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Supporting Information

Solvatochromism and linear solvation energy relationship of diol- and proline-functionalized azo dyes using the KAMLET–TAFT and CATALÁN solvent parameter sets

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Solvent Parameter Sets:

Table S1. KAMLET–TAFT [S1] and CATALÁN [S2,3] parameter set.

solvent	KAMLET–TAFT parameter			CATALÁN parameter[a,b]			
	α	β	π^*	*SA*	*SB*	*SPP*	*SP*
cyclohexane	0.00	0.00	0.00	0.000	0.073	0.557	0.6830
n-hexane	0.00	0.00	–0.04	0.000	0.056	0.519	0.6164
triethylamine	0.00	0.71	0.14	0.000	0.885	0.617	0.6603
tetrachloromethane	0.00	0.10	0.28	0.000	0.044	0.632	0.7677
toluene	0.00	0.11	0.54	0.000	0.128	0.655	0.7816
benzene	0.00	0.10	0.59	0.000	0.124	0.667	0.7929
diethyl ether	0.00	0.47	0.27	0.000	0.562	0.694	0.6167
1,4-dioxane	0.00	0.37	0.55	0.000	0.444	0.701	0.7374
anisole	0.00	0.32	0.73	0.084	0.299	0.823	0.8204
tetrahydrofurane	0.00	0.55	0.58	0.000	0.591	0.838	0.7139
ethyl acetate	0.00	0.45	0.55	0.000	0.542	0.795	0.6558
chloroform	0.20	0.10	0.53	0.047	0.071	0.786	0.7833
pyridine	0.00	0.64	0.87	0.033	0.581	0.922	0.8416
dichloromethane	0.13	0.10	0.82	0.040	0.178	0.876	0.7612
1,2-dichloroethane	0.00	0.10	0.81	0.030	0.126	0.890	0.7711
benzonitrile	0.00	0.37	0.90	0.047	0.281	0.960	0.8507
acetone	0.08	0.43	0.71	0.000	0.475	0.881	0.6510
N,*N*-dimethylacetamide	0.00	0.76	0.88	0.028	0.650	0.930	0.7632
N,*N*-dimethylformamide	0.00	0.69	0.88	0.031	0.613	0.939	0.7589
dimethyl sulfoxide	0.00	0.76	1.00	0.072	0.647	1.000	0.8295
acetonitrile	0.19	0.40	0.75	0.044	0.286	0.895	0.6448
nitromethane	0.22	0.06	0.85	0.078	0.236	0.907	0.7096
1-decanol	0.70	0.82	0.45	0.259	0.912	0.765	0.7221
1-butanol	0.84	0.84	0.47	0.341	0.809	0.837	0.6742
2-propanol	0.76	0.84	0.48	0.283	0.830	0.848	0.6334
1-propanol	0.84	0.90	0.52	0.367	0.782	0.847	0.6581
ethanol	0.86	0.75	0.54	0.400	0.658	0.853	0.6334
methanol	0.98	0.66	0.60	0.605	0.545	0.857	0.6079
2,2,2-trifluoroethanol	1.51	0.00	0.73	0.893	0.107	0.908	0.5431

[a] *SA*, *SB*, and *SPP* values for all solvents were taken from ref. 10b.
[b] *SP* values for all solvents were taken from ref. 10c.

Results of the multiple linear regression analyses:

Table S2. Solvent-independent correlation coefficients a, b and s of the Kamlet–Taft parameters α, β and π^*, respectively, solute property of the reference system $\tilde{\nu}_{max,0}$, correlation coefficient (r), significance (f), standard deviation (sd), and number of solvents (n) calculated for the solvatochromism of compounds **2a** and **2c**.

compound	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*F*	*R*	*SD*
2a	23.254 (±0.178)	0.602 (±0.078)	–0.695 (±0.142)	0.248 (±0.215)	26	<0.0001	0.892	0.211
2a	23.091 (±0.071)	0.607 (±0.113)	-	-	26	<0.0001	0.731	0.305
2a	23.665 (±0.136)	-	–0.784 (±0.248)	-	26	0.004	0.535	0.378
2a	23.153 (±0.293)	-	-	0.231 (±0.277)	26	0.599	0.406	0.444
2a	23.438 (±0.082)	0.586 (±0.079)	–0.732 (±0.139)	-	26	<0.0001	0.885	0.212
2a	22.765 (±0.206)	0.634 (±0.111)	-	0.489 (±0.292)	26	<0.0001	0.763	0.294
2a	23.684 (±0.309)	-	–0.788 (±0.259)	–0.026 (±0.386)	26	0.017	0.445	0.385
2c	22.678 (±0.140)	0.555 (±0.091)	–0.375 (±0.131)	–0.523 (±0.178)	27	<0.0001	0.832	0.189
2c	22.182 (±0.054)	0.533 (±0.109)	-	-	27	<0.0001	0.699	0.234
2c	22.388 (±0.118)	-	–0.135 (±0.217)	-	27	0.540	0.123	0.325
2c	22.715 (±0.184)	-	-	–0.615 (±0.277)	27	0.035	0.406	0.299
2c	22.320 (±0.080)	0.588 (±0.104)	–0.334 (±0.149)	-	27	<0.0001	0.760	0.217
2c	22.487 (±0.141)	0.498 (±0.102)	-	–0.468 (±0.202)	27	<0.0001	0.763	0.216
2c	22.831 (±0.218)	-	–0.200 (±0.201)	–0.653 (±0.279)	27	0.071	0.445	0.300

Table S3. Solvent-independent correlation coefficients *a*, *b* and *s* of the CATALÁN parameters *SA*, *SB* and *SPP*, respectively, solute property of the reference system $\tilde{\nu}_{max,0}$, correlation coefficient (*r*), significance (*f*), standard deviation (*sd*), and number of solvents (*n*) calculated for the solvatochromism of compounds **2a** and **2c**.

compound	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*F*	*R*	*SD*
2a	23.194 (±0.406)	1.116 (±0.217)	–0.708 (±0.177)	0.283 (±0.476)	26	<0.0001	0.809	0.233
2a	23.109 (±0.070)	1.029 (±0.270)	-	-	26	5.773E–4	0.614	0.300
2a	23.537 (±0.134)	-	–0.626 (±0.257)	-	26	0.023	0.445	0.340
2a	22.570 (±0.622)	-	-	0.821 (±0.740)	26	0.299	0.278	0.370
2a	23.429 (±0.092)	1.143 (±0.210)	–0.712 (±0.174)	-	26	<0.0001	0.806	0.230
2a	22.800 (±0.514)	0.996 (±0.280)	-	0.376 (±0.612)	26	0.004	0.622	0.303
2a	22.879 (±0.581)	-	-0.620 (±0.256)	0.7839 (±0.677)	26	0.041	0.492	0.337
2c	23.132 (±0.337)	1.128 (±0.200)	–0.097 (±0.158)	–1.104 (±0.407)	27	<0.0001	0.773	0.217
2c	22.191 (±0.055)	0.991 (±0.216)	-	-	27	1.082E–4	0.676	0.241
2c	22.333 (±0.125)	-	–0.015 (±0.235)	-	27	0.949	0.013	0.328
2c	22.840 (±0.489)	-	-	–0.620 (±0.585)	27	0.299	0.207	0.321
2c	22.247 (±0.095)	1.013 (±0.220)	–0.129 (±0.177)	-	27	5.038E-4	0.685	0.244
2c	23.105 (±0.329)	1.113 (±0.196)	-	–1.123 (±0.400)	27	<0.0001	0.769	0.214
2c	22.837 (±0.502)	-	0.010 (±0.236)	–0.623 (±0.600)	27	0.590	0.208	0.327

Table S4. Solvent-independent correlation coefficients *a*, *b* and *s* of the CATALÁN parameters *SA*, *SB* and *SP*, respectively, solute property of the reference system $\tilde{\nu}_{max,0}$, correlation coefficient (*r*), significance (*f*), standard deviation (*sd*), and number of solvents (*n*) calculated for the solvatochromism of compounds **2a** and **2c**.

compound	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*F*	*R*	*SD*
2a	25.254 (±0.397)	0.637 (±0.187)	–0.835 (±0.129)	–2.382 (±0.510)	26	<0.0001	0.908	0.167
2a	25.254 (±0.525)	-	-	–2.792 (±0.729)	26	8.122E–4	0.616	0.299
2a	24.413 (±0.652)	0.637 (±0.321)	-	–1.743 (±0.868)	26	6.755E–4	0.686	0.282

2a	26.068 (±0.384)	-	–0.855 (±0.156)	–3.391 (±0.503)	26	<0.0001	0.855	0.201
2c	25.036 (±0.200)	0.235 (±0.091)	–0.352 (±0.060)	–3.594 (±0.254)	27	<0.0001	0.972	0.080
2c	24.939 (±0.226)	-	-	–3.640 (±0.313)	27	<0.0001	0.919	0.130
2c	24.590 (±0.285)	0.263 (±0.140)	-	–3.203 (±0.379)	27	<0.0001	0.929	0.124
2c	25.357 (±0.174)	-	–0.360 (±0.067)	–3.992 (±0.225)	27	<0.0001	0.964	0.089

Single crystal X-ray structure analysis:

Crystal data was collected on a Oxford Gemini Diffractometer at low temperature (100 K) using Cu-K_α-radiation (λ = 1.54 Å). The structure was solved by direct methods using SHELXS-97[S4]. The structure was refined by full-matrix least squares procedures on F^2, using SHELXL-97[S5]. All non hydrogen atoms were refined anisotropically. All hydrogen atoms were added on calculated positions, except of OH and NH which were found in difference fourier synthesis.

Table S5: Crystallographic data and collection parameters for **2a**

empirical formula	$C_{18}H_{20}N_6O_9$
formula weight	464.40
color	orange
wavelength (Å)	1.54184
temperature (K)	100 (0)
crystal system	triclinic
space group	*P1*
a [Å]	6.7800 (10)
b [Å]	8.0970 (15)
c [Å]	19.7070 (16)
α [°]	95.732 (8)
β [°]	96.607 (9)
γ [°]	92.11 (6)
volume (Å^3)	1068.0 (2)
Z	2
calcd density (g*cm^{-3})	1.444
absorption coeffizient (mm^{-1})	1.012
F(000)	484
crystal size (mm^3)	0.2 x 0.2 x 0.01
Θ range for data collection(°)	4.54–60.46
index ranges	$-7\leq h\leq 7$, $-8\leq k\leq 8$, $-22\leq l\leq 22$
reflections collected	7626
independent reflections	3106

R_{int}	0.0194
data/restraints/parameter	3106/0/310
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	0.941
final *R* indicates [$I>2\sigma(I)$]	R1 = 0.0343, *w*R2 = 0.0852
R indicates all data	R1 = 0.0487, *w*R2 = 0.0917
largest diff. peak and hole (e^* Å^3	0.192, -0.193

Table S6. Bond lengths [A] and angles [deg] for **2a**

N(3)-N(4)	1.2631(19)
N(3)-C(4)	1.424(2)
O(1)-N(1)	1.2280(19)
O(2)-N(1)	1.2288(19)
N(1)-C(1)	1.468(2)
N(6)-O(8)	1.227(2)
N(6)-O(7)	1.2382(19)
N(6)-C(11)	1.449(2)
O(3)-N(2)	1.2248(18)
N(4)-C(7)	1.404(2)
C(11)-C(12)	1.386(2)
C(11)-C(10)	1.427(2)
C(7)-C(12)	1.379(2)
C(7)-C(8)	1.409(2)
O(4)-N(2)	1.2300(18)
N(5)-C(10)	1.340(2)
N(5)-C(14)	1.456(2)
C(1)-C(2)	1.386(2)
C(1)-C(6)	1.389(2)
C(4)-C(5)	1.394(2)
C(4)-C(3)	1.404(2)
C(3)-C(2)	1.379(2)
C(3)-N(2)	1.470(2)
C(5)-C(6)	1.378(2)
O(6)-C(15)	.422(3)
(5)-C(13)	1.425(2)
C(8)-C(9)	1.362(2)
C(9)-C(10)	1.432(2)
C(14)-C(13)	1.522(3)
C(14)-C(15)	1.522(3)
O(9)-C(17)	1.217(3)
C(17)-C(16)	1.487(3)
C(17)-C(18)	1.498(4)

N(4)-N(3)-C(4)	112.04(13)
O(1)-N(1)-O(2)	123.58(14)
O(1)-N(1)-C(1)	118.17(14)
O(2)-N(1)-C(1)	118.25(14)
O(8)-N(6)-O(7)	121.43(15)
O(8)-N(6)-C(11)	118.66(14)
O(7)-N(6)-C(11)	119.91(14)
N(3)-N(4)-C(7)	114.61(14)
C(12)-C(11)-C(10)	121.51(16)
C(12)-C(11)-N(6)	116.48(15)
C(10)-C(11)-N(6)	122.01(14)

C(12)-C(7)-N(4)	115.49(15)
C(12)-C(7)-C(8)	119.18(15)
N(4)-C(7)-C(8)	125.31(15)
C(10)-N(5)-C(14)	126.53(16)
C(2)-C(1)-C(6)	122.14(15)
C(2)-C(1)-N(1)	118.46(15)
C(6)-C(1)-N(1)	119.39(15)
C(5)-C(4)-C(3)	117.69(15)
C(5)-C(4)-N(3)	124.35(15)
C(3)-C(4)-N(3)	117.89(15)
C(2)-C(3)-C(4)	122.68(15)
C(2)-C(3)-N(2)	116.55(15)
C(4)-C(3)-N(2)	120.73(14)
C(6)-C(5)-C(4)	121.03(16)
O(3)-N(2)-O(4)	124.34(15)
O(3)-N(2)-C(3)	119.29(14)
O(4)-N(2)-C(3)	116.33(14)
C(7)-C(12)-C(11)	120.84(16)
C(9)-C(8)-C(7)	120.66(16)
C(5)-C(6)-C(1)	119.16(16)
C(3)-C(2)-C(1)	117.29(16)
C(8)-C(9)-C(10)	122.02(16)
N(5)-C(10)-C(11)	123.36(16)
N(5)-C(10)-C(9)	120.88(16)
C(11)-C(10)-C(9)	115.75(15)
N(5)-C(14)-C(13)	109.36(16)
N(5)-C(14)-C(15)	107.01(15)
C(13)-C(14)-C(15)	113.48(16)
O(6)-C(15)-C(14)	111.51(17)
O(5)-C(13)-C(14)	111.53(18)
O(9)-C(17)-C(16)	120.7(2)
O(9)-C(17)-C(18)	122.7(2)
C(16)-C(17)-C(18)	116.6(2)

Table S7. torsion angles [deg] for **2a**

C(4)-N(3)-N(4)-C(7)	178.51(12)
O(8)-N(6)-C(11)-C(12)	0.1(2)
O(7)-N(6)-C(11)-C(12)	179.45(15)
O(8)-N(6)-C(11)-C(10)	179.80(16)
O(7)-N(6)-C(11)-C(10)	−0.8(2)
N(3)-N(4)-C(7)-C(12)	175.10(13)
N(3)-N(4)-C(7)-C(8)	−6.1(2)
O(1)-N(1)-C(1)-C(2)	1.8(2)
O(2)-N(1)-C(1)-C(2)	−177.71(14)
O(1)-N(1)-C(1)-C(6)	−179.52(14)
O(2)-N(1)-C(1)-C(6)	1.0(2)
N(4)-N(3)-C(4)-C(5)	6.3(2)
N(4)-N(3)-C(4)-C(3)	−176.73(13)
C(5)-C(4)-C(3)-C(2)	0.1(2)
N(3)-C(4)-C(3)-C(2)	−177.08(14)
C(5)-C(4)-C(3)-N(2)	177.75(14)
N(3)-C(4)-C(3)-N(2)	0.6(2)
C(3)-C(4)-C(5)-C(6)	0.5(2)
N(3)-C(4)-C(5)-C(6)	177.42(14)
C(2)-C(3)-N(2)-O(3)	−136.36(15)
C(4)-C(3)-N(2)-O(3)	45.8(2)

C(2)-C(3)-N(2)-O(4)	41.73(19)
C(4)-C(3)-N(2)-O(4)	−136.09(15)
N(4)-C(7)-C(12)-C(11)	179.51(14)
C(8)-C(7)-C(12)-C(11)	0.7(2)
C(10)-C(11)-C(12)-C(7)	−1.6(2)
N(6)-C(11)-C(12)-C(7)	178.10(14)
C(12)-C(7)-C(8)-C(9)	1.0(2)
N(4)-C(7)-C(8)-C(9)	−177.74(15)
C(4)-C(5)-C(6)-C(1)	−0.3(2)
C(2)-C(1)-C(6)-C(5)	−0.3(2)
N(1)-C(1)-C(6)-C(5)	−179.02(14)
C(4)-C(3)-C(2)-C(1)	−0.7(2)
N(2)-C(3)-C(2)-C(1)	−178.49(14)
C(6)-C(1)-C(2)-C(3)	0.9(2)
N(1)-C(1)-C(2)-C(3)	179.54(14)
C(7)-C(8)-C(9)-C(10)	−1.7(3)
C(14)-N(5)-C(10)-C(11)	173.76(17)
C(14)-N(5)-C(10)-C(9)	−7.7(3)
C(12)-C(11)-C(10)-N(5)	179.58(15)
N(6)-C(11)-C(10)-N(5)	−0.1(3)
C(12)-C(11)-C(10)-C(9)	0.9(2)
N(6)-C(11)-C(10)-C(9)	−178.79(14)
C(8)-C(9)-C(10)-N(5)	−177.96(16)
C(8)-C(9)-C(10)-C(11)	0.7(2)
C(10)-N(5)-C(14)-C(13)	−81.7(2)
C(10)-N(5)-C(14)-C(15)	155.05(18)
N(5)-C(14)-C(15)-O(6)	50.0(2)
C(13)-C(14)-C(15)-O(6)	−70.7(2)
N(5)-C(14)-C(13)-O(5)	175.74(15)
C(15)-C(14)-C(13)-O(5)	−64.9(2)

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