Solvation properties of protic ionic liquids and molecular solvents

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Supporting Information

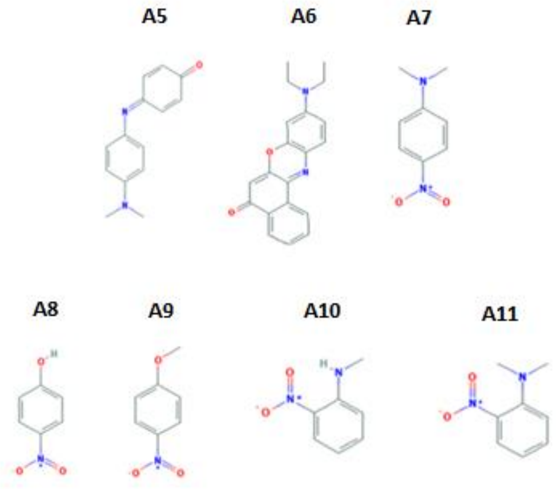

Figure S1. Chemical structures of the other dye molecules used in this study. **A5.** Phenol blue (PB), **A6.** Nile red (NR), **A7.** N,N-dimethyl-4-Nitroaniline (DM4A), **A8.** 4-nitrophenol (4NP), **A9.** 4-nitroanisole (4NAni), **A10.** N-methyl-2-Nitroaniline (M2A) and **A11.** N,N-dimethyl-2-Nitroaniline (DM2A)

Table S1. Solvatochromic and solvatofluorochromic dye molecules used in this study

No	Probe molecule	Abb.	Molecular weight (g/mol)	H Bond Donor Count	H Bond Acceptor Count	type of solvatochromic shift	Final concentration in transferring solvent (mM)
A1	N,N-diethyl-4-Nitroaniline	DE4A	194.23	0	3	positive (bathochromic)	0.014
A2	4-nitroaniline	4NA	138.12	1	3	positive (bathochromic)	0.020
A3	Reichardt`s Dye (Dimroth's Betaine)	RD30	551.68	0	1	negative (hypsochromic)	0.540
A4	Reichardt`s Dye 33	RD33	468.37	0	1	negative (hypsochromic)	0.630
A5	Phenol Blue	PB	226.27	0	3	positive (bathochromic)	0.033
A6/F3	Nile Red	NR	318.37	0	4	Positive (bathochromic) and solvatofluorochromic	0.010
A7	N,N-dimethyl-4-Nitroaniline	DM4A	166.18	0	3	Positive (bathochromic)	0.093
A8	4-nitrophenol	4NP	139.11	1	3	positive (bathochromic)	0.037
A9	4-nitroanisole	4NAni	153.14	0	3	positive (bathochromic)	0.039
A10	N-methyl-2-Nitroaniline	M2A	152.15	1	3	positive (bathochromic)	0.088
A11	N,N-dimethyl-2-Nitroaniline	DM2A	166.18	0	3	positively (bathochromic)	0.233
F1	Pyrene	Pyr	202.25	0	0	positive solvatofluorochromic	0.037
F2	Coumarin 153	C153	309.28	0	6	positive solvatofluorochromic	0.004

Table S2. The wavelengths of absorbance maxima for dyes in various molecular solvents (Uncertainty in λ_{max} ± 1.0 nm)

	4NAni	**4NA**	**4NP**	**M2A**	**NR**	**PB**	**DE4A**	**DM4A**	**DM2A**	**RD33**	**RD30**
cyclohexane	297	325	297	409	491	554	367	358	397	LS[a]	924
HMPA	316	393	329	433	551	580	404	397	434	471	BD[b]
DMSO	317	390	319	439	552	604	413	407	434	528	632
acetonitrile	310	367	310	429	536	582	402	394	421	501	604
cyclohexanol	LS[a]	378	315	424	551	612	393	389	416	510	595
2-propanol	306	376	316	422	544	604	392	388	414	498	589
ethanol	304	372	315	424	550	606	393	389	415	468	550
methanol	304	370	314	426	554	607	397	391	417	441	515
water	318	381	398	446	561	658	430	421	439	408	LS

[a, b] The abbreviations LS and BD refer to limited solubility, and band disappearance of dyes in specific solvents. 4NAni has limited solubility in cyclohexanol. RD30 (pK_a=8.6) is scarcely soluble in water and sensitive to acidic medium[1]. The phenolate oxygen of RD30 is protonated in acidic medium causing the intermolecular charge transfer band to disappear. Therefore, its dichloro- substituted derivative, RD33 with a lower pK_a (4.78) is usually used in water and more acidic medium[2]. Both Reichardt's dyes had limited solubility in pentylamine. NR with pK_a value of 1.00[3], is also known to be a suitable probe for the overall polarity measurement of acidic environments and protic molecular solvents[4].

Table S3. Electronic transition energies (E_T, kcal/mol) of the molecular solvents obtained based on RD30, RD33, NR and PB (Uncertainty of ±0.02 kcal/mol).

	Relative polarity[a], E_T^N	**E_T (33) (kcal/mol)**	**E_T (30) (kcal/mol)**	**E_T (30)$_{calc}$ (kcal/mol)**	**E_T (NR) (kcal/mol)**	**E_T (PB) (kcal/mol)**
cyclohexane	(0.006[5])	nd[b]	30.94; (30.9[5])	nd	58.23; (58.63[3])	51.61; (51.81[6])
HMPA	(0.315[5])	60.70	(40.9[5])	51.58	51.89	49.30
DMSO	(0.444[5])	54.15	45.24; (45.1[5])	45.40	51.79; (52.06[3])	47.34; (47.19[6])
acetonitrile	(0.460[5])	57.07	47.34; (45.6[5])	48.15	53.34; (53.78[3])	49.13; (48.97[6])
cyclohexanol	(0.509[5])	56.06	48.05; (47.2[5])	47.20	51.89	46.72
2-propanol	(0.546[5])	57.41	48.54; (48.4[5])	48.48	52.56; (53.02[3])	47.34; (47.91[6])
ethanol	(0.654[5])	61.09	51.98; (51.9[5])	51.95	51.98; (52.15[3])	47.18; (47.18[6])
methanol	(0.762[5])	64.83	55.52; (55.4[5])	55.48	51.61; (52.02[3])	47.10; (47.03[6])
water	(1.00[5])	70.08	(63.1[5])	60.43	50.97; (48.21[3])	43.45

[a]The dimensionless relative/normalized polarity (E_T^N) values were extracted from the literature, where normalization is done based on the E_T (30) values for water (E_T^N=1.00) and tetramethylsilane (E_T^N=0.00) as extreme polar and nonpolar reference solvents. [b]Not determined due to no dye response in Table S2. Numbers in parenthesis were extracted from literature.

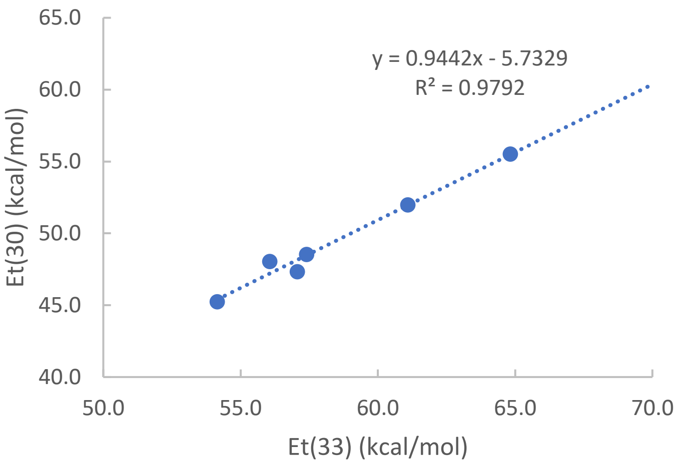

Figure S2. Electronic transition energy correlation based on the responses of RD30 and RD33

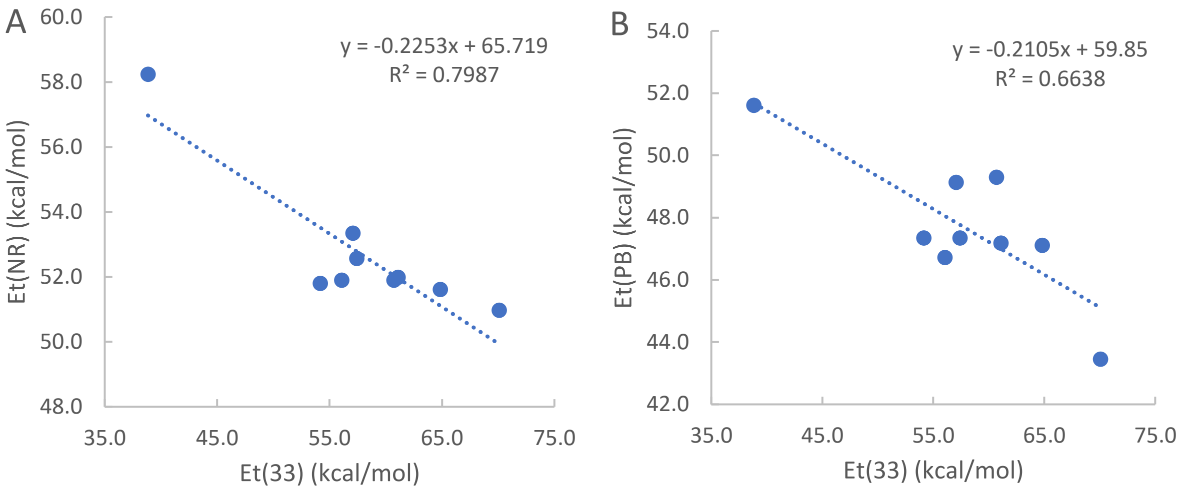

Figure S3. Electronic transition energies based on positively solvatochromic dyes A. NR and B. PB with respect to those of RD33. Dashed lines are a guide to the eye.

Table S4. The spectral correlation coefficients for non-H bonding dyes[7]

	v0, kK	-s
4Nani	34.17	2.410
DE4A	27.52	3.182
DM4A	28.10	3.436
DM2A	25.30	2.023

Table S5. Solvent dipolarity/polarizability, π^* values of molecular solvents based on 4 different solvatochromic dyes (all values have an uncertainty of ±0.02).

	4NAani[a]	**DE4A**	**DM4A**	**DM2A**	**π^* (ave)[b]**	**π^* (ave)**
cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00
HMPA	0.95	0.82	0.82	1.00	0.87	n/a[c]
DMSO	1.00	1.00	1.00	1.00	1.00	1.00
acetonitrile	0.66	0.78	0.76	0.67	0.71	0.75[d,e]
cyclohexanol	LS	0.59	0.66	0.54	n/a	n/a
2-propanol	0.47	0.57	0.64	0.48	0.51	0.50[e]
ethanol	0.36	0.59	0.66	0.51	0.54	0.51[d]
methanol	0.36	0.68	0.70	0.56	0.59	0.73[d]; 0.61[e]
water	1.05	1.32	1.24	1.12	1.09	1.33[d]; 1.17[e]

[a] 4-nitroanisole limited solubility (LS) in cyclohexanol. [b] π^*_{ave} represents the average π^* values obtained by several dyes and were taken from the original Kamlet-Taft's paper[7]. [c] n/a: not available. [d] from Ref. 2[8]. [e] from Ref. 3 where the average values were calculated using the results of 5 dyes 4-nitroanisole, N,N-diethyl-3-nitroaniline, 4-ethylnitrobenzene, N-methyl-2-nitroaniline, and 2-nitroanisole[9].

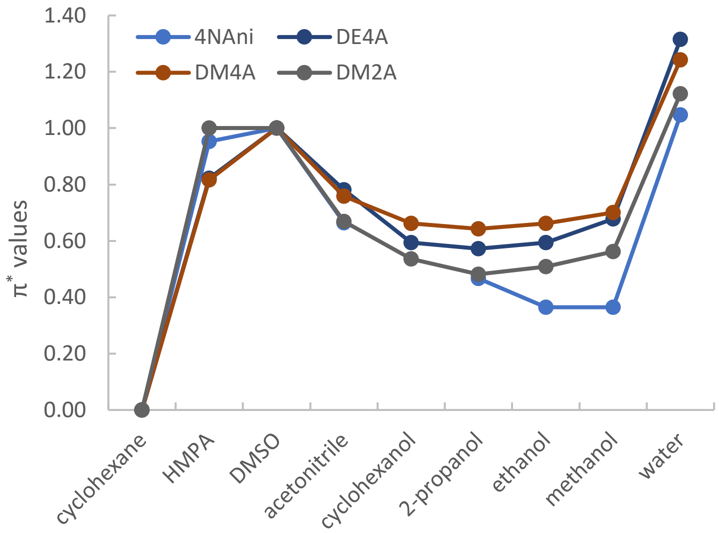

Figure S4. π^* values of molecular solvents based on 4 different solvatochromic dyes

Table S6. HBD acidity and HBA basicity of molecular solvents (±0.04)

	HBD acidity, α (in this study)	**α (literature)**	**HBA basicity, β (in this study)**	**β (literature)**
cyclohexane	0.02	0.0[10]	0.03	0.0[10]
HMPA	0.69	-	1.00	1.00[10]
DMSO	0.17	0.0[11]	0.74	0.76[11]
acetonitrile	0.50	0.29[10]; 0.19[11]	0.41	0.40[11]
cyclohexanol	0.56	-	0.90	-
2-propanol	0.66	0.76[8]	0.87	0.84-0.93[8]
ethanol	0.87	0.83-0.98[8]	0.75	0.75-0.83[8]
methanol	1.04	1.05[11]; 0.93-1.14[8]	0.60	0.61[11]; 0.66-0.74[8]
water	0.93	1.12[11]; 1.17-1.23[8]	0.17	0.50[11]; 0.14-0.47[8]

Table S7. The initial water content of PILs and the wavelengths of absorbance maxima for dyes in PILs

	Water content, (wt %) (±0.05)	**4NA, (λ_{max} ± 1.0 nm)**	**DE4A, (λ_{max} ± 1.0 nm)**	**RD33, (λ_{max} ± 1.0 nm)**	**RD30, (λ_{max} ± 1.0 nm)**
EAF	0.05	385	408	423	nd
EtAF	0.72	389	416	422	478
DEAF	0.10	391	406	418	nd
DEtAF	1.15	387	416	418	nd
BAF	0.34	384	398	438	493
PeAF	0.33	382	396	440	502
PAA	0.75	385	397	440	502
PeAA	0.46	385	393	449	513
EAN	0.29	386	417	408	463
EtAN	0.12	386	422	401	461
PAN	0.49	384	415	411	466
BAN	0.06	381	410	418	474

nd: not detected

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