Supporting Information (SI)

Aggregation of a model porphyrin within poly(ethylene glycol) (PEG): Effect of water, PEG molecular weight, ionic liquid, salt, and temperature

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Table S1. Recovered rate constants for the decay of absorbance at 490 nm (corresponding to decay of J-aggregates) and growth of absorbance at 448 nm (corresponding to formation of diprotonated form) of 10 µM TSPP in 10 wt% water added PEGs with and without 0.3 M additive at mixture pH 1. r^2 shows the goodness-of-fit for the fitted data. Error estimated in rate constants ≤ 10%.

PEGs	Additives	$\lambda_{\max}^{abs}(nm)$	$k \times 10^4$ (s^{-1})	r^2
200	None	490	~ 0	_ _
		448	~ 0	_ _
	NaCl	490	14.8	0.9963
		448	21.3	0.9984
	$NaBF_4$	490	6.2	0.9994
		448	8.8	0.9981
	[bmim][BF_4]	490	11.8	0.9949
		448	18.8	0.9872
	[bmim][OTf]	490	8.5	0.9673
		448	16.2	0.9898
	[bmim][PF_6]	490	9.6	0.9960
		448	13.7	0.9940
	[bmim][Tf_2N]	490	8.8	0.9721
		448	33.7	0.9861
400	None	490	8.6	0.9989
		448	9.8	0.9990
	NaCl	490	9.4	0.9994
		448	14.1	0.9983
	$NaBF_4$	490	2.8	0.9997
		448	4.1	0.9992
	[bmim][BF_4]	490	5.6	0.9948
		448	14.0	0.9984
	[bmim][OTf]	490	7.5	0.9992
		448	12.8	0.9983

	[bmim][PF$_6$]	490	5.0	0.9987
		448	10.5	0.9994
	[bmim][Tf$_2$N]	490	8.4	0.9954
		448	15.6	0.9957
600	None	490	7.3	0.9994
		448	12.2	0.9995
	NaCl	490	9.6	0.9987
		448	13.9	0.9989
	NaBF4	490	2.7	0.9964
		448	5.3	0.9989
	[bmim][BF$_4$]	490	9.4	0.9869
		448	11.6	0.9994
	[bmim][OTf]	490	15.5	0.9776
		448	17.5	0.9919
	[bmim][PF$_6$]	490	9.5	0.9948
		448	16.8	0.9950
	[bmim][Tf$_2$N]	490	12.7	0.9859
		448	13.6	0.9947
1000	None	490	9.0	0.9987
		448	16.2	0.9963
	NaBF4	490	4.3	0.9957
		448	11.0	0.9839
	[bmim][BF$_4$]	490	12.1	0.9973
		448	21.0	0.9887
	[bmim][OTf]	490	17.7	0.9958
		448	15.7	0.9921
	[bmim][PF$_6$]	490	8.1	0.9989
		448	13.3	0.9996
	[bmim][Tf$_2$N]	490	29.3	0.9902
		448	19.7	0.9959
1450	None	490	15.6	0.9923

		448	19.0	0.9892
	[bmim][BF$_4$]	490	17.8	0.9881
		448	21.2	0.9834
	[bmim][OTf]	490	26.5	0.9934
		448	24.7	0.9958
	[bmim][PF$_6$]	490	22.5	0.9954
		448	21.8	0.9787
	[bmim][Tf$_2$N]	490	15.1	0.9469
		448	39.2	0.9855
2000	None	490	13.2	0.9932
		448	34.8	0.9863
	[bmim][BF$_4$]	490	6.1	0.9959
		448	33.5	0.9887
	[bmim][OTf]	490	3.6	0.9845
		448	< 50	
	[bmim][PF$_6$]	490	14.9	0.9885
		448	27.8	0.9957
	[bmim][Tf$_2$N]	490	8.8	0.9831
		448	68.5	0.8865
3000	None	490	16.6	0.9563
		448	44.7	0.9374

Table S2. Specific conductance (mS.cm^{-1}) of 10 wt% water added PEGs (PEG200, PEG600 and PEG2000) with and without 0.3 M additive (NaCl, $NaBF_4$ and [bmim][BF_4]) at mixture pH 1. Temperatures are provided in the parenthesis.

Solvent	**Specific Conductance (mS.cm^{-1})**	
	10 wt % water in PEG 200 at pH 1	
No additive	0.41 (27ºC)	0.82 (80ºC)
NaCl	0.63 (27ºC)	1.52 (80ºC)
$NaBF_4$	0.87 (27ºC)	2.86 (80ºC)
[bmim][BF_4]	0.83 (27ºC)	3.25 (80ºC)
	10 wt % water in PEG 600 at pH 1	
No additive	0.23 (27ºC)	0.59 (80ºC)
NaCl	0.29 (27ºC)	1.07 (80ºC)
$NaBF_4$	0.47 (27ºC)	2.01 (80ºC)
[bmim][BF_4]	0.52 (27ºC)	2.03 (80ºC)
	10 wt % water in PEG 2000 at pH 1	
No additive	0.15 (40ºC)	0.34 (80ºC)
[bmim][BF_4]	0.61 (40ºC)	1.59 (80ºC)

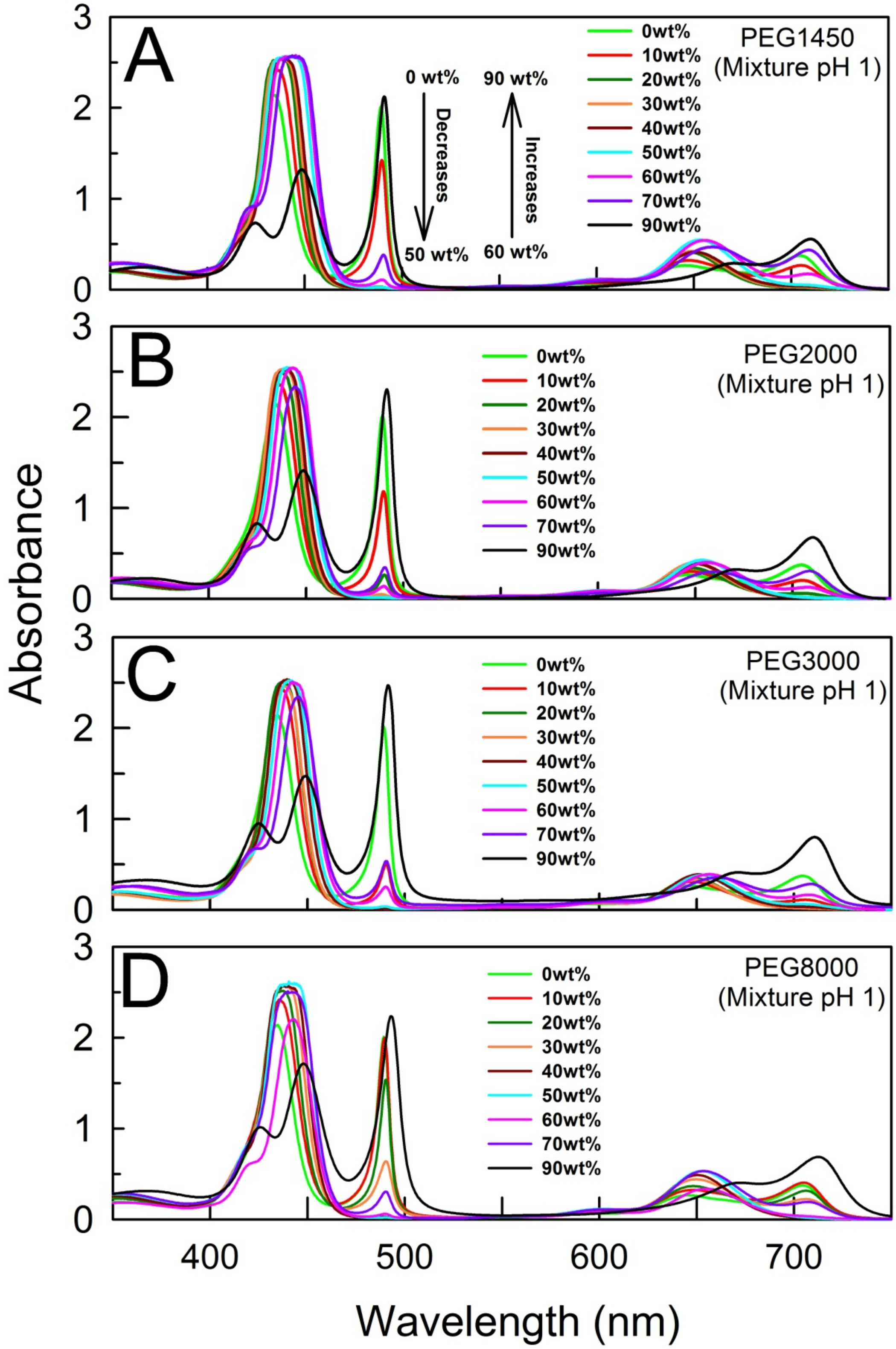

Figure S1. Absorbance spectra of 10 μM TSPP dissolved in aqueous mixture of PEGs (PEG1450, PEG2000, PEG 3000 and PEG8000) at pH 1 as a function of wt% of water.

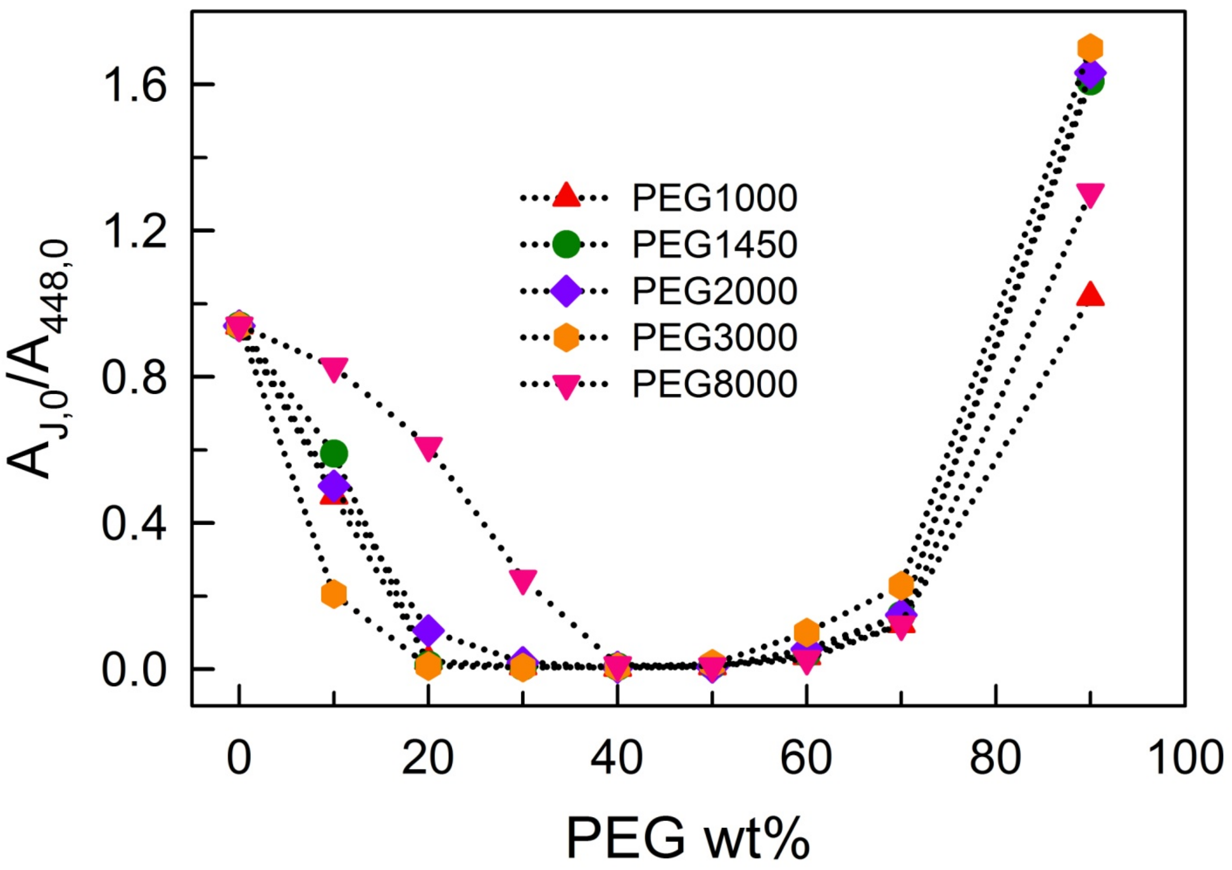

Figure S2. Ratio of the absorbance at 490 nm corresponding to initially formed J-aggregates ($A_{J,0}$) to the absorbance at 448 nm corresponding to diprotonated form exist initially ($A_{448,0}$) of 10 μM TSPP in aqueous mixture of PEGs at pH 1 as a function of wt% of PEG.

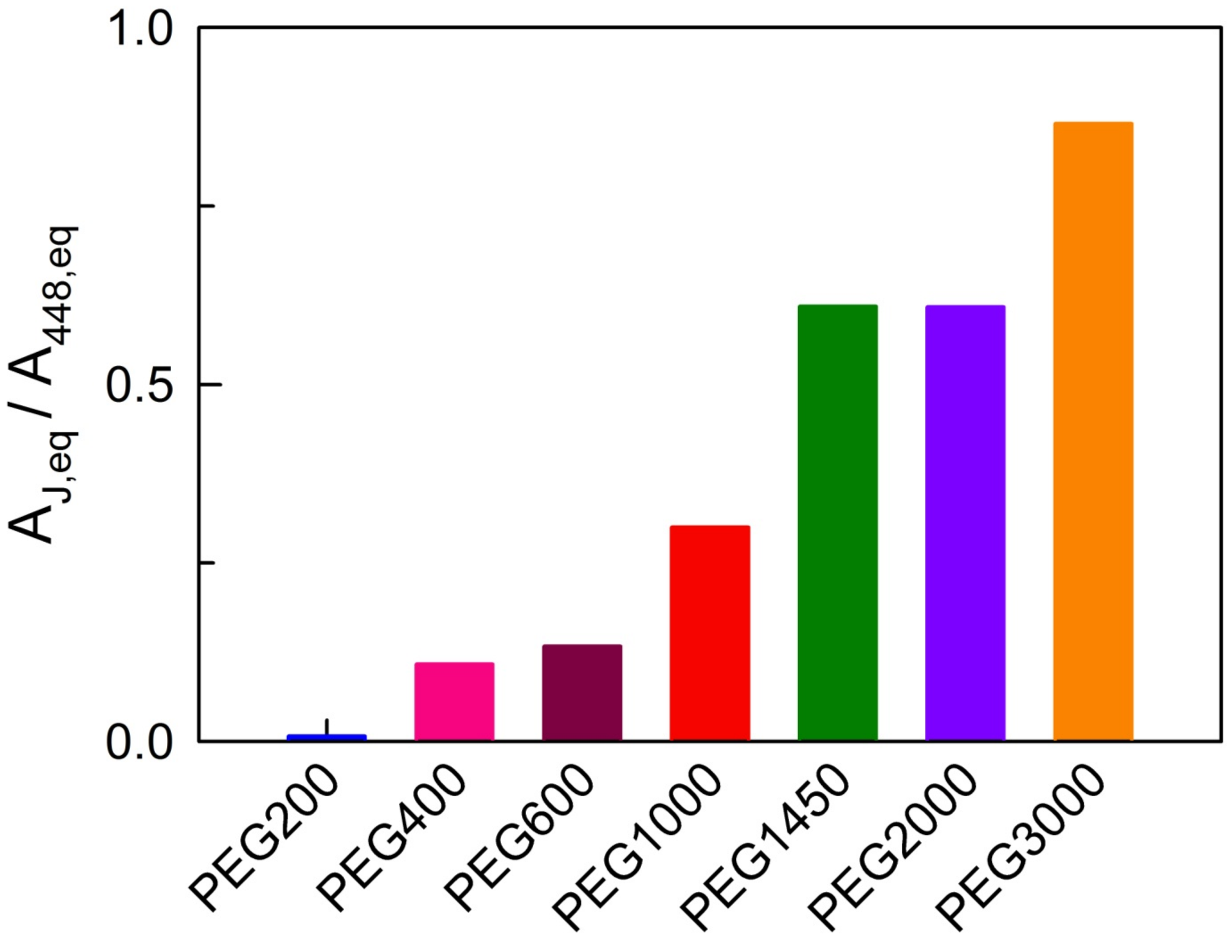

Figure S3. Ratio of the absorbance at 490 nm ($A_{J,eq}$) corresponding to J-aggregates after reaching equilibrium to the absorbance at 448 nm ($A_{448,eq}$) corresponding to diprotonated form after reaching equilibrium in 10 wt% water-added PEG mixtures at pH 1.

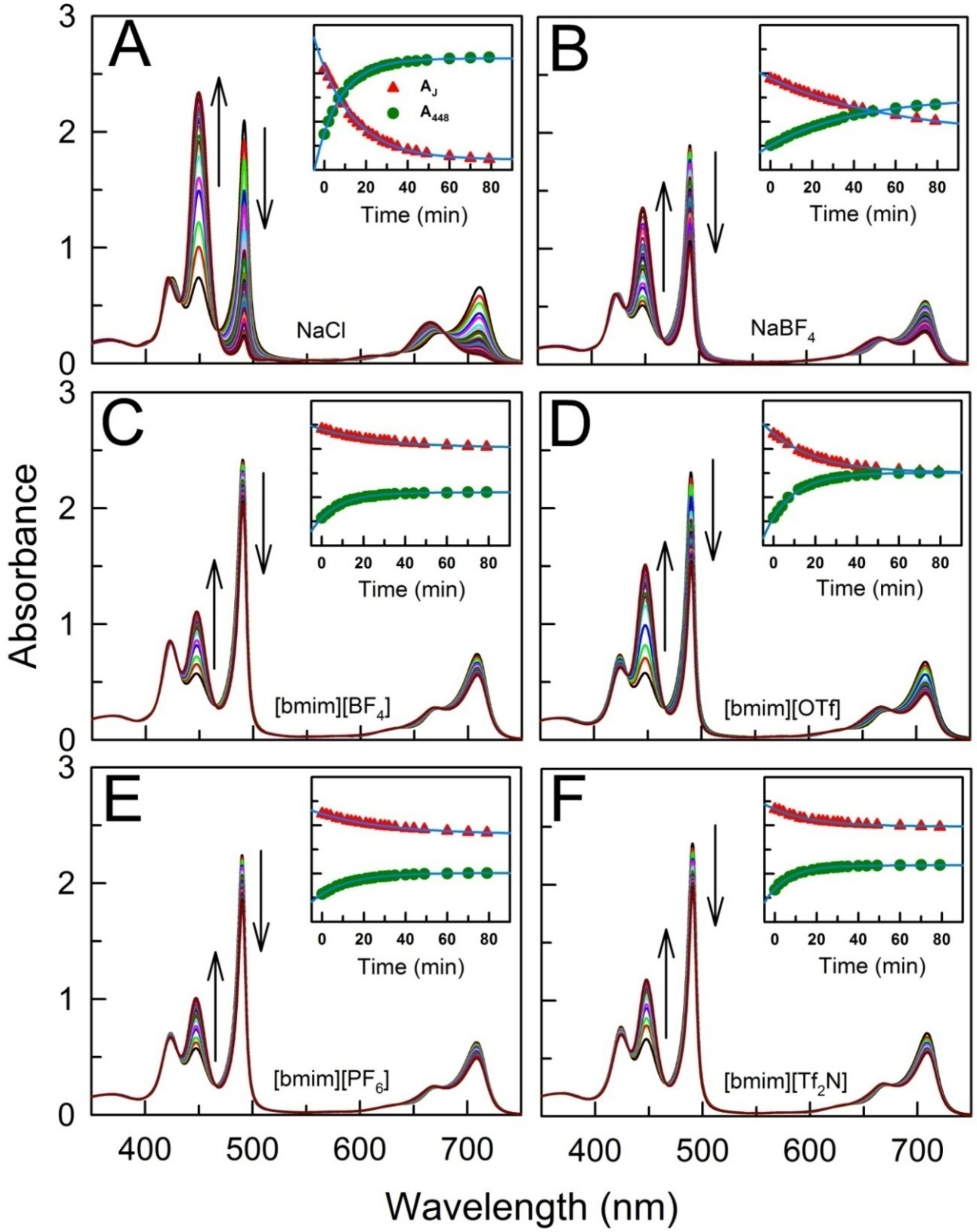

Figure S4. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG400 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth of diprotonated form) with time. Solid lines represent the fit of the data to a psuedo-first order kinetics.

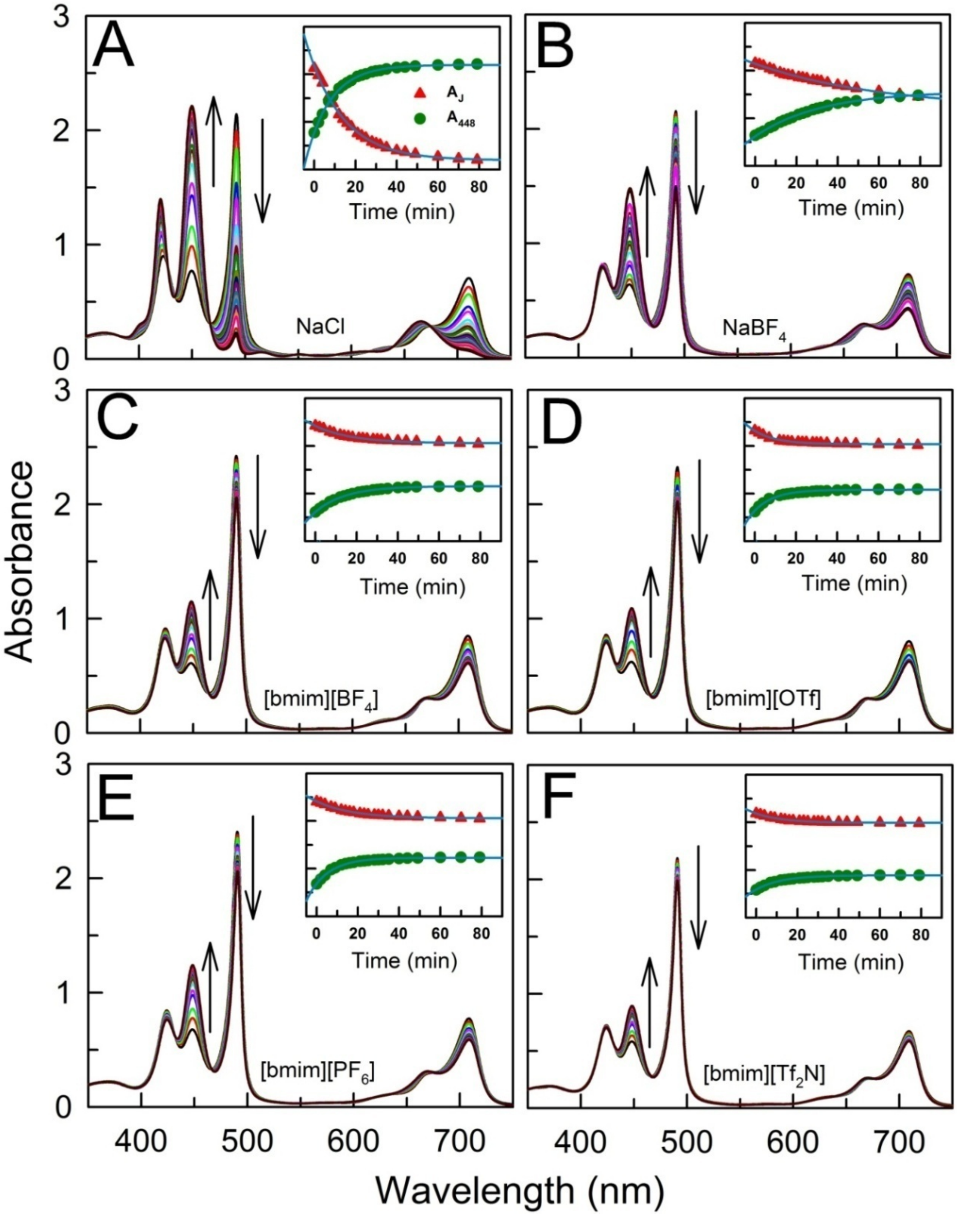

Figure S5. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG600 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth of diprotonated form) with time. Solid lines represent the fit of the data to a psuedo-first order kinetics.

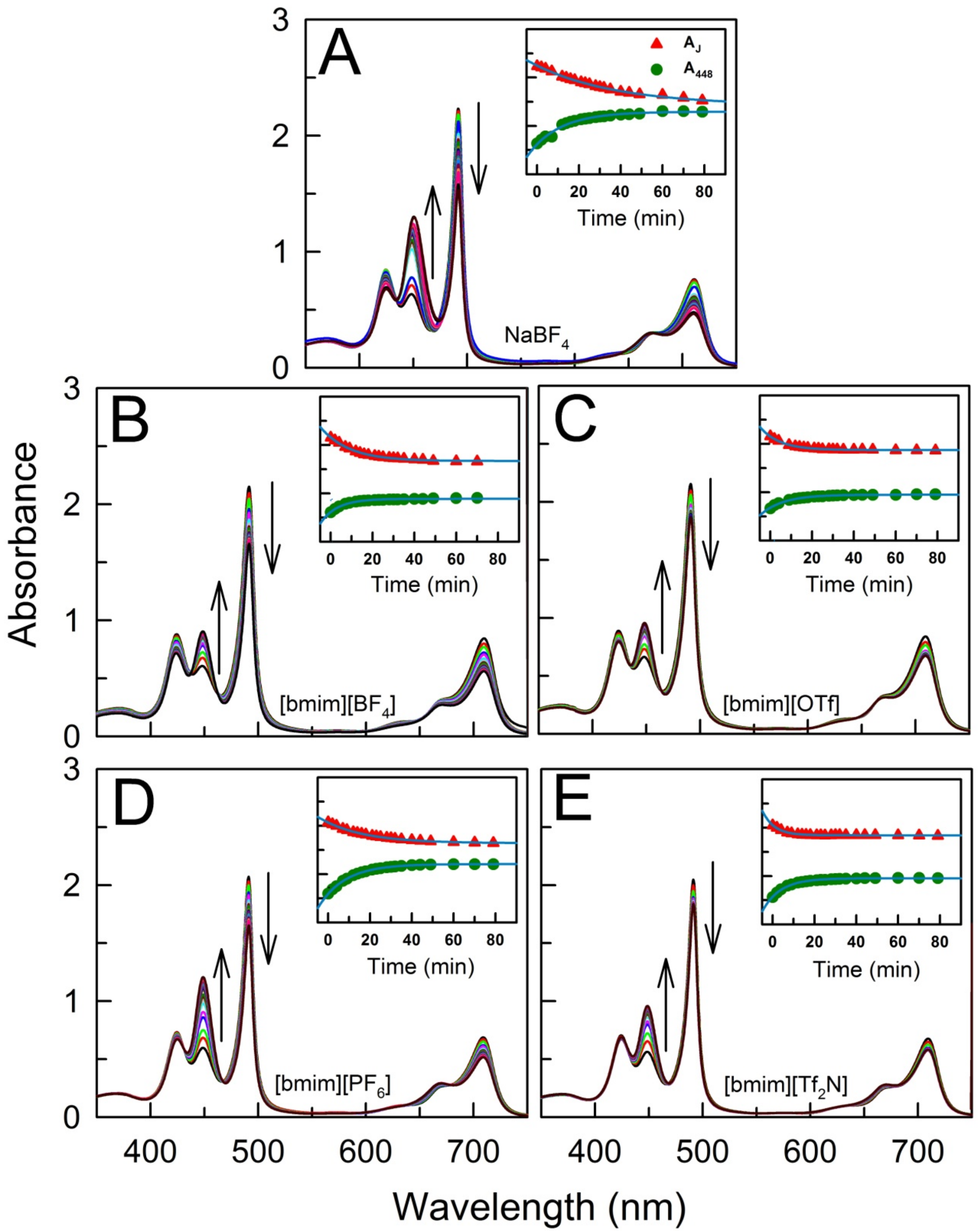

Figure S6. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG1000 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth of diprotonated form) with time. Solid lines represent the fit of the data to a psuedo-first order kinetics.

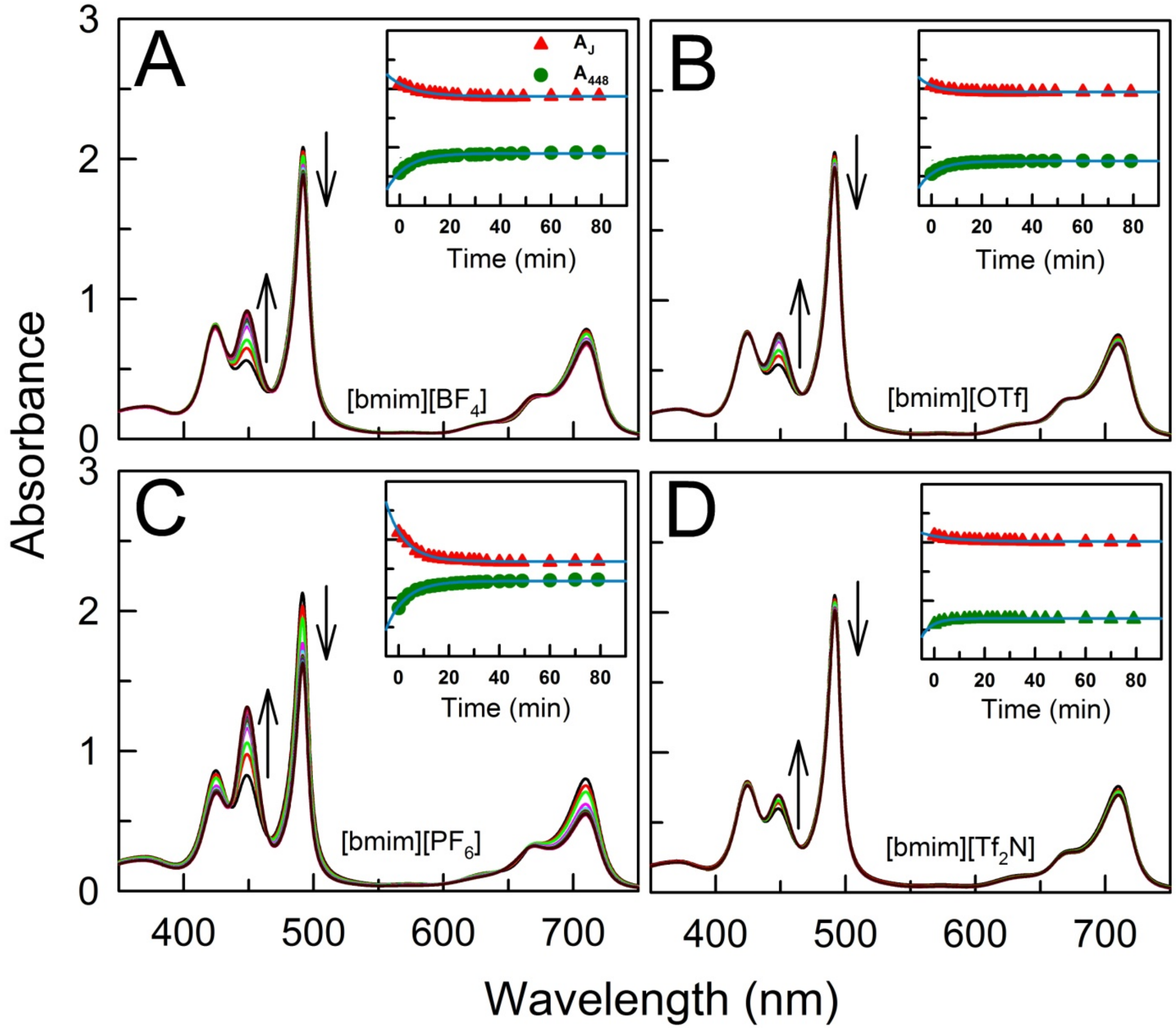

Figure S7. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG1450 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth of diprotonated form) with time. Solid lines represent the fit of the data to a psuedo-first order kinetics.

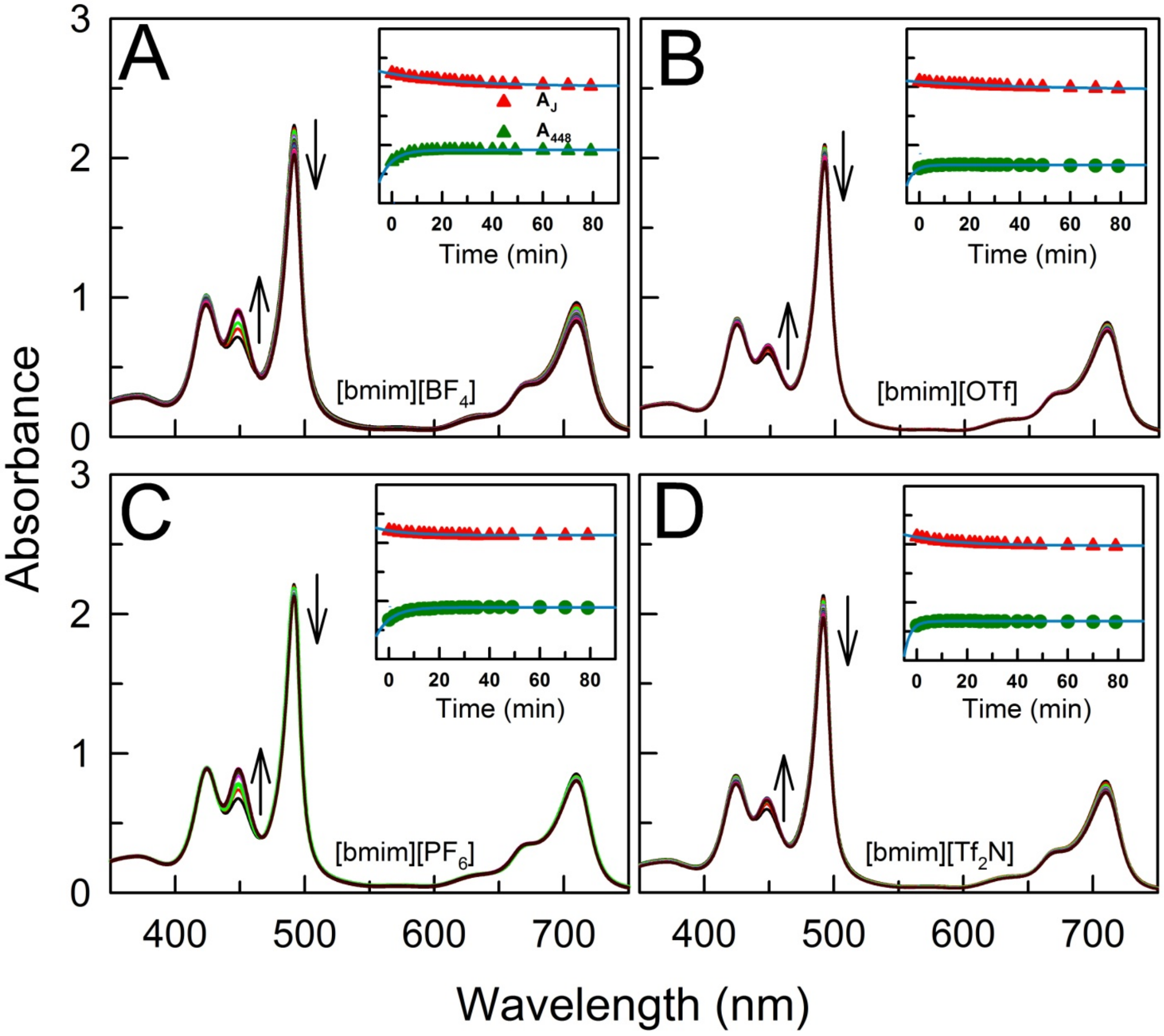

Figure S8. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG2000 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth of diprotonated form) with time. Solid lines represent the fit of the data to a psuedo-first order kinetics.

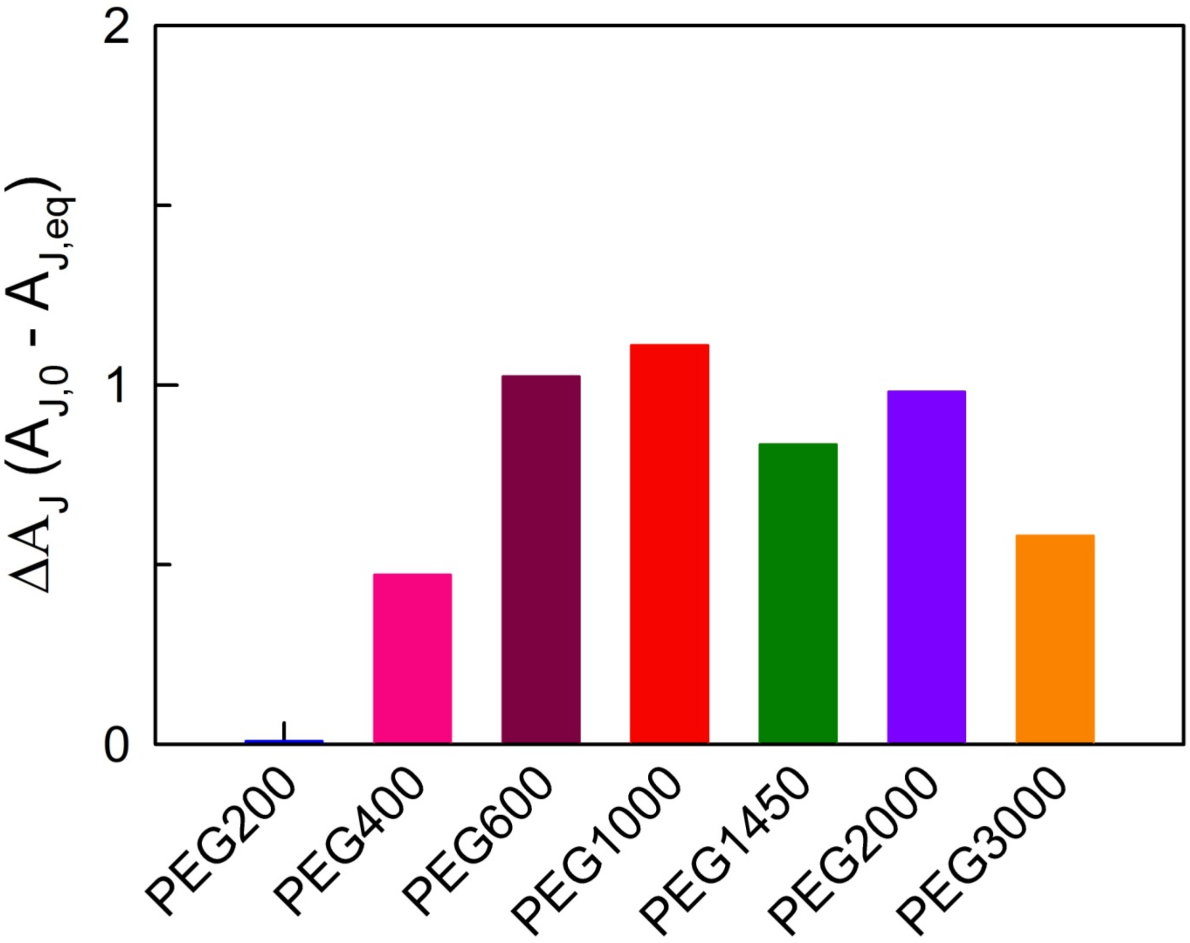

Figure S9. Difference (ΔA_J) between the absorbance of initially formed J-aggregates ($A_{J,0}$) and the absorbance of J-aggregates formed at equilibrium ($A_{J,eq}$) for 10 μM TSPP dissolved in 10 wt% water-added PEG mixtures at pH 1.