SUPPORTING INFORMATION

Effect of ionic liquids on the conformation of a porphyrin-based viscometer

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TABLE OF CONTENTS

Materials and methods

All reagents and solvents were from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar) and were used as received. Ionic liquids were synthesized and purified according to literature procedures, see below for details.[1] **PD** was prepared according to literature procedure;[2] the structure and purity were confirmed by MALDI-TOF spectrometry and HPLC, respectively (Figure S8).

A 1 mM concentration stock solution of **PD** in DMSO was prepared fresh prior to experiments, used within 48 h for all spectroscopic measurements, and protected from direct light exposure during storage. All solutions of **PD** in ILs were prepared by addition of the DMSO stock solution to the ionic liquid, followed by vortexing at 3000 rpm for 10-30 seconds.

NMR spectra were recorded on a Varian (300 MHz) spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) downfield from residual DMSO in DMSO-d_6; ^{19}F resonances are reported relative to trifluoroacetic acid ($\delta = -76.5$ ppm).

Absorption spectra were acquired on an Agilent 8453 UV-vis instrument using 1.0 cm quartz cells. The absorption maxima of the Soret band in molecular solvents and their mixtures was centered around 470 nm, for ionic liquids at 475 nm.

Fluorescence measurements were performed using a Shimadzu RF-5301PC as follows: for all molecular solvents and molecular solvent mixtures λ_{ex} was 470 nm; for all ionic liquids λ_{ex} was 475 nm; emission spectra were collected from 600 to 900 nm; excitation and emission slit widths were 3 nm and 3 nm; sensitivity – high; 1.0 cm quartz cell. All spectra were background subtracted using appropriate blanks, and subsequently smoothed using manufacturer provided software. Temperature dependent measurements were performed using Agilent-Cary spectrophotometer with a Peltier temperature controller as follows: λ_{ex} was 470 nm; emission spectra were collected from 600 to 900 nm using 5 scans; excitation and emission slit widths were 10 nm and 10 nm; 1.0 cm quartz cell. The samples were equilibrated for 5 min at a given temperature before the emission spectra were measured. All spectra were background subtracted using the appropriate blanks.

Percent of the twisted PD conformation (twisted PD / %) was calculated as follows:

$$\text{twisted PD} / \% = (F^{max}_{\text{twisted}}) / (F^{max}_{\text{twisted}} + F^{max}_{\text{planar}}) \bullet 100\%$$

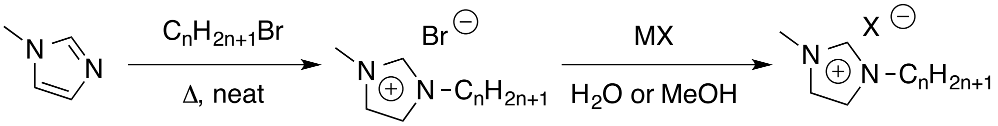
where F^{max}_{twisted} is the maximum fluorescence intensity of the twisted conformation; F^{max}_{planar} is the maximum fluorescence intensity of the planar conformation

Water content of ILs was measured using Aquamax KF coulometric titrator from GRS Scientific according to manufacturer provided protocols, using 0.4 or 0.5 ml of sample.

Viscosity and density of ILs was measured using Anton-Paar Lovis 4500M microviscometer. Fluorescence measurements were performed concurrently with the water content measurements.

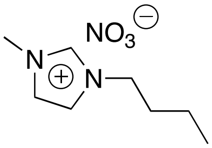
Synthesis and characterization of ionic liquids

All ionic liquids were prepared according to literature procedures or modified literature procedures[1] following the general sequences shown below. All ionic liquids were purified as follows: ionic liquids were dissolved in CH_2Cl_2, followed by filtration to get rid of inorganic impurities. Next, ionic liquids were repeatedly treated with charcoal in EtOH at elevated temperatures followed by filtration and removal of EtOH in vacuo (for an azeotropic removal of residual water). Finally, the ionic liquids were dried under vacuum for 8-12 hours. All sample preparations and spectroscopic measurements were conducted immediately after removing the ionic liquids from the vacuum with care to minimize the exposure to moisture.



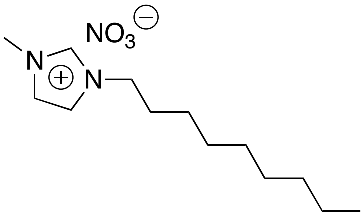
$X = NO_3$: $MX = AgNO_3$, MeOH
$X = NTf_2$: $MX = LiNTf_2$, H_2O
$X = PF_6$: $MX = KPF_6$, H_2O

[C_4-mim]NO_3:[3]



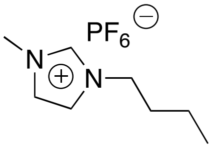
^1H NMR (300 MHz, DMSO-d_6): δ = 9.16 (s, 1H), 7.78 (t, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 1.8 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.74 (pent, *J* = 7.4 Hz, 2H), 1.23 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 6.9 Hz, 3H)

[C_9-mim]NO_3:[4]



^1H NMR (300 MHz, DMSO-d_6) δ = 9.15 (s, 1H), 7.78 (t, *J* = 1.8 Hz, 1H), 7.71 (t, *J* = 1.8 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.77 (pent, *J* = 7.2 Hz, 2H), 1.24 (m, 12H), 0.85 (t, *J* = 6.6 Hz, 3H)

[C_4-mim]PF_6:[5]



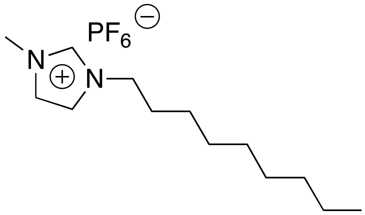
^1H NMR (300 MHz, DMSO-d_6): δ = 9.08 (s, 1H), 7.74 (s, 1H), 7.67 (s, 1H), 4.14 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 1.75 (pent, *J* = 7.2 Hz, 2H), 1.24 (sext, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H);

^{19}F NMR (300 MHz, DMSO-d_6): δ = –70.2 (d, *J* = 710.4 Hz)

[C_9-mim]PF_6:[5]

^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.07 (s, 1H), 7.74 (m, 1H), 7.68 (m, 1H), 4.13 (t, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.76 (pent, *J* = 7.5 Hz, 2H), 1.23 (m, 12H), 0.84 (t, *J* = 7.5 Hz, 3H);

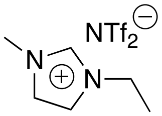
^{19}F NMR (DMSO-d_6): δ = –70.2 (d, *J* = 713.5 Hz)



[C_2-mim]NTf_2:[5]

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.09 (s, 1H), 7.56 (s, 1H), 7.67 (s, 1H), 4.17 (q, *J* = 7.5 Hz), 3.83 (s, 2H), 1.40 (t, *J* = 7.5 Hz, 3H);

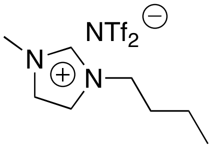
^{19}F NMR (300 MHz, DMSO-d_6): δ = –78.8 (s)



[C_4-mim]NTf_2:[5]

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.09 (s, 1H), 7.75 (t, *J* = 1.8 Hz, 1H), 7.68 (t, *J* = 1.8 Hz, 1H), 4.14 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 1.75 (pent, *J* = 7.5 Hz, 2H), 1.24 (sext, *J* = 7.5 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H);

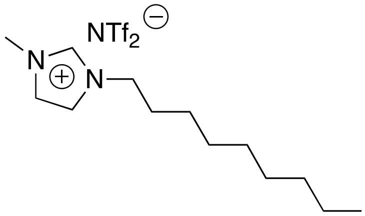
^{19}F NMR (300 MHz, DMSO-d_6): δ = –78.8 (s)



[C_9-mim]NTf_2:[5]

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.08 (s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 4.13 (t, *J* = 7.5 Hz, 2H), 3.83 (s, 3H), 1.76 (m, 2H), 1.23 (m, 12H), 0.87 (m, 3H).

^{19}F NMR (300 MHz, DMSO-d_6): δ = –78.8 (s)



[C_{12}-mim]NTf_2:[6]

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.08 (s, 1H), 7.75 (s, 1H), 7.68 (s, 1H), 4.13 (t, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 1.75 (m, 2H), 1.22 (m, 18H), 0.84 (m, 3H);

^{19}F NMR (300 MHz, DMSO-d_6): δ = –78.8 (s)

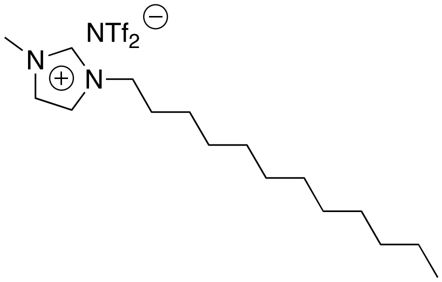


Table S1. Properties of glycerol-ethanol mixtures[a]

Entry	Glycerol – EtOH (v/v)	Viscosity, mPa•s	Density, g/cm^3
1	0 – 10	1.2	0.78942
2	1 – 9	2.4	0.84845
3	3 – 7	7.6	0.94313
4	5 – 5	39	1.05342
5	7 – 3	108	1.11474
6	8 – 2	241	1.16188
7	9 – 1	664	1.22316
8	10 – 0	1457	1.23008

a – viscosity and density measurements performed at 20°C.

Table S2. Properties of molecular solvents[a]

Entry	solvent	Viscosity, mPa•s	Density, g/cm^3
1	decanol	15	0.82977
2	ethylene glycol	21	1.11328
3	tetraethylene glycol	59	1.12453

a – viscosity and density measurements performed at 20°C.

Table S3. Properties of ionic liquids[a]

Entry	Ionic Liquid	Viscosity, mPa•s	Density, g/cm^3	Water content, ppm
1	[C_4-mim]NO_3	262	1.15545	4140
2	[C_9-mim]NO_3	791	1.05085	5473
3	[C_4-mim]PF_6	381	1.37045	347
4	[C_9-mim]PF_6	1324	1.21513	290
5	[C_2-mim]NTf_2	38	1.51923	590
6	[C_4-mim]NTf_2	60	1.43579	469
7	[C_9-mim]NTf_2	116	1.29499	628
8	[C_{12}-mim]NTf_2	202	1.24681	223

a – viscosity and density measurements performed at 20°C.

Table S4. Properties of glycerol-ethanol (80-20 v/v) mixture as a function of temperature

Entry	**T, °C**	**Viscosity, mPa•s**	**Density, g/cm^3**
1	20	241	1.16188
2	30	122	1.15515
3	40	68	1.14826
4	50	42	1.41274
5	60	28	1.13419

Table S5. Properties of tetraethylene glycol as a function of temperature

Entry	**T, °C**	**Viscosity, mPa•s**	**Density, g/cm^3**
1	20	59	1.12483
2	30	35	1.11688
3	40	23	1.10890
4	50	16	1.10093
5	60	11	1.09295

Table S6. Properties of [C_4-mim]NO_3[a] as a function of temperature

Entry	**T, °C**	**Viscosity, mPa•s**	**Density, g/cm^3**
1	20	258	1.15545
2	30	144	1.14913
3	40	85	1.14280
4	50	55	1.13657
5	60	37	1.13040

a – water content: 4140 ppm

Table S7. Properties of [C_4-mim]PF_6[a] as a function of temperature

Entry	**T, °C**	**Viscosity, mPa•s**	**Density, g/cm^3**
1	20	403	1.37004
2	30	209	1.36168
3	40	122	1.35333
4	50	77	1.34505
5	60	52	1.33685

a – water content: 252 ppm

Table S8. Properties of [C_9-mim]PF_6[a] as a function of temperature

Entry	**T, °C**	**Viscosity, mPa•s**	**Density, g/cm^3**
1	20	1346	1.214991
2	30	641	1.20741
3	40	334	1.19993
4	50	189	1.19250
5	60	114	1.18509

a – water content: 308 ppm

Table S9. Effect of water on the properties of [C_4-mim]NO_3[a]

Entry	**Ionic Liquid**	**Viscosity, mPa•s**	**Density, g/cm^3**	**Water content, ppm (%, v/v)**
1	[C_4-mim]NO_3	262	1.15545	4140 (0.5)
2	[C_4-mim]NO_3	148	1.15839	14600 (1.7)
3[b]	[C_4-mim]NO_3	32	1.14704	– (10)

a – viscosity and density measurements performed at 20°C; water content in v/v was recalculated using the amount of water (density = 1 g/cm^3) in a given volume of IL;

b – [C_4-mim]NO_3 was mixed with water (v/v), and viscosity and density were determined in the same manner as for the other ILs; water content of this sample was not determined by KF-titration.

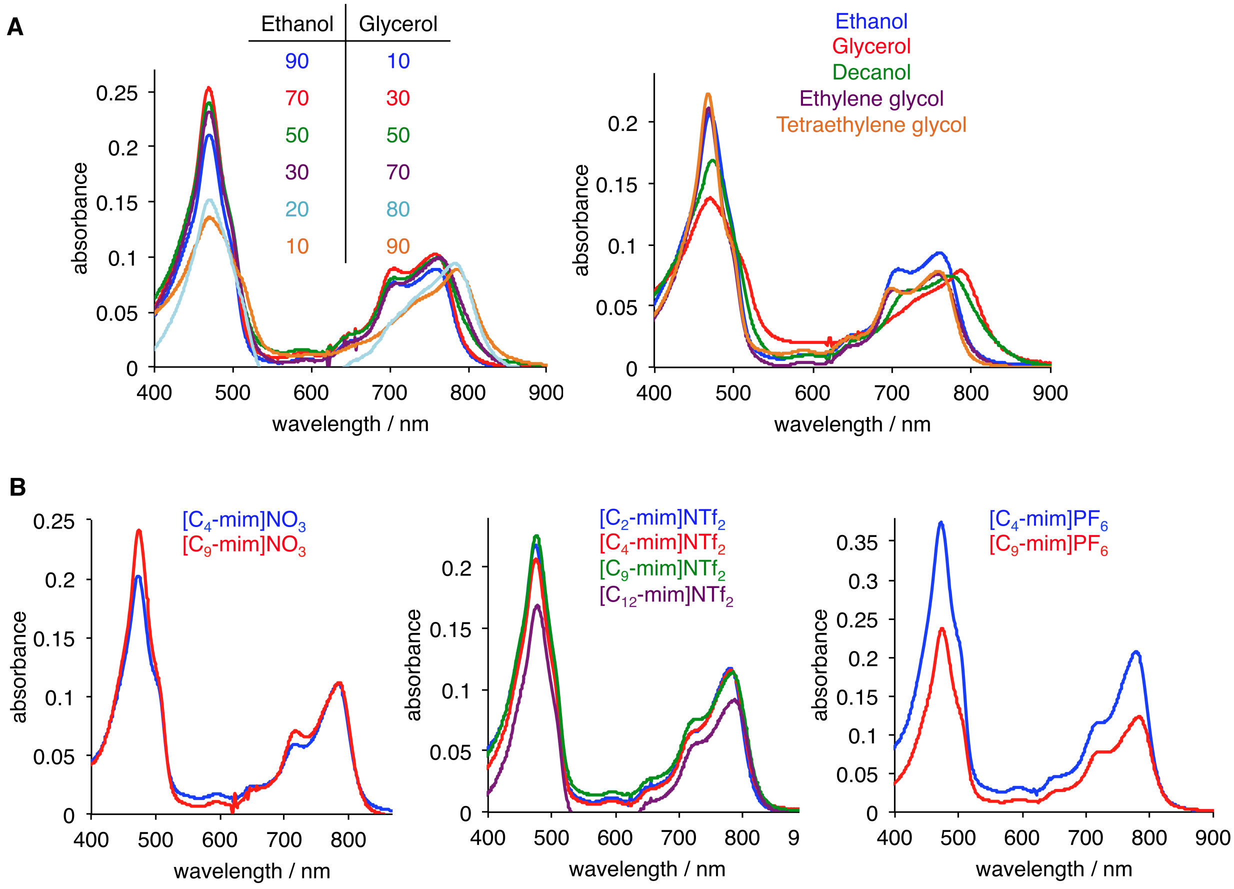


Figure S1. Absorption spectra of **PD** in molecular (**A**) and ionic (**B**) liquids. Conditions: [**PD**] = 1 μM, all mixtures contain 0.1 % DMSO (v/v)

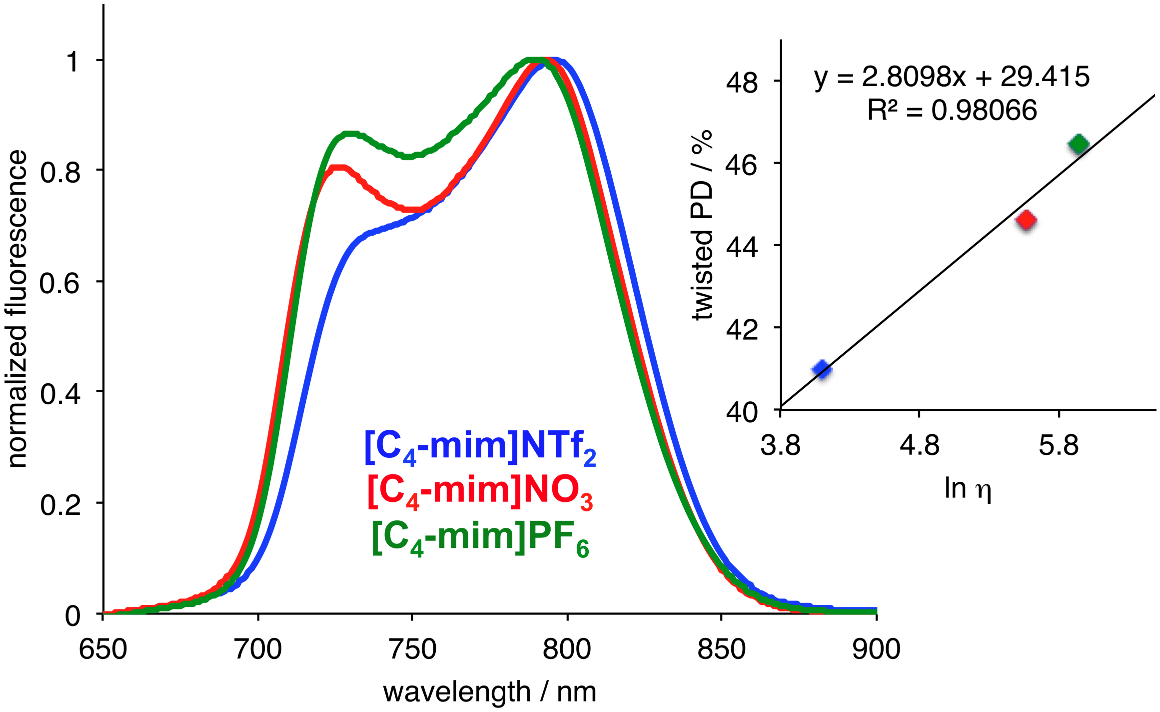


Figure S2. Emission spectra of **PD** in [C_4-mim]-containing ionic liquids; overlaid spectra of [C_4-mim]NTf_2, [C_4-mim]PF_6 and [C_4-mim]NO_3. Insert: **PD** conformation as a function of IL viscosity (blue symbol – C_4-mim]NTf_2; red symbol – [C_4-mim]NO_3 and green – [C_4-mim]PF_6). Conditions: λ_{ex} = 475 nm, [**PD**] = 1 μM, all mixtures contain 0.1 % DMSO (v/v)

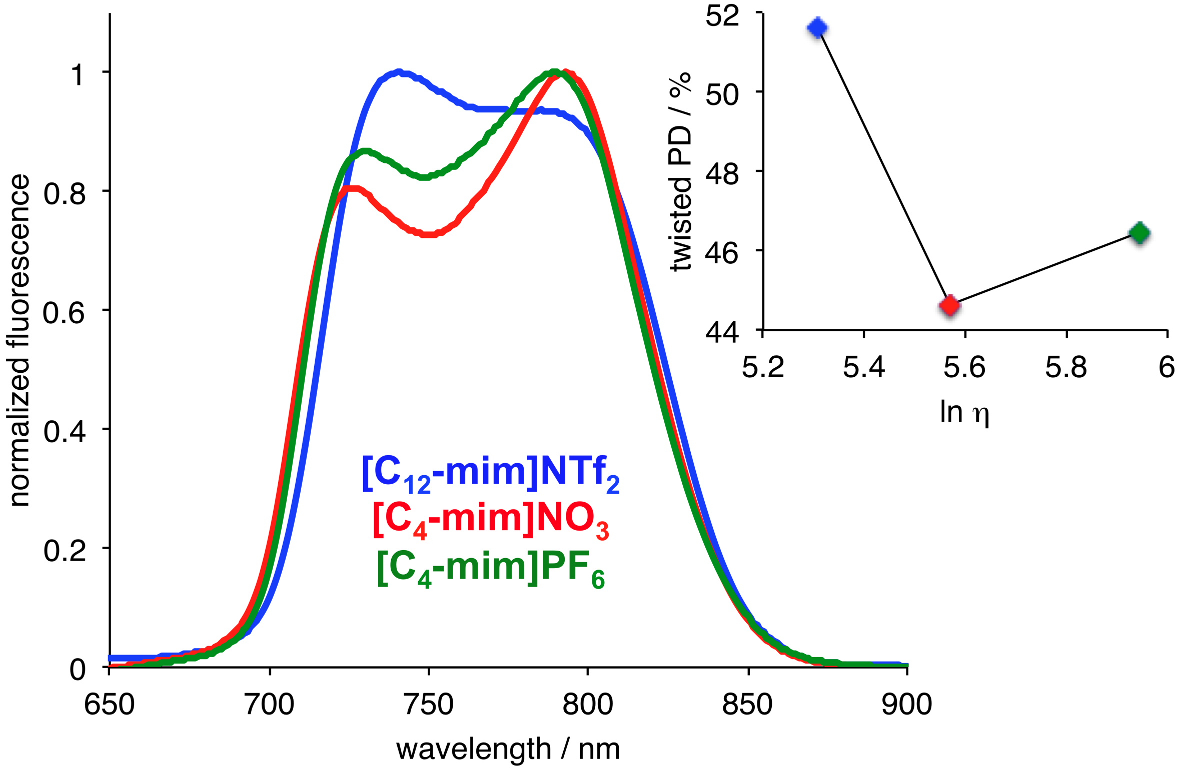


Figure S3. Emission spectra of **PD** in various ionic liquids; overlaid spectra of [C$_{12}$-mim]NTf$_2$, [C$_4$-mim]NO$_3$ and [C$_4$-mim]PF$_6$. Insert: **PD** conformation as a function of IL viscosity (blue symbol – C$_{12}$-mim]NTf$_2$; red symbol – [C$_4$-mim]NO$_3$ and green – [C$_4$-mim]PF$_6$). Conditions: λ_{ex} = 475 nm, [**PD**] = 1 μM, all mixtures contain 0.1 % DMSO (v/v)

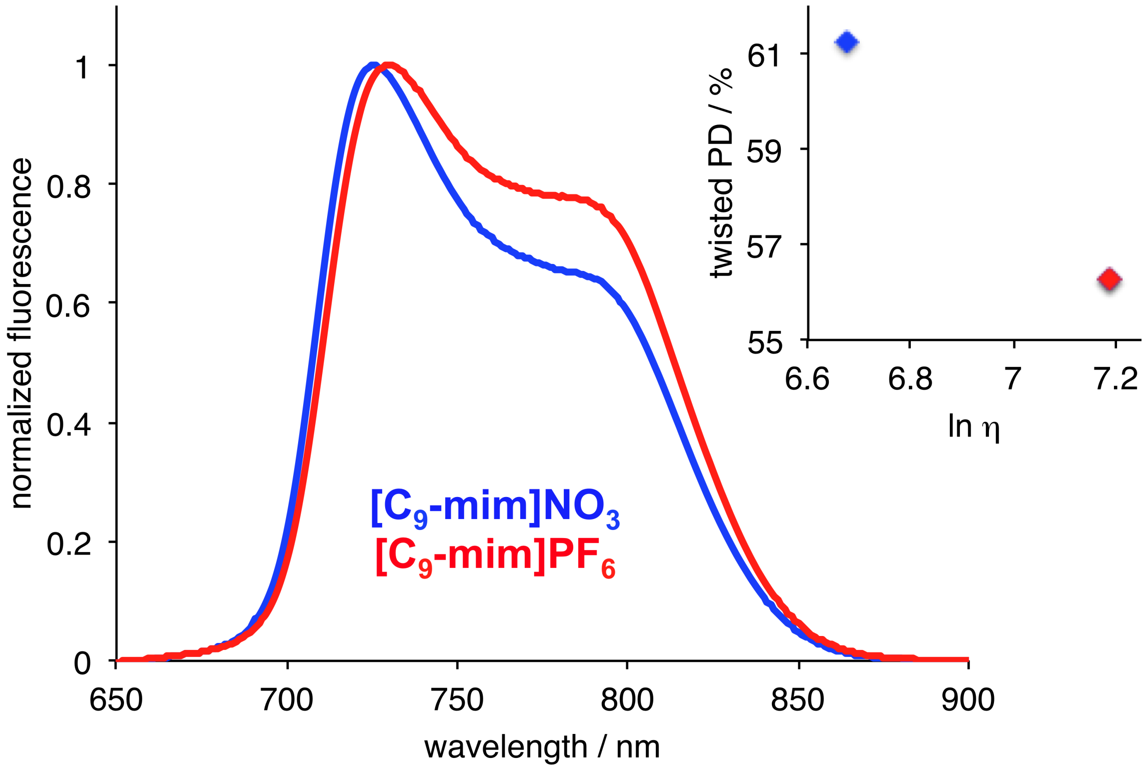


Figure S4. Emission spectra of **PD** in some [C_9-mim]-containing ionic liquids; overlaid spectra of [C_9-mim]PF_6 and [C_9-mim]NO_3. Insert: **PD** conformation as a function of IL viscosity (blue symbol – [C_9-mim]NO_3; red symbol – [C_9-mim]PF_6). Conditions: λ_{ex} = 475 nm, [**PD**] = 1 μM, all mixtures contain 0.1 % DMSO (v/v)

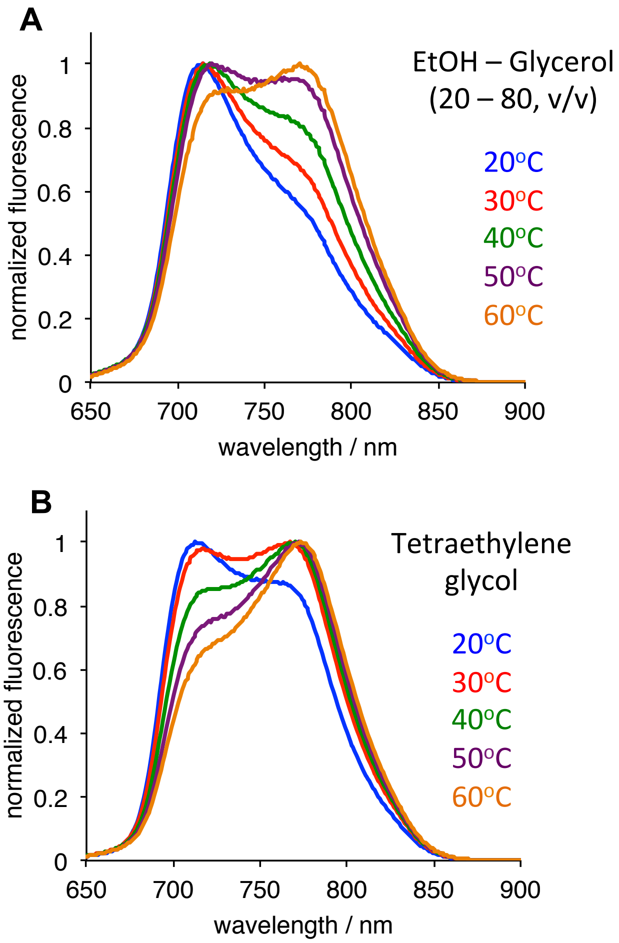


Figure S5. Emission spectra of **PD** in molecular solvents as a function of temperature: **A**: EtOH-glycerol (20/80 v/v); **B**: tetraethylene glycol. Conditions: [**PD**] = 1 μM, λ_{ex} = 470 nm, [DMSO] = 0.1 % (v/v). See Tables S4 and S5 for viscosity data

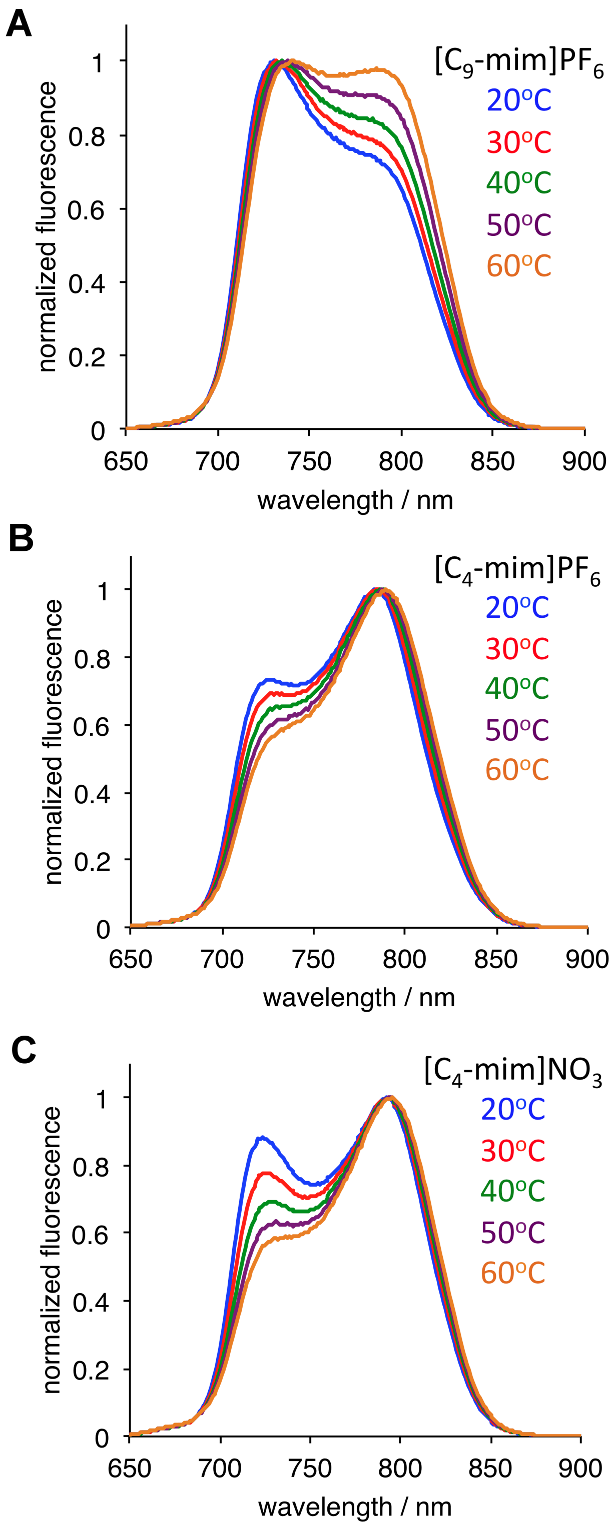


Figure S6. Emission spectra of **PD** in ionic liquids as a function of temperature; **A**: [C$_9$-mim]PF$_6$; **B**: [C$_4$-mim]PF$_6$; **C**: [C$_4$-mim]NO$_3$. Conditions: [**PD**] = 1 μM, λ_{ex} = 475 nm, [DMSO] = 0.1 % (v/v). See Tables S6, S7, S8 for viscosity data

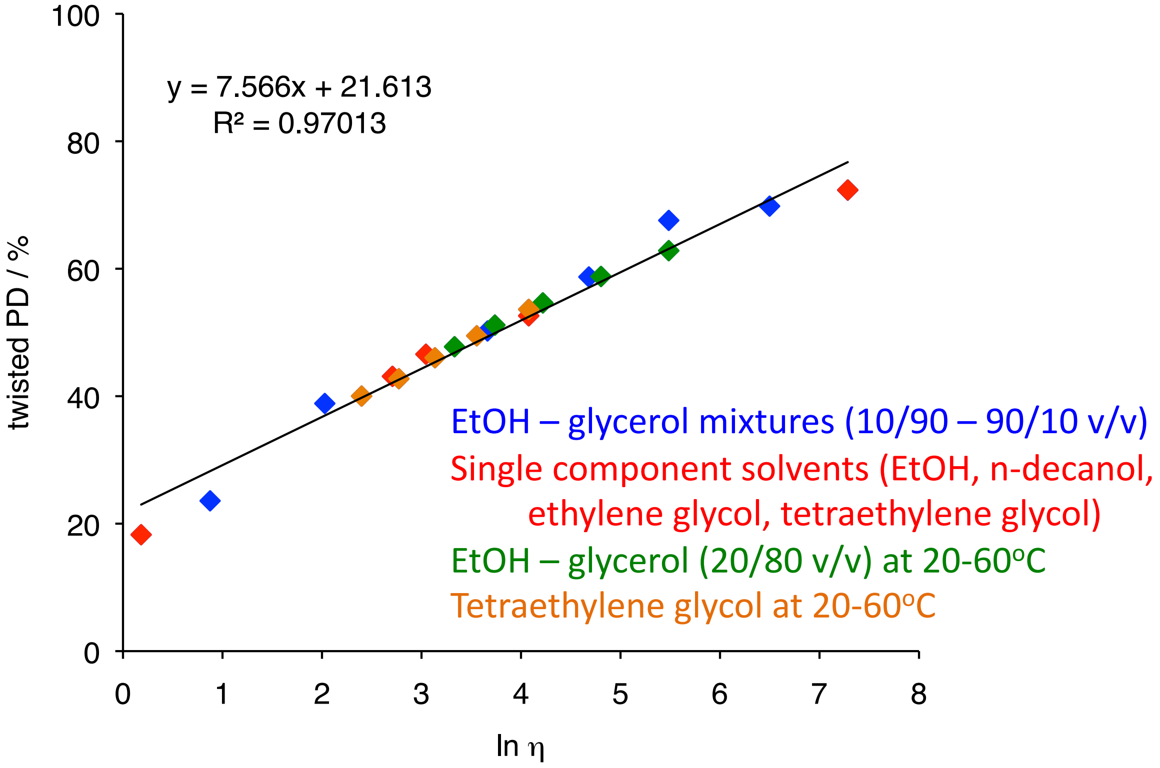
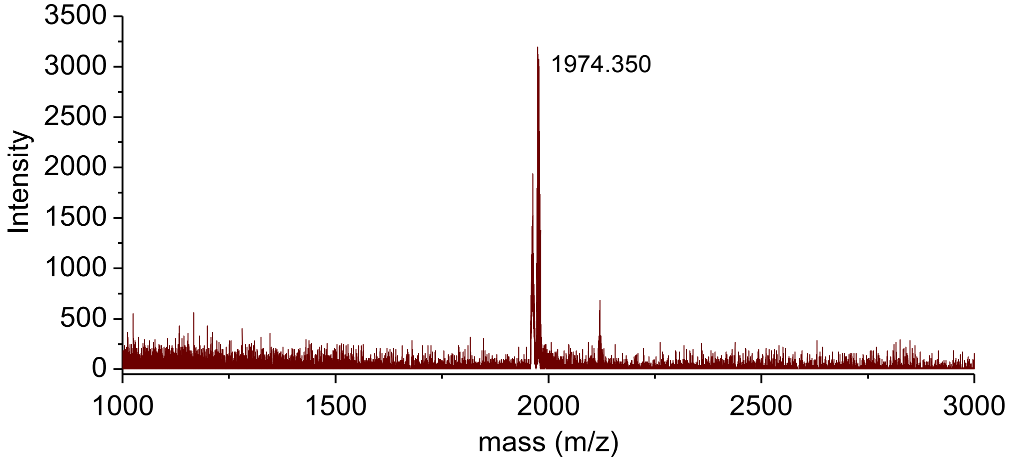
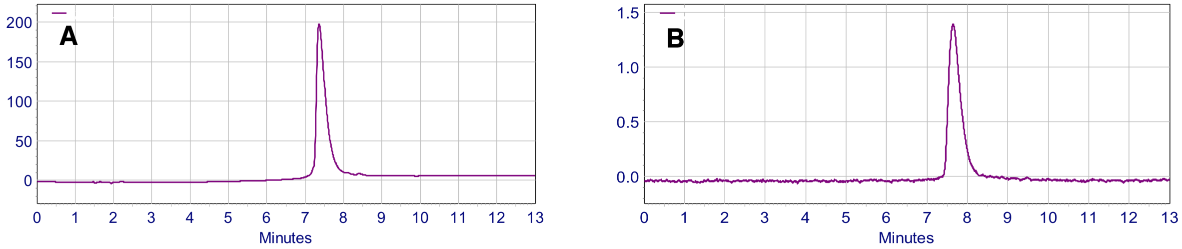


Figure S7. Effect of molecular solvent viscosities on the conformation of **PD** (combined data). Conditions: [**PD**] = 1 μM, λ_{ex} = 470 nm, [DMSO] = 0.1 % (v/v)

MALDI-TOF spectrum of **PD**: m/z 1974.350 ($C_{112}H_{106}N_{10}O_{16}Zn_2$, $[M-2]^+$, requires 1974.636)



(A) absorption (λ = 469 nm) and (B) emission (λ_{ex} = 469 nm, λ_{em} = 775 nm) HPLC chromatograms of **PD**.



Solvent gradient used for HPLC of **PD**. Conditions: flow rate: 1 mL/min, Temperature: 30 °C

Time (min)	**1% CH_3CO_2H in H_2O (%)**	**CH_3OH (%)**	**THF (%)**
0	70	25	5
8.0	15	25	60
10.0	15	25	60
11.0	70	25	5
13.0	70	25	5

Figure S8. MALDI-TOF and HPLC of **PD**.

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