Extended π conjugation in 2*H*-1,4,2-diazaphosphole complexes

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Supplementary material
Details on TD-DFT calculations

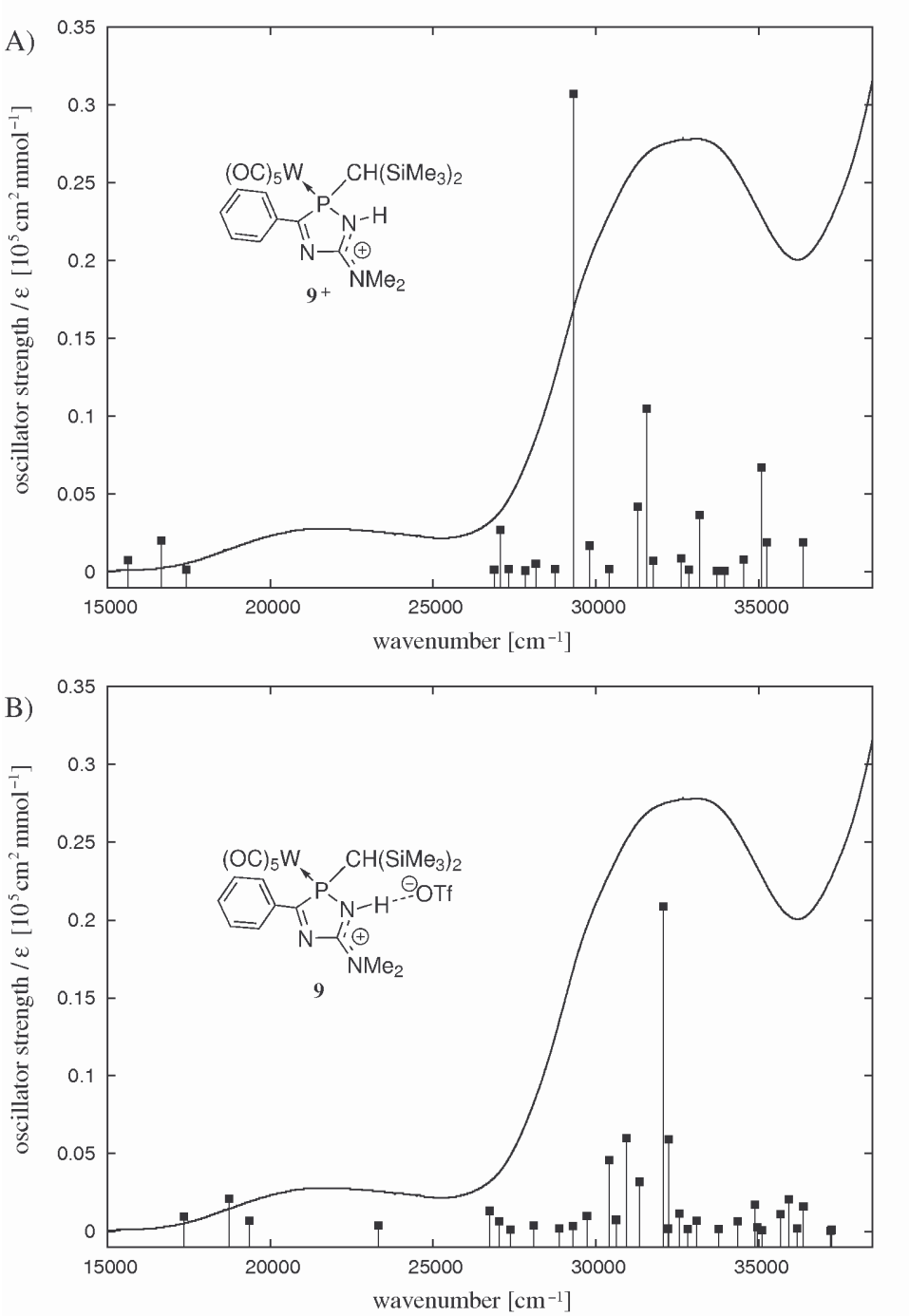

Fig. S.1 Comparison of the experimental UV/Vis spectrum of **9** (CH_2Cl_2; solid line) with calculated vertical singlet excitations for cation $\mathbf{9^+}$ (A) and contact ion pair **9** (B) (TD-B3LYP/SV(P)/ECP-60-MWB(W) // RI-BLYP/SV(P)/ECP-60-MWB(W)).

Table S.1 Selected vertical singlet excitations calculated for the cation **9**$^+$ (only the major orbital contributions given).

No.	ν [cm^{-1}]	Oscillator strength	Orbital contributions	$\|c\|^2$ [%]
1	15630	0.008	**HOMO** (d_2) → **LUMO** (π*)	84
2	16661	0.020	**HOMO–1** (d_1) → **LUMO** (π*)	84
5	27071	0.027	**HOMO–5** (π_3) → **LUMO** (π*)	74
			HOMO–3 (π_2) → **LUMO** (π*)	15
10	29317	0.307	**HOMO–3** (π_2) → **LUMO** (π*)	44
			HOMO–4 (π_1) → **LUMO** (π*)	28

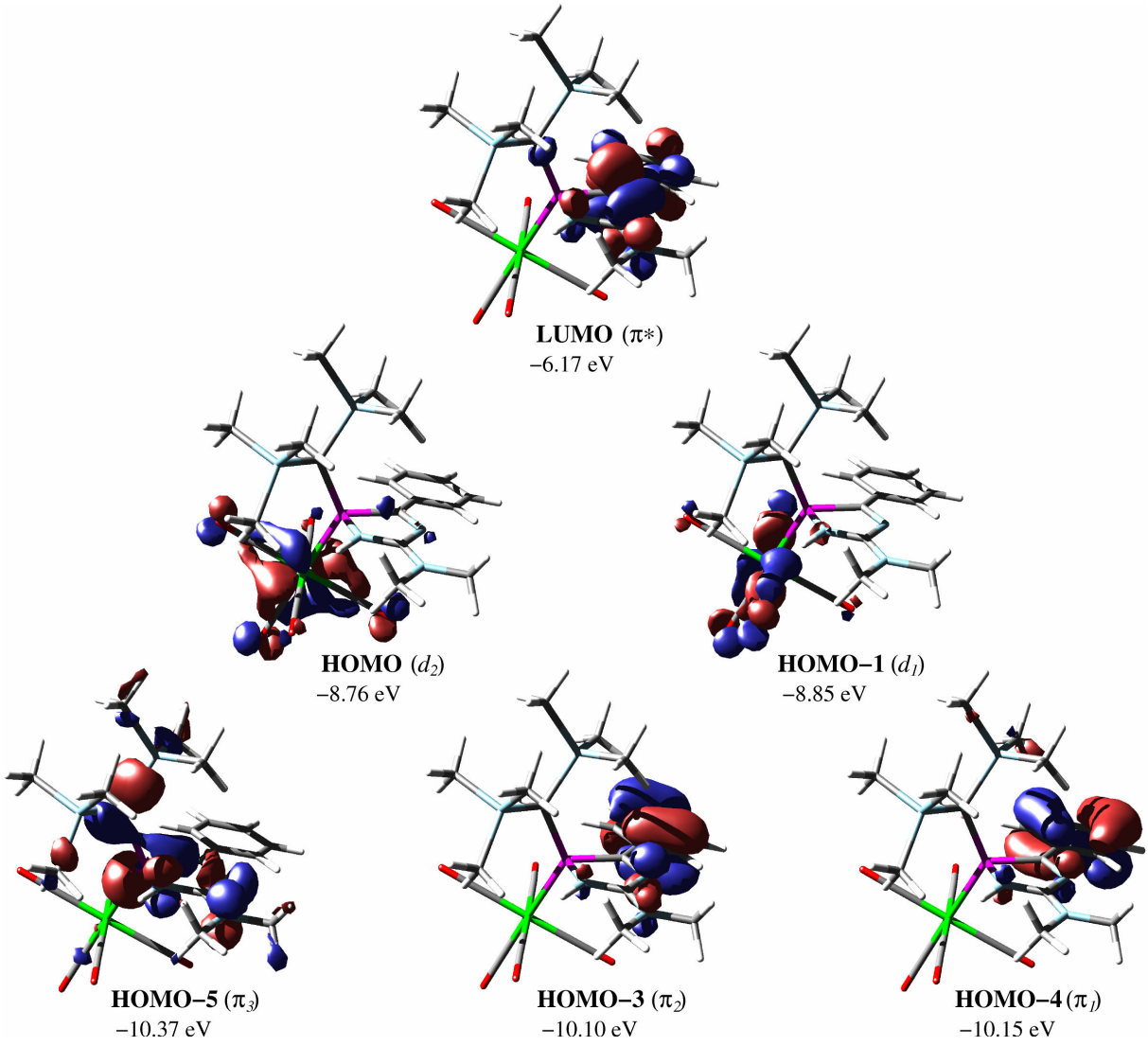

Fig. S.2 Visualization of selected molecular orbitals calculated for the cation **9**$^+$ (B3LYP/SV(P)/ECP-60-MWB(W); isovalue 0.04 au).

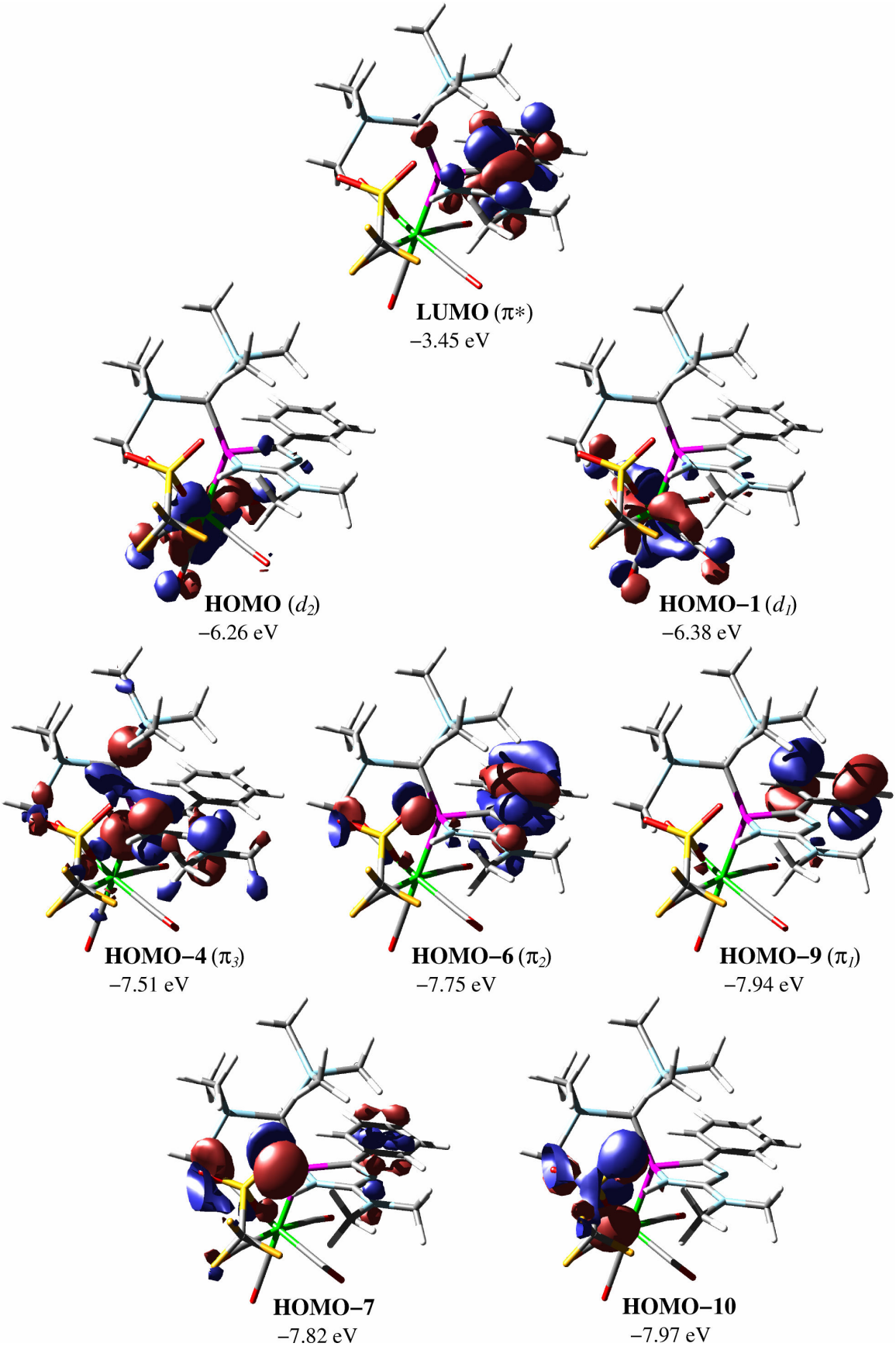

Fig. S.3 Visualization of selected molecular orbitals calculated for the contact ion pair **9** (B3LYP/SV(P)/ECP-60-MWB(W); isovalue 0.04 au).

Table S.2 Selected vertical singlet excitations calculated for **3b** (only the major orbital contributions given).

No.	ν [cm^{-1}]	Oscillator strength	Orbital contributions	$\|c\|^2$ [%]
1	20596	0.002	**HOMO** (d_2) → **LUMO** (π*)	99
2	21326	0.017	**HOMO–1** (d_1) → **LUMO** (π*)	99
4	24498	0.051	**HOMO–3** (π_3) → **LUMO** (π*)	96
13	30564	0.147	**HOMO–4** (π_2) → **LUMO** (π*)	48
19	33960	0.051	**HOMO–6** (π_1) → **LUMO** (π*)	87

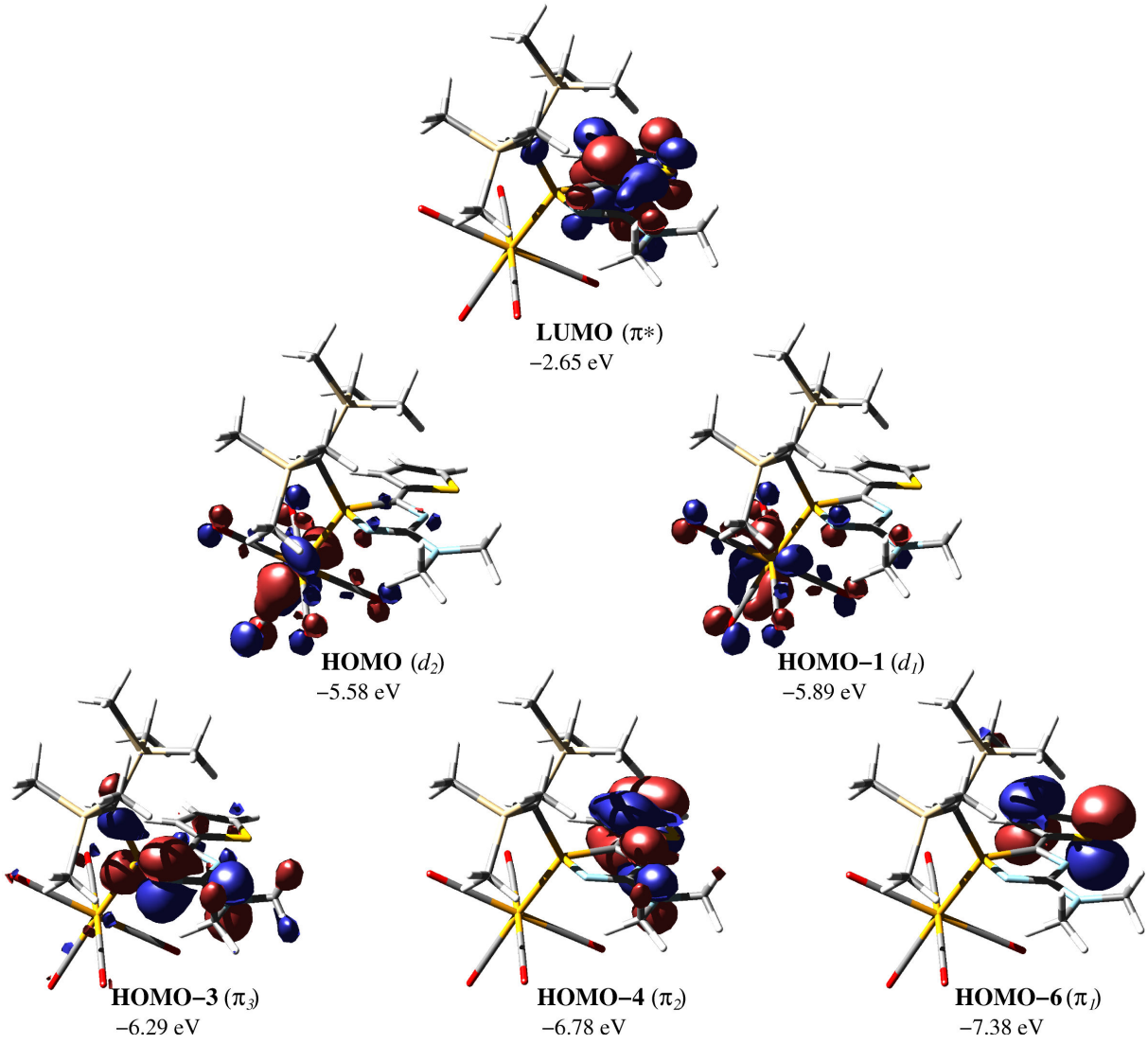

Fig. S.4 Visualization of selected molecular orbitals calculated for **3b** (B3LYP/SV(P)/ECP-60-MWB(W); isovalue 0.04 au).

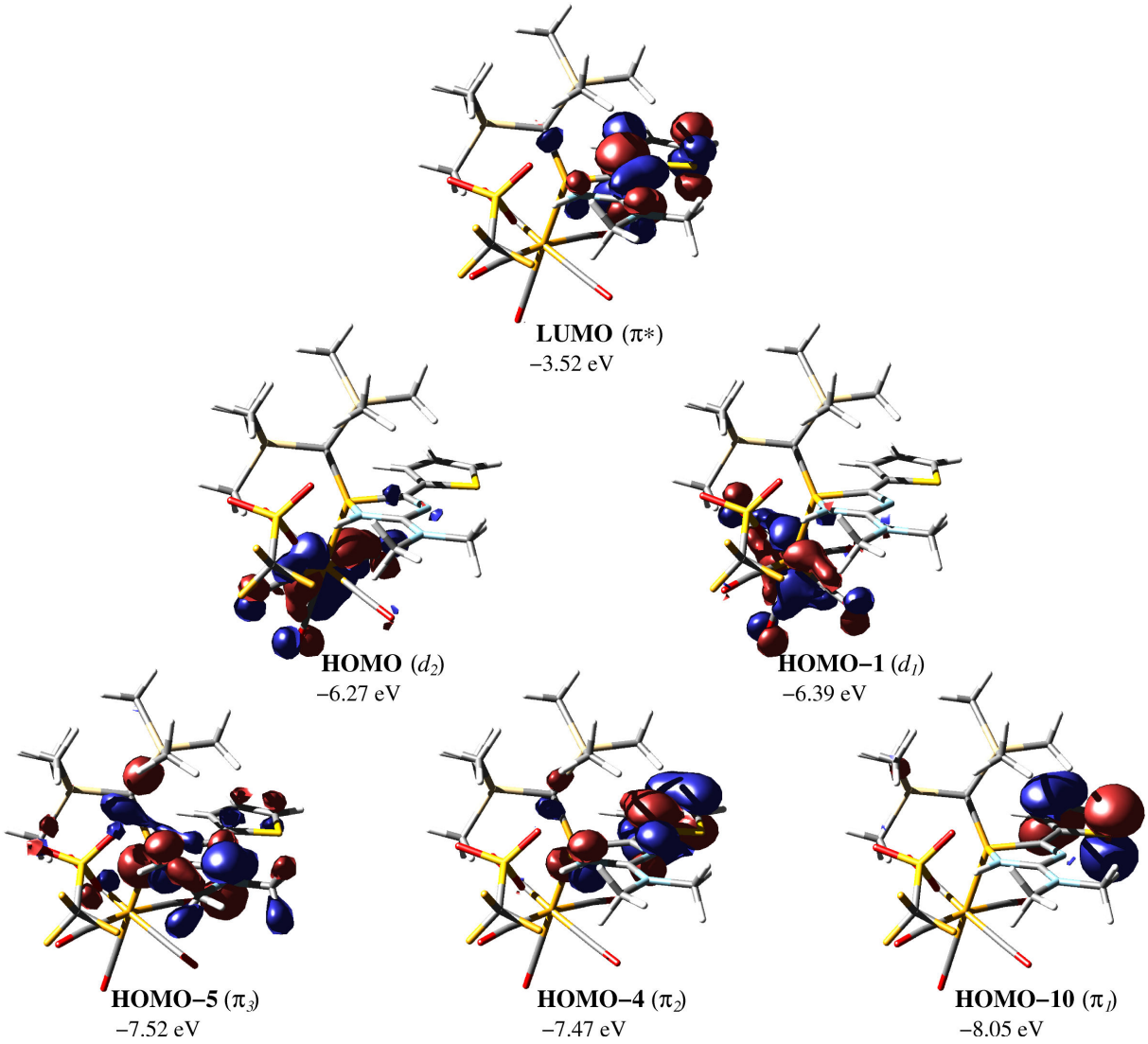

Fig. S.5 Visualization of selected molecular orbitals calculated for **4** (B3LYP/SV(P)/ECP-60-MWB(W); isovalue 0.04 au).