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Date: Feb. 18, 2014

Dr. Tanya Smekal
Publishing Editor - Physical Chemistry Chemical Physics
Royal Society of Chemistry, Thomas Graham House
Science Park, Cambridge CB4 0WF.

RE: Submission of the Revised Manuscript CP-ART-01-2014-000103

Dear Dr. Smekal,

Thank you for your e-mail dated February 12, 2014 informing us about the minor revisions required on our manuscript CP-ART-01-2014-000103 prior to its further consideration for publication. We thank all three reviewers for their valuable time and suggestions. We are submitting the revised manuscript addressing the reviewers' comments to the best of our abilities.

Following are the details of the changes incorporated in the revised manuscript as suggested by the reviewers (for your convenience, reviewers' comments are provided in red).

Referee 1:

Comments to the author:

Manuscript represents a very interesting and novel study of the aggregation behavior of a common porphyrin, 5,10,15,20-tetrakis-(4-sulfonatophenyl) porphyrin (TSPP), dissolved in a solvent media composed of poly(ethylene glycols) (PEGs) up to an average molecular weight (MW) of 8000 as the major chemical component. The authors study the aggregation behavior in the different neat poly(ethylene glycols), and as a function of added water, electrolyte salts (sodium chloride and sodium tetrafluoroborate), and ionic liquids (1-butyl-3-methylimidazoium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoro borate, 1-butyl-3-methylimida-zolium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium trifluoromethane-sulfonate). Absorption measurements were recorded from ambient room temperature upto approximately 90 ^{o}C.

The authors' study significantly contributes to our understanding of solute aggregation in organic solvent media. Important experimental observations and conclusions were that small amounts of water mixed with high MW PEGs facilitate J-aggregation of a model porphyrin TSPP under acidic conditions. J-aggregation of the dye was evidenced by the appearance of batho-chromically-shifted sharp absorbance in 485-495 nm region (Soret band) as well as a band in 700-725 nm region (Q-band). The J-aggregation efficiency appears to be a complex interplay of interactions between the ethylene groups, ethoxy units and the terminal hydroxyls on PEG molecular framework along with the water present within the solvent media. The decay of the J-aggregates and subsequent formation of deprotonated form follows pseudo-first order kinetics with reactions reaching equilibrium within approximately 80 minutes. Electrolyte salts and ionic liquids additives facilitate TSPP J-aggregation by decreasing inherent electrostatic repulsion between the negative and positive charge centers of the porphyrin, respectively.

The experimental measurements were carefully performed , and the authors' explanations seem reasonable given the measured absorption data and molecular structures of the compounds studied. I did not notice any errors or omissions in the discussion. I did notice though that there was a problem in the manuscript in that open boxes appeared in the open file instead of what I believe should be long hyphens, for example see the first, second, third, fourth and sixth lines of page 10. Negative subscripts are missing in the numerical values in lines 5 and 7 on page 12. This is likely an error in converting the manuscript to a pdf file. (perhaps an incompatible font style?) I mention the problem to alert the authors to potential problem that might happen in a typesetting stage.

My recommendation is that the manuscript is suitable for publication in its present form.

Response: We thank Referee for her/his time and effort. We have checked the boxes as mentioned by the Referee and made sure they do not appear in the revised manuscript.

Referee 2:

Comments to the author:

The manuscript depicts a comprehensive study of conditions for the formation of J-aggregates of a literature known porphyrin in environment friendly solvent mixtures, i.e. water containing poly(ethylene glycol) (PEG), basically by means of UV-vis absorption spectroscopy. The most suited solvent composition has been explored to be PEG solutions of this porphyrin dye with 10 m.w.-% water content. However, such solutions referred to a non-equilibrated state and, thus, show a time-dependent absorption decrease of the aggregated species as well as an absorption increase for the monomeric one. This J-aggregate degradation has been shown to be dependent on the molecular weight of the applied PEG and was less pronounced for high molecular weight PEGs, for instance PEG3000. Furthermore, the influence of additives, such as salts and ionic liquids, on this J-aggregate degradation has been investigated. Interestingly, these additives enabled the J-band formation even for low molecular weight PEGs and hindered the J-aggregate dissociation the more effectively the higher the molecular weight of the PEGs has been. While for PEG 3000 as most suited solvent component even at high temperatures stable J-aggregates exist, the additives, in particular ionic liquids, seemed to rather stabilize these aggregates for the PEGs of lower molecular weight. The work presented in this manuscript is based on former studies of the same porphyrin and is an extension of a published work (reference 38) of the same group. It provides a comprehensive study about the stabilization of a J-aggregated porphyrin dependent on solvent conditions of applied environment friendly PEG-water mixtures. Since this is a basic value for a broad readership interested in supramolecular dye chemistry, in particular with focus on biological applications, I recommend accepting the manuscript for publication in Physical Chemistry Chemical Physics. Nevertheless some corrections have to be taken into account:

- From a referee's point of view, the time-dependent UV-vis spectra show isosbestic points and thus, one would expect same rate constants derived from both J-aggregate degradation and monomer band increase. However, rate constants differ in case of higher molecular weight PEGs, which is explained by a contribution of a third component, namely the deprotonated form of the porphyrin. This section may not be easy to understand for the reader and therefore I recommend a reconsideration of this part, where this issue is explained in more detail.

Response: As suggested, the appropriate portion is re-written (please see page 11 of the revised manuscript).

- Since the J-aggregates immediately start to dissociate, it is important to point out under which conditions these aggregates have been prepared. If I got it right, J-aggregates have been formed by acidifying aqueous solutions of the porphyrin according to earlier publications, before PEG was added. However, this is not clearly pointed out and should also be mentioned in the experimental section. In the same way, the word "initially" in the underline of Figure 1 is misleading and can easily been read over. Please, make clear, that the UV-vis measurement has been performed immediately after sample preparation, since this does not clearly emanate from the text.

Response: J-aggregates are formed immediately after addition of dye into aqueous mixture of 90 wt% PEGs at mixture pH 1. Therefore, we first prepared the aqueous mixture of 90 wt% PEGs with or without additives, maintained pH 1 of mixture using HCl and then collected absorbance immediately after mixing solution properly. We have added the procedure of sample preparation in experimental section. The word initially in the underline of Figure 1 has been mentioned because we collected absorbance just after addition of dye into mixture and proper mixing of dye took less than 15s.

- The journal of reference 12 is “Chem. Commun.”.

Response: We have checked and corrected this in revised manuscript.

- The second name of the first author of reference 13 is De Zorzi. Thus “De” should not be abbreviated.

Response: We have checked and have corrected this in revised manuscript.

- The name of the second author in reference 14 is “Rudine”.

Response: We have checked and corrected this in revised manuscript.

- The volume number of reference 22 and 39 must be written in bold.

Response: We have checked and have written in bold in revised manuscript.

- Last author in reference 29 is H. L. Pan.

Response: We have checked and corrected this in revised manuscript.

- For reference 32, the international edition must be cited: Angew. Chem. Int. Ed., 2011, 50, 3376.

Response: We have checked and corrected the name of journal.

- The surname of penultimate author in reference 34 is Campos.

Response: We have checked and corrected this in revised manuscript.

- Starting page of reference 48 is 54.

Response: We have checked and corrected this in revised manuscript.

- In general, if the first name contains a hyphen, the name must be abbreviated like A.-B. This is missing in several cases. Therefore, I request the authors to go carefully through the abbreviations in the reference part.

Response: We have carefully checked all the references and have made corrections wherever needed.

- In the text many special characters are not indicated correctly, for example superscripted negative charges as well as hyphen between reference number.

Response: We have checked all special characters and have indicated them correctly in revised manuscript.

Referee 3:

Comments to the author:

"Aggregation of a model porphyrin within poly(ethylene glycol) (PEG): Effect of water, PEG molecular weight, ionic liquid, salt, and temperature" by Rai et al. studies the J-aggregation of 5,10,15,20-tetrakis-(4-sulfonato phenyl)porphyrin (TSPP) in the parameters listed w/in the title. Results regarding TSSP and the effect of ionic liquids on supporting its J-aggregation were reported in refs 37 and 38, The focus of this paper concerns the effects of PEG MW on the J-aggregation via a similar experimental approach. Here, ionic liquids are admixed with solutions of increasing PEG MW solutions.

In the case of added PEG MW conditions, the J-aggregation increases from PEG 250-PEG 3000, but then decreases at PEG 8000. So whatever factors used to explain the initial observations become less relevant at higher MW. Which leads the authors to provide the unsatisfactory conclusion, "The J-aggregation efficiency appears to be a complex interplay of interactions afforded by ethylene groups, ethoxy units and terminal hydroxyls on PEG molecular framework along with the water present within the system." Although the experiments appear to be carried with high precision, since no clear hypothesis concerning the effects of PEG is stated (as perhaps in earlier cases utilizing only ionic liquids), the paper falls short in providing important physical insights.

Response: We agree with the Referee that for samples containing higher MW PEGs, the interactions present within the system become fairly complex. Subsequently, proposing a simple explanation or stating a clear and straight-forward hypothesis becomes increasingly difficult. We recognize this, and in turn, offer this as an important insight that comes out of this work.

Please let me know if you need any further regarding this. Hope you find the revised article suitable for consideration.

Sincerely,

Siddharth Pandey

(SIDDHARTH PANDEY)

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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ABSTRACT. Understanding molecular aggregation within environmentally-benign media is of utmost importance. Aggregation of a common porphyrin, 5,10,15,20-tetrakis-(4-sulfonato phenyl)porphyrin (TSPP), dissolved in media composed of poly(ethylene glycols) (PEGs) up to an average molecular weight (MW) of 8000 as major component, is investigated. J-aggregates of TSPP are well-manifested via the bathochromically-shifted uv-vis absorbance band of TSPP. As media, 10 wt% water-added PEGs at pH 1 show excellent efficiency for TSPP J-aggregation. The J-aggregation efficiency increases as the PEG MW is increased and it is found to be the maximum for the medium constituted of PEG3000. Once formed, some of the J-aggregates decay back to the diprotonated form via pseudo-first order kinetics. Addition of salts NaCl and $NaBF_4$, and ionic liquids [bmim][PF_6], [bmim][Tf_2N], [bmim][BF_4], and [bmim][OTf] [bmim = 1-butyl-3-methylimidazolium, PF_6 = hexafluorophosphate, Tf_2N = bis(trifluoromethylsulfonyl) imide, BF_4 = tetrafluoroborate, and OTf = trifluoromethanesulfonate], respectively, to TSPP dissolved in 10 wt% water added PEGs at pH 1 results in increased J-aggregation efficiency. Ionic liquids are found to protect porphyrin J-aggregates from decaying to its diprotonated form. Increasing temperature from ambient to 90°C results in decreased J-aggregation efficiency of TSPP in the presence of salts NaCl and $NaBF_4$, respectively; concentration of J-aggregates does not change much with temperature when an ionic liquid as additive is present in the medium. Polymer chain length and electrostatic interactions appear to play major role in porphyrin J-aggregation efficiency and kinetics within water-added acidic mixtures of PEG.

INTRODUCTION

Porphyrins constitute one of the most important classes of compounds in chemical sciences.[1,2] Besides their important role in supporting aerobic life, porphyrins have many interesting applications. Porphyrins and their complexes are known to catalyze a variety of reactions in chemistry.[3–7] The strong light absorbing capabilities of porphyrins have resulted in their use in photodynamic therapy.[8–10] Porphyrins and related compounds have shown applications in molecular electronics and as supramolecular building blocks.[11–13] Applications of various porphyrins as dye-sensitized solar cells have demonstrated remarkable solar conversion efficiencies that were close to those of silicon-based photovoltaic devices.[14–16] Other applications of porphyrin-based compounds are in photonic devices, in magnetic resonance imaging, and in the treatment of psoriasis, blocked arteries, and viral and bacterial infections.[17–21]

Several of the applications of porphyrins and related compounds are based on their interesting aggregation behavior.[9–16] Since the aggregation strongly alters the physicochemical and optical properties that exist with single molecules, the aggregation of molecular dyes broadens their technological applications. The molecular aggregates of porphyrins have been employed as potential sensitizers in the photographic industries and to mimic light harvesting arrays or artificial photosynthetic systems.[22–25] They have found use in nonlinear optics, in opto-electronics, and in energy/charge transfer processes in biological systems.[26–28] These closed-stacked molecular structures also possess properties suitable for superconductivity, as organic photoconductors, as markers of biological and artificial membrane systems, in optical frequency conversion, and in information processing, transmission and storage.[28–31] One of the most powerful tools to recognize these aggregates is the electronic absorption spectroscopy where the absorbance band shifts dramatically as a result of the formation of the aggregates.[32] J-aggregates, formed by ‘head-to-tail’ stacking of molecules, are easily identified by an absorption band that is bathochromically-shifted relative to the absorption band of the single monomer.[32–34]

The aggregation phenomenon of porphyrins, in general, is found to highly depend on the properties of the solubilizing milieu, such as, polarity, pH, ionic strength, etc.[35–38] Among few reports on J-aggregation of one of the most common and popular porphyrins, 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (TSPP), it is shown that the ions of inorganic salts, surfactant assemblies, microemulsions, proteins, nucleic acids, etc., can promote aggregation of porphyrins in acidic medium.[35–45] Due to the dramatic effect that the medium can have on the aggregation of porphyrins, it is of immense importance and interest to investigate porphyrin aggregation within alternate media. Poly(ethylene glycols) (PEGs), one of the many such alternatives (others being supercritical fluids, ionic liquids, renewable bio-feedstocks, etc.), have importance and associated applications due to their environmentally-benign properties.[46] Several favorable physiochemical features, such as, low vapor pressure, high chemical stability, non-toxicity, biodegradability, and low melting point, of PEGs have attracted great deal of attention and have rendered them useful in many industrial, pharmaceutical, and biomedical applications.[47–49] In contrast to many alternative solvents, PEGs are usually water-miscible, can be easily recovered or recycled by extraction, and are available in a wide range of molecular weight (MW). Even higher MW PEGs that are solid under ambient conditions can be utilized as media either by making them liquid by heating or can be used as their aqueous mixtures. PEG is indeed a ‘benign’ media and has been approved by the FDA for internal consumption.[50]

In this paper, we present outcomes of our detailed investigation of the aggregation behavior of TSPP within the ‘hybrid green’ media comprising of water and a PEG. For this purpose, several PEGs of different average MWs are used. We have varied the composition of the aqueous PEG mixture under acidic conditions to assess the effect of water content on the J-aggregation efficiency of TSPP. Effect of additives, specifically salts and ionic liquids, on both efficiency and kinetics of J-aggregation of TSPP is studied within acidic aqueous PEG mixtures. We also report the effect of temperature on J-aggregation of TSPP within water added PEG medium under acidic conditions.

EXPERIMENTAL

Materials. Sodium salt of TSPP (high purity) was obtained from Sigma-Aldrich and was used as received. Lower MW PEGs with average MW 200 (PEG200), 400 (PEG400), 600 (PEG600), and 1000 (PEG1000) were obtained from Merck and higher MW PEGs with average MW 1450 (PEG1450), 2000 (PEG2000), 3000 (PEG3000), and 8000 (PEG8000) were obtained from Sigma-Aldrich in highest purity possible and were stored under dry conditions. Ionic liquids; 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methyl imidazolium trifluoromethanesulfonate ([bmim][OTf]), 1-butyl-3-methylimidazolium hexafluoro phosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) were obtained from Merck in highest purity possible and were stored under argon atmosphere in dry conditions. The molecular structures of TSPP, PEGs and ILs used are shown in **Scheme 1**. Doubly-distilled deionized water was obtained from a Millipore Milli-Q Academic water purification system having ≥18 MΩ.cm resistivity. Ethanol (99.9%) of HPLC grade and HCl in highest purity possible, were obtained from Merck Ltd. NaCl was purchased from Qualigens in highest purity possible and was used as received. $NaBF_4$ was purchased from Sigma-Aldrich in highest purity possible and was used as received.

Methods. The stock solution of TSPP was prepared in water (1.0 mM) and stored under refrigeration at 4 ± 1 °C in pre-cleaned amber glass vials. Before acquisition of uv–vis molecular absorbance spectra, the aqueous mixture of 90 wt% PEGs was prepared with or without additives maintaining the mixture pH at 1 with HCl using CyberScan pH 510 meter from EUTECH Instruments with ±0.01 pH accuracy. The absorption spectra were collected immediately after adding the mixture into the sample tube containing the required amount of stock solution in water such that the concentration of the dye is 10 μM. The sample was stirred to ensure complete solubilization of TSPP. The mixing of dye into the mixture took < 20s. In order to prepare the aqueous mixture of PEGs in the absence and presence of 0.3 M additives, the required amount of material was weighed using Mettler-Toledo AB104-S balance with a precision of ±0.1 mg. A Perkin-Elmer Lambda bio 35 double beam spectrophotometer with variable bandwidth was used for the acquisition of uv–vis molecular absorbance spectra. The temperature was controlled with Perkin-Elmer PCB1500 water peltier system having a stability of ±0.01 ºC. The respective solutions without TSPP were used as blank for baseline correction and recording the absorbance spectra. The mixtures of 90 wt% of higher MW PEGs with water are not transparent at room temperature and this problem increases with the increase of PEG MW. Therefore, in aqueous mixture of 90 wt% of PEG1450, PEG2000 and PEG3000, absorbance is collected at the lowest temperatures where the mixture became transparent. All data were collected at least in triplicate starting from the sample preparation. All data analysis was performed using Microsoft Excel 2007 and/or Sigma Plot v10.0 softwares. All the structures have been drawn using the ChemBioDraw Ultra v11.0 software.

RESULTS AND DISCUSSIONS

In aqueous medium, depending on the pH of the solution, two prototropic forms of TSPP exist in equilibrium (**Scheme 2**). The pK_a of this aqueous prototropic equilibrium is reported to be ~4.8 at ambient conditions.[51] At lower pH (i.e., at pH < 4.8), due to the protonation of the two pyrrole nitrogens of the ionic porphyrin the diprotonated form (H_4TSPP^{2-}) dominates the deprotonated form (H_2TSPP^{4-}). The absorption spectrum of the deprotonated or the tetra-anionic species (H_2TSPP^{4-}) consists of an intense Soret peak at *ca.* 415 nm and four Q-band peaks at 515, 551, 580 and 645 nm.[52,53] Whereas the diprotonated species or the dianion (H_4TSPP^{2-}) in water consists of a bathochromically-shifted B band (Soret) at *ca.* 435 nm and three Q bands at 550, 595 and 644 nm. More interestingly, TSPP may form J- and/or H-aggregates depending on the concentration of the porphyrin as well as on the pH and the ionic strength of the aqueous medium. These two aggregates are differentiated on the basis of monomer transition dipoles alignment. The parallel alignment of monomer transition dipole to the hypothetical line connecting adjacent molecules in aggregates corresponds to J-aggregates whereas the perpendicular alignment of same corresponds to H-aggregates.[32] The lower pH and higher ionic strength usually help the process of J-aggregation in water.[35,37,38,45]

Effect of water and PEG molecular weight on J-aggregation of TSPP.

Efficiency of J-aggregation. The relatively higher average MW PEGs used in this investigation (PEG1000, PEG1450, PEG2000, PEG3000, and PEG8000, respectively) are solid at ambient conditions. However, addition of only 10 wt% (6.17 *m*) water to these PEG at mixture pH 1 results in significant J-aggregation of TSPP (**Figs. 1, S1,** and **S2**). This J-aggregation is highlighted by the appearance of bathochromically-shifted sharp absorbance in 485-495 nm region (Soret band) as well as a band in 700-725 nm region (Q-band). It is in agreement with earlier report that while within low average MW neat PEGs (average MW < 1000) that are liquid at ambient conditions, no aggregation of TSPP is observed, addition of small amount of water significantly facilitates J-aggregation at low mixture pH.[38] It was also found that the J-aggregation becomes more efficient as the average MW of the PEG is increased to 1000. A careful examination of the data presented in **Figs. 1** and **S1** clearly reveals the J-aggregate formation to be highly efficient within 10 wt% water-added PEGs at mixture pH 1. The absorbance corresponding to initially formed J-aggregates ($A_{J,0}$) decreases as the amount of water is increased at mixture pH 1 and almost no J-aggregates are formed in the presence of 50-60 wt% water (**Fig. 1B**). For water >60-70 wt% the J-aggregate formation efficiency again increases and becomes significant in aqueous solution at pH 1. Within 10 wt% water-added PEGs at mixture pH 1, interestingly, the J-aggregation efficiency is found to increase with increasing average MW of the PEG from 1000 to 3000 before decreasing for PEG8000 (**Fig. 1B** and inset). As the diprotonated TSPP is the precursor that forms J-aggregates, the ratio of the absorbance due to J-aggregates to that due to the diprotonated form (i.e., $A_{J,0}/A_{448,0}$, **Fig. S2**) also reveals the J-aggregation efficiency to be the maximum within 10 wt% water-added PEG3000 at pH 1 – it is decreased within 10 wt% water-added PEGs of lower as well as higher average MWs.

The diprotonated form of TSPP is known to readily self-aggregate to form J-aggregates in water at low pH.[35,39] Initial addition of PEG of average MW 1000-8000 clearly disrupts these J-aggregates. We believe the presence of □CH_2CH_2□ functionality on the backbone of PEGs that disrupts H-bonded water network around porphyrin J-aggregates to be responsible for this observation as solvents other than water, including aqueous-organic mixtures, are known to support the J-aggregates of porphyrins in less efficient manner.[38] Interestingly, as the PEG is increased in the mixture to the extent (i.e., 90 wt%) where it becomes the bulk component and the water becomes the minor component ([water] = 6.17 m), the porphyrin J-aggregation becomes highly efficient (for PEG MW > 1000, $A_{J,0}$ in 10 wt% water added PEG are even higher than that in water at pH 1). When PEG is present as bulk, it appears the abundance of □O□ of the ethoxy functionalities as well as termini □OH groups protect the porphyrin J-aggregates by forming water-like network around them. The □O□ of the ethoxy functionalities may have major contribution as compared to □OH in facilitating J-aggregates as $A_{J,0}$ is the highest for system constituting of PEG3000 (equal weight of PEG3000 will have more ethoxy units and less □OH groups as compared to PEG200). The □CH_2CH_2□ functionality may begin to dominate again and result in reduced $A_{J,0}$ for systems with PEG MW > 3000. Acidic PEG mixtures containing small amount of water readily support J-aggregation of the porphyrin nonetheless.

Kinetics of J-aggregation. Due to significant J-aggregation efficiency of TSPP, the kinetics of the aggregation is investigated within 10 wt% (6.17 m) water-added PEGs at pH 1.

TSPP dissolved in 10 wt% water-added PEG200 at pH 1 neither shows formation of J-aggregates nor exhibits any changes in the absorbance corresponding to the diprotonated species with time (0 – 80 min, **Fig. 2A**). We believe the presence of small polymer chains and/or too many termini □OH groups may be hindering the J-aggregation process (*vide supra*). As PEG200 is replaced with a higher average MW PEG (PEG400, PEG600, PEG1000, PEG1450, PEG2000, and PEG3000, respectively) in the solubilizing milieu, some of the J-aggregates that are initially formed dissociate back to diprotonated TSPP (**Fig. 2B-2G**). The kinetics of the J-aggregates dissociating into unaggregated diprotonated form appears to be complete in an hour or so. This rather slow decomposition of J-aggregates into unaggregated diprotonated TSPP appears to be caused by PEG. In order to assess the effect of PEG MW, if any, on dissociation kinetics of J-aggregates, the decay of the J-aggregated TSPP as well as the growth of the monomeric diprotonated species with time were best fit to a pseudo-first order kinetics (as PEG may be considered to be in abundance). Since the absorbance at 490 nm is almost entirely due to J-aggregates, the variation in absorbance at 490 nm (A_J) with time was fitted to a simplistic expression: $A_J = A_{J,0} + a_1 e^{-k_J t}$, where k_J is the pseudo first-order rate constant for the decay of absorbance at 490 nm which corresponds to the dissociation of J-aggregates into the diprotonated unaggregated form. A generalized expression is also used for the increase in the absorbance at 448 nm (A_{448}) with time keeping in mind that it may not be solely due to the increase in the diprotonated unaggregated species (the decrease in the deprotonated form corresponding to absorbance at 420□425 nm with time may interfere with increase in diprotonated form corresponding to the absorbance at 448 nm): $A_{448} = A_{448,0} + a_2(1 - e^{-k_{448} t})$, where k_{448} is the pseudo first-order rate constant for the growth of absorbance at 448 nm which, under certain severe assumptions, may correspond to the growth of the unaggregated diprotonated form. The dark curves in insets of **Fig. 2B-2G** show the results of the fit, which appear to be satisfactory. **Table 1** presents recovered rate constants, *k*, the parameter of utmost importance to us (the goodness-of-the-fit in terms of r^2 is presented in **Table S1**).

A careful examination of the rate constants provides insights to the effect of PEG average MW on the kinetics of J-aggregation of TSPP within 10 wt% water added PEG mixtures at pH 1. While the rate constants recovered from the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) are fairly similar for milieu constituted of PEG400, PEG600, and PEG1000, they are appreciably higher for systems with higher PEG average MWs (PEG1450, PEG2000, and PEG3000). Interestingly, the rate constants are fairly similar for the three higher

PEG average MW media. It is inferred that the decay of J-aggregates becomes almost twice as fast when the medium is constituted of PEG1450 as opposed to PEG1000. It appears that for PEG MW > 1000, the arrangement of PEG moieties within the medium is in such a manner to expedite the dissociation of J-aggregates of TSPP. It is interesting to note that rate of increase in absorbance at 448 nm corresponding to the growth of diprotonated TSPP increases monotonically with the MW of the PEG. While the absorbance at 448 nm does not change at all with time ($k \sim 0$) within 10 wt% water added PEG200 at pH 1, it shows appreciable increase with time ($k = 9.8\times10^{-4}$ s^{-1}) when PEG200 is replaced with PEG400. When the medium is constituted of PEG3000, the rate of increase of absorbance at 448 becomes significantly high ($k = 44.7\times10^{-4}$ s^{-1}). Higher MW PEGs, in general, appear to expedite the decomposition of J-aggregates and the growth of diprotonated form. Simple chemical kinetics tells us that in the absence of any interfering effect, the rate constants k_J and k_{448}, should be similar to each other if the molar absorptivities of the two species are similar. The two rate constants, k_J and k_{448}, are fairly similar for the system constituted of PEG400, however, they are different for systems with higher PEG MW. This is easy to conceive as decrease in deprotonated form with time is negligible within system with PEG400 (band at 420–425 nm, **Fig. 2B**), whereas this decrease is significant within systems constituted of PEG MW > 400 (**Fig. 2C-2G**). In the absence of contribution from kinetics of deprotonated TSPP, the rate of decomposition of J-aggregates into the unaggregated diprotonated form becomes similar to the rate of growth of diprotonated form.

It is clear from **Fig. 2** that both the decrease in absorbance at 490 nm and increase in absorbance at 448 nm with time slow down and achieve a constant value at longer times ($t \geq 80$ min). It appears the equilibrium is attained by the species involved beyond this time period. A plot of absorbance at 490 nm ($A_{J,eq}$) corresponding to J-aggregates of TSPP after the equilibrium is attained (**Fig. 3**) again shows the increase in J-aggregation with increase in PEG MW with highest A_J observed within milieu constituted of PEG3000. Interestingly, the absorbance corresponding to diprotonated TSPP ($A_{448,eq}$) does not appear to depend on the MW of the PEG in the solubilizing milieu (**Fig. 3** inset). The ratio, $A_{J,eq}/A_{448,eq}$, showing the efficiency of J-aggregation from diprotonated form at equilibrium increases monotonically with increase in PEG MW (**Fig. S3**). It can be inferred that while the presence of equilibrium concentration of diprotonated TSPP is independent of the PEG MW within 10 wt% water added PEG at pH 1, the higher the MW of the PEG (in the MW range 200-3000) constituting the medium, the higher the equilibrium concentration of J-aggregates. Longer is the chains of the polymer PEG (up to MW 3000), the more the J-aggregation of the porphyrin.

Effect of additive on J-aggregation of TSPP. TSPP dissolved in 10 wt% water added PEG200 at pH 1 does not J-aggregate to any extent though most of the TSPP exists in diprotonated form. Further, there is no change in absorbance of the solution with time (*vide supra*). Interestingly, addition of 0.3 M of $NaBF_4$, NaCl, and ionic liquids (of same cation but different anions), [bmim][PF_6], [bmim][BF_4], [bmim][OTf], and [bmim][Tf_2N], respectively, to 10 wt% water-added PEG200 at pH 1 results in significant formation of J-aggregates (**Fig. 4**). This is in agreement with what is reported earlier.[38] The dissolved salts and ionic liquids will produce ions in the system that are known to decrease the electrostatic repulsion between the negatively charged sulfonate groups and the positively charged protonated *N*-units of the pyrrole ring of TSPP, respectively, by acting as the counter ions. This decrease in electrostatic repulsion results in better stacking of the diprotonated TSPP, increasing J-aggregation efficiency in the process.[38,39,42,45] Some of the initially formed J-aggregates in the presence of 0.3 M of any of the salts or the ionic liquids decay back to the diprotonated species. It appears that the deprotonated species may also decay and help the formation of diprotonated TSPP.

Addition of aforementioned additives to 10 wt% water-added PEG at pH 1 with higher MW PEGs also results in decay of initially formed J-aggregates into diprotonated form of TSPP (**Figs. S4-S8** and **Fig. 5**, deprotonated TSPP decays and contributes to the formation of the diprotonated form). However, as the PEG MW is increased within the medium, the extent of the decay of the J-aggregates (and the growth of the diprotonated TSPP) becomes less. Interestingly, for 10 wt% water added PEG3000 at pH 1 the decay of J-aggregates and the growth of the diprotonated form in the presence of 0.3 M of any of the four ionic liquids become negligible (**Fig. 5**). Increasing the MW of the PEG constituting the medium clearly hinders the dissociation of the J-aggregates back into the diprotonated unaggregated TSPP. It is important to mention that while all four of the ionic liquids are readily miscible with all the PEGs at 0.3 M concentration, it is not so for the two salts; 0.3 M NaCl and 0.3 M $NaBF_4$ samples could not be prepared in 10 wt% water added PEG systems at pH 1 for PEG MW > 600 and PEG MW > 1000, respectively. This highlights an important advantage of ionic liquids over common salts as far as miscibility in PEGs is concerned.

It is interesting to note that the dissociation of J-aggregates within 10 wt% water-added PEG medium at pH 1 is in complete contrast to what was observed in acidic water.[39] Addition of ionic liquids to acidic aqueous solutions of TSPP showed build-up of J-aggregates and decay of diprotonated form. Addition of 0.221 M of a water soluble ionic liquid, [bmim][BF_4], to pH 2 aqueous solution of TSPP resulted in the decay of the monomeric species and the growth of the J-aggregates with both these processes following pseudo-first order kinetics. It is clear that PEG present as the bulk component in the medium triggers the decay of the J-aggregates into the diprotonated TSPP irrespective of the presence of salts or ionic liquids, whereas, the addition of ionic liquid to aqueous solution of TSPP triggers the growth of J-aggregates from the diprotonated species.

The decrease and increase in absorbances at 490 nm and 448 nm, respectively, of TSPP dissolved in 10 wt% water added PEG in the presence of additives $NaBF_4$, NaCl, [bmim][PF_6], [bmim][BF_4], [bmim][OTf], and [bmim][Tf_2N], respectively, were again best fit to the simplistic expressions for first-order reaction kinetics (*vide supra*). The results of the fits are presented in insets of **Figs. 4-5** and **Figs. S4-S8** as solid curves (**Table 1** presents the recovered rate constants and the corresponding r^2 representing the goodness-of-the-fits are presented in **Table S1**). Addition of ionic liquid or salt does not have any clear-cut effect on the rate of decay of TSPP J-aggregates within 10 wt% water-added PEG at pH 1. However, it appears that the rate constant of the decay of J-aggregates has the highest value when the solubilizing milieu is constituted of PEG1450 for additive 0.3 M [bmim][BF_4], [bmim][OTf], and [bmim][PF_6], respectively, and PEG1000 for additive 0.3 M [bmim][Tf_2N]. Further increase in PEG MW results in decrease of rate constant for the decay of J-aggregates. A careful examination of the rate constant data reveals that, in general, the rate of growth of the diprotonated TSPP is relatively higher for 0.3 M ionic liquid added 10 wt% water-added PEG at pH 1 for PEG MW > 1000.

The initially formed J-aggregates of TSPP within 10 wt% water added PEG at pH 1 in the presence of aforementioned additives decay with time and appear to attain equilibrium concentrations when the time exceeds 80 min. The extent of decay of TSPP J-aggregates, i.e., the difference in the absorbance values (ΔA_J) between the J-aggregates formed initially ($A_{J,0}$) and those formed at equilibrium ($A_{J,eq}$) reveals interesting features (**Fig. 6**). In the presence of 0.3 M NaCl, decomposition of TSPP J-aggregates to diprotonated form is fairly significant within solubilizing milieu constituted of either of PEG200, PEG400, or PEG600 (**Fig. 6A**). The J-aggregate decomposition becomes less when the additive is 0.3 M $NaBF_4$ (**Fig. 6B**). Interestingly, in the presence of 0.3 M ionic liquid with $[bmim]^+$ cation and $[BF_4]^{\square}$, $[OTf]^{\square}$, $[PF_6]^{\square}$, and $[Tf_2N]^{\square}$, respectively, the J-aggregate decomposition becomes significantly hindered as compared to that observed for salts NaCl and $NaBF_4$ (**Fig. 6C-6F**). It is clear that in the presence of ionic liquids, the J-aggregates decompose to much less extent and especially when the medium contains high average MW PEGs, such as, PEG2000 and PEG3000, the decomposition of J-aggregates to diprotonated form is severely restricted.

The J-aggregates decay into unaggregated diprotonated TSPP within 10 wt% water added PEGs at pH 1 (**Fig. 2** and **Fig. S9**). However, ionic liquids as additives restrict this decomposition of J-aggregates – more so in systems composed of higher MW PEGs (**Figs. 5** and **6**). After initial formation of J-aggregates, which is facilitated by addition of salt or ionic liquid (**Figs. 4-5** and **Figs. S4-S8**), the extent of decomposition induced by salts appears to be very different from that induced by ionic liquids. The nature of the cation/anion and the degree of dissociation of the additive appear to contribute to this observation. In order to support this hypothesis, we measured electrical conductance of certain 10 wt% water added PEG mixtures at pH 1 (**Table S2**). In general, the electrical conductance of ionic liquid $[bmim][BF_4]$ added aqueous PEG mixtures is found to be higher than that of NaCl added aqueous PEG mixtures. This difference in electrical conductance becomes more as the PEG MW is increased in the milieu. It can be inferred that the favorable electrostatic interactions that stabilize the J-aggregates are more pronounced when ionic liquids are present as additives as opposed to NaCl. J-aggregates once formed in the system are protected by ionic liquids and they cannot dissociate back to the diprotonated porphyrin.

Effect of temperature on J-aggregation of TSPP. Changing temperature is another possible way to affect the J-aggregation of a porphyrin. We increased the temperature of the mixture of TSPP dissolved in 10 wt% water added PEG at pH 1 to 90°C at 10 deg increments in the absence and presence of additives. The plots of absorbance corresponding to the J-aggregates ($A_{J,0}$) as a function of temperature for systems constituted of different average MW PEGs in the absence of any additive are presented in **Fig. 7A**. A careful examination of the data reveals that except for the medium constituted of PEG1000, changing temperature does not seem to have much effect on J-aggregation efficiency of TSPP within 10 wt% water-added PEG at pH 1. System constituted of PEG1000, the J-aggregation efficiency decreases to some extent with increasing temperature. However in the presence of 0.3 M NaCl, the absorbance corresponding to J-aggregates decreases rapidly irrespective of the PEG average MW as the temperature is increased up to ~50°C - the decrease is not as rapid for $T > 50°C$ (**Fig. 7B**). The absorbance corresponding to J-aggregates decreases in the presence of 0.3 M $NaBF_4$ also, however, the decrease becomes less gradual as the average MW of the PEG constituting the system is increased from 200 to 1000 (**Fig. 7C**).

While the presence of 0.3 M of any of the four ionic liquids results in significant J-aggregation of TSPP as indicated by the high absorbance values corresponding to the J-aggregates when dissolved in 10 wt% water added PEG at pH 1, interestingly, unlike what is observed for the two salts as additives, the increase in temperature to 90°C results in only a very small decrease in absorbance corresponding to J-aggregates (**Fig. 7D-7G**). It is clear that increased temperature results in decreased TSPP J-aggregation in the presence of NaCl or $NaBF_4$, it is not so when the additive is an ionic liquid – ionic liquids, unlike salts, as additives appear to support J-aggregates even at higher temperatures. This can again be tentatively attributed to the relatively higher electrical conductance of ionic liquid added aqueous PEG mixtures as compared to that of NaCl added (**Table S2**). Ionic liquids, as additives, protect J-aggregates within aqueous acidic PEG mixtures even at higher temperatures.

CONCLUSIONS

Media composed of small amount of water mixed with high MW PEGs facilitate J-aggregation of a model porphyrin TSPP under acidic conditions. J-aggregation efficiency increases with increasing PEG MW and attains maxima within system composed of PEG3000 before decreasing again when mixture has PEG8000 as the major component. The J-aggregation efficiency appears to be a complex interplay of interactions afforded by ethylene groups, ethoxy units and terminal hydroxyls on PEG molecular framework along with the water present within the system. The decay of some of the J-aggregates and subsequent formation of diprotonated form follows pseudo-first order kinetics with reactions reaching equilibrium within ~80 minutes. More the MW of the PEG, faster is the kinetics of the growth of the diprotonated form. Salts NaCl and $NaBF_4$, and ionic liquids [bmim][PF_6], [bmim][Tf_2N], [bmim][BF_4], and [bmim][OTf], as additives facilitate TSPP J-aggregation by decreasing inherent electrostatic repulsion between negative and positive charge centers, respectively, of the porphyrin. Increasing PEG MW or adding ionic liquids hinder the decay of porphyrin J-aggregates. In the presence of ionic liquid, J-aggregates decay when the medium is aqueous acidic PEG mixture, in complete contrast, J-aggregates grow when the medium is simply acidic water. Ionic liquids, as additives, protect J-aggregates from decaying even as the temperature is increased to 90°C. The knowledge and understanding of factors affecting aggregation of porphyrins can help increase application potential of this important class of molecules. It is established that water mixtures of PEG as environmentally-benign media are capable of assisting aggregation processes.

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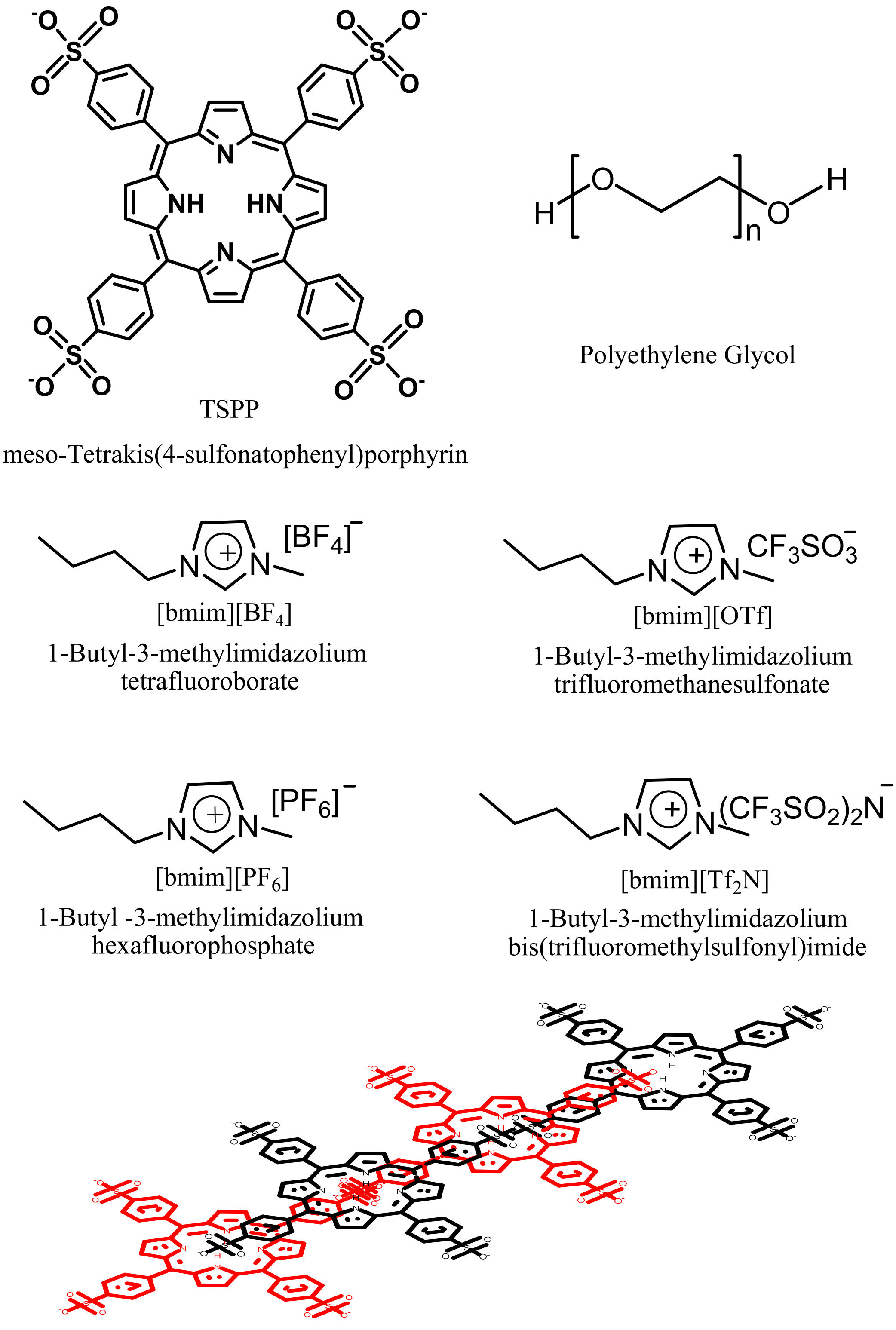
Table 1. Recovered rate constants for the decay of absorbance at 490 nm (corresponding to decay of J-aggregates) and growth of absorbance at 448 nm (corresponding to formation of diprotonated form) of 10 μM TSPP in 10 wt% water added PEGs with and without 0.3 M additive at mixture pH 1. Error estimated in a rate constant is ≤10%.

	Rate Constants ($k \times 10^4$ s^{-1})						
Event	**PEG200**	**PEG400**	**PEG600**	**PEG1000**	**PEG1450**	**PEG2000**	**PEG3000**
			No additive				
J-aggregate decay (A_{490})	~ 0	8.6	7.3	9.0	15.6	13.2	16.6
Diprotonated growth (A_{448})	~ 0	9.8	12.2	16.2	19.0	34.8	44.7
			+ 0.3 M [bmim][BF_4]				
J-aggregate decay (A_{490})	11.8	5.6	9.4	12.1	17.8	6.1	~ 0
Diprotonated growth (A_{448})	18.8	14.0	11.6	21.0	21.2	33.5	~ 0
			+ 0.3 M [bmim][OTf]				
J-aggregate decay (A_{490})	8.5	7.5	15.5	17.7	26.5	3.6	~ 0
Diprotonated growth (A_{448})	16.2	12.8	17.5	15.7	24.7	< 50.0	~ 0
			+ 0.3 M [bmim][PF_6]				
J-aggregate decay (A_{490})	9.6	5.0	9.5	8.1	22.5	14.9	~ 0
Diprotonated growth (A_{448})	13.7	10.5	16.8	13.3	21.8	27.8	~ 0
			+ 0.3 M [bmim][Tf_2N]				
J-aggregate decay (A_{490})	8.8	8.4	12.7	29.3	15.1	8.8	~ 0
Diprotonated growth (A_{448})	33.7	15.6	13.6	19.7	39.2	68.5	~ 0
			+ 0.3 M $NaBF_4$				
J-aggregate decay (A_{490})	6.2	2.8	2.7	4.3	not soluble	not soluble	not soluble
Diprotonated growth (A_{448})	8.8	4.1	5.3	11.0			
			+ 0.3 M NaCl				
J-aggregate decay (A_{490})	14.8	9.4	9.6	not soluble	not soluble	not soluble	not soluble
Diprotonated growth (A_{448})	21.3	14.1	13.9				



TSPP

meso-Tetrakis(4-sulfonatophenyl)porphyrin

Polyethylene Glycol

[bmim][BF_4]
1-Butyl-3-methylimidazolium tetrafluoroborate

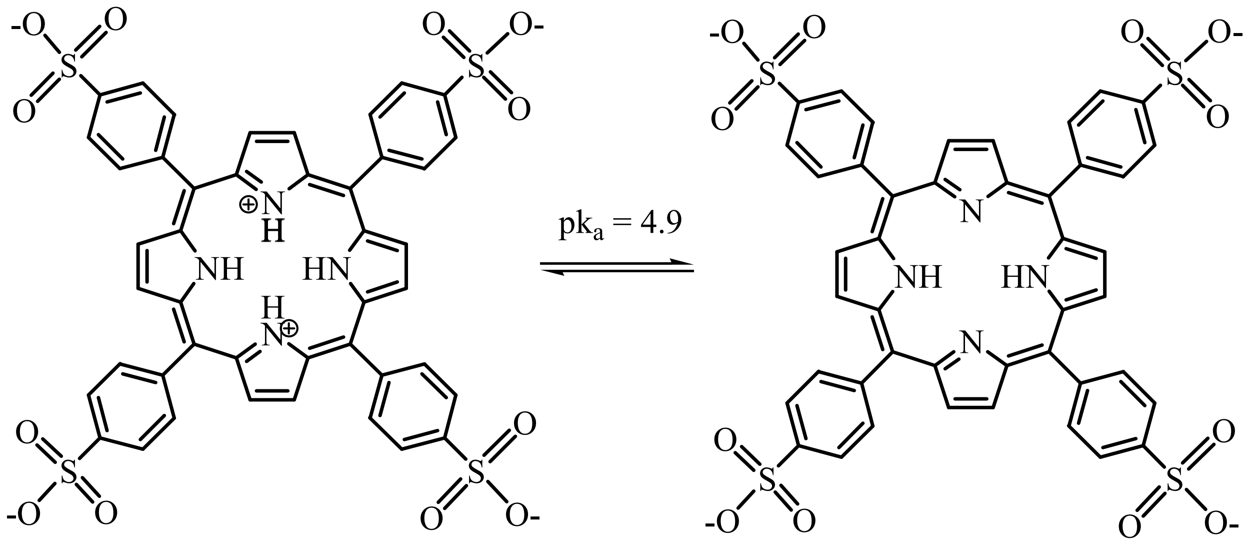
[bmim][OTf]
1-Butyl-3-methylimidazolium trifluoromethanesulfonate

[bmim][PF_6]
1-Butyl -3-methylimidazolium hexafluorophosphate

[bmim][Tf_2N]
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

J-aggregates of TSPP

Scheme 1.



(a) $H_4TSPP^{2□}$ (b) $H_2TSPP^{4□}$

Scheme 2.

Figure and Scheme Captions.

Scheme 1. Molecular structures of *meso*-tetrakis(4-sulfonatophenyl)porphyrin (TSPP), J-aggregates of TSPP, poly(ethylene glycol), and various ionic liquids used.

Scheme 2. Equilibrium between the two prototropic forms of TSPP, the diprotonated form (a) and the deprotonated form (b), in aqueous media.

Figure 1. Absorbance spectra of 10 μM TSPP dissolved in aqueous mixture of PEG3000 at pH 1 as a function of wt% of water (panel A). Absorbance at 490 nm corresponding to initially formed J-aggregates ($A_{J,0}$) in aqueous PEG mixtures at pH 1 as a function of wt% of water (panel B). Inset shows $A_{J,0}$ in 10 wt% water-added PEG mixtures at pH 1. Error estimated in $A_{J,0} \leq 0.05$.

Figure 2. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG mixtures at pH 1. 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 3. Absorbance at 490 nm ($A_{J,eq}$) corresponding to J-aggregates after reaching equilibrium for 10 μM TSPP dissolved in 10 wt% water-added PEG mixtures at pH 1. Inset shows the absorbance at 448 nm ($A_{448,eq}$) corresponding to diprotonated form after reaching equilibrium for the same samples.

Figure 4. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG200 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 5. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG3000 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 6. 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 in the presence of 0.3 M additives at mixture pH 1.

Figure 7. Change in absorbance corresponding to initially formed J-aggregates ($A_{J,0}$) with temperature for 10 μM TSPP dissolved in 10 wt% water-added PEG mixtures in the absence and presence of 0.3 M additives at mixture pH 1.

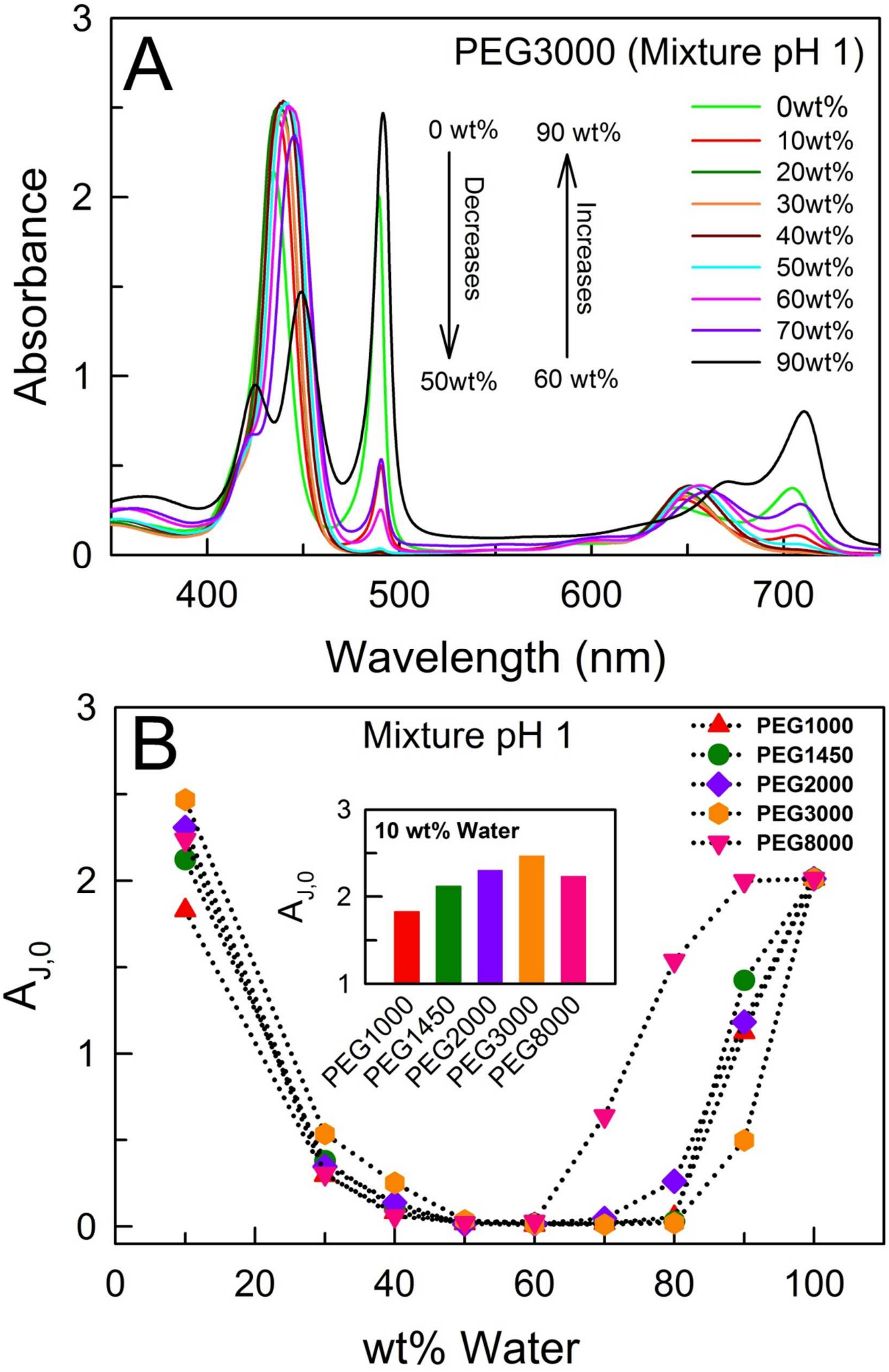

A
PEG3000 (Mixture pH 1)
0 wt%
Decreases
50wt%
90 wt%
Increases
60 wt%
0wt%
10wt%
20wt%
30wt%
40wt%
50wt%
60wt%
70wt%
90wt%
Absorbance
Wavelength (nm)
0
1
2
3
400
500
600
700
B
Mixture pH 1
PEG1000
PEG1450
PEG2000
PEG3000
PEG8000
10 wt% Water
$A_{J,0}$
1
2
3
PEG1000
PEG1450
PEG2000
PEG3000
PEG8000
$A_{J,0}$
0
1
2
3
0
20
40
60
80
100
wt% Water

Figure 1.

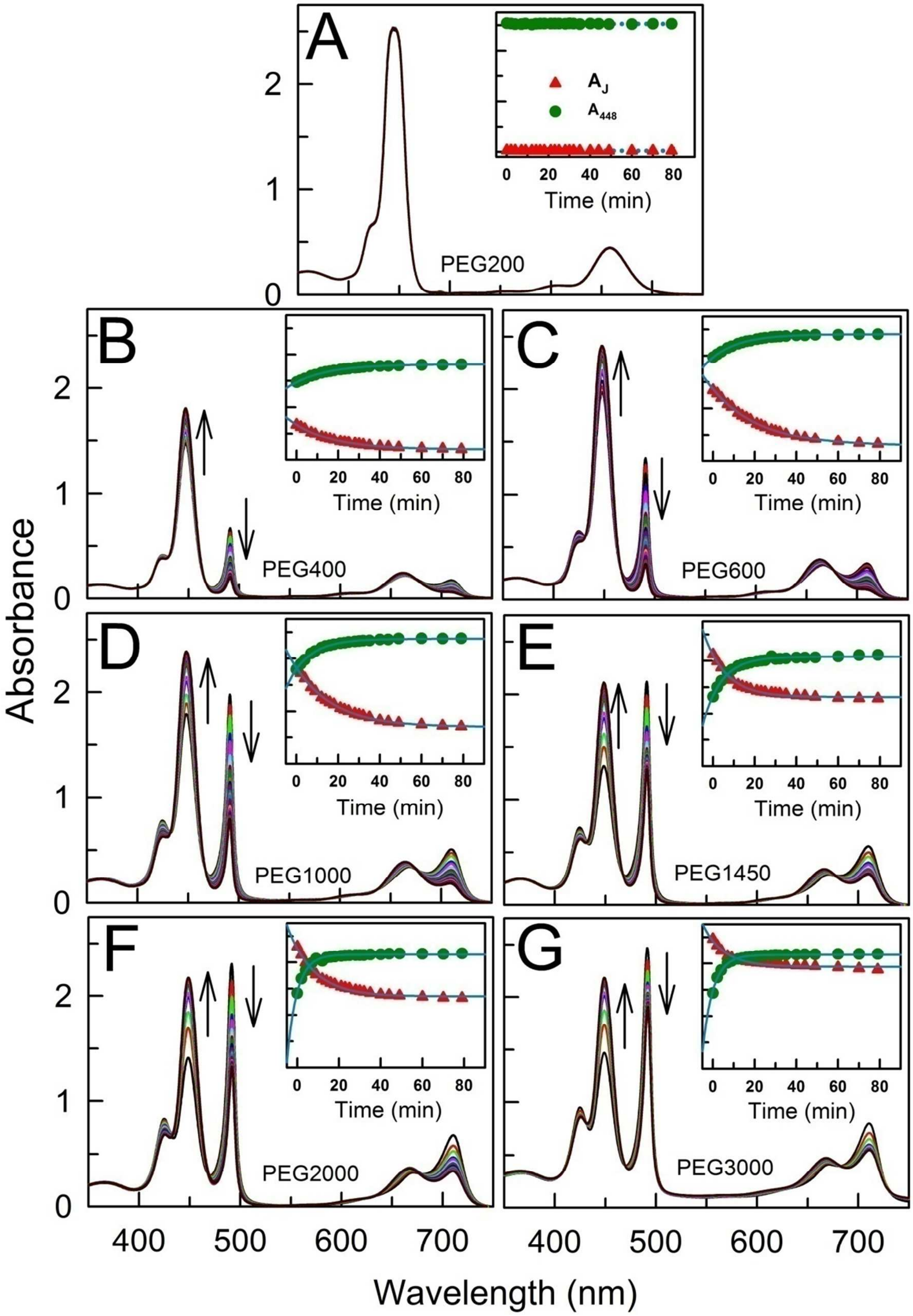

A
B
C
D
E
F
G
Absorbance
Wavelength (nm)
Time (min)
A_J
A_{448}
PEG200
PEG400
PEG600
PEG1000
PEG1450
PEG2000
PEG3000
0
1
2
400
500
600
700
20
40
60
80

Figure 2.

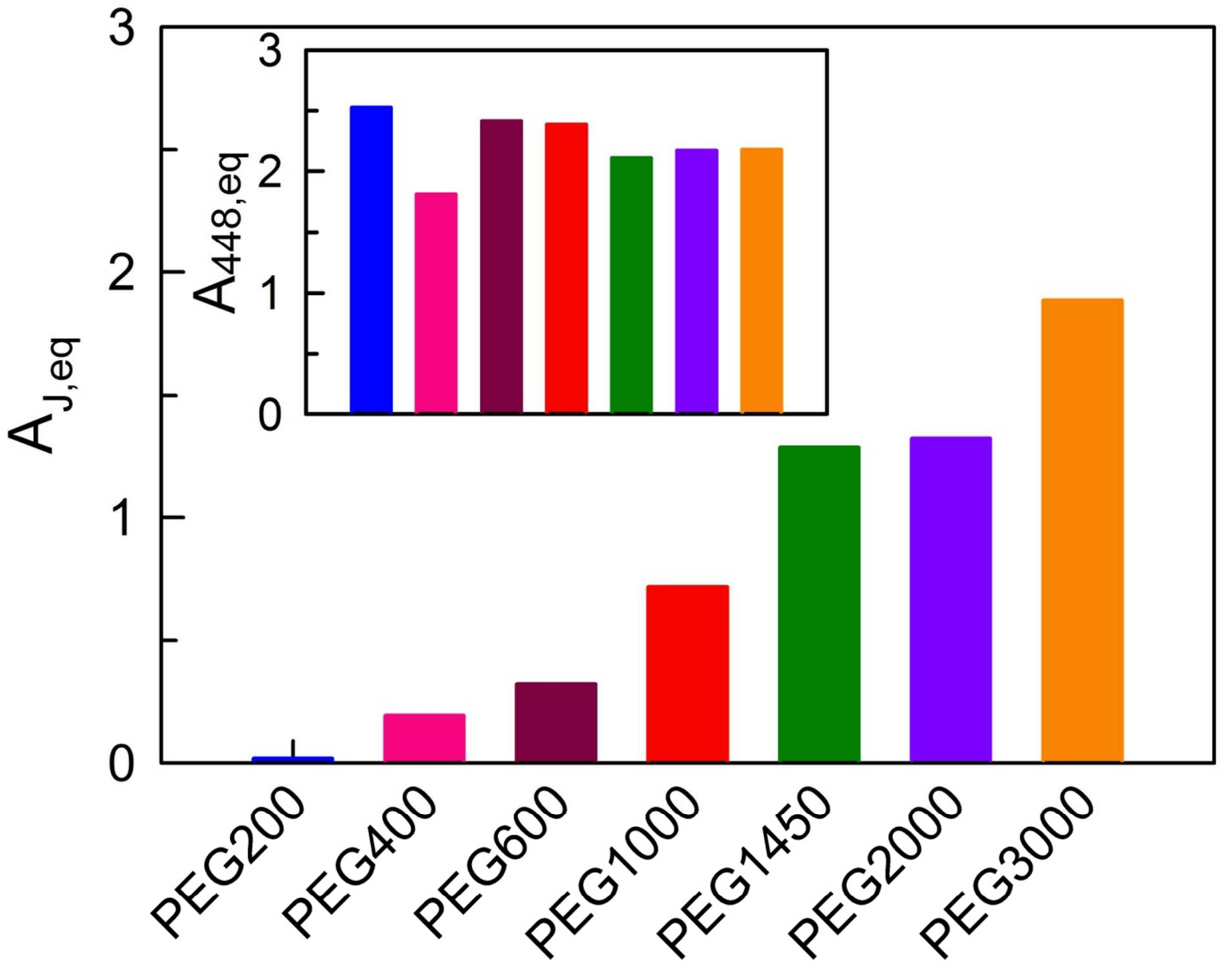

3
2
1
0
$A_{J,eq}$
$A_{448,eq}$
3
2
1
0
PEG200
PEG400
PEG600
PEG1000
PEG1450
PEG2000
PEG3000

Figure 3.

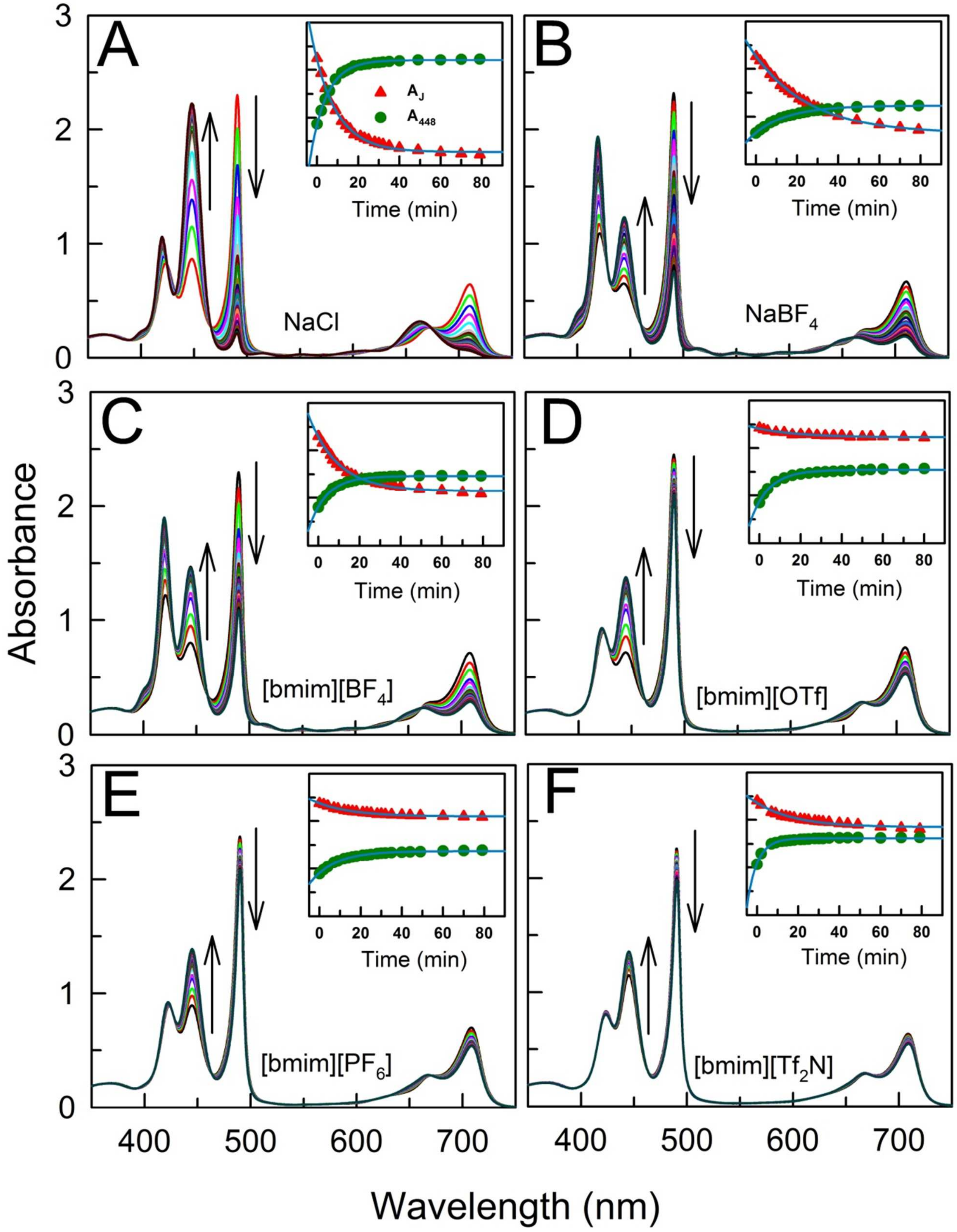

A
B
C
D
E
F
NaCl
NaBF$_4$
[bmim][BF$_4$]
[bmim][OTf]
[bmim][PF$_6$]
[bmim][Tf$_2$N]
A$_J$
A$_{448}$
Time (min)
0
20
40
60
80
Absorbance
0
1
2
3
400
500
600
700
Wavelength (nm)

Figure 4.

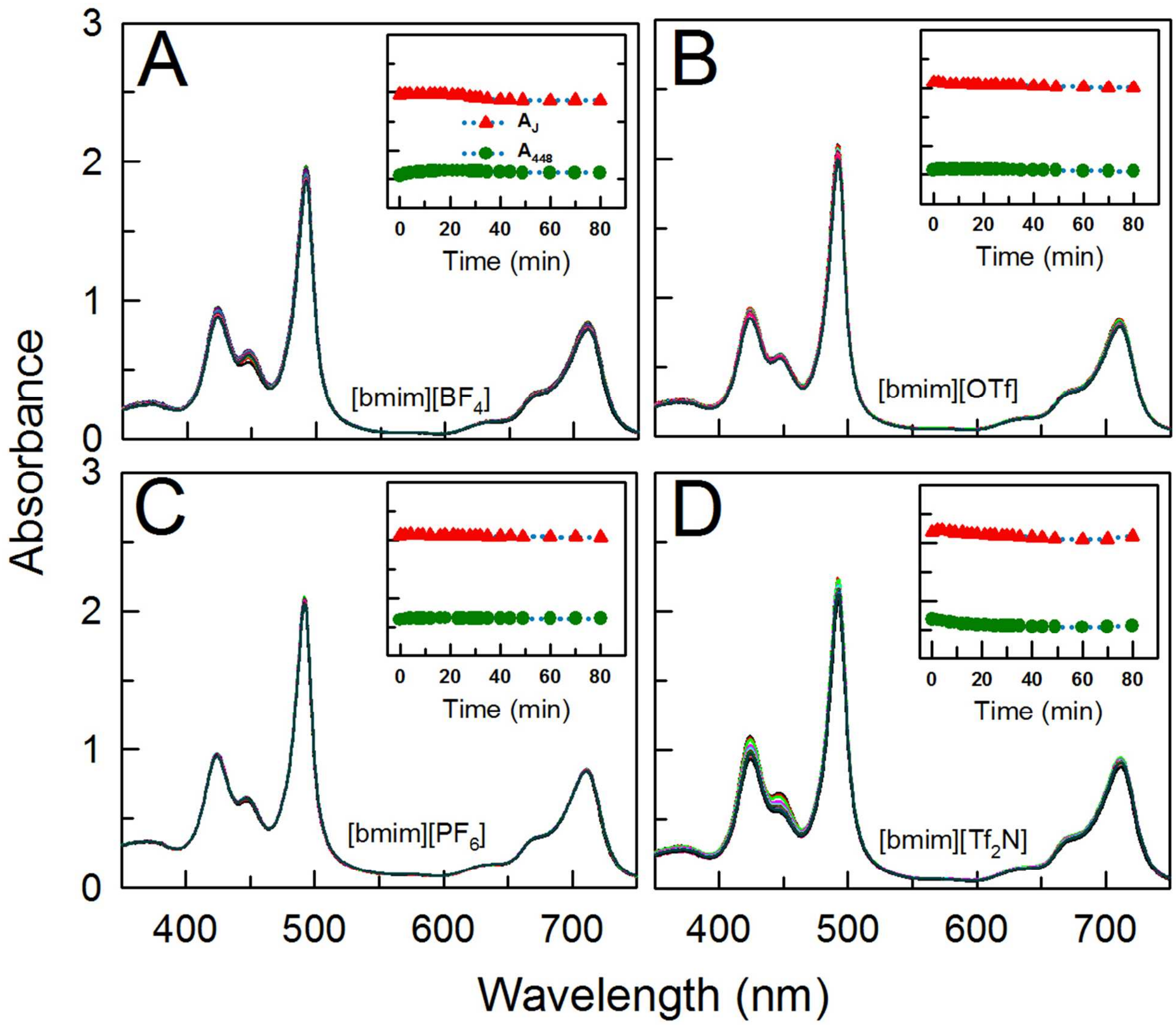

A
B
C
D
Absorbance
Wavelength (nm)
Time (min)
A_J
A_{448}
[bmim][BF$_4$]
[bmim][OTf]
[bmim][PF$_6$]
[bmim][Tf$_2$N]
0
1
2
3
400
500
600
700
0
20
40
60
80

Figure 5.

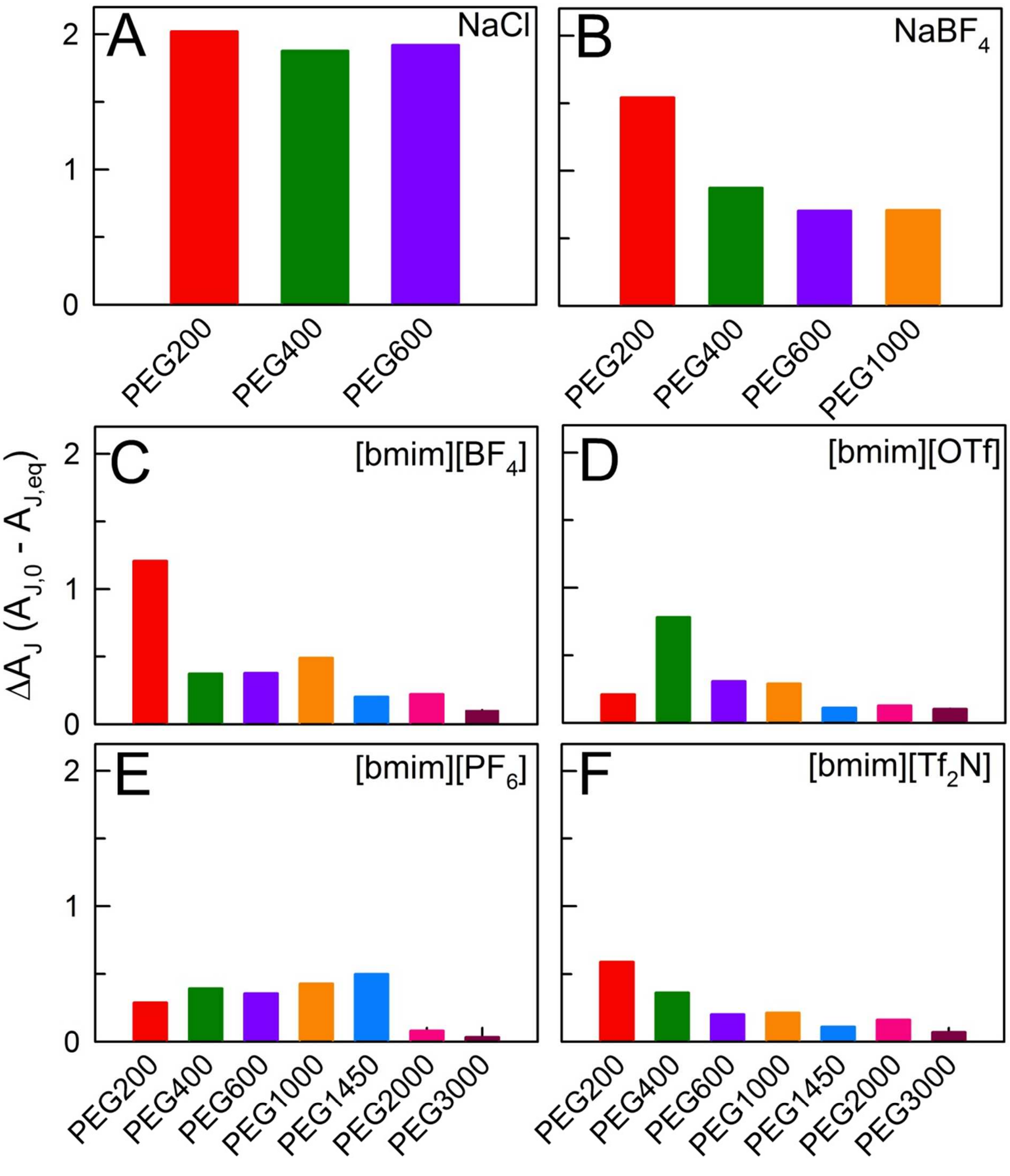

A
NaCl
B
NaBF$_4$
C
[bmim][BF$_4$]
D
[bmim][OTf]
E
[bmim][PF$_6$]
F
[bmim][Tf$_2$N]
ΔA_J ($A_{J,0}$ - $A_{J,eq}$)
0
1
2
PEG200
PEG400
PEG600
PEG1000
PEG1450
PEG2000
PEG3000

Figure 6.

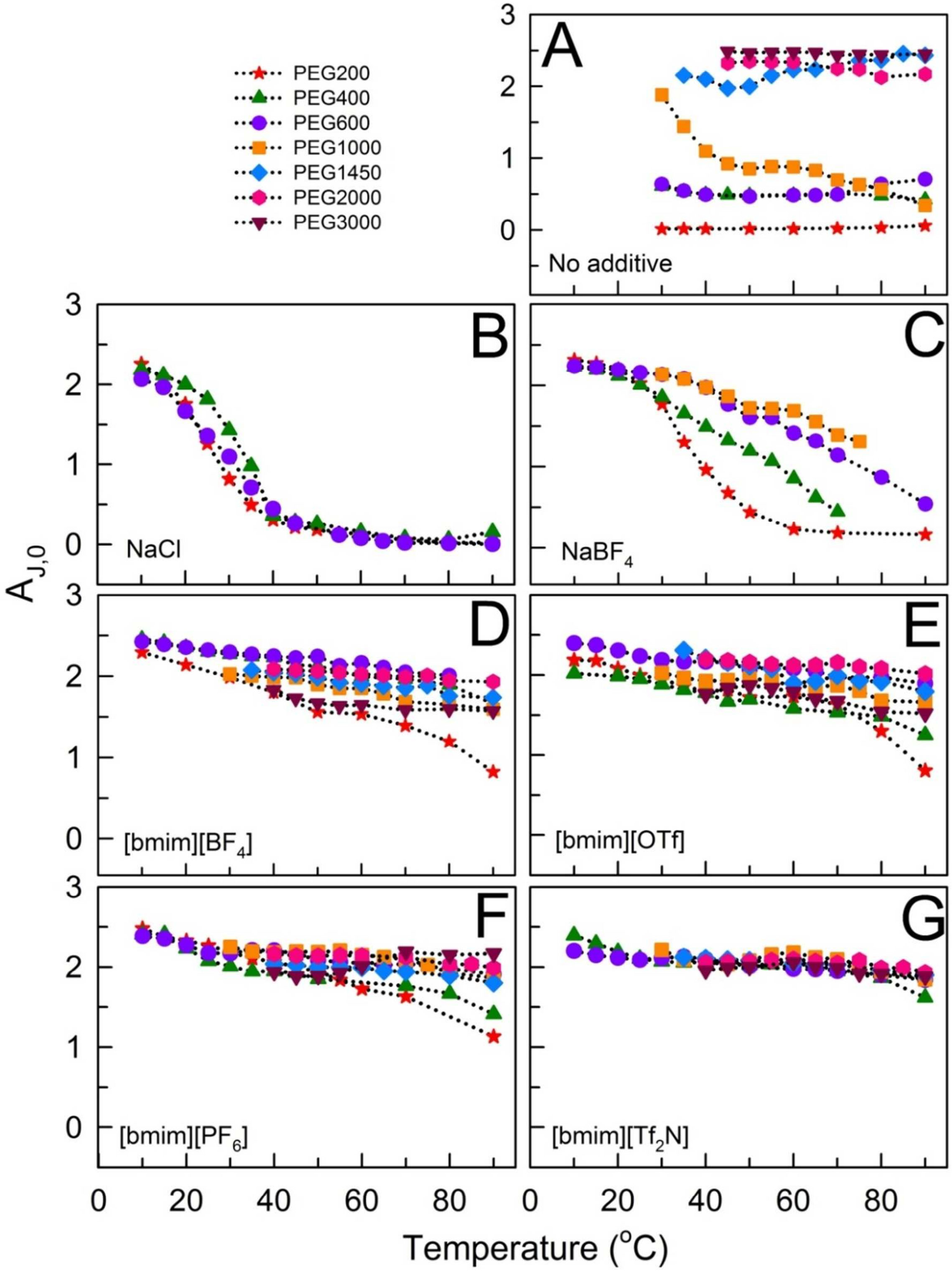
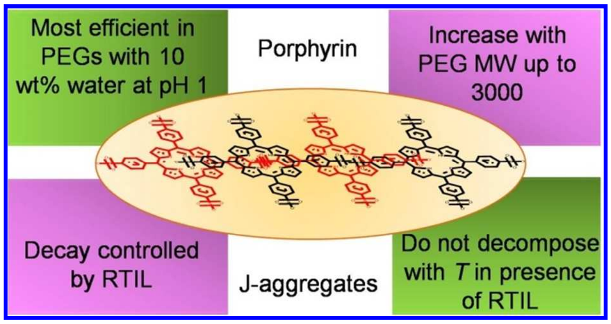

PEG200
PEG400
PEG600
PEG1000
PEG1450
PEG2000
PEG3000
A
No additive
B
NaCl
C
$NaBF_4$
D
$[bmim][BF_4]$
E
[bmim][OTf]
F
$[bmim][PF_6]$
G
$[bmim][Tf_2N]$
$A_{J,0}$
0
1
2
3
0
20
40
60
80
Temperature (°C)

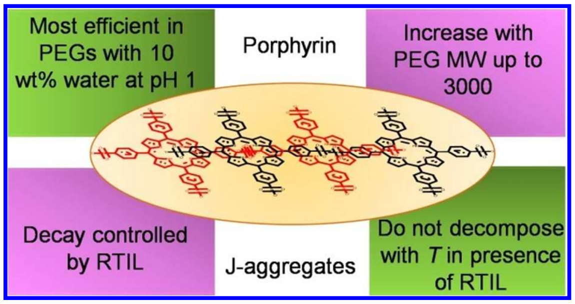
Figure 7.

Table of Contents Entry



Porphyrin J-aggregation is facilitated in 10 wt% water-added PEGs at pH 1; it increases with PEG MW and is controlled by RTILs.

Table of Contents Entry



Porphyrin J-aggregation is facilitated in 10 wt% water-added PEGs at pH 1; it increases with PEG MW and is controlled by RTILs.

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

	[bmim][PF_6]	490	5.0	0.9987
		448	10.5	0.9994
	[bmim][Tf_2N]	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_2N]	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_2N]	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_2N]	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_2N]	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)

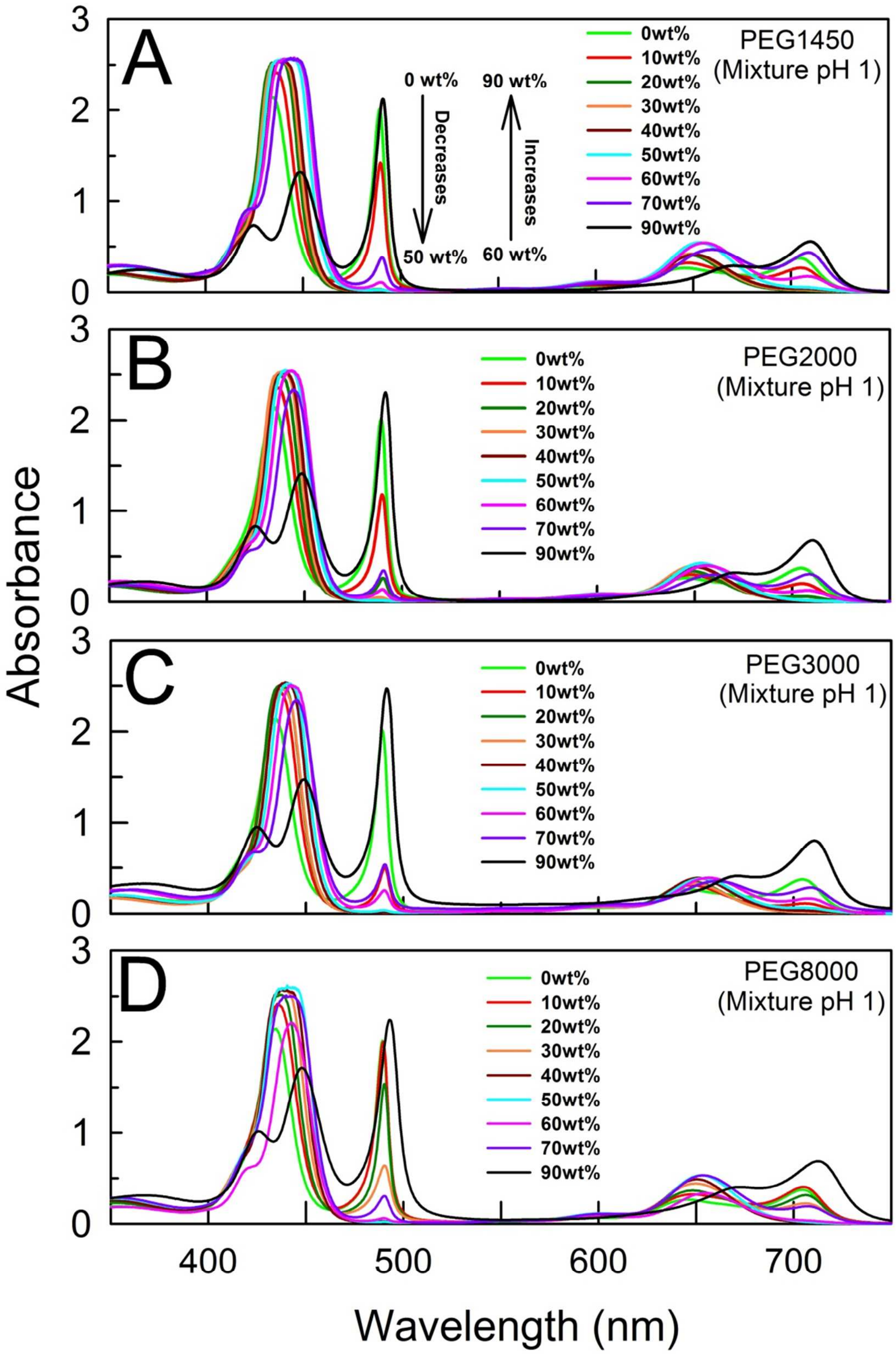

Figure S1. Absorbance spectra of 10 μM TSPP dissolved in aqueous mixture of PEGs (PEG1450, PEG2000, PEG 3000 and PEG8000) at pH 1 as a function of wt% of water.

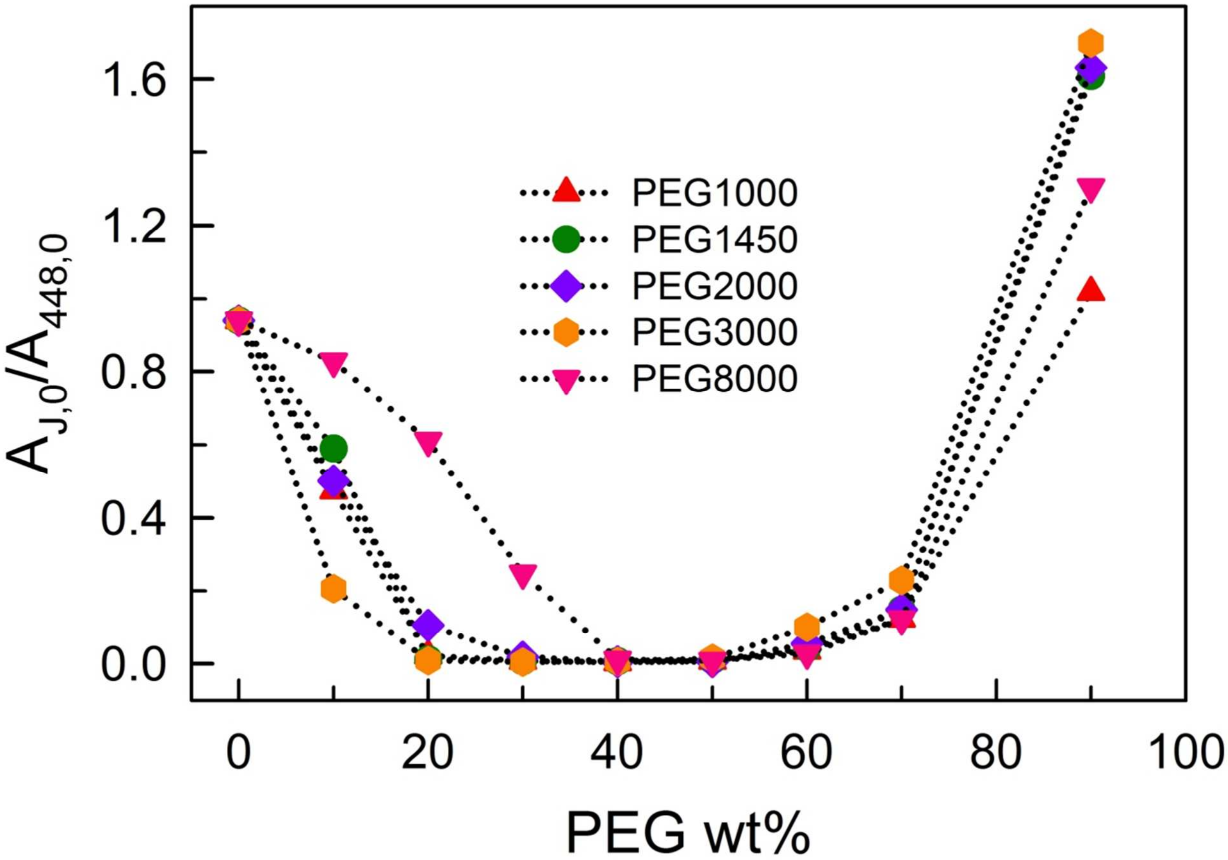

Figure S2. Ratio of the absorbance at 490 nm corresponding to initially formed J-aggregates ($A_{J,0}$) to the absorbance at 448 nm corresponding to diprotonated form exist initially ($A_{448,0}$) of 10 μM TSPP in aqueous mixture of PEGs at pH 1 as a function of wt% of PEG.

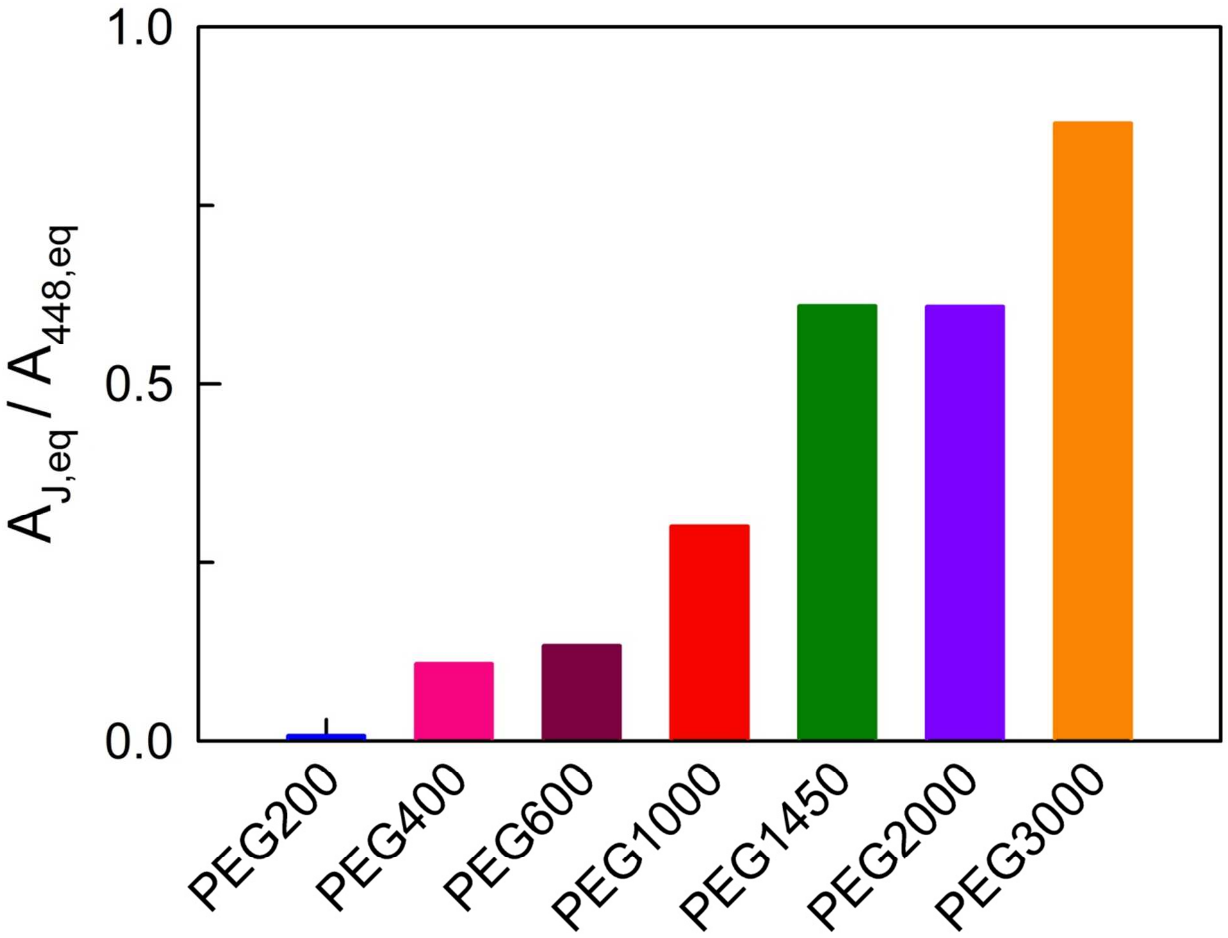

Figure S3. Ratio of the absorbance at 490 nm ($A_{J,eq}$) corresponding to J-aggregates after reaching equilibrium to the absorbance at 448 nm ($A_{448,eq}$) corresponding to diprotonated form after reaching equilibrium in 10 wt% water-added PEG mixtures at pH 1.

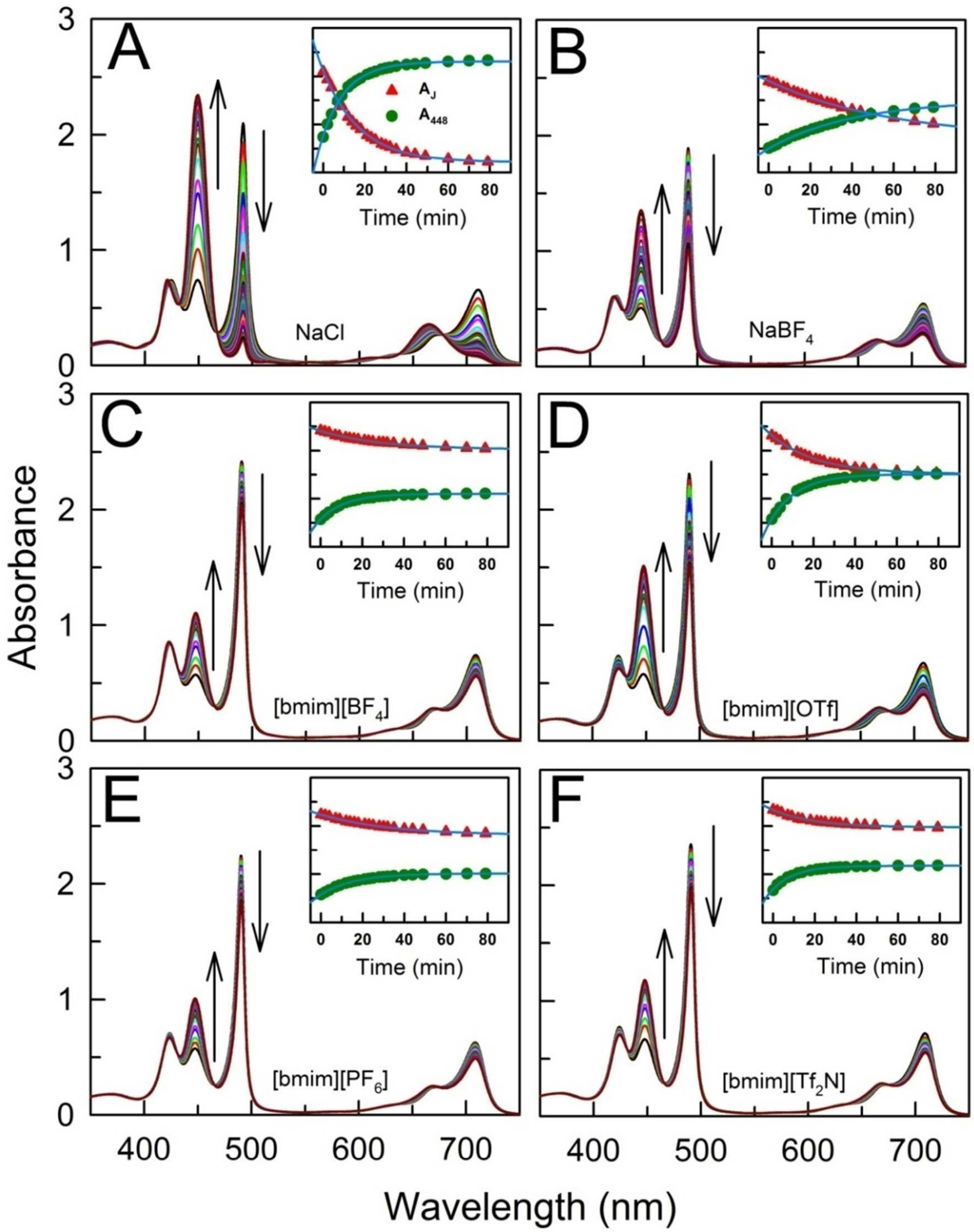

Figure S4. Change in absorbance of 10 μM TSPP with time within 10 wt% water-added PEG400 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth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

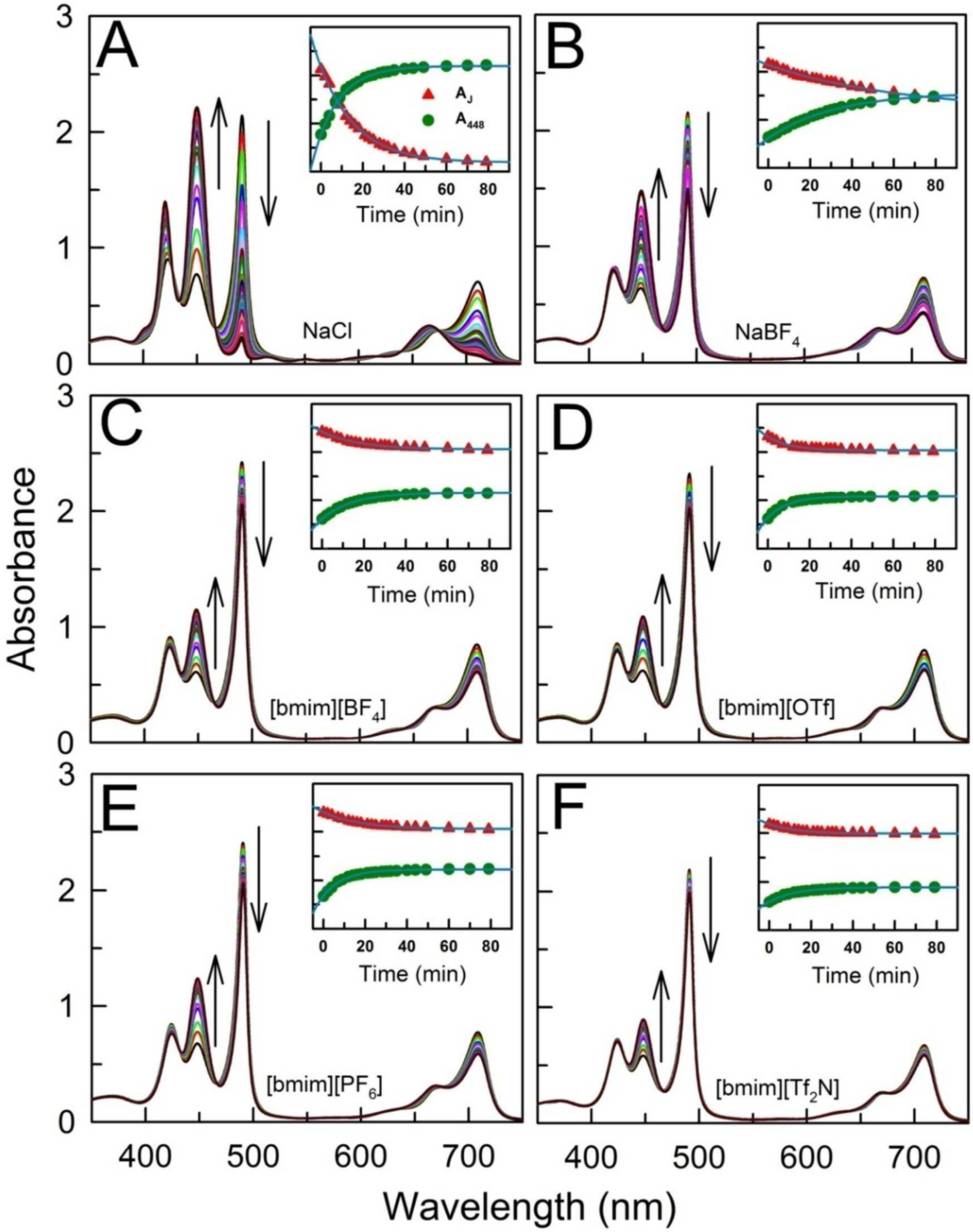

Figure S5. Change in absorbance of 10 µM TSPP with time within 10 wt% water-added PEG600 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth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

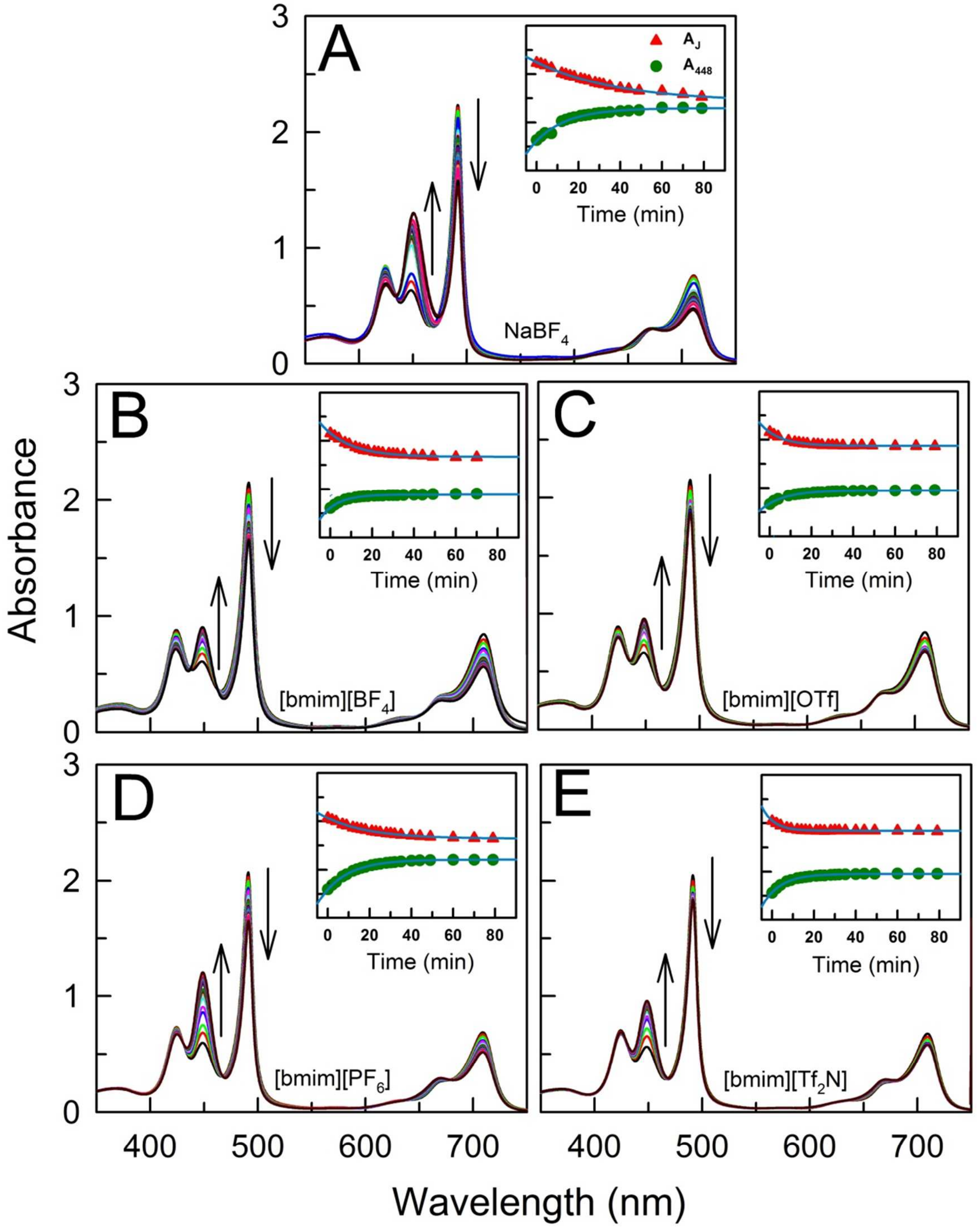

Figure S6. Change in absorbance of 10 µM TSPP with time within 10 wt% water-added PEG1000 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth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

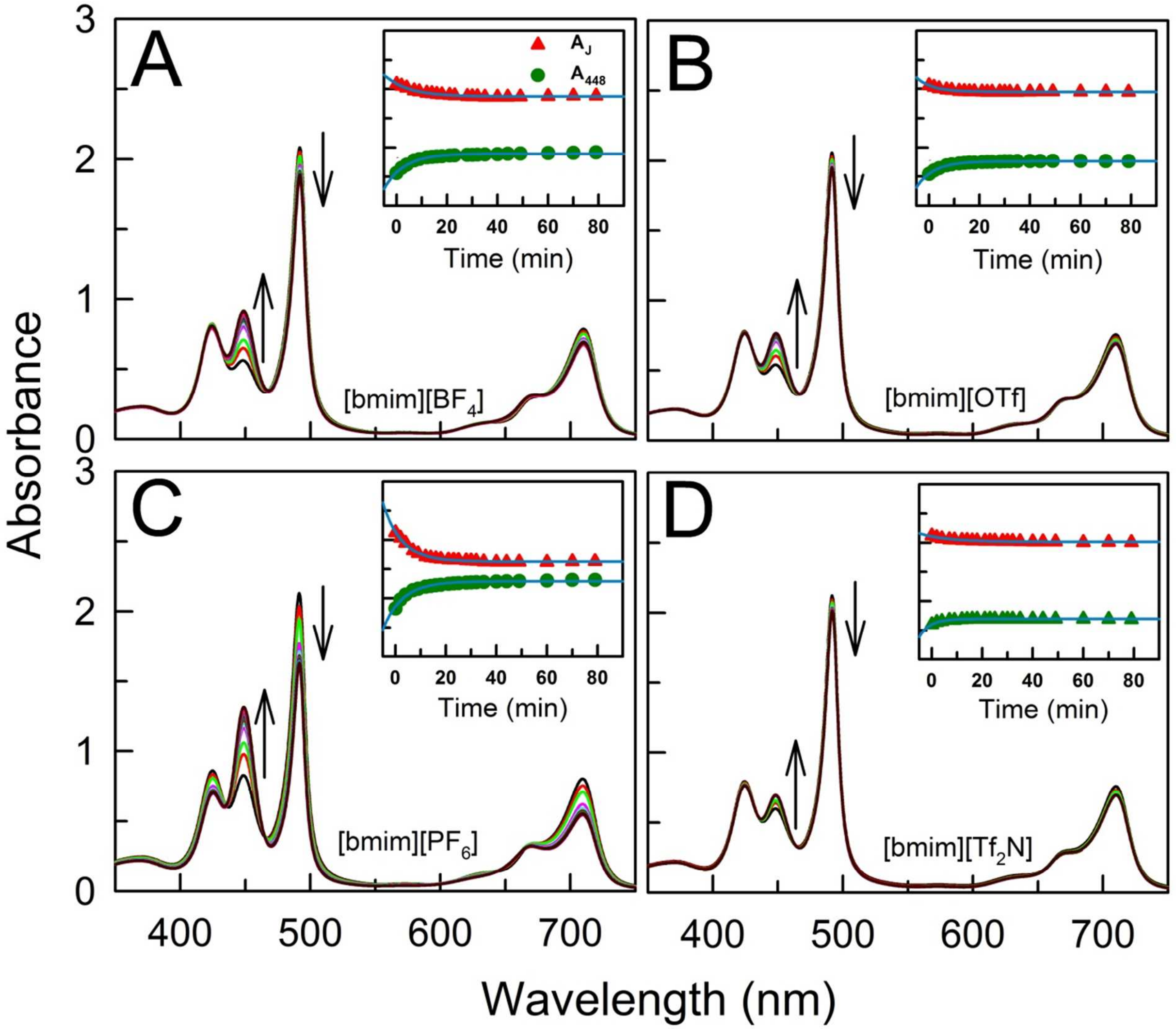

Figure S7. Change in absorbance of 10 µM TSPP with time within 10 wt% water-added PEG1450 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth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

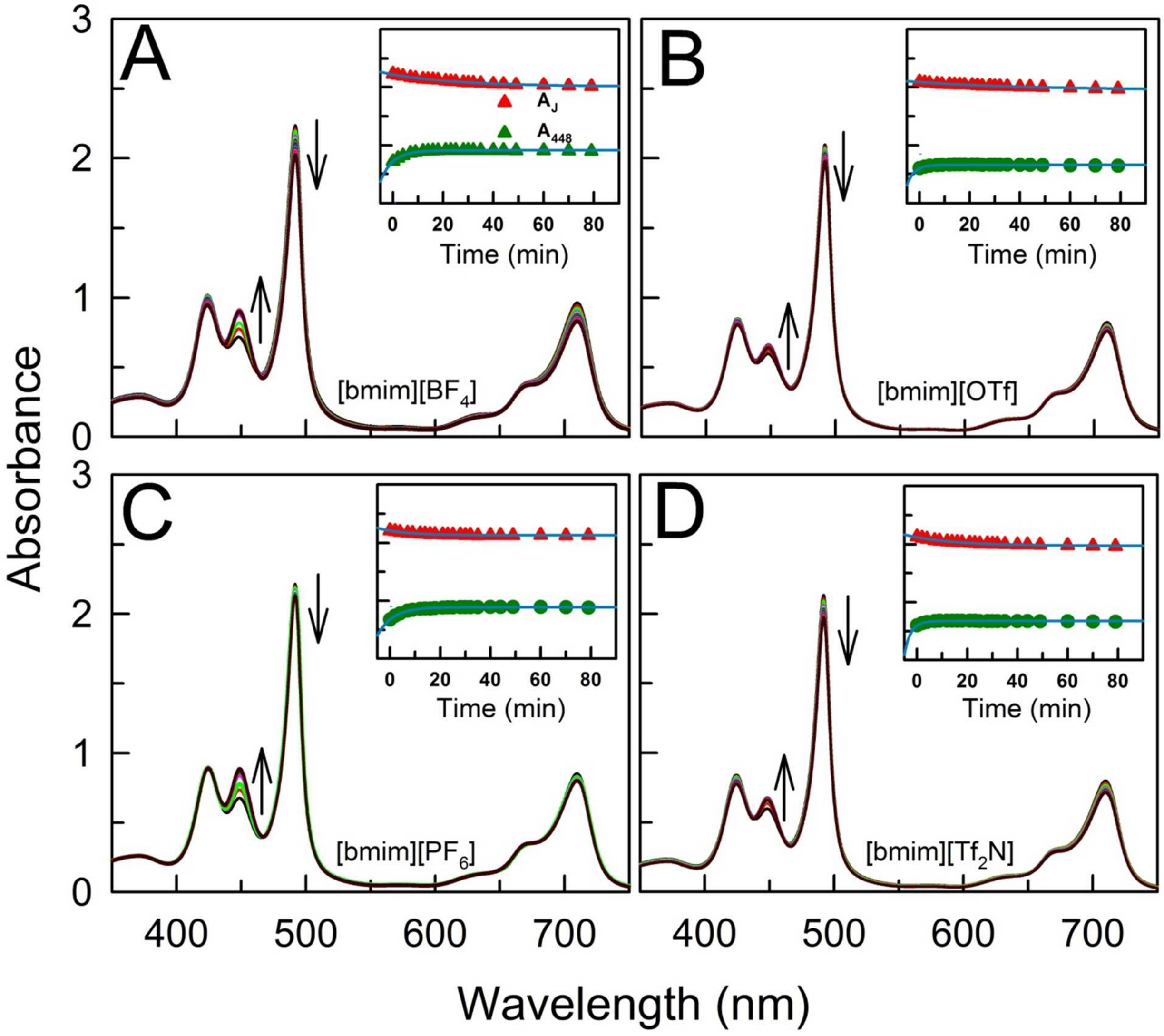

Figure S8. Change in absorbance of 10 µM TSPP with time within 10 wt% water-added PEG2000 mixtures at pH 1 in the presence of 0.3 M additives. Insets show the decrease in absorbance at 490 nm (corresponding to the decay of J-aggregates) and increase in absorbance at 448 nm (corresponding to the growth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

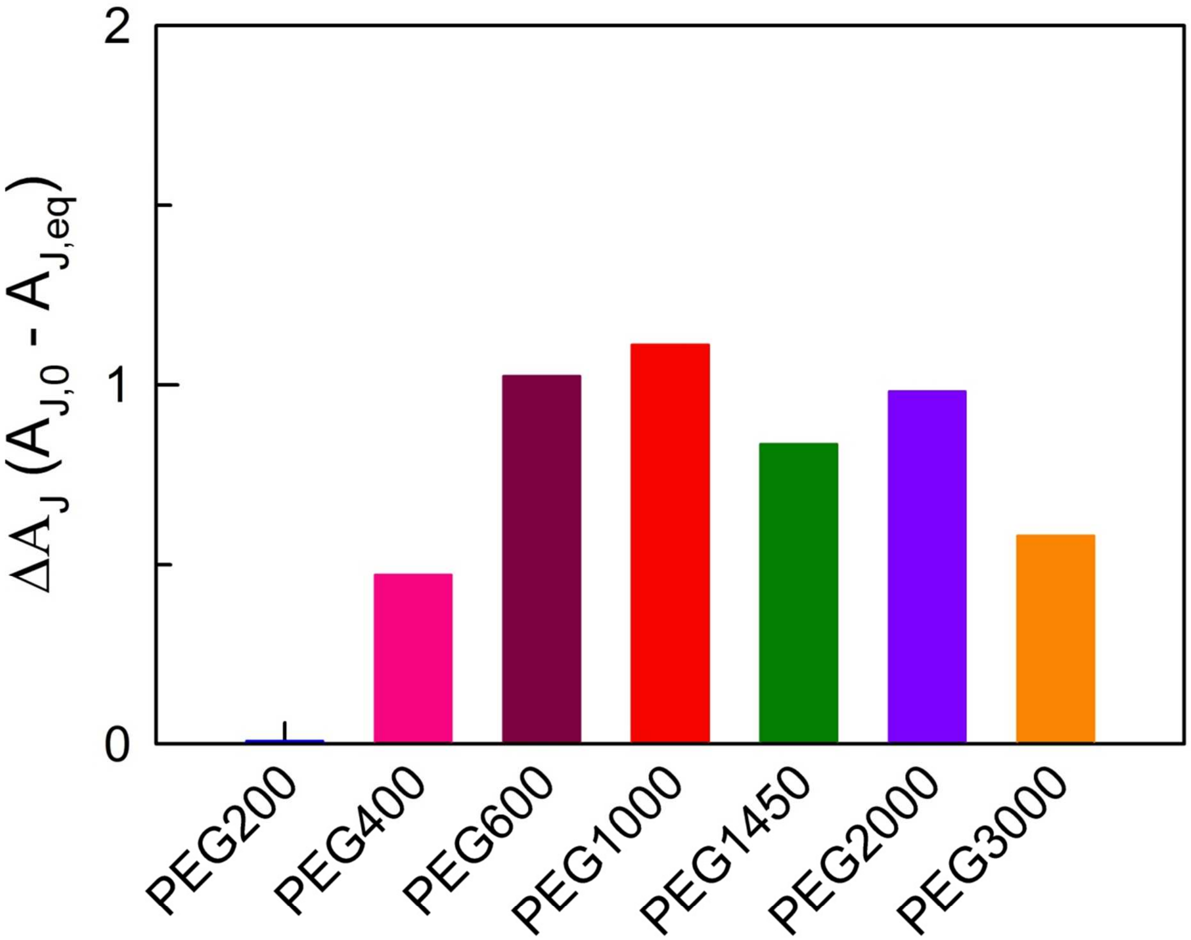

Figure S9. Difference (ΔA_J) between the absorbance of initially formed J-aggregates ($A_{J,0}$) and the absorbance of J-aggregates formed at equilibrium ($A_{J,eq}$) for 10 μM TSPP dissolved in 10 wt% water-added PEG mixtures at pH 1.