Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Crystal Environment Induced Symmetry Reduction (CEISR): Deep Analysis of *Para*-Chloroacetophenone Azine and Generalization

Harmeet Bhoday,[a] Kaidi Yang,[a,b] Steven P. Kelley,[b] and Rainer Glaser[a,*]

[a] Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri, 65409. Email: glaserr@mst.edu

[b] Department of Chemistry, University of Missouri, Columbia, Missouri, 65211

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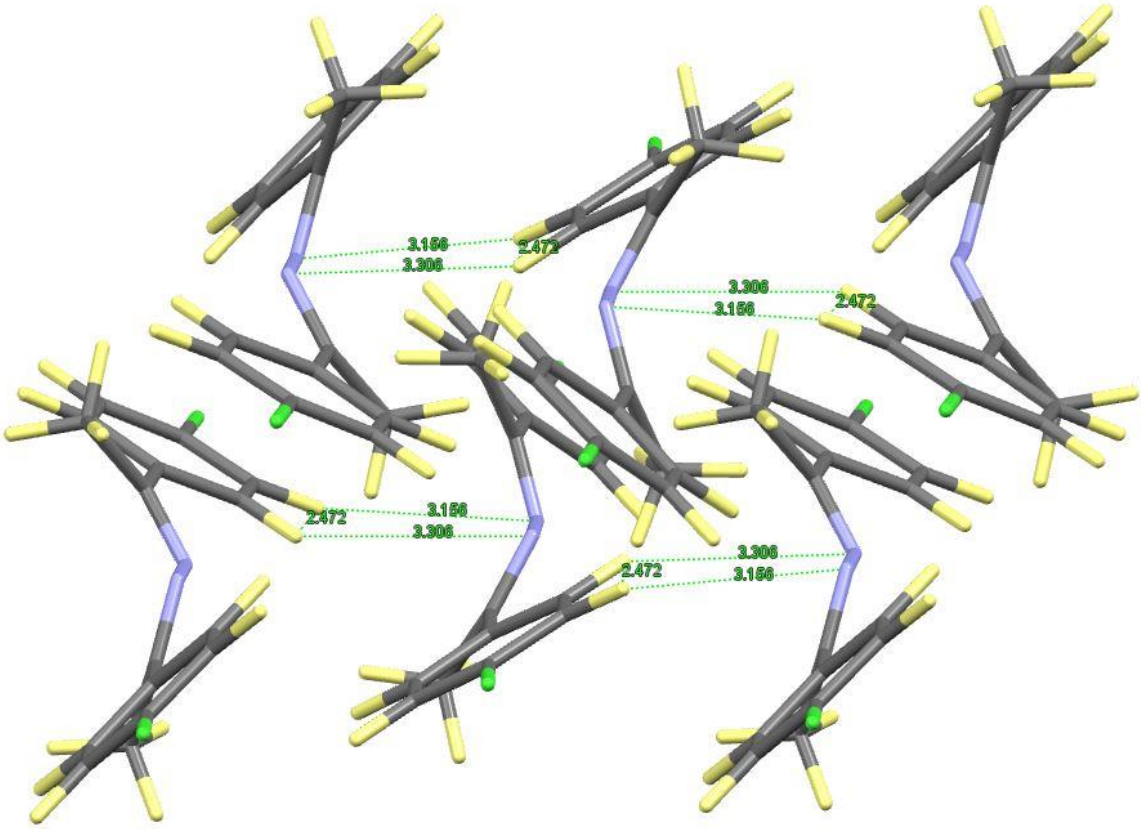

Fig. S1 The directed AAz chain containing molecules **V** and **W** is shown as in Fig. 4 and contains only *P* helicity molecules. The neighboring AAz chain is directed anti-parallel and comprises of only *M* helicity molecules.

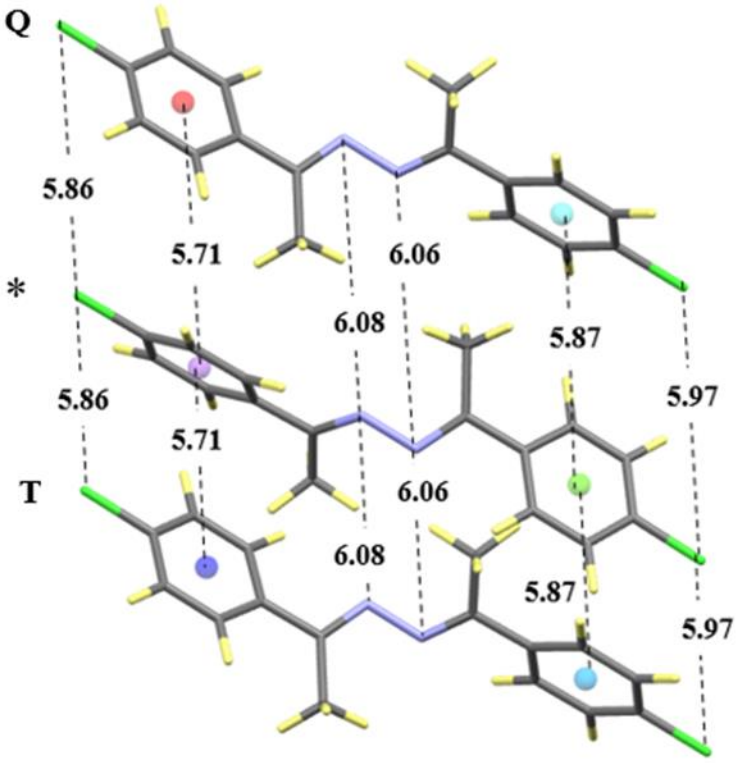

Fig. S2 The interatomic distances between the pair **Q**, * and pair **T**, *.

Table S1 Helicity of the Phenyl Twist in Optimized Structures of **1**

Starting from Different Trial Structures

		Ia		**I**b	
		starting struc.	optimized struc.	starting struc.	optimized struc.
Ia1	Azine helicity	*P*	*P*	*M*	*M*
	τ	134.71	132.39	-134.71	-132.39
	Ph1 helicity	*P*	*M*	*M*	*P*
	ϕ_1	29.31	-15.61	-29.31	15.66
	Ph2 helicity	*M*	*M*	*P*	*P*
	ϕ_2	-30.53	-15.58	30.53	15.65
Ia2	Azine helicity	*P*	*P*	*M*	*M*
	τ	134.71	132.39	-134.71	-132.39
	Ph1 helicity	*M*	*M*	*P*	*P*
	ϕ_1	-29.31	-15.65	29.31	15.65
	Ph2 helicity	*P*	*M*	*M*	*P*
	ϕ_2	30.53	-15.66	-30.53	15.66
Ia3	Azine helicity	*P*	*P*	*M*	*M*
	τ	134.71	132.39	-134.71	-132.39
	Ph1 helicity	*P*	*M*	*M*	*P*
	ϕ_1	29.31	-15.66	-29.31	15.66
	Ph2 helicity	*P*	*M*	*M*	*P*
	ϕ_2	30.53	-15.65	-30.53	15.65

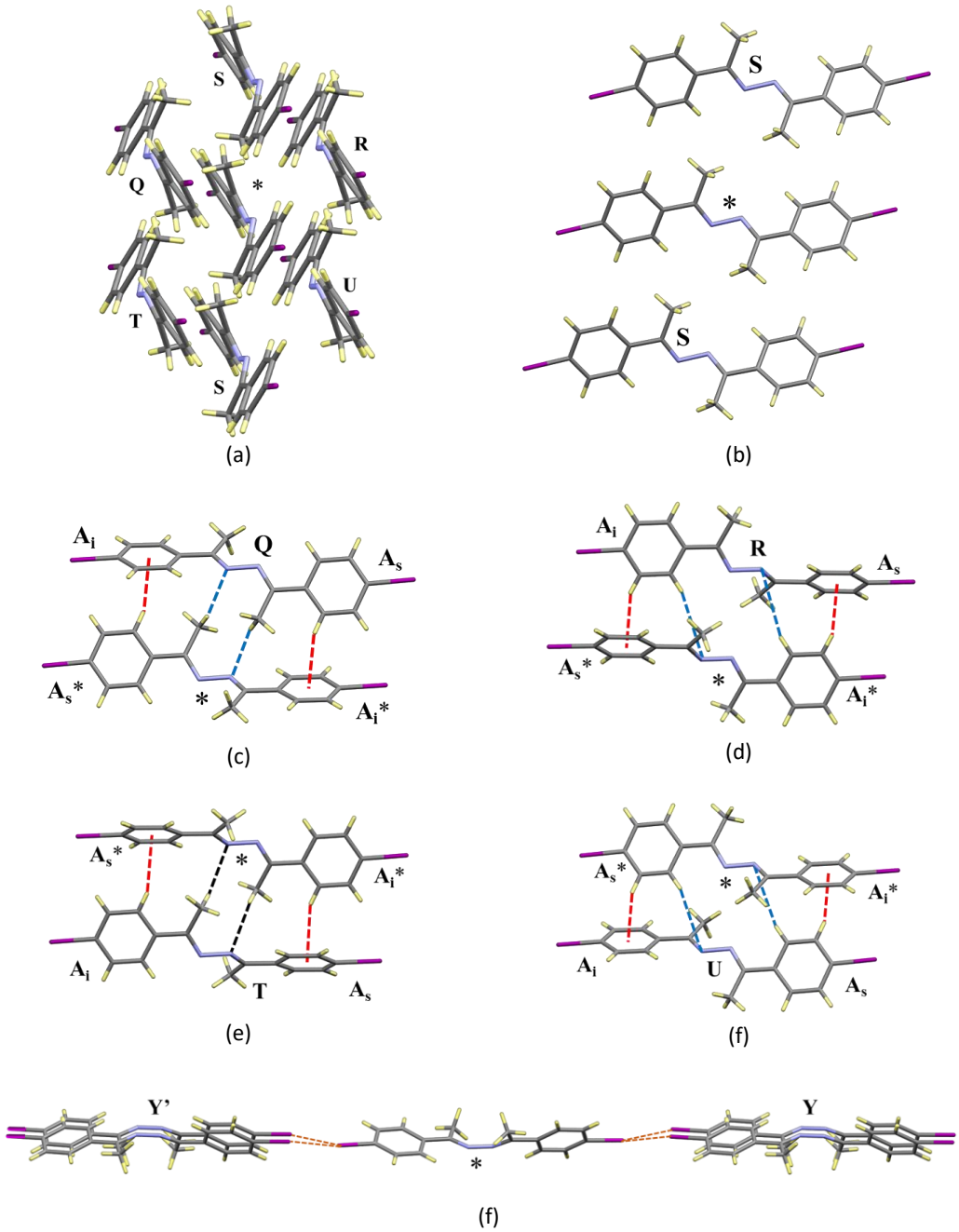

Fig. S3 The starred molecule in (I, I)-azine **3** with neighbors (a) **Q** - **U** in the *intra*layer and (b) **Y** in the *inter*layer. The molecule possesses C_2-symmetry, so the arenes are indistinguishable.

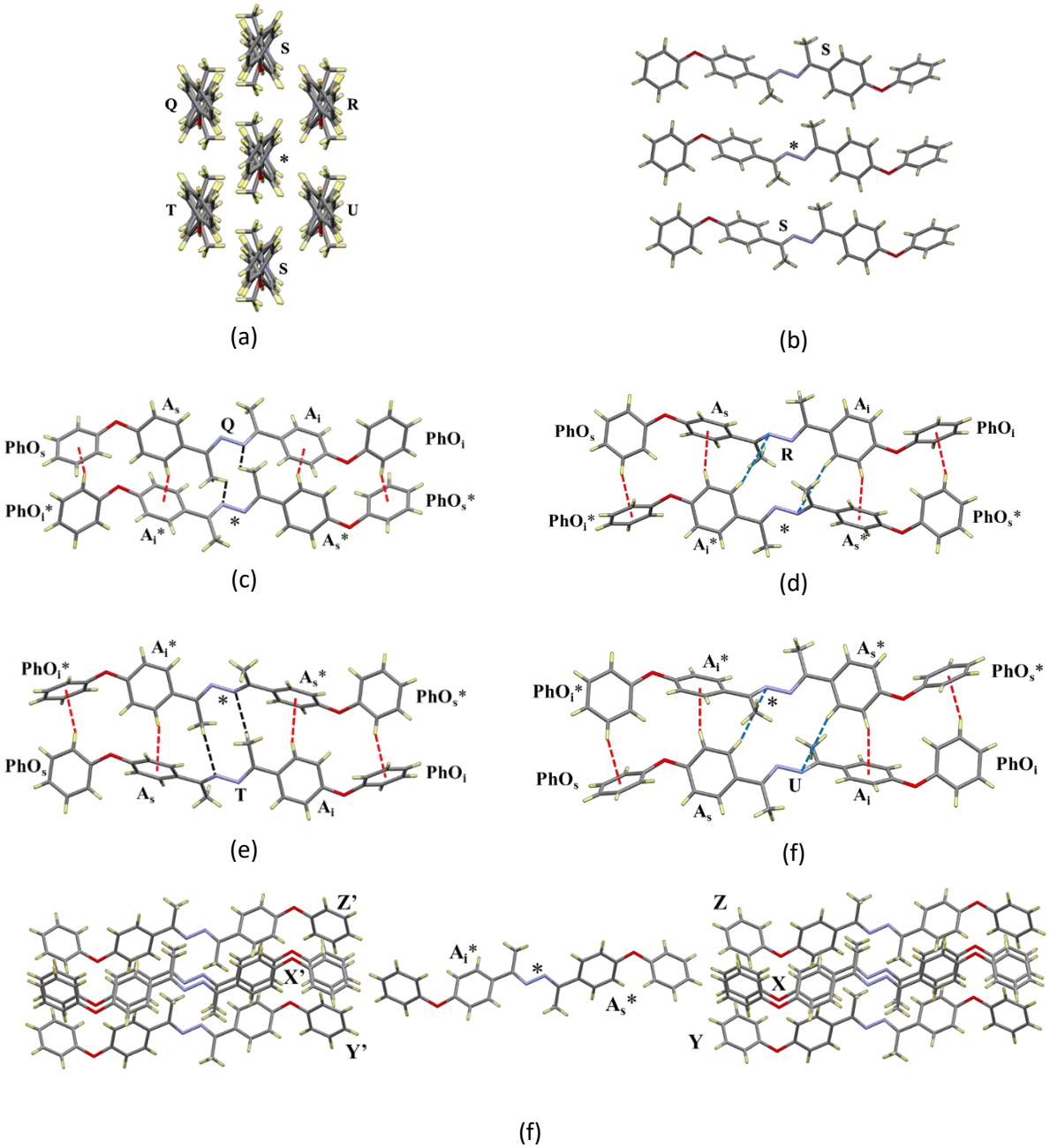

Fig. S4 The starred molecule in (PhO, PhO)-azine **5** with neighbors (a) **Q** - **U** in the *intra*layer and (b) **X** - **Z** in the *inter*layer. The molecule possesses C_2-symmetry, so the arenes A_i and A_s are indistinguishable.

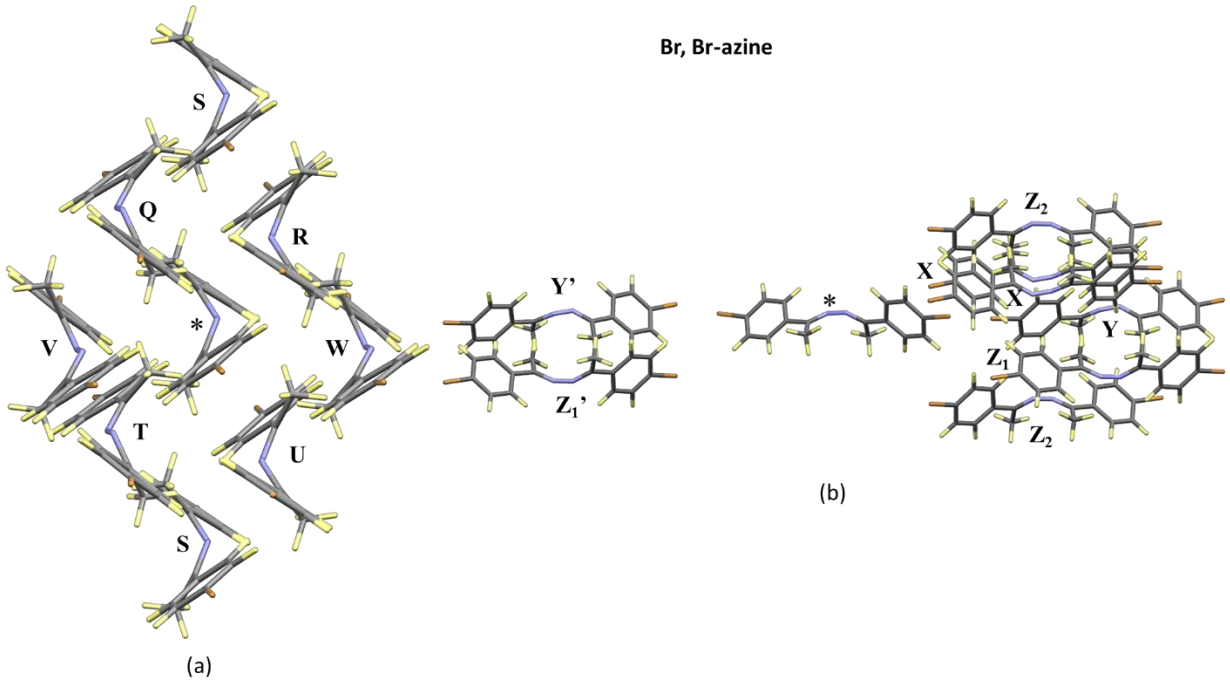

Fig. S5 The starred molecule in (Br, Br)-azine **2-Ia** with neighbors (a) **Q** - **W** in the intralayer and (b) **X** - **Z** in the interlayer.

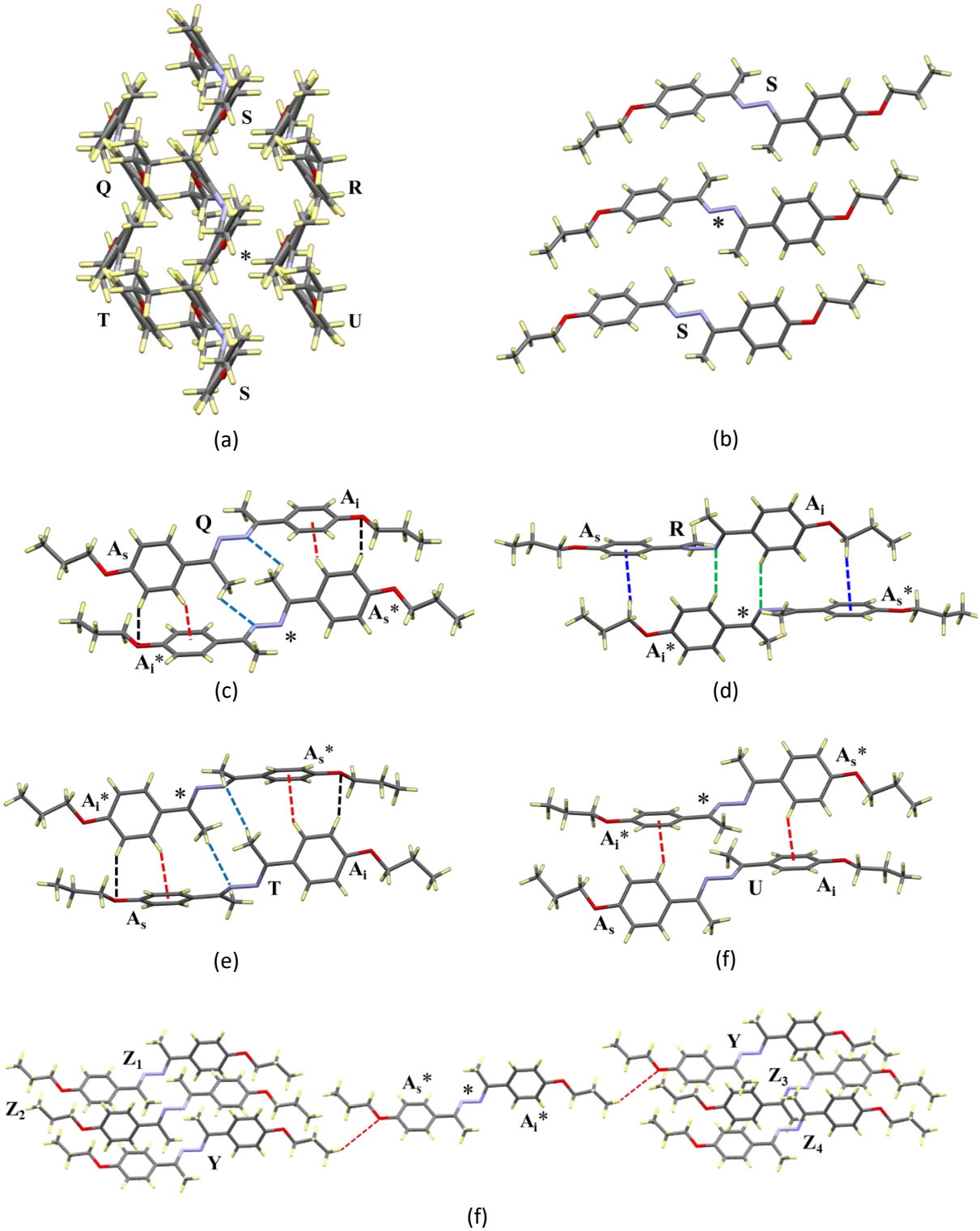

Fig. S6 (a)-(e) The starred molecule in (PrO, PrO)-azine **10** with neighbors **Q** - **U** in the *intra*layer. (f) **Y** - **Z4** in the *inter*layer.

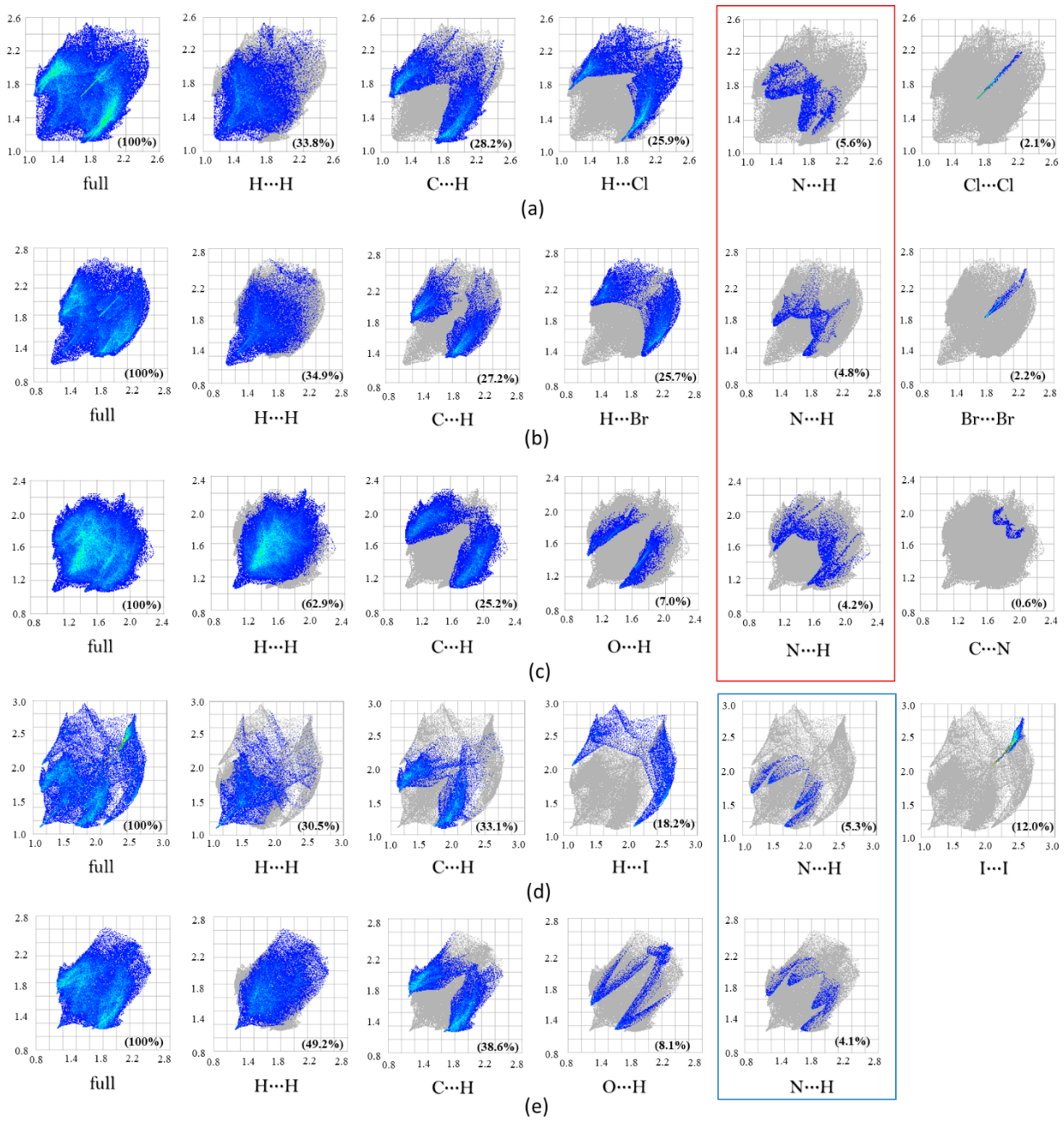

Fig. S7 Hirshfeld surfaces for C_1-symmetric azines (a) (Cl, Cl)-azine **1-I**, (b) (Br, Br)-azine **2-Ia**, and (c) (PrO, PrO)-azine **10** and C_2-symmetric azines (d) (I, I)-azine **3** and (e) (PhO, PhO)-azine **10**.

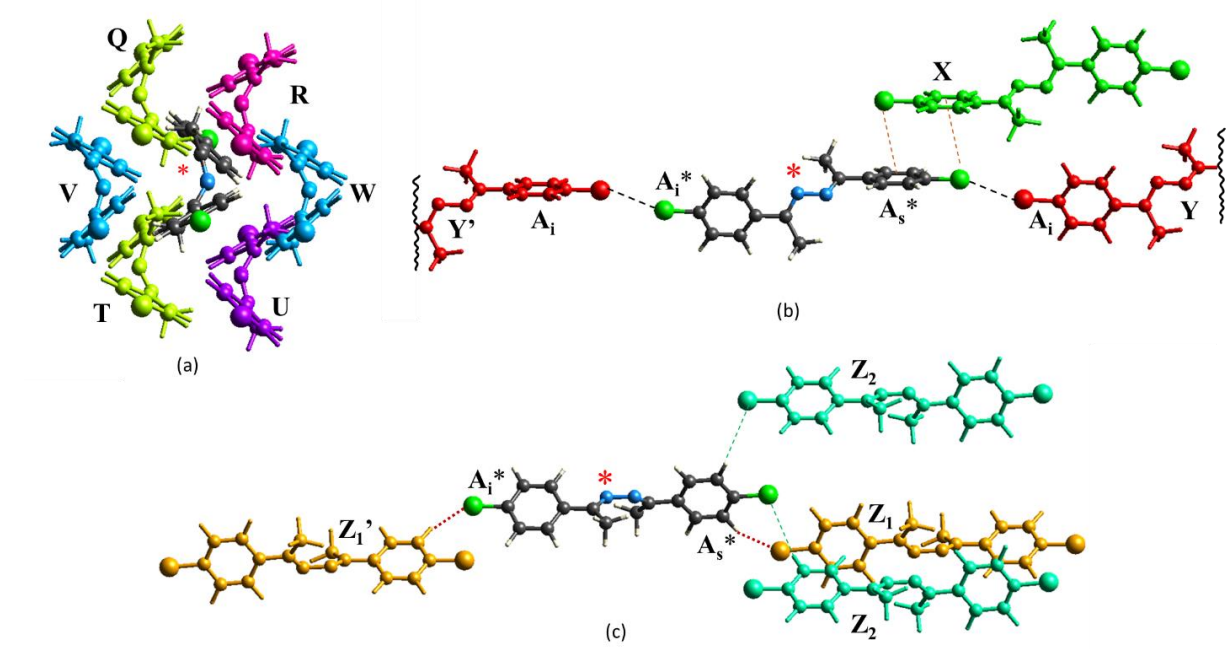

Fig. S8 Color-coded interaction mapping within 3.8 Å of the starred molecule in **I**.

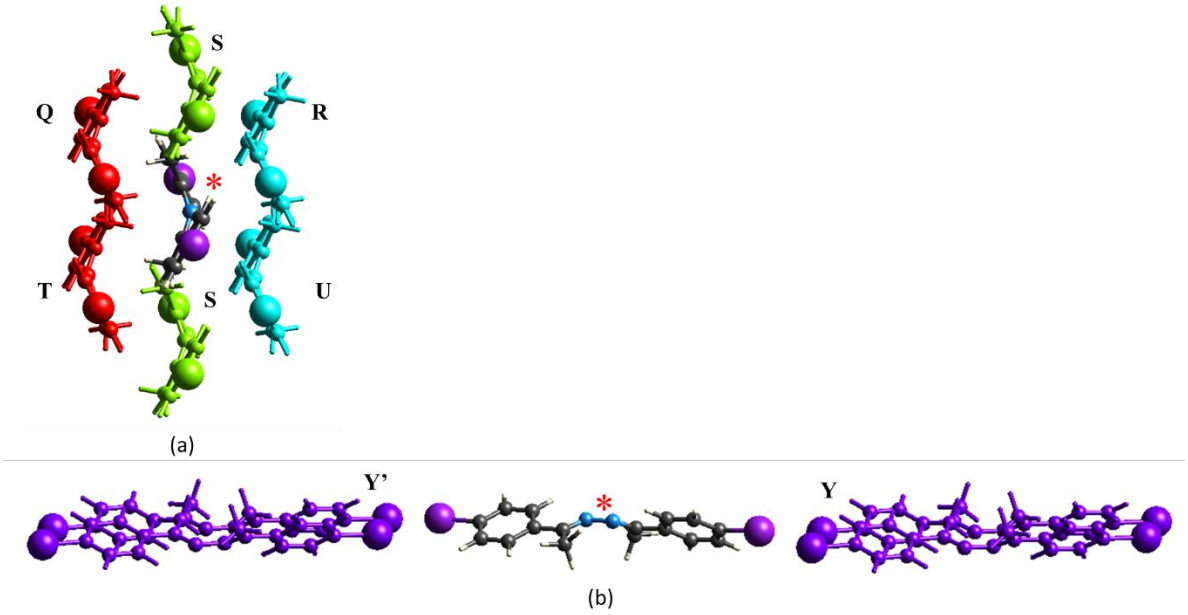

Fig. S9 Color-coded interaction mapping within 3.8 Å of the starred molecule in (I, I)-azine **3**.

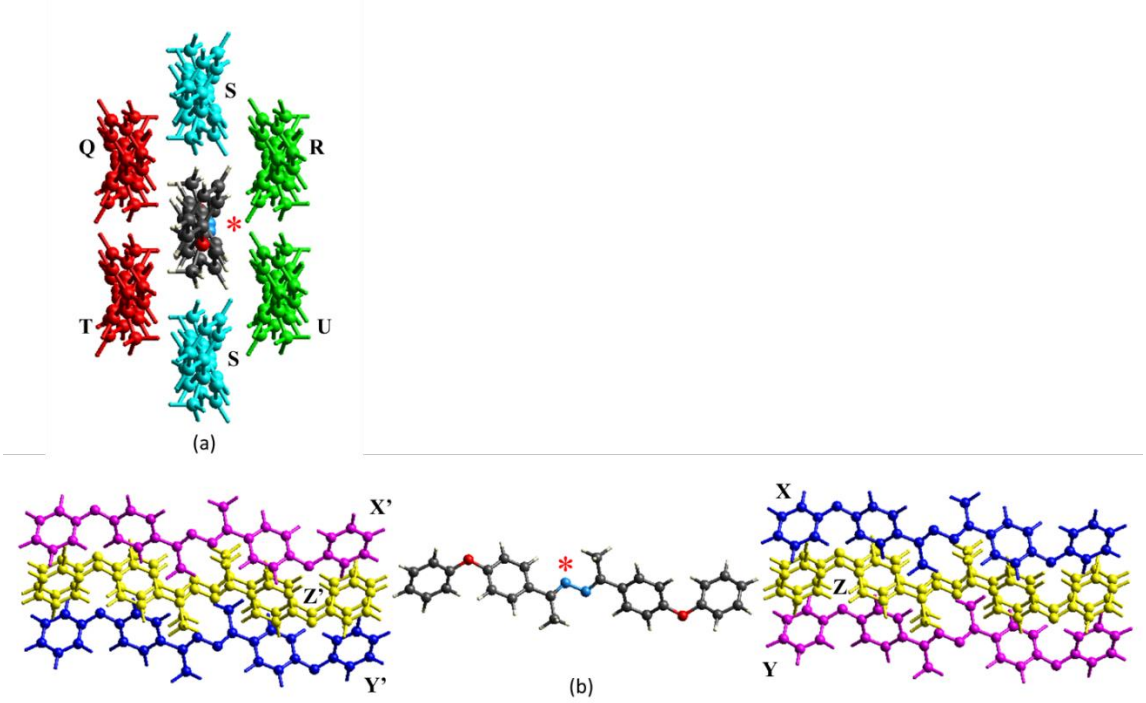

Fig. S10 Color-coded interaction mapping within 3.8 Å of the starred molecule in (PhO, PhO)-azine **5**.

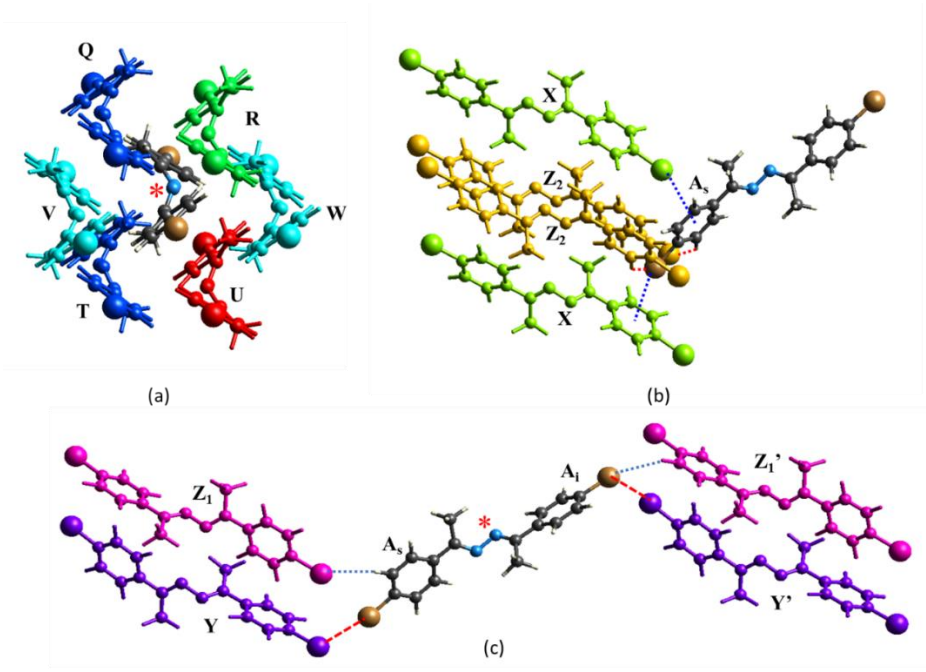

Fig. S11 Color-coded interaction mapping within 3.8 Å of the starred molecule in (Br, Br)-azine **2-Ia**.

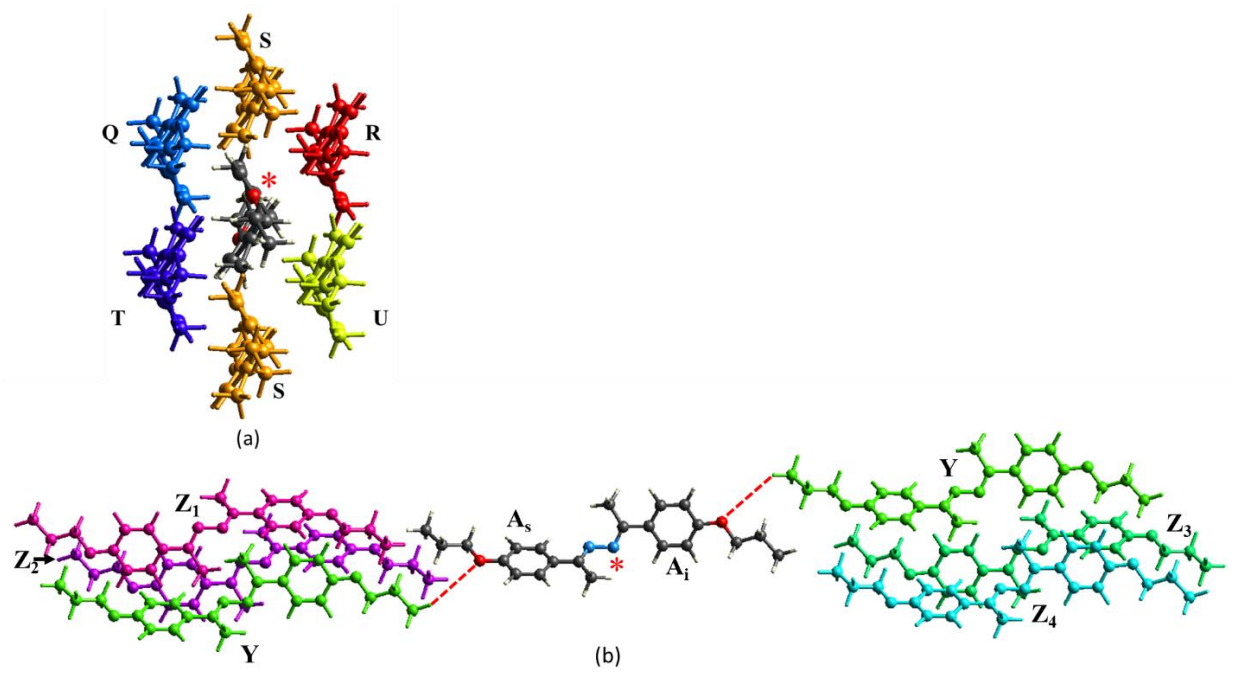

Fig. S12 Color-coded interaction mapping within 3.8 Å of the starred molecule in (PrO, PrO)-azine **10**.

Table S2 Color-coded pairwise interaction energies relative to starred molecule in **5** (PhO), **3** (I), **1-I** (Cl), **2-Ia** (Br) and **10** (PrO)

	N[a]	R[b]	E_{ele}	E_{pol}	E_{dis}	E_{xrep}	E_{tot}
PhO							
Q, T	2	4.90	-21.6	-3.5	-94.4	60.0	**-70.6**
R, U	2	4.89	-20.0	-3.3	-91.7	57.4	**-67.9**
S	2	6.54	-5.8	-0.6	-32.1	13.8	-26.0
Y	2	23.87	1.8	-0.3	-10.9	0	-7.9
X	2	23.57	0	-0.2	-6.7	0	-6.0
Z	4	23.78	0	-0.1	-5.0	0	-4.4
I							
R, U	2	4.66	-15.5	-3.6	-72.3	37.4	**-52.9**
Q, T	2	5.01	-15.7	-4.3	-68.3	38.4	-49.2
S	2	6.37	-7.3	-1.6	-35.6	16.0	-27.5
Y	4	17.55	13.8	-0.2	-8.6	0	6.2
Cl							
U	1	4.89	-10.8	-1.7	-62.2	34.3	**-45.6**
Q, T	2	5.76	-8.6	-1.7	-44.9	24.6	**-34.4**
V, W	2	6.13	-5.7	-1.6	-49.1	26.3	**-33.7**
R	1	8.51	-2.9	-0.5	-16.3	9.5	-11.8
Z_1	2	14.53	-2.6	-0.2	-5.2	0	-7.5
Z_2	2	15.78	2.5	-0.4	-7.5	0	-4.2
X	1	12.16	17.2	-0.8	-23.7	0	-3.0
Y	2	17.72	2.9	0	-3.4	0	0.2
Br							
U	1	4.95	-9.2	-1.6	-60.7	32.8	**-43.5**
Q, T	2	5.85	-11.8	-2.0	-52.1	34.9	**-37.7**
V, W	2	6.55	-5.5	-1.6	-43.4	23.7	**-30.3**
X	2	12.91	-16.4	-0.3	-14.7	0	**-30.3**
R	1	8.56	-3.5	-0.6	-23.8	9.6	**-19.0**
Z_1	2	15.80	-4.0	-0.1	-3.6	0	-7.4
Y	2	15.49	2.3	-0.3	-8.8	0	-5.5
Z_2	2	12.67	4.6	-0.4	-9.8	0	-3.9
PrO							
U	1	5.78	-25.2	-5.3	-89.8	65.8	**-68.1**
T	1	4.90	-25.1	-3.3	-92.7	68.9	**-67.2**
Q	1	4.87	-21.0	-3.0	-84.2	52.3	**-65.4**
R	1	4.65	-10.6	-5.7	-94.1	56.7	**-62.3**
S	2	6.32	-12.1	-1.8	-49.9	33.3	**-37.0**
Y	2	21.13	-2.4	-0.2	-10.7	0	-11.9
Z_1	1	22.35	-2.1	-0.1	-8.7	0	-9.9
Z_2	1	20.55	-1.7	-0.2	-4.9	0	-6.2
Z_3	1	23.74	-0.1	0	-4.2	0	-3.7
Z_4	1	24.55	-0.7	0	-1.7	0	-2.3

[a]**N** = number of neighboring molecules with same E_{tot}.
[b]**R** = distance between molecular centroids expressed in Å.
[c]Electrostatic (E_{ele}), polarization (E_{pol}), dispersion (E_{dis}), exchange-repulsion (E_{xrep}), and total energies (E_{tot}) in kJ/mol.
[d]E_{tot} (CE-B3LYP) = 1.057 E_{ele} + 0.740 E_{pol} + 0.871 E_{dis} + 0.618 E_{xrep} for **5** (PhO), **1-I** (Cl), **2-Ia** (Br) and **10** (PrO).
[e]E_{tot} (CE-HF) = 1.019 E_{ele} + 0.651 E_{pol} + 0.901 E_{dis} + 0.811 E_{xrep} for **3** (I).