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. Such applications include fluorescence microscopy and photodynamic therapy with two-photon excitation, 3D microfabrication, and sensor protection. 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. In this report, we consider the effect of transition metal ions on the porphyrin γ and δ values. 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(III), Mn(II), and Co(II) TPP are shown in Figure 1A. The widely used four orbital model (a1u, a2u, HOMO and e1g LUMO, Figure 1B) qualitatively explains the origin of porphyrin B and Q bands. For Fe(III) and Mn(II) TPP, mixing of the metal d and macrocycle π orbitals leads to additional peaks in the absorption spectrum. For Fe(III) TPP, these CT transitions involve the π (a1u, a2u) orbitals of the macrocycle and the metal ion’s dxz orbital (π−dxy). For Mn(II) TPP, the CT bands include the π (b2g)−dxz (λmax = 432 nm) and π (a1u−a2u)−dxz (λmax = 638 nm) transitions. 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(II) TPP absorption spectrum suggests that the mixing of the Co(II) ion’s d orbitals with the macrocycle’s π system is less efficient. Thus, comparison of Co(II) TPP and Mn(II) Fe(III) 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(III) TPP and ~1250 nm for Mn(II) TPP. The Co(II) 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.

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:

\[
\gamma \propto - \frac{M_{01}^2}{(\omega_1 - \omega - i\Gamma)^3} + \frac{M_{01}^2 M_{12}^2}{(\omega_1 - \omega - i\Gamma)(\omega_2 - 2\omega - i\Gamma)}
\]

(1)

where \(M_{01}\) and \(M_{12}\) are the transition dipole moments for the 0→1 and 1→2 transitions, \(\omega\) is the experimental frequency, \(\omega_1\) and \(\omega_2\) 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 \(\Gamma\) accounts for the linewidths. Analysis of the γ spectra yields the \(M_{12}\), \(E_2\), and \(\Gamma\) 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(III) TPP two-photon state has a higher energy than that of Mn(II) TPP. Both porphyrins have \(M_{12}\) values of 4.2 D.
Table 1. Linear and Nonlinear Spectroscopic Properties of the Metalloporphyrin Films

<table>
<thead>
<tr>
<th>Metal</th>
<th>(M_0(\Omega)^\text{a} )</th>
<th>(M_2(\Omega)^\text{b} )</th>
<th>(\epsilon_1(\text{cm}^2/\text{M})^\text{a} )</th>
<th>(\epsilon_2(\text{cm}^2/\text{M})^\text{a} )</th>
<th>(\Gamma(\text{cm}^{-1})^\text{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{3+})</td>
<td>3.85</td>
<td>4.2</td>
<td>15868</td>
<td>16050</td>
<td>1150</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>1.3</td>
<td>4.2</td>
<td>14300</td>
<td>17400</td>
<td>900</td>
</tr>
</tbody>
</table>

\(^{a}\) 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, \(\delta\), we consider the imaginary component of hyperpolarizability, \(\text{Im}\ \gamma\). The cross-section \(\delta\) can be obtained from:

\[
\delta = \frac{6\pi^2\hbar^4}{\epsilon_0^2\lambda^3} \text{Im}\ \gamma
\]

where \(\epsilon_0\) is the electric constant, \(\eta\) is the index of refraction, and \(\lambda\) is the wavelength. Application of eq 2 to the \(\gamma\) data yields \(\delta_{\text{max}} = 82\ \text{GM for Fe}^{2+}\ \text{TPP and } \delta_{\text{max}} = 164\ \text{GM for Mn}^{3+}\ \text{TPP (Figure 3; 1 GM = 1 x 10}\^{-50}\ \text{cm}^2/\text{M}^2/\text{s}). The difference in \(\delta_{\text{max}}\) values can be attributed to the increase in the transition dipole moment, \(M_{\text{01}}\), of Mn\(^{3+}\) TPP over that of Fe\(^{3+}\) TPP. For metal-free TPP, \(\delta < 10\ \text{GM in the spectral range of our experiments}^\text{f}.\) 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 \(\pi\) 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.\(^\text{g}\) 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.\(^\text{h}\)

Shifts in the energies of the two-photon states, \(E_T\), 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 \(d_M\), \(d_N\), and \(d_{\pi}\) orbitals are in the HOMO/LUMO gap of the macrocycle’s \(\pi\) orbitals. The Fe\(^{3+}\) ion’s \(d_{\pi}\) orbital is very close in energy to the \(\pi_{1u}\) and \(\pi_{2u}\) orbitals,\(^\text{h}\) 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 \(d_{\pi}\) orbital in the two-photon transition, \(d_{\pi}\rightarrow\pi^*\). For the Mn\(^{3+}\) ion, the \(d_{\pi}\) orbital is at a higher energy than the macrocycle’s \(\pi_{1u}\) and \(\pi_{2u}\) orbitals.\(^\text{h}\) If the two-photon transition originates from the \(d_{\pi}\) 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 prediction (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.\(^\text{i}\)

While the Co\(^{2+}\) \(d_{\pi}\) orbital is at an energy similar to those of the Mn\(^{3+}\) and Fe\(^{3+}\) ions,\(^\text{j}\) we did not observe CT transitions in Co\(^{3+}\) TPP \(\gamma\) spectra. The much weaker transition dipole moment, \(M_{01}\), of this metalloporphyrin could account for this result. While the CT absorption bands have \(e = 2300\ \text{M}^{-1}\ \text{cm}^{-1}\) for Fe\(^{3+}\) TPP and \(e = 10000\ \text{M}^{-1}\ \text{cm}^{-1}\) for Mn\(^{3+}\) TPP, the corresponding extinction coefficient of Co\(^{3+}\) TPP was only \(e \approx 75\ \text{M}^{-1}\ \text{cm}^{-1}\). The small \(e\) value implies that the \(M_{01}\) of Co\(^{3+}\) 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 \(M_{01}\).\(^\text{j}\)

In summary, Fe\(^{3+}\) and Mn\(^{3+}\) ions enhance the second hyperpolarizability, \(\gamma\), and two-photon absorption cross-section, \(\delta\), 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 \(d_{\pi\rightarrow\pi^*}\) 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 \(\gamma\) spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References