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Amplified Optical Nonlinearity in a Self-Assembled Double-Strand Conjugated Porphyrin Polymer Ladder

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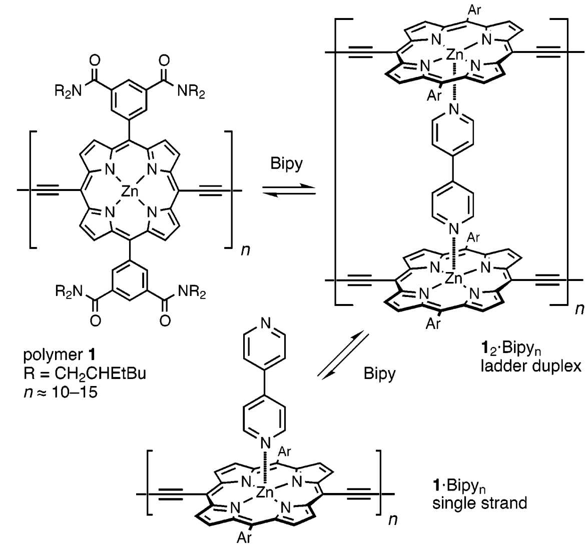
Received March 15, 2002

Materials with large third-order optical susceptibility, $\chi^{(3)}$, have numerous applications in nonlinear optics. High values of the real component result in nonlinear refraction, leading to scope for ultrafast all-optical signal processing,[1] while the imaginary component Im$\chi^{(3)}$ controls two-photon absorption, which is useful for optical limiting,[2] two-photon fluorescence microscopy,[3] and 3D microfabrication.[4] Strong third-order nonlinearity is exhibited by materials with long conjugated π-systems and is enhanced by resonance with one- and two-photon transitions.[5] Conjugated porphyrin polymers[6] have the largest one-photon off-resonant $\chi^{(3)}$ values reported for organic materials, due to two-photon resonance.[7,8] Here we demonstrate that self-assembly of double-strand ladder complexes achieves a 9-fold amplification in the nonlinearity of these polymers by holding the π-systems in a planar conformation. There is great interest in the use of self-assembly to control the structure and function of synthetic polymers;[9] this is the first time this strategy has been applied to amplify optical nonlinearity.

Previously we have demonstrated that butadiyne-linked zinc porphyrin oligomers form double-strand ladder complexes with linear bidentate ligands such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and 4,4′-bipyridyl (Bipy).[10] We were unable to extend this approach to porphyrin polymers due to solubility problems, until we prepared polymer **1**. This new polymer dissolves in noncoordinating solvents, such as chloroform, even in the absence of amines, although under these conditions it exists as an aggregate. Addition of Bipy breaks up this aggregate, generating the double-strand ladder complex $\mathbf{1}_2$•Bipy$_n$. At higher Bipy concentration this duplex dissociates into a single-strand complex, **1**•Bipy$_n$, as shown in Scheme 1. The near-IR spectral evolution during titration of polymer **1** with Bipy is shown in Figure 1a. There is an initial red-shift in the Q-band maximum, from 827 to 856 nm, due to ladder formation, followed by a blue-shift to 781 nm at higher Bipy concentrations due to single-strand formation.[11] The binding isotherm in Figure 1b was obtained by plotting the absorption at 856 nm against Bipy concentration. The data fit surprisingly well to the calculated curve for all-or-nothing formation of a tetramer ladder, as illustrated in Figure 1b,[12] but higher ladders give similar isotherms, and we suspect the experimental curve is the sum of many polydisperse ladder-forming and -breaking equilibria. Hill plots provide a way of quantifying the cooperativity of a binding process, even when the stoichiometry is unknown;[10] in this case the Hill coefficients for the formation and breaking of the ladder are highly cooperative ($n_{\mathrm{H}} = 3.0$ and 3.7, respectively), as expected for a self-assembly process of this type. ^{1}H NMR titrations confirmed the formation of a ladder duplex. When a solution of **1** in CDCl$_3$ is treated with 0.5 equiv of Bipy per macrocycle, new signals appear at 5.05 and 2.65 ppm, typical chemical shifts for a Bipy ligand between two porphyrins.[13] These signals broaden and shift downfield when more Bipy is added, as the ladders dissociate. The ladders are stable enough to survive on an analytical size-exclusion column in CHCl$_3$, giving molecular weights of $M_{\mathrm{n}} = 5.6 \times 10^4$ and 2.1×10^4 respectively for $\mathbf{1}_2$•Bipy$_n$ and **1**•(pyridine)$_n$. We have also characterized these assemblies by small-angle neutron scattering (SANS) in CDCl$_3$. The scattering profiles fit a rigid rod model (see Supporting Information); the ladder $\mathbf{1}_2$•Bipy$_n$ behaves as a rod with a diameter of 31 ± 2 Å and a length of 105 ± 7 Å (corresponding to about seven repeat units), whereas the **1**•(pyridine)$_n$ single strand behaves as a rod with a diameter of 14 ± 2 Å and a length of 68 ± 5 Å. The double-strand nature of $\mathbf{1}_2$•Bipy$_n$ is reflected in its greater diameter, while the shorter apparent length of **1**•(pyridine)$_n$, despite its identical covalent length, reflects its greater flexibility.

Scheme 1



The Q-band absorption of the ladder $\mathbf{1}_2$•Bipy$_n$ is sharper and red-shifted, by 75 nm, compared with that of the single-strand **1**•Bipy$_n$ (Figure 1a), yet the local coordination environment of each porphyrin is identical in these two polymers. Three factors may contribute to these spectral changes: (a) interchain coupling via the molecular orbitals of the Bipy, (b) through-space exciton coupling between the transition dipoles of the two chains, and (c) increased intrachain conjugation due to planarization. Studies on simpler zinc porphyrin complexes[13] indicate that factors (a) and (b) should result in a ca. 2 nm blue-shift, so we believe that the observed 75 nm red-shift in $\mathbf{1}_2$•Bipy$_n$ is mainly due to planarization. To test whether this increased conjugation would alter the nonlinear optical behavior, degenerate four-wave mixing (DFWM) measure-

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10.1021/ja026205k CCC: $22.00

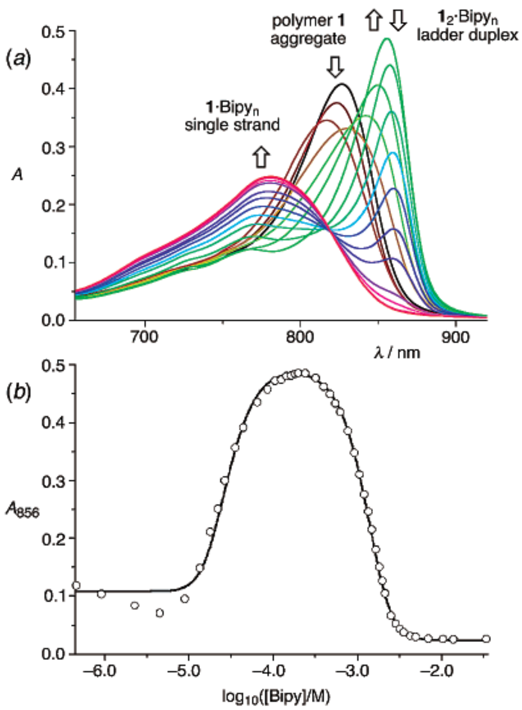
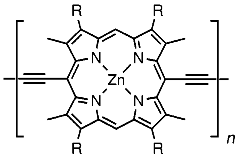


Figure 1. Near-IR titration of polymer **1** with Bipy in $CHCl_3$ at 298 K: (a) spectral evolution and (b) absorption at 856 nm vs ligand concentration, with a curve fit for an all-or-nothing tetramer ladder model.[12]

ments were carried out with solutions of the ladder $\mathbf{1}_2$·Bipy$_n$ and the single-strand quinuclidine complex **1**·Quin$_n$ at 1064 nm as described previously.[7,14] This gave the nonlinear optical parameters (per macrocycle unit) compared with those of our original conjugated porphyrin polymer **2**[7] in Table 1.



polymer **2**
R = $CH_2CH_2CO_2(CH_2)_2CHMe(CH_2)_3CHMe_2$

Both the real and imaginary components of $\chi^{(3)}$ are strongly amplified by ladder formation. It is reasonable to assume that the DFWM response is dominated by the three-level two-photon contribution,[7b,15] so the value of Im$\gamma_{yyyy}(-\omega;\omega,\omega,-\omega)$ for $\mathbf{1}_2$·Bipy$_n$ corresponds to a large two-photon absorption cross section of $\delta = 5 \times 10^{-46}$ cm^4 s (photon-macrocycle)$^{-1}$ = 5×10^4 GM per macrocycle at 1064 nm. For resonant two-photon absorption, a simplified expression[5c] for the susceptibility (in terms of the ground- and excited-state transition moments, M, the line width of the resonant two-photon state, Γ_{02}, and the off-resonant energy difference between the one-photon state and the measurement frequency, $\omega_{01} - \omega_L$) is

$$\delta(\omega) \propto \mathrm{Im}\gamma_{yyyy}(-\omega;\omega,\omega,-\omega) \propto [M_{01}{}^2/(\omega_{01} - \omega_L)^2][M_{12}{}^2/\Gamma_{02}] \quad (1)$$

The enhanced nonlinearity per macrocycle in the ladder is a reflection of the greater conjugation in *both* the one- and two-photon near-resonant states, according to eq 1. The increased delocalization in the one-photon state (Q-band) is observable in the red-shift and slight increase in oscillator strength f_Q. From the first term of eq 1, this would lead to a 3-fold enhancement in γ and δ. The observed 7-fold increase implies that the enhanced conjugation in the ladder also increases the excited-state transition dipole moment M_{12}. The greater nonlinearity of $\mathbf{1}_2$·Bipy$_n$ compared to **2**·Quin$_n$ must be due to this enhanced excited-state transition dipole since their linear optical properties are similar.

Table 1. Linear and Nonlinear Optical Parameters[a]

polymer	f_Q/N	$\lvert\gamma_{xyyx}\rvert/N$ ($\times 10^{-45}$ m^5 V^{-2})	$\lvert\chi^{(3)}{}_{xyyx}\rvert$ ($\times 10^{-17}$ m^2 V^{-2})	Im$\chi^{(3)}$/Re$\chi^{(3)}$	Imγ_{yyyy}/N ($\times 10^{-45}$ m^5 V^{-5})
1·Quin$_n$	0.55	0.84	0.66	−2.0	2.0
$\mathbf{1}_2$·Bipy$_n$	0.69	7.6	6.0	−1.2	14
2·Quin$_n$	0.52	2.8	2.2	−1.6	6.1

[a] f_Q is the oscillator strength of the Q-band; γ/N and $\chi^{(3)}$ are molecular and bulk susceptibilities per porphyrin macrocycle at 1064 nm in $CHCl_3$.

In summary, we have used near-IR, NMR, GPC, and SANS to show that polymer **1** binds Bipy to form a double-strand ladder. DFWM measurements demonstrate that this self-assembly process amplifies the optical nonlinearity per macrocycle by an order of magnitude. Thus, double-strand formation may be useful for creating advanced optoelectronic materials.

Acknowledgment. We thank EPSRC for support and EPSRC mass spectrometry service (Swansea) for mass spectra.

Supporting Information Available: Details of synthesis, complexation experiments, SANS, and DFWM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) When **1** is titrated with monodentate ligands such as pyridine and quinuclidine, the Q-band maximum shifts directly from that of the aggregate at 827 nm to that of the single-strand at ca. 780 nm.
(12) The data in Figure 1 are fitted to the tetramer ladder model $2A + 4B \rightleftharpoons A_2B_4$, with $K_F = 1.7 \times 10^{24}$ M^{-5}; $A_2B_4 + 4B \rightarrow 2AB_4$ with $K_B = 1.0 \times 10^5$ M^{-3}, using a set of 46 spectra with [Bipy] = 0.4 μM−34 mM, [porphyrin] = 4.0 μM in the range 350−1000 nm using SPECFIT version 3 (Spectrum Software Associates, P.O. Box 4494, Chapel Hill, NC 27515-4494).
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JA026205K