Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Is the origin of green fluorescence in unsymmetrical four-ring bent-core liquid crystals single or double proton transfer?

Venkatesh Gude,*[a] Manobina Karmakar,[b] Avishek Dey,[a] Prasanta Kumar Datta[b] and

Kumar Biradha*[a]

[a]Department of Chemistry, [b]Department of Physics, Indian Institute of Technology-Kharagpur, Kharagpur, West Bengal, 721302, India.

E-mail: venkatesh.gude@gmail.com, kbiradha@chem.iitkgp.ernet.in

Table of contents

Fig. S1: Steady-state absorption and emission spectra of 4-PABA, 4-AP, 4-4 and 12-12 in toluene

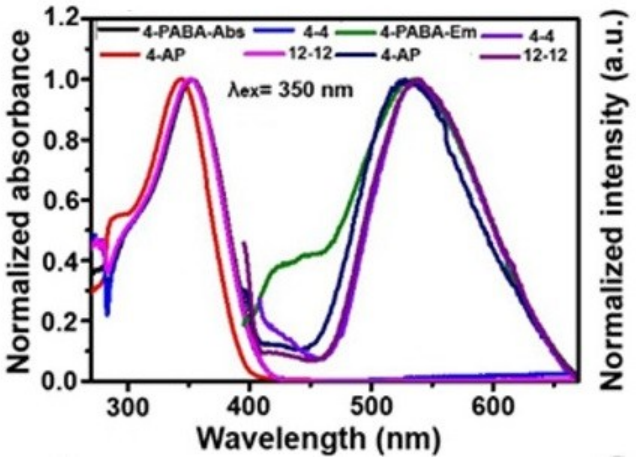


Fig. S2: Calculated (TD-DFT) absorption spectra of 4-4 (a) using optimized geometry at the respective functional and (b) using B3LYP optimized geometry at various functional/6-31++G(d,p) level in chloroform solvent.

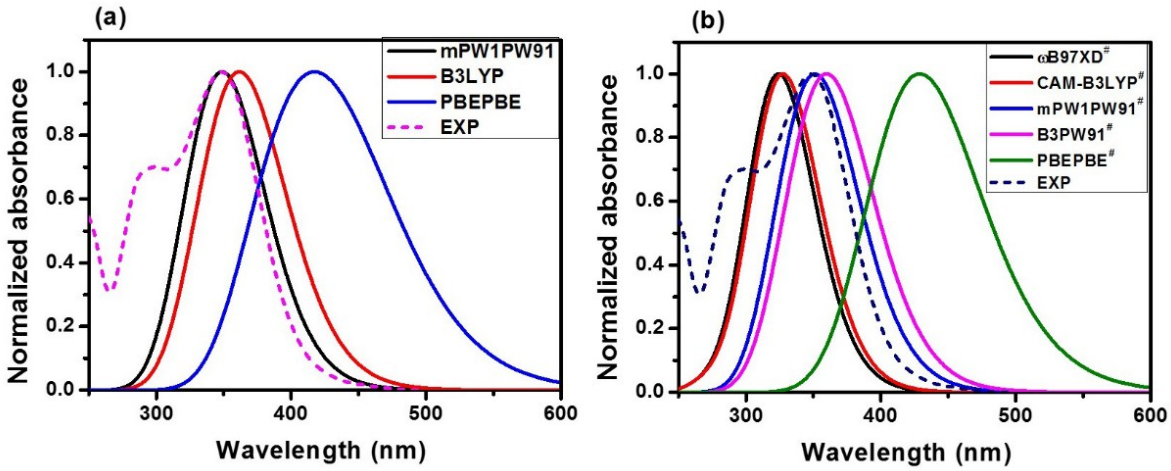


Table S1: Calculated (TD-DFT) absorption properties of different tautomers with various functional. # represents the B3LYP optimized geometry used with various functional; & represents the mPW1PW91 optimized geometry used with 6-311++G (d) basis set.

Structure	Functional	S_1 (hartree)	S_0 (hartree)	S_1-S_0 (hartree)	S_1-S_0 (in kcal)	λ_{abs} (nm)	Exp. λ_{abs} (nm)
DE	B3LYP	-1916.29980	-1916.42278	0.12298	77.17	370	350
	PBE	-1914.00789	-1914.09159	0.0837	52.52	544	
	PBE#	-1913.99852	-1914.08714	0.08862	55.61	514	
	mPW1PW91	-1915.83163	-1915.95951	0.12788	80.24	356	
	mPW1PW91#	-1915.83074	-1915.95769	0.12695	79.66	359	
	mPW1PW91&	-1916.13979	-1916.26965	0.12986	81.48	351	
	B3PW91#	-1915.55465	-1915.67819	0.12354	77.52	369	
	CAM-B3LYP#	-1915.29993	-1915.43705	0.13712	86.04	332	
	ωB97XD#	-1915.64427	-1915.78292	0.13865	87	328	
MK-C	B3LYP	-1916.31424	-1916.42128	0.10704	67.16	425	(415-500)
	PBE	-1914.01339	-1914.09122	0.07783	48.84	585	
	PBE#	-1914.00553	-1914.08695	0.08142	51.09	560	
	mPW1PW91	-1915.84574	-1915.95701	0.11127	69.82	410	
	mPW1PW91#	-1915.84483	-1915.95518	0.11035	69.24	413	
	mPW1PW91&	-1916.15872	-1916.27036	0.11164	70.05	408	
	B3PW91#	-1915.56862	-1915.67612	0.1075	67.45	424	
	CAM-B3LYP#	-1915.31518	-1915.43391	0.11873	74.50	384	
	ωB97XD#	-1915.66006	-1915.77989	0.11983	75.19	380	
MK-O	B3LYP	-1916.30837	-1916.42110	0.11273	70.74	404	
	PBE	-1914.01500	-1914.09110	0.0761	47.75	598	
	PBE#	-1914.00737	-1914.08689	0.07952	49.9	573	
	mPW1PW91	-1915.84017	-1915.95684	0.11667	73.21	391	
	mPW1PW91#	-1915.83937	-1915.95501	0.11564	72.56	394	
	mPW1PW91&	-1916.15315	-1916.27012	0.11697	73.39	390	
	B3PW91#	-1915.56267	-1915.67596	0.11329	71.09	402	
	CAM-B3LYP#	-1915.31140	-1915.43364	0.12224	76.71	373	
	ωB97XD#	-1915.65666	-1915.77965	0.12299	77.18	370	
DK	B3LYP	-1916.31297	-1916.41961	0.10664	66.92	427	
	PBE	-1914.02022	-1914.09073	0.07051	44.24	646	
	PBE#	-1914.01407	-1914.08666	0.07259	45.55	628	
	mPW1PW91	-1915.84336	-1915.95428	0.11092	69.60	411	
	mPW1PW91#	-1915.84254	-1915.95251	0.10997	69.00	414	
	mPW1PW91&	-1916.15956	-1916.27084	0.11128	69.83	410	
	B3PW91#	-1915.56680	-1915.67389	0.10709	67.2	425	
	CAM-B3LYP#	-1915.31211	-1915.43053	0.11842	74.31	385	
	ωB97XD#	-1915.65714	-1915.77665	0.11951	74.99	381	

Table S2: Calculated (TD-DFT) emission properties of different tautomers with various functional. # represents the B3LYP optimized geometry used with various functional; & and % represents the mPW1PW91 optimized geometry used with 6-311++G (d) and DZVP basis set.

Structure	Functional	S_1 (hartree)	S_0 (hartree)	S_1-S_0 (hartree)	S_1-S_0 (in kcal)	λ_{em} (nm)	Exp. λ_{em} (nm)
DE*	B3LYP	-1916.31328	-1916.41555	0.10227	64.17	445	430
	PBE	-1914.02187	-1914.07954	0.05767	36.18	790	
	PBE#	-1914.00925	-1914.08378	0.07453	46.77	611	
	mPW1PW91	-1915.84635	-1915.95172	0.10537	66.12	432	
	mPW1PW91#	-1915.84136	-1915.94956	0.1082	67.89	421	
	mPW1PW91&	-1916.15540	-1916.26119	0.10579	66.38	431	
	B3PW91#	-1915.56496	-1915.67086	0.1059	66.45	430	
	CAM-B3LYP#	-1915.31184	-1915.42636	0.11452	71.86	398	
	ωB97XD#	-1915.65599	-1915.77189	0.1159	72.73	393	
MK-C*	B3LYP	-1916.32409	-1916.41186	0.08777	55.08	519	(460-660)
	PBE	-1914.02387	-1914.08105	0.05718	35.88	796	
	PBE#	-1914.00761	-1914.07957	0.07196	45.15	633	
	mPW1PW91	-1915.85529	-1915.94810	0.09281	58.24	491	
	mPW1PW91#	-1915.85168	-1915.94452	0.09284	58.26	491	
	mPW1PW91&	-1916.16864	-1916.26108	0.09244	58	493	
	mPW1PW91%	-1915.88228	-1915.97411	0.09183	57.62	496	
	B3PW91#	-1915.57636	-1915.66611	0.08975	56.32	508	
	CAM-B3LYP#	-1915.31848	-1915.42210	0.10362	65.02	440	
	ωB97XD#	-1915.66327	-1915.76817	0.1049	65.82	434	
MK-O*	B3LYP	-1916.31856	-1916.41127	0.09271	58.17	491	
	PBE	-1914.02797	-1914.07946	0.05149	32.31	885	
	PBE#	-1914.00557	-1914.07876	0.07319	45.92	622	
	mPW1PW91	-1915.85007	-1915.94754	0.09747	61.16	467	
	mPW1PW91#	-1915.84650	-1915.94390	0.0974	61.12	468	
	mPW1PW91&	-1916.16349	-1916.26054	0.09705	60.89	469	
	B3PW91#	-1915.57061	-1915.66547	0.09486	59.52	480	
	CAM-B3LYP#	-1915.31559	-1915.42148	0.10589	66.44	430	
	ωB97XD#	-1915.66100	-1915.76770	0.1067	66.95	427	
DK*	B3LYP	-1916.32266	-1916.41013	0.08747	54.88	521	
	PBE	-1914.02974	-1914.08089	0.05115	32.07	891	
	PBE#	-1914.01613	-1914.07919	0.06306	39.57	722	
	mPW1PW91	-1915.85285	-1915.94531	0.09246	58.01	493	
	mPW1PW91#	-1915.84921	-1915.94177	0.09256	58.08	492	
	mPW1PW91&	-1916.16942	-1916.26148	0.09206	57.76	495	
	B3PW91#	-1915.57439	-1915.66381	0.08942	56.11	509	
	CAM-B3LYP#	-1915.31512	-1915.41864	0.10352	64.96	440	
	ωB97XD#	-1915.66007	-1915.76489	0.10482	65.77	435	

Table S3: Calculated (TD-DFT) whole absorption and emission properties of different tautomers with various functional. # represents the B3LYP optimized geometry used with various functional

Structure	B3LYP λ(nm)	PBE λ(nm)	PBE# λ(nm)	mPW1 PW91 λ(nm)	mPW1 PW91# λ(nm)	B3P W91# λ(nm)	CAM-B3LYP# λ(nm)	ωB97 XD# λ(nm)	Exp. $\lambda_{abs/em}$
4-4 (**DE)**	370	544	514	356	359	369	332	328	350(λ_{abs})
MK-C	425	585	560	410	413	424	384	380	415-500 ($\lambda_{trans-abs}$)
MK-O	404	598	573	391	394	402	373	370	
DK	427	646	628	411	414	425	385	381	
4-4 (**DE*)**	445	790	611	432	421	430	398	393	430 (λ_{em}) (enol)
MK-C*	519	796	633	491	491	508	440	434	460-660 (λ_{em}) (keto)
MK-O*	491	885	622	467	468	480	430	427	
DK*	521	891	722	493	492	509	440	435	

Computational details: It was found that the popular B3LYP functional has a good record for satisfactory molecular geometries (https://sites.google.com/site/orcainputlibrary/dft). Therefore, in order to verify the accuracy of experimental and calculated absorption and emission properties, single-point energy calculations were performed with various functional such as the PBEPBE, mPW1PW91, CAM-B3LYP, B3PW91, and ωB97XD on B3LYP optimized geometries (Table S1, S2, S3). In order to verify the emission properties, We also studied the effect of basis set changing from 6-31++G (d,p) to 6-311++G(d) and double zeta valence plus polarization function(DZVP) with mPW1PW91 functional on DE and keto structures. However, the obtained results (Table S1, S2, and S3) are almost similar to all basis sets.

Table S4: Natural Bond Orbital (NBO) charge analysis of ground (S_0) and excited (S_1) state optimized DE (4-4) with mPW1PW91 and B3LYP functional.

Structure	Electronic state-Functional	atoms	NBO charges (a.u.)
DE	**S_0-** mPW1PW91	O1, H2, N3, O4, H5, N6 and Carbonyl O	-0.720, 0.532, -0.540, -0.722, 0.532, -0.536 and -0.614
DE*	**S_1-** mPW1PW91	O1, H2, N3, O4, H5, N6 and Carbonyl O	-0.716, 0.524, -0.565, -0.722, 0.532, -0.534 and -0.617
DE	**S_0-** B3LYP	O1, H2, N3, O4, H5, N6 and Carbonyl O	-0.718, 0.529, -0.535, -0.720, 0.528, -0.531 and -0.616
DE*	**S_1-** B3LYP	O1, H2, N3, O4, H5, N6 and Carbonyl O	-0.718, 0.524, -0.559, -0.720, 0.529, -0.530 and -0.621

Fig. S8: View of total electron density isosurface mapped with molecular electrostatic potential (MEP) surface for the S_0 and S_1 optimized DE with mPW1PW91 and B3LYP functional.

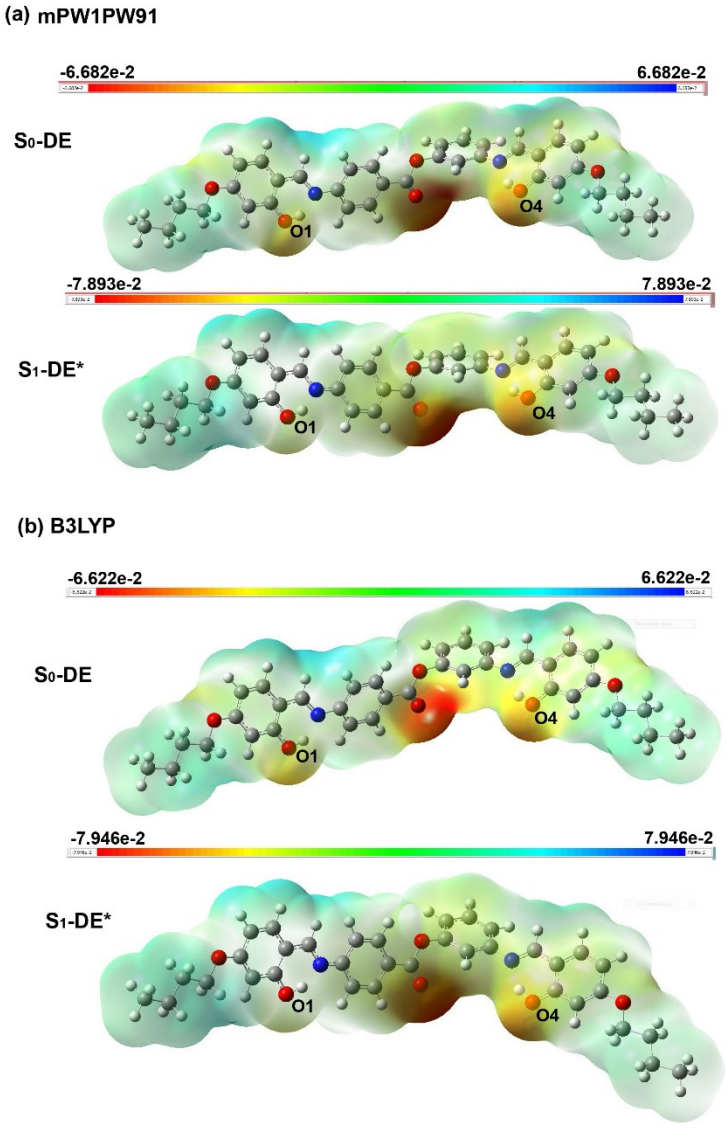


Fig. S9: Frequency analysis of ground (S_0) and excited state (S_1) optimized DE structure with mPW1PW91 and B3LYP functional**.**

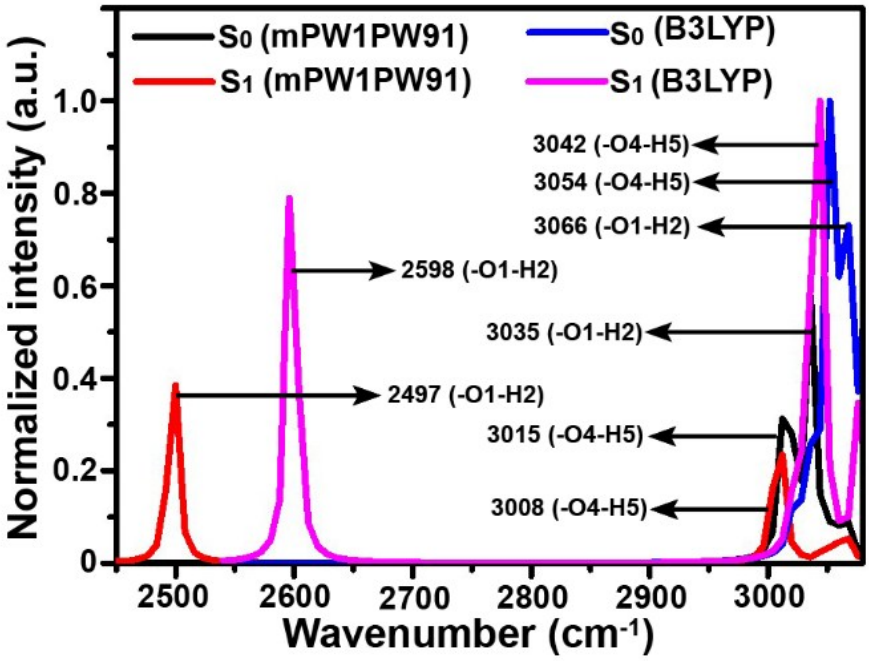


Table S5: Variation in the geometrical parameters of hydrogen bonds of different tautomers in the ground (S_0) and first excited state (S_1).

Electronic State-Tautomer-Functional	Geometrical parameters		
	Donor (D) to hydrogen distance (d) Å	Donor to acceptor (A) distance (D) Å	D-H…A angle (°) (θ)
S_0-**DE**-mPW1PW91	-O1-H2 = 1.003 -O4-H5 = 1.004	-O1-N3 = 2.580 -O4-N6 = 2.578	-O1-H2…N3 = 149.19 -O4-H5…N6 = 149.35
S_1-**DE**-mPW1PW91	-O1-H2 = 1.033 -O4-H5 = 1.004	-O1-N3 = 2.525 -O4-N6 = 2.577	-O1-H2…N3 = 152.55 -O4-H5…N6 = 149.30
S_0-**DE**-B3LYP	-O1-H2 = 1.002 -O4-H5 = 1.003	-O1-N3 = 2.611 -O4-N6 = 2.609	-O1-H2…N3 = 148.33 -O4-H5…N6 = 148.49
S_1-**DE**-mPW1PW91	-O1-H2 = 1.028 -O4-H5 = 1.004	-O1-N3 = 2.558 -O4-N6 =2.609	-O1-H2…N3 = 151.56 -O4-H5…N6 = 148.41
S_0-**MK-C**-mPW1PW91	-N3-H2 = 1.042 -O4-H5 = 1.004	-N3-O1 = 2.575 -O4-N6 =2.578	-N3-H2…O1 = 141.13 -O4-H5…N6 = 149.37
S_1-**MK-C**-mPW1PW91	-N3-H2 = 1.034 -O4-H5 = 1.004	-N3-O1 = 2.657 -O4-N6 =2.576	-N3-H2…O1 = 139.95 -O4-H5…N6 = 149.45
S_0-**MK-C**-B3LYP	-N3-H2 = 1.039 -O4-H5 = 1.003	-N3-O1 = 2.609 -O4-N6 =2.610	-N3-H2…O1 = 139.65 -O4-H5…N6 = 148.48
S_1-**MK-C**-B3LYP	-N3-H2 = 1.034 -O4-H5 = 1.004	-N3-O1 = 2.689 -O4-N6 =2.608	-N3-H2…O1 = 138.82 -O4-H5…N6 = 148.59
S_0-**MK-O**-mPW1PW91	-O1-H2 = 1.003 -N6-H5 = 1.044	-O1-N3 = 2.579 -N6-O4 = 2.570	-O1-H2…N3 = 149.20 -N6-H5…O4 = 141.56
S_1-**MK-O**-mPW1PW91	-O1-H2 = 1.003 -N6-H5 = 1.032	-O1-N3 = 2.579 -N6-O4 = 2.665	-O1-H2…N3 = 149.22 -N6-H5…O4 = 139.71
S_0-**MK-O**-B3LYP	-O1-H2 = 1.002 -N6-H5 = 1.040	-O1-N3 = 2.611 -N6-O4 = 2.606	-O1-H2…N3 = 148.32 -N6-H5…O4 = 139.93
S_1-**MK-O**-B3LYP	-O1-H2 = 1.003 -N6-H5 = 1.032	-O1-N3 = 2.610 -N6-O4 = 2.697	-O1-H2…N3 = 148.36 -N6-H5…O4 = 138.68
S_0-**DK**-mPW1PW91	-N3-H2 = 1.043 -N6-H5 = 1.044	-N3-O1 = 2.575 -N6-O4 = 2.571	-N3-H2…O1= 141.15 -N6-H5…O4= 141.56
S_1-**DK**-mPW1PW91	-N3-H2 = 1.035 -N6-H5 = 1.043	-N3-O1 = 2.656 -N6-O4 = 2.573	-N3-H2…O1= 140.05 -N6-H5…O4= 141.44
S_0-**DK**-B3LYP	-N3-H2 = 1.039 -N6-H5 = 1.040	-N3-O1 = 2.610 -N6-O4 = 2.607	-N3-H2…O1= 139.61 -N6-H5…O4= 139.96
S_1-**DK**-B3LYP	-N3-H2 = 1.034 -N6-H5 = 1.039	-N3-O1 = 2.688 -N6-O4 = 2.610	-N3-H2…O1= 138.88 -N6-H5…O4= 139.81

Table S6: Quantitative assessment of strength of hydrogen bond both in the ground (S_0) and excited (S_1) state of optimized DE with mPW1PW91 and B3LYP functional.

Structure	Electronic state-Functional	Hydrogen bonds under investigation	Potential energy density at the bond critical point $V(r_{bcp})$	Approximate Hydrogen bond energy (E_{HB}) $E_{HB}= V(r_{bcp})/2*2625.5$ KJ/mol	(E_{HB}) kcal/mol
DE	**S_0-** mPW1PW91	O1-H2…N3 O4-H5…N6	-0.04632895310 -0.04718136673	-60.8 -61.9	-14.53 -14.79
DE*	**S_1-** mPW1PW91	O1-H2…N3 O4-H5…N6	-0.06938507804 -0.04726790543	-91.1 -62.1	-21.77 -14.84
DE	**S_0-** B3LYP	O1-H2…N3 O4-H5…N6	-0.04035413455 -0.04098895096	-52.9 -53.8	-12.64 -12.85
DE*	**S_1-** B3LYP	O1-H2…N3 O4-H5…N6	-0.05759322709 -0.04100019953	-75.6 -53.9	-18.06 -12.88

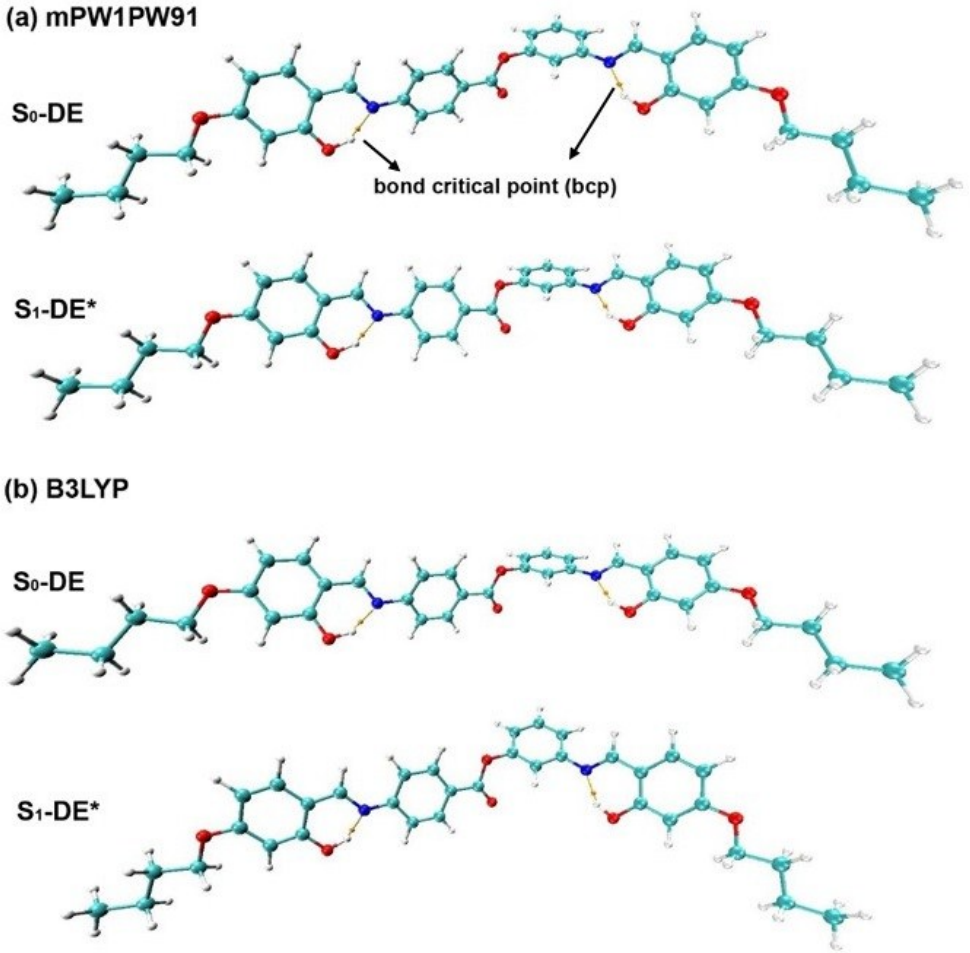


Fig. S10: The Intrinsic Reaction Coordinate (IRC) calculated for various target reactions in the ground state.

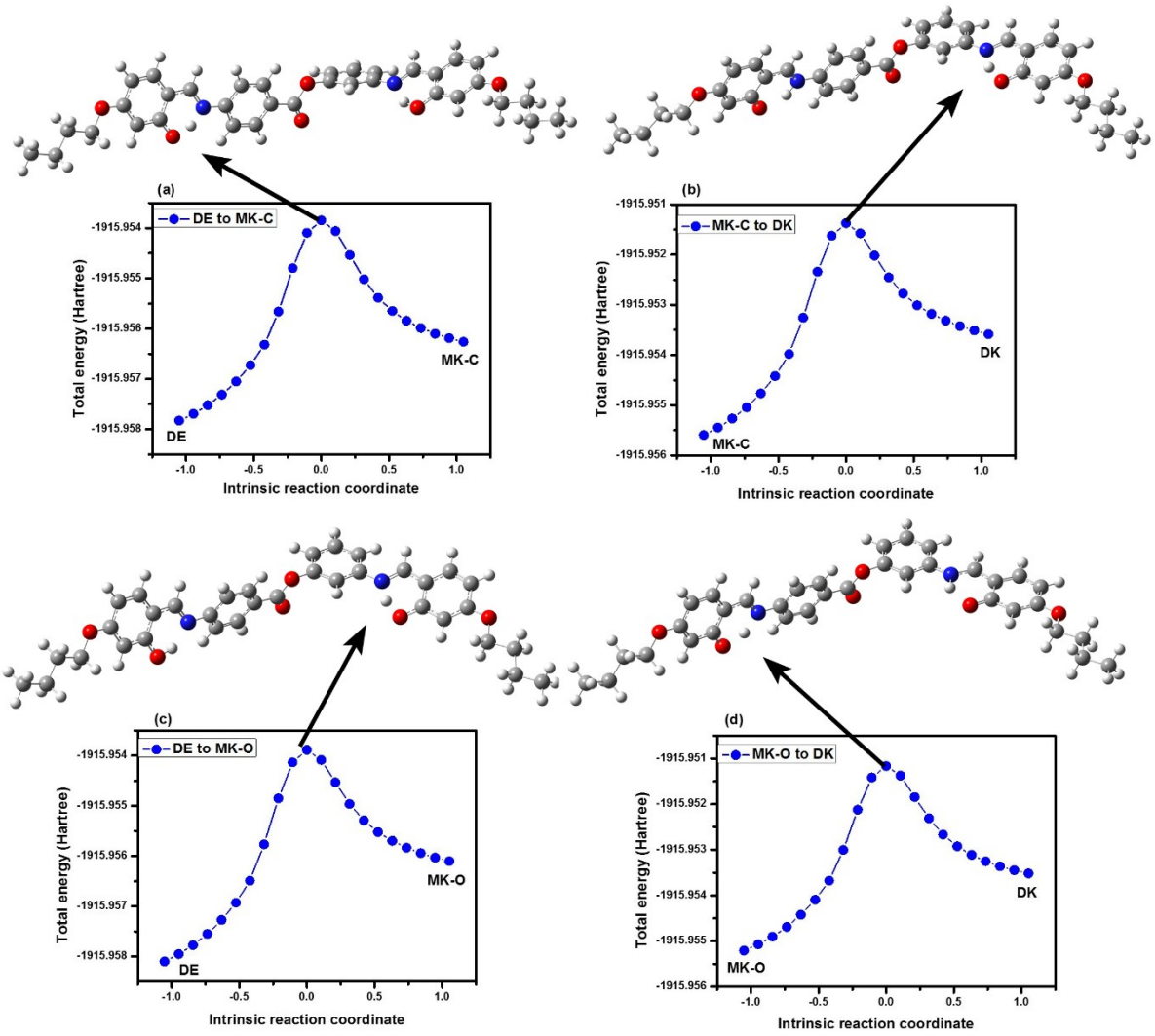


Table S7: Vertical excitation energies of S_0 optimized structures with mPW1PW91 and B3LYP functional.

Structure	Functional	S_2 (hartree)	S_1 (hartree)	S_0 (hartree)	S_1-S_0 (in kcal)	S_2-S_0 (in kcal)	S_2-S_1 (in kcal)
DE	mPW1PW91	-1915.82350	-1915.83163	-1915.95951	80.24	85.34	5.1
DE	B3LYP	-1916.29721	-1916.29980	-1916.42278	77.17	78.80	1.63
MK-C	mPW1PW91	-1915.82878	-1915.84574	-1915.95701	69.82	80.46	10.64
MK-C	B3LYP	-1916.30344	-1916.31424	-1916.42128	67.17	73.94	6.77
MK-O	mPW1PW91	-1915.82988	-1915.84017	-1915.95684	73.21	79.67	6.46
MK-O	B3LYP	-1916.30504	-1916.30837	-1916.42110	70.74	72.83	2.09

Fig. S11: Proton transfer processes in S_0 and S_1 state. (a), (b) representing the sequential and (c) concerted process. Numerical numbers on the horizontal lines representing the energies in kcal/mol calculated at B3LYP/6-31++G (d,p) level in chloroform solvent. S_1 state DE structure has 68.7 kcal/mol from S_0 state. Vertical arrows representing the Frank-Condon transition from the ground state optimized structure.

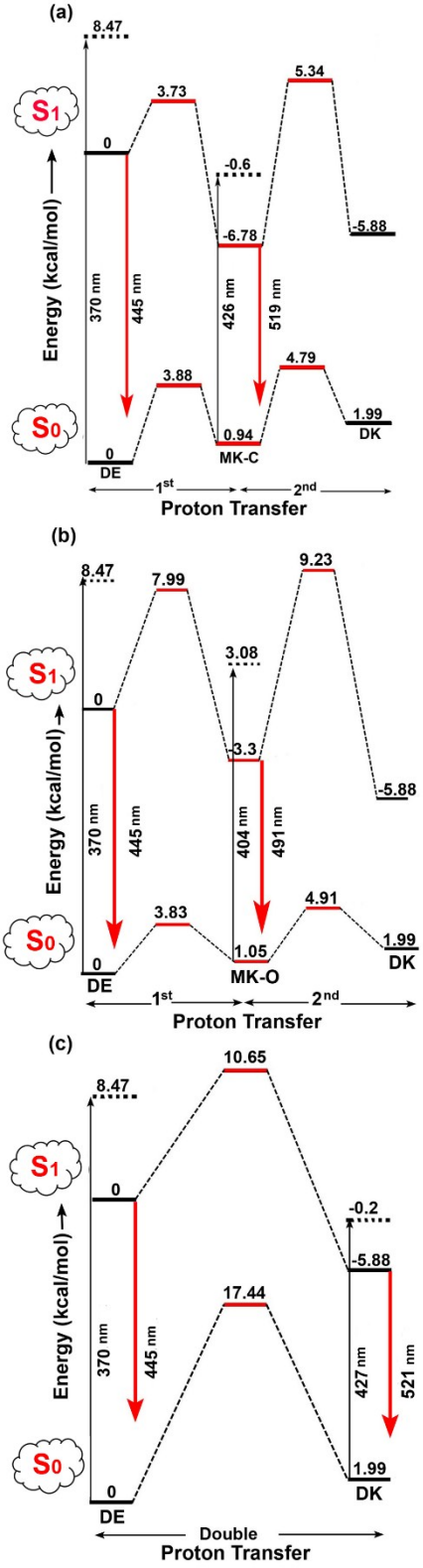
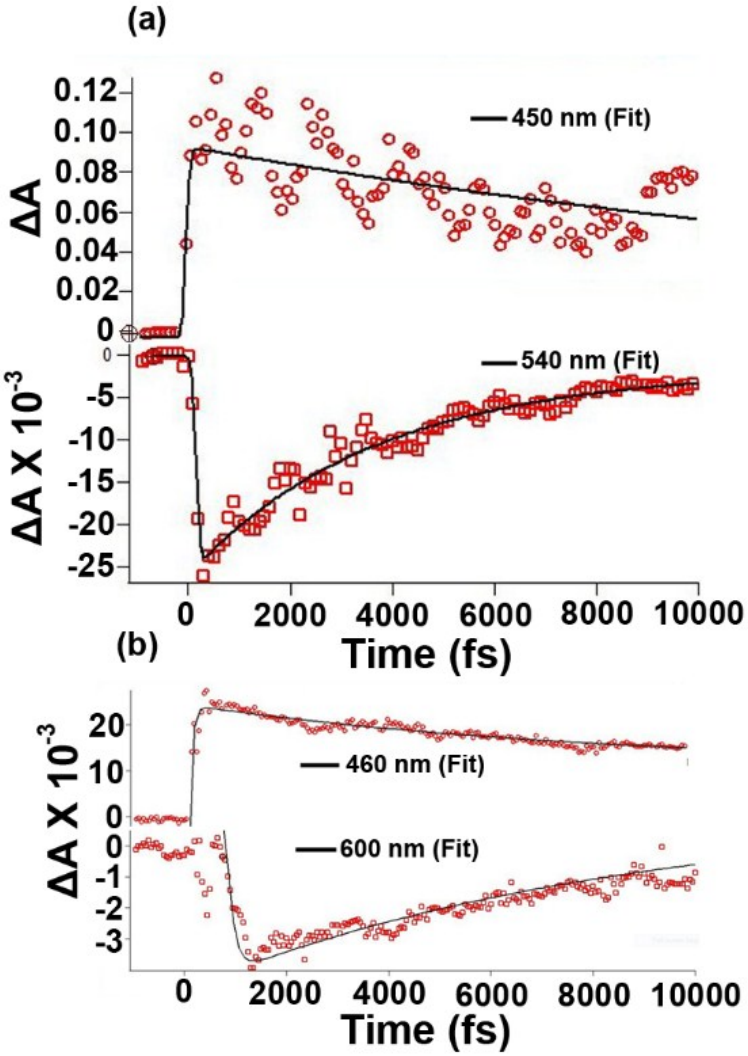
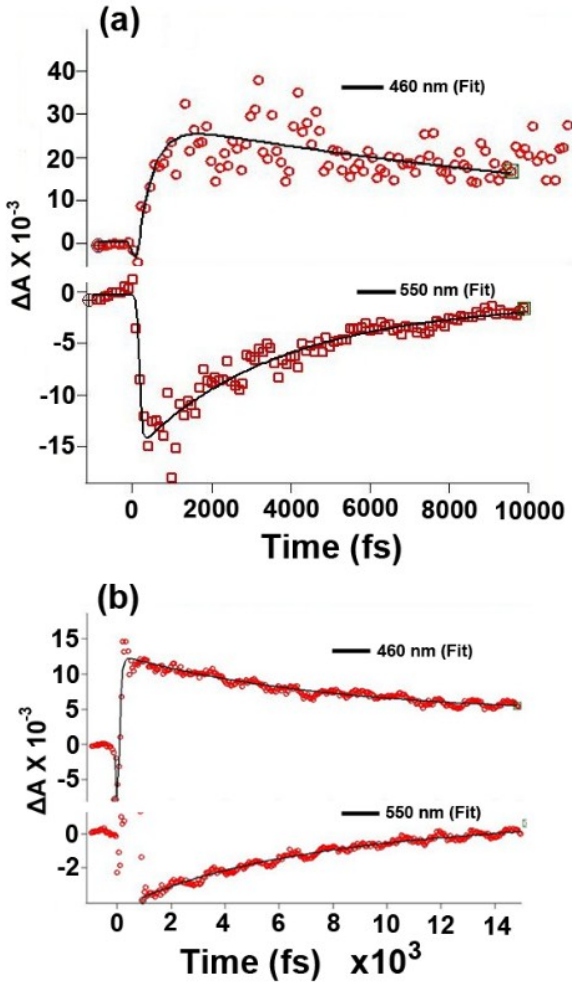


Fig. S12: Transient absorption decay traces of 4-PABA in Chloroform (a) and Toluene (b)



4-PABA in $CHCl_3$	$\lambda_{abs}/\lambda_{em}$ (nm)	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)
	450	<100	21 (±3)	
	540	-	1.6 (±0.6)	21 (±3)
4-PABA in Toluene	460	<100	8.3 (±0.001)	
	600	150 (±25)	8.3	

Fig. S13: Transient absorption decay traces of 4-AP in Chloroform (a) and Toluene (b)



4-AP in $CHCl_3$	$\lambda_{abs}/\lambda_{em}$ (nm)	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)
	460	346.52 (± 94.3)	15.15 (± 0.95)	
	550	-	2.09 (± 0.24)	15
4-AP in Toluene	460	<100	10 (± 2)	
	550	-	2.5 (± 0.95)	10 (± 2)

Fig. S14: Calculated (TD-DFT) absorption spectra for various keto tautomers with (a) mPW1PW91 and (b) B3LYP functional.

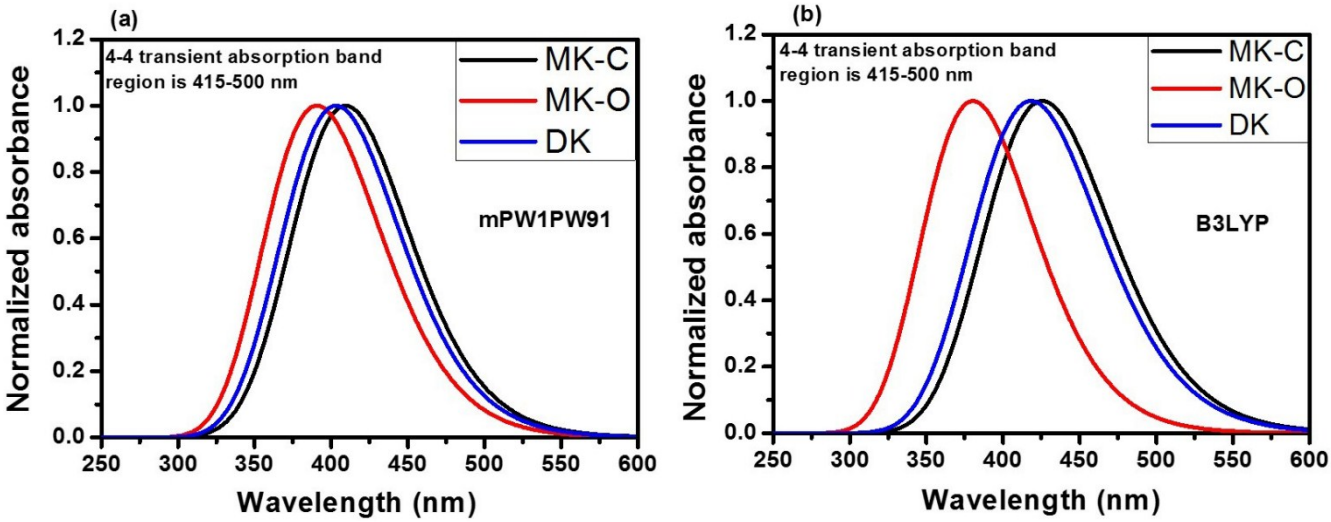
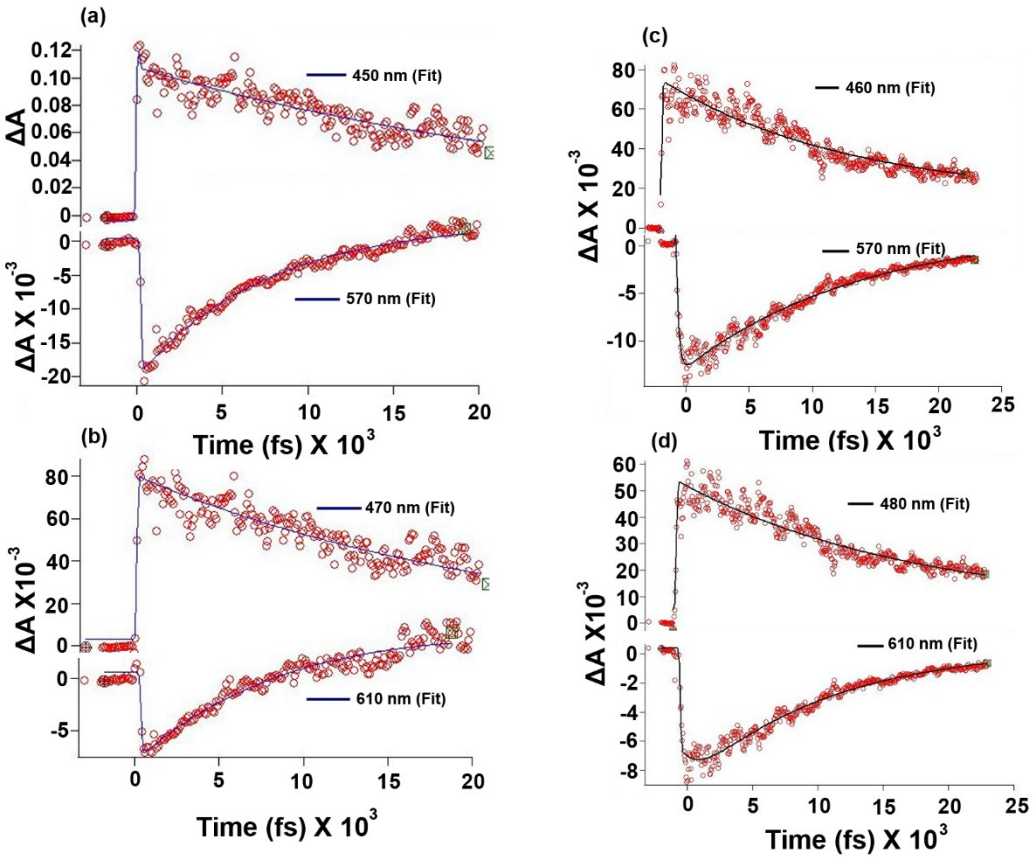
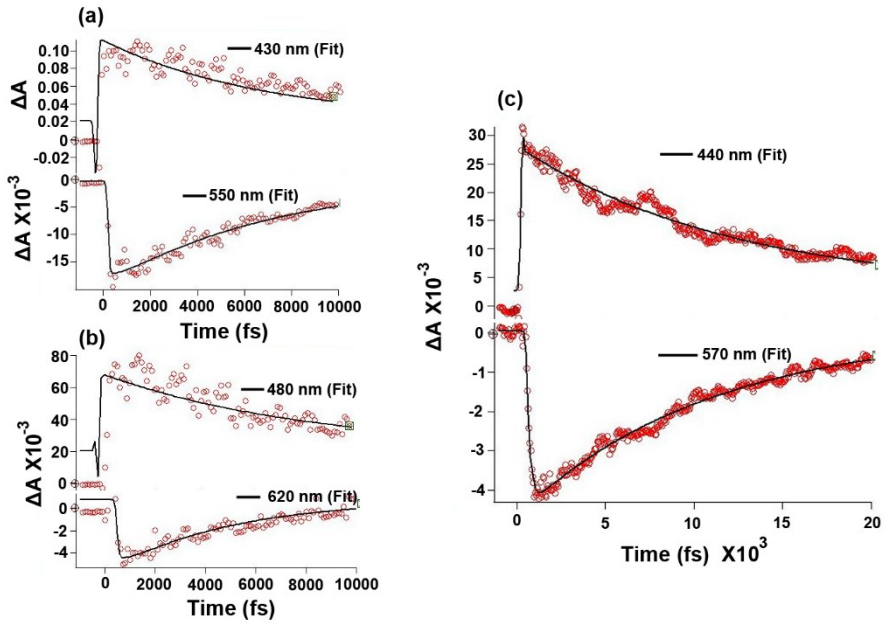


Fig. S15: Transient absorption decay traces of 4-4 in chloroform (a), (b) and toluene (c), (d)



4-4 in $CHCl_3$	$\lambda_{abs}/\lambda_{em}$ (nm)	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)
	450	<100	22 (± 2)	
	470	<100	22 (± 2)	
	520	-	1.6 (± 0.2)	22
	570	-	3.9 (± 0.5)	22
	610	-	4.06 (± 0.8) (~30%)	22 (~70%)
4-4 in Toluene	460	<100	13.8 (± 0.5)	
	480	<100	13.5 (± 0.5)	
	570	170-250	13.5	
	610	170-250	13.5	

Fig. S16: Transient absorption decay traces of 12-12 in Chloroform (a,b) and Toluene (c)



12-12 in $CHCl_3$	$\lambda_{abs}/\lambda_{em}$ (nm)	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)
	430	<100	9 (± 0.5)	
	480	185	8.5 (± 0.5)	
	550		1.2 (± 0.5)	8.5 (± 0.5)
	620		1 (± 0.5)	8.5 (± 0.5)
12-12 in Toluene	440	<100	10.74 ± 0.13	
	570	180-250	10.88 ±0.07	

Fig. S17: Diffuse reflectance spectra (DRS) of 4-PABA, 4-AP, 4-4 and 12-12