Monatsh Chem (2009) 140:335–337
DOI 10.1007/s00706-008-0028-z

ORIGINAL PAPER

Inhibition of J-aggregation of *meso*-tetra (4-sulfonatophenyl)porphyrin by an ionic liquid with π-conjugated character

Qing-Xia Wan · Ye Liu · Sa-Sa Wang

Received: 9 June 2008 / Accepted: 13 June 2008 / Published online: 17 September 2008

Abstract UV–visible spectral observations indicate that the J-aggregation of protonated *meso*-tetra(4-sulfonatophenyl)porphyrin ($[H_2TSPP]^{2+}$) under acidic conditions is completely inhibited by the π–π counteraction between 1-butyl-pyridinium tetrafluoroborate ($[bpy]BF_4$) and $[H_2TSPP]^{2+}$. The studies also suggest that the intermolecular π–π force is of relative importance for the J-aggregates of $[H_2TSPP]^{2+}$ and the intermolecular electrostatic force for the H-aggregates.

Keywords Porphyrin · Ionic liquids · Aggregation · UV–visible spectrophotometer

Introduction

Porphyrins with a well-extended π-conjugate system are expected to form highly ordered self-aggregates through non-covalent interactions, including π–π and electrostatic force, hydrogen bonding, and charge-transfer interactions [1–5]. A variety of factors can influence the extent of self-aggregation, including the nature of porphyrin itself (metal ion, number and nature of peripheral groups) as well as external changes like ionic strength, pH, solvent nature, concentration, etc. [3, 4]. Conventional nomenclature distinguished J (redshifted)- and H (blueshifted)-aggregate transitions in which the monomer transition dipoles are aligned parallel and perpendicular, respectively, to the line connecting neighboring molecules in the aggregates [5–9].

Q.-X. Wan · Y. Liu (✉) · S.-S. Wang
Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China
e-mail: yliu@chem.ecnu.edu.cn

In the literature, the aggregation of the ionic water-soluble *meso*-tetra(4-sulfonatophenyl)porphyrin sodium ($[TSPP]Na_4$) [3–5, 10–15] was significantly investigated under suitable conditions of pH, ionic strength, and different acids by spectroscopic techniques. However, it is difficult to determine the relatively important driving force for the aggregation among the non-covalent interactions like π–π force, electrostatic force, hydrogen bonding, and charge-transfer interactions, and the mechanism of aggregation is of continuing interest.

In this work we try to prove that π–π interaction is the predominant driving force for the formation of J-aggregates of $[H_2TSPP]^{2+}$, whereas the electronstatic force is contributing to the H-aggregation through investigating the influence of the ionic liquid 1-butyl-pyridinium tetrafluoroborate ($[bpy]BF_4$) on the aggregation of protonated $[H_2TSPP]^{2+}$.

Results and discussion

In NaOH aqueous solution, TSPP exists as an unprotonated monomer anion with a charge of −4 from the sulfonato groups, and the Soret band appears at 413 nm. Fig. 1 shows how the Soret band of protonated diacid of $[H_2TSPP]^{2+}$ evolves as $[bpy]BF_4$ is added in HNO_3 aqueous solution (at pH = 5.1–0.8). At pH 5.1, the diacid monomer corresponding to the weak Soret band at 437 nm just begins to form (line 1) because the p*K*a for the protonated diacid of TSPP is about 5 [16]. At lower pH of 0.8, the characteristic absorbances of J-aggregates of $[H_2TSPP]^{2+}$ at 490 nm (Soret band) and 707 nm (Q band) coexist with those of the diacid monomer (line 2) [6–8]. When $[bpy]BF_4$ is added gradually, the absorbance of 490 nm decays, accompanied by the concurrent increase at the absorbance of 437 nm

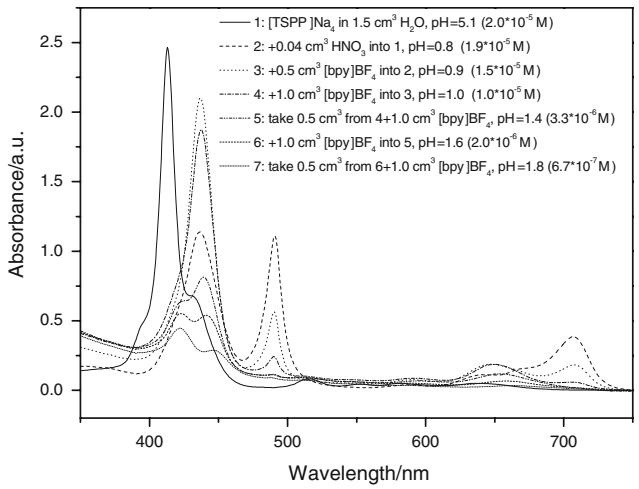

Fig. 1 UV–visible spectra of TSPP in acid aqueous solution treated with $[bpy]BF_4$

(lines 3–5). In 2.4 M $[bpy]BF_4$ at pH 1.1, the J-aggregates totally dissociated into the diacid monomer (437 nm, line 5), which is split into two components at about 422 and 438 nm with the further increased concentration of $[bpy]BF_4$ (line 6). The latter absorbance band ascribed to the diacid monomer of $[H_2TSPP]^{2+}$ continuously decays and shows redshifts to about 450 nm due to the presence of the large amount of $[bpy]BF_4$ salt (line 7), accompanied by the concurrent increase at 422 nm. It has been shown that the structure of the J-aggregates shows the monomer units stacked as in a slipped deck of cards, with the negative charges on the periphery of one molecule overlapping the positive charges in the center of the neighboring porphyrin [6, 7, 16]. Close association of the π orbitals of neighboring molecules leads to strong exciton coupling, and the resulting J-aggregate absorption at 490 nm exhibits the narrowed line width [8] as shown in Fig. 1. Reasonably, the presence of $[bpy]BF_4$ with the conjugated character could counteract the π–π interaction of porphyrin itself, leading to the dissociation of J-aggregates of $[H_2TSPP]^{2+}$ into the diacid monomer. This result implies that among many non-covalent interactions, including π–π force, electrostatic force, hydrogen bonding, and charge-transfer interactions for the formation of the highly ordered J-aggregates of $[H_2TSPP]^{2+}$, the π–π force is dominantly important over the others. Whenever the π–π force in the porphyrins is broken down, the J-aggregate network collapses.

The unexpected peak at 422 nm in Fig. 1 was tentatively assigned to represent the H-aggregates of $[H_2TSPP]^{2+}$, according to the observation of Choi et al. [8]. It is considered that the monomer transition dipoles in the H-aggregate are aligned perpendicularly to the line connecting neighboring molecules in the aggregates. In this situation, the electrostatic interaction becomes a dominant driving force for the formation of H-aggregates instead of π–π force. Hence, the presence of $[bpy]BF_4$ could not suppress the formation of H-aggregates $[H_2TSPP]^{2+}$. On the contrary, the presence of $[bpy]BF_4$ at high concentration as a kind of ionic salt led to the dramatically increased ionic strength, which favored H-aggregation of $[H_2TSPP]^{2+}$ [8].

In order to compare the roles of $[bpy]BF_4$ as a π-conjugated unit and a common ionic salt, respectively, for the contribution of J, H-aggregation, the influence of inorganic salt $NaBF_4$ on the aggregation of $[H_2TSPP]^{2+}$ was investigated in Fig. 2. The addition of $NaBF_4$ led to the increased intensity both at 490 (J-aggregates) and 422 nm (H-aggregates), due to the increased ionic strength [1, 2, 8]. Without the π-conjugated character in $NaBF_4$, the inhibition of J-aggregates of TSPP through π–π counteraction could not be observed.

In pure $[bpy]BF_4$, TSPP surely exists as an unprotonated monomer anion with the indication of the spectral pattern of four Q bands for the free-base porphyrin with D_{2h} symmetry (Fig. 3, line 1). The typical Soret band of the unprotonated TSPP monomer appeared at 420 nm with several nanometer redshifts compared to that in aqueous solution (413 nm, in Figs. 1, 2). When the concentrated nitric acid was added, TSPP was protonated to become a diacid monomer, showing the Soret band at 450 nm. Comparing the Soret bands for the unprotonated monomer (TSPP) and the protonated monomer ($[H_2TSPP]^{2+}$) in $[bpy]BF_4$ to those in aqueous solution, the obvious redshift was observed in $[bpy]BF_4$ solution, suggesting the strong π–π interaction between $[bpy]BF_4$ and TSPP through π orbital mixing [8]. Resultantly, the J-aggregation of TSPP dominantly derived from π–π interaction of porphyrino rings was completely inhibited (Fig. 3, lines 2 and 3). When H_2O was added to dilute the IL solution, the absorbance band at 450 nm for $[H_2TSPP]^{2+}$ diacid monomer shifted back to 438 nm as a normal one in aqueous solution (line 5). However, the

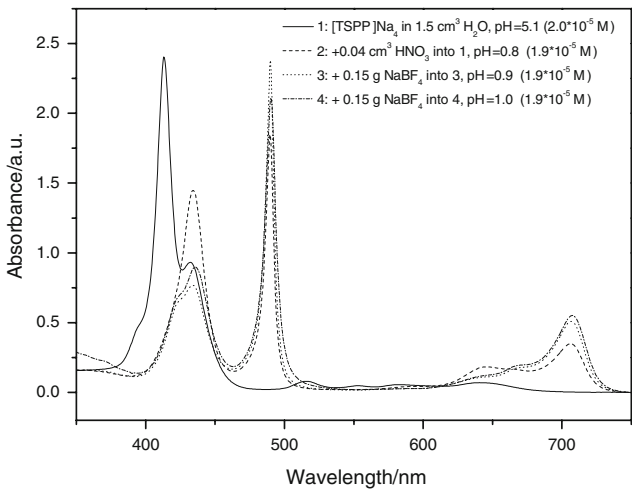

Fig. 2 UV–visible spectra of TSPP in acid aqueous solution treated with $NaBF_4$

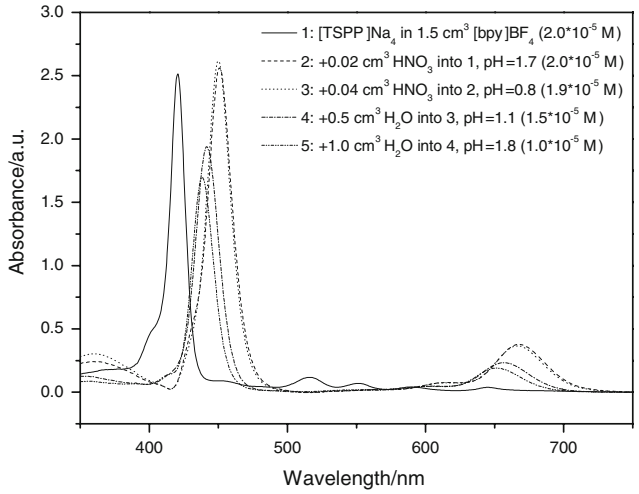

Fig. 3 UV–visible spectra of TSPP in $[bpy]BF_4$ solution treated with H_2O

H-aggregates, in which the monomer transition diploes are aligned perpendicularly to benefit the intermolecular electrostatic interaction between $[H_2TSPP]^{2+}$ molecules, could not be formed anymore, suggesting that the highly ordered π–π super-network established in $[bpy]BF_4$ solution of $[H_2TSPP]^{2+}$ prevents the realignment of the monomer transition diploes in $[H_2TSPP]^{2+}$ from parallel to perpendicular. In contrast, when TSPP dissolved in the acidic aqueous solution was treated with $[bpy]BF_4$ afterwards, the π–π facial interaction between $[bpy]BF_4$ and $[H_2TSPP]^{2+}$ established in small-scale makes the monomer transition dipoles in $[H_2TSPP]^{2+}$ much easier to be realigned perpendicularly, leading to the formation of H-aggregate $[H_2TSPP]^{2+}$ as observed in Fig. 1, with increased ionic strength ($[bpy]BF_4$ salt).

In conclusion, we investigated the influence of $[bpy]BF_4$ with conjugated character on the aggregation of $[H_2TSPP]^{2+}$ under acid conditions and found that J-aggregation of $[H_2TSPP]^{2+}$ derived from the π–π interaction of porphyrin itself was completely inhibited independent of pH values due to the π–π counteraction between $[bpy]BF_4$ and $[H_2TSPP]^{2+}$. The studies also suggest that J-aggregates of $[H_2TSPP]^{2+}$ are dominantly held together by intermolecular π–π force and H-aggregates of $[H_2TSPP]^{2+}$ by intermolecular electrostatic force.

Experimental

The evolving processes of $[TSPP]Na_4$ solution under different conditions in a UV cuvette (3 cm^3) were monitored in situ by a SHIMADZU-UV 2550 spectrophotometer at ambient temperature (ca. 25 °C). The spectral resolution was about 1 nm. $[TSPP]Na_4$ was dissolved into 1.5 cm^3 deionized water (or $[bpy]BF_4$) with a concentration of 2.0×10^{-5} M, which was protonated by concentrated nitric acid to pH 0.8. Consequently, the buffer was added gradually into the protonated $[H_2TSPP]^{2+}$ solution. The pH value of the solution was measured by accuracy pH test paper.

The porphyrin derivative $[TSPP]Na_4$ and the IL $[bpy]BF_4$ were prepared according to [17] and [18].

Acknowledgments The National Natural Science Foundation of China (nos. 20673039, 20533010, 20590366) and the Science and Technology Commission of Shanghai Municipality (06JC14023, 06SR07101) are gratefully acknowledged for financial support.

References

1. Kano K, Fukuda K, Wakami H, Nishiyabu R, Pasternack RF (2000) J Am Chem Soc 122:7494
2. Kano K, Kobayashi T (2001) J Chem Phys 116:184
3. Andrade SM, Teixeira R, Costa SMB, Sobral AJFN (2008) Biophys Chem 133:1
4. Rahman M, Harmon HJ (2007) J Porp Phthal 11:125
5. Higgins DA, Barbara PF (1995) J Phys Chem 99:3
6. Akins DL, Zhu HR, Guo C (1996) J Phys Chem 100:5420
7. Akins DL, Zhu HR, Guo C (1994) J Phys Chem 98:3612
8. Choi MY, Pollard JA, Webb MA, McHale JL (2003) J Am Chem Soc 125:810
9. Yildirim H, Iseri EI, Gülen D (2004) Chem Phys Lett 391:302
10. Egawa Y, Hayashida R, Anzai J (2007) Langmuir 23:13146
11. Wu J-J, Ma HL, Mao H-S, Wang Y, Jin W-J (2005) J Photochem Photobiol B 173:296
12. Ohno O, Kaizu Y, Kobayashi H (1993) J Chem Phys 99:4128
13. Ribó JM, Crusats J, Farrera J-A, Valero ML (1994) Chem Commun 6:681
14. Rubires R, Crusats J, El-Hachemi Z, Jaramillo T, López M, Valls E, Farrera J-A, Ribó JM (1999) New J Chem 23:189
15. Maiti NC, Mazumdar S, Periasamy N (1998) J Phys Chem B 102:1528
16. Maiti NC, Ravikanth M, Mazumdar S, Periasamy N (1995) J Phys Chem 99:17192
17. Sutter TPG, Rahimi R, Hambright P, Bommer JC, Kumar M, Neta P (1993) J Chem Soc Faraday Trans 89:495
18. Behar D, Neta P, Carl S (2002) J Phys Chem A 106:3139