

A Theoretical Investigation of Heavy Atom and Oxidation Effects in MR-TADF Emitters for OLEDs: A Combined DFT, Double hybrid DFT, CCSD, and QM/MM Approaches

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Spin-orbit coupling (SOC) calculation

The spin-orbit coupling (SOC) calculations were performed utilizing the ORCA 5.0 software.¹ The SOC values were determined for T₁ geometries using the M06/def2-SVP level of theory. The equation is,

$$\text{SOC} = \sqrt{(\langle S_n | \widehat{H_{\text{SOC}}}^x | T_n \rangle^2 + \langle S_n | \widehat{H_{\text{SOC}}}^y | T_n \rangle^2 + \langle S_n | \widehat{H_{\text{SOC}}}^z | T_n \rangle^2)/3} \quad (1)$$

For instance, the calculated SOC values for molecule **1**, specifically between the S₁ and T₁ states, use the optimized T₁ geometry.

Molecule	SOCx	SOCy	SOCz	x ²	y ²	z ²	x ² + y ² + z ²	(x ² + y ² + z ²)/3	SQRT ((x ² + y ² + z ²)/3)
1	0.00	0.59	0.00	0.00	0.3481	0.00	0.3481	0.1160	0.34

Rate calculation

The reverse intersystem crossing rates (RISC) were calculated by using semiclassical Marcu's equation,²

$$k_{(R)ISC} = \frac{2\pi}{\hbar} \left| \langle I_{\psi_1^0} | \widehat{H_{SO}} | 3_{\psi_F^0} \rangle \right|^2 \frac{1}{\sqrt{4\pi\lambda K_B T}} \exp \left(-\frac{(AE_{ST} + \lambda)^2}{4\lambda K_B T} \right) \quad (2)$$

\hbar	-	Reduced Planck's constant.
K_B	-	Boltzmann constant.
$ H_{SO} $	-	Spin-orbit coupling
T	-	Temperature.
λ	-	Reorganization energy.

The intramolecular re-organization energy for ISC rate is,

$$\lambda^{ISC} = E_S^T - E_T^T \quad (3)$$

where E_S^T represent the energy of triplet state at single state geometry, and E_T^T represent the energy of triplet state at triplet state geometry. In this regard, the intramolecular reorganization energy for ISC is calculated for experimentally reported molecules.

Molecules	E_S^T	E_T^T	λ^{ISC} (in Hartree) S_1-T_1	λ^{ISC} (in eV) S_1-T_1
5	-2083.1679	-2083.1662	0.0017	0.05
9	-1685.0250	-1685.0229	0.0021	0.06
17	-2186.0507	-2186.0489	0.0018	0.05
21	-1802.8612	-1802.8594	0.0018	0.05
29	-6085.3833	-6085.3820	0.0014	0.04
33	-3686.1315	-3686.1299	0.0016	0.04
37	-4000.3942	-4000.3927	0.0014	0.04

The intramolecular re-organization energy for the RISC rate is,

$$\lambda^{RISC} = E_T^S - E_S^S \quad (4)$$

where E_T^S represent the energy of singlet state at triplet state geometry, and E_S^S represent the energy of the singlet state at singlet state geometry. In this regard, the intramolecular reorganization energy for RISC is calculated for experimentally reported molecules.

Molecules	E_T^S	E_S^S	λ^{RISC} (in Hartree) S_1-T_1	λ^{RISC} (in eV) S_1-T_1
5	-2083.1562	-2083.1567	0.0005	0.01
9	-1685.0133	-1685.0144	0.0010	0.03
17	-2186.0388	-2186.0393	0.0005	0.01
21	-1802.8490	-1802.8495	0.0005	0.01
29	-6085.3716	-6085.3725	0.0008	0.02
33	-3686.1202	-3686.1213	0.0011	0.03
37	-4000.3828	-4000.3837	0.0009	0.02

The energy gap ΔE_{ST} (calculated using the M06 functional) reflects the difference in energy levels between the pertinent excited states. In our calculations for rates, we integrated the SOC values obtained from optimizing the geometry of the T_1 state. The overall reorganization energy

encompasses both intramolecular reorganization and contributions from the external environment. Therefore, when determining the rates of ISC and RISC, we factored in a total reorganization energy of 0.16 eV. This value encapsulates the effects of relaxations induced by the medium, a topic extensively discussed in previous studies.³ Therefore, the SOC value between these states for molecule 1 is determined to be 0.000042155 eV.

For ISC:

$$\frac{2\pi}{\hbar} |H_{so}|^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} = 7.44 * 10^{+07} \text{ eV s}^{-1}$$

$$\exp\left(-\frac{(\lambda - \Delta E_{ST})^2}{4\lambda k_B T}\right) = 2.57 * 10^{-01} \text{ eV}^{-1}$$

$$k(ISC) = 1.91 \times 10^{+07} \text{ s}^{-1}$$

For RISC:

$$\frac{2\pi}{\hbar} |H_{so}|^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} = 7.44 * 10^{+07} \text{ eV s}^{-1}$$

$$\exp\left(-\frac{(\lambda + \Delta E_{ST})^2}{4\lambda k_B T}\right) = 1.59 * 10^{-06} \text{ eV}^{-1}$$

$$k(RISC) = 1.18 \times 10^{+02} \text{ s}^{-1}$$

The numerical values used in ISC and RISC rate calculation:

π	-	3.141
V	-	SOC values (in eV)
\hbar	-	6.5821×10^{-16} eV s
K_B	-	8.6173×10^{-5} eV K ⁻¹
λ	-	0.16 eV
T	-	300 K

Delayed fluorescence rate, Quantum yields, Internal, and External quantum efficiency

The delayed fluorescence rate constant can be calculated theoretically by using the equation,

$$K_{TADF}^{-1} = K_{PF}^{-1} + K_{RISC}^{-1} \quad (5)$$

The external quantum efficiency (ϕ_{EQE}) can be calculated by,

$$\phi_{EQE} = \phi_{IQE} * \eta_{out} \quad (6)$$

The value of the output sheet coupling (η_{out}) typically ranges between 0.2 and 0.3.

The internal quantum efficiency (ϕ_{IQE}) can be calculated by,

$$\phi_{IQE} = \eta_r(S_1) \phi_{PF} + \eta_r(T_1) \phi_{ISC} \phi_{RISC} + \eta_r(T_1) \phi_{RISC} \quad (7)$$

where $\eta_r(S_1) = 0.25$ and $\eta_r(T_1) = 0.75$ are the branching ratios of the formation of singlet and triplet excitons, respectively. The efficiency of prompt fluorescence (ϕ_{PF}), inter-system crossing (ϕ_{ISC}), and reverse-intersystem crossing rate (ϕ_{RISC}) can be calculated by,

$$\phi_{PF} = 1 - \phi_{ISC} \quad (8)$$

$$\phi_{ISC} = \frac{K_{ISC}}{K_{PF}} \quad (9)$$

$$\phi_{RISC} = \frac{\phi_{TADF}}{\phi_{ISC}} \quad (10)$$

$$\phi_{TADF} = \frac{K_{ISC} * \phi_{PF} * K_{RISC}}{K_{PF} * K_{TADF}} \quad (11)$$

The photoluminescence quantum yield (PLQY) can be calculated by,

$$PLQY = \phi_{PF} + \phi_{TADF} \quad (12)$$

Table S1. Calculated HOMO and LUMO energy for reference molecules at 6-31+G(d) basis set. (All energies are in eV)

Molecules	BH & HLYP	BP86	BMK	O3LYP	B3LYP	PBE0	M06	M06-2X	CAM-B3LYP	WB97XD	Exp.
HOMO											
5	-6.24	-4.76	-5.98	-4.97	-5.32	-5.52	-5.59	-6.48	-6.57	-7.13	-5.04⁴
9	-6.31	-4.86	-6.07	-5.06	-5.41	-5.62	-5.68	-6.58	-6.65	-7.20	-
17	-6.16	-4.72	-5.91	-4.92	-5.27	-5.48	-5.55	-6.43	-6.50	-7.06	-5.18⁴
21	-6.15	-4.71	-5.90	-4.91	-5.26	-5.46	-5.55	-6.42	-6.49	-7.04	-5.15⁴
29	-6.31	-4.81	-6.02	-5.02	-5.38	-5.58	-5.67	-6.56	-6.64	-7.21	-5.21⁵
33	-6.35	-4.90	-6.09	-5.10	-5.45	-5.67	-5.74	-6.62	-6.69	-7.25	-
37	-6.25	-4.82	-6.00	-5.01	-5.37	-5.57	-5.66	-6.53	-6.59	-7.15	-5.36⁶
LUMO											
5	-1.03	-2.74	-1.49	-2.19	-2.06	-1.95	-1.89	-1.32	-0.97	-0.39	-2.61⁴
9	-1.11	-2.81	-1.58	-2.27	-2.13	-2.04	-1.97	-1.42	-1.06	-0.48	-
17	-0.93	-2.66	-1.41	-2.11	-1.98	-1.88	-1.82	-1.25	-0.89	-0.30	-2.72⁴
21	-0.91	-2.64	-1.38	-2.08	-1.95	-1.85	-1.80	-1.22	-0.86	-0.28	-2.68⁴
29	-1.05	-2.76	-1.50	-2.21	-2.08	-1.98	-1.93	-1.35	-0.99	-0.41	-2.72⁵
33	-1.11	-2.82	-1.58	-2.28	-2.14	-2.05	-1.98	-1.43	-1.07	-1.43	-
37	-1.05	-2.75	-1.52	-2.19	-2.07	-1.98	-1.93	-1.38	-1.00	-0.43	-2.81⁶

Table S2. Calculated the vertical singlet (S_1) and triplet (T_1) energies, and singlet-triplet energy differences (ΔE_{ST}) of reference molecules at 6-31+G(d) basis set along with experimental values. (All energies are in eV)

Molecules	BH&HLYP	BP86	BMK	O3LYP	B3LYP	PBE0	M06	M06-2X	CAM-B3LYP	WB97XD	Exp.
S_1											
5	3.34	2.24	3.04	2.54	2.70	2.80	2.83	3.18	3.24	3.30	2.45 ⁴
9	3.37	2.25	3.07	2.26	2.39	2.83	2.86	3.22	3.26	3.33	2.63 ⁷
17	3.35	2.28	3.05	2.58	2.73	2.83	2.86	3.20	3.25	3.31	2.45 ⁴
21	3.36	2.30	3.06	2.59	2.74	2.84	2.87	3.21	3.26	3.32	2.45 ⁴
29	3.39	2.26	3.08	2.56	2.73	2.83	2.87	3.23	3.28	3.34	2.63 ⁵
33	3.39	2.26	3.10	2.58	2.76	2.86	2.90	3.24	3.29	3.35	2.60 ⁷
37	3.36	2.27	3.07	2.58	2.74	2.84	2.87	3.21	3.26	3.32	2.61 ⁶
T_1											
5	2.67	1.97	2.62	2.22	2.35	2.41	2.49	2.76	2.73	2.80	2.29 ⁴
9	2.46	2.01	2.66	2.26	2.39	2.45	2.52	2.80	2.72	2.81	2.53 ⁷
17	2.69	2.02	2.64	2.26	2.38	2.44	2.52	2.77	2.74	2.81	2.30 ⁴
21	2.69	2.03	2.64	2.27	2.38	2.44	2.53	2.77	2.75	2.82	2.31 ⁴
29	2.69	2.01	2.67	2.26	2.39	2.45	2.54	2.81	2.78	2.85	2.46 ⁵
33	2.46	2.04	2.70	2.29	2.42	2.48	2.56	2.83	2.73	2.83	2.48 ⁷
37	2.43	2.03	2.67	2.29	2.41	2.47	2.54	2.80	2.73	2.83	2.52 ⁶
ΔE_{ST}											
5	0.68	0.27	0.42	0.32	0.35	0.39	0.34	0.43	0.50	0.50	0.16 ⁴
9	0.91	0.25	0.41	0.30	0.34	0.38	0.34	0.42	0.55	0.51	0.11 ⁷
17	0.66	0.26	0.41	0.31	0.35	0.39	0.34	0.42	0.50	0.49	0.14 ⁴
21	0.67	0.27	0.42	0.32	0.36	0.40	0.35	0.43	0.51	0.50	0.14 ⁴
29	0.70	0.25	0.41	0.30	0.34	0.38	0.33	0.42	0.50	0.49	0.17 ⁵
33	0.94	0.23	0.41	0.29	0.33	0.38	0.34	0.41	0.56	0.52	0.11 ⁷
37	0.93	0.24	0.40	0.29	0.33	0.37	0.33	0.41	0.53	0.50	0.09 ⁶

Table S3. Calculated bond length (Å), bond angles (°), and dihedral angles (°) for designed molecules at optimized S₀ state at B3LYP/6-31+G(d) level of theory.

Molecules	Θ_1	Θ_2	Θ_3	δ_1	δ_2	δ_3	l_1
1	122.86	104.90	104.90	180.00	-	-	1.55
2	125.57	99.37	99.38	179.99	-	-	1.56
3	121.38	98.78	98.78	180.00	-	-	1.42
4	122.33	94.92	94.92	180.00	-	-	1.41
5	130.15	97.52	97.52	180.00	165.07	164.62	1.52
	(129.91)	(97.65)	(97.49)	(179.98)	(164.69)	(165.63)	(1.52)
6	130.26	93.55	93.55	180.00	164.41	163.84	1.52
7	120.16	105.66	105.66	180.00	177.72	177.84	1.41
8	120.46	178.45	178.52	180.00	100.24	100.24	1.41
9	129.42	97.35	-	176.14	-	172.43	1.53
	(125.59)	(106.77)	-	(177.19)	-	(176.42)	(1.55)
10	129.47	93.39	-	176.55	163.73	172.47	1.53
11	119.41	105.76	-	175.12	177.56	168.57	1.42
12	119.57	100.40	-	176.66	178.37	166.57	1.42
13	129.46	97.38	-	176.01	164.56	172.49	1.53
14	129.52	93.41	-	176.42	162.94	173.30	1.53
15	119.51	105.76	-	175.14	177.57	168.20	1.42
16	119.67	100.40	-	176.60	178.50	166.14	1.42
17	130.27	97.50	-	179.73	164.80	170.53	1.52
	(129.85)	(97.12)	-	(179.12)	(160.52)	(170.02)	(1.51)
18	130.33	93.56	-	179.84	164.02	170.22	1.52
19	120.21	105.74	-	178.65	177.38	178.70	1.41
20	128.05	100.23	-	179.58	179.22	178.29	1.41
21	129.00	97.52	-	179.12	164.95	170.11	1.49
	(128.97)	(97.76)	-	(178.64)	(163.68)	(174.87)	(1.50)
22	130.32	93.59	-	179.94	163.58	170.66	1.52
23	120.05	105.66	-	179.43	177.89	175.55	1.41
24	120.23	100.11	-	178.88	177.81	175.16	1.41
25	120.79	100.48	100.48	180.00	-	-	1.56
26	123.80	95.54	95.53	180.00	-	-	1.57
27	120.63	95.00	95.00	180.00	-	-	1.42
28	121.37	91.67	91.67	179.99	-	-	1.42
29	130.21	93.39	93.39	180.00	160.52	159.99	1.52
	(129.78)	(93.51)	(93.73)	(178.87)	(163.17)	(163.95)	(1.51)
30	130.34	90.09	90.09	180.00	159.89	159.26	1.52
31	120.40	101.78	101.78	180.00	179.98	179.98	1.41
32	120.61	98.15	98.15	180.00	176.59	176.37	1.41
33	129.45	93.17	-	175.97	-	172.41	1.53
	(123.92)	(101.84)	-	(179.56)	-	(169.76)	(1.54)
34	129.52	89.85	-	176.48	159.49	172.39	1.53
35	119.53	101.96	-	174.94	179.70	167.85	1.42
36	119.65	98.25	-	176.30	176.11	166.70	1.42
37	129.52	93.18	-	175.84	160.44	172.31	1.53

38	129.58	89.88	-	176.40	159.61	172.11	1.53
39	119.62	101.98	-	175.05	179.73	167.44	1.42
40	119.72	98.27	-	176.49	176.11	166.25	1.42
41	130.28	93.38	-	179.57	160.05	170.65	1.52
42	130.34	90.03	-	179.98	159.68	170.34	1.52
43	120.33	101.91	-	178.55	178.77	179.64	1.41
44	120.43	98.13	-	179.84	176.14	179.25	1.41
45	130.30	93.38	-	179.35	160.37	170.13	1.52
46	130.36	90.05	-	179.77	160.16	170.29	1.52
47	120.16	101.77	-	179.34	179.72	175.52	1.41
48	120.34	97.93	-	179.32	175.51	175.18	1.41

Parentheses represent the experimental values.⁴⁻⁷

Table S4. Calculated bond length (Å), bond angles (°), and dihedral angles (°) for designed molecules in crystal phase.

Molecules	Θ_1	Θ_2	Θ_3	δ_1	δ_2	δ_3	l_1
5	130.05	97.36	97.23	-179.74	164.16	168.97	1.52
9	125.23	105.74	-	-176.05	-	175.67	1.54
17	129.10	96.65	-	179.80	162.21	169.39	1.51
29	129.87	93.12	93.84	-178.30	160.61	165.94	1.52
33	124.90	100.88	-	177.99	-	172.80	1.55

Table S5. Calculated the excited state properties of the reported molecules in crystal phases.

Molecules	PBE0				M06			
	S ₁	T ₁	ΔE_{ST}	f ₀	S ₁	T ₁	ΔE_{ST}	f ₀
5	2.83	2.41	0.42	0.23	2.86	2.49	0.37	0.22
9	3.00	2.52	0.47	0.23	3.01	2.58	0.43	0.22
17	2.90	2.47	0.43	0.31	2.93	2.55	0.38	0.30
29	2.84	2.42	0.42	0.24	2.88	2.50	0.37	0.23
33	2.97	2.53	0.44	0.20	2.99	2.58	0.41	0.20

Table S6. Calculated the absorption (λ_{abs}) and emission (λ_{emi}) wavelength (in nm) mean separation distance (Δr in Å), overlap extent (λ_{OC} in %) for vertical singlet (S_1) and triplet (T_1) energies), and the intersystem crossing rates (k_{ISC} in s^{-1}), reverse intersystem crossing rates (k_{RISC} in s^{-1}), at M06/6-31+G(d) level of theory.

Molecules	λ_{abs}	λ_{emi}	S_1		T_1		$k_{\text{ISC}} (S_1-T_1)$	$k_{\text{RISC}} (T_1-S_1)$ $\lambda = 0.20 \text{ eV}$
			λ_{OC}	S_1	T_1	Δr		
1	411	431	0.58	0.58	1.10	1.10	$6.54*10^{+07}$	$2.30*10^{+02}$
2	397	450	0.44	0.49	1.18	1.31	$9.48*10^{+06}$	$8.81*10^{+02}$
3	348	428	0.62	0.61	0.12	0.24	$2.04*10^{+07}$	$8.60*10^{+01}$
4	319	353	0.61	0.65	1.23	0.91	$5.61*10^{+05}$	$1.10*10^{+02}$
5	438	479	0.57	0.57	1.28	1.28	$2.04*10^{+07}$	$8.30*10^{+02}$
6	378	452	0.57	0.57	1.49	1.49	$1.16*10^{+07}$	$3.40*10^{+02}$
7	410	484	0.54	0.54	1.37	1.35	$6.43*10^{+06}$	$1.93*10^{+03}$
8	389	458	0.62	0.62	0.38	0.89	$7.73*10^{+07}$	$7.10*10^{+02}$
9	432	491	0.55	0.56	2.37	2.39	$4.51*10^{+07}$	$0.20*10^{+05}$
10	420	443	0.58	0.58	1.47	1.48	$3.68*10^{+07}$	$7.30*10^{+01}$
11	452	485	0.55	0.55	3.03	3.11	$4.02*10^{+07}$	$0.11*10^{+05}$
12	436	534	0.59	0.58	1.93	3.16	$1.07*10^{+07}$	$2.32*10^{+02}$
13	436	485	0.56	0.56	1.85	1.85	$3.30*10^{+07}$	$0.21*10^{+05}$
14	427	448	0.58	0.58	1.46	1.46	$3.68*10^{+06}$	$7.30*10^{+01}$
15	451	536	0.55	0.52	2.67	3.46	$2.01*10^{+07}$	$0.13*10^{+05}$
16	440	543	0.57	0.61	2.63	2.75	$1.34*10^{+06}$	$8.01*10^{+02}$
17	434	475	0.57	0.57	1.51	1.51	$1.45*10^{+07}$	$6.23*10^{+02}$
18	427	459	0.58	0.58	1.66	1.66	$9.09*10^{+06}$	$1.80*10^{+02}$
19	449	472	0.55	0.55	2.08	2.08	$6.06*10^{+06}$	$8.60*10^{+02}$
20	437	475	0.61	0.61	2.02	2.02	$3.68*10^{+06}$	$7.30*10^{+01}$
21	432	472	0.58	0.58	1.39	1.39	$3.62*10^{+07}$	$0.34*10^{+05}$
22	426	458	0.58	0.58	1.74	1.74	$2.59*10^{+06}$	$0.10*10^{+01}$
23	449	472	0.55	0.55	1.89	1.89	$3.68*10^{+07}$	$0.24*10^{+05}$
24	438	481	0.61	0.61	2.06	2.06	$7.51*10^{+06}$	$1.50*10^{+02}$
25	432	457	0.55	0.55	1.12	1.12	$2.05*10^{+08}$	$1.30*10^{+03}$
26	394	507	0.36	0.52	1.52	0.94	$1.13*10^{+08}$	$3.23*10^{+02}$
27	337	409	0.56	0.55	0.52	0.64	$1.57*10^{+08}$	$4.50*10^{+02}$
28	314	343	0.58	0.64	1.27	0.39	$6.85*10^{+05}$	$3.94*10^{-04}$
29	384	472	0.56	0.56	1.35	1.35	$3.79*10^{+07}$	$1.63*10^{+03}$
30	373	449	0.57	0.57	1.55	1.55	$1.36*10^{+07}$	$4.00*10^{+02}$
31	414	492	0.52	0.52	1.37	1.34	$8.29*10^{+06}$	$3.62*10^{+03}$
32	387	456	0.61	0.61	0.89	0.89	$3.68*10^{+06}$	$7.30*10^{+01}$
33	427	480	0.54	0.54	1.37	1.35	$3.79*10^{+08}$	$0.24*10^{+06}$
34	418	442	0.62	0.62	0.89	0.89	$1.27*10^{+07}$	$2.51*10^{+02}$
35	457	488	0.52	0.58	0.52	0.58	$3.55*10^{+08}$	$0.23*10^{+06}$
36	435	533	0.59	0.58	1.82	3.21	$8.42*10^{+05}$	$2.30*10^{+02}$
37	431	474	0.56	0.56	1.61	1.61	$2.45*10^{+08}$	$0.34*10^{+06}$
38	425	447	0.59	0.59	1.57	1.57	$1.08*10^{+07}$	$2.14*10^{+02}$
39	455	484	0.53	0.52	2.96	3.52	$3.08*10^{+08}$	$0.20*10^{+06}$
40	439	542	0.57	0.6	2.54	2.85	$1.34*10^{+06}$	$8.01*10^{-02}$

41	430	466	0.57	0.57	1.42	1.42	$4.05 \times 10^{+07}$	$2.50 \times 10^{+01}$
42	426	459	0.58	0.58	1.77	1.77	$1.47 \times 10^{+07}$	$2.91 \times 10^{+02}$
43	454	477	0.53	0.53	2.33	2.33	$1.71 \times 10^{+08}$	$1.60 \times 10^{+03}$
44	436	473	0.60	0.60	1.96	1.96	$1.58 \times 10^{+07}$	$4.61 \times 10^{+02}$
45	428	464	0.58	0.58	1.36	1.36	$1.42 \times 10^{+08}$	$0.20 \times 10^{+06}$
46	425	459	0.58	0.58	1.86	1.86	$1.56 \times 10^{+07}$	$2.10 \times 10^{+02}$
47	454	477	0.53	0.54	2.10	2.10	$2.03 \times 10^{+08}$	$0.28 \times 10^{+06}$
48	435	478	0.60	0.60	2.00	2.00	$2.57 \times 10^{+06}$	7.22×10^{-01}

Table S7. Calculated the delayed fluorescence rate (K_{TADF} in 10^{+05} s^{-1}), internal quantum efficiency (Φ_{IQE}), external quantum efficiency ($\Phi_{\text{EQE}} \%$), and photoluminescence quantum yield (PLQY %) for eight molecules.

Molecules	K_{TADF}	Φ_{IQE}	Φ_{EQE}	PLQY
11	0.11	0.84	21.10	96.18
13	0.04	0.69	17.35	86.75
15	0.05	0.89	22.37	98.19
23	0.14	0.86	21.62	97.09
35	2.23	-	-	-
39	19.9	-	-	-
45	1.30	-	-	-
47	1.20	-	-	-

Table S8. Calculated the singlet (S_1), triplet (T_1) energies, ΔE_{ST} , (all values are in eV), and oscillator strength (f_0) at the B2PLYP/PBE0-2/STEOM-DLPNO-CCSD//def2-SVP level of theory.

Molecules	B2PLYP				PBE0-2				STEOM-DLPNO-CCSD			
	S_1	T_1	ΔE_{ST}	f_0	S_1	T_1	ΔE_{ST}	f_0	S_1	T_1	ΔE_{ST}	f_0
11	2.79	2.59	0.20	0.28	3.49	2.70	0.79	0.00	2.66	2.33	0.33	0.38
13	2.84	2.39	0.45	0.32	3.12	3.11	0.01	0.37	2.75	2.62	0.13	0.41
15	3.09	2.55	0.54	0.04	3.41	2.67	0.74	0.00	2.64	2.27	0.37	0.38
23	2.74	2.33	0.41	0.34	3.02	3.03	-0.01	0.37	2.63	2.55	0.08	0.35
35	2.71	2.59	0.12	0.29	3.49	2.70	0.79	0.00	2.65	2.33	0.32	0.38
39	3.07	2.55	0.52	0.02	3.41	2.67	0.74	0.00	2.62	2.26	0.36	0.38
45	2.88	2.35	0.53	0.27	3.15	3.14	0.01	0.29	2.79	2.62	0.17	0.34
47	2.70	2.31	0.39	0.09	2.93	2.99	-0.06	0.00	2.63	2.54	0.09	0.36

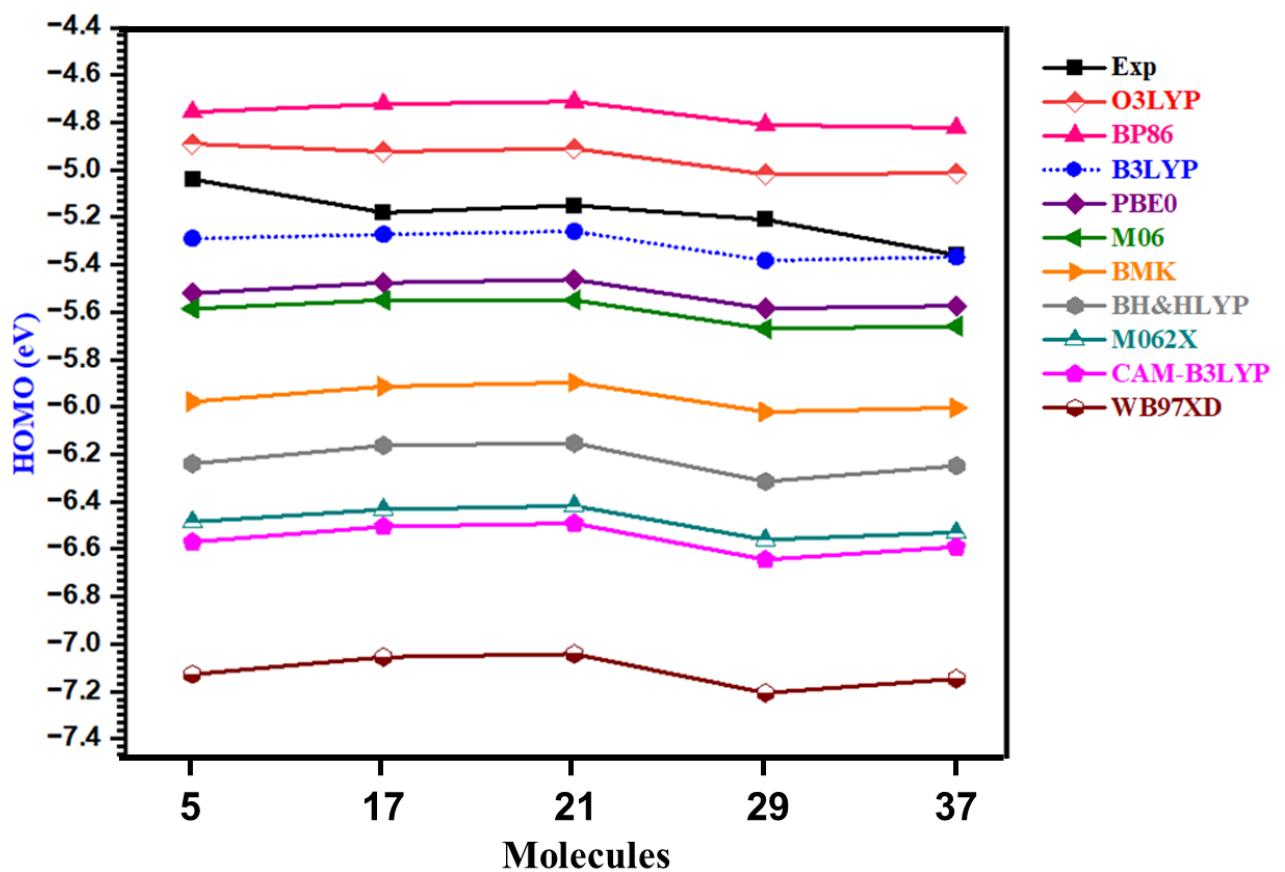


Figure S1. Comparison of HOMO energy for experimental molecules with computed results at different functionals with 6-31+G(d) basis set. (All energies are in eV)

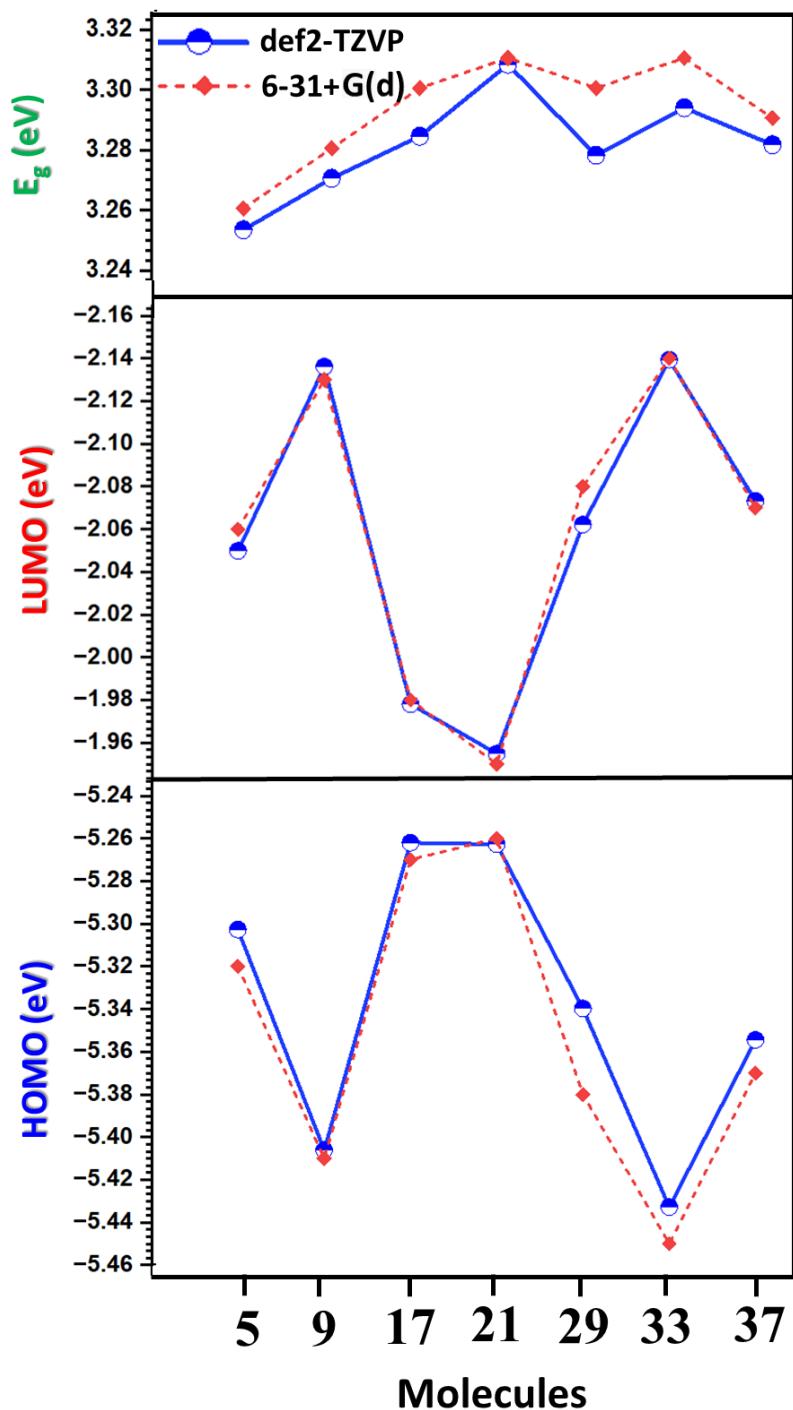


Figure S2. Comparison of HOMO, LUMO, and E_g gap for experimental molecules at B3LYP functional with def2-TZVP/6-31+G(d) level of theory. (All energies are in eV)

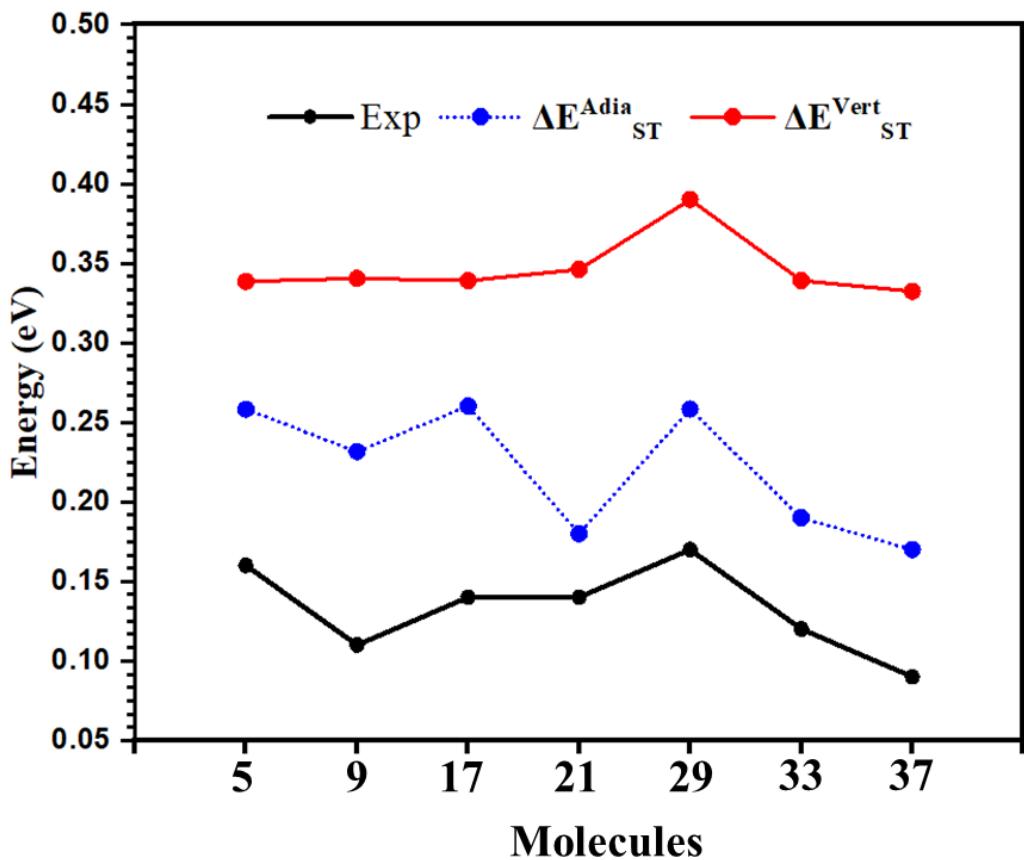


Figure S3. Comparison of vertical and adiabatic energy gap (ΔE_{ST}) for experimental molecules at M06/6-31+G(d) level of theory. (All energies are in eV)

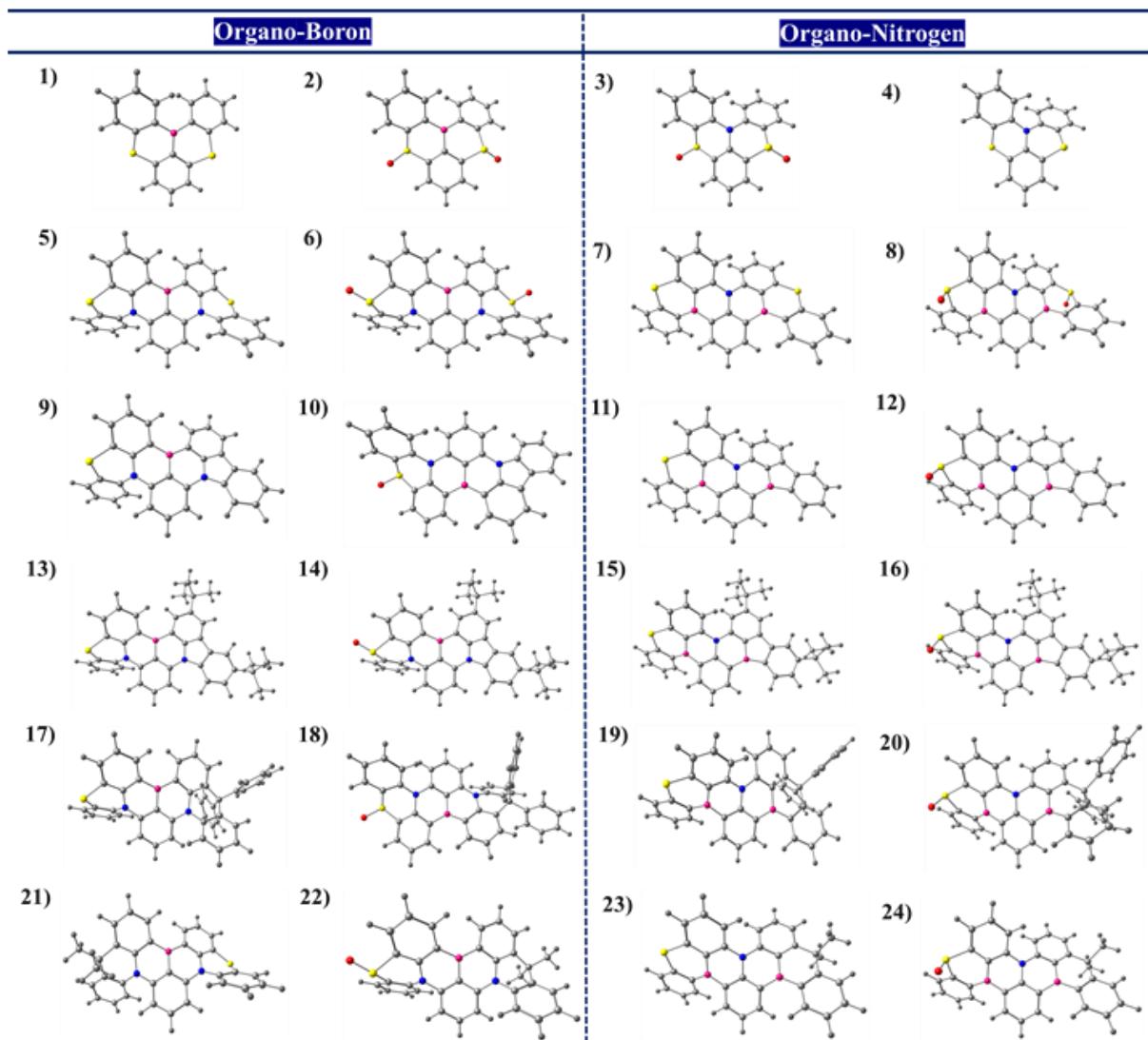


Figure S4. Optimized geometry of sulfur-incorporated OB/ON molecules at B3LYP/6-31+G(d) level of theory.

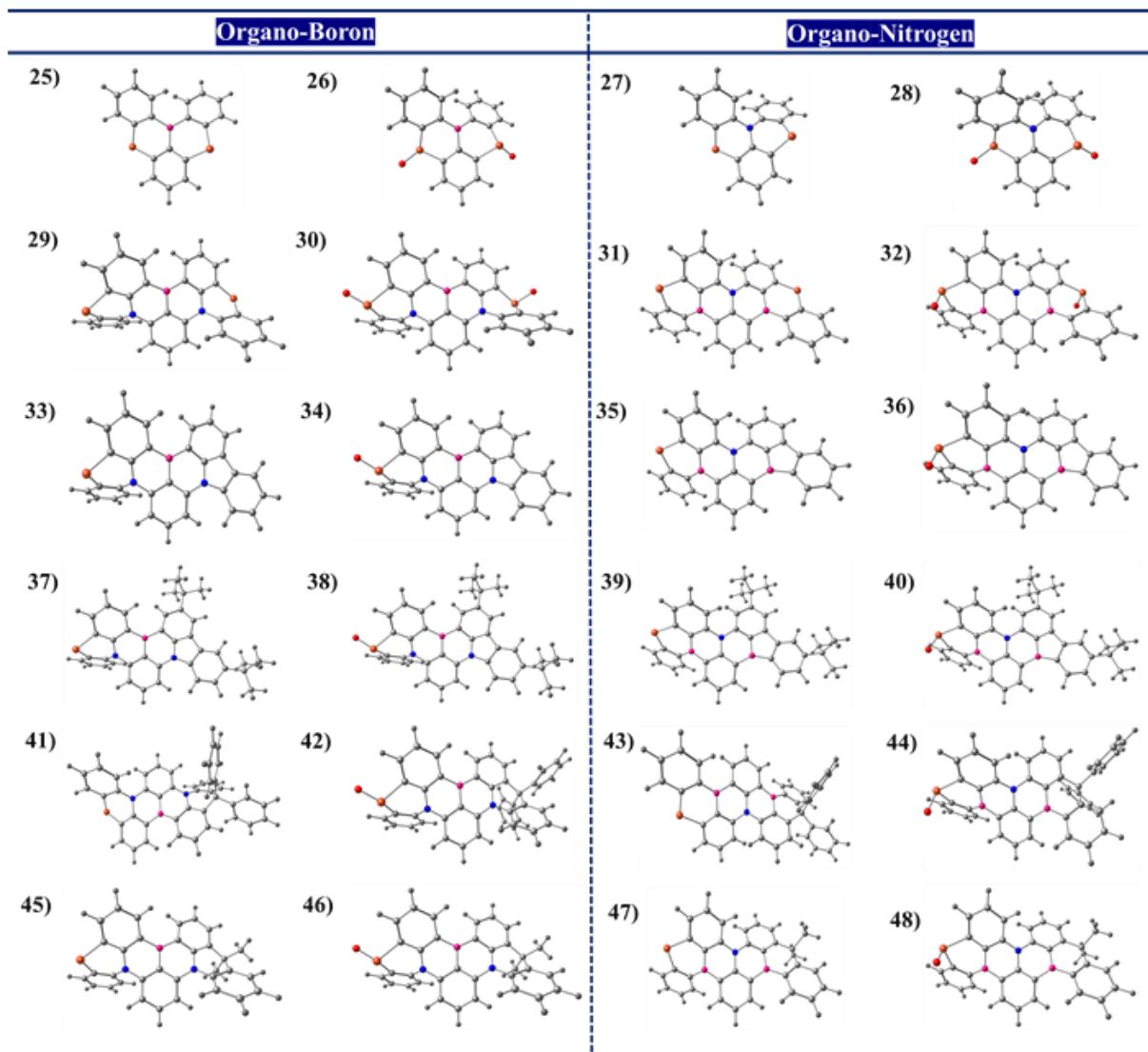


Figure S5. Optimized geometry of selenium-incorporated OB/ON molecules at B3LYP/6-31+G(d) level of theory.

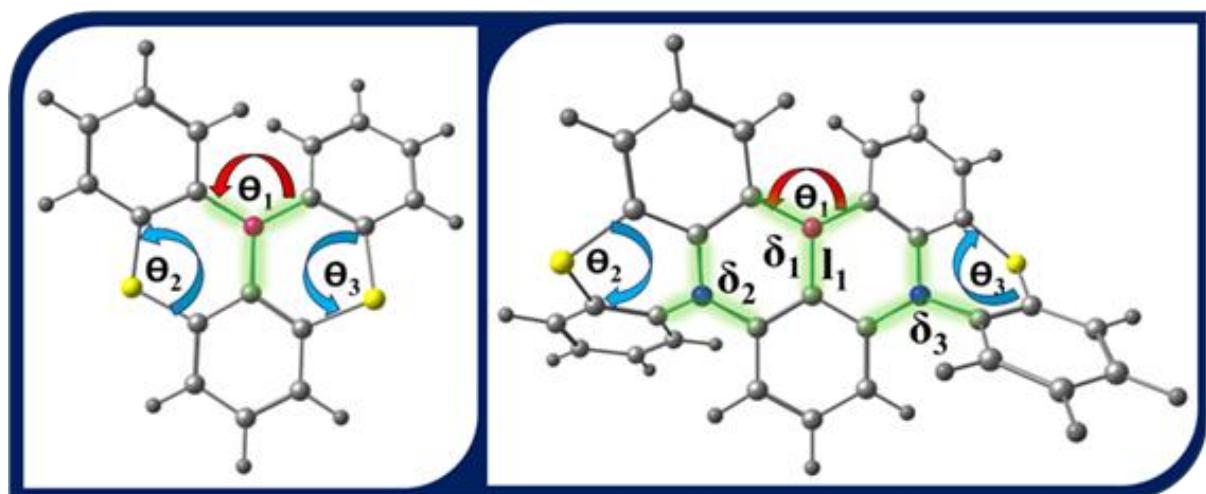


Figure S6. The selected bond length (l), dihedral angles (δ), and bond angle (θ) for designed molecules.

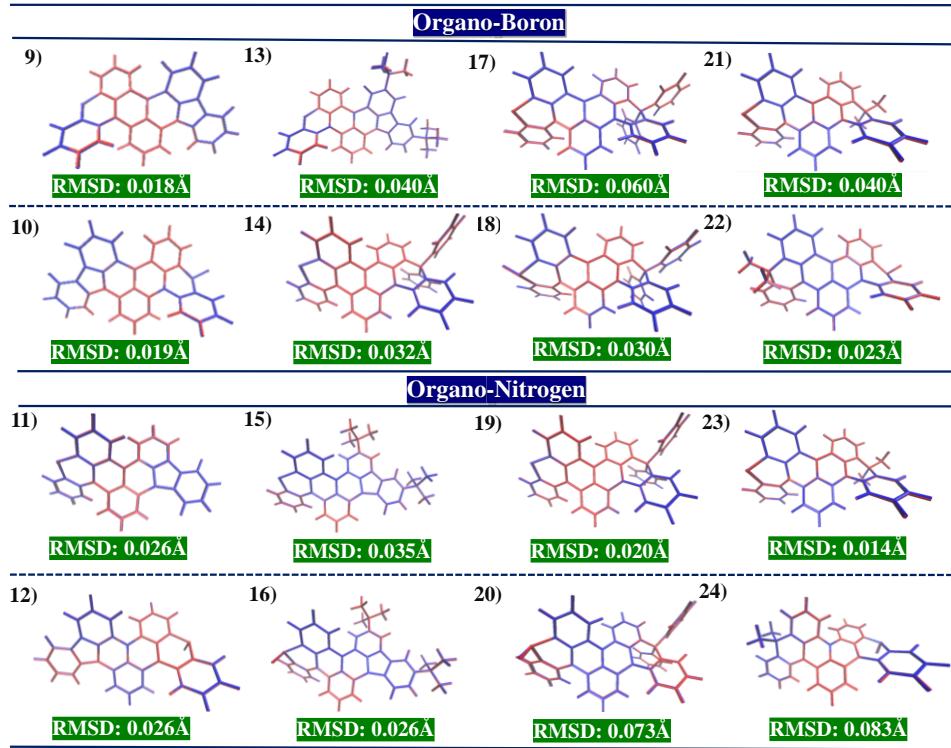


Figure S7: Structural differences between the S₁ and T₁ states for sulfur-incorporated molecules (color codes: blue for S₁ and red for T₁).

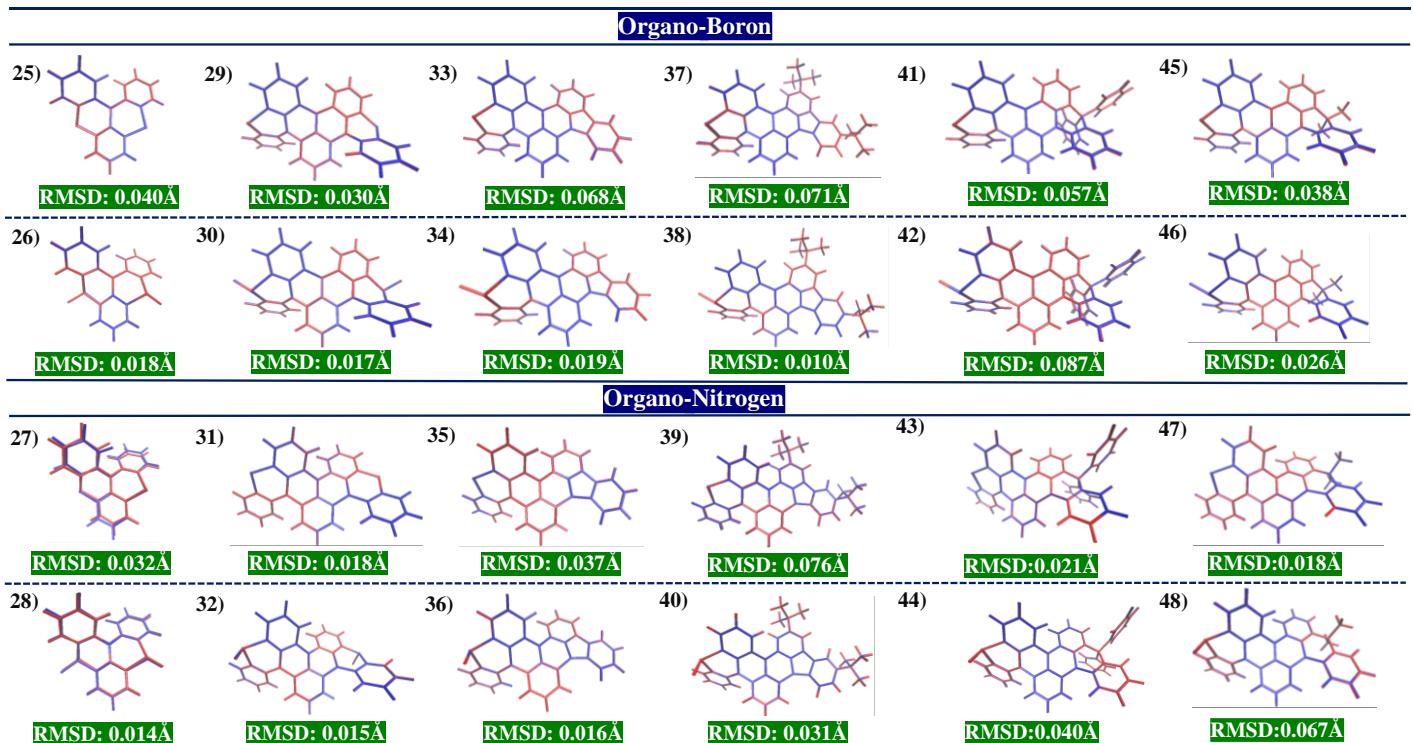


Figure S8: Structural differences between the S₁ and T₁ states for selenium-incorporated molecules (color codes: blue for S₁ and red for T₁).

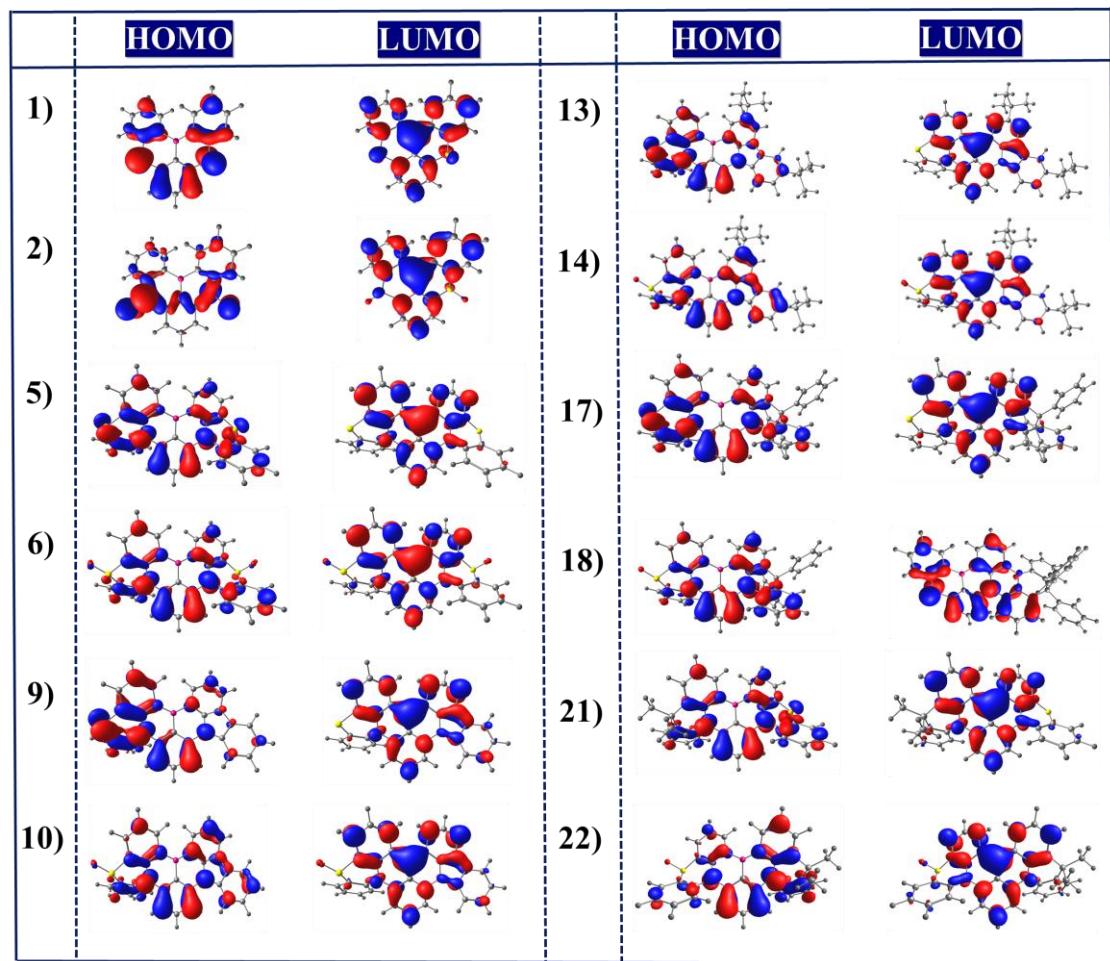


Figure S9. FMO diagram of sulfur-incorporated OB molecules at B3LYP/6-31+G(d) level of theory. (isosurface value = 0.02 a.u.)

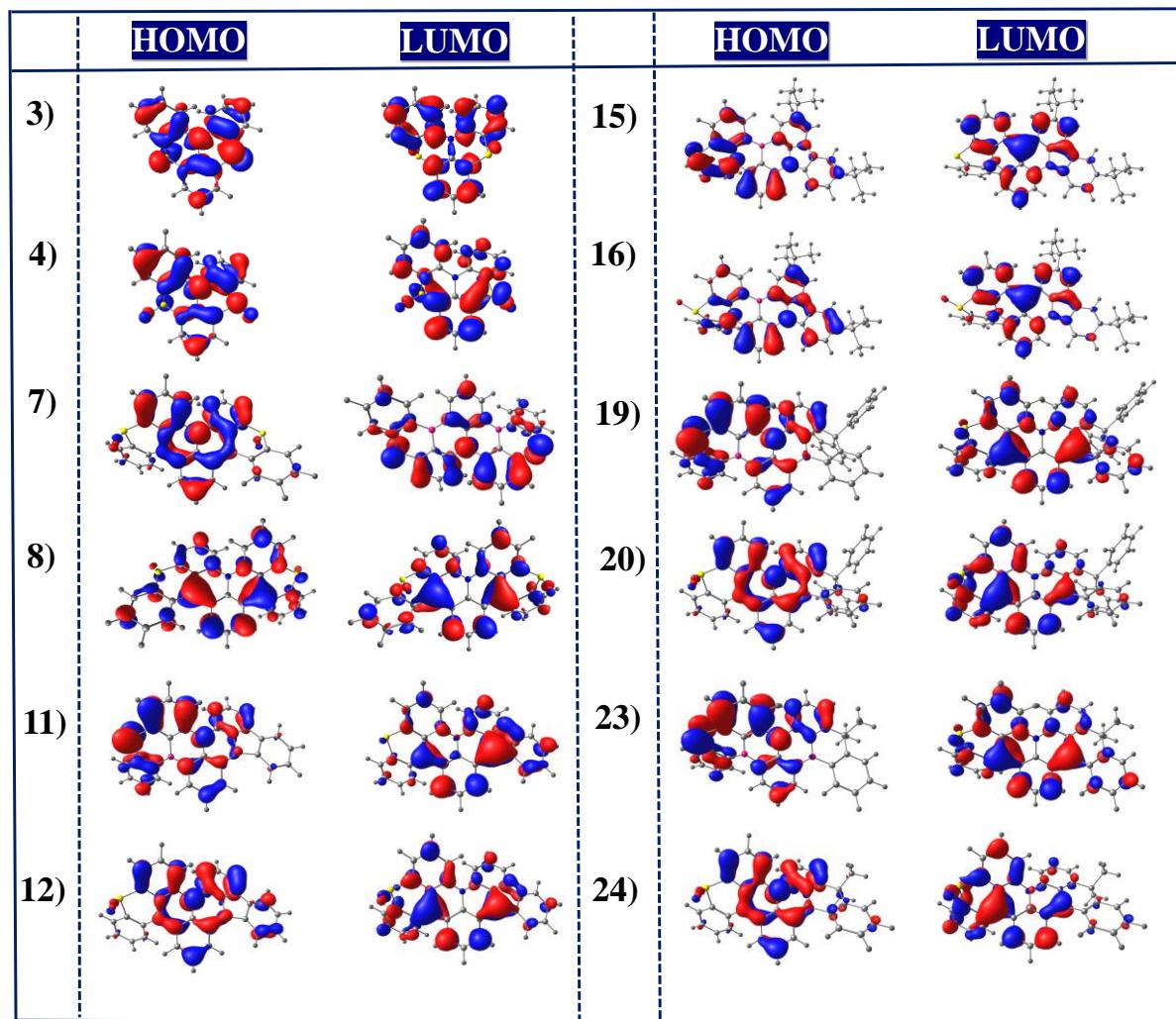


Figure S10. FMO diagram of sulfur-incorporated ON molecules at B3LYP/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

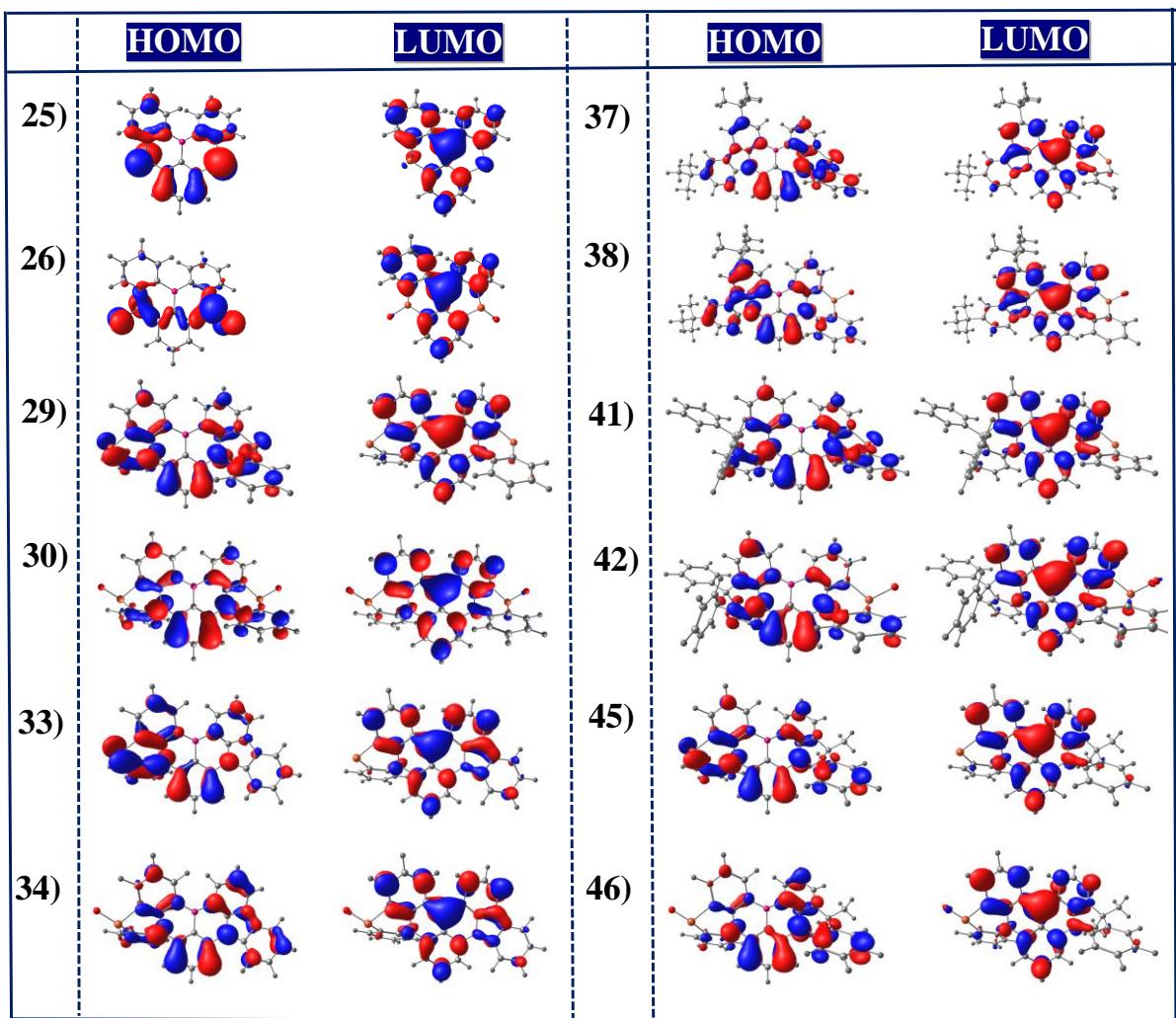


Figure S11. FMO diagram of selenium-incorporated OB molecules at B3LYP/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

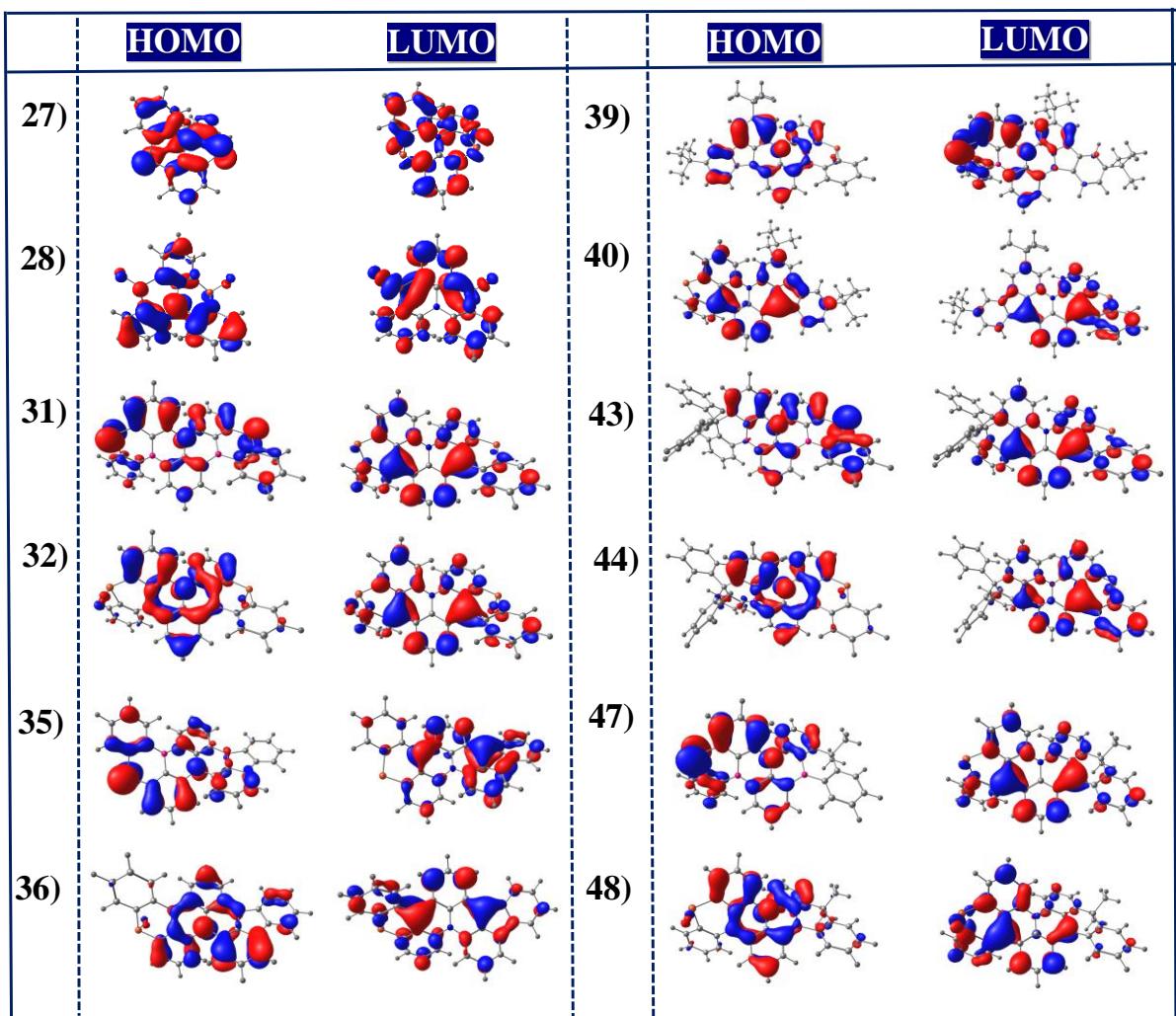


Figure S12. FMO diagram of selenium-incorporated ON molecules at B3LYP/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

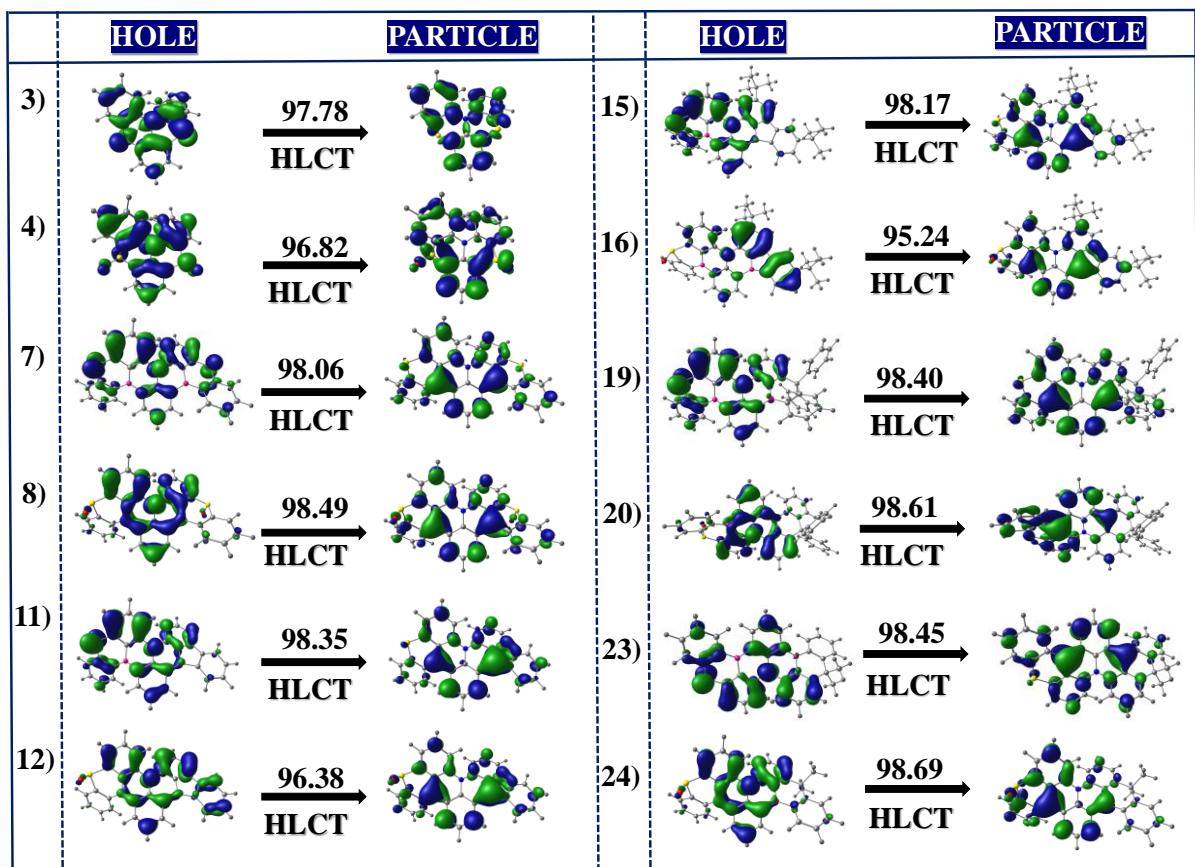


Figure S13. NTOs of sulfur-incorporated ON molecules for the S₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

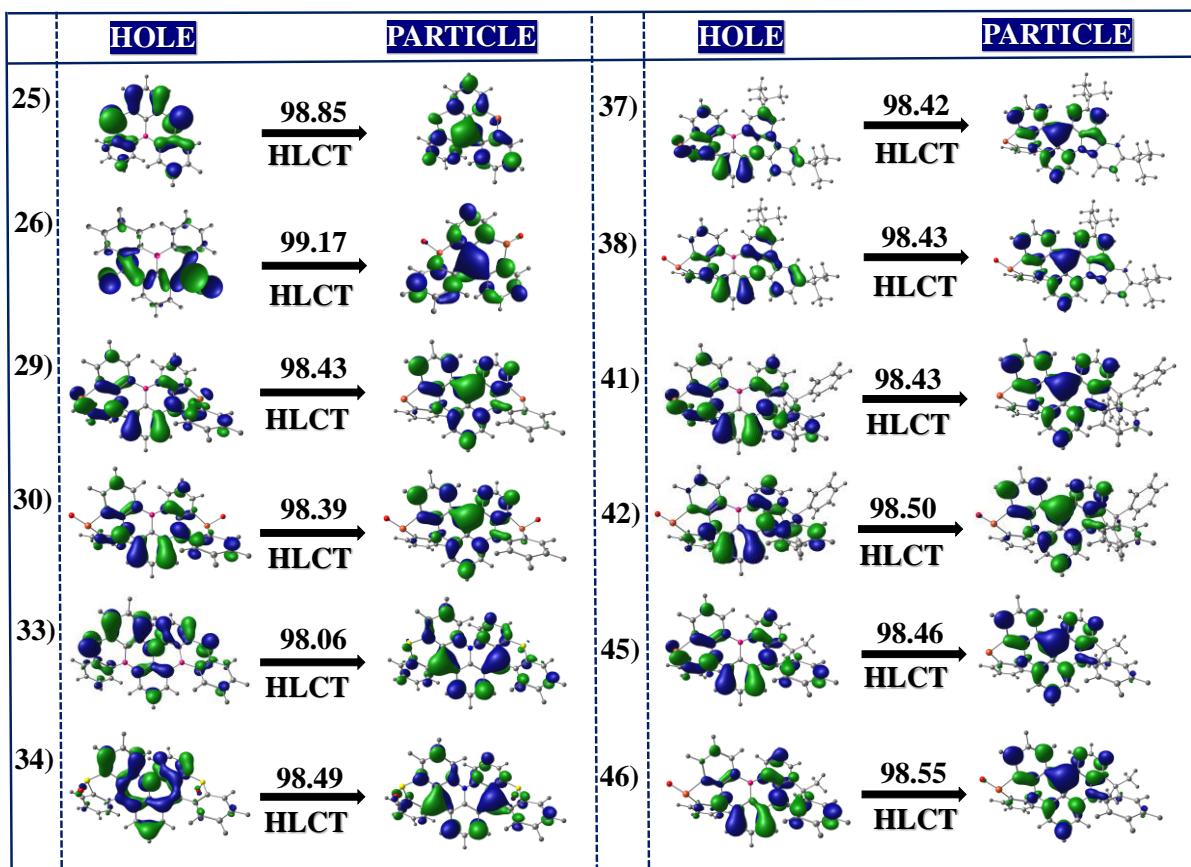


Figure S14. NTOs of selenium-incorporated OB molecules for the S₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

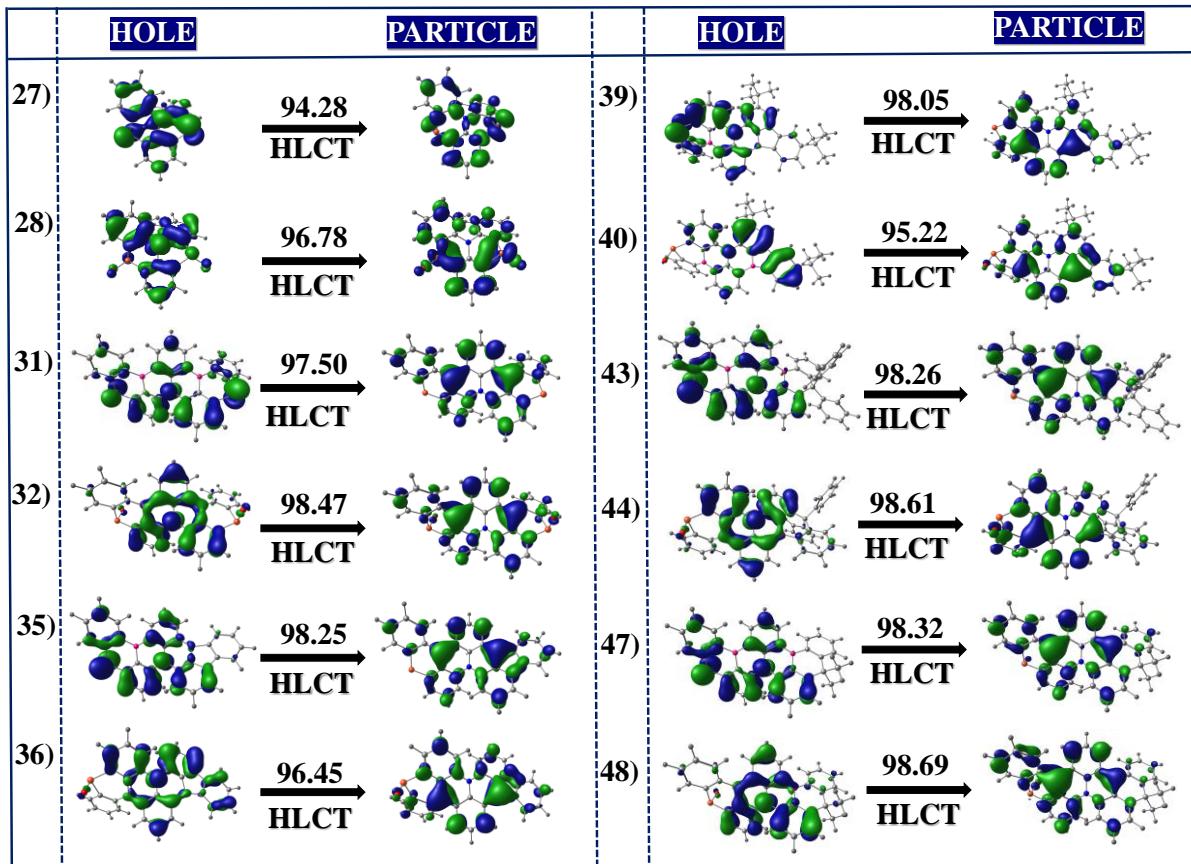


Figure S15. NTOs of selenium-incorporated ON molecules for the S₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

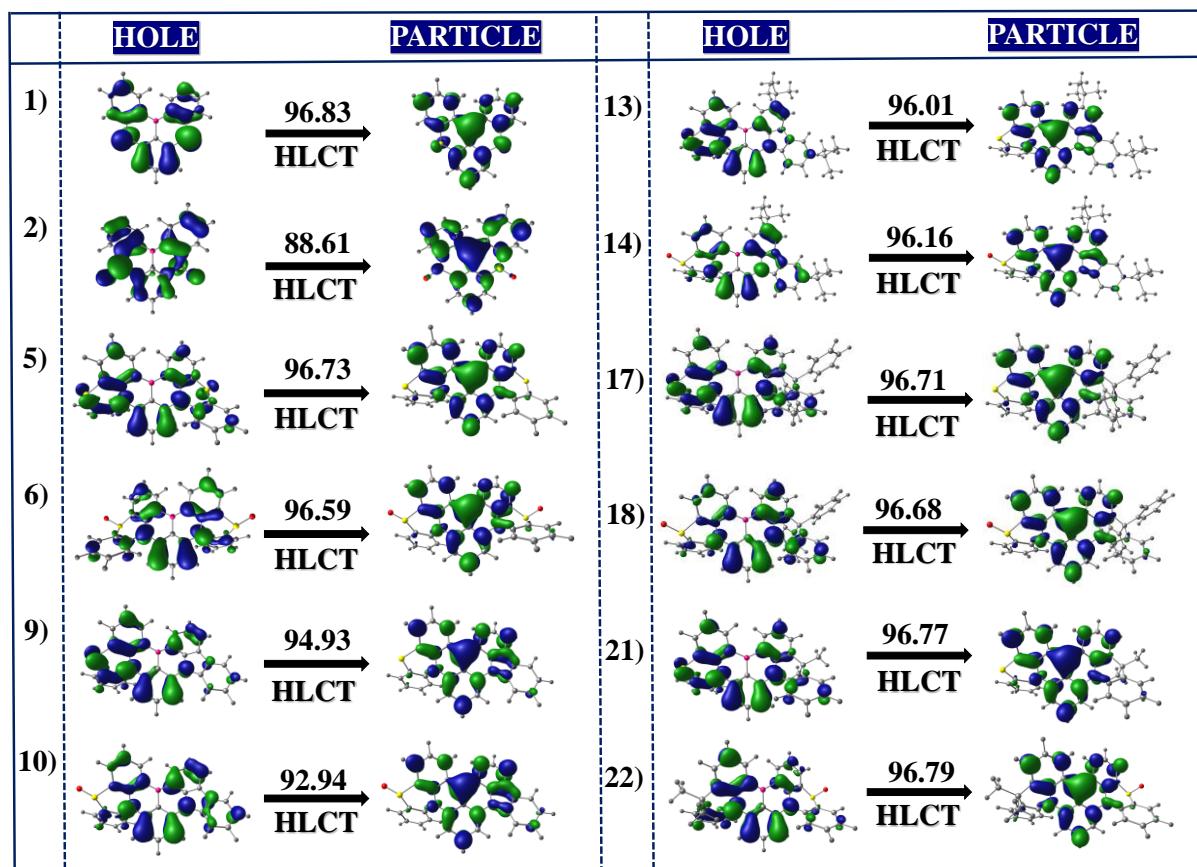


Figure S16. NTOs of sulfur-incorporated OB molecules for the T₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

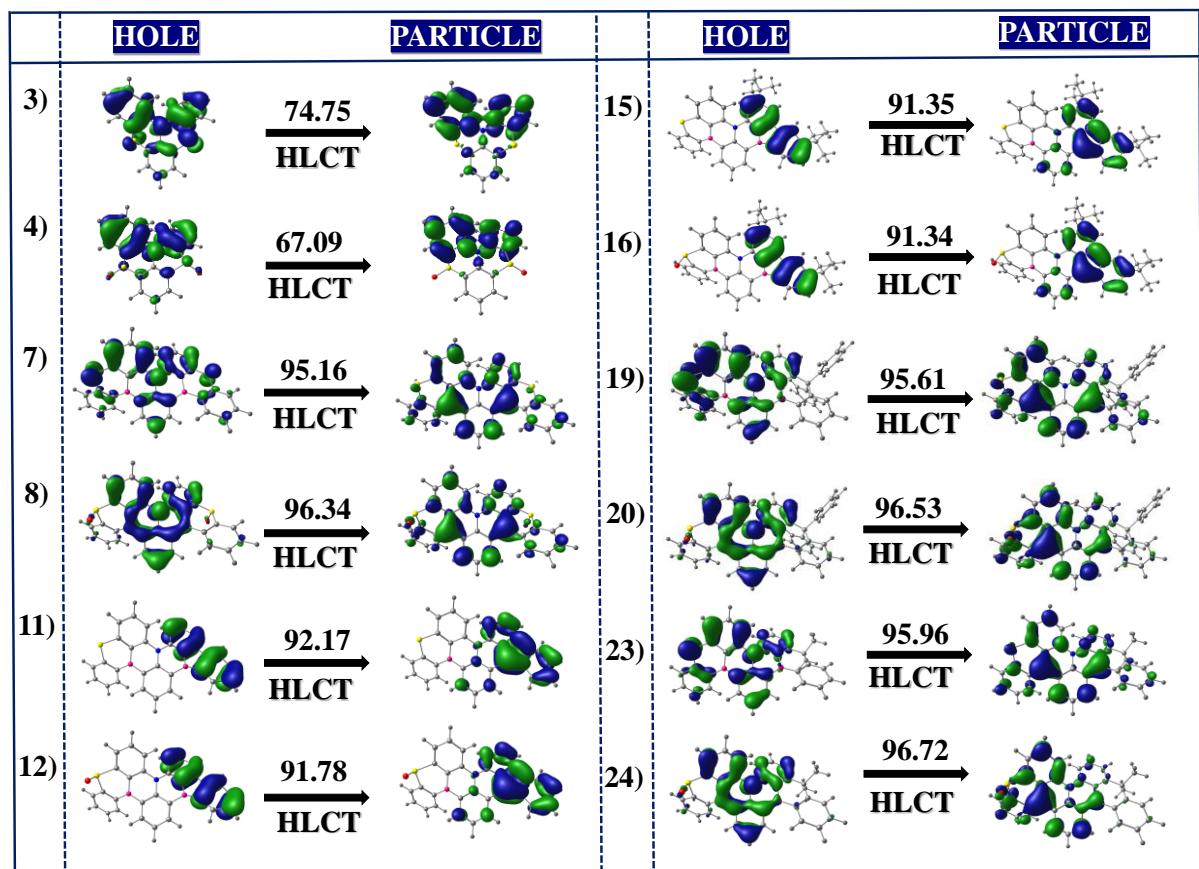


Figure S17. NTOs of sulfur-incorporated ON molecules for the T₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

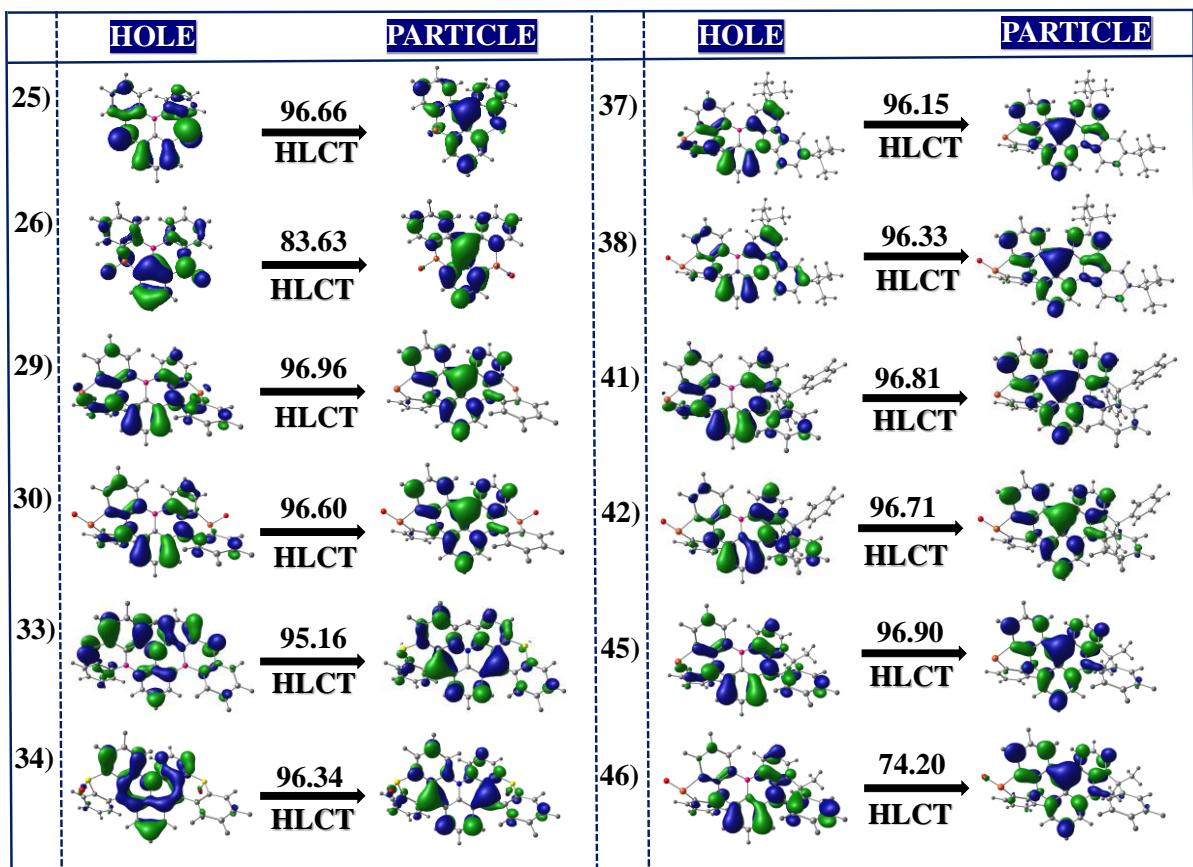


Figure S18. NTOs of selenium-incorporated OB molecules for the T₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

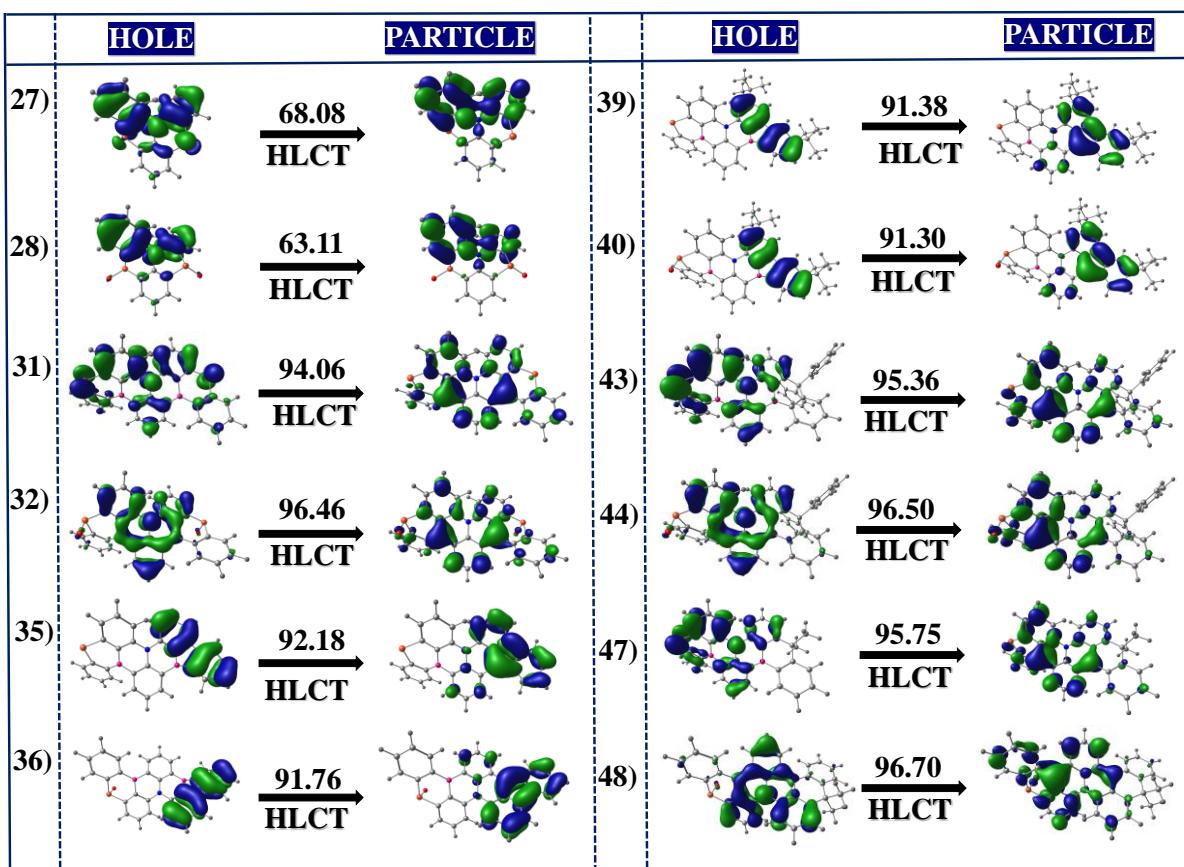


Figure S19. NTOs of selenium-incorporated ON molecules for the T₁ state at M06/6-31+G(d) level of theory. (iso-surface value = 0.02 a.u.)

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