Electronic Supplementary Information

First 1-hydroxy-1*H*-imidazole-based ESIPT emitter with an O–H···O intramolecular hydrogen bond: ESIPT-triggered TICT and speciation in solution

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Experimental part

X-ray crystal structure data

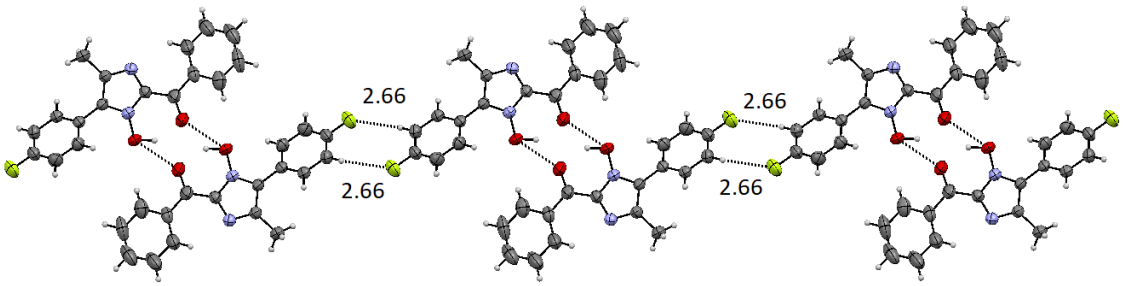


Figure S1. A supramolecular ribbon in the structure of **HL**.

IR spectra

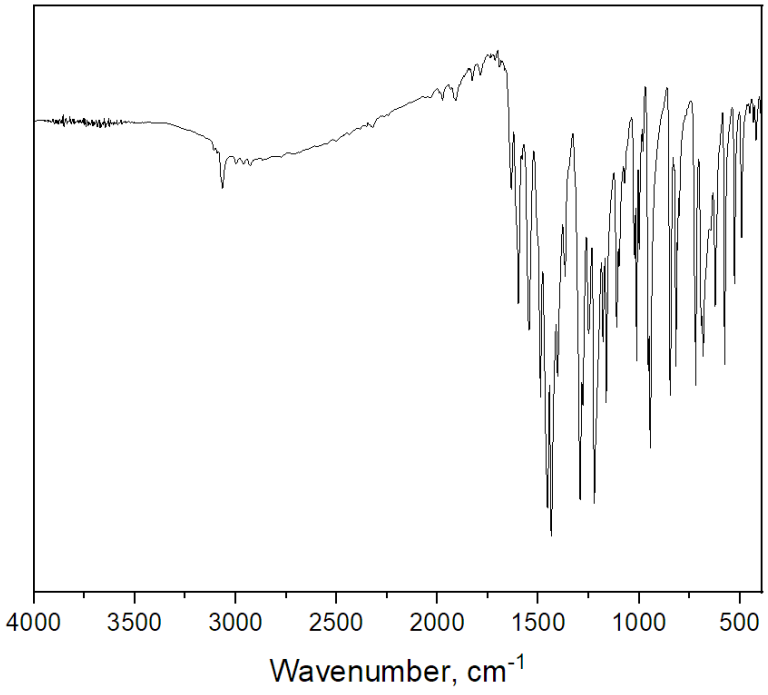


Figure S2. The IR spectrum of **HL** in the 4000 – 390 cm^{-1} region.

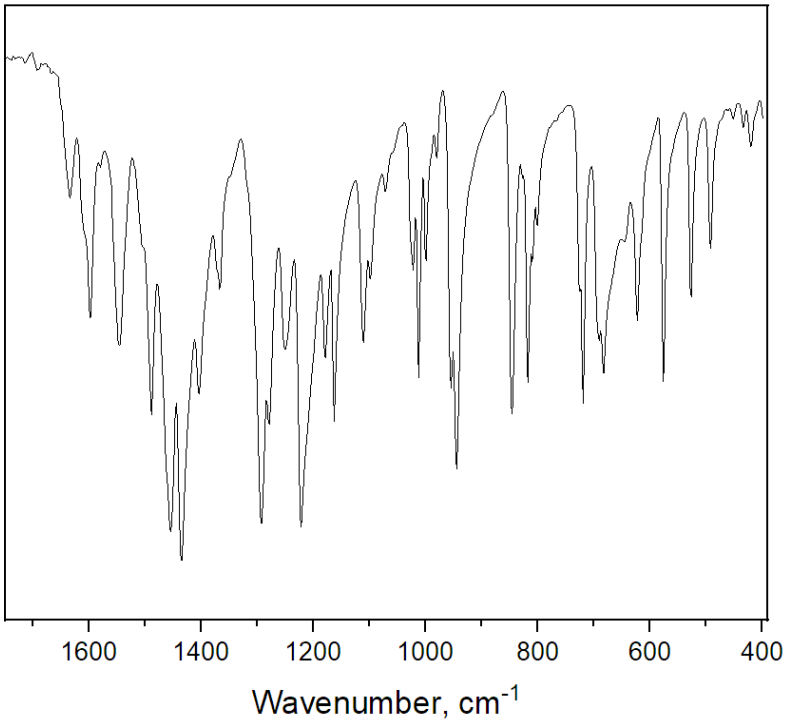


Figure S3. The IR spectrum of **HL** in the 1750 – 390 cm^{-1} region.

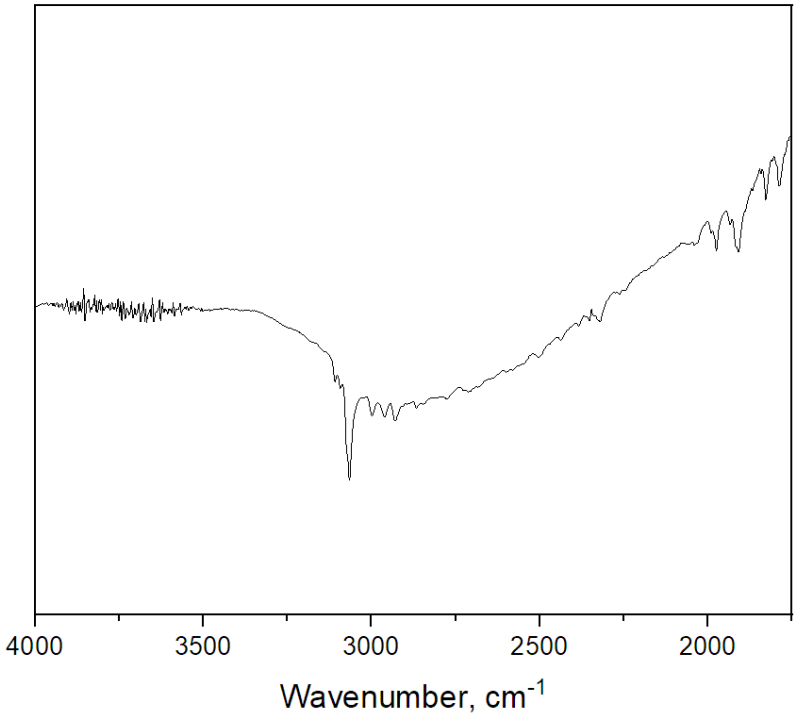


Figure S4. The IR spectrum of **HL** in the 4000 – 1750 cm^{-1} region.

Photoluminescence data

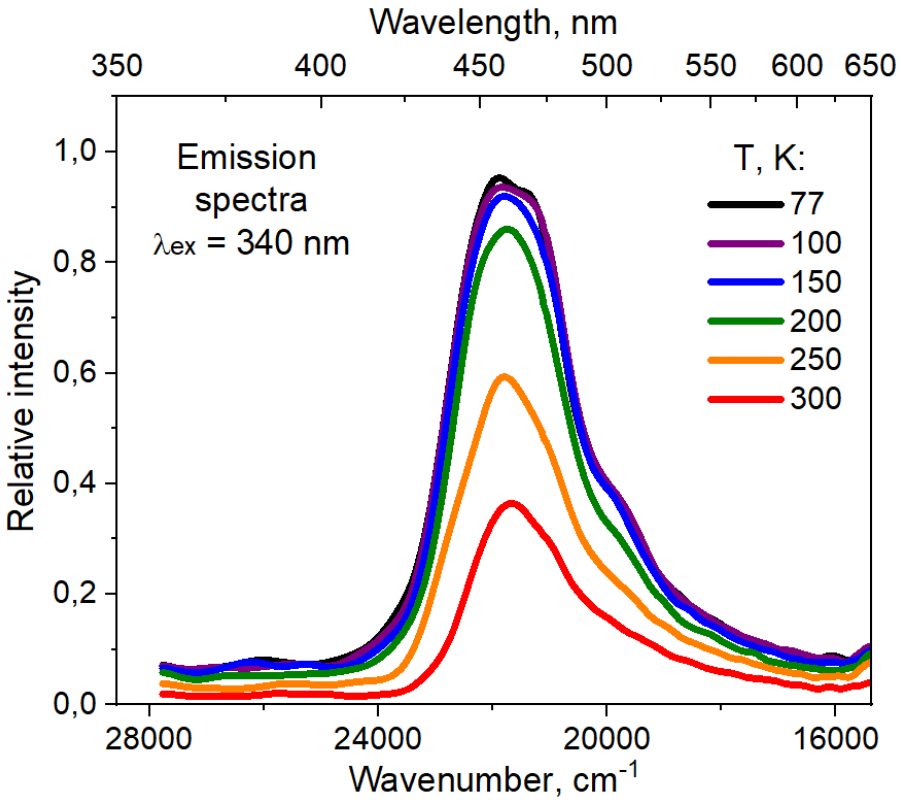


Figure S5. Temperature dependence of the emission spectrum of **HL** at λ_{ex} = 340 nm in the solid state.

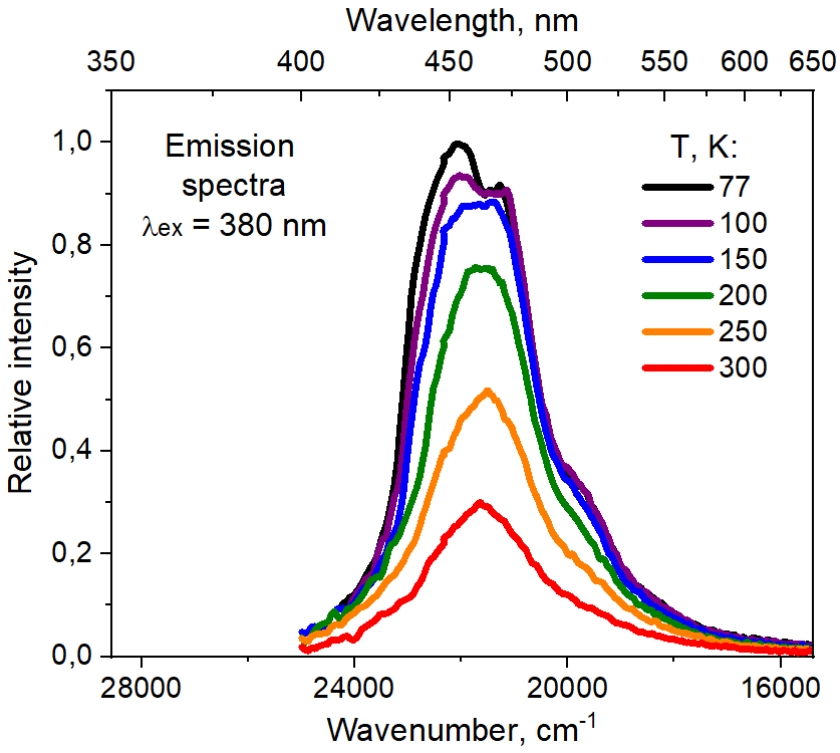


Figure S6. Temperature dependence of the emission spectrum of **HL** at λ_{ex} = 380 nm in the solid state.

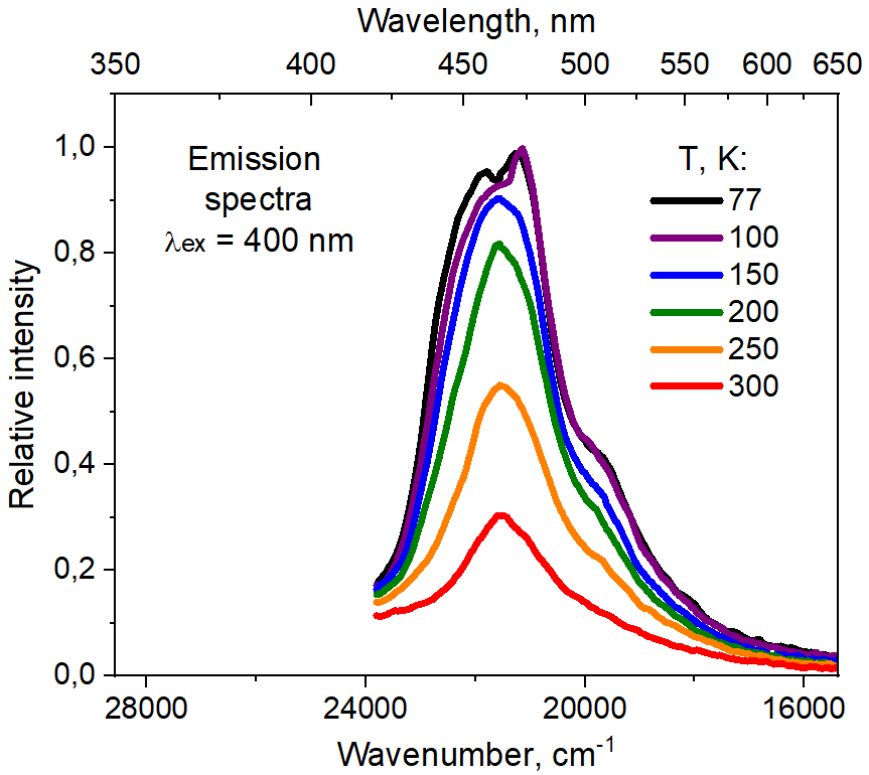


Figure S7. Temperature dependence of the emission spectrum of **HL** at λ_{ex} = 400 nm in the solid state.

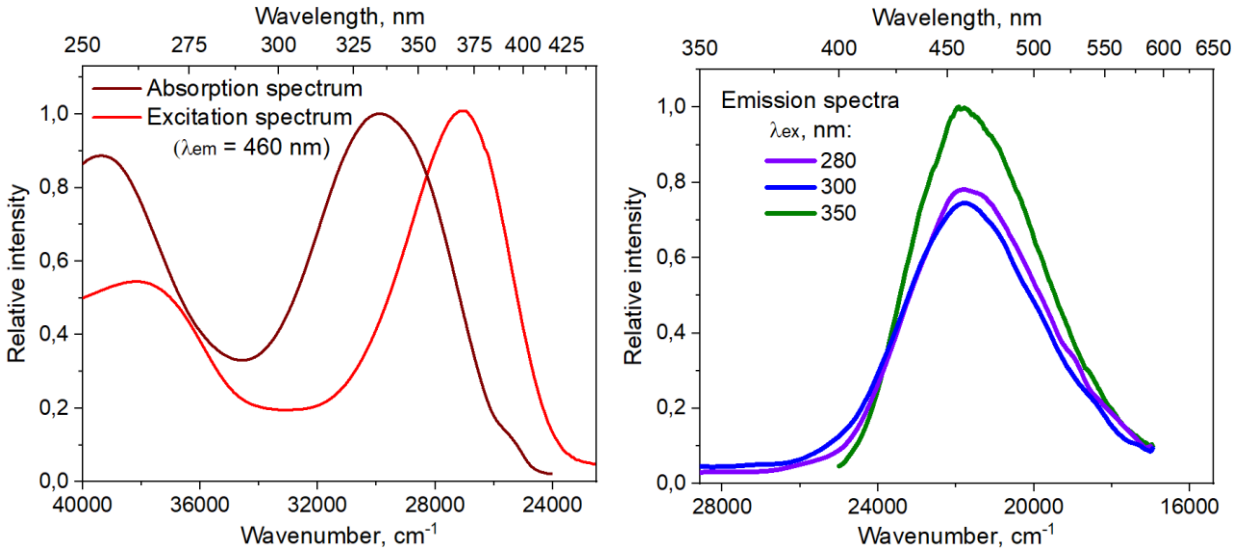


Figure S8. Absorption, excitation and emission spectra of **HL** in CH_2Cl_2 solution at 300 K.

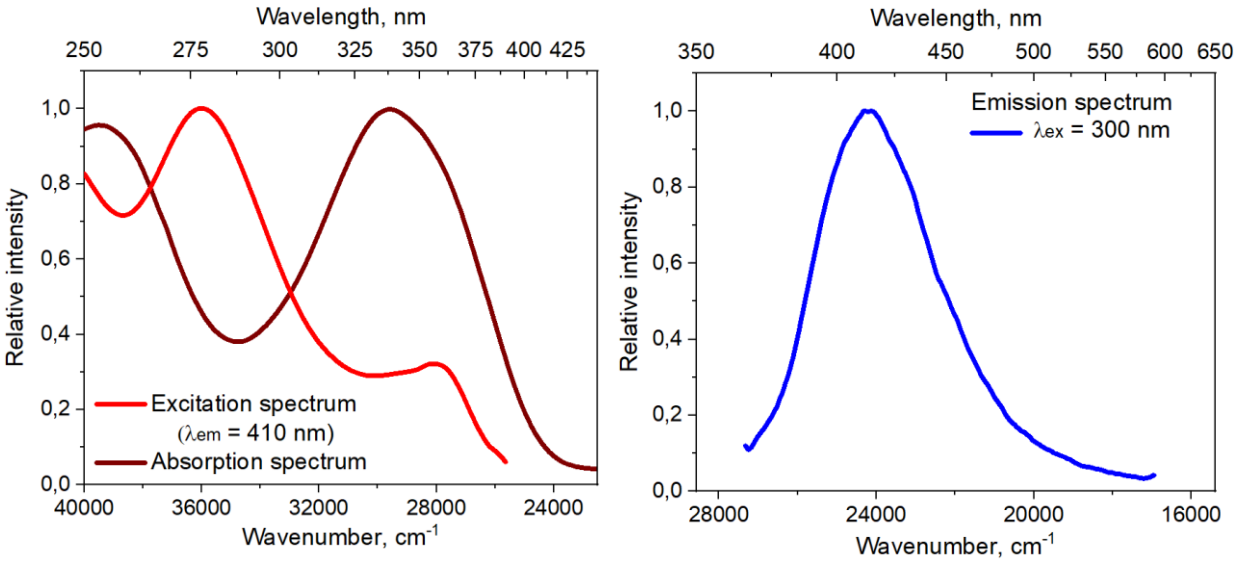


Figure S9. Absorption, excitation and emission spectra of **HL** in EtOH solution at 300 K.

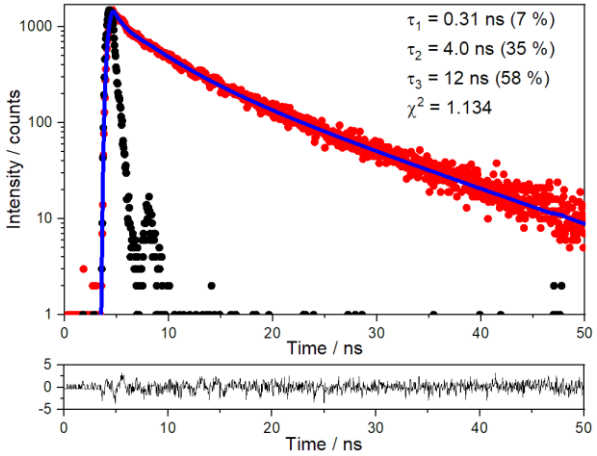


Figure S10. Fluorescence decay curves recorded for **HL** in EtOH solution at 300 K (λ_{ex} = 250 nm, λ_{det} = 410 nm): approximation (blue), experimental points (red) and instrument response function (black).

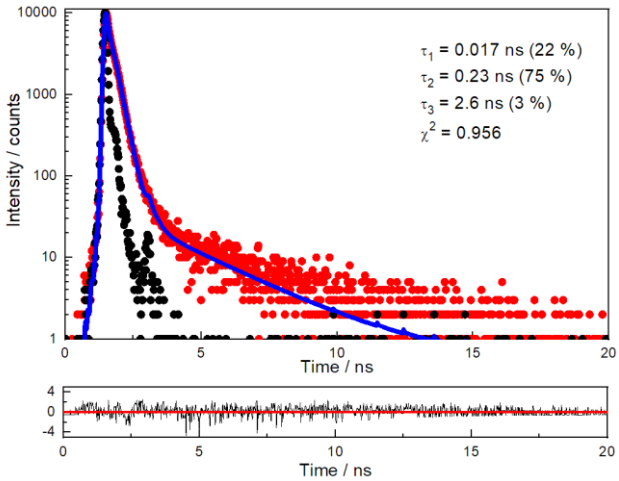


Figure S11. Fluorescence decay curves recorded for **HL** in MeCN solution at 300 K (λ_{ex} = 375 nm, λ_{det} = 450 nm): approximation (blue), experimental points (red) and instrument response function (black).

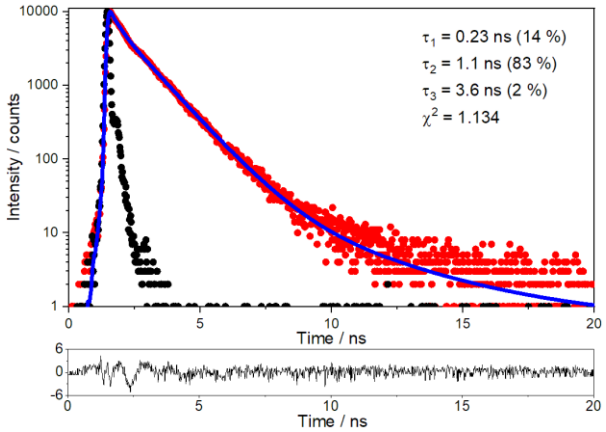


Figure S12. Fluorescence decay curves recorded for **HL** in CH_2Cl_2 solution at 300 K (λ_{ex} = 375nm, λ_{det} = 460 nm): approximation (blue), experimental points (red) and instrument response function (black).

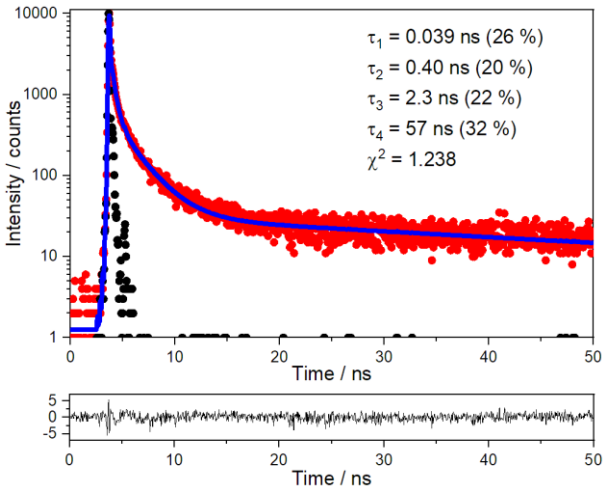


Figure S13. Fluorescence decay curves recorded for **HL** in the solid state at 300 K (λ_{ex} = 375 nm, λ_{det} = 470 nm): approximation (blue), experimental points (red) and instrument response function (black).

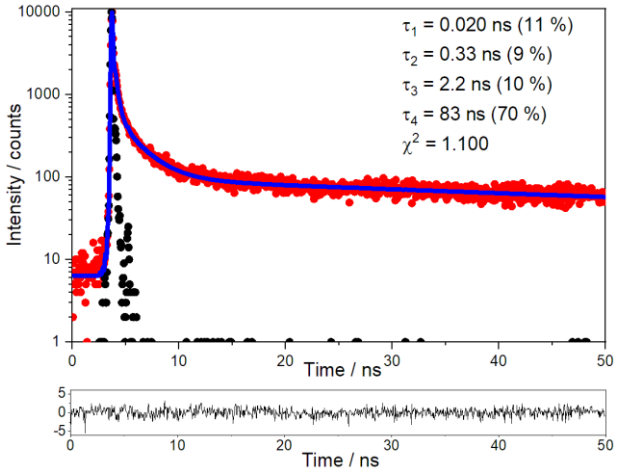


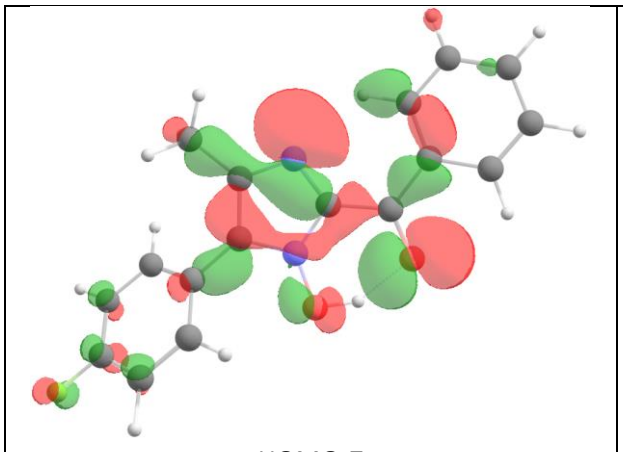
Figure S14. Fluorescence decay curves recorded for **HL** in the solid state at 300 K (λ_{ex} = 375 nm, λ_{det} = 545 nm): approximation (blue), experimental points (red) and instrument response function (black).

Theoretical part

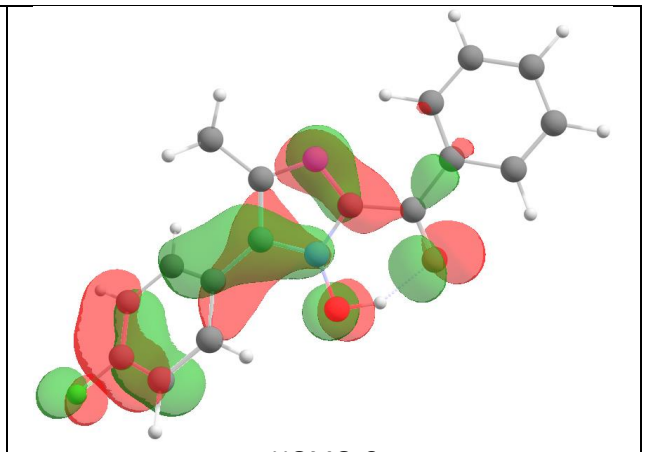
Table S1. Excited state properties of **HL-A** at the relaxed ground state geometry (S_0^N) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**. Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.4043	364.20	HOMO -> LUMO (98 %)	0.7407	$\pi - \pi^*$
S2	3.9893	310.79	HOMO-5 -> LUMO (63 %) HOMO-6 -> LUMO (12 %)	0.0068	$\sigma - \pi^*$, $n - \pi^*$
S3	4.1006	302.35	HOMO-1 -> LUMO (87 %)	0.0091	$\pi - \pi^*$
S4	4.1991	295.26	HOMO-2 -> LUMO (94 %)	0.0276	$\pi - \pi^*$
S5	4.5545	272.22	HOMO-3 -> LUMO (84 %)	0.1813	$\pi - \pi^*$
S6	4.6284	267.88	HOMO-4 -> LUMO (78 %) HOMO -> LUMO+2 (13 %)	0.0012	$\pi - \pi^*$
S7	4.7805	259.35	HOMO-7 -> LUMO (57 %) HOMO-5 -> LUMO (20 %) HOMO-6 -> LUMO (14 %)	0.0153	$\sigma - \pi^*$, $n - \pi^*$
S8	4.9605	249.94	HOMO -> LUMO+2 (61 %) HOMO -> LUMO+1 (16 %) HOMO-4 -> LUMO (13 %)	0.042	$\pi - \pi^*$
S9	4.9751	249.21	HOMO -> LUMO+1 (70 %) HOMO -> LUMO+2 (15 %)	0.1411	$\pi - \pi^*$
S10	5.1660	240.00	HOMO-6 -> LUMO (59 %) HOMO-7 -> LUMO (23 %)	0.0736	$\pi - \pi^*$

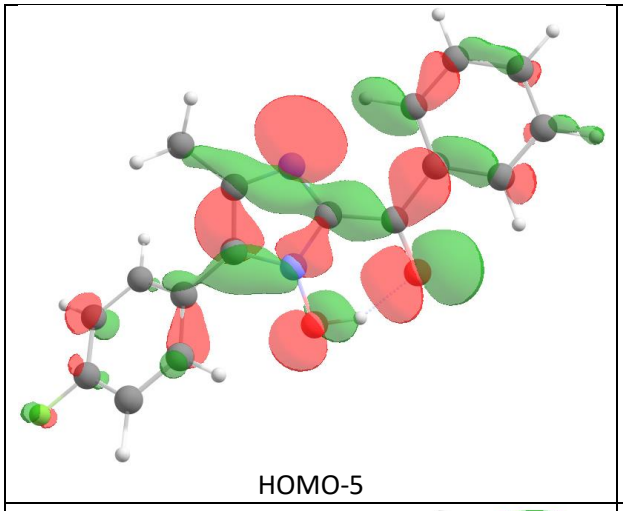
Table S2. Isosurface contour plots of the molecular orbitals of **HL-A** at the relaxed ground state geometry (S_0^N) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.



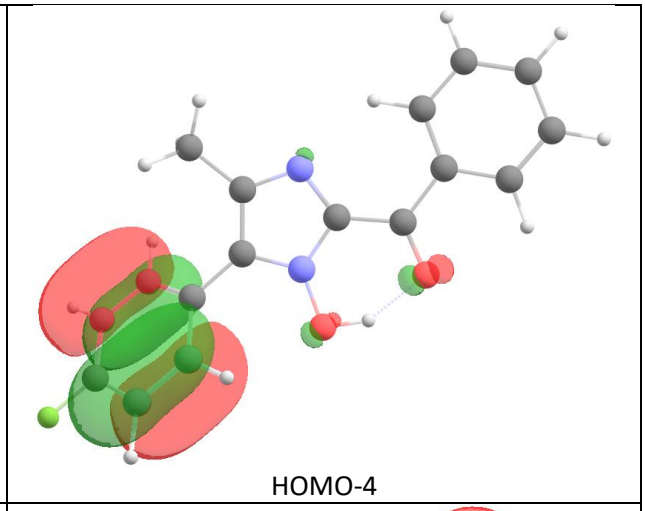
HOMO-7



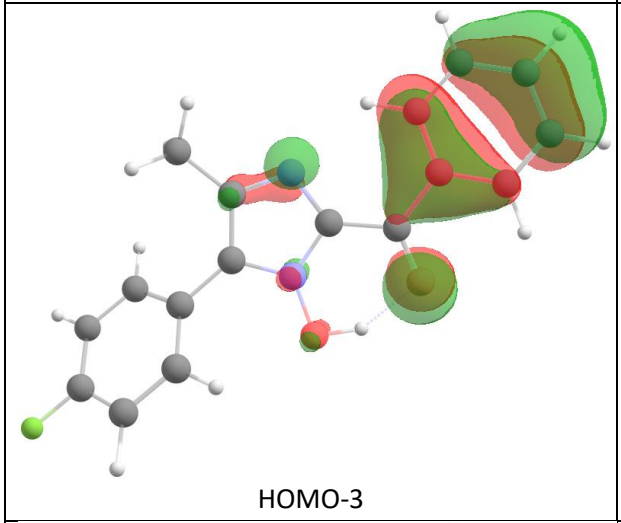
HOMO-6



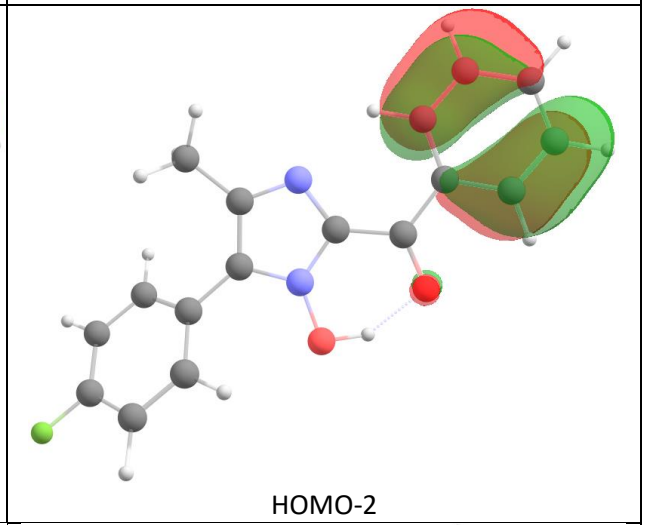
HOMO-5



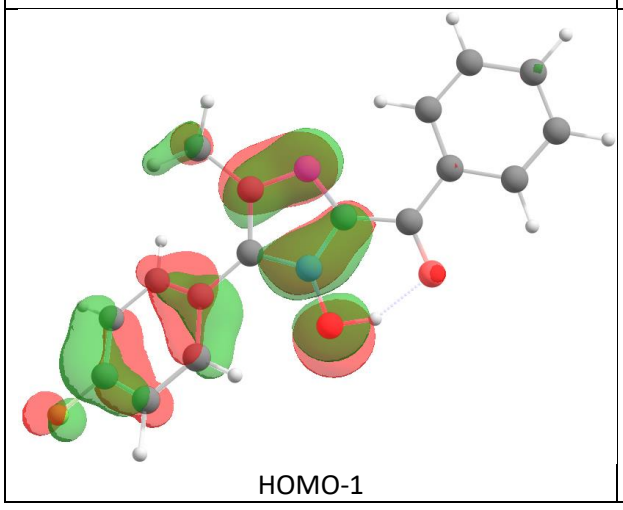
HOMO-4



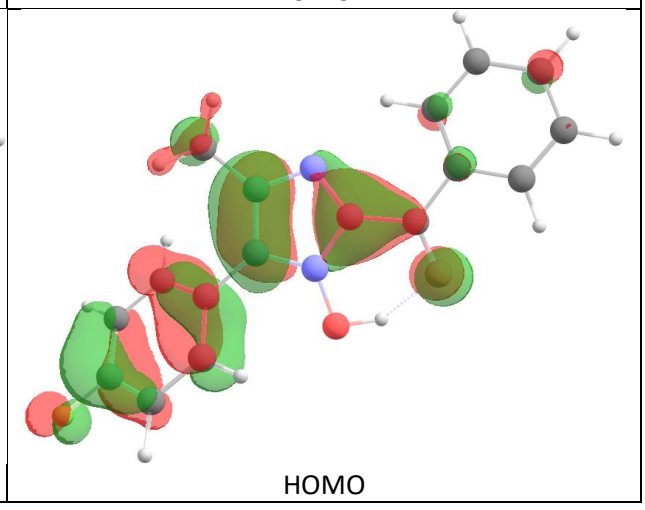
HOMO-3



HOMO-2



HOMO-1



HOMO

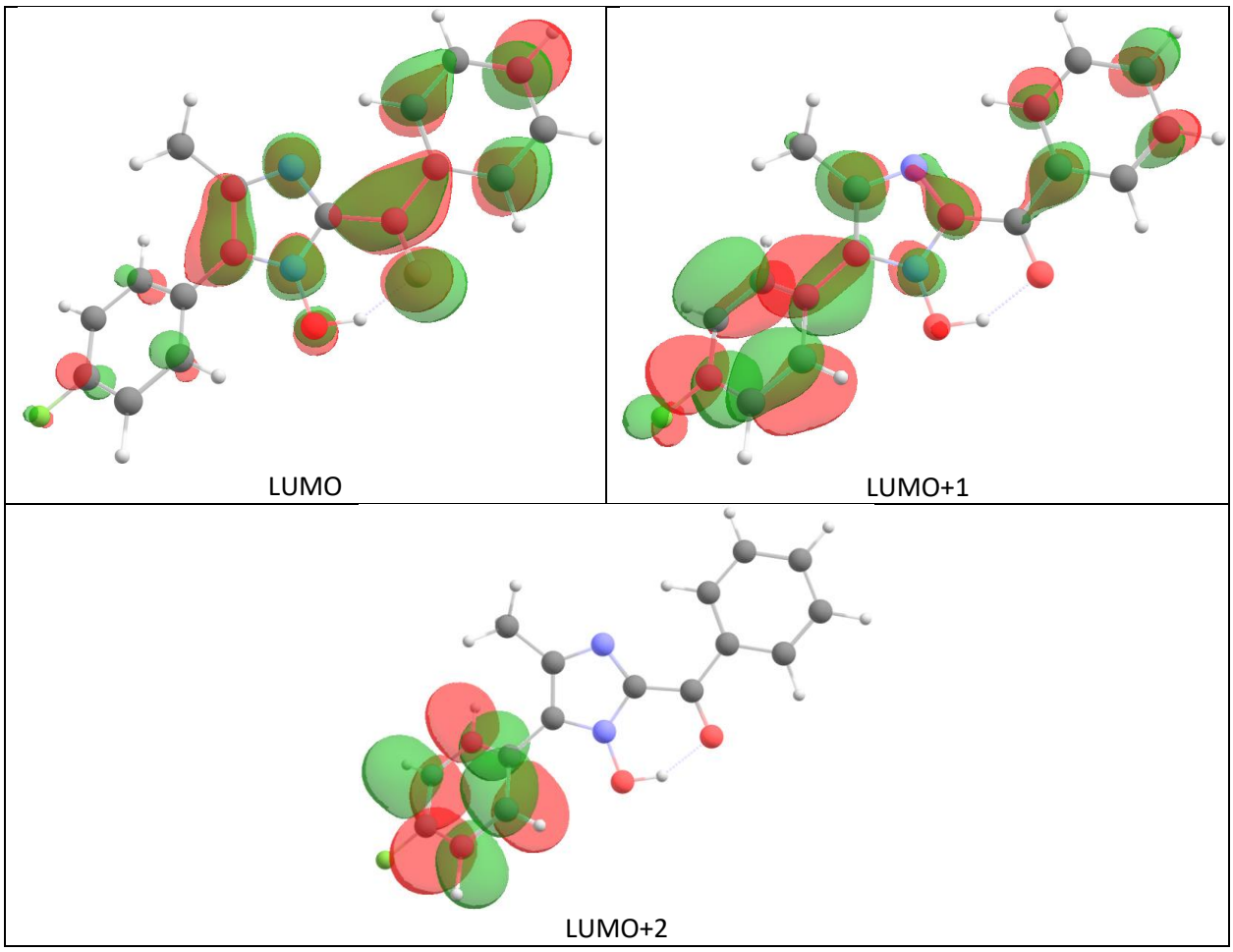
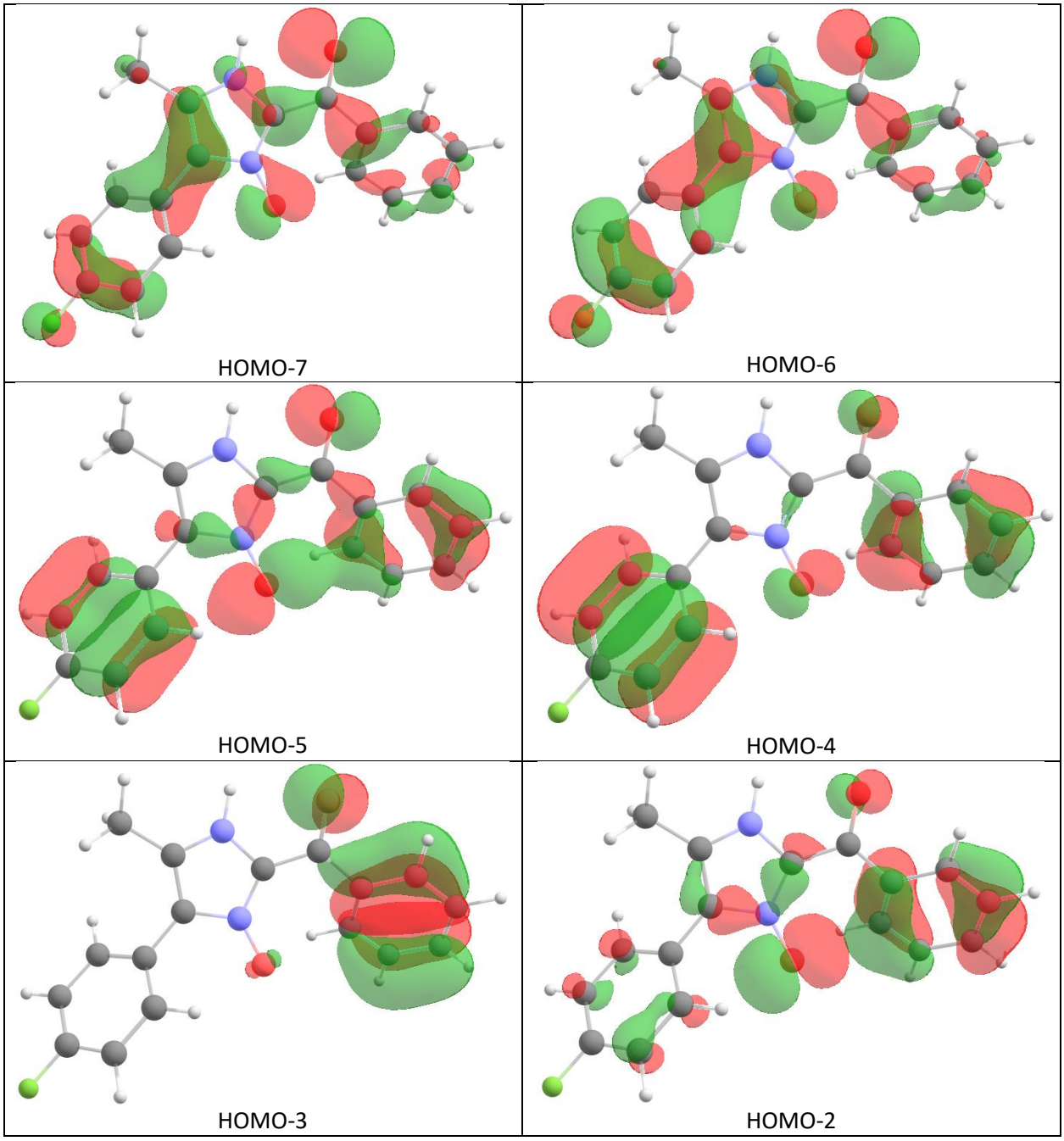


Table S3. Excited state properties of **HL-B** at the relaxed ground state geometry (S_0) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**. Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.3590	369.11	HOMO -> LUMO (93 %)	0.0571	$\pi - \pi^*$
S2	3.6532	339.39	HOMO-2 -> LUMO (39 %) HOMO-1 -> LUMO (38 %)	0.1168	$\pi - \pi^*$, $n - \pi^*$
S3	3.7702	328.85	HOMO-1 -> LUMO (58 %) HOMO-2 -> LUMO (25 %)	0.2910	$\pi - \pi^*$, $n - \pi^*$
S4	3.9382	314.82	HOMO-3 -> LUMO (30 %) HOMO-7 -> LUMO (28 %) HOMO-6 -> LUMO (18 %) HOMO-2 -> LUMO (16 %)	0.0439	$\pi - \pi^*$, $n - \pi^*$
S5	4.3613	284.28	HOMO-3 -> LUMO (40 %) HOMO-5 -> LUMO (26 %) HOMO-4 -> LUMO (20 %)	0.0208	$\pi - \pi^*$, $n - \pi^*$
S6	4.6422	267.08	HOMO-4 -> LUMO (34 %) HOMO-6 -> LUMO (19 %) HOMO-3 -> LUMO (18 %) HOMO-7 -> LUMO (14 %)	0.1435	$\pi - \pi^*$, $n - \pi^*$
S7	4.7057	263.48	HOMO -> LUMO+1 (91 %)	0.0849	$\pi - \pi^*$
S8	4.8007	258.26	HOMO-5 -> LUMO (38 %) HOMO-4 -> LUMO (28 %)	0.0043	$\pi - \pi^*$, $n - \pi^*$

			HOMO -> LUMO+2 (12 %)		
S9	4.9097	252.53	HOMO -> LUMO+2 (66 %)	0.0213	$\pi - \pi^*$
S10	5.0819	243.97	HOMO-1 -> LUMO+1 (31 %) HOMO-7 -> LUMO (29 %) HOMO-6 -> LUMO (28 %)	0.1573	$\pi - \pi^*$, $n - \pi^*$

Table S4. Isosurface contour plots of the molecular orbitals of **HL-B** at the relaxed ground state geometry ($\mathbf{S_0}$) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.



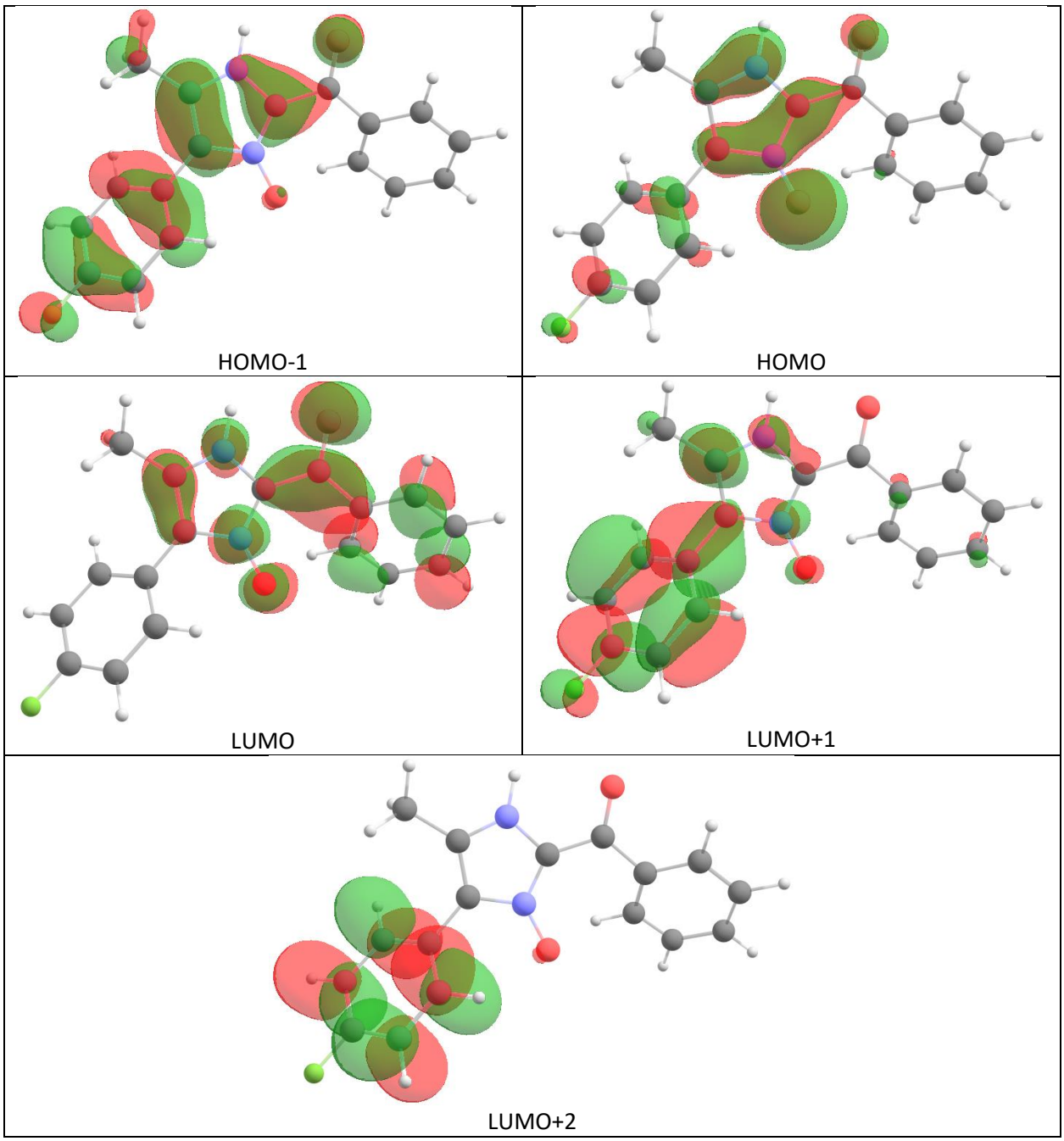
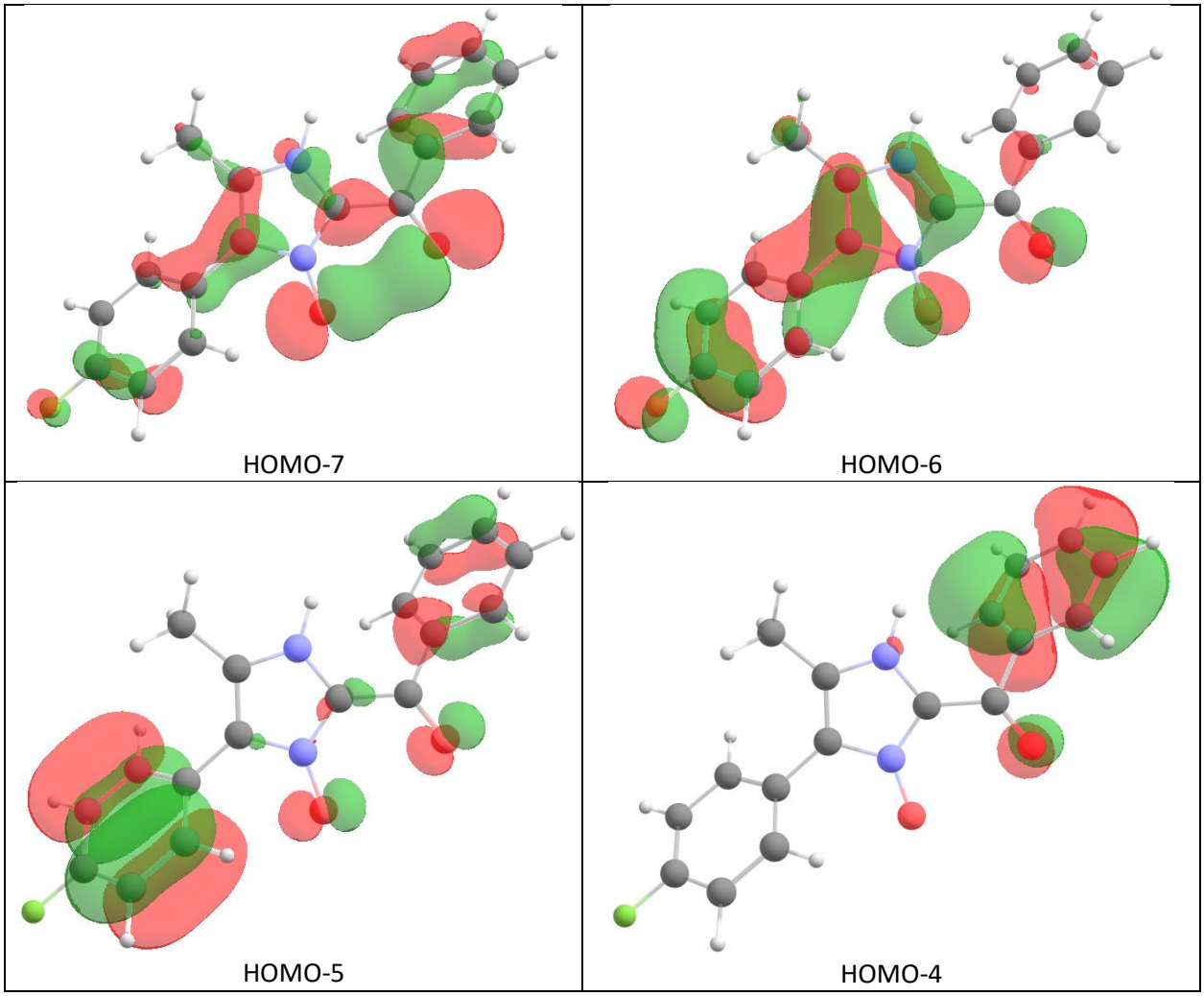


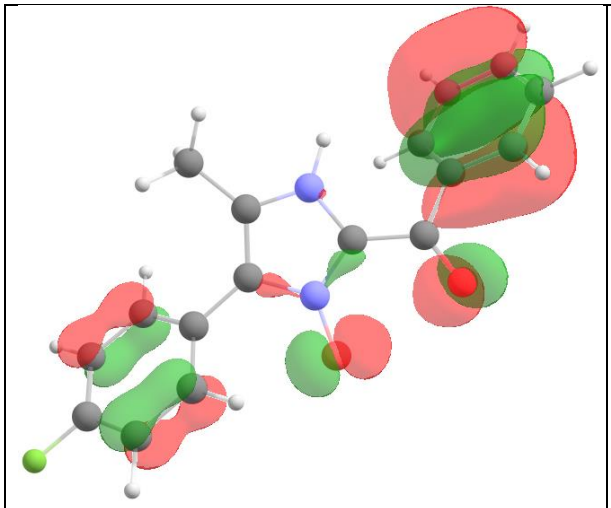
Table S5. Excited state properties of **HL-C** at the relaxed ground state geometry (S_0) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**. Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.4229	362.22	HOMO-2 -> LUMO (79 %) HOMO -> LUMO (12 %)	0.0151	$\sigma - \pi^*$, $n - \pi^*$
S2	3.6066	343.77	HOMO -> LUMO (86 %)	0.0741	$\pi - \pi^*$
S3	3.8976	318.11	HOMO-1 -> LUMO (94 %)	0.4738	$\pi - \pi^*$
S4	4.1955	295.52	HOMO-3 -> LUMO (45 %) HOMO-7 -> LUMO (38 %)	0.0419	$\pi - \pi^*$, $\sigma - \pi^*$, $n - \pi^*$
S5	4.5904	270.09	HOMO-4 -> LUMO (67 %) HOMO-3 -> LUMO (19 %)	0.0105	$\pi - \pi^*$

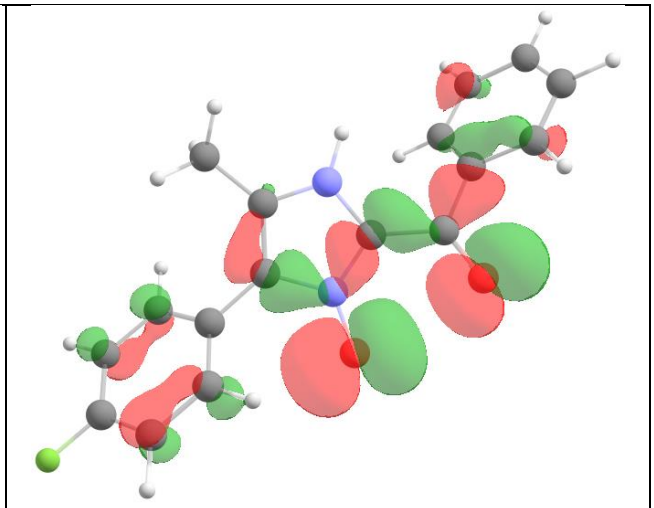
S6	4.6878	264.48	HOMO -> LUMO+1 (90 %)	0.1972	$\pi - \pi^*$
S7	4.8087	257.83	HOMO-5 -> LUMO (29 %) HOMO-4 -> LUMO (17 %) HOMO-3 -> LUMO (14 %) HOMO-7 -> LUMO (12 %)	0.0616	$\pi - \pi^*$, $\sigma - \pi^*$, $n - \pi^*$
S8	4.8483	255.73	HOMO -> LUMO+3 (42 %) HOMO-1 -> LUMO+3 (11 %)	0.0160	$\pi - \pi^*$
S9	4.9756	249.18	HOMO-5 -> LUMO (48 %) HOMO -> LUMO+3 (37 %)	0.0077	$\pi - \pi^*$
S10	5.0390	246.05	HOMO -> LUMO+2 (81 %)	0.0009	$\pi - \pi^*$

Table S6. Isosurface contour plots of the molecular orbitals of **HL-C** at the relaxed ground state geometry ($\mathbf{S_0}$) as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

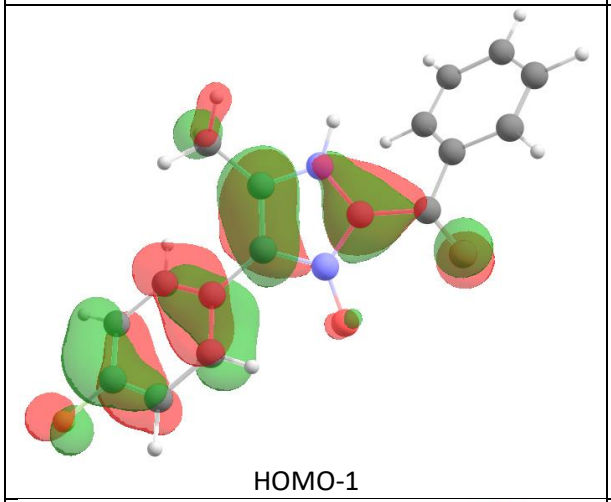




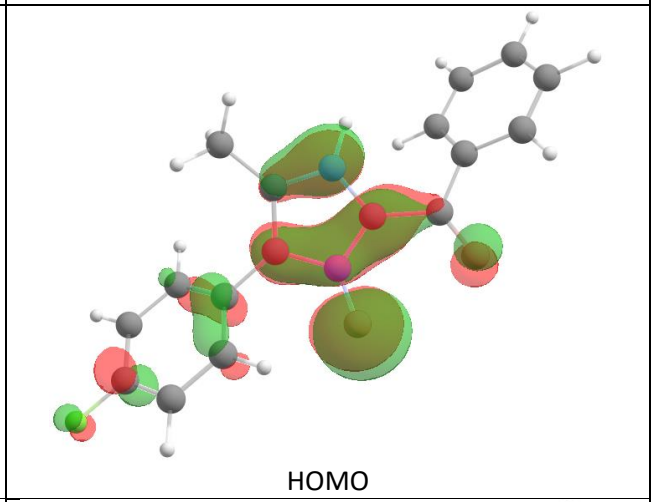
HOMO-3



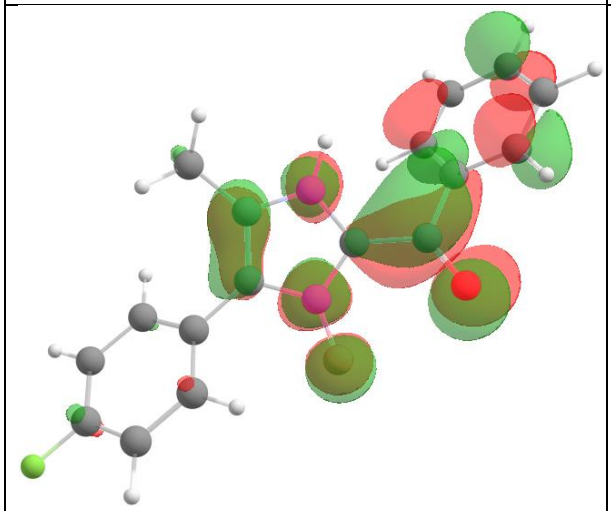
HOMO-2



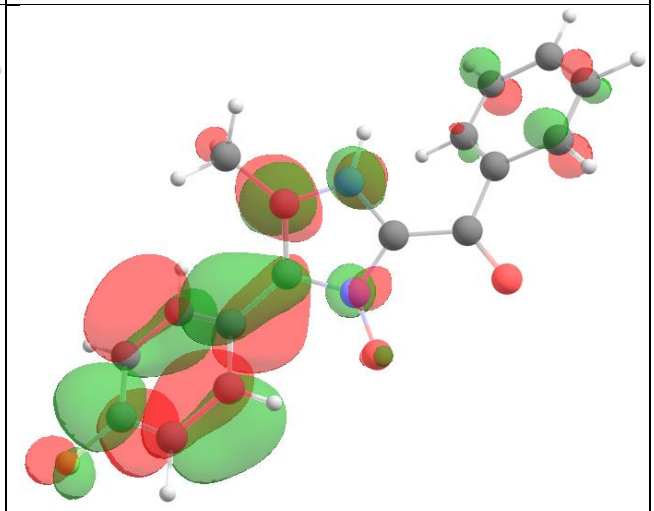
HOMO-1



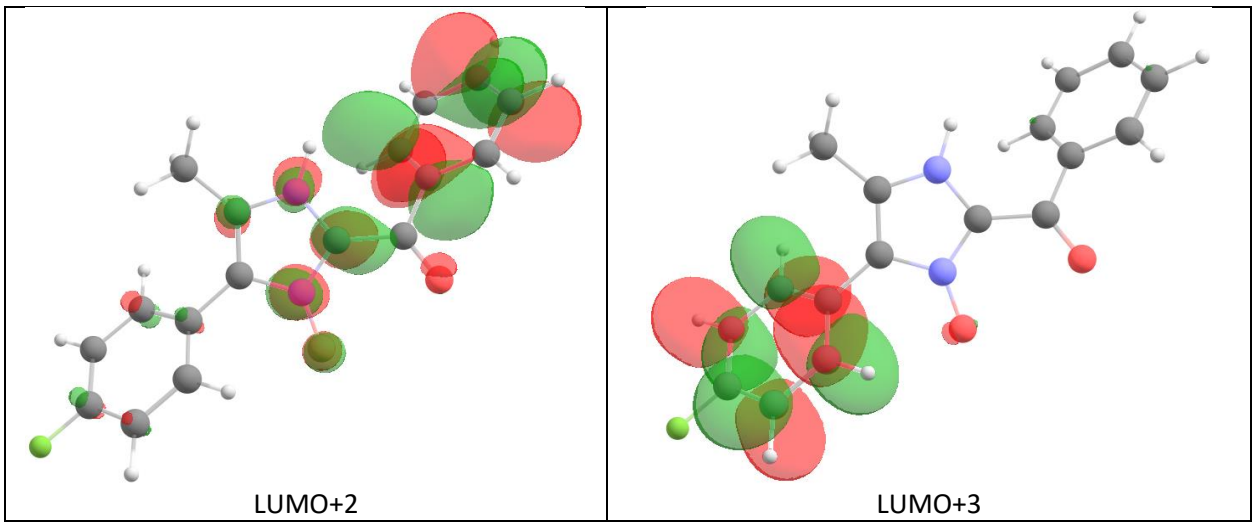
HOMO



LUMO



LUMO+1



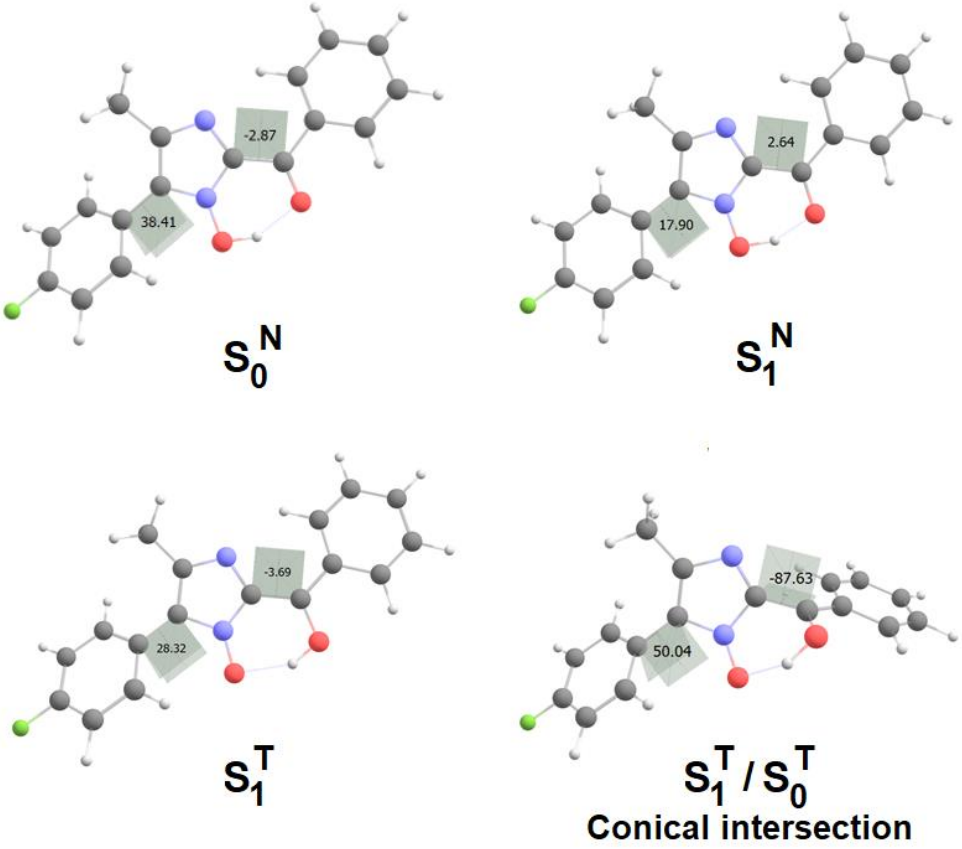
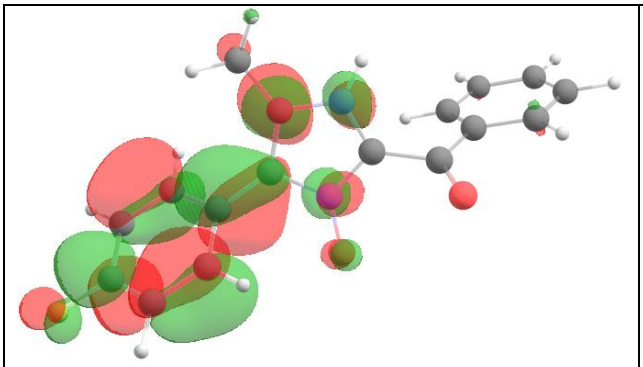


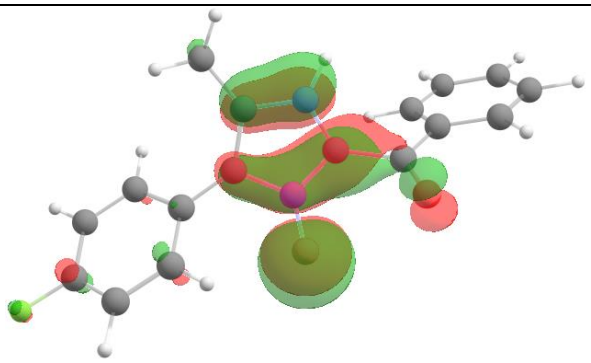
Figure S15. The optimized geometries of the ground state (S_0^N), of the first singlet excited state in both forms (S_1^N, S_1^T), of the S_1^T/S_0^T conical intersection for the **HL-A** molecule. The torsion angles C19–C14–C5–N1 and N3–C2–C6–C7 are also shown.

Table S7. Isosurface contour plots of the molecular orbitals of **HL–C** at the relaxed **third singlet excited state** geometry as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

S_3 → S_0 is LUMO+1 → HOMO transition, λ = 344 nm, f = 0.1569



LUMO+1



HOMO

Table S8. Optimized geometry of the **ground state** of **HL-A** (**normal form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	3.117099000000	0.646992000000	14.610070000000
O	-1.132374000000	5.196198000000	15.951399000000
N	-0.363336000000	5.536925000000	17.016018000000
O	-2.518938000000	7.169701000000	16.734273000000
C	-0.629041000000	6.541025000000	17.911570000000
N	0.340438000000	6.568042000000	18.835924000000
C	1.197753000000	5.578825000000	18.532391000000
C	0.774365000000	4.897397000000	17.372021000000
C	-1.798636000000	7.377632000000	17.738187000000
C	-2.158432000000	8.457293000000	18.684125000000
C	-1.598812000000	8.587030000000	19.964499000000
H	-0.843848000000	7.883436000000	20.295537000000
C	-2.014819000000	9.616951000000	20.803742000000
H	-1.582566000000	9.707490000000	21.796623000000
C	-2.980671000000	10.527809000000	20.376330000000
H	-3.298686000000	11.332344000000	21.034469000000
C	-3.540242000000	10.404978000000	19.102675000000
H	-4.291739000000	11.113789000000	18.765634000000
C	-3.136981000000	9.373010000000	18.264940000000
H	-3.568618000000	9.264727000000	17.274757000000
C	2.420684000000	5.324545000000	19.346656000000
H	2.713421000000	6.244195000000	19.860931000000
H	3.256920000000	4.990505000000	18.724354000000
H	2.248661000000	4.556621000000	20.111177000000
C	1.361930000000	3.780808000000	16.634001000000
C	1.973023000000	2.730049000000	17.335008000000
H	1.969671000000	2.727089000000	18.420608000000

C	2.569376000000	1.669986000000	16.659625000000
H	3.039440000000	0.851268000000	17.195298000000
C	2.542251000000	1.673401000000	15.274053000000
C	1.945733000000	2.689606000000	14.542900000000
H	1.949893000000	2.655026000000	13.457893000000
C	1.355604000000	3.744501000000	15.230113000000
H	0.892700000000	4.549168000000	14.668692000000
H	-1.854264000000	5.899544000000	15.995880000000

Table S9. Optimized geometry of the **ground state** of **HL-B** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	3.543575000000	0.709104000000	14.705793000000
O	-0.621580000000	5.391088000000	15.774634000000
N	-0.125765000000	5.547734000000	16.945052000000
O	-1.358721000000	8.396667000000	18.761415000000
C	-0.515762000000	6.455821000000	17.878053000000
N	0.312932000000	6.296962000000	18.948249000000
C	1.198296000000	5.302701000000	18.730378000000
C	0.932736000000	4.807637000000	17.460538000000
C	-1.478469000000	7.550292000000	17.868132000000
C	-2.573013000000	7.655504000000	16.873765000000
C	-3.239045000000	6.532440000000	16.369915000000
H	-2.905585000000	5.535598000000	16.638330000000
C	-4.334606000000	6.696041000000	15.526536000000
H	-4.859883000000	5.822612000000	15.149493000000
C	-4.753583000000	7.975878000000	15.161011000000
H	-5.600684000000	8.098450000000	14.490890000000
C	-4.088003000000	9.098799000000	15.656479000000
H	-4.412321000000	10.096127000000	15.371842000000
C	-3.012053000000	8.939208000000	16.522874000000
H	-2.497215000000	9.804440000000	16.930833000000
C	2.225398000000	4.910804000000	19.729467000000
H	2.553173000000	5.781064000000	20.305923000000
H	3.096461000000	4.476500000000	19.232576000000
H	1.833478000000	4.168599000000	20.434839000000
C	1.589621000000	3.730585000000	16.720832000000
C	1.956232000000	2.550444000000	17.383781000000
H	1.706769000000	2.417084000000	18.432506000000
C	2.621239000000	1.527424000000	16.713164000000
H	2.905724000000	0.610341000000	17.219484000000
C	2.902836000000	1.699027000000	15.367683000000
C	2.548202000000	2.845180000000	14.672033000000
H	2.788060000000	2.937593000000	13.617226000000
C	1.890017000000	3.861720000000	15.356104000000
H	1.603735000000	4.764609000000	14.828290000000
H	0.255215000000	6.892342000000	19.765097000000

Table S10. Optimized geometry of the **ground state** of **HL-C** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	2.825278000000	0.338922000000	15.116551000000
O	-0.770844000000	5.531679000000	15.797687000000
N	-0.107597000000	5.839189000000	16.845975000000
O	-1.843457000000	8.176003000000	16.381837000000
C	-0.325999000000	6.910970000000	17.653888000000
N	0.588169000000	6.826515000000	18.668502000000
C	1.377395000000	5.740638000000	18.512928000000
C	0.936647000000	5.086608000000	17.371927000000
C	-1.288792000000	7.983177000000	17.461670000000
C	-1.562950000000	8.876443000000	18.628139000000
C	-1.716634000000	8.381215000000	19.929738000000
H	-1.626438000000	7.315470000000	20.126345000000
C	-2.037146000000	9.247798000000	20.973281000000
H	-2.172442000000	8.855205000000	21.977341000000
C	-2.190165000000	10.611386000000	20.727052000000
H	-2.431913000000	11.286850000000	21.543408000000
C	-2.040539000000	11.108926000000	19.430745000000
H	-2.161381000000	12.171455000000	19.237584000000
C	-1.739954000000	10.244498000000	18.383863000000
H	-1.632779000000	10.619284000000	17.369668000000
C	2.494882000000	5.426761000000	19.440316000000
H	2.969085000000	6.345389000000	19.799458000000
H	3.252496000000	4.822986000000	18.935090000000
H	2.142705000000	4.866971000000	20.314684000000
C	1.406403000000	3.841273000000	16.767384000000
C	1.747457000000	2.753334000000	17.584057000000
H	1.617720000000	2.820501000000	18.660408000000
C	2.232606000000	1.569011000000	17.036174000000
H	2.495829000000	0.722098000000	17.662087000000
C	2.360135000000	1.486632000000	15.659183000000
C	2.023919000000	2.534553000000	14.815156000000
H	2.138890000000	2.426461000000	13.741028000000
C	1.545900000000	3.713770000000	15.376593000000
H	1.276493000000	4.542800000000	14.731720000000
H	0.716352000000	7.541422000000	19.372696000000

Table S11. Optimized geometry of the **ground state** of **HL-D** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	6.783332000000	6.955621000000	15.229412000000
O	0.637639000000	8.297109000000	16.306164000000
N	0.601192000000	7.213900000000	17.134046000000
O	-2.460417000000	7.446807000000	18.914207000000

C	-0.474737000000	6.813118000000	17.869602000000
N	-0.127821000000	5.784582000000	18.630899000000
C	1.183600000000	5.524825000000	18.378962000000
C	1.682643000000	6.425953000000	17.441957000000
C	-1.828028000000	7.415422000000	17.863176000000
C	-2.416821000000	7.919298000000	16.596842000000
C	-2.055648000000	7.387179000000	15.352725000000
H	-1.293609000000	6.615057000000	15.288224000000
C	-2.691686000000	7.825862000000	14.194980000000
H	-2.418564000000	7.399402000000	13.233636000000
C	-3.676702000000	8.810896000000	14.270223000000
H	-4.165592000000	9.159032000000	13.363996000000
C	-4.038000000000	9.348321000000	15.507842000000
H	-4.803999000000	10.116918000000	15.565630000000
C	-3.419656000000	8.895656000000	16.667686000000
H	-3.698943000000	9.296303000000	17.638083000000
C	1.889988000000	4.390872000000	19.042134000000
H	2.297098000000	4.683293000000	20.018190000000
H	2.720021000000	4.022065000000	18.432088000000
H	1.189798000000	3.567124000000	19.210896000000
C	3.010217000000	6.592526000000	16.853331000000
C	3.176200000000	6.881291000000	15.488998000000
H	2.306944000000	6.999807000000	14.850325000000
C	4.446304000000	7.007351000000	14.936754000000
H	4.584547000000	7.226221000000	13.882492000000
C	5.547325000000	6.836533000000	15.762433000000
C	5.428347000000	6.549885000000	17.113106000000
H	6.315714000000	6.431243000000	17.726965000000
C	4.151591000000	6.433072000000	17.653871000000
H	4.043681000000	6.232102000000	18.715551000000
H	0.954241000000	9.042232000000	16.848638000000

Table S12. Optimized geometry of the **ground state** of **HL-E** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	3.371447000000	0.628083000000	14.776779000000
O	-1.021309000000	5.061082000000	15.998141000000
H	-0.969145000000	5.717127000000	15.277948000000
N	-0.224297000000	5.528152000000	17.005311000000
O	-2.309791000000	7.730171000000	18.880866000000
C	-0.586245000000	6.456823000000	17.942391000000
N	0.287296000000	6.443404000000	18.939132000000
C	1.199489000000	5.475942000000	18.656249000000
C	0.887774000000	4.857879000000	17.446820000000
C	-1.747796000000	7.361927000000	17.855198000000
C	-2.196151000000	7.832518000000	16.517050000000
C	-3.557349000000	8.079957000000	16.304993000000
H	-4.262179000000	7.890577000000	17.109729000000

C	-3.996762000000	8.546869000000	15.070447000000
H	-5.056205000000	8.721297000000	14.903763000000
C	-3.078889000000	8.790720000000	14.047031000000
H	-3.424188000000	9.159259000000	13.084830000000
C	-1.717975000000	8.568861000000	14.259578000000
H	-0.999946000000	8.778106000000	13.471549000000
C	-1.276280000000	8.084855000000	15.488917000000
H	-0.209996000000	7.945970000000	15.661904000000
C	2.354628000000	5.208592000000	19.560814000000
H	2.699374000000	6.144732000000	20.010417000000
H	3.190508000000	4.753888000000	19.021103000000
H	2.076931000000	4.532128000000	20.378781000000
C	1.518127000000	3.751816000000	16.728542000000
C	1.972249000000	2.632138000000	17.441549000000
H	1.817080000000	2.575925000000	18.514939000000
C	2.602261000000	1.575408000000	16.791502000000
H	2.952721000000	0.704305000000	17.336142000000
C	2.764414000000	1.651046000000	15.417253000000
C	2.327771000000	2.737136000000	14.673650000000
H	2.481356000000	2.759568000000	13.599291000000
C	1.705962000000	3.788586000000	15.338101000000
H	1.382951000000	4.652369000000	14.765772000000

Table S13. Optimized geometry of the **first singlet excited state** of **HL-A** (**normal form**, $\mathbf{S_1^N}$) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	3.015945000000	0.666227000000	14.638685000000
O	-0.475241000000	5.910502000000	15.761931000000
H	-1.069994000000	6.785452000000	15.850815000000
N	0.093855000000	5.915849000000	16.992775000000
O	-1.612037000000	7.930808000000	16.497065000000
C	-0.178699000000	6.819523000000	17.968707000000
N	0.483701000000	6.485544000000	19.101637000000
C	1.130174000000	5.342671000000	18.853273000000
C	0.903368000000	4.917152000000	17.499895000000
C	-1.108312000000	7.931136000000	17.689003000000
C	-1.440708000000	8.942668000000	18.645144000000
C	-0.907928000000	9.008083000000	19.964687000000
H	-0.195856000000	8.258741000000	20.289463000000
C	-1.294699000000	10.021372000000	20.829380000000
H	-0.875543000000	10.051513000000	21.832506000000
C	-2.209202000000	11.001832000000	20.428046000000
H	-2.503848000000	11.792830000000	21.112560000000
C	-2.739751000000	10.953773000000	19.129237000000
H	-3.450682000000	11.711244000000	18.807226000000
C	-2.367522000000	9.950868000000	18.253106000000
H	-2.779789000000	9.913702000000	17.249753000000

C	2.004849000000	4.730471000000	19.885873000000
H	2.165509000000	5.457310000000	20.685830000000
H	2.976734000000	4.431733000000	19.479286000000
H	1.542577000000	3.840253000000	20.332601000000
C	1.421282000000	3.824052000000	16.749721000000
C	1.929902000000	2.674397000000	17.419796000000
H	1.869875000000	2.603298000000	18.498634000000
C	2.463290000000	1.615592000000	16.715475000000
H	2.839722000000	0.731706000000	17.219829000000
C	2.497196000000	1.690801000000	15.322877000000
C	2.005506000000	2.787632000000	14.617626000000
H	2.056842000000	2.800778000000	13.533702000000
C	1.466260000000	3.843262000000	15.324434000000
H	1.087491000000	4.705374000000	14.790079000000

Table S14. Optimized geometry of the **first singlet excited state** of **HL-A** (**tautomeric form**, S_1^T) in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	2.960105000000	0.627340000000	14.638421000000
O	-0.569364000000	5.752546000000	15.850371000000
H	-1.388188000000	7.250912000000	15.955638000000
N	0.007934000000	5.863405000000	16.995489000000
O	-1.644272000000	8.044652000000	16.488238000000
C	-0.206932000000	6.811086000000	17.935484000000
N	0.522317000000	6.523967000000	19.030330000000
C	1.201249000000	5.369223000000	18.812190000000
C	0.936105000000	4.908147000000	17.528368000000
C	-1.103405000000	7.931366000000	17.716541000000
C	-1.455313000000	8.935625000000	18.660139000000
C	-0.977135000000	8.961198000000	19.998921000000
H	-0.302874000000	8.184613000000	20.338437000000
C	-1.366181000000	9.970243000000	20.867252000000
H	-0.987015000000	9.965610000000	21.886476000000
C	-2.233453000000	10.986075000000	20.452011000000
H	-2.531034000000	11.772305000000	21.140300000000
C	-2.712853000000	10.975606000000	19.136491000000
H	-3.388158000000	11.758264000000	18.798969000000
C	-2.337712000000	9.976224000000	18.254304000000
H	-2.718082000000	9.980081000000	17.238413000000
C	2.121318000000	4.817812000000	19.846980000000
H	2.398862000000	5.614974000000	20.542032000000
H	3.036189000000	4.412819000000	19.401560000000
H	1.651001000000	4.016793000000	20.430966000000
C	1.437490000000	3.804978000000	16.761060000000
C	1.859653000000	2.628480000000	17.424168000000
H	1.748789000000	2.543687000000	18.499447000000
C	2.367791000000	1.555003000000	16.714236000000
H	2.678020000000	0.641690000000	17.211185000000

C	2.462224000000	1.662828000000	15.330295000000
C	2.067513000000	2.801113000000	14.635798000000
H	2.178151000000	2.843666000000	13.557082000000
C	1.556542000000	3.870040000000	15.351519000000
H	1.262615000000	4.773156000000	14.829942000000

Table S15. Optimized geometry of the **first singlet excited state** of **HL-B** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	4.071575000000	0.733510000000	14.879114000000
O	0.246517000000	5.809814000000	15.221277000000
N	0.345210000000	5.749399000000	16.471701000000
O	-0.210733000000	8.843610000000	16.746297000000
C	-0.312067000000	6.636639000000	17.321583000000
N	0.016439000000	6.245303000000	18.540205000000
C	0.869533000000	5.139783000000	18.524119000000
C	1.076432000000	4.816180000000	17.212302000000
C	-1.021738000000	7.855872000000	16.888309000000
C	-2.431885000000	7.839745000000	16.663037000000
C	-3.226050000000	6.675930000000	16.844176000000
H	-2.764622000000	5.746130000000	17.172496000000
C	-4.593478000000	6.700837000000	16.610871000000
H	-5.174166000000	5.792708000000	16.758098000000
C	-5.229651000000	7.875406000000	16.190255000000
H	-6.300662000000	7.889396000000	16.009106000000
C	-4.459390000000	9.031976000000	16.008288000000
H	-4.938489000000	9.952988000000	15.682039000000
C	-3.091896000000	9.022974000000	16.236821000000
H	-2.501781000000	9.923660000000	16.092805000000
C	1.386160000000	4.544229000000	19.774994000000
H	1.805502000000	5.319618000000	20.425320000000
H	2.166287000000	3.813885000000	19.553587000000
H	0.584028000000	4.040670000000	20.327410000000
C	1.856475000000	3.746587000000	16.586341000000
C	1.723134000000	2.427984000000	17.039448000000
H	1.017492000000	2.193676000000	17.831430000000
C	2.473606000000	1.403683000000	16.470583000000
H	2.379759000000	0.377262000000	16.810380000000
C	3.343924000000	1.721429000000	15.439749000000
C	3.495654000000	3.013545000000	14.958442000000
H	4.190525000000	3.216096000000	14.149744000000
C	2.745890000000	4.029205000000	15.540555000000
H	2.861356000000	5.047421000000	15.182155000000
H	-0.311479000000	6.709269000000	19.380180000000

Table S16. Optimized geometry of the **first singlet excited state** of **HL-C** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	2.786234000000	0.628062000000	14.556147000000
O	-0.688439000000	5.801594000000	16.059802000000
N	0.012434000000	5.840182000000	17.177012000000
O	-1.728094000000	7.681946000000	16.648671000000
C	-0.203279000000	6.795104000000	18.108751000000
N	0.678535000000	6.538404000000	19.118912000000
C	1.444744000000	5.441518000000	18.808971000000
C	1.016646000000	4.975910000000	17.580789000000
C	-1.180823000000	7.771875000000	17.831233000000
C	-1.570034000000	8.854293000000	18.721000000000
C	-1.375848000000	8.804791000000	20.117269000000
H	-0.979263000000	7.911946000000	20.592061000000
C	-1.760549000000	9.871230000000	20.921272000000
H	-1.607046000000	9.809650000000	21.995696000000
C	-2.358469000000	11.003637000000	20.362976000000
H	-2.657588000000	11.833974000000	20.996723000000
C	-2.581668000000	11.050680000000	18.984778000000
H	-3.055558000000	11.922328000000	18.540091000000
C	-2.198630000000	9.991703000000	18.171304000000
H	-2.365842000000	10.035983000000	17.099176000000
C	2.523510000000	4.962641000000	19.709659000000
H	3.049551000000	5.808162000000	20.165095000000
H	3.252509000000	4.370137000000	19.151754000000
H	2.127120000000	4.339606000000	20.520646000000
C	1.460124000000	3.835047000000	16.782480000000
C	1.819699000000	2.632039000000	17.408087000000
H	1.723708000000	2.528545000000	18.484764000000
C	2.275536000000	1.547956000000	16.663951000000
H	2.552853000000	0.612750000000	17.140167000000
C	2.351388000000	1.678869000000	15.286483000000
C	1.990214000000	2.844771000000	14.628223000000
H	2.061847000000	2.904697000000	13.546651000000
C	1.545955000000	3.924203000000	15.384106000000
H	1.265446000000	4.845629000000	14.883652000000
H	0.872407000000	7.166331000000	19.885811000000

Table S17. Optimized geometry of the **third singlet excited state** of **HL-C** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	2.264972000000	0.130575000000	15.129404000000
O	-0.686499000000	5.738903000000	16.040383000000
N	0.150756000000	6.014944000000	16.950523000000
O	-0.847915000000	8.705764000000	16.291830000000

C	0.077616000000	7.135706000000	17.734176000000
N	0.974140000000	6.978528000000	18.690849000000
C	1.711605000000	5.792491000000	18.507666000000
C	1.147829000000	5.119115000000	17.430198000000
C	-0.772575000000	8.331401000000	17.451120000000
C	-1.421324000000	9.010298000000	18.585145000000
C	-1.679517000000	8.352109000000	19.797573000000
H	-1.404941000000	7.309341000000	19.932545000000
C	-2.332218000000	9.025383000000	20.825774000000
H	-2.543313000000	8.511018000000	21.758737000000
C	-2.716966000000	10.355225000000	20.654365000000
H	-3.219156000000	10.881099000000	21.461899000000
C	-2.463388000000	11.013673000000	19.447660000000
H	-2.764470000000	12.049399000000	19.318795000000
C	-1.825327000000	10.344041000000	18.412920000000
H	-1.622206000000	10.840591000000	17.468700000000
C	2.838673000000	5.449408000000	19.401627000000
H	3.439164000000	6.336421000000	19.636265000000
H	3.487833000000	4.719206000000	18.912186000000
H	2.504054000000	5.015583000000	20.355532000000
C	1.374821000000	3.846314000000	16.836851000000
C	1.824941000000	2.738097000000	17.639139000000
H	1.899769000000	2.852729000000	18.717501000000
C	2.096021000000	1.509866000000	17.077967000000
H	2.403682000000	0.669451000000	17.694581000000
C	1.949203000000	1.344507000000	15.688416000000
C	1.581551000000	2.404211000000	14.855975000000
H	1.530921000000	2.251525000000	13.780555000000
C	1.307765000000	3.642681000000	15.404234000000
H	1.051615000000	4.468295000000	14.748682000000
H	1.182217000000	7.678294000000	19.394389000000

Table S18. Estimated geometry of the **S_1/S_0 conical intersection** of **HL-A** in Cartesian (XYZ) coordinates as calculated in Gaussian at the PBE0/6-31+g(d) level of theory **in MeCN continuum solvation model**.

F	1.510360000000	0.242800000000	15.005614000000
O	-0.429934000000	6.294758000000	16.356002000000
H	0.070532000000	8.150967000000	16.029626000000
N	0.346442000000	6.160110000000	17.353094000000
O	0.114877000000	8.945702000000	16.618163000000
C	0.617741000000	7.268826000000	18.172369000000
N	1.686724000000	7.070012000000	18.860686000000
C	2.116454000000	5.749284000000	18.558989000000
C	1.332219000000	5.192903000000	17.590744000000
C	-0.168560000000	8.478744000000	17.854800000000
C	-1.206617000000	9.008880000000	18.639098000000
C	-1.442658000000	8.510035000000	19.948775000000
H	-0.801819000000	7.729704000000	20.349336000000

C	-2.474871000000	9.022557000000	20.719347000000
H	-2.647757000000	8.624015000000	21.715478000000
C	-3.279908000000	10.055778000000	20.231134000000
H	-4.079386000000	10.461579000000	20.844011000000
C	-3.044866000000	10.570846000000	18.948303000000
H	-3.668998000000	11.374601000000	18.566414000000
C	-2.033294000000	10.059270000000	18.155995000000
H	-1.863742000000	10.447381000000	17.156746000000
C	3.284455000000	5.187400000000	19.277109000000
H	4.096814000000	5.921596000000	19.304498000000
H	3.645796000000	4.273422000000	18.799514000000
H	3.026503000000	4.949632000000	20.317371000000
C	1.362531000000	3.896932000000	16.904820000000
C	1.508322000000	2.715927000000	17.644682000000
H	1.562867000000	2.760380000000	18.728721000000
C	1.566578000000	1.477720000000	17.010615000000
H	1.679435000000	0.557465000000	17.575170000000
C	1.461074000000	1.440988000000	15.629577000000
C	1.304268000000	2.585127000000	14.862262000000
H	1.227528000000	2.510660000000	13.781969000000
C	1.259553000000	3.816572000000	15.508616000000
H	1.149407000000	4.721614000000	14.919774000000