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Research article

Photophysical studies of Zn(II) tetra, *tert*-butyl phthalocyanine

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Abstract. Phthalocyanine derivatives have attracted significant attention due to their unique chemical properties and applications in various fields, including photodynamic therapy. However, the synthesis and purification of phthalocyanines remain challenging. Among these derivatives, zinc(II) tetra, *tert*-butyl phthalocyanine (*tert*-ZnPc(II)) is noteworthy for its straightforward synthesis, making it a cost-effective option. *tert*-ZnPc(II) is often synthesized as a second-generation byproduct in the synthesis of asymmetric phthalocyanines when *tert*-butyl moieties are introduced to enhance the solubility of derivatives in a wide range of organic solvents. The practical applications of phthalocyanine derivatives depend mainly on their photophysical properties, which in turn influence key parameters such as absorption and fluorescence emission. This study investigates the ultraviolet-visible (UV-vis) absorption and fluorescence emission spectroscopies of *tert*-ZnPc(II), focusing on the impact of solvent polarity and the effect of different concentrations of water on UV-vis absorption behavior.

Keywords. UV-vis absorption, *tert*-ZnPc(II), Photophysical properties.

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1. Introduction

Phthalocyanines (Pcs) and their derivatives represent aromatic macrocycles with an 18- π -electron delocalization system characterized by high chemical and thermal stability. These compounds possess diverse coordination properties, exhibit low toxicity, and have the ability to absorb within the visible region (600–800 nm). The versatility of Pcs is featured in a wide range of applications [1–5], such as semiconductor devices [6], liquid crystals [7–9], sensors [10–12], catalysts [13], and dye-sensitized solar cells [14,15]. Furthermore, Pcs have emerged as

highly promising photosensitizers in the context of photodynamic therapy (PDT) [16–22].

The photophysical characteristics of Pcs are notably influenced by the central metal ion, with zinc (Zn) proving particularly valuable due to its ability to confer Pcs with enhanced fluorescence and singlet oxygen production properties. These attributes make them suitable for applications in tumor detection and treatment [23].

The solubility of Pcs is a pivotal factor for diverse applications. Introducing functional groups such as alkyl, tertiary butyl groups, crown ethers, alkoxy, alkylthio, and amide groups into peripheral benzene rings of the Pc structure enhances solubility in both protic and non-protic solvents [24–32]. Notably, water solubility assumes a crucial role in PDT applications [33–35]. While sulfonates [36],

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carboxylates [37,38], and quaternized amino groups [39–41] are commonly employed to achieve water solubility in dyes, *tert*-butyl groups confer Pcs with hydrophobic properties [42].

An important consideration in the study of Pcs is their tendency to form aggregates, especially in aqueous solutions [43]. This property proves unfavorable as it reduces solubility and adversely impacts photophysical characteristics, such as shortening the triplet state lifetime and hindering the efficient generation of singlet oxygen. In the context of *in vivo* activity as photosensitizers, aggregation not only diminishes photoactivity but also restricts access to neoplastic cells [44]. The degree of this effect is significantly influenced by the molecular structure, particularly the nature of the central metal ion and functional groups present in the peripheral substituents [45,46]. Since photochemical activity is important only for Pc monomers, assessing aggregation parameters becomes essential for accurately determining the photophysical properties of these compounds. The formation of aggregates is primarily driven by π - π stacking between the nearly planar Pc macrocycles and van der Waals forces. Depending on their geometry, H-type (sandwich) and J-type (head-to-tail) aggregates can be distinguished, exhibiting significant differences in optical properties according to Kasha's exciton model [47,48].

Considering the cost-effectiveness and commercial availability of *tert*-ZnPc(II), it emerges as an intriguing compound with a vast field of applications. In this study, we aim to explore the impact of solvent polarity on the photophysical properties (absorption and fluorescence emission spectroscopies) of *tert*-ZnPc(II). This work explores its photophysical properties, with special attention given to the effect of different concentrations of water on absorption behavior and aggregation in homogeneous solutions.

2. Results and discussion

The most important properties of Pcs as materials lie in their exceptional thermal, chemical, and photochemical stabilities. Typically, unsubstituted Pc complexes exhibit low solubility across a wide range of solvents. Solubility in organic solvents is crucial for exploring the diverse applications of these molecules. Enhancing solubility in water or common

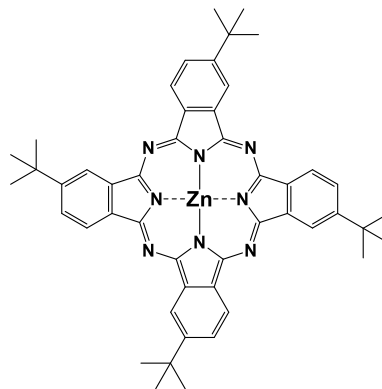


Figure 1. Chemical structure of *tert*-ZnPc(II).

organic solvents can be effectively achieved through peripheral modifications of Pcs, particularly by introducing the right substitutions on benzene rings [49–51].

In contrast to unsubstituted Pc metal complexes, *tert*-ZnPc(II), despite existing as a mixture of four positional isomers [52–57], stands out due to the incorporation of bulky *tert*-butyl substituents. This modification mitigates the aggregation tendencies of Pcs and enables an increase in their solubility across various common organic solvents without causing a significant shift in their ultraviolet–visible (UV–vis) spectra [58]. The chemical structure of *tert*-ZnPc(II) is shown in Figure 1.

2.1. Effect of the solvent

2.1.1. Ground-state electronic absorption spectra

The photophysical characteristics of Pc macrocycles are primarily influenced by their molecular structure and their interaction with the surrounding environment [59]. The UV–vis absorption spectra of *tert*-ZnPc(II), as illustrated in Figure 2, were measured in various solvents. Solvent polarity is quantified by the $E_T(30)$ parameter, with higher $E_T(30)$ values indicating increased solvent polarity ($E_T(30)$ water = 63.1, $E_T(30)$ glycerol = 57, $E_T(30)$ methanol = 55.4, $E_T(30)$ ethanol = 51.9, $E_T(30)$ acetonitrile = 45.6, $E_T(30)$ DMF = 43.8, $E_T(30)$ chloroform = 39.1, $E_T(30)$ ethyl acetate = 38.1, $E_T(30)$ toluene = 33, $E_T(30)$ FBS = unknown) [60,61].

A DMSO stock solution ($m_{tert-ZnPc(II)} = 4.75$ mg, $V_{DMSO} = 4.75$ mL) was prepared, ensuring compound solubility. This stock solution was further diluted in

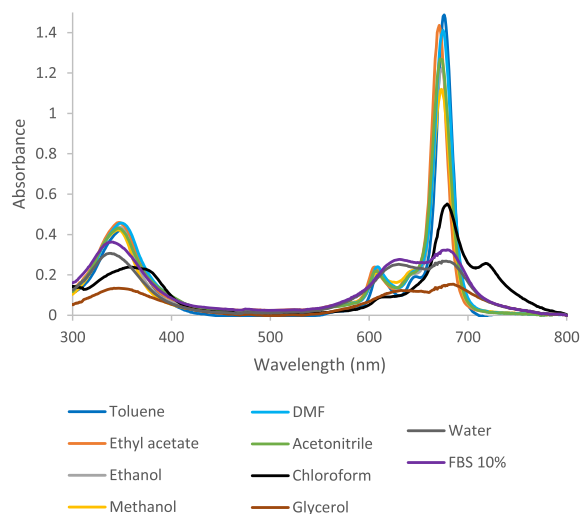


Figure 2. Absorption spectra of *tert*-ZnPc(II) in 10 different solvents ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$).

10 different solvents to investigate the specific impact of solvent polarity on photophysical properties. Concentration standardization was achieved in toluene by adjusting the peak absorbance at 610 nm to approximately 0.2, equivalent to $6 \times 10^{-3} \text{ mg}\cdot\text{mL}^{-1}$. The solvents include toluene, ethyl acetate, ethanol, methanol, DMF, acetonitrile, chloroform, glycerol, water, and a 10% dilution of fetal bovine serum (FBS) in a biological medium. The absorption spectra are presented in Figure 2.

The pronounced tendency of Pcs to form dimers and trimers in solution leads to a reduction in its photoactivity as a photosensitizer. This is attributed to the fact that the monomer structure is responsible for optimal photochemical activity [44–46]. In Figure 2, the absorption spectra of *tert*-ZnPc(II) in toluene, ethyl acetate, ethanol, methanol, DMF, and acetonitrile are depicted. The Soret and Q bands exhibit consistent shapes with minor shifts, aligning with the characteristic UV–vis spectra of Pcs.

On the other hand, absorption spectra of *tert*-ZnPc(II) in chloroform, glycerol, water, and FBS show a significant alteration in the shape, intensity, and split absorption peaks in comparison to the spectra in toluene, indicating an aggregation effect. *tert*-ZnPc(II) exhibits two main absorption bands at 350 nm and 610 nm. These bands exhibit diminished intensity in aqueous medium, glycerol, and chloroform, coupled with a red shift. Con-

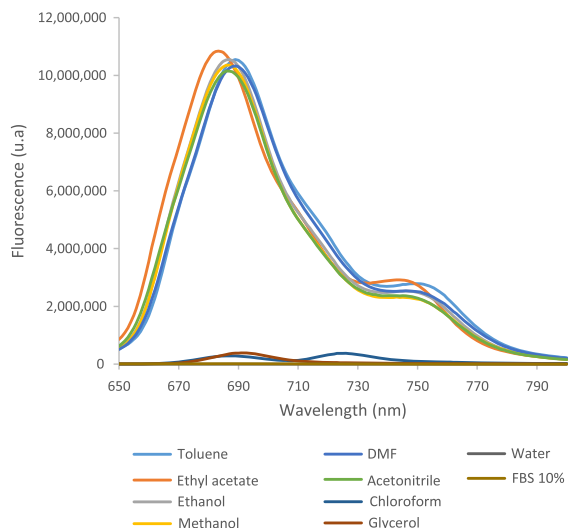


Figure 3. Fluorescence spectrum of *tert*-ZnPc(II) in 10 solvents excited at 610 nm ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$).

versely, the spectra appear quite similar in the other solvents.

The molar extinction coefficient (ϵ) is an intrinsic property of molecules depending mostly on their structure and composition. It assesses how chemical species absorb photons at specific wavelengths. The molar extinction coefficients of *tert*-ZnPc(II) are calculated and depicted in Table 1.

2.1.2. Fluorescence quantum yields

The fluorescence spectra in different solvents after excitation at 610 nm are shown in Figure 3.

The fluorescence spectra of *tert*-ZnPc(II) reveal two distinct groups of solvents (Figure 3). In FBS, chloroform, and glycerol, the spectra exhibit two peaks of very low intensity at 690 nm and 725 nm while no fluorescence is observed in water. Conversely, in the remaining solvents, the emission spectra show the characteristic patterns of Pc macrocycles. The first maxima spectra are situated between 680 nm and 690 nm and the second between 740 nm and 750 nm, with both peaks exhibiting higher intensity in alignment with the absorption spectra of Pcs.

The fluorescence quantum yields in toluene, ethyl acetate, ethanol, methanol, DMF, and acetonitrile exhibit close values, ranging from 0.35 to 0.27 (Table 2). In contrast, chloroform, glycerol, and FBS show fluorescence quantum yields less than 0.1 while

Table 1. Absorbance B and Q bands and molar extinction coefficient of *tert*-ZnPc(II) in different solvents

Solvents	B band (nm)	Q band 1 (nm)	Q band 2 (nm)	ϵ_{350}	ϵ_{610}
Toluene	350	610	676	56,802	29,403
Ethyl acetate	347	606	671	60,277	28,067
Ethanol	347	608	674	57,738	28,067
Methanol	346	608	673	55,064	27,933
DMF	349	609	675	61,079	31,675
Acetonitrile	346	606	672	56,535	27,933
Chloroform	357	679	718	30,740	11,494
Glycerol	349	633	685	17,776	12,162
Water	338	630	678	37,422	25,527
FBS	339	630	679	45,174	26,998

as expected, the fluorescence quantum yield is zero for water. Notably, the fluorescence quantum yields at 350 nm closely mirror those at 610 nm, indicating that the quantum yield remains consistent irrespective of the wavelength at which it is measured. This emphasizes the wavelength-independent nature of fluorescence quantum yield.

2.2. Effect of pH medium

The UV-vis spectrum of *tert*-ZnPc(II) in water reveals a broader absorption profile with split peaks, exhibiting an extensive broadening of the Q band (Figure 4). This is accompanied by a red shift in the absorption maximum, compared to toluene, and a blue shift in the Soret band from 350 nm to 336 nm (Table 3), indicative of H-aggregate formation. The H-aggregate, characterized by a face-to-face arrangement, features a large contact area and strong π - π forces. Previous research has shown that nonaxial modified phthalocyanines, such as tetra(4-*tert*-butyl)phthalocyanine (abbreviated as TbPc), tend to form H-aggregates during self-assembly [15].

Moreover, pH is identified as a factor that could influence photophysical properties. UV-vis absorption and fluorescence emission of *tert*-ZnPc(II) in water at a concentration of $7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ were measured under different pH conditions (pH 4, 7, and 10). The absorption spectra are relatively similar for pH 7 and 10, whereas a significant decrease in intensity is observed for pH 4. In water, $7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ exhibits no fluorescence across all pH ranges, indicating the presence of aggregation (Figure 5).

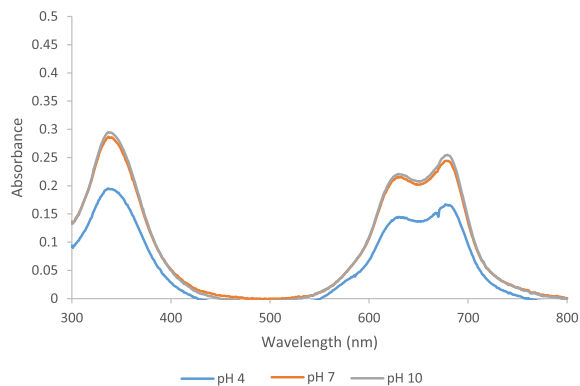
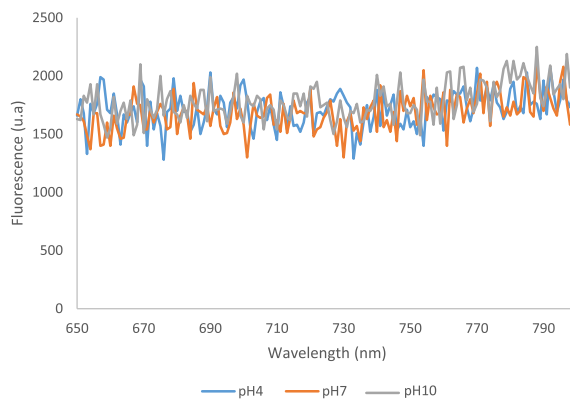
**Figure 4.** UV-vis absorption spectra of *tert*-ZnPc(II) in water at different pH ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$).**Figure 5.** Fluorescence spectrum of *tert*-ZnPc(II) in water excited at 610 nm ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$) at different pH.

Table 2. Emission band, fluorescence quantum yield of *tert*-ZnPc(II) in different solvents

Solvents	Λ_{ext} (nm)	Λ_{em} Band 1 (nm)	Λ_{em} Band 2 (nm)	Λ_{em} Band 3 (nm)	Φ_f 610
Toluene	610	689	749	-	0.35
Ethyl acetate	610	683	743	-	0.31
Ethanol	610	687	746	-	0.29
Methanol	610	686	745	-	0.27
DMF	610	689	746	-	0.29
Acetonitrile	610	687	741	-	0.28
Chloroform	610	687	-	-	0.03
Glycerol	610	692	-	-	0.02
Water	610	700	720	738	0
FBS	610	686	-	-	<0.1

Table 3. Absorbance B and Q bands of *tert*-ZnPc(II) in water at different pH ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$)

Water	B band (nm)	Q band 1 (nm)	Q band 2 (nm)
pH4	336	630	677
pH7	337	630	677
pH10	337	630	677

2.3. Effect of water concentration on UV-vis absorption properties of *tert*-ZnPc(II)

The observation of a notable change in the Q band shape within the UV-vis absorption spectrum of *tert*-ZnPc(II) in a water environment motivated us to examine the impact of water on the absorption intensity for detecting trace amounts of water in diverse organic solvents, including ethanol, methanol, and acetonitrile.

Indeed, water stands as an important and indispensable substance, holding significance not only in the realm of everyday human existence but also within the domain of chemistry. It serves as a critical impurity requiring elimination from numerous chemical and industrial production processes.

Water possesses distinctive characteristics that engender specific interactions with excited molecules owing to its substantial dielectric constant and ability to donate and accept protons. This makes it a potential sensor for detecting moisture in organic solvents. Another important factor that needs to be considered is the strong tendency of *tert*-ZnPc(II) to form aggregates.

The probe solution of *tert*-ZnPc(II) ($7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$) is dissolved in each of the dry organic solvents ethanol, methanol, and acetonitrile, and various concentrations of water (0–70%, v/v) were added. All spectra were obtained immediately after the addition of water to each solvent at 25 °C.

Various concentrations of water in ethanol, methanol, and acetonitrile solutions containing *tert*-ZnPc(II) did not lead to significant wavelength shifts or notable changes in spectral shape; the only difference lay in the absorption coefficient magnitudes. Dicelio and colleagues conducted a study on the aggregation of tetra, *tert*-butyl phthalocyanine, revealing that both the monomer and dimer of tetra, *tert*-butyl phthalocyanine exhibited nearly identical UV-vis absorption spectra [62]. Consequently, the addition of water to *tert*-ZnPc(II) induced the formation of *tert*-ZnPc(II) aggregates without entirely altering the UV-vis absorption spectra. Explaining the shapes and intensities of the dimer spectra accurately would necessitate a comprehensive theoretical investigation, extending Kasha's exciton theory to degenerate excited states and incorporating vibronic coupling into the model as proposed by previous research [47,63].

The UV-vis absorption spectra of *tert*-ZnPc(II) in ethanol, methanol, and acetonitrile (Figures 6–8) exhibited a nearly identical absorption shape even after the addition of varying concentrations of water. However, the notable alteration was observed in the absorption intensity. Specifically, the introduction of small aliquots of water (0.1%) into ethanol, methanol, and acetonitrile resulted in a decrease in

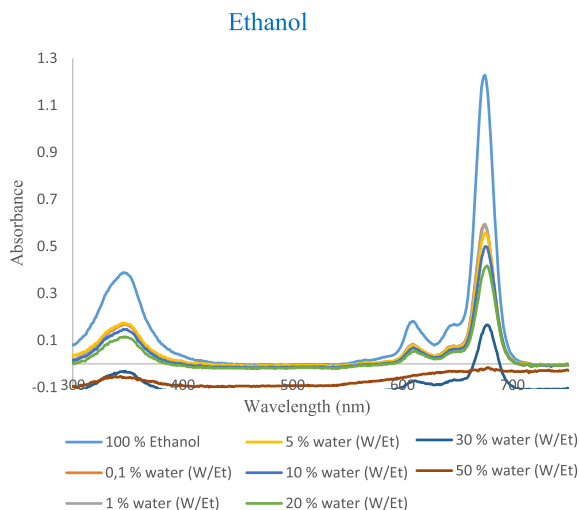


Figure 6. UV-vis absorption spectra as a function of water content of *tert*-ZnPc(II) in ethanol at $7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$.

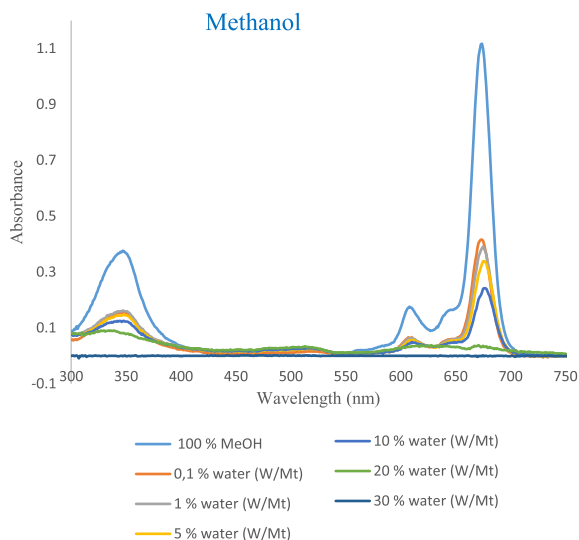


Figure 7. UV-vis absorption spectra as a function of water content of *tert*-ZnPc(II) in methanol at $7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$.

absorption intensity from 1.228 to 0.593, 1.115 to 0.415, and 1.270 to 0.632, respectively. These values were 2, 2.60, and 2 times lower than those observed in pure ethanol, methanol, and acetonitrile, respectively (Tables 4–6 in Supplementary Material).

This diminished intensity, attributed to the addition of a minimal quantity of water, emphasizes

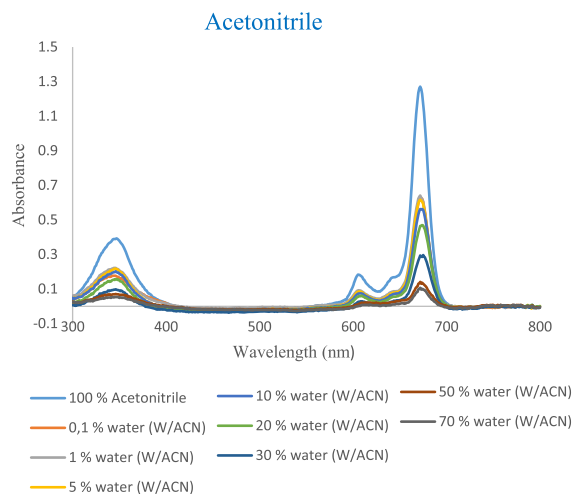


Figure 8. UV-vis absorption spectra as a function of water content of *tert*-ZnPc(II) in acetonitrile at $7.5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$.

the high sensitivity of *tert*-ZnPc(II) to water content. The absorption intensity at 674 nm, 673 nm, and 672 nm in ethanol, methanol, and acetonitrile progressively decreased with increasing water content from 0.1% to (30%, 10%, and 70%), reaching a plateau at each respective concentration. At the 30%, 10%, and 70% water content levels, the absorption intensity at 674 nm, 673 nm, and 672 nm were approximately 7-, 4.62-, and 12-fold lower than in pure ethanol, methanol, and acetonitrile, respectively (Figures 6–8). Evidently, a linear decrease in absorption intensity was observed across all wavelengths with increasing percentage of water content.

It is noteworthy that despite the likely occurrence of aggregation, the spectra maintained their consistent absorption shapes even when incorporating 30%, 10%, and 70% water into homogeneous solvents of ethanol, methanol, and acetonitrile, respectively.

3. Conclusion

This study focuses on the exploration of *tert*-ZnPc(II) photophysical properties. The investigation highlights the influence of solvent polarity on ground-state electronic absorption spectra and fluorescence capability. It is noteworthy that *tert*-ZnPc(II) exhibits typical UV-vis spectra in all organic solvents examined except chloroform, water, glycerol, and FBS. In

these specific solvents, a significant alteration in the shape of absorption spectra is observed coupled with a notable absence of fluorescence, likely attributed to well-known aggregation phenomena inherent in phthalocyanines. Additionally, the UV–vis spectra of *tert*-ZnPc(II) in water demonstrate high sensitivity to water content, maintaining consistent absorption shapes even with the incorporation of a substantial amount of water into the solvents.

4. Materials and methods

All solvents and reagents were of reagent grade quality and obtained commercially from Aldrich, TCI, Fluka, and Merck.

4.1. Photophysical properties

Absorption spectra were recorded on a UV-3600 UV–visible double beam spectrophotometer (Shimadzu, Marne la Vallée, France). Fluorescence spectra were recorded on a Fluorolog FL3-222 spectrofluorometer (HORIBA Jobin Yvon, Longjumeau, France) equipped with a 450 W xenon lamp, a thermostated cell compartment (25 °C), a UV–visible photomultiplier R928 (HAMAMATSU, Japan), and an InGaAs infrared detector (DSS-16A020L, Electro-Optical Systems Inc, PA, USA).

The excitation beam and the emission beam were diffracted by a double-ruled grating SPEX monochromator with 1200 grooves/mm blazed at 330 nm and 1200 grooves/mm blazed at 500 nm, respectively. All spectra were measured in four-face quartz cuvettes. All the emission spectra have been displayed with the same absorbance (less than 0.2) with the lamp and photomultiplier correction.

4.2. Parameters for fluorescence quantum yields

The fluorescence quantum yields of *tert*-ZnPc(II) (Φ_f) were calculated in different solvents by Equation (1) [64]:

$$\Phi_f = \Phi_{f_o} \cdot \frac{I_f}{I_{f_o}} \cdot \frac{DO_o}{DO} \cdot \left(\frac{n}{n_o}\right)^2, \quad (1)$$

where Φ_f and Φ_{f_o} , I_f and I_{f_o} , DO and DO_o , and n and n_o are the quantum yields, fluorescence intensities, optical densities, and refractive indices respectively of the sample and the standard.

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Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

Supplementary data

Supporting information for this article is available on the journal's website under <https://doi.org/10.5802/crchim.364> or from the author.

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