Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Table S1: The complete NBO characteristics of Resazurin molecule

Bond orbital	Occupancy	*Atom*	Contribution from Parent NBO (%)	Coefficients	Atomic Hybrid Contribution (%)
H1 – C2	1.97568	*H1*	35.98	0.5998	s(99.96)+p $^{0.00}$(0.04)
		C2	64.02	0.8002	s(30.41)+p $^{2.29}$(69.57)+d $^{0.00}$(0.02)
C2 – C4	1.97012	*C2*	48.37	0.6955	s(32.96)+p $^{2.03}$(67.01)+d $^{0.00}$(0.03)
		C4	51.63	0.7186	s(37.67)+p $^{1.65}$(62.31)+d $^{0.00}$(0.02)
C2 – C5	1.97656	*C2*	50.59	0.7112	s(36.62)+p $^{1.73}$(63.35)+d $^{0.00}$(0.03)
		C5	49.41	0.7030	s(36.33)+p $^{1.75}$(63.64)+d $^{0.00}$(0.03)
C2=C5	1.76532	*C2*	47.30	0.6878	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C5	52.70	0.7259	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
C3 – C6	1.97444	*C3*	50.88	0.7133	s(35.00)+p $^{1.86}$(64.98)+d $^{0.00}$(0.03)
		C6	49.12	0.7008	s(35.92)+p $^{1.78}$(64.05)+d $^{0.00}$(0.03)
C3=C6	1.58796	*C3*	58.92	0.7676	s(0.00)+p $^{1.00}$(99.97)+d $^{0.00}$(0.03)
		C6	41.08	0.6409	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
C3 - C7	1.97271	*C3*	48.78	0.6984	s(34.87)+p $^{1.87}$(65.10)+d $^{0.00}$(0.03)
		C7	51.22	0.7157	s(39.15)+p $^{1.55}$(60.83)+d $^{0.00}$(0.02)
C3 - H9	1.97490	*C3*	62.74	0.7921	s(30.11)+p $^{2.32}$(69.86)+d $^{0.00}$(0.02)
		H9	37.26	0.6104	s(99.96)+p $^{0.00}$(0.04)
C4 - C7	1.97394	*C4*	50.54	0.7109	s(35.14)+p $^{1.85}$(64.83)+d $^{0.00}$(0.03)
		C7	49.46	0.7033	s(36.60)+p $^{1.73}$(63.37)+d $^{0.00}$(0.03)
C4= C7	1.60434	*C4*	56.06	0.7488	s(0.00)+p $^{1.00}$(99.98)+d $^{0.00}$(0.02)
		C7	43.94	0.6628	s(0.00)+p $^{1.00}$(99.97)+d $^{0.00}$(0.03)
C4- N10	1.98411	*C4*	37.74	0.6143	s(27.08)+p $^{2.69}$(72.83)+d $^{0.00}$(0.09)
		N10	62.26	0.7890	s(34.60)+p $^{1.89}$(65.38)+d $^{0.00}$(0.02)
C5 - C6	1.97933	*C5*	50.42	0.7101	s(33.87)+p $^{1.95}$(66.10)+d $^{0.00}$(0.03)
		C6	49.58	0.7041	s(35.71)+p $^{1.80}$(64.26)+d $^{0.00}$(0.03)
C5 -H8	1.97936	*C5*	62.35	0.7896	s(29.77)+p $^{2.36}$(70.21)+d $^{0.00}$(0.03)
		H8	37.65	0.6136	s(99.96)+p $^{0.00}$(0.04)
C6 - O22	1.99283	*C6*	34.20	0.5848	s(28.06)+p $^{2.56}$(71.78)+d $^{0.01}$(0.16)
		O22	65.80	0.8112	s(40.24)+p $^{1.48}$(59.71)+d $^{0.00}$(0.05)
C7 - O13	1.98910	*C7*	32.24	0.5678	s(24.04)+p $^{3.15}$(75.77)+d $^{0.01}$(0.19)
		O13	67.76	0.8232	s(31.98)+p $^{2.12}$(67.96)+d $^{0.00}$(0.06)
N10- C11	1.98588	*N10*	62.39	0.7899	s(37.17)+p $^{1.69}$(62.80)+d $^{0.00}$(0.02)
		C11	37.61	0.6132	s(28.17)+p $^{2.55}$(71.74)+d $^{0.00}$(0.09)
N10= C11	1.76261	*N10*	60.65	0.7788	s(0.00)+p $^{1.00}$(99.97)+d $^{0.00}$(0.03)
		C11	39.35	0.6273	s(0.00)+p $^{1.00}$(99.92)+d $^{0.00}$(0.08)
N10- O24	1.99273	*N10*	50.24	0.7088	s(27.99)+p $^{2.57}$(71.93)+d $^{0.00}$(0.08)
		O24	49.76	0.7054	s(22.18)+p $^{3.50}$(77.69)+d $^{0.01}$(0.13)
C11 - C12	1.97283	*C11*	50.69	0.7120	s(34.69)+p $^{1.88}$(65.28)+d $^{0.00}$(0.03)
		C12	49.31	0.7022	s(35.51)+p $^{1.82}$(64.46)+d $^{0.00}$(0.03)
C11 – C14	1.96887	*C11*	51.85	0.7201	s(37.03)+p $^{1.70}$(62.96)+d $^{0.00}$(0.02)
		C14	48.15	0.6939	s(32.02)+p $^{2.12}$(67.95)+d $^{0.00}$(0.04)
C12 – O13	1.98867	*C12*	31.86	0.5645	s(23.62)+p $^{3.23}$(76.19)+d $^{0.01}$(0.20)

		O13	68.14	0.8255	s(31.68)+p $^{2.15}$(68.26)+d $^{0.00}$(0.06)
C12 – C19	1.97601	*C12*	51.61	0.7184	s(40.67)+p $^{1.46}$(59.31)+d $^{0.00}$(0.02)
		C19	48.39	0.6956	s(35.45)+p $^{1.82}$(64.51)+d $^{0.00}$(0.04)
C12 = C19	1.80551	*C12*	48.02	0.6930	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C19	51.98	0.7210	s(0.00)+p $^{1.00}$(99.95)+d $^{0.00}$(0.05)
C14 – H15	1.97608	*C14*	63.98	0.7999	s(30.62)+p $^{2.27}$(69.36)+d $^{0.00}$(0.02)
		H15	36.02	0.6002	s(99.96)+p $^{0.00}$(0.04)
C14 – C16	1.98034	*C14*	50.97	0.7139	s(37.36)+p $^{1.68}$(62.62)+d $^{0.00}$(0.03)
		C16	49.03	0.7002	s(36.86)+p $^{1.71}$(63.11)+d $^{0.00}$(0.03)
C14 = C16	1.80419	*C14*	50.46	0.7104	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C16	49.54	0.7038	s(0.00)+p $^{1.00}$(99.95)+d $^{0.00}$(0.05)
C16 – H17	1.97919	*C16*	62.86	0.7929	s(30.11)+p $^{2.32}$(69.86)+d $^{0.00}$(0.03)
		H17	37.14	0.6094	s(99.96)+p $^{0.00}$(0.04)
C16 – C18	1.98240	*C16*	51.34	0.7165	s(33.01)+p $^{2.03}$(66.96)+d $^{0.00}$(0.03)
		C18	48.66	0.6976	s(34.25)+p $^{1.92}$(65.72)+d $^{0.00}$(0.04)
C18 – C19	1.97457	*C18*	48.31	0.6950	s(34.76)+p $^{1.88}$(65.20)+d $^{0.00}$(0.03)
		C19	51.69	0.7190	s(33.98)+p $^{1.94}$(65.99)+d $^{0.00}$(0.03)
C18 – O21	1.99534	*C18*	35.74	0.5979	s(30.72)+p $^{2.25}$(69.20)+d $^{0.00}$(0.08)
		O21	64.26	0.8016	s(38.65)+p $^{1.58}$(61.08)+d $^{0.01}$(0.27)
C18 = O21	1.93418	*C18*	33.51	0.5789	s(0.00)+p $^{1.00}$(99.88)+d $^{0.00}$(0.12)
		O21	66.49	0.8154	s(0.00)+p $^{1.00}$(99.75)+d $^{0.00}$(0.25)
C19 – H20	1.97359	*C19*	63.18	0.7949	s(30.56)+p $^{2.27}$(69.42)+d $^{0.00}$(0.02)
		H20	36.82	0.6068	s(99.96)+p $^{0.00}$(0.04)

Table S2: Same as Table S1, for resorufin molecule

Bond Orbital	Occupancy	Atom	Contribution from Parent NBO (%)	Coefficients	Atomic Hybrid Contribution (%)
H1-C2	1.97872	H1	36.75	0.6062	s(99.96)+p $^{0.00}$(0.04)
		C2	63.25	0.7953	s(30.35)+p $^{2.29}$(69.62)+d $^{0.00}$(0.03)
C2-C4	1.97185	C2	48.63	0.6973	s(33.17)+p $^{2.01}$(66.80)+d $^{0.00}$(0.03)
		C4	51.37	0.7168	s(35.86)+p $^{1.79}$(64.12)+d $^{0.00}$(0.02)
C2-C5	1.97878	C2	50.31	0.7093	s(36.47)+p $^{1.74}$(63.51)+d $^{0.00}$(0.03)
		C5	49.69	0.7049	s(36.34)+p $^{1.75(}$ 63.63)+d $^{0.00}$(0.03)
C2=C5	1.77603	C2	47.08	0.6861	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C5	52.92	0.7275	s(0.00)+p $^{1.00}$(99.97)+d $^{0.00}$(0.03)
C3-C6	1.97220	C3	50.88	0.7133	s(34.34)+p $^{1.91}$(65.65)+d $^{0.00}$(0.01)
		C6	49.12	0.7009	s(35.56)+p $^{1.81}$(64.37)+d $^{0.00}$(0.07)
C3=C6	1.57554	C3	59.50	0.7713	s(0.00)+p $^{1.00}$(99.97)+d $^{0.00}$(0.03)
		C6	40.50	0.6364	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
C3-C7	1.97450	C3	48.87	0.6991	s(34.50)+p $^{1.90}$(65.46)+d $^{0.00}$(0.03)
		C7	51.13	0.7151	s(39.68)+p $^{1.52}$(60.30)d $^{0.00}$(0.02)
C3-H9	1.97733	C3	62.78	0.7923	s(31.16)+p $^{2.21}$(68.82)+d$^{0.00}$(0.02)
		H9	37.22	0.6101	s(99.96)+p $^{0.00}$(0.04)

C4-C7	1.97679	C4	49.74	0.7053	s(33.28)+p $^{2.00}$(66.69)+d $^{0.00}$(0.03)
		C7	50.26	0.7089	s(36.47)+p $^{1.74}$(63.50)+d $^{0.00}$(0.03)
C4=C7	1.52421	C4	53.71	0.7329	s(0.00)+p $^{1.00}$(99.99)+d $^{0.00}$(0.01)
		C7	46.29	0.6804	s(0.00)+p $^{1.00}$(99.98)+d $^{0.00}$(0.02)
C4-N10	1.98120	C4	42.11	0.6489	s(30.70)+p $^{2.26}$(69.23)+d $^{0.00}$(0.07)
		N10	57.89	0.7608	s(33.30)+p $^{2.00}$(66.64)+d $^{0.00}$(0.06)
C5-C6	1.97704	C5	50.33	0.7094	s(33.12)+p $^{2.02}$(66.87)+d $^{0.00}$(0.01)
		C6	49.67	0.7048	s(35.42)+p $^{1.82}$(64.52)+d $^{0.00}$(0.06)
C5-H8	1.98101	C5	62.49	0.7905	s(30.53)+p $^{2.27}$(69.44)+d $^{0.00}$(0.03)
		H8	37.51	0.6124	s(99.96)+p $^{0.00}$(0.04)
C6-O22	1.99367	C6	35.04	0.5919	s(28.50)+p $^{2.50}$(71.32)+d $^{0.01}$(0.18)
		O22	64.96	0.8060	s(39.41)+p $^{1.54}$(60.52)+d $^{0.00}$(0.07)
C7-O13	1.98909	C7	31.93	0.5651	s(23.70)+p $^{3.21}$(76.12)+d $^{0.01}$(0.19)
		O13	68.07	0.8250	s(32.16)+p $^{2.11}$(67.78)+d $^{0.00}$(0.06)
N10-C11	1.98400	N10	58.10	0.7622	s(35.85)+p $^{1.79}$(64.10)+d $^{0.00}$(0.06)
		C11	41.90	0.6473	s(31.85)+p $^{2.14}$(68.08)+d $^{0.00}$(0.07)
N10=C11	1.75298	N10	54.80	0.7403	s(0.00)+p $^{1.00}$(99.82)+d $^{0.00}$(0.18)
		C11	45.20	0.6723	s(0.00)+p $^{1.00}$(99.92)+d $^{0.00}$(0.08)
C11-C12	1.97606	C11	50.08	0.7076	s(32.94)+p $^{2.04}$(67.04)+d $^{0.00}$(0.02)
		C12	49.92	0.7066	s(35.42)+p $^{1.82}$(64.53)+d $^{0.00}$(0.06)
C11-C14	1.97147	C11	51.52	0.7178	s(35.08)+p $^{1.85}$(64.89)+d $^{0.00}$(0.02)
		C14	48.48	0.6963	s(32.08)+p $^{2.12}$(67.88)+d $^{0.00}$(0.03)
C12-O13	1.98764	C12	31.64	0.5625	s(23.07)+p $^{3.33}$(76.70)+d $^{0.01}$(0.24)
		O13	68.36	0.8268	s(32.02)+p $^{2.12}$(67.93)+d $^{0.00}$(0.05)
C12-C19	1.97231	C12	51.53	0.7179	s(41.05)+p $^{1.43}$(58.91)+d $^{0.00}$(0.04)
		C19	48.47	0.6962	s(35.28)+p $^{1.83}$(64.67)+d $^{0.00}$(0.06)
C12=C19	1.80671	C12	47.62	0.6900	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C19	52.38	0.7238	s(0.00)+p $^{1.00}$(99.95)+d $^{0.00}$(0.05)
C14-H15	1.97855	C14	63.33	0.7958	s(30.65)+p $^{2.26}$(69.32)+d $^{0.00}$(0.03)
		H15	36.67	0.6055	s(99.96)+p $^{0.00}$(0.04)
C14-C16	1.98253	C14	50.67	0.7118	s(37.25)+p $^{1.68}$(62.72)+d $^{0.00}$(0.03)
		C16	49.33	0.7024	s(37.07)+p $^{1.70}$(62.90)+d $^{0.00}$(0.03)
C14=C16	1.81504	C14	49.98	0.7070	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
		C16	50.02	0.7072	s(0.00)+p $^{1.00}$(99.96)+d $^{0.00}$(0.04)
C16-H17	1.98035	C16	63.11	0.7944	s(30.93)+p $^{2.23}$(69.05)+d $^{0.00}$(0.03)
		H17	36.89	0.6073	s(99.96)+p $^{0.00}$(0.04)
C16-C18	1.98023	C16	50.85	0.7131	s(31.99)+p $^{2.12}$(67.97)+d $^{0.00}$(0.03)
		C18	49.15	0.7011	s(34.03)+p $^{1.94}$(65.94)+d $^{0.00}$(0.04)
C18-C19	1.97344	C18	48.89	0.6992	s(34.60)+p $^{1.89}$(65.37)+d $^{0.00}$(0.02)
		C19	51.11	0.7149	s(33.11)+p $^{2.02}$(66.83)+d $^{0.00}$(0.06)
C18-O21	1.99576	C18	36.12	0.6010	s(31.23)+p $^{2.20}$(68.71)+d $^{0.00}$(0.06)
		O21	63.88	0.7993	s(38.04)+p $^{1.62}$(61.64)+d $^{0.01}$(0.32)
C18=O21	1.93761	C18	32.64	0.5713	s(0.00)+p $^{1.00}$(99.89)+d $^{0.00}$(0.11)
		O21	67.36	0.8207	s(0.00)+p $^{1.00}$(99.75)+d $^{0.00}$(0.25)
C19-H20	1.97548	C19	63.37	0.7960	s(31.50)+p $^{2.17}$(68.46)+d $^{0.00}$(0.04)
		H20	36.63	0.6052	s(99.97)+p $^{0.00}$(0.03)

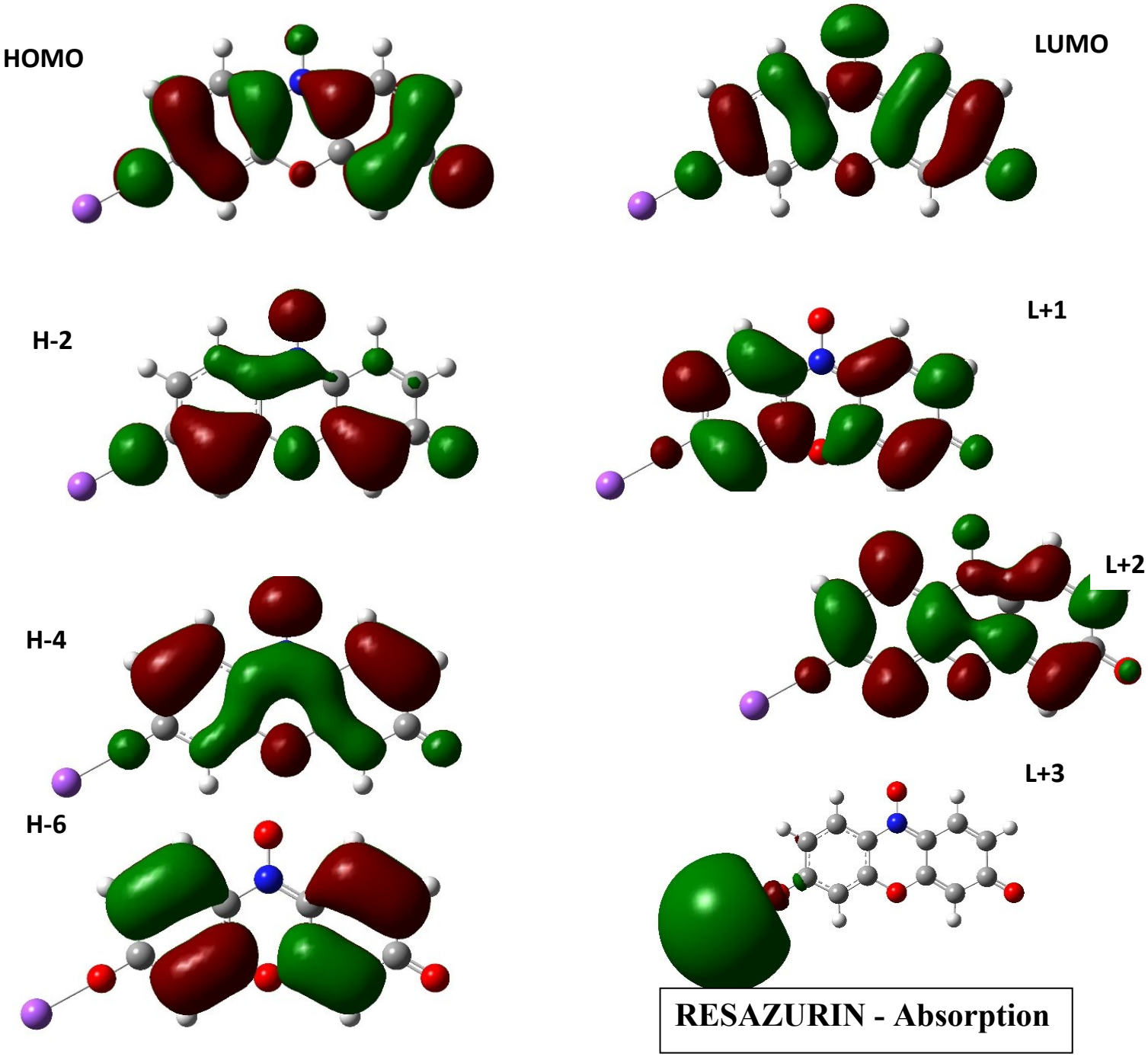
Table S3: Absorption and Emission properties of dihydroresorufin

TDDFT Absorption				TDDFT Emission				
E_α (eV)	f_α	λ_{max} (nm)	Transition (α- State)	E_α (eV)	f_α	λ_{max}	Transition (α- State)	Stoke's shift (cm^{-1})
2.69	0.0009	461.11	H(A) →L+1(A) (99%)(1)	1.57	0.0013	785.30	H(A) →L(A) (99%)(1)	
2.72	0.0173	455.82	H(A)→L(A) (96%) (2)	2.32	0.0007	534.44	H(A) →L+1(A) (100%)(2)	
3.12	0.0271	396.82	H (A) →L +2(A) (93%) (3)	2.69	0.1527	460.72	H(A) →L+2(A) (96%)(3)	
3.44	**0.2501**	**360.54**	**H(A) →L+3(A) (88%) (4)**	3.14	0.0808	394.31	H(A) →L+4(A) (46%)(4)	
3.51	0.0039	353.52	H(A) →L+4(A) (99%)(5)	3.18	0.1176	389.40	H(A) →L+4(A) (52%)(5)	
3.63	0.0007	341.29	H (A) →L+5 (A) (99%) (6)	3.25	0.0507	381.98	H-2(A) →L(A) (53%)(6)	
3.65	0.0096	339.63	H (A) →L+6(A) (97%) (7)	3.26	0.0013	380.09	H(A) →L+5(A) (98%)(7)	
3.78	0.0002	327.58	H (A) →L+7 (A) (100%) (8)	**3.31**	**0.2135**	**374.95**	**H-2(A) →LA) (42%)(8)**	**1065.9**
3.88	0.0001	319.17	H(A) →L+8 (A) (100%) (9)	3.33	0.0257	372.67	H(A) →L+6(A) (70%)(9)	
3.90	0.0014	318.13	H-1(A) →L+1(A) (100%)(10)	3.42	0.0007	362.03	H(A) →L+7(A) (100%)(10)	
4.01	0.0964	309.26	H-1(A) →L (A)(78%) (11)	3.51	0.0002	352.87	H(A) →L+8(A) (100%)(11)	
4.03	0.0008	307.54	H(A) →L+9(A)(99%) (12)(12)	3.66	0.001	339.16	H(A) →L+9(A) (100%)(12)	

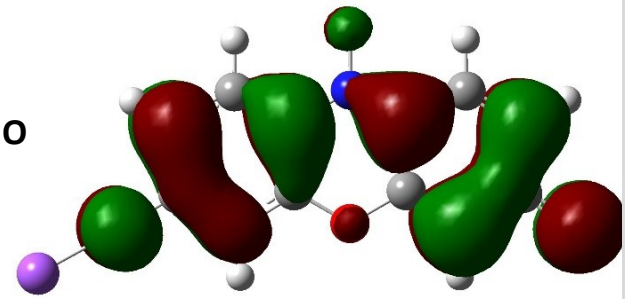
Table S4: Comparison of different functionals to obtain the photophysical (in aniline solvent) and NLO properties (in gas phase) of both Rz and Rf dyes. The experimental values obtained from Ref. [14] are also included for the most dominant transitions, and the results from present study are highlighted in bold format for clarity.

Dye	Method	Photophysical properties			Energy Gap (eV)	NLO properties		
		Absorption /nm	Emission /nm	Stokes shift /cm^{-1}		μ (Debye)	α ($\times 10^{-24}$ esu)	β_{tot} ($\times 10^{-30}$ esu)
Rz	B3LYP	516.5	590.3	2423	2.526	20.816	24.017	33.797
	PBE1PBE	497.0	564.0	2108	3.049	20.877	23.345	34.267
	PBEPBE	558.2	657.4	2704	1.571	21.117	25.369	23.955
	BPW91	**558.3**	**658.2**	**2718**	**1.586**	**21.240**	**25.123**	**25.687**
	Expt.	602	634	838	-	-	-	-
Rf	B3LYP	493.2	558.4	2363	2.382	19.884	23.998	23.029
	PBE1PBE	481.9	542.9	2330	2.906	19.922	23.372	25.665
	PBEPBE	524.1	612.3	2746	1.542	20.424	25.469	10.654
	BPW91	**524.2**	**612.6**	**2753**	**1.642**	**20.602**	**25.117**	**12.477**
	Expt.	572	585	389	-	-	-	-

Figure S1: The density distribution diagram of transition orbitals (both absorption and emission in aniline solvent) for resazurin molecule



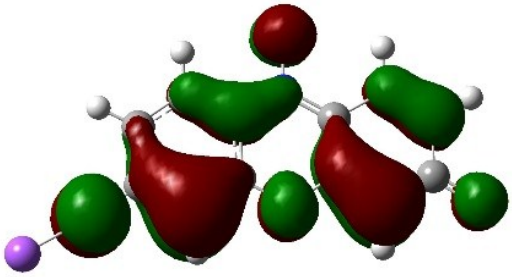
HOMO



LUMO

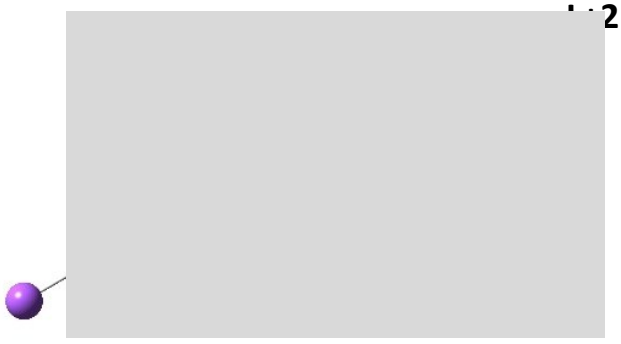
L+1

H-2



H-4

L+2

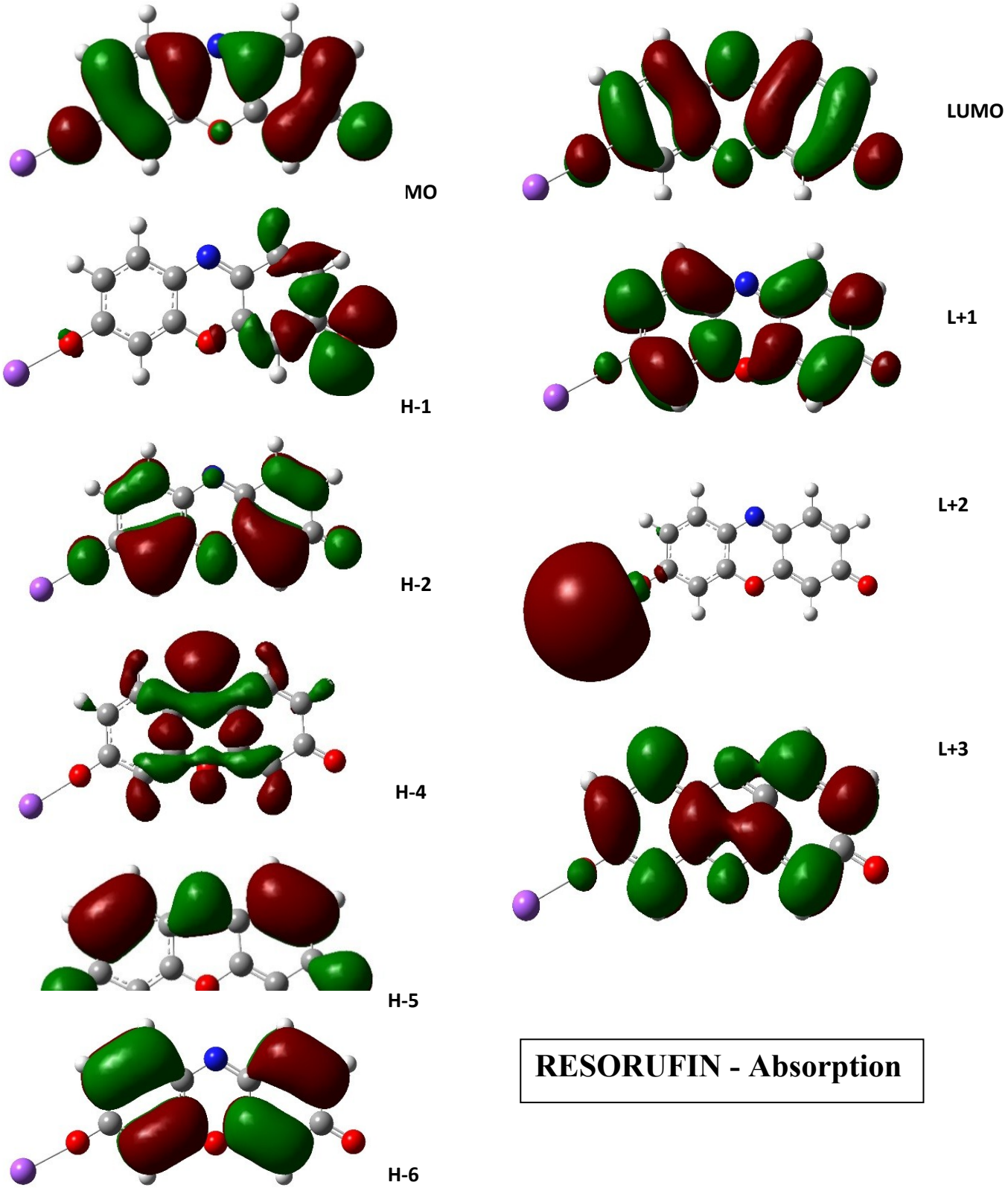


L+3

H-6

RESAZURIN - Emission

Figure S2: Same as Fig. S1, for resorufin molecule



RESORUFIN - Absorption

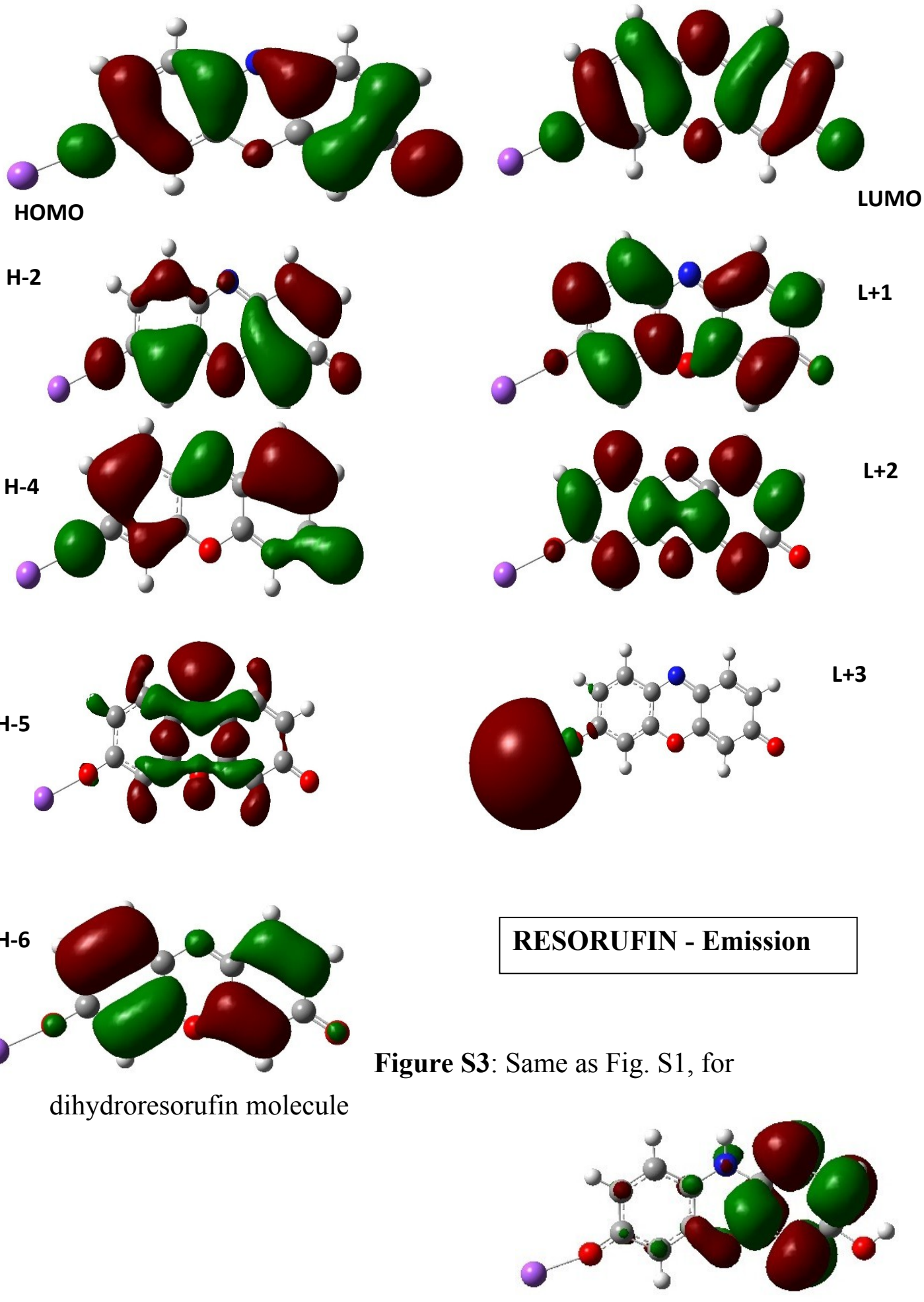
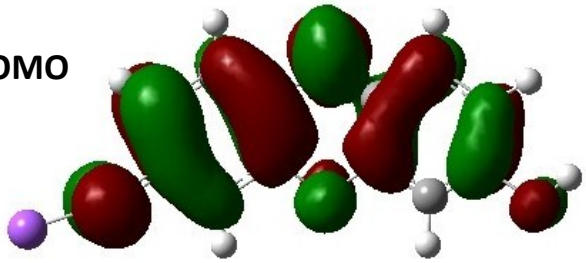


Figure S3: Same as Fig. S1, for dihydroresorufin molecule

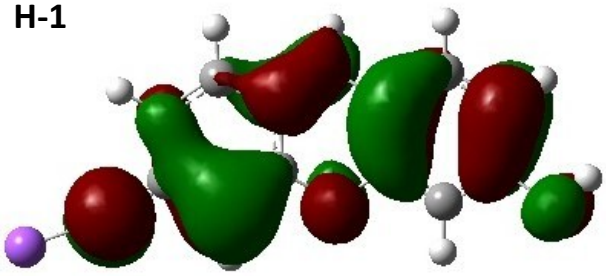
LUMO

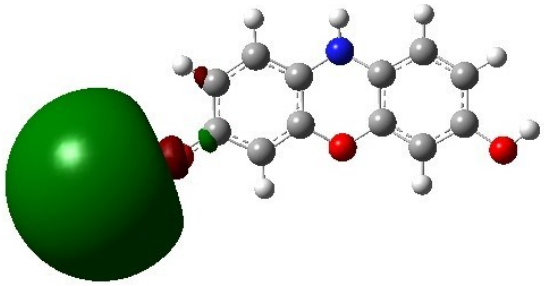
HOMO



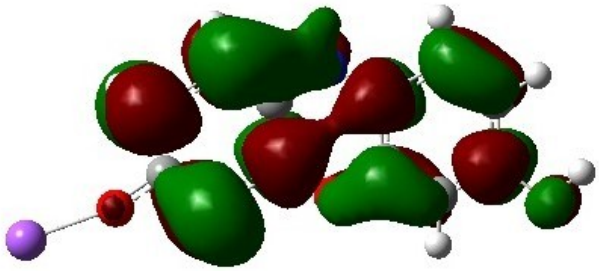
L+1

H-1

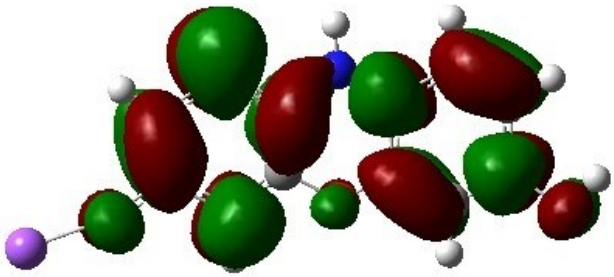




L+2

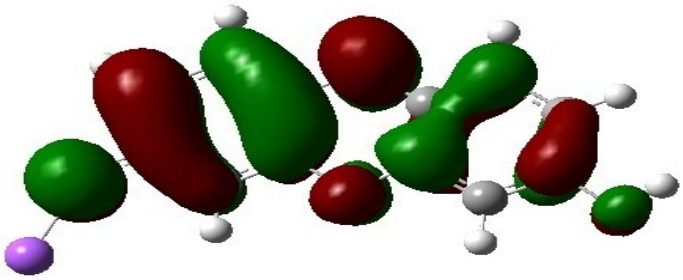


L+3

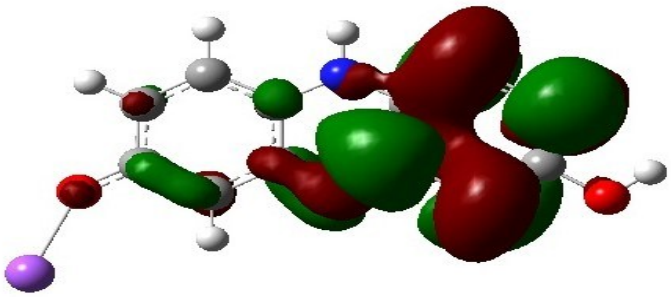


Dihydroresorufin -Absorption

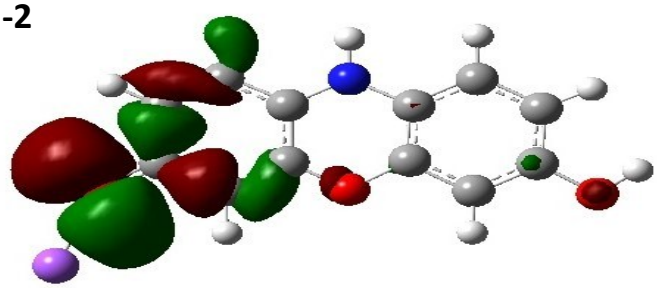
HOMO



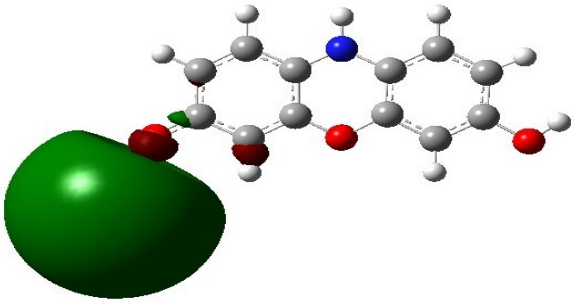
LUMO



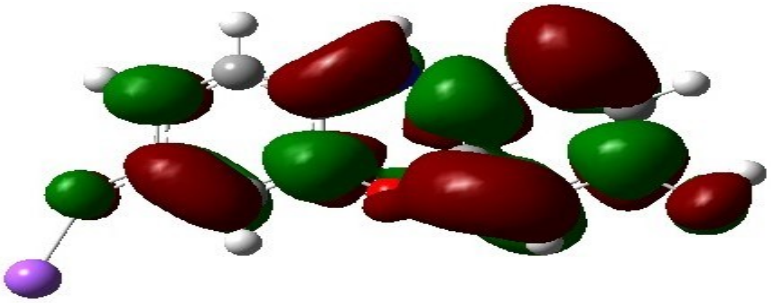
H-2



L+1



L+2



Dihydroresorufin - Emission