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Charge Transfer Enhances Two-Photon Absorption in Transition Metal Porphyrins

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Porphyrin-based materials are promising for applications that require strong two-photon absorption.[1] Such applications include fluorescence microscopy and photodynamic therapy with two-photon excitation, 3D microfabrication, and sensor protection.[1] Enhancement of the optical properties that determine two-photon absorption efficiency (molecular second hyperpolarizability, γ, and two-photon absorption cross-section, δ) have been achieved through modifications to the π network of the porphyrin macrocycle.[1] In this report, we consider the effect of transition metal ions on the porphyrin γ and δ values.[2] We show that metalloporphyrins with strong charge transfer (CT) transitions in their one-photon absorption spectra have δ values that are an order of magnitude larger than those of the free base porphyrin. We attribute this effect to CT transitions between the metal ion's d orbitals and the π system of the porphyrin.

Electropolymerized thin films of Fe^{3+},[3] Mn^{3+}, and Co^{2+} 5,10,15,20-tetrakis-(4-hydroxytetraphenyl)porphyrins (TPP) were studied. Because these metalloporphyrins have low emission yields, degenerate four wave mixing (DFWM) experiments with 100 fs laser pulses were used to determine γ and δ. Details of the film preparation and optical studies are given in the Supporting Information.

The absorption spectra of Fe^{3+}, Mn^{3+}, and Co^{2+} TPP are shown in Figure 1A. The widely used four orbital model (a_{1u},a_{2u} HOMO and e_g LUMO, Figure 1B) qualitatively explains the origin of porphyrin B and Q bands.[4] For Fe^{3+} and Mn^{3+} TPP, mixing of the metal d and macrocycle π orbitals leads to additional peaks in the absorption spectrum.[5,6] For Fe^{3+} TPP, these CT transitions involve the π (a_{1u},a_{2u}) orbitals of the macrocycle and the metal ion's d_π orbitals ($\pi \rightarrow d_\pi$).[6] For Mn^{3+} TPP, the CT bands include the π $(b_{2u}) \rightarrow d_\pi$ ($\lambda_{max} = 432$ nm) and π $(a_{1u},a_{2u}) \rightarrow d_{z^2}$ ($\lambda_{max} = 638$ nm) transitions.[6] These CT transitions are allowed as they occur between electronic states of opposite symmetry (*g*→*u*). The absence of similar CT bands in the Co^{2+} TPP absorption spectrum suggests that the mixing of the Co^{2+} ion's d orbitals with the macrocycle's π system is less efficient. Thus, comparison of Co^{2+} TPP and Mn^{3+}/Fe^{3+} TPP optical properties allows the role of metal ion/macrocycle interactions on two-photon effects to be investigated.

The metalloporphyrin second hyperpolarizability, γ, spectra are shown in Figure 2. (DFWM data are provided in Supporting Information. The ~100 fs response time of each material indicates a purely electronic process.) Peaks are observed in the near-IR region of the γ spectra at ~1150 nm for Fe^{3+} TPP and ~1250 nm for Mn^{3+} TPP. The Co^{2+} TPP γ spectrum does not have this feature. The molecular orbital model shown in Figure 1B suggests that the peaks in the γ spectra could be related to two-photon transitions between metal d and macrocycle π^* orbitals. As both orbitals have *g* symmetry, two-photon transitions are allowed. In contrast, one-photon transitions between these orbitals are forbidden and are not seen in the absorption spectra in Figure 1A.

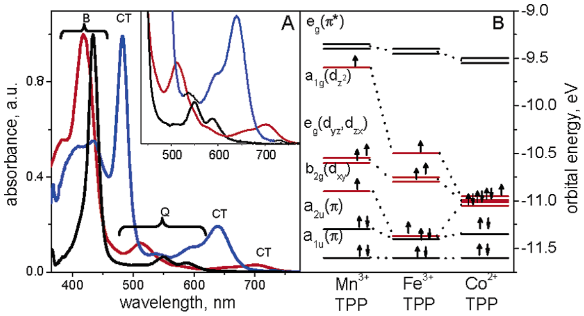

Figure 1. (A) One-photon absorption spectrum of Mn^{3+} (−), Fe^{3+} (−), and Co^{2+} (−) TPP. (B) Molecular orbital diagram for Mn^{3+} and Fe^{3+} TPP. Metal orbitals are shown in red. Adapted from refs 11−13

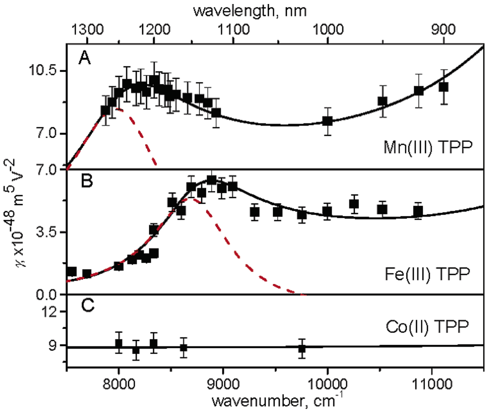

Figure 2. Second hyperpolarizability, γ, of (A) Mn^{3+}, (B) Fe^{3+}, and (C) Co^{2+} TPP determined by DFWM studies on thin films. The solid lines are fitting results according to eq 1. The two-photon component (Im γ, dashed red line) is also shown.

A sum-over-states model was used to estimate the two-photon state energies and dipole moments. A three-state model (ground, one-, and two-photon excited states) was previously applied to porphyrin materials:[7]

$$\gamma \propto -\frac{M_{01}{}^4}{(\omega_1 - \omega - i\Gamma)^3} + \frac{M_{01}{}^2 M_{12}{}^2}{(\omega_1 - \omega - i\Gamma)^2(\omega_2 - 2\omega - i\Gamma)} \tag{1}$$

where M_{01} and M_{12} are the transition dipole moments for the 0→1 and 1→2 transitions, ω is the experimental frequency, ω_1 and ω_2 are frequencies derived from the excited-state energies E_1 and E_2 ($\omega_1 = E_1/h$ and $\omega_2 = E_2/h$; h is the reduced Planck's constant). Parameter Γ accounts for the linewidths. Analysis of the γ spectra yields the M_{12}, E_2, and Γ values (Table 1; E_1 and M_{01} were obtained from absorption spectra in Figure 1A). As suggested by the γ spectra in Figure 2, the Fe^{3+} TPP two-photon state has a higher energy than that of Mn^{3+} TPP. Both porphyrins have M_{12} values of 4.2 D.

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Table 1. Linear and Nonlinear Spectroscopic Properties of the Metalloporphyrin Films

	M_{01} (D)^a	M_{12} (D)^b	E_1 (cm^{-1})^a	E_2 (cm^{-1})^b	Γ (cm^{-1})^a
Mn^{3+}	3.85	4.2	15686	16050	1150
Fe^{3+}	1.3	4.2	14300	17400	900

[a] The errors are ±3.5% in these values. [b] ±10% error.

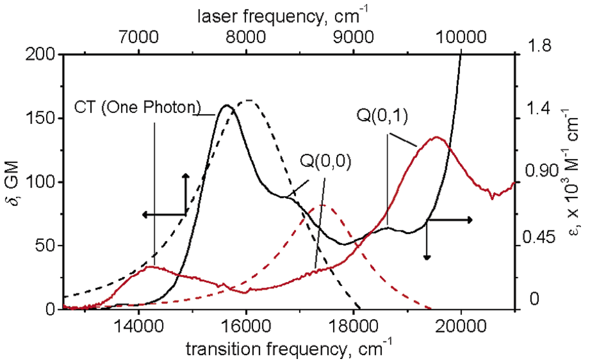

Figure 3. One- (—) and two-photon (- - -) spectra of Mn^{3+} TPP (black) and Fe^{3+} TPP (red).

To determine the effect of the metalloporphyrin two-photon states on the two-photon absorption cross-section, δ, we consider the imaginary component of hyperpolarizability, Im γ. The cross-section δ can be obtained from:[8]

$$\delta = \frac{6\pi^2\hbar}{\epsilon_0 n^2 \lambda^2} f^4 \mathrm{Im}\gamma \qquad (2)$$

where ϵ_0 is the electric constant, n is the index of refraction, and λ is the wavelength. Application of eq 2 to the Im γ data yields $\delta_{\max} = 82$ GM for Fe^{3+} TPP and $\delta_{\max} = 164$ GM for Mn^{3+} TPP (Figure 3; 1 GM $= 1 \times 10^{-50}$ cm^4 s^{-1}). The difference in $\delta_{\max}$ values can be attributed to the increase in the transition dipole moment, M_{01}, of Mn^{3+} TPP over that of Fe^{3+} TPP. For metal-free TPP, $\delta < 10$ GM in the spectral range of our experiments.[9] Therefore, Mn^{3+} and Fe^{3+} ions enhance two-photon absorption intensity by at least an order of magnitude.

A comparison of the one- and two-photon spectra (Figure 3, the energy scale in the upper axis reflects a two-photon process) offers further support for the assignment of the two-photon absorption bands (dashed lines) to intramolecular charge transfer. The two-photon transitions do not originate in the π network of the macrocycle, as they are not allowed by the selection rules. If the selection rules for the two-photon processes are relaxed due to symmetry breaking from distortion of the macrocycle in the solid state, two-photon absorption would be stronger into the vibronic Q(0,1) band than into the purely electronic Q(0,0) band.[9] Our results show the opposite trend: two-photon absorption is stronger into the region of the Q(0,0) band than into that of the Q(0,1) band. Additionally, the porphyrin macrocycle's two-photon states were predicted to have much higher energies than those observed in our experiments.[10]

Shifts in the energies of the two-photon states, E_2, suggest which molecular orbitals give rise to the two-photon CT transitions (according to the four orbital model, Figure 1B). For Fe^{3+} and Mn^{3+} TPP, the metal d_{xy}, d_π, and d_{z^2} orbitals are in the HOMO/LUMO gap of the macrocycle's π orbitals. The Fe^{3+} ion's d_{xy} orbital is very close in energy to the a_{1u},a_{2u} orbitals,[11] and the Fe^{3+} TPP two-photon state energy determined in our experiments is very close in energy to the Q(0,0) state. This suggests involvement of the d_{xy} orbital in the two-photon transition, $d_{xy} \rightarrow \pi^*$. For the Mn^{3+} ion, the d_{xy} orbital is at a higher energy than the macrocycle's a_{1u},a_{2u} orbitals.[11] If the two-photon transition originates from the d_{xy} orbital, the Mn^{3+} TPP state will be at a lower energy than that observed for Fe^{3+} TPP. The experimental results agree with this predicition (Table 1 and Figure 3). Definite assignment of the molecular orbitals involved in the two-photon transition will require quantum chemical computations for molecular excited states. Such studies are difficult for transition metal complexes with an unfilled d electron shell.[12]

While the Co^{2+} d_{xy} orbital is at an energy similar to those of the Mn^{3+} and Fe^{3+} ions,[13] we did not observe CT transitions in Co^{2+} TPP γ spectra. The much weaker transition dipole moment, M_{01}, of this metalloporphyrin could account for this result. While the CT absorption bands have $\epsilon = 2300$ M^{-1} cm^{-1} for Fe^{3+} TPP and $\epsilon = 10000$ M^{-1} cm^{-1} for Mn^{3+} TPP, the corresponding extinction coefficient of Co^{2+} TPP was only $\epsilon \approx 75$ M^{-1} cm^{-1}.[14] The small ϵ value implies that the M_{01} of Co^{2+} TPP is too small to promote amplification of the two-photon processes. The two-photon absorption enhancement in linear conjugated oligomers is also dependent on M_{01}.[15]

In summary, Fe^{3+} and Mn^{3+} ions enhance the second hyperpolarizability, γ, and two-photon absorption cross-section, δ, of transition metal porphyrins by at least an order of magnitude. The enhancement is dependent on the one-photon transition dipole moment. A two-photon $d_{xy} \rightarrow \pi^*$ charge-transfer transition was observed for Fe^{3+} and Mn^{3+} tetraphenyl porphyrins for the first time, and suggest a new approach to enhance optical properties of porphyrin materials.

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Supporting Information Available: Metalloporphyrin film characterization, DFWM kinetics and spectra, data analysis used to obtain γ spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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