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“*Synthesis of Porphyrin Materials with Optimized Excited State Absorption Properties*”

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Final Report on period October 2001 – January 2005

Introduction. An ideal reverse saturable absorber (RSA) should have the following properties: small, but measurable, ground state absorption throughout the visible or near infrared (NIR) spectral regions, large excited state absorption cross-section over the same wavelength range, and long ($>1 \mu\text{s}$) excited state lifetime. Porphyrins are one of the most promising classes of RSA materials because their excited states have large absorption cross-sections and their molecular structure can be modified to obtain the desired spectral properties. Much progress has been made in establishing structure-property relationships among porphyrins in the visible spectral region (400–700 nm), but little has been done in the development of these materials for the NIR (700–900 nm). The aim of this project was to synthesize highly conjugated porphyrin oligomers with strong RSA behavior in this NIR region. Increasing the conjugation shifts the ground state, and excited state, absorption to longer wavelengths.

Summary of Results. This final report summarizes the contents of 13 quarterly reports. During the period of the project, 8 out of the 12 target milestones set in the original proposal were fully achieved; 3 out of the 4 remaining target milestones were partially achieved, and all the compounds targeted in the proposal were successfully synthesized, except for the cumulenyl trimer (**2**) and the push-pull quinoidal dimer (**10**). Substantial effort was invested in pursuing these two elusive targets, and our failure to prepare them leads us to conclude that they are too unstable to be isolated. We also synthesized and tested many compounds not envisaged at the time of the proposal. 26 of the most interesting new materials generated from this research were tested by Dr Paul Fleitz’s team at AFRL/MLPJ. The structures of these compounds, and the conclusions from their photophysical behavior, are summarized briefly in the Appendix to this report. Three of these compounds appear to be promising materials for RSA in the NIR (**Ander4**, **Ander4-I**, and **C2H2-dimer**). The following themes have emerged from this work:

(1) Control of Triplet Yield. Four key parameters need to be controlled in the design of an RSA dye: (i) the ground state S_0-S_n absorption spectrum, (ii) the triplet excited state T_1-T_n absorption spectrum, (iii) the triplet yield and (iv) the triplet lifetime. At the outset of this project we expected the main challenge to be control of the S_0-S_n and T_1-T_n absorption spectra, because most known porphyrins already had suitable triplet yields and triplet lifetimes. However the main challenge has been to maintain a high triplet yield while achieving a suitable shift in the absorption spectra. Shifting the S_0-S_n and T_1-T_n absorption to longer wavelengths generally results in faster S_1-S_0 internal conversion, reducing the triplet yield. This effect is most prominent in the edge-fused systems (**Ander1**, **Ander4**, **Ander6**, **Pb-TIPS triple-link dimer**, **Zn-TIPS triple-link trimer**, **Ander4-I**, **Ar6-dimer** and **D18Ar6-dimer**). We found that satisfactory triplet yields could be achieved by attaching heavy atoms to the *meso*-positions of the dimers (as in **Ander4** and **Ander4-I**), so as to increase the rate of S_1-T_1 intersystem crossing. It

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14. ABSTRACT

This report results from a contract tasking The Chancellor, Masters and Scholars of the University of Oxford as follows: The contractor will investigate the nonlinear response of porphyrin-based materials to intense laser illumination. Porphyrin-based materials have shown nonlinear coefficients an order of magnitude greater than other organic compounds. The contractor will synthesize and analyze various forms of these materials to optimize their nonlinear optics properties.

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is interesting that this strategy is more effective than the insertion of heavy atoms at the center of the porphyrin (as in **Pb-TIPS triple-link dimer**).

The deuterated compound **D18Ar6-dimer** was synthesized to test whether coupling with C-H vibrations has a significant role in facilitating internal conversion in these systems. Pump-probe experiments detected no significant triplet absorption with either **D18Ar6-dimer** or **Ar6-dimer**, and fluorescence experiments (by Dr Nicola Armaroli, Istituto ISOF/CNR, Bologna, Italy) showed that these two compounds have identical fluorescence quantum yields in both dichloromethane and toluene. We still plan to investigate whether there is a difference in fluorescence efficiency in hydrogen-free solvents (such as CCl_4), but the current data indicate that coupling with C-H vibrations has little effect on the rate of internal conversion in these systems. There seems to be a need for theoretical work to gain a better understanding of the factors controlling the rates of internal conversion and intersystem crossing in these dyes.

(2) Use of Two-Photon Absorption and Excited State Absorption. During the course of this project, collaborative experiments with Prof. Aleks Rebane (Montana, USA) showed that some of our conjugated porphyrin dimers (e.g. **PNT-dimer**, **C4-dimer** and **C2-dimer**) exhibit extremely strong two-photon absorption (TPA) in the 800-900 nm region (these results were published in *J. Am. Chem. Soc.* 2004, 126, 15325). This suggests that these materials might be able to exhibit RSA by a combination of TPA and ESA, so we synthesized highly soluble derivatives (**C4/MJF-dimer** and **PNT/CJW-dimer**) for testing at high concentrations. The results showed that the materials exhibit nonlinear absorption at 800, 840 and 880 nm, but the mechanism seems to be purely TPA because the T_1-T_n band at around 1000 nm does not overlap well with the TPA band. Recently we have synthesized an alkene-linked structure (**C2H2-dimer**) which exhibits a T_1-T_n band at shorter wavelengths (ca. 750–1000 nm). It will be interesting to see whether this provides better overlap with the two-photon absorption (TPA experiments are in progress).

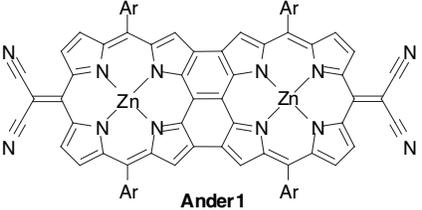
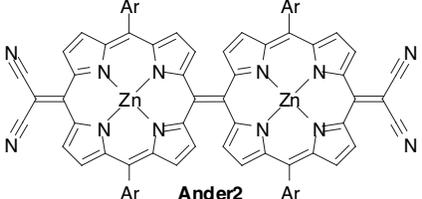
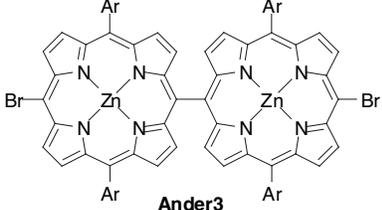
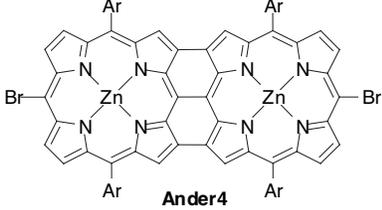
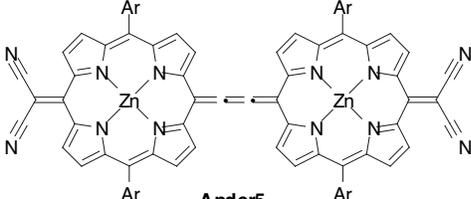
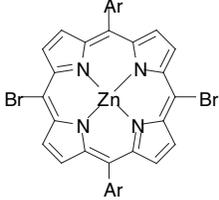
Publications. Three articles have been published on work directly resulting from this project:

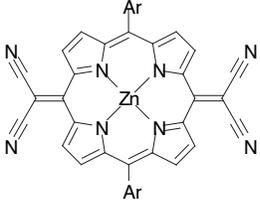
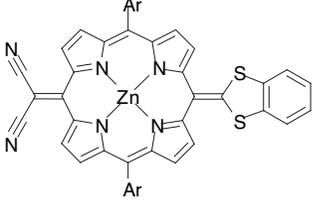
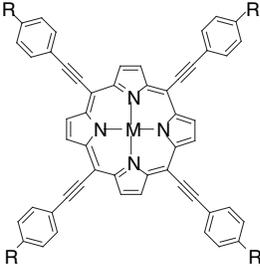
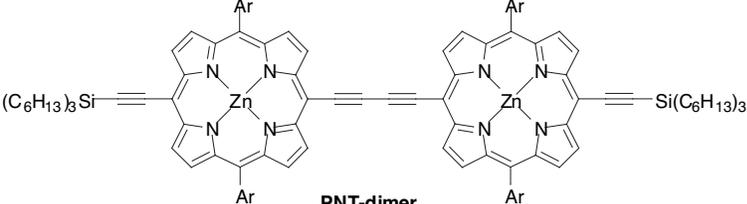
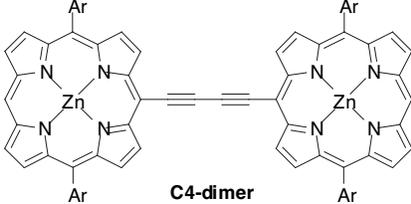
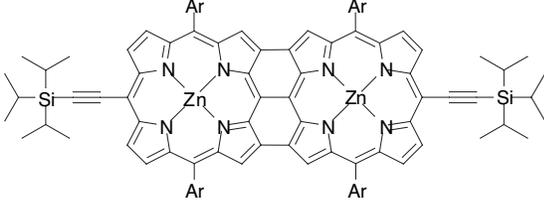
- (i) “*Fusion and planarization of a quinoidal porphyrin dimer*”, I. M. Blake, A. Krivokapic, M. Katterle and H. L. Anderson, *Chem. Commun.* **2002**, 1662–1663.
- (ii) “*Reverse saturable absorption in the near infrared by fused porphyrin dimers*”, K. J. McEwan, P. A. Fleitz, J. E. Rogers, J. E. Slagle, D. G. McLean, H. Akdas, M. Katterle, I. M. Blake and H. L. Anderson, *Adv. Mater.* **2004**, 16, 1933–1935.
- (iii) “*Synthesis and crystal structure of a push-pull quinoidal porphyrin: a nanoporous framework assembled from cyclic trimer aggregates*”, M. J. Smith, W. Clegg, K. A. Nguyen, J. E. Rogers, R. Pachter, P. A. Fleitz and H. L. Anderson, *Chem. Commun.* **2005**, in press.

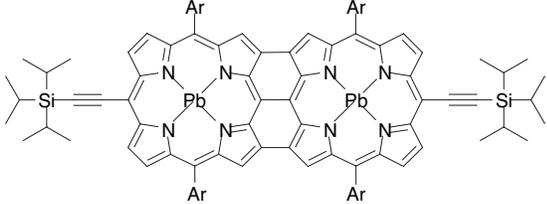
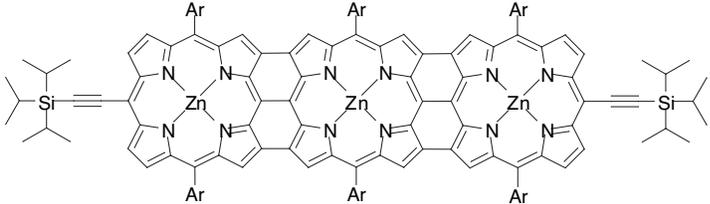
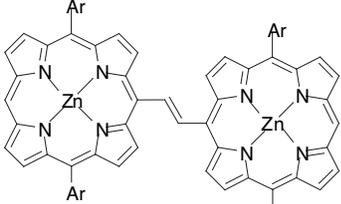
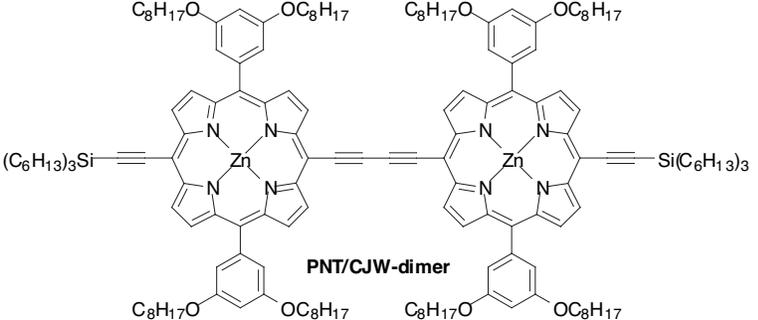
The following articles are in various stages of preparation:

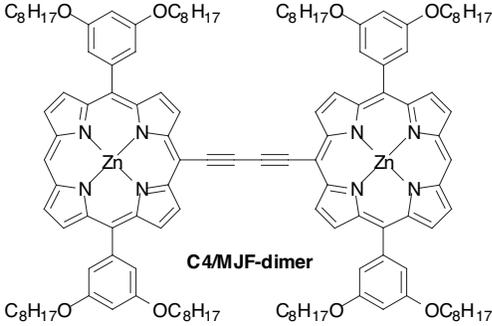
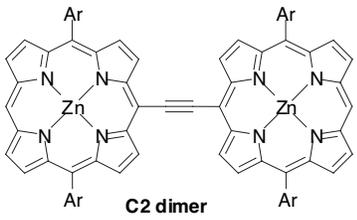
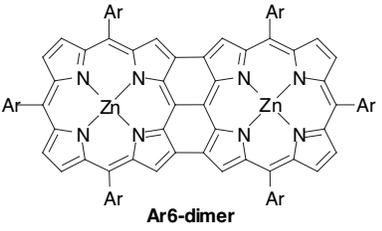
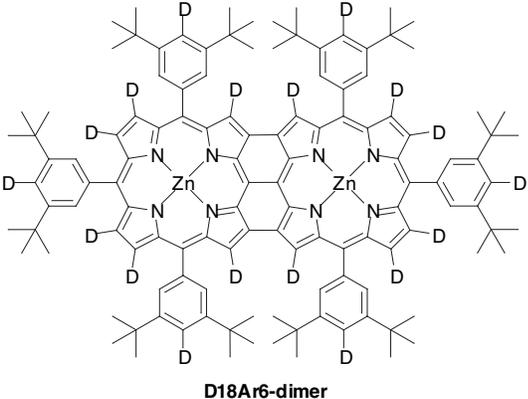
- (iv) “*Pull-pull, push-pull and push-push quinoidal porphyrins: synthesis, crystallography and electronic structure*”, M. J. Smith, L. Thoresen, H. Akdas, I. M. Blake, A. Krivokapic, A. R. Cowley, W. Clegg, H. L. Anderson and other authors — a full paper related to the above communication, in preparation for *Chem. Eur. J.*
- (v) “*A conjugated porphyrin dimer with a C_2H_2 -meso bridge*”, M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, P. A. Fleitz, H. L. Anderson and other authors — a communication including a comparison of the T_1-T_n spectra of the C2H2- and C2-dimers; in preparation for *Chem. Commun.*
- (vi) “*Synthesis of a deuterated porphyrin dimer*”, M. J. Frampton, H. L. Anderson, J. E. Rogers, P. A. Fleitz and other authors.
- (vii) “*Electron donating and withdrawing substituents in meso-tetra-ethynyl porphyrins*”, C. J. Wilson, J. E. Rogers, P. A. Fleitz and H. L. Anderson — a full paper on some data from the first year of this project.

Appendix. List of compounds sent for photophysical testing at AFRL/MLPJ, Dayton, Ohio.

Date sample sent from Oxford	Compound	Date of report from AFRL and comments
17 May 2002	 <p style="text-align: center;">Ander1</p>	18 Dec 2003 no ESA detected synthesis and crystal structure published in <i>Chem. Comm.</i> 2002, 1662.
17 May 2002	 <p style="text-align: center;">Ander2</p>	18 Dec 2003 complex ESA behavior indicating decomposition
17 May 2002	 <p style="text-align: center;">Ander3</p>	24 Nov 2003 ESA in visible region $\Phi_T = 0.85$
17 May 2002	 <p style="text-align: center;">Ander4</p>	24 Nov 2003, 18 Dec 2003 and 25 May 2004 RSA at 610–930 nm $\Phi_T = 0.12$
17 May 2002	 <p style="text-align: center;">Ander5</p>	18 Dec 2003 complex ESA behavior indicating decomposition
28 Oct 2002		ESA similar to Ander3 $\Phi_T = 0.86$

28 Oct 2002		18 Jan 2003 and 1 Feb 2005 no ESA observed
3 Jan 2003		18 Jan 2003 and 1 Feb 2005 no ESA observed
7 July 2003	 <p> HLA/CJW1 M = Zn, R = <i>n</i>-Bu HLA/CJW2 M = Pb, R = <i>n</i>-Bu HLA/CJW3 M = Zn, R = SO₂Bu HLA/CJW4 M = Pb, R = SO₂Bu HLA/CJW5 M = Zn, R = NHBu HLA/CJW6 M = Pb, R = NHBu </p>	24 Nov 2003 donor and acceptor groups do not have a strong effect on RSA results in preparation for publication
8 Oct 2003	 <p style="text-align: center;">PNT-dimer</p>	10 Feb 2004 ESA around 1000 nm $\Phi_T = 0.31$
8 Oct 2003	 <p style="text-align: center;">C4-dimer</p>	10 Feb 2004 ESA around 1000 nm $\Phi_T = 0.52$
8 Oct 2003	 <p style="text-align: center;">Ander6 TIPS triple-link dimer</p>	18 Dec 2003 no ESA observed

19 Dec 2003	 <p style="text-align: center;">Pb-TIPS triple-link dimer</p>	17 Feb 2004 no ESA observed
19 Dec 2003	 <p style="text-align: center;">Zn-TIPS triple-link trimer</p>	17 Feb 2004 no ESA observed strong ground state absorption at 1500 nm
5 April 2004	 <p style="text-align: center;">Ander4-I</p>	25 May 2004 RSA at 604–973 nm $\Phi_T = 0.20$ results published in <i>Adv. Mater.</i> 2004, 16, 1933.
3 Sep 2004	 <p style="text-align: center;">C2H2-dimer</p>	15 Dec 2004 and 16 Mar 2005 promising ESA at 750-1000 nm $\Phi_T = 0.21$
3 Sep 2004	 <p style="text-align: center;">PNT/CJW-dimer</p>	31 Jan 2005 NLA at 850–950 nm due to TPA

7 Sept 2004	 <p style="text-align: center;">C4/MJF-dimer</p>	31 Jan 2005 NLA at 800–900 nm due to TPA
29 Jan 2005	 <p style="text-align: center;">C2 dimer</p>	16 Mar 2005 ESA at >900 nm $\Phi_T = 0.44$
29 Jan. 2005	 <p style="text-align: center;">Ar6-dimer</p>	14 Mar 2005 no detectable ESA experiments on measurement of Φ_F in progress
29 Jan 2005	 <p style="text-align: center;">D18Ar6-dimer</p>	14 Mar 2005 no detectable ESA experiments on measurement of Φ_F in progress