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Modified (22π) Smaragdyrins with Large Two-Photon Absorption Cross Section: A Structure Function Correlation

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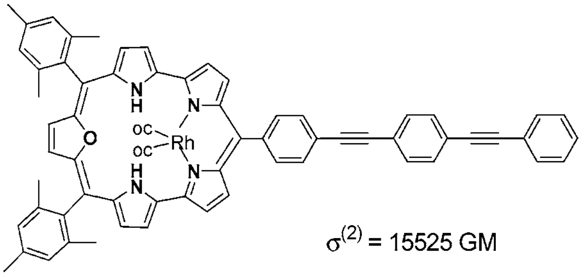
ABSTRACT



Two-photon absorption (TPA) cross-section values for a series of 22π smaragdyrins bearing phenylacetylenylphenyl and [(phenylacetylenyl)-phenylacetylenyl]phenyl meso links and their Rh(I) derivatives are reported.

Molecules which exhibit large third-order nonlinear optical response have attracted considerable attention because of their diverse technological applications.[1] Recent research on such molecules has concentrated on understanding the structure−function correlation with an aim of ultimately assembling an optical device. Various organic molecules which contain π-conjugated electrons with appropriate donor acceptor groups exhibit moderate to large two photon absorption (TPA) cross section $\sigma^{(2)}$. Many organic dyes based on hetroaromatics,[2] dendritic triphenylamine,[3] and anthracene derivatives with a variety of donor−acceptor substituents[4] exhibit $\sigma^{(2)}$ value in the range of (100−5000 GM). More recently, various porphyrin systems have been studied for their two photon absorption cross section because of their large π electron delocalization, flat structure, and high thermal stability. For example, fused diporphyrins,[5] meso-meso- and alkyne-linked porphyrins,[6] butadiyne linked-self-assembeled porphyrins,[7] and aggregated porphyrins[8] have been investigated, and the $\sigma^{(2)}$ value in these range from 100 to 15400 GM. To understand a correlation between two photon absorption cross-section values and molecular structures of porphyrins, more studies are required on porphyrins of diverse architecture. Very recently, we have reported large TPA cross-section values for expanded porphyrin[9] systems

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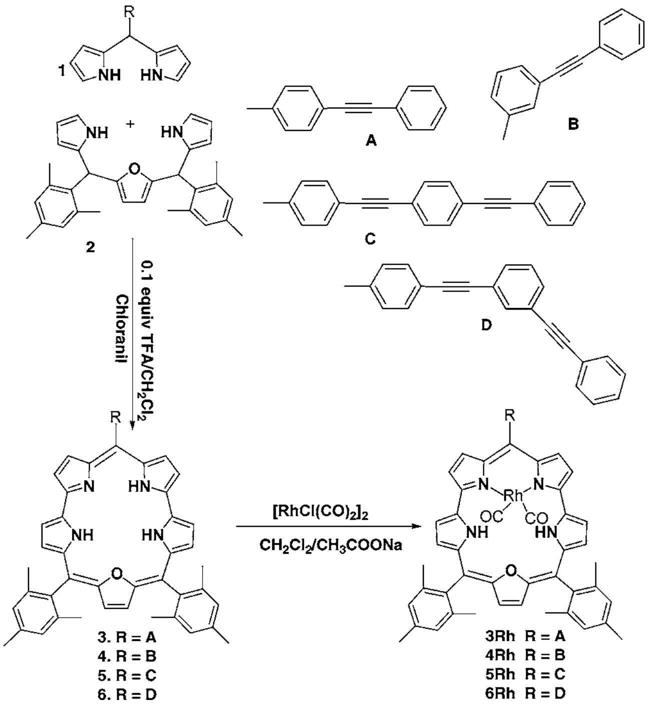
containing 26π and 34π electrons. Another idea we wanted to try is the effect of extended conjugation at the meso carbon of an 22π macrocycle. In this work, we have used phenylacetylenyl substituents at one of the meso positions of 22π smaragdyrin and measured their two photon absorption (TPA) cross-section values. It has been shown that the extension of conjugation at the meso position significantly enhances the $\sigma^{(2)}$ values. Furthermore, substitution of Rh metal in the cavity of the macrocycle results in an increase of $\sigma^{(2)}$ values by 2−3 orders of magnitude.

The synthetic strategy involved well-known [3 + 2] acid-catalyzed oxidative coupling methodology using appropriate precursors. The desired phenylacetylenylphenyl and [(phenylacetylenyl)phenylacetylenyl]phenyl substituents were incorporated in the dipyrromethane unit **1** by standard methods, and this was coupled with the oxatripyrrane **2** using 0.1 equiv of trifluoracetic acid in dichloromethane followed by chloranil oxidation to get the desired smaragdyrins[10] (**3**−**6**) Scheme 1. The metalation of free base derivatives was done using di-μ-chlorobis[dicarbonylrhodium(I)], and the purification was done by silica gel column chromatography. In the present study the $\sigma^{(2)}$ value are measured by using a standard open aperture Z-scan technique for 1 cm long sample cells (for details, see the Supporting Information). Figure 1 shows the open aperture trace of **5 Rh**. The TPA spectra at the 780 nm region indicate that two photon-allowed states exist at 390 nm, which corresponds to the high energy soret band region; this feature is an analogous result observed in other porphyrin systems.[5]

Scheme 1. Synthesis of Smaragdyrins and Their Metal Derivatives



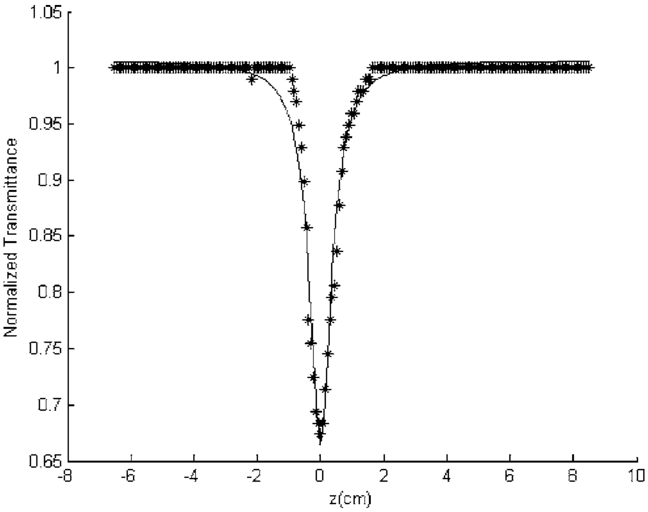


Figure 1. Open aperture Z-scan traces of **5Rh**. Solid lines are the best fitted curves of experimental data.

At 780 nm, the one-photon absorption spectral intensity of smaragdyrins is nearly zero. The one-photon absorption spectra of **4** and **4Rh** is shown in Figure 2. The $\sigma^{(2)}$ value for compounds **3**−**6** and their rhodium derivatives were measured at 780 nm wavelength and 100 fs pulse width and are listed in Table 1. The general features of these findings are as follows. (a) The TPA cross section $\sigma^{(2)}$ value increases with conjugation length and depends on the nature of isomers and the number of phenylacetylene units attached to the meso phenyl of smaragdyrin skeleton. In general, the para isomer

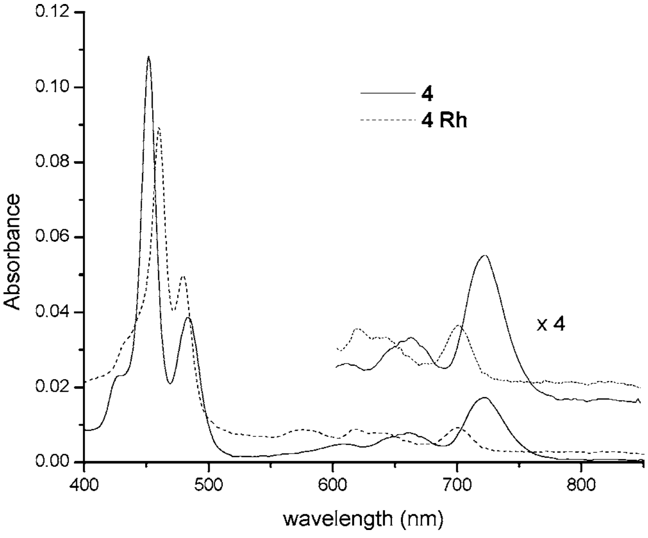


Figure 2. UV−vis absorption spectra of **4** and **4Rh**.

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Table 1. Observed $\sigma^{(2)}$ Values for Smaragdyrins and Their Metal Derivatives

compd	$\sigma^{(2)}$(GM)
3	1215
4	926
5	7839
6	6226
3Rh	4496
4Rh	1537
5Rh	15525
6Rh	10523

show larger values relative to the meta isomer. This is attributed to the disruption in the conjugation for the meta isomer relative to the para isomer. From absorption spectral studies, Melinger and co-workers have recently shown that upon meta branching there is loss of vibronic structure resulting in the disruption of π electron delocalization over the three linear benzene rings.[11] (b) The large increase in the $\sigma^{(2)}$ value observed for **5** and **6** relative to **3** and **4** are attributed to the increase in the number of phenylacetylene unit from one to two resulting in increased conjugation. (c) Upon metalation, there is increase in the value of $\sigma^{(2)}$ relative to corresponding free base smaragdyrin. The substitution of the transition metal is expected to perturb the π electron system of the ring resulting in the reduction in HOMO−LUMO gap. Metal−ligand charge-transfer interaction (both MLCT or LMCT) and metal d−d interactions are known to contribute to the perturbation of the π electron system.[12] (d) **5Rh** shows largest $\sigma^{(2)}$ value in this series.

Thus, the observed increase in $\sigma^{(2)}$ value upon metalation is consistent with these results. To the best of our knowledge, the $\sigma^{(2)}$ value of 15525 GM observed for **5 Rh** is highest in the literature for a 22 π macrocycle. The 380 cm^{-1} red shift of the Soret band upon metalation is consistent with the reduction in HOMO−LUMO gap.

In summary, this paper reports syntheses of four new 22π smaragdyrin systems and their Rh(I) derivatives. It has been shown that the TPA cross section $\sigma^{(2)}$ value depends on the nature of the links (meta vs para), the number of phenylacetylene units link to the meso phenyl group, and metal coordination.

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Supporting Information Available: Experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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