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Types of interaction of *meso*-tetraphenylporphyrin with alkali and alkaline-earth metal ions

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ABSTRACT: The cavity in a porphyrin can accommodate metal ions through electron donor-acceptor (EDA) interaction in acetonitrile media without any specially designed fabrication with the porphyrin subunit. Alkali metal ion forms a complex with *meso*-tetraphenylporphyrin (TP) in 2:1 stoichiometry, while the bivalent Mg^{2+} ion follows a 1:1 stoichiometry. A fluorescence interaction study indicated that TP can behave like a chemosensor for these ions present in the blood electrolytes. Specifically, for the alkali metal ions intensity-based sensing was observed, due to inhibition of photoinduced electron transfer (PET), entailing enhancement of fluorescence intensity, and for the alkaline-earth Mg^{2+} a mixed quenching was observed. Na⁺ and K⁺ ions can be differentiated depending upon the extent of fluorescence enhancement. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: meso-tetraphenylporphyrin; blood electrolyte sensor; 2:1 and 1:1 stoichiometry for alkali and alkaline-earth metal ions

Introduction

Since Na⁺, K⁺ and Mg²⁺ are well-known blood electrolytes, their sensing by chelating agents such as porphyrin, which is present within the core of haem proteins, is of great importance. The porphyrins and related macrocycles have rich coordination chemistry and are of much interest because of their significance in biology, specifically in biological oxidation and reduction reactions (1,2). Their metal complexes participate in the primary photosynthetic process, oxygen transport, electron transport and in the metabolism of drugs and xenobiotics (3-6). Porphyrin with cation radicals have been identified as intermediates in many catalytic cycles (3). It has further been suggested that future electronic devices used in memory or logic application could rely specifically on tuning the electronic properties of porphyrins and their π -cation radicals (7,8). Many porphyrins and metalloporphyrins have been used in the last few years as ionophores (9-18) because of the importance of developing new polymeric membrane ion-selective electrodes. Thus, polymeric membrane was shown to be the best working medium for free-base porphyrins to work as ionophores for heavy metal sensors (19).

The porphyrin dianion ligand (P^{2-}) can coordinate with two alkali metal atoms to form dimetallic complexes, M_2P (where M = Li, Na, K), which were originally characterized by absorption spectra many years ago (20–22). These alkali metal complexes have been found to be useful reagents for syntheses of early transition metal complexes of the porphyrins (23–25) and porphyrin (and/or phthalocyanine) sandwich compounds (26,27). However, isolation and structural study of these alkali metal complexes are difficult, since they are chemically labile and can quickly change to the free-base porphyrin (H_2P) in the presence of water or dilute weak acids. Previously, Arnold and co-workers (28,29) found that the reaction of free-base porphyrins, such as octaethylporphyrin (OEP), meso-tetraphenylporphyrin (TP) and meso-tetrakis(3,4,5-trimethoxylphenyl) porphyrin (TMPP), with Mn (SiMe₃)₂ (Li, Na, K) in tetrahydrofuran (THF) or dimethoxyethane (DME) yields $M_2P(THF)_4$ and $M_2P(DME)_2$ complexes. The structures of Na₂(OEP)(THF)₄ and $K_2(OEP)(pyr)_2$ have been determined by X-ray crystal studies; the structures and properties of the alkali metal porphyrin complexes are still not well understood in comparison with other metalloporphyrins.

Very recently De Luca and co-workers (30) have succeeded in detecting and spectroscopically characterizing two novel sittingatop (SAT) complexes of sodium as metal ions in the organic phase. The interplay of low-polarity solvents and bulky and weakly coordinating anions favours the stabilization of these new species, in which the sodium ion is interacting with the N atoms of the porphyrin core without the concomitant loss of the N–H groups.

This study explores whether the biologically important freebase *meso*-tetraphenylporphyrin (TP) can interact with blood electrolytes as such, or whether it needs the environment to form dianions, as reported earlier, without using polymeric membrane as the working medium. It is also to nullify the effect of bulky anions by replacing with perchlorate, so that the sitting-atop situation can be modified. To our knowledge, this is the first

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intensive spectroscopic study of blood electrolytes interacting with the TP molecule in polar acetonitrile medium, where various types of interactions exist.

Experimental

Reagents

The TP was prepared according to the reported method (31). Purity of the prepared compound was checked by IR (Perkin-Elmer FTIR, Model No. RXI), by ¹H-NMR (Bruker AV300; 300 MHz in CD₃CN) spectral measurements and also by thin-layer chromatography. All the solvents (HPLC grade; Merck) were used without further purification. Sodium, potassium and magnesium perchlorates (Aldrich) were dried in the oven before use. The samples were preserved in a dry box so as to avoid contamination from moisture.

Apparatus

Absorption (UV-vis) spectral measurements were performed on a Shimadzu UV 1601 PC spectrophotometer fitted with an electronic temperature controller unit (TCC-240A). The steadystate fluorescence emission and excitation spectra were recorded on a Hitachi F-4500 spectrofluorometer equipped with a temperature-controlled cell holder.



Figure 1. CT absorption spectra of NaClO₄ $(1.677 \times 10^{-5} \text{ mo/L}) + \text{TP}$ $(1.315 \times 10^{-4} \text{ mol/L})$ and Mg(ClO₄)₂ $(2.0 \times 10^{-5} \text{ mol/L}) + \text{TP}$ $(1.315 \times 10^{-4} \text{ mol/L})$ against pristine acceptor solutions as reference.



Figure 2. Gaussian analysis curve of the shoulder region of CT band for the $\rm K^+/\rm TP$ system.

Table 1. Gaussian curve analysis for the CT spectra of TP and metal perchlorates at a temperature of 298K; CT absorption maxima, transition energies, oscillator strengths (*f*), transition dipole ($\mu_{\rm EN}$) and resonance energies ($R_{\rm N}$) of the same complexes

Gaussian curve analysis data	Systems Na ⁺ /TP K ⁺ /TP		Mg ²⁺ /TP	
10 ⁻⁶ Area of curve (A), L.mol ⁻¹	177.37	55.06	40.03	
Width of curve (<i>w</i>), cm ⁻¹	1674.7	2031.5	602.99	
Centre of curve (x_c) , cm ⁻¹	22901.31	22932.00	22857.00	
y_0 , L.mol ⁻¹ .cm ⁻¹	0.0004	0.0010	0.0556	
λ _{ct} , nm	436.65	436.07	438.00	
hv _{CT} , eV	2.5828	2.5862	2.5700	
f, L.mol ⁻¹ .cm ⁻²	0.7662	0.2379	0.1729	
$\mu_{\sf EN}$, Debye	0.031	0.015	0.025	
R _N , eV	0.4761	0.4652	0.7314	



Figure 3. Job's plot for: (a) TP/K^+ system indicating 1:2 complexation; and (b) TP/Mg^{+2} system indicating 1:1 complexation.





Figure 4. Fluorescence enhancement of TP ($8.22 \times 10^{-6} \text{ mol/L}$) in presence of alkali metal perchlorate solutions (concentration increases from 10^{-8} to 10^{-7} mol/L).

Quantum chemical calculations

Experimental findings were rationalized through density-based quantum chemical calculations, using the Unix version of Gaussian '03 software in a Silicon Graphics computer work station.

Results and discussion

Observation of charge transfer (CT) bands

Figure 1 shows the electronic absorption spectra of mixtures containing $TP + NaClO_4$ and $TP + Mg(ClO_4)_2$ in acetonitrile medium. To obtain the CT bands, spectra of the above solution (in acetonitrile medium) were recorded against the pristine acceptor (metal ions) solution as reference to cancel out the acceptor absorbance, if any. It was observed that new absorption peaks were in the visible region. The CT absorption spectra were analysed by fitting to the Gaussian function:

$$y = y_0 + \left[\frac{A}{\left(w\sqrt{\left(\pi/2\,\exp\left[-2(x-x_c)^2/w^2\right]}\right)}\right]$$
(1)

where x and y denote wavenumber and molar extinction coefficient, respectively. When such a Gaussian fit (approximated

by the above approximation) is applied over a wide range of (x, y) points, y_0 obviously represents the lowest bound value above which the y values of all other points in the range will appear, because the remaining term in the expression is a definitely positive quantity. At the value of $x = x_{cr}$ the derivative dy/dx disappears, giving $y_c = y_0 + A/\{w\sqrt{(\pi/2)}\}$, which has numerical significance in the context of plot only. However, as $x \to \infty$, then $y \rightarrow y_0$, which may give a significance of hypothetical absorbance value in the limit of infinite wavelength, provided that the data are included within the range. One such plot is shown in Figure 2. The results of the Gaussian analysis for all the TP-acceptor systems under study are shown in Table 1. The wavelengths at these new absorption maxima ($\lambda_{max} = 1/x_c$) and the corresponding transition energies (hv) are summarized in the same table. The Gaussian analysis fitting was done in accordance with the method developed by Gould et al. (32). One important point to mention here is that Gaussian analysis of a curve generally gives a reasonably acceptable result near the maximum of the curve, spread over a very small region. For this reason, although the errors in the centres of the CT spectra for the complexes of TP with various electron acceptors were very small, there are appreciable errors in the y_0 value. Although metal ions and TP undergo CT interaction with great ease, one can still argue that the way they approach each other is dictated by the acidic nature of the pyrrolic protons of TP. For this reason,

we have investigated the affinity of alkali metal ions as well as the bivalent alkaline-earth metal ion for TP in a polar solvent, such as acetonitrile. Acetonitrile was chosen as the solvent primarily to obtain practical levels of solubility, but it serves another important purpose. The choice of a polar solvent undoubtedly promotes aggregation of the less polar TP and metal ion entities, which may be viewed as an artificial enhancement of their mutual affinity. The demonstration of M^{n+}/TP binding in acetonitrile is therefore considered a particularly stringent test for spontaneous attraction.

Determination of oscillator strength (f), resonance energy (R_N) and transition dipolar strength (μ_{EN})

From the CT absorption spectra, we could estimate oscillator strength for the transition. The oscillator strength f was estimated using the formula:

$$f = 4.32 \times 10^{-9} \left[\varepsilon_{\rm CT} d\nu \right] \tag{2}$$

where $\int \varepsilon_{CT} dv$ is the area under the curve of the molar absorbance of the absorption band in question, plotted against frequency. The integral has to be evaluated between zero and infinity. To a first approximation:

$$f = 4.32 \times 10^{-9} \varepsilon_{\rm max} \ \Delta v_{1/2}$$
 (3)

where ε_{max} is the extinction coefficient at maximum absorbance of the band and $\Delta v_{1/2}$ is the half-width, i.e. the width of the band at half the maximum absorbance. The observed oscillator strengths of the CT bands are summarized in Table 1.

The extinction coefficient is related to the transition dipole by:

$$\mu_{\rm EN} = 0.0952 \left[\varepsilon_{\rm max} \Delta v_{1/2} / \Delta v \right]^{1/2} \tag{4}$$

where $\Delta v \approx v'$ at ε_{max} and μ_{EN} is defined as $e \int \psi_{ex} \sum r_i \psi_g d\tau$, μ_{EN} for all the complexes given in Table 1. It has been observed that transition dipole strength (μ_{EN}) for the Na⁺ complex is somewhat higher than that of corresponding K⁺ and Mg⁺² complexes.

Briegleb and Czekalla (33) theoretically derived the relation:

$$\varepsilon_{\rm max} = 7.7 \times 10^4 / (h v_{\rm CT} / |R_{\rm N}| - 3.5)$$
 (5)

where ε_{max} is the molar extinction coefficient of the complex at the maximum of the CT absorption, v_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state which, obviously, is a contributing factor to the stability of the complex (a ground state property). The values of R_N for the complexes under study are provided in Table 1. The trend in R_N values shows that Mg²⁺ forms the strongest complex with TP in acetonitrile as compared to that of Na⁺ and K⁺ complexes.

Job's plot in Figure 3 indicated that the alkali metal ions form a 2:1 complex with TP, while Mg²⁺ forms a 1:1 complex with the same TP. Thus, the stoichiometry is totally different for the two systems of alkali and alkaline-earth metal ions.

Fluorescence interaction with metal ions

Alkali metal ions. The binding process of TP to an alkali metal ion was monitored by fluorescence spectroscopy. A solution of TP was titrated with a stock solution of metal perchlorate in acetonitrile, keeping the TP concentration fixed. For TP, the intensity of maximum emission increased steadily by adding Na^+ or K^+ salt solution, as shown in Figure 4; the spectral pattern and the position of the emission band remained unaltered, with the enhancement of fluorescence intensity only. The emission intensity of TP was abruptly enhanced by the addition of NaClO₄, as shown in Figure 4A, while the enhancement was more pronounced with KCIO₄ (Figure 4B). A relative account for the extent of enhancement in emission intensity of TP in presence of Na⁺ and K⁺ is represented in Figure 4C. It can be concluded that TP can efficiently discriminate Na⁺, which reaches maximum enhanced emission at a comparatively lower concentration than that of K⁺ and thus can be used as a fluorescent chemosensor for alkali metals. TP can sense zinc ion through wavelength ratiometric sensing, as we get in our laboratory, but for alkali metal ions it is only intensity-based sensing in such a medium as acetonitrile.

Alkaline-earth metal ions. With incremental addition of Mg $(CIO_4)_2$ to a fixed concentration of TP, a progressive quenching of the fluorescence intensity of TP was observed, corresponding to excitation at 590 nm (Figure 5a). It is well known that fluorescence quenching is of two types, static and dynamic. They can be distinguished from one another on the basis of their different temperature dependences and preferably on their lifetime measurements. To explore the mechanism of



Figure 5. (a) Fluorescence quenching of TP $(1.1 \times 10^{-6} \text{ mol/L})$ on addition of Mg $(CIO_4)_2$. (b) Stern–Volmer plots at two different temperatures for the Mg²⁺/TP system.



Figure 6. MMFF-optimized geometry of: (a) Na⁺/TP/Na⁺; (b) Mg²⁺/TP; and (c) K⁺/TP/K⁺ complexes.

quenching, steady-state emission studies at two different temperatures have been performed. Figure 5b shows that with increase in temperature the slopes of linear Stern–Volmer (SV) plots are increased, indicating that mixed dynamic and static quenching takes place. Out of this overall quenching process, the dynamic contribution could be evaluated by means of time-resolved measurements. Thus, it was revealed that alkaline-earth metal ion, Mg²⁺, follows a mixed dynamic and static mechanism of quenching with TP in acetonitrile medium.

Theoretical rationalization

Since molecular mechanics has a demonstrated history of success in determining the equilibrium structure of porphyrin (34), TP and its three complexes have been optimized by a molecular mechanics force field (MMFF) calculation. As experiments showed that alkali metal ions form complexes with TP in 2:1 stoichiometry, quantum chemical optimizations were done in this way (Figure 6). However, with Mg²⁺ the experimental stoichiometry is 1:1 and the complex has been so optimized. Figure 6b shows that Mg²⁺ was precisely centred over the pyrrolic nitrogen moiety with donor-acceptor separation distance of only 3.09 Å, while in the case of alkali metal ion complexes the two metal ions, instead of lying in the centre over the pyrrolic nitrogen moieties, are rather shifted towards the opposite nitrogen centres that have pyrrolic protons attached to them

Table 2.	Calculated	ground-state	parameters	of TP a	nd its	
three metal ion complexes						

System	TP	Na ⁺ /TP/Na ⁺	K ⁺ /TP/K ⁺	TP/Mg ²⁺
E _{gr} (a.u)	-1903.12	-2225.33	-3096.63	-2113.31
Е _{номо} (eV)	-4.95	-10.58	-10.32	-10.94
E _{LUMO} (eV)	-2.93	-8.62	-8.36	-9.97
Band gap (eV)	2.02	1.96	1.96	0.97
μ (D) ^a	0.0006	1.80	1.49	4.34
^a D, Debye				

(Figure 6a, c). The donor–acceptor separation distance is only 2.99 Å in the case of Na⁺/TP and for K⁺/TP system it is a bit longer, 3.37 Å (from the nearest N centre). To obtain information about the frontier molecular orbitals in studying the extent of interaction, a single-point density-based calculation by the DFT/B3LYP/ 3-21G* method (35–38) has been employed for all the systems and several ground state parameters are presented in Table 2. It was experimentally observed that the band gap of TP was shifted to low energy, i.e. to longer wavelength, on interaction with metal ion. Again, in the case of Na⁺ and K⁺, both complexes have an almost similar band gap (1.96 eV) and an even closer λ_{CT} (436.65 and 436.06 nm, respectively), while in case of Mg²⁺ the band gap further decreased (0.97 eV) along with the measured, relatively longer λ_{CT} (438 nm). The difference

between the theoretically calculated band gap and experimental excitation parameters might be due to solvation.

The frontier molecular orbital picture of Figure 7a indicates that for TP, the highest occupied molecular orbital (HOMO), however, delocalized over the pyrrolic ring, was mainly centred over the two pyrrolic nitrogen centres without H. The lowest unoccupied molecular orbital (LUMO) was essentially localized over the pyrrolic unsaturation part and had almost no amplitude on the nitrogens without H. On interaction with alkali metal ions, the features of LUMO remained unaltered. In alkali metal ion complexes the metal ions were closer to the pyrrolic nitrogens with H, thus positioning near the location of higher LUMO density (Figure 7b). The decrease in HOMO density upon complexation is associated with electron transfer from the pyrrole rings without pyrrolic protons to the meso-carbons and partly to the metal ions. The fluorescence quenching of TP can be linked to the PET process from the TP moiety to the quencher. The quenching efficiency is better when the quencher energy level is similar to that of LUMO of TP. Occupancy of the dominant LUMO positions by Na⁺/K⁺ thereby inhibits the PET. Thus, through inhibition of PET, simple *meso*-tetraphenylporphyrin can sense alkali metal ions and the intensity of fluorescence of TP is enhanced in the presence of such metal ions.

In the case of th4 Mg²⁺–TP interacting system, HOMO density was concentrated on TP and LUMO on the metal ion (Figure 7c); thus, intermolecular HOMO to LUMO electron transfer was clearly an EDA-type interaction. This was what we have obtained experimentally.



Figure 7. Frontier molecular orbital of: (a) TP; (b) $Na^+/TP/Na^+$; and (c) Mg^{2+}/TP systems.

Conclusion

With both types of metal ions: alkali and alkaline-earth, *meso*tetraphenylporphyrin can form charge transfer complexes in the ground state, while in the excited state the modes of interaction are totally different. With Mg^{2+} a mixed quenching of fluorescence was observed, while with Na^+ and K^+ there was enhancement of fluorescence intensity. Again, TP can efficiently discriminate the two alkali metal ions through the extents of enhancement for the same concentration of metal ions in solution. Density functional theory (DFT)-based calculation could rationalize the sensing through electron density changes explaining the inhibition of the PET mechanism.

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