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Luminescent Zn and Pd Tetranaphthaloporphyrins

Vladimir V. Rozhkov, Mazdak Khajehpour, and Sergei A. Vinogradov*

Department of Biochemistry and Biophysics, University of Pennsylvania,
Philadelphia, Pennsylvania 19104

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Zn and Pd complexes of *meso*-tetraphenyltetranaphthaloporphyrins (Ph_4TNP) exhibit strong infrared absorption bands and luminesce in solutions at room temperature. S1 → S0 fluorescence (λ_{max} = 732 nm, ϕ = 5.3%) is the predominant emission in the case of ZnPh_4TNP (**1**). This emission is in part due to the delayed fluorescence (ϕ = 1.1%). Phosphorescence (T1 → S0) of **1** (λ_{max} = 973 nm) is very weak (ϕ = 0.04%) and occurs with lifetime of about 440 μs in deoxygenated DMF. In the case of PdPh_4TNP (**2**), almost no S1 → S0 fluorescence could be observed, while the main emission detected was T1 → S0 phosphorescence (λ_{max} = 938 nm). The phosphorescence of **2** occurs with lifetime of about 65 μs and (ϕ=6.5%) in deoxygenated DMF solution. Metalloporphyrins **1** and **2** are promising near infrared dyes biomedical applications.

Interest in porphyrins fused with external aromatic rings has been steadily increasing in the past several years.[1] Symmetrically extended porphyrins, such as tetrabenzoporphyrins (TBPs), exhibit particularly red-shifted absorption bands and strong infrared luminescence and possess interesting nonlinear optical properties, suggesting applications in biomedicine[2] and various branches of optical technology.[3] *meso*-Tetraarylated tetrabenzoporphyrins (Ar_4TBPs) and tetranaphthaloporphyrins (Ar_4TNPs) have an advantage of increased solubility and relative ease of derivatization. Considerable progress has been achieved lately in the synthesis of functionalized Ar_4TBPs,[4] and some of their applications have been described.[2b−f,3] Ar_4TNPs, on the other hand, are studied only minimally,[5] although their synthesis has also been recently improved.[6] In this work, we report on Zn and Pd tetraphenyltetra[2,3]naphthaloporphyrins (Ph_4TNPs), which possess remarkably red-shifted absorption Q-bands and exhibit considerable room temperature emission, suggesting applications in PDT and biological oxygen sensing by phosphorescence quenching.

The symmetrical tetraphenyltetra[2,3]naphthaloporphyrins (MPh_4TNPs; M = Zn (**1**), Pd (**2**)) studied in this work are shown in Scheme 1 together with the homologous tetraphenyltetrabenzoporphyrin (MPh_4TBP).

Synthesis of Ar_4TNPs was originally proposed by Kopranenkov et al.[7] It was based on the template condensation of 2,3-naphthalenedicarboximide with phenylacetic acids in the presence of Zn salts. A much improved higher yield synthesis of Ar_4TNPs has been recently developed by Ono et al.,[6] allowing for the introduction of substituents in the *meso*-phenyl rings, but requiring rather elaborate synthesis of the precursor compounds. In this work, we followed the older method, which has an advantage of a simpler single-

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* Corresponding author. E-mail: vinograd@mail.med.upenn.edu.

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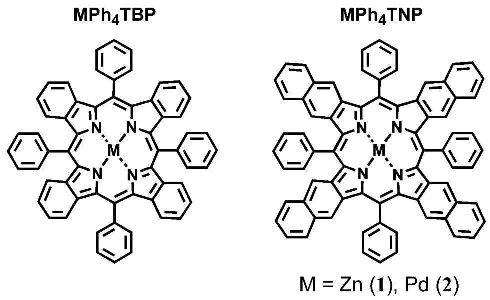
10.1021/ic034257k CCC: $25.00

Scheme 1



Scheme 2

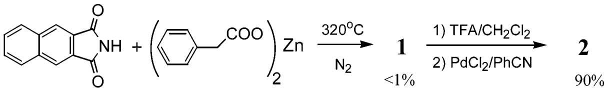


Table 1. Photophysical Properties of **1** and **2** in DMF Solutions at Room Temperature

	absorption λ_{max}, nm ($\log_{10} \epsilon$)	emission			
		type	λ_{max} (λ_{ex}),[b] nm	ϕ,[c] %	τ, μs
1	720 (4.82)	S1 → S0	732, 809 (494)	5.3 ± 0.7[d]	
	659 (3.90)	S1 → S0[e]	732, 809 (494)	1.1 ± 0.2	442
	494 (4.98)				
	R[a] = 2.3	T1 → S0	973 (720)	0.04 ± 0.01	438
2	704 (5.01)	S1 → S0	715 (440)	<0.02[d]	
	640 (4.12)				
	459 (4.98)	T1 → S0	938 (704)	6.5 ± 0.1	65
	R[a] = 1.2				

[a] $R = I_{Soret}/I_Q$ = ratio of the integral intensities. [b] λ_{ex} = wavelength used for excitation, shown in parentheses. [c] ϕ = emission quantum yield, determined relative to the fluorescence of Zn tetraphenylporphyrin (ZnTPP) in deaerated benzene, $\phi = 3.3\%$.[10] [d] Quantum yield is shown for combined fast and delayed fluorescence in deoxygenated solution. [e] Delayed fluorescence due to thermal repopulation of singlet state.

step synthetic procedure. Our goal was to examine basic photophysical properties of Ph_4TNPs, for which the materials were required only in minimal amounts. The synthesis is shown in Scheme 2.

A similar synthesis of Ph_4TBPs[8] has been reported to give mixtures of products, consisting of porphyrins with two to four *meso*-phenyl rings.[9] Although not directly demonstrated, synthesis of Ph_4TNPs is likely to suffer from the same problem. As a consequence, a very tedious purification was required to obtain pure $ZnPh_4TNP$ (**1**), which could be isolated only in a very low yield (<1%). A much higher yield (25%) has been reported originally,[7] along with the blue-shifted Q-band of **1** (λ_{Qmax} = 710 nm). For comparison, λ_{Qmax} of **1** in CH_2Cl_2, reported by Ono et al.,[6] is 723 nm. It is likely that the material obtained in ref. 7 contained porphyrins with fewer *meso*-phenyl substituents, $ZnPh_nTNP$ (n = 2−4), whose presence resulted in the overall Q-band blue-shift.

The photophysical properties of $ZnPh_4TNP$ (**1**) and $PdPh_4TNP$ (**2**) are summarized in Table 1. The absorption spectra of **1** and **2** are shown in Figure 1.

The absorption Q-bands of both complexes are significantly red-shifted, compared to those of tetraphenylporphyrins (TPPs) and Ph_4TBPs. For example, the principal Q-band peaks of PdTPP[11] and $PdPh_4TBP$[2b] are at 522 and 628 nm, respectively, while the Q-band peak of **2** is at 704 nm. The red-shifted absorption of Ph_4TBPs versus TPPs is due to the π-extension[12a] and nonplanar distortion[12b] of the Ph_4TBP macrocycle. In the case of Ph_4TNP versus Ph_4TBP, however, it is only the extra π-extension that causes the absorption red-shift, which reaches 75 nm for Pd complexes and 63 nm for Zn complexes (λ_{Qmax} $ZnPh_4TBP$ = 657 nm).[9] The magnitudes of the predominant saddle type distortions (d_{sad}'s) are practically the same in **1** and in $ZnPh_4TBP$, as seen from the calculated structures, depicted in Figure 2, and evidenced by the results of NSD (normal-coordinate structural decomposition) analyses.[13]

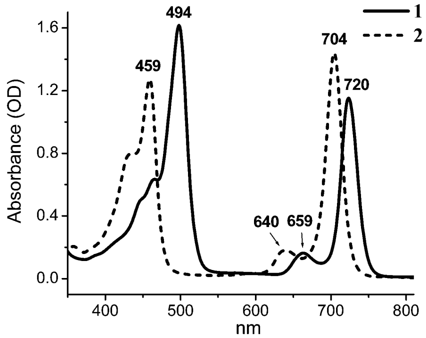


Figure 1. Absorption spectra of porphyrins **1** and **2** in DMF solutions.

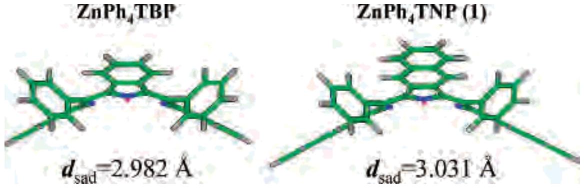


Figure 2. Side views of the calculated structures of $ZnPh_4TBP$ and $ZnPh_4TNP$ (**1**). d_{sad} values indicate the magnitudes of the saddle type (B_{2u}) normal distortion modes, as calculated by NSD.[13]

Presently, no structural data are available for Ar_4TNPs, and only a few X-ray analyses are reported for Ar_4TBPs.[14] Therefore, making structural comparisons was possible only by using computed structures. The geometries of the corresponding Zn-complexes were optimized at the DFT B3LYP/6-31G level. It has to be mentioned that the degree of the saddle type distortion in the calculated $ZnPh_4TBP$ is higher than that found in the reported[14a] experimental structure $ZnPh_4TBP\cdot THF$ (d_{sad} = 2.34 Å).

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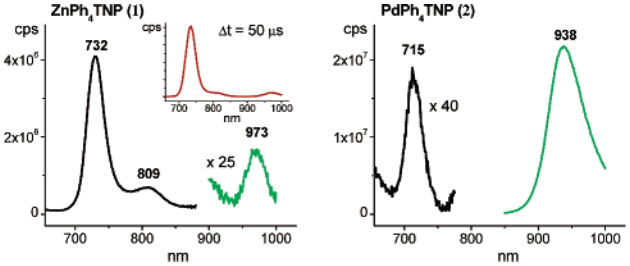

Figure 3. Corrected emission spectra of ZnPh$_4$TNP (**1**) and PdPh$_4$TNP (**2**) in DMF. (**1**) Black line indicates fluorescence in aerated solution (λ_{ex} = 460 nm); green line indicates phosphorescence in deoxygenated solution (λ_{ex} = 720 nm). Inset: Red line indicates emission in deoxygenated solution (uncorrected); spectrum delayed by 50 μs (λ_{ex} = 494 nm). (**2**) Black line indicates fluorescence (λ_{ex} = 440 nm); green line indicates phosphorescence (λ_{ex} = 704 nm).

The Soret transitions are less affected by the macrocycle extension/distortion than the Q-bands. For example, the red-shift of the Soret band of **1** versus that of ZnTPP is only 71 nm (λ_{Soret} ZnTPP = 423 nm), while for the corresponding Q-bands this difference is more than 120 nm ($\lambda_{Q(0,0)}$ ZnTPP = 596 nm).[10] Porphyrins **1** and **2** are, therefore, far surpassed in terms of Soret red-shifts by, for instance, tetraaryltetraacenaphthoporphyrins, whose Soret bands reach as far as 550 nm and above.[15] However, the locations of extremely strong and narrow Q-bands make **1** and **2** almost ideally suited for biological in vivo applications, such as PDT, where absorption between 630 and 800 nm, in the so-called "near infrared window of tissue", is highly desirable. Another interesting and useful feature of **1** and **2** is that, compared to the corresponding TPPs and Ph$_4$TBPs, they exhibit large increases in the oscillator strengths (I_λ) of the Q-bands versus Soret bands. In the case of Pd complexes, for example, the ratio I_{Soret}/I_Q (see Table 1) changes from PdTPP to PdPh$_4$TBP to **2** as 13.8 → 2.6 → 1.2. In fact, the extinction at the Q-band peak of **2** is higher than that at the Soret peak, offering a possibility for very effective near infrared excitation.

Luminescence of metalloporphyrins **1** and **2** is significantly red-shifted and could be accurately measured only using specialized infrared enhanced detection systems, such as Hamamatsu R2685 PMT. The results of the measurements are summarized in Table 1, and the emission spectra are shown in Figure 3. In all cases, the origins of the emission bands were confirmed by comparing the absorption and excitation spectra.

The obvious difference between compounds **1** and **2** is that the major emission from the former is fluorescence, while the latter mainly exhibits phosphorescence from the T1 state. This difference is due to the enhanced intersystem crossing, which is known to be amplified in porphyrins by heavy metals such as Pd and Pt.[11]

Fluorescence of **1** (λ_{max} = 732 nm) has a Stokes shift of 12 nm and presents almost an ideal mirror image of the absorption Q-band. Such a small Stokes shift (227 cm^{-1}) is rather surprising in a view of the highly distorted molecular structure of **1**. It has been observed that other nonplanar Zn porphyrins, such as Zn dodecaphenylporphyrin (ZnDPP) and Zn octaethyltetraphenylporphyrin (ZnOETPP), exhibit significant increases (up to 1660 cm^{-1}) in the gaps between fluorescence and absorption maxima.[16] S1 → S0 fluorescence quantum yield of **1** (ϕ = 5.3%), is comparable to that of ZnTPP (3.3%),[10] and higher than that of ZnDPP (1%) and ZnOETPP (0.3%).[16] Interestingly, a large portion of fluorescence (~20%) is delayed. Phosphorescence of Zn complex **1** is very weak (ϕ = 0.04%). The inset in Figure 3 shows the delayed emission spectrum of **1** in deoxygenated DMF, where both the phosphorescence and the fluorescence peaks are clearly present. The time-resolved measurements at the emission maxima (732 and 973 nm) resulted in practically the same lifetimes, 442 and 438 μs, suggesting that emitting S1 species are formed in this case as a result of thermal equilibrium between T1 and S1 states. Delayed fluorescence has been previously observed for metalloporphyrins by Gouterman and co-workers.[17]

Because of the greatly enhanced intersystem crossing, S1 → S0 fluorescence of **2** (λ_{max} = 715 nm) is extremely weak (ϕ < 0.02%). Instead, T1 → S0 phosphorescence constitutes the major emission from this porphyrin, similar to what has been previously observed for PdTPP[11] and PdPh$_4$TBP.[2b] The quantum yield of this emission, ϕ = 6.5%, is somewhat lower than that reported for PdPh$_4$TBP phosphorescence (ϕ = 8−12%).[2b] The phosphorescence lifetime of **2** in the absence of oxygen is 65 μs, and in aerated solutions, the emission is almost fully quenched. Considering the extremely strong absorption Q-band of **2** (704 nm, $\log_{10} \epsilon \approx 5.0$), these characteristics suggest that **2** can be very effective as a near infrared phosphor for biological oxygen measurements.

Finally, we would like to point out that, upon excitation at the Soret bands, both compounds **1** and **2** exhibit broad and weak emissions (ϕ = 0.1−0.3%) in the 520−570 nm region, i.e., blue-shifted compared to the corresponding S1 → S0 bands. The excitation spectra showed that these peaks were due to impurity (or impurities) with absorption bands at 510−515 nm.

In summary, Zn and Pd *meso*-tetraphenyl[2,3]tetranaphthaloporphyrins exhibit strong near infrared absorption bands and luminesce in solutions at room temperature. These compounds present an interest as chromophores for biomedical applications, such as in vivo oxygen imaging and PDT.

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Supporting Information Available: Synthesis and characterization of porphyrins, details of optical measurements, description of the calculations, and NSD analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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