Alternative selection rules for one- and two-photon transitions in tribenzotetraazachlorin: Quasi-centrosymmetrical π -conjugation pathway of formally non-centrosymmetrical molecule

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We compare the two-photon absorption (2PA) spectra of non-centrosymmetrical metal-free tribenzotetraazachlorin (H_2TBTAC) and analogous symmetrical tetra-*tert*-butyl-phthalocyanine ($H_2TtBuPc$). Surprisingly, despite formal lack of center of inversion, the 2PA spectrum of H_2TBTAC displays a two-photon allowed transition at 935 nm, similar to *gerade-gerade* ($g-g$) transitions observed in $H_2TtBuPc$ and in other symmetrical phthalocyanines. This transition is even better resolved in the singlet-singlet excited-state absorption spectrum. We tentatively explain the survival of the $g-g$ transition in H_2TBTAC by assuming that the main π -electron conjugation pathway in the tetraaza-substituted tetrapyrrole macrocycle bypasses the outer parts of the two oppositely located isoindole rings and thus renders the optically responsive core of the chromophore quasi-centrosymmetrical. By using the independently measured ground- and excited-state absorption extinction coefficients, we also show that the two-photon absorptivity can be quantitatively explained by a simple three-level model with the lowest energy Q_1 state serving as an intermediate level. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4807594>]

I. INTRODUCTION

Tetraaza-substituted tetrapyrrolic compounds such as tetraazaporphyrins (TAPs), phthalocyanines (Pcs), and naphthalocyanines (NPs) demonstrate remarkable photophysical and photochemical properties, such as high photostability,^{1,2} ability to photosensitize cells,^{3,4} strong one-photon absorption (1PA) in the red (650–750 nm),^{1,2} as well as strong two-photon absorption (2PA) in near-IR (750–1000 nm).^{5–8} These molecules are very attractive for applications based on nonlinear absorption, such as optical power limiting,^{9,10} high-density volumetric data storage,^{11,12} and deep tissue photodynamic therapy.^{13,14} We have recently studied the 2PA spectra of a series of symmetrically substituted Pcs, and found strong, *gerade-gerade* ($g-g$) 2PA transitions in the energy region between the Q- and B-bands.⁶ Maximum transition frequencies were in good correspondence with earlier theoretical calculations.^{15–24} The best agreement between the experimental 2PA transition (observed between 880 and 940 nm)⁶ and theoretical calculation is obtained when the time-dependent density functional theory (TDDFT) method was used (910 nm²¹). In comparison, $g-g$ transitions of symmetrical porphyrins are harder to access by direct degenerate two-photon fluorescence excitation technique because they tend to lie at higher energies, i.e., above the B-band.²⁵ Symmetrical tetraaza-substituted tetrapyrroles present a good model

system for studying the parity selection rules predicting that the 1PA and 2PA transitions are alternatively allowed, i.e., the $g \leftrightarrow u$ transitions are allowed in 1PA spectra and forbidden in 2PA spectra, while the $g \leftrightarrow g$ (and $u \leftrightarrow u$) transitions are allowed in 2PA, but forbidden in 1PA spectra. Non-centrosymmetrical hydrogenated tetraazaporphyrins and phthalocyanines have recently become available.²⁶ To shed light on the actual π -conjugation pattern of the tetrapyrrole macrocycle,²⁷ it is of great interest to compare one- and two-photon absorption properties of centrosymmetrical and corresponding non-centrosymmetrical tetraaza-substituted compounds.

Here we study the degenerate simultaneous 2PA spectrum of the non-centrosymmetrical metal-free tribenzotetraazachlorin (H_2TBTAC) in the region of $\lambda_{2PA} = 850$ –1600 nm and demonstrate that, surprisingly from the first glance, the $g-g$ transition typical for symmetrical phthalocyanines is still present in the H_2TBTAC spectrum between the Q- and B-bands. This suggests that despite the apparent lack of inversion symmetry, the core of the chromophore still behaves very similarly to that of symmetrical Pcs. We corroborate our finding by quantitative femtosecond transient excited-state absorption (ESA) spectroscopy and show that the $S_1 \rightarrow S_n$ transition frequency and cross section are in quantitative agreement with the 2PA data. We also show that a few-level model of two-photon transition, where the Q_1 -band plays a role of a virtual intermediate excited state quantitatively describes the observed 2PA intensity and spectral shapes.

We tentatively explain this observation by assuming a particular π -electron conjugation pathway in the

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metal-free tetra-*tert*-butyl-phthalocyanine (H_2TtBuPc), which bypasses two opposite isoindole rings. This pathway should not change upon reduction of one of these rings and therefore the core of the H_2TBTAC chromophore should remain quasi-centrosymmetrical. This picture agrees with previous quantum-chemical calculations that suggest that the main pathway of the π -electron ring currents in tetraazaporphyrins and phthalocyanines does not encounter the outer part of the two oppositely located isoindole rings.²⁸ In this regard, tetraazaporphyrins and phthalocyanines differ from the non-centrosymmetrical porphyrins and chlorins, where much larger part of the π -electron ring current flows through the outer part of the all four pyrrole rings.

II. EXPERIMENTAL

H_2TBTAC was synthesized as described earlier.²⁹ H_2TtBuPc (2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine), fullerene (C_{60}), rhodamine B, styryl-9M, carbon tetrachloride, methanol, toluene, and chloroform were purchased from Sigma-Aldrich and were used without further purification. The purity of the dyes was better than 97%, and the solvents used were of the spectral grade quality.

2PA spectra and cross sections were measured using fluorescence excitation technique as described previously.³⁰ Briefly, our laser system consists of a 1-kHz pulse repetition rate Ti:Sapphire regenerative amplifier (Coherent, Legend-HE) seeded with a Ti:Sapphire femtosecond oscillator (Coherent, Mira 900). The amplified femtosecond pulses (center wavelength = 795 nm, pulse duration = 120 fs, and pulse energy = 1.3 mJ) are used to pump an optical parametric amplifier (OPA, Quantronix TOPAS-C). The output of the OPA (~ 100 mW average power) is tunable in the wavelength range 550–1600 nm. The fluorescence excited in the sample was collected with a spherical mirror in the direction perpendicular to the direction of the excitation laser beam, and was focused on the entrance slit of a 550-mm focal length grating spectrometer (Horiba Jobin Yvon, HR 550) coupled with a liquid nitrogen cooled CCD detector (SpectrumOne). The spectrometer recorded the fluorescence spectrum at each excitation wavelength, which allowed us collecting the fluorescence signal emitted only by the chromophore, and not by some impurity or stray laser light. In case of H_2TBTAC the fluorescence was monitored at 758 ± 5 nm and in case of H_2TtBuPc at 704 ± 5 nm, corresponding to the respective $S_1 \rightarrow S_0$ 0–0 emission peaks.³¹ An Ophir Nova II power meter with a 3A-SH thermoelectric probe was used to measure the average laser power.

The 1PA, 2PA, and ESA spectra of H_2TBTAC and H_2TtBuPc were obtained in carbon tetrachloride solution to avoid artifacts related to the absorption in the near-IR exhibited by common organic solvents. Rhodamine B dissolved in methanol was used as the reference standard to correct for wavelength-dependent variations of the laser beam profile and pulse duration. The 2PA cross sections were measured relative to Styryl-9M dissolved in chloroform.

The experimental pump-probe setup with femtosecond resolution is shown in Fig. 1. The setup utilizes the same wavelength-tunable femtosecond laser system described

FIG. 1. Schematic of the femtosecond pump-probe setup. QPD1, QPD2 are quad photo-detectors used for the alignment of the beam overlap; SPD1, SPD2 are sandwich photo-detectors; NDFW1, NDFW2 are neutral density filter wheels; M1, M2, M3 are computer-controlled mirrors; BS1 is a computer-controlled beam splitter. SM1 is a spherical focusing mirror; SH1, SH2 are computer-controlled shutters; SHG BBO is a frequency doubling BBO crystal.

above. The sample is excited with a fixed wavelength pump pulse, $\lambda_{\text{pump}} = 397$ nm, and with a time-delayed wavelength-tunable probe pulse, $\lambda_{\text{probe}} = 550\text{--}1600$ nm. For the pump beam we frequency-doubled a small fraction (4%) of the Ti:Sapphire amplifier output that we split off with a glass plate. Attenuated OPA output served as a wavelength-tunable probe beam. The time delay between the pump and probe pulse was adjusted by directing the pump beam through a computer-controlled 0–2.8 ns variable optical delay line. A 500 Hz mechanical chopper (Thorlabs MC1000A) synchronized with the Ti:Sapphire amplifier blocked every second pump pulse. The pump and probe beams were aligned to propagate collinearly with the help of a home-built computer-controlled automatic beam aligning system that comprised three stepper-motor driven mirrors (M1, M2, and M3), one stepper-motor driven beam splitter (BS1), and two InGaAs photodiode quadrant detectors (QPD1 and QPD2). The two spatially overlapped beams were focused into the sample with a 200-mm focal length spherical mirror (SM1), with the probe beam diameter being slightly smaller than that of the pump beam.

The sample was contained in a 2-mm thick quartz cuvette, and was constantly stirred by a motor driven bar magnet. A color filter placed after the sample blocked the pump beam. The transmitted probe beam was focused on an amplified Si/InGaAs sandwich signal detector (SPD1). The second sandwich reference detector (SPD2) was used to measure the energy of the probe pulses before the sample. Computer-controlled continuously variable neutral density filter wheels (NDFW1 and NDFW2) were placed in front of each of the sandwich detectors to compensate for the variation of the probe pulse energy as a function of λ_{probe} .

The output of the detectors was analyzed using a 16-bit, 10 Mega sample per second digitizer (GaGe Dynamic Signal CompuScope 8420). Two computer-operated shutters were used to block the pump and the probe beams separately in order to minimize the sample bleaching during the experiment. TOPAS wavelength tuning, alignment of the beams, and collection of the data were computer-controlled with the LabView program.

The principle of measuring of the ESA spectra is described in many papers (see, for example, Ref. 32), and is

FIG. 2. 1PA (blue solid line), 2PA (red symbols) spectra, and fluorescence anisotropy as a function of one-photon excitation wavelength (solid line, upper panels) of H₂TBTAC (left panel) and H₂TtBuPc (right panel). Vertical dashed lines indicate locations of the quasi $g-g$ and $g-u$ transitions (see text for details).

based on the following expression for the change of the optical density at the probe wavelength:

$$\Delta OD(\lambda_{probe}) = -\log_{10} \left[\frac{I_{ref}^0(\lambda_{probe}) I_{sig}^1(\lambda_{probe})}{I_{sig}^0(\lambda_{probe}) I_{ref}^1(\lambda_{probe})} \right], \quad (1)$$

where $I_{ref}^0(\lambda)$ and $I_{sig}^0(\lambda)$ are the probe pulse energy on the reference detector and on the signal detector when the pump beam path is blocked by the chopper, while $I_{ref}^1(\lambda)$ and $I_{sig}^1(\lambda)$ are the corresponding values when the pump beam is present. The value of ΔOD was evaluated for each pulse pair (with and without the pump pulse) at 500 Hz rate and then averaged over 10–100 acquisitions for each probe wavelength.

The sample concentration was adjusted to correspond to the linear optical density value at the pump wavelength of $OD \sim 0.1$ – 0.4 . The pump pulse energy was ~ 1 – $5 \mu\text{W}$ and the pump beam diameter at the sample was about 200–400 μm . The diameter of the probe beam was about 100–200 μm . The delay between the pump and the probe pulses was kept at a few picoseconds to ensure that only the singlet-singlet transient absorption is present in the ESA spectrum. Estimated error of the measurement of absorbance change ΔOD was less than 0.001.

The values of the excited-state extinction coefficient were determined using relative technique, similar to that described in Ref. 33. This method is based on the assumption that if the absorbance of the reference sample matches that of the sample, then the number of excited molecules will be also the same in both cases. Fullerene C₆₀ in toluene, for which the ground- and excited state extinction coefficient values are known from literature,³⁴ was used as a reference. The linear optical density of the reference solution at the pump wavelength was adjusted to match that of the sample solution. Under such conditions, the extinction of the sample can be calculated from the relation,

$$\varepsilon_{sample}(\lambda_0) = \varepsilon_{ref}(\lambda_0) \frac{\Delta OD_{sample}(\lambda_0)}{\Delta OD_{ref}(\lambda_0)}, \quad (2)$$

where $\varepsilon_{sample}(\lambda_0)$ and $\varepsilon_{ref}(\lambda_0)$ are the extinction coefficients of the sample and the reference, $\Delta OD_{sample}(\lambda_0)$ and $\Delta OD_{ref}(\lambda_0)$

are the differential optical densities of the sample and the reference, and $\varepsilon_{ref}(759 \text{ nm}) = 3700 \text{ M}^{-1} \text{ cm}^{-1}$.³³ The measured ESA spectra of the samples were calibrated to the extinction coefficient value determined at 759 nm.

Linear absorption and fluorescence emission spectra were measured with a Perkin Elmer Lambda 900 spectrophotometer and a Perkin Elmer LS-50B spectrofluorimeter, respectively. The spectrofluorimeter was also used to determine one-photon absorption (1PA) components parallel and perpendicular to the fluorescence emission transition dipole moment using the fluorescence anisotropy method.³⁵ The anisotropy was measured in olive oil to increase its absolute value at room temperature. The 1PA spectra of the molecules in both CCl₄ and in olive oil virtually coincide.

III. RESULTS AND DISCUSSION

A. Linear and two-photon absorption spectra

Figure 2 presents the 1PA and degenerate 2PA spectra, as well as fluorescence anisotropy as a function of excitation wavelength for H₂TBTAC ((a) and (b), left panel) and H₂TtBuPc ((c) and (d), right panel). The structure of the molecules is shown in insets. The x-axis at the bottom of the graphs represents the 2PA laser wavelength, and the top x-axis represents the 1PA transition wavelength, equal to one-half of the laser wavelength. The fluorescence emission spectra are presented in the supplementary material.³¹

The linear, one-photon, absorption spectra show two distinct transition regions, typical for most of tetrapyrrolic compounds: the B-band between 300 and 400 nm, and the stronger Q-bands in the region from 550 to 800 nm. In H₂TBTAC, the lowest energy Q₁-band at 752 nm is by far the strongest and corresponds to the pure electronic (0–0) $S_0 \rightarrow S_1$ transition. The accompanying vibronic components at 720 nm and 670 nm are much weaker compared to the pure electronic one. Another, relatively weak band at 605 nm belongs to the electronic $S_0 \rightarrow S_2$ (Q₂) transition.^{36,37} The vibronic transitions of the Q₁ band are polarized at small angles to the pure

electronic $S_0 \rightarrow S_1$ transition, whereas the Q_2 band transitions are polarized in the perpendicular direction, as confirmed by the circular dichroism³⁶ and anisotropy measurements, Fig. 2(a).

Compared to H_2TBTAC , $H_2TtBuPc$ shows two almost equally strong Q -bands that belong to two orthogonally polarized electronic transitions (Q_x and Q_y),^{1,2} see Figs. 2(c) and 2(d). Because of larger overlap between the bands the corresponding vibronic components are less resolved. In both chromophores there are no strong one-photon transitions present in the range between 400 nm and 510 nm.

The 2PA spectra were measured in the laser wavelength range from 800 to 1600 nm. Similar to what was observed before in symmetrical Pcs,^{6,30} the 2PA spectrum of $H_2TtBuPc$ possesses an extremely weak longest wavelength 2PA peak at 1410 nm (with the cross section, $\sigma_2 \sim 1$ GM, $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s}$) which coincides with the 0–0 Q_1 transition of the linear absorption spectrum. The broad feature at ~ 1300 nm with the maximum cross section value, $\sigma_2 \sim 20$ GM, is probably due to a combination of a vibronic Q_1 transition and overlapping Q_2 band. The weakness of the 0–0 Q_1 two-photon transition is explained by its $g-u$ nature. It is not completely forbidden ($\sigma_2 \neq 0$) probably because of small perturbations caused, e.g., by solute-solvent interactions, molecular vibrations, or non-symmetrical conformations, and positions of butyl substituents, which all can slightly distort the symmetry of the wave function in the ground and/or excited state. In contrast, the corresponding one-photon transition is strongly allowed. It is convenient to introduce an empirical parameter that has dimensionality of dipole moment (in Debye units),

$$\alpha = 1.27 \times 10^{25} (\sigma_2 \nu_{\max} / \epsilon_{\max})^{1/2}, \quad (3)$$

where $\nu_{\max}$ is the frequency of pure electronic transition (in cm^{-1}), σ_2 is the 2PA cross section (in $\text{cm}^4 \text{ s}$), and $\epsilon_{\max}$ is the extinction coefficient (in $\text{M}^{-1} \text{ cm}^{-1}$) both determined at $\nu_{\max}$. This parameter has the physical meaning of how much the permanent dipole moment changes upon excitation in two-level system.³⁸ Our estimation shows that α varies from 0.4 D ($H_2TtBuPc$) and 0.9 D (H_2TBTAC) to 1.8 D in free base tetraphenylporphyrin (H_2TPP),³⁰ and 5.8 D in strongly push-pull-substituted porphyrin no. 7 in Ref. 39. Comparing these numbers, we can suppose that the inevitable presence of structural isomers (with different positions of butyl groups) in the flat and rigid $H_2TtBuPc$ ring causes less effect than a small asymmetry of the electronic conjugation path in H_2TBTAC (see Fig. 3(a)), which in turn is still less than the asymmetry of non-symmetrical isomers of H_2TPP (where the 60° twisting of phenyl rings causes a perturbation of otherwise centrosymmetric wavefunction of the tetrapyrrole ring).^{40,41} Therefore, both $H_2TtBuPc$ and H_2TBTAC can be considered as quasi-centrosymmetrical, compared to stronger perturbed H_2TPP and even non-centrosymmetrical porphyrin no. 7 of Ref. 39.

Slightly lower in energy from the B-band, there are two distinct 2PA-allowed peaks, at 945 nm ($\sigma_2 \sim 200$ GM) and 865 nm ($\sigma_2 \sim 800$ GM), previously assigned to the $g-g$ transitions.⁶ Neither of these strong peaks has a counterpart in the 1PA spectrum, one more time confirming alternative parity selection rules.

FIG. 3. Prevalent theoretical π -conjugation pathway (thick lines) in H_2TBTAC (a) and $H_2TtBuPc$ (b). Numbers shown next to the bonds symbols in $H_2TtBuPc$ depict relative induced current density calculated in Ref. 28.

As far as the 2PA spectrum of the formally non-centrosymmetrical H_2TBTAC is concerned, we observe a distinct peak at 1500 nm coinciding with the pure electronic Q_1 transition peak in the 1PA spectrum. Although the corresponding cross section is larger than in the case of $H_2TtBuPc$, $\sigma_2 = 6$ GM, it is still quite small to be considered as corresponding to fully allowed 2PA transition. Similar to $H_2TtBuPc$, the accompanying broad vibronic feature at 1400 nm is stronger than the 0–0 transition ($\sigma_2 = 10$ GM). The 2PA spectrum in the $S_0 \rightarrow S_2$ transition region (1020–1220 nm) has similar features and cross section values as for the $S_0 \rightarrow S_1$ region, but shifted to shorter wavelengths. At even shorter wavelengths, slightly below the B-band in energy, H_2TBTAC shows a distinct strong peak at 935 nm. The large peak cross section value ($\sigma_2 = 480$ GM) and spectral position indicate that this allowed two-photon transition has similar nature as the 945-nm peak of $H_2TtBuPc$. Similar to $H_2TtBuPc$, this transition has no counterpart in the linear absorption spectrum.

A surprising finding of this experiment is that a nominally non-centrosymmetrical molecule may still exhibit the property that is expected only for symmetrical systems. The apparent preservation of the parity selection rule indicates that the π -conjugation structure, which is mostly responsible for optical electronic transitions in this system, still remains quasi-symmetrical in H_2TBTAC . (Strictly speaking, the symmetry of H_2TBTAC is further perturbed compared to $H_2TtBuPc$, and hence the higher σ_2 value in the pure electronic Q_1 transition.) This conclusion is supported by quantum-chemical calculations of the π -electron ring currents in symmetrical tetraazaporphyrins and phthalocyanines that are induced by external static magnetic field. These induced currents follow the path of the highest electron density, and may be considered indicative of the symmetry of the core electronic structure.^{28,42} According to calculations performed by Vysotsky *et al.*²⁸ the π -electron ring currents are concentrated in the inner part of symmetrical phthalocyanine macrocycle thus avoiding the outer part of the two isoindole rings, see Fig. 3. (Only $\sim 10\%$ of ring current flows into the outer isoindole rings.) Since these rings are responsible for the apparent symmetry breaking in H_2TBTAC , this latter molecule should generally preserve the central symmetry. It is also worth noting that tetraazaporphyrins and phthalocyanines differ in this

FIG. 4. ESA spectra (symbols) of H₂TBTAC (a) and H₂TtBuPc (b). Linear absorption spectra are shown for comparison (blue line). Vertical arrows indicate the positions of the tentative $S_1 \rightarrow S_f$ transitions relevant to the 2PA spectra.

regard from regular porphyrins, where almost one third of the π -electron ring current goes through these rings.^{28,42}

B. Excited state absorption

Figure 2 shows that the 2PA cross section of both compounds generally increases upon tuning the laser from 1000 nm to shorter wavelengths. This effect can be qualitatively explained by the resonance enhancement effect of the 2PA, and is typically observed when the laser frequency approaches the lowest energy 1PA-allowed (Q_1) transition (see, e.g., Ref. 6). The shapes of the 2PA g - g spectra, described above, are likely altered by this effect. Alternatively, the same final states may be probed by transient singlet–singlet ESA spectroscopy, which is not subject to the resonance distortion. Figure 4(a) shows the transient ESA spectrum of H₂TBTAC in CCl₄ plotted as a function of the probe frequency (bottom x-axis). Top x-axis represents the corresponding probe wavelength. Left vertical axis shows an absolute effective excited-state extinction coefficient. The transient ESA spectrum of symmetrical H₂TtBuPc is presented for comparison in Fig. 4(b). Both H₂TBTAC and H₂TtBuPc molecules show a pronounced ESA signal at frequencies larger than 15 000 cm^{−1} ($\lambda < 670$ nm), which is typical for the high-energy $S_1 \rightarrow S_n$ transitions in phthalocyanines.⁴³ In the Q-bands region the ESA signal is negative due to the saturation of the $S_0 \rightarrow S_1$ transition. The smaller amplitude negative peaks at 11 700 cm^{−1} (H₂TBTAC) and 12 700 cm^{−1} (H₂TtBuPc) likely correspond to stimulated emission in the $S_1 \rightarrow S_0$ transition. The same effect may explain the slight redshift of the main negative ESA peak relative to the linear 0–0 absorption maximum. At

lower probe frequencies H₂TBTAC shows a single peak at 7870 cm^{−1} (1270 nm) that is accompanied by a broader shoulder extending over the range 8700–10 000 cm^{−1} (1000–1150 nm). H₂TtBuPc shows two distinct ESA peaks, one at 6540 cm^{−1} (1530 nm) and another at 8030 cm^{−1} (1245 nm) which is accompanied by a broad shoulder extending up to the point where the negative ESA takes over at 12 200 cm^{−1} (820 nm).

The excited-state absorption peak positions of both molecules closely match those observed in the simultaneous two-photon absorption spectra discussed in Sec. III A. Indeed, the sum of the frequencies of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_f$ transitions (where S_f is a final singlet state) of H₂TBTAC (21 170 cm^{−1}) is very close to the frequency of the $S_0 \rightarrow S_f$ transition found above from the 2PA spectrum (~ 21 400 cm^{−1}), see Table I. Similarly, both 2PA peaks of H₂TtBuPc correlate with the observed ESA (see Table I). We therefore conclude that the same final excited state is reached in both the 2PA and ESA processes in these molecules. Furthermore, based on the similarity of the $S_0 \rightarrow S_f$ transition frequency in H₂TBTAC and H₂TtBuPc, as well as on the fact that the 1PA spectrum of H₂TBTAC shows no distinct features in this spectral range, we ascribe *gerade* symmetry to the S_f state of this latter molecule. It is also noteworthy that, as it was expected, the u - g transitions appear to be better resolved in ESA spectra than in the corresponding 2PA measurement. Related arguments were previously used to rationalize observed 2PA cross sections in some symmetric compounds (see, for example, Refs. 44–47), however, to the best of our knowledge, this is the first direct experimental study of the g - g transition in tetrapyrrolic molecules with simultaneous probing of the same final state by 2PA and ESA.

TABLE I. Transition frequencies calculated as a sum of GS and ESA peaks ($\bar{\nu}_{10} + \bar{\nu}_{f1}$) and 2PA ($\bar{\nu}_{f0}$), dipole moments, symmetry factor A with the symmetry of the final state shown in parentheses, and calculated and measured peak 2PA cross sections of the g - g transition.

Compound	$\bar{\nu}_{10}$ (cm ^{−1})	$\bar{\nu}_{f1}$ (cm ^{−1})	$\bar{\nu}_{10} + \bar{\nu}_{f1}$ (cm ^{−1})	$\bar{\nu}_{f0}$ (2PA) (cm ^{−1})	$ \bar{\mu}_{10} $ (D)	$ \bar{\mu}_{f1} $ (D)	A	σ_2^{calc} (GM)	σ_2^{exp} (GM)
H ₂ TBTAC	13 300	7870	21 170	21 400	5.8	3.0	3(A _g)	360	480
H ₂ TtBuPc									
1st peak	14 230	6300	20 530	21 100	5.7 (Q ₁)	1.0 (S _{f1})	8(A _g)	80	160
2nd peak	15 060	7900	22 960	23 040	5.7 (Q ₂)	2.5 (S _{f2})	4(B _{1g})	200	780
							8(A _g)	400	

C. Few essential states model

To shed more light on the mechanism of the 2PA process and the role of real intermediate states in the enhancement of the low energy 2PA g - g transition of H₂TBTAC versus H₂TtBuPc, we apply here a few-essential-states model. This model has been previously used to explain the 2PA properties of symmetrical Pcs⁶ as well as a number of other symmetrical and non-symmetrical chromophores.^{5-7,25,38,39} Even though ultimate theoretical proof of when such simplified models may be used is still outstanding, we can apply the measured experimental extinction values for both the ground-state and excited-state transitions, to check the validity of the few-states approximation in our case. Another advantage that this simple approach may have over more sophisticated (and presumably more accurate) computational methods^{23,27} is that it offers a relatively simple physical picture of the 2PA process.⁴⁸

Following the approach developed in Ref. 6, we start our analysis by considering four essential states in both molecules, including the ground, 0, the two intermediate, 1 and 2 (corresponding to Q₁ and Q₂ states, respectively), and the final, f , states. Note that in the case of H₂TtBuPc, we consider two different final states, i.e., at 945 and 865 nm in Fig. 2(d). In the case of the simultaneous two-photon absorption resulting from a single beam with linear polarization, the 2PA cross section reads

$$\sigma_2(2\nu) = 2 \frac{(2\pi)^4}{(hc)^2} \frac{f^4}{n^2} \nu^2 \langle |S_{f0}|^2 \rangle g(2\nu), \quad (4)$$

where ν is the photon frequency (in Hz), $g(2\nu)$ is the line shape of the final state (in s) normalized such that $\int_{-\infty}^{\infty} g(2\nu) d(2\nu) = 1$, h is the Planck constant, c is the speed of light, n is the refractive index of the solvent, f is the local field factor, and S_{f0} is the two-photon tensor (see Ref. 6 for its definition). The angle brackets in (4) denote the orientational averaging. To perform the orientational averaging we apply the classical method of Monson and MacClain.^{49,50} According to Sec. III A, both molecules possess quasi-D_{2h} symmetry. For this group of symmetry, there are formally four possible types of *gerade-gerade* transitions starting from the A_g ground state: A_g → A_g, A_g → B_{1g}, A_g → B_{2g}, and A_g → B_{3g}.

Since the molecules under consideration are quasi-planar, the A_g → B_{2g} and A_g → B_{3g} types result in $\langle |S_{f0}|^2 \rangle \approx 0$.⁵⁰ For the A_g → A_g type of transitions in the four-level system we will have⁶

$$\begin{aligned} \langle |S_{f0}|^2 \rangle = & \frac{1}{15} \left(3 \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu - \nu_{10})^2} + 3 \frac{|\mu_{f2}|^2 |\mu_{20}|^2}{(\nu - \nu_{20})^2} \right. \\ & \left. + 2 \frac{|\mu_{f1}| |\mu_{10}| |\mu_{f2}| |\mu_{20}|}{(\nu - \nu_{10})(\nu - \nu_{20})} \right). \end{aligned} \quad (5)$$

In the case of H₂TtBuPc this expression is simplified⁶ by noticing that $|\mu_{10}| \approx |\mu_{20}|$ and that near the 2PA maximum $\nu - \nu_{10} \approx \nu - \nu_{20}$, and $|\mu_{f1}| \approx |\mu_{f2}|$,

$$\langle |S_{f0}|^2 \rangle \approx \frac{8}{15} \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu - \nu_{10})^2}. \quad (6)$$

In the case of H₂TBTAC, noticing that $|\mu_{10}|^2 \gg |\mu_{20}|^2$ and $(\nu - \nu_{10})^2 \ll (\nu - \nu_{20})^2$, allows us to approximate (5) with

$$\langle |S_{f0}|^2 \rangle \approx \frac{3}{15} \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu - \nu_{10})^2}. \quad (7)$$

Note that the last expression corresponds in effect to a three-level system and represents the lower limit estimation for the 2PA strength for H₂TBTAC.

For the A_g → B_{1g} type of transitions the corresponding tensor will read^{49,50}

$$\langle |S_{f0}|^2 \rangle = \frac{1}{15} \left(\frac{|\mu_{f1}| |\mu_{10}|}{(\nu - \nu_{10})} + \frac{|\mu_{f2}| |\mu_{20}|}{(\nu - \nu_{20})} \right)^2, \quad (8)$$

which in the case of H₂TtBuPc can be approximated by

$$\langle |S_{f0}|^2 \rangle \approx \frac{4}{15} \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu - \nu_{10})^2} \quad (9)$$

and in the case of H₂TBTAC, by

$$\langle |S_{f0}|^2 \rangle \approx \frac{1}{15} \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu - \nu_{10})^2}. \quad (10)$$

Substituting (6), (7) or (9), (10) into (4) one can finally get the few-state model expression for the 2PA spectrum:

$$\sigma_2(2\nu) \approx A \frac{2}{15} \frac{(2\pi)^4}{(hc)^2} \frac{f^4}{n^2} \frac{|\mu_{f1}|^2 |\mu_{10}|^2}{(\nu_{10}/\nu - 1)^2} g(2\nu), \quad (11)$$

where A is the symmetry-defined factor, shown in Table I for each particular case.

Now we can quantitatively compare the 2PA spectrum measured experimentally with the predictions of a few-state model. For that purpose we first note that $|\mu_{10}|^2$ can be obtained by integrating the ground-state (GS) absorption spectrum in the region of the lowest energy, Q₁ transition^{38,51}:

$$|\mu_{10}|^2 = \frac{3 \times 10^3 \ln 10 h c n}{(2\pi)^3 N_A f^2} \int_{Q_1} \frac{\varepsilon_{10}(\bar{\nu})}{\bar{\nu}} d\bar{\nu}, \quad (12)$$

where $\varepsilon_{10}(\bar{\nu})$ is the molar extinction coefficient (in cm⁻¹ M⁻¹), $\bar{\nu}$ is the wavenumber (in cm⁻¹), and N_A is the Avogadro number. Second, we can substitute the combination $|\mu_{f1}|^2 g(2\nu)$ found in Eq. (11) with the ESA measured in independent experiment,

$$|\mu_{f1}|^2 g(2\nu) = \frac{3 \times 10^3 \ln 10 h n}{(2\pi)^3 N_A f^2} \frac{\varepsilon_{f1}(2\bar{\nu} - \bar{\nu}_{10})}{2\bar{\nu} - \bar{\nu}_{10}} \quad (13)$$

Here $\varepsilon_{f1}(2\bar{\nu} - \bar{\nu}_{10})$ is the excited-state extinction coefficient determined as a function of the probe frequency, $2\bar{\nu} - \bar{\nu}_{10}$. In our model we assume that during few picoseconds time delay between the pump and probe pulses the system is able to completely relax to the lowest excited singlet state, from where the subsequent excited-state absorption occurs. We also neglect a partial polarization-dependent photo-selection caused by linearly polarized pump. Instead, we assume that the excited-state transition dipole moments remain as virtually isotropically distributed (hence factor 3 in the numerator of Eq. (13)).

FIG. 5. Experimental 2PA spectra (red symbols) and 2PA spectra simulated as a stepwise GS + ESA absorption (solid line) of H₂TBTAC (a) and H₂TtBuPc (b) using the parameters summarized in Table I. Insets show the energy level diagrams with the corresponding degenerate 2PA (red arrows) and singlet-singlet ESA with the pump photon shown by a blue arrow and the probe photon shown by a maroon arrow. Two states labeled as S₁₁ and S₁₂ in the case of H₂TtBuPc correspond to two different final states of the 2PA transition, as described in the text. The solid brown curve in panel (b) shows the result obtained by assuming that both the 1st and 2nd peak having A_g → A_g symmetry; whereas the dashed brown line corresponds to the A_g → B_{1g} character of the 2nd peak.

Combining (12), (13), and (11), we finally obtain

$$\begin{aligned} \sigma_2(2\nu) &\approx A \frac{2}{15} \frac{9 \times 10^6 (\ln 10)^2}{(2\pi)^2 N_A^2 c} \frac{\varepsilon_{f1}(2\bar{\nu} - \bar{\nu}_{10})}{(\bar{\nu}_{10}/\bar{\nu} - 1)^2 (2\bar{\nu} - \bar{\nu}_{10})} \\ &\times \int_{Q_1} \frac{\varepsilon_{10}(\bar{\nu})}{\bar{\nu}} d\bar{\nu} = \\ &= 1.48 \times 10^{-53} A \frac{\varepsilon_{f1}(2\bar{\nu} - \bar{\nu}_{10})}{(\bar{\nu}_{10}/\bar{\nu} - 1)^2 (2\bar{\nu} - \bar{\nu}_{10})} \\ &\times \int_{Q_1} \frac{\varepsilon_{10}(\bar{\nu})}{\bar{\nu}} d\bar{\nu} \end{aligned} \quad (14)$$

Note that because we are relating the measured 2PA cross section with the measured one-photon extinction coefficients, the common uncertainty related to local field factor is absent from this expression. To the best of our knowledge, there are only a few quantum calculations of *one-photon forbidden* molecular orbitals of the metal free phthalocyanine.^{15,18,52} Transitions between the HOMO and one of those orbitals would correspond to the 2PA in a one-electron approximation. All these papers predict the lowest energy one-electron transition in H₂Pc to be of the A_g → A_g type. Taking into account configurational interaction (CI) in the relative molecule, i.e., free-base porphyrazine, at the CNDO/S⁵³ and TDDFT⁵⁴ levels of theory also predicts that the lowest *g*-*g* transition with non-vanishing 2PA strength is of the A_g → A_g type. The authors^{53,54} also found that the one-electron approximation works quantitatively for this particular transition in porphyrazine. Therefore, we assume the A_g → A_g symmetry for the lowest energy 2PA-allowed transition in both H₂TtBuPc and H₂TBTAC. For the higher energy peak observed in 2PA (~23 000 cm⁻¹) spectrum of H₂TtBuPc we consider both possibilities, i.e., either A_g → A_g or A_g → B_{1g}, because the information available about its symmetry is much less certain.^{15,18,52} Table I summarizes the transition dipole moment values and the peak frequencies related to the *g*-*g* transitions of the H₂TBTAC and H₂TtBuPc. In the last case

we show separately the lower energy (1st peak) and the higher energy (2nd peak) transitions.

Figure 5 shows the experimentally measured degenerate 2PA spectra (in the range ~830–1020 nm) re-plotted from Fig. 2 as a function of laser frequency (symbols) and the 2PA spectra simulated according to a few-level model, Eq. (14).

For H₂TBTAC molecule (Fig. 5(a)) the model predicts a 2PA maximum near $\bar{\nu} = 10\,700\text{ cm}^{-1}$, which matches well with the peak value and shape of the measured 2PA transition. The fact that the few-level model appears to work so well indicates that the higher excited states (such as Q₂ and B states) do not have a strong contribution to the two-photon absorptivity. This may be explained by a weak transition strength between the Q₂-state and the final *gerade* state (see above) and almost vanishing transition strength between the B-state and the same final state.⁵⁵ The fact that at higher frequencies the model predicts a lower 2PA cross section may be explained by the presence of transitions to higher energy states, which are not probed by the current ESA measurement. In case of the H₂TtBuPc Eq. (14) was applied separately for each of the two final transitions. The combined result is shown in Fig. 5(b). The comparison of the experimental 2PA spectrum (red dots) with the four-level model suggests that the higher energy transition (2nd peak) in the 2PA spectrum is better described by the A_g → A_g transition (solid brown line in Fig. 5(b)). Although the simulated peak σ_2 values fall somewhat below what was measured directly in the 2PA experiment, the overall agreement is still remarkably good, especially considering that the combined maximum experimental uncertainty may approach 30%–50%.

IV. CONCLUDING REMARKS

The 2PA and singlet-singlet ESA properties of non-symmetrical metal-free H₂TBTAC were studied and compared to its symmetrical counterpart H₂TtBuPc. Contrary to what might be expected based solely on symmetry considerations, both molecules show strong evidence of the alternative

parity selection rules for the 1PA-allowed and 2PA-allowed transitions. This indicates that despite the apparent lack of inversion symmetry, the core of the H₂TBTAC molecule still behaves very much like that of the symmetrical Pcs. This interpretation is further supported by previous quantum mechanical calculations of the induced π -electron current patterns in phthalocyanines.²⁸ To the best of our knowledge, this is the first experimental support of the theoretically predicted π -conjugation pathway in this class of tetrapyrroles. This methodology may prove useful for assessing symmetry properties and associated π -conjugation routes in cyclic chromophores including other porphyrinoid compounds.

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