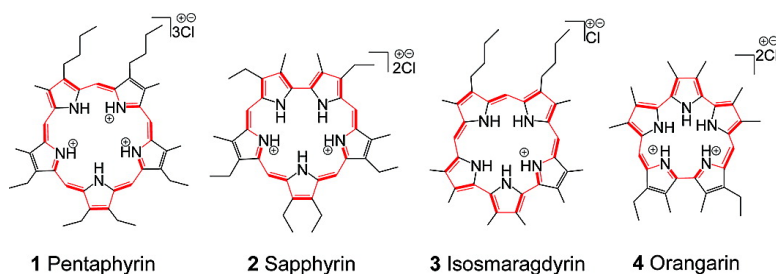


## Nonlinear Optical Properties as a Guide to Aromaticity in Congeneric Pentapyrrolic Expanded Porphyrins: Pentaphyrin, Sapphyrin, Isosmaragdyrin, and Orangarin

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# Nonlinear Optical Properties as a Guide to Aromaticity in Congeneric Pentapyrrolic Expanded Porphyrins: Pentaphyrin, Sapphyrin, Isosmaragdyrin, and Orangarin

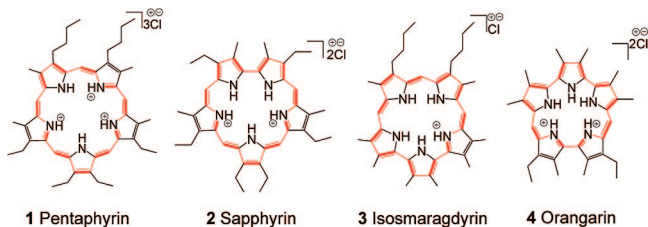
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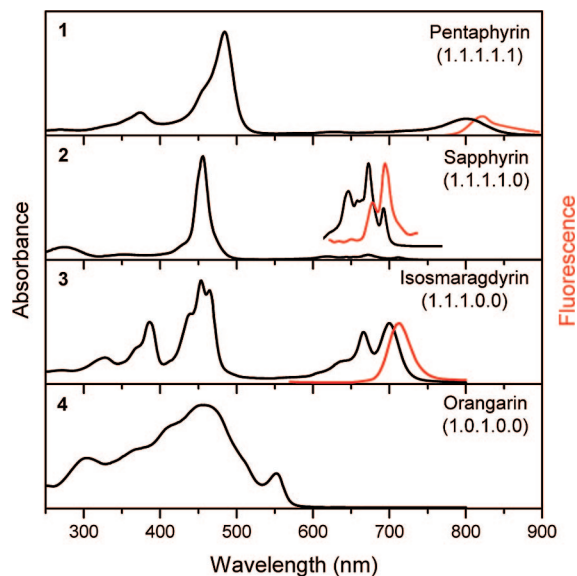
Many expanded porphyrins are characterized by extended  $\pi$ -conjugation pathways and, as a consequence, display absorption and emission features in the NIR (near-infrared) region.<sup>1</sup> Recently, we have explored the relationship between the nonlinear optical (NLO) properties (two-photon absorption (TPA)) and aromaticity in expanded porphyrins using femtosecond Z-scan analyses and NICS (nucleus-independent chemical shifts) calculations.<sup>2</sup> However, such correlations, which could provide key insights into structure–aromaticity effects, have yet to be extended in a systematic way to expanded porphyrins containing five pyrrole rings, even though these are among the most widely studied of all expanded porphyrins<sup>3</sup> and a class of pyrrolic macrocycles that has attracted recent attention as potential drug leads.<sup>4</sup> In this Communication, we report the two-photon absorption properties of a set of four pentapyrrolic expanded porphyrins. We find that the NLO properties, defined by the TPA cross-section values of **1–4**, correlate well with the corresponding calculated NICS(0) values and thus provides a useful quantitative guide to aromaticity in this closely matched series of conjugated macrocycles.

## Chart 1. Pentapyrrolic Expanded Porphyrins Used in This Study<sup>a</sup>



<sup>a</sup> Bold double bonds, shown in red, indicate the  $\pi$ -bonding interactions involved in the proposed overall conjugation pathway.

While a large number of oligopyrrolic macrocycles are now known, series **1–4** was specifically chosen because it represents a set of congeners with (i) essentially the same local chemical environment for the constituent pyrrole rings, (ii) good solubility in the same solvent ( $\text{CH}_2\text{Cl}_2$ ), and (iii) two different, albeit well-defined, electronic configurations (i.e., 22  $\pi$ -electrons for **1–3**, and 20  $\pi$ -electrons for **4**). This means these compounds may be qualitatively assigned as aromatic (pentaphyrin **1**, sapphyrin **2**, and isosmaragdyrin **3**) or antiaromatic (orangarin **4**), respectively, according to Hückel's  $[4n + 2]$  rule. Within the context of this broad assessment, however, it is important to quantify the degree of aromaticity and to find new experimental probes for this key molecular feature. The goal of this study is to probe the extent to which nonlinear optical effects could provide this information.



**Figure 1.** Absorption and emission spectra of **1–4** in  $\text{CH}_2\text{Cl}_2$ .

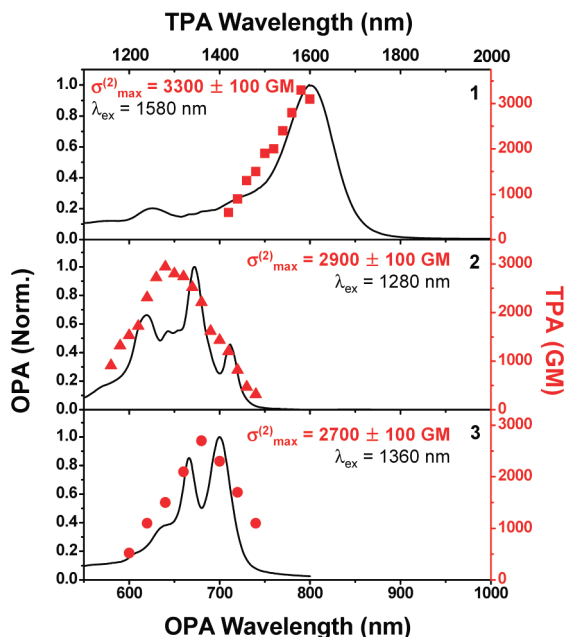
The absorption maxima of the Q-like bands appear at 801, 712, 700, 552 nm for **1–4**, respectively. If the  $\pi$ -electrons within the respective monocyclic conjugation pathways are the sole contributors to the absorption bands in accord with a simplistic particle-in-a-box model, the three aromatic species **1–3** would be expected to exhibit the similar HOMO–LUMO gaps. However, the experimental findings reveal differences in the Q-like band maxima that reflect, presumably, either (i) additional delocalized conjugation effects due to, for example, extra  $\pi$ -electrons present in the pyrrole rings or (ii) more complex  $\pi$ -electronic resonance structures that change the effective monocyclic  $\pi$ -conjugation pathways in **1–3**, or some combination thereof.

Compared to the Hückel aromatic species **1–3**, the absorption spectrum of the antiaromatic expanded porphyrin **4** is extremely broad (see Supporting Information (SI)).<sup>2–5</sup> The aromatic pentapyrrolic macrocycles **1–3** also display appreciable fluorescence, whereas no appreciable fluorescence is seen for the antiaromatic species **4**.

The nonfluorescent nature of **4** is consistent with the fact that the excited singlet ( $\pi, \pi^*$ ) state undergoes an ultrafast decay with a time constant of 8.7 ps, as determined using femtosecond transient absorption techniques. The fast decay in **4** is thought to reflect the greater density of states resulting from the presence of partially unoccupied orbitals, a feature that distinguishes this species from its aromatic congeners **1–3**.<sup>6</sup> In contrast, **1–3** exhibit decay time constants greater than 2 ns for the excited ( $\pi, \pi^*$ ) and a few tens of microseconds for the respective triplet ( $\pi, \pi^*$ ) states (see SI).

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**Figure 2.** One-photon absorption (OPA) and two-photon absorption (TPA) spectra of **1–3** in  $\text{CH}_2\text{Cl}_2$ .

As can be inferred from their chemical structures, the  $\pi$ -conjugation pathways become longer on going from **3** to **1**. As a consequence, the HOMO–LUMO energy gap becomes smaller, and the molecular polarizability is expected to be larger, according to Koopmans' theorem.<sup>2</sup> The TPA cross-section values were found to follow the same tendency, namely 3300, 2900, 2700 GM for **1**, **2**, and **3**, respectively. In other words, larger TPA values were seen for molecules containing smaller HOMO–LUMO gaps; these showed similar one-photon absorption (OPA) and TPA wavelength maxima, presumably as the result of accessing the same excited-state with allowed symmetry.

The NICS(0) values, a quantitative measure of aromaticity,<sup>7</sup> were found to follow the same trend, namely  $-16.2$ ,  $-14.9$ ,  $-14.1$  ppm for **1**, **2**, and **3**, respectively. Such findings are consistent with the diatropic ring current in **1** being higher than in **3**. In contrast, the antiaromatic system **4** exhibits a relatively small TPA value of 1200 GM, and a strong paratropic ring current (NICS(0) =  $+42.9$  ppm). On the basis of these experimental and computational results, we suggest that the TPA cross-section values can serve as a quantitative measure of aromaticity, at least within an appropriately matched set of aromatic and antiaromatic compounds.

Because of their congeneric nature, we felt that compounds **1–3** could be used to explore in greater depth the molecular origins of the observed aromaticity. Specifically we noted that even though the number of methine bridges increases on going from **3** to **1**, the associated monocyclic conjugation pathways should be similar across the series **1–3**; this is because all three systems contain 22  $\pi$ -electron peripheries. Since, as reported previously,<sup>2</sup> the TPA cross-section values are expected to be dependent on the  $\pi$ -conjugation pathways, the enhanced TPA cross-section value seen for **1** can be considered to reflect an increased diatropic ring current relative to **3**. In this context, it should be noted that a previous theoretical report by Cho et al., involving a series of octupolar electron donor–acceptor molecular systems, also concludes that the first hyperpolarizability is linearly proportional to the TPA cross-section values.<sup>8</sup> Although these workers did not directly mention the correlation between hyperpolarizability and BLA (bond length alternation) or between the hyperpolarizabilities, we can infer from

**Table 1.** Number of  $\pi$ -Electrons, Absorption and Emission Maxima, NICS(0) Values, and TPA Values of **1–4**<sup>a</sup>

	$\pi$ e <sup>-b</sup>	$\lambda_{\text{abs}}$ (nm) <sup>c</sup>	$\lambda_{\text{emi}}$ (nm) <sup>c</sup>	NICS (ppm) <sup>d</sup>	$\sigma^{(2)}$ (GM) <sup>e</sup>	$\tau_{\text{S}}$ (ns) <sup>f</sup>	$\tau_{\text{T}}$ ( $\mu\text{s}$ ) <sup>g</sup>
<b>1</b>	22	801	815	$-16.2$	$3300 \pm 100$	$>2$	6.6
<b>2</b>	22	712	716	$-14.9$	$2900 \pm 100$	2.43	14.9
<b>3</b>	22	700	713	$-14.1$	$2700 \pm 100$	2.40	6.8
<b>4</b>	20	552	<sup>h</sup>	$+42.9$	$1200 \pm 100$	0.0087	<sup>h</sup>

<sup>a</sup> The solvent was dichloromethane unless indicated otherwise. <sup>b</sup> Number of  $\pi$ -electrons in the monocyclic conjugation pathways. <sup>c</sup> Absorption and emission maxima. <sup>d</sup> NICS(0) values calculated at the B3LYP/6–31G\* level. <sup>e</sup> TPA values. <sup>f</sup> Singlet excited-state lifetimes. <sup>g</sup> Triplet excited-state lifetimes. <sup>h</sup> Not observed.

their results that the imaginary part of  $\gamma$  (second-order hyperpolarizability) determines the TPA cross-section values. In even earlier work, Brédas et al. showed that the BLA is a key determinant of the NLO response exhibited by conjugated organic molecules.<sup>9</sup>

In conclusion, using various spectroscopic and theoretical methods, we have demonstrated that a strong correlation exists between the experimentally determined TPA cross-section values and the presumed aromaticity, at least in the present set of pentapyrrolic expanded porphyrins. The fluorescent (aromatic) and nonfluorescent (antiaromatic) nature of the species in question was found to offer a convenient qualitative guide to the number of  $\pi$ -electrons in the periphery (i.e., Hückel's  $[4n + 2]$  rule), while more quantitative indices of aromaticity were found to correlate to the TPA cross-section values. Specifically, we found that compounds with greater aromatic character give rise to higher TPA cross-section values. Accordingly, independent of what baseline criterion is chosen to define aromaticity, we propose that the TPA cross-section values provide a useful experimental measure of conjugation effects, at least within a closely related series of compounds. Efforts to generalize this conclusion and extend it to other systems are currently underway.

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**Supporting Information Available:** Complete ref 4b, details of the syntheses, and spectroscopic measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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