Investigation of Reverse-Saturable Absorption in Brominated Porphyrins

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Introduction

Optical limiters are devices containing dyes that undergo nonlinear absorption of light at high incident fluence. A type of dye used in an optical limiter is a reverse-saturable absorber (RSA). An RSA has excited states that behave according to a five-level model (Figure 1). When the ground state (S_g) of the RSA is excited to the first singlet state (S_1) by a laser of pulse width τ, intersystem crossing occurs to the triplet state (T_1). For an RSA material to be an efficient nonlinear absorber, it is desirable to have a high ratio of excited state ($T_1 \rightarrow T_2$) to ground state ($S_g \rightarrow S_1$) absorption cross section($\sigma_{ex}/\sigma_g \gg 1$), a rapid intersystem crossing rate ($\tau_{ISC} \ll \tau$), a long internal conversion lifetime ($\tau_{IC} \gg \tau$), a high intersystem crossing quantum yield ($\phi_{S_1 \rightarrow T_1} \sim 1$), and a long triplet lifetime ($\tau_{T_1} \gg \tau$). When these conditions are not met, insufficient triplet state population results in poor nonlinear absorption.

Perry et al.[1,2] have demonstrated that phthalocyanines exhibit good nonlinear absorption. Insertion of heavy atoms ("heavy atom effect") into the phthalocyanine ring causes significant effects on RSA performance by increasing spin−orbit coupling, leading to a high intersystem crossing rate and $\phi_{S_1 \rightarrow T_1}$. In our laboratory, we have been investigating the RSA properties of porphyrins.[3] The ease of porphyrin synthesis makes possible extensive structure−property studies, including studies of the effects of variation of the inserted metal, increasing ring size, adding conjugated groups, attachment of another chromophore, and halogenation. The RSA properties of some porphyrins have already been investigated by other groups. Blau *et al.*[4] have shown RSA in tetraphenylporphyrins (TPP), including H_2TPP, CoTPP, and ZnTPP. Reverse-saturable absorption has also been reported in FeTPP[5] and tetrabenzoporphyrins.[6] These porphyrins have a small cross section ratio and therefore an insufficient dynamic range to be used in optical limiters. Besides, some halogenated porphyrins were extensively synthesized and studied recently.[7−15] Bonnett et al. investigated the effect of bromination on the intersystem crossing rate of octaethyl porphyrins.[10] They have shown that by merely incorporating one bromine atom at the pyrrole position, $\phi_{S_1 \rightarrow T_1}$ is increased to virtually unity. Despite growing interest in these porphyrins and their application in catalysis, brominated porphyrins have not been investigated as RSA dyes. On the basis of the literature data, we expected that porphyrin bromination would enhance RSA performance and give porphyrins potential for use in optical limiters. In this communication, we give nonlinear absorption data for both octabromotetraphenylporphyrin (H_2OBP) and some metallooctabromotetraphenylporphyrins (MOBP). In particular, ZnOBP had strong nonlinear absorption comparable to state-of-the-art phthalocyanine dyes.

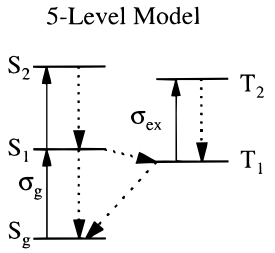
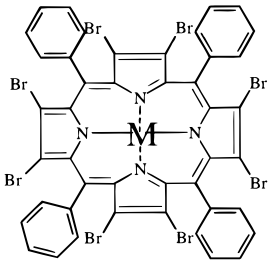


Figure 1. Five-level model describing RSA chromophore.



Experimental Section

Synthesis. H_2OBP was synthesized via bromination of CuTPP, followed by an acid demetalation reaction using a

(1) Perry, J. W.; Mansour, K.; Marder, S. R.; Perry, K. J.; Alvarez, D.; Choong, I. *Opt. Lett.* **1994**, *19*, 625.
(2) Perry, J. W.; Mansour, K.; Lee, I.-Y. S.; Wu, X.-L.; Bedworth, P. V.; Chen, C.-T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533.
(3) Su, W.; Cooper, T. M.; Tang, N.; Krein, D.; Jiang, H.; Brandelik, D.; Fleitz, P.; Brant, M. C.; McLean, D. J. *MRS Proc.* **1997**, *479*, 313.
(4) Blau, W.; Byrne, H.; Dennis, W. M.; Kelly, J. M. *Opt. Commun.* **1985**, *56*, 25.
(5) Fei, H. S.; Han, L.; Ai, X. C.; Yin, R.; Shen, J. C. *Chin. Sci. Bull.* **1992**, *37*, 298.
(6) Guha, S.; Kang, K.; Porter, P.; Roach, J. F.; Remy, D. E.; Aranda, F. J.; Rao, D. V. G. L. N. *Opt. Lett.* **1992**, *17*, 264.
(7) D'Souza, F.; Villard, A.; Van Caemelbecke, E.; Franzen, M.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4042.
(8) Bhyrappa, P.; Nethaji, M.; Krishnan, V. *Chem. Lett.* **1993**, 869.
(9) Takeuchi, T.; Gray, H. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 9730.
(10) Bonnett, R.; Harriman, A.; Kozyrev, A. N. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 763.
(11) Mandon, D.; Ochsenbein, P.; Fischer, J.; Weiss, R.; Jayaraj, K.; Austin, R. N.; Gold, A.; White, P. S.; Brigaud, O.; Battioni, P.; Mansuy, D. *Inorg. Chem.* **1992**, *31*, 2044.
(12) Hodge, J. A.; Hill, M. G.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 809.
(13) Baskigia, K. M.; Barber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851.
(14) Ochsenbein, P.; Ayougou, K.; Mandon, D.; Fischer, J.; Weiss, R.; Austin, R. N.; Jayaraj, K.; Gold, A.; Terner, J.; Fajer, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 348.
(15) Bonnett, R.; Campion-Smith, I. H.; Kozyrev, A. N.; Mironov, A. F. *J. Chem. Res.* **1990**, 138.

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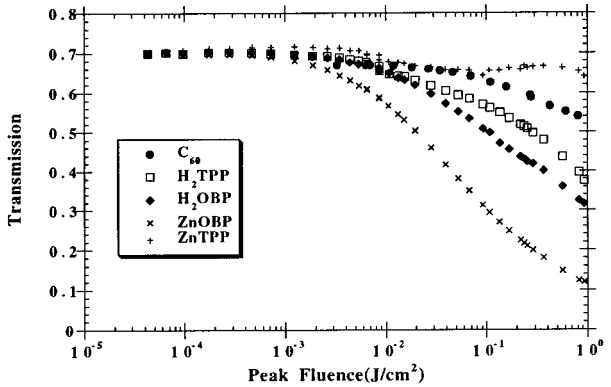

Figure 2. Nonlinear absorption data for TPP, ZnTPP, C_{60}, H_2OBP, and ZnOBP.

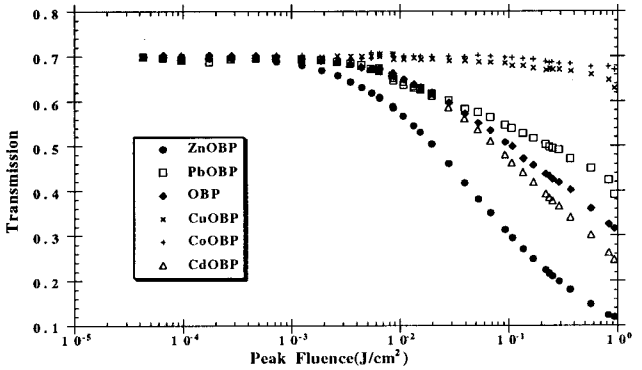

Figure 3. Nonlinear absorption data for H_2OBP, CoOBP, CuOBP, ZnOBP, CdOBP, and PbOBP.

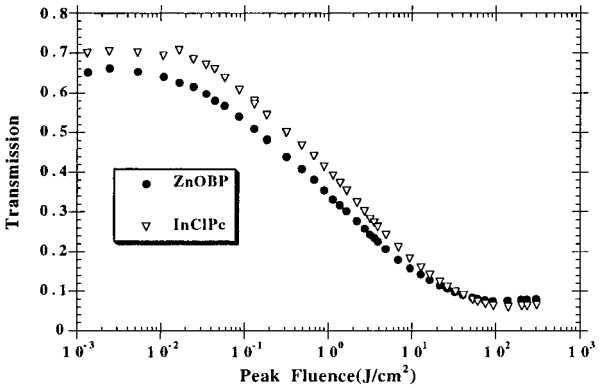

Figure 4. Nonlinear absorption data for ZnOBP, InClPc, and C_{60}.

minor modification of a procedure by Bhyrappa.[8] Zn-, Co-, Cu-, Cd-, and PbOBP were also made by Bhyrappa's method. ZnOBP, CoOBP, and CuOBP were purified by using flash column chromatography over basic alumina/CH_2Cl_2. Because CdOBP and PbOBP were not stable on an alumina column, they were chromotographed over Florisil/CH_2Cl_2. InCl-phthalocyanine(*tert*-butyl)$_4$(InClPc) was obtained from Jet Propulsion Laboratory and used without further purification.

Nonlinear Absorption Measurements. The experiment was designed to measure the nonlinear optical absorption of samples as thick as 1 cm. A 532-nm, 6.8-ns (fwhm) pulsed laser was focused to a 106 mm radius waist Gaussian beam in the sample. We used a long focal length lens (500 mm) to provide a collimated beam throughout the sample. The incident and transmitted energies were measured for 10 laser pulses at a 10-Hz repetition rate. This was repeated at increasing laser energies up to an energy 10^5 times greater than the lowest energy. Linear operation of the silicon energy meters over this large energy range was maintained by inserting calibrated neutral density filters as needed. The transmission of the system with no sample was also measured over this energy range to ensure the linearity of the experiment to within 1%. In addition, an integrating sphere was used to collect forward-scattered light within a *f*/2 cone angle. Any reduction in transmission was due to absorption of light within the sample. The porphyrins were dissolved in CH_2Cl_2, and the concentration was adjusted to a linear transmission of 70% at 532 nm. C_{60} and InClPc were dissolved in toluene.

Results and Discussion

Nonlinear absorption efficiency was estimated by measuring the transmittance change on going from 0 to 0.1 J/cm^2 peak fluence. In Figure 2, efficiency scaled as ZnOBP > OBP > TPP > C_{60} > ZnTPP. ZnOBP showed superior performance compared to the benchmark RSA dye C_{60}. ZnTPP and TPP are both planar, while H_2OBP has a saddle shape[8] and ZnOBP has a ruffled saddle conformation.[11,16] Ring nonplanarity increases the matrix element $\langle S_1|\ \mathbf{H}\ |T_1\rangle$, allowing for mixing of $\pi\sigma^*$ and $\sigma\pi^*$ triplet states with $S_1(\pi\pi^*)$ and the "free rotor effect", simultaneously shortening the intersystem crossing and triplet lifetimes.[10,17,18] The data in Figure 3 give a comparison of a series of MOBPs. In this case the efficiency scaled as ZnOBP > CdOBP > H_2OBP > PbOBP > CuOBP ≅ CoOBP. The trend reflected the spin state of the metals. Gouterman classifies three types of metals forming complexes with porphyrins: closed shell metals, open shell paramagnetic metals, and open shell diamagnetic metals.[19] Both Cu^{2+} and Co^{2+} are open shell paramagnetic ions with unfilled d orbitals. Spin−orbit coupling through Coulombic exchange terms could decrease the triplet lifetime, thereby lowering nonlinear absorption. In contrast, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions have closed shells. In heavy-atom-containing phthalocyanines, spin−orbit coupling and nonlinear absorption increases with *Z*.[20] However, in the closed shell metal OBP series, a reversed trend $Zn^{2+} > Cd^{2+} > Pb^{2+}$ appeared. Contributions to spin−orbit coupling come from the central metal ion, the bromines, and the distortion of the porphyrin ring. The factors that increase the intersystem crossing rate also decrease the triplet lifetime.[10,18] ZnOBP also showed nonlinear absorption comparable to that of the state-of-the-art phthalocyanine dye InClPc (Figure 4). A detailed presentation of kinetic parameters and $T_1 \rightarrow T_2$ spectra will be given in a later publication.

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(16) Birnbaum, E. R.; Hodge, J. A.; Grinstaff, M. W.; Schaefer, W. P.; Henling, L.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 3625.

(17) Gentemann, S.; Medforth, C. J.; Forsyth, T. P.; Nurco, D. J.; Smith, K. M.; Fajer, J.; Holten, D. *J. Am. Chem. Soc.* **1994**, *116*, 7363.

(18) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, 1994; pp 153−198.

(19) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.

(20) Mansour, K.; Alvarez, D.; Perry, K. J.; Choong, I.; Marder, S. R.; Perry, J. W. *SPIE Org. Biol. Optoelectron.* **1993**, *1853*, 132.