Supporting Information

For

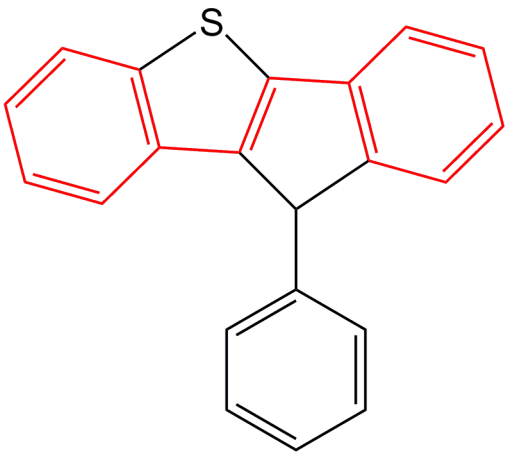
How Dual Bridging Atoms Tune Structural and Optoelectronic Properties of Ladder-type Heterotetracenes? — A Theoretical Study

Xian-Kai Chen, Lu-Yi Zou, Ai-Min Ren*, Jian-Xun Fan

State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

Correspondence to: A.-M. Ren; e-mail: *aimin_ren@yahoo.com*

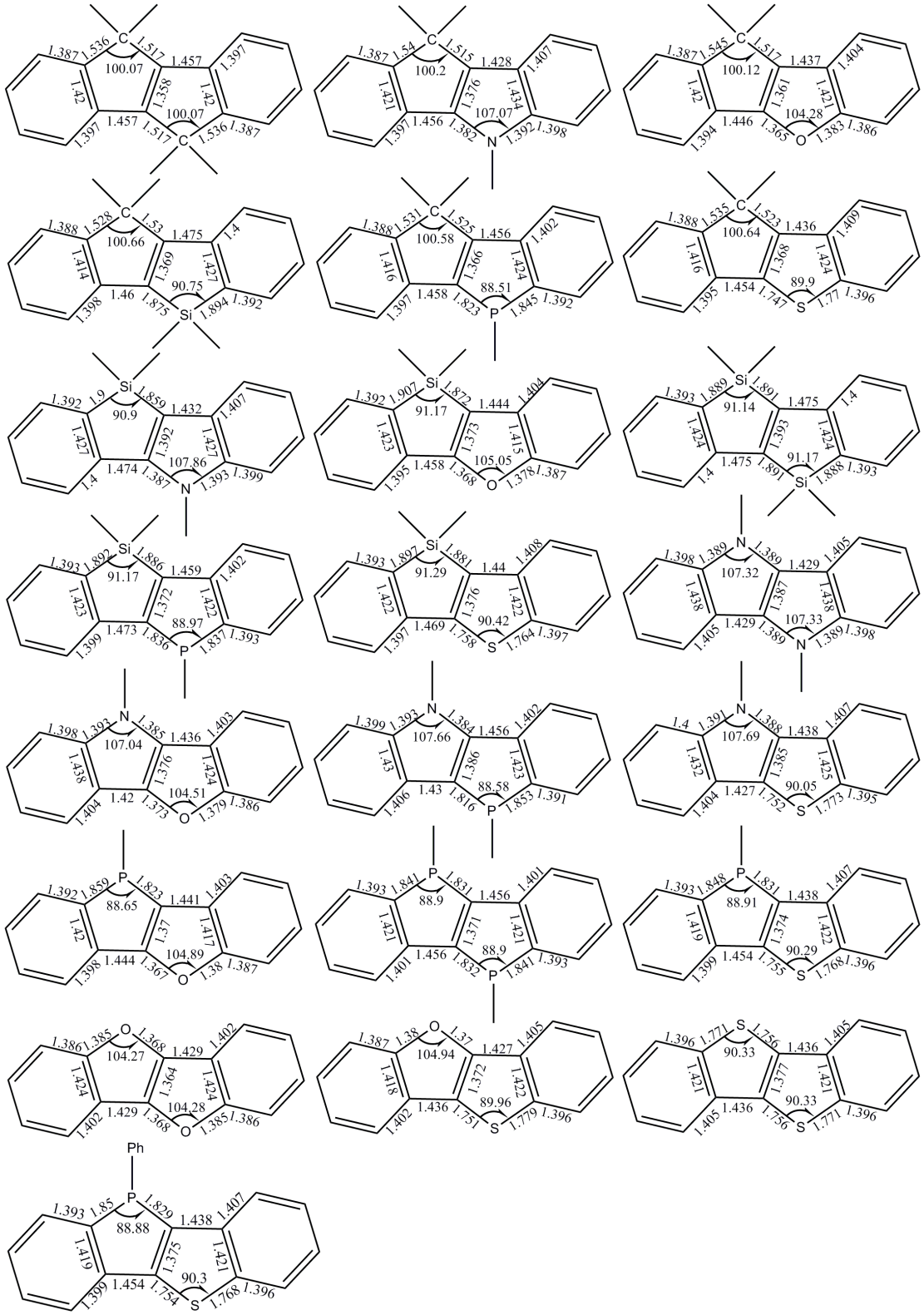
Fig. S1 Chemical structures of PS-Ph



PS-Ph

Fig. S2

(a) The selected important bond lengths and bond angles of these optimized compounds in the neutral states



(b) The selected important bond lengths and bond angles of these optimized compounds in S_1 states

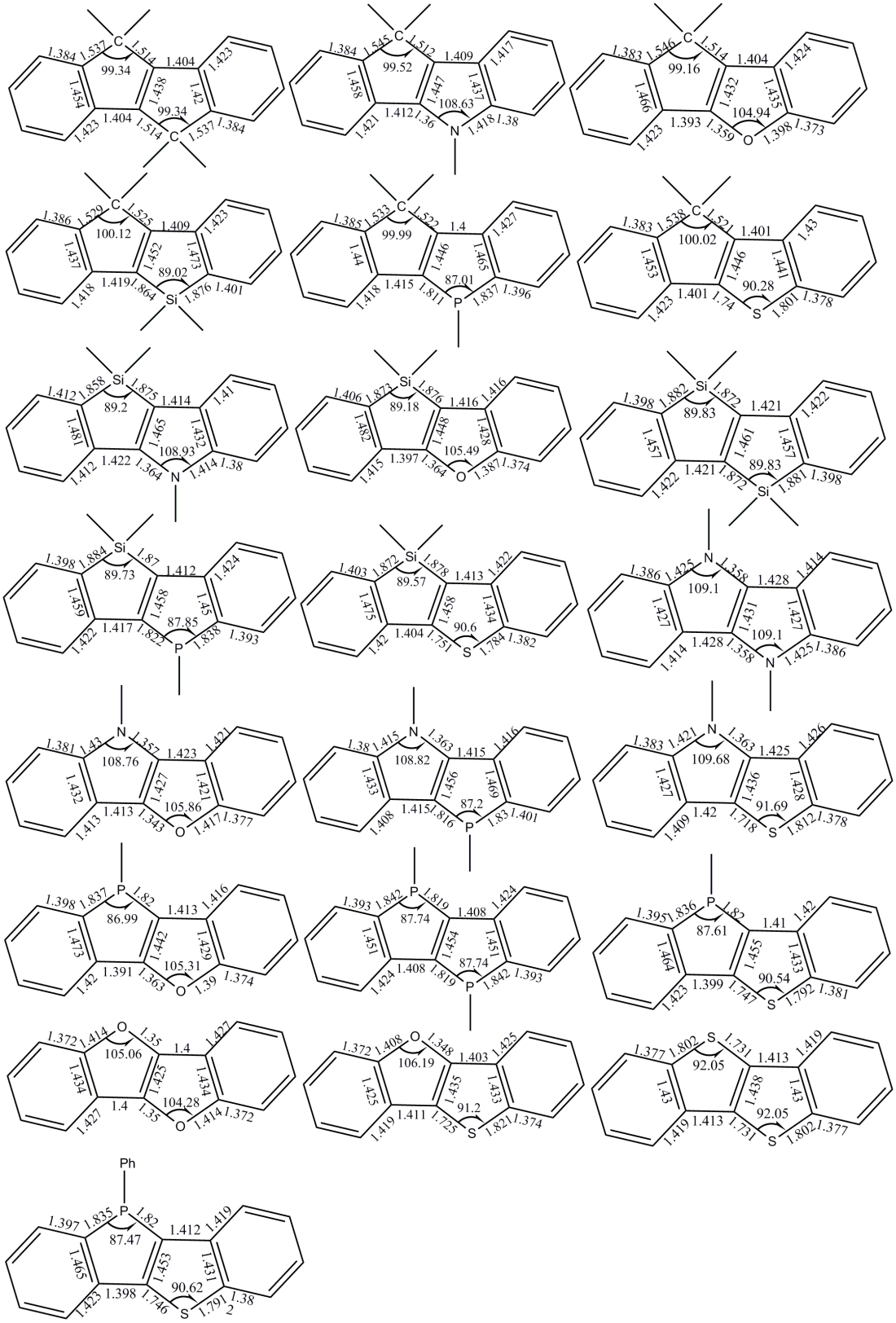
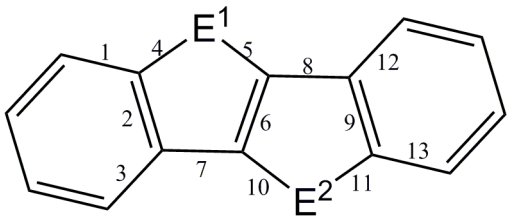


Fig. S3 (a) The bond numbers of the selected important bond lengths.



(b) The differences of bond lengths selected between the ground and singlet excited state geometries.

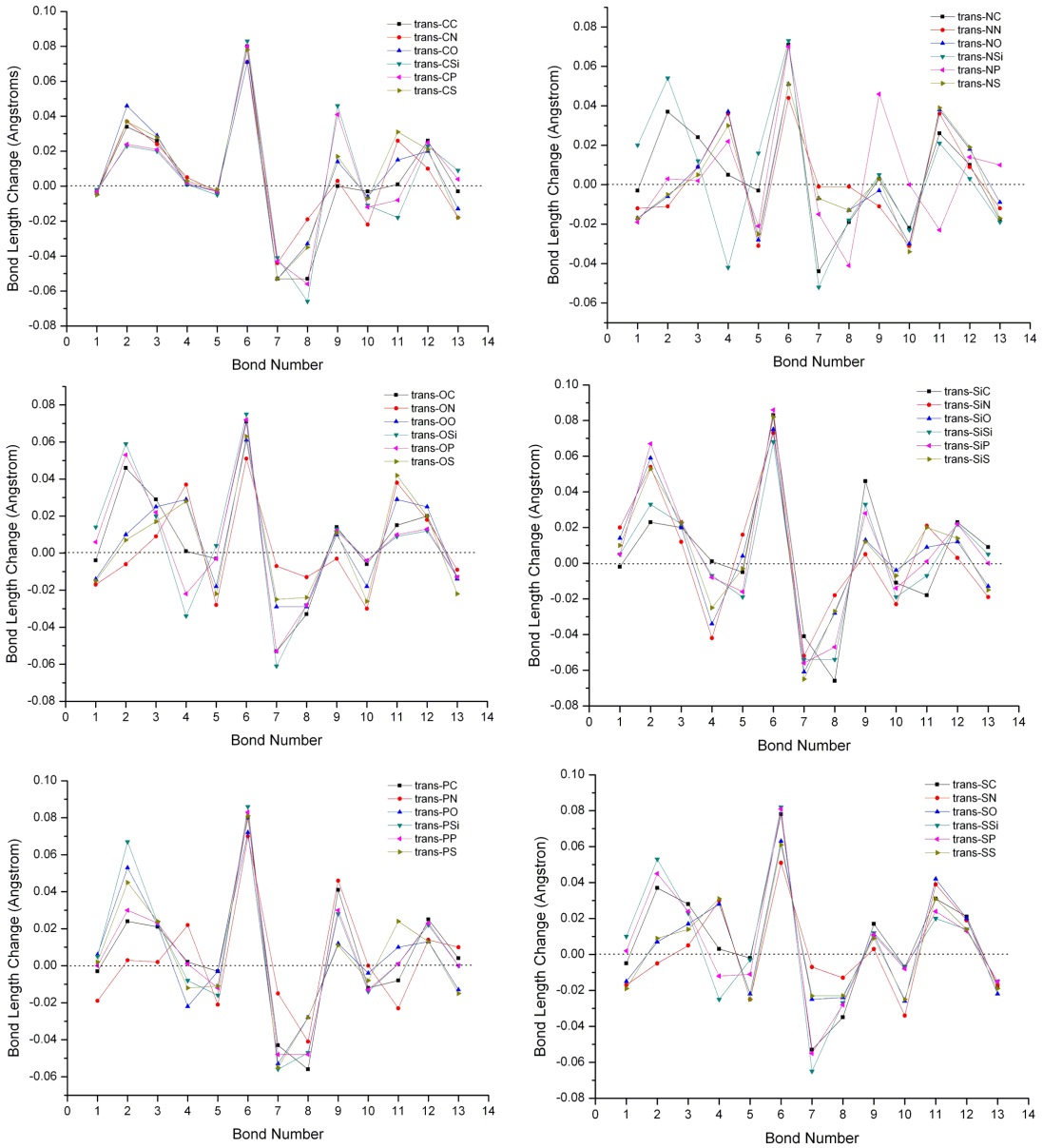


Figure S4 The electronic density contours of FMOs of the studied molecules.

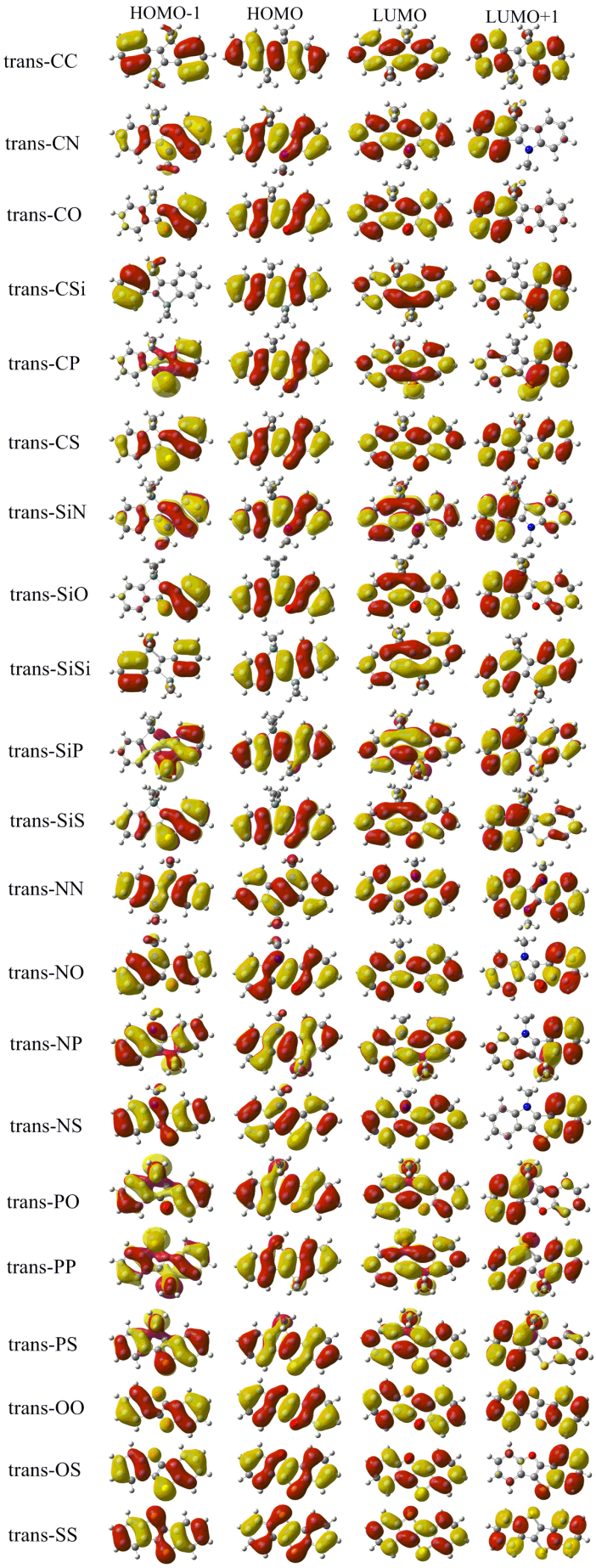
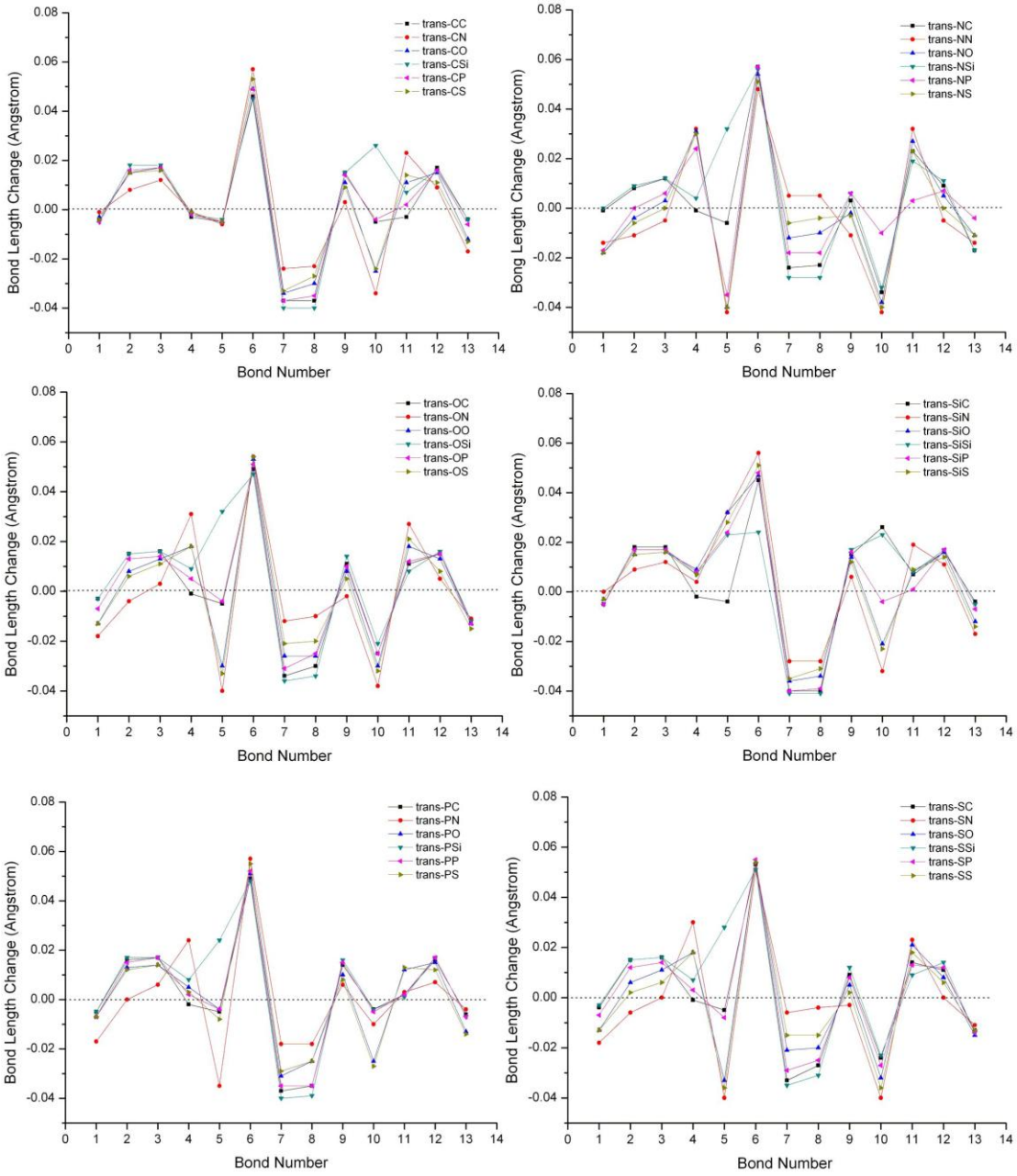


Fig. S5 The differences of bond lengths selected between the neutral and ionized geometries, (a) for hole and (b) for electron.

(a)



(b)

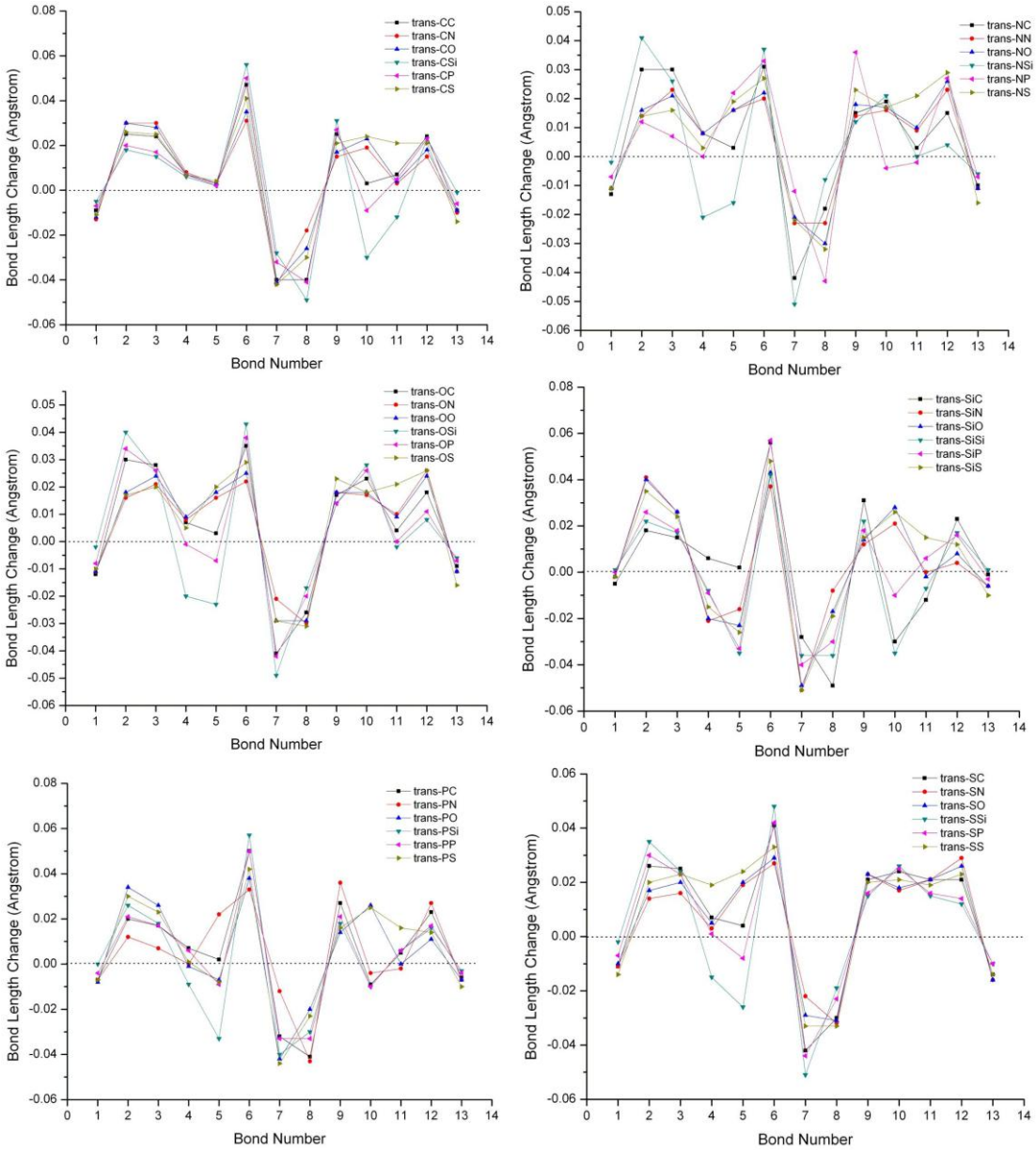


Table S1 HOMO and LUMO energies, Ionization Potentials (IPs) and Electronic Affinities (EAs) obtained by LC-BLYP and CAM-B3LYP functionals; the suffixes (v) indicate vertical values. (in eV)

Species	E_{HOMO}	IP(v)	E_{LUMO}	EA(v)
trans-CC	-7.67[a]/-6.41[b]	7.21[a]/7.04[b]	1.19[a]/0.15[b]	-0.12[a]/-0.08[b]
trans-CN	-7.43[a]/-6.20[b]	6.99[a]/6.85[b]	1.40[a]/0.39[b]	-0.36[a]/-0.33[b]
trans-CO	-7.84[a]/-6.59[b]	7.46[a]/7.29[b]	1.16[a]/0.14[b]	-0.15[a]/-0.12[b]
trans-CSi	-7.77[a]/-6.50[b]	7.31[a]/7.13[b]	0.96[a]/-0.09[b]	0.14[a]/0.18[b]
trans-CP	-7.85[a]/-6.59[b]	7.39[a]/7.21[b]	0.89[a]/-0.13[b]	0.17[a]/0.20[b]

trans-CS	-7.92[a]/-6.66[b]	7.49[a]/7.31[b]	1.01[a]/0.01[b]	-0.01[a]/0.00[b]

The superscripts a and b denote the values calculated by LC-BLYP and CAM-B3LYP functionals, respectively.

To validate the reliability of HOMOs and LUMOs energies, IP(v) and EA(v) values calculated by B3LYP functional, these values for series molecules *C* taken as the example are compared with those calculated by LC-BLYP and CAM-B3LYP functionals. It can be found that the relative orderings of these values obtained (in Tables 1 and 2) by B3LYP functional are accordant with those obtained by LC-BLYP and CAM-B3LYP functionals. It should be pointed out that the values obtained by the later two functionals are probably non-reasonable, because most of LUMOs energies are positive values and most of EA(v) values are negative.

Table S2 the ground-state dipole moment (μ) values of the studied molecules. (in Debye)

	trans-CC	trans-CN	trans-CO	trans-CSi	trans-CP	trans-CS	trans-SiN
μ	0.0004	1.6209	1.1380	0.4639	1.3953	1.1891	1.7505
	trans-SiO	trans-SiSi	trans-SiP	trans- SiS	trans-NN	trans-NO	trans-NP
μ	1.2627	0.0019	1.4519	1.3382	0.0906	2.5034	2.6980
	trans-NS	trans-PO	trans-PP	trans-PS	trans-OO	trans-OS	trans-SS
μ	2.6525	1.2625	0.0013	1.2460	0.0004	0.2371	0.0000

Table S3 HOMO and LUMO energies obtained by B3LYP/6-311+G(d) method (in eV)

	trans-CC	trans-CN	trans-CO	trans-CSi	trans-CP	trans-CS	trans-SiN
HOMO	-5.47	-5.28	-5.65	-5.56	-5.63	-5.69	-5.39
LUMO	-1.41	-1.18	-1.42	-1.64	-1.66	-1.50	-1.36

	trans-SiO	trans-SiSi	trans-SiP	trans- SiS	trans-NN	trans-NO	trans-NP
HOMO	-5.75	-5.63	-5.71	-5.79	-5.01	-5.44	-5.44
LUMO	-1.58	-1.85	-1.85	-1.68	-1.02	-1.26	-1.40
	trans-NS	trans-PO	trans-PP	trans-PS	trans-OO	trans-OS	trans-SS
HOMO	-5.42	-5.79	-5.82	-5.85	-5.86	-5.86	-5.86
LUMO	-1.31	-1.88	-1.64	-1.73	-1.52	-1.56	-1.63

Table S4 The absorption (a) and emission (b) spectra calculated by TDDFT method in vacuum and solvent (CH_2Cl_2) of trans-E^1E^2.

(a) absorption spectra

in vacuum

Species	Electronic transitions	λ_{max}(nm)	Band gaps (eV)	f	Main configurations	Coefficient
trans-CC	$S_0 \rightarrow S_1$	325.7	3.80	0.46	H→L	0.7
	$S_0 \rightarrow S_5$	243.0	5.10	0.19	H-1→L	0.6
trans-CN	$S_0 \rightarrow S_1$	320.7	3.87	0.34	H→L	0.7
	$S_0 \rightarrow S_3$	285.3	4.35	0.17	H-1→L	0.6
trans-CO	$S_0 \rightarrow S_1$	307.5	4.03	0.55	H→L	0.7
	$S_0 \rightarrow S_5$	235.0	5.28	0.11	H-2→L	0.6
trans-CSi	$S_0 \rightarrow S_1$	350.2	3.54	0.29	H→L	0.7
	$S_0 \rightarrow S_5$	250.9	4.94	0.27	H-2→L	0.4
trans-CP	$S_0 \rightarrow S_1$	340.3	3.64	0.31	H→L	0.7
	$S_0 \rightarrow S_8$	234.9	5.28	0.22	H-1→L+1	0.6
trans-CS	$S_0 \rightarrow S_1$	312.7	3.96	0.43	H→L	0.7
	$S_0 \rightarrow S_4$	257.3	4.82	0.12	H-1→L	0.3
trans-SiN	$S_0 \rightarrow S_1$	340.8	3.64	0.18	H→L	0.7
	$S_0 \rightarrow S_3$	288.5	4.30	0.29	H→L+1	0.5
trans-SiO	$S_0 \rightarrow S_1$	325.7	3.81	0.31	H→L	0.7
	$S_0 \rightarrow S_2$	280.9	4.41	0.11	H→L+1	0.6
trans-SiSi	$S_0 \rightarrow S_1$	370.9	3.34	0.24	H→L	0.7
	$S_0 \rightarrow S_7$	254.6	4.87	0.41	H→L+2	0.5
trans-SiP	$S_0 \rightarrow S_1$	359.3	3.45	0.25	H→L	0.7
	$S_0 \rightarrow S_9$	236.1	5.25	0.2	H-1→L+2	0.5
trans-SiS	$S_0 \rightarrow S_1$	330.3	3.75	0.28	H→L	0.7
	$S_0 \rightarrow S_3$	278.9	4.45	0.11	H→L+1	0.6
trans-NN	$S_0 \rightarrow S_1$	339.0	3.66	0.10	H→L	0.7
	$S_0 \rightarrow S_2$	297.7	4.17	0.20	H-1→L	0.6
trans-NO	$S_0 \rightarrow S_1$	313.6	3.95	0.26	H→L	0.7
	$S_0 \rightarrow S_2$	288.2	4.30	0.21	H-1→L	0.6

trans-NP	$S_0 \rightarrow S_1$	335.4	3.70	0.18	H→L	0.7
	$S_0 \rightarrow S_2$	301.7	4.11	0.17	H-1→L	0.7
trans-NS	$S_0 \rightarrow S_1$	325.6	3.81	0.13	H→L	0.7
	$S_0 \rightarrow S_2$	295.1	4.20	0.20	H-1→L	0.6
trans-PO	$S_0 \rightarrow S_1$	320.2	3.87	0.32	H→L	0.7
	$S_0 \rightarrow S_2$	288.9	4.29	0.12	H-1→L	0.6
trans-PP	$S_0 \rightarrow S_1$	350.4	3.54	0.25	H→L	0.7
	$S_0 \rightarrow S_3$	307.1	4.04	0.12	H-1→L	0.7
trans-PS	$S_0 \rightarrow S_1$	325.7	3.81	0.26	H→L	0.7
	$S_0 \rightarrow S_2$	301.6	4.11	0.16	H-1→L	0.7
trans-OO	$S_0 \rightarrow S_1$	295.2	4.20	0.62	H→L	0.7
	$S_0 \rightarrow S_4$	237.2	5.23	0.34	H→L+2	0.6
trans-OS	$S_0 \rightarrow S_1$	303.2	4.09	0.35	H→L	0.7
	$S_0 \rightarrow S_2$	283.7	4.37	0.18	H-1→L	0.6
trans-SS	$S_0 \rightarrow S_1$	314.5	3.94	0.16	H→L	0.7

in solvent

Species	Electronic transitions	λ_{max}(nm)	Band gaps (eV)	f	Main configurations	Coefficient
trans-CC	$S_0 \rightarrow S_1$	331.5	3.74	0.60	H→L	0.7
	$S_0 \rightarrow S_5$	244.2	5.08	0.25	H-1→L	0.6
trans-CN	$S_0 \rightarrow S_1$	325.9	3.80	0.47	H→L	0.7
	$S_0 \rightarrow S_3$	285.7	4.34	0.16	H→L+1	0.5
trans-CO	$S_0 \rightarrow S_1$	313.8	3.95	0.72	H→L	0.7
	$S_0 \rightarrow S_5$	236.5	5.24	0.14	H-2→L	0.6
trans-CSi	$S_0 \rightarrow S_1$	353.3	3.51	0.40	H→L	0.7
	$S_0 \rightarrow S_5$	252.5	4.91	0.28	H→L+2	0.4
trans-CP	$S_0 \rightarrow S_1$	344.7	3.60	0.43	H→L	0.7
	$S_0 \rightarrow S_8$	234.5	5.29	0.26	H-1→L+1	0.6
trans-CS	$S_0 \rightarrow S_1$	317.9	3.90	0.59	H→L	0.7
	$S_0 \rightarrow S_4$	257.9	4.81	0.15	H→L+1	0.4
trans-SiN	$S_0 \rightarrow S_1$	341.6	3.63	0.27	H→L	0.7
	$S_0 \rightarrow S_3$	288.5	4.30	0.33	H→L+1	0.6
trans-SiO	$S_0 \rightarrow S_1$	328.2	3.78	0.45	H→L	0.7
	$S_0 \rightarrow S_2$	280.4	4.42	0.12	H→L+1	0.6
trans-SiSi	$S_0 \rightarrow S_1$	373.9	3.32	0.33	H→L	0.70
	$S_0 \rightarrow S_6$	257.1	4.82	0.53	H→L+2	0.5
trans-SiP	$S_0 \rightarrow S_1$	362.8	3.42	0.35	H→L	0.7
	$S_0 \rightarrow S_5$	259.7	4.77	0.14	H-2→L	0.4
trans-SiS	$S_0 \rightarrow S_1$	333.3	3.72	0.41	H→L	0.7
	$S_0 \rightarrow S_3$	278.6	4.45	0.11	H→L+1	0.6
trans-NN	$S_0 \rightarrow S_1$	339.0	3.66	0.10	H→L	0.7

	$S_0 \rightarrow S_2$	297.7	4.17	0.20	H-1→L	0.6
trans-NO	$S_0 \rightarrow S_1$	313.6	3.95	0.26	H→L	0.7
	$S_0 \rightarrow S_2$	288.2	4.30	0.21	H-1→L	0.6
trans-NP	$S_0 \rightarrow S_1$	335.4	3.70	0.18	H→L	0.7
	$S_0 \rightarrow S_2$	301.7	4.11	0.17	H-1→L	0.7
trans-NS	$S_0 \rightarrow S_1$	325.6	3.81	0.13	H→L	0.7
	$S_0 \rightarrow S_2$	295.1	4.20	0.20	H-1→L	0.6
trans-PO	$S_0 \rightarrow S_1$	323.8	3.83	0.47	H→L	0.7
	$S_0 \rightarrow S_2$	289.1	4.29	0.14	H-1→L	0.6
trans-PP	$S_0 \rightarrow S_1$	354.3	3.50	0.36	H→L	0.7
	$S_0 \rightarrow S_3$	307.2	4.04	0.16	H-1→L	0.7
trans-PS	$S_0 \rightarrow S_1$	328.9	3.77	0.40	H→L	0.7
	$S_0 \rightarrow S_2$	302.1	4.10	0.20	H-1→L	0.7
trans-OO	$S_0 \rightarrow S_1$	301.5	4.11	0.81	H→L	0.7
	$S_0 \rightarrow S_4$	238.6	5.20	0.39	H→L+2	0.6
trans-OS	$S_0 \rightarrow S_1$	306.9	4.04	0.54	H→L	0.7
	$S_0 \rightarrow S_2$	284.6	4.36	0.20	H-1→L	0.6
trans-SS	$S_0 \rightarrow S_1$	315.8	3.93	0.28	H→L	0.7
	$S_0 \rightarrow S_2$	293.2	4.23	0.45	H-1→L	0.7

(b) emission spectra

in vacuum

Species	Electronic transitions	λ_{max}(nm)	Excitation energies (eV)	f	Main configurations	Coefficient
trans-CC	$S_1 \rightarrow S_0$	388.4	3.19	0.44	L→H	0.7
trans-CN	$S_1 \rightarrow S_0$	367.3	3.38	0.34	L→H	0.7
trans-CO	$S_1 \rightarrow S_0$	353.8	3.50	0.53	L→H	0.7
trans-CSi	$S_1 \rightarrow S_0$	439.9	2.82	0.26	L→H	0.7
trans-CP	$S_1 \rightarrow S_0$	422.3	2.94	0.28	L→H	0.7
trans-CS	$S_1 \rightarrow S_0$	360.3	3.44	0.47	L→H	0.7
trans-SiN	$S_1 \rightarrow S_0$	422.4	2.94	0.13	L→H	0.7
trans-SiO	$S_1 \rightarrow S_0$	402.4	3.08	0.25	L→H	0.7
trans-SiSi	$S_1 \rightarrow S_0$	474.8	2.61	0.23	L→H	0.7
trans-SiP	$S_1 \rightarrow S_0$	456.3	2.72	0.24	L→H	0.7
trans-SiS	$S_1 \rightarrow S_0$	404.4	3.07	0.26	L→H	0.7
trans-NN	$S_1 \rightarrow S_0$	396.5	3.13	0.12	L→H	0.7
trans-NO	$S_1 \rightarrow S_0$	357.6	3.47	0.27	L→H	0.7
trans-NP	$S_1 \rightarrow S_0$	411.4	3.01	0.15	L→H	0.7
trans-NS	$S_1 \rightarrow S_0$	369.2	3.36	0.17	L→H	0.7
trans-PO	$S_1 \rightarrow S_0$	391.4	3.17	0.27	L→H	0.7
trans-PP	$S_1 \rightarrow S_0$	433.2	2.86	0.25	L→H	0.7

trans-PS	$S_1 \rightarrow S_0$	394.2	3.15	0.27	L→H	0.7
trans-OO	$S_1 \rightarrow S_0$	328.2	3.78	0.64	L→H	0.7
trans-OS	$S_1 \rightarrow S_0$	338.9	3.66	0.40	L→H	0.7
trans-SS	$S_1 \rightarrow S_0$	349.8	3.54	0.23	L→H	0.7

in solvent

Species	Electronic transitions	λ_{max}(nm)	Excitation energies (eV)	f	Main configurations	Coefficient	τ (ns)
trans-CC	$S_1 \rightarrow S_0$	397.9	3.12	0.58	L→H	0.7	4.09
trans-CN	$S_1 \rightarrow S_0$	374.9	3.31	0.46	L→H	0.7	4.58
trans-CO	$S_1 \rightarrow S_0$	363.1	3.41	0.70	L→H	0.7	2.84
trans-CSi	$S_1 \rightarrow S_0$	445.8	2.78	0.36	L→H	0.7	8.30
trans-CP	$S_1 \rightarrow S_0$	429.4	2.89	0.39	L→H	0.7	7.09
trans-CS	$S_1 \rightarrow S_0$	369.1	3.36	0.63	L→H	0.7	3.25
trans-SiN	$S_1 \rightarrow S_0$	421.7	2.94	0.19	L→H	0.7	14.06
trans-SiO	$S_1 \rightarrow S_0$	405.3	3.06	0.36	L→H	0.7	6.85
trans-SiSi	$S_1 \rightarrow S_0$	481.0	2.58	0.31	L→H	0.7	11.19
trans-SiP	$S_1 \rightarrow S_0$	462.8	2.68	0.32	L→H	0.7	10.05
trans-SiS	$S_1 \rightarrow S_0$	409.3	3.03	0.37	L→H	0.7	6.80
trans-NN	$S_1 \rightarrow S_0$	404.7	3.06	0.17	L→H	0.7	14.51
trans-NO	$S_1 \rightarrow S_0$	364.3	3.40	0.37	L→H	0.7	5.40
trans-NP	$S_1 \rightarrow S_0$	414.3	2.99	0.21	L→H	0.7	12.3
trans-NS	$S_1 \rightarrow S_0$	372.2	3.33	0.24	L→H	0.7	8.68
trans-PO	$S_1 \rightarrow S_0$	396.2	3.13	0.38	L→H	0.7	6.20
trans-PP	$S_1 \rightarrow S_0$	440.1	2.82	0.35	L→H	0.7	8.30
trans-PS	$S_1 \rightarrow S_0$	400.0	3.10	0.38	L→H	0.7	6.32
trans-OO	$S_1 \rightarrow S_0$	337.3	3.68	0.83	L→H	0.7	2.05
trans-OS	$S_1 \rightarrow S_0$	344.8	3.60	0.58	L→H	0.7	3.07
trans-SS	$S_1 \rightarrow S_0$	352.7	3.52	0.36	L→H	0.7	5.18