Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information

Functional group induced excited state intramolecular proton transfer process in 4-amino-2-methylsulfanyl-pyrimidine-5-carboxylic acid ethyl ester: A combined spectroscopic and Density Functional Theory study

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Contents:

1. Chemicals and solvent used

Spectroscopic grade of all solvents such as cyclohexane (CY), methylcyclohexane (MCH), n-heptane (n-hept), n-hexane (n-hex), tetrahydrofuran (THF), 1,4-dioxane (DOX), chloroform ($CHCl_3$), carbontetrachloride (CCl_4), 1,2-dichloromethane (DCM), N,N-dimethylformamide (DMF), dimethylsuophoxide (DMSO), methanol (MeOH), isopropanol (^{i}PrOH), butanol (BuOH), and acetonitrile (ACN) were purchased from Spectrochem and were used after proper distillation as required. Ethanol (EtOH), sulphuric acid (H_2SO_4), acetic acid (AcOH) and sodium hydroxide from E. Merck were used as received. Triple distilled water was used for the preparation of all aqueous solutions. AMPCE is totally soluble in almost all the solvents used except non polar (n-hex, n-hept, MCH, CY and CCl4) and water solvents in which it is partially soluble. Therefore, 5% ethanol solution has been used for those solvents in which AMPCE is partially soluble.

2. Absorption spectra of AMPCE with increasing AcOH concentration in n-hex solvent

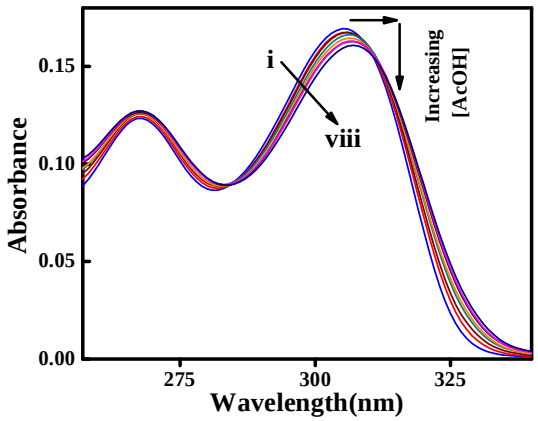

Fig. S1. Changes of absorption profile of AMPCE as a function of AcOH concentration in n-hex solvent (i→viii; 0, 0.1, 1.9, 4.2, 8.13, 16.83, 25.1, 35.4 mM AcOH).

3.

Table S1: Atomic charge on different atoms of AMPCE with different forms involving in PT process in vacuo and MeOH solvent

Atom with numbering	Vacuo				MeOH			
	A	**A***	**I**	**I***	**A**	**A***	**I**	**I***
C_1	-0.123	-0.293	-0.106	-0.231	-0.122	-0.266	-0.091	-0.18
C_2	1.312	1.408	1.785	1.721	1.342	1.449	1.809	1.781
C_3	-0.169	-0.185	-0.195	-0.159	-0.162	-0.189	-0.180	-0.153
N_4	-0.015	0.077	-0.029	0.002	-0.068	-0.008	-0.087	-0.046
C_5	-0.198	-0.099	-0.173	-0.152	-0.162	0.072	-0.133	-0.106
N_6	-0.016	0.014	0.025	0.001	-0.069	-0.051	-0.056	-0.089
N_7	-0.453	-0.448	-0.665	-0.708	-0.475	-0.473	-0.728	-0.785
C_8	-0.736	-0.735	-1.223	-1.102	-0.710	-0.735	-1.201	-1.116
S_{10}	-0.103	-0.345	-0.100	-0.101	-0.132	-0.457	-0.137	-0.129
C_{11}	-0.661	-0.578	-0.668	-0.664	-0.666	-0.576	-0.673	-0.671
O_{12}	-0.046	-0.048	-0.042	-0.016	-0.057	-0.065	-0.032	-0.016
O_{13}	-0.313	-0.299	-0.254	-0.231	-0.355	-0.346	-0.245	-0.226
H_{24}	0.299	0.298	0.438	0.424	0.311	0.308	0.441	0.424
H_{25}	0.284	0.286	0.257	0.247	0.313	0.316	0.267	0.254

4. Ground and excited state energy optimized different forms of AMPCE in vacuo

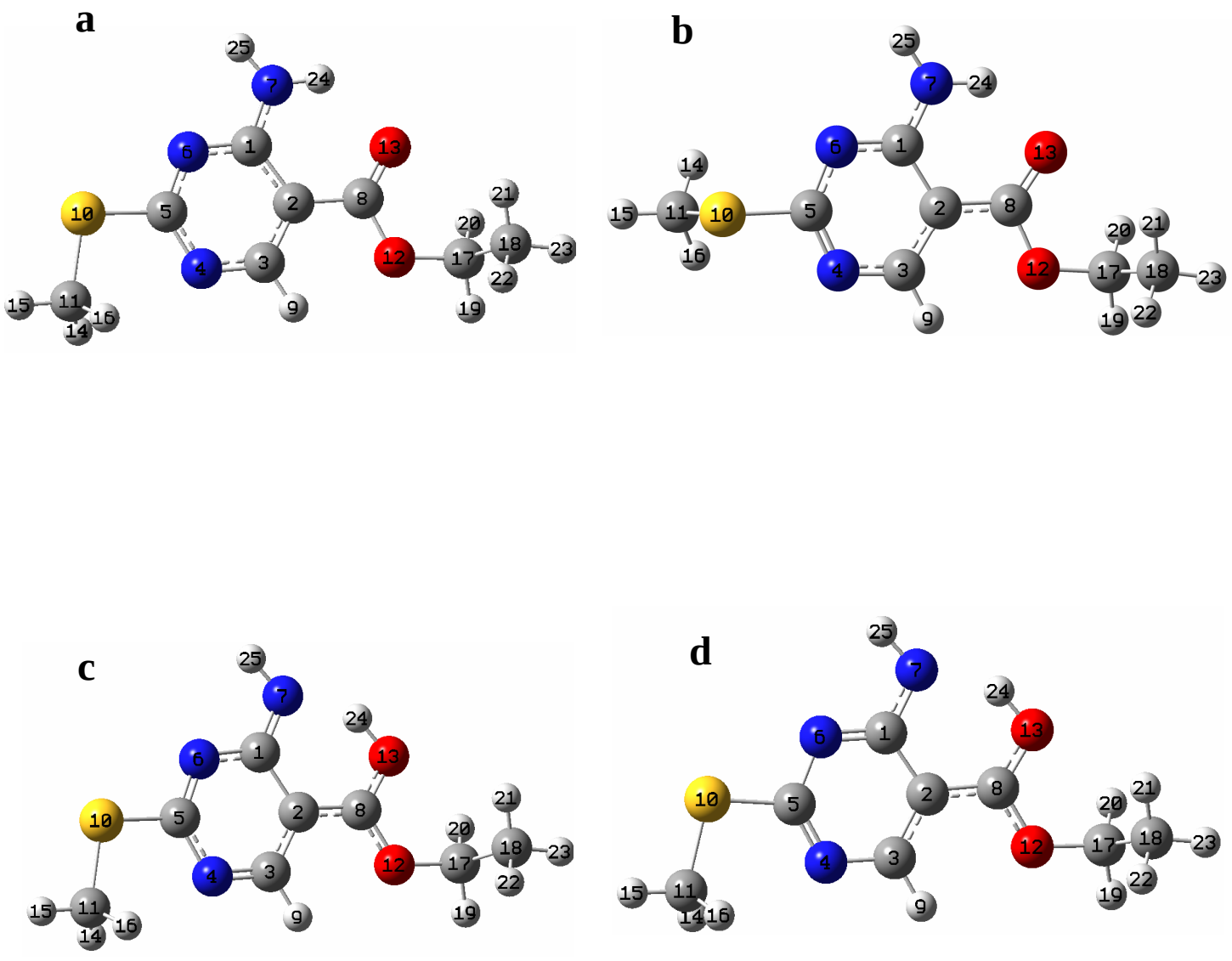

Fig. S2: Optimized structure of AMPCE with different forms in vacuo (a) Amine form in ground state [A] (b) Amine form in the excited state [A^*] (c) Imine form in ground state [I] (d) Imine form in the excited state [I^*].

5. Ground and excited state energy optimized different forms of AMPCE in methanol solvent

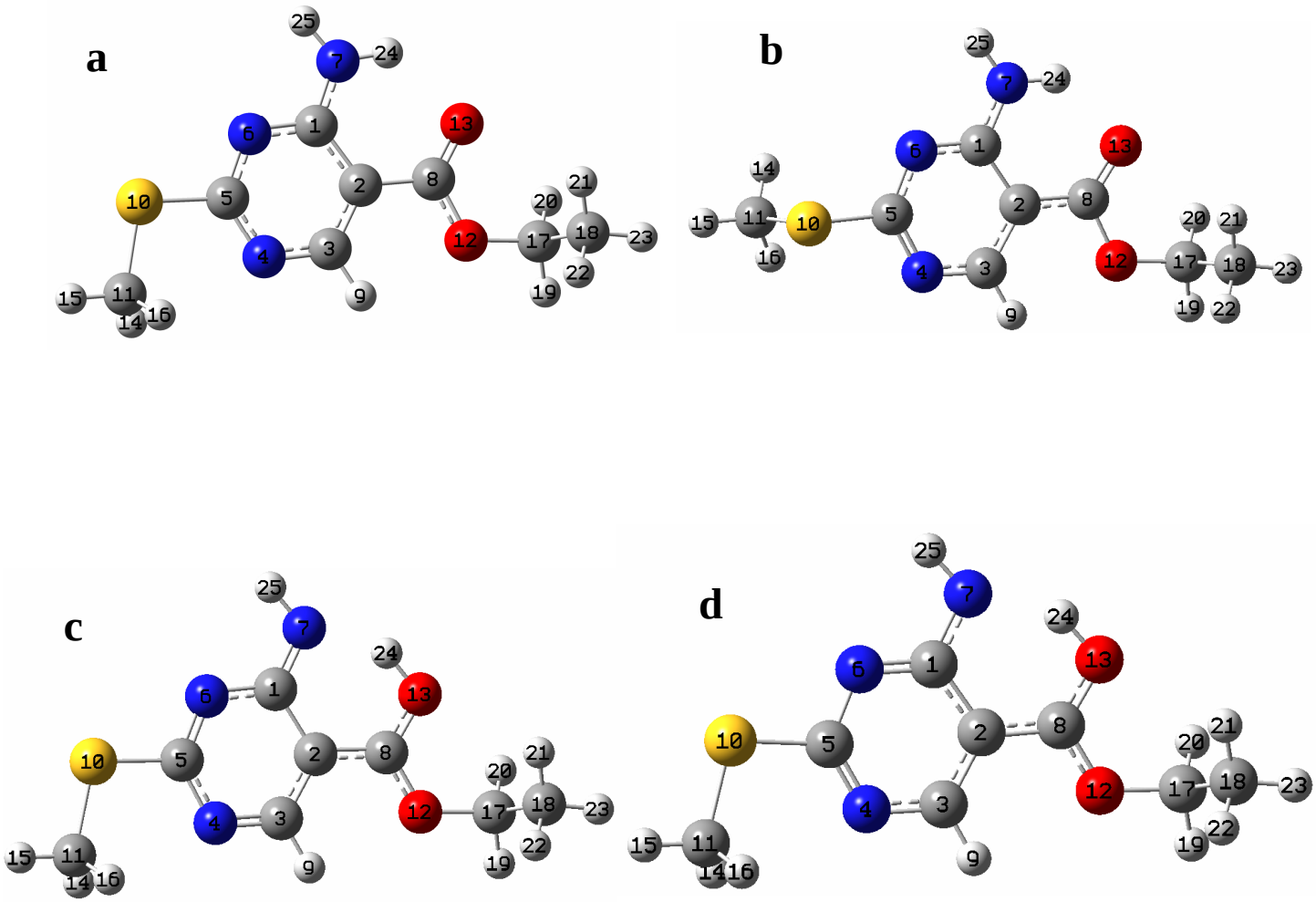

Fig. S3: Optimized structure of AMPCE with different forms in mthanol solvent (a) Amine form in ground state [A] (b) Amine form in the excited state [A^*] (c) Imine form in ground state [I] (d) Imine form in the excited state [I^*].

6.

Table S2: Ground and excited state optimized parameters of A, A*, I, I* forms of AMPCE molecule in vacuo and MeOH solvent

Parameter	Vacuo				MeOH			
	A	A*	I	I*	A	A*	I	I*
N_7–H_{24}	1.010	1.010	1.710	1.710	1.010	1.010	1.710	1.710
N_7–O_{13}	2.730	2.686	2.617	2.602	2.739	2.716	2.618	2.601
O_{13}–H_{24}	1.991	1.897	1.020	1.005	2.003	1.942	1.017	1.002
O_{13}–C_8	1.221	1.242	1.301	1.322	1.223	1.245	1.298	1.323
N_7–C_1	1.344	1.346	1.300	1.364	1.340	1.347	1.303	1.359
C_2–C_8	1.468	1.434	1.404	1.424	1.471	1.430	1.416	1.422
C_1–C_2	1.430	1.448	1.466	1.447	1.431	1.451	1.462	1.446
C_8–O_{12}	1.348	1.374	1.319	1.325	1.341	1.372	1.305	1.322
N_7–H_{25}	1.006	1.005	1.015	1.019	1.007	1.007	1.016	1.020
C_5–S_{10}	1.767	1.796	1.769	1.758	1.771	1.773	1.774	1.766
C_{11}–S_{10}	1.824	1.809	1.825	1.818	1.823	1.812	1.824	1.819
N_7–H_{24}–O_{13}	127.83	132.60	145.67	145.53	127.57	131.20	146.18	145.72
H_{24}–N_7–C_1	119.40	117.64	101.14	103.61	119.51	118.35	100.69	103.48
O_{13}–C_8–C_2	124.42	126.50	123.57	126.72	124.06	126.42	122.93	126.02
N_7–C_1–C_2	122.62	120.62	120.18	117.30	122.82	120.73	120.47	117.20
C_8–C_2–C_1	121.78	120.91	121.29	120.65	122.01	121.75	121.34	121.23
H_{25}–N_7–H_{24}	122.46	123.17	146.83	146.89	121.43	122.18	147.18	146.39
O_{13}–C_8–O_{12}	122.72	121.07	116.89	116.49	123.12	120.87	117.76	117.04
C_5–S_{10}–C_{11}	102.07	102.72	102.97	100.99	102.94	104.08	103.70	102.01
C_4–C_5–S_{10}	118.96	113.27	117.11	122.57	119.23	113.95	117.63	122.70
H_{25}–N_7–C_1	118.13	118.89	112.02	109.48	119.04	119.45	112.12	110.11
O_{12}–C_8–C_2	112.85	112.41	119.52	116.77	112.80	112.69	119.30	116.92
H_{24}–N_7–C_1–C_2	0.28	-2.49	-0.09	0.25	0.06	-0.01	-0.25	0.15
O_{13}–C_8–C_2–C_1	-0.37	0.32	0.09	0.11	-0.22	0.06	-0.09	-0.14
N_7–H_{24}–C_{13}–C_8	0.14	-1.24	0.43	0.26	-0.02	-0.76	0.24	-0.12
N_7–C_1–C_2–C_8	0.10	1.11	0.11	-0.23	0.08	-0.36	0.32	-0.08
H_{25}–N_7–C_{24}–C_1	-179.57	173.84	179.57	-178.87	179.95	179.34	179.32	-179.10
O_{13}–C_8–O_{12}–C_2	-179.71	-179.53	-179.63	-179.67	-179.71	-179.51	-179.70	-179.35
C_{11}–S_{10}–C_5–C_4	-0.30	-89.35	-0.31	0.08	-0.23	-93.77	0.09	0.08
O_{13}–C_8–O_{12}–C_{17}	0.40	1.10	1.49	0.45	0.72	1.54	0.64	2.88

7.

Table S3: Difference in parameter between A and I form in ground state and between A^* and I^* form in excited state

Parameter	vacuo		MeOH	
	A ~ I	**A^* ~ I^***	**A ~ I**	**A^* ~ I^***
N_7–O_{13}	0.113	0.084	0.121	0.115
O_{13}–H_{24}	0.971	0.892	0.986	0.940
O_{13}–C_8	0.080	0.080	0.075	0.078
N_7–C_1	0.044	0.018	0.037	0.012
C_2–C_8	0.064	0.010	0.055	0.008
C_1–C_2	0.036	0.001	0.031	0.005
N_7–H_{24}–O_{13}	18.84	12.93	18.61	14.52
H_{24}–N_7–C_1	18.26	14.03	18.82	14.87
O_{13}-C_8–C_2	0.85	0.22	1.13	0.40
C_8–C_2–C_1	0.49	0.26	0.67	0.52

8. Double y-axis plot for non-monotonic nature of PT process along PT coordinate

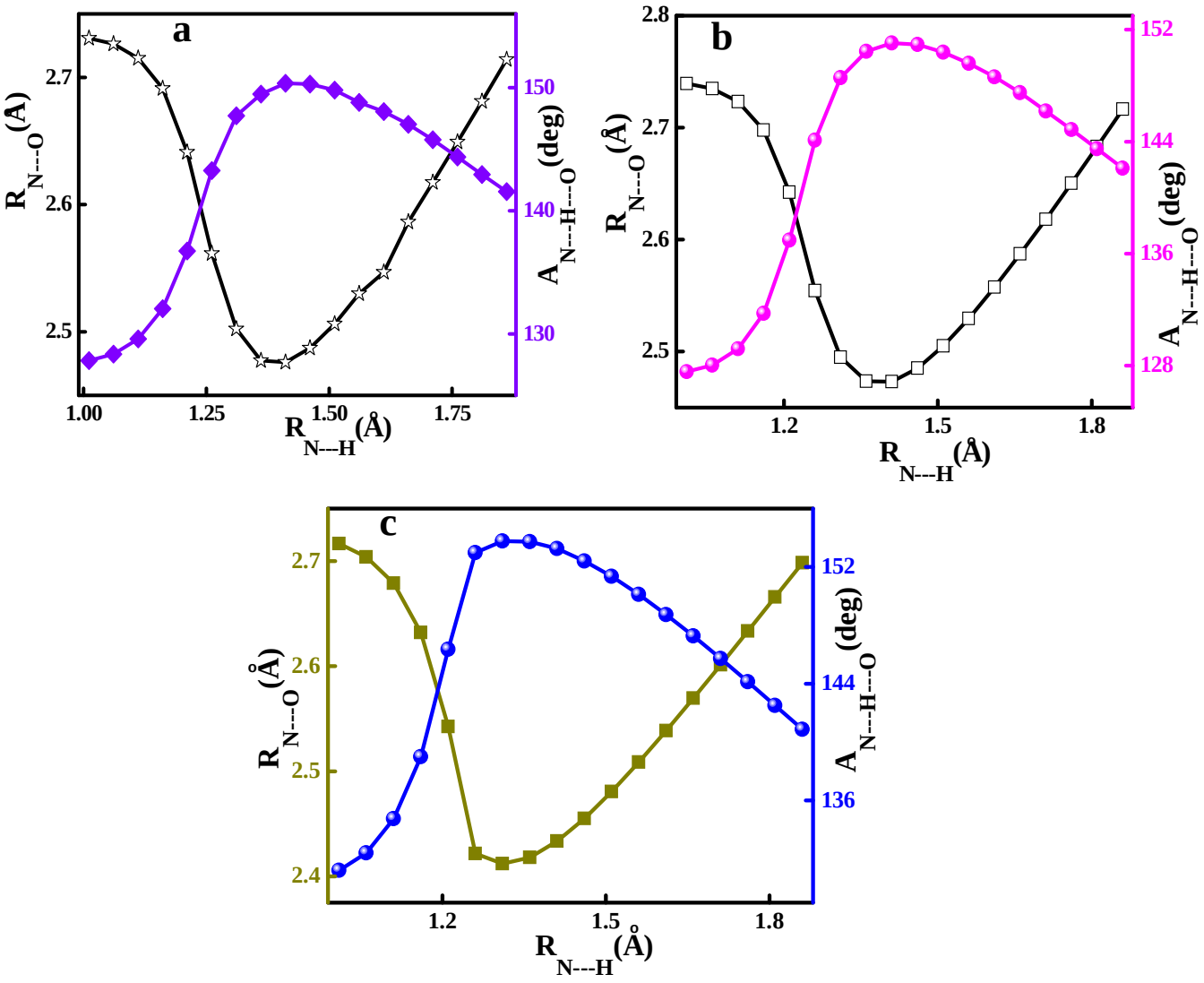

Fig. S4. Variation of N_7---O_{13} bond distance and N_7---H_{24}---O_{13} angle against N_7---H_{24} bond distance (a) in the S_0 state in vacuo (b) S_0 state in methanol and (c) S_1 state in methanol solvent.

9. Ground and excited state potential energy surfaces of AMPCE in methanol solvent

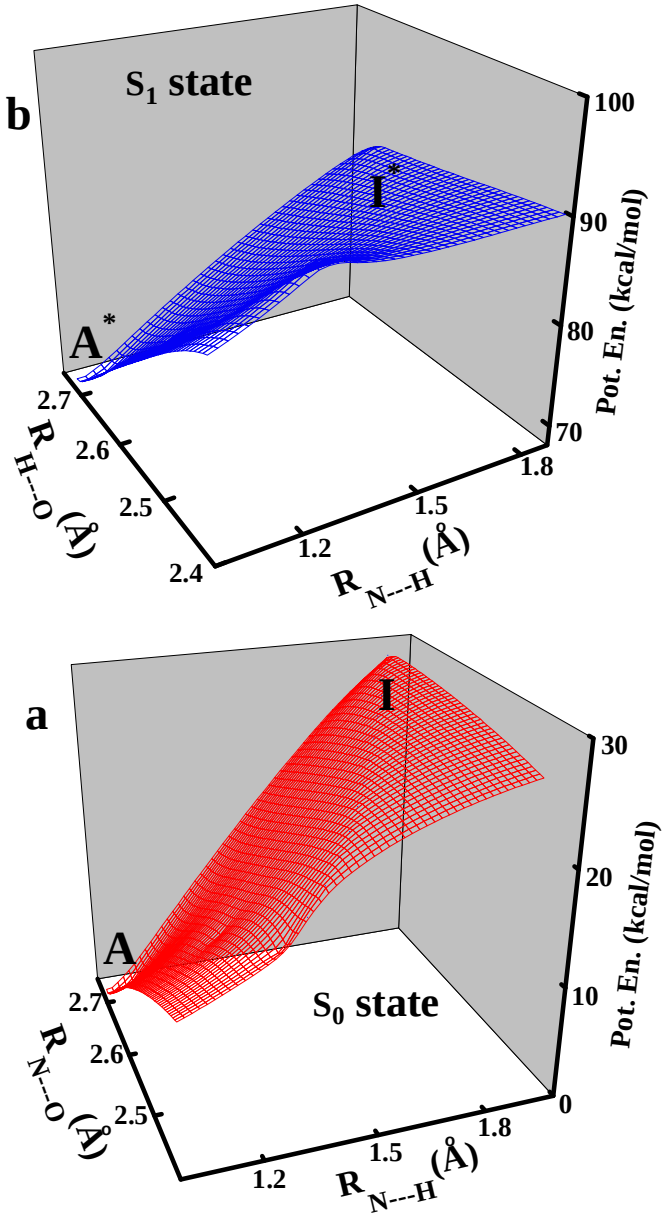

Fig. S5. 3D Potential energy surfaces for the (a) ground state and (b) first excited singlet state of AMPCE with variation of N_7---H_{24} and N_7---O_{13} bond distances in methanol solvent.