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## Two-photon absorption in porphycenic macrocycles: the effect of tuning the core aromatic electronic structure†

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**Changing the core heteroatoms in porphycenic macrocycles can have a dramatic effect on the two-photon absorption properties via tuning of resonance enhancement between Q-band and Soret-band states.**

Two-photon absorption (TPA) is becoming an increasingly important area of research with many diverse potential applications including three-dimensional data storage and optical power limiting as well as biological applications such as fluorescence imaging, mechanistic studies of cell death, and non-linear photodynamic therapy (PDT).<sup>1–5</sup> In studies of cell death and PDT light is used to excite a sensitizer molecule, which ultimately undergoes intersystem crossing from a singlet to a triplet state, and subsequently energy transfer occurs to create the highly reactive singlet molecular oxygen that can induce apoptotic cell death.<sup>6,7</sup>

For biological applications a non-linear excitation process offers up several advantages. For example, the absorption range for the molecular system of interest can be extended into the tissue transparency window (700–1000 nm) where water does not strongly absorb. The quadratic dependence of absorption upon the intensity of the laser field also allows for a much greater spatial resolution. Finally, TPA can populate otherwise ‘dark’ electronic states, and these may have desired properties for the application at hand.

Of the few one-photon absorption (OPA) PDT sensitizers in current clinical use most are based around porphyrinoid ring systems or their close analogues.<sup>8</sup> These systems however do not appear to exhibit optimal optical properties for TPA applications. However, recent work has highlighted porphycence (**Pc**) based systems as displaying the desired characteristics of excellent TPA sensitizers.<sup>9</sup> From this and similar studies it is clear that the TPA cross-section at a given wavelength can be very sensitive to molecular structure. Below we report how the TPA can be tuned by changing the nature of the core heteroaromatic rings. This subtle change in the core electronics can finely tune resonance-enhancement between the Q- and Soret-states.

We have used density functional theory (DFT) to optimise the molecular structures of interest, and subsequently linear and quadratic response theory to obtain the one- and two-photon absorption strength. Previous work has shown that the Coulomb-attenuated variant of the popular B3LYP functional (CAM-B3LYP) is very accurate at modelling TPA due to the correct asymptotic behaviour in the exchange–correlation potential giving a good description of absorption to and from the virtual state in TPA (which can be written as a linear combination of the real eigenstates of the system).<sup>10,11</sup> The one-electron basis set used was the Pople type 6-31G\*, although we note the results are not particularly sensitive to basis set.

From the first residue of the quadratic response function one retrieves the two-photon transition tensor  $T$ , the calculated values of which then can be used to obtain the two-photon absorption cross-section,  $\delta$ , as shown in eqn (1.1)

$$\begin{aligned}\delta &= F\delta^F + G\delta^G + H\delta^H \\ \delta^F &= \frac{1}{30} \sum_{\alpha,\beta} T_{\alpha\alpha} T_{\beta\beta}^* \\ \delta^G &= \frac{1}{30} \sum_{\alpha,\beta} T_{\alpha\beta} T_{\alpha\beta}^* \\ \delta^H &= \frac{1}{30} \sum_{\alpha,\beta} T_{\alpha\beta} T_{\beta\alpha}^*\end{aligned}\quad (1.1)$$

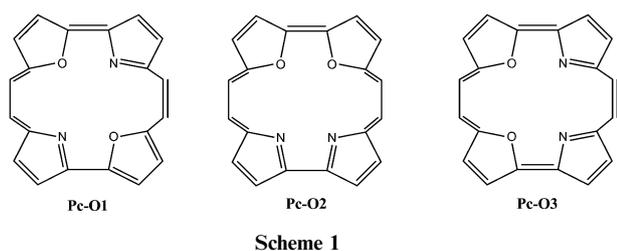
The summations are carried out over the molecular axes (*i.e.*,  $\alpha$  and  $\beta$  refers to the Cartesian coordinates  $x$ ,  $y$  and  $z$ ) and the values of  $F$ ,  $G$  and  $H$  depend on the polarisation of the incident photons. The conditions applied in this work was linear polarisation, where  $F = G = H = 2$ . The spatially dependent components of  $T$  can be expressed in a sum-over-states expression, as in eqn (1.2), where  $T$  is expressed in terms of the transition moments between initial,  $i$ , virtual,  $v$ , and final states,  $f$ .

$$T_{\alpha\beta} = \sum_v \frac{\langle i|\mu_\alpha|v\rangle\langle v|\mu_\beta|f\rangle}{\omega_v - \omega} + \frac{\langle i|\mu_\beta|v\rangle\langle v|\mu_\alpha|f\rangle}{\omega_v - \omega}\quad (1.2)$$

The excitation frequency of the  $v$ -th state is denoted by  $\omega_v$ , the frequency of the irradiating light  $\omega$  and  $\mu_\alpha$  and  $\mu_\beta$  are components of the electric dipole moment operator. The sum-over-states expression is useful when interpreting and discussing data, but it

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is important to note that the response calculation provides a value of  $T$  without carrying out the summation explicitly.

The **Pc** systems investigated here were dioxaporphycenes, where pyrrolic nitrogen atoms in **Pc** were substituted for oxygen atoms systematically, as per Scheme 1. All geometry optimisations in the Gaussian 09 program<sup>12</sup> at B3LYP//6-31G\* level of theory yielded completely planar structures with symmetries ranging from  $C_{2h}$  to  $C_{2v}$  depending on aromaticity pattern (Fig. 1).

The OPA results, retrieved from the linear response CAM-B3LYP//6-31G\* calculations, are summarised in the simulated absorption spectra in Fig. 2, and show clear Soret ( $\sim 300$ – $350$  nm) and Q-bands ( $\sim 500$ – $600$  nm) for all species. There are no major effects observed on the spectral profile upon substitution of the core heteroatoms, compared with porphycene. This is an expected behaviour as the substitution of nitrogen atoms in porphyrins has been demonstrated previously to have little effect upon the linear electronic spectra.<sup>13</sup> This also holds true for extended porphyrins where core nitrogens have been systematically substituted for S and Se heteroatoms, with little effect on the OPA spectra.<sup>14</sup>

The TPA spectra from the quadratic response CAM-B3LYP//6-31G\* calculations, calculated in a local version of the Dalton software,<sup>15</sup> are presented in Fig. 3. It is important to note that the absorption wavelength indicated is the total for the two-photon process, *i.e.* the actual excitation takes place at twice the wavelength. The spectra all show a main absorption in the Soret-region ( $\sim 250$ – $270$  nm), and there is a significant disparity between the calculated TPA cross-sections for the four isomers. These two facts can be explained in terms of one-photon resonance enhancement of the absorption. This phenomenon is best discussed in terms of the sum-over-states expression in eqn (1.2), where the magnitude of  $T$  depends on the difference between the excitation frequency of the  $\nu$ -th state and the frequency of the total excitation, from the magnitude of the denominator in the expression. As the virtual state can be described as a linear combination of all real eigenstates in the system, a TPA *via* a virtual state that can be described mainly in terms of a real state will be significantly enhanced. Thus, an allowed OPA Q-band transition accidentally degenerate at half the Soret excitation energy will greatly enhance the Soret TPA transition.

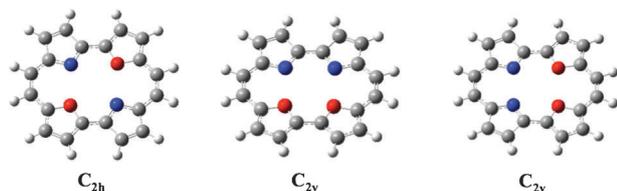


Fig. 1 Core porphycene-like heteroatom substitution pattern in systems studied for TPA.

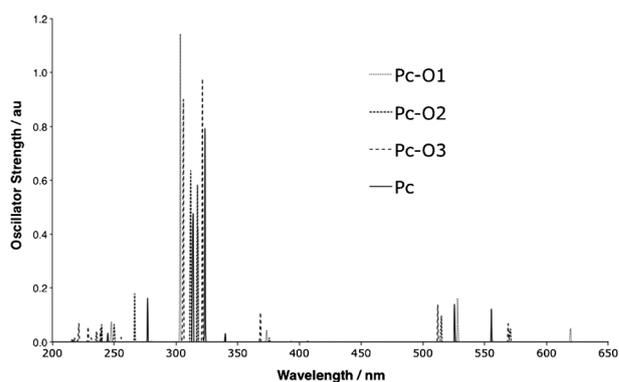


Fig. 2 One photon absorption (OPA) for porphycene and core substituted analogues.

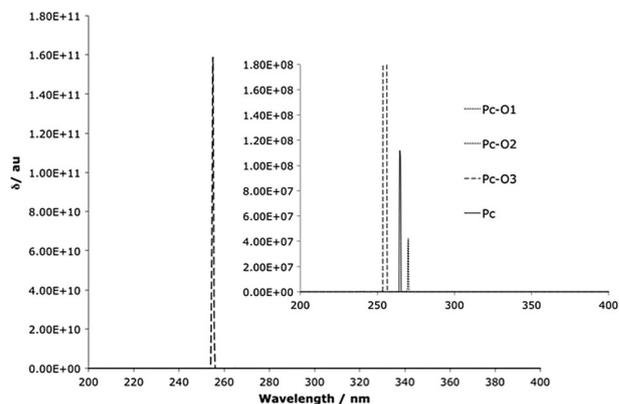


Fig. 3 Dominant two-photon absorption (TPA) for porphycene, and core-substituted analogues. Resonant absorption of two-photons of half the excitation energy to the final state is assumed.

This feature has been used to explain the greater TPA cross-section in tetraphenyl porphycene compared to tetraphenyl porphyrins. This feature also accounts for the whole series investigated here exhibiting strong absorption in the Soret-region, as a result of near resonance with a state in the Q-band, as seen on the corresponding OPA spectrum. There is no corresponding enhancement of TPA into the Q-region as there are no allowed one-photon transitions to a state  $\nu$  at a frequency near that of the total excitation frequency. This leads to very small TPA cross-sections in the Q-region, at wavelengths longer than 350 nm.

The resonance enhancement argument also rationalises the very large disparity between the total TPA cross-section of the systems described. The main TPA peak in the **Pc-O2** molecule has a cross-section of  $\delta \sim 4.95 \times 10^5$  a.u. at  $\sim 240$  nm, whilst **Pc-O3** has a significantly larger cross section value of  $\delta \sim 1.64 \times 10^{11}$  a.u. at  $\sim 255$  nm (Table 1). This enormous difference, by nearly six orders of magnitude, can be explained by inspection of the OPA spectra for these two systems. They reveal an allowed transition in the Q-region at 514 nm and 512 nm for **Pc-O2** and **Pc-O3** respectively. These correspond to two-photon transitions *via* a virtual state that is separated from a real state by  $\sim 18$  nm in **Pc-O2** and a virtual state that is separated by only  $\sim 1$  nm from a real state in **Pc-O3**.

One important point to note is that **Pc** and **Pc-O1** are centrosymmetric and thus may naively be expected to have a

**Table 1** Two-photon absorption data for porphycene and core-substituted analogues

<b>Pc-O1</b>		<b>Pc-O2</b>	
Wavelength/nm	$\delta/a.u.$	Wavelength/nm	$\delta/a.u.$
389	1.03E+03	570	1.64E+03
270	4.34E+07	393	6.43E+02
254	1.04E+06	317	1.86E+01
247	2.01E+05	247	8.64E+02
242	2.89E+05	<b>239</b>	<b>4.94E+05</b>
241	2.92E+03	439	7.50E+00
230	2.34E+04	264	3.84E+01
214	1.99E+03	195	4.52E+01
210	6.38E+03	191	7.02E-02
202	2.01E+04	181	1.32E-01
<b>Pc-O3</b>		<b>Pc</b>	
Wavelength/nm	$\delta/a.u.$	Wavelength/nm	$\delta/a.u.$
568	2.19E+03	359	8.42E+02
368	7.35E+02	300	3.42E+04
306	4.93E+02	265	2.37E+08
<b>255</b>	<b>1.64E+11</b>	248	3.78E+05
241	3.46E+05	239	2.42E+04
340	1.68E+01	298	8.51E+02
317	6.03E+01	226	1.93E+01
211	1.90E+01	179	1.10E-01
188	1.30E+00	175	2.93E+01
179	7.52E+00	169	3.62E-01

TPA to a state higher in energy than the OPA, due to the parity selection rules being reversed in a non-linear excitation process compared to a linear one. This is not the case here, as also found in a previous experimental and theoretical study on a related Pc system.<sup>9</sup> This is due to the fact there is a large density of states in this spectral region, and several close lying states of different parity. As shown in ref. 9 the use of parity arguments when detailing TPA in such large systems requires careful consideration.

We also note that in cases of strong resonance absolute values of the cross-section can be problematic, and so called damped response functions are currently being developed.<sup>16</sup> Here though the main point is that the subtle shifts in the Q-band states, by changing the core heteroatoms, are enough to bring the Soret TPA transitions into and out of resonance. The transition moments between the excited states contributing to the resonance can be calculated from the double-residue of the quadratic response function, and here we find much larger values for the core-modified porphycenes. Such large changes in TPA behaviour involving relatively minor changes in molecular structure highlight that such non-linear optical properties can be much more sensitive to structural features,

and this will be important for the development of systems having the desired spectral properties.

In conclusion, we have demonstrated that the changes in electronic core structure of a series of dioxaporphycene macrocycles, whilst not having a very large impact on the linear absorption spectra, affords an unexpected effect upon the non-linear absorption. These results suggest that the tuning of TPA does not have to be carried out through large structural changes, and small electronic factors can be utilised to improve the magnitude of the TPA cross-section. The theoretical data presented here indicates that there is a significant amount of information on the photochemical behaviour of molecules to be gained from computations that can be valuable as foundations for future experimental research and development.

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