SUPPORTING INFORMTION

Probing the Heterogeneity of Molecular Level Organization of Ionic Liquids: A Comparative Study Using Neutral Nile Red and Cationic Nile Blue Sulfate as Fluorescent Probes, for Butyrolactam-based Protic Ionic Liquids

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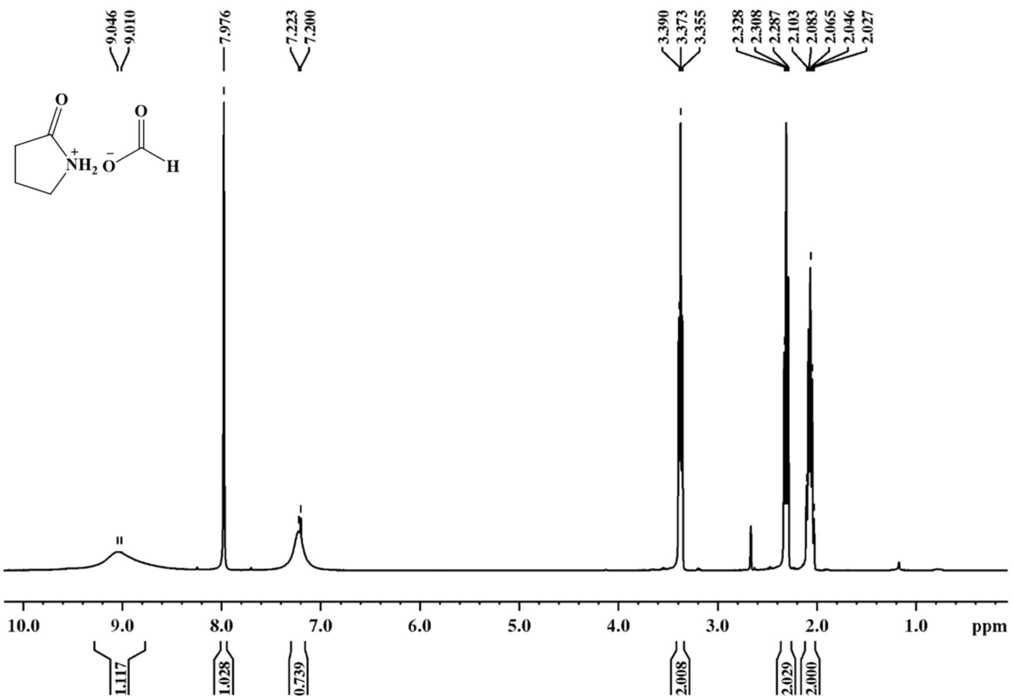

Fig. S1. ^{1}H NMR spectrum of BTF ionic liquid in $CDCl_3$ solvent

^{1}H NMR ($CDCl_3$, δ ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.97 (s, 1H),7.22 (d, J = 8.9 Hz, 1H), 3.35 (t, J = 7.0 Hz, 2H), 2.28 (t, J = 8.1 Hz, 2H), 2.10 – 1.99 (m, 2H)

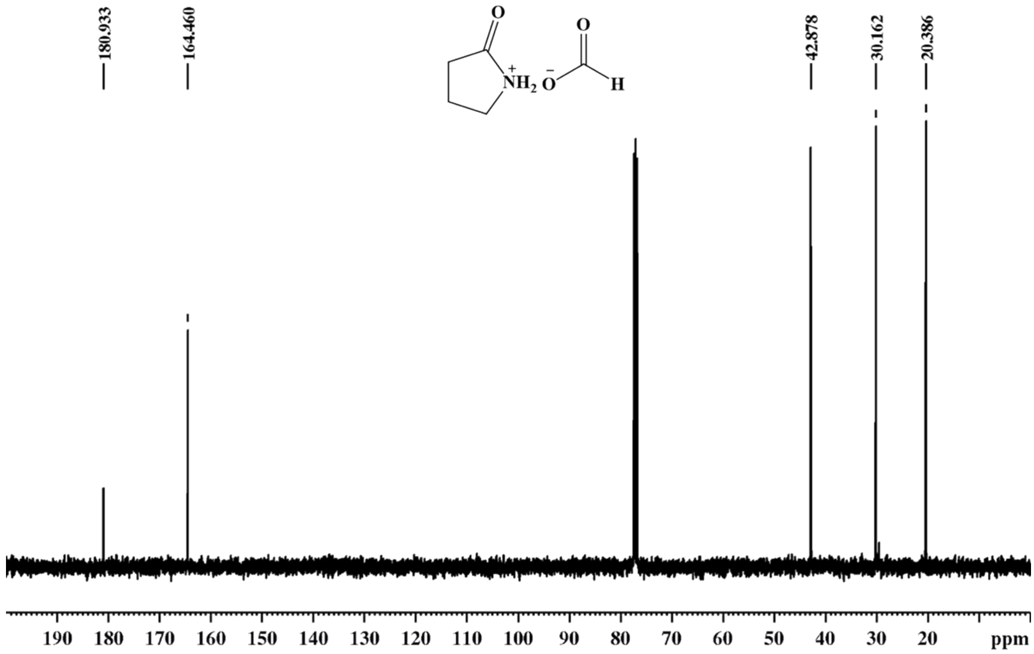

Fig. S2. ^{13}C NMR spectrum of BTF ionic liquid in $CDCl_3$ solvent

^{13}C NMR ($CDCl_3$, δ ppm) = 180.93 (s), 164.46 (s), 42.87 (s), 30.16 (s), 20.38 (s)

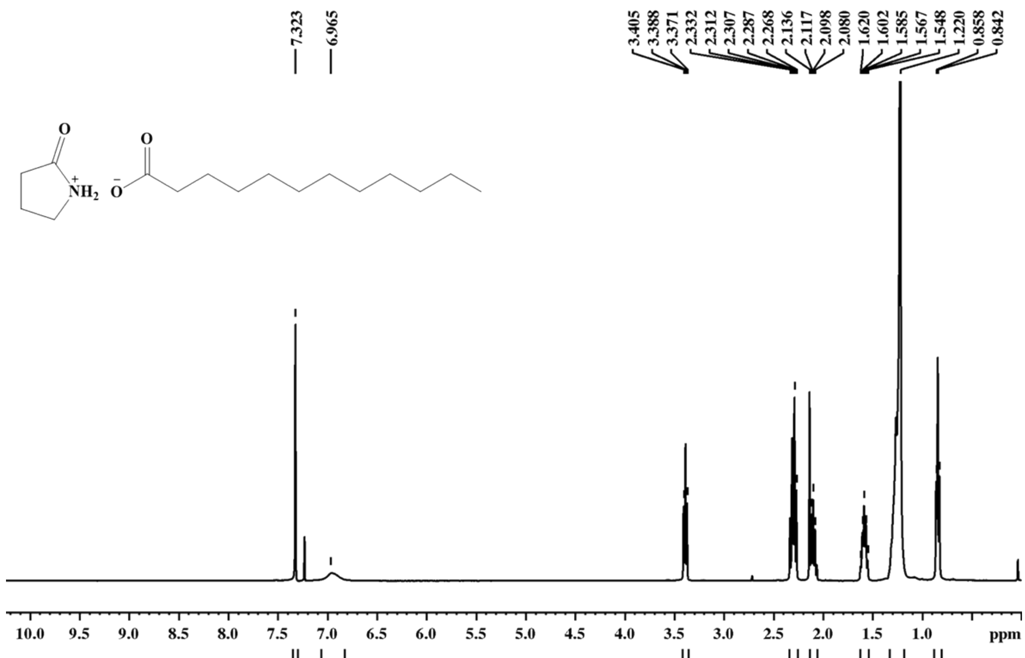

Fig. S3. ^{1}H NMR spectrum of BTD ionic liquid in $CDCl_3$ solvent

^{1}H NMR ($CDCl_3$, δ ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.96 (s, 1H), 3.40 (t, *J* = 7.0 Hz, 2H), 2.40 – 2.26 (m, 4H), 2.14 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.25 (s, 16H), 0.85 (t, *J* = 6.6 Hz, 3H)

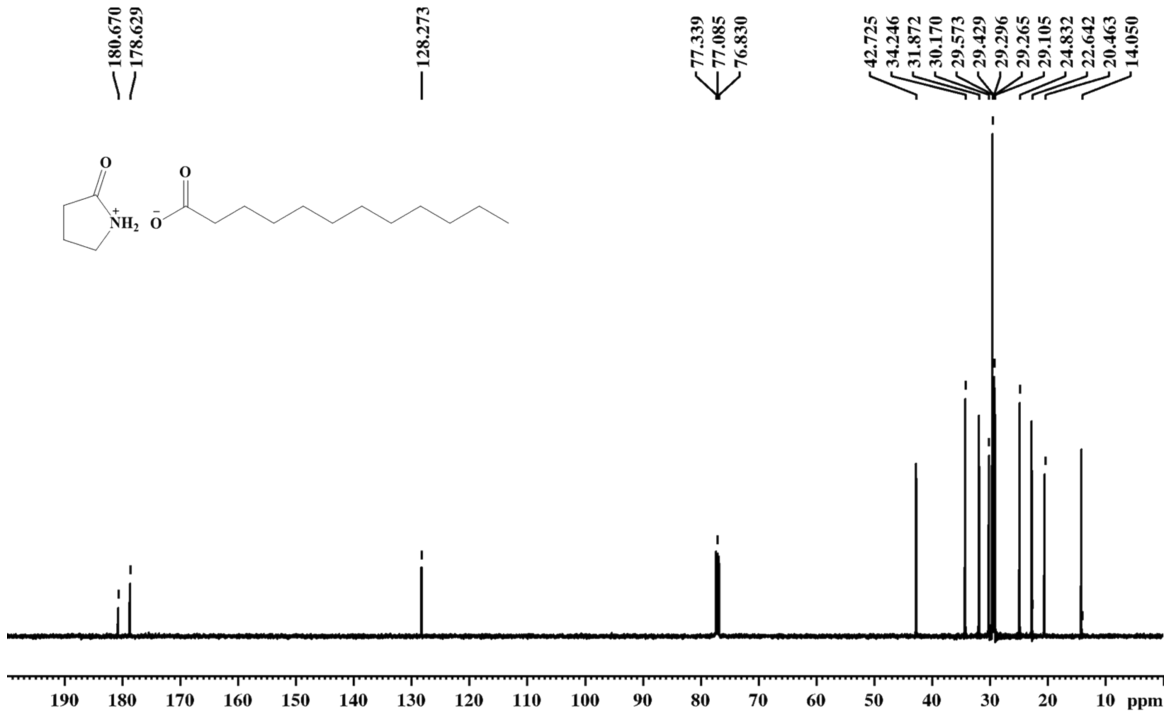

Fig. S4. ^{13}C NMR spectrum of BTD ionic liquid in $CDCl_3$ solvent

^{13}C NMR ($CDCl_3$, δ ppm) = 180.67 (s), 178.62 (s), 128.27 (s), 77.25 (s), 77.00 (s), 76.75 (s), 42.72 (s), 34.16 (s), 31.79 (s), 30.08 (s), 29.49 (s), 29.19 (d, *J* = 3.9 Hz), 24.75 (s), 22.56 (s), 20.38 (s), 13.05 (s)

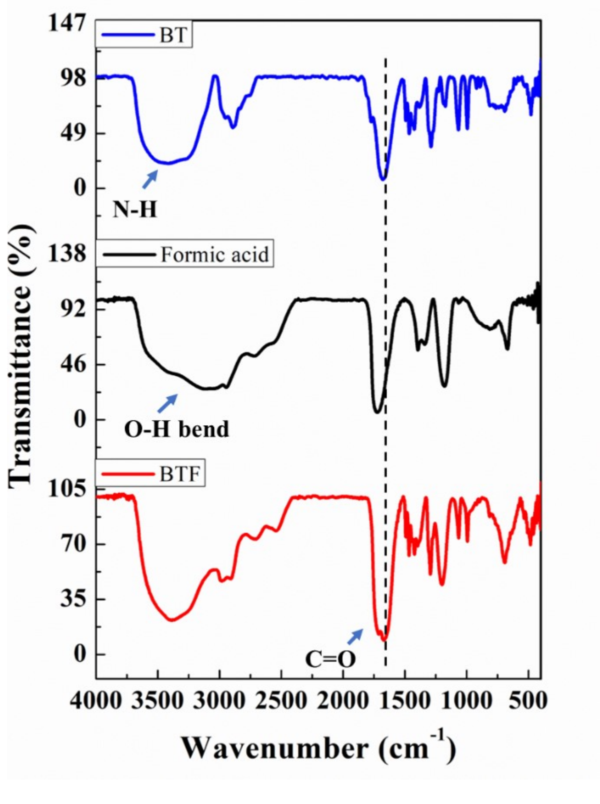

Fig. S5. IR spectrum of BTF ionic liquid

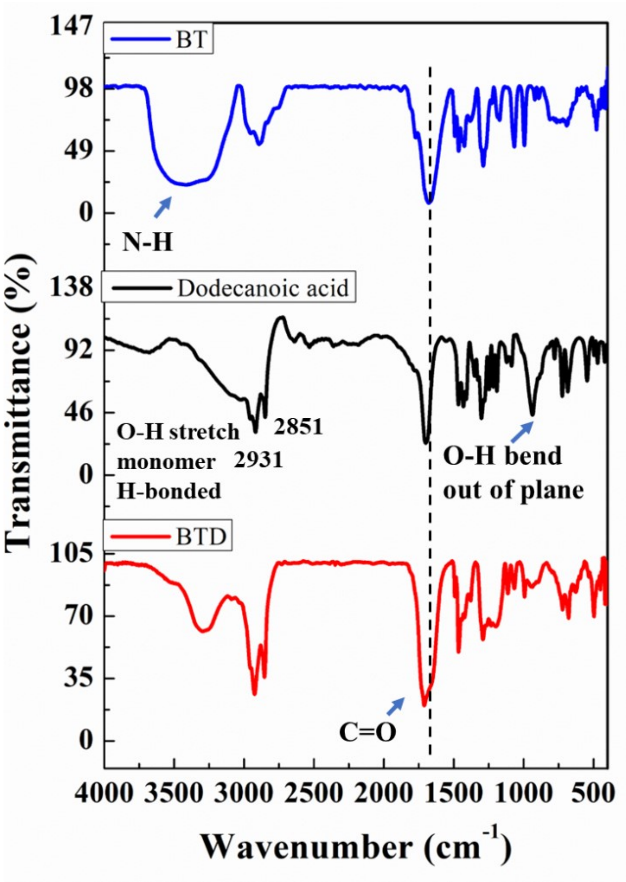

Fig. S6. IR spectrum of BTD ionic liquid

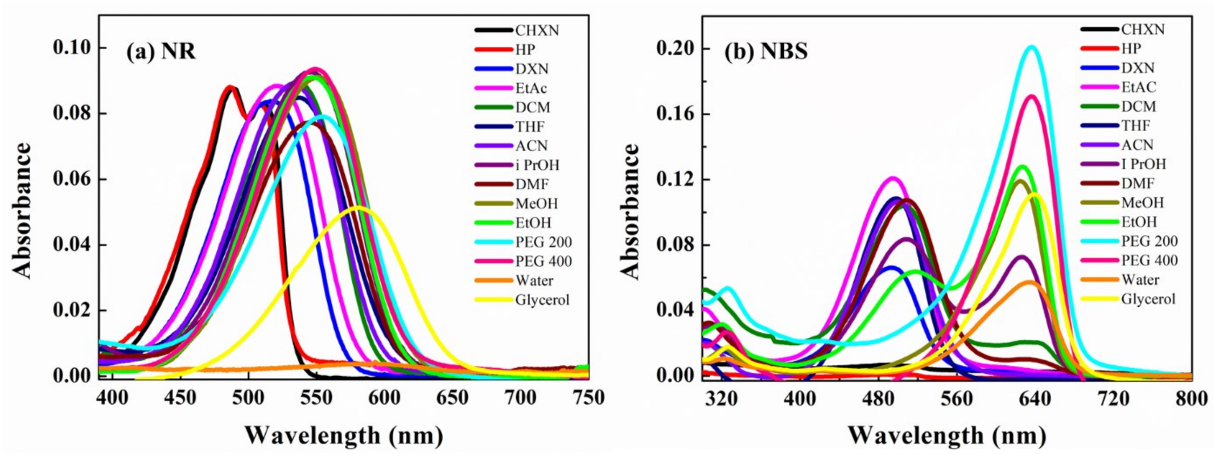

Fig. S7. Steady-state absorption spectra of a) NR and b) NBS in different solvents (Concentration = 2 μM)

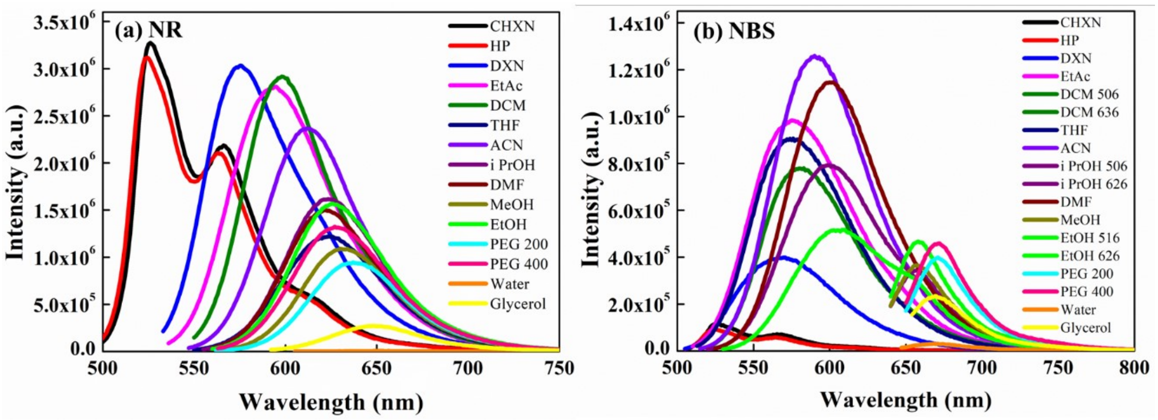

Fig. S8. Steady-state emission spectra of a) NR and b) NBS in different solvents (Concentration = 2 μM)

Table S1. Solvatochromic behaviour of absorption maxima, fluorescence emission maxima,

Solvent	NR		Stokes shift (cm^{-1})	NBS		Stokes shift (cm^{-1})
	λ_{max} *abs* (nm)	λ_{max} *emi* (nm)		λ_{max} *abs* (nm)	λ_{max} *emi* (nm)	
CHXN	488,512	526,565	1481	491	525,567	1319
HP	486,510	525,564	1529	491	525,563	1219
DXN	517	576	1981	492	567	2689
EtAc	521	594	2359	494	575	2852
DCM	535	598	1969	506,636	581	2551
THF	537	623	2571	498	575	2689
ACN	533	612	2422	501	590	3010
i PrOH	545	623	2297	506, 626	599, 657	3068
DMF	544	622	2341	510	600	2941
MeOH	550	632	2359	625	657	779
EtOH	546	626	2305	516, 626	658, 605	777
PEG 200	555	635	2270	636	673	864
PEG 400	548	627	2299	636	672	842
Water	590	-	-	632	668	853
Glycerol	578	648	1869	639	667	657

and Stokes shift of NR and NBS in different solvents

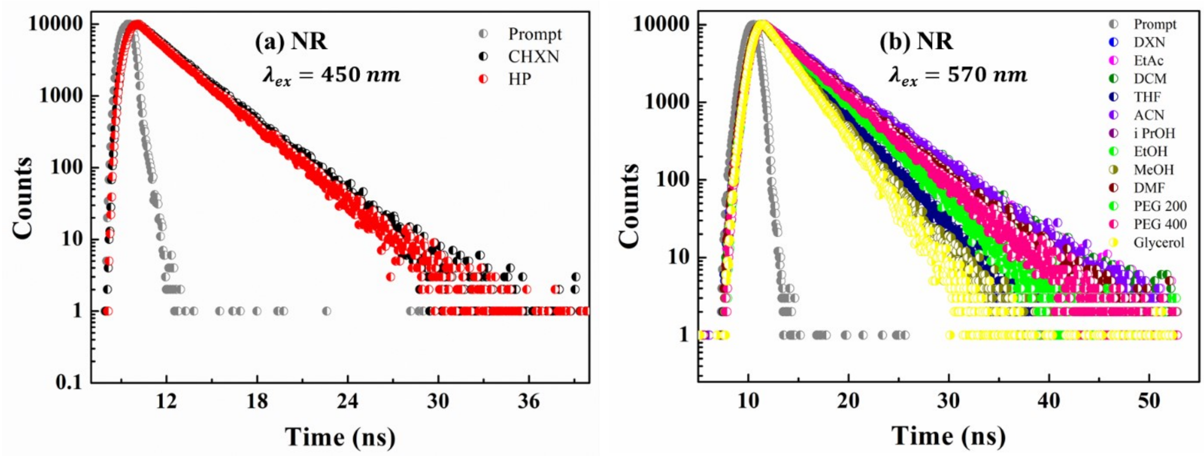

Fig. S9. Fluorescence lifetime decay of **a)** NR (λ_{ex} = 450 nm and **b)** λ_{ex} = 570 nm at room temperature

Solvent	NR	
	τ (ns)	**χ^2**
CHXN	2.55	1.09
HP	2.40	1.26
DXN	4.08	1.21
EtAc	4.43	1.28
DCM	4.41	1.29
THF	3.11	1.24
ACN	4.45	1.28
i PrOH	3.78	1.15
EtOH	3.55	1.12
MeOH	2.73	1.03
DMF	4.11	1.21
PEG-200	3.60	1.09
PEG-400	3.91	1.23
Water	-	-
Glycerol	2.49	1.05

Table S2. Fluorescence lifetime value of NR in different solvents

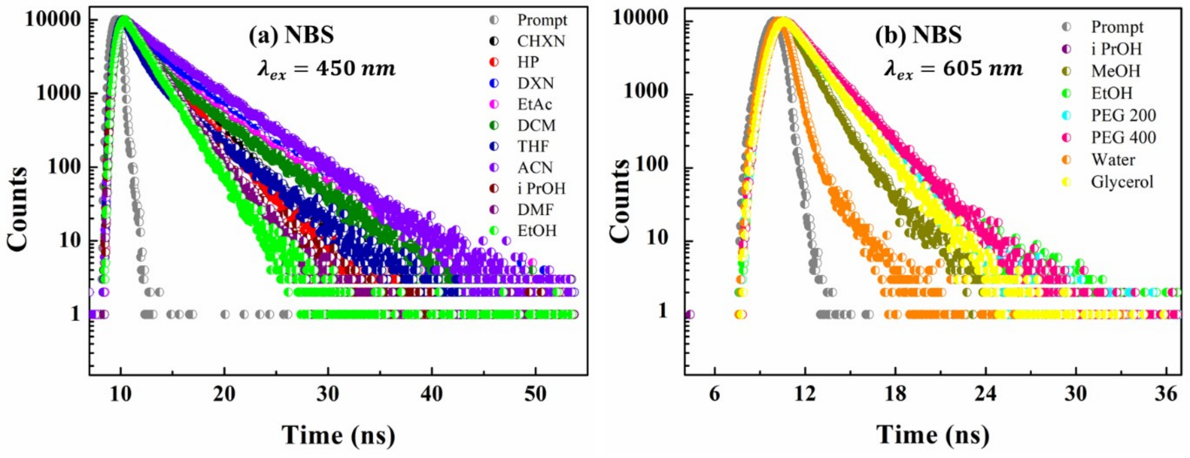

Fig. S10. Fluorescence lifetime decay of **a)** NBS (λ_{ex} = 450 nm and **b)** λ_{ex} = 605 nm at room temperature.

Table S3. Fluorescence lifetime value of NBS in different solvents

Solvent	**NBS**		
	τ_1(ns) (α_1)	**τ_2(ns) (α_2)**	**χ^2**
CHXN	1.96 (35.23)	3.07 (64.77)	1.04
HP	1.81 (36.44)	2.88 (63.56)	1.10
DXN	0.61 (14.30)	3.95 (85.70)	1.07
EtAc	0.85 (29.88)	4.29 (70.12)	1.08
DCM	1.27 (41.24)	4.25 (58.76)	1.02
THF	1.03 (55.81)	3.76 (44.19)	1.07
ACN	1.52 (8.25)	4.40 (91.75)	1.12
iPrOH	1.73 (73.66)	2.87 (26.34)	1.01
iPrOH	1.77 (100)	-	1.13
DMF	2.06 (100)	-	1.26
MeOH	1.02 (80.54)	1.80 (19.46)	1.18
EtOH	1.40 (82.68)	2.56 (17.32)	1.01
EtOH	1.90 (100)	-	1.20
PEG 200	1.64 (100)	-	1.23
PEG 400	1.87 (100)	-	1.33
H2O	0.41 (90)	1.57 (10)	1.00
Glycerol	1.58 (100)	-	1.26

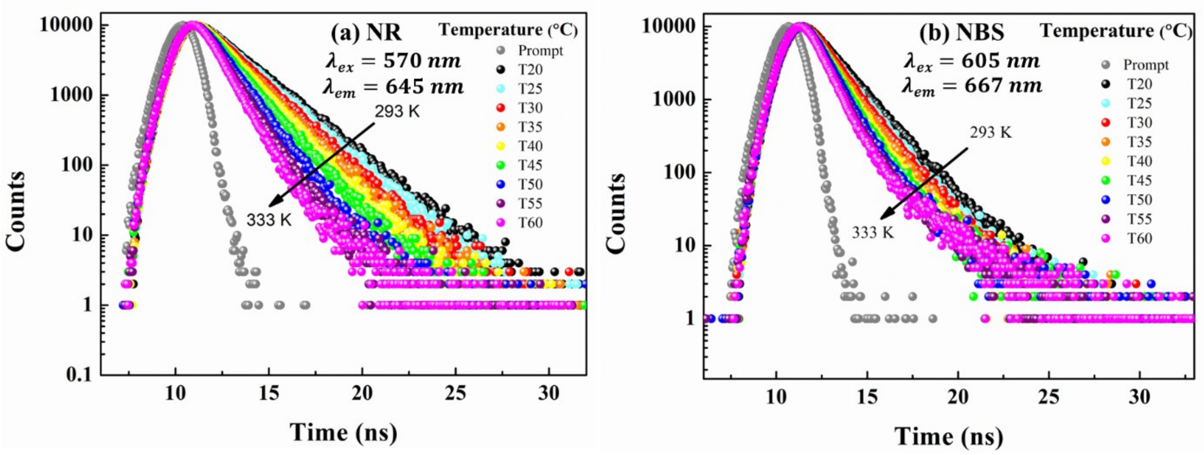

Fig. S11. Fluorescence lifetime decay of (a) NR (λ_{ex} = 570 nm, Concentration = 4 μM) and (b) NBS (λ_{ex} = 605 nm, Concentration = 0.5 μM) in BTF IL with varying temperature

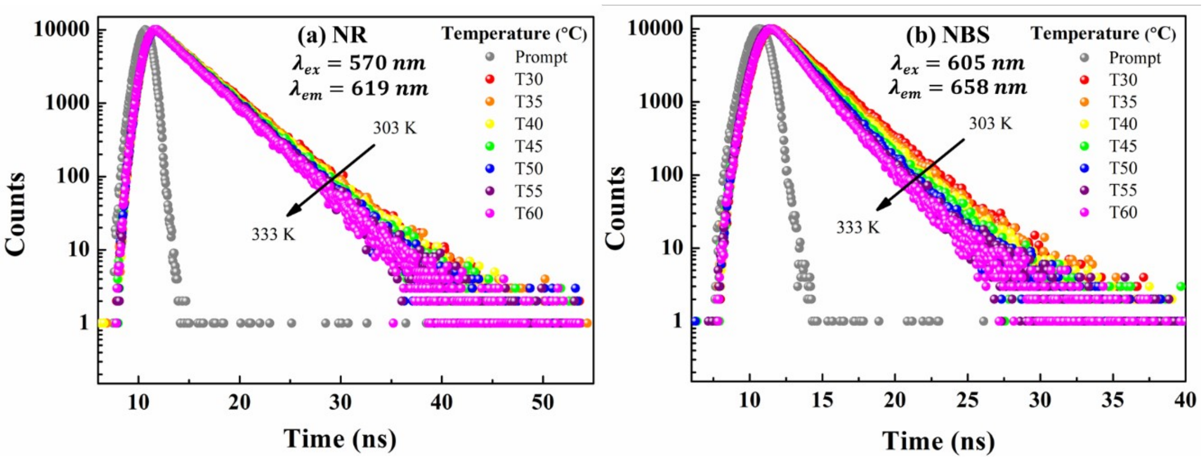

Fig. S12. Fluorescence lifetime decay of (a) NR (λ_{ex} = 570 nm, Concentration = 4 μM) and (b) NBS (λ_{ex} = 605 nm, Concentration = 0.5 μM) in BTD IL with varying temperature

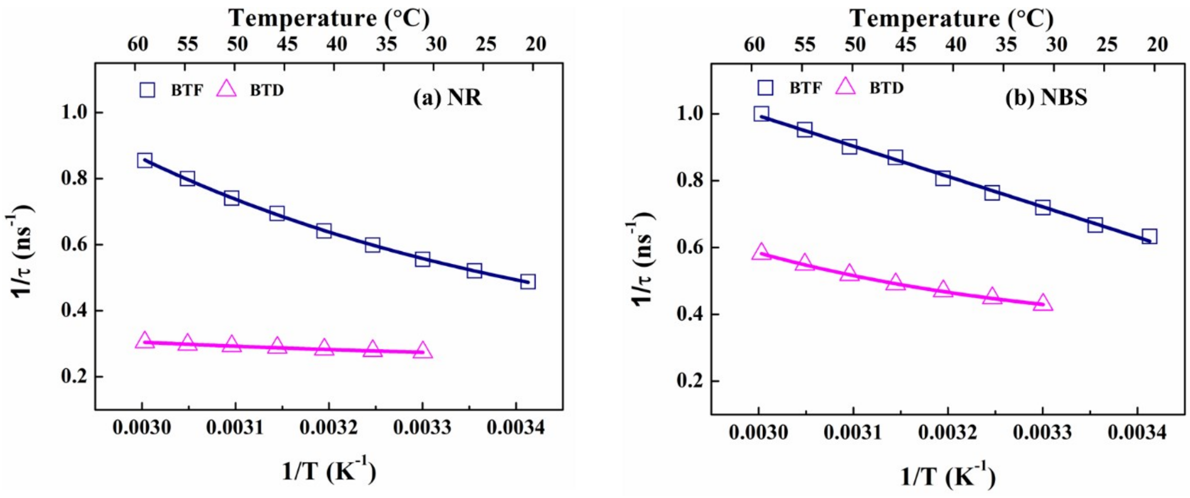

Fig. S13. Arrhenius plots for the determination of activation energies of nonradiative decay of (a) NR and (b) NBS in BTF and BTD ILs

Table S4. The variation of bulk viscosity with temperature and related parameters obtained from Arrhenius plot and activation energy of nonradiative decay

System	Temperature (K)	Viscosity (η) (mPa.s)	E_{η} (kJmol^{-1}) $\pm$ σ	E_{nr} (kJmol^{-1}) $\pm$ σ
NR in BTF	293	7.17		
	298	6.14		
	303	5.32		
	308	4.64		
	313	4.09	22 $\pm$ 0.4	18 $\pm$ 1.18
	318	3.53		
	323	3.12		
	328	2.72		
	333	2.45		
NR in BTD	303	18.98		
	308	15.72		
	313	13.2		
	318	11.2	27 $\pm$ 1.10	16.81 $\pm$ 0.005
	323	9.6		
	328	8.3		
	333	7.2		

Standard uncertainties u is u (T) = 0.002 K, u (η) = 0.005 mPa.s, σ = Standard deviation

Table S5. The variation of bulk viscosity with temperature and related parameters obtained from Arrhenius plot and activation energy of nonradiative decay

System	Temperature (K)	Viscosity (η) (mPa.s)	E_{η} (kJmol^{-1}) $\pm$ σ	E_{nr} (kJmol^{-1}) $\pm$ σ
NBS in BTF	293	7.17		
	298	6.14		
	303	5.32		
	308	4.64		
	313	4.09	22 $\pm$ 0.4	12 $\pm$ 1.41
	318	3.53		
	323	3.12		
	328	2.72		
	333	2.45		
NBS in BTD	303	18.98		
	308	15.72		
	313	13.2		
	318	11.2	27 $\pm$ 1.10	23 $\pm$ 2.12
	323	9.6		
	328	8.3		
	333	7.2		

Standard uncertainties u is u (T) = 0.002 K, u (η) = 0.005 mPa.s, σ = Standard deviation

Microviscosity Calculation: Experimental Study

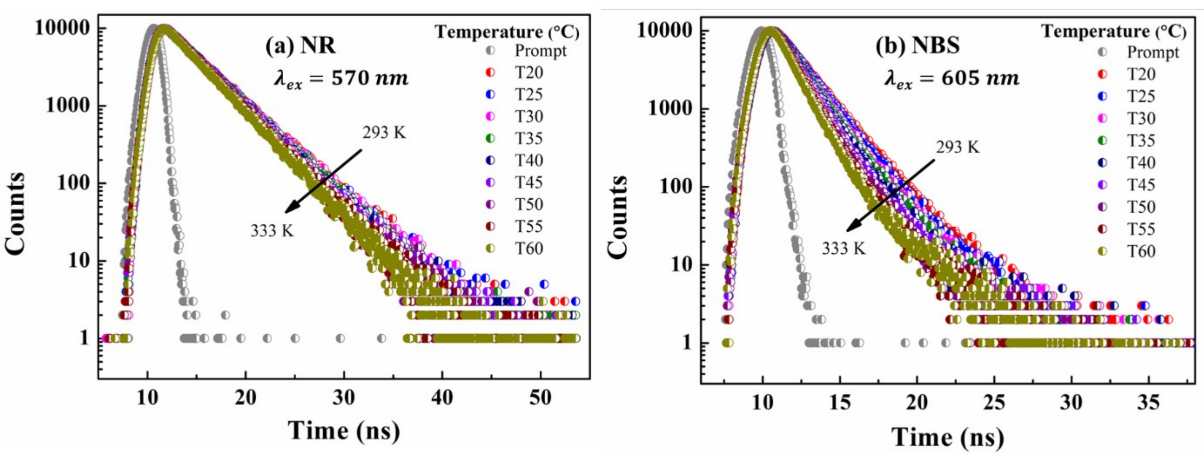

Fig. S14. Fluorescence lifetime decay of **a)** NR (λ_{ex} = 570 nm and **b)** NBS (λ_{ex} = 605 nm) in PEG 200 by varying temperature

Table S6. Fluorescence lifetime value of NR and NBS in PEG 200 at different temperature

Temperature (˚C)	PEG 200				
	NR		NBS		
	τ_1(ns)	χ^2	τ_1(ns) (α_1)	τ_2(ns) (α_2)	χ^2
20	3.65	1.12	1.77 (100)	-	1.29
25	3.61	1.16	1.70 (100)	-	1.17
30	3.57	1.18	1.61 (100)	-	1.33
35	3.53	1.13	1.53 (100)	-	1.35
40	3.48	1.15	1.45 (100)	-	1.38
45	3.43	1.23	1.20 (84)	2.12 (16)	1.04
50	3.37	1.33	1.14 (85)	2.05 (15)	0.99
55	3.31	1.16	1.09 (89)	2.25 (11)	0.99
60	3.23	1.16	1.03 (91)	2.38 (9)	0.97

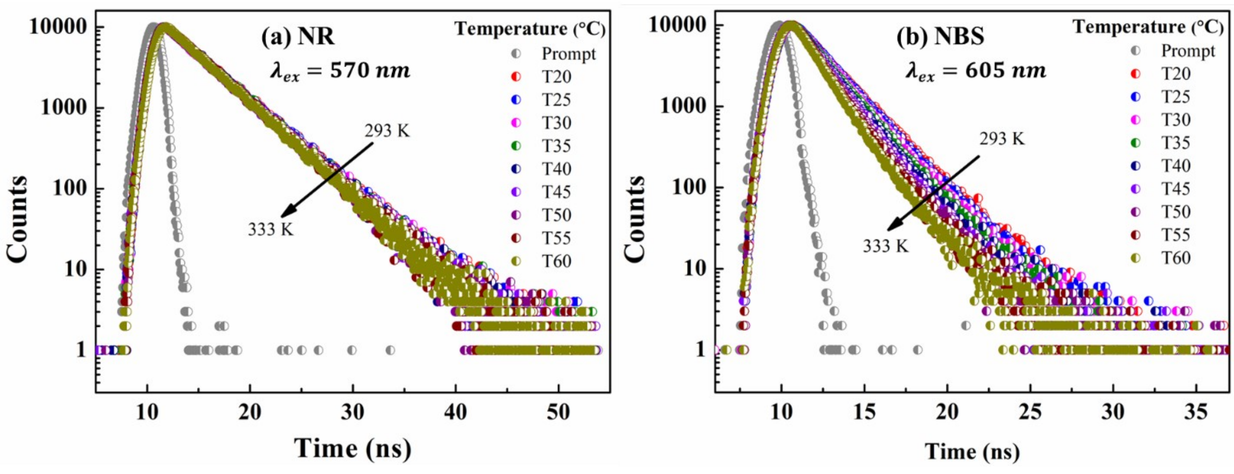

Fig. S15. Fluorescence lifetime decay of **a)** NR (λ_{ex} = 570 nm and **b)** NBS (λ_{ex} = 605 nm) in PEG 400 by varying temperature

Table S7. Fluorescence lifetime value of NR and NBS in PEG 400 at different temperature

Temperature (˚C)	PEG 400				
	NR		NBS		
	τ_1(ns)	χ^2	τ_1(ns) (α_1)	τ_2(ns) (α_2)	χ^2
20	3.91	1.24	1.99 (100)	-	1.04
25	3.89	1.35	1.91 (100)	-	1.27
30	3.87	1.28	1.84 (100)	-	1.20
35	3.85	1.13	1.76 (100)	-	1.33
40	3.85	1.15	1.68 (100)	-	1.25
45	3.82	1.21	1.43 (75)	2.09 (25)	1.13
50	3.79	1.22	1.36 (76)	2.04 (24)	1.25
55	3.76	1.14	1.26 (80)	2.11 (20)	0.99
60	3.73	1.16	1.20 (82)	2.02 (18)	1.04

Table S8. Limiting anisotropy value of NR in PEG 400, PEG 200, BTD, and BTF IL at room temperature

NR	PEG 200	PEG 400	BTD IL	BTF IL
r_0	0.38	0.35	0.32	0.34

Table S9. Limiting anisotropy value of NBS in PEG 400, PEG 200, BTD, and BTF IL at room temperature

NBS	PEG 200	PEG 400	BTD IL	BTF IL
r_0	0.4	0.38	0.34	0.36