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

Solvation properties of protic ionic liquid - molecular solvent mixtures

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Electronic Supplementary Information

- **Spectral data used for KAT solvatochromic comparison method**

Table S1. Wavelengths of absorbance maxima of solvatochromic dyes in binary mixtures of water

Mole fractions		λ_{max} (nm) (±0.5)			
		4NA	DE4A	RD33	RD30
water	**methanol**				
1.0	0	381	430	408	
0.75	0.25	384	423	417	481
0.50	0.50	381	416	430	502
0.25	0.75	375	409	438	511
0.10	0.90	372	402	440	514
0	1.0	370	397	441	515
water	**acetonitrile**				
1.0	0	381	430	408	
0.75	0.25	375	416	432	502
0.50	0.50	372	412	444	514
0.25	0.75	369	407	460	532
0.10	0.90	367	403	466	554
0	1.0	367	402	501	604
water	**DMSO**				
1.0	0	381	430	408	
0.75	0.25	390	422	447	526
0.50	0.50	390	417	477	573
0.25	0.75	390	415	501	604
0.10	0.90	390	414	514	622
0	1.0	390	413	528	632

*Dye concentrations in stock solutions were 0.020 mM, 0.014 mM, 0.630 mM and 0.540 mM for 4NA, DE4A, RD33 and RD30, respectively.

Table S2. Wavelengths of absorbance maxima of solvatochromic dyes in binary mixtures of EAN

Mole fractions		λ_{max} (nm) (±0.5)			
		4NA	DE4A	RD33	RD30
EAN	**water**				
1.0	0	386	417	408	463
0.75	0.25	386	419	407	463
0.50	0.50	386	421	406	462
0.25	0.75	387	427	403	460
0.10	0.90	385	432	401	
0	1.0	381	430	408	
EAN	**methanol**				
1.0	0	386	417	408	463
0.75	0.25	384	416	410	464
0.50	0.50	382	414	412	464
0.25	0.75	378	411	414	466
0.10	0.90	375	406	417	466
0	1.0	370	397	441	515
EAN	**acetonitrile**				
1.0	0	386	417	408	463
0.75	0.25	383	416	410	463
0.50	0.50	380	414	413	463
0.25	0.75	373	409	415	464
0.10	0.90	369	404	418	470
0	1.0	367	402	501	604
EAN	**DMSO**				
1.0	0	386	417	408	463
0.75	0.25	385	415	413	463
0.50	0.50	386	415	417	466
0.25	0.75	389	415	437	487
0.10	0.90	390	414	454	520
0	1.0	390	413	528	632

Table S3. Wavelengths of absorbance maxima of solvatochromic dyes in binary mixtures of PAN

Mole fractions		λ_{max} (nm) (±0.5)			
		4NA	DE4A	RD33	RD30
PAN	**water**				
1.0	0	384	415	411	466
0.75	0.25	385	415	414	467
0.50	0.50	386	418	413	467
0.25	0.75	388	423	412	466
0.10	0.90	388	431	407	598
0	1.0	381	430	408	
PAN	**methanol**				
1.0	0	384	415	411	466
0.75	0.25	382	412	415	467
0.50	0.50	381	412	415	467
0.25	0.75	378	411	416	467
0.10	0.90	374	404	419	469
0	1.0	370	397	441	515
PAN	**acetonitrile**				
1.0	0	384	415	411	466
0.75	0.25	383	414	415	467
0.50	0.50	380	413	415	467
0.25	0.75	372	408	417	467
0.10	0.90	370	403	420	463
0	1.0	367	402	501	604
PAN	**DMSO**				
1.0	0	384	415	411	466
0.75	0.25	384	414	415	466
0.50	0.50	386	414	419	469
0.25	0.75	389	413	439	490
0.10	0.90	390	413	456	526
0	1.0	390	413	528	632

Table S4. Solvation parameters for binary mixtures of water with methanol, acetonitrile, and DMSO

Mole fractions		E_T (33) (kcal/mol) (±0.02)	E_T (30) (kcal/mol) (±0.02)	$E_T(30)_{calc}$ (kcal/mol) (±0.02)	π* (±0.02)[a]	α (±0.04)	β (±0.04)
water	**methanol**						
1.0	0	70.08	nd[b]	60.43	1.32	0.93	0.17
0.75	0.25	68.56	59.44	59.01	1.19	0.92	0.38
0.50	0.50	66.49	56.96	57.05	1.06	0.88	0.45
0.25	0.75	65.28	55.95	55.90	0.92	0.90	0.46
0.10	0.90	64.98	55.63	55.62	0.78	0.98	0.54
0	1.0	64.83	55.52	55.48	0.68	1.04	0.60
water	**acetonitrile**						
1.0	0	70.08	nd	60.43	1.32	0.93	0.17
0.75	0.25	66.18	56.96	56.76	1.06	0.87	0.30
0.50	0.50	64.40	55.63	55.07	0.98	0.81	0.31
0.25	0.75	62.16	53.74	52.95	0.88	0.74	0.35
0.10	0.90	61.36	51.61	52.20	0.80	0.75	0.38
0	1.0	57.07	47.34	48.15	0.78	0.50	0.41
water	**DMSO**						
1.0	0	70.08	nd	60.43	1.32	0.93	0.17
0.75	0.25	63.96	54.36	54.66	1.17	0.65	0.54
0.50	0.50	59.94	49.90	50.86	1.08	0.47	0.65
0.25	0.75	57.07	47.34	48.15	1.04	0.32	0.69
0.10	0.90	55.63	45.97	46.79	1.02	0.25	0.71
0	1.0	54.15	45.24	45.40	1.00	0.17	0.74

[a] Data was normalized with 0 (for cyclohexane) and 1.0 (for DMSO); [b] Not detected.

Table S5. Solvation parameters for binary mixtures of EAN with water, methanol, acetonitrile, and DMSO

Mole fractions		E_T (33) (kcal/mol) (±0.02)	E_T (30) (kcal/mol) (±0.02)	$E_T(30)_{calc}$ (kcal/mol) (±0.02)	π* (±0.02)[a]	α (±0.04)	β (±0.04)
EAN	**water**						
1.0	0	70.08	61.75	60.43	1.08	1.09	0.55
0.75	0.25	70.25	61.75	60.60	1.11	1.08	0.51
0.50	0.50	70.42	61.89	60.76	1.15	1.06	0.47
0.25	0.75	70.95	62.16	61.25	1.26	1.02	0.37
0.10	0.90	71.30	nd[b]	61.59	1.35	0.98	0.22
0	1.0	70.08	nd	60.43	1.32	0.93	0.17
EAN	**methanol**						
1.0	0	70.08	61.75	60.43	1.08	1.09	0.55
0.75	0.25	69.74	61.62	60.11	1.06	1.08	0.53
0.50	0.50	69.40	61.62	59.79	1.02	1.09	0.52
0.25	0.75	69.06	61.36	59.48	0.96	1.11	0.49
0.10	0.90	68.56	61.36	59.01	0.86	1.15	0.52
0	1.0	64.83	55.52	55.48	0.68	1.04	0.60
EAN	**acetonitrile**						
1.0	0	70.08	61.75	60.43	1.08	1.09	0.55
0.75	0.25	69.74	61.75	60.11	1.06	1.08	0.50
0.50	0.50	69.23	61.75	59.63	1.02	1.08	0.47
0.25	0.75	68.90	61.62	59.32	0.92	1.13	0.41
0.10	0.90	68.40	60.83	58.85	0.82	1.16	0.41
0	1.0	57.07	47.34	48.15	0.78	0.50	0.41
EAN	**DMSO**						
1.0	0	70.08	61.75	60.43	1.08	1.09	0.55
0.75	0.25	69.23	61.75	59.63	1.04	1.07	0.57
0.50	0.50	68.56	61.36	59.01	1.04	1.02	0.60
0.25	0.75	65.43	58.71	56.04	1.04	0.83	0.67
0.10	0.90	62.98	54.98	53.73	1.02	0.70	0.71
0	1.0	54.15	45.24	45.40	1.00	0.17	0.74

[a] Data was normalized with 0 (for cyclohexane) and 1.0 (for DMSO); [b]Not detected

Table S6. Solvation parameters for binary mixtures of PAN with water, methanol, acetonitrile, and DMSO

Mole fractions		E_T (33) (kcal/mol) (±0.02)	E_T (30) (kcal/mol) (±0.02)	$E_T(30)_{calc}$ (kcal/mol) (±0.02)	π* (±0.02)[a]	α (±0.04)	β (±0.04)
PAN	**water**						
1.0	0	69.57	61.36	59.95	1.04	1.09	0.55
0.75	0.25	69.06	61.22	59.48	1.04	1.06	0.57
0.50	0.50	69.23	61.22	59.63	1.10	1.03	0.53
0.25	0.75	69.40	61.36	59.79	1.19	0.97	0.48
0.10	0.90	70.25	47.81	60.60	1.33	0.93	0.31
0	1.0	70.08	nd[b]	60.43	1.32	0.93	0.17
PAN	**methanol**						
1.0	0	69.57	61.36	59.95	1.04	1.09	0.55
0.75	0.25	68.90	61.22	59.32	0.98	1.08	0.57
0.50	0.50	68.90	61.22	59.32	0.98	1.08	0.54
0.25	0.75	68.73	61.22	59.16	0.96	1.09	0.49
0.10	0.90	68.24	60.96	58.70	0.82	1.15	0.54
0	1.0	64.83	55.52	55.48	0.68	1.04	0.60
PAN	**acetonitrile**						
1.0	0	69.57	61.36	59.95	1.04	1.09	0.55
0.75	0.25	68.90	61.22	59.32	1.02	1.06	0.55
0.50	0.50	68.90	61.22	59.32	1.00	1.07	0.49
0.25	0.75	68.56	61.22	59.01	0.90	1.12	0.40
0.10	0.90	68.08	61.75	58.54	0.80	1.16	0.46
0	1.0	57.07	47.34	48.15	0.78	0.50	0.41
PAN	**DMSO**						
1.0	0	69.57	61.36	59.95	1.04	1.09	0.55
0.75	0.25	68.90	61.36	59.32	1.02	1.06	0.57
0.50	0.50	68.24	60.96	58.70	1.02	1.02	0.62
0.25	0.75	65.13	58.35	55.76	1.00	0.84	0.71
0.10	0.90	62.70	54.36	53.47	1.00	0.69	0.74
0	1.0	54.15	45.24	45.40	1.00	0.17	0.74

[a] Data was normalized with 0 (for cyclohexane) and 1.0 (for DMSO); [b]Not detected.

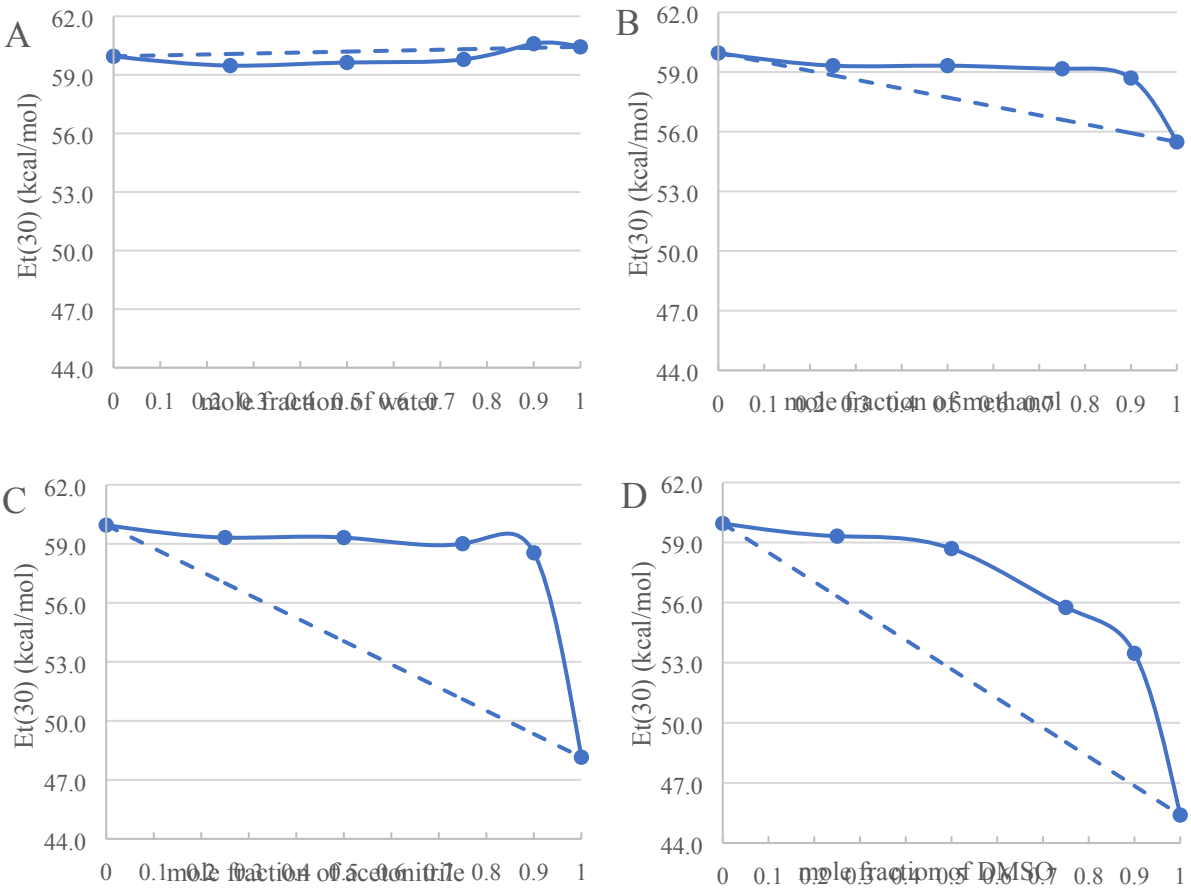

Figure S1. $E_T(30)$ values as a function of the mole fraction of added solvent into PAN (A. PAN-water, B. PAN-methanol, C. PAN-acetonitrile, D. PAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

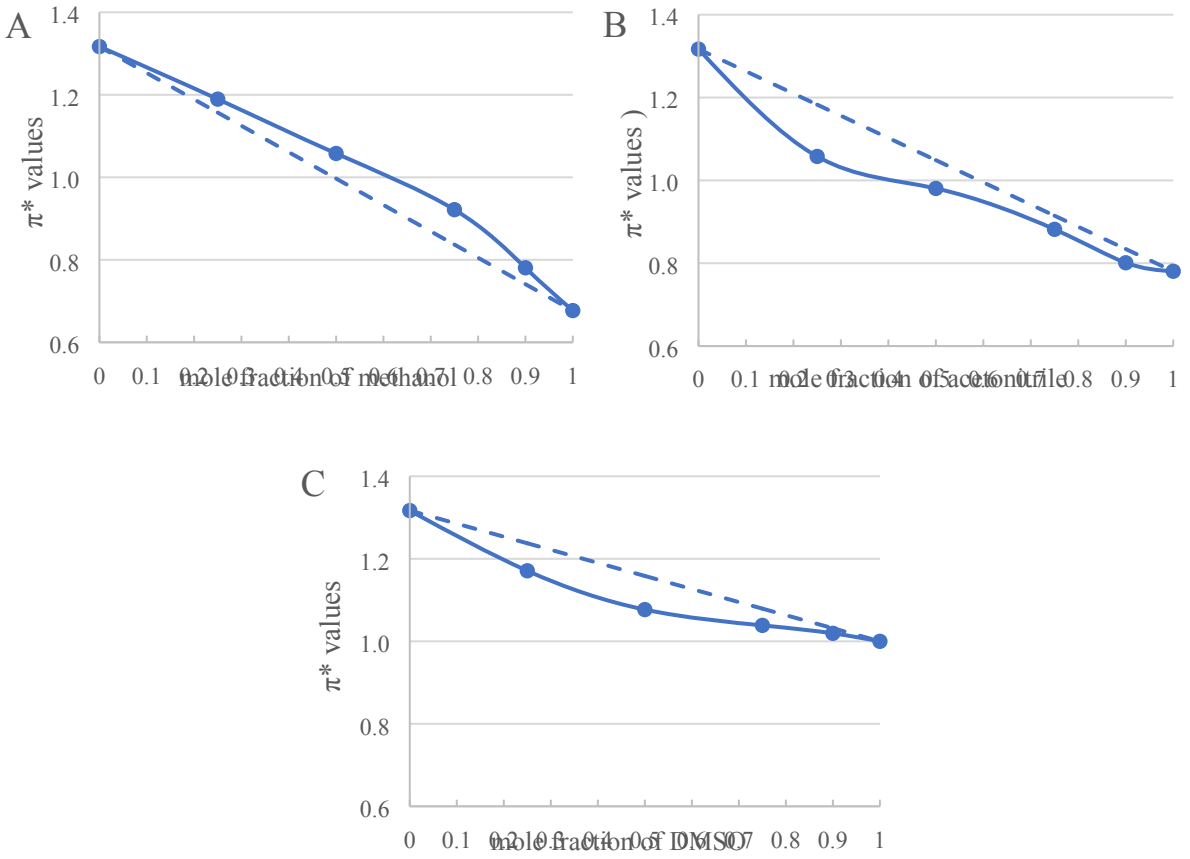

Figure S2. π* values as a function of mole fraction of added solvent into water (A. water-methanol, B. water-acetonitrile and C. water-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

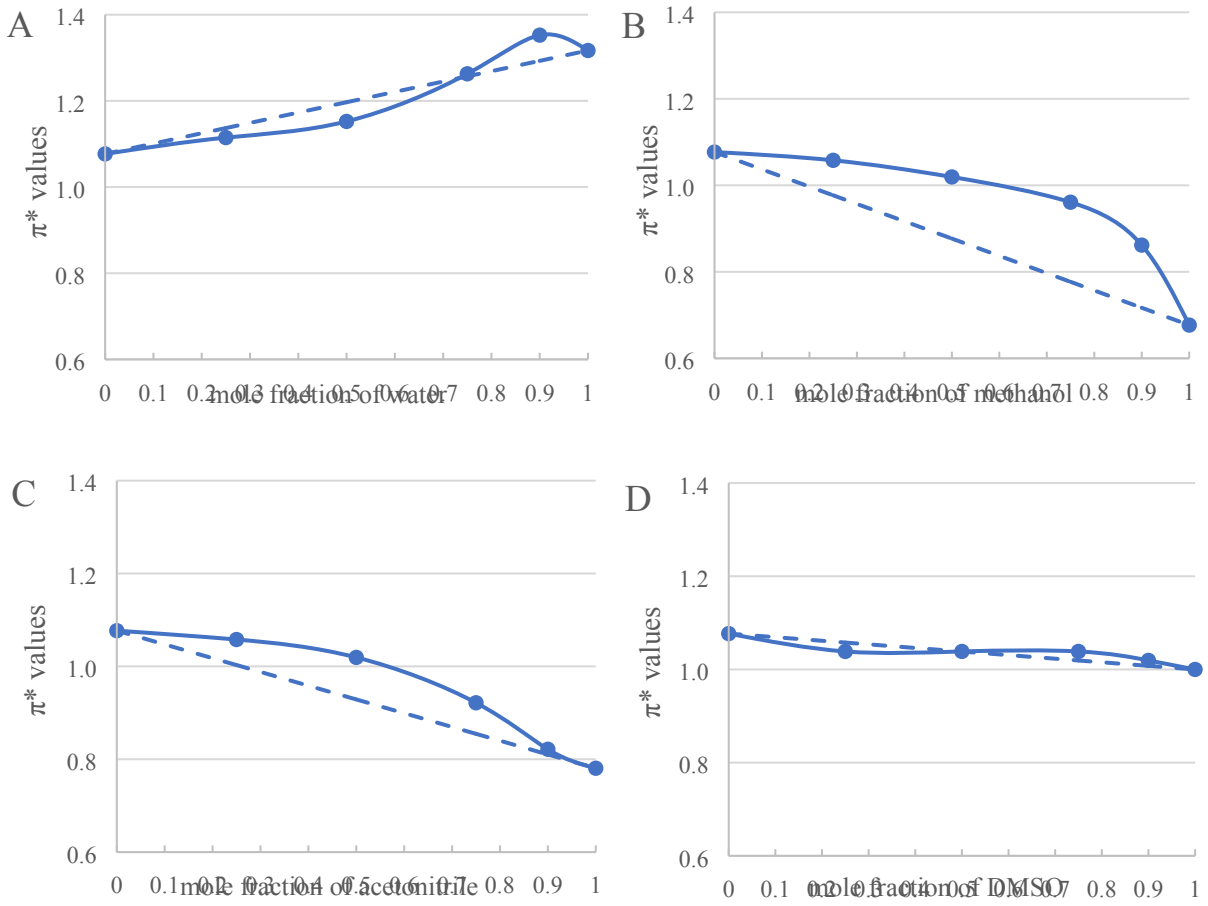

Figure S3. π* values as a function of mole fraction of added solvent into EAN (A. EAN-water, B. EAN-methanol, C. EAN-acetonitrile and D. EAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

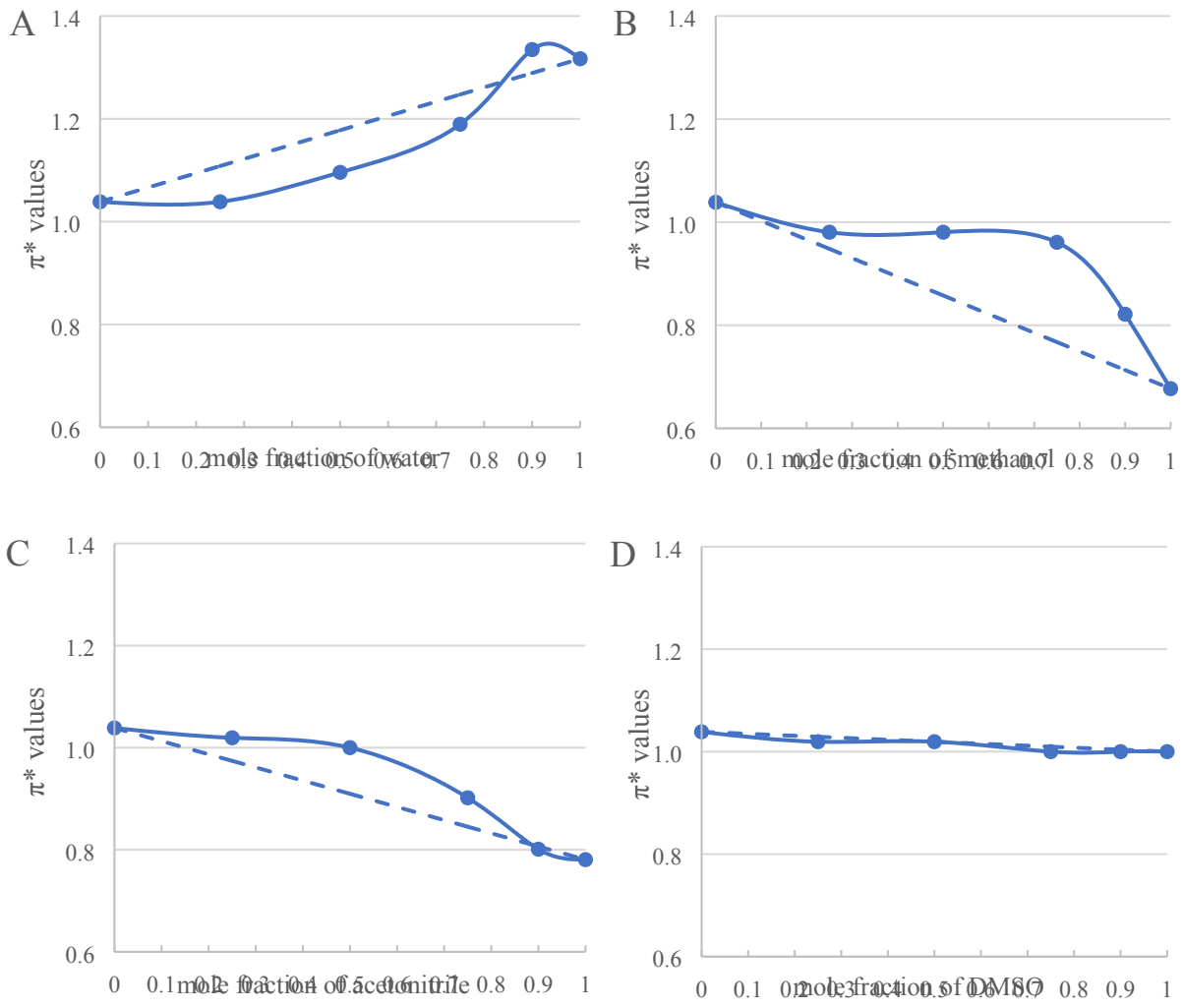

Figure S4. π* values as a function of mole fraction of added solvent into PAN (A. PAN-water, B. PAN-methanol, C. PAN-acetonitrile and D. PAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

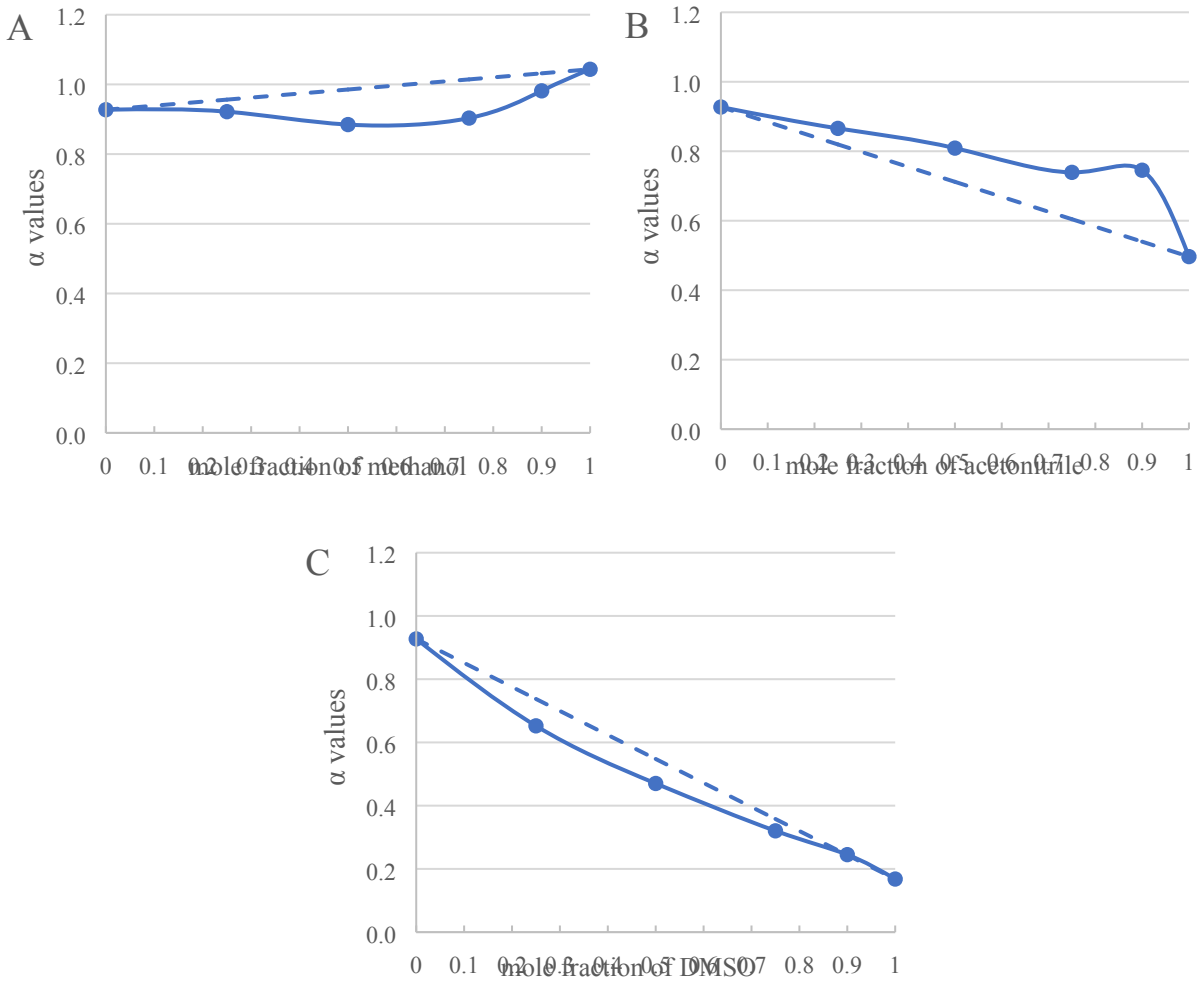

Figure S5. α values as a function of mole fraction of added solvent into water (A. water-methanol, B. water-acetonitrile and C. water-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

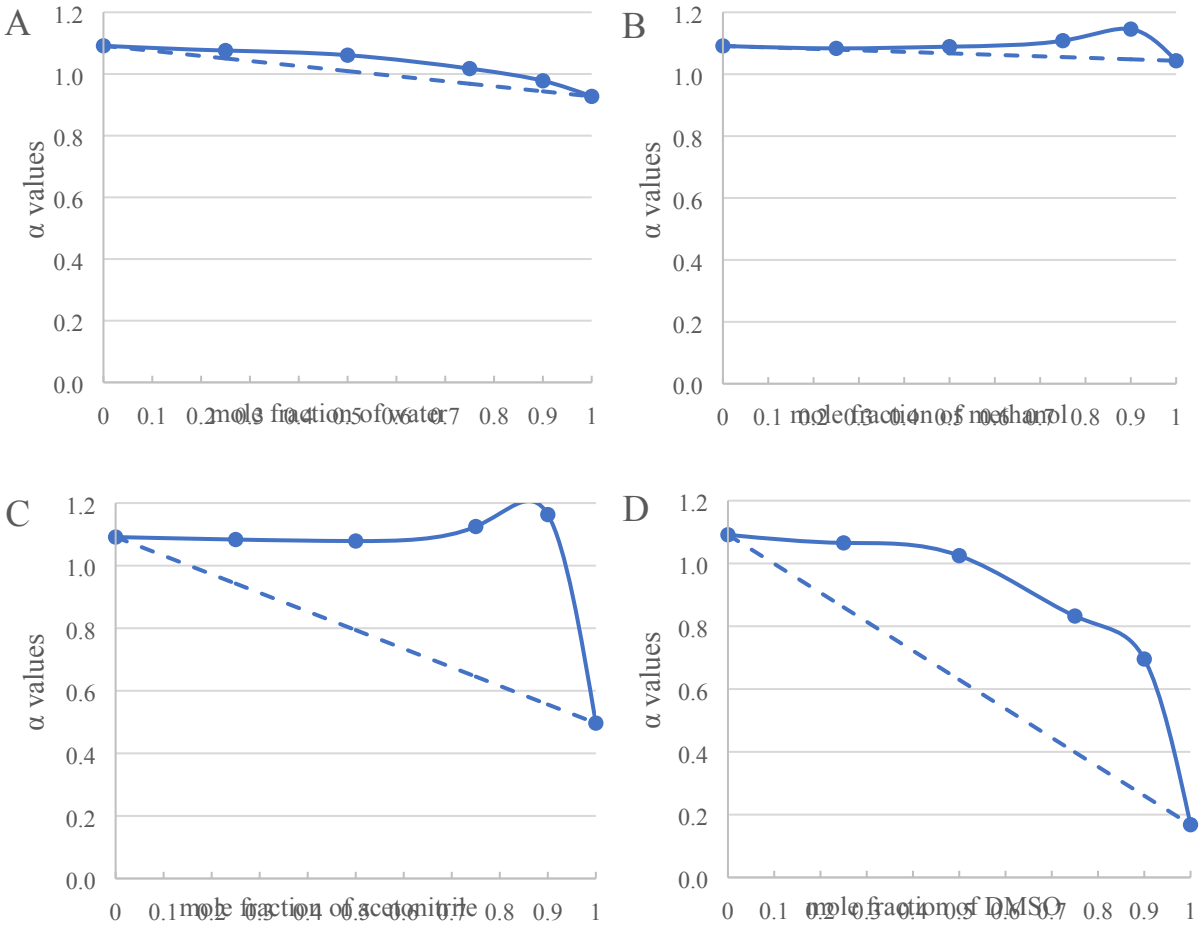

Figure S6. α values as a function of mole fraction of added solvent into EAN (A. EAN-water, B. EAN-methanol, C. EAN-acetonitrile and D. EAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

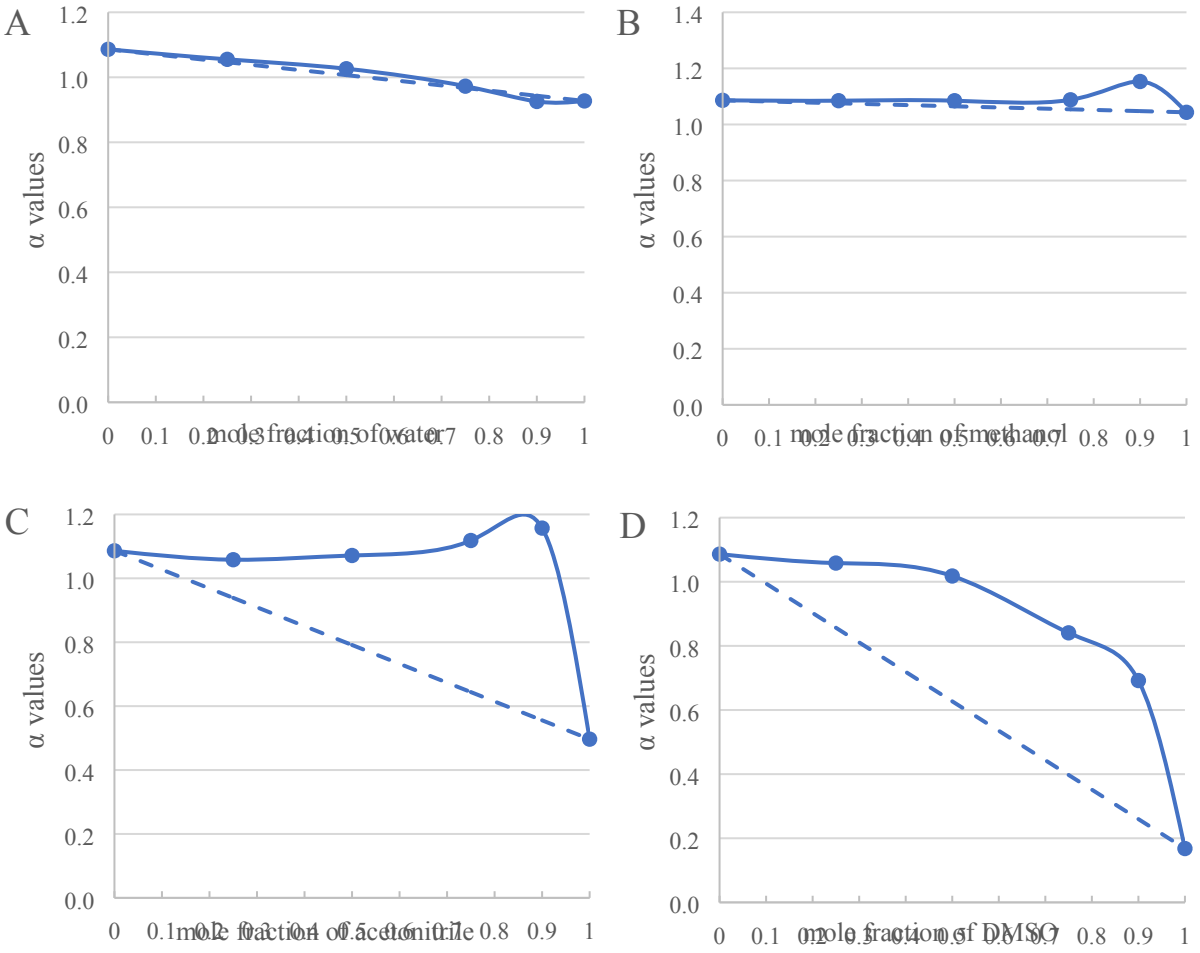

Figure S7. α values as a function of mole fraction of added solvent into PAN (A. PAN-water, B. PAN-methanol, C. PAN-acetonitrile and D. PAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

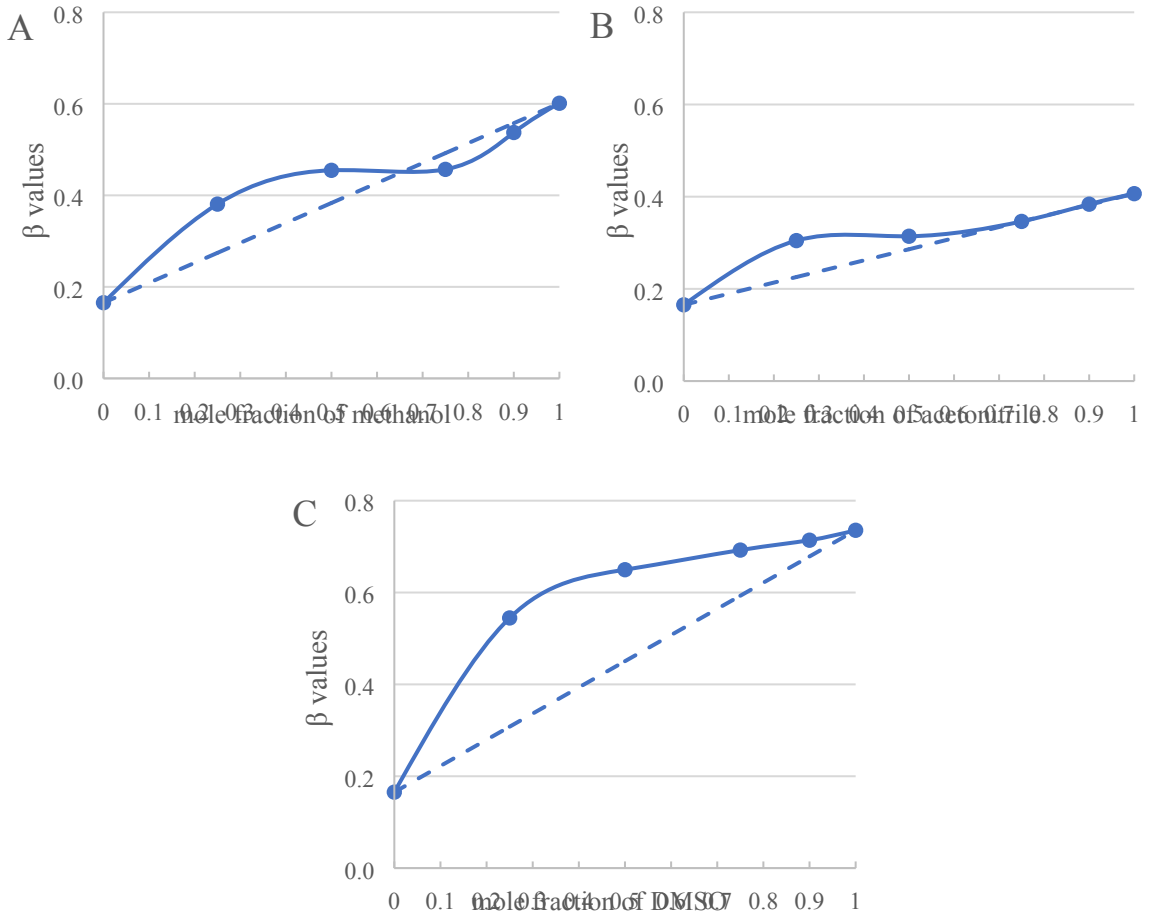

Figure S8. β values as a function of mole fraction of added solvent into water (A. water-methanol, B. water-acetonitrile and C. water-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

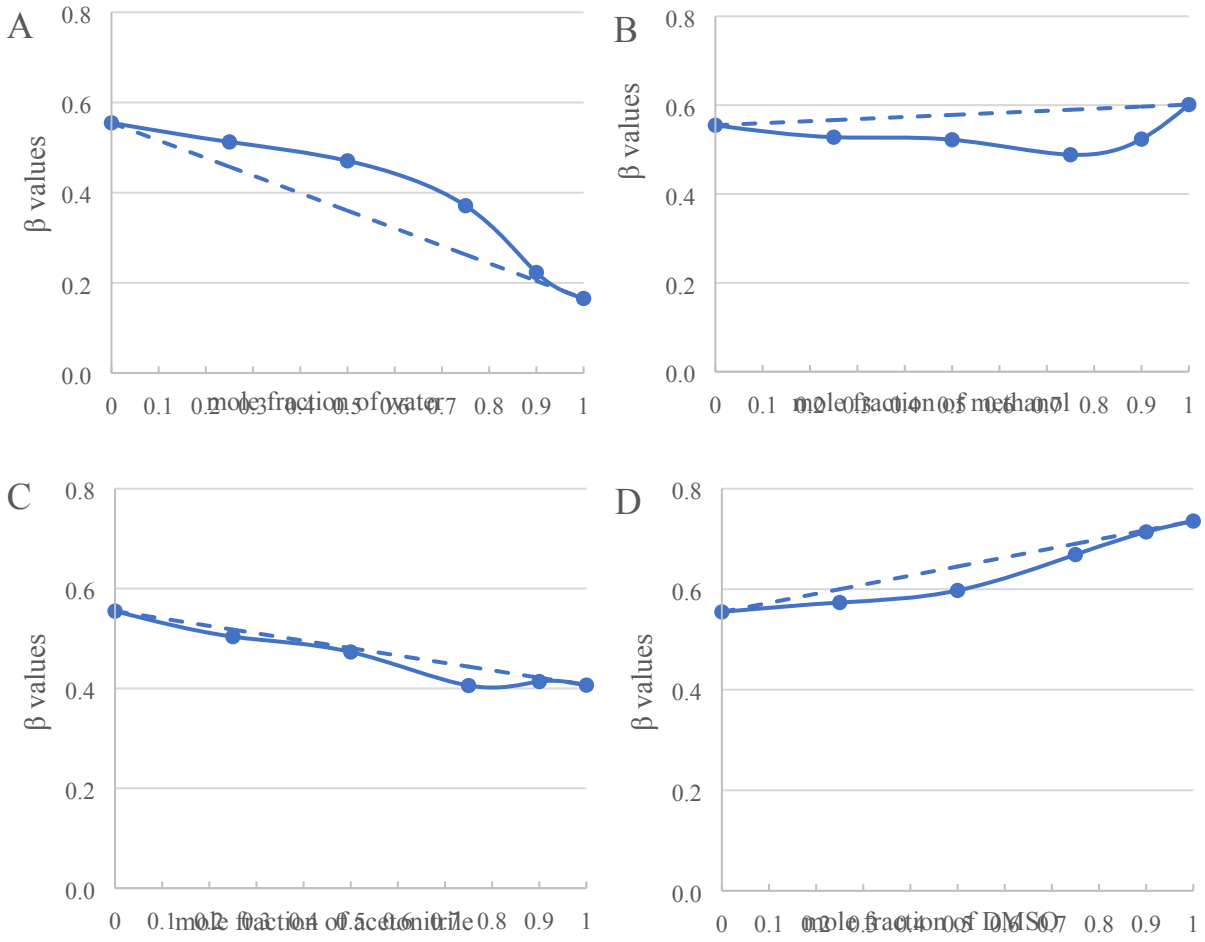

Figure S9. β values as a function of mole fraction of added solvent into EAN (A. EAN-water, B. EAN-methanol, C. EAN-acetonitrile and D. EAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

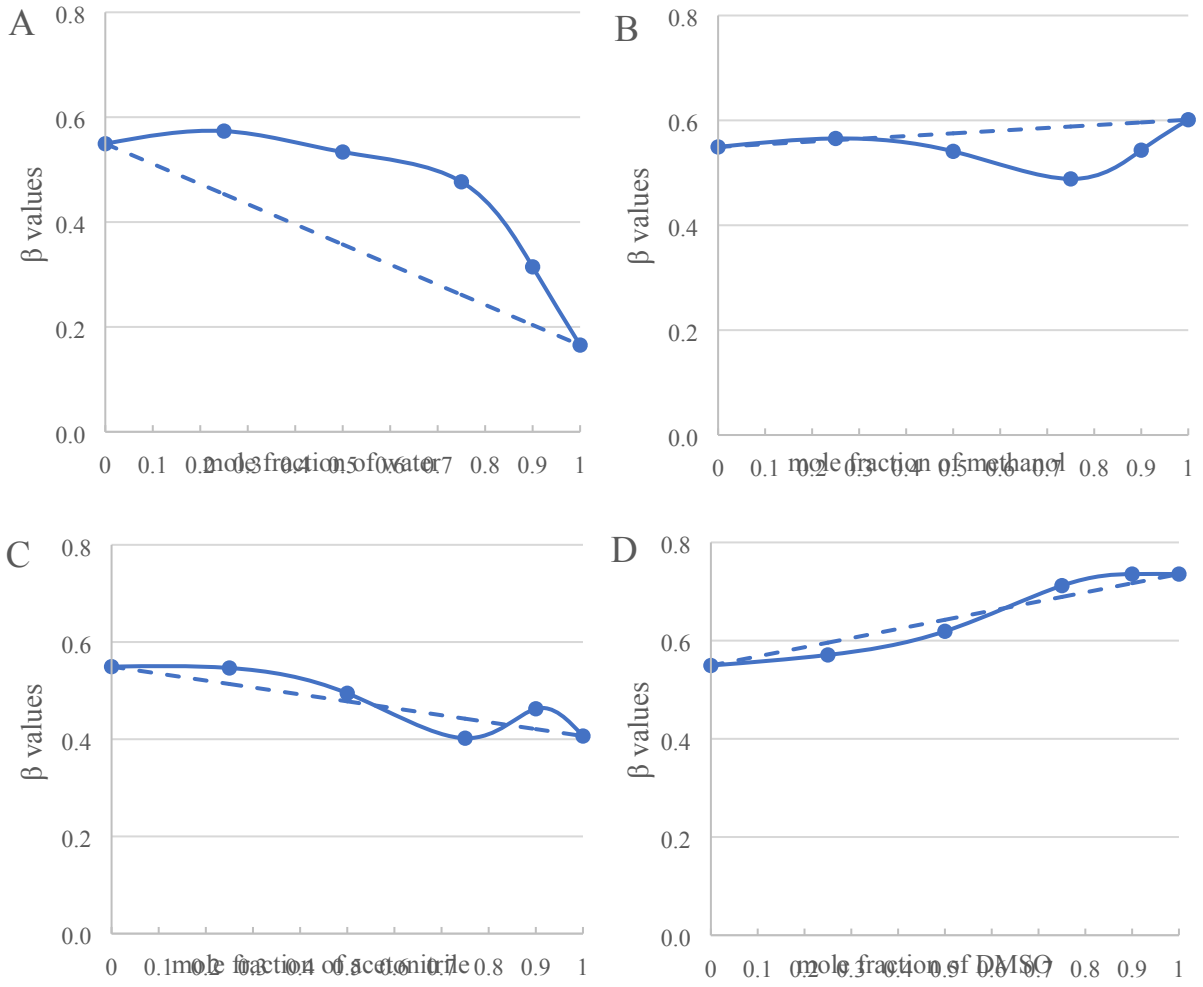

Figure S10. β values as a function of mole fraction of added solvent into PAN (A. PAN-water, B. PAN-methanol, C. PAN-acetonitrile and D. PAN-DMSO). Solid lines are a guide to the eye and the dashed lines represent the ideal trend.

- **Spectral data (via fluorescent dyes)**

The final concentrations of the fluorescent dyes Nile Red (NR), Pyrene (Pyr) and Coumarin 153 (C153) in the binary mixtures were 0.010 mM, 0.037 mM and 0.004 mM, respectively. The spectral ranges for each dye were determined separately. First, excitation scans were performed in each solvent to find out the excitation maxima and the resulting spectra for NR and C153 are plotted in Figure S11 and Figure S12, respectively. Then, the maximum excitation wavelengths (λ_{max}ex) were accordingly set at 530, 335 and 415 nm for NR, Pyr and C153, respectively whereas the ranges of the emission wavelength were 545 – 700 nm, 350 – 450 nm and 435 – 600 nm for the same dyes. For NR and C153 dyes, the results are discussed in terms of the intermolecular charge transfer band shifts based on emission maxima to understand that dye-solvent interactions at the excited state. The higher emission maxima indicate the higher solvent polarity. For Pyr, the polarity of solvents is attributed to

the intensity ratio of the first (I_I) and the third (I_{III}) vibronic fluorescence bands, where a higher ratio corresponds to a higher polarity.

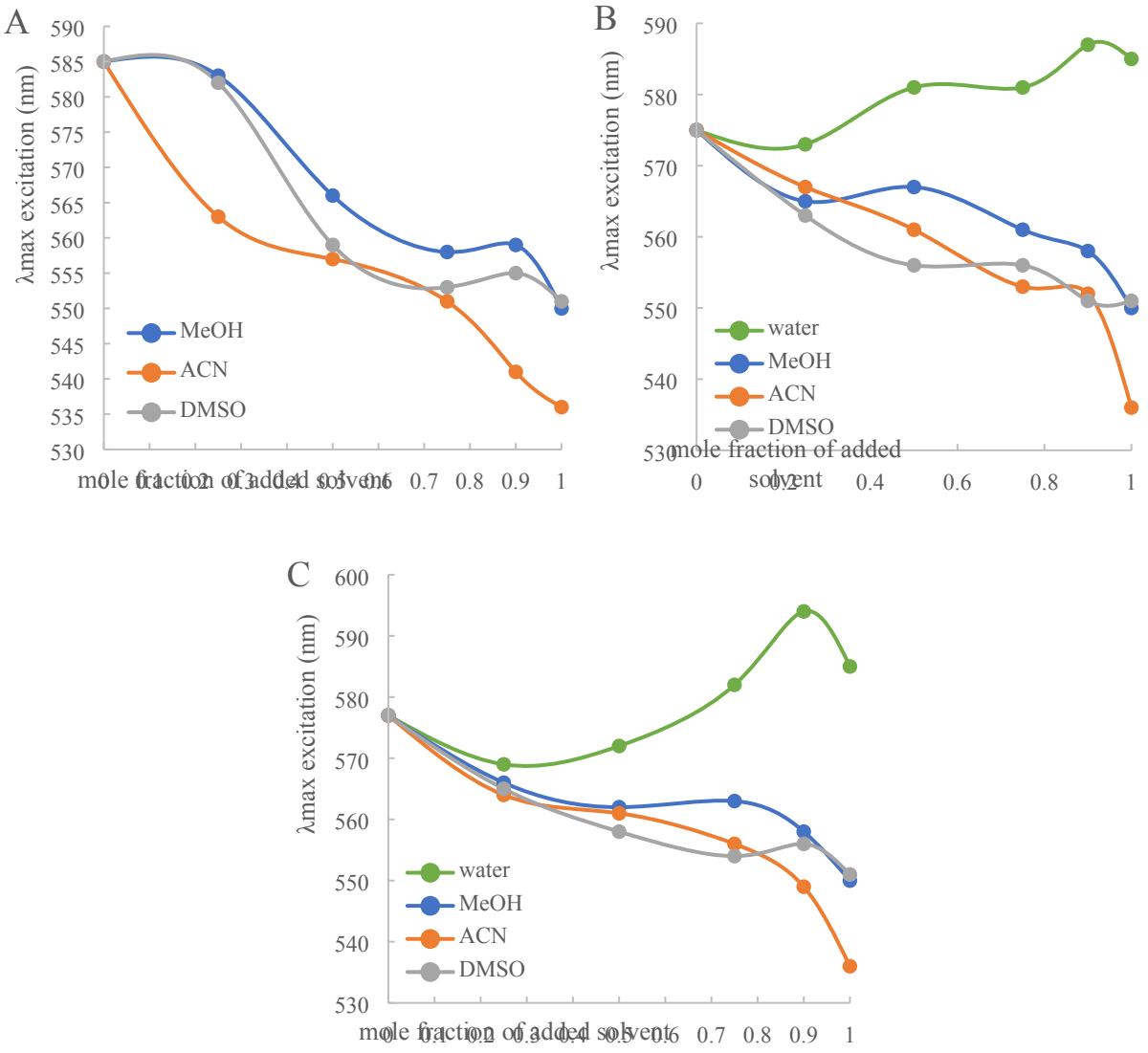

Figure S11. λ_{ex} of NR in A. mixtures of water, B. mixtures of EAN and C. mixtures of PAN. Solid lines are a guide to the eye.

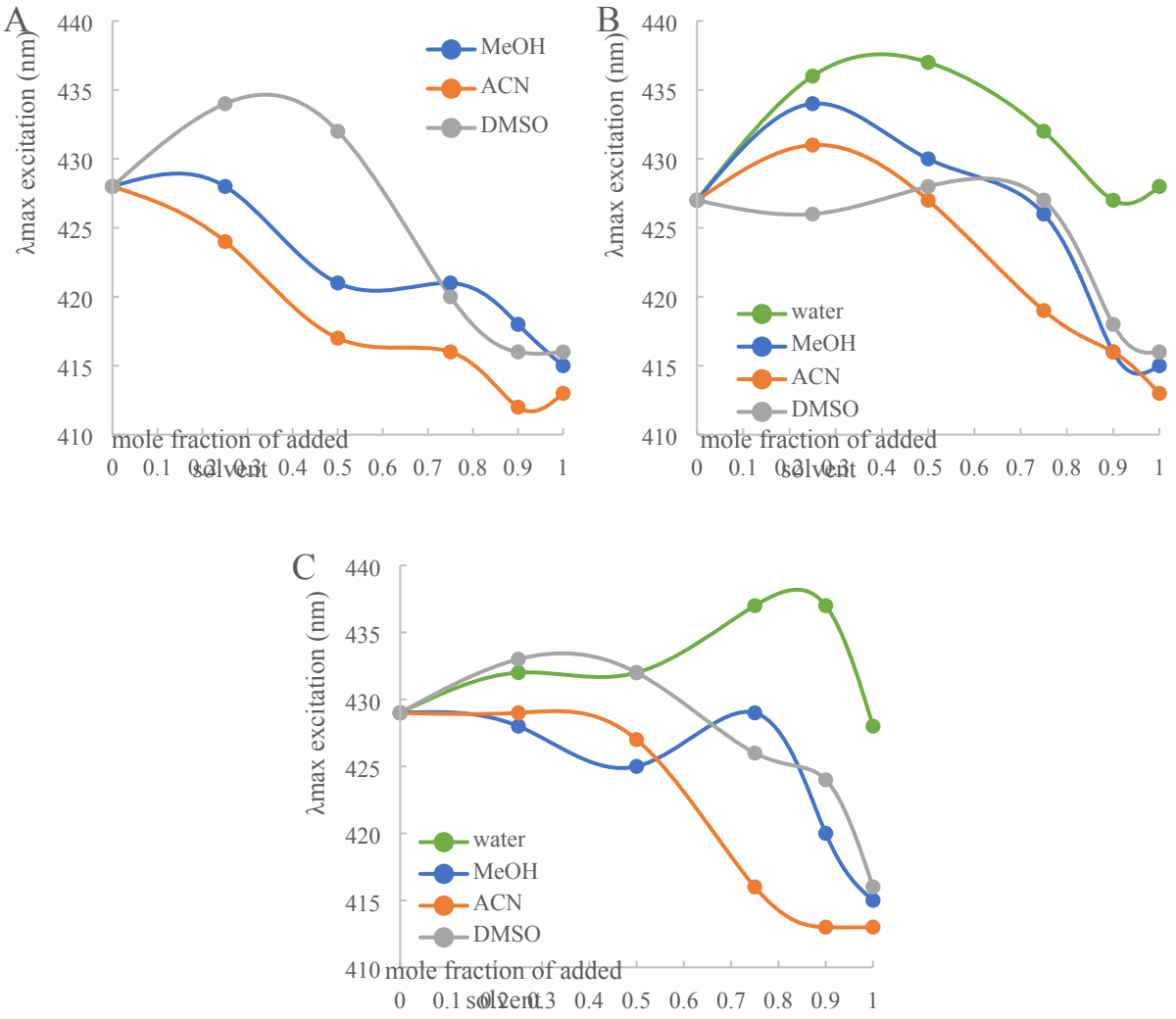

Figure S12. λ_{ex} of C153 in A. mixtures of water, B. mixtures of EAN and C. mixtures of PAN. Solid lines are a guide to the eye.

Nile Red (NR) emission spectra

The polarity responses of NR were in all 66 solvent environments is shown in Figure S13. The decreasing order of polarities for pure solvents is water (666 nm) > EAN (647 nm) > PAN (645 nm) > methanol (635 nm) > DMSO (628 nm) > acetonitrile (619 nm) showing a great consistency with those reported for molecular solvents by Fletcher et al[1]. The presence of preferential solvation is evident in all aqueous mixtures from the sudden decrease in emission maxima upon addition of 0.25 mol of secondary solvents, and in all cases, NR seems to be preferably solvated by the added solvent (Figure S13A). Upon further addition, the compositions in the solvation shell changed almost ideally. Figure S13B and Figure S13C show the changes in emission maxima of NR in binary mixtures of EAN and PAN with molecular solvents, respectively. It is apparent that the dye preferred to be solvated by PILs upon addition of methanol, acetonitrile and DMSO at almost all compositions. In contrast, the PIL

preference of dye was also observed in PIL-water mixtures up to 0.5 mol of water present, the NR-water interactions are slightly stronger in the presence of higher water concentrations.

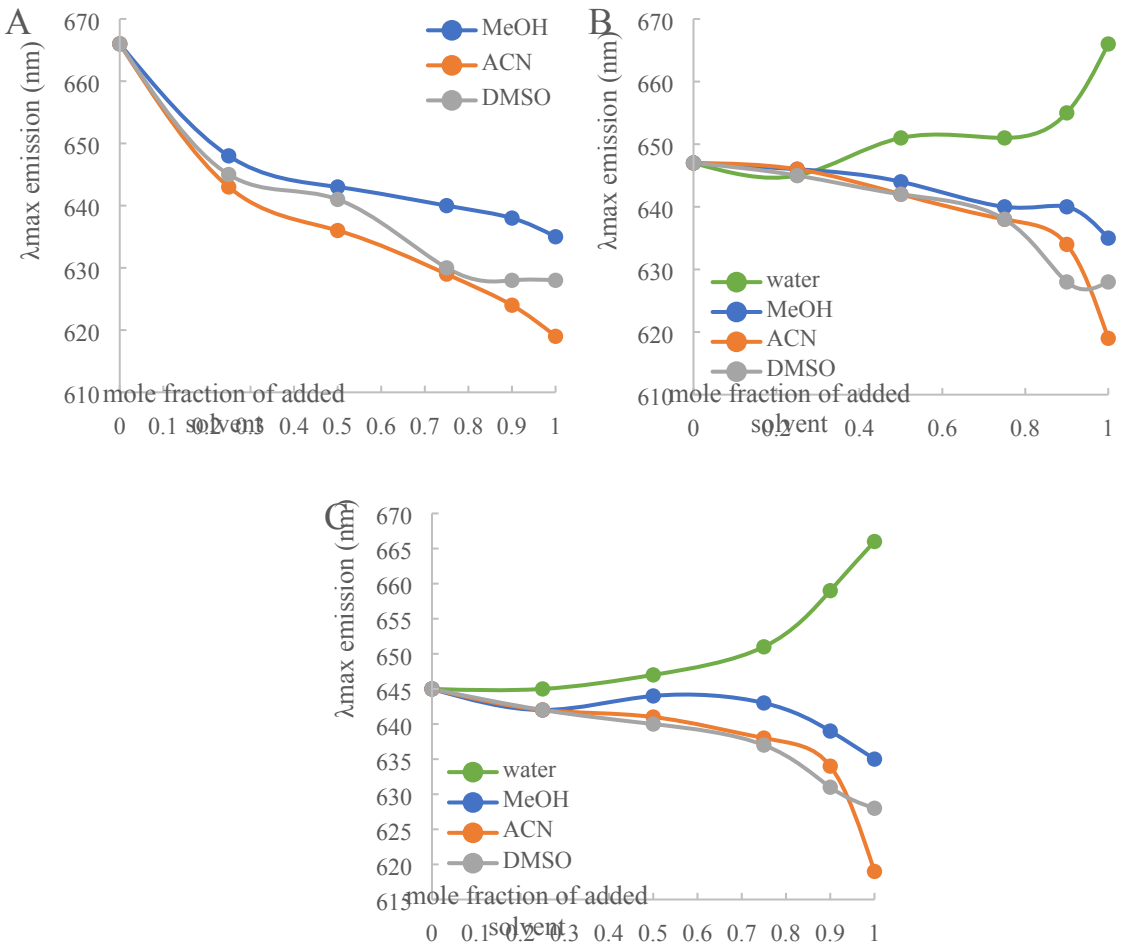

Figure S13. λ_{em} of NR in A. mixtures of water, B. mixtures of EAN and C. mixtures of PAN. Solid lines are a guide to the eye.

Coumarin 153 (C153) emission spectra

The scarcely water soluble and low dipolar fluorescent compound C153 with dipole moment of 6.55 D at ground state[2], is more sensitive towards probing hydrophobic environments compared to NR with dipole moment of 8.2 D[3]. The polarity responses of C153 in all 66 binary mixtures are given in Figure S14. In the pure solvents, the overall polarity is found to decrease in the following order: water (548 nm) > EAN = PAN (544 nm) > methanol (533 nm) > DMSO (528 nm) > acetonitrile (520 nm), which was the same order of response as obtained with NR, and shows good agreement with the corresponding literature values[4-6]. Moreover, the relative ordering is similar to the molar transition energies calculated based on RD30.

The polarity responses of C153 in aqueous mixtures (Figure S14A) shows a decrease on mixing with acetonitrile and DMSO at all compositions. In water-methanol mixtures, C153 prefers solvation by water at 0.25 mol of methanol present, then with increasing methanol proportion C153 shows a preference towards methanol. In EAN-solvent mixtures (Figure S14B), a synergistic effect was observed on addition of molecular solvents, with higher polarity response values than either neat solvent at certain concentrations. Although the polarity values of pure EAN and PAN were close to each other, the values on mixing the IL with molecular solvents were significantly different. As shown in Figure S14C, C153 had a strong dye preference towards PAN over the entire composition range, for all added molecular solvents. This was attributed to the high sensitivity of C153 to hydrophobic domains and hence increasing the alkyl chain length possibly enables orientation of propylammonium solvent species around the dye, with minimal presence of the added molecular solvent.

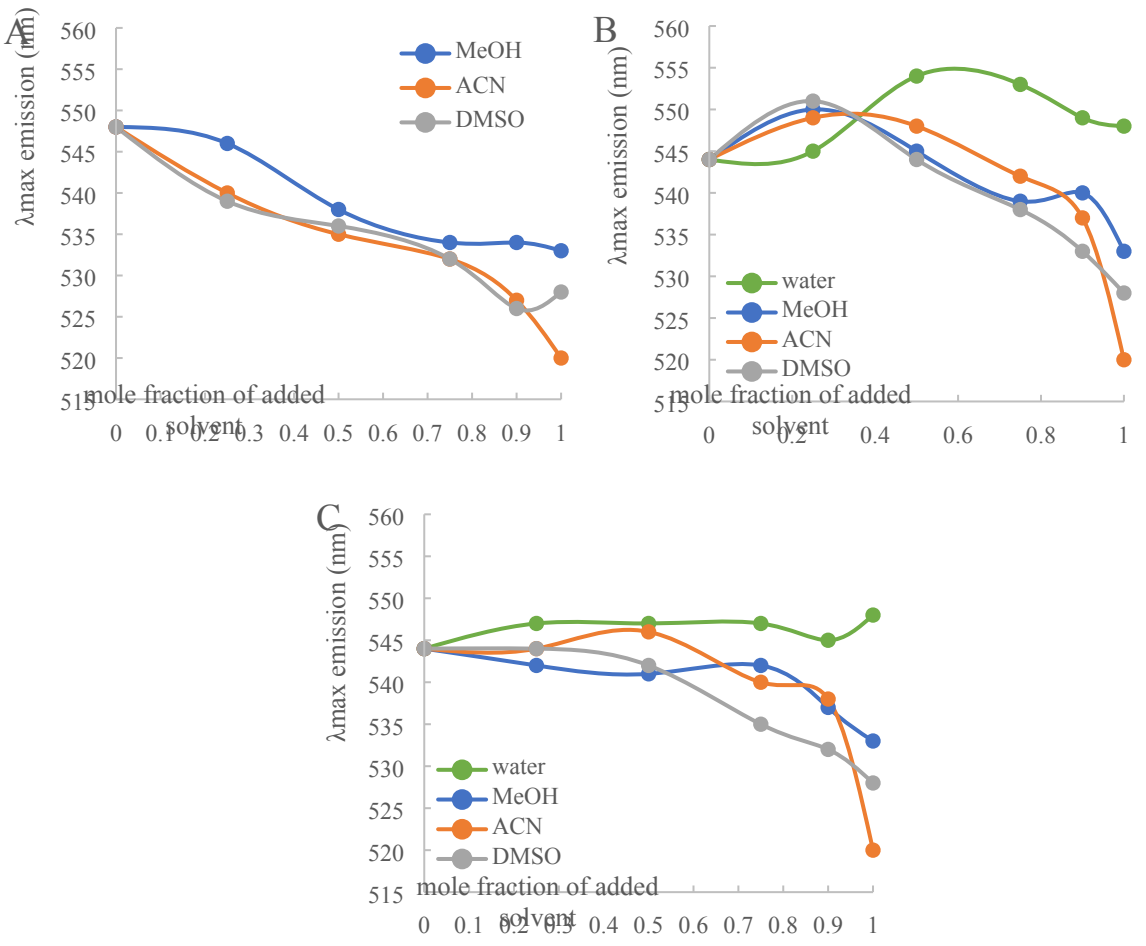

Figure S14. λ_{em} of C153 in A. mixtures of water, B. mixtures of EAN and C. mixtures of PAN. Solid lines are a guide to the eye.

Pyrene (Pyr)

Pyrene was used as a neutral fluorescent probe alternative to the solvatochromic non-H bonding dye DE4A[7]. The key advantages of using this probe is that it can eliminate or minimize probe-probe interactions and enables direct comparison with the responses obtained in the π* scale. The decreasing order of dipolarity for the neat solvents based on Pyr was DMSO(1.22) > EAN(1.15) > acetonitrile ≈ PAN(1.02) > water(0.92) > methanol(0.86)[8] and the relative ordering shows a good accordance with the literature values[1, 9-10]. When compared to the values obtained in the π* scale, responses based on Pyrene show a greater sensitivity to solvent change than those based on DE4A.

The relative dipolarity changes in binary mixtures of water, EAN and PAN with molecular solvents based on Pyr were given in Figure S15. It is evident that mixing water with 0.25 mol of additional solvent led to a significant increase in dipolarity, as measured by pyrene solvation. In all cases, pyrene showed a greater preference towards the added molecular solvents than water, with the greatest preference towards DMSO.

The change in the dipolarity of binary mixtures of EAN and PAN with molecular solvents can be seen in Figures S15B and S15C, respectively. In the mixtures of both PILs with DMSO, the dipolarity of mixtures increase almost linearly and ideally. Pyrene had a preference towards PILs for up to 0.5 mol of acetonitrile being added, then at higher acetonitrile concentrations, pyrene-acetonitrile interactions became stronger. Upon methanol addition, pyrene is preferentially solvated by either EAN or PAN, up to 0.75 mol of methanol present in the EAN mixtures and 0.9 mol of methanol in PAN mixtures (Figure S15B and Figure S15C). In aqueous mixtures of EAN and PAN the solvation of pyrene is predominantly controlled by the PILs up to 0.5 mol of water present in the mixtures. However, at higher water concentrations, the dipolarity of EAN-water mixtures decreases whereas those of PAN-water mixtures increases with evident synergism.

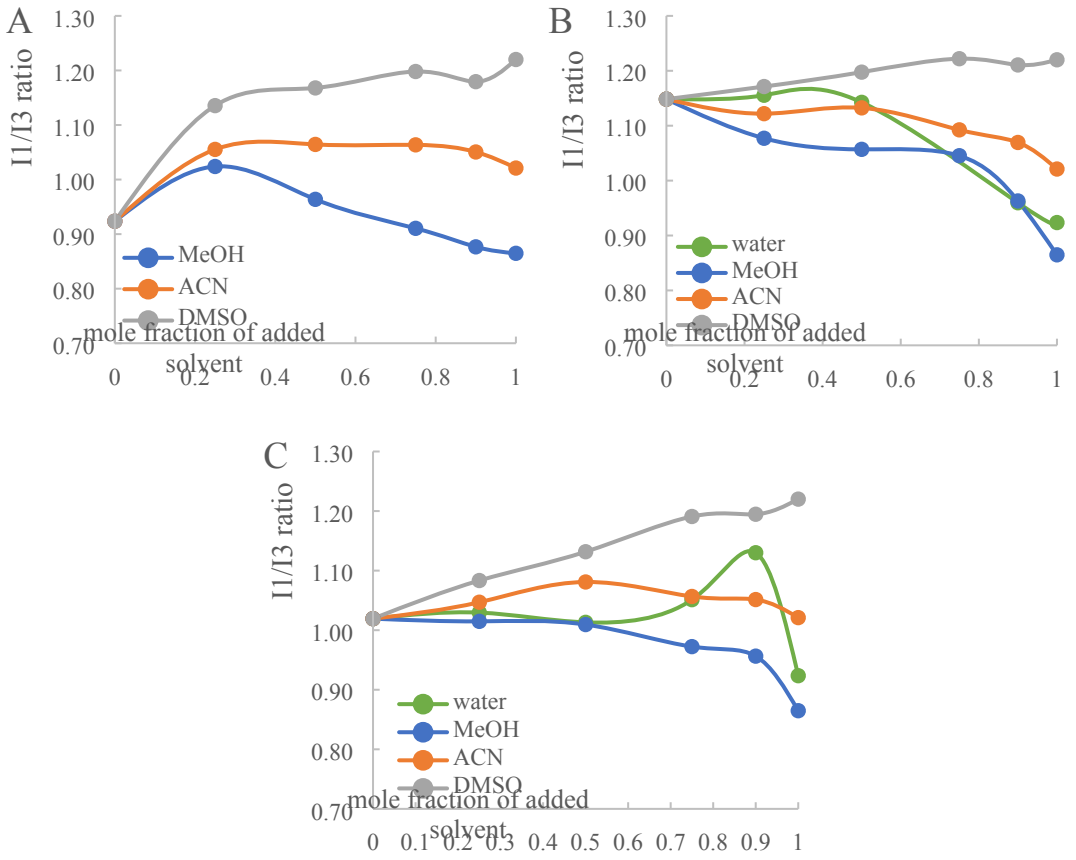

Figure S15. I_I/I_{III} fluorescence band intensity ratio of Pyr in A. mixtures of water, B. mixtures of EAN and C. mixtures of PAN. Solid lines are a guide to the eye.

Table S7. Characteristic vibrational modes and wavenumbers (ν) for solvents

IR modes[a]	Wavenumber (cm^{-1}), (ν ± 0.5 cm^{-1})					
	water	**methanol**	**acetonitrile**	**DMSO**	**EAN**	**PAN**
ν(O-H)	3231	3305				
ν(N-H)					3062	3060
ν(C-H)		2940 - 2830	3000 - 2945	2995 - 2913	2985-2946	2967-2937-2883
ν(C≡N)			2253			
δ(O-H)	1634	1654				
δ(N-H)					1618	1618
ω(N-H)					1515	1518
τ(CH_3)			1442-1375	1436-1407-1309		
ν(NO_3), as					1291	1287
ρ(C-H)/ρ(CH_3)			1038	1017-952-929-896	1216-1190	1186-1157
ν(S=O)				1042-1017		
ν(NO_3), s					1040	1038
ν(C-O)		1020				
ν(C-C)			918			
δ(NH_3)					977	990-953
δ(C-N)						
ν(C-N), s					871	865
ω(NO_3), op					825	825
ρ(NH_3)					793	752
δ(C-C≡N)			748			
ρ(NO_3), ip					718	718
ν(C-S-C), as				697		
ν(C-S-C), s				667		
ω(CH_3)					411	450

[a] The symbols ν, δ, ω, τ and ρ denote stretching, bending, wagging, twisting and rocking modes. The asymmetric, symmetric, out-of-plane and in-plane vibrations are abbreviated as “as”, “s”, “op” and “ip”, respectively.

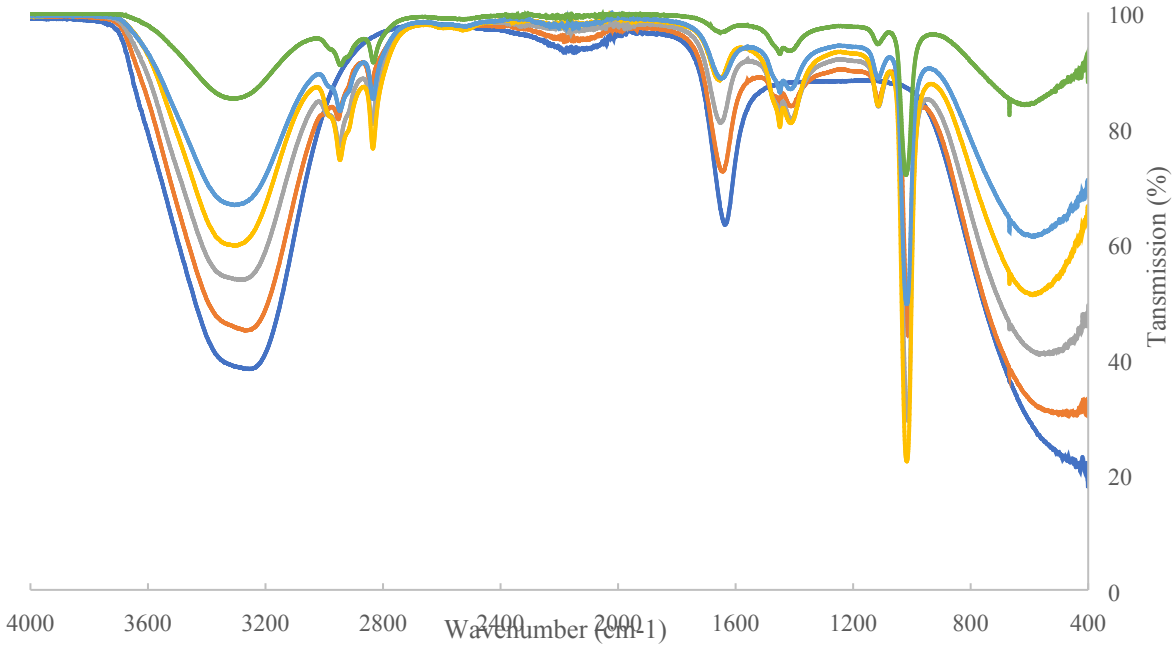

Figure S16. IR spectra of water-methanol mixtures. Methanol mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

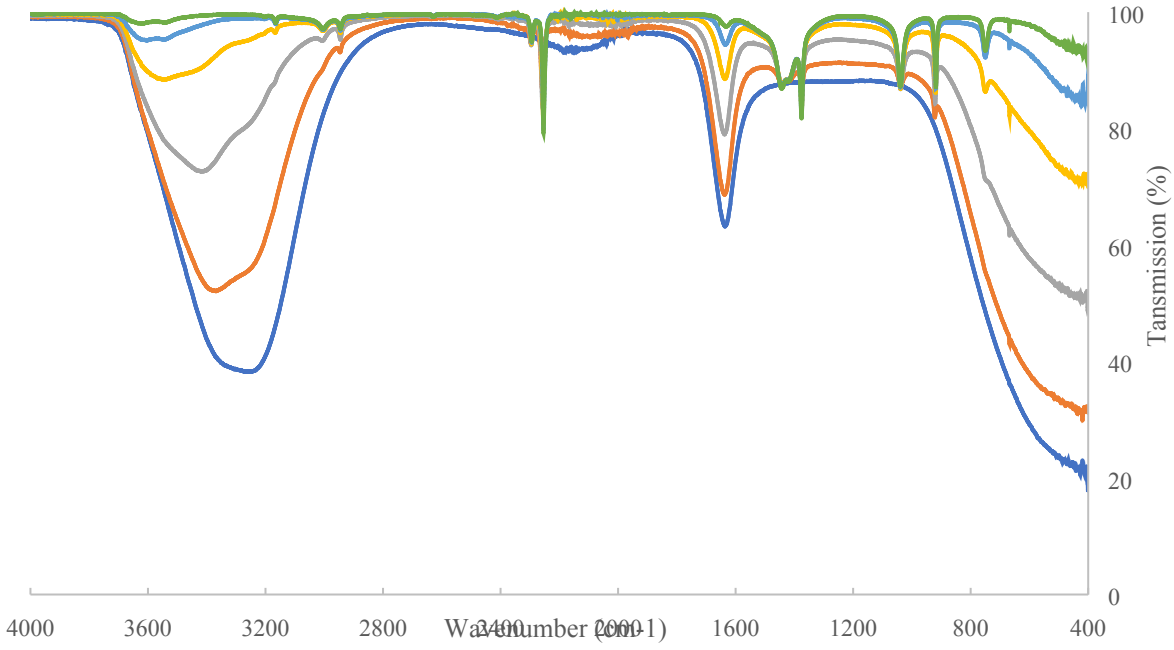

Figure S17. IR spectra of water-acetonitrile mixtures. Acetonitrile mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

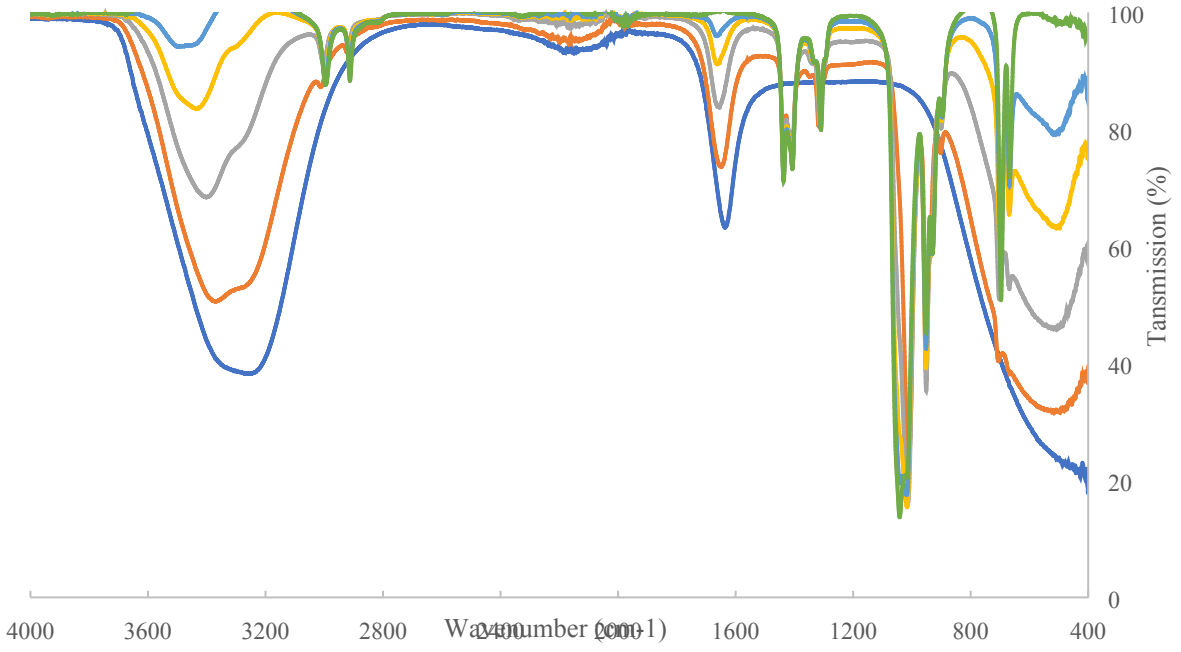

Figure S18. IR spectra of water-DMSO mixtures. DMSO mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

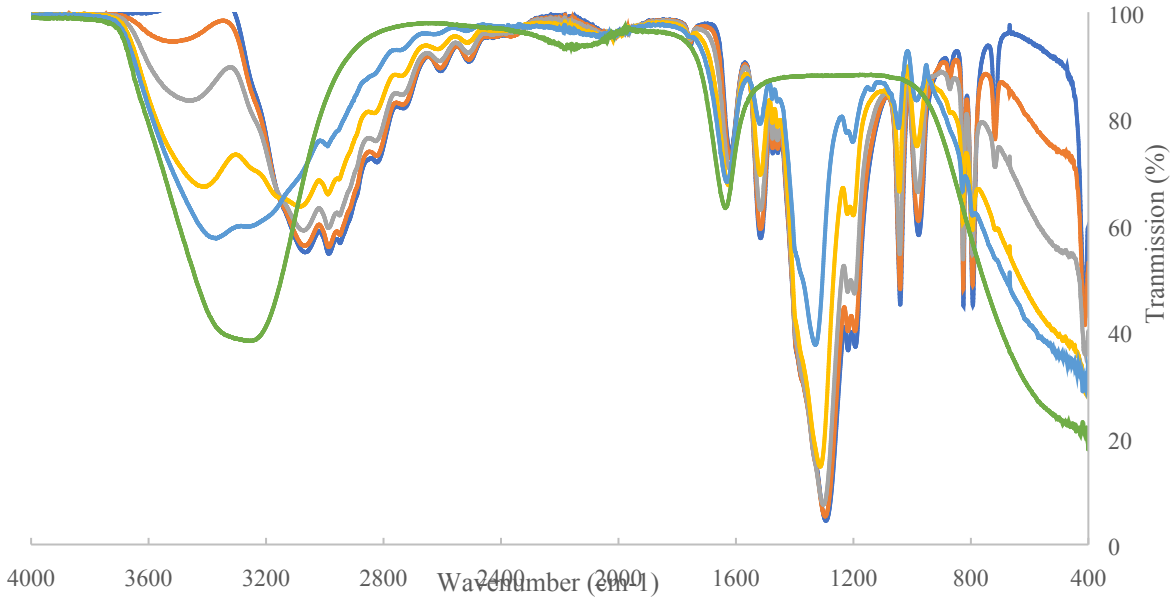

Figure S19. IR spectra of EAN-water mixtures. Water mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

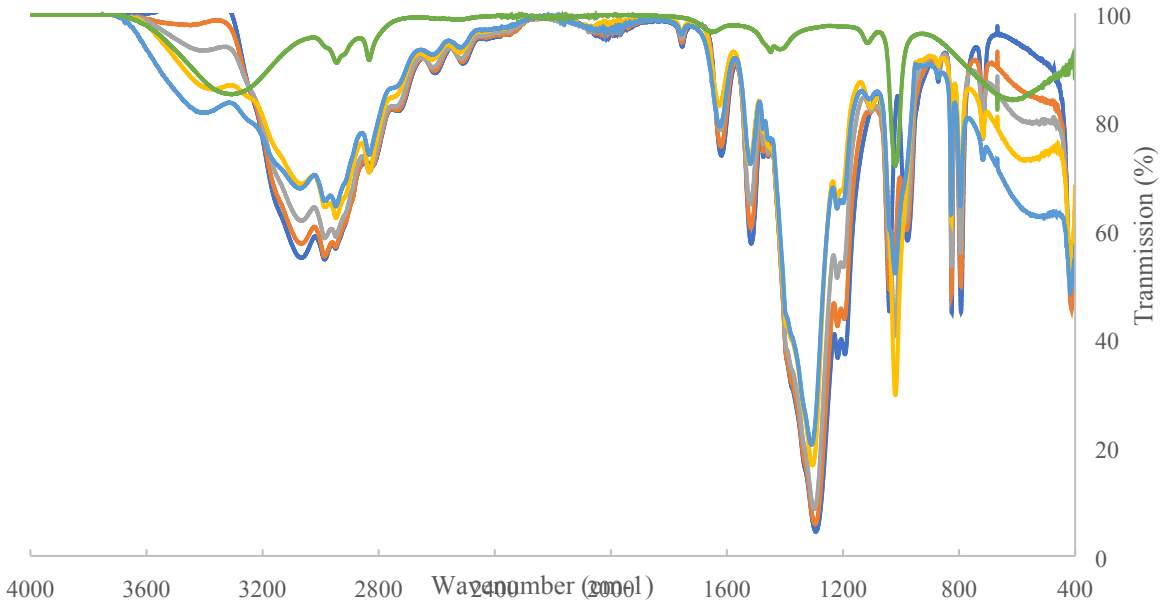

Figure S20. IR spectra of EAN-methanol mixtures. Methanol mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

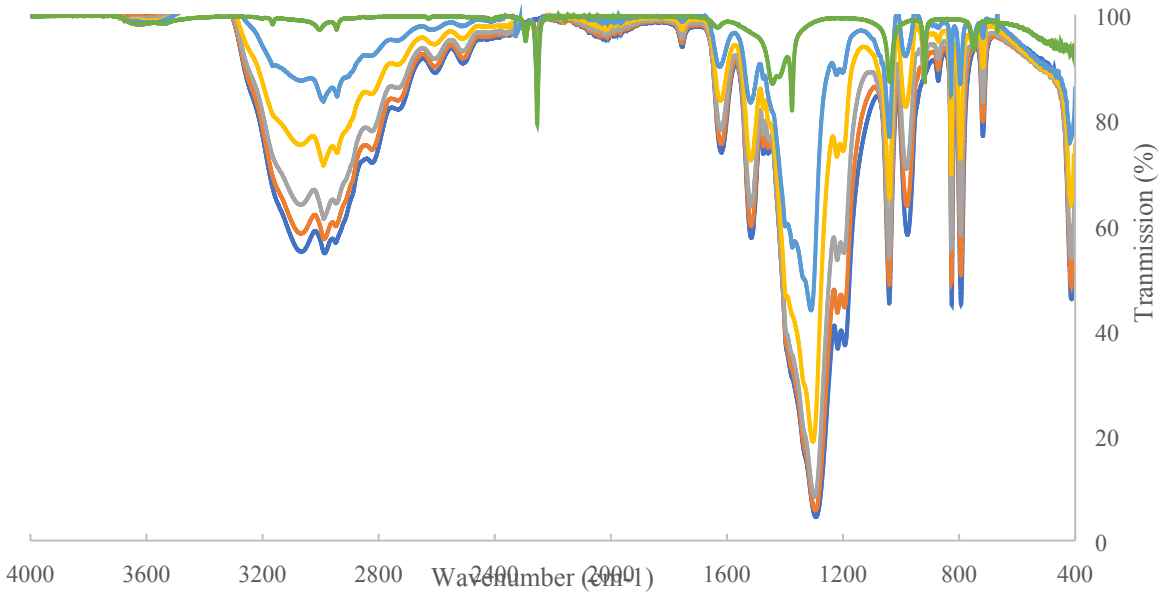

Figure S21. IR spectra of EAN-acetonitrile mixtures. Acetonitrile mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

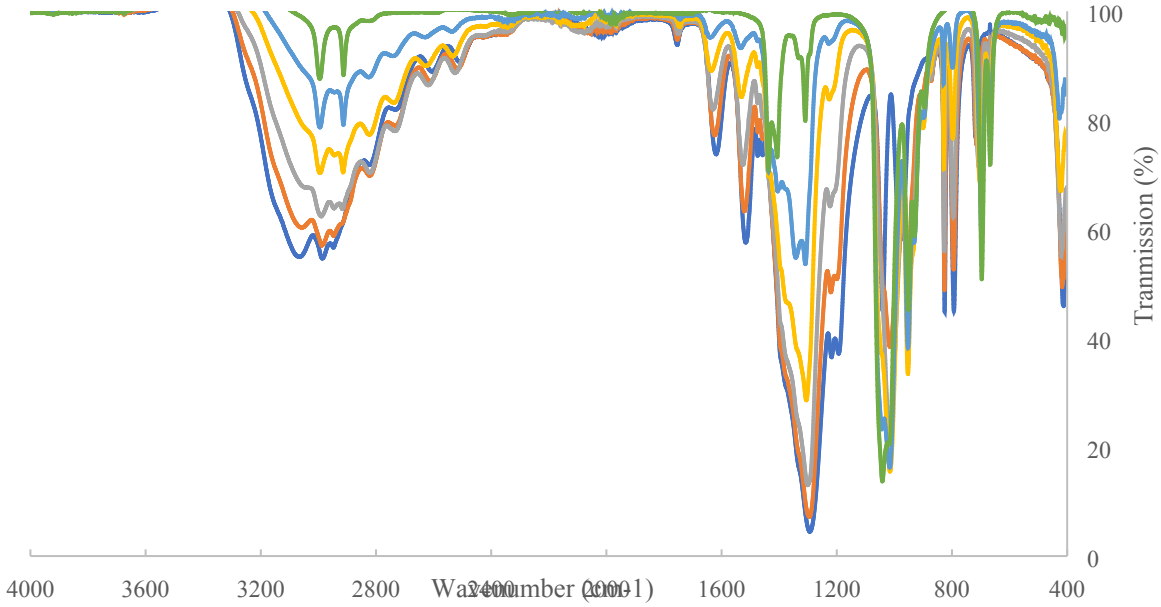

Figure S22. IR spectra of EAN-DMSO mixtures. DMSO mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

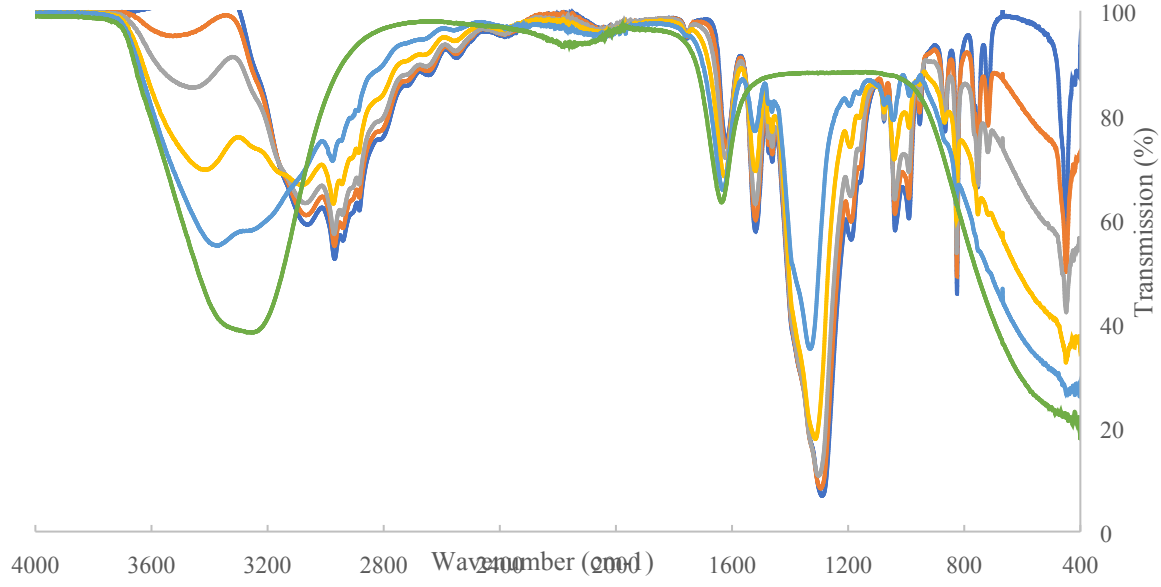

Figure S23. IR spectra of PAN-water mixtures. Water mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

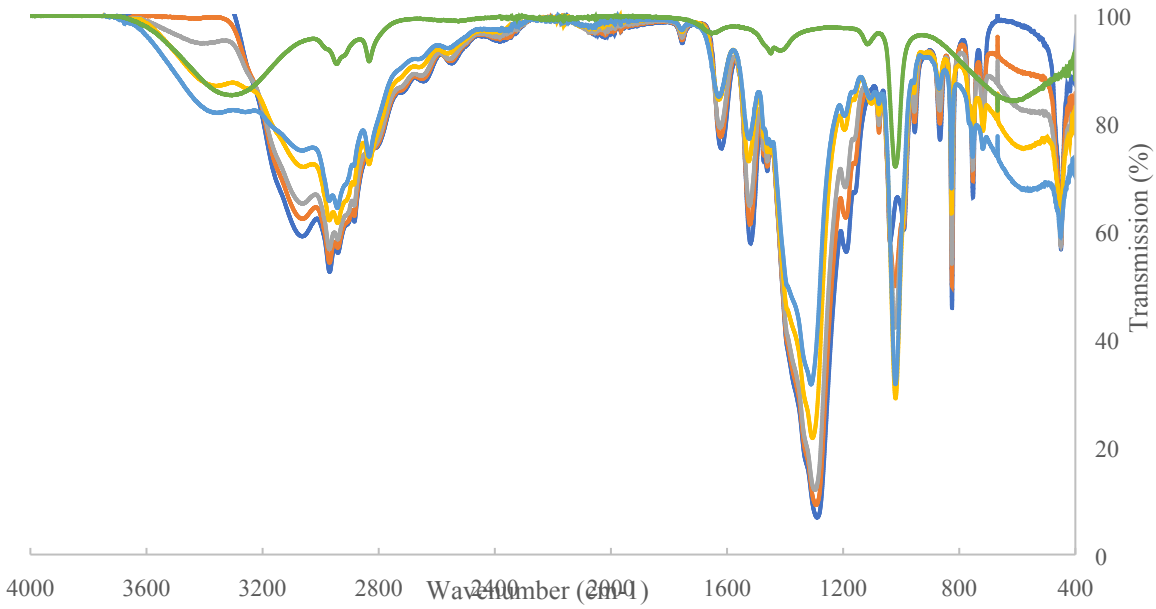

Figure S24. IR spectra of PAN-methanol mixtures. Methanol mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

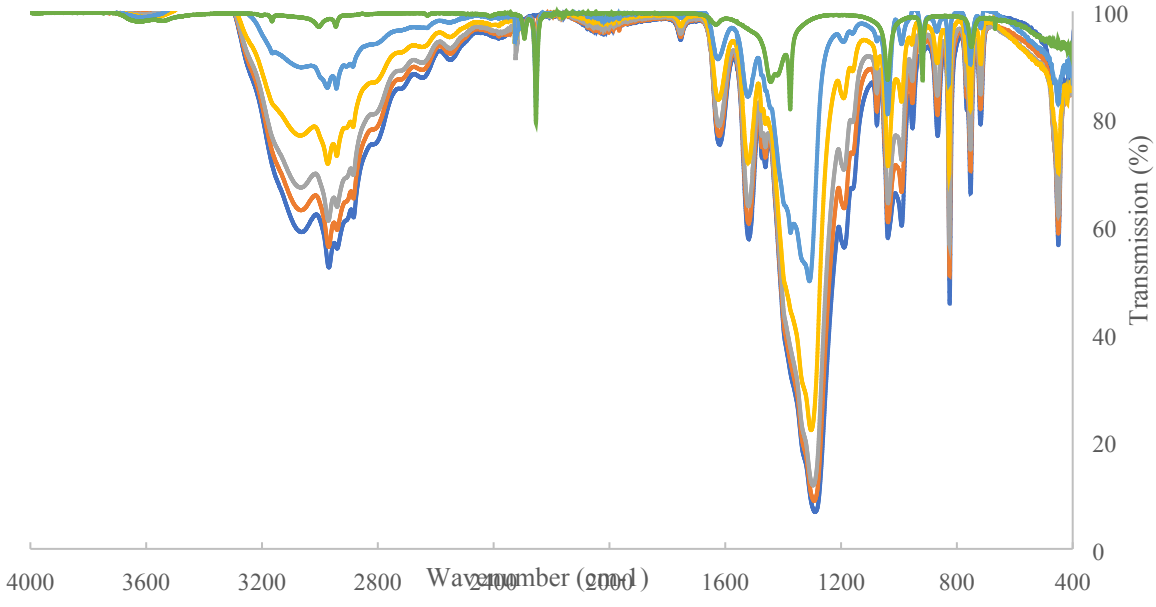

Figure S25. IR spectra of PAN-acetonitrile mixtures. Acetonitrile mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

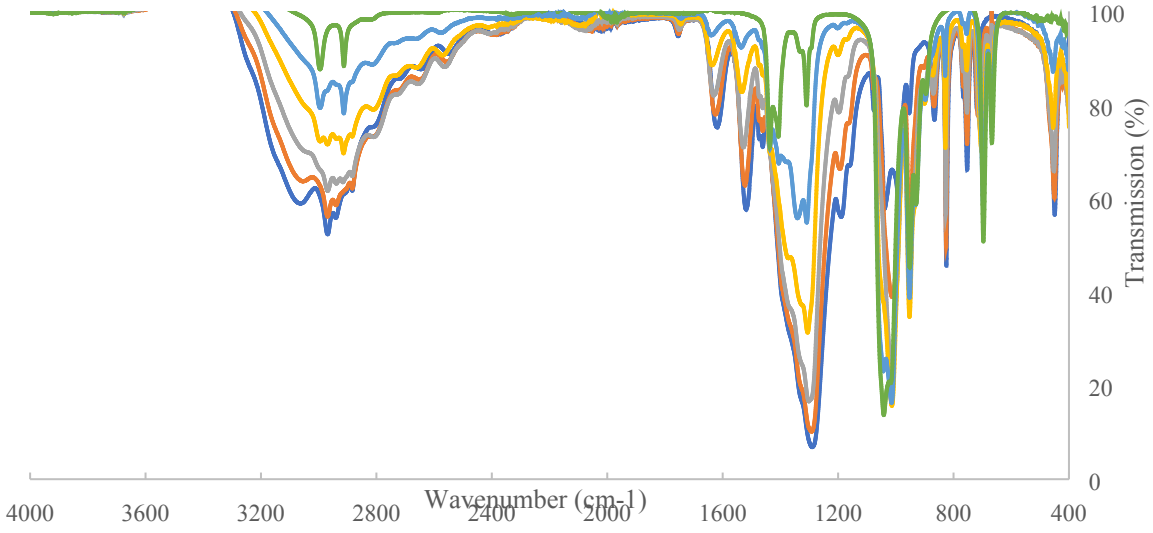

Figure S26. IR spectra of PAN-DMSO mixtures. DMSO mol fraction was 0, 0.25, 0.5, 0.75, 0.9 and 1 from bottom to top

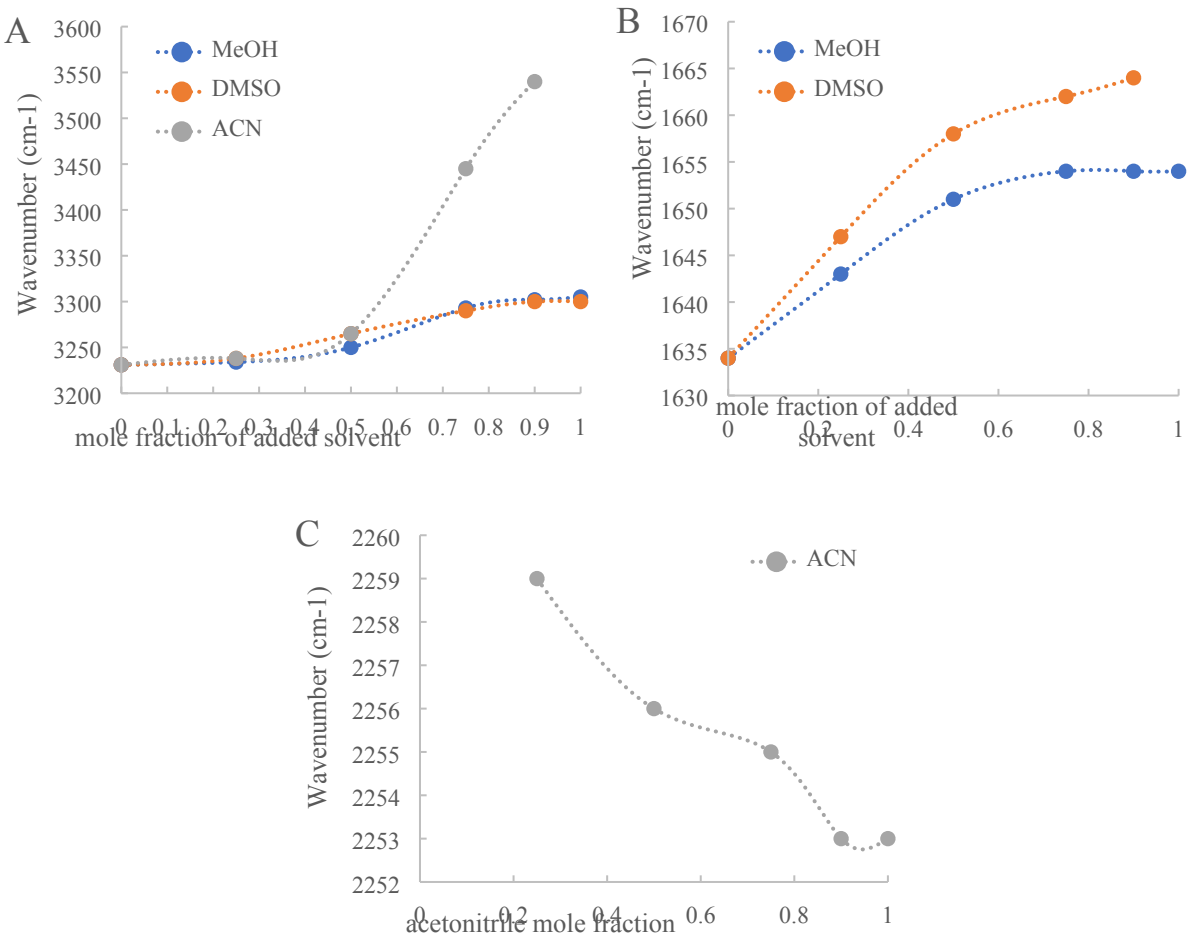

Figure S27. Vibrational band shifts in water-solvent mixtures. A. O-H stretching, B. O-H bending and C. C≡N stretching. Dashed lines are a guide to the eye.

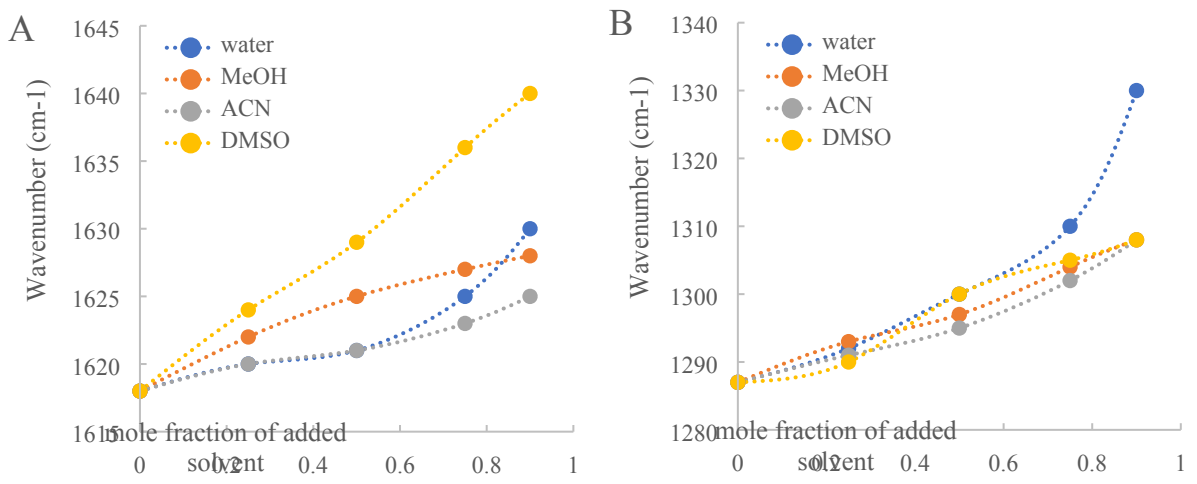

Figure S28. Vibrational band shifts in PAN-solvent mixtures. A. N-H bending and B. NO_3 asymmetric stretching. Dashed lines are a guide to the eye.

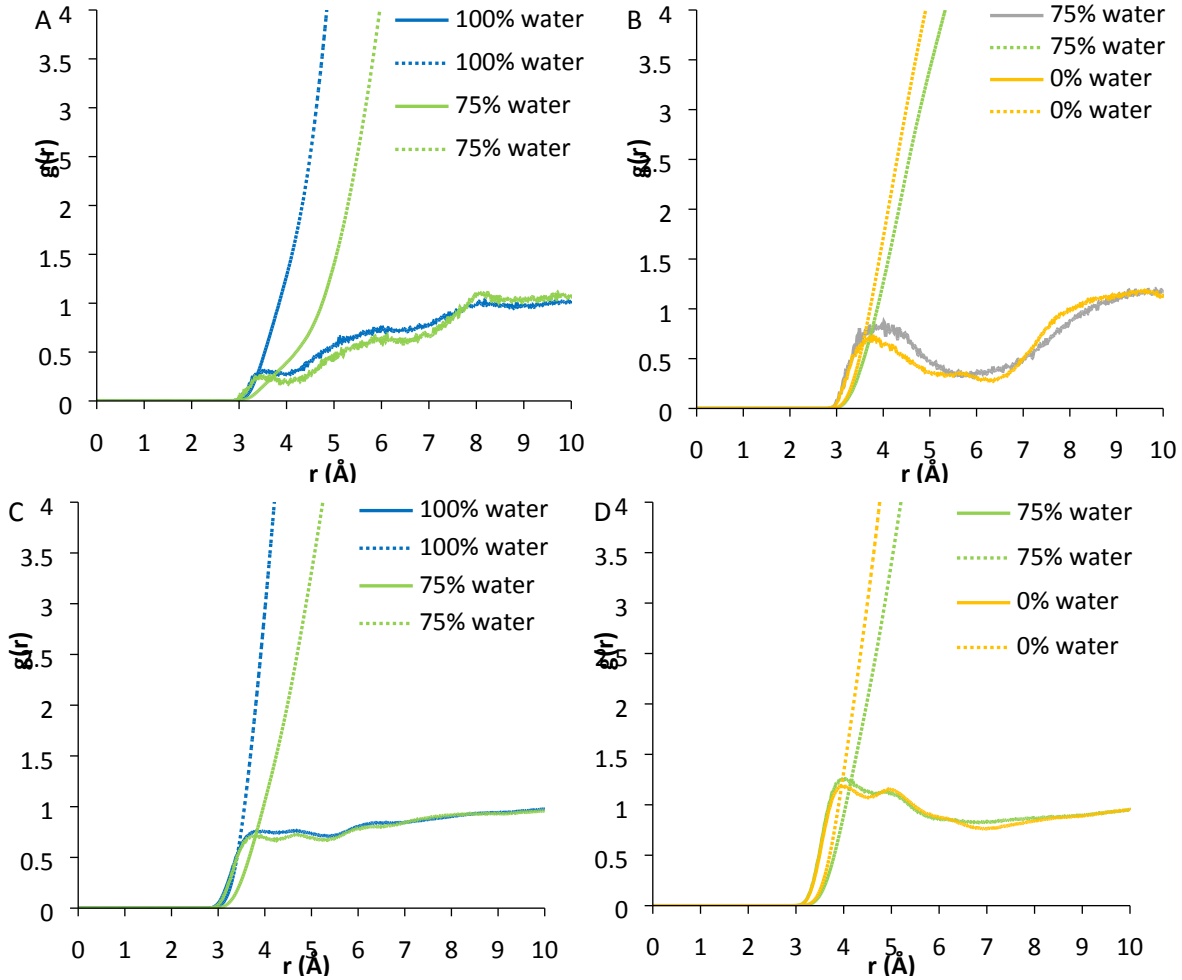

Figure S29. Radial distribution functions for the pairwise interactions between RD30 and solvents. A. RD30 nitrogen with water oxygen. B. RD30 nitrogen with ethylammonium nitrogen. C. RD30 carbon with water oxygen. D. RD30 carbon with ethylammonium carbon. The integral of g(r) is shown as a dotted line.

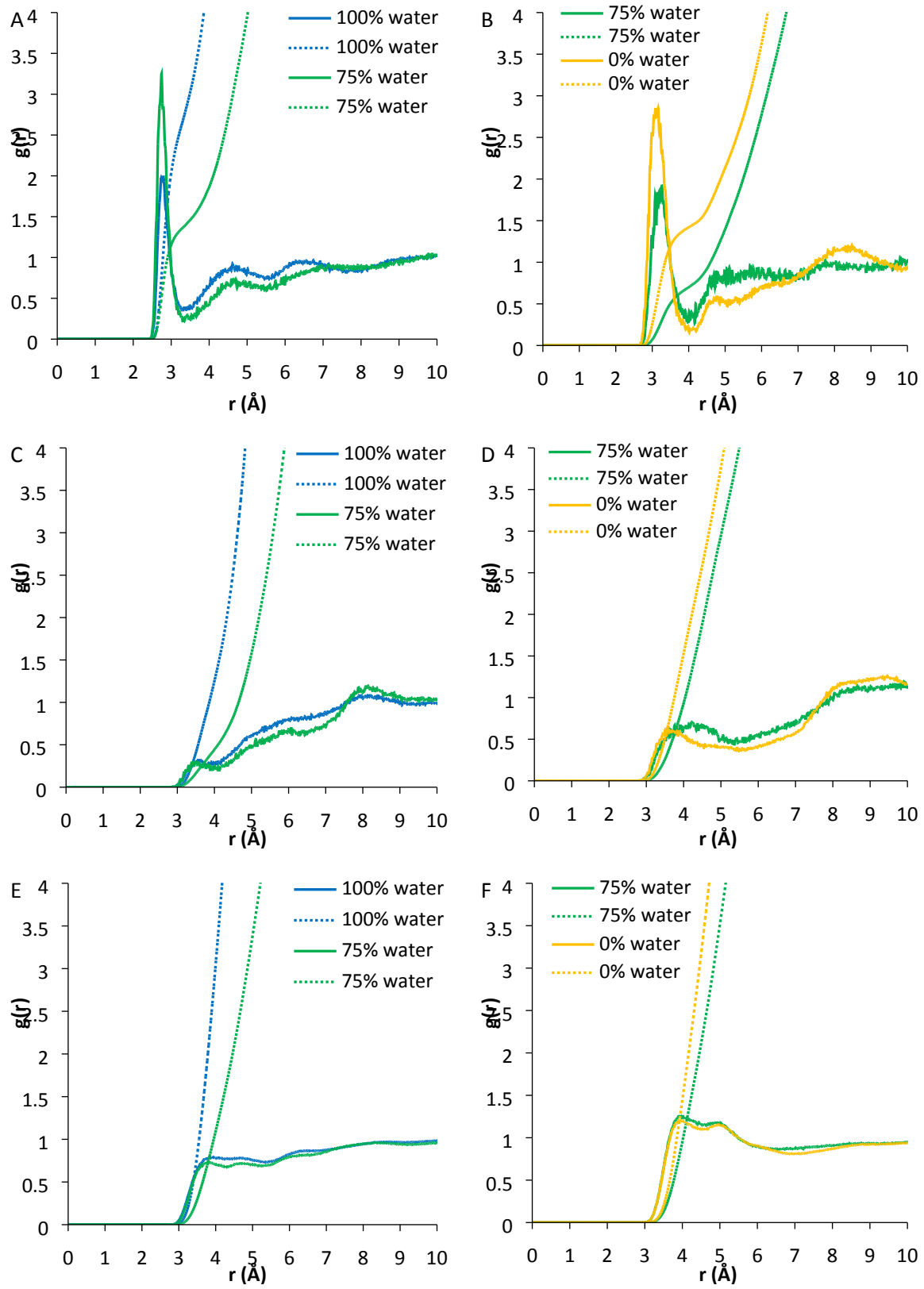

Figure S30. Radial distribution functions for the pairwise interactions between RD33 and solvents. A. RD33 oxygen with water oxygen. B. RD33 oxygen with ethylammonium nitrogen. C. RD33 nitrogen with water oxygen. D. RD33 nitrogen with ethylammonium nitrogen. E. RD33 carbon with water oxygen. F. RD33 carbon with ethylammonium carbon. The integral of g(r) is shown as a dotted line.

Table S8. Estimated number of solvent atoms in the first solvation shell of RD33 atoms based on radial distribution functions.

RD33 atom	Solvent atom	Solvent system (mol %)	Radius of first solvation shell (Å)	# of listed atoms in the first solvation shell
Carbon	Water oxygen	100% water	4.2	4.2
		75% water	4.3	1.6
	Ethylammonium carbon	100% EAN	4.6	3.7
		25% EAN	4.7	2.5
Oxygen	Water oxygen	100% water	3.4	2.7
		75% water	3.3	1.4
	Ethylammonium nitrogen	100% EAN	4.0	1.4
		25% EAN	4.0	0.7
Nitrogen	Water oxygen	100% water	4.0	1.2
		75% water	3.9	0.4
	Nitrate oxygen	100% EAN	5.5	5.2
		25% EAN	5.4	3.7

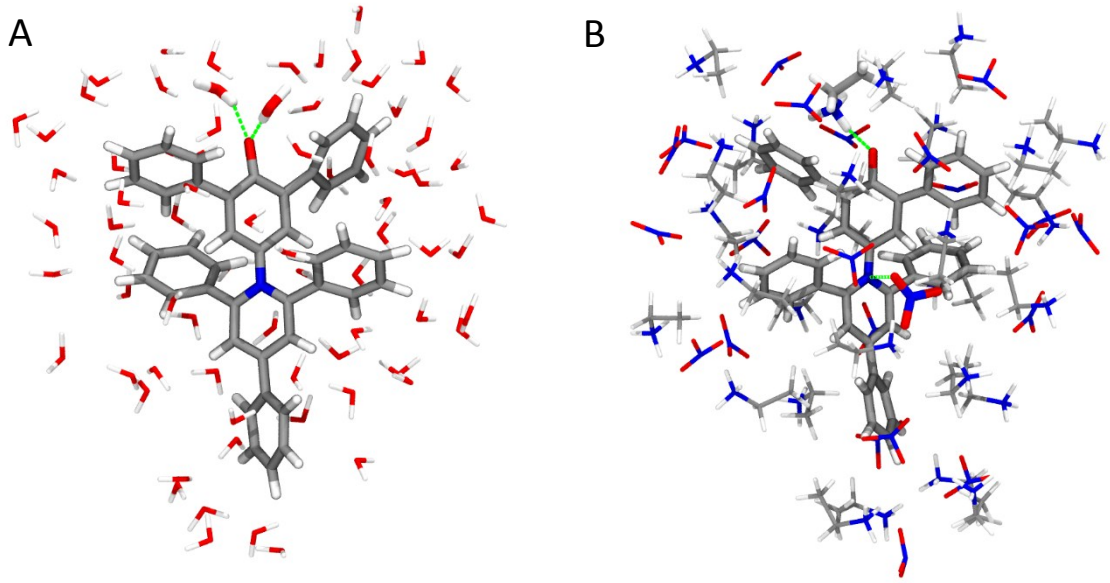

Figure S31. Representative snapshot of RD30 in the first solvation shell of A. water and B. EAN. Oxygen, carbon, nitrogen, and hydrogen are coloured red, grey, blue, and white, respectively. Key interactions are highlighted in green. Only solvent molecules within 4 Å of RD30 are shown.

- **Force Field Parameters for the dyes and solvents**

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 HC      HC          0.00000     0.00000     A      2.50000e-01    1.25520e-01
 N       N           0.00000     0.00000     A      3.25000e-01    7.11280e-01
 HN      HN          0.00000     0.00000     A      2.50000e-01    1.25520e-01
 ON      ON          0.00000     0.00000     A      3.06000e-01    8.78640e-01
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EAM.itp

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    5    CT    1     EAM    CA1     5       0.190000        12.01000
    6    HC    1     EAM    HA4     6       0.060000        1.00800
    7    HC    1     EAM    HA5     7       0.060000        1.00800
    8    N     1     EAM    NA      8       -0.300000       14.01000
    9    HN    1     EAM    HA1     9       0.330000        1.00800
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   11    HN    1     EAM    HA3     11      0.330000        1.00800

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[pairs]

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3	7	1 ;	HA7 - HA5
3	8	1 ;	HA7 - NA
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4	7	1 ;	HA8 - HA5
4	8	1 ;	HA8 - NA
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6	10	1 ;	HA4 - HA2
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7	10	1 ;	HA5 - HA2
7	11	1 ;	HA5 - HA3

[angles]

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[dihedrals] ; propers

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3	1	5	7	3	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000	;	HA7-	CA2-	CA1-	HA5
3	1	5	8	3	0.80333	2.40999	0.00000	-3.21331	0.00000	0.00000	;	HA7-	CA2-	CA1-	NA
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RD3.itp

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4    opls_263    1 RD3   C3       3        -0.1221
5    opls_166    1 RD3   C4       4        0.4652
6    opls_263    1 RD3   C5       5        -0.1221
7    opls_145    1 RD3   C6       6        -0.1793
8    opls_146    1 RD3   H6       6        0.0461
9    opls_520    1 RD3   N        7        0.1992
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11   opls_264    1 RD3   Cl5      9        -0.043
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13   opls_145B   1 RD3   C19      11       0.0877
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17	opls_145	1	RD3	C22	14	-0.1749
18	opls_146	1	RD3	H22	14	0.0768
19	opls_145B	1	RD3	C23	15	0.0877
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27	opls_145	1	RD3	C28	20	-0.1219
28	opls_146	1	RD3	H28	20	0.1216
29	opls_145	1	RD3	C29	21	-0.1208
30	opls_146	1	RD3	H29	21	0.1065
31	opls_145B	1	RD3	C30	22	0.1156
32	opls_145	1	RD3	C31	23	-0.1208
33	opls_146	1	RD3	H31	23	0.1065
34	opls_145	1	RD3	C32	24	-0.1219
35	opls_146	1	RD3	H32	24	0.1216
36	opls_145	1	RD3	C33	25	-0.0776
37	opls_146	1	RD3	H33	25	0.1165
38	opls_145	1	RD3	C34	26	-0.1219
39	opls_146	1	RD3	H34	26	0.1216
40	opls_145	1	RD3	C35	27	-0.1208
41	opls_146	1	RD3	H35	27	0.1065
42	opls_145B	1	RD3	C36	28	0.0969
43	opls_145	1	RD3	C37	29	-0.1311
44	opls_146	1	RD3	H37	29	0.1291
45	opls_145	1	RD3	C38	30	-0.1146
46	opls_146	1	RD3	H38	30	0.1169
47	opls_145	1	RD3	C39	31	-0.0679
48	opls_146	1	RD3	H39	31	0.1118
49	opls_145	1	RD3	C40	32	-0.1146
50	opls_146	1	RD3	H40	32	0.1169
51	opls_145	1	RD3	C41	33	-0.1311
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[angles]
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[dihedrals]
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