Supplementary Information

Theoretical exploration of bromine substitution effect and hydrostatic pressure responsive mechanism for room temperature phosphorescence

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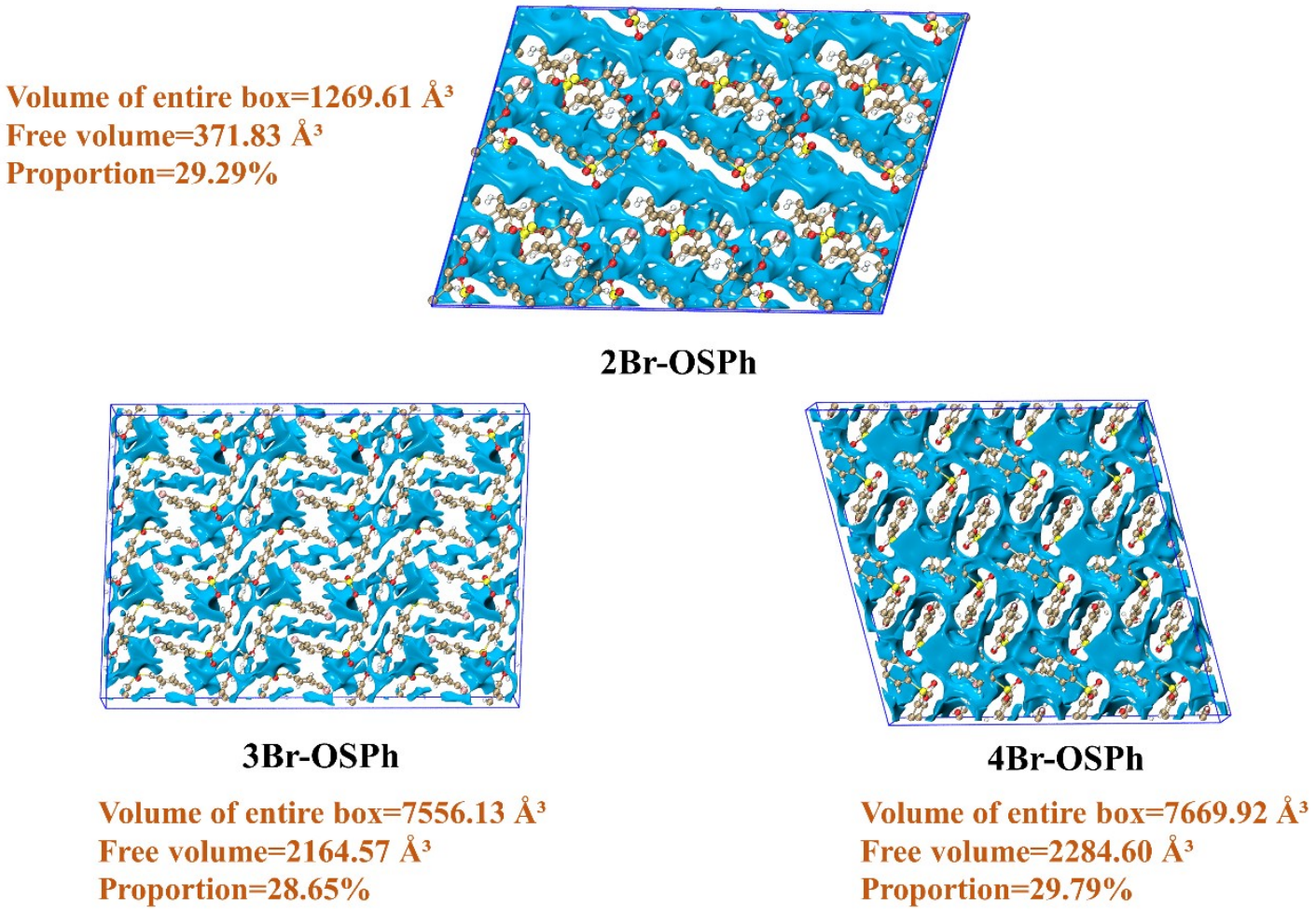

Figure S1. The free volume for 2Br-OSPh, 3Br-OSPh and 4Br-OSPh.

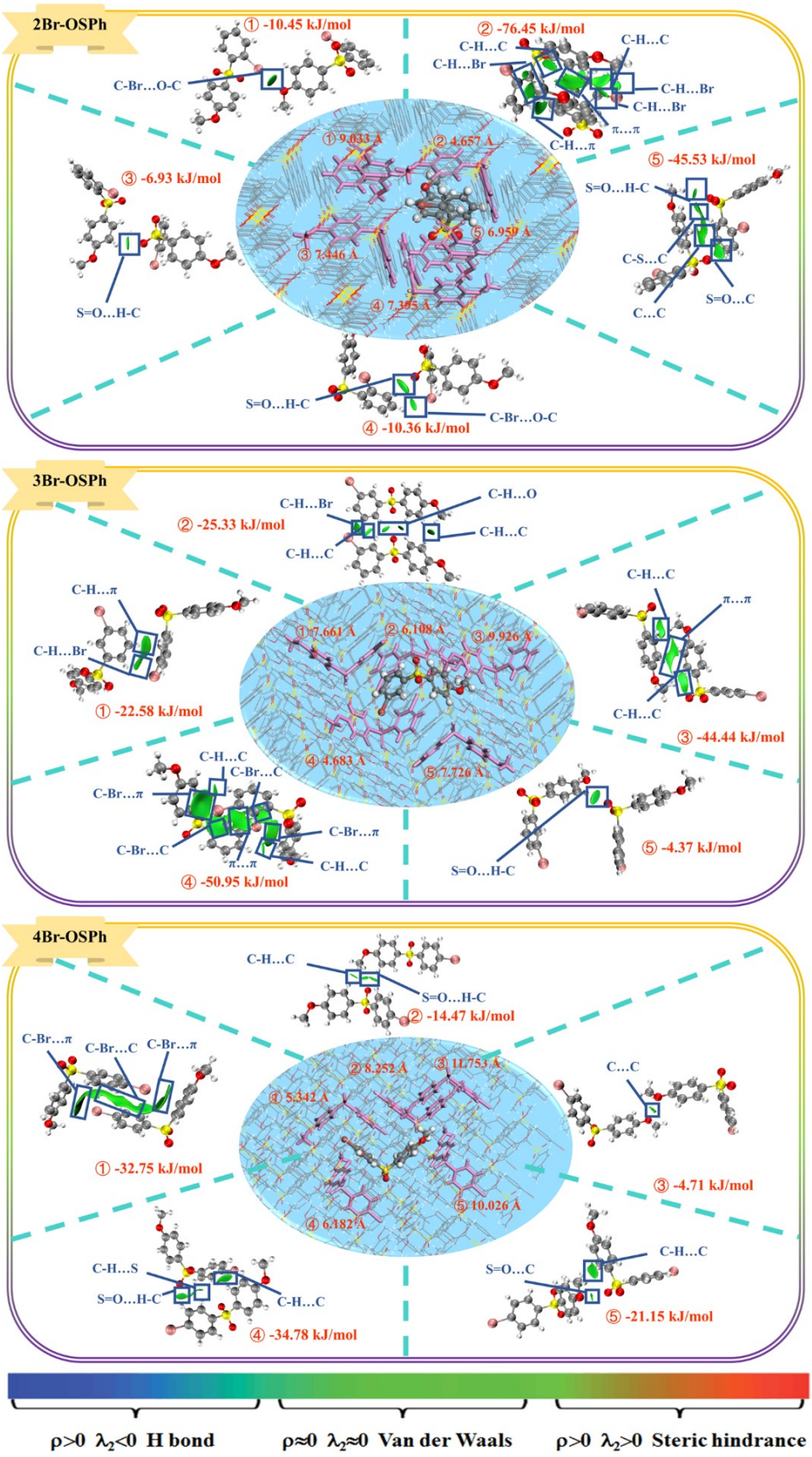

Figure S2. Intermolecular interactions for selected dimers of 2Br-OSPh, 3Br-OSPh and 4Br-OSPh described by IGMH method.

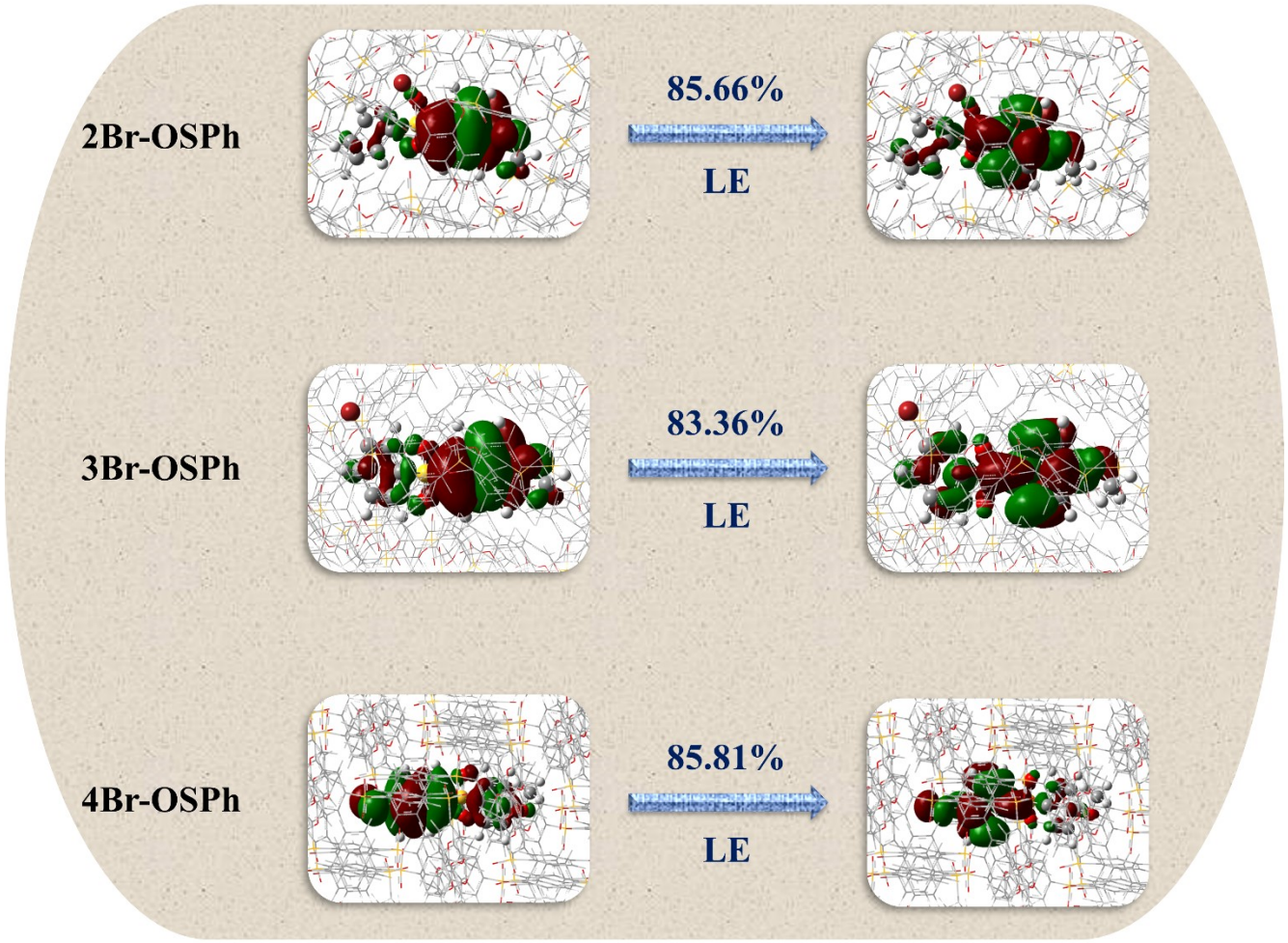

Figure S3. Natural transition orbitals (NTOs) of the T_1 state for 2Br-OSPh, 3Br-OSPh and 4Br-OSPh in the crystal.

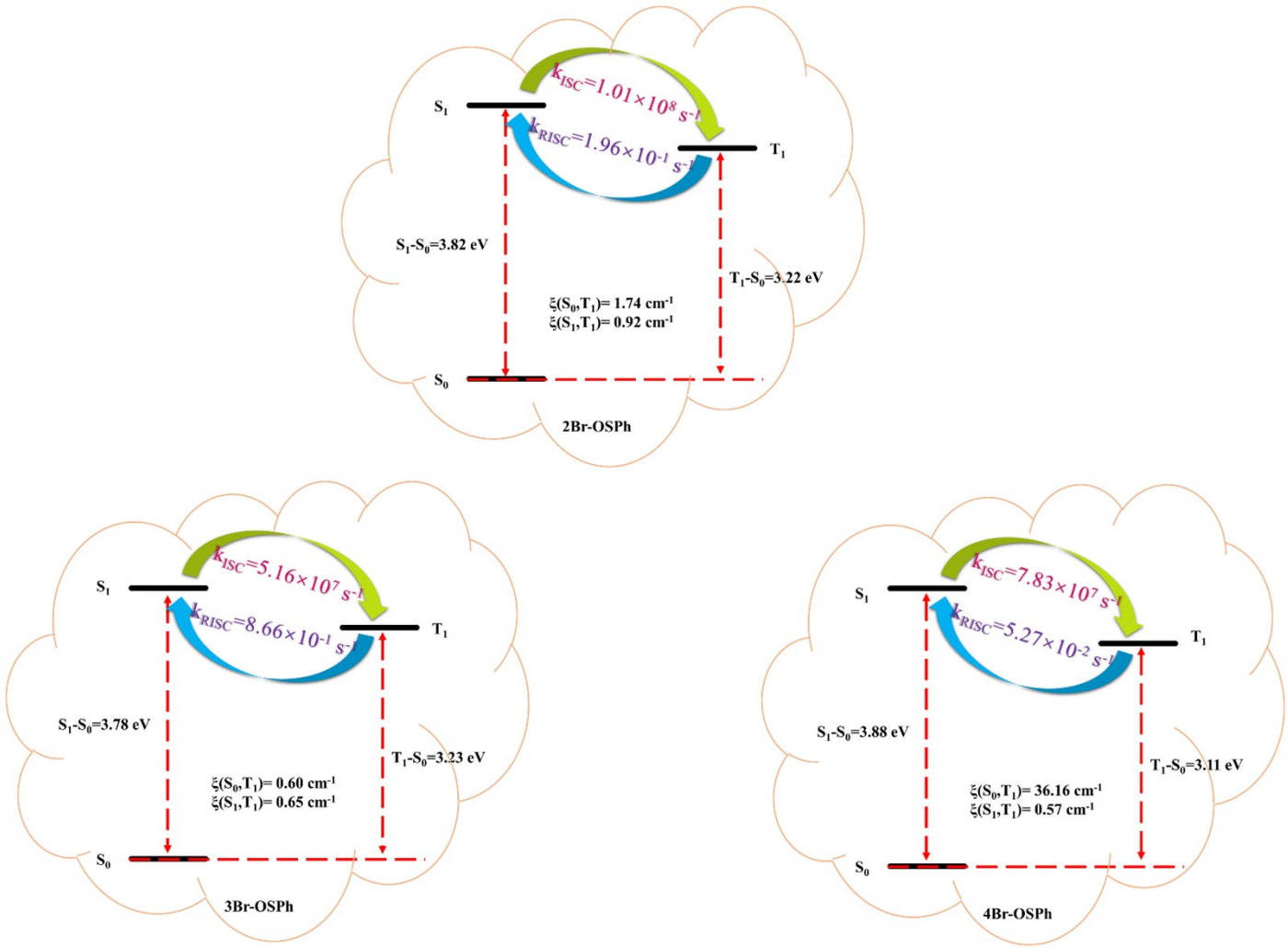

Figure S4. Adiabatic excitation energy diagrams for 2Br-OSPh, 3Br-OSPh and 4Br-OSPh in the crystal. Corresponding SOC constants are also listed.

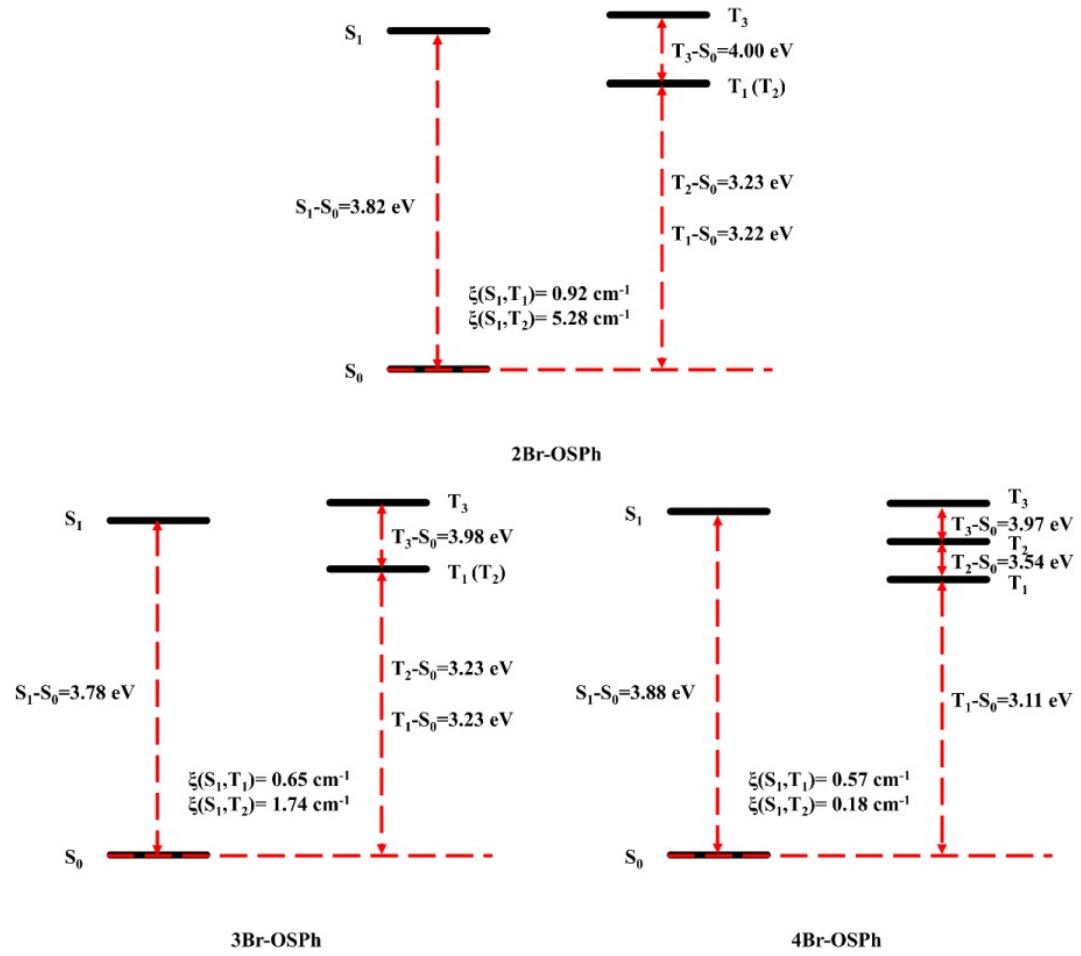

Figure S5. Adiabatic excitation energy diagrams for 2Br-OSPh, 3Br-OSPh and 4Br-OSPh in the crystal. Corresponding SOC constants are also listed.

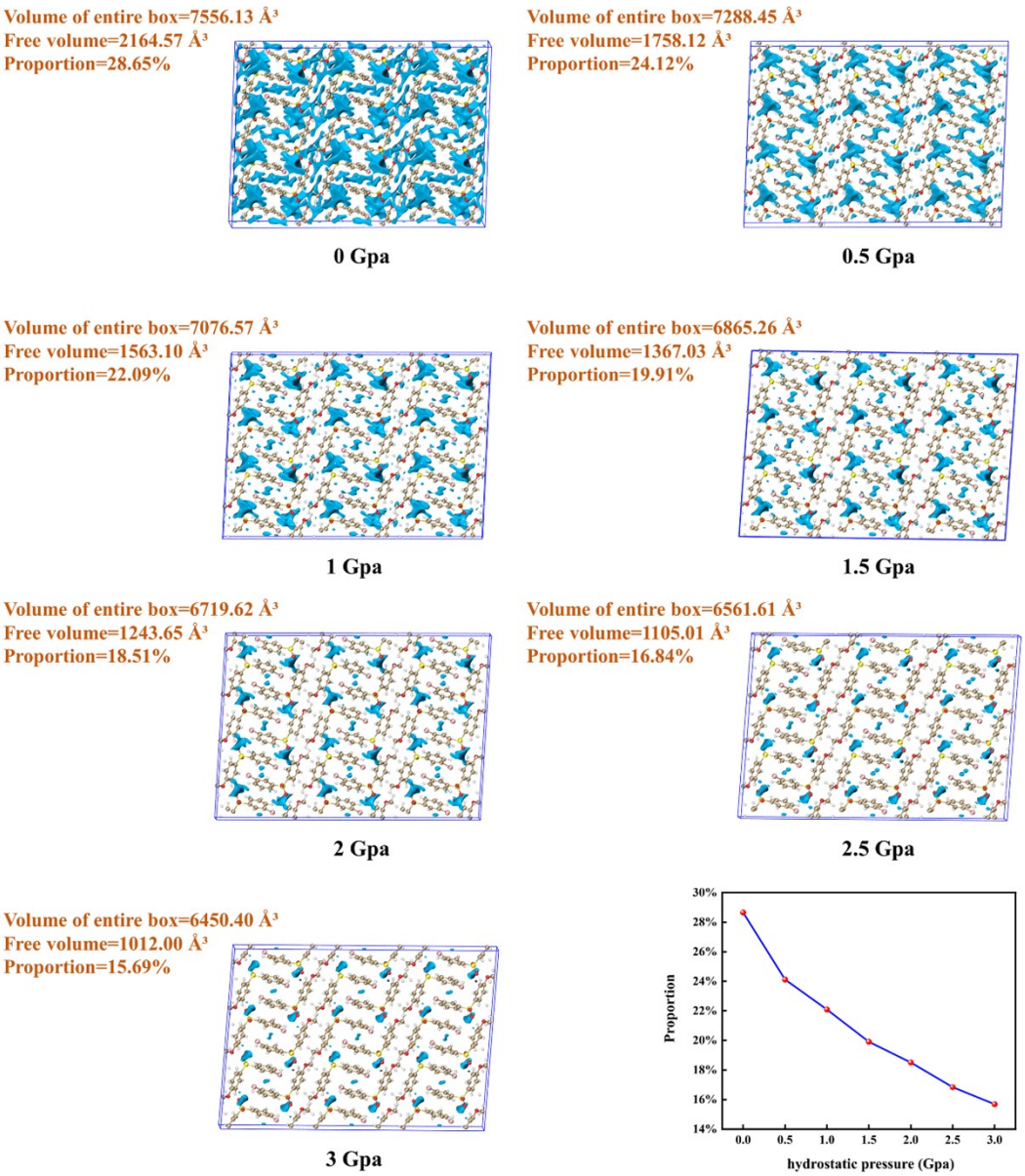

Figure S6. The free volume for 3Br-OSPh at different pressures.

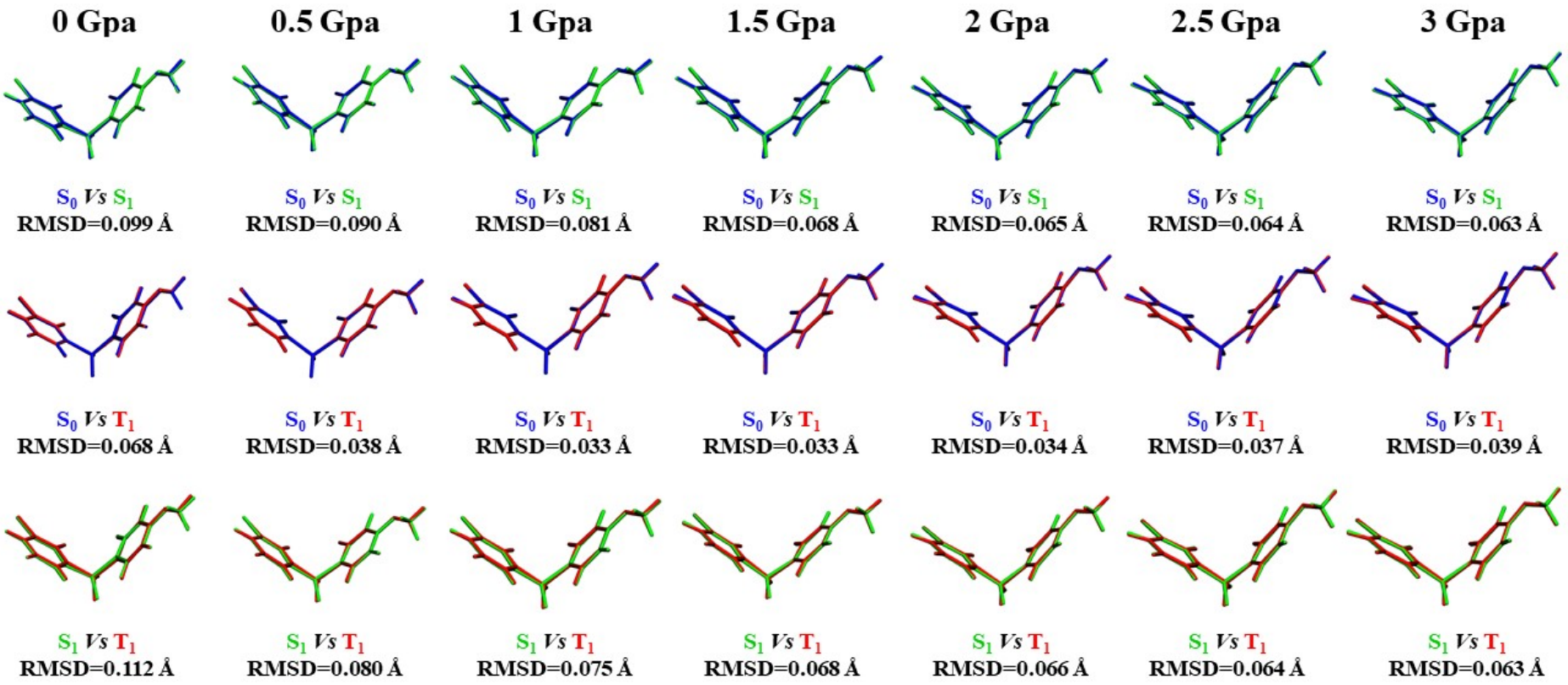

Figure S7. Geometry comparisons and RMSD values among S_0 (blue), S_1 (green) and T_1 (red) for 3Br-OSPh at different pressures.

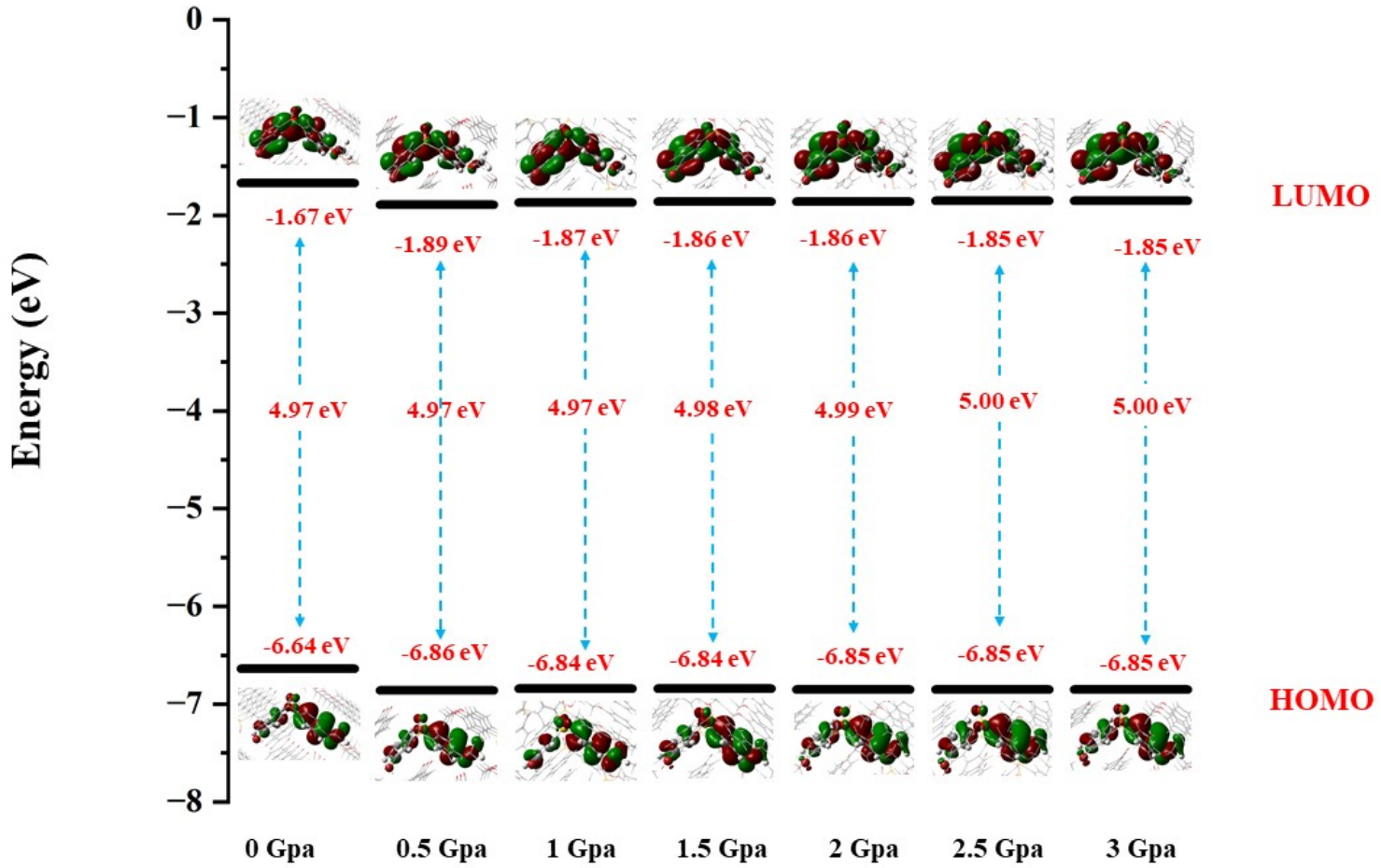

Figure S8. Calculated frontier orbital distributions and energies for 3Br-OSPh at different pressures.

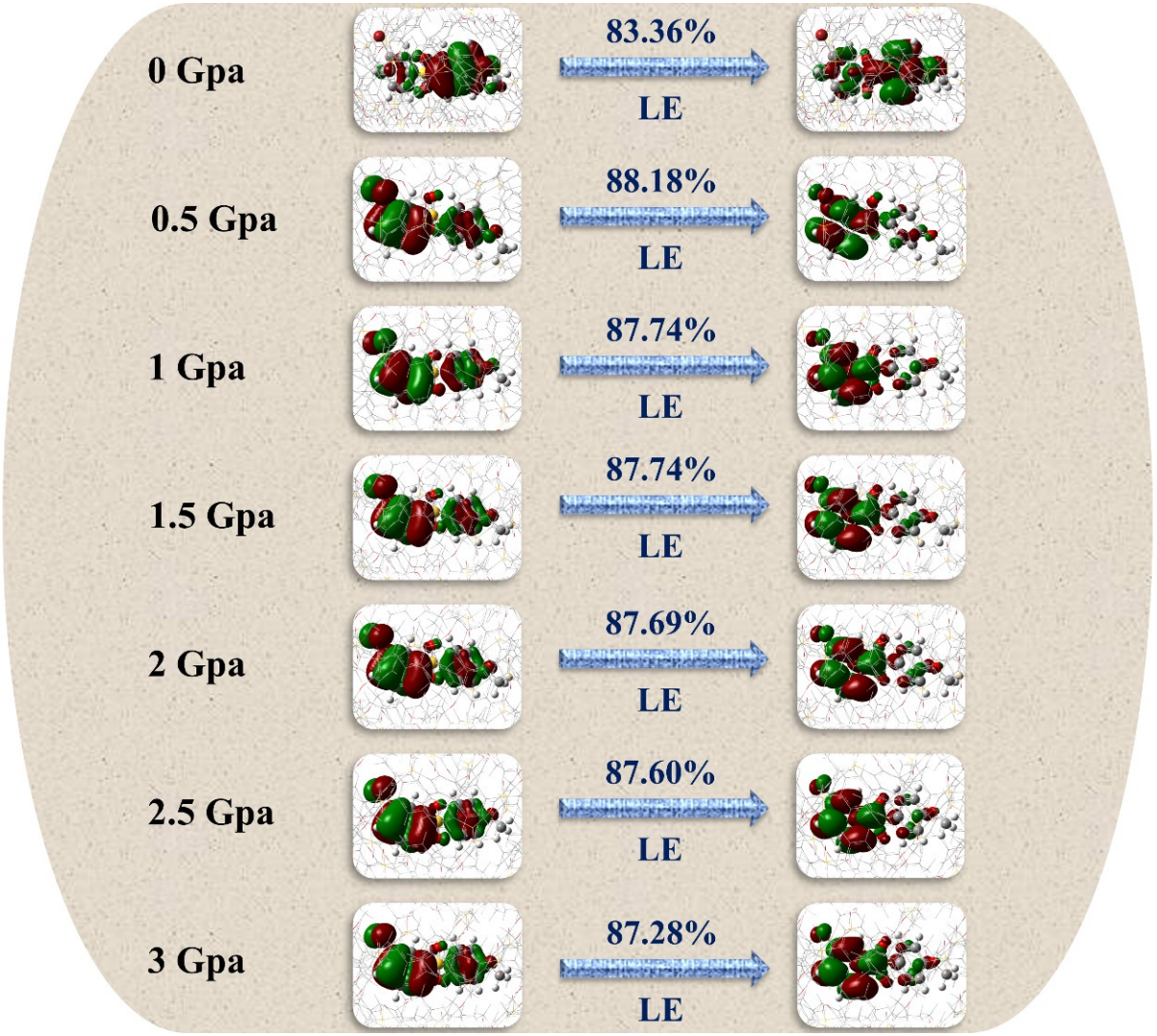

Figure S9. Natural transition orbitals (NTOs) of the T_1 state for 3Br-OSPh at different pressures.

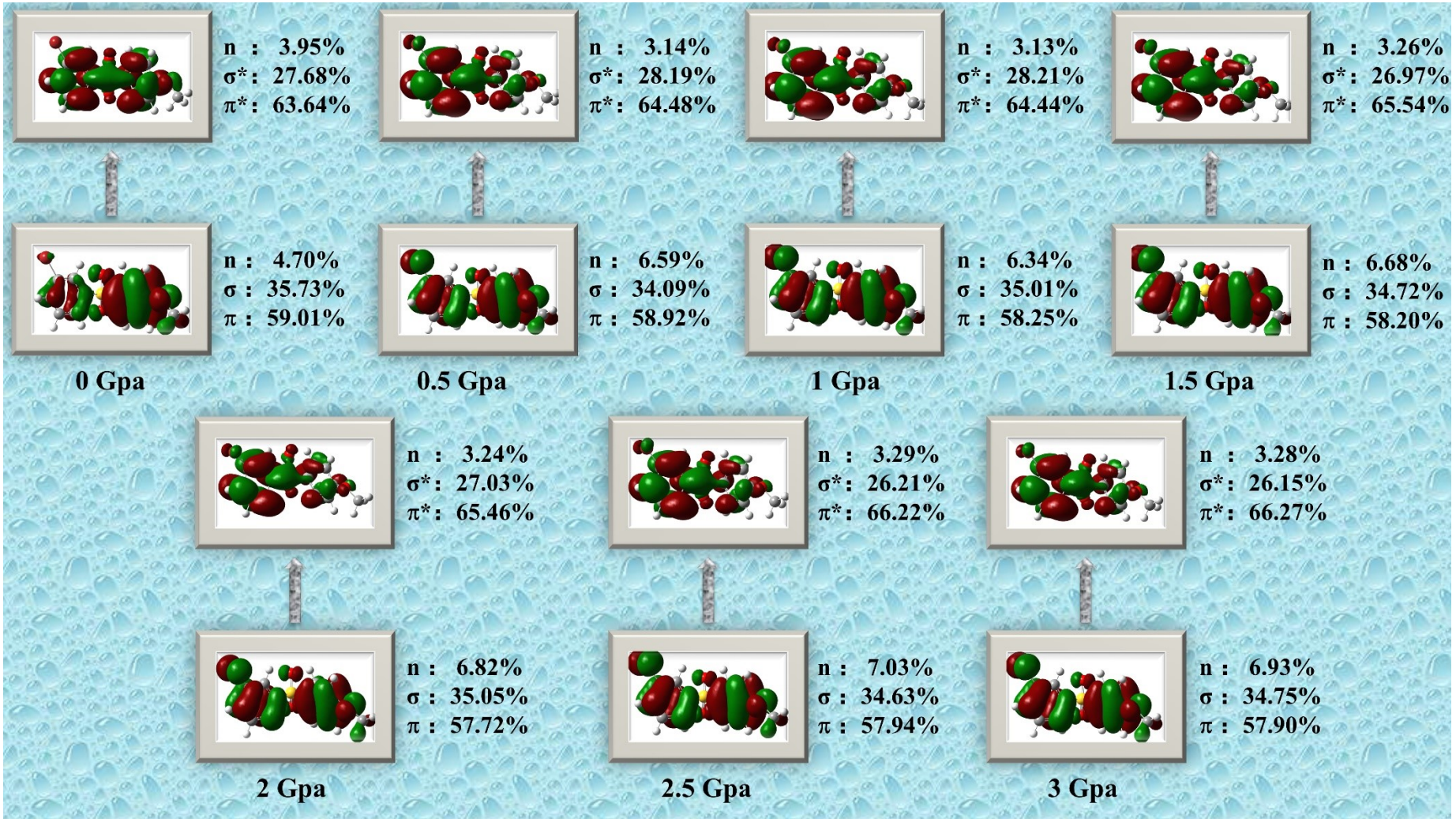

Figure S10. Composition (%) of atoms in frontier MOs for 3Br-OSPh at different pressures calculated by NAO method in the crystal.

Table S1. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 2Br-OSPh.

		Electrostatic	Repulsion	Dispersion	Total
2Br-OSPh	Dimer-1	-1.71	3.62	-12.37	-10.45 kJ/mol
	Dimer-2	-2.00	45.40	-119.86	-76.45 kJ/mol
	Dimer-3	4.44	6.06	-17.42	-6.93 kJ/mol
	Dimer-4	-2.43	14.37	-22.30	-10.36 kJ/mol
	Dimer-5	-6.63	20.61	-59.50	-45.53 kJ/mol

Table S2. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh.

		Electrostatic	Repulsion	Dispersion	Total
3Br-OSPh	Dimer-1	0.15	18.01	-40.74	-22.58 kJ/mol
	Dimer-2	2.49	16.53	-44.34	-25.33 kJ/mol
	Dimer-3	-6.55	22.51	-60.40	-44.44 kJ/mol
	Dimer-4	-0.24	41.17	-91.87	-50.95 kJ/mol
	Dimer-5	1.71	8.30	-14.38	-4.37 kJ/mol

Table S3. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 4Br-OSPh.

		Electrostatic	Repulsion	Dispersion	Total
4Br-OSPh	Dimer-1	0.49	45.63	-78.86	-32.75 kJ/mol
	Dimer-2	-2.46	11.42	-23.43	-14.47 kJ/mol
	Dimer-3	5.76	4.52	-14.98	-4.71kJ/mol
	Dimer-4	-7.06	19.58	-47.30	-34.78 kJ/mol
	Dimer-5	1.66	11.62	-34.42	-21.15 kJ/mol

Table S4. Calculated adiabatic singlet and triplet energies and SOC constants (cm^{-1}) among S_0, S_1 and T_1 for all studied molecules in the crystal and gas phase.

		Gas phase			**Crystal**		
		2Br-OSPh	3Br-OSPh	4Br-OSPh	2Br-OSPh	3Br-OSPh	4Br-OSPh
E (eV)	S_1	3.80	3.75	3.76	3.82	3.78	3.88
	T_1	3.46	3.38	3.36	3.22	3.23	3.11
$\langle S_0 \vert \hat{H}_{so} \vert T_1 \rangle$		2.11	0.23	0.83	1.74	0.60	36.16
$\langle S_1 \vert \hat{H}_{so} \vert T_1 \rangle$		1.07	0.31	0.38	0.92	0.65	0.57

Table S5. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 0.5 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
0.5 Gpa	Dimer-1	0.46	24.75	-45.76	-20.54 kJ/mol
	Dimer-2	1.62	30.05	-53.62	-21.93 kJ/mol
	Dimer-3	-10.52	32.04	-66.92	-45.40 kJ/mol
	Dimer-4	-1.35	49.69	-98.56	-50.22 kJ/mol
	Dimer-5	-0.66	27.84	-19.70	7.47 kJ/mol

Table S6. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 1 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
1 Gpa	Dimer-1	0.46	28.07	-48.44	-19.91 kJ/mol
	Dimer-2	1.81	37.13	-58.67	-19.73 kJ/mol
	Dimer-3	-10.84	40.66	-73.59	-43.77 kJ/mol
	Dimer-4	-1.33	59.52	-106.55	-48.36 kJ/mol
	Dimer-5	-0.58	34.55	-21.25	12.72 kJ/mol

Table S7. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 1.5 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
1.5 Gpa	Dimer-1	0.41	36.17	-54.78	-18.20 kJ/mol
	Dimer-2	1.92	40.56	-60.79	-18.31 kJ/mol
	Dimer-3	-10.77	43.38	-75.41	-42.80 kJ/mol
	Dimer-4	-1.33	70.34	-115.12	-46.12 kJ/mol
	Dimer-5	-0.57	36.10	-23.08	12.45 kJ/mol

Table S8. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 2 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
2 Gpa	Dimer-1	0.44	39.05	-56.97	-17.48 kJ/mol
	Dimer-2	2.05	48.31	-65.30	-14.94 kJ/mol
	Dimer-3	-10.94	48.18	-78.41	-41.17 kJ/mol
	Dimer-4	-1.32	77.94	-120.72	-44.10 kJ/mol
	Dimer-5	-0.49	41.86	-24.60	16.77 kJ/mol

Table S9. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 2.5 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
2.5 Gpa	Dimer-1	0.43	43.25	-60.61	-16.93 kJ/mol
	Dimer-2	2.25	55.08	-68.30	-10.97 kJ/mol
	Dimer-3	-10.88	54.75	-82.39	-38.52 kJ/mol
	Dimer-4	-1.33	90.60	-129.71	-40.44 kJ/mol
	Dimer-5	-0.56	44.86	-26.46	17.84 kJ/mol

Table S10. Intermolecular interaction energy analysis for selected dimers extracted from the crystal of 3Br-OSPh at 3 Gpa.

		Electrostatic	Repulsion	Dispersion	Total
3 Gpa	Dimer-1	0.41	47.12	-63.25	-15.71 kJ/mol
	Dimer-2	2.31	62.16	-71.60	-7.13 kJ/mol
	Dimer-3	-10.98	59.44	-85.08	-36.61 kJ/mol
	Dimer-4	-1.35	100.87	-136.07	-36.55 kJ/mol
	Dimer-5	-0.53	49.30	-27.74	21.03 kJ/mol