Supporting information

A detailed UV-Vis spectral investigation of six azo dyes derived from benzoic- and cinnamic acids: experimental and theoretical insight

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Table S1. *The relative energies (ΔE) in kcal/mol of fully optimized geometries at B3LYP and M06-2X/6-311++G(d,p) and statistical Boltzmann distribution weights (ω) in % for all possible tautomeric forms of the investigated azo dye molecules in vacuum, ethanol and DMSO.*

		B3LYP		B3LYP		M06-2X		M06-2X		M06-2X	
Compound		Vacuum		Ethanol		Vacuum		Ethanol		DMSO	
Tautomer	**Conformer**	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω
A2											
Hydrazone	s-*cis*,s-*cis*	0.000	32.60	0.000	35.75	0.776	7.38	0.000	19.93	0.000	19.26
	s-*cis*,s-*trans*	0.020	31.55	0.118	29.32	0.783	7.30	0.034	18.84	0.064	17.31
	s-*trans*,s-*cis*	0.532	13.35	0.433	17.30	1.168	3.83	0.372	10.68	0.275	12.15
	s-*trans*,s-*trans*	0.545	13.07	0.471	16.21	1.243	3.37	0.427	9.74	0.319	11.29
		Σ	**90.56**	**Σ**	**98.59**	**Σ**	**21.88**	**Σ**	**59.18**	**Σ**	**60.01**
Azo	s-*cis*,s-*cis*	1.319	3.57	2.527	0.52	0.000	27.14	0.217	13.84	0.243	12.81
	s-*cis*,s-*trans*	1.390	3.17	2.677	0.40	0.049	25.01	0.297	12.12	0.331	11.05
	s-*trans*,s-*cis*	1.858	1.44	2.919	0.27	0.392	14.05	0.557	7.82	0.494	8.42
	s-*trans*,s-*trans*	1.939	1.26	3.013	0.23	0.490	11.93	0.621	7.04	0.545	7.72
		Σ	**9.44**	**Σ**	**1.41**	**Σ**	**78.12**	**Σ**	**40.82**	**Σ**	**39.99**
A2a											
Hydrazone	*cis*,*cis*	0.000	38.07	0.000	40.10	0.845	7.50	0.000	20.86	0.000	20.35
	cis,*trans*	0.045	35.29	0.094	34.26	0.854	7.40	0.072	18.49	0.037	19.14
	trans,*cis*	0.890	8.55	0.680	12.81	1.522	2.41	0.493	9.12	0.514	8.59
	trans,*trans*	0.962	7.58	0.758	11.25	1.551	2.30	0.566	8.06	0.491	8.93
		Σ	**89.50**	**Σ**	**98.42**	**Σ**	**19.60**	**Σ**	**56.54**	**Σ**	**57.00**
Azo	*cis*,*cis*	1.277	4.47	2.460	0.65	0.000	30.97	0.151	16.18	0.180	15.05
	cis,*trans*	1.324	4.13	2.569	0.54	0.026	29.63	0.251	13.70	0.211	14.29
	trans,*cis*	2.152	1.03	3.136	0.21	0.661	10.22	0.632	7.23	0.649	6.85
	trans,*trans*	2.250	0.87	3.186	0.19	0.699	9.58	0.708	6.36	0.653	6.81
		Σ	**10.50**	**Σ**	**1.58**	**Σ**	**80.40**	**Σ**	**43.46**	**Σ**	**43.00**
B2											

Azo	s-*cis*,s-*cis*	0.000	37.17	0.000	30.97	0.000	36.30	0.000	32.24	0.000	40.20
	s-*cis*,s-*trans*	0.056	33.84	0.063	27.86	0.102	30.59	0.091	27.66	0.315	23.71
	s-*trans*,s-*cis*	0.532	15.24	0.129	24.96	0.454	16.95	0.213	22.54	0.404	20.42
	s-*trans*,s-*trans*	0.593	13.75	0.422	15.27	0.482	16.16	0.362	17.57	0.562	15.67
B2a											
Azo	s-*cis*,s-*cis*	0.000	43.02	0.000	39.88	0.000	39.51	0.000	38.49	0.000	37.68
	s-*cis*,s-*trans*	0.071	38.20	0.131	32.00	0.041	36.89	0.166	29.15	0.100	31.88
	s-*trans*,s-*cis*	0.861	10.14	0.522	16.61	0.711	12.00	0.409	19.39	0.512	15.97
	s-*trans*,s-*trans*	0.957	8.64	0.767	11.01	0.730	11.60	0.648	12.97	0.570	14.47

$\Delta E = E_{ZPE}$ (i) - E_{ZPE} (0); E_{ZPE} - zero point corrected energy; E_{ZPE} (0) - energy of most stable conformer-

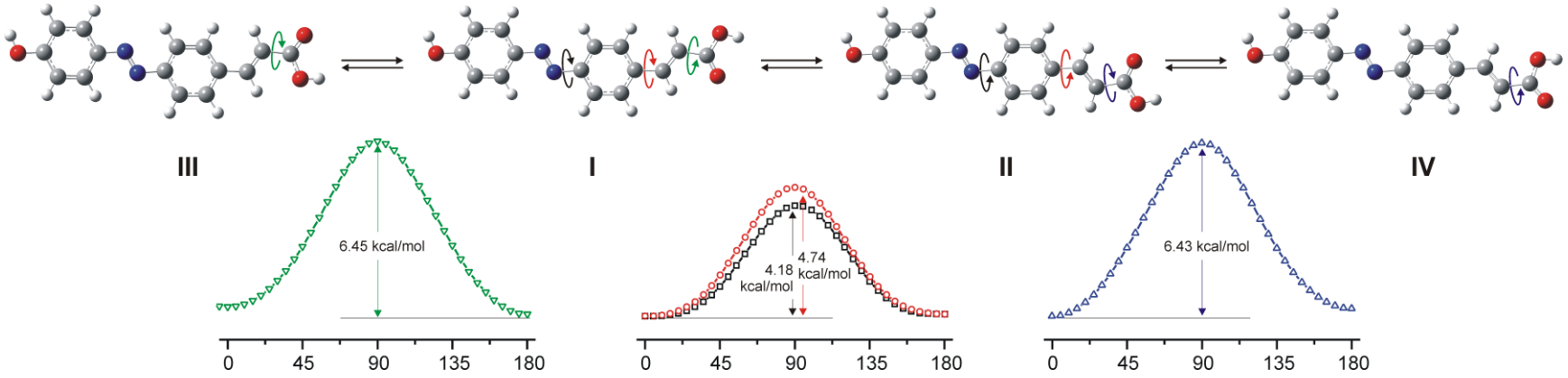
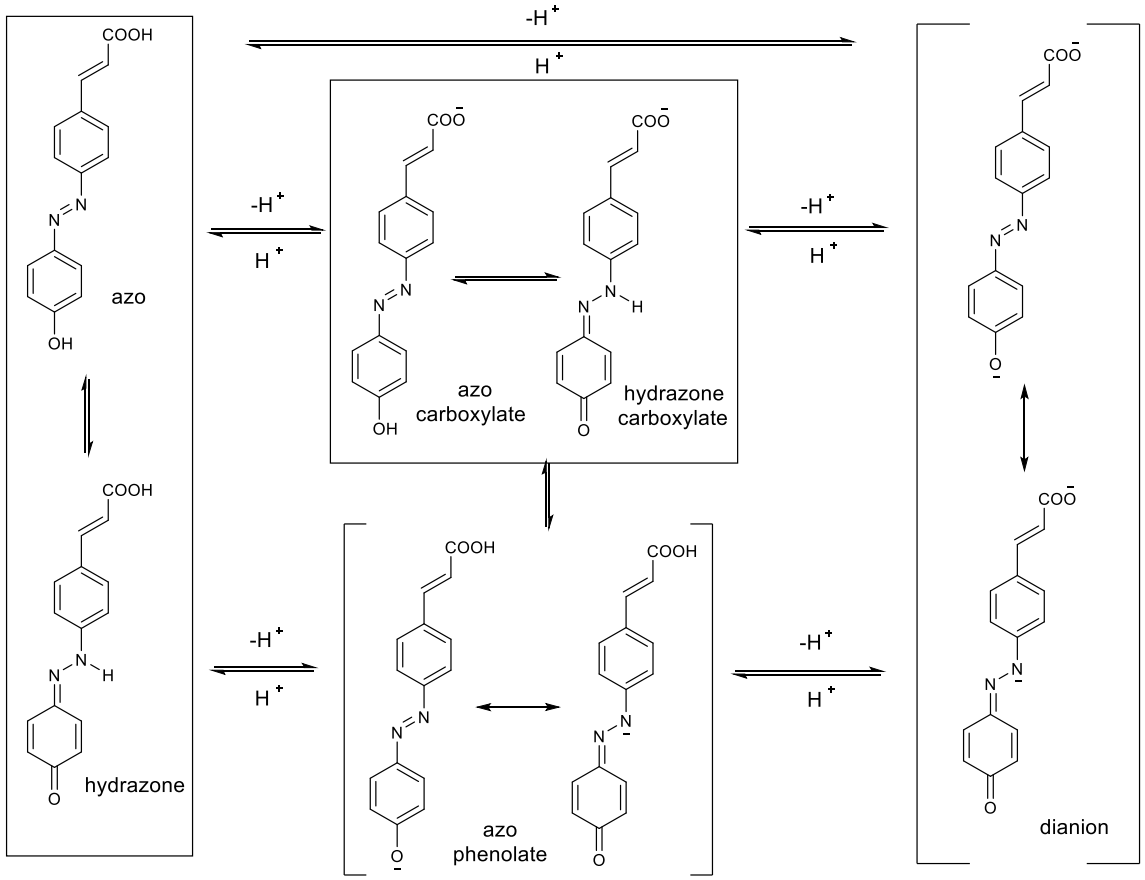


Figure S1. *The geometries of hydrazone tautomer of molecule* ***B2*** *and relaxed reaction coordinates for transition between them.*



Scheme S2. *The neutral and the theoretical possible anionic/dianionic molecular forms of* ***B2***

Table S2. *The relative energies (ΔE) in kcal/mol of fully optimized geometries at B3LYP and M06-2X/6-311++G(d,p) and statistical Boltzmann distribution weights (ω) in % for all possible anionic species in vacuum, ethanol and DMSO*

		B3LYP		B3LYP		M06-2X		M06-2X		M06-2X	
Compound		Vacuum		Ethanol		Vacuum		Ethanol		DMSO	
Anion species	**Conformer**	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω	Δ*E*	ω
A2											
Azo-Carboxylate	s-*cis*	2.911	0.25	1.964	1.87	3.184	0.14	0.000	37.87	0.000	35.22
	s-*trans*	2.951	0.23	1.976	1.83	3.285	0.12	0.076	33.34	0.029	33.55
		Σ	**0.48**	**Σ**	**3.71**	**Σ**	**0.26**	**Σ**	**71.22**	**Σ**	**68.78**
Hydrazone-Carboxylate	s-*cis*	2.849	0.28	0.057	45.84	5.795	0.00	0.616	13.47	0.534	14.39
	s-*trans*	2.881	0.26	0.000	50.45	5.714	0.00	0.540	15.31	0.440	16.83
		Σ	**0.54**	**Σ**	**96.29**	**Σ**	**0.00**	**Σ**	**28.78**	**Σ**	**31.22**
Azo-anion	s-*cis*,s-*cis*	0.045	30.51	9.653	0.00	0.000	29.20	7.336	0.00	7.419	0.00
	s-*cis*,s-*trans*	0.000	32.91	9.698	0.00	0.001	29.17	7.357	0.00	7.520	0.00
	s-*trans*,s-*cis*	0.376	17.50	10.037	0.00	0.226	19.99	7.546	0.00	7.716	0.00
	s-*trans*,s-*trans*	0.358	18.06	10.074	0.00	0.186	21.38	7.591	0.00	7.757	0.00
		Σ	**98.98**	**Σ**	**0.00**	**Σ**	**99.74**	**Σ**	**0.00**	**Σ**	**0.00**
Dianion	s-*trans*	0.000	47.06					0.000	45.76	0.000	45.81
	s-*cis*	-0.070	52.94					-0.101	54.24	-0.100	54.19
A2a											
Azo-anion	s-*cis*,s-*cis*	0.000	36.77	0.000	36.54	0.000	36.68	0.000	34.13	0.000	34.08
	s-*cis*,s-*trans*	-0.024	38.31	0.010	35.93	0.068	32.74	0.002	34.03	0.000	34.07
	s-*trans*,s-*cis*	0.661	12.13	0.596	13.45	0.525	15.20	0.443	16.24	0.444	16.19
	s-*trans*,s-*trans*	0.630	12.79	0.568	14.08	0.518	15.38	0.466	15.61	0.463	15.67
B2											
Azo carboxylate	s-*cis*	18.293	0.00	1.097	5.08	15.022	0.00	0.000	47.12	0.000	49.37
	s-*trans*	18.352	0.00	1.258	3.88	15.037	0.00	0.061	42.50	0.061	44.58

		Σ	**0.00**	**Σ**	**8.96**	**Σ**	**0.00**	**Σ**	**89.62**	**Σ**	**93.95**
Azo phenolate	s-*cis*,s-*cis*	0.019	32.09	0.000	32.01	0.000	33.24	1.518	3.69	1.867	2.15
	s-*cis*,s-*trans*	0.000	33.15	0.110	26.64	0.098	28.23	1.736	2.56	2.087	1.49
	s-*trans*,s-*cis*	0.431	16.09	0.339	18.12	0.330	19.12	1.766	2.44	2.113	1.43
	s-*trans*,s-*trans*	0.342	18.68	0.482	14.27	0.321	19.41	1.982	1.69	2.334	0.98
		Σ	**100.00**	**Σ**	**91.04**	**Σ**	**100.00**	**Σ**	**10.38**	**Σ**	**6.05**
Dianion		0.000	53.56					0.000	53.26	0.000	53.38
		0.085	46.44					0.078	46.74	0.081	46.62
B2a											
Azo phenolate	s-*cis*,s-*cis*	0.000	35.92	0.000	37.30	0.000	36.18	0.000	37.67	0.000	41.73
	s-*cis*,s-*trans*	-0.056	39.43	-0.006	37.68	0.021	34.95	0.086	32.62	0.252	27.37
	s-*trans*,s-*cis*	0.663	11.81	0.669	12.14	0.621	12.76	0.579	14.27	0.532	17.11
	s-*trans*,s-*trans*	0.613	12.84	0.634	12.88	0.482	16.11	0.532	15.44	0.660	13.79

$\Delta E = E_{ZPE}$ (i) - E_{ZPE} (0); E_{ZPE} - zero point corrected energy; E_{ZPE} (0) - energy of most stable conformer

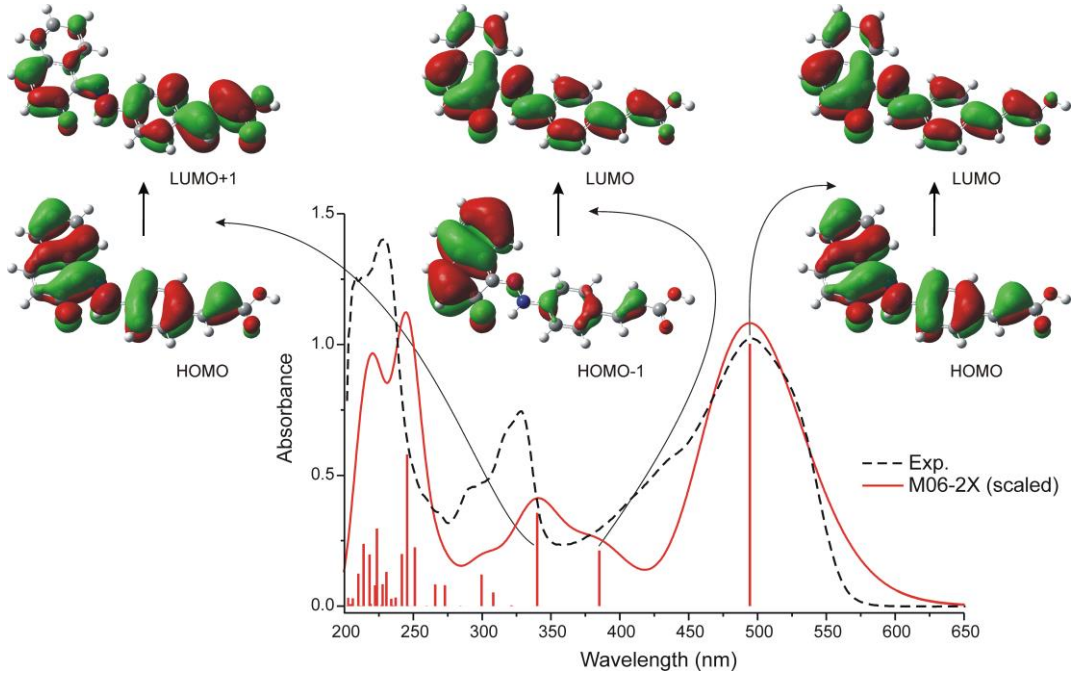


Figure S2. *Experimental and scaled theoretical UV-Vis spectra with corresponding transitions in ethanol for hydrazone form of dye* ***A2*** *at the TD-CPCM-M06-2X/6-311++G(d,p) level.*

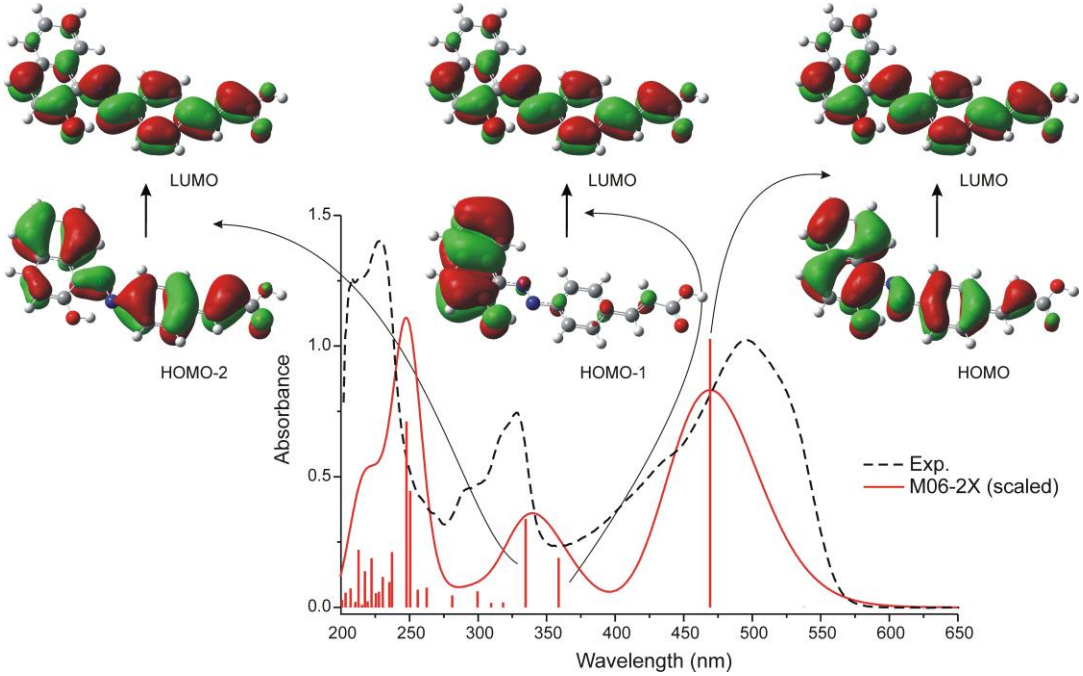


Figure S3. *Experimental and scaled theoretical UV-Vis spectra with corresponding transitions in ethanol for azo form of dye* ***A2*** *at the TD-CPCM-M06-2X/6-311++G(d,p) level.*

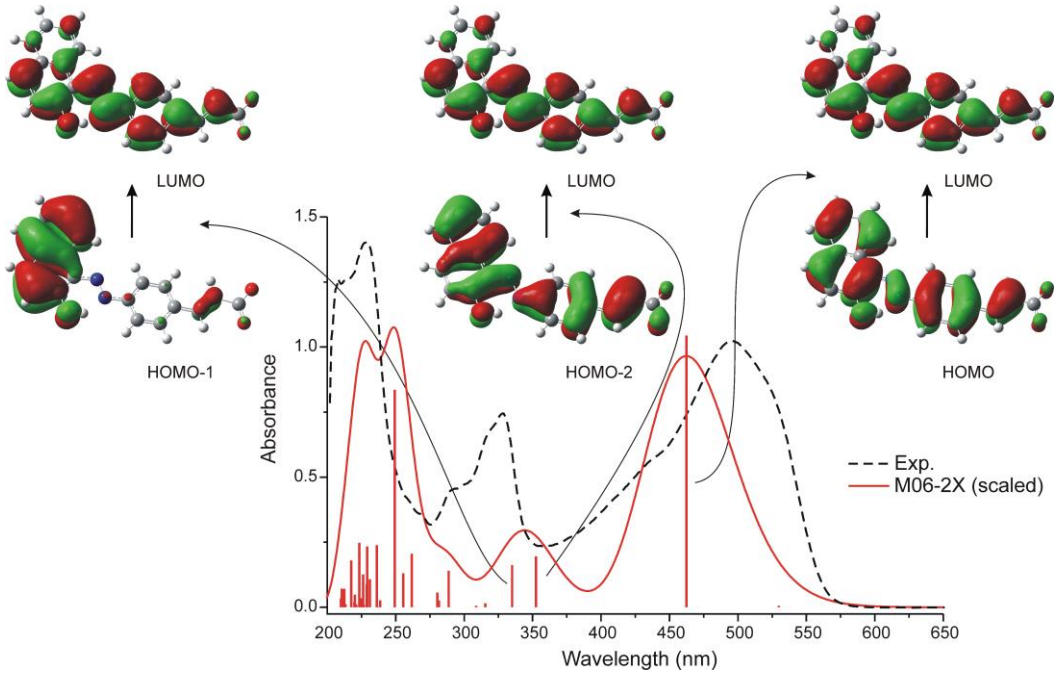


Figure S4. *Experimental and scaled theoretical UV-Vis spectra with corresponding transitions in ethanol for azo carboxylate form of dye* ***A2*** *at the TD-CPCM-M06-2X/6-311++G(d,p) level.*

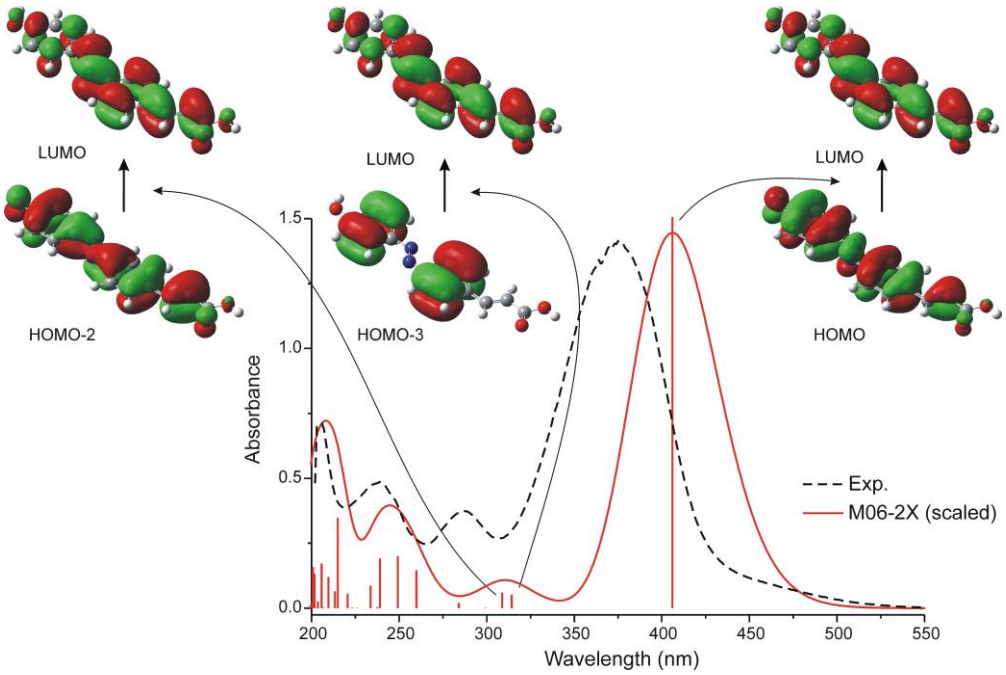


Figure S5. *Experimental and scaled theoretical UV-Vis spectra with corresponding transitions in ethanol for azo form of dye* ***B2*** *at the TD-CPCM-M06-2X/6-311++G(d,p) level.*

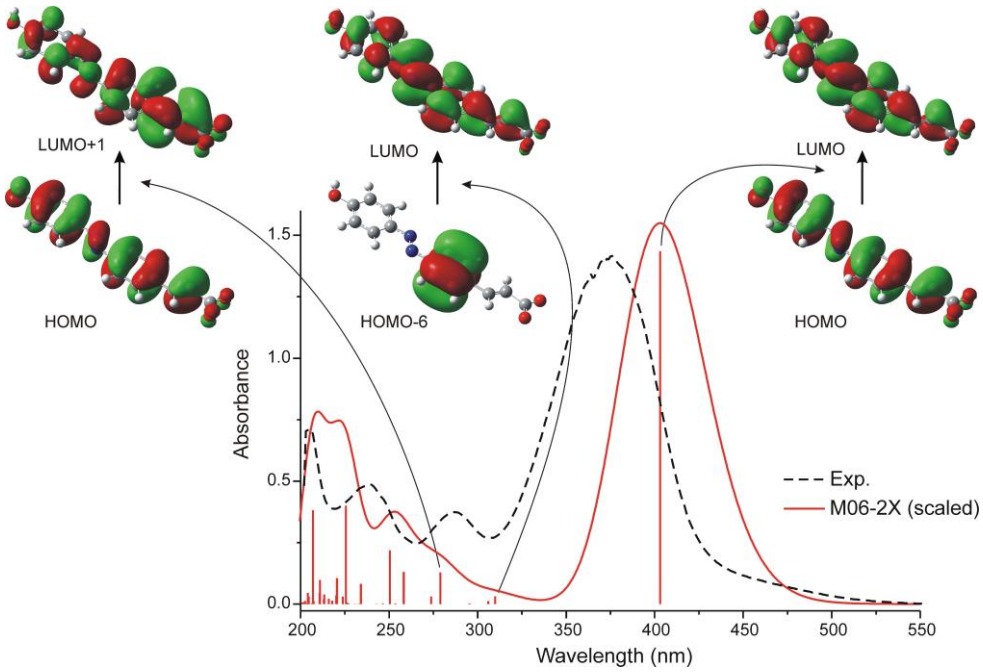


Figure S6. *Experimental and scaled theoretical UV-Vis spectra with corresponding transitions in ethanol for azo carboxylate form of dye* ***B2*** *at the TD-CPCM-M06-2X/6-311++G(d,p) level.*

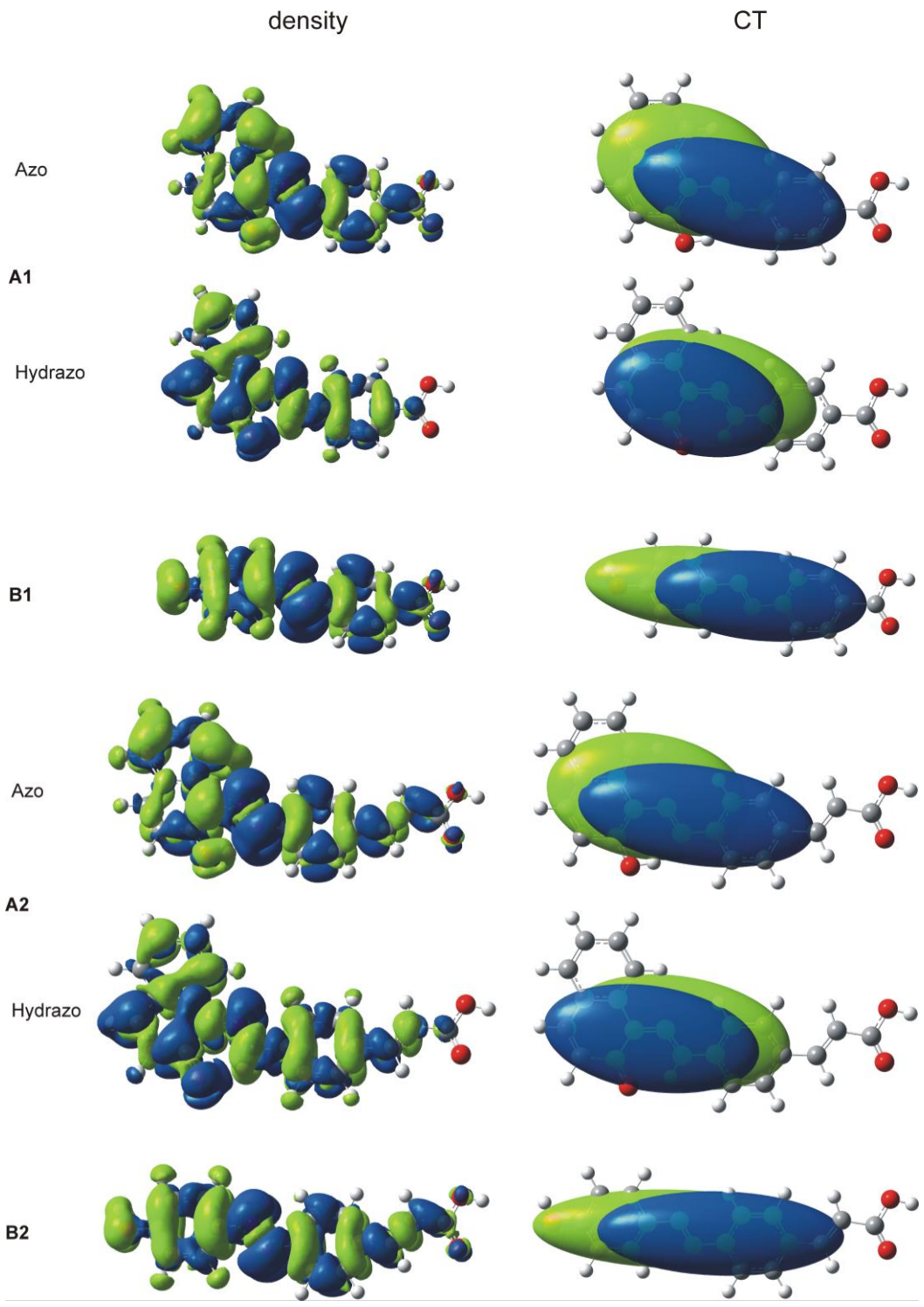
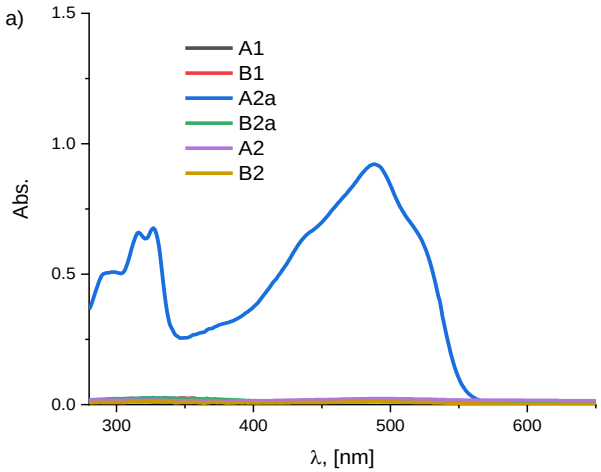
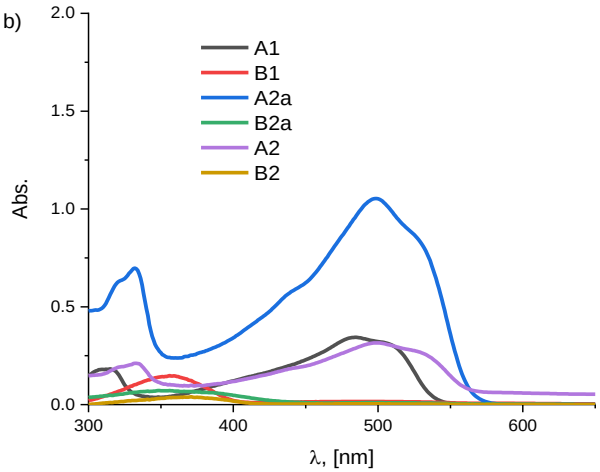
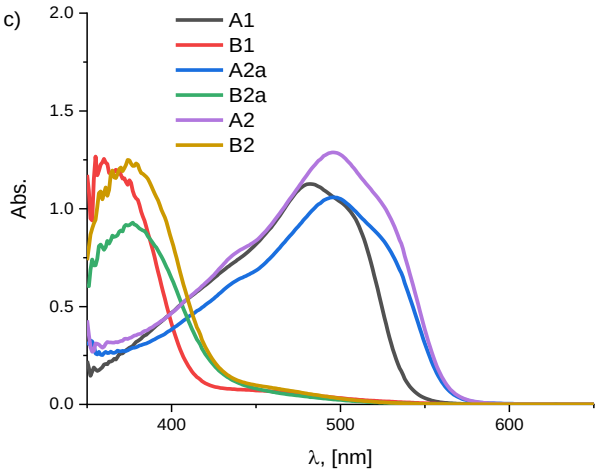
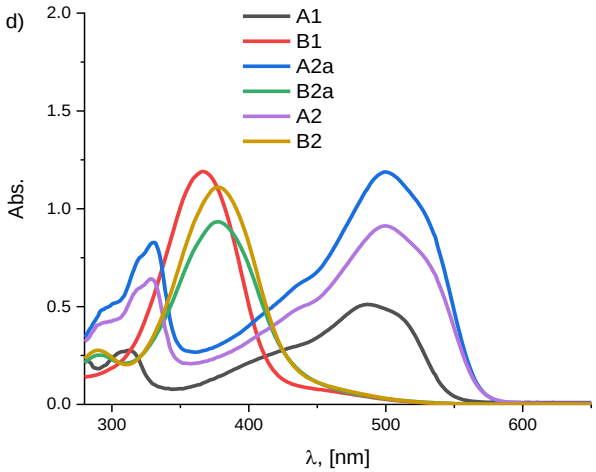


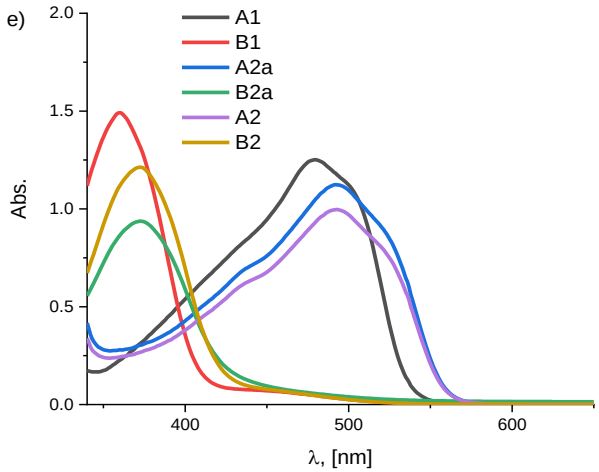
Figure S7. *The computed charge density difference between ground state and first excited states and centroids of charge $C_{+}(r)/C_{-}(r)$ calculated at the CPCM/TD-M06-2X/6-311++G(d,p) level the for dyes **A1**, **A2**, **B1** and **B2**. The blue and green zones correspond to density decrement and increment, respectively.*


a)
Abs.
λ, [nm]
A1
B1
A2a
B2a
A2
B2
0.0
0.5
1.0
1.5
300
400
500
600


b)
Abs.
λ, [nm]
A1
B1
A2a
B2a
A2
B2
0.0
0.5
1.0
1.5
2.0
300
400
500
600


c)
A1
B1
A2a
B2a
A2
B2
Abs.
λ, [nm]


d)
A1
B1
A2a
B2a
A2
B2
Abs.
λ, [nm]


e)
A1
B1
A2a
B2a
A2
B2
Abs.
λ, [nm]

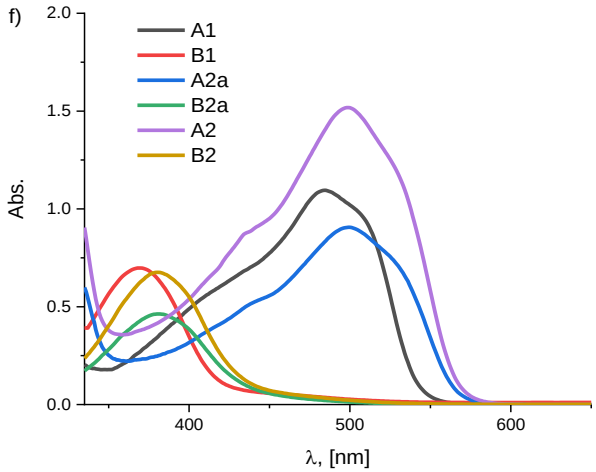

f)
A1
B1
A2a
B2a
A2
B2
Abs.
λ, [nm]

Figure S8. *The experimental UV-Vis absorption spectra of the investigated azo dye molecules in some selected solvents: a) hexane b) toluene c) cyclohexanone d) cyclohexanol, e) 2-butanone, f) 1-methyl-2-pyrrolidinone*

Table S3. *UV-Vis spectroscopic data of the dominant UV-Vis maxima of the investigated compounds*

	A1		**B1**		**A2a**		**B2a**		**A2**		**B2**	
	λ, [nm]	log ε[a]	λ, [nm]	log ε[a]	λ, [nm]	log ε[a]	λ, [nm]	log ε[a]	λ, [nm]	log ε[a]	λ, [nm]	log ε[a]
Acetone	478.0	4.24	359.0	4.33	491.0	4.30	370.0	4.31	492.0	4.26	371.0	4.29
Acetonitrile[c]	479.0	4.20	356.0	4.36	492.0	4.35	368.0	4.32	492.0	4.37	368.0	4.34
n-Butanol	485.0	4.08	362.0	4.23	497.0	4.28	372.0	4.01	497.0	4.17	375.0	4.27
2-Butanon	479.0	4.40	361.0	4.48	492.0	4.35	373.0	4.28	493.0	4.30	372.0	4.39
tert-Butanol	484.0	4.25	361.0	4.46	497.0	4.38	374.0	4.35	497.0	4.37	373.0	4.44
Cyclohexanol	486.0	4.01	366.0	4.38	499.0	4.38	378.0	4.27	499.0	4.26	378.0	4.35
Cyclohexanone	482.0	4.35	365.0	4.40	496.0	4.33	377.0	4.27	496.0	4.41	374.0	4.40
Dioxane	482.0	4.29	359.0	4.49	496.0	4.51	371.0	4.43	496.0	4.39	371.0	4.39
Diisopropyl ether	477.0	4.06	359.0	4.26	489.0	4.17	371.0	3.38	488.0	4.26	371.0	4.31
DMA	483.0	4.24	367.0	4.40	497.0	4.37	380.0	4.45	496.0	4.36	380.0	4.25
DMF	483.0	4.35	366.0	4.40	497.0	4.40	380.0	4.45	497.0	4.31	378.0	4.50
DMSO[c]	486.0	4.32	369.0	4.18	501.0	4.27	381.0	4.51	500.0	4.29	379.0	4.36
Ethanol[c]	482.0	4.21	362.0	4.40	495.0	4.36	374.0	4.46	495.0	4.28	373.0	4.45
Ethyl acetate	478.0	4.24	357.0	4.35	492.0	4.40	369.0	4.03	492.0	4.36	369.0	4.30
Chloroform	486.0	4.40	358.0	4.03	501.0	4.43	368.0	4.44	501.0	4.43	371.0	4.05
n-Hexane	/[b]	/[b]	/[b]	/[b]	488.0	4.27	/[b]	/[b]	/[b]	/[b]	/[b]	/[b]
Isobutanol	487.0	4.02	363.0	4.49	498.0	4.32	374.0	3.84	498.0	4.04	374.0	4.37
Methanol	483.0	4.04	358.0	4.47	495.0	4.15	371.0	4.45	495.0	4.37	372.0	4.41
Propanol	486.0	4.03	361.0	4.48	497.0	4.26	372.0	4.25	497.0	4.25	373.0	4.36
Acetic acid	487.0	4.48	359.0	4.44	504.0	4.42	371.0	4.41	505.0	4.42	369.0	4.41
1-Methyl-2-pyrolidinone	484.0	4.34	371.5	4.15	499.5	4.26	380.5	3.97	499.0	4.48	381.0	4.13
2-Pentanone	479.5	4.11	360.5	4.06	492.5	4.48	372.0	4.32	493.5	4.48	374.0	4.12
Anisole	486.5	4.29	361.0	4.16	500.5	4.45	/[b]	/[b]	501.5	4.34	375.5	3.97
Benzyl alcohol	494.0	4.37	368.0	4.24	510.5	4.46	380.5	3.92	511.5	4.56	377.0	4.20
Diethyl ether	477.5	4.05	358.5	4.13	489.5	4.39	/[b]	/[b]	489.5	4.24	372.0	4.27
Xylene	484.5	4.09	/[b]	/[b]	499.0	4.44	/[b]	/[b]	499.0	3.89	/[b]	/[b]
Methyl acetate	479.0	4.17	355.5	3.96	492.0	4.42	368.5	4.14	492.5	4.43	371.0	4.21
Dichloromethane	483.5	4.03	353.0	3.95	499.5	4.48	/[b]	3.40	498.5	4.37	368.5	3.69
n-Pentane	/[b]	/[b]	/[b]	/[b]	488.0	4.33	/[b]	/[b]	/[b]	/[b]	/[b]	/[b]
Tetrahydrofuran	480.5	4.40	360.0	3.97	494.5	4.44	372.5	3.95	494.0	4.45	375.0	3.97
Toluene	484.5	3.84	356.0	3.47	498.5	4.32	/[b]	/[b]	499.5	3.80	/[b]	/[b]
Triethylamine	480.5	4.04	362.5	4.46	491.0	4.05	375.0	4.41	488.5	4.27	375.0	4.50
Pyridine	486.5	4.33	370.0	4.46	501.5	4.48	381.5	4.44	501.5	4.33	380.5	4.54
Formamide	492.0	4.42	359	4.45	507.5	4.38	374.0	4.35	507.5	4.25	371.0	4.33

[a] ε, $dm^3\,mol^{-1}\,cm^{-1}$

[b] insoluble

[c] data taken from ref. [6]

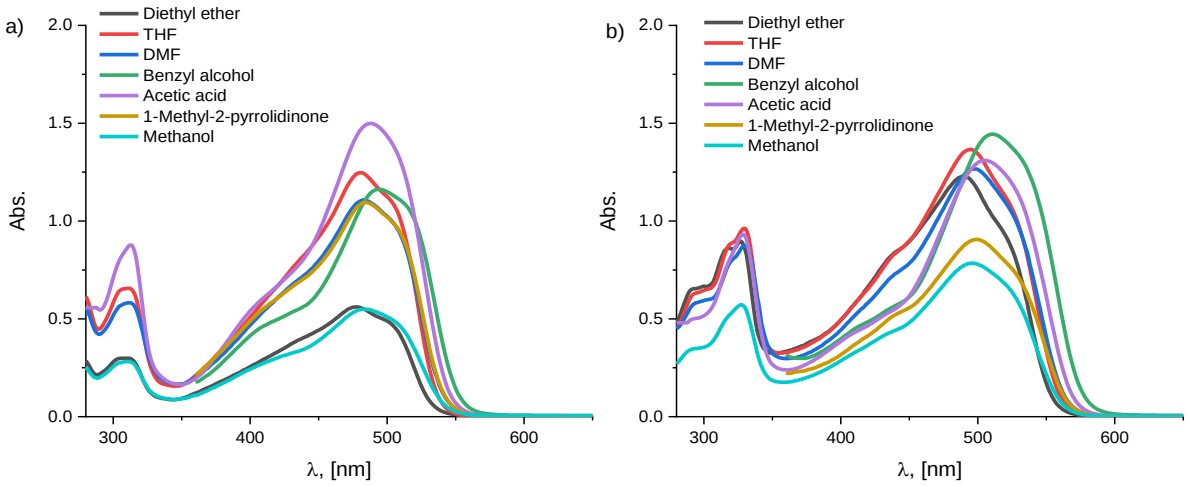


Figure S9. *The experimental UV-Vis absorption spectra of the a)* ***A1*** *and b)* ***A2a*** *in selected solvents*

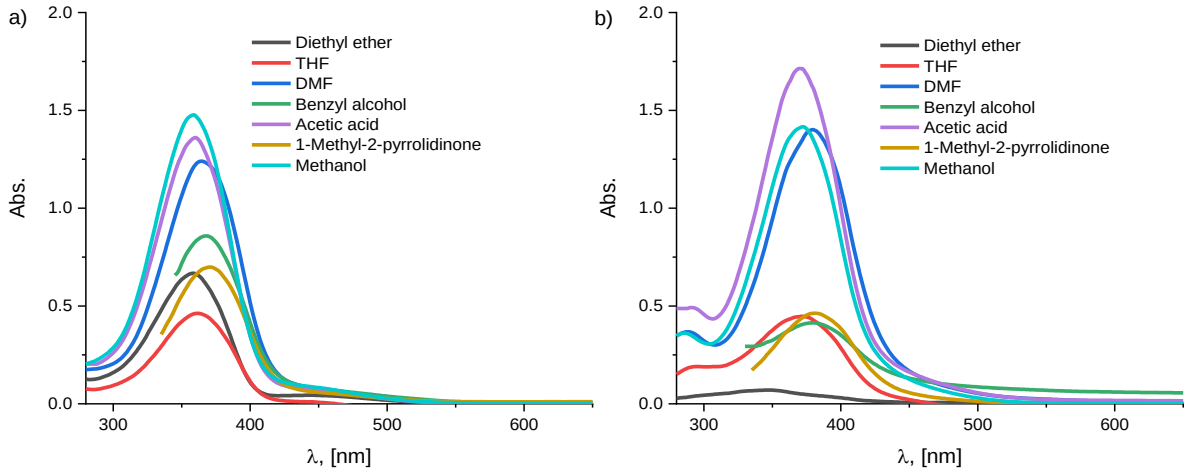


Figure S10. *The experimental UV-Vis absorption spectra of the a)* ***B1*** *and b)* ***B2a*** *in selected solvents*

Table S4. *Physical parameters of the corresponding solvents used for LSER analyses*

Solvent	*SP*	*SdP*	*SB*	*SA*
2-Butanone	0.669	0.872	0.52	0
Acetone	0.651	0.907	0.475	0
Acetonitrile	0.645	0.974	0.286	0.044
1-Butanol	0.674	0.655	0.809	0.341
Cyclohexanone	0.766	0.745	0.482	0
Dioxane	0.737	0.312	0.444	0
Diizopropyl ether	0.625	0.324	0.657	0
DMA	0.763	0.987	0.65	0.028
DMF	0.759	0.977	0.613	0.031
DMSO	0.83	1	0.647	0.072
Ethanol	0.633	0.783	0.658	0.4
Ethyl acetate	0.656	0.603	0.542	0
Chloroform	0.783	0.614	0.071	0.047
Isobutanol	0.657	0.684	0.828	0.311
Methanol	0.608	0.904	0.545	0.605
Hexane	/	/	/	/
1-Propanol	0.658	0.748	0.782	0.367
Acetic acid	0.651	0.676	0.39	0.689
tert-Butanol	0.632	0.732	0.928	0.145
2-Pentanone	0.689	0.783	0.537	0.01
1-Methyl-2-pyrrolidinone	0.812	0.959	0.613	0.024
Anisole	0.82	0.543	0.299	0.084
Benzyl alcohol	0.861	0.788	0.461	0.409
Xylene	0.78	0.215	0.16	0
Methyl acetate	0.645	0.637	0.527	0
Diethyl ether	0.617	0.385	0.562	0
Pentane	0.593	0	0.073	0
Toluene	0.782	0.284	0.128	0
Dichloromethane	0.761	0.769	0.178	0.04
Tetrahydrofuran	0.714	0.634	0.591	0
Cyclohexanol	/	/	/	/
Triethylamine	0.660	0.108	0.885	0
Pyridine	0.842	0.761	0.581	0.033
Formamide	0.814	1.006	0.414	0.549

Table S5. *Percentage contribution of solvatochromic parameters according to the Catalán equation*

	P_{SP} (%)	P_{SdP} (%)	P_{SB} (%)	P_{SA} (%)
A1	68.5	3.3	5.2	23.0
A2a	77.9	0.0	0.0	22.1
A2	71.6	0.0	5.8	22.6
B1	68.7	8.1	23.2	0.0
B2a	70.1	13.2	12.4	4.2
B2	71.4	5.4	23.2	0.0

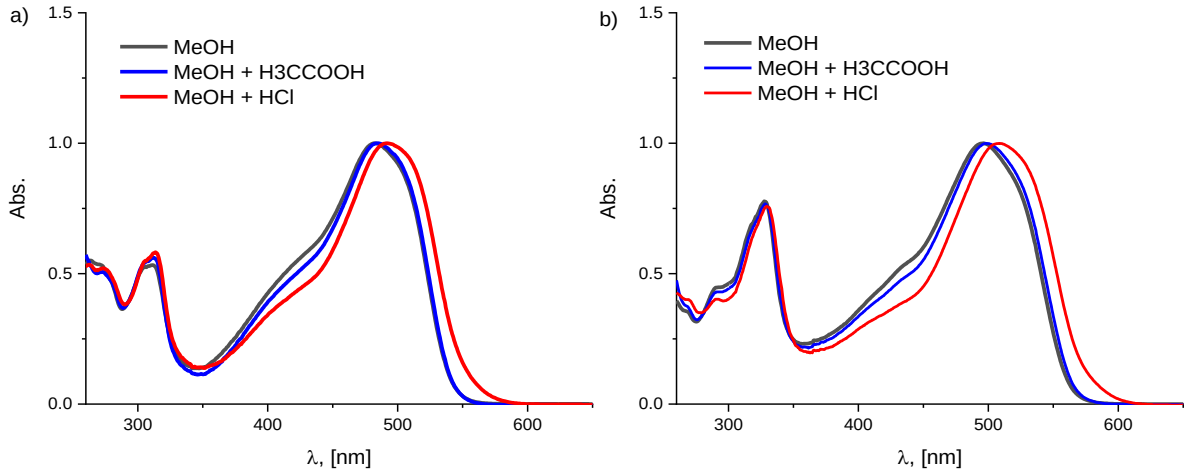


Figure S11. *The normalized experimental UV-Vis absorption spectra in methanol upon addition of the HCl and the acetic acid of a)* ***A1*** *and b)* ***A2a***

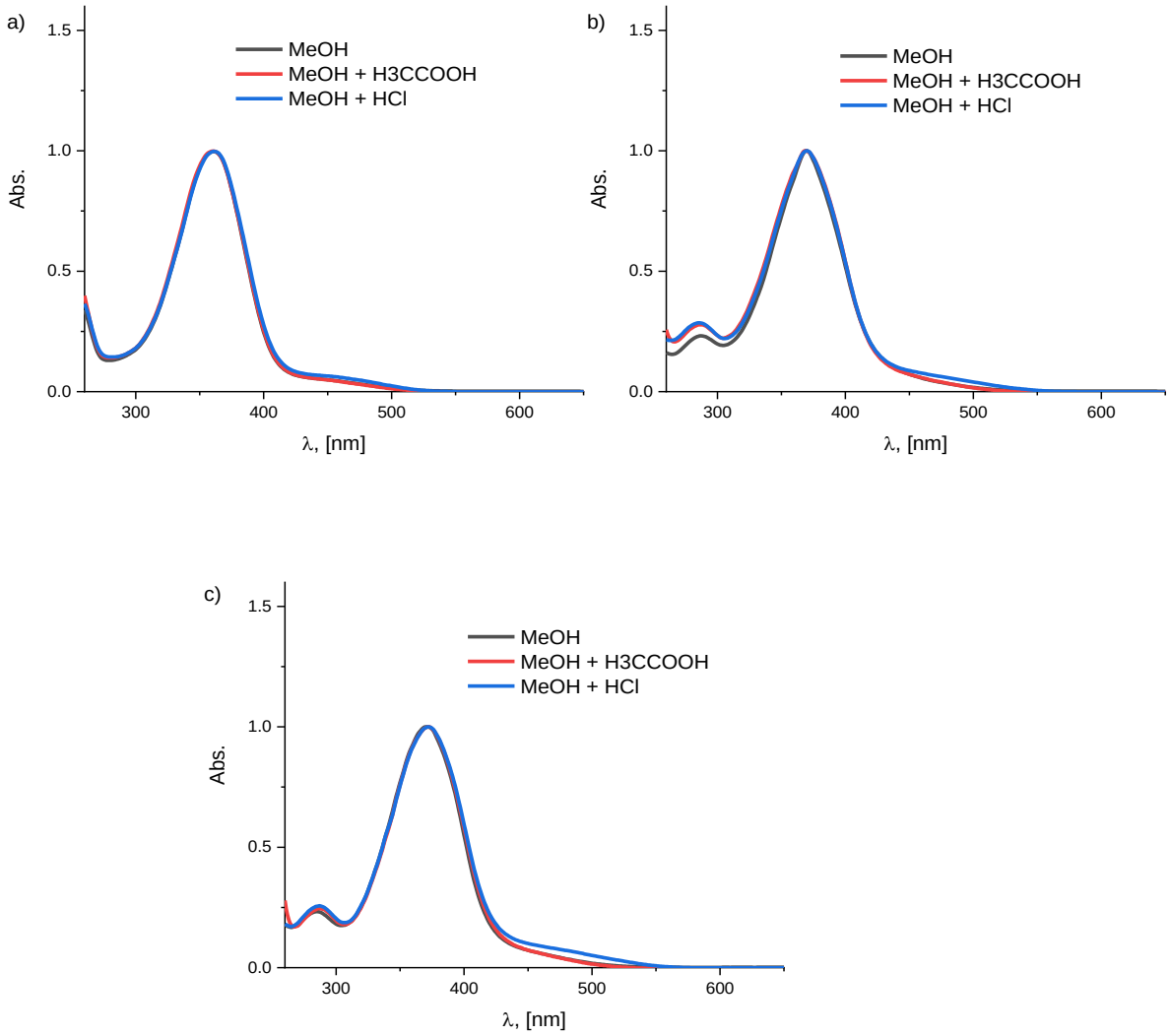


Figure S12. *The normalized experimental UV-Vis absorption spectra in methanol upon addition of the HCl and the acetic acid of a)* ***B1****, b)* ***B2a*** *and c)* ***B2***

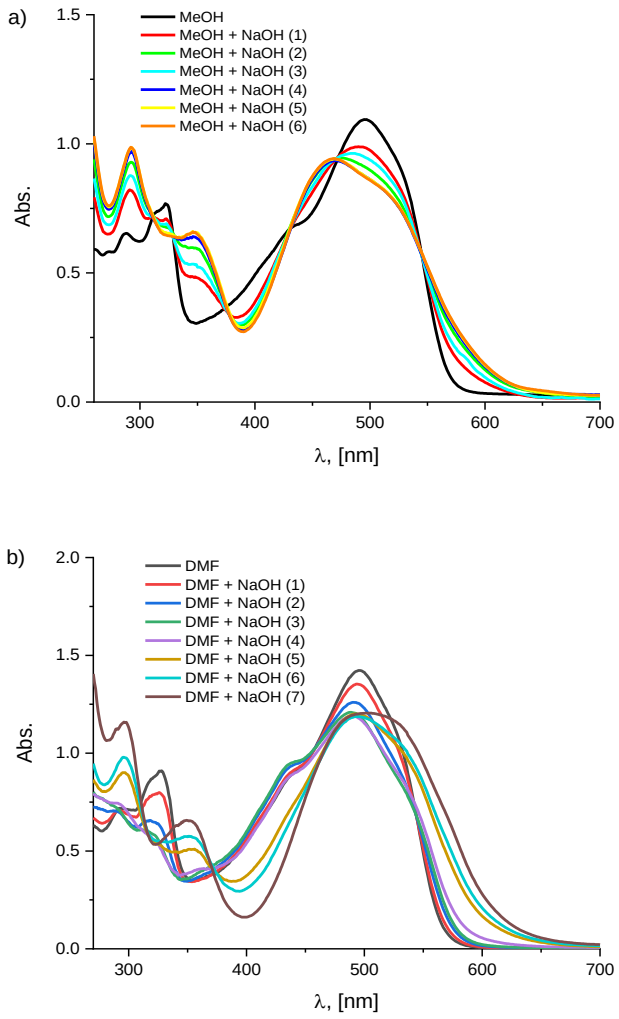


Figure S13. *The experimental UV-Vis spectra of* ***A2*** *after the gradual addition of NaOH in: a) methanol and b) DMF*

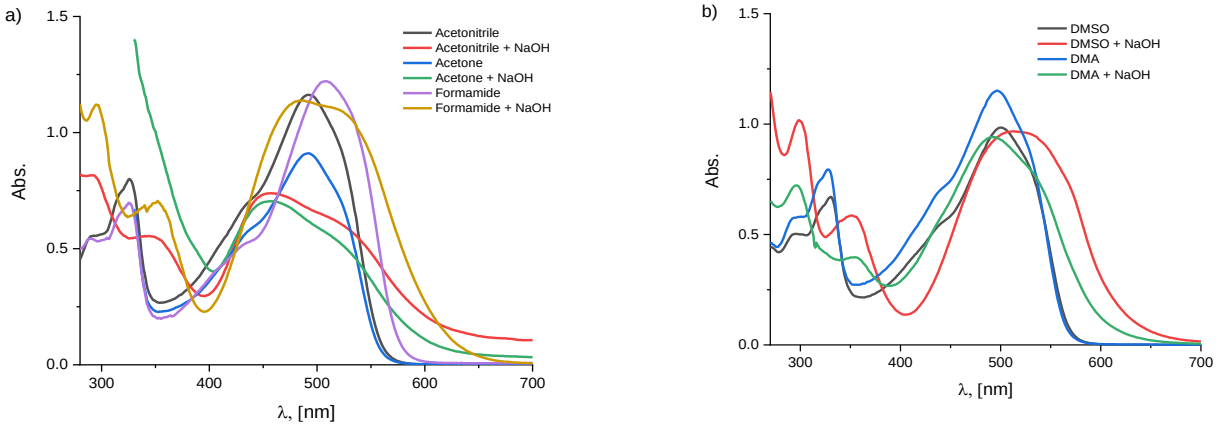


Figure S14. *The experimental UV-Vis spectra displaying the influence of the alkaline medium (NaOH) on the compound* ***A2*** *in the selected solvents*

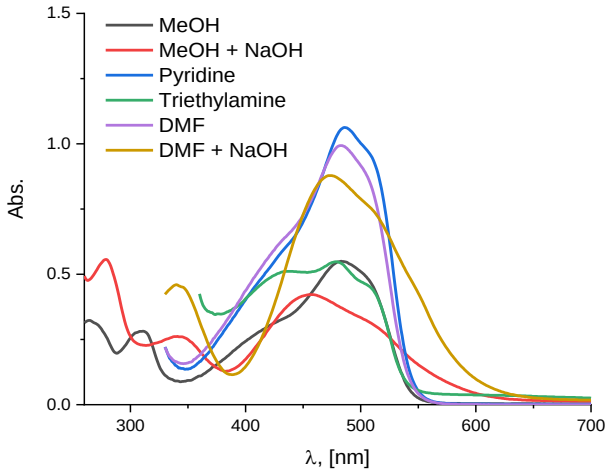


Figure S15. *The experimental UV-Vis spectra of* ***A1*** *in different alkaline media*

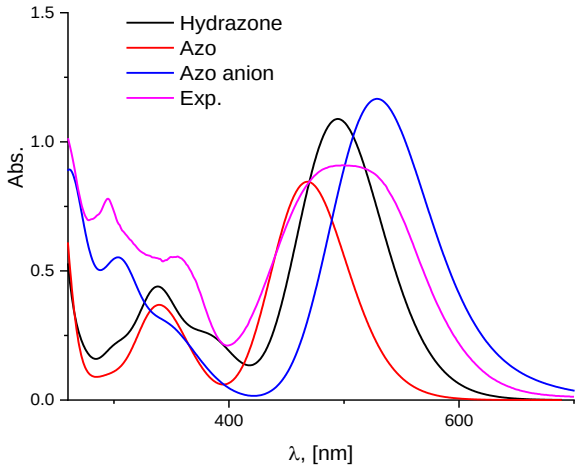


Figure S16. *The comparison of experimentally obtained UV-Vis spectrums in ethanol upon the addition of NaOH and theoretically obtained ones by the DFT method of* ***A2a***

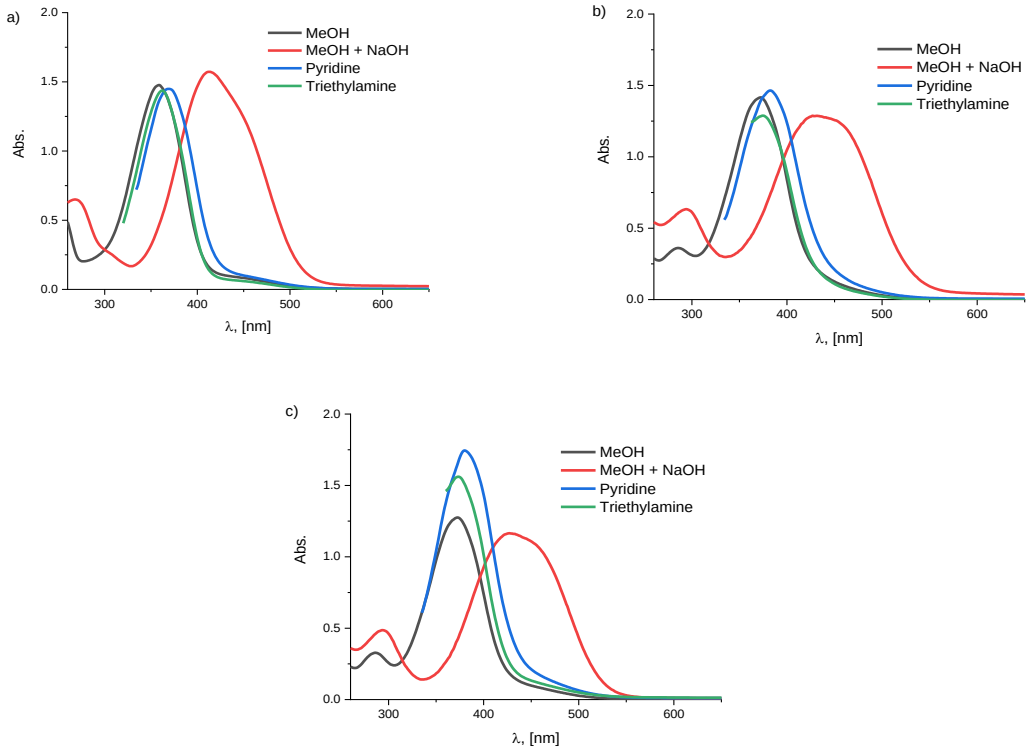


Figure S17. *A comparison of the experimental UV-Vis absorption spectra of the a)* ***B1****, b)* ***B2a****, and c)* ***B2*** *in three different alkaline media*

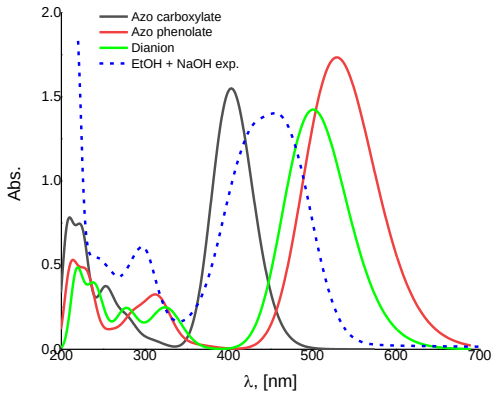


Figure S18. *The comparison of experimentally obtained UV-Vis spectrums in ethanol upon the addition of NaOH and theoretically obtained ones by the DFT method of* ***B2***