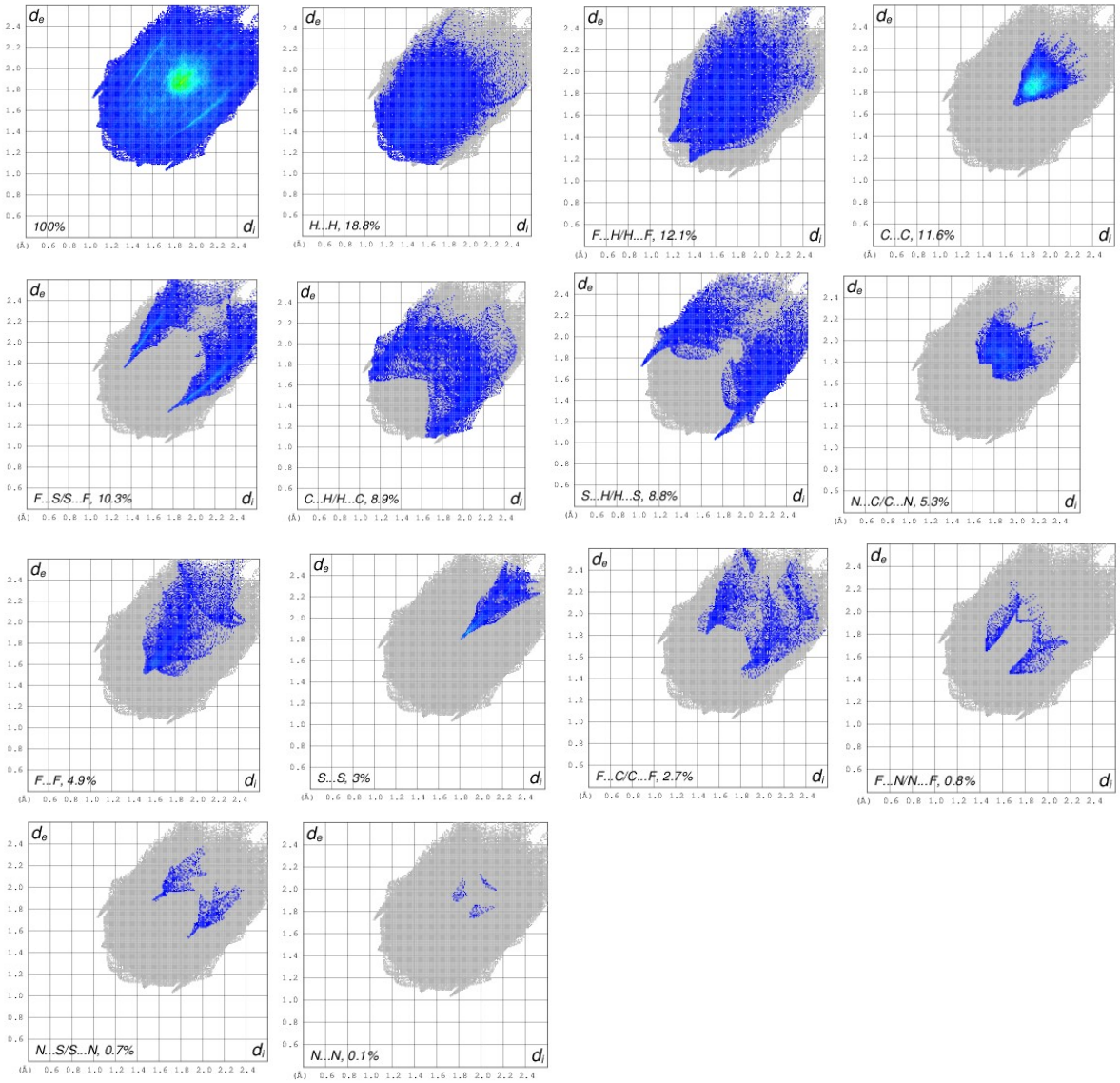

Figure S8. Fingerprint plots for **compound β F–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

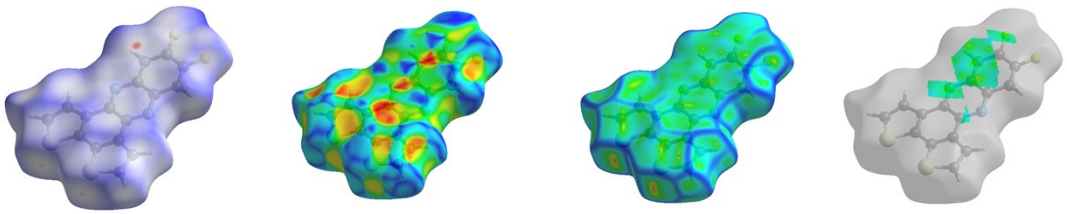

Figure S9. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle) and π-stacking area (right) for compound **γ F–DTPhz.**

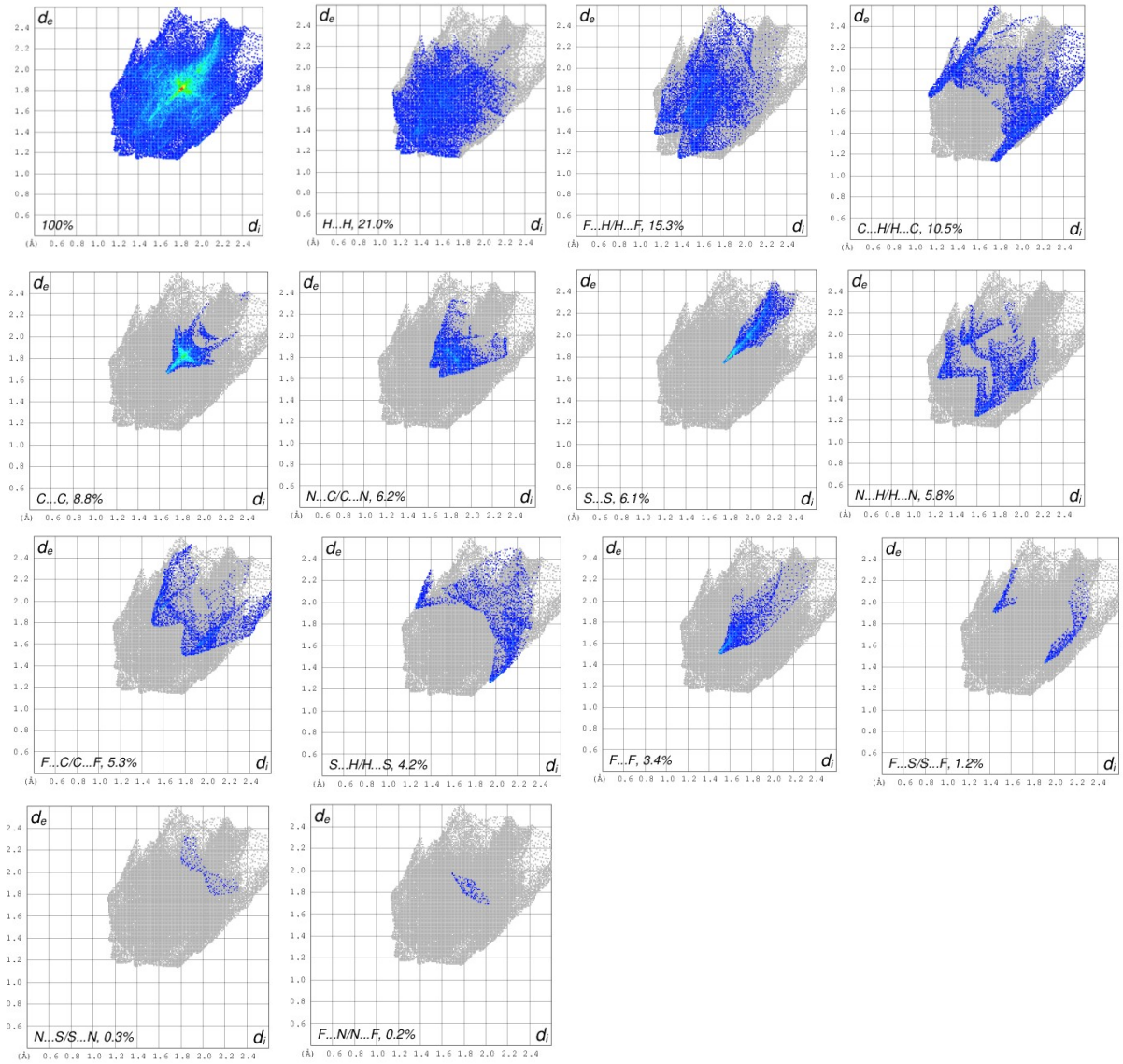

Figure S10. Fingerprint plots for compound **γ F–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

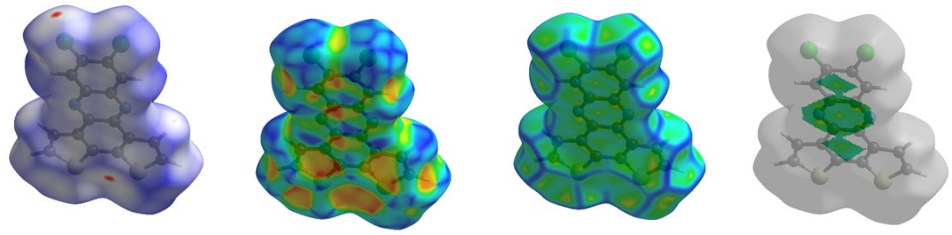

Figure S11. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle) and π-stacking area (right) for compound **α Cl–DTPhz.**

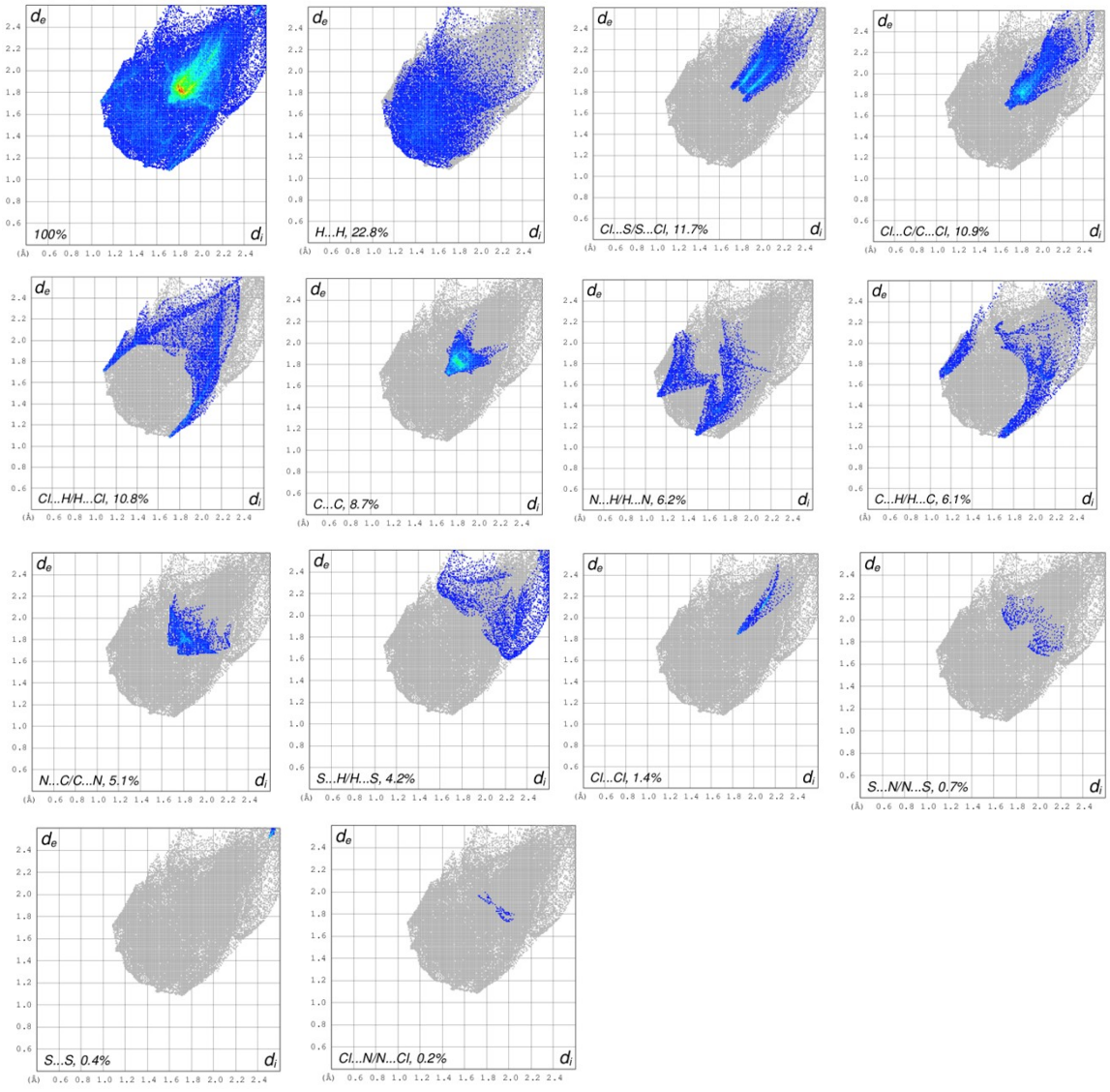

Figure S12. Fingerprint plots for compound **α Cl–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

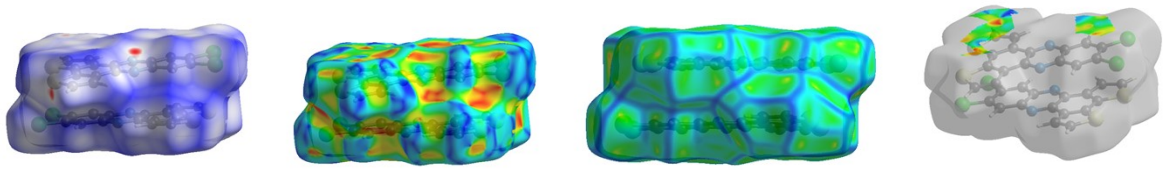

Figure S13. Hirshfeld surface mapped with d_{norm} (left), shape index (middle), curvedness (middle) and π-stacking area (right) for compound **β Cl–DTPhz.**

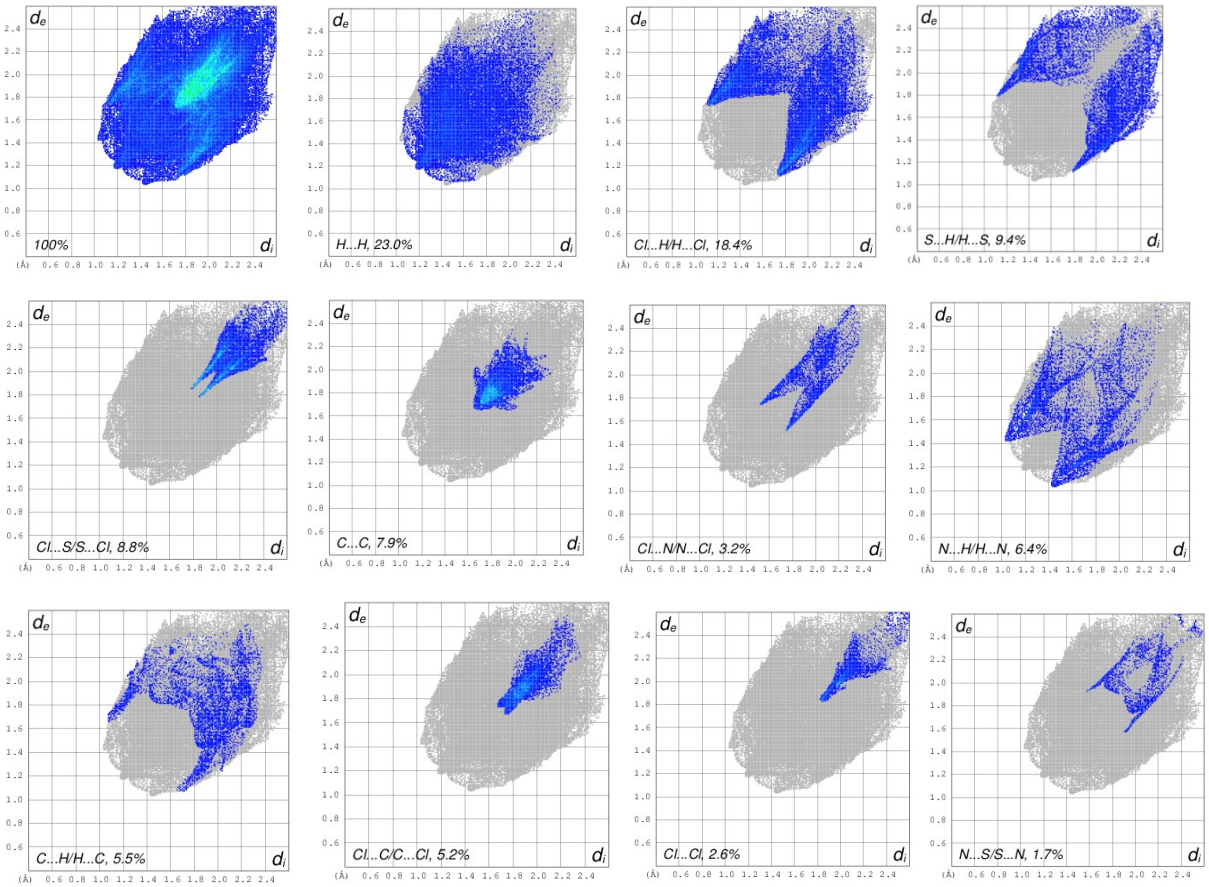

Figure S14. Fingerprint plots for compound **β Cl–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

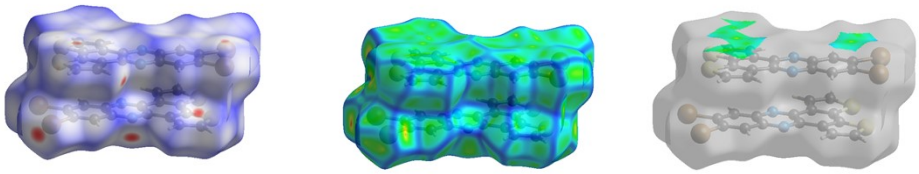

Figure S15. Hirshfeld surface mapped with d_{norm} (left), curvedness (middle) and π-stacking area (right) for compound **Br–DTPhz.**

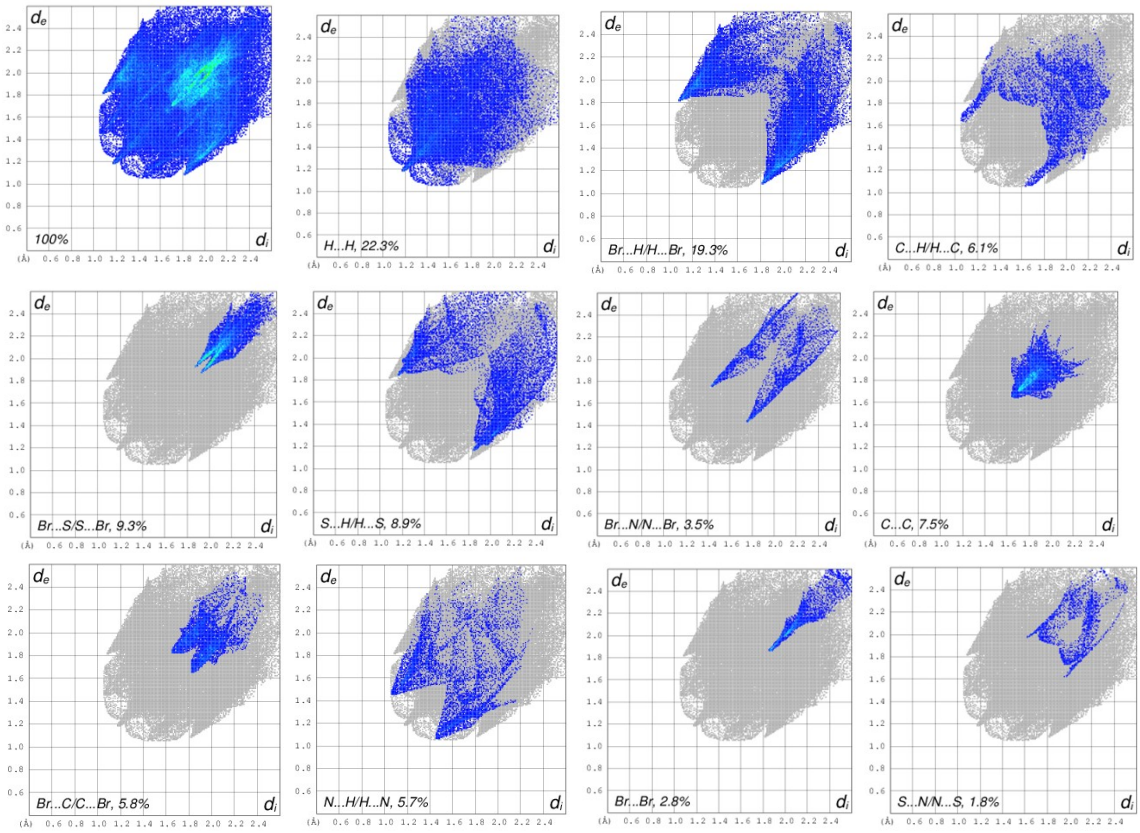

Figure S16. Fingerprint plots for compound **Br–DTPhz**: full and resolved into the most meaningful interactions showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules.

Table S2. Percent distribution of meaningful interactions in the studied polymorphs.

Compound	H…H ,%	C…H /H…C, %	S…H/ H…S, %	C… C	N…H/ H…N, %	N…C/ C…N, %	S…S, %	N…S /S…N,%	Hal…S /S…Hal, %	Hal…C/ C…Hal,%	Hal…H/ H…Hal, %	Hal…Hal ,%	Hal…N/ N…Hal, %	N…N, %
α H–DTPhz	35.7	16.2	9.0	8.8	6.6	6.9	4.6	0.2	-	-	-	-	-	-
β H–DTPhz	34.6	18.5	12.1	12.6	7.2	3.3	2.4	2.5	-	-	-	-	-	-
α F-DTPhz	20.8	7.7	7.3	15.0	5.3	4.1	3.9	0.3	5.9	5.3	13.9	2.8	0.6	0.9
β F-DTPhz	18.8	8.9	8.8	11.6	4.8	5.3	3.0	0.7	10.3	2.7	12.1	4.9	0.8	0.1
γ F–DTPhz	21.0	10.5	4.2	8.8	5.8	6.2	6.1	0.3	1.2	5.3	15.3	3.4	0.2	-
α Cl-DTPhz	22.8	6.1	4.2	8.7	6.2	5.1	0.4	0.7	11.7	10.9	10.8	1.4	0.2	-
β Cl-DTPhz	23.0	5.5	9.4	7.9	6.4	-	-	1.7	8.8	5.2	18.4	2.6	3.2	-
Br-DTPhz	22.3	6.1	8.9	7.5	5.7	-	-	1.8	9.3	5.8	19.3	2.8	3.5	-
Range	18.8-35.7	5.5-18.5	4.2-12.1	7.5-15.0	5.3-6.4	3.3-6.9	0.4-6.1	0.2-2.5	1.2-11.7	2.7-10.9	10.8-19.3	1.4-4.9	0.2-3.5	0.1-0.9

Table S3. Lattice energy of polymorphs (Rydberg) calculated with PBE-D method using pbe-rrkjus ultrasoft pseudopotentials.

structure type	**α H-DTPhz**	**β H-DTPhz**	**α F-DTPhz**	**β F-DTPhz**	**γ F-DTPhz**	**α Cl-DTPhz**	**β Cl-DTPhz**
H	-277.0118	-277.0089	-276.9962	-277.0064	-277.0064	-277.0073	-276.9948
F	-373.7560	-373.7478	-373.7555	-373.7565	-373.7565	-373.7562	-373.7554
Cl	-343.9434	-343.9291	-343.9429	-343.9472	-343.9461	-343.9546	-343.9549
Br						-342.3669	-342.3684