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ARTICLE

Two-Photon Absorption in Butadiyne-Linked Porphyrin Dimers: Torsional and Substituent Effects

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Dyes exhibiting efficient two-photon absorption (2PA) are in demand for a wide range of applications, and *meso-meso* butadiyne-linked porphyrin dimers (bis-porphyrins) are promising chromophores in this area. As part of an investigation of the structure-property relationships controlling the performance of these dyes, we present the synthesis of eight π -extended dimers, with substituents providing diverse push and pull electronic effects, and high solubility. We show that the peak 2PA cross sections can be increased from 3,000 GM to 20,000 GM by attaching terminal electron-withdrawing or -donating groups, and by converting the free-base dimers to zinc complexes. The two-photon excited fluorescence spectra of porphyrin dimers in viscous media, under conditions such that excited states do not planarize prior to emission, reveal that dimers in planar conformations dominate the two-photon absorption.

Introduction

Materials with strong two-photon absorption (2PA) are increasingly important at the frontiers of microscopy, photodynamic therapy (PDT), telecommunications, 3D data storage, light-activated drugs and optical power limiting.¹⁻⁶ There have been significant advances in the elucidation of molecular design principles for maximizing the 2PA cross section (σ_2),^{1,2,7-9} however structure-property relationships are still poorly understood for all but the simplest chromophores. The nonlinear optical properties of porphyrins have attracted much interest over the past 20 years.^{2,10-13} Monomeric porphyrins exhibit only modest 2PA cross-sections,^{14,15} even with optimized substitution patterns,^{16,17} but dimers and higher oligomers have been found to offer substantial increases in σ_2 .^{11,15,18-22} Several varieties of conjugated porphyrin oligomers have been explored, resulting in 10^2 – 10^3 fold enhancements in σ_2 per porphyrin unit.^{2,11} Butadiyne-linked porphyrin dimers offer a good compromise between high 2PA cross section, long excited state lifetimes, high solubility and synthetic accessibility.²⁴⁻²⁸

A common design strategy for optimizing σ_2 is the use of centrosymmetric quadrupolar architectures, of the type A-D-A or D-A-D, featuring strong π -conjugated “push” electron-donating (D) and “pull” electron-accepting (A) groups.^{1,2,7-9,29} Previously we have reported a butadiyne-linked dimer, Oxidime (Fig. 1) with terminal pyridinium electron-acceptor groups which exhibits enhanced 2PA ($\sigma_2 = 17,000$ GM

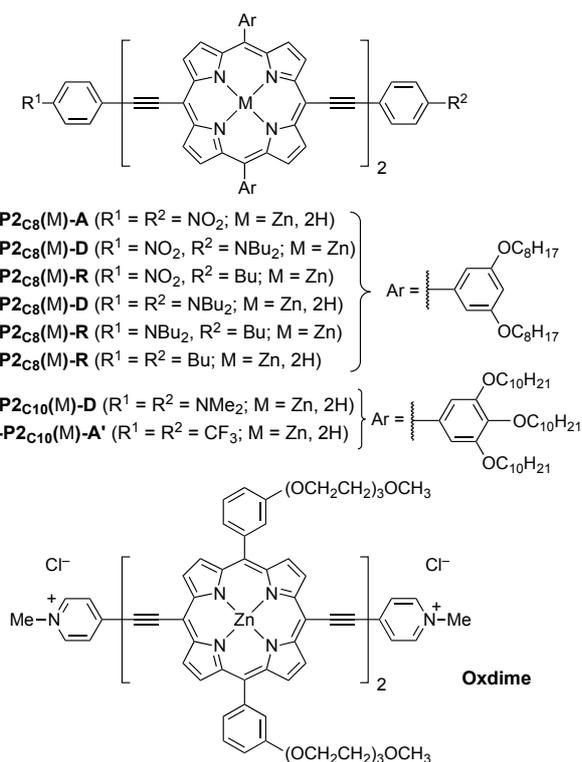
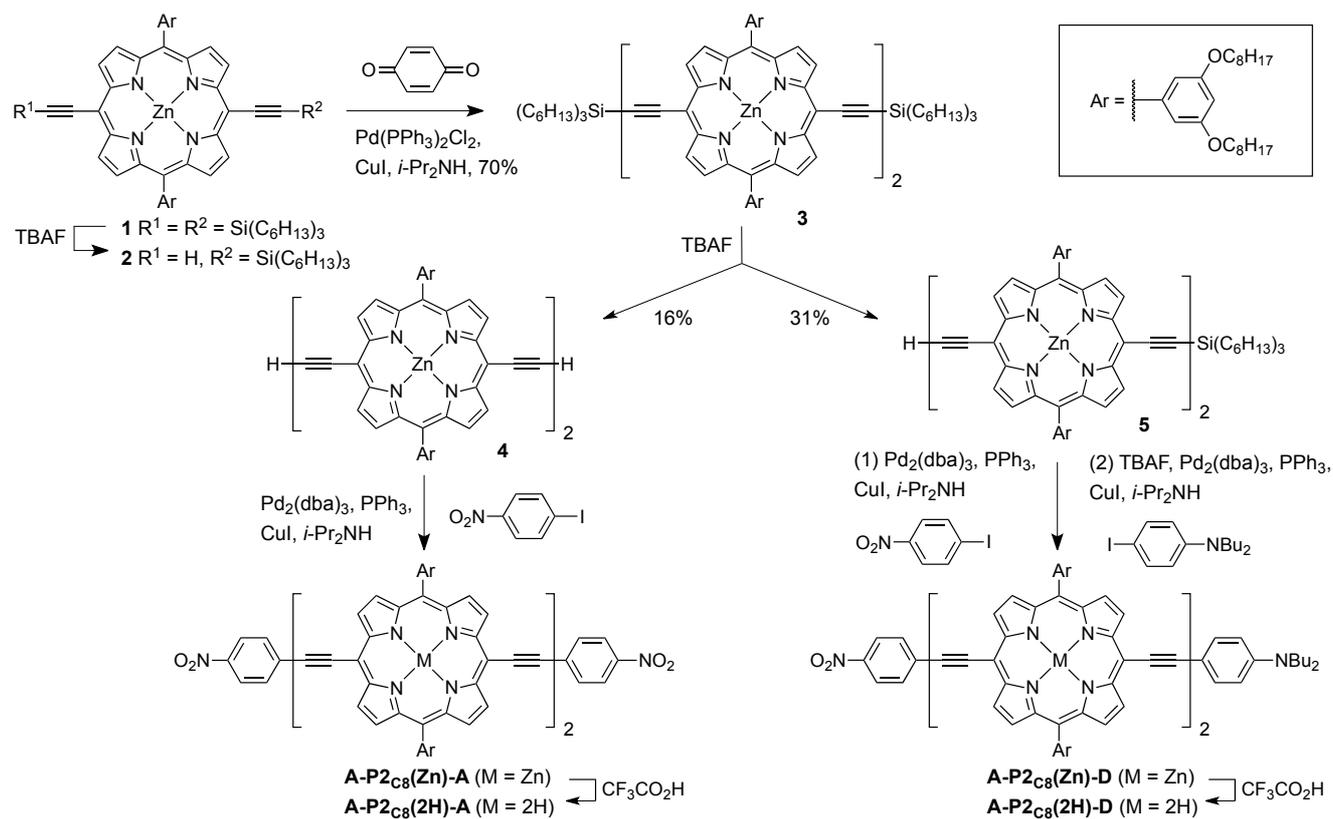
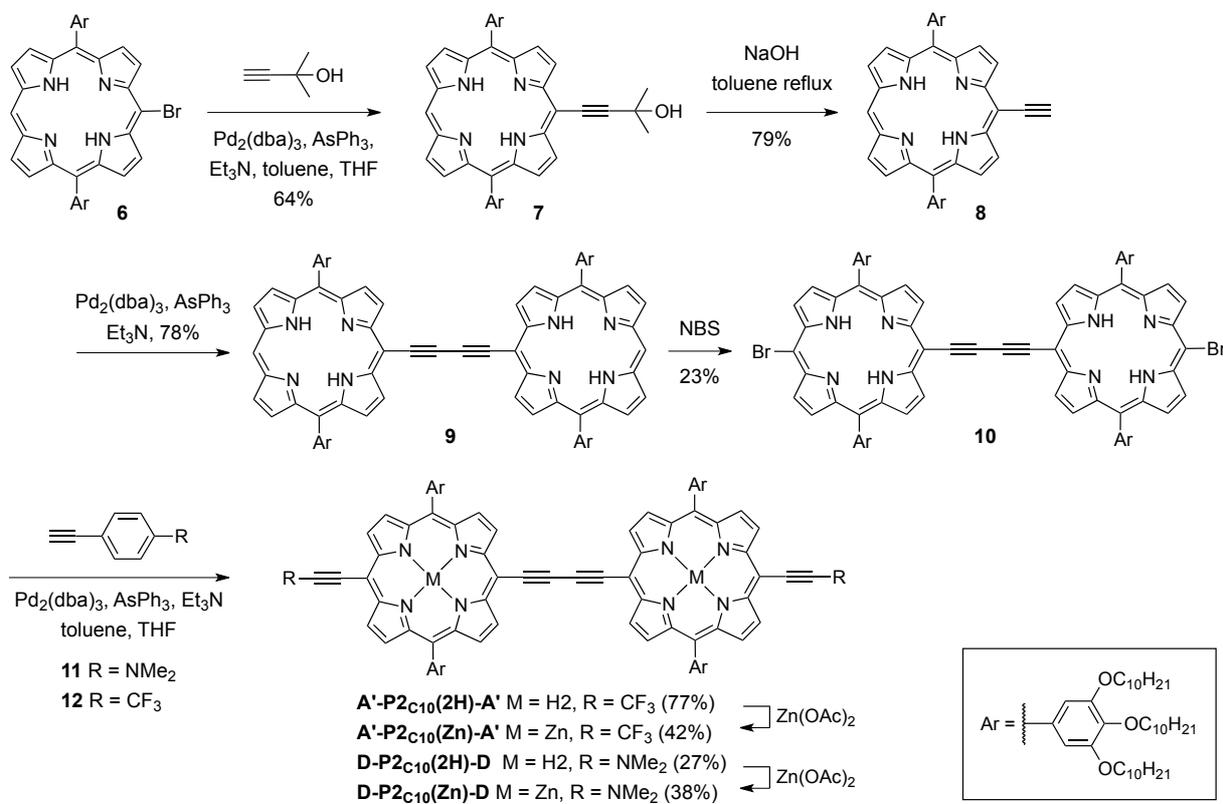


Fig. 1. Structure of the compounds studied in this work and the previously reported two-photon PDT sensitiser Oxidime.^{5,24-26,30}



Scheme 1. Synthesis of A-P2c8(Zn)-A, A-P2c8(Zn)-D, A-P2c8(2H)-A and A-P2c8(2H)-D.



Scheme 2. Synthesis of A'-P2c10(2H)-A', A'-P2c10(Zn)-A', D-P2c10(2H)-D and D-P2c10(Zn)-D.

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at 916 nm),^{5,24-26,30} but the effect of terminal electron acceptors and donors has not been systematically tested.³¹ Here we present a study of the effect of electron-donating and -withdrawing groups on σ_2 in butadiyne-linked porphyrin dimers.

Efficient 2PA requires strong electronic coupling over a large π -system, making it sensitive to conformational changes which alter π -orbital overlap. Various strategies have been used to enhance 2PA by constraining the conformations of π -systems, including the synthesis of multiply-linked porphyrin tapes (e.g. β -to- β 1,3-butadiyne doubly-linked,³² meso- β doubly-linked,³³ and triply-linked tapes³⁴), ladder-complex formation,^{35,36} straps and host-guest chemistry.³⁷ Butadiyne-linked porphyrin dimers consist of mixtures of conformations due to rotation about the central butadiyne link, and the different conformations have characteristic absorption and fluorescence spectra.³⁸⁻⁴³ Here we use this feature to compare the 2PA cross sections of planar and twisted conformations.

Results and discussion

Synthesis

Porphyrin dimers sometimes exhibit poor solubility, which can make it difficult to investigate and apply of their photophysical properties, so in this work we have tested two different types of solubilizing groups: 3,5-dioctyloxyphenyl and 3,4,5-tridecyloxyphenyl. The family of six **P2**_{C8} octyloxy-solubilized zinc porphyrin dimers shown in Figure 1 was synthesized from porphyrin monomer **1** using a combination of statistical desilylation and Sonogashira coupling steps, as illustrated in Scheme 1.^{38,44} Desilylation of **1** yielded a mixture from which the singly desilylated monomer **2** was separated and subjected to a Pd-catalyst in the presence of 1,4-benzoquinone as oxidant to give butadiyne-linked dimer **3**. This dimer was then similarly desilylated, and the doubly- and singly-desilylated dimers **4** and **5** separated. Coupling **4** and **5** to 4-iodonitrobenzene yielded **A-P2**_{C8}(Zn)-**A** and a silyl/nitro dimer, respectively; the latter was desilylated and *in situ* coupled to *N,N*-dibutyl-4-iodoaniline yielding **A-P2**_{C8}(Zn)-**D**. The synthesis can also be performed without separating **4** and **5**, by isolating **A-P2**_{C8}(Zn)-**A** and the silyl/nitro dimer precursor to **A-P2**_{C8}(Zn)-**D** after the next step. The free-base porphyrin dimers were prepared either by demetalation of the final zinc compound, or by demetalation of intermediate **3**, followed by the application of Cu-free Sonogashira coupling steps⁴⁵ (see ESI Fig. S1 and S2).

Another series of porphyrin dimers (**P2**_{C10}, Fig. 1) with electron-withdrawing CF₃ terminals, or NMe₂ electron-donors, was prepared as shown in Scheme 2. Bromoporphyrin **6**^{17,46} was subjected to Sonogashira coupling followed by removal of

the protecting group, to give intermediate **8**. Palladium-catalyzed homocoupling, under copper-free conditions, gave dimer **9** in 78% yield. Subsequent bromination at the two remaining *meso*-positions followed by Sonogashira coupling with alkynes **11** and **12** gave dimers **A'-P2**_{C10}(2H)-**A'** and **D-P2**_{C10}(2H)-**D**. In this approach, zinc was inserted at the end of the synthesis.

One-photon absorption spectra

The absorption spectra of the bis-porphyrins show the typical features of butadiyne-linked porphyrin dimers (Table 1 and Fig. 2).^{21,47-52} For the zinc family, the peak of the Soret (B) band is shifted bathochromically by up to 5 nm to 469 nm in the “pull-push” chromophore **A-P2**_{C8}(Zn)-**D**, compared to the “push” chromophore **D-P2**_{C8}(Zn)-**R**. The trend in peak wavelength of this band [**A'-P2**_{C10}(Zn)-**A'** \approx **D-P2**_{C8}(Zn)-**R** \approx **R-P2**_{C8}(Zn)-**R** < **A-P2**_{C8}(Zn)-**R** \approx **D-P2**_{C10}(Zn)-**D** \approx **D-P2**_{C8}(Zn)-**D** \approx **A-P2**_{C8}(Zn)-**A** < **A-P2**_{C8}(Zn)-**D**] suggests that the electron-accepting nitro group has a greater influence on the π -system, than the electron-donor. The CF₃ acceptor has less influence on the absorption spectra, as seen by comparing **A-P2**_{C8}(Zn)-**A** with **A'-P2**_{C10}(Zn)-**A'**. The Soret bands of the free-base family also span a 7 nm range, but the electron-donating group has the greatest effect on the π -system, dramatically broadening the Soret band in **D-P2**_{C8}(2H)-**D** and **D-P2**_{C10}(2H)-**D**. The extinction coefficients of the Soret transition are large and correlate well with the inverse of the bandwidth for the zinc dyes; the oscillator strengths (f_B) are all similar as expected.

The Q bands of all the free-base dimers show an extra peak at 620–650 nm, as expected from the lower symmetry of the free-base chromophore. The Q band transitions are more sensitive to changes in the electronic substitution, with a maximum red shift in the lowest-energy band of 12 nm from **R-P2**_{C8}(Zn)-**R** to **A-P2**_{C8}(Zn)-**D**, and 19 nm from **R-P2**_{C8}(2H)-**R** to **D-P2**_{C10}(2H)-**D**. There is again distortion in this region for the **D-P2**_{C8}(2H)-**D** free-base dye, with significant broadening and loss of structure in the Q band accompanied by increased oscillator strength (Fig. 2b).

Table 1. One- and two-photon absorption data (in CHCl₃, plus 1% pyridine for M = Zn)

dimer	$\lambda_{\text{max,1PA}}$ (nm) [ϵ ($\mu\text{M}^{-1}\text{cm}^{-1}$)]	f_{B}^a	f_{Q}^a	$\lambda_{\text{max,2PA}}$ (nm)	σ_2 (10^3 GM)
A-P2C₈(Zn)-A	468 [0.34], 494 [0.16] 694 [0.10], 748 [0.10]	2.96	0.67	904	15
A'-P2C₁₀(Zn)-A'	464 [0.24], 499 [0.08], 686 [0.05], 749 [0.05]	1.79	0.35	920	6
A-P2C₈(Zn)-D	469 [0.30], 495 [0.19] 702 [0.09], 756 [0.10]	2.68	0.65	902	12
A-P2C₈(Zn)-R	466 [0.35], 498 [0.15] 690 [0.09], 748 [0.09]	2.67	0.58	900	13
D-P2C₈(Zn)-D	468 [0.25], 496 [0.17] 704 [0.08], 752 [0.08]	2.54	0.57	902	13
D-P2C₁₀(Zn)-D	466 [0.22], 496 [0.14], 703 [0.06], 744 [0.06]	2.50	0.52	920	21
D-P2C₈(Zn)-R	464 [0.32], 497 [0.18] 697 [0.08], 745 [0.09]	2.67	0.58	900	12
R-P2C₈(Zn)-R	465 [0.46], 499 [0.16] 681 [0.09], 744 [0.10]	2.82	0.55	890	9.1
A-P2C₈(2H)-A	458 [0.27], 484 [0.11] 622 [0.06], 708 [0.06] 738 [0.07]	2.88	0.58	920	10
A'-P2C₁₀(2H)-A'	455 [0.31], 483 [0.09] 625 [0.05], 709 [0.05] 740 [0.07]	2.55	0.47	915	3.4
D-P2C₈(2H)-D	460 [0.22], 646 [0.08] 747 [0.10]	3.42	0.85	925	17
D-P2C₁₀(2H)-D	463 [0.23], 644 [0.07], 725 [0.08], 754 [0.09]	2.75	0.66	926	10
R-P2C₈(2H)-R	456 [0.29], 481 [0.09] 623 [0.05], 706 [0.05] 736 [0.06]	2.39	0.47	915	7.7

^aCalculated using $f = 4.319 \times 10^{-9} A/n$ where n is the solvent refractive index (1.45 for CHCl₃) and A is the integrated absorption band (units: mol⁻¹ L cm⁻²; integration range for M = Zn f_{B} 18,020–26,670 cm⁻¹/375–555 nm; range for f_{Q} 11,830–16,450 cm⁻¹/608–845 nm; integration range for M = 2H f_{B} 17,699–30,030 cm⁻¹/333–565 nm; range for f_{Q} 11,111–17,699 cm⁻¹/565–900 nm).

Two-photon absorption spectra

The 2PA cross-sections and spectra were measured by two-photon excited fluorescence (2PEF) under dilute conditions (concentration ca. 10⁻⁶ M) in chloroform, in the presence of 1% pyridine in the case of the zinc complexes, to suppress aggregation. We can be confident that there is no aggregation under these conditions, because aggregation was not detected when the same compounds were examined by ¹H NMR in the same solvents at much higher concentrations (ca. 10⁻³ M). The entire series of dimers was found to have large σ_2 (~10⁴ GM at ~900 nm; Table 1) with maxima lying between 890 and 926 nm, in accordance with literature values^{5,15,19-21,36,51,52} and representing an hundred-fold enhancement compared to typical porphyrin monomers.¹⁴⁻¹⁷ The 2PA spectra feature a second, broader peak at lower intensity at 1050–1150 nm. The strongly quadrupolar **A-P2C₈(Zn)-A** dimer exhibits a peak cross section of 1.5 × 10⁴ GM, which is 1.7-fold larger than that of the **R-P2C₈(Zn)-R** reference system, and similar to that of Oxidime.^{5,30} However this enhanced 2PA is not observed in **A'-P2C₈(Zn)-A'**, illustrating the weaker effect of the CF₃ acceptor. **D-P2C₈(2H)-D** shows a 2.2-fold increase in peak cross section over the free-base reference compound **R-P2C₈(2H)-R**.

A three-level model has previously been invoked to describe the 2PA spectra of centrosymmetric porphyrin dimers, with the lowest-energy Q_x(0-0) transition assigned to the

intermediate state.^{15,20} Resonance enhancement due to the presence of this state is in part responsible for the large σ_2 observed for porphyrin dimers compared to monomers.^{15,20} Besides the centrosymmetry supporting the role of the Q_x(0-0) transition, the close match between the difference in the shortest and longest wavelengths of the 2PA maxima and the difference in the wavelengths of the lowest energy Q_x(0-0) transition of the corresponding compounds further implies this state is significant in 2PA [comparing **R-P2C₈(Zn)-R** with **A-P2C₈(Zn)-A**, and **R-P2C₈(2H)-R** with **D-P2C₁₀(2H)-D**]. It is also observed that the oscillator strength of the Q band is strongest in **A-P2C₈(Zn)-A** and **D-P2C₈(2H)-D**, contributing to their large σ_2 values.

The 2PA cross section of the butadiyne-linked porphyrin dimer core is found to be quite insensitive to substitution. This is emphasized by comparing the factor of ~2-fold difference between σ_2 of **A-P2C₈(Zn)-A** and **R-P2C₈(Zn)-R**, and between **D-P2C₈(2H)-D** and **R-P2C₈(2H)-R**, and the factor of ~20 between analogously modified porphyrin monomers.¹⁶ Commonly held design principles, such as the advantage of a quadrupolar system over a dipolar system, are thus strongly dependent upon the core π -system. The tetrapyrrole core has elsewhere been found to be surprisingly unperturbed by peripheral substitutions; in a recent study of metal-free tribenzo-tetraazachlorin, distinct *gerade-gerade* 2PA transitions are maintained, despite the formal lack of a center of inversion.¹⁵

Table 2. Electrochemical potential data for selected dimers

dimer	E_{ox}	$E_{\text{ox}} - E_{\text{ox,ref}}$	E_{red}	$E_{\text{red}} - E_{\text{red,ref}}$	$E_{\text{ox}} - E_{\text{red}}$
A-P2C₈(Zn)-A	0.43	0.04	-1.41	0.06	1.84
D-P2C₈(Zn)-D	0.23	-0.16	-1.53	-0.06	1.76
R-P2C₈(Zn)-R	0.39	0	-1.47	0	1.86
A-P2C₈(2H)-A	0.61	0.06	-1.18	0.10	1.79
A'-P2C₁₀(2H)-A'	0.63	0.08	-1.23	0.05	1.86
D-P2C₈(2H)-D	0.27	-0.28	-1.31	-0.03	1.58
D-P2C₁₀(2H)-D	0.27	-0.28	-1.32	-0.04	1.59
R-P2C₈(2H)-R	0.55	0	-1.28	0	1.83

All data are in volts against internal ferrocene (Fc/Fc⁺) and were acquired using square wave voltammetry in THF containing Bu₄NPF₆ (0.1 M). $E_{\text{ox,ref}}$ and $E_{\text{red,ref}}$ refer to the oxidation and reduction potentials respectively for the relevant **R-P2C₈(M)-R** reference compound. Square wave frequency 8 Hz; glassy carbon working electrode, Pt counter electrode, Ag/AgNO₃ reference electrode.

The largest 2PA cross sections are found when two acceptor groups are attached to the electron-rich zinc porphyrin dimers, as in **A-P2C₈(Zn)-A**, or when two donor groups are attached to the electron-poor free-base dimers, as in **D-P2C₈(2H)-D**. The effects of electron accepting and donating substituents can be quantified by the changes in redox potentials of the porphyrin dimers (Table 2). The quantity $E_{\text{ox}} - E_{\text{ox,ref}}$ is the difference between the first oxidation potential of a specific dimer and that of the reference dimer **R-P2C₈(M)-R**. $E_{\text{ox}} - E_{\text{ox,ref}}$ acts as a

measure of the electronic effect of the acceptor or donor groups upon the porphyrin dimer core, and reveals that the aniline donor group induces the greatest electronic perturbation on the dimer core, both in **D-P2_{C8}(Zn)-D** and **D-P2_{C8/10}(2H)-D**, but this perturbation is only translated into the one- and two-photon absorption profiles for the free-base core. Relative to the zinc core, the free-base core is electron poor, and **D-P2_{C8}(2H)-D** is thus a stronger quadrupolar “push-pull-push” system than **A-P2_{C8}(2H)-A**; as a result, an enhanced σ_2 is observed. However, based on this electrochemical analysis of the “push” and “pull” effect alone, the bis-donor dimer would also be expected to exhibit the highest σ_2 in the zinc series, as the magnitude of $E_{ox} - E_{ox,ref}$ is again greater for **D-P2_{C8}(Zn)-D** than **A-P2_{C8}(Zn)-A**. Instead **A-P2_{C8}(Zn)-A** dominates the σ_2 trend, itself also highly polarizable and benefitting from the longest π -system due to complete conjugation of the strong “pull-pull” nitro groups to the phenyl rings. The importance of a long conjugation pathway is also seen from the low value of σ_2 of **A'-P2_{C10}(2H)-A'** (with -CF₃ σ -acceptors) compared with **A-P2_{C8}(2H)-A** (with -NO₂ π -acceptors).

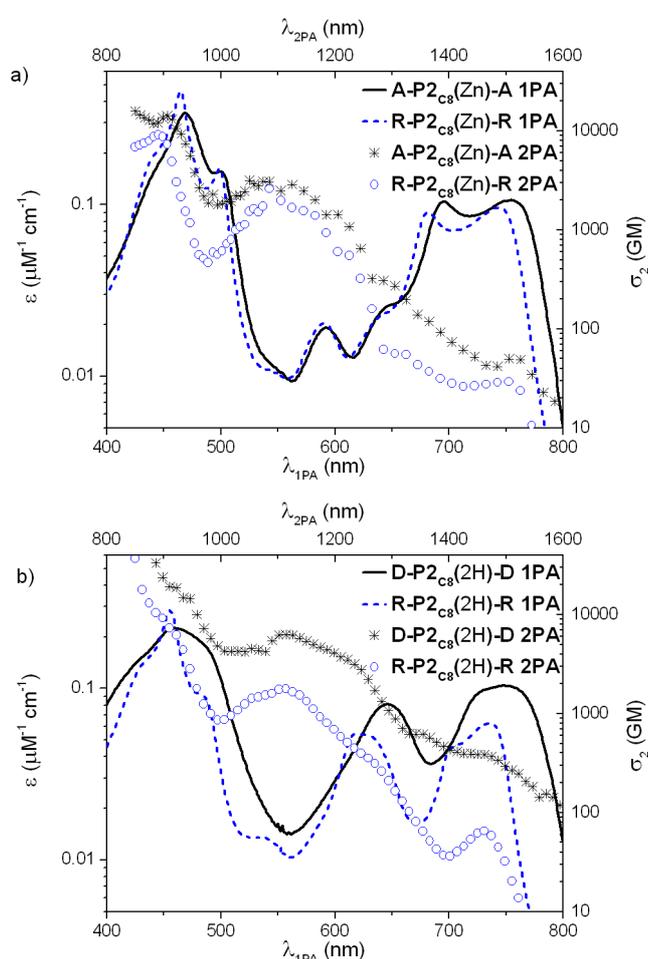


Fig 2. One- and two-photon absorption spectra of a) **A-P2_{C8}(Zn)-A** and **R-P2_{C8}(Zn)-R** in CHCl₃ containing 1% pyridine and b) **D-P2_{C8}(2H)-D** and **R-P2_{C8}(2H)-R** in CHCl₃.

D-P2_{C8}(2H)-D and **D-P2_{C10}(2H)-D** are indistinguishable by electrochemistry, suggesting little difference in “push” between the dibutyl and dimethyl aniline groups, but these dimers exhibit different cross sections. The **P2_{C10}** variant does not display as heightened Q band oscillator strength as the **P2_{C8}** variant, and thus resonance enhancement is weaker, suggesting subtle effects upon the optical properties originating from the bulkier side groups.

The effects of the π -core and the quadrupolar nature of the structure upon σ_2 are consistent with other studies,³⁴ but do not account for all of the subtle variation within the series. The design principles derived for simple organic moieties cannot be simply applied to more complex π -cores, and do not play such an obvious role in butadiyne-linked porphyrin dimers.

Conformation effects

Previously it has been found that there is a poor match between the one- and two-photon transition energies in butadiyne-linked porphyrin dimer, as is confirmed by the data in Table 1 and Figure 2; for example values of $\lambda_{max,2PA}$ do not correlate well with $\lambda_{max,1PA}$. This implies that 2PA involves transitions to a *gerade* final state,^{15,20} and that the chromophores are effectively centrosymmetric, which is surprising because these dimers exist in solution as broad distributions of conformations, due to free rotations about the butadiyne link,³⁸ and only the conformation in which both porphyrins are co-planar is centrosymmetric.

The different torsional conformations of a butadiyne-linked porphyrin dimer have different fluorescence spectra. In the ground state, the barrier to rotation about the butadiyne link is less than kT at room temperature, whereas this barrier becomes higher in the singlet excited state.³⁸ In low-viscosity solvents, the excited states undergo planarization faster than radiative decay, so that most of the emission originates from the planar conformation, regardless of which conformation was excited, but in viscous media torsional rotation becomes slow on the time-scale of emission and the shape of the observed fluorescence spectrum provides information on the conformations that were excited.³⁹ Although there is a continuous distribution of conformations, the spectra can be adequately analyzed in terms of just two extreme conformations with twisted and planar geometries.

We analyzed the one- and two-photon excited fluorescence spectra of **R-P2_{C8}(Zn)-R** in a viscous chloroform/polymer medium, in order to test which conformations contribute most to the 2PA. The normalized one-photon excitation and fluorescence spectra of **R-P2_{C8}(Zn)-R** in Figure 3 show that twisted and planar conformations fluoresce at 685 and 755 nm respectively. One photon excitation at 500 nm generates exclusively the planar excited state, whereas excitation at 460 nm gives predominantly the twisted excited state, with also some planar excited state due to competing absorption by both conformations at 460 nm, and possibly due to partial planarization in the excited state.

This viscous solution was then used to acquire a 2D 2PEF emission-excitation spectrum (Fig. 4). The two-photon excitation emission map reveals that upon excitation at the 2PA

maximum (890 nm), emission is seen exclusively from the planar form (755 nm), implying that this conformation is the stronger two-photon absorber. The tail of the contour reveals a second 2PA peak clearly emitting at the wavelength of the twisted conformation (685 nm) with excitation shifted bathochromically by 15 nm, as expected for a twisted conformation.⁵³

Whereas the one-photon excited emission spectra at various excitation wavelengths demonstrate that both conformations absorb strongly, in ratios reflected in the varying emission ratio of the two peaks (685:755), under two-photon excitation there is very little variation in the emission ratio, as the planar form is the dominant 2P absorber (Fig. 5). Plotting the individual two-photon excitation spectra confirms the dominance of the planar form over the twisted form in σ_2 (Fig. 6).

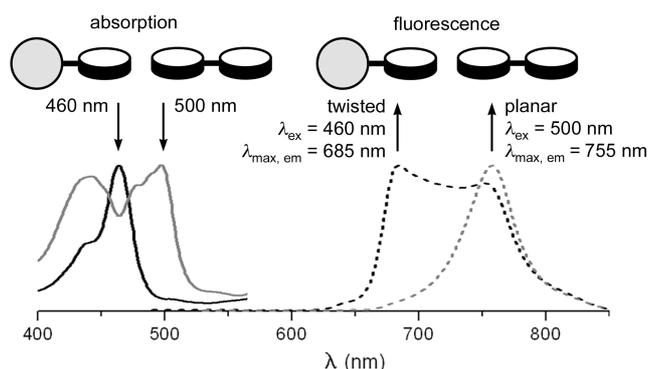


Fig 3. Normalized one-photon excitation spectra (solid lines, detection at 685 and 755 nm) and fluorescence spectra (dashed lines, excitation at 460 and 500 nm) spectra of **R-P2_{c8}(Zn)-R** in viscous solution; twisted conformation in black and planar conformation in grey.

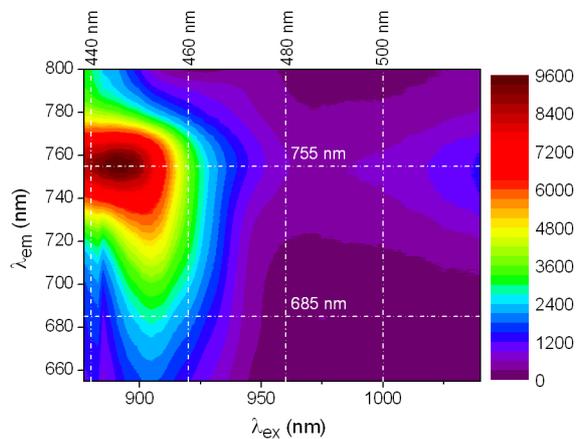


Fig 4. 3D two-photon excitation-emission plot of **R-P2_{c8}(Zn)-R** in viscous chloroform/polymer solution.

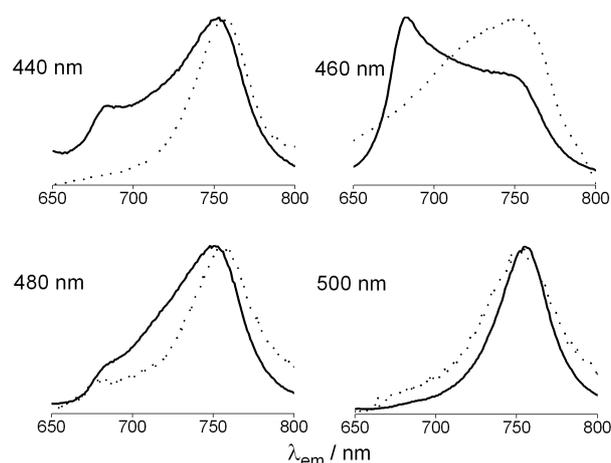


Fig 5. Emission spectra of **R-P2_{c8}(Zn)-R** in viscous solution under 1P (solid) and 2P (dots) excitation at the energy indicated.

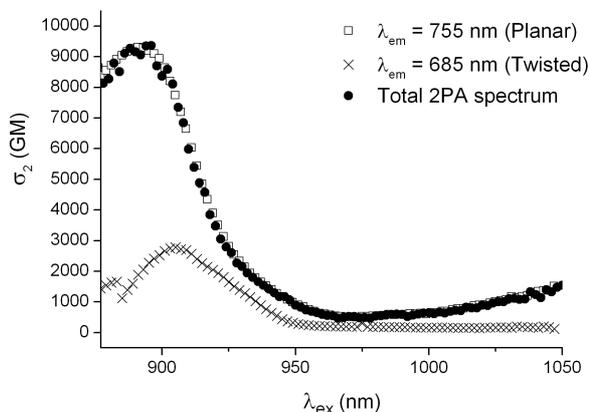


Fig 6. Two-photon excitation spectra of the planar and twisted conformations of **R-P2_{c8}(Zn)-R** acquired in viscous solution (values normalized to σ_2 measured in solution), compared to the total 2PA spectrum (integrated across all emission wavelengths) in normal solution.

Conclusions

This systematic study of donor- and acceptor-substituted butadiyne-linked porphyrin dimers shows that the attachment of electron acceptors and donors can increase the 2PA cross section by about a factor of three in zinc and free-base dimers. However the nonlinear optical properties of these dimers are much less sensitive to donor/acceptor substituents than has been found for the corresponding porphyrin monomers.^{16,17,54-56} These insights will be useful in the design of applied two-photon absorbers, as optimizing features such as biocompatibility can be prioritized. We have also provided direct spectroscopic evidence that the 2PA of these dimers is dominated by the contribution from the planar form. This result is in accord both with inferences made from the 2PA spectra regarding the planarity of related dimers,¹⁵ theoretical work on butadiyne-linked dimers,⁵¹ and with systems modified to enhance planarity.^{29,33-37} This work indicates that the σ_2 of

butadiyne-linked dimers can be increased by synthetic modifications to suppress twisted conformations.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: One- and two-photon absorption spectra, synthetic procedures and characterization, square-wave and cyclic voltammetry. See DOI: 10.1039/b000000x/

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