SUPPORTING INFORMATION

Conformational preference of a porphyrin rotor in confined environments

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Materials and methods

All reagents and solvents were from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar, Wako, Tokyo Chemical Industries Co.) and were used as received. Ionic liquids (ILs) were synthesized and purified according to literature procedures, see below for details.[1] [C_2-mim]BF_4 was purchased from Tokyo Chemical Industries Co. and used as received. **PD** was prepared according to literature procedure;[2] the structure and purity were confirmed by MALDI-TOF spectrometry and HPLC, respectively (Figure S11).

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 and sample preparations. All solutions of **PD** in ILs were prepared by addition of the DMSO stock solution to the ionic liquid or DMSO, followed by vortexing at 3000 rpm for 10-30 seconds.

NMR spectra were recorded on a Varian (300 MHz) spectrometer. ^1H NMR chemical shifts are reported in ppm (δ) downfield from residual DMSO (δ = 2.51 ppm) in DMSO-d_6; ^{19}F resonances are reported relative to trifluorochloromethane (δ = 0.00 ppm).

Dynamic light scattering (DLS) for characterization of the reverse micelles (RMs) was done using a Malvern Zetasizer Nano ZS light scattering instrument employing a 532 nm laser. The scattering angle was set at 90^o. Tween-80/Span-20/IL or DMSO/IPM reverse micelle systems were prepared as follows: a mixture of Tween-80 and Span-20 in a 2:3 ratio by weight was prepared. Next, IPM was filtered using a 0.2 μM Millipore Millex-PTFE filter to remove any traces of dust or contaminants, then an appropriate amount of IPM was added to produce a solution with the surfactants concentration of 20 % by weight. The mixture was vortexted and sonicated to produce a macroscopically homogeneous solution. RMs with various contents (DMSO, DMSO-**PD**, IL-DMSO, or IL-**PD**) were prepared by injecting an appropriate amount of media or media stock, followed by thorough mixing until a clear and optically transparent solution was obtained. No macroscopic heterogeneity was visible before measurements. Measurements were conducted at 25 ^{o}C. Samples were equilibrated for 5 minutes before data collection. The size and polydispersity of the RMs were evaluated with the aid of Malvern DTS software. In this study, the micelle content (R) was expressed as the molar ratio of media to surfactants (Tween-80 + Span-20).

Concurrent with DLS measurements, absorbance and fluorescence of **PD**-containing RM or the appropriate background (DMSO-RMs or IL-DMSO) were obtained.

Absorption spectra were acquired on JascoV-550 UV-vis instrument with a resolution of 1 nm using 1.0 cm quartz cells.

Fluorescence measurements were performed using a Hitachi F-700; the measurements were carried out as follows: λ_{ex} = 460, 470, 475, 480 and 490 nm; emission collected from 600 to 850 nm; excitation and emission slit widths were 5 nm and 10 nm respectively; 700 volts; 1.0 cm quartz cells. All spectra were background subtracted using appropriate blanks, and subsequently smoothed using manufacturer provided software.

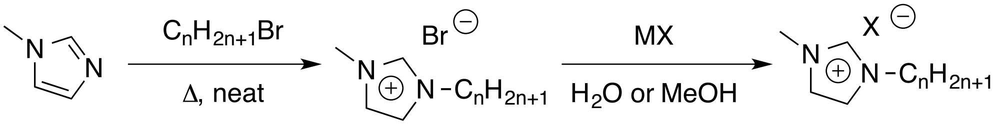
Percent of the twisted **PD** conformation was calculated as follows:

twisted **PD** % = F max twisted / (F max twisted + F max planar) * 100 ,

where F max twisted is the maximum emission intensity of the twisted conformation and F max planar is the maximum fluorescence intensity of the planar conformation.

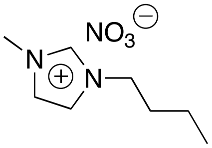
Synthesis and characterization of ILs

All ILs were prepared according to literature procedures or modified literature procedures[1] following the general sequence shown below. ILs were purified as follows: ILs were dissolved in CH_2Cl_2, followed by filtration to get rid of inorganic impurities. Next, ILs 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 ILs were dried under vacuum for 8-12 hours. All sample preparations and spectroscopic measurements were conducted immediately after removing the ILs from the vacuum with care to minimize the exposure to moisture.

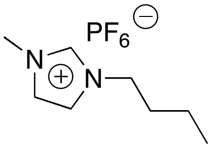


X = NO_3: MX = $AgNO_3$, MeOH
X = NTf_2: MX = $LiNTf_2$, H_2O
X = PF_6: MX = KPF_6, H_2O

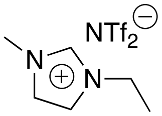
[C_4-mim]NO_3:[3]
^1H NMR (300 MHz, DMSO-d_6): δ = 9.16 (s, 1H), 7.78 (t, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 1.8 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.74 (pent, *J* = 7.4 Hz, 2H), 1.23 (sext, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 6.9 Hz, 3H)



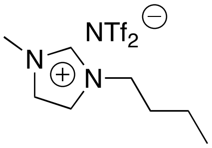
[C_4-mim]PF_6:[3]
^1H NMR (300 MHz, DMSO-d_6): δ = 9.08 (s, 1H), 7.74 (s, 1H), 7.67 (s, 1H), 4.14 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 1.75 (pent, *J* = 7.2 Hz, 2H), 1.24 (sext, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H);
^{19}F NMR (300 MHz, DMSO-d_6): δ = –70.2 (d, *J* = 710.4 Hz)



[C_2-mim]NTf_2:[3]
^1H 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:[3]
^1H 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)



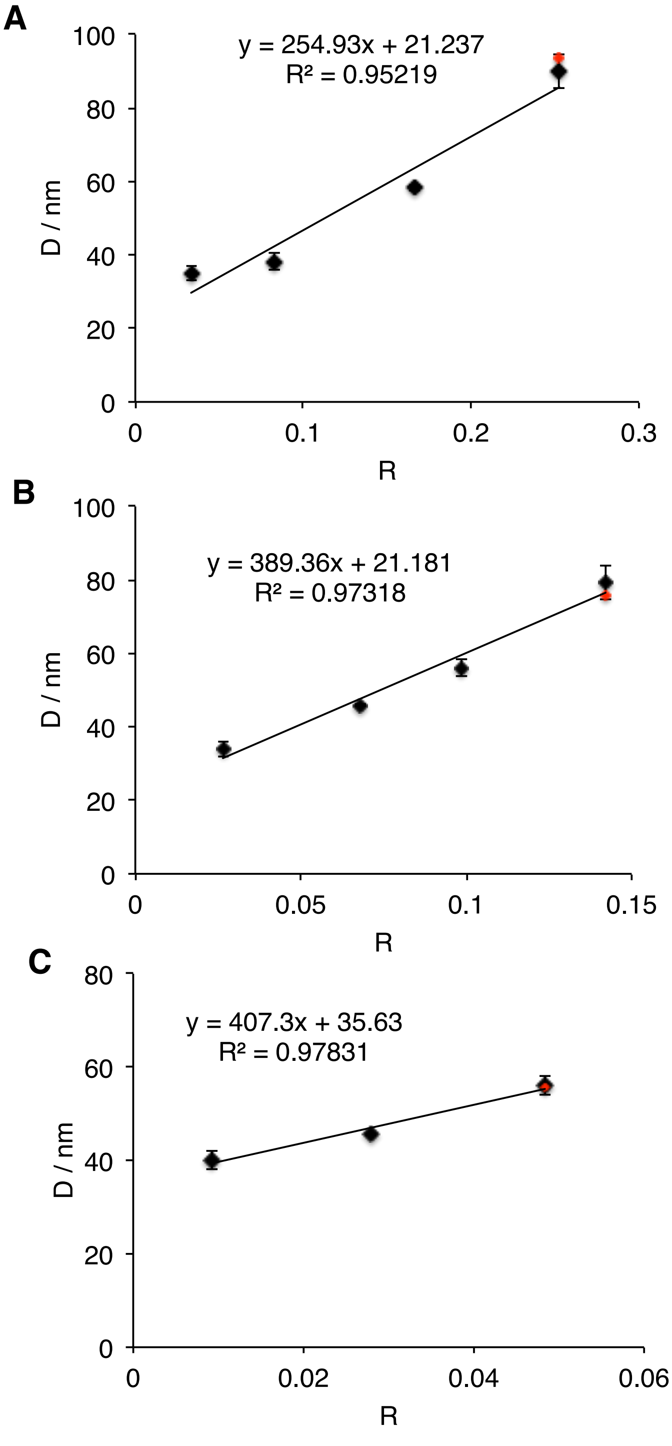


Figure S1. Diameter of ionic liquid–reverse micelles as a function of the amount of the [C_4-mim]-based ionic liquids: **A** – [C_4-mim]NO_3, **B** – [C_4-mim]PF_6, **C** – [C_4-mim]NTf_2. Data are reported as averages of two to six independent preparations of the IL-RMs (±SD as error bars). Overlaying red symbols in **A**–**C** indicate representative size of a **PD**-containing IL-RM.

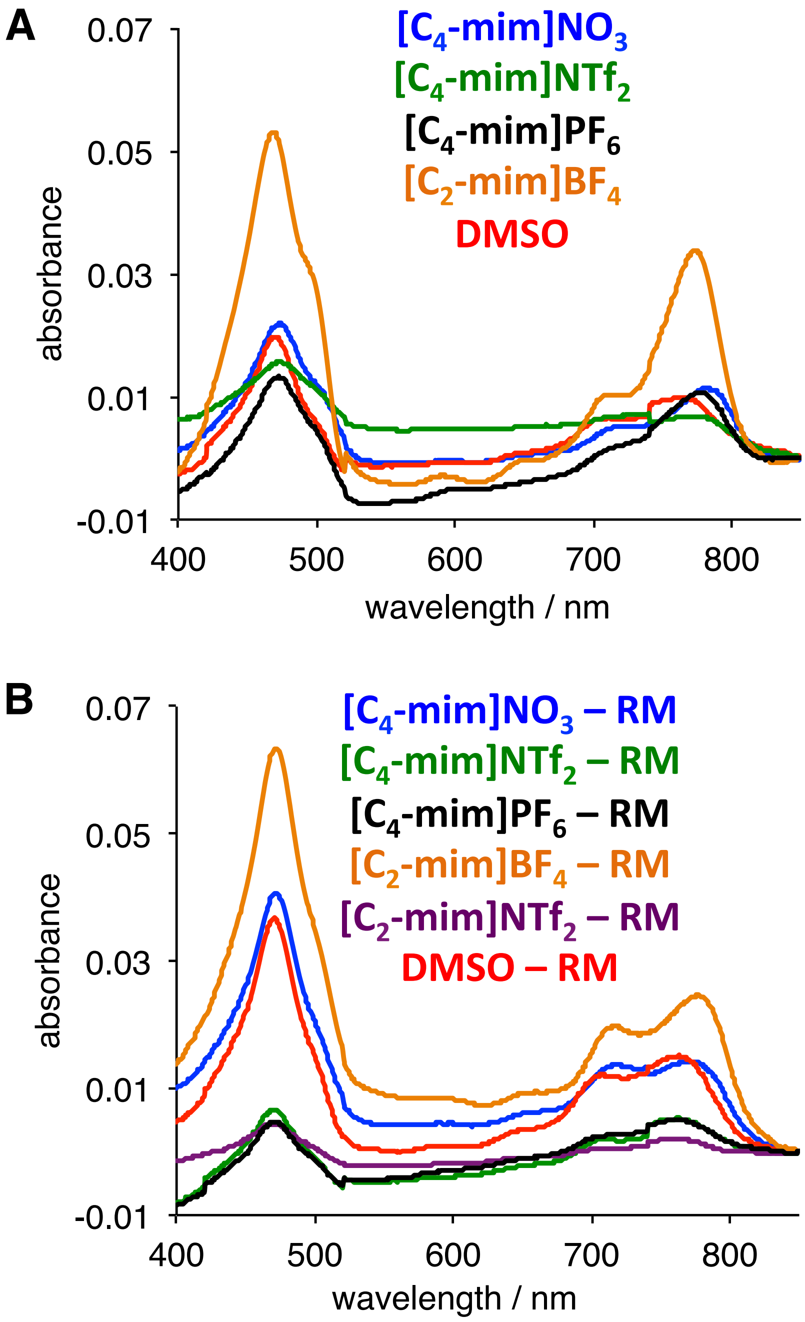


Figure S2. Absorption spectra of **PD** in neat solvents (**A**), and in IL-RMs and DMSO-RMs (**B**). The absorption of **PD** in neat [C_2-mim]NTf_2 was too low to be measured.

Conditions:

[C_4-mim]PF_6 and [C_4-mim]PF_6–RM: [**PD**] = 0.10 μM, 0.010 % of DMSO (v/v).
[C_4-mim]NTf_2 and [C_4-mim]NTf_2–RM: [**PD**] = 0.05 μM, 0.005 % of DMSO (v/v).
[C_4-mim]NO_3 and [C_4-mim]NO_3–RM: [**PD**] = 0.15 μM, 0.015 % of DMSO (v/v).
[C_2-mim]BF_2 and [C_2-mim]BF_4–RM: [**PD**] = 0.30 μM, 0.03 % of DMSO (v/v).
[C_2-mim]NTf_2 and [C_2-mim]NTf_2–RM: [**PD**] = 0.03 μM, 0.003 % of DMSO (v/v).
DMSO: [**PD**] = 0.15 μM; DMSO–RM: [**PD**] = 0.15 μM, 1.5 % of DMSO (v/v).

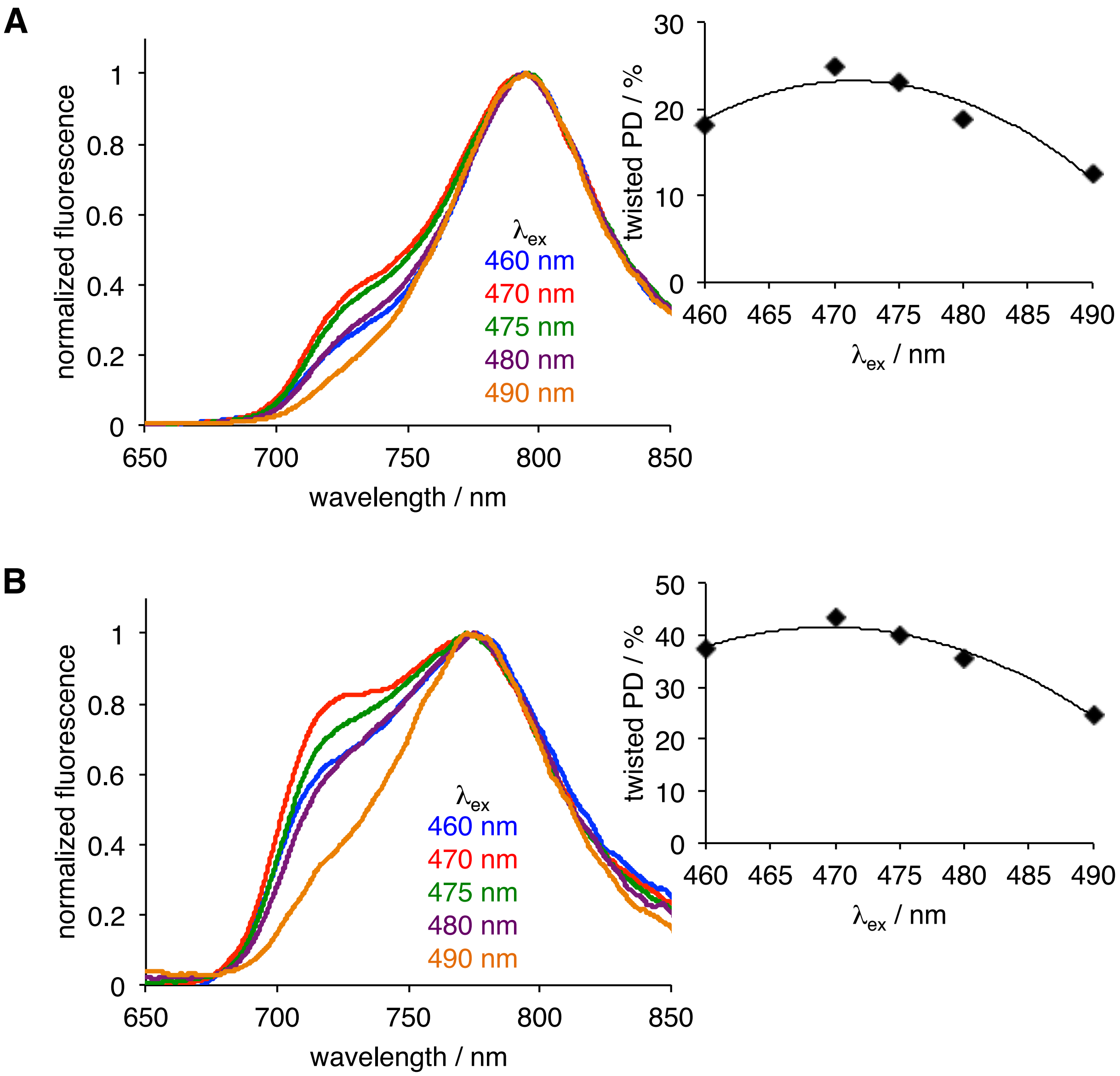


Figure S3. Emission spectra of **PD** in [C_4-mim]PF_6 (**A**) and [C_4-mim]PF_6–reverse micelles (**B**); insets show the amount of twisted **PD** as a function of excitation wavelength. Conditions: [**PD**] = 0.10 μM, all mixtures contained 0.010 % of DMSO (v/v).

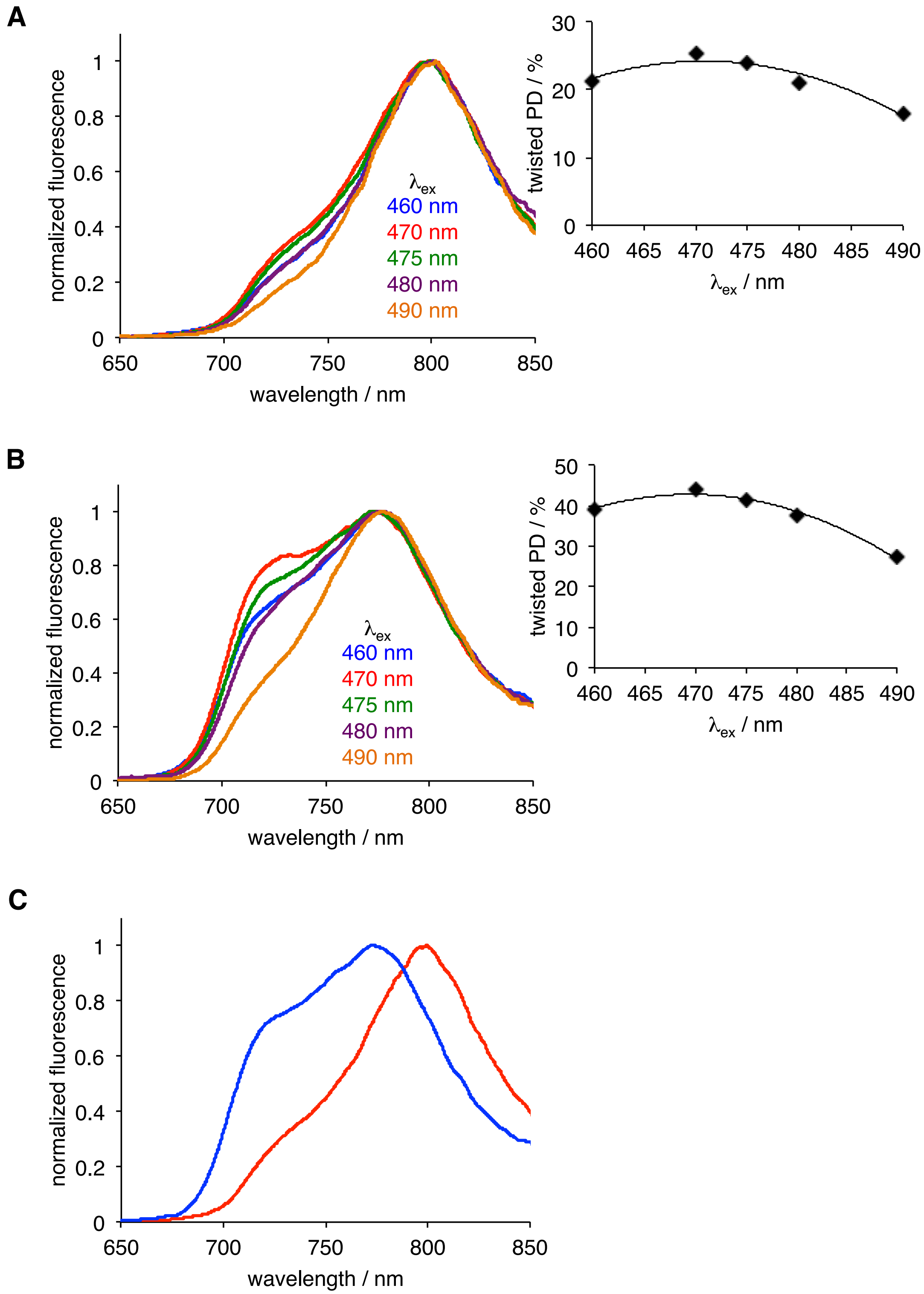


Figure S4. Emission spectra of **PD** in [C_4-mim]NTf_2 (**A**) and [C_4-mim]NTf_2–reverse micelles (**B**); insets show the amount of twisted **PD** as a function of excitation wavelength. Overlaid emission spectra of **PD** in [C_4-mim]NTf_2 (red) and [C_4-mim]NTf_2–reverse micelles (blue) upon excitation at 475 nm (**C**). Conditions: [**PD**] = 0.05 μM, all mixtures contained 0.005 % of DMSO (v/v).

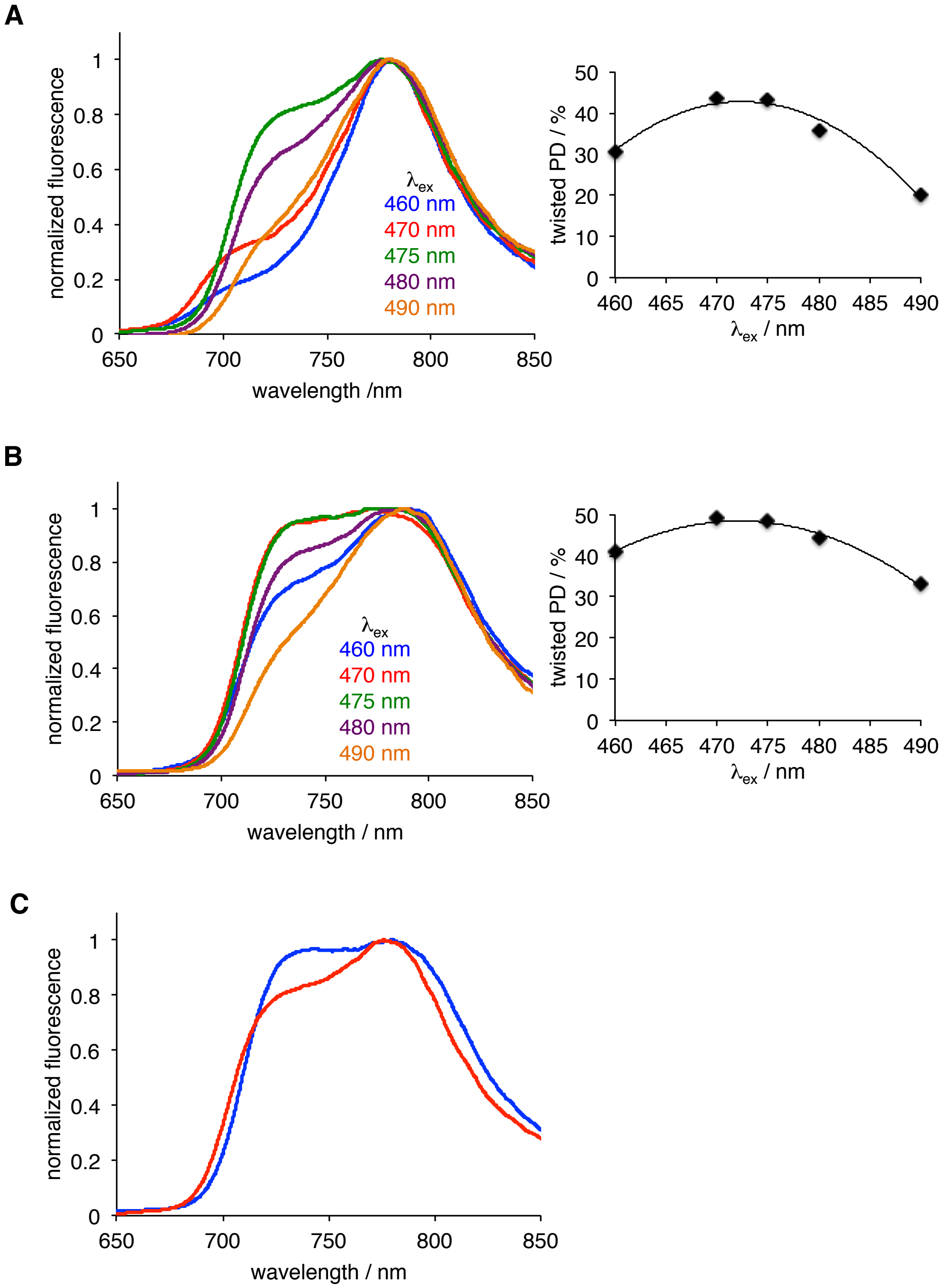


Figure S5. Emission spectra of **PD** in [C_4-mim]NO_3 (**A**) and [C_4-mim]NO_3–reverse micelles (**B**); insets show the amount of twisted **PD** as a function of excitation wavelength. Overlaid emission spectra of **PD** in [C_4-mim]NO_3 (red) and [C_4-mim]NO_3–reverse micelles (blue) upon excitation at 475 nm (**C**). Conditions: [**PD**] = 0.15 μM, all mixtures contained 0.015 % of DMSO (v/v).

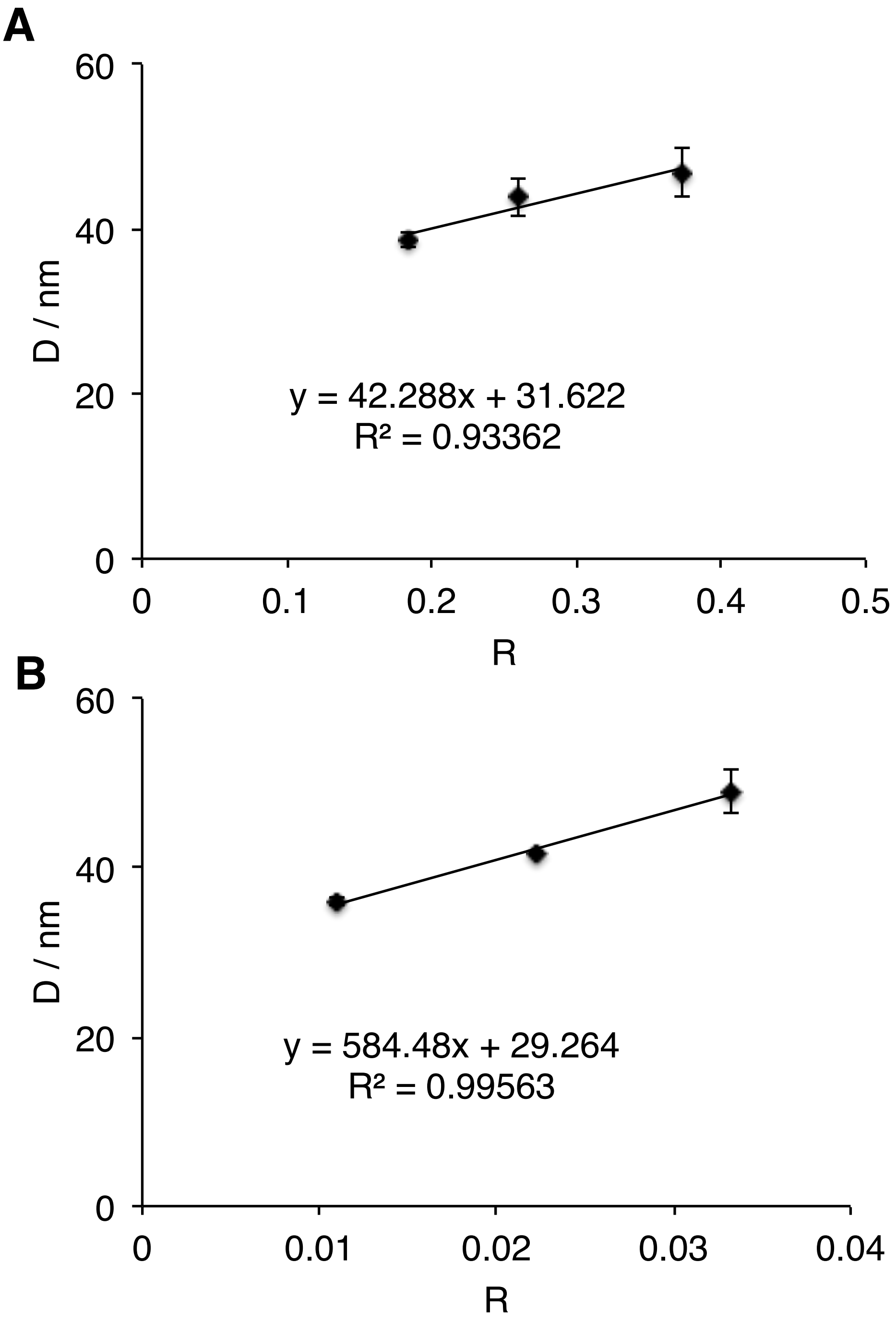


Figure S6. Diameter of ionic liquid–reverse micelles as a function of the amount of the [C_2-mim]-based ionic liquids. **A** – [C_2-mim]BF_4, **B** – [C_2-mim]NTf_2. Data are reported as averages of two to four independent preparations of the IL-RMs (±SD as error bars).

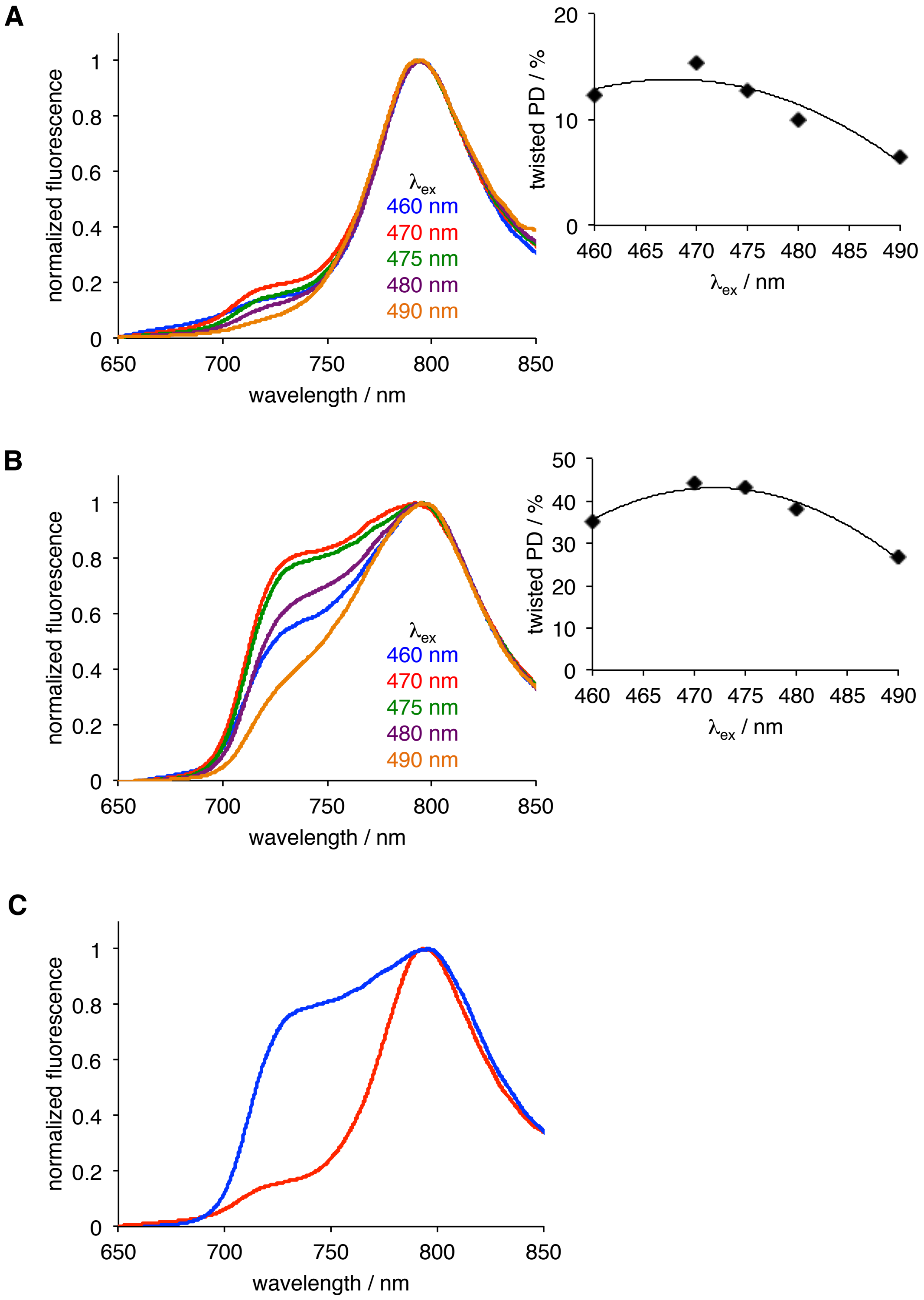


Figure S7. Emission spectra of **PD** in [C_2-mim]BF_4 (**A**) and [C_2-mim]BF_4–reverse micelles (**B**); Insets show the amount of twisted **PD** as a function of excitation wavelength. Overlaid emission spectra of **PD** in [C_2-mim]BF_4 (red) and [C_2-mim]BF_4–reverse micelles (blue) upon excitation at 475 nm (**C**). Conditions: [**PD**] = 0.30 μM, all mixtures contained 0.03 % of DMSO (v/v).

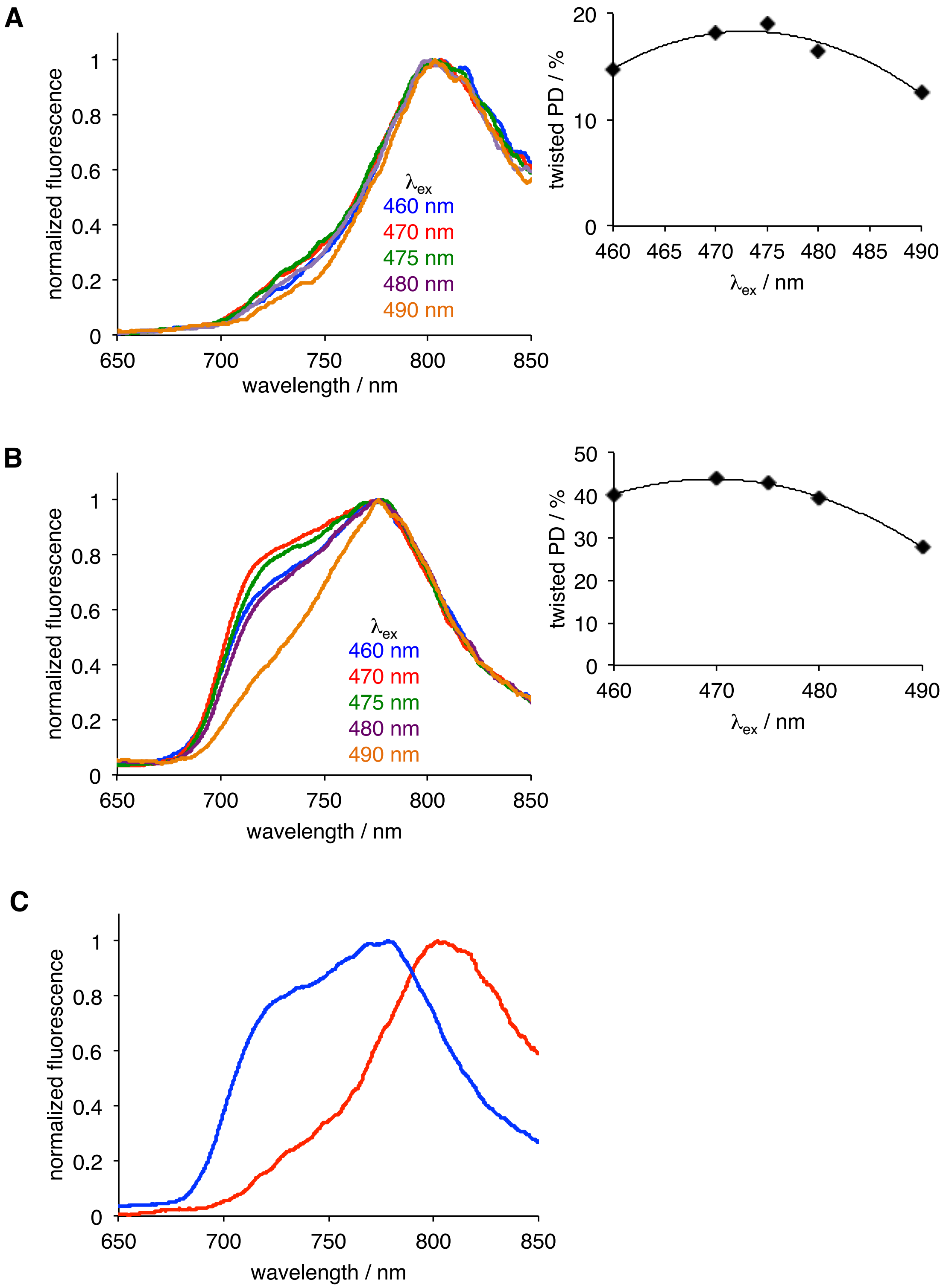


Figure S8. Emission spectra of **PD** in [C_2-mim]NTf_2 (**A**) and [C_2-mim]NTf_2–reverse micelles (**B**); insets show the amount of twisted **PD** as a function of excitation wavelength. Overlaid emission spectra of **PD** in [C_2-mim]NTf_2 (red) and [C_2-mim]NTf_2–reverse micelles (blue) upon excitation at 475 nm (**C**). Conditions: [**PD**] = 0.03 μM, all mixtures contained 0.003 % of DMSO (v/v).

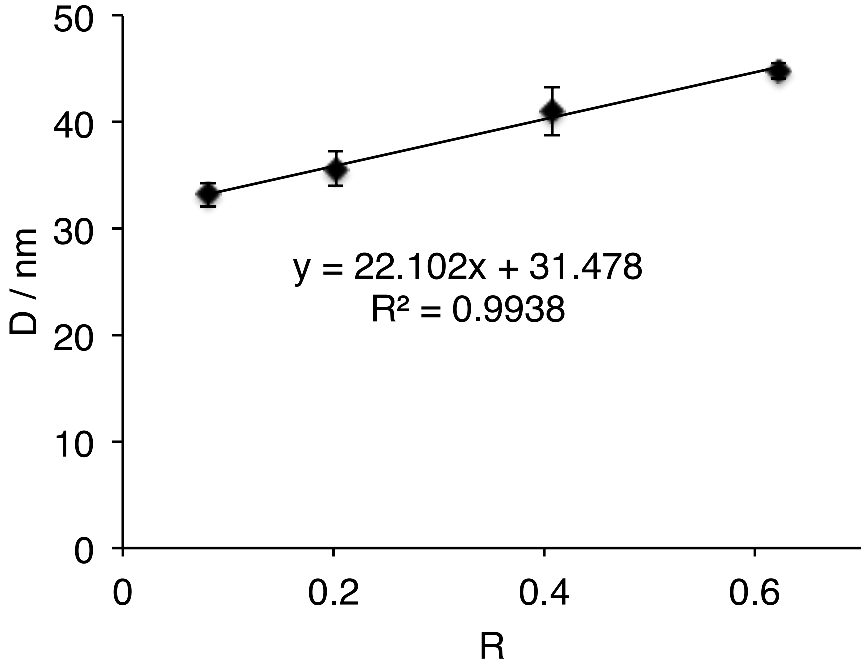


Figure S9. Diameter of DMSO–reverse micelles as a function of the amount of DMSO. Data are reported as averages of four to six independent preparations of the DMSO-RMs (±SD as error bars).

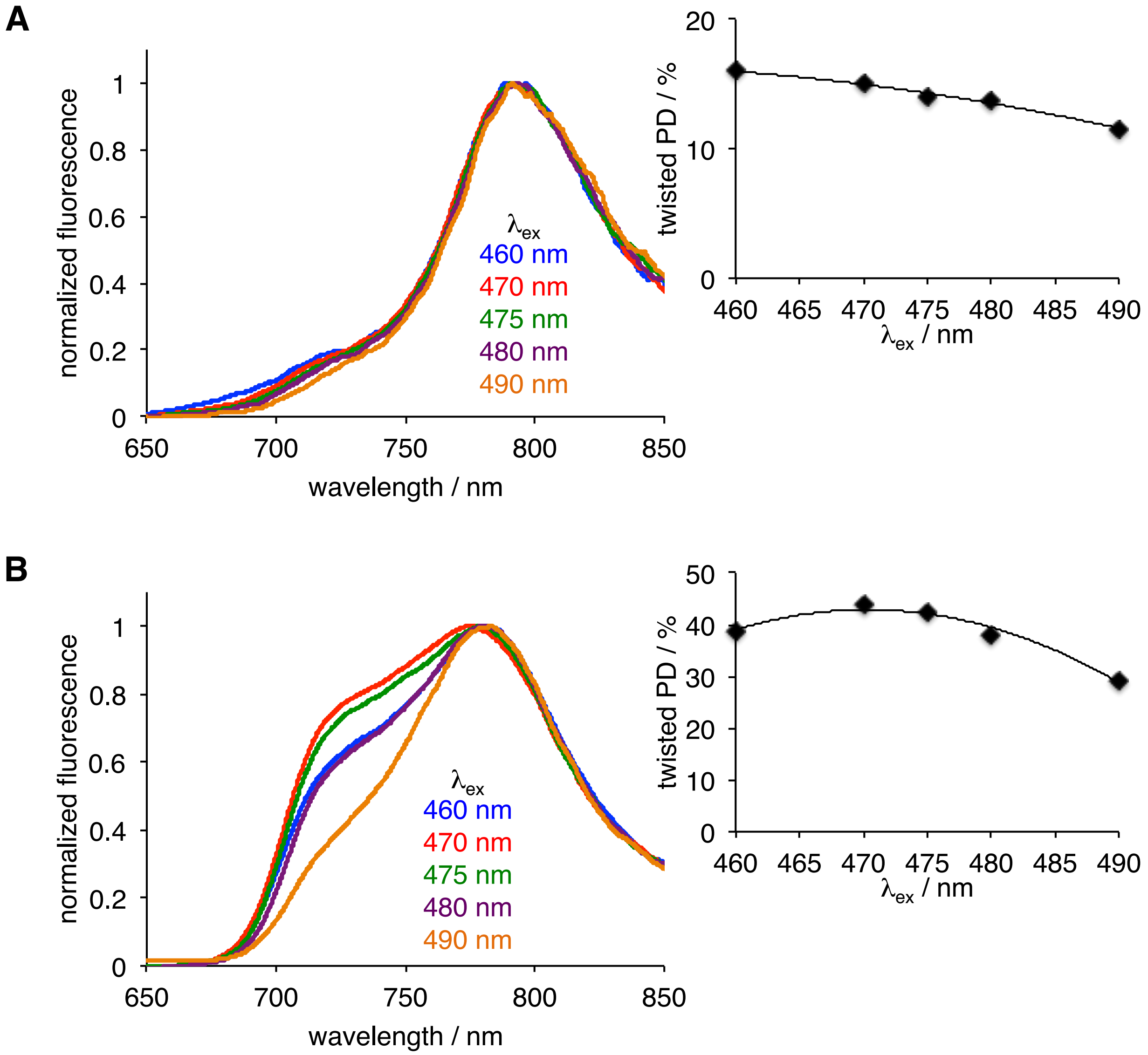
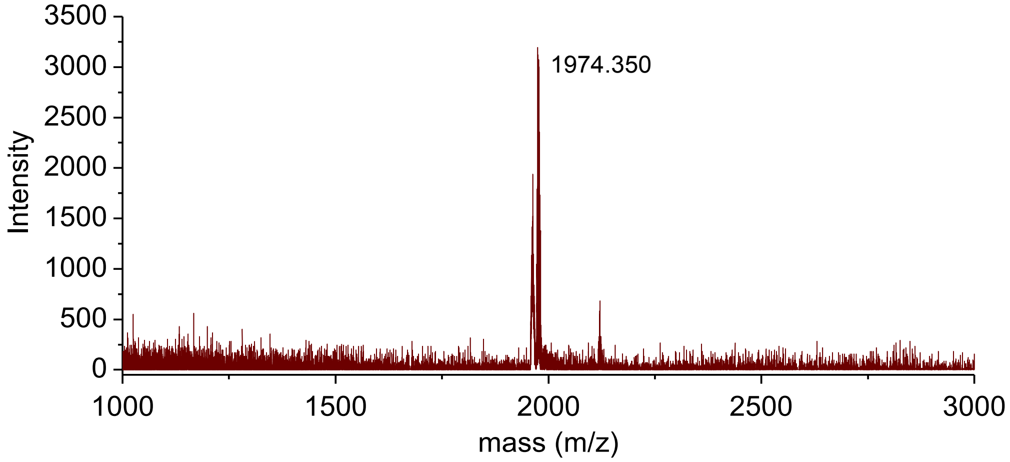
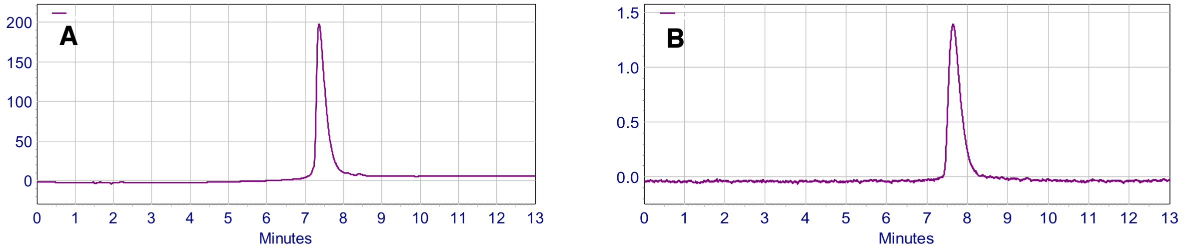


Figure S10. Emission spectra of **PD** in DMSO (**A**) and DMSO–reverse micelles (**B**); insets show the amount of twisted **PD** as a function of excitation wavelength. Conditions: [**PD**] = 0.15 μM, all mixtures of DMSO-RMs contained 1.5 % of DMSO (v/v).

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 S11. MALDI-TOF and HPLC of **PD**.

References

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2. M. Balaz, H. A. Collins, E. Dahlstedt and H. L. Anderson, *Org. Biomol. Chem.,* 2009, **7**, 874.

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