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Absorption and fluorescence properties of aryl substituted porphyrins in different media

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ABSTRACT

Absorption and fluorescence properties of aryl substituted porphyrins, 5,10,15,20-tetra-4-oxy(aceticacid)phenylporphyrin (TAPP), 5,10,15,20-tetra-(4-phenoxyphenyl) porphyrin (TPPP), 5,10,15,20-tetra-(3-bromo-4-hydroxyphenyl) porphyrin (TBHPP), and 5,10,15,20-tetra-p-chloromethylphenyl porphyrin (CMPP) were investigated. The UV/vis absorption, fluorescence and excited spectra as the fluorescence quantum yields and fluorescence lifetimes for the compounds were measured in organic solvents (chloroform ($CHCl_3$), tetrahydrofuran (THF)) and immobilized media (PVC film, sol–gel matrix). The fluorescence quantum yields of TAPP and TPPP were higher than the others. The fluorescence lifetimes of all studied porphyrin derivates were found to be fifty percent lower and their fluorescence intensities were increased fifty percent more in both of immobilized mediums, as compared to organic solvents.

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1. Introduction

Photophysical and photochemical studies of porphyrins have been of increasing interest in fields extending from chemistry to biology [1,2]. Besides this the interest to study of porphyrin photophysical characteristics is stimulated by their medical applications, especially due to their efficacy in photodynamic therapy (PDT) of cancer [3,4], psoriasis, atheromatous plaque, viral and bacterial infections including HIV [5,6] and blood substitutes [7].

The porphyrin efficacy in photonic devices and PDT depends on its photophysical characteristics, such as lifetimes and quantum yields of the excited (singlet and triplet) states [8–13], which in turn depend on the environmental characteristics: pH, ionic strength, interaction with other molecules, etc. To apply these materials in photonics and medicine in the most effective way it is necessary to know the behavior of all their photophysical characteristics in the function of external conditions.

In recent years, doping of organic dye molecules within polymer matrices has gained interest. These matrices are easily prepared and provide immobilization. Also, by this immobilization the ground and excited state properties of single molecules can be understandable [14]. In favourable cases, the immobilization of fluorescent molecules in the solid matrix may reduce intramolecular motions and rearrangements, thus leading to enhanced photostability and fluorescence capability. Entrapment of fluorescent molecules in solid matrix allows the investigation of both photophysical and photochemical properties and sensor applications [15].

Plasticized PVC membranes are believed to be useful for sensor applications because of their good mechanical properties, homogeneity, simplicity of preparation and optical transparency [16,17]. A sol–gel matrix is very attractive because of its low preparation temperature and high chemical and mechanical stabilities [18,19]. In the sol–gel process, transparent oxide glasses are prepared by hydrolysis and condensation of tetra alkyl orthosilicates and in one sol–gel preparation technique molecules can become entrapped in the growing covalent silica network.

In this study, the photophysical characteristics of aryl substituted porphyrins, TAPP, TBHPP, CMPP and TPPP, in organic solvents (chloroform ($CHCl_3$), tetrahydrofuran (THF)) and immobilized media (PVC film, sol–gel matrix) were examined.

2. Experimental and method

2.1. Materials

PVC (high molecular weight) and the plasticizer bis-(2-ethyl-hexyl)phalate (DOP) were supplied by Fluka (Buchs SG, Switzerland). The polyester support (Mylar type) was provided from Hostaphan Films, Germany. The sol–gel precursor tetraethylorthosilicate (tetraethoxysilane, TEOS), the surfactant additive Triton X-100 were obtained from Fluka (Buchs SG, Switzerland). All other chemicals were obtained from Fluka and Merck. Deionized water was used throughout the studies. The copper nitrate salt used in quenching experiments was supplied by Merck and was used without any further purification.

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Table 1
Absorption characteristics of porphyrins in organic solvents and immobilized media.

		λ_{max}(nm) ε (L mol^{-1} cm^{-1})				
		B(0–0)	Q*x*(1–0)	Q*y*(1–0)	Q*x*(0–0)	Q*y*(0–0)
TAPP	THF	421 (1.17×10^5)	515 (4.50×10^3)	550 (3.20×10^3)	590 (1.30×10^3)	644 (1.20×10^3)
	$CHCl_3$	423 (1.16×10^5)	512 (4.30×10^3)	555 (3.12×10^3)	589 (1.20×10^3)	650 (1.15×10^3)
	PVC	427 (1.80×10^5)	516 (6.93×10^3)	557 (4.98×10^3)	593 (2.01×10^3)	651 (1.79×10^3)
	Sol–gel	429 (2.07×10^5)	518 (7.98×10^3)	559 (5.70×10^3)	595 (2.32×10^3)	652 (2.10×10^3)
TBHPP	THF	420 (1.14×10^5)	514 (4.65×10^3)	545 (3.25×10^3)	585 (1.20×10^3)	650 (1.30×10^3)
	$CHCl_3$	423 (1.13×10^5)	517 (4.60×10^3)	550 (3.10×10^3)	586 (1.15×10^3)	650 (1.18×10^3)
	PVC	429 (1.76×10^5)	520 (7.08×10^3)	555 (4.65×10^3)	591 (1.80×10^3)	651 (2.00×10^3)
	Sol–gel	430 (2.02×10^5)	521 (8.08×10^3)	559 (5.35×10^3)	593 (2.07×10^3)	653 (2.31×10^3)
CMPP	THF	416 (1.22×10^5)	512 (4.60×10^3)	546 (3.30×10^3)	589 (1.20×10^3)	645 (8.00×10^2)
	$CHCl_3$	416 (1.20×10^5)	514 (4.41×10^3)	551 (3.15×10^3)	590 (1.15×10^3)	646 (8.00×10^2)
	PVC	420 (1.94×10^5)	519 (8.05×10^3)	554 (5.51×10^3)	592 (2.02×10^3)	649 (1.45×10^3)
	Sol–gel	423 (2.20×10^5)	521 (9.09×10^3)	557 (6.35×10^3)	593 (2.38×10^3)	652 (1.68×10^3)
TPPP	THF	421 (1.35×10^5)	517 (4.60×10^3)	554 (3.40×10^3)	591 (1.20×10^3)	651 (1.60×10^3)
	$CHCl_3$	420 (1.30×10^5)	515 (4.25×10^3)	555 (3.30×10^3)	590 (1.20×10^3)	649 (1.50×10^3)
	PVC	425 (2.00×10^5)	519 (7.10×10^3)	558 (5.70×10^3)	593 (2.10×10^3)	652 (1.78×10^3)
	Sol–gel	429 (2.50×10^5)	521 (8.80×10^3)	559 (4.50×10^3)	595 (2.62×10^3)	653 (2.20×10^3)

2.2. *Porphyrins (Fig. 1)*

TAPP was synthesized accordance with literature given before [20]. The synthesis procedure of others were given below.

TBHPP

A 0.170 g of tetrahydroxyphenylporphyrin was mixed with 1.2 mL concentrated H_2SO_4 and 150 mL of tetrahydrofuran (THF) in a round-bottomed flask and refluxed for 3 h at 70 °C. The reaction mixture was left to cool, and 5 mL of 0.6 M NaOH solution and 250 μL of bromine were added drop by drop. The mixture was refluxed for 1 h at 70 °C and left to cool, then 5 mL of 1.0 M H_2SO_4 was also added and mixed for 30 min. The reaction mixture was extracted with diethyl ether and the THF in the upper phase was evaporated by rotary evaporator. After 10 mL of distilled water was added, the formed residue was filtered off and finally dried under vacuum. The yield of TBHPP was 75%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.88 ppm (s, 4H), 7.55 ppm (s, 2H), 7.05–6.70 ppm (m, 20H). FTIR (KBr): 3125 cm^{-1} (C-OH), 897 cm^{-1}(C-Br). Elemental analysis, expected (calculated): C-49.55 (49.67), H-2.76 (2.82), N-5.01 (5.26).

TPPP

A 0.2 g of tetrahydroxyphenylporphyrin was stirred in 15 mL dimethylformamide with 0.120 g of crushed sodium hydroxide. 0.4 g of chlorobenzene was added over 1 h using a dropping funnel. After 30 h, 10 mL of ethanol was added to the solution, followed by 80 mL of distilled water. The product was filtered off and washed with absolute ethanol and then dried. It was chromatographed on alumina with chloroform. TPPP was eluted with the solvent front and separated easily from any unreacted starting material. The yield of TPPP was 82%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.30 ppm (s, 2H), 8,28–7,77 ppm (m, 44H). FTIR (KBr): 2100 cm^{-1} (Ar-O-Ar). Elemental analysis, expected (calculated): C-77.49 (77.86), H-4.65 (4.28), N-5.16 (5.82).

CMPP

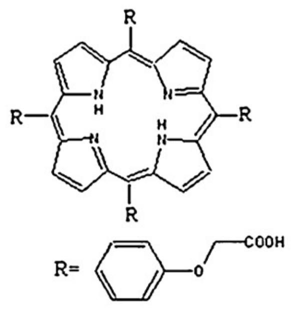
A 0.123 g of tetraphenylporphyrin was mixed with 0.002 g of *p*-formaldehyde, 0.027 g of anhydrous $ZnCl_2$ powder and 150 mL of THF in a round-bottomed flask and refluxed for 30 min at 75 °C. 10 mL of 1.0 M HCl was added to the reaction mixture drop by drop and refluxed for more than 15 min. Then the reaction mixture was transferred to a separatory funnel and washed with 2.0–3.0 mL of cold distilled water, 2.0–3.0 mL of saturated Na_2CO_3 solution and 2.0–3.0 mL of distilled water. After filtration the mixture, the product was dried under vacuum. The yield of CMPP was 71%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.28 ppm (s, 2H), 8,05–7,54 ppm (m, 34H). FTIR (KBr): 2920 cm^{-1} (Ar-CH_2-Cl), 895 cm^{-1}(C-Cl). Elemental analysis, expected (calculated): C-65.52 (65.97), H-4.20 (4.54), N-5.66 (5.26).

2.3. *Spectroscopic analysis*

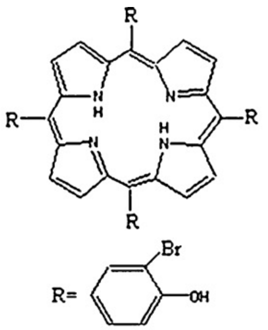
Visible spectra were obtained using Shimadzu UV-1601 spectrophotometer, with cuvets of 1 cm optical length. Fluorescence emission spectra were recorded on a Varian-Cary Eclipse spectrofluorimeter (Mulgrave, Australia), equipped with a Xenon lamps source and 1.0 cm quartz, excitation and emission slit at 10 nm at medium voltage of the photomultiplier. Fluorescence quantum yields were determined by using tetraphenylporphyrin (TPP) in benzene ($\Phi_f = 0.13$) [21] as standard. The PVC film and sol–gel matrix were placed in diagonal position in the quartz cell. All measurements were carried out at room temperature.

Table 2
Fluorescence properties of porphyrins in organic solvents and immobilized media.

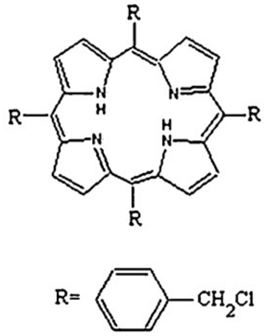
	Medium	λ_{max} (ex) (nm)	λ_{max} (fl) (nm)	$\Delta\lambda$ (nm)	τ_0 (ns)	Φ_{exp}
TAPP	THF	570	660	90	0.07 ± 0.01	0.07 ± 0.01
	$CHCl_3$	570	658	88	0.07 ± 0.01	0.07 ± 0.01
	PVC	572	659	88	0.04 ± 0.01	0.08 ± 0.02
	Sol–gel	570	660	89	0.04 ± 0.01	0.08 ± 0.01
TBHPP	THF	559	659	100	0.06 ± 0.01	0.06 ± 0.01
	$CHCl_3$	559	657	98	0.07 ± 0.01	0.05 ± 0.01
	PVC	565	666	101	0.04 ± 0.01	0.07 ± 0.01
	Sol–gel	550	660	110	0.04 ± 0.01	0.08 ± 0.01
CMPP	THF	550	660	110	0.03 ± 0.01	0.04 ± 0.01
	$CHCl_3$	550	660	110	0.04 ± 0.01	0.04 ± 0.01
	PVC	560	660	100	0.03 ± 0.01	0.05 ± 0.01
	Sol–gel	560	657	97	0.02 ± 0.01	0.04 ± 0.01
TPPP	THF	570	659	89	0.04 ± 0.01	0.11 ± 0.01
	$CHCl_3$	570	658	88	0.05 ± 0.01	0.10 ± 0.01
	PVC	570	659	89	0.03 ± 0.01	0.12 ± 0.01
	Sol–gel	570	658	88	0.03 ± 0.01	0.12 ± 0.01



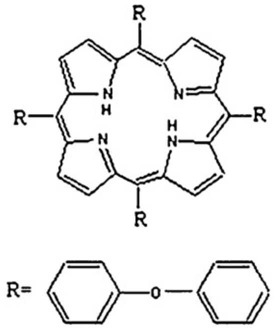
5,10,15,20-tetra-4-oxy(aceticacid) phenylporphyrin (TAPP)



5,10,15,20-tetra-(3-bromo-4-hydroxyphenyl) porphyrin (TBHPP)



5,10,15,20-tetra-p-chloromethylphenyl porphyrin (CMPP)



5,10,15,20-tetra-(4-phenoxyphenyl) porphyrin (TPPP)

Fig. 1. The porphyrins determined photophysical properties.

2.4. *PVC film preparation*

PVC films were prepared from a mixture of 120 mg of PVC, 240 mg of plasticizer (DOP) and 1.5 mL of 1×10^{-6} mol L^{-1} porphyrin in THF. The concentration of the porphyrins in mixture was 1×10^{-4} mol L^{-1}. The resulting polymer cocktails were spread onto a polyester support (Mylar type). PVC films were kept in THF containing desiccator to avoid damage from the air. Each PVC film was placed diagonally into the sample cuvette to improve the reproducibility of the measurements.

2.5. *Sol–gel process*

Porphyrin doped sol–gel glasses were derived from a starting composition of 4 mol of high quality acidic water (pH = 2, adjustment is done by HCl) and 1 mol of TEOS. These constituents were sonicated for 40 min in closed vials. 1.5 mL dopant was then added in the concentration range of 1×10^{-6} mol L^{-1} in THF. The resulting dopant concentration in sol was 1×10^{-4} mol L^{-1}. The addition of a few drops of Triton X-100, to improve the homogeneity of the sol–gel and to give a crack-free monolith, was also performed. The doped sol was stirred until the dye was completely dissolved before coating a glass slide (11 × 40 × 1 mm) which had been activated by treatment with concentrated HNO_3 for 24 h, washed with deionized water and then ethanol. Then the glass slides doped with porphyrin were dried at room temperature. After evaporation of the solvent, the coated glass slides were fixed diagonally in a quartz sample cuvette.

3. Results and discussion

3.1. *Spectral characterization studies*

The absorption and emission based spectral data of all four porphyrin derivatives in different host matrices are summarized in Tables 1 and 2. Also, as an example, the fluorescence spectra of TAPP in solution media and immobilized media were given in Fig. 2. The absorption spectra and the molar extinction coefficients of the Soret and Q bands of all porphyrin synthesized are quite similar under the same conditions, indicating that the differences in substituting groups as halogen, alkoxy or acid hydrocarbon do not affect greatly the absorption properties. It is noted that their absorption properties are similar in THF and $CHCl_3$, in which the molar extinction coefficients of all studied porphyrins in $CHCl_3$ are slightly lower than in THF. In comparison to the solution phase, the absorption maxima of porphyrin derivatives in PVC film and sol–gel matrix exhibited red shifts ranging from 4 to 9 nm. This result can be attributed to the restricted vibrational rotational motions in solid phase. The values of molar extinction coefficients increased for all of the porphyrin derivatives in PVC film and sol–gel matrix. The reason can be the enhanced rigidity in immobilized medium.

Additionally the excitation and emission related data: excitation and emission wavelengths, λ (nm), Stokes shift values, $\Delta\lambda$ (nm), radiative life times, τ_0 (ns), fluorescence quantum yields, Φ_f of all

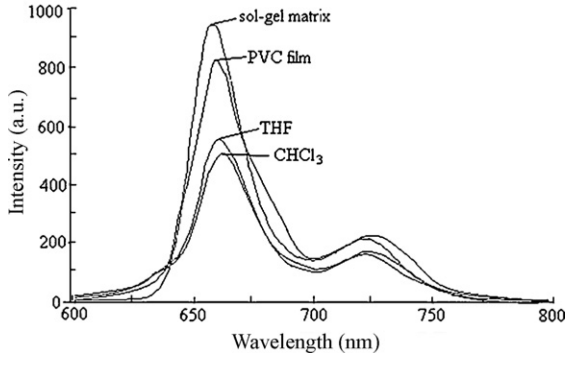


Fig. 2. The emission spectra of 1×10^{-6} mol L^{-1} TAPP in all of media.

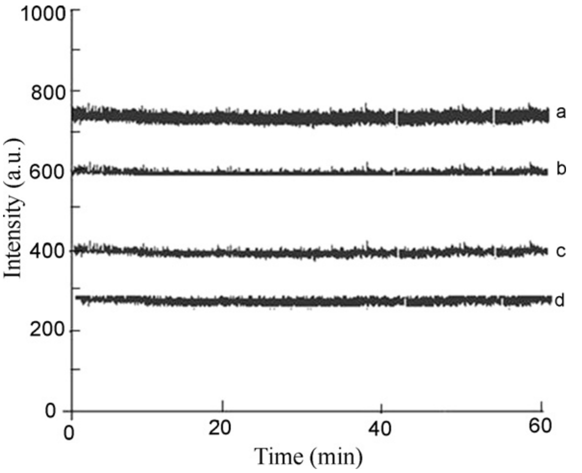


Fig. 3. Photostability test results of 1×10^{-6} mol L^{-1} TAPP in (a) sol–gel matrix, (b) PVC film, (c) THF, (d) CHCl$_3$ after 1 h of monitoring.

porphyrins in all studied media were summarized in Table 2. In all of the employed solvents and immobilized media, the excitation wavelength was chosen at between 550 and 572 nm and the emission spectra were recorded.

Two fluorescence bands around 657–666 and 720–728 nm, corresponding to Q transitions, were observed in the all studied porphyrins. The studied porphyrins derivatives exhibited Stokes shift ranging from 88 to 101 nm in all of the employed media. In halogen derivated porphyrins, TBHPP and CMPP, the degree of Stokes shift was seen higher.

Fluorescence quantum yield (Φ_{exp}) was calculated from

$$\Phi_{\mathrm{exp}} = \Phi_{\mathrm{ref}} \frac{F\{1-\exp(-A_{\mathrm{ref}}\ \ln 10)\}n^2}{F_{\mathrm{ref}}\{1-\exp(-A\ \ln 10)\}n_{\mathrm{ref}}^2}$$

where F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium. The reference system used were tetraphenylporphyrin ($\lambda_{\mathrm{ex}} = 560$ nm, $\Phi_{\mathrm{f}} = 0.13$ in benzene).

The radiative lifetime ($\tau_{0,}$ in ns) was calculated from the modified Strickler–Berg equation [22]:

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \frac{\int_{\mathrm{f1.spec}} F(\tilde{\nu})d\tilde{\nu}}{\int_{\mathrm{f1.spec}} F(\tilde{\nu})\tilde{\nu}^{-3}d\tilde{\nu}} \int_{\mathrm{abs.spec}} \varepsilon(\tilde{\nu})\tilde{\nu}^{-1}d\tilde{\nu}$$

where $F(\nu)$,ν and $\varepsilon(\nu)$ denote the corrected fluorescence spectrum, the wavenumber of the light (cm^{-1}), and the molar absorptivity, respectively.

The radiative lifetimes values, $\tau_{0,}$ for all the porphyrin derivatives in immobilized media were highly low with respect to solution media. This decrease in the solid phase arises from lowered difference of equilibrium geometries between ground and excited states in immobilized media with respect to solutions and can be attributed to the same reason of restricted vibrational rotational motions. In addition, the lowest radiative lifetime value, τ_0, in all host matrices was seen in CMPP.

The quantum yield values calculated were shown in Table 2. The TPPP exhibited high quantum yield. Moreover, the quantum yield values in PVC film and sol–gel matrix were higher than solution media for the all porphyrin derivatives.

3.2. Photostability test results

The photostability of porphyrin derivatives in solution and immobilized media were monitored and recorded with a steady-state spectrofluorimeter in the mode of time based measurements. The data were acquired at the maximum emission wavelength of porphyrin derivatives in all of media. As an example, only the data collected for TAPP after 1 h monitoring is shown in Fig. 3. The experimental results revealed that the porphyrin derivatives exhibited excellent photostability in all of the employed solvents and PVC film and sol–gel matrix.

4. Conclusion

The aim of this work was to investigate the photophysical properties of aryl substituted porphyrins including halogen, alkoxy or acid hydrocarbon groups in organic solvents and immobilized media. Thus, UV/vis absorption and fluorescence spectra, fluorescence quantum yield, lifetimes and photostabilities of porphyrins were measured in organic solvents and immobilized media. The absorption maxima of porphyrin derivatives in PVC film and sol–gel matrix exhibited red shifts ranging from 4 to 9 nm. Radiative lifetime values, $\tau_{0,}$ in PVC film and sol–gel matrix were obtained as the lower for all the porphyrin derivatives. The quantum yield values in PVC film and sol–gel matrix was higher than solution media for the all porphyrin derivatives.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.11.019.

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