Table S1. Relative energies of **L1-L5** (R1-5= −H, $-NH_2$, $-OCH_3$, $-CF_3$, and –CN) at the S_0 and S_1 states calculated at CAM-B3LYP/6-31++G(d,p) level

		CAM-B3LYP				
Media	Molecule	S_0-E	S_1(FC)	S_1-E	S_0-K	S_1-K
Gas	**L1**	0.00	81.44	75.42	8.67	76.40
	L2	0.00	80.97	74.90	7.13	77.75
	L3	0.00	81.25	75.13	6.57	76.91
	L4	0.00	79.84	73.91	8.08	75.36
	L5	0.00	78.35	72.45	8.30	74.30
DMSO	**L1**	0.00	78.66	67.99	5.96	68.71
	L2	0.00	77.88	66.90	4.25	69.01
	L3	0.00	83.22	67.84	4.00	68.54
	L4	0.00	77.24	66.53	5.37	66.89
	L5	0.00	75.59	64.67	5.60	65.34
MeOH	**L1**	0.00	78.97	68.09	6.01	68.82
	L2	0.00	.78.21	67.02	4.30	69.14
	L3	0.00	78.84	67.94	4.04	68.66
	L4	0.00	77.53	66.64	5.41	67.00
	L5	0.00	75.88	64.78	5.65	65.47
Toluene	**L1**	0.00	78.78	71.69	7.44	72.76
	L2	0.00	78.17	70.88	5.83	73.49
	L3	0.00	78.66	71.44	5.38	72.76
	L4	0.00	77.18	70.20	6.82	71.16
	L5	0.00	75.56	68.47	7.05	69.85

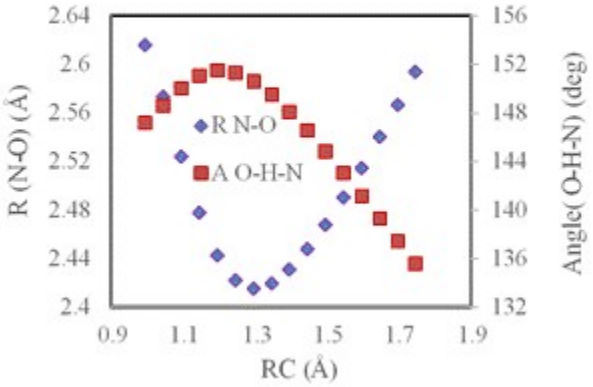
Table S2. The calculated absorption and emission wavelengths (λ) and oscillator strength (*f*) of **L1-L5** (R1-5= −H, $-NH_2$, $-OCH_3$, $-CF_3$, and –CN) in the gas phase

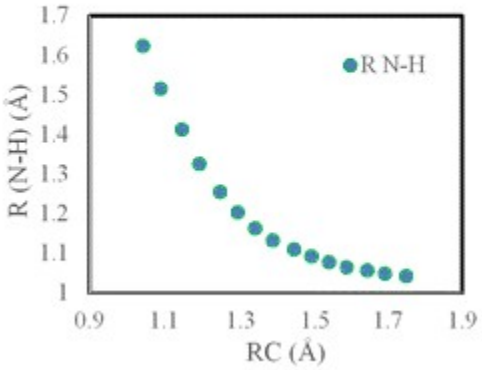
	S_0-E	S_1-E	S_0-K	S_1-K
L1	CAM-B3LYP			
λ1 (nm)	351	411	397	451
λ1 (eV)	3.53	3.01	3.12	2.74
λ2 (nm)	303	350	331	357
λ3 (nm)	295	319	329	356
f1	1.431	1.563	1.038	0.937
f2	0.001	0.003	0.002	0.566
f3	0.03	0.016	0.409	0.012
L2				
λ1 (nm)	353	416	380	432
λ1 (eV)	3.51	2.98	3.25	2.87
λ2 (nm)	298	343	327	356
λ3 (nm)	296	313	314	335
f1	1.693	1.823	1.366	1.361
f2	0.003	0.003	0.373	0.416
f3	0.043	0.043	0	0
L3				
λ1 (nm)	351	414	382	433
λ1 (eV)	3.52	2.99	3.24	2.86
λ2 (nm)	299	345	320	346
λ3 (nm)	296	313	314	331
f1	1.612	1.749	1.369	1.408
f2	0.002	0.003	0.235	0.263
f3	0.041	0.041	0	0
L4				
λ1 (nm)	358	419	401	450
λ1 (eV)	3.46	2.96	3.09	2.75
λ2 (nm)	306	354	333	357
λ3 (nm)	295	320	331	354
f1	1.464	1.574	1.128	1.171
f2	0.001	0.003	0.004	0.366
f3	0.033	0.044	0.336	0.002
L5				
λ1 (nm)	364	428	410	457
λ1 (eV)	3.4	2.89	3.02	2.71
λ2 (nm)	309	358	339	362
λ3 (nm)	301	325	338	360
f1	1.555	1.691	1.111	1.18
f2	0.001	0.003	0.024	0.436
f3	0.027	0.038	0.402	0.003

Table S3. The calculated absorption and fluorescence emission properties of **L1-L5** (R1-5= −H, $-NH_2$, $-OCH_3$, $-CF_3$, and –CN) in different solvents.

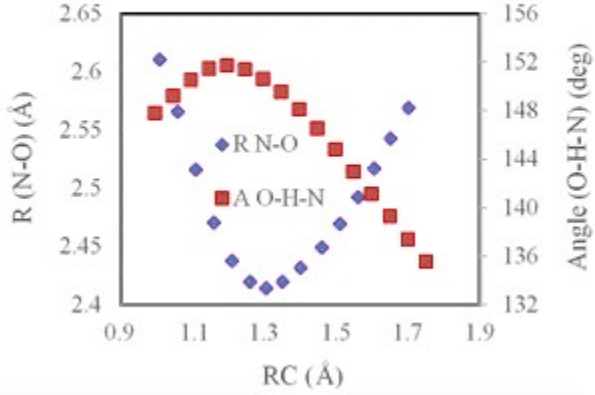
		CAM-B3LYP			
		S_0-E	S_1-E	S_0-K	S_1-K
L1	**DMSO**				
	λ1 (nm)	363	481	404	500
	fl	1.61	2.012	1.276	1.644
	MeOH				
	λ1 (nm)	362	480	409	499
	fl	1.587	2.007	1.303	1.637
	Toluene				
	λ1 (nm)	362	443	409	470
	fl	1.616	1.82	1.224	1.347
L2	**DMSO**				
	λ1 (nm)	367	492	388	490
	fl	1.921	2.244	1.721	2.024
	MeOH				
	λ1 (nm)	365	491	387	489
	fl	1.893	2.24	1.694	2.017
	Toluene				
	λ1 (nm)	365	450	392	458
	fl	1.912	2.065	1.64	1.774
L3	**DMSO**				
	λ1 (nm)	364	484	391	490
	fl	1.784	2.123	1.611	1.911
	MeOH				
	λ1 (nm)	362	482	389	489
	fl	1.761	2.12	1.591	1.906
	Toluene				
	λ1 (nm)	363	446	394	459
	fl	1.792	1.968	1.568	1.708
L4	**DMSO**				
	λ1 (nm)	370	493	411	512
	fl	1.621	2.039	1.318	1.679
	MeOH				
	λ1 (nm)	368	491	409	511
	fl	1.600	2.031	1.303	1.674
	Toluene				
	λ1 (nm)	370	452	414	477
	fl	1.625	1.843	1.286	1.47
L5	**DMSO**				
	λ1 (nm)	378	512	423	526
	fl	1.716	2.181	1.281	1.687
	MeOH				
	λ1 (nm)	376	511	421	525
	fl	1.694	2.176	1.265	1.682
	Toluene				
	λ1 (nm)	378	465	425	488
	fl	1.724	1.975	1.265	1.479

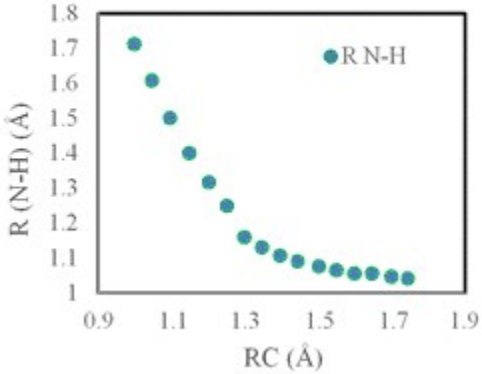
L1


R (N-O) (Å)
Angle(O-H-N) (deg)
R N-O
A O-H-N
RC (Å)

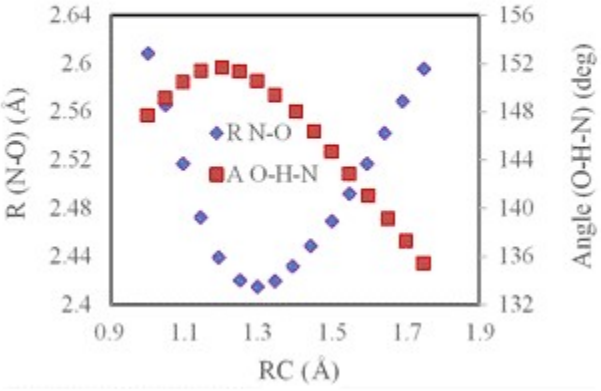

R (N-H) (Å)
R N-H
RC (Å)

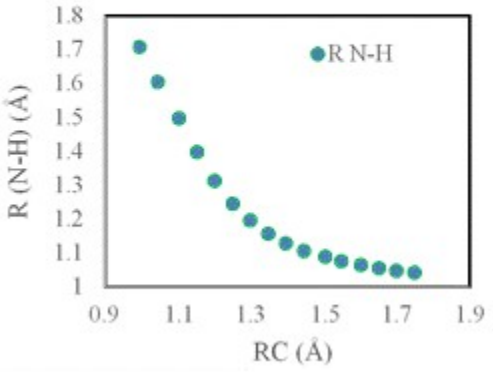
L2


R (N-O) (Å)
Angle (O-H-N) (deg)
R N-O
A O-H-N
RC (Å)


R (N-H) (Å)
R N-H
RC (Å)

L3


R (N-O) (Å)
Angle (O-H-N) (deg)
R N-O
A O-H-N
RC (Å)


R (N-H) (Å)
R N-H
RC (Å)

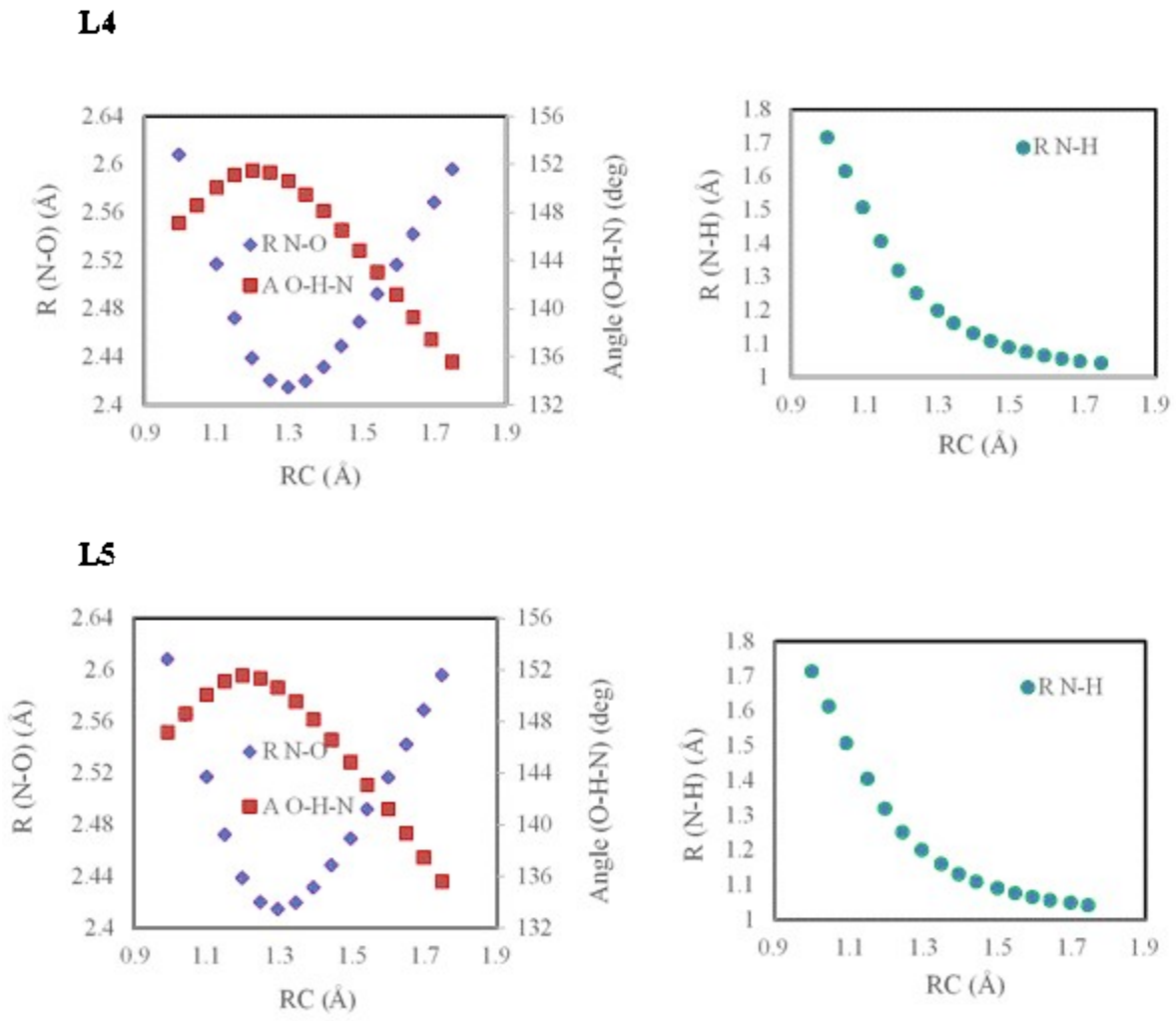


Fig. S1. Variations of (N–H and O–N) bond lengths and (O–H–N) bond angle in terms of RC (d_{OH}) along the proton transfer for **L1**, **L2, L3, L4** and **L5** in the S_0 state at PBE0/6-31++G(d,p) level.

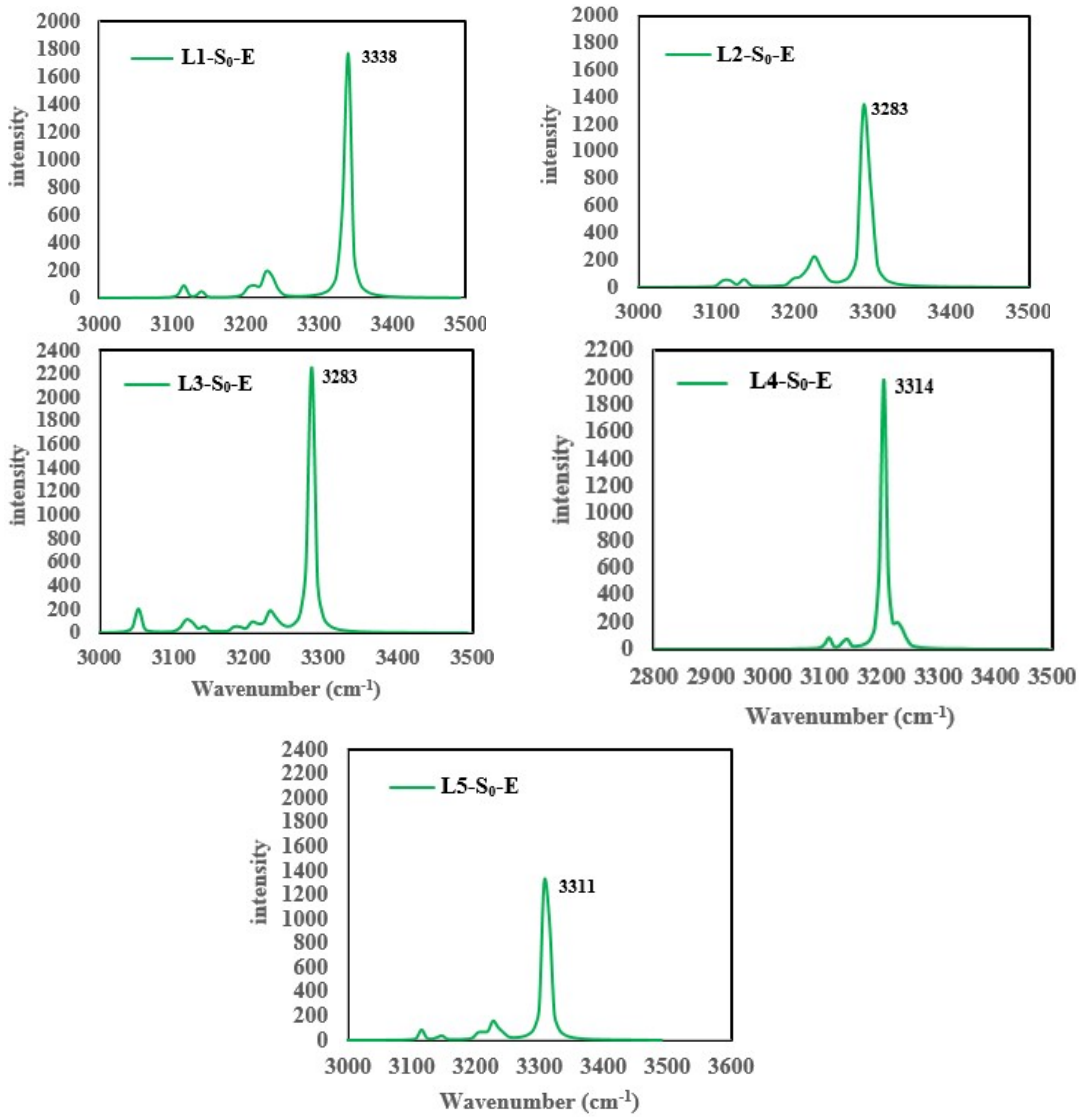


Fig. S2. Calculated vibrational spectra of O−H bond at the S_0-E state of azine derivatives **L1-L5** (R1-5= −H, $-NH_2$, $-OCH_3$, $-CF_3$, and –CN) at CAM-B3LYP/6-31++G(d,p) level.

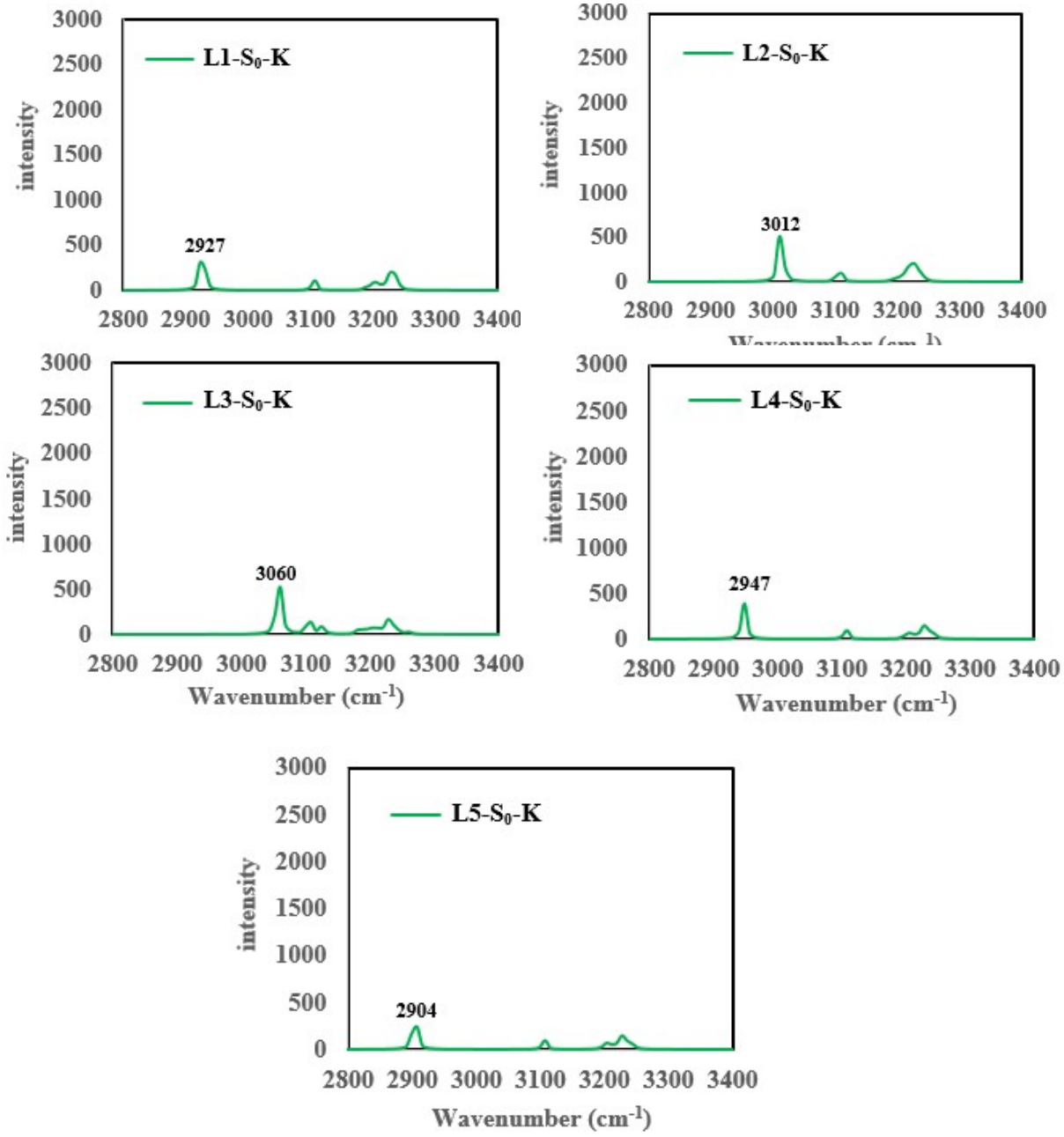
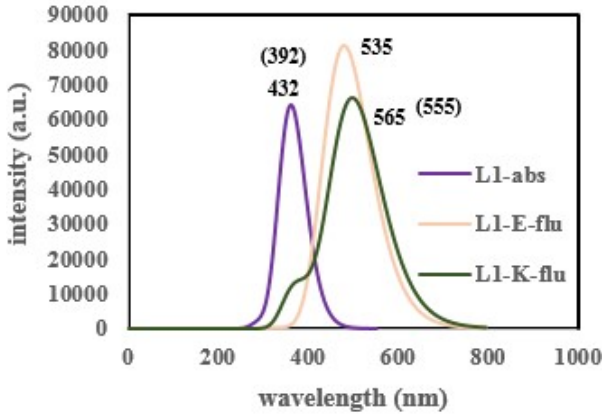
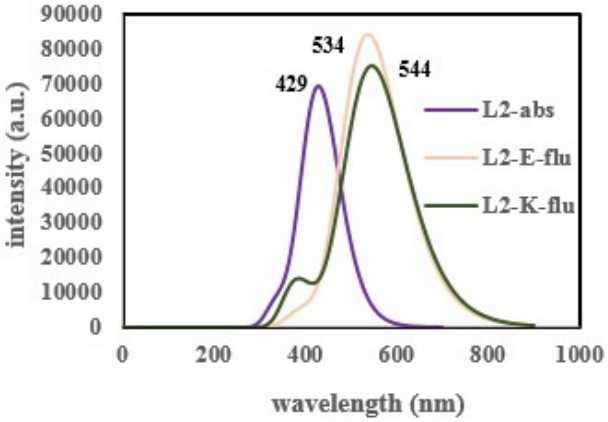
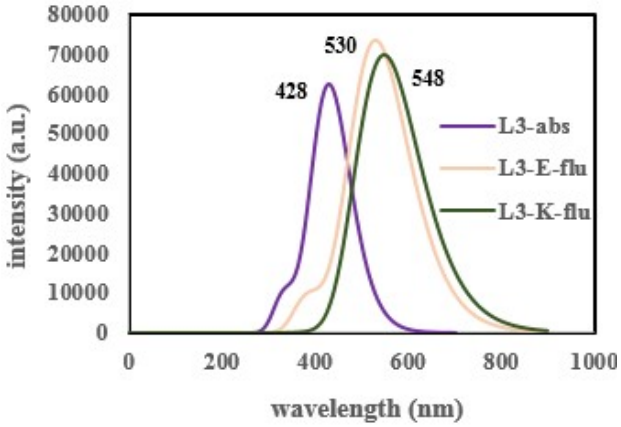
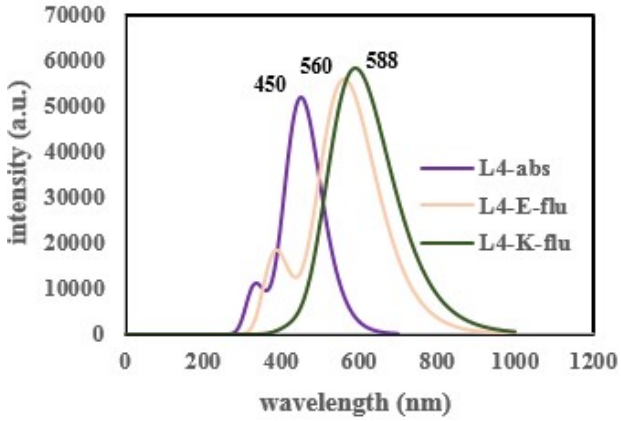


Fig. S3. Calculated vibrational spectra of N−H bond at the S_0-K state of azine derivatives **L1**-**L5** (R1-5= −H, $-NH_2$, $-OCH_3$, $-CF_3$, and –CN) at CAM-B3LYP/6-31++G(d,p) level.


intensity (a.u.)
wavelength (nm)
(392)
432
535
565
(555)
L1-abs
L1-E-flu
L1-K-flu


intensity (a.u.)
wavelength (nm)
429
534
544
L2-abs
L2-E-flu
L2-K-flu


intensity (a.u.)
wavelength (nm)
428
530
548
L3-abs
L3-E-flu
L3-K-flu


intensity (a.u.)
wavelength (nm)
450
560
588
L4-abs
L4-E-flu
L4-K-flu

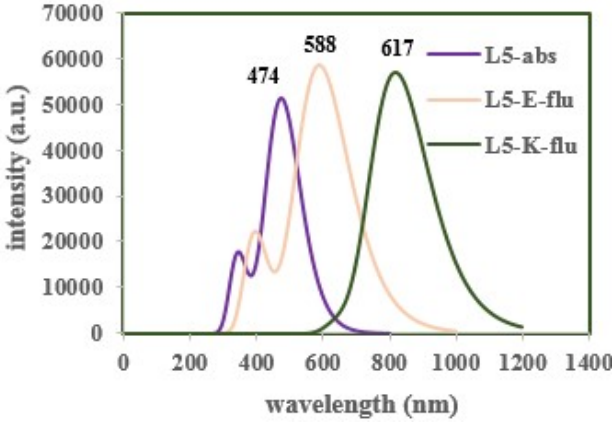

intensity (a.u.)
wavelength (nm)
474
588
617
L5-abs
L5-E-flu
L5-K-flu

Fig. S4. The absorption and emission spectra of **L1-L5** in MeOH solvent at PBE0/6-31++G(d,p) level. The values in parentheses are experimental data (abs: absorption spectrum; and flu: fluorescence spectrum).

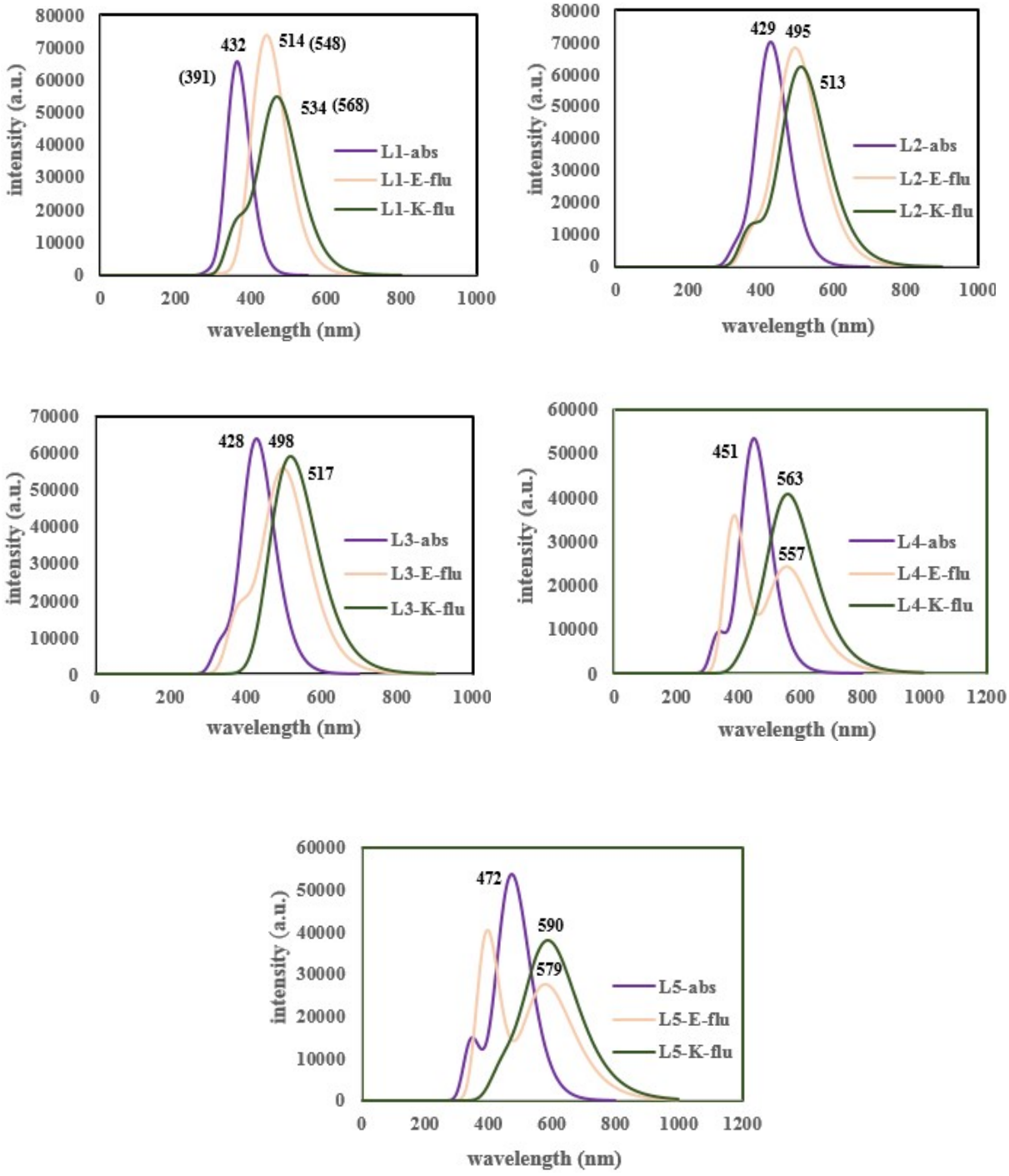


Fig. S5. The absorption and emission spectra of **L1-L5** in toluene solvent at PBE0/6-31++G(d,p) level. The values in parentheses are experimental data (abs: absorption spectrum; and flu: fluorescence spectrum).

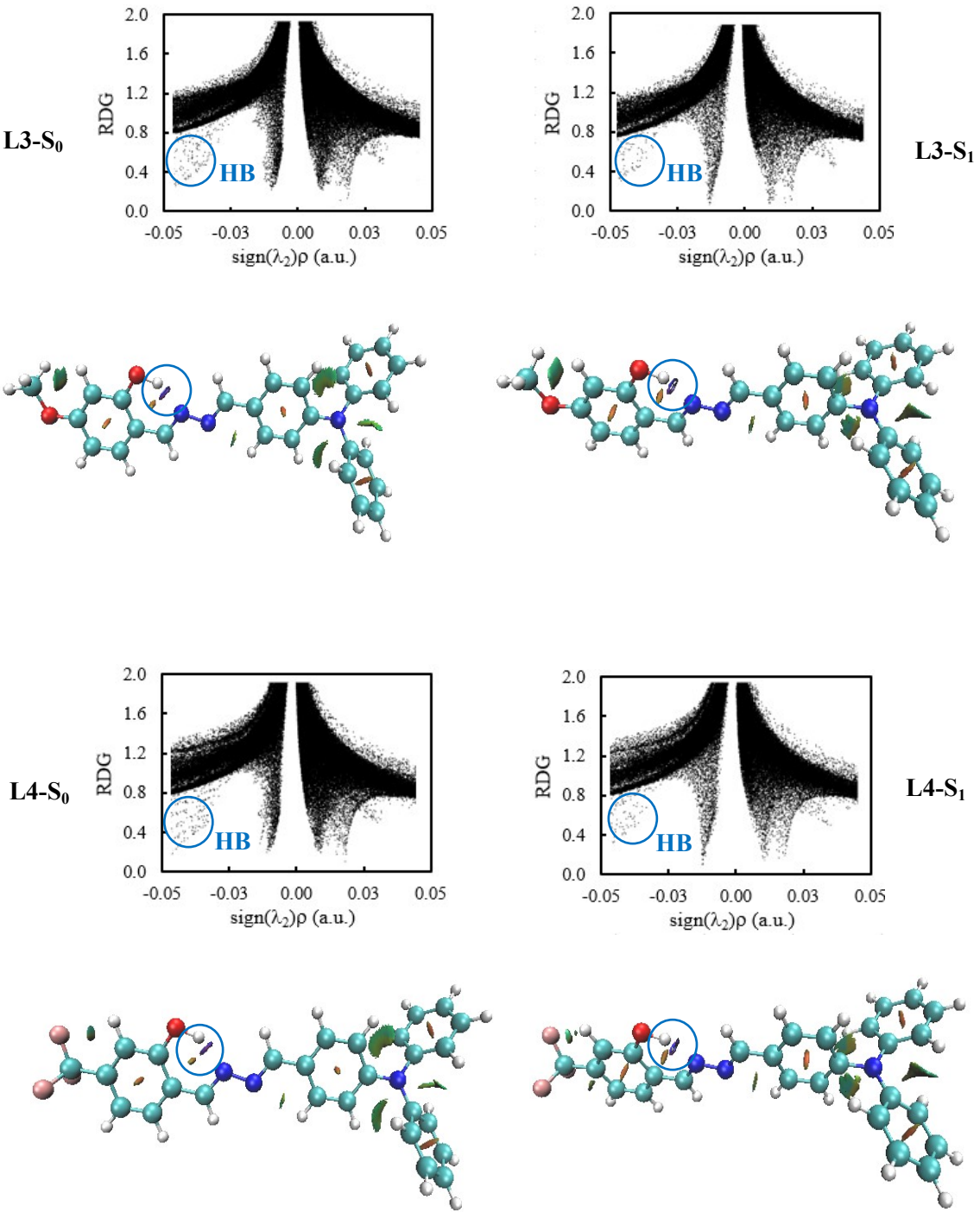


Fig. S6. RDG scatter plots and isosurfaces of **L3** and **L4** in the S_0 and S_1 states.