Strong Cooperative Enhancement of Two-Photon Absorption in Double-Strand Conjugated Porphyrin Ladder Arrays

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Simultaneous two-photon absorption (2PA) in macromolecular nanostructures, such as π-conjugated oligomers,[1] polymers,[2] and dendrimers,[3] has attracted considerable interest because the corresponding 2PA cross sections are usually very high and sometimes increase nonlinearly with the number of constituent building blocks.[1,3] We have recently found that butadiyne-linked porphyrin dimers show particularly large intrinsic (femtosecond) 2PA cross sections, $\sigma_2 \approx 10^4$ GM, which corresponds to a 500-fold cooperative enhancement compared to the parent monomer.[4] Similarly large σ_2 values have been reported for other conjugated porphyrin oligomers and polymers,[5,6] but the relationship between structure and conjugation length in these systems has yet to be elucidated.

Here we report the intrinsic 2PA spectra of a series of butadiyne-linked porphyrin oligomers, Zn$_2$**1**, Zn$_4$**2**, Zn$_8$**3**, and Zn$_N$**4**, containing 2, 4, 8, and ca. 13 monomer units. In solution, the conjugation lengths of single-strand chains can be strongly limited by rotational disorder (noncoplanarity),[7] but these oligomers become almost coplanar when they self-assemble into double-strand ladders.[5,8] We demonstrate that ladder formation dramatically increases the conjugation length, leading to strong cooperative enhancement of 2PA.
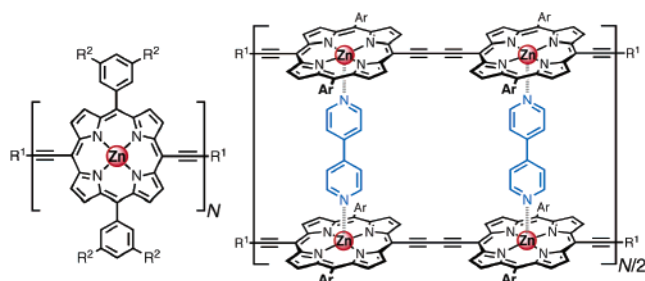
single strands
Zn$_2$**1** ($N = 2$, $R^1 =$ SiHex$_3$, $R^2 =$ OC$_8$H$_{16}$)
Zn$_4$**2** ($N = 4$, $R^1 =$ SiHex$_3$, $R^2 =$ OC$_8$H$_{16}$)
Zn$_8$**3** ($N = 8$, $R^1 =$ SiHex$_3$, $R^2 =$ OC$_8$H$_{16}$)
Zn$_N$**4** ($N = 10$-15, $R^1 =$ H, $R^2 =$ CON(CH$_2$CHEtBu)$_2$)

double strands
(Zn$_2$**1**)$_2$·Bipy$_2$
(Zn$_4$**2**)$_2$·Bipy$_4$
(Zn$_8$**3**)$_2$·Bipy$_8$
(Zn$_N$**4**)$_2$·Bipy$_N$

The changes in one-photon absorption (1PA) and 2PA upon transition from a single- to double-strand structure are illustrated by the spectra of the octamer complexes, Zn$_8$**3** and (Zn$_8$**3**)$_2$·Bipy$_8$, in Figure 1. The red shift and narrowing of the 1PA Q-band are accompanied by dramatic changes in the 2PA spectrum. The 2PA peak moves to longer wavelengths, from $\lambda_{2PA} \approx 890$ to 1315 nm. The 2PA maximum wavelengths (λ_{2PA}^m) and cross sections (σ_2^m) of the oligomers are summarized in Table 1. A new red-shifted 2PA band is apparent in the ladder complexes of all the longer

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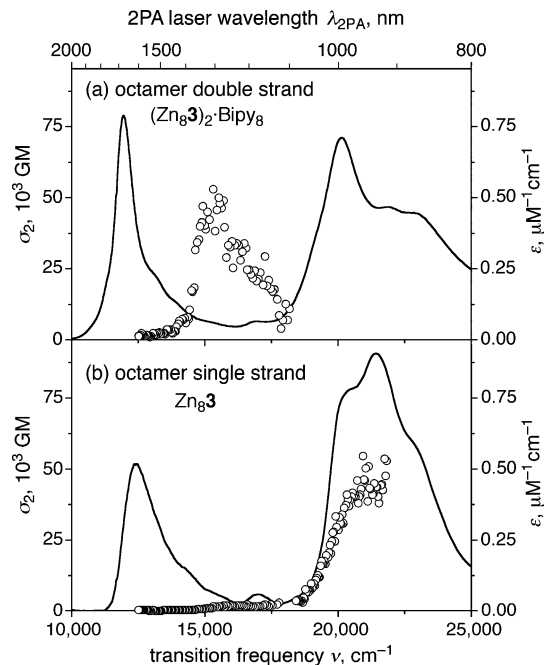[§] University of Oxford.

Figure 1. 2PA spectra (symbols) of octamer double strand (a) and single strand (b). 1PA spectra are also shown (solid lines).

Table 1. 2PA Properties of Single- and Double-Strand Porphyrin Oligomer Arrays with N Porphyrin Units[a]

N	compound	λ_{2PA}^m (nm)	σ_2^m (10^3 GM)	σ_2^m/N (10^3 GM)	S (10^5 GM cm^{-1})
2	Zn$_2$**1**	890	7.5	3.75	3.5
	(Zn$_2$**1**)$_2$·Bipy$_2$	880	6.6	3.3	2.9
4	Zn$_4$**2**	960	22	5.5	17.6
	(Zn$_4$**2**)$_2$·Bipy$_4$	1305	8.8	2.2	43.8
8	Zn$_8$**3**	980	37	4.6	45.1
	(Zn$_8$**3**)$_2$·Bipy$_8$	1315	49	6.1	212
13 ± 3	Zn$_N$**4**	980	83	6.4	67.7
	(Zn$_N$**4**)$_2$·Bipy$_N$	1325	115	8.9	517

[a] These 2PA peak cross sections σ_2^m and "conjugation signature" S are expressed per covalent oligomer chain, rather than per supramolecular unit, for direct comparison of single- and double-strand arrays.

oligomers but is not observed with the dimer. This difference in behavior can be explained by assuming that, in the dimer, the conjugation strength does not change much from single strand to double strand, as found previously in DABCO ladder complexes.[8] In the single-strand arrays, the peak cross section per macrocycle, σ_2^m/N, virtually does not change with the number of units N (Table 1). On the other hand, in the double-strand systems, σ_2^m/N drops
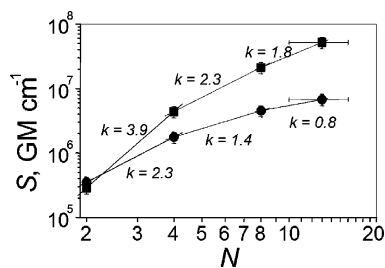
Figure 2. Scaling of 2PA conjugation signature S with the number of monomer units N for single-strand (circles) and double-strand oligomers (squares). Horizontal error bars on the polymer point reflect the uncertainty in the chain length ($N \approx 13$) of the polymer.

from dimer to tetramer and then gradually increases from tetramer to octamer and polymer.

For a quantitative analysis of these results, we turn to the three-level model that was shown to work well with related porphyrin dimers.[4] This simple model includes the ground state 0, one intermediate state i, which we identify with the lowest Q-state, and the final state f, which is a one-photon-forbidden but two-photon-allowed mA_g state, common for one-dimensional conjugated polymers.[9,10] Second-order perturbation theory gives, then, for the peak 2PA cross section:[4]

$$\sigma_2{}^m = C \frac{|\mu_{i0}|^2 |\mu_{fi}|^2}{(2\nu_{i0}/\nu_{f0} - 1)^2 \Gamma_f} \tag{1}$$

where μ_{nm} is the transition dipole moment between states m and n, ν_{nm} is the corresponding transition frequency, C is a constant, depending on relative orientation of transition dipole moments μ_{i0} and μ_{fi}, and Γ_f is the line width of state f.

If one applies eq 1 to an oligomer with N repeat units, the integrated 2PA strength will increase nonlinearly with N only if the conjugation length L_c increases with oligomer size. Furthermore, as far as L_c is proportional to the number of monomer units N, or, alternatively, $|\mu_{i0}| \propto N$ (cf. particle-in-a-box model), the electronic delocalization can be considered as spread over the whole chain in both the 0 and i states. The second transition dipole moment, $|\mu_{fi}|$, will also scale linearly with N as far as the electron and the hole are only weakly correlated in both the i and f states.[7] On the other hand, there is no simple power dependence describing the denominator of eq 1. The main reason for this is the complicated behavior of ν_{i0} and ν_{f0} as functions of L_c.[10] Therefore, we define here a "conjugation signature" S, which depends only on the product of transition dipole moments involved in 2PA, such that $S = C|\mu_{i0}|^2|\mu_{fi}|^2$. Its value can be obtained from experimentally measured $\sigma_2{}^m$, Γ_f, ν_{i0}, and ν_{f0} as follows: $S = \sigma_2{}^m \Gamma_f (2\nu_{i0}/\nu_{f0} - 1)^2$ (see eq 1). According to our above consideration, $S \propto N^4$ for fully conjugated systems and $S \propto N$ for uncoupled systems. Any power exponent between 1 and 4 implies that the conjugation length, while still increasing with N, encompasses not the whole oligomer chain but a certain fraction thereof.

Experimentally, ν_{i0} was determined as the frequency of the lowest Q-band, and $\sigma_2{}^m$, Γ_f, and ν_{f0} were found from 2PA spectra as described in ref 4. The S values obtained for both series of oligomers are presented in the last column of Table 1. Figure 2 demonstrates, in double logarithmic coordinates, the scaling behavior of S for both single- and double-strand oligomers. The numbers near the segments, connecting data points, designate the power exponent k of the corresponding scaling law $S \propto N^k$. In both cases, S first increases nonlinearly and then starts to saturate for longer oligomers.

For all $N \geq 4$, double-strand arrays perform much better in terms of the conjugation length. Also, in double strands $k \approx 4$ up to tetramer. This suggests that the conjugation length embraces the whole molecule up to $N = 4$ and then gets smaller for $N \geq 8$, while still increasing. This saturation behavior of long oligomers may be due to conformational inhomogeneity. One possibility is the formation of "slipped" ladders, where one chain is laterally displaced with respect to the other, but for smaller oligomers, $N \leq 6$, such structures were ruled out by ^{1}H NMR and spectrophotometric titrations,[5,8] in good agreement with the 2PA data. In the single strands, the conjugation length is always less than N, except for $N = 2$, but keeps increasing until $N = 8$. Similar "effective conjugation lengths" ($N_c \approx 2-5$) have been recently predicted theoretically for butadiyne-linked porphyrin oligomer series.[11]

We have shown that the 2PA "conjugation signature" acquires much larger values and increases faster with N for double-strand arrays, which is expected from their better coplanarity. However, this does not result in a dramatic increase of the $\sigma_2{}^m$ values in double strands compared to single ones because of worse detuning factors in the former case. The double-strand oligomers show extremely large 2PA cross sections at 1.3 μm, which may be of great importance for optical switching and signal processing in fiber-optic communications technologies.

Supporting Information Available: Details of synthesis, complexation titrations, 2PA measurements method, and 2PA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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