Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanism of Intramolecular Halogen Bonding Enhancing Quantum Efficiency of Ultralong Organic Phosphorescence in Aggregated State

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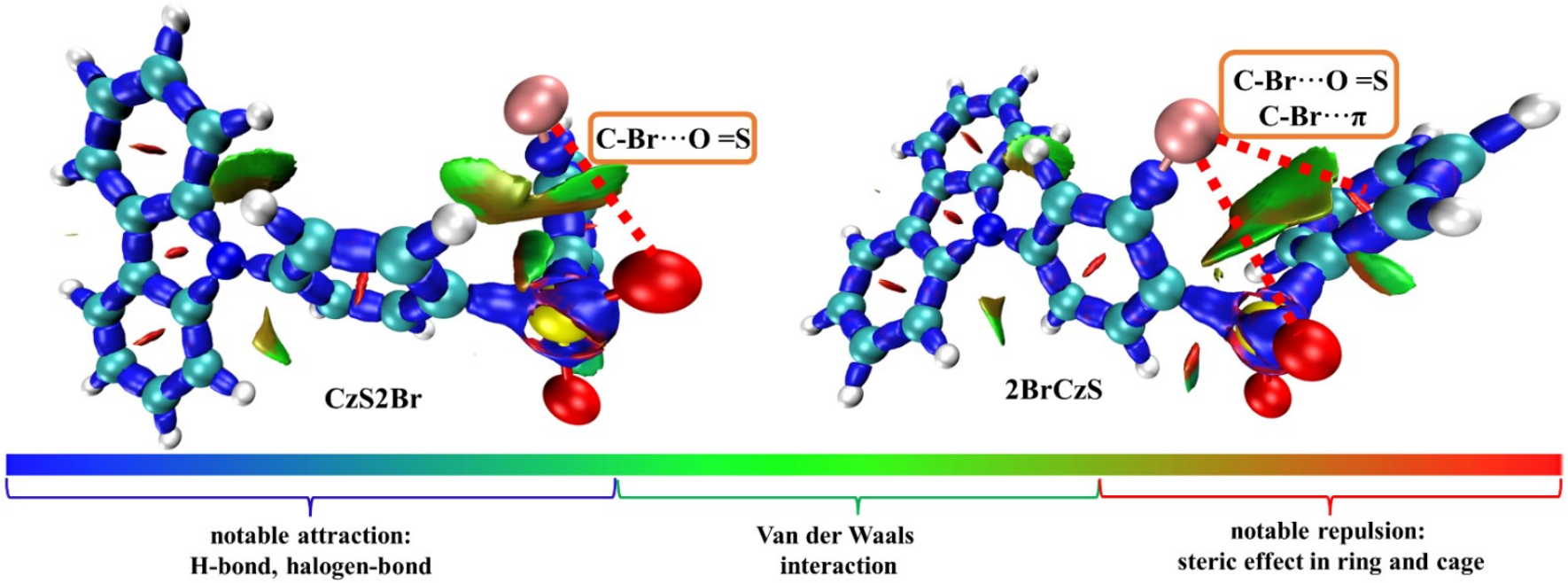

Figure S1 IRI graphical analysis of weak interactions in CzS2Br and 2BrCzS in the aggregated state.

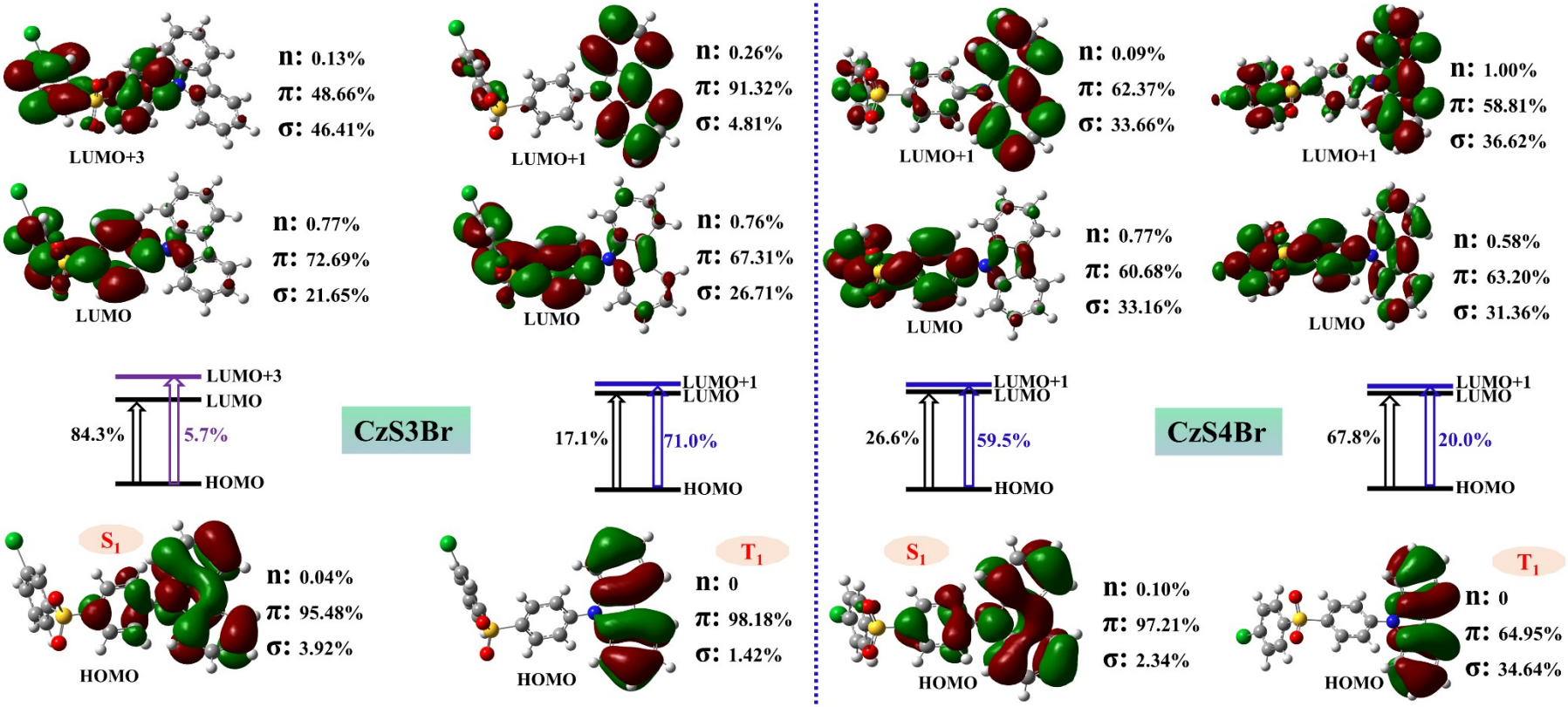

Figure S2 Involved molecular orbitals with energy levels, proportions and charge density distributions for CzS3Br and CzS4Br in the aggregated state.

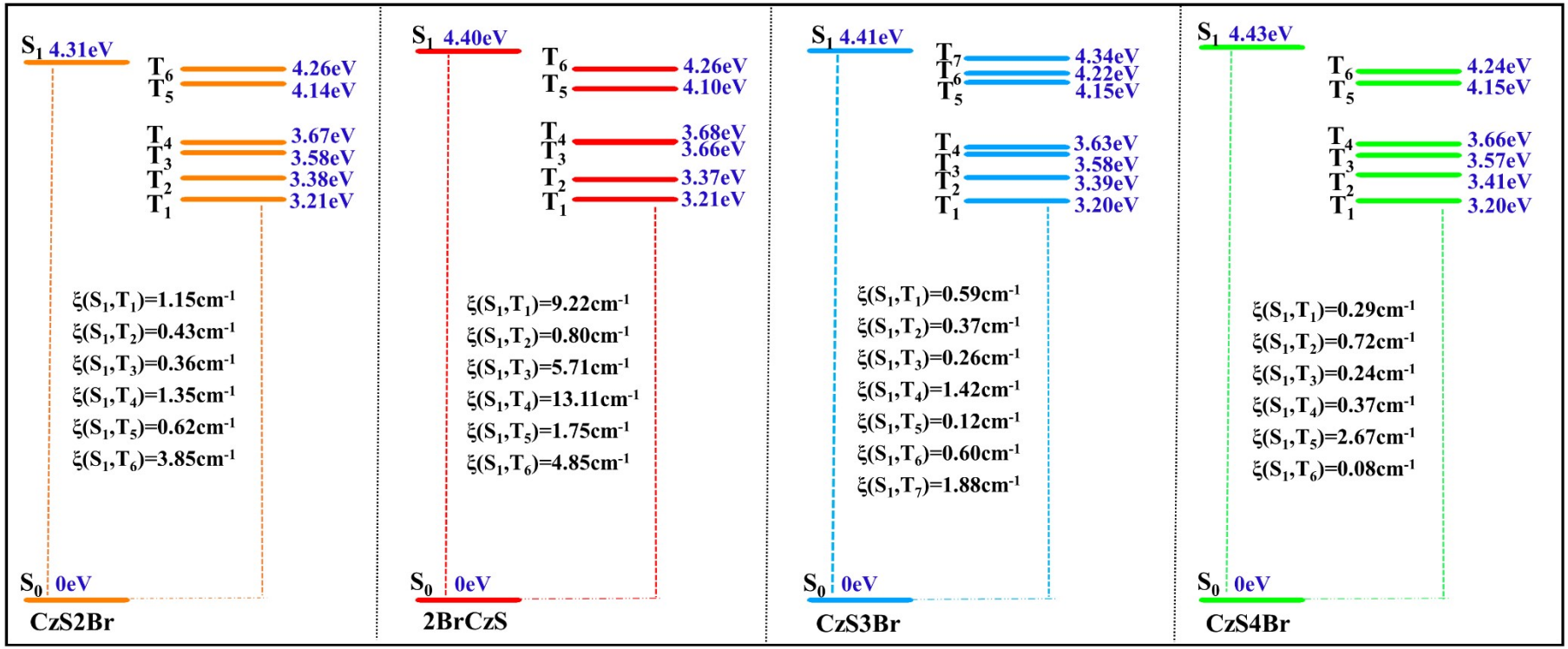

Figure S3 Excitation energy levels and spin-orbit coupling (SOC) matrix elements (ξ) between S_1 and T_n for CzS2Br, 2BrCzS, CzS3Br and CzS4Br in the aggregated state.

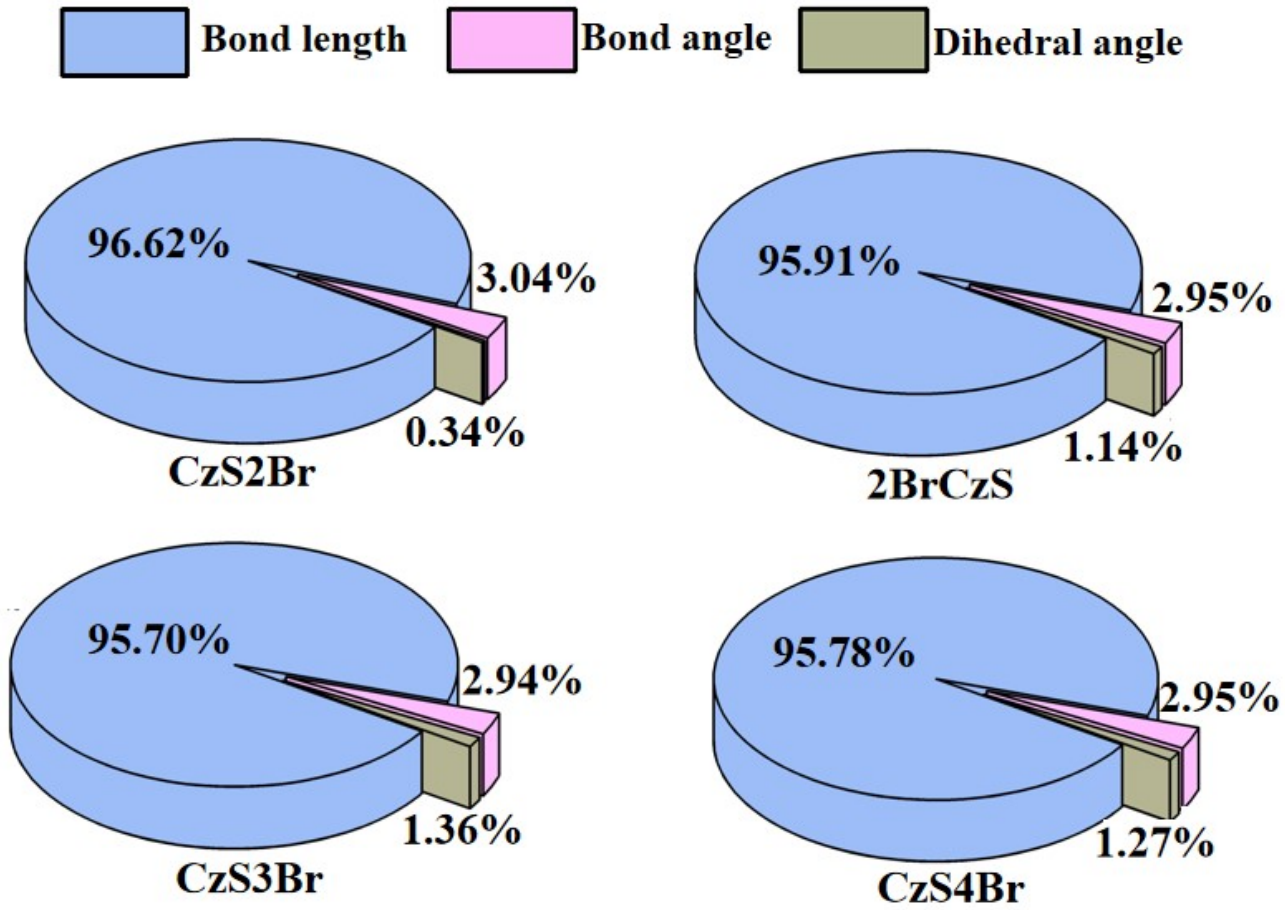

Figure S4 Contribution ratios to the reorganization energies from the bond lengths (red), bond angles (green) and dihedral angles (blue) for CzS2Br, 2BrCzS, CzS3Br and CzS4Br in the aggregated state.

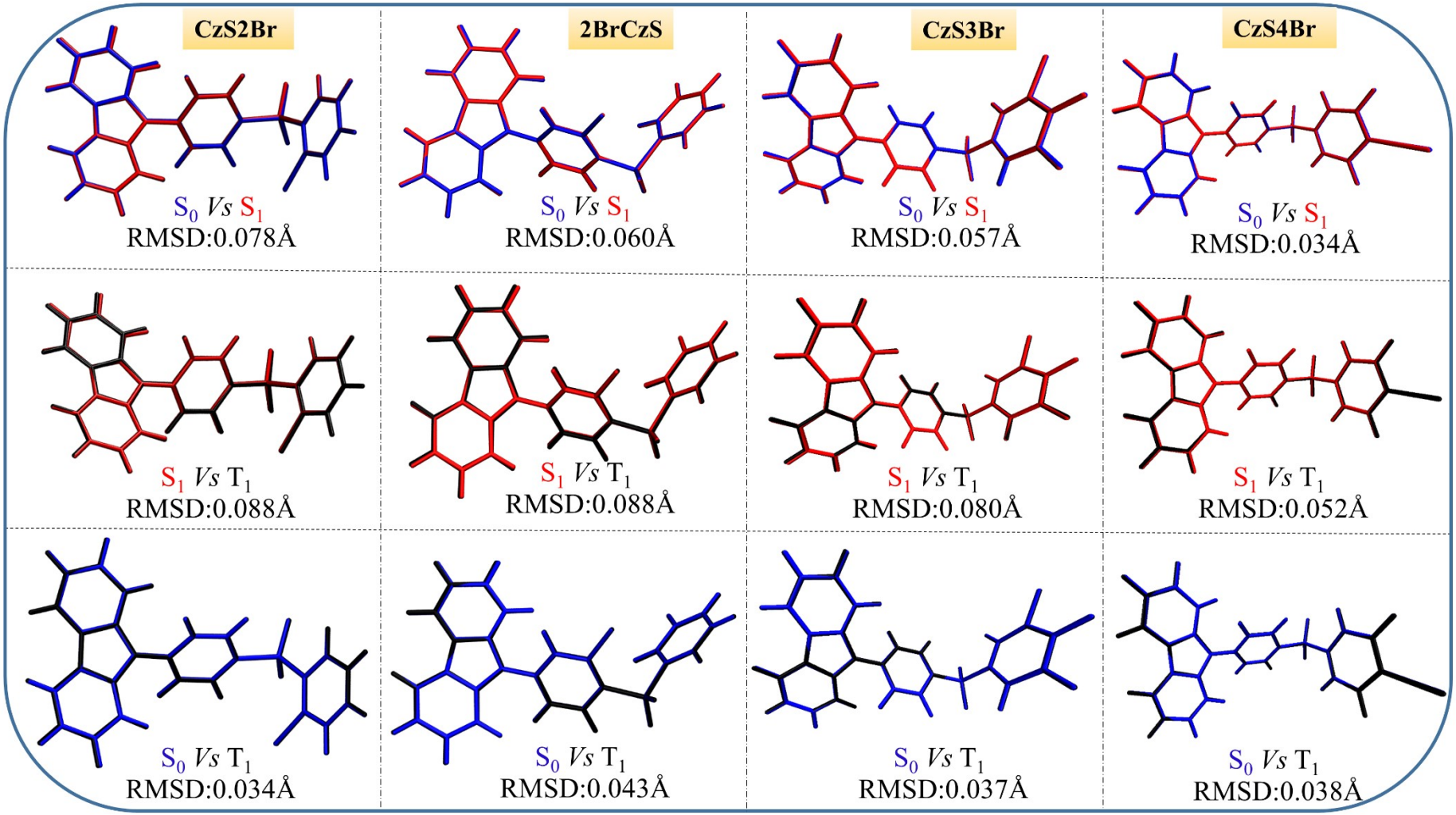

Figure S5 RMSD of S_0 (blue), S_1 (red) and T_1 (black) for CzS2Br, 2BrCzS, CzS3Br and CzS4Br in the aggregated state.

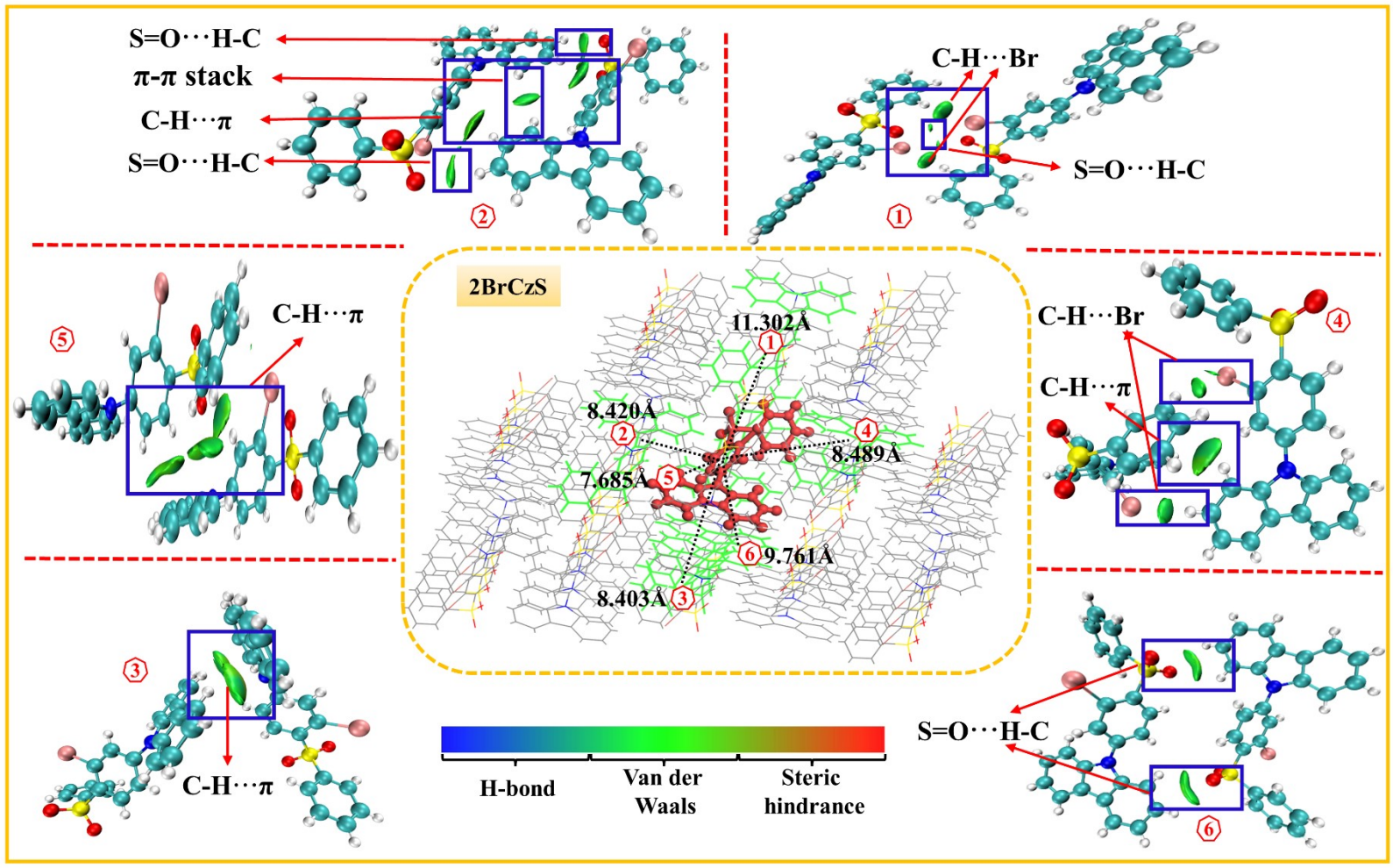

Figure S6 Intermolecular interactions for selected dimers of 2BrCzS described by IGM method in the aggregated state.

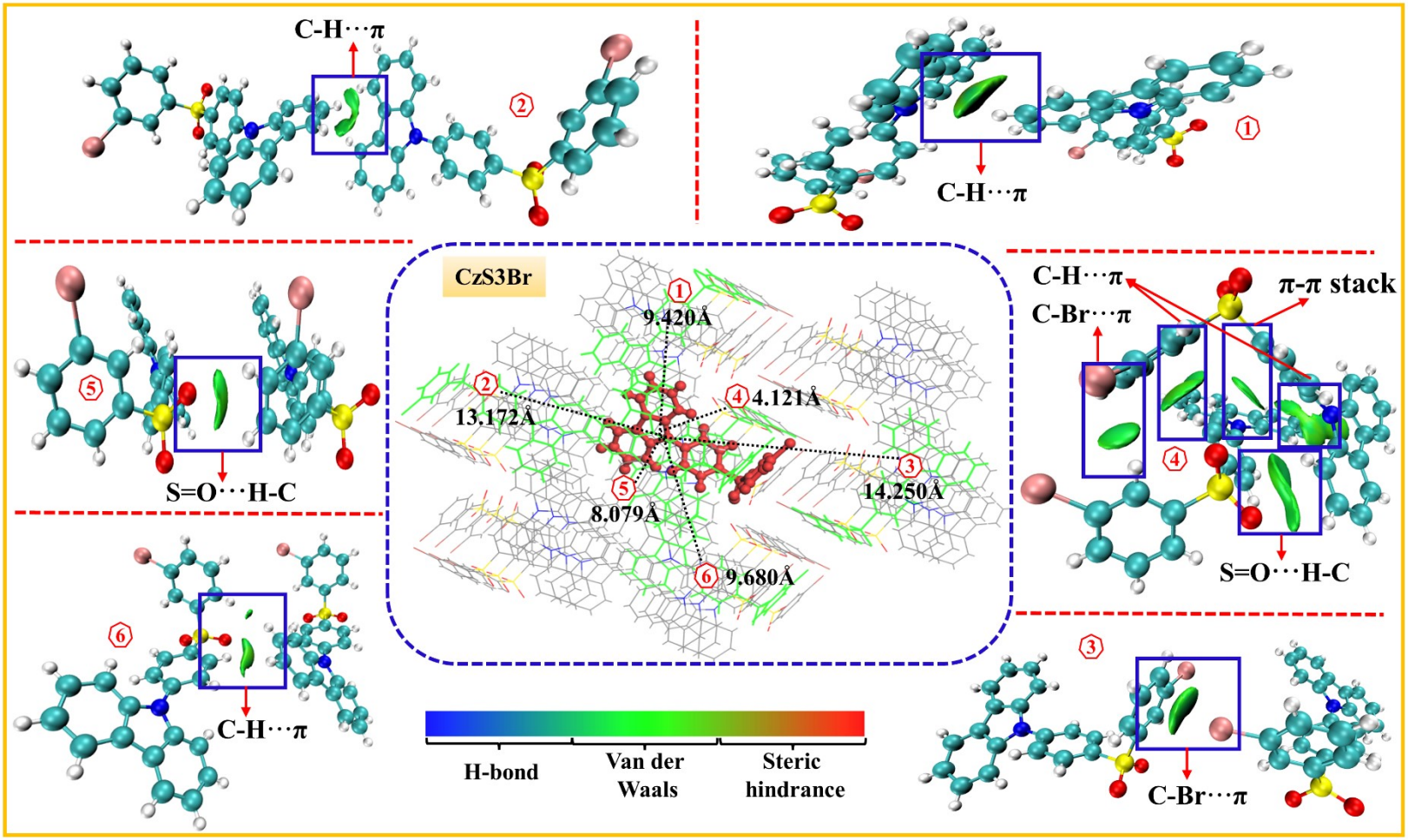

Figure S7 Intermolecular interactions for selected dimers of CzS3Br described by IGM method in the aggregated state.

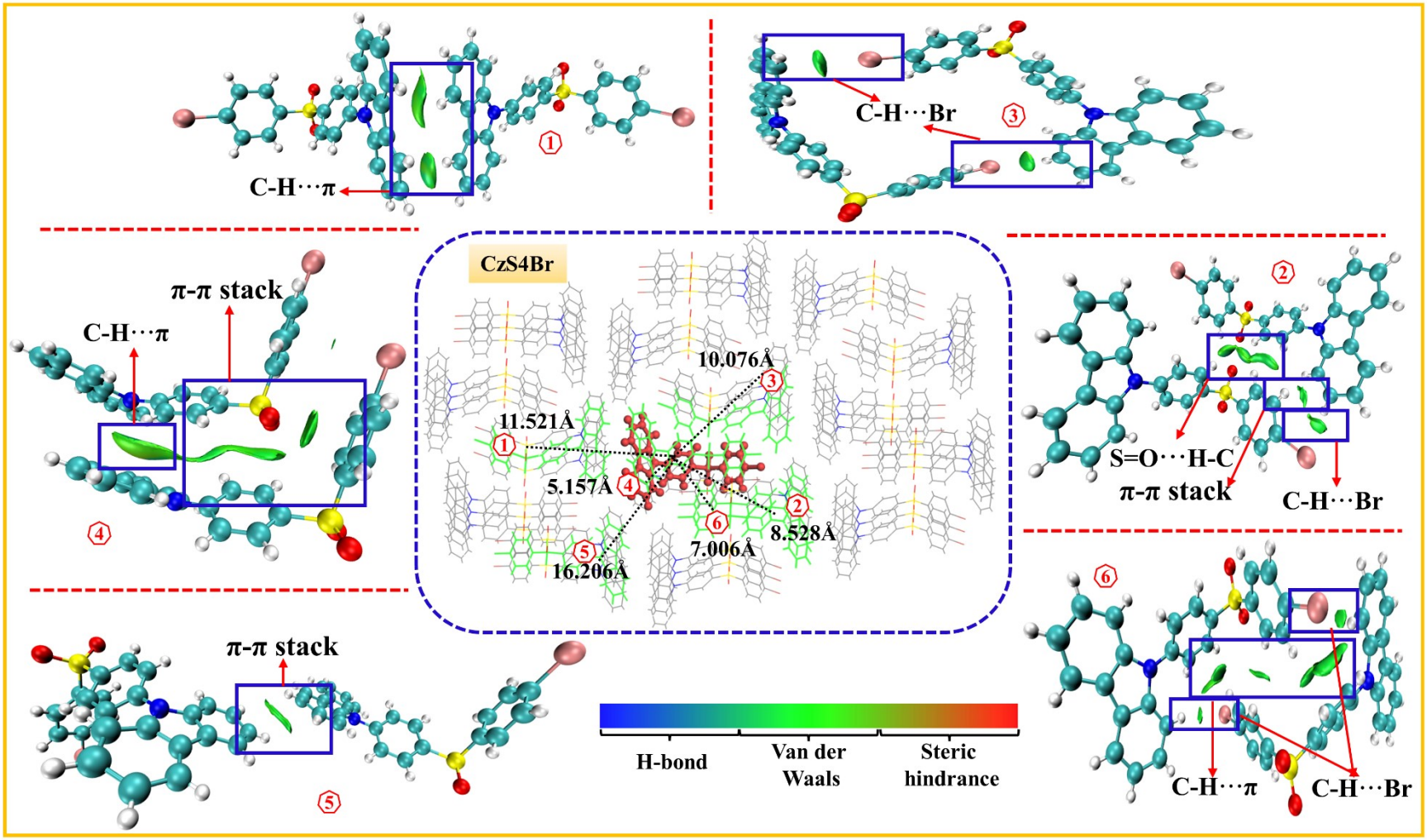

Figure S8 Intermolecular interactions for selected dimers of CzS4Br described by IGM method in the aggregated state.

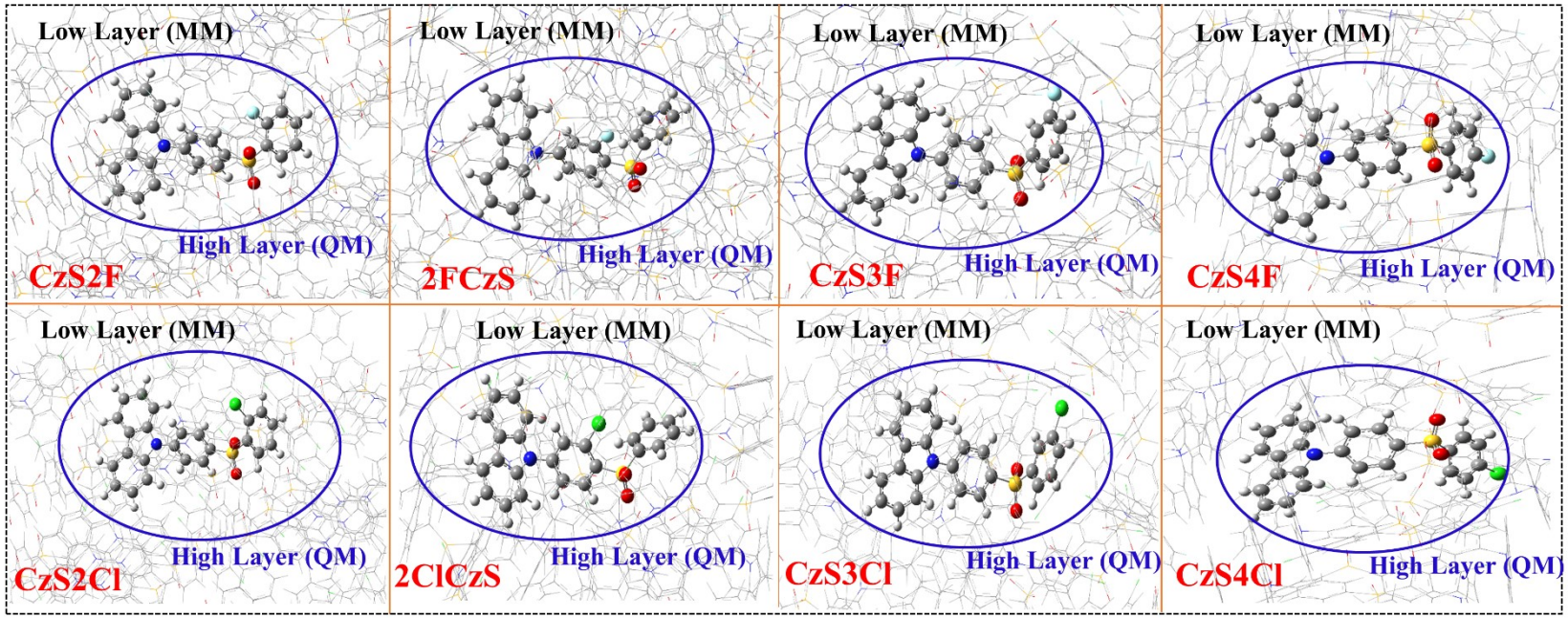

Figure S9 ONIOM model for simulating the aggregated states of CzS2F, 2FCzS, CzS3F, CzS4F, CzS2Cl, 2ClCzS, CzS3Cl and CzS4Cl: the central molecule is treated as a high layer and the surrounding molecules are chosen a low layer.

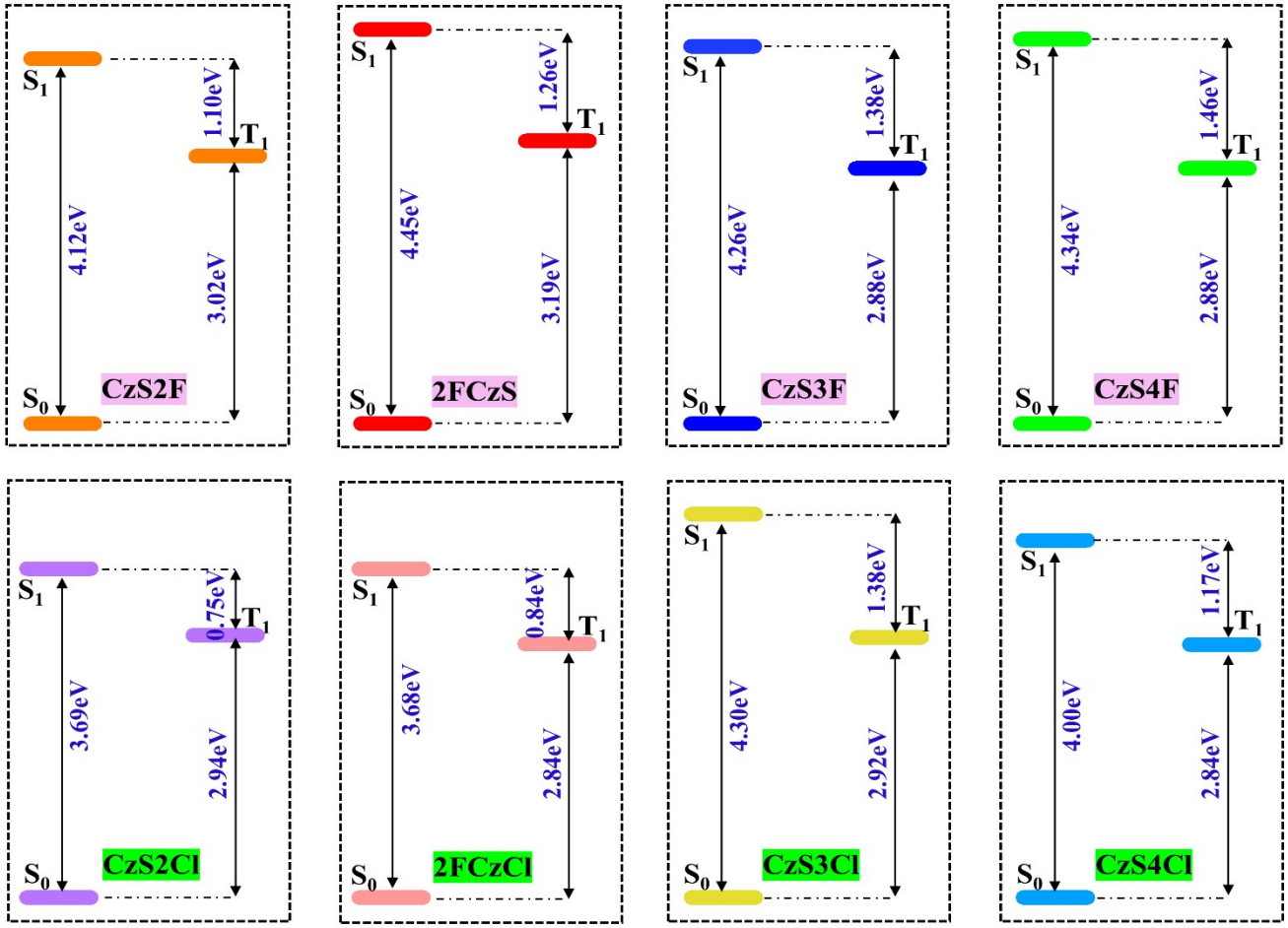

Figure S10 Excitation energy levels and energy difference between different states for CzS2F, 2FCzS, CzS3F, CzS4F, CzS2Cl, 2ClCzS, CzS3Cl and CzS4Cl in the aggregated state.

Table S1 Calculated SOC constants (cm^{-1}) between selected states for CzS2Br, 2BrCzS, CzS3Br and CzS4Br in the gas phase and liquid phase.

	Gas		Liquid	
	$\langle S_1 \vert H_{S0} \vert T_1 \rangle$	$\langle T_1 \vert H_{S0} \vert S_0 \rangle$	$\langle S_1 \vert H_{S0} \vert T_1 \rangle$	$\langle T_1 \vert H_{S0} \vert S_0 \rangle$
CzS2Br	0.84	0.37	1.53	0.37
2BrCzS	1.56	0.38	9.57	0.38
CzS3Br	0.26	0.34	0.56	0.34
CzS4Br	0.06	0.33	0.58	0.32

Table S2 Intermolecular interaction energy (kJ/mol) analysis for selected dimers extracted from the aggregates of 2BrCzS.

Dimer	Electrostatic	Repulsion	Dispersion	Total
1	-1.56	15.90	-28.33	-13.99
2	-9.59	18.47	-54.67	-45.79
3	-5.30	16.50	-43.06	-31.86
4	-1.94	14.29	-37.21	-24.85
5	-4.96	25.00	-70.02	-49.98
6	-15.39	8.82	-24.29	-30.86

Table S3 Intermolecular interaction energy (kJ/mol) analysis for selected dimers extracted from the aggregates of CzS3Br.

Dimer	Electrostatic	Repulsion	Dispersion	Total
1	0.56	17.77	-36.01	-17.69
2	-0.26	3.75	-13.13	-9.64
3	1.09	17.28	-22.44	-4.07
4	-13.64	88.61	-139.32	-64.35
5	-8.94	3.20	-12.59	-18.34
6	-0.67	8.72	-20.82	-12.76

Table S4 Intermolecular interaction energy (kJ/mol) analysis for selected dimers extracted from the aggregates of CzS4Br.

Dimer	Electrostatic	Repulsion	Dispersion	Total
1	-2.77	9.10	-27.33	-21.00
2	2.87	18.89	-46.42	-24.67
3	-1.48	15.39	-25.91	-12.00
4	-16.62	41.28	-113.00	-88.34
5	0.20	1.63	-6.51	-4.68
6	0.23	19.87	-54.6	-34.49