Supporting Information

Spectroscopic Evidence for Through-Space Arene-Sulfur-Arene Bonding Interaction in *m*-Terphenyl Thioether Radical Cations

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complete references 43 and 45:

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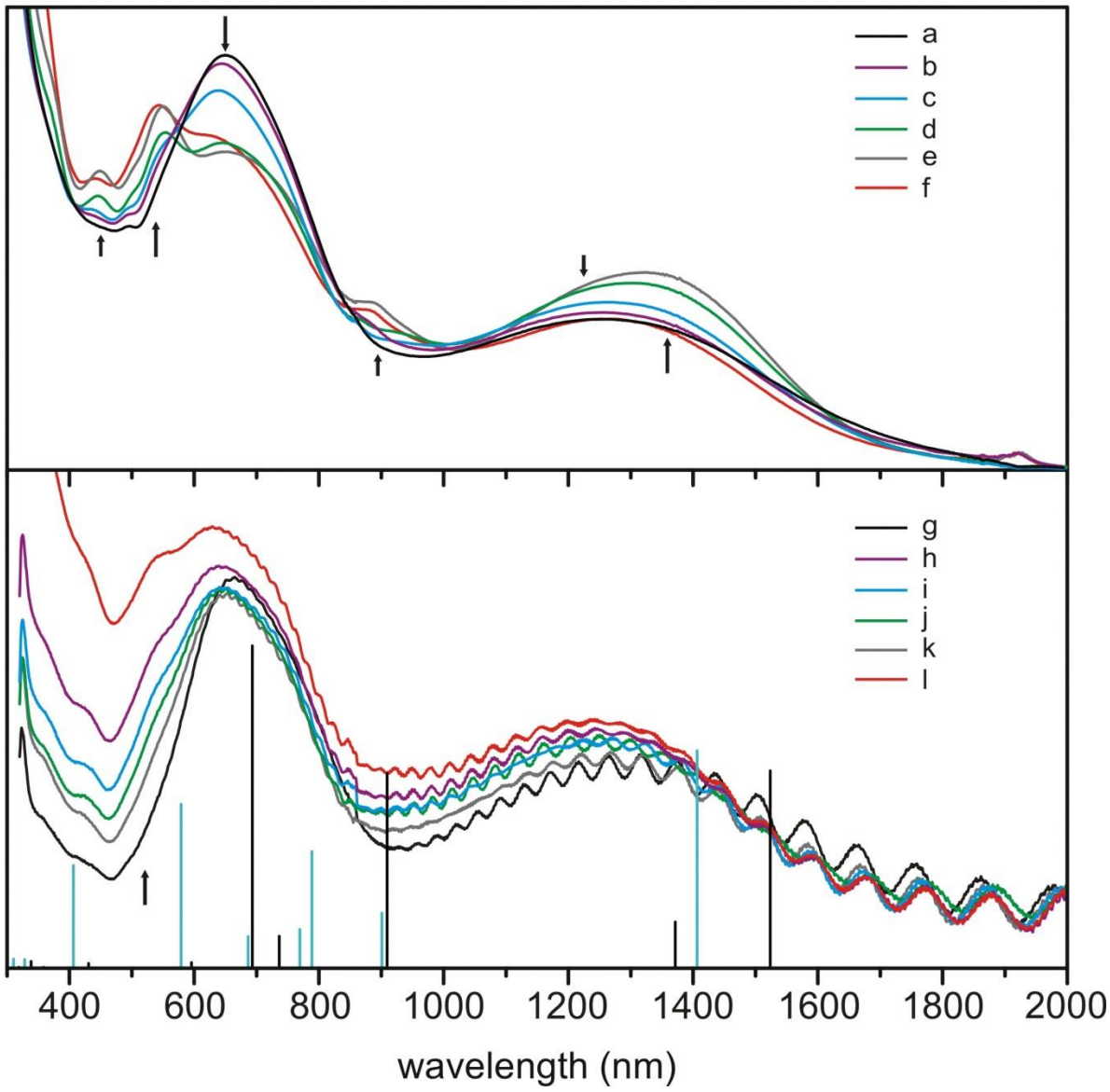

Figure S1: Annealing experiments on **1a**$^{\bullet+}$ in Freon (top) and argon matrix (bottom). Difference spectra taken after: 200 min γ-irradiation (a), 1.5 h @ 77.5 K (b), 1h @ 78 K (c), 15 min @ 79 K (d), 15 min @ 79.5 K (e), 1h @ 80 K (f), 2h X-irradiation (g), 5 min @ 25 K (h), 1h @ 27 K (i), 45 min @ 29 K (j), 45 min @ 30 K (k), 5 min @ 34 K (l). The bars indicate the main excitation energies and transition moments of **1a**$^{\bullet+}$ of the perpendicular conformer (black bars) and twisted conformer (turquoise bars).

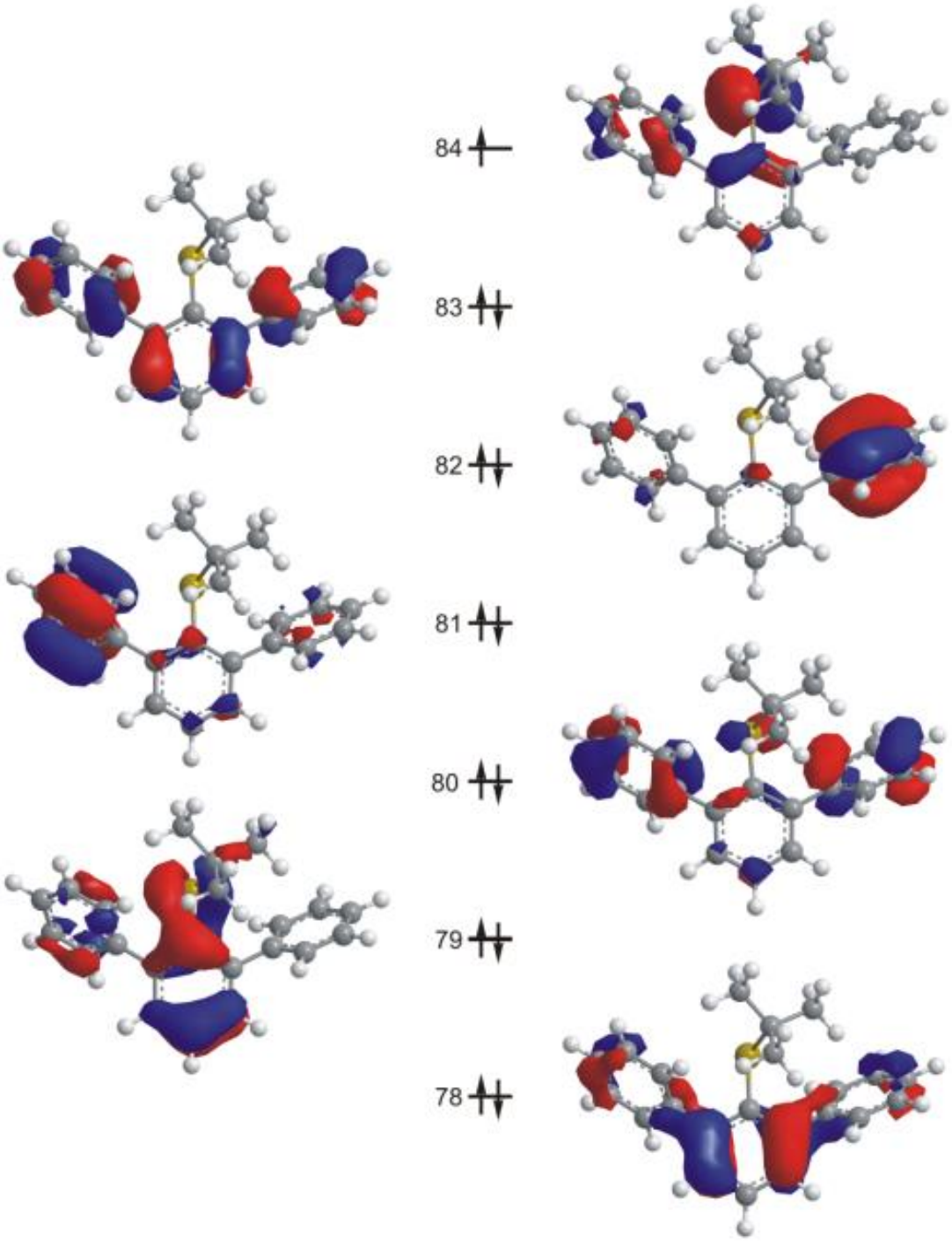

Figure S2: MOs of **1a**$^{\bullet+}$ (twisted conformation) that are involved in the main electronic excitations that appear in the EA spectrum in Figure S1.

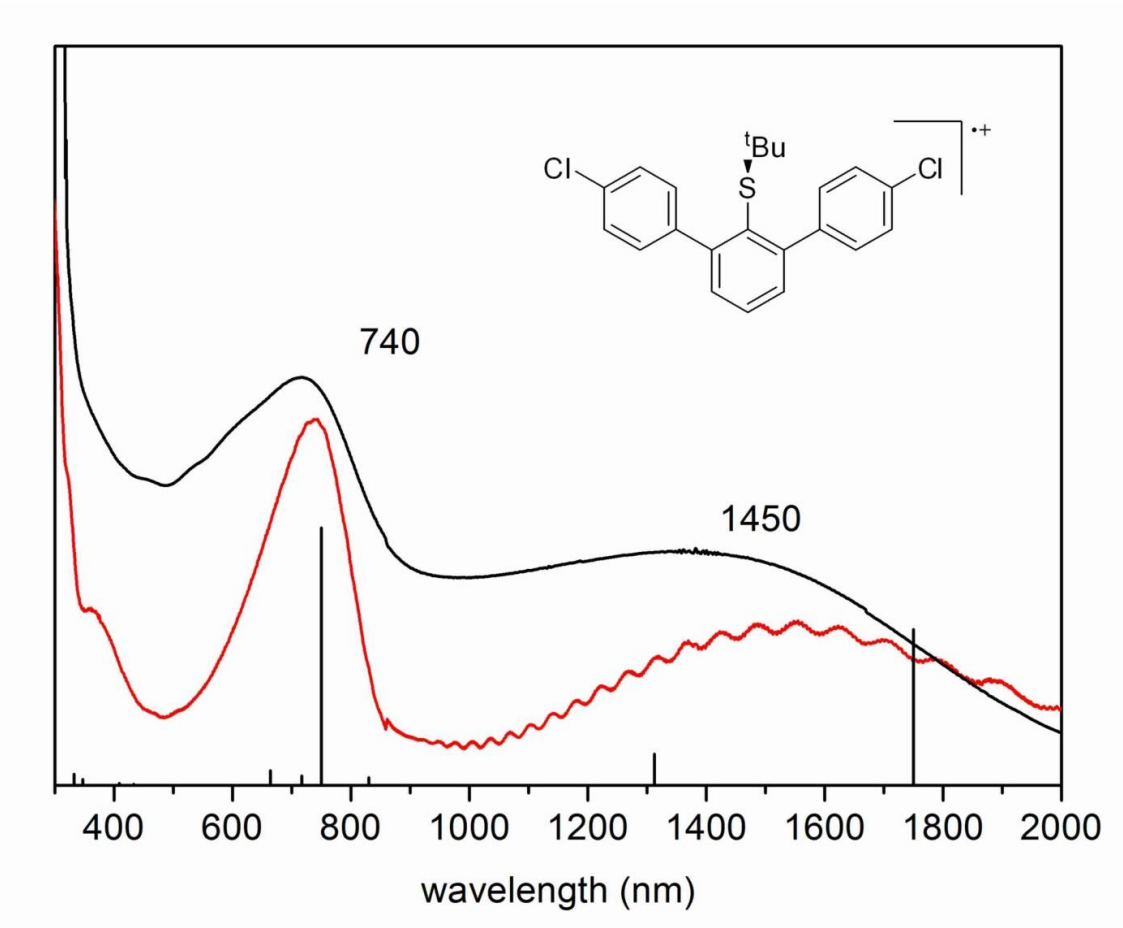

Figure S3: Difference spectrum obtained on γ-irradiation of **1b**$^{\bullet+}$ in a Freon mixture (5mM) at 77 K (black) and on X-irradiation of an argon matrix containing **1b** (red). The bars indicate the main excitation energies and transition moments of **1b**$^{\bullet+}$ calculated by TD-B2PLYP (Table S1)

Table S1: Excited states of **1b**$^{\bullet+}$ calculated by TD-B2PLYP/cc-pVDZ. Orbital 100 corresponds to the SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.71	1750	0.1267	95β → 100β 99β → 100β	0.13 0.84
2nd	0.95	1313	0.0254	98β → 100β	0.95
3rd	1.49	830	0.0065	95β → 100β 97β → 100β	0.22 0.72
4th	1.65	750	0.2091	95β → 100β 97β → 100β 99β → 100β	0.60 0.26 0.10
5th	1.73	717	0.0079	94β → 100β 96β → 100β	0.24 0.74
6th	1.87	664	0.0121	94β → 100β 96β → 100β	0.71 0.22
7th	3.57	347	0.0051	highly mixed	

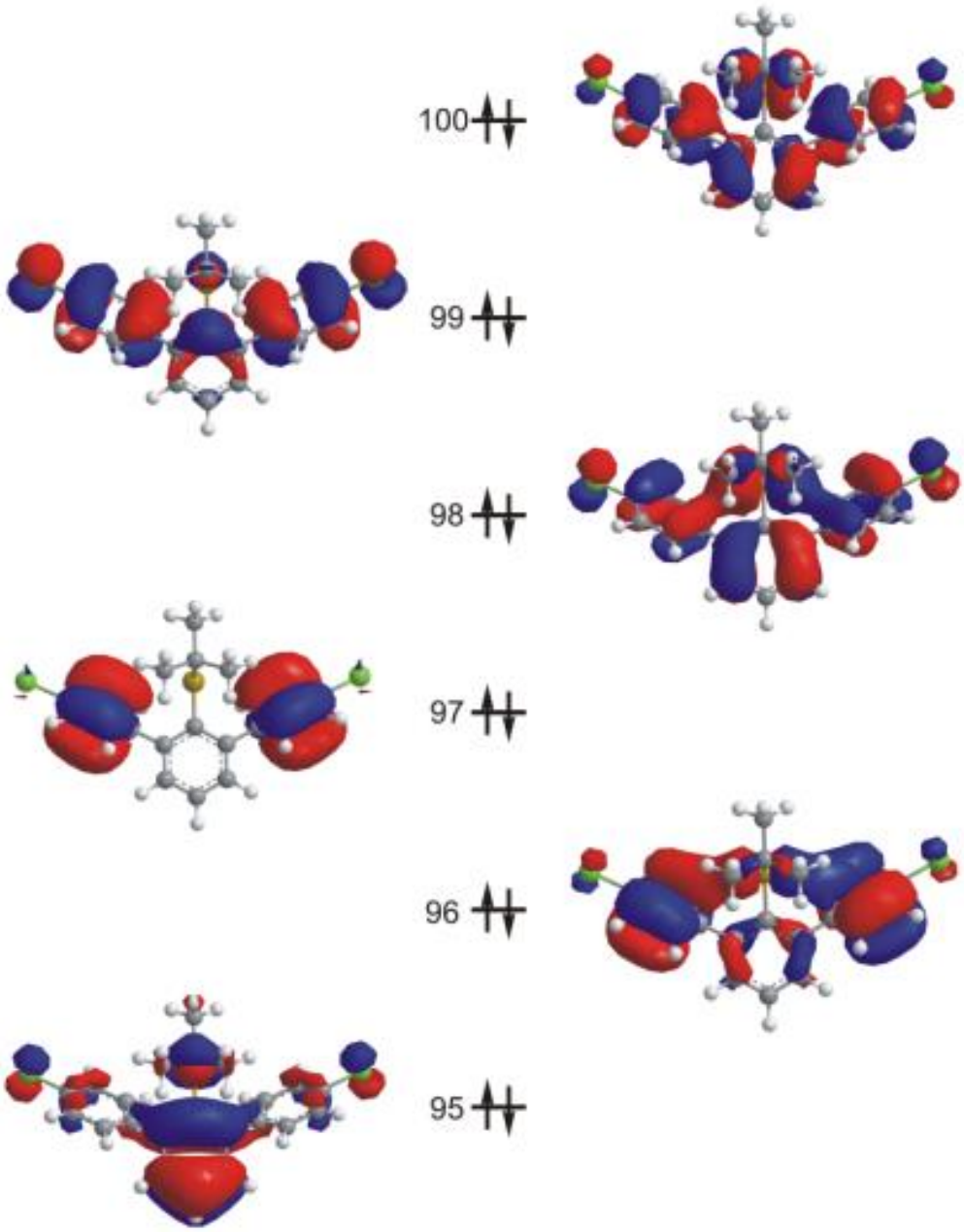

Figure S4: MOs of **1b**$^{\bullet+}$ that are involved in the main electronic excitations that appear in the EA spectrum in Figure S.

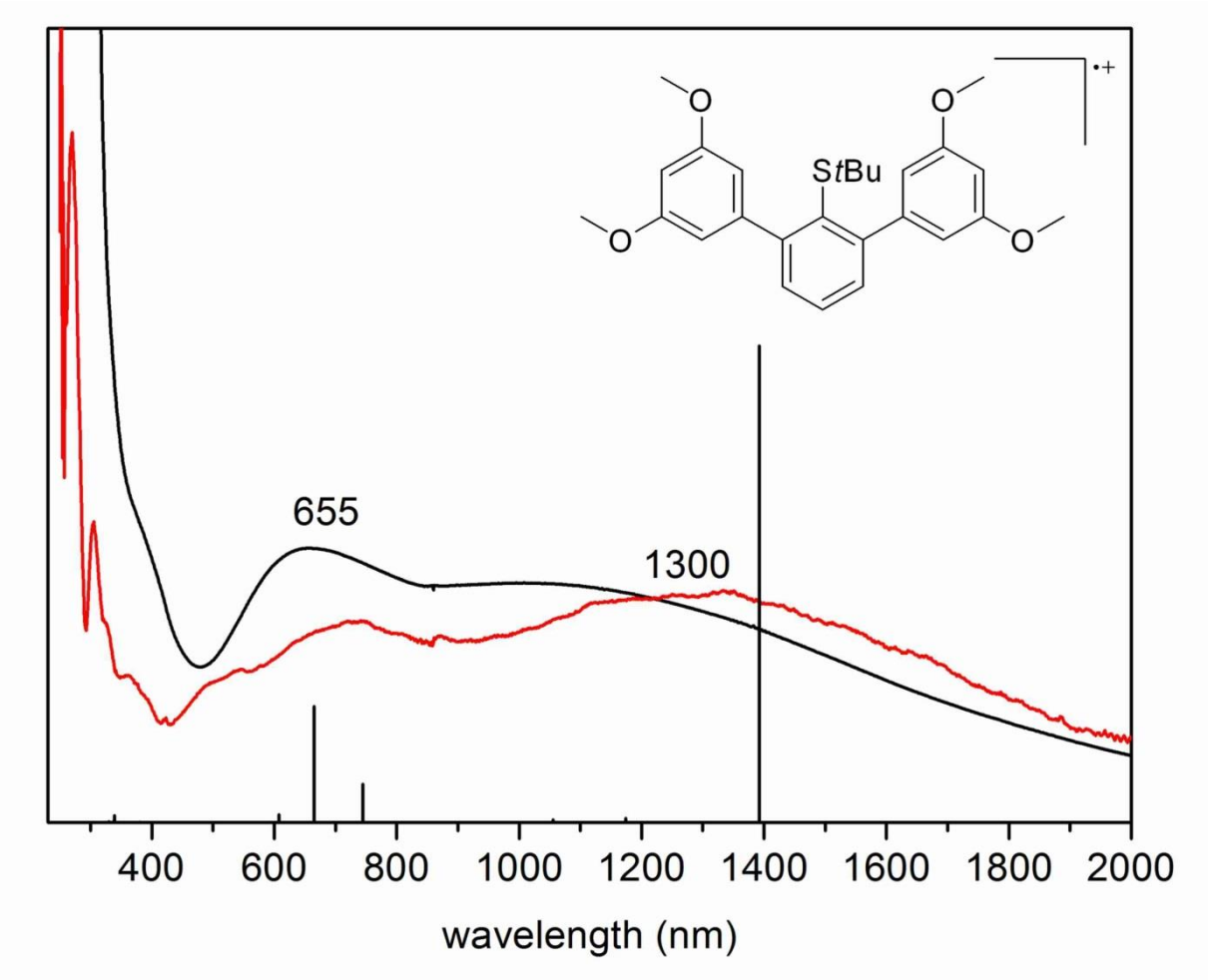

Figure S5: Difference spectrum obtained on γ-irradiation of **1c**$^{\bullet+}$ in a Freon mixture (5mM) at 77 K (black) and on X-irradiation of an argon matrix containing **1c** (red). The bars indicate the main excitation energies and transition moments of **1c**$^{\bullet+}$ calculated by TD-B2PLYP (Table S2)

Table S1: Excited states of **1b**$^{\bullet+}$ calculated by TD-B2PLYP/cc-pVDZ. Orbital 116 corresponds to the SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.89	1392	0.2642	111β → 116β 115β → 116β	0.03 0.93
4th	1.67	745	0.0213	112β → 116β 113β → 116β	0.49 0.45
5th	1.86	665	0.0644	111β → 116β	0.74
6th	2.04	608	0.0045	110β → 116β	0.89
10th	3.66	339	0.0039	highly mixed	

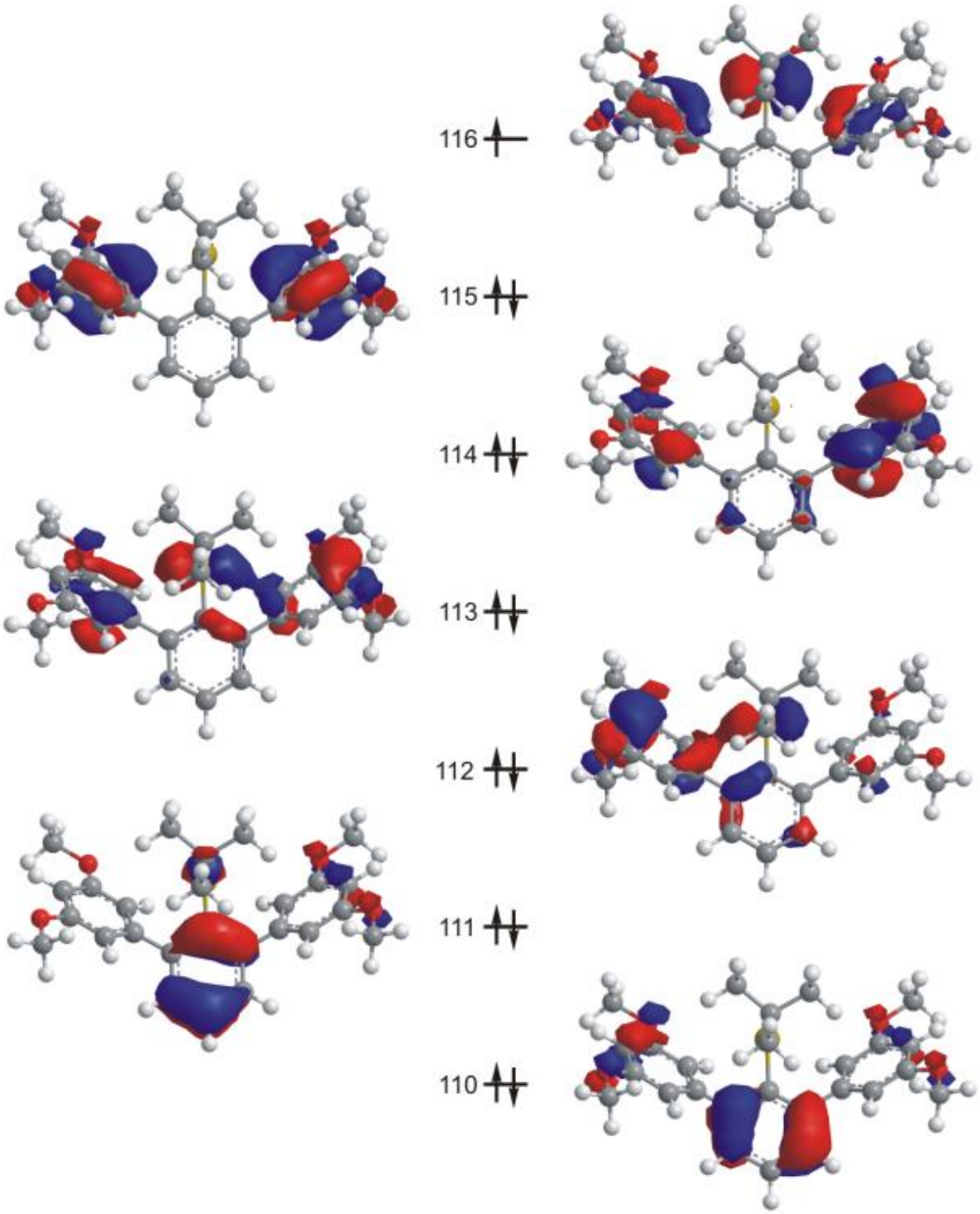

Figure S6: MOs of **1b**$^{\bullet+}$ that are involved in the main electronic excitations that appear in the EA spectrum in Figure S5

Table S4: Excited states of **2A**$^{\bullet+}$ calculated by TD-B2PLYP/cc-pVDZ. Orbital 72 = SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.90	1377	0.1074	67β → 72β 69β → 72β 71β → 72β	0.06 0.09 0.81
2nd	0.90	1377	0.0138	70β → 72β	0.97
3rd	1.33	929	0.0772	69β → 72β 71β → 72β	0.89 0.08
4th	1.73	718	0.0078	66β → 72β 68β → 72β	0.02 0.95
5th	1.77	699	0.0909	67β → 72β 71β → 72β	0.89 0.07

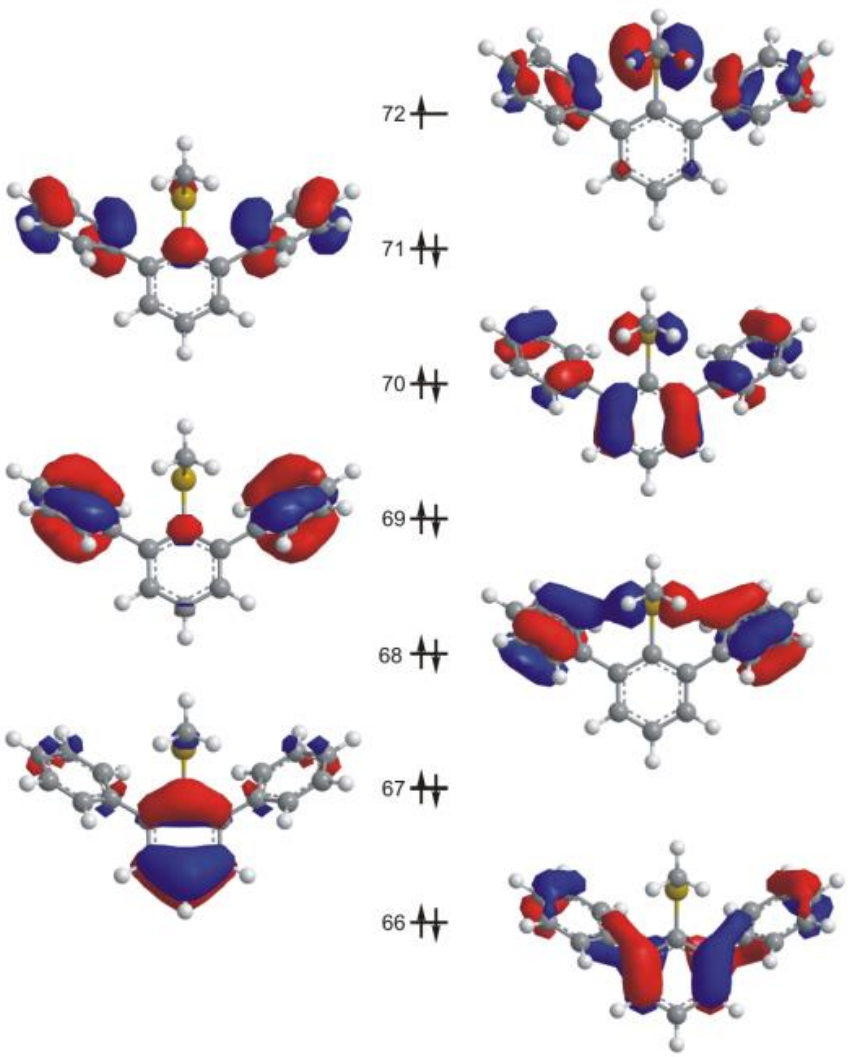

Figure S7: MOs of **2A**$^{\bullet+}$ (perpendicular conformation) that are involved in the main electronic excitations that appear in the EA spectrum in Figure 8 and are listed in Table S4.

Table S5: Excited states of **2B**$^{\bullet+}$ calc. by TD-B2PLYP/cc-pVDZ. Orbital 72 corresponds to the SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.91	1358	0.0628	68β → 72β 71β → 72β	0.02 0.91
2nd	1.41	875	0.0295	68β → 72β 69β → 72β 70β → 72β	0.75 0.10 0.08
3rd	1.55	799	0.0171	68β → 72β 69β → 72β	0.13 0.78
4th	1.40	887	0.0095	68β → 72β 69β → 72β 70β → 72β	0.06 0.04 0.87
5th	2.24	554	0.0423	66β → 72β 67β → 72β	0.28 0.60
6th	2.20	559	0.0626	66β → 72β 67β → 72β	0.61 0.29

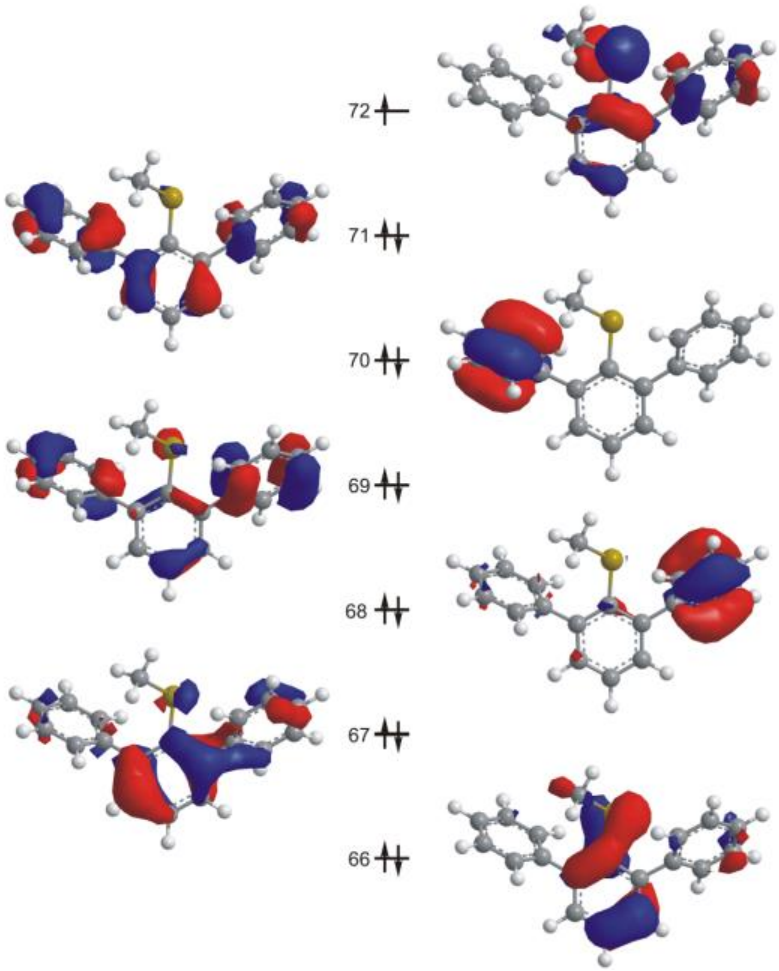

Figure S8: MOs of **2B**$^{\bullet+}$ (twisted conformation) that are involved in the main electronic excitations that appear in the EA spectrum in Figure 8 and are listed in Table S5

Table S6: Excited states of **2C**$^{\bullet+}$ calculated by TD-B2PLYP/cc-pVDZ. Orbital 72 corresponds to the SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.89	1395	0.0402	67β → 72β 71β → 72β	0.06 0.91
2nd	1.46	852	0.0060	68β → 72β 70β → 72β	0.12 0.84
3rd	1.60	774	0.0042	68β → 72β 70β → 72β	0.76 0.14
5th	2.28	544	0.0306	66β → 72β 67β → 72β 71β → 72β	0.04 0.80 0.06
6th	2.85	436	0.118	68β → 72β 66β → 72β 67β → 72β	0.02 0.83 0.05
8th	3.78	328	0.0377	highly mixed	

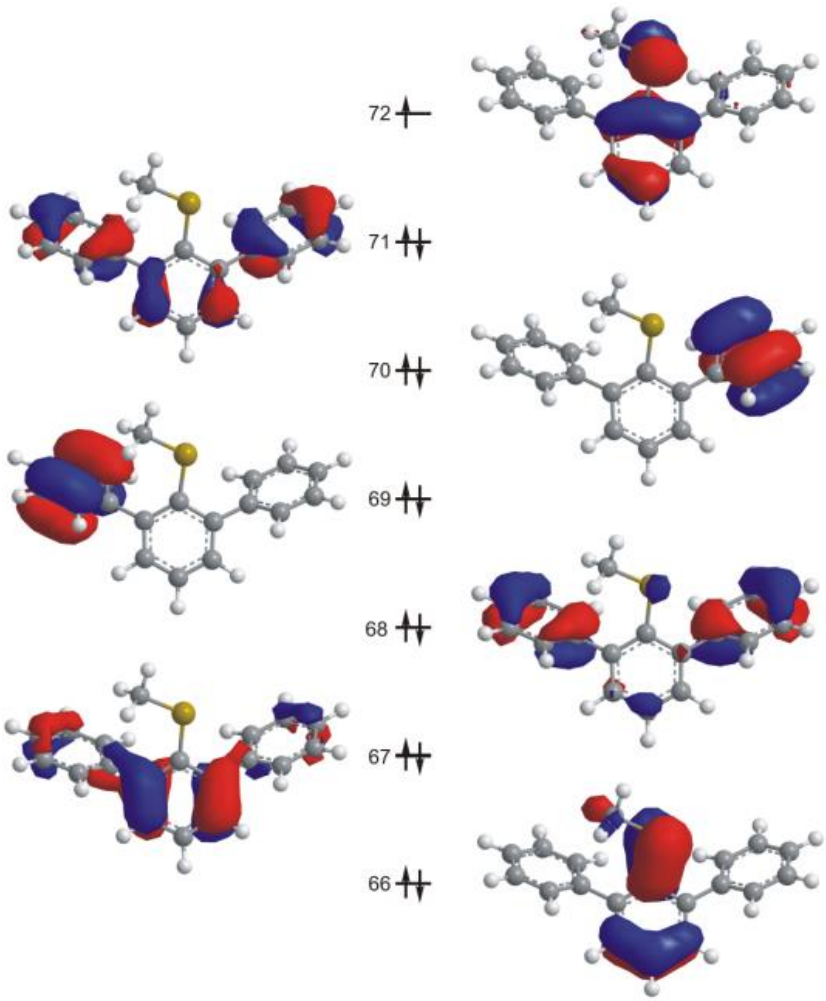

Figure S9: MOs of **2C**$^{\bullet+}$ (parallel conformation) that are involved in the main electronic excitations that appear in the EA spectrum in Figure 8 and are listed in Table S6

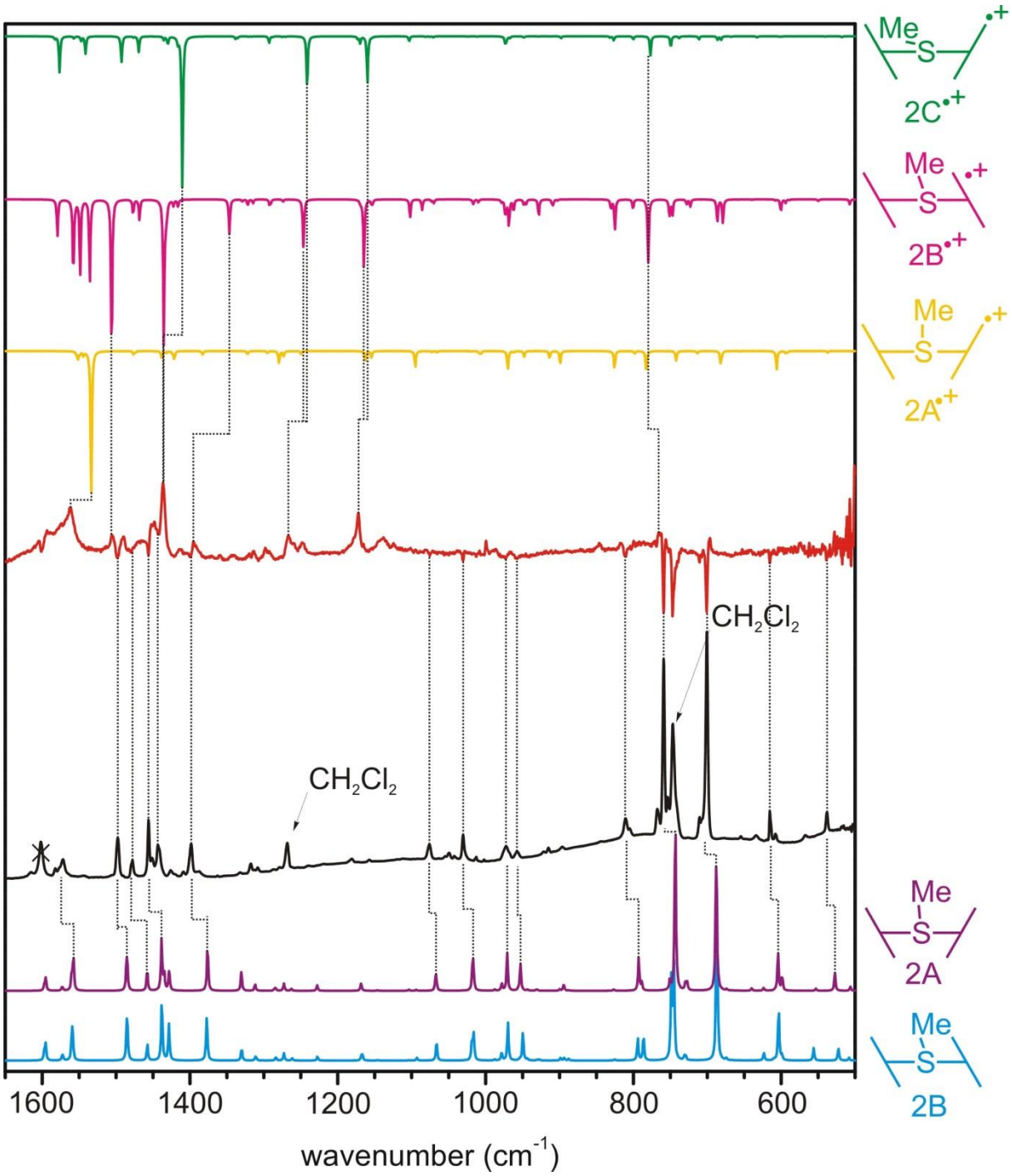

Figure S10: IR spectra of **2** in an argon matrix at 9 K (black) and difference spectrum after 1h30 X-irradiation (red) with B3LYP/6-31G* simulations for the neutral **2B** twisted conformer (blue) and **2A** perpendicular conformer (purple), and **2A**$^{\bullet+}$ perpendicular (yellow), **2B**$^{\bullet+}$ twisted (pink) and **2C**$^{\bullet+}$ parallel (green).

Table S7: Excited states of **3**$^{\bullet+}$ calculated by TD-B3LYP/6-31G*. Orbital 165 corresponds to the SOMO.

Excited State	Energy eV	nm	Oscillator strength	Main excitations	Coefficient
1st	0.43	2851	0.1619	164β → 165β	1.03
3rd	0.81	1532	0.0827	162β → 165β 164β → 165β	0.96 0.34
7th	1.35	921	0.0807	158β → 165β 164β → 165β	0.98 0.11

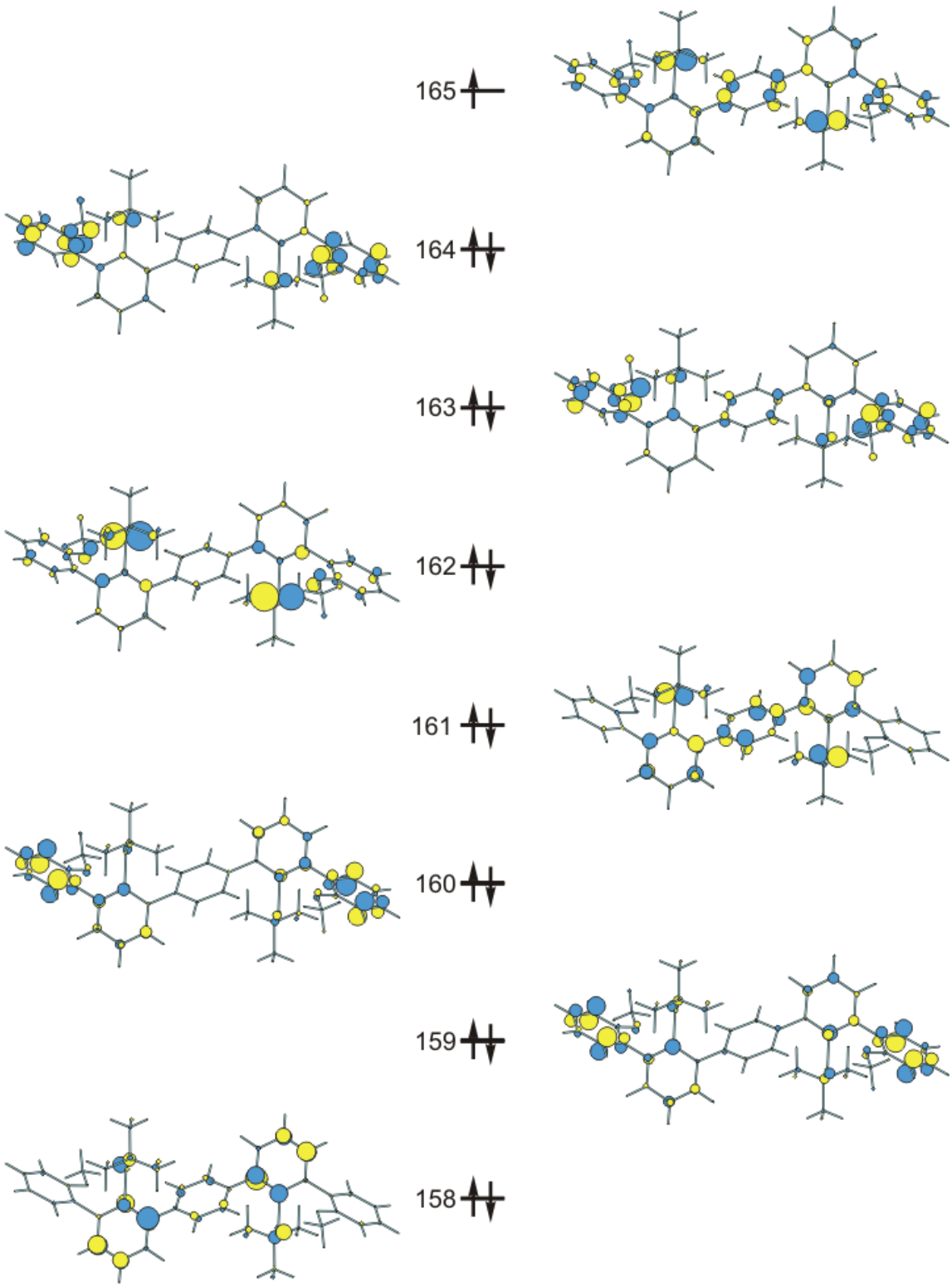

Figure S11: Orbitals of **3**$^{\bullet+}$ calculated with B3LYP/6-31G*.

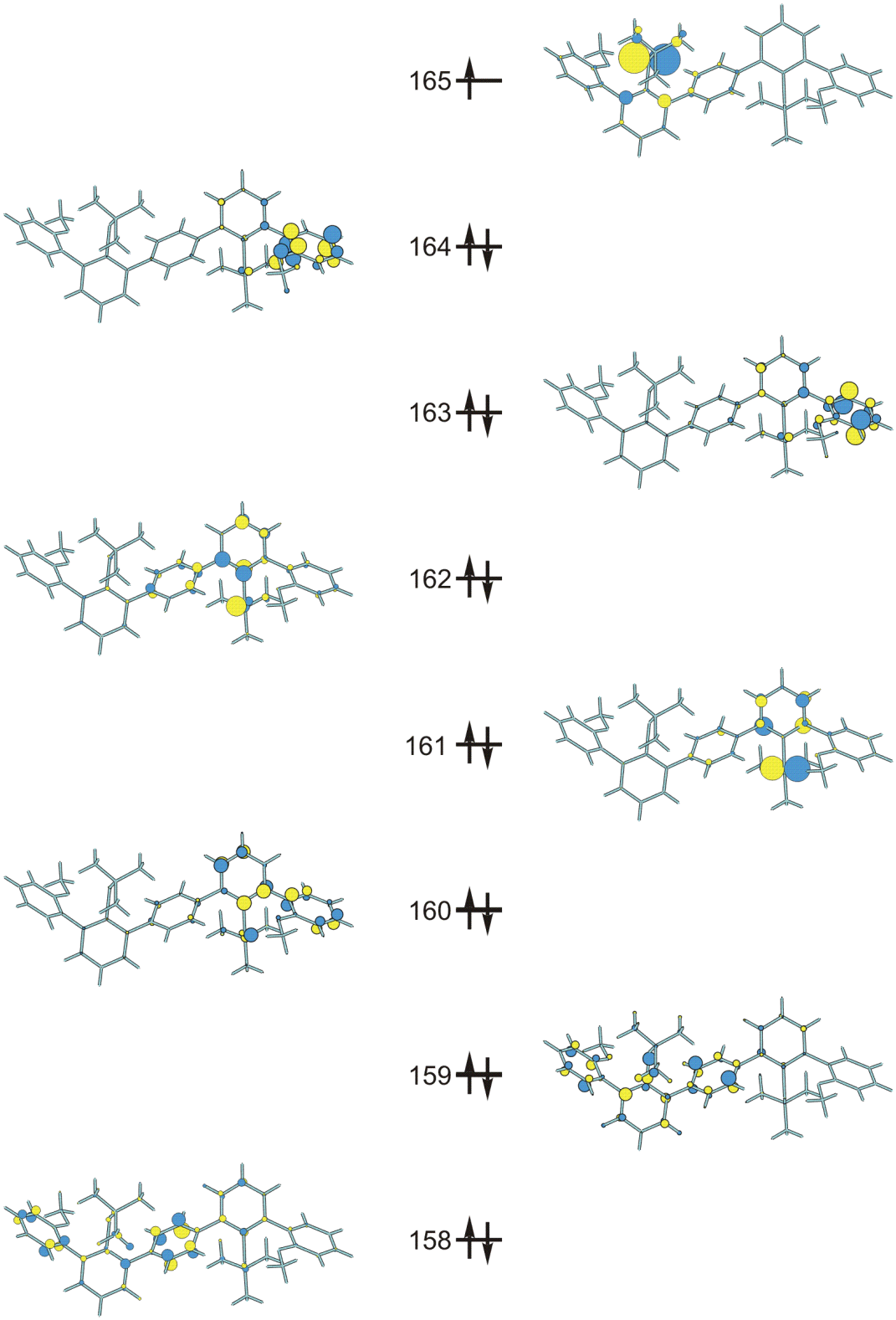

Figure S12: Orbitals of **3**$^{\bullet+}$ calculated with UHF/6-31G.