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Fluorescence spectroscopic studies on substituted porphyrins in homogeneous solvents and cationic micellar medium

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ABSTRACT

Steady state and time-resolved fluorescence properties of porphyrin appended 1,3,4-oxadiazoles and thiazoles were described in homogeneous medium as well as in presence of cationic surfactant cetyltrimethylammonium bromide (CTAB). The electron withdrawing substituent on the porphyrin moiety in both the cases make a donor–spacer–acceptor type of intramolecular photoinduced electron transfer (PET) system resulting substantial quenching in porphyrin fluorescence due to partial energy migration towards the acceptor in the excited state. The increase in fluorescence yield as well as appreciable difference in fluorescence decay behavior in aqueous buffer solution of pH 4.2 from that in chloroform solution is believed due to partial protonation of the porphyrin ring. All the investigated systems show preferential binding into the interfacial region of the micellar sub-domain with varying degree of penetration depending on the nature of the substituent. Almost 2–4 fold increase in fluorescence yield for the probes is explained on the basis of restricted flexibility and corresponding decrease in total nonradiative rate inside the micellar interface layer.

1. Introduction

Photochemistry of substituted porphyrins is a subject of renewed interest in recent times due to its wonderful repertoire of optical and electronic properties which allow them to play a variety of roles in nature as well as in technical applications [1,2]. Tetraphenylporphyrins (TPPs) have been examined most intensively due to their easy synthesis as well as relevance to biologically important properties [3]. The knowledge on the photophysical behavior of such systems is useful for a better understanding on the natural phenomenon and designing various molecular devices of medical, bio-medical or environmental importance. Recently, the photophysical properties of dithiaporphyrins were reported in comparison to tetraphenylporphyrins (TPP) [4–6]. The aggregation and/or dimerization of porphyrins and metalloporphyrins in aqueous solutions are also well-known [7–16]. Micellar effect on the aggregation of porphyrins with cationic, anionic and nonionic surfactants in aqueous media was also reported in the literature [17]. The investigated porphyrins were tetra-anionic *meso-tetrakis*-(4-sulfonatophenyl) porphyrin (TPPS), H_2TPPS, (TPPS)VO, (TPPS)Cu, and (TPPS)Zn. An additional interest in examining the properties of H_2TPPS and (TPPS)M (with M=Zn(II), Cu(II), VO^{2+}) in micellar media comes from possible use of these systems in photodynamic therapy (PDT) and magnetic resonance imaging. H_2TPPS is known to localize in certain tumors to a high absolute concentration with favorable tumor to other tissue ratios. It is also known that a direct interaction and a strong binding of H_2TPPS with tubulin are involved in the biochemical mechanism for its selective uptake [18,19]. In addition, (TPPS)M, with M=Fe(III), Mn(III) and Cu(II), are being investigated as contrast agents for NMR imaging of solid tumors [20–22]. Tabak et al. studied the behavior of charged porphyrin in micellar systems which may shed more light on the interaction of charged porphyrin with liposomes and can potentially be used for porphyrin drug delivery [23].

To act as effective photodynamic therapeutic drug, the porphyrin derivatives need to be specifically administered to the targeted site. Normally, the albumins and/or lipoproteins present in the blood serum act as endogenous carrier for this purpose. However, because of their strong affinity, the proteins may either aid in the delivery and access of the porphyrins to the affected cell via receptor mechanism or decrease the availability of the drug towards PDT by its rapid removal from circulation. A critical balance between these two, which might differ from one carrier to the other and also from one porphyrin species to another, drives scientists to design for the newer systems. In the present

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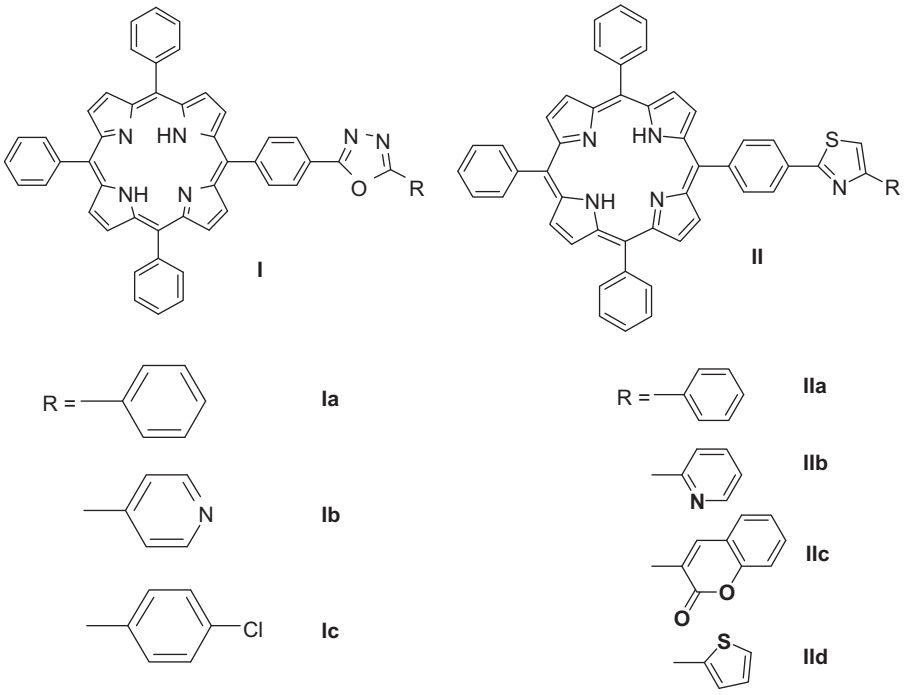

Scheme 1. Structure of the systems investigated.

work, we report the photophysical behavior of several porphyrin appended 1,3,4-oxadiazoles (**I**) and thiazoles (**II**) (Scheme 1, for structures) in chloroform by steady state and time resolved fluorescence spectroscopy. Detail investigations are also done for all the systems in aqueous buffer solution of pH 4.2 to verify any possibility for the formation of dimer and/or other higher order aggregates. Also, some of the representative systems from both the groups were investigated in presence of cationic surfactant namely, cetyltrimethylammonium bromide (CTAB). This study is done with an intention to gather information on the mechanism of biological effects of the synthesized porphyrin derivatives and their possible involvement in penetration through membranes and binding to plasma proteins. Simple micellar models are used to evaluate the binding efficiency of these porphyrin appended systems into the natural membrane mimetic cell components provided by the micellar sub-domain.

2. Experimental

*2.1. General synthetic procedure and characterization of porphyrin appended 1,3,4-oxadiazoles (**Ia–c**) and thiazoles (**IIa–d**).*

*2.1.1. Porphyrin appended oxadiazoles (**Ia–c**): The corresponding porphyrin hydrazones in dichloromethane were cyclized to porphyrin appended 1,3,4-oxadiazoles using iodobenzenediacetate (IBD) with constant stirring for eight hours at room temperature [24].*

5-[4-phenyl-{2-phenyl-1,3,4-oxadiazol-5-yl}]-10,15,20-triphenylporphyrin **(Ia):** Yield 66%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J=4 Hz), 8.86 (s, 8H), 8.57 (d, 2H, J=12 Hz), 8.42 (d, 2H, J=8 Hz), 8.23 (d, 6H, J=8 Hz), 7.77 (d, 9H, J=8 Hz), 7.61 (t, 3H, J=8 Hz), −2.75 (s, 2H). MS: m/z 759.1574, calcd. for $[M+H]^+$ −759.2872. 5-[4-phenyl-{4-pyridyl-1,3,4-oxadiazol-5-yl}]-10,15,20-triphenyl-porphyrin **(Ib):** Yield 75%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.94 (d, 2H, J=8 Hz), 8.84 (s, 8H), 8.63 (d, 2H, J=8 Hz), 8.52 (d, 2H, J=8 Hz), 8.24 (d, 6H, J=8 Hz), 8.21 (d, 2H, J=8 Hz), 7.85 (m, 9H), −2.86 (s, 2H). MS: m/z 760.1547, calcd. for $[M+H]^+$ −760.2825. 5-[4-phenyl-{2-(4-chloro-phenyl)-1,3,4-oxadiazol-5-yl}]-10,15,20-triphenyl-porphyrin **(Ic):** Yield 74%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.89 (d, 2H, J=4 Hz), 8.85 (s, 8H), 8.55 (d, 2H, J=8 Hz), 8.42 (d, 2H, J=8 Hz), 8.23 (d, 6H, J=8 Hz), 7.79 (d, 9H, J=8 Hz), 7.61 (d, 2H, J=8 Hz), −2.75 (s, 2H). MS: m/z 793.1147, calcd. for $[M+H]^+$ −793.2483.

*2.1.2. Porphyrin appended thiazoles (**IIa-d**):*
*The facile and high yielding synthesis of **II** involved the reaction of 5-(4-thiocarboxamidophenyl)-10,15,20-triphenylporphyrin with α-bromo ketones in ethanol [25].*

5-{4-phenyl-(4′-Phenyl)-2′-thiazolyl}-10,15,20-triphenylporphyrin (**IIa**): Yield 82%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δH ppm 8.87–8.92 (m, 8H), 8.45 (d, 2H, J=7.3 Hz), 8.34 (d, 2H, J=8.2 Hz), 8.21–8.24 (m, 6H), 8.12–8.14 (m, 2H), 7.73–7.79 (m, 9H), 7.64 (s, 1H), 7.54 (t, 2H, J=7.6 Hz), 7.41–7.45 (m, 1H), −2.77 (s, 2H). MS: m/z 774.2920, calcd. for $[M+H]^+$ −774.2613. 5-{4-phenyl-4′-(pyridin-2-yl)-2′-thiazolyl}-10,15,20-triphenyl porphyrin (**IIb**): Yield 79%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H ppm 8.86–8.91 (m, 8H), 8.69–8.71 (m, 1H), 8.45–8.41 (m, 3H), 8.34 (dd, 2H, J=1.7 Hz, J=6.4 Hz), 8.21–8.25 (m, 7H), 7.89 (t, 1H, J=7.7 Hz), 7.73–7.81 (m, 9H), 7.29–7.32 (m, 1H), −2.76 (s, 2H). MS: m/z 775.2920, calcd. for $[M+H]^+$ −775.2566. 5-{4-phenyl-4′-(coumarin-3-yl)-2′-thiazolyl}-10,15,20-triphenylporphyrin (**IIc**): Yield 77%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H 9.05 (s, 1H), 8.86–8.92 (m, 8H), 8.64 (s, 1H), 8.47 (dd, 2H, J=1.8 Hz, J=6.4 Hz), 8.37 (dd, 2H, J=1.7 Hz, J=6.4 Hz), 8.22–8.24 (m, 6H), 7.74–7.81 (m, 10H), 7.57–7.58 (m, 1H), 7.45 (d, 1H, J=8.4 Hz), 7.35–7.38 (m, 1H), −2.76 (s, 2H). MS: m/z 842.2730, calcd. for $[M+H]^+$ −842.2511. 5-{4-phenyl-4′-(thiophen-2-yl)-2′-thiazolyl}-10,15,20-triphenylporphyrin (**IId**): Yield 80%; ^{1}HNMR (400 MHz; $CDCl_3$; Me_4Si): δ_H 8.85–8.90 (m, 8H), 8.42 (d, 2H, J=7.0 Hz), 8.33 (d, 2H, J=8.0 Hz), 8.21–8.23 (m, 6H), 7.73–7.81 (m, 9H), 7.64 (dd, 1H, J=3.5 Hz, J=1.0 Hz), 7.49 (s, 1H), 7.38 (dd, 1H, J=5.2 Hz, J=1.0 Hz), 7.16 (dd, 1H, J=3.9 Hz, J=5.0 Hz), −2.76 (s, 2H). MS: m/z 780.2522, calcd. for $[M+H]^+$ −779.2177.