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Drastic enhancement of two-photon absorption in porphyrins associated with symmetrical electron-accepting substitution

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Abstract

We observe a dramatic enhancement of simultaneous two-photon absorption (TPA) in a series of substituted tetraazaporphyrins with multiple electron-accepting groups and show for the first time that the TPA cross-section increases in linear proportion with the substituent's Hammett constant. The measured cross-section amounts to $\sigma_2 = 1.6 \times 10^{-47}$ cm^4 s/photon for octakis(4-nitrophenyl)-tetraazaporphine at 770 nm. This large value is explained by both the resonance enhancement by a strong $Q_x(0–0)$ linear transition and the presence in the same spectral region of a strong two-photon allowed *gerade–gerade* transition. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Two-photon absorption (TPA) is a third-order nonlinear process, in which two photons are absorbed simultaneously, without population of any real intermediate state [1, and references therein]. Due to its nonlinear (square) dependence on the instantaneous intensity of the illumination, TPA has important potential applications in 3D-optical memory, 3D-microfabrication, 3D-fluorescence imaging and photo-medicine [1,2, and references therein]. It has been suggested that TPA in tetra-pyrrolic compounds, which are the primary photosensitizers used in photodynamic therapy (PDT), can be applied to increase the depth of light penetration in tissue, and thus significantly improve the efficacy of cancer treatment [3–5].

During the past two decades there have been extensive studies of two-step absorption in tetra-pyrroles. In the process of two-step absorption, the first photon brings the molecule from the ground state to some excited electronic state. After non-radiative relaxation to the lowest excited state, the second, time-delayed photon, promotes the molecule to some higher-excited state. Tetrapyrrolic compounds which have *weak ground-state absorption* for the first photon (in visible or near-IR), but *strong excited-state absorption* for the second

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photon (at the same wavelength) have been used as reverse saturable absorbers (RSA) in power limiting experiments [6,7]. Spectroscopically, the above mentioned condition suggests that the first Q-band has to be lower in energy and *far from resonance with respect to the laser photon energy*, while the excited-state transition has to be as strong as possible and *in resonance with the laser photon energy*.

The distinctive feature of TPA is that the intermediate state is not populated at all and that two photons are absorbed simultaneously, i.e., without any time delay. Although TPA has some common features with RSA in singlet manifold, especially in terms of selection rules, efficient TPA requires two consecutive transitions which are strong for both the first and the second photons and *both close to resonance with the laser frequency*. Despite this marked difference between the requirements for the stepwise- and the simultaneous two-photon absorption, one can still use the information collected in the stepwise absorption experiments [7–9] on the strength and the position of the ground- and excited-singlet-state transitions, to predict the efficiency of TPA. Also, it has been recently shown [7] that it is possible to manipulate the wavelength and strength (red shift and enhancement) of both ground- and excited-state absorption by special chemical modification.

In contrast to the extensive studies performed on the stepwise absorption in tetrapyrrolic molecules, there are only relatively few communications available, which are reporting the measurement of the instantaneous TPA cross-section. In [3,4,10,11] it was found that the cross-section does not exceed, $\sigma_2 \sim 1$–10 GM (1 GM = 10^{-50} cm^4 s/photon). In view of large σ_2 values (10^3–10^4 GM) obtained in some new TPA-chromophores [12,13], the TPA efficiency of porphyrins appears to be very small and still needs to be optimized.

In our recent study [14] we found that in porphyrins the two-photon absorption is well described by a three-level model involving the ground, the lowest *ungerade* excited singlet and one of the low-lying *gerade* excited singlet states, which are playing the role of the initial (0), intermediate (i) and final (f) state, respectively. We also found that the TPA can be significantly enhanced

by optimizing the resonance condition for virtual transition between the ground and the intermediate state. Increased σ_2 is achieved by tuning the laser closer to the real one-photon Q(0–0) transition frequency, as well as by increasing the transition dipole moment squared, $|\boldsymbol{\mu}_{i0}|^2$, by means of chemical modification of the structure of the molecule. This approach allowed us to achieve σ_2 value up to $\sim 10^2$ GM for *meso*-phenyl-substituted tetrabenzoporphyrins [14]. To further increase σ_2, one can try to optimize the strength, $|\boldsymbol{\mu}_{fi}|^2$, and to tune the spectral position of the second virtual transition between the intermediate and final states.

In this Letter, we show that for tetraazaporphyrins it is possible to spectrally separate the shape of the 'pure' two-photon $0 \to f$ transition from the effect of resonance enhancement resulting from Q(0–0) band. This allowed us to observe the spectral peak of the two-photon-allowed *gerade–gerade* transition, what is to our knowledge the first time for porphyrins. Furthermore, by using multiple symmetrical substitution of the porphyrazine ring with different kinds of electron-accepting group, we demostarte a drastic increase of the σ_2 value in the series: tetra-*t*-butyl-tetraazaporphyrin–octa(*p*-bromophenyl)tetraazaporphyrin–octa(*p*-nitrophenyl)tetraazaporphyrin. We explain this effect by decrease of the energy detuning and by simultaneous increase of the dipole moment of both $0 \to i$ and $i \to f$ virtual transitions. We also compare our observations to the results of recent theoretical calculations [15–18], which considered the effect of attaching electron-donating or electron-accepting groups to the π-conjugated core of the porphyrin molecule.

2. Experimental

2,7,12,17-Tetra-*tert*-butyl-tetraazaporphine (Bu$_4$TAP) was purchased from Aldrich and used as received. Octakis(4-nitrophenyl)-tetraazaporphine ((NO$_2$Ph)$_8$TAP) and Octakis(4-bromophenyl)-tetraazaporphine ((BrPh)$_8$TAP) were synthesized as described in [19,20], respectively.

Our experimental setup comprised a Ti:sapphire regenerative amplifier (CPA-1000, Clark

MXR), which was operated at 1 kHz repetition rate and produces 150-fs pulses of 0.8 mJ energy per pulse. These pulses were parametrically down-converted using an optical parametric amplifier, OPA (TOPAS, Quantronix), which yields 100-fs pulses in the wavelength range from 1100 to 1600 nm. TPA spectra of molecules were obtained as fluorescence excitation spectra either by tuning the OPA or by tuning the Ti:sapphire amplifier. Relative spectra measured by this method were normalized to an absolute σ_2 value measured at one particular wavelength. Absolute cross-section values of Bu_4TAP and $(NO_2Ph)_8TAP$ were obtained by comparing fluorescence intensity under one- and two-photon excitation (see [21] and references therein for details). We usually employ the fundamental amplifier wavelength for two-photon excitation and its second harmonic for one-photon excitation. In both cases a small central part of the beam's spatial cross-section was selected with a pinhole and passed through a 1-cm cell with the sample solution. Fluorescence was collected at a right angle and focused on the entrance slit of a Jobin–Yvon TRIAX 550 monochromator with a spherical mirror. Fluorescence intensity was measured at its spectral maximum, i.e., 640 nm for Bu_4TAP and 690 nm for $(BrPh)_8TAP$ and $(NO_2Ph)_8TAP$. To justify the validity of this method, we have measured the cross-section of Rhodamine B in methanol at 782 nm. The value measured by us coincides within experimental error with that presented in [22]. For two-photon cross-section measurements all substances were dissolved in dichloromethane to such a concentration that the optical density at the second harmonic wavelength (≈ 390 nm) was less than 0.1. To measure fluorescence quantum yields, we used dilute ($<10^{-5}$ M) dichloromethane solutions of $(NO_2Ph)_8TAP$ and $(BrPh)_8TAP$ and toluene solution of Bu_4TAP and 392-nm excitation. Singlet oxygen luminescence was recorded with a liquid nitrogen-cooled Ge-detector.

3. Results and discussion

Fig. 1 shows linear absorption spectra (continuous lines) of the three compounds in dichlorom-

ethane. These spectra are consistent with literature data [19,20,23]. Note a low-frequency shift and broadening of the spectrum for $(NO_2Ph)_8TAP$ and $(BrPh)_8TAP$, as compared to Bu_4TAP. About 2-fold broadening and almost the same maximum extinction coefficient give rise to about 2-fold enhancement of the oscillator strength of Q-transitions in $(NO_2Ph)_8TAP$ and $(BrPh)_8TAP$. The same figure also presents the two-photon absorption spectra (symbols) of Bu_4TAP and $(NO_2Ph)_8TAP$. It is evident that the TPA does not follow the pure electronic $Q_x(0–0)$ bands in both cases. More likely, it corresponds to some vibronic satellite of the $Q_x(0–0)$ band with a maximum offset of 1200–1400 cm^{-1}. This observation unambiguously demonstrates that the selection rules for one-photon and two-photon pure electronic transitions are mutually exclusive for these compounds. Indeed, for centro-symmetric molecules, two-photon transitions are allowed between the states of similar parity (i.e., in our case, between *gerade* states), whereas one-photon transitions are allowed between the states of opposite parity (i.e., *gerade → ungerade*). Therefore, we can state that the *tetraazaporphyrins under consideration do possess a center of symmetry*, which is very important for the foregoing discussion. Concerning the vibronic TPA transitions, observed in Fig. 1, they can be allowed for some odd molecular vibrations, which change the symmetry of the first excited state to *gerade* one.

We now turn our attention to a region of higher excitation frequencies, adjacent to the linear $Q_x(0–0)$ band from below. For porphyrins, in this spectral region one probably starts to excite some lowest electronic *gerade–gerade* transition(s) and, furthermore, approaching the $Q_x(0–0)$ band one observes strong resonant enhancement of TPA [14]. Fig. 2 demonstrates the TPA spectra of Bu_4TAP and $(NO_2Ph)_8TAP$ in this, high-frequency spectral region. Note that the abscissa axis in Fig. 2 corresponds to the excitation frequency, which in the case of TPA is equal to one-half of the transition frequency. For all the experimental points shown in Fig. 2, we attested that the two-photon-excited fluorescence intensity had a quadratic dependence on laser power. At higher excitation frequencies, the power law gradually
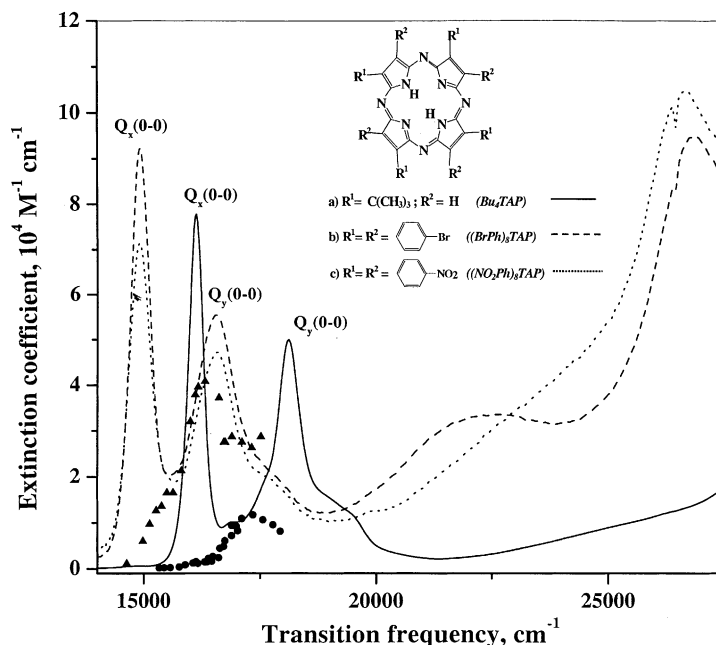
Fig. 1. Absorption spectra of Bu_4TAP (solid line), $(BrPh)_8TAP$ (dashed line) and $(NO_2Ph)_8TAP$ (dotted line). Two-photon absorption spectra of Bu_4TAP (circles) and $(NO_2Ph)_8TAP$ (triangles) are normalized such that their peak intensity roughly coincides with the peak of the corresponding linear vibronic spectra. For two-photon absorption spectra, an abscissa axis corresponds to twice excitation wavelength. Inset shows the corresponding chemical structures.

transformed into a linear one because a 'hot' one-photon absorption in Q-band started to compete with TPA.

Similarly to other porphyrins [14], the TPA efficiency of tetraazaporphyrins continuously increases towards higher frequencies, see Fig. 2. In order to get deeper insight into the nature of this behavior, we consider the frequency dependence of TPA, derived from a simple three-level approximation [24]:

$$\sigma_2(v_p) = A v_p^2 \frac{|\boldsymbol{\mu}_{i0}|^2 |\boldsymbol{\mu}_{fi}|^2}{(v_{i0} - v_p)^2 + \Gamma_{i0}^2} g(2v_p). \tag{1}$$

Here A is a combination of the universal constants, refractive index of the medium and a factor describing the mutual orientation of $\boldsymbol{\mu}_{i0}$ and $\boldsymbol{\mu}_{fi}$,

$$g(2v_p) = \frac{1}{\pi} \frac{\Gamma_{f0}}{(2v_p - v_{f0})^2 + \Gamma_{f0}^2}, \tag{2}$$

is the normalized line shape function for the two-photon transition, v_p is the photon frequency, v_{mn}

and Γ_{mn} is the frequencies and homogeneous linewidths of the $m \to n$ transition ($m, n = 0, i, f$).

In order to determine the spectral region where the TPA response of tetraazaporphyrins is completely dominated by resonance enhancement via $Q_x(0–0)$ transition, we apply the following analysis. Suppose that that (a) $\Gamma_{i0} \ll v_{i0} - v_p \ll v_p$ and (b) $| 2v_p - v_{f0} | \ll \Gamma_{f0}$ and $v_{i0} - v_p \ll \Gamma_{f0}$. The first inequality is normally fulfilled for our experimental conditions, because $\Gamma_{i0} = 100–200$ cm^{-1}, $v_{i0} - v_p = 2000–4000$ cm^{-1} and $v_p = 12000–14000$ cm^{-1}. However, the validity of condition (b) is not obvious a priori and is a subject of the following investigation. Let us first suppose that this condition is valid, then

$$\sigma_2(v_p) \propto \frac{|\boldsymbol{\mu}_{i0}|^2 |\boldsymbol{\mu}_{fi}|^2}{(v_{i0} - v_p)^2}. \tag{3}$$

The normalized spectral derivative of the two-photon molecular absorptivity depends in that case only on the value of detuning:
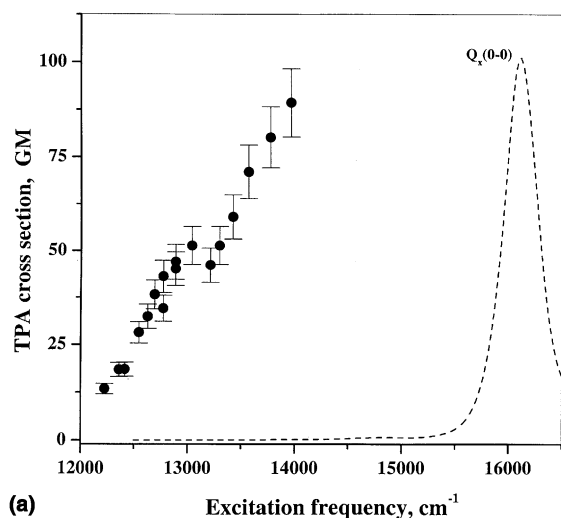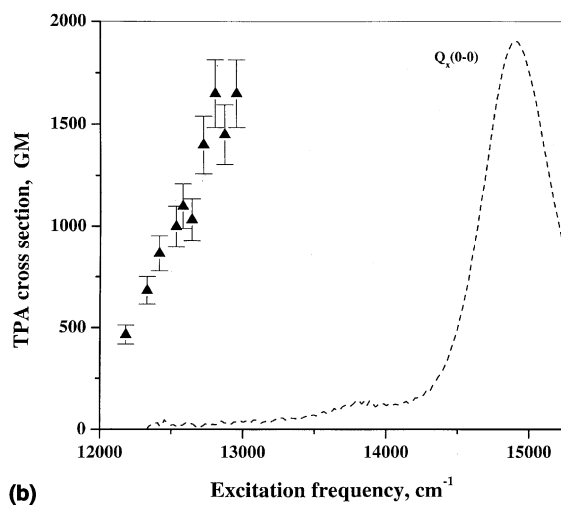
(a)

(b)

Fig. 2. Two-photon absorption spectra of Bu_4TAP (a) and $(NO_2Ph)_8TAP$ (b). Abscissa axis corresponds to excitation photon frequency. Onset of linear photon absorption (dashed lines) is presented in relative units for comparison.

$$\frac{1}{\sigma_2}\frac{d\sigma_2}{dv_p} = \frac{2}{v_{i0} - v_p}. \tag{4}$$

Therefore we can obtain from the measured TPA spectrum an expected frequency of the most important one-photon transition as follows

$$v_{i0} = v_p + 2\frac{\sigma_2}{d\sigma_2/dv_p}. \tag{5}$$

An advantage of this approach lies in using only relative values of TPA and therefore does not include an error of the absolute cross-section measurement.

Fig. 3 presents the dependence of v_{i0} on v_p for Bu_4TAP and $(NO_2Ph)_8$ TAP, recalculated from the plots in Fig. 2, according to (4). The straight horizontal line represents an actual position of the $Q_x(0–0)$ maximum frequency determined from the linear absorption spectrum for both molecules. One can see that for Bu_4TAP, the calculated v_{i0} value coincides within experimental error with the real $Q_x(0–0)$ transition frequency in the range of v_p from 12 900 to 13 700 cm^{-1}. This observation unambiguously demonstrates that in this spectral
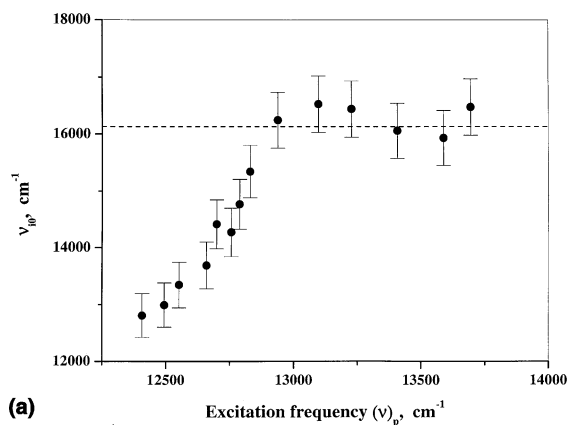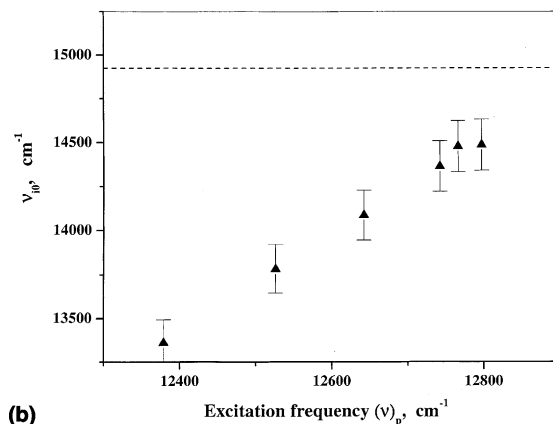

(a)

(b)

Fig. 3. The dependence of expected position of resonance frequency v_{i0} on excitation laser frequency v_p, calculated according to (4) from experimental data in Fig. 2 for Bu_4TAP (a) and $(NO_2Ph)_8TAP$ (b). Dashed horizontal lines show actual position of the first $Q_x(0–0)$ transition.

range the TPA of Bu_4TAP is completely determined by resonance enhancement by a linear $Q_x(0–0)$ transition and the $\sigma_2(v_p)$ dependence is just described by a resonance denominator in (2). On the other hand, for lower photon frequencies, $v_p = 12400–12900$ cm^{-1}, the condition $|2v_p - v_{f0}| \ll \Gamma_{f0}$ and $v_{i0} - v_p \ll \Gamma_{f0}$ is probably not fulfilled and the spectral behavior of TPA becomes sensitive to $g(2v_p)$. As for $(NO_2Ph)_8$ TAP molecule, the above condition probably fails in the entire spectral range studied here.

The fact that in a sufficiently large spectral range the TPA of both molecules is sensitive to $g(2v_p)$ allows us to obtain the spectral shape of the latter from experimental data. For this purpose we plot the quantity $\sigma_2(v_p)(v_{i0} - v_p)^2/v_p^2$ against $2v_p$ for Bu_4TAP and $(NO_2Ph)_8TAP$ in Fig. 4. According to (1), this representation should give us $g(2v_p)$. Interestingly, in both cases the $g(2v_p)$ shows a distinctive spectral peak with a maximum at $2v_p = 26450$ for Bu_4TAP and $2v_p = 25460$ cm^{-1} for $(NO_2Ph)_8TAP$, respectively. Note a red shift of about 1000 cm^{-1} for $(NO_2Ph)_8$ TAP with respect to Bu_4TAP. It is reasonable to assign this peak to one of the lowest *gerade–gerade* electronic transitions. This assignment is based first on the mutual exclusion rule for one- and two-photon transitions discussed earlier. Second, quantum-mechanical calculations for tetraazaporphin free base (TAP) [25] predict the first *gerade* level of A_g symmetry at 25500 cm^{-1} and the next one, of B_{1g} symmetry, at 26500 cm^{-1}. The corresponding transitions are shown by bars in Fig. 4 and agree very well with our experimental result obtained for Bu_4TAP. Another paper [26] gives for the first two-photon allowed transition in TAP a frequency of 27700 cm^{-1}, which is also close to our experimental result.

A question about an exact symmetry of the excited state under consideration (A_g or B_{1g}) can be solved by using polarization measurements. We emphasize at this point that most of the data of this Letter are obtained with linearly polarized light. However, we have also measured the polarization ratio $\Omega = \sigma/\sigma_\uparrow$, where σ is the TPA cross-section for circularly polarized light and $\sigma_\uparrow$ is that for linearly polarized light. These data, obtained at different wavelengths for Bu_4TAP, are shown in
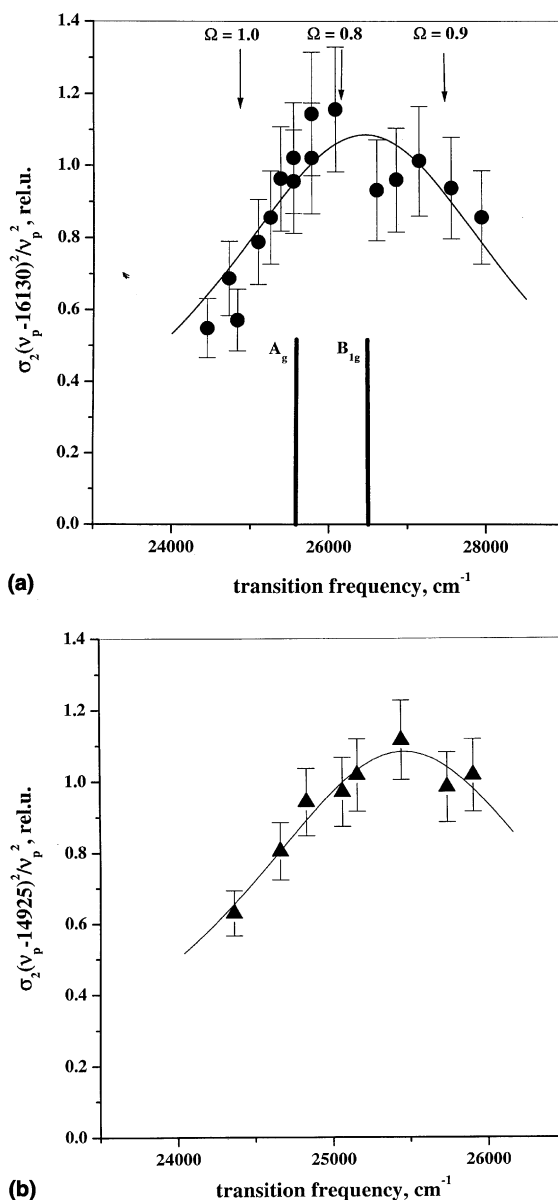

(a)

(b)

Fig. 4. Spectral shape of a two-photon transition $g(2v_p)$ free from resonance enhancement contribution for Bu_4TAP (a) and $(NO_2Ph_8)TAP$ (b). In part (a) polarization ratio Ω measured in our independent experiment at three different frequencies is presented. Also, the positions of gerade states predicted in [25] for tetraazaporphyrin molecule are shown by vertical bars.

Fig. 4. As can be seen, Ω does not vary much within the TPA band, and is equal to 0.9 ± 0.1. This value suggests that the transition into A_g state

probably dominates the observed TPA band, because in porphyrins with D_{2h} symmetry $\Omega = 1.5$ for $A_g \rightarrow B_{1g}^*$ transitions and $\Omega \sim 1.0$ (which is ill defined in this case) for $A_g \rightarrow A_g^*$ transitions [27].

Thus, the above analysis allows us to spectrally extract the 'pure' contribution of two-photon-allowed transition from that of resonance enhancement by the Q(0–0) band. With the information about the spectral maxima of TPA in hand, we can now quantitatively compare the absolute TPA cross-section values for tetraazaporphyrins under study. This is the single way to establish a reliable structure–property relationship, because in this case the cross-section value does not depend on photon frequency, but includes only molecular parameters:

$$\sigma_2(\nu_{fi}) \propto \nu_{fi}^2 \frac{|\mu_{i0}|^2 |\boldsymbol{\mu}_{fi}|^2}{(\nu_{i0} - \nu_{fi}/2)^2 \Gamma_{f0}}. \qquad (6)$$

Table 1 presents experimental TPA cross-sections, obtained near spectral maximum of *gerade–gerade* transition (underlined values) as well as linear absorption coefficients and fluorescence quantum yields for all three porphyrins.

The most important thing is that the σ_2 value dramatically increases with the electron-accepting ability of substituents. Qualitatively, such tendency has been observed previously for some stilbene derivatives with the acceptor–donor–acceptor (A–D–A) linear structure [12]. Also, the effect of continuously increasing strength of electron acceptors (or donors) on TPA efficiency has been considered theoretically for linear quadrupolar centro-symmetrical molecules [15,16], and for three-branch octupolar molecules with C_3 sym-

metry [17]. In these papers, it has been predicted that the TPA transition amplitude is a monotonically increasing function of the acceptor or the donor strength. In particular, Lee et al. [17] predicted a linear correlation between σ_2 and the Hammett constant (characterizing electron-accepting or donating ability) of the substituent group.

In our particular situation, we deal with multiple (eight in the case of $(NO_2Ph)_8 TAP$ and $(BrPh)_8 TAP$) electron acceptors symmetrically attached to the porphyrin ring. Fig. 5 shows the dependence of σ_2 on the substituent Hammett constant (taken from [29]) for the three porphyrin molecules studied here. In good agreement with theory, the σ_2 value linearly increases with the acceptor strength. Model calculations, accom-
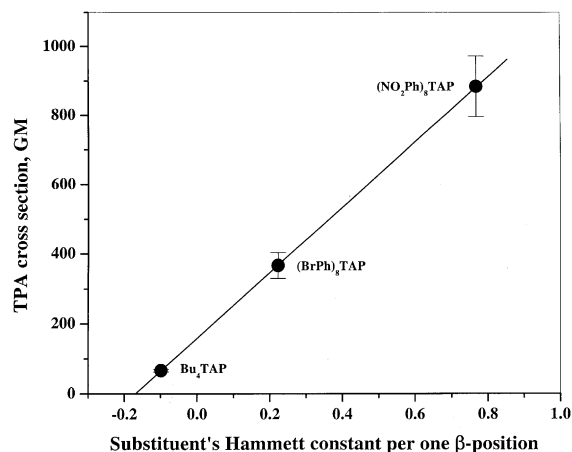

Fig. 5. The dependence of two-photon absorption cross-section near transition maximum on the substituent's Hammett constant per one β-position for the three molecules studied.

Table 1
Two-photon cross-section (σ_2), linear extinction coefficient in $Q_x(0–0)$ band maximum (ε_{max}) and quantum yield of fluorescence at room temperature (φ_F) for three molecules studied

Molecule	σ_2, GM (λ, nm)	ε_{max}, M^{-1} cm^{-1} (λ, nm)	φ_F (solvent)
Bu$_4$TAP	<u>70</u> (783)	8.0×10^4 (620)	0.18 (toluene)[c]
(BrPh)$_8$TAP	<u>380</u> (802)	9.1×10^4 (670)[b]	2.2×10^{-3} (CH$_2$Cl$_2$)
(NO$_2$Ph)$_8$TAP	<u>900</u> (802)	7.1×10^4 (670)[a]	3.0×10^{-2} (CH$_2$Cl$_2$)
	<u>1600</u> (770)		

[a] Data from [20].
[b] Data from [19].
[c] Data from [28].

plished for linear quadrupolar [15] molecules, show that the increase of charge-transfer ability of substituent groups results in an increase of the product $\mu_{i0}^2\mu_{fi}^2$, and a decrease of detuning $(\nu_{i0} - \nu_{fi}/2)^2$ in (6).

Our result shows that when we go from Bu$_4$TAP to (NO$_2$Ph)$_8$TAP, the σ_2 value increases by $\sim$13 times. At the same time, μ_{i0}^2 increases only by about 1.5 times, and the improvement of denominator in (6) provides a $\sim$3 times enhancement. Therefore, the remaining factor of 3 is presumably due to the enhancement of μ_{fi}^2.

We would like to emphasize here that p-NO$_2$ substituent used in the (NO$_2$Ph)$_8$TAP molecule is one of the strongest electron acceptors [29]. Therefore, for this particular porphyrazine structure, one could not expect much higher σ_2 values in the case if one just exchanges the NO$_2$ group by some other acceptor group.

From the point of view of applications, it also makes sense to briefly discuss the quantum efficiencies of fluorescence obtained here. For example, for two-photon imaging and diagnostics applications, fluorescence quantum yield needs to be as high as possible. On the other hand, in photodynamic therapy, one looks for a high singlet–triplet interconversion yield to photosensitize singlet oxygen more efficiently.

We observe a strong reduction of φ_F upon introduction of p-nitrophenyl- and p-bromophenyl substituents in the β-positions of porphyrin, see Table 1. It has been assumed [30,31] that nitrogroups quench fluorescence of porphyrins by an intramolecular charge-transfer mechanism resulting in internal conversion (S$_1$S$_0$) of excitation. On the other hand, bromophenyl groups are shown to quench fluorescence of porphyrins by an internal heavy atom effect, i.e., by intensifying interconversion (S$_1$T$_1$) process [32]. For two-photon-induced singlet oxygen generation, a higher interconversion efficiency in (BrPh)$_8$TAP than in (NO$_2$Ph)$_8$TAP could be even more important factor than a larger TPA cross-section in the latter.

We note that we were able to observe singlet oxygen luminescence near 1.27 μm upon two-photon excitation of both (BrPh)$_8$TAP and (NO$_2$Ph)$_8$TAP at 780 nm. Its efficiency compares with our recent result obtained with another porphyrin molecule [5]. A more detail study of this effect will be a subject of our foregoing work.

To conclude, we measured two-photon absorption spectra of three substituted tetraazaporphyrins. In the excitation region close to the linear Q$_x$(0–0) band, we observed strong resonance enhancement of the TPA efficiency. We compared our experimental data with the theoretical description of the resonance enhancement effect, and used this to retrieve the spectral peak of the *gerade–gerade* transition. Our result constitutes to the best of our knowledge the first observation of two-photon-allowed *gerade–gerade* transition in porphyrins. Furthermore, we showed that in the current compounds the absolute value of TPA is dramatically enhanced by strong electron-accepting substitution at the eight pyrrole positions of the porphyrazine ring. The cross-section value is found to be proportional to the substituent's Hammett constant and amounts 1600 GM for (NO$_2$Ph)$_8$TAP upon approaching one-photon transition (at 770 nm).

Acknowledgements

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