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Electronic Supplementary Material (ESI)

Structure, Dynamics and Free Energy Analysis of 5-Hydroxymethylfurfural in Aprotic Solvents and Imidazolium Ionic liquids using All Atom Molecular Dynamics Simulations

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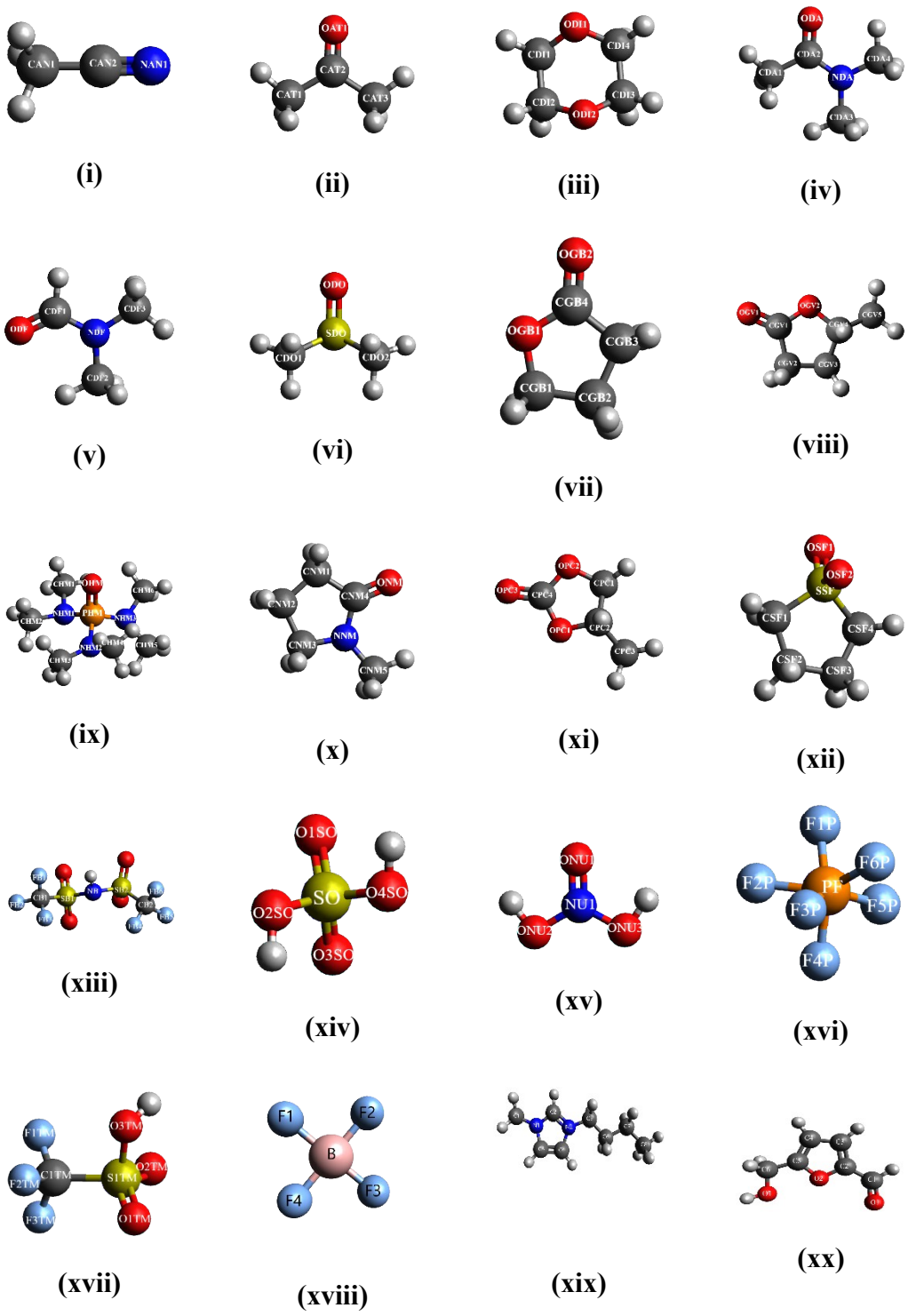


Figure S1. Atomistic labeling of the molecules (i) AN, (ii) AT, (iii) DI, (iv) DMA, (v) DMF, (vi) DMSO, (vii) GBL, (viii) GVL, (ix) HMPA, (x) NMP, (xi) PC, (xii) SF, (xiii) HSO_4, (xiv) BF_4, (xv) BIS, (xvi) NO_3, (xvii) PF_6, (xviii) TFS, (xix) BMIM, (xx) 5-HMF.

Table S1. Partial atomic charges of the molecules.

GBL		**GVL**		**HMPA**	
CGB1	0.161848	CGV1	0.845146	PHM	1.057563
CGB2	-0.06736	CGV2	-0.27009	OHM	-0.75665
CGB3	-0.16096	CGV3	-0.07694	NHM1	-0.12862
H1G2	0.032333	H1V2	0.086346	NHM2	-0.18255
H2G2	0.05191	H2V2	0.09768	NHM3	-0.12762
CGB4	0.859377	CGV4	0.509778	CHM1	-0.30323
H1G3	0.069726	H1V3	0.028952	H1H1	0.139238
H2G3	0.060051	H2V3	0.051093	H2H1	0.098193
OGB1	-0.47683	CGV5	-0.53838	H3H1	0.093038
H1G1	0.054042	H1V5	0.151306	CHM2	-0.23919
H2G1	0.043679	H2V5	0.16014	H1H2	0.069869
OGB2	-0.62782	H3V5	0.11779	H2H2	0.079451
SF		OGV1	-0.61102	H3H2	0.104463
		OGV2	-0.53064	CHM3	-0.30777
SSF	1.342063	H1V4	-0.01515	H1H3	0.139928
OSF1	-0.69498	**DMF**		H2H3	0.09339
OSF2	-0.69025			H3H3	0.099653
CSF1	-0.25994	NDF	0.016461	CHM4	-0.22964
CSF2	-0.05444	CDF1	0.427893	H1H4	0.099558
H1S1	0.106174	CDF2	-0.41342	H2H4	0.077871
H2S1	0.117359	H1F2	0.132658	H3H4	0.069192
CSF3	-0.06013	H2F2	0.140526	CHM5	-0.27245
H1S2	0.057926	H3F2	0.141401	H1H5	0.112622
H2S2	0.055877	CDF3	-0.23803	H2H5	0.08493
CSF4	-0.24674	H1F3	0.132161	H3H5	0.104129
H1S3	0.054867	H2F3	0.09126	CHM6	-0.28826
H2S3	0.057309	H3F3	0.092312	H1H6	0.087805
H1S4	0.103394	ODF	-0.56862	H2H6	0.115381
H2S4	0.111513	H1F1	0.045391	H3H6	0.109682

AT		DI		DMA		AN	
CAT1	-0.56424	CDI1	0.216397	CDA1	0.737587	CAN1	-0.49882
CAT2	0.865241	CDI2	0.200483	CDA2	-0.52853	CAN2	0.483921
H1C1	0.141075	ODI1	-0.47104	H1M1	0.141246	NAN1	-0.52178
H2C1	0.140945	H1D1	0.014454	H2M1	0.140015	HCA1	0.178802
H3C1	0.149522	H2D1	0.013278	H3M1	0.155961	HCA2	0.178862
CAT3	-0.55977	ODI2	-0.47223	ODA	-0.63731	HCA3	0.179021
H1C3	0.148088	H1D2	-0.01045	NDA	-0.10159		
H2C3	0.139783	H2D2	0.040236	CDA3	-0.32662		
H3C3	0.140176	CDI4	0.182856	H1M3	0.147896		
OAT1	-0.60082	CDI3	0.215472	H2M3	0.113061		
NMP		H1D4	0.046087	H3M3	0.117772		
		H2D4	-0.00468	CDA4	-0.31858		
CNM1	-0.23553	H1D3	0.014631	H1M4	0.118137		
CNM2	-0.10924	H2D3	0.014513	H2M4	0.116657		
CNM3	-0.60687	**PC**		H3M4	0.124299		
H1N2	0.058132			**DMSO**			
H2N2	0.06433	CPC1	0.203753				
NNM	-0.81736	CPC2	0.448712	SDO	0.40293		
H1N3	0.069911	CPC3	-0.54855	CDO1	-0.45682		
H2N3	0.061749	H1P3	0.161491	H1DA	0.188754		
CNM4	0.644409	H2P3	0.180395	H2DA	0.151838		
H1N1	0.096702	H3P3	0.109941	H3DA	0.188012		
H2N1	0.094362	OPC1	-0.55326	CDO2	-0.44741		
CNM5	-0.36696	H1P2	0.009534	H1DB	0.185957		
H1N5	0.163923	OPC2	-0.52824	H2DB	0.185383		
H2N5	0.11867	H1P1	0.04714	H3DB	0.149664		
H3N5	0.121783	H2P1	0.030731	ODO	-0.54831		
ONM	-0.63983	CPC4	1.071014				
		OPC3	-0.63267				

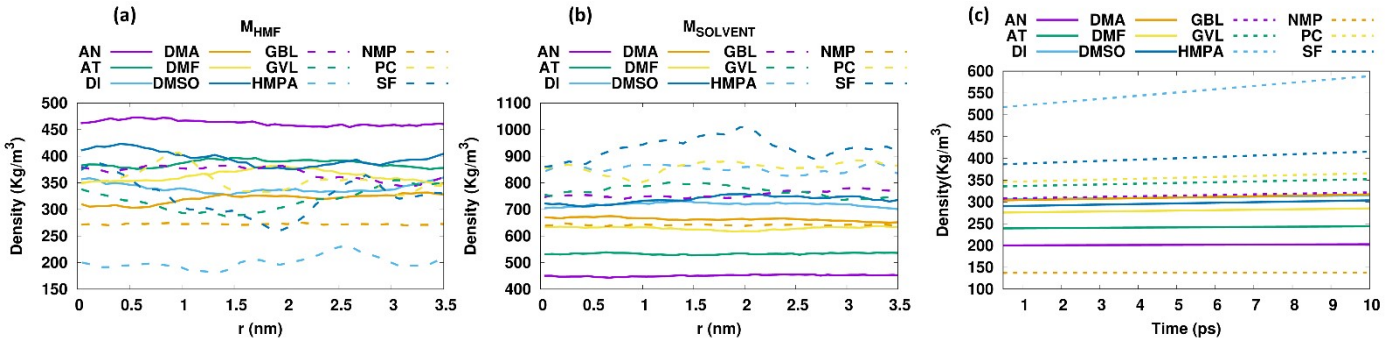


Figure S2. System density profiles of (a) 5-HMF and (b) Solvents at different combinations of solvent systems, with respect to distance (nm) and (c) system density with respect to time (ps).

Table S2. The radius of gyration (Rg) values at different combinations of solvent systems. The standard deviation values are given in parentheses.

Simulated system	Rg (nm)	
AN	1.801	(0.085191)
DMSO	1.879	(0.044227)
AT	1.901	(0.029263)
GBL	1.933	(0.062752)
DMF	1.936	(0.023625)
PC	1.967	(0.032642)
DI	1.978	(0.050074)
SF	1.995	(0.023584)
GVL	2.013	(0.026021)
DMA	2.016	(0.021775)
NMP	2.140	(0.02958)
HMPA	2.367	(0.014023)

Table S3. RDF_COM coordination number (N_{cr}) with different combinations of solvent systems.

Mixed system in the presence of 5-HMF	Pairs	Peak Position	Coordination numbers\N_{cr}
AN	**AN-AN**	0.48	2.569
	AN-5-HMF	0.53	0.933
	5-HMF-5-HMF	0.66	2.125
DMSO	**DMSO-DMSO**	0.53	2.952
	DMSO-5-HMF	0.56	1.079
	5-HMF-5-HMF	0.64	1.546
AT	**AT-AT**	0.51	2.163
	AT-5-HMF	0.54	0.831
	5-HMF-5-HMF	0.64	1.497
GBL	**GBL-GBL**	0.56	3.234
	GBL-5-HMF	0.59	1.213
	5-HMF-5-HMF	0.64	1.465
DMF	**DMF-DMF**	0.55	2.811
	DMF-5-HMF	0.57	1.016
	5-HMF-5-HMF	0.65	1.475
PC	**PC-PC**	0.46	0.712
	PC-5-HMF	0.63	1.497
	5-HMF-5-HMF	0.60	1.090
DI	**DI-DI**	0.57	3.051
	DI-5-HMF	0.54	0.698
	5-HMF-5-HMF	0.66	1.475
SF	**SF-SF**	0.51	0.844
	SF-5-HMF	0.59	1.033
	5-HMF-5-HMF	0.62	1.158
GVL	**GVL-GVL**	0.55	2.058
	GVL-5-HMF	0.62	1.262

	5-HMF-5-HMF	0.66	1.528
DMA	**DMA-DMA**	0.40	0.140
	DMA-5-HMF	0.60	1.118
	5-HMF-5-HMF	0.65	1.253
NMP	**NMP-NMP**	0.60	3.984
	NMP-5-HMF	0.56	0.828
	5-HMF-5-HMF	0.64	1.355
HMPA	**HMPA-HMPA**	0.72	3.239
	HMPA-5-HMF	0.55	0.344
	5-HMF-5-HMF	0.65	0.713

Table S4. Iso-surface value of a mixed system.

Mixed system	Iso-surface value	Iso-surface range
AN-5-HMF	3.00176	0 - 4.61809
DMSO-5-HMF	2.48059	0 - 4.13432
AT-5-HMF	2.00097	0 - 3.2574
GBL-5-HMF	0.092729	0 - 0.188145
DMF-5-HMF	1.27001	0 - 3.48631
PC-5-HMF	0.061868	0 - 0.120298
DI-5-HMF	1.17296	0 - 3.28428
SF-5-HMF	0.058163	0 - 0.135714
GVL-5-HMF	0.032946	0 - 0.079526
DMA-5-HMF	2.11172	0 - 3.14511
NMP-5-HMF	0.033501	0 - 0.74446
HMPA-5-HMF	0.041592	0 - 0.102156

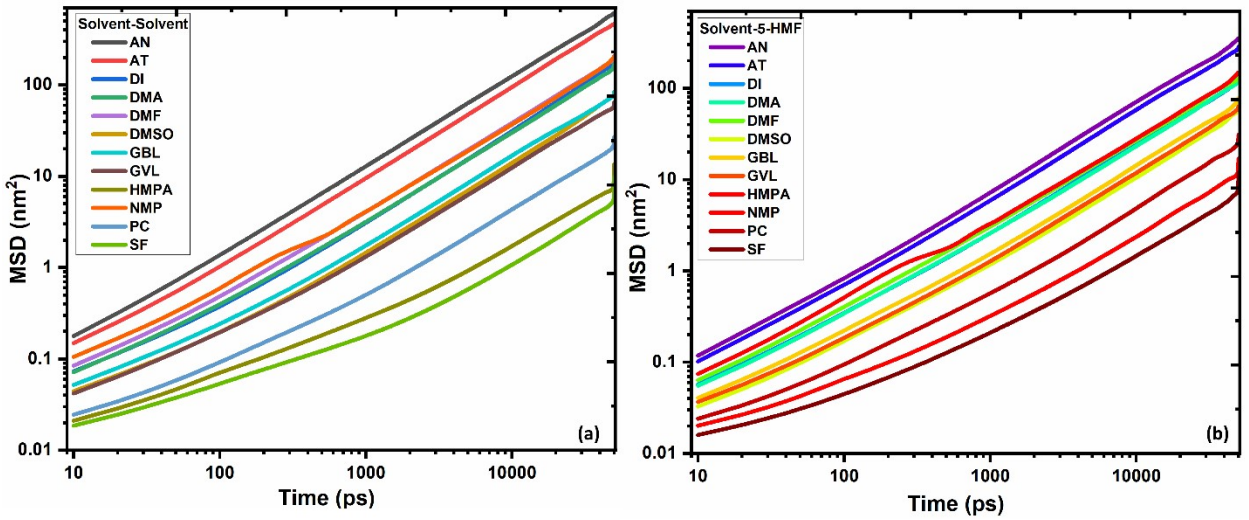


Figure S3. Mean square displacement on a log-log scale of 5-HMF with (a) different solvent systems, and (b) 5-HMF.

Table S5. Diffusion behavior of solvents and 5-HMF in the system. The standard deviation values are given in parentheses.

Self-diffusivity, $D*10^5$; cm^2/s					Literature, $D*10^5$; cm^2/s
Mixed system	**Solvent**		**HMF**		**Pure Solvent**
AN	1.9811	(0.03)	1.0532	(0.0002)	4.31[1] [a]
DMSO	0.2561	(0.0426)	0.1794	(0.0145)	0.0231[2] [b]
AT	1.5757	(0.0438)	0.8677	(0.0017)	0.0692[3] [c]
GBL	0.2427	(0.0102)	0.2208	(0.021)	0.86[4] [d]
DMF	0.6225	(0.0083)	0.4357	(0.003)	1.28[5] [e]
PC	0.0671	(0.0027)	0.0792	(0.007)	0.52[4] [f]
DI	0.5775	(0.063)	0.3695	(0.0057)	1.091[6] [g]
SF	0.017	(0.0001)	0.0223	(0.0014)	0.0008[7] [h]
GVL	0.1915	(0.016)	0.1962	(0.0061)	-----
DMA	0.5072	(0.0062)	0.3894	(0.0159)	0.03[8] [i]
NMP	0.6247	(0.0367)	0.4458	(0.0055)	0.775[9] [j]
HMPA	0.0246	(0.0027)	0.0384	(0.0011)	0.344[10] [k]

[a] Acetonitrile under various pressures.
[b] DMSO+ water+ poly-acrylonitrile.
[c] CO_2+ water+ acetone.
[d] Pure GBL.
[e] Pure DMF at different temperatures and pressures.
[f] Pure PC.
[g] Water+ dioxane.
[h] Li-BF_4+ sulfolane.
[i] DMA+ hydroxide based ammonium IL+ TEAH+ TPAH+ TBAH.
[j] NMP+ water.
[k] Ethylene glycol+ HMPA.

Table S6. Density values for 5-HMF-Solvent mixtures for excess molar volume (kg/m^3). The

standard deviation values are given in parentheses.

Mixed system	ρ_solvent		ρ_hmf		ρ_system	
AN	451.512	(4.6317)	445.54	(6.833)	897.052	(11.4647)
DMSO	725.603	(1.344)	404.547	(1.3662)	1130.15	(2.7102)
AT	530.968	(2.996)	381.609	(6.4105)	912.577	(9.4065)
GBL	746.99	(1.1772)	377.877	(1.2108)	1124.867	(2.388)
DMF	634.519	(5.886)	346.799	(1.0604)	981.318	(6.9464)
PC	859.946	(2.111)	349.638	(1.942)	1209.584	(4.053)
DI	698.592	(8.959)	362.072	(1.038)	1060.664	(9.997)
SF	877.052	(3.708)	362.221	(3.296)	1239.273	(7.004)
GVL	747.437	(2.159)	343.137	(2.225)	1090.574	(4.384)
DMA	665.218	(6.042)	312.356	(8.1892)	977.574	(14.2312)
NMP	638.049	(1.925)	271.085	(1.328)	909.134	(3.253)
HMPA	824.01	(1.5127)	199.578	(1.09)	1023.588	(2.6027)

Table S7. Excess molar volume (m^3/Kmol) in a mixed system.

Mixed system	V_m^E
AN	-0.06948
DMSO	-0.07894
AT	-0.08238
GBL	-0.08444
DMF	-0.08931
PC	-0.08984
DI	-0.08964
SF	-0.09163
GVL	-0.09458
DMA	-0.10007
NMP	-0.11637

HMPA	-0.15897

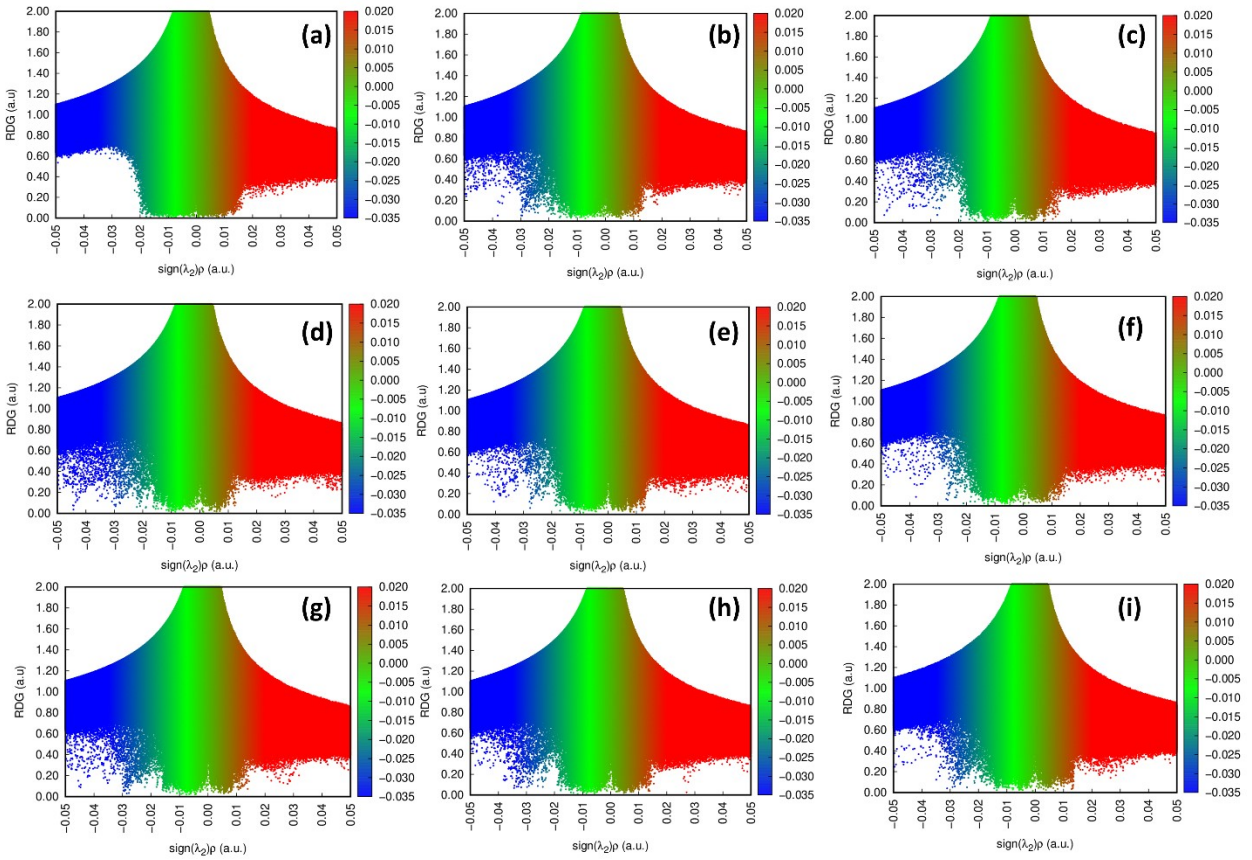


Figure S4: RDG plot versus the electron density multiplied by the sign of the second Hessian eigenvalue represented by (a) AN, (b) AT, (c) DI, (d) DMA, (e) DMF, (f) GBL, (g) GVL, (h)PC, and (i) SF.

Table S8. Free-energy solvation in the mixture and ionic liquid.

Free-energy solvation						
Mixed system	**Electrostatic interaction (KJ/mol)**		**Van der Waals interaction (KJ/mol)**		**Total ΔG**	
	Value	**Std. deviation**	**Value**	**Std. deviation**	**Value**	**Std. deviation**
Aprotic solvent + 5-HMF						
AN	-147.26	0.16	-18.08	0.24	-165.34	0.4
DMSO	-151.95	0.27	-14.31	0.32	-166.26	0.59
AT	-146.09	0.17	-19.28	0.18	-165.37	0.35
GBL	-148.58	0.38	-16.94	0.23	-165.52	0.61
DMF	-147.75	0.13	-18.37	0.19	-166.12	0.32

PC	-148.77	0.2	-15.5	0.19	-164.27	0.39
DI	-144.96	0.17	-19.89	0.14	-164.85	0.31
SF	-151.66	0.19	-14.4	1.22	-166.06	1.41
GVL	-147.62	0.12	-17.77	0.28	-165.39	0.4
DMA	-147.1	0.18	-18.77	0.15	-165.87	0.33
NMP	-147.47	0.15	-18.25	0.13	-165.72	0.28
HMPA	-146.17	0.67	-20.54	0.69	-166.71	1.36
5-HMF + [BMIM] + Different anions						
BF_4	-151.44	0.23	-12.86	1.55	-164.3	1.78
BIS	-147.72	0.48	-18.2	1.99	-165.92	2.47
HSO_4	-150.06	0.41	-24.44	0.59	-174.5	1
NO_3	-152.42	0.32	-15.07	2.03	-167.49	2.35
PF_6	-154.95	0.91	-21.04	1.18	-175.99	2.09
TFS	-149.05	0.26	-15.7	2.08	-164.75	2.34

Table S9: Partition coefficient (log P) of solvents with 5-HMF and their literature report data.

Solvents	**BF4**	**BIS**	**HSO4**	**NO3**	**PF6**	**TFS**	**Literature report**
AN	0.18	-0.10	-1.59	-0.37	-1.85	0.10	0.43[9] [l]
DMSO	0.34	0.06	-1.43	-0.21	-1.69	0.26	-1.35[11] [m]
AT	0.19	-0.10	-1.59	-0.37	-1.85	0.11	-------
GBL	0.21	-0.07	-1.56	-0.34	-1.82	0.13	-0.64[12] [n]
DMF	0.32	0.03	-1.46	-0.24	-1.72	0.24	-1.01[11] [o]
PC	-0.01	-0.29	-1.78	-0.56	-2.04	-0.08	------
DI	0.10	-0.19	-1.68	-0.46	-1.94	0.02	-0.27[10] [p]
SF	0.31	0.02	-1.47	-0.25	-1.73	0.23	-0.77[15] [q]
GVL	0.19	-0.09	-1.59	-0.37	-1.85	0.11	-0.27[13] [r]
DMA	0.27	-0.01	-1.50	-0.28	-1.76	0.19	-0.77[11] [s]
NMP	0.25	-0.03	-1.53	-0.31	-1.79	0.17	0.88[14] [t]
HMPA	0.42	0.14	-1.36	-0.14	-1.62	0.34	0.28[11] [u]

[l] Mixture of chloroform+ water+ acetonitrile

[m] Mixture of EC_{50}+ DMSO.

[n] Mixture of allyl-amine+ water+ GBL

[o] Mixture of EC_{50}+ DMF.

[p] Mixture of glycerol+ water+ 1,4-dioxane+ o-

[q] Mixture of di-isopropanol-amine+ hydroponic acid+ SF.

[r] Mixture of syringic acid+ ferulic acid+ aqueous solution+ GVL.

[s] Mixture of EC_{50}+ DMA.

[t] Mixture of water+ NMP

[u] Mixture of EC_{50}+ HMPA.

Solvents	BF_4	BIS	HSO_4	NO_3	PF_6	TFS
AN	0.18	-0.10	-1.59	-0.37	-1.85	0.10
DMSO	0.34	0.06	-1.43	-0.21	-1.69	0.26
AT	0.19	-0.10	-1.59	-0.37	-1.85	0.11
GBL	0.21	-0.07	-1.56	-0.34	-1.82	0.13
DMF	0.32	0.03	-1.46	-0.24	-1.72	0.24
PC	-0.01	-0.29	-1.78	-0.56	-2.04	-0.08
DI	0.10	-0.19	-1.68	-0.46	-1.94	0.02
SF	0.31	0.02	-1.47	-0.25	-1.73	0.23
GVL	0.19	-0.09	-1.59	-0.37	-1.85	0.11
DMA	0.27	-0.01	-1.50	-0.28	-1.76	0.19
NMP	0.25	-0.03	-1.53	-0.31	-1.79	0.17
HMPA	0.42	0.14	-1.36	-0.14	-1.62	0.34

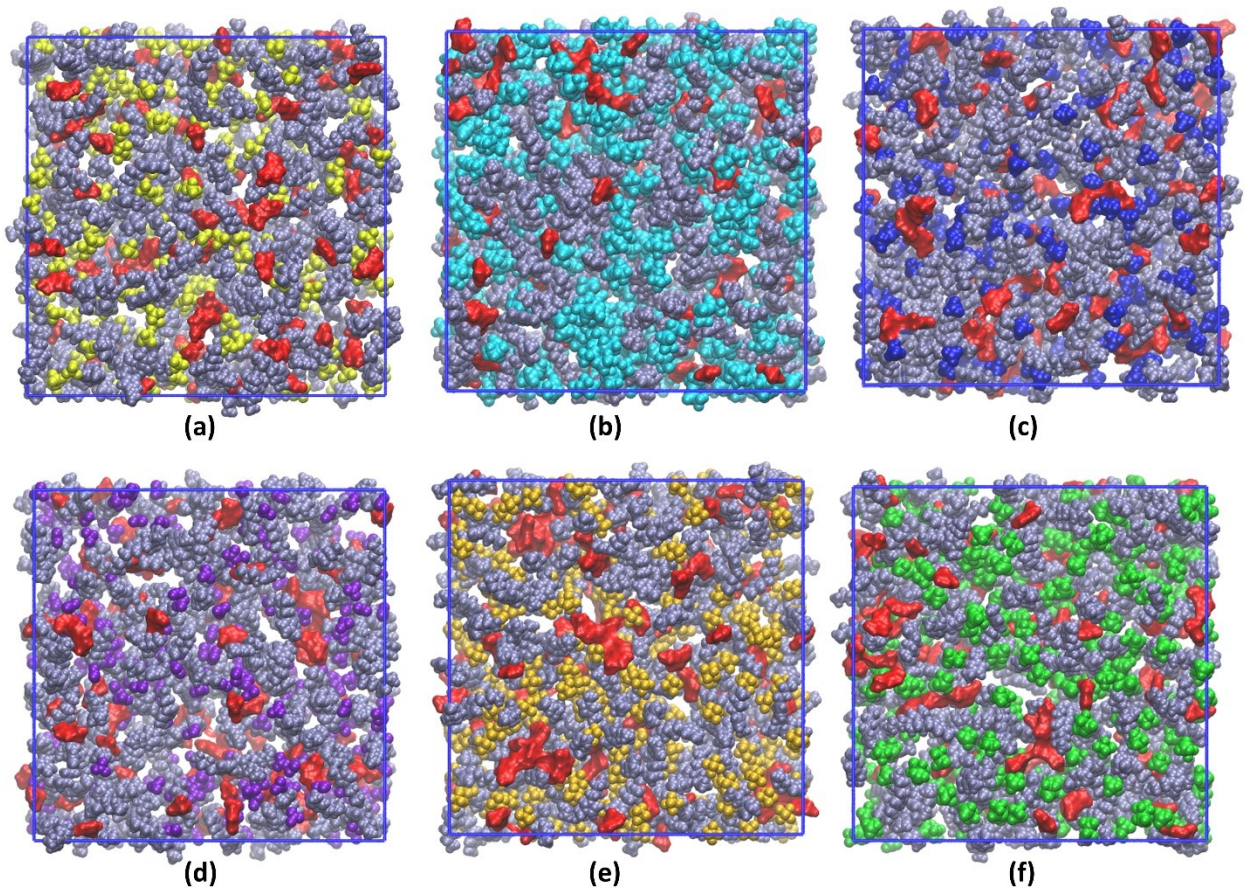


Figure S5. Snapshots of initial systems with different combinations of IL in single [5-HMF] shown (a) 1HMF_[BMIM]_[BF_4], (b) 1HMF_[BMIM]_[BIS], (c) 1HMF_[BMIM]_[HSO_4], (d) 1HMF_[BMIM]_[NO_3], (e) 1HMF_[BMIM]_[PF_6], and (f) 1HMF_[BMIM]_[TFS]. Color codes: HMF- red, [BMIM] – ice blue, BF_4- yellow2, BIS- cyan2, HSO_4- blue3, NO_3- violet2, PF_6- orange3, and TFS-green2.

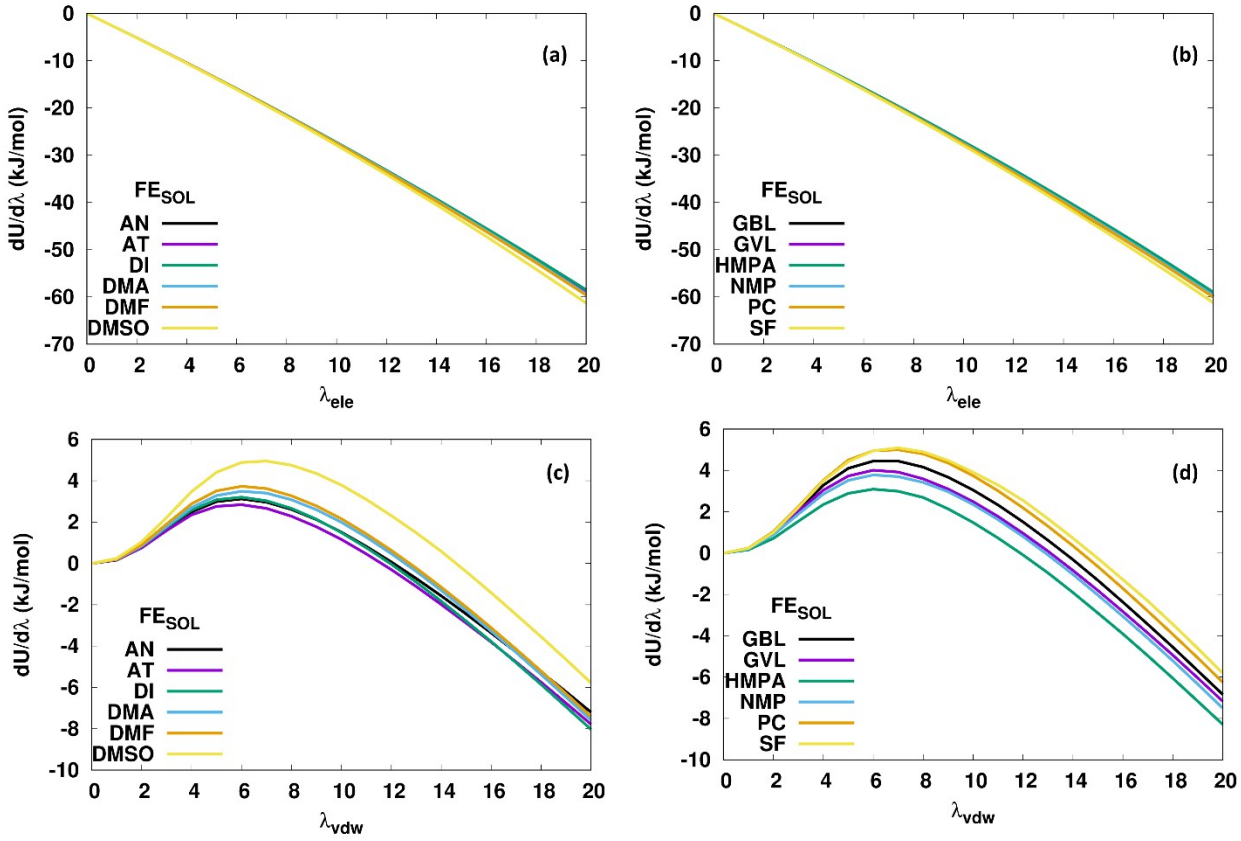
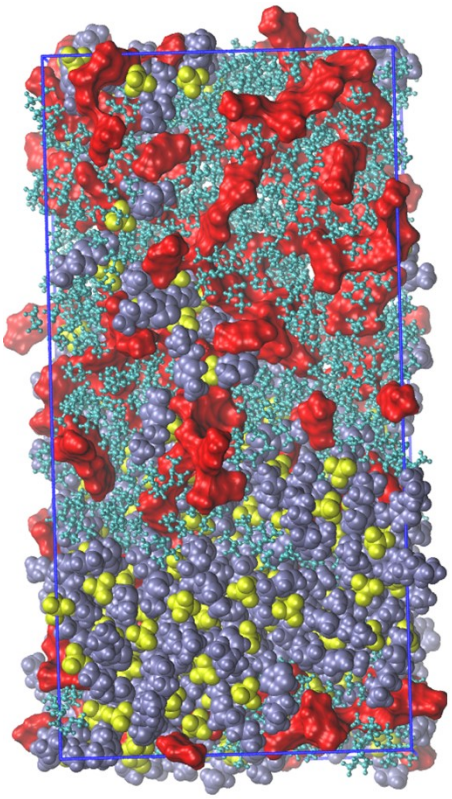
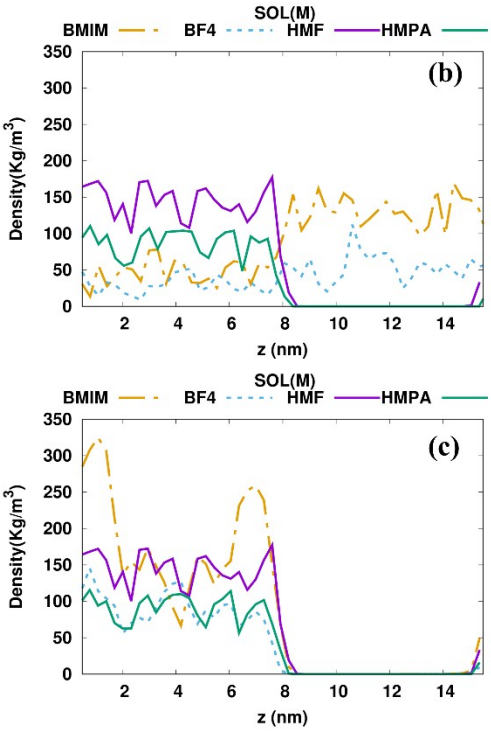
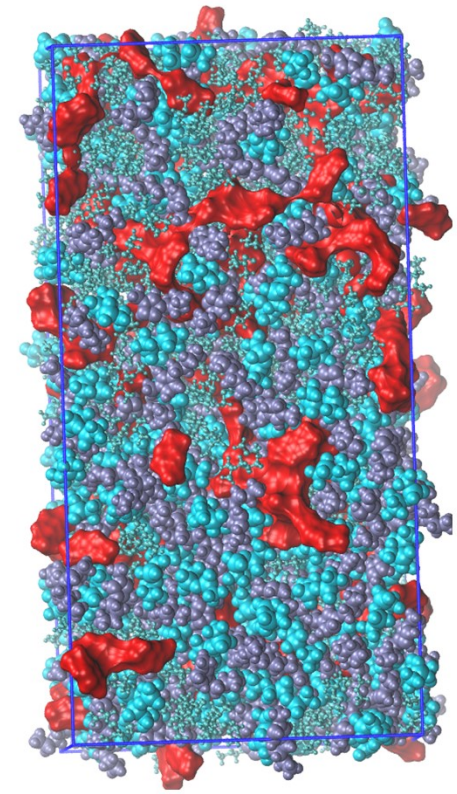


Figure S6. The dU/dλ as a function of (a) λ_{ele} for 5-HMF, (b) λ_{vdw} for 5-HMF in the solvents system.

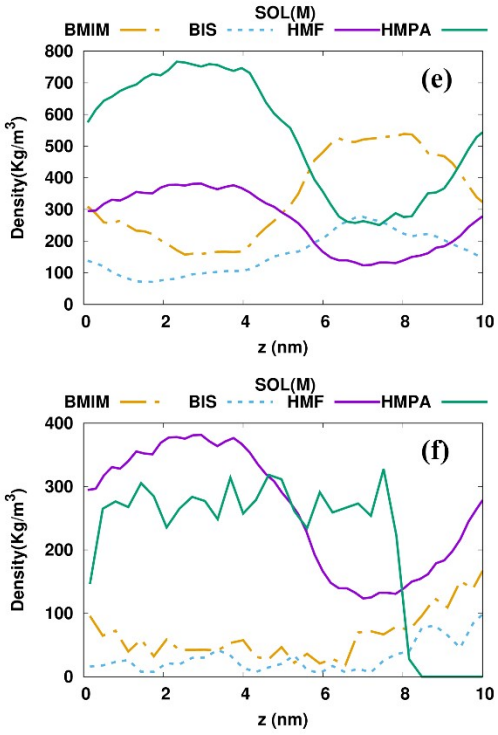


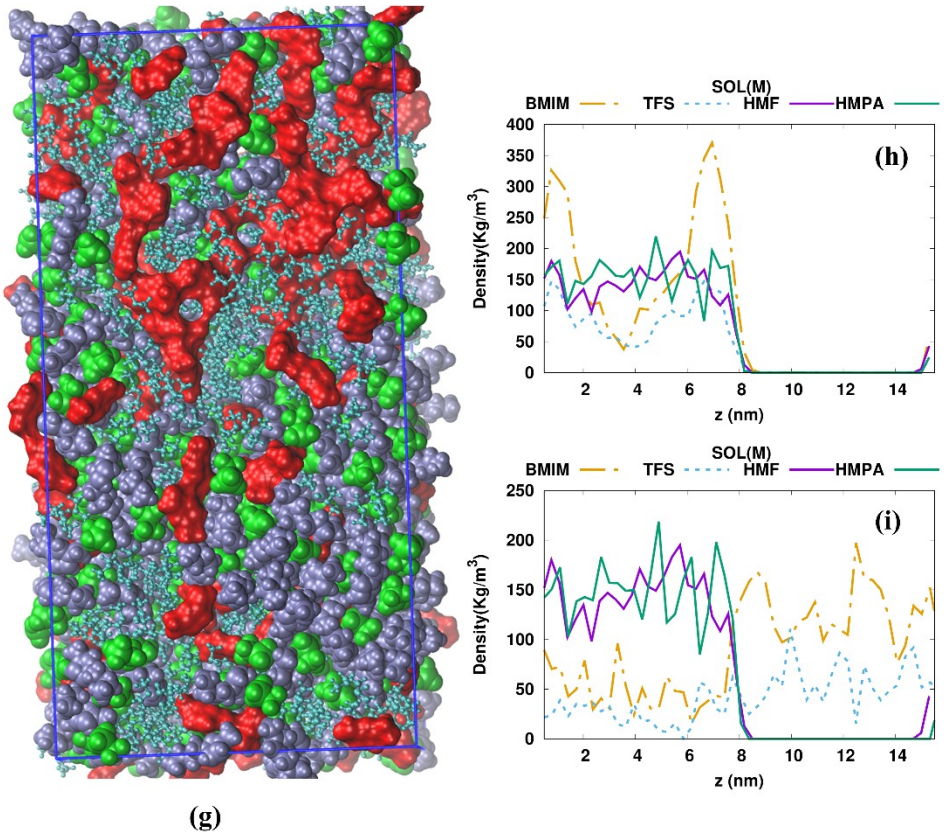
(a)


SOL(M)
BMIM
BF4
HMF
HMPA
(b)
Density(Kg/m3)
z (nm)
(c)



(d)


SOL(M)
BMIM
BIS
HMF
HMPA
(e)
Density(Kg/m3)
z (nm)
(f)



(g)

Figure S7: Biphasic system of 5-HMF with HMPA solvent with their initial and final mass density distribution (a) 5-HMF_HMPA_[BMIM]_[BF_4], (b) initial mass density of 5-HMF_HMPA_[BMIM]_[BF_4], (c) final mass density of 5-HMF_HMPA_[BMIM]_[BF_4], (d) HMF_HMPA_[BMIM]_[BIS], (e) initial mass density of 5-HMF_HMPA_[BMIM]_[BIS], (f) final mass density of 5-HMF_HMPA_[BMIM]_[BIS] and (g) HMF_HMPA_[BMIM]_[TFS], (h) initial mass density of 5-HMF_HMPA_[BMIM]_[TFS], and (i) final mass density of 5-HMF_HMPA_[BMIM]_[TFS].

Color codes: HMF- red, HMPA- cyan, BF_4- yellow2, BIS- cyan2, TFS-green2.

Table S10. Density (ρ) of biphasic system. The standard deviation values are given in parentheses.

Biphasic system	**Density**	
HMPA_HMF_BMIM_BF_4	1123.97	(2.1073)
HMPA_HMF_BMIM_BIS	1293.09	(2.73175)
HMPA_HMF_BMIM_TFS	1194.77	(5.14705)

References:

(1) Hurle, R. L.; Woolf, L. A. Self-diffusion in liquid acetonitrile under pressure. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1982**, *78* (7), 2233-2238.
(2) Yi, K.; Li, Q. F.; Zhang, L.; Li, N.; Zhou, Y.; Ryu, S. K.; Jin, R. G. Diffusion coefficients of dimethyl sulphoxide (DMSO) and H2O in PAN wet spinning and its influence on morphology of nascent polyacrylonitrile (PAN) fiber. *Journal of Engineered Fibers and Fabrics* **2013**, *8* (1), 155892501300800113.
(3) Bellaire, D.; Großmann, O.; Münnemann, K.; Hasse, H. Diffusion coefficients at infinite dilution of carbon dioxide and methane in water, ethanol, cyclohexane, toluene, methanol, and acetone: A PFG-NMR and MD simulation study. *The Journal of Chemical Thermodynamics* **2022**, *166*, 106691.
(4) Koverga, V. A.; Voroshylova, I. V.; Smortsova, Y.; Miannay, F.-A.; Cordeiro, M. N. D.; Idrissi, A.; Kalugin, O. N. Local structure and hydrogen bonding in liquid γ-butyrolactone and propylene carbonate: A molecular dynamics simulation. *Journal of Molecular Liquids* **2019**, *287*, 110912.
(5) Easteal, A. J.; Woolf, L. A. Self-diffusion and volumetric measurements for N-methylformamide and N, N-dimethylformamide at temperatures from 240 to 313 K and pressures up to 300 MPa. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1985**, *81* (11), 2821-2833.
(6) Holz, M.; Heil, S. R.; Sacco, A. Temperature-dependent self-diffusion coefficients of water and six selected molecular liquids for calibration in accurate 1H NMR PFG measurements. *Physical Chemistry Chemical Physics* **2000**, *2* (20), 4740-4742.
(7) Dokko, K.; Watanabe, D.; Ugata, Y.; Thomas, M. L.; Tsuzuki, S.; Shinoda, W.; Hashimoto, K.; Ueno, K.; Umebayashi, Y.; Watanabe, M. Direct evidence for Li ion hopping conduction in highly concentrated sulfolane-based liquid electrolytes. *The Journal of Physical Chemistry B* **2018**, *122* (47), 10736-10745.
(8) Reddy, T. D. N.; Mallik, B. S. Nanostructure domains, voids, and low-frequency spectra in binary mixtures of N, N-dimethylacetamide and ionic liquids with varying cationic size. *RSC advances* **2020**, *10* (3), 1811-1827.
(9) Ambrosone, L.; D'Errico, G.; Sartorio, R.; Vitagliano, V. Analysis of velocity cross-correlation and preferential solvation for the system N-methylpyrrolidone–water at 20° C. *Journal of the Chemical Society, Faraday Transactions* **1995**, *91* (9), 1339-1344.
(10) Rodnikova, M.; Idiyatullin, Z. S.; Barthel, J.; Solonina, I.; Sirotkin, D. Self-diffusion of molecules in ethylene glycol solutions of dimethyl sulfoxide. *Journal of Molecular Liquids* **2017**, *248*, 898-901.