

Metal-free phthalocyanine aggregation and binding with amines: Specific and general solvent effects on absorption and fluorescence properties



Tao Wang^a, Xian-Fu Zhang^{a,b,*}, Xulin Lu^a

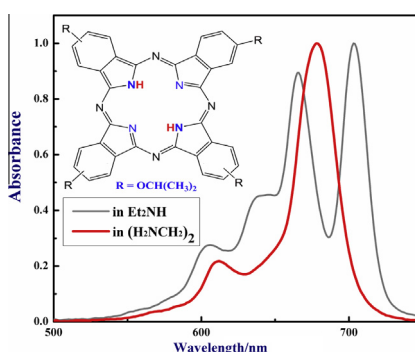
^a Institute of Applied Photochemistry & Center of Analysis and Measurements, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei Province 066004, China

^b MPC Technologies, Hamilton, ON L8S 3H4, Canada

HIGHLIGHTS

- The spectral properties of metal and metal-free phthalocyanines (Pcs) were compared.
- Metal-free Pcs show very specific solvent effect in amines, while metal Pcs do not.
- Metal-free Pcs show strong molecular aggregation in alcohols, while metal Pcs do not.
- Increase of solvent polarity decreases both Φ_f and τ_f , but increases the Stoke's shift.
- Metal-free Pcs show stronger solvent polarity dependence in spectra than metal Pcs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 October 2014
 Received in revised form 12 November 2014
 Accepted 12 November 2014
 Available online 23 December 2014

Keywords:

Phthalocyanine
 Fluorescence
 Absorption
 Solvent effect
 Aggregation

ABSTRACT

The fluorescence and absorption properties of a metal-free phthalocyanine (Pc) H_2PcR_4 and its zinc-centered complex $ZnPcR_4$ (R is the isopropoxy at the β -position of a Pc ring) were measured and compared in protic and aprotic solvents. H_2PcR_4 shows strong bonding interaction with amines and aggregation in alcohols in addition to the general solvent effect in aprotic solvents due to polarity change. The specific solvent effect leads to substantial changes in its spectra, fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ_f) values. In contrast, $ZnPcR_4$ does not show the specific effects due to the presence of a central element in a Pc cavity. For H_2PcR_4 the change of solvents caused a large variation of Φ_f (0.050–0.48) and τ_f (3.45–6.88 ns), in contrast to the slight changes for $ZnPcR_4$. On the other hand, the general solvent effect of H_2PcR_4 due to polarity is also more significant than that of $ZnPcR_4$. The increase of solvent polarity decreases both Φ_f and τ_f , but increases the Stoke's shift.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Phthalocyanine (Pc) and its metal complexes (Scheme 1) have been the focus of many studies [1–5]. Pc materials are used as

photosensitizers in photodynamic therapy of Tumor (PDT) [6–12], electron donor/acceptors in dye-sensitized solar cells (DSSC) [13–16], nonlinear optical materials for preventing laser weapons [17–19], catalysts in industry [20–22], liquid crystals in display devices [23–25], and photoconductors in copy machines and laser printers [6,26,27].

Most of the applications are based on their photophysical properties, which are closely related to the generation and decay of

* Corresponding author at: Institute of Applied Photochemistry & Center of Analysis and Measurements, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei Province 066004, China. Tel./fax: +86 3358387040.

E-mail address: zhangxianfu@tsinghua.org.cn (X.-F. Zhang).

excited singlet state (S_1) of Pcs which are affected by solvents. The fluorescence properties of a Pc compound can be influenced by solvents in many different ways, but attentions in past reports are usually paid to the general solvent effect due to polarity. For example, some studies have explored the effect of solvent polarity on the UV–vis absorption and fluorescence spectral positions of ZnPc [28–30], CuPc [31], PbPc [32] and CdPc [33]. In addition to polarity effect, a solvent may also affect Pc's spectra and photophysical properties through specific solvent effect (SSE), including hydrogen bonding, acid–base equilibrium and aggregation effect. However, there has been no systematic study about these SSEs on Pc compounds. Therefore the focus of this report is placed on the SSEs, including amine–Pc acid–base binding and alcohol hydrogen bonding, on the Pc's spectra and photophysical properties.

Another emphasis in this study is on metal-free Pc (H_2Pc), since most investigations in literature are about metal Pcs. H_2Pc is different from its metal Pc in several aspects, (i) a metal coordinated Pc complex is more or less ionic, the negative charge (-2) of Pc ligand is fully delocalized over the Pc ring which makes the four N atoms in inner core are equal. On the other hand, H_2Pc is a covalent compound, and the four N atoms in inner core are different (Scheme 1). (ii) The shape of the UV–vis absorption band of an H_2Pc compound is different from that of ZnPc due to different molecular symmetry. H_2Pc is C_{2v} symmetrical in comparison to the D_{4h} symmetry of ZnPc. (iii) H_2Pc is a weak organic acid. Therefore H_2Pc must exhibit different solvent effect from that of a metal Pc. Indeed we found in this study that H_2Pc showed two specific SSEs which are different from that of ZnPc. This study is based on our previous studies on the various properties of Pc compounds [6–10,12].

Experimental section

Reagents and apparatus

Zinc phthalocyanine (ZnPc) was purchased from TCI. H_2PcR_4 and $ZnPcR_4$ were home made and the procedure for the synthesis and characterization are the same as that reported previously [34,35]. All organic solvents were of analytical grade, dried by appropriate methods and distilled before use. UV–vis absorption measurements were made with a StellarNet Black Comet CSR diode array miniature spectrophotometer, which is connected to deuterium and halogen lamp by optical fiber in 10 mm quartz cuvettes. Fluorescence spectra were monitored using FLS920 Fluoro-spectrometer (Edinburgh Instruments Ltd.). Fluorescence lifetimes of Pc compounds were measured by time-correlated single photon counting method using FLS920.

Sample preparation

The compound (H_2PcR_4 or $ZnPcR_4$) was first dissolved in a vial (5 ml) to get the concentrated stock solution, the solution was son-

icated for 2 min. It was then diluted in another vial to reach the desirable absorbance at the selected wavelength immediately before measurements.

Photophysical measurements

The absorption and fluorescence spectra, fluorescence quantum yields and fluorescence lifetimes were investigated at room temperature, ca. 22 °C. All solutions were air-saturated.

Absorption spectra

UV–vis absorption measurements were made in 1 cm quartz cuvettes using blank solvent as the reference, sample concentrations were diluted so that the absorbance at Q band maxima was 1.0 ± 0.1 .

Fluorescence spectra

Fluorescence spectra (650–830 nm) were monitored with both excitation and emission slits of 1 nm. All spectra were corrected for the sensitivity of the photo-multiplier tube. Excitation wavelength is 600 nm for H_2PcR_4 and 605 nm for $ZnPcR_4$. The absorbance at an excitation wavelength is 0.090 ± 0.010 to avoid self absorption in measuring fluorescence and keep the absorbance accuracy.

Fluorescence quantum yields

Fluorescence quantum yields (Φ_f) were measured according to equation: $\Phi_f = \Phi_f^0 \cdot F_s \cdot A_0 \cdot n_s^2 / (F_0 \cdot A_s \cdot n_0^2)$, in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. Zinc phthalocyanine in DMF was used as the reference ($\Phi_f = 0.30$) [36]. The sample and reference solutions were prepared to have the same absorbance (A_i) at the excitation wavelength (near 0.090 per cm).

Fluorescence lifetimes

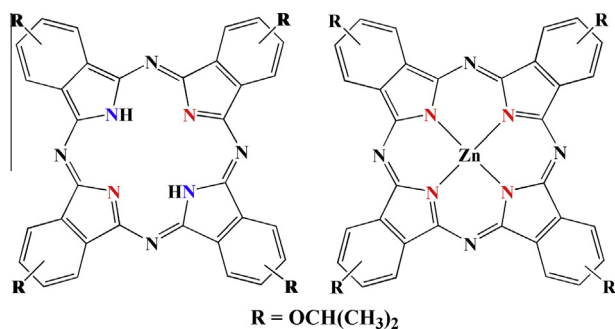
Fluorescence lifetimes were measured by time-correlated single photon counting method with excitation by a 672 nm diode laser (50 ps FWHM) and emission was typically monitored at the band maximum. Fluorescence lifetimes were obtained by fitting the experimental data to $I(t) = A_1 \exp(-t/\tau_f) + C_1$ or $I(t) = A_1 \exp(-t/\tau_1) + B_1 \exp(-t/\tau_2) + C_2$ by deconvolution method using the software F900 supplied by the instrument seller.

Results and discussion

In literature aprotic solvents were usually adopted to study the polarity effect on the peak positions of absorption and fluorescence spectra [28–33]. We use both protic and aprotic solvents in the study. In particular, two types of protic solvents, including alcohols and amines, are selected and both of them showed very different specific solvent effects on the Pc photophysical properties, as discussed below.

Aggregation in alcohols

The most remarkable effect of alcohols as solvents is the aggregation occurrence of H_2PcR_4 observed from UV–vis absorption spectra. Seven alcohols with different chain lengths ($C_nH_{2n+1}OH$, $n = 1–6, 8$) were tested. Fig. 1 shows the absorption spectra. In the least polar $n-C_8H_{17}OH$, H_2PcR_4 showed the typical UV–vis absorption spectrum of H_2Pc , in which the Q band is split into Q_x and Q_y bands (690 and 705 nm, respectively) [37,38]. The increase in the polarity of the alcohols (or the decrease in chain length)



Scheme 1. Chemical structure of H_2PcR_4 and $ZnPcR_4$.

Download English Version:

<https://daneshyari.com/en/article/1405411>

Download Persian Version:

<https://daneshyari.com/article/1405411>

[Daneshyari.com](https://daneshyari.com)