

Synthesis and photophysical properties of peripherally metallated bis(dimethylamino)porphyrazines

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Abstract

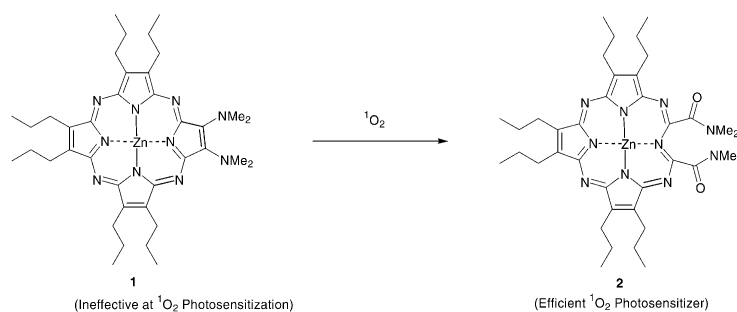
The photophysics of the two novel solitaire porphyrazines **3** and **4** (obtained via coordination of PdCl₂ and PtCl₂ to the peripheral bis(dimethylamino) entity of the Zn-porphyrazine **1**, respectively) have been examined using absorption, emission and transient absorption spectroscopy. While the free ligand **1** exhibits neither fluorescence nor triplet absorption, the peripherally metallated derivatives **3** and **4** display both fluorescence as well as intersystem crossing. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrinoids; Complexes; Fluorescence; Intersystem crossing

1. Introduction

The design and study of coordination compounds prepared from ligand systems containing photo-active units are of great importance in areas such as photodynamic therapy [1], electron transfer [2] and nonlinear optics [3]. Our efforts in this field utilize the tetraazaporphyrin (porphyrazine, pz) ligand as a structural motif for the rigid organization of the metal centers, and we have developed a new family of

tetraaza-macrocycles that have metal-binding heteroatoms (S, N and O) attached to the pz periphery [4]. Recently we reported the synthesis [5] and photophysical properties [6] of the zinc-seco-porphyrazine **2**. In contrast to the precursor macrocycle **1**, pigment **2** exhibits fluorescence as well as intersystem crossing ($\phi_T = 0.64$). As a consequence, seco-porphyrazine **2** is a superb photosensitizer for the formation of singlet oxygen with a quantum yield of $\phi_\Delta = 0.54$. Herein we now report the effects of peripheral metallation upon the photophysical properties of ligand **1**.



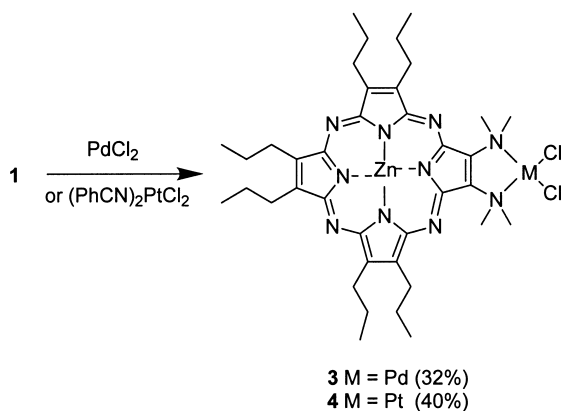
2. Experimental details

Hexapropyl bis(dimethylamino) zinc porphyrazine **1** was synthesized as previously described [5]. The two novel soli-

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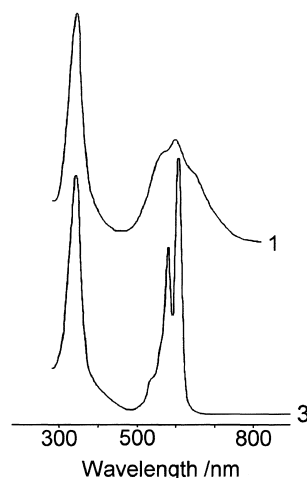
Scheme 1.

taire porphyrazines **3** and **4**, employed in this study, were prepared following methods developed in our laboratories [7].

The experimental conditions and instrumentation for the photophysical measurements: steady-state absorption and emission, fluorescence lifetime and triplet state properties have been previously described [6]. For the present study, an excitation wavelength, λ_{ex} , of 595 nm was used to measure the fluorescence lifetime. Triplet state measurements were carried out on a nanosecond, flash-photolysis apparatus using an excitation wavelength of 605 nm and a repetition rate of 10 Hz.

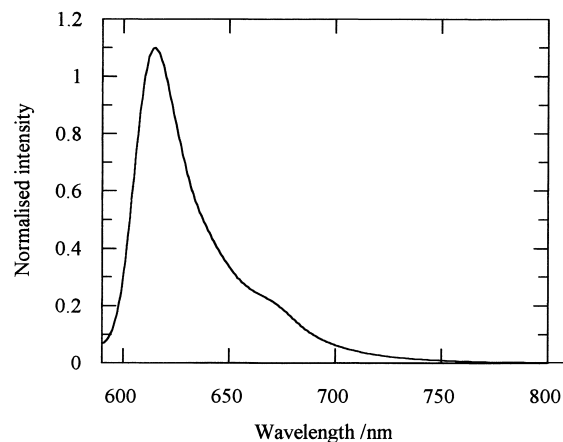
3. Results and discussion

The palladium solitaire porphyrazine **3** was readily obtained through reaction of equimolar amounts of Zn-porphyrazine **1** with PdCl_2 in chloroform and acetonitrile (3:1) at reflux (Scheme 1). Similarly, treatment of the free ligand **1** with a stoichiometric amount of bis(benzonitrile)platinum(II) chloride in 1,2-dichloroethane at reflux gave the corresponding solitaire porphyrazine **4** in moderate yield (Scheme 1). The electronic absorption spectrum of compound **1** has a distinct Q-band at 597 nm which is severely broadened. This broadening obscures the expected "split" of the Q-band which is normally observed for macrocycles of less than D_{4h} symmetry [8], and is presumably due to overlap of underlying $n-\pi^*$ transitions that arise from the nonbonding electrons associated with the peripheral nitrogens. As previously observed [7,9], removal of the broadening effect upon peripheral metallation lends credence to the assignment of the $n-\pi^*$ transition and indeed, both **3** and **4** exhibit a sharp, split Q-band having Q_x and Q_y absorbances at 605 and 578 nm, respectively (see representative spectra in Fig. 1). In addition, the metal coordination to the peripheral dimethylamino chelate has also a profound effect on the photophysical properties of the macrocycle. While the photophysical data for the free ligand **1** suggests that the dominant deactivation process for the first excited

Fig. 1. Absorption spectra of porphyrazines **1** and **3** in CH_2Cl_2 .

singlet state is nonradiative (neither fluorescence nor triplet absorption was detected although ground-state bleaching was observed) [6], both **3** and **4** exhibit fluorescence as well as intersystem crossing. The fluorescence quantum yields, ϕ_f , for the solitaire complexes **3** and **4** were determined to be 0.05 and 0.08 ± 0.01 , respectively (a representative fluorescence spectrum of the complex **3** is shown in Fig. 2) with lifetimes of 0.4 and 0.65 ± 0.05 ns. However, while ϕ_{ISC} is promoted, determination of the triplet state quantum yield, ϕ_T , proved difficult due to the pigments **3** and **4** undergoing photodegradation. Fig. 3 for example shows the electronic absorption spectrum of complex **3** before (a) and after (b) intense irradiation. The new absorption at 607 nm is the photoproduct(s) and may be a result of the triplet state of solitaire porphyrazine **3** being photochemically active. The spectrum resembles the one of the free ligand **1**, thus suggesting the loss of the metal cation. This is currently under further investigation.

As the lone pair electrons on the $(\text{NMe}_2)_2$ moiety are now bonded datively to the metal ions they can no longer interact

Fig. 2. Fluorescence emission spectrum of porphyrazine **3** in toluene. Excitation wavelength, $\lambda_{\text{ex}} = 595$ nm.

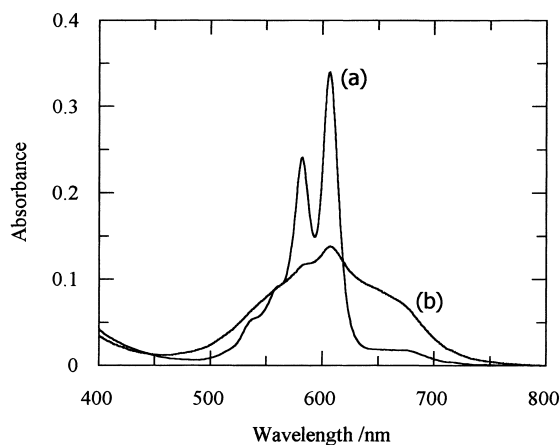


Fig. 3. Absorption spectra of solitaire porphyrazine **3** before (a) and after illumination (b).

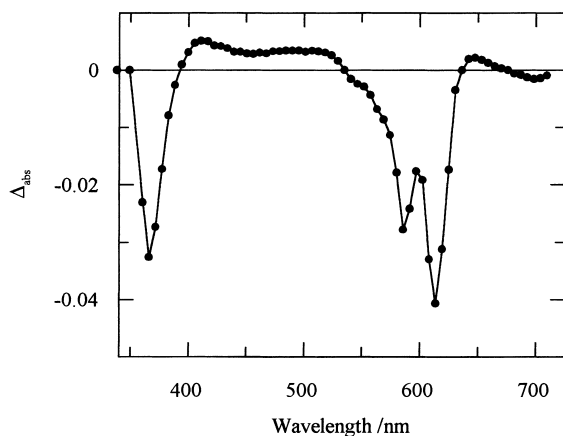


Fig. 4. Transient absorption spectrum of solitaire porphyrazine **4**. Excitation wavelength $\lambda_{\text{ex}} = 605$ nm.

strongly with the porphyrazine π -system. This combined with the fixed geometry of the chelating unit may suppress internal conversion as the dominant deactivation pathway and we therefore observe fluorescence for the solitaire complexes **3** and **4** in contrast to the free ligand **1**. In addition, the heavy atom effect is expected to increase intersystem crossing ($S_1 \rightarrow T_1$) and at the same time the decay rates for phosphorescence ($T_1 \rightarrow S_0$) and nonradiative quenching ($T_1 \rightarrow S_0$). Thus, although triplet state formation is observed

(Fig. 4), intersystem crossing back to the ground state followed by vibrational relaxation rather than phosphorescence seems to be the dominant deactivation process for the first excited triplet states of solitaire complexes **3** and **4**.

In summary, we herein demonstrate that the photophysical properties of porphyrazines substituted with a single bidentate dimethylamino chelating group can not only be switched through seco-porphyrazine formation but also via peripheral metallation. This represents a powerful strategy which will allow us to effectively design and synthesize potential molecular photonic devices.

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