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<b>1. AGENCY USE ONLY (Leave blank)</b>		<b>2. REPORT DATE</b> 9/30/06	<b>3. REPORT TYPE AND DATES COVERED</b> Final Technical Report 7/1/05 - 10/31/08	
<b>4. TITLE AND SUBTITLE</b> (DEPSCOR-05) TWO PHOTON PORPHYRIN CORE DENDRIMERS FOR OPTICAL POWER LIMITING			<b>5. FUNDING NUMBERS</b> Grant No. FA9550-05-1-0357  Purchase Request No.	
<b>6. AUTHOR(S)</b> Professor Aleksander Rebane				
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Physics Department Montana State University EPS Building Bozeman, MT 59717  Tel: (406) 994 7831 Fax: (406) 994 4452 Email: Rebane@physics.montana.edu			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  Charles Y-C Lee AFOSR/NL Suite 325, Room 3112 Arlington, VA 22203-1954  Email: charles.lee@afosr.af.mil Fax: (703) 696-8449 Phone: (703) 696-7779			<b>10. SPONSORING / MONITORING AGENCY REPORT NUMBER</b>	
<b>11. SUPPLEMENTARY NOTES</b>				
<b>12a. DISTRIBUTION / AVAILABILITY STATEMENT</b>				<b>12b. DISTRIBUTION CODE</b> A
<b>13. ABSTRACT (Maximum 200 Words)</b>  This research is to establish novel nonlinear-absorbing materials with large intrinsic two-photon cross section for fast response optical power limiting in the photon wavelength range 700 - 900nm. We synthesize novel porphyrin core dendrimers, which combine the large 2PA efficiency of conjugated dendrites with the high efficiency of excited state absorption of the core tetrapyrrole. The goal of this project is to (a) establish structure property relationships for the novel class of two-photon assisted reverse saturable absorption materials and (b) optimize the chromophores for practical use, including high number density and solubility requirements. Our materials and results are transferred for further testing and evaluation at the Wright-Patterson AFB/MLPJ (Dr. A. Urbas).				
<b>14. SUBJECT TERMS</b>				<b>15. NUMBER OF PAGES</b>
				<b>16. PRICE CODE</b>
<b>17. SECURITY CLASSIFICATION OF REPORT</b>	<b>18. SECURITY CLASSIFICATION OF THIS PAGE</b>	<b>19. SECURITY CLASSIFICATION OF ABSTRACT</b>	<b>20. LIMITATION OF ABSTRACT</b>	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

# 20090319196

## Final Technical Report 7/1/05 - 10/31/08

Grant No. FA9550-05-1-0357

### ***Two-Photon Porphyrin Core Dendrimers for Optical Power Limiting***

A. Rebane, Physics Department, Montana State University, Bozeman, MT 59717

Tel. (406) 994 7831, Fax: (406) 994 4452, Email: rebane@physics.montana.edu

### **2. Objectives** (not changed)

This research was to establish novel nonlinear-absorbing materials with enhanced intrinsic (100 femtosecond pulse) two-photon cross section in the photon wavelength range 700 - 900nm. The goal is to develop new materials that facilitate optical power limiting with a low clamping pulse energy <10 nJ in visible- and near-IR range of wavelength. The approach was to synthesize novel porphyrin core dendrimers, which combine the large 2PA efficiency of conjugated dendrites with the high efficiency of excited state absorption of the core tetrapyrrole. The goal of this project was to (a) establish structure property relationships for the novel class of two-photon assisted reverse saturable absorption materials and (b) optimize the chromophores for practical use, including high number density and solubility requirements. Our materials and results are transferred for further testing and evaluation at the Wright-Patterson AFB/MLPJ .

### **3. Accomplishments & New Findings**

#### **3.1. Main results**

1. We synthesized a series of **new porphyrins-core dendrimers** and studied their linear- and nonlinear 2PA photophysical properties in broad range of wavelengths [1].
2. We have established structure-property relationships for 2PA cross sections of  $\pi$ -conjugated porphyrin oligomers and polymers [2].
3. We have completed a detailed study of 2PA in symmetrical and asymmetrical (push-pull) phthalocyanines [3,4,5].
4. We have performed a quantitative 2PA structure-property relationship study for a broad range of dipolar molecules [6].
5. In collaboration with WPAFB and Dr. Schanze (U of Florida), we explored 2PA and related multi-photon photophysics of platinum acetylide chromophores [7, 8].
6. In collaboration with Dr. Gryko (Polish Acad. Sci.), we studied 2PA of novel corroles [9].
7. We studied the requirements imposed on organic photochromes for 2PA terabyte rewritable volumetric optical storage [10].
8. We have developed a femtosecond 2PA spectrometer and a set of two-photon reference compounds with high absolute accuracy and broad range of wavelengths 550 – 1600 nm [11].

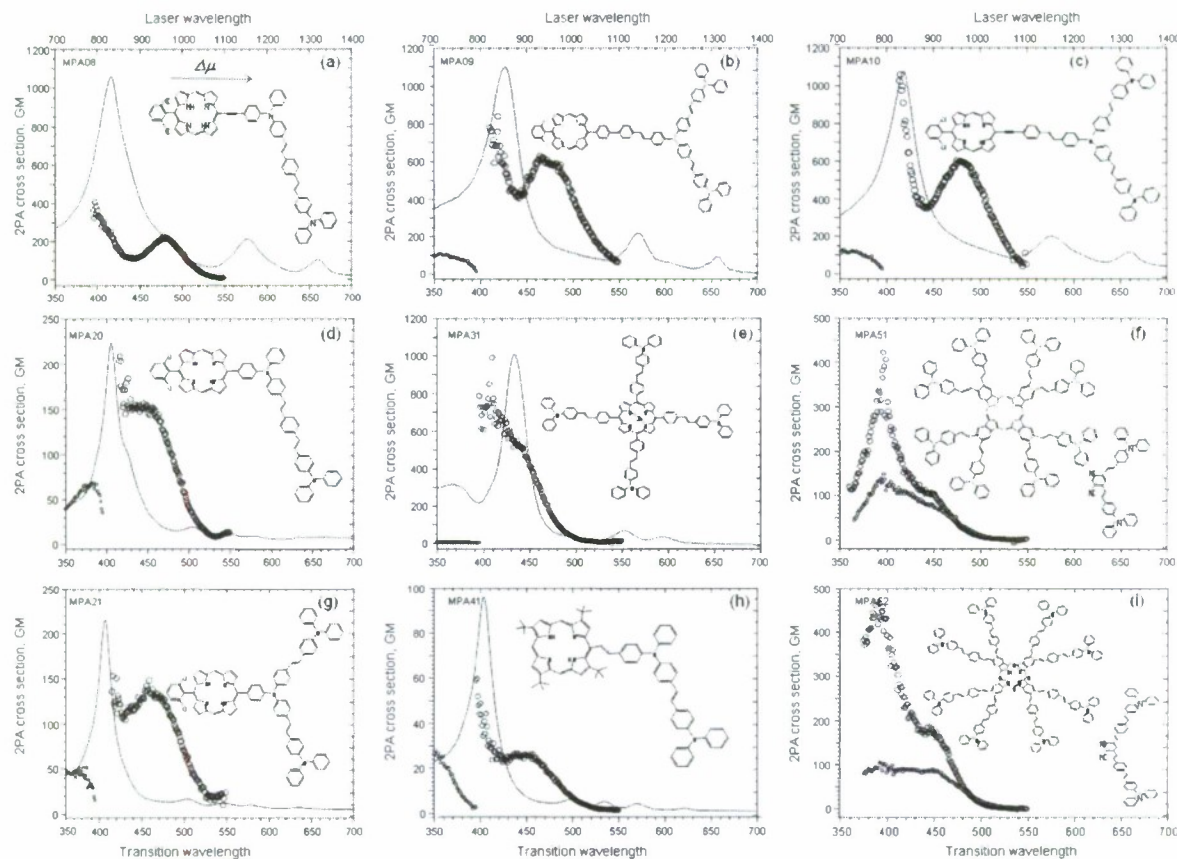
#### **3.2. Summary and detailed description of main results**

##### **3.2.1. New porphyrin core dendrimers [1]**

We have synthesized and characterized a family of new branched porphyrin-core dendrimers shown in **Figure 1**. Some of these systems show enhanced 2PA properties in the wavelength range 750 – 1000 nm. Taken alone, the porphyrin core has rather low 2PA cross section, of the order of 10 GM or less. However, when the core is linked to one- or more DPAS, BDPAS, or BDPADSB-type of groups, then the cross section increases dramatically, in some cases up to



1000 GM. The most significant result is that the total 2PA of such constructs may be many times larger than the sum of the constituent parts. For example, compound MPA 31 in Figure 2(a) comprises four symmetrically *meso*-attached DPAS chromophores, the peak 2PA of each is about 30 GM. The measured peak cross section of the dendrimer is  $\sigma_2 \sim 800$  GM at 800 nm, which is

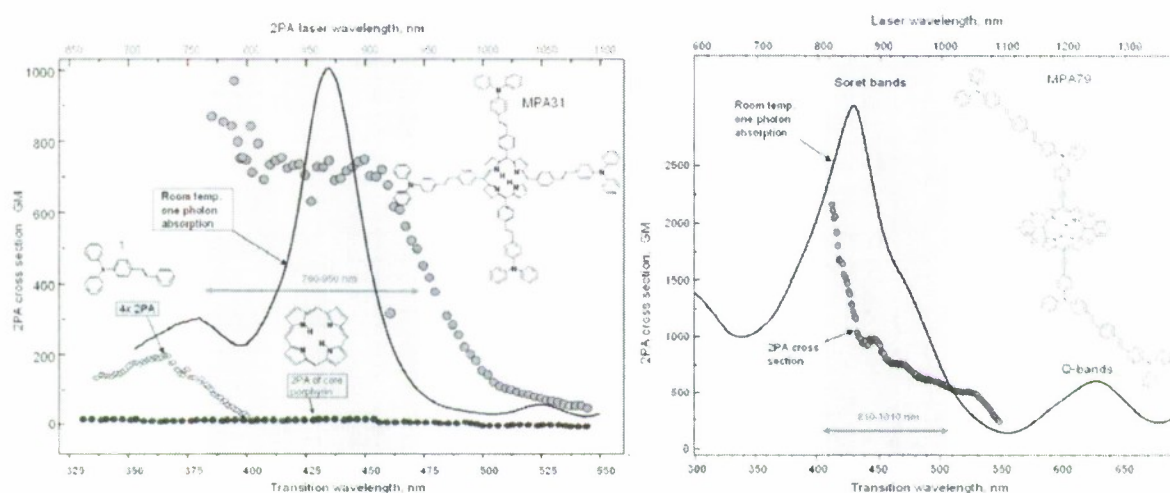


**Figure 1.** 2PA spectra (empty circles) and linear absorption (solid line) of porphyrin core dendrimers. 2PA spectra of the attached chromophores (filled circles) are shown for comparison. 2PA of the bare porphyrin is at the zero baseline level. *Meso*-substituted compounds demonstrate a varying degree of the cooperative enhancement. Compounds with  $\beta$ -substitution (f) and (i) show no cooperative enhancement (purely additive effect).

almost an order of magnitude (!) larger than the mere sum of the cross sections of the constituent units. Also, the 2PA spectrum of the dendrimer is notably red-shifted with respect to the 2PA of the attached chromophores and the porphyrin core itself.

Even though the substituents are connected to the porphyrin through single bonds, the observed effect implies rather strong coupling between different parts of the molecule. Furthermore, such new dendrimer constructs retain practically all other useful signature properties of the porphyrin – the characteristic linear absorption spectrum, high quantum yield of triplet formation, and strong excited-state absorption. Many of these properties are essential for optical limiting, which makes porphyrin core dendrimers interesting candidates for further investigations.

**Figure 2** shows detailed 2PA spectrum of dendrimer MPA31 and MPA79 along with 2PA of the core tetraphenylporphyrin ( $H_2TPP$ ) and DPAS molecule. The dendrimers show strong 2PA up to  $\sigma_1 = 700\text{--}800\text{ GM}$  in the broad spectral range, 770–950 nm. Most significant is the strong cooperative enhancement, which manifest as the 2PA of the dendrimer is at least an order of magnitude stronger than the mere sum of its substituents. It is also significant that such enhancement occurs with meso-substitution. In contrast, the dendrimers where the 2PA chromophores are attached at  $\beta$ -positions (compounds *f* and *i* in Figure 1) show practically no cooperative enhancement. In this case, the 2PA of the dendrimer is mostly described as superposition of 2PA of the constituent parts.



**Figure 2.** 2PA spectra of four-branched MPA31 (a) and two-branched MPA79 (b). 1PA spectrum and 2PA spectra of the core porphyrin and the attached chromophore unit are shown for comparison. Shaded region shows the wavelength range of strong 2PA enhancement.

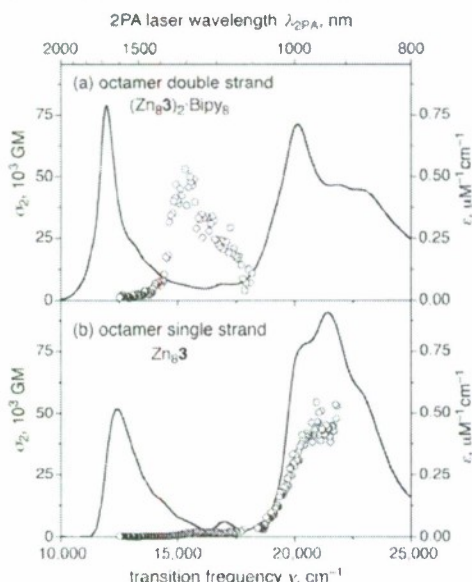
The results of comprehensive studies, performed in this project, allow us to formulate the following key guidelines for successful design of novel advanced nonlinear absorbers:

- For the systems with sufficiently strong 2PA ( $\sigma_2 > 100\text{ GM}$ ), few-essential-states models can predict almost quantitatively the peak cross section values.
- According to this description, in order to enhance the 2PA, one needs to (a) increase all transition dipole moments involved in 2PA process; (b) tune (by chemical modifications) the final 2PA state close to double-resonance conditions (such that the final state energy would be slightly less than the twice the energy of intermediate state in the three-level system); (c) increase the difference between permanent dipole moments in the final and ground states;
- Enhancement of transition dipole moments is usually attained by more efficient  $\pi$ -conjugation between different parts of a molecule.
- 2PA strength increases faster than linearly with the size of  $\pi$ -conjugated pool of electrons (cooperative enhancement).
- Cooperative enhancement is more pronounced for more co-planar systems, but tends to saturate (or even reverse) as soon as co-planarity is lost.



### 3.2.2. $\pi$ -conjugated porphyrin oligomers and polymers [2]

2PA cross sections of  $\pi$ -conjugated oligomers and polymers are often relatively high and sometimes show cooperative enhancement, i.e. increase faster than linearly with the number of constituent building blocks. We studied 2PA of self-assembling double-strand conjugated porphyrin ladder arrays (in collaboration with H. Anderson, UK). We found that butadiyne-linked porphyrin dimers show particularly large intrinsic (femtosecond) 2PA cross sections,  $\sigma_2 \sim 10^4$  GM, which corresponds to a 500-fold cooperative enhancement compared to the parent monomer. Similarly large  $\sigma_2$  values have been reported for other conjugated porphyrin oligomers and polymers, but the relationship between structure and conjugation length in these systems has yet



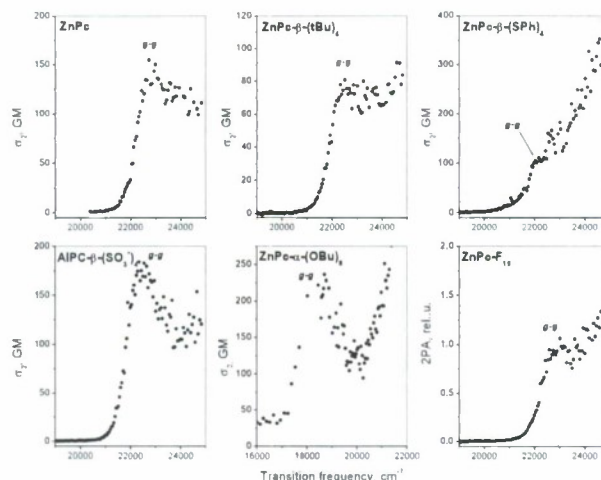
**Figure 3.** 2PA spectra (symbols) of octamer double strand (a) and single strand (b). 1PA spectra are also shown (solid lines).

interesting to note that the double-strand oligomers show extremely large 2PA cross sections at 1.3  $\mu\text{m}$ . This finding may be of great importance for optical switching and signal processing in fiber-optic communications technologies.

### 3.2.3. Symmetrical and asymmetrical (push-pull) phthalocyanines [3,4,5]

We studied two-photon absorption (2PA) spectra of a number of symmetrically-substituted phthalocyanines in the excitation wavelength region from  $\lambda_{\text{ex}} = 800$  to 1600 nm. This is the first time such measurements have been reported for phthalocyanines. We study commercially available substances that vary by position of substitution ( $\alpha$ - or  $\beta$ -), number of substituent groups (4, 8, or 16), and presence or absence of metal (Zn or Al) in the center. For all phthalocyanines we find a moderately strong ( $\sigma_2 \sim 100$ –200 GM), pure electronic, *gerade* - *gerade* (*g-g*) 2PA transition. The two-photon allowed transition shows up as a well-resolved relatively narrow peak in the energy region between Q- and B-bands ( $\lambda_{\text{ex}} = 870$ –1100 nm). In metallo-phthalocyanines (MPcs) this lowest *g-g* transition is followed by the onset of other higher-frequency 2PA transitions. In some metal-free phthalocyanines ( $\text{H}_2\text{Pcs}$ ) we also reveal a second, broader 2PA transition at slightly higher frequency. In both MPcs and  $\text{H}_2\text{Pcs}$ , we find a strong monotonic increase of integrated strength of the lowest *g-g* transition as a function of electron-accepting

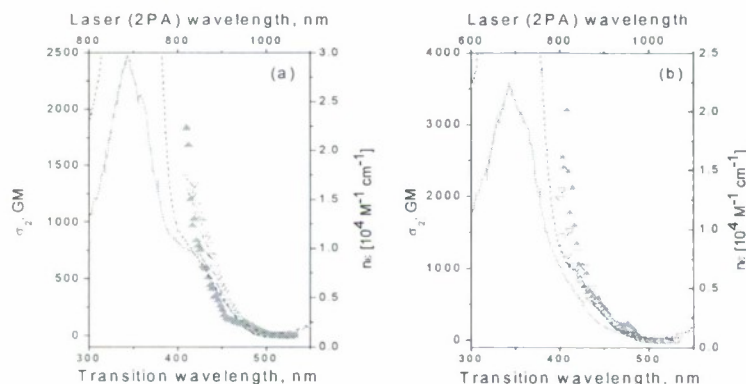
to be elucidated. The new finding concern the intrinsic 2PA spectra of a series of butadiyne-linked porphyrin oligomers,  $\text{Zn}_2$ ,  $\text{Zn}_4$ ,  $\text{Zn}_8$  and  $\text{Zn}_N$  containing 2, 4, 8 and ca. 13 monomer units. In solution the conjugation lengths of single-strand chains can be strongly limited by rotational disorder (non-coplanarity), but these oligomers become almost co-planar when they self-assemble into double-strand ladders. We found that ladder formation dramatically increases the conjugation length, leading to strong cooperative enhancement of 2PA. Our analysis shows that the 2PA “conjugation signature” acquires much larger values and increases faster with  $N$  for double-strand arrays, which is expected from better co-planarity. However, this does not result in dramatic increase of  $\sigma_2^{\text{m}}$  values in double strands, compared to single ones, because of worse detuning factors in the former case. It is



**Figure 4.** 2PA of metal-substituted symmetrical phthalocyanines in the lowest *g-g* transition (marked by *g-g*).

ability of peripheral substituents, expressed as their aggregated Hammett constant. By using few essential states models (three states for MPes and four states for H<sub>2</sub>Pes) we demonstrate the primary role of excited-state transition dipole moment in this effect.

In a closely related study we investigated near-IR 2PA spectra of non-symmetrically substituted metal-free push-pull type phthalocyanines, NSPc and NPEPc. The special feature of these



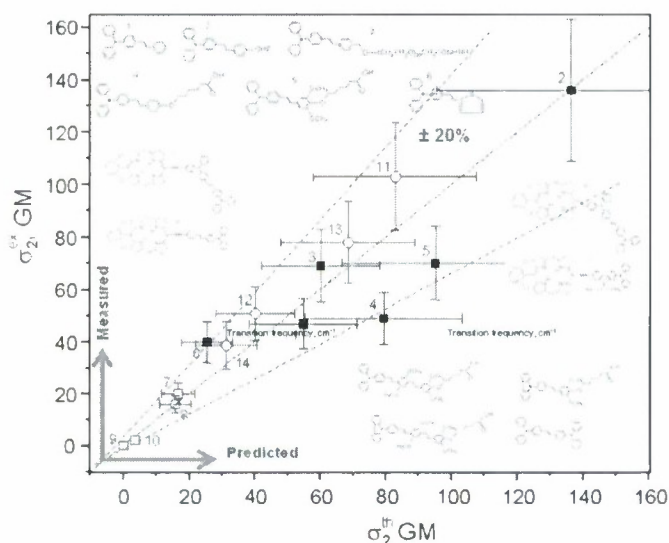
**Figure 5.** 2PA spectra (symbols, left y-axis) in B-region of NSPc (a) and NPEPc (b) in octane. Filled symbols are for T1 tautomer, open symbols – for T2 tautomer. 1PA spectra in octane are also shown for comparison (continuous lines, right y-axis). Solid line presents T1 tautomer, dashed – T2 tautomer. Bottom x-axis represents the transition wavelength (equal for both 1PA and 2PA). Top x-axis corresponds to the laser wavelength.

molecules is that they are present in solution at room temperature as a mixture of two spectrally non-equivalent tautomers T1 and T2. Large 2PA cross sections,  $\sigma_2 = (1-3) \times 10^3 \text{ GM}$  are obtained in the excitation wavelength region  $\lambda_{\text{ex}} = 815-850 \text{ nm}$  (**Figure 5**) and are explained by (a) new charge transfer state appearing in one-photon absorption (1PA) spectrum of these compounds at 420-430 nm and (b) strong resonance enhancement within quasi-three-level system when the Q-state(s) serve as the real intermediate state(s). In B-region, where higher 2PA cross sections,  $\sigma_2 =$

$(1-3) \times 10^3$  GM (Figure 5), were obtained for both tautomers and both NSPc and NPEPc molecules, we find a new CT-transition which is 2PA allowed. Despite large change of permanent dipole moment,  $|\Delta\mu_{00}| \sim 10$  D, the strength of this transition is better described within the framework of a quasi-three-level system, involving the lowest Q-states (at 675-720 nm) as real intermediate state(s). Since the laser wavelength is tuned rather close to this transition, the 2PA becomes very strong due to resonance enhancement effect. The role of asymmetric electron-withdrawing substitution consists in making this new CT transition two-photon allowed and enhancing excited-state transition dipole, compared to symmetrical analogue,  $H_2Pc-\beta(tBu)_4$ . A combination of strong 2PA in near-IR region with potentially efficient excited state absorption in the same region due to phthalocyanine cation-radical formation upon photoinduced electron transfer makes this type of materials particularly attractive for OPL of near-IR pulses on ps - ns timescale.

### 3.2.4. Quantitative 2PA for dipolar molecules [6]

We studied 2PA in nonsymmetrical molecules possessing a large permanent dipole moment difference between ground- and excited electronic states. We show for the first time that the peak 2PA cross section in the lowest dipole-allowed transition may be predicted with high degree of accuracy based on molecular parameters obtained solely from linear spectroscopic measurements for a broad class of molecules. We measure 2PA spectrum in a series of substituted diphenylaminostilbenes, push-pull porphyrins and a push-pull porphyrin dimer. A two-level model can be used to describe only the low-lying singlet-singlet transitions, where 2PA and 1PA peaks coincide. We measure the corresponding transition dipole moments and permanent dipole moment difference by using standard linear spectroscopic techniques. By using appropriate local field correction factor, we obtain a better than 50% quantitative correspondence between the theoretical and experimental 2PA cross section values.



**Figure 6.** Quantitative correspondence between the measured (vertical axis) and the predicted (horizontal axis) 2PA cross section in a selection of 14 chromophores of largely varying structure and properties. In all cases, the peak 2PA of the lowest-energy dipole-allowed transition falls within 20% of the predicted value. All chromophores but 1,2, and 13 are newly synthesized by our group.



Theoretical 2PA cross section of dipolar transition is given by:

$$\sigma_2^{two-state} = C_1 (1 + 2 \cos^2 \alpha_1) |\vec{\mu}_{f0}|^2 |\Delta \vec{\mu}_{f0}|^2 g(2\nu) \quad (1)$$

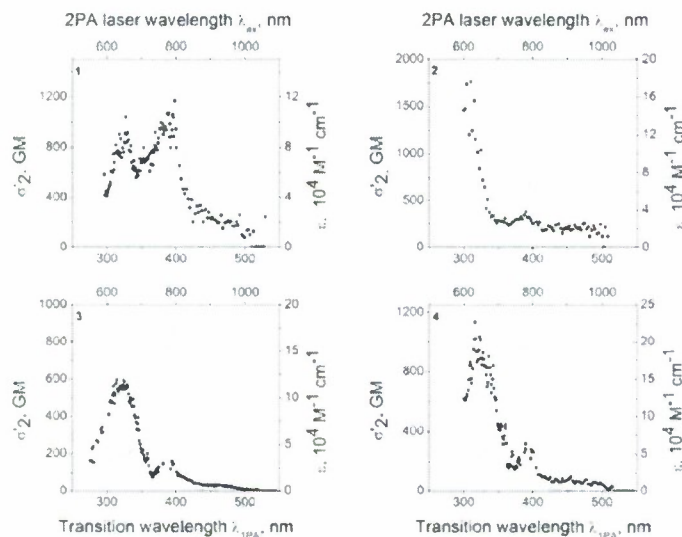
where  $\vec{\mu}_{f0}$  is the transition dipole moment vector between the ground state  $0$  and the final excited state  $f$ ,  $\Delta \vec{\mu}_{f0}$  is the difference between the permanent dipole moments in the ground- and excited state,  $\alpha_1$  is the angle between the above two vectors,  $g(2\nu)$  is the normalized line shape function, and the proportionality constant,

$$C_1 = \frac{2}{15} \frac{(2\pi)^4}{(hc)^2} \frac{(n^2 + 2)^4}{3^4 n^2}, \quad (2)$$

depends on the index of refraction,  $n$ , the speed of light  $c$ , the Planck's constant,  $h$ , and the Lorentz model is considered for the local field factor.

### 3.2.5. Femtosecond 2PA in platinum acetylide chromophores [7,8]

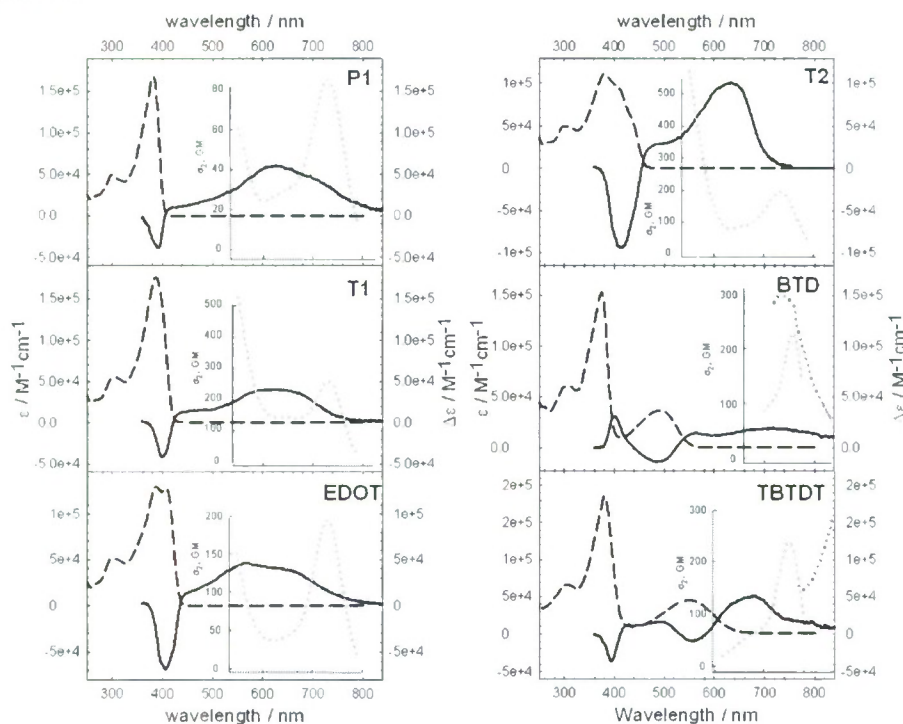
In collaboration with AFRL group at WPAFB, we have explored the photophysics of platinum acetylide chromophores having strong two photon cross section. We have investigated the synthesis and spectroscopic characterization of a series of platinum acetylide complexes that feature highly  $\pi$ -conjugated ligands substituted with  $\pi$ -donor or -acceptor moieties. The molecules are NLO-functionalized analogs of bis(phenylethynyl)bis(tributylphosphine) platinum (II) complexes. The conjugated ligands impart the complexes with effective two-photon absorption cross sections, while the heavy metal platinum centers give rise to efficient intersystem crossing to afford long lived triplet states. Photophysical studies demonstrate that one-photon excitation of the chromophores produces an  $S_1$  state that is delocalized across the two conjugated ligands, with weak (excitonic) coupling through the platinum center(s). Femtosecond pulses were



**Figure 7.** Two-photon absorption spectra of compounds 1-4 dissolved in benzene at ambient conditions (symbols). As described in the Experimental section, the samples were excited with 100-fs pulses with  $\lambda_{ex} = 550$  -1100 nm. The absolute two-photon absorption cross sections were measured using the sample fluorescence relative to a bis-diphenylaminostilbene solution in methylene chloride. This method gives the cross section value  $\sigma'_2$ , which, according to definition, is twice that would be obtained with nonlinear absorption techniques ( $\sigma'_2 = 2 \sigma_2$ ). One-photon absorption spectra (solid lines) are also shown for comparison. Bottom x-axis presents transition wavelength (which is equal to 1PA wavelength) and top x-axis presents laser wavelength, used for 2PA excitation.

used to characterize the two-photon absorption properties of the complexes (**Figure 7**), and all of the chromophores are relatively efficient two photon absorbers in the visible and near-infrared region of the spectrum (600–800 nm). The complexes exhibit maximum two-photon absorption at a shorter wavelength than  $2\lambda$  for the one-photon band, consistent with the dominant two photon transition arising from a two-photon allowed gerade-gerade transition. Nanosecond transient absorption experiments carried out on several of the complexes with excitation at 803 nm confirm that the long-lived triplet state can be produced efficiently via a sequence involving two-photon excitation to produce  $S_1$  followed by intersystem crossing to afford  $T_1$ .

In collaboration with Kirk Schanze group, we studied two-photon absorption properties of a series of Pt-acetylide dimers, which are symmetrically end-capped with electron-donating diphenylamino-groups (D), which are, in turn, connected through  $\pi$ -conjugating fluorenes to both ends of a core Ar- units via Pt-acetylide linkages. The central  $\pi$ -conjugated arylene units include electron-accepting (A) oligothiophenes (**T1**, **T2**), 2,1,3-benzothiadiazole (**BTD**), 4,7-dithien-2-yl-2,1,3-benzothiadiazole (**TBTD**), electron-donating 3,4-ethylenedioxythiophene (**EDOT**), as well as neutral phenol (**P1**). Structure-property relationships are obtained, besides 2PA, also for the core conjugation length, D to A charge transfer, singlet-singlet absorption, intersystem crossing and triplet-triplet absorption. Here again we showed that the lowest-energy 2PA spectrum and cross section are well described by two-level model. **Figure 8** shows how the spectral overlap between 2PA and triplet-triplet absorption varies within the series. Achieving maximum overlap is critical for efficient optical limiting by 2PA-induced excited state absorption mechanism.

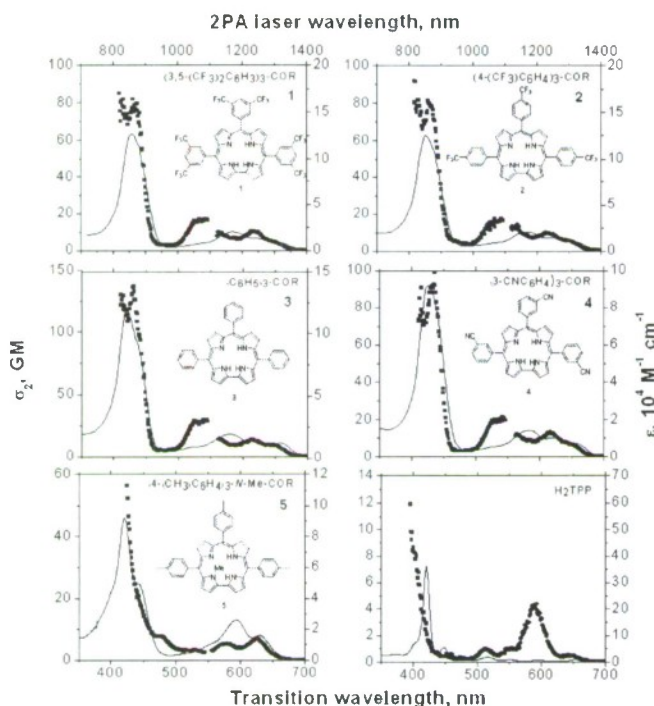


**Figure 8.** Spectral overlap of two-photon absorption spectra (orange dotted line, inset) and transient triplet-triplet absorption (black solid line) in a series of Pt-dimer complexes. One-photon absorption spectra (dashed lines) are also shown for comparison.

### 3.2.6. 2PA spectroscopy of corroles [9]

In collaboration with Dr. Daniel Gryko (Polish Academy of Sciences), we studied 2PA cross sections and spectra of corroles within a broad spectral range of excitation wavelengths, 800 – 1400 nm. Compared to symmetrically-substituted porphyrins, the 2PA spectrum of corroles contains a distinct peak at the laser wavelength close to twice the wavelength of Soret maximum ( $\sim 850$  nm), with a quite significant cross section,  $\sigma_2 = 60 - 130$  GM. We explain this observation in terms of decreased symmetry of the contracted macrocycle as compared to centro-symmetric porphyrins. Lowering of the symmetry relaxes the parity selection rules for 2PA, thus making the

Soret band allowed for two-photon transition. We also observe that the strength of the 2PA peak in Soret region strongly decreases with the electron-withdrawing ability (increasing Hammett constant) of the side substituents. This effect can be explained by assuming that the corrole core itself reveals a certain electron-accepting ability. The 2PA cross sections in the Q-region are much less than in Soret-region, and they can be quantitatively described within the two-level approximation taking into account permanent dipole moments in the ground and excited states.

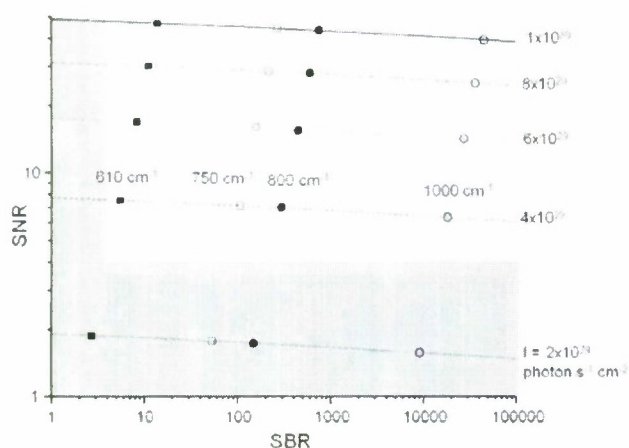


**Figure 9.** One-photon (line) and two-photon (symbols) absorption spectra of corroles. Left y-axis presents 2PA cross section, right y-axis presents extinction coefficient.

### 3.2.7. 2PA terabyte rewritable volumetric optical storage [10]

We completed a quantitative study of the requirements imposed on organic photochromes for two-photon absorption (2PA) terabyte volumetric optical storage. We present a quantitative model of signal-to-noise ratio (SNR) and signal-to-background ratio (SBR) when 2PA-induced photochromic switching is used for writing, and 2PA-induced fluorescence is used for read-out. We show that single-channel data access rate  $>100$  MHz at minimum SNR  $>4$  implies minimum intrinsic 2PA cross section,  $\sigma_2 > 10^3$  GM. Resonance enhancement allows  $\sigma_2 \sim 10^5$  GM, however, it also lowers SBR due to thermally-activated one-photon absorption (1PA). We model the critical trade-off between SNR and SBR as a function of laser frequency, intensity and temperature. Acceptable parameter space may be achieved by careful choice of the above variables. We perform experiments with non-symmetrical free-base phthalocyanines, which show efficient 2PA-induced photochromic switching between two tautomer forms and large  $\sigma_2 \sim 10^4$  GM, and shows good potential for high capacity data storage.

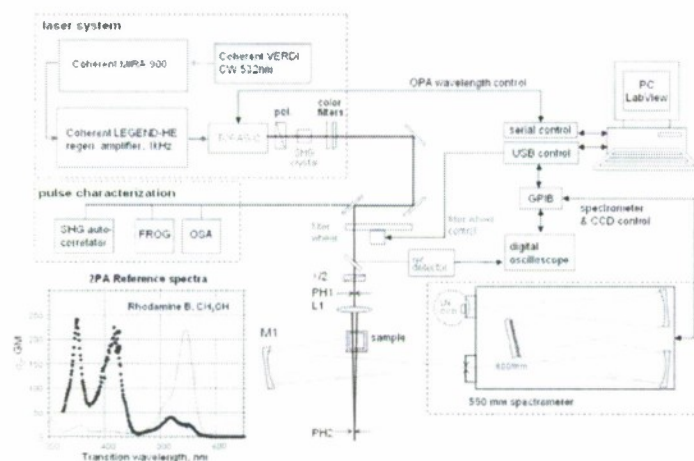




**Figure 10.** Calculated SNR versus SBR for  $\text{Pc}_3\text{Ne}$  at  $T = 77 \text{ K}$ . Each curve corresponds to the particular laser peak intensity, indicated on top of the curve. Different symbols on the curves label the particular values of frequency detuning from 1PA maximum. Shaded regions correspond to forbidden values, i.e. if either signal-to-noise ratio is too low ( $\text{SNR} < 4$ ) or/and signal-to-background ratio is too low ( $\text{SBR} < 4$ ).

### 3.2.8. Femtosecond 2PA spectrometer and 2PA references in 550 – 1600 nm [11]

Key experimental issue for the success of the current project is the ability to measure absolute two-photon cross sections and 2PA spectra in a broad range of wavelengths and with high fidelity and reproducibility. In our lab, we have recently developed an advanced femtosecond two-photon spectrometer that allows accurate measurement of 2PA in the excitation laser wavelength range 500 - 2200 nm with absolute accuracy better than 10-15% (depending on wavelength). We use the fluorescence excitation method, which allows for direct measurement of 2PA in a broad variety of compounds and under a broad range of excitation conditions. Currently, this is a unique one-in-kind measurement system in the world. **Figure 11** presents a detailed scheme of the apparatus developed in our laboratory. To facilitate better measurements by other groups, we have also recently published the 2PA spectra of 15 commercial dyes that can be used as reference standards in the wavelength range 550 - 1600 nm. The reference dyes enable accurate and reproducible 2PA cross section measurements not only in fluorescing systems, but also in those which do not emit fluorescence.



**Figure 11.** Schematic of the 2PA spectrometer. 100-fs pulses from optical parametric amplifier (OPA) are focused with the lens L1 on the sample in a  $1 \times 1 \text{ cm}^2$  spectroscopic cell. PH1, PH2 – pinholes for beam alignment. M1 – spherical mirror. The laser system, the spectrometer and the data collection are controlled via a PC by the LabView routine. Insert (lower left) shows a representative reference 2PA spectrum (symbols) of Rhodamine B. The fidelity of the absolute cross sections throughout the spectrum is better than 15%.

#### 4. Personnel involved in the project:

Prof. Aleksander Rebane (MSU Faculty, P.I.)

Prof. Charles Spangler (MSU Research Faculty, Co-P.I.)

Dr. Mikhail Drobizhev (MSU Assistant Research Professor in Rebane group)

Dr. Yuryi Stepanenko (post-doc 2005)

Nikolay Makarov (graduate student, physics)

Daniel Koepke (graduate student, physics)

Ben Skerik-Borg (graduate student, chemistry)

#### 5. Publications in refereed journals:

1. "Strong two-photon absorption in new asymmetrically-substituted porphyrins: interference between charge-transfer and intermediate-resonance pathways." M. Drobizhev, F. Meng, A. Rebane, Y. Stepanenko, E. Nickel, and C. W. Spangler, *J. Phys. Chem. B* 110 (20), 9802-9814 (2006).
2. "Strong cooperative enhancement of two-photon absorption in double-strand conjugated porphyrin ladder arrays," M. Drobizhev, Y. Stepanenko, A. Rebane, C.J. Wilson, T. E.O. Screen, H.L. Anderson, *J. Am. Chem. Soc.*, 128 (38), 12432-12433 (2006).
3. "Near-infrared two-photon absorption in phthalocyanines: Enhancement of lowest gerade-gerade transition by symmetrical electron-accepting substitution," M. Drobizhev, N. Makarov, Y. Stepanenko and A. Rebane, *J. Phys. Chem.* 124 (22), 224701 (2006).
4. "Very efficient two-photon induced photo-tautomerization in non-symmetrical phthalocyanines," M. Drobizhev, N. Makarov, A. Rebane, et al., *J. Luminescence*, 128(2), pp. 217-222 (2008).
5. "Strong two-photon absorption in push-pull phthalocyanines: Role of low symmetry and permanent dipole moment change upon excitation," M. Drobizhev, N. S. Makarov, A. Rebane, G. de la Torre, T. Torres, *J. Phys. Chem. C* 112(3), pp. 848-859 (2008).
6. "Quantitative prediction of two-photon absorption cross section based on linear spectroscopic properties," A. Rebane, N. S. Makarov, M. Drobizhev, B. Spangler, E. S. Tarter, B. D. Reeves, Ch.W. Spangler, F. Meng, Z. Suo, *J. Phys. Chem. C* 112, pp. 7997-8004 (2008).
7. "Platinum acetylide two photon chromophores," J. E. Rogers, J. E. Slagle, D. M. Krein, A. R. Burke, B. C. Hall, A. Fratini, D. G. McLean, P. A. Fleitz, T. M. Cooper, M. Drobizhev, N. S. Makarov, A. Rebane, K.-Y. Kim, R. Farley, and K. S. Schanze, *Inorg. Chem.* 46(16), pp. 6483-6494 (2007).
8. "Optimizing simultaneous two-photon absorption and transient triplet-triplet absorptions in platinum acetylide chromophores," Kye-Young Kim, Kirk S. Schanze, M. Drobizhev, N. Makarov, A. Rebane, (in preparation).
9. "Two-photon absorption properties of meso-substituted A3-corroles," D.T. Gryko, A. Rebane, M. Drobizhev, N. S. Makarov, B. Koszarna, M. Tasior, *Chem Phys Lett.* 462 (4-6), pp. 246-250 (2008).
10. "Optimizing two-photon absorption for volumetric optical data storage," N. S. Makarov, A. Rebane, M. Drobizhev, H. Wolleb, and H. Spahn, *JOSA B*, 24 (8), pp. 1874-1885 (2007).
11. "Two-photon absorption standards in the 550-1600 nm excitation wavelength range," Nikolay S. Makarov, M. Drobizhev, A. Rebane, *Optics Express* 16 (6), pp. 4029-4047 (2008).
12. "New fluorophores based on triphenylamine for three-photon absorption," Z. Suo, M. Drobizhev, C.W. Spangler, N. Christensson, and A. Rebane, *Organic Letters*, 7 (22), 4807-4810 (2005).



13. "Quantum interference between multi photon absorption pathways in organic solid," A. Rebane, N. Christensson, M. Drobizhev, Y. Stepanenko, C.W. Spangler, J. of Luminescence **127** (1), pp. 28-33 (2007).
14. "Synthesis, crystal structure and nonlinear optical behavior of *meso-meso* E-vinylene-linked porphyrin dimers without  $\beta$ -substituents," M. J. Frampton, H. Akdas, A. R. Cowley, J. E. Rogers, P. A. Fleitz, M. Drobizhev, A. Rebane and H. L. Anderson, Organic Letters, **7** (24), 5365-5368 (2005).

## 6. Interactions/Transitions:

### a. Participation/presentations at meetings, conferences, seminars, etc.

1. "Coherent domain structure in linear and dendrimer chromophores studied by one- and three-photon absorption spectroscopy," M. Drobizhev, N. Christensson, A. Rebane, Z. Suo, C.W. Spangler, O. Mongin, M. Blanchard-Desce, Proc. SPIE Vol. 5934, Nonlinear Optical Transmission and Multiphoton Processes in Organics III; A. Todd Yeates; Ed. , p. 104-112 (2005)
2. "Quantum interference by femtosecond multi-photon absorption in conjugated dendrimers," A. Rebane, N. Christensson, M. Drobizhev, Y. Stepanenko, C. W. Spangler, Proc. SPIE Vol. 5934, Nonlinear Optical Transmission and Multiphoton Processes in Organics III; A. T. Yeates; Ed., p. 113-120 (2005).
3. "Experimental characterization of two-photon materials for fast rewritable optical data storage," Nikolay Makarov, Mikhail Drobizhev, Aleks Rebane, Desiree Peone, Heinz Wolleb\*, Heinz Spahni, Proc. SPIE Vol. 6330, Nonlinear Optical Transmission and Multiphoton Processes in Organics IV; A. T. Yeates, K. D. Belfield, F. Kajzar; Eds. (2006).
4. "Phthalocyanine molecules with extremely strong two-photon absorption for 3D rewritable optical information storage," M. Drobizhev, N. S. Makarov, A. Rebane, H. Wolleb, H. Spahni, Proc. SPIE Vol. 6308, 630803, Photonics for Space Environments XI; Edward W. Taylor; Ed. (2006).
5. "Fluorescence from upper excited states of porphyrins with one- and two-photon excitation," M. Kruk, M. Drobizhev, A. Karotki, A. Rebane, Proc. SPIE Vol. 6727, pp. in: Nonlinear Laser Spectroscopy and High-Precision Measurements; and Fundamentals of Laser Chemistry and Biophotonics, S. Tikhomirov; T. Udem; V.I. Yudin; M. Pshenichnikov; O. Sarkisov, Eds. (2007).
6. "Resonance enhancement of two-photon absorption of phthalocyanines for 3D optical storage in the presence of hot-band absorption," N. Makarov, M. Drobizhev, A. Rebane, D. Peone, H. Wolleb, H. Spahni, E. A. Makarova, E.A. Lukyanets, Proc. SPIE Vol. 6470, in: Organic Photonic Materials and Devices IX, J. G. Grote, F. Kajzar, N. Kim, Eds. (2007).
7. "Broad bandwidth near-IR two-photon absorption in conjugated porphyrin-core dendrimers," A. Rebane, N. Makarov, M. Drobizhev, C. W. Spangler, A. Gong, F. Meng, SPIE Proceedings v.6653 (2007).
8. "Narrowing of the homogeneous two-photon absorption line width in two-level dipolar system," Aleks K. Rebane, Mikhail A. Drobizhev, Nikolay S. Makarov, SPIE Proceedings, vol. 6903, Advanced Optical Concepts in Quantum Computing, Memory, and Communication (2008).
9. "Narrowing of the homogeneous two-photon absorption line width in two-level dipolar system," Aleks K. Rebane, Mikhail A. Drobizhev, Nikolay S. Makarov, SPIE Proceedings, vol. 6903, Advanced Optical Concepts in Quantum Computing, Memory, and Communication (2008).
10. (INVITED TALK) "Multi-photon quantum interference in organic solid," A. Rebane, 14th Annual Laser Physics Workshop, July 4 -8, 2005, Kyoto, Japan.
11. "Quantum interference in organic solid," A. Rebane, CLEO/QELS Pacific Rim, July 11 -15, 2005, Tokyo, Japan.



12. (INVITED TALK) "Quantum interference in organic solid," A. Rebane, Colloquium at the Department of Organic and Polymeric Materials, Tokyo Institute of Technology, July 14, 2005, Tokyo, Japan.
13. "Coherent domain structure in linear and dendrimer chromophores studied by one- and three-photon absorption spectroscopy," M. Drobizhev, N. Christensson, A. Rebane, Z. Suo, C.W. Spangler, O. Mongin, M. Blanchard-Desce, SPIE Annual Meeting, San Diego, July 30 -August 4, 2005.
14. "Quantum interference by femtosecond multi-photon absorption in conjugated dendrimers," SPIE Annual Meeting, San Diego, July 30 -August 4, 2005.
15. "Optimization of femtosecond two-photon storage by spectral pulse shaping,," N. Makarov, M. Drobizhev, A. Rebane, SPIE Annual Meeting, San Diego, July 30 -August 4, 2005.
16. "Two-photon porphyrin core dendrimers for optical power limiting," AFOSR Polymer Chemistry & Polymer Matrix Composites Program Review, San Diego, CA, 8-13 August, 2005.
17. (INVITED TALK) "Tetrapyrroles: From Quantum Interference to Cancer Therapy," Dept. of Physics, Texas A&M University, April 6, 2006.
18. (INVITED TALK) "Multi Photon Quantum Interference Holography," Seminar on Zero Phonon Lines: Recent Developments and Future Prospects, Tartu, Estonia, April 11, 2006.
19. "Quantum interference of multi photon absorption pathways in organic solid," A. Rebane, N. Christensson, M. Drobizhev, Y. Stepanenko, C.W. Spangler, 9<sup>th</sup> Int. Conf. on Hole Burning and Single Molecules, June 24-29, 2006, Assois, France.
20. "Very efficient two-photon induced photo-tautomerization in non-symmetrical phthalocyanines," M. Drobizhev, N. S. Makarov, A. Rebane H. Wolleb, H. Spahni, , 9<sup>th</sup> Int. Conf. on Hole Burning and Single Molecules, June 24-29, 2006, Assois, France.
21. (INVITED TALK) "Two-photon absorption in tetrapyrroles," M.Drobizhev, A. Rebane and C. W. Spangler, 4<sup>th</sup> Int. Conf. on Porphyrins and Phthalocyanines, July 2 -7, 2006, Rome, Italy.
22. "The effect of electron-withdrawing substituents on two-photon absorption properties of A3-corroles, " A. Rebane, M. Drobizhev, N.S. Makarov, B. Koszarna, D. T. Gryko, 4<sup>th</sup> Int. Conf. on Porphyrins and Phthalocyanines, July 2 -7, 2006, Rome, Italy.
23. "Modulation of two-photon absorption of asymmetrically-substituted phthalocyanines by the position of inner protons (tautomerization) and structure of linking group," A. Rebane, M. Drobizhev, N. S. Makarov, G. de la Torre and T. Torres, 4<sup>th</sup> Int. Conf. on Porphyrins and Phthalocyanines, July 2 -7, 2006, Rome, Italy
24. "Two-photon absorption in tetraazachlorin and its benzo- and 2,3-naphtho-fused derivatives: effective symmetry of  $\pi$ -conjugation pathway," M. Drobizhev, N. S. Makarov, A. Rebane, E. A. Makarova, E. A. Luk'yanets, 4<sup>th</sup> Int. Conf. on Porphyrins and Phthalocyanines, July 2 -7, 2006, Rome, Italy
25. "Strong cooperative enhancement of two-photon absorption in a series of conjugated porphyrin oligomers arranged in a double-stranded conformation," M. Drobizhev, Y. Stepanenko, A. Rebanc, C.J. Wilson, T. E.O. Screen, H.L. Anderson, 4<sup>th</sup> Int. Conf. on Porphyrins and Phthalocyanines, July 2 -7, 2006, Rome, Italy.
26. "Experimental characterization of two-photon materials for fast rewritable optical data storage," N. Makarov, M. Drobizhev, A. Rebane, D. Peone, H. Wolleb, H. Spahni, SPIE Optics & Photonics Annual Meeting, San Diego, August 13-17, 2006.
27. "Phthalocyanine molecules with extremely strong two-photon absorption for 3D rewritable optical information storage," M. Drobizhev, N. S. Makarov, A. Rebane, H. Wolleb, H. Spahni, SPIE Optics & Photonics Annual Meeting, San Diego, August 13-17, 2006.

28. "Two photon absorption in conjugated tetrapyrroles: spectroscopy and applications," A.Rebane, M. Drobizhev, 7th Int. Conf. on Optical Probes of p-Conjugated Polymers and Functional Self-Assemblies, Turku, Finland, June 10- 15, 2007.
29. "Two-photon absorption in organic chromophores: Spectroscopy and applications" Colloquium at the Department of Physics of the University of Utah, Salt Lake City, July 10, 2007.
30. "Quantitative description two-photon absorption in dipolar molecules with two-level model," N. Makarov, A. Rebane, M. Drobizhev, Z. Suo, C.W. Spangler, B. D. Spangler, F. Meng, H. L. Anderson, C.J. Wilson, SPIE Optics & Photonics Annual Meeting, San Diego, August 26-31, 2007.
31. "Two-photon and excited-state absorption in asymmetric phthalocyanines, push-pull phthalocyanines, and phthalocyanine: electron-acceptor diads," M. Drobizhev, N. Makarov, A. Rebane, G. de la Torre, T. Torres, H. Wolleb, H. Spahni, SPIE Optics & Photonics Annual Meeting, San Diego, August 26-31, 2007.
32. "Broad bandwidth near-IR two-photon absorption in conjugated porphyrins core dendrimers," A. Rebane, M. Drobizhev, N. Makarov, C. W. Spangler, A. Gong, SPIE Optics & Photonics Annual Meeting, San Diego, August 26-31, 2007.
33. "Broad bandwidth near-IR two-photon absorption in conjugated porphyrin-core dendrimers," A. Rebane, N. Makarov, M. Drobizhev, C. W. Spangler, A. Gong, F. Meng, SPIE Proceedings v. 6653 (2007).
34. "Fluorescence from upper excited states of porphyrins with one- and two-photon excitation," M. Kruk, M. Drobizhev, A. Karotki, A. Rebane, Proc. SPIE Vol. 6727, pp. in: Nonlinear Laser Spectroscopy and High-Precision Measurements; and Fundamentals of Laser Chemistry and Biophotonics, S. Tikhomirov; T. Udem; V.I. Yudin; M. Pshenichnikov; O. Sarkisov, Eds. (2007).
35. "Resonance enhancement of two-photon absorption of phthalocyanines for 3D optical storage in the presence of hot-band absorption," N. Makarov, M. Drobizhev, A. Rebane, D. Peone, H. Wolleb, H. Spahni, E. A. Makarova, E.A. Lukyanets, Proc. SPIE Vol. 6470, in: Organic Photonic Materials and Devices IX, J. G. Grote, F. Kajzar, N. Kim, Eds. (2007).
36. "Optimizing two-photon optical storage in the presence of hot band absorption", Makarov N.S., Rebane A., Drobizhev M., Wolleb H., Spahni H., Photonics West 2007, 20-25 January 2007.
37. "Resonance enhancement of two-photon cross section for optical storage in the presence of hot band absorption", Makarov N.S., Rebane A., Drobizhev M., Wolleb H., Spahni H., Photonics West 2007, 20-25 January 2007.
38. Tri-Service Information Exchange Meeting on Optical Limiting, Hilton Head Island, South Carolina, April 14-16, 2008.

**b. Consultative and advisory functions to Air Force and other DoD laboratories.**

Over the duration of this project, we have performed at our laboratory measurements of AFRL supplied compounds (see below) for purpose of common projects and common publications [7,14]. We have on numerous occasions met with the AFRL personnel both at conferences as well as on site at the Wright-Patterson AFB, and performed other consulting functions for the AFRL scientists.

DoD contacts: Dr. Thomas Cooper (group leader), Dr. Joy E. Haley, Dr. Ruth Pachter, Dr. Daniel McLean, Dr. Augustine Urbas (former group leader), AFRL/MLPJ Bldg 651, 3005 Hobson Way, Wright-Patterson AFB, OH 45433-7702

Phone (937) 255-3808 x3179, Fax (937) 255-1128.

Approximate dates the interactions occurred:



**August 2005:** Discussed triplet-triplet absorption measurements with Dr. Joy Rogers at the AFOSR Program Review meeting in San Diego, CA.

**July-August 2006:** Performed 2PA spectrum measurements of samples sent by WPAFB group (J. Rogers, T. Cooper) and also by K. Schanze (U of Florida). A paper is being prepared for publication.

**July 2006.** Discussed 2PA absorption measurements with Dr. Joy Rogers and theory calculations with Dr. Ruth Pachter at the ICPP-4 meeting in Rome, Italy.

4. Site visit and presentations by Montana State University Two-Photon Spectroscopy group at WPAFB, May 10, 2007.

*Dr. Aleks Rebane: "Chromophores for Broad-Band Two-Photon Absorption in Near-IR"*

This presentation will give a brief overview of our program on the design and spectroscopic characterization of new organic chromophores with efficient two-photon absorption (2PA) in broad range of wavelengths. I will start by reviewing the basic principles of 2PA in two- and three energy level systems, including the methodology of measuring the 2PA spectra and absolute 2PA cross sections in 500 – 2000nm wavelength range by fluorescence excitation method. Recent progress in porphyrin-based near-IR two-photon absorbers will be described.

*Dr. Mikhail Drobizhev: "Two-Photon Spectroscopy of Porphyrins and Phthalocyanines"*

This talk will give an overview in recent progress in understanding 2PA properties of porphyrins, porphyrin-based dimers and oligomers, as well as symmetrical and non-symmetrical phthalocyanines. We will show that lowering the molecular symmetry, in combination with resonance enhancement can give very large 2PA cross sections  $\sigma_2=10^3$ - $10^5$  GM at 800 – 1500 nm. Possibilities of adding strong excited-state absorption in the same region for efficient power limiting will be discussed.

*Dr. Charles W. Spangler: "Design of Porphyrins with Enhanced Multi-Photon Absorption - Using What We Have Learned from Linear and Branched Chain Structures"*

Over the past decade we have developed several paradigms for the design of extended conjugation systems with greatly enhanced multi-photon absorption (MPA). Several of these systems yielded models for how these lessons could be incorporated into the design of other molecules that have notoriously low multi-photon cross-sections, such as porphyrins. Our success with porphyrins has led to a pre-clinical program employing these porphyrins for the noninvasive treatment of subcutaneous cancerous tumors in the NIR tissue transparency window.

**December 2007 and January 2008.** Discussed with Dr. Urbas modeling of ultra short pulse propagation in NLO media.

**October 2008** Phone conference with Dr. Cooper, Dr. Rogers and Dr. Daniel McLean about development of 2PA-enhanced chromophores.

**October 2008** Email exchange with Dr. Daniel McLean concerning construction of 2PA spectrometer.

### **c. Transitions to technology application.**

#### **7. New discoveries, inventions, or patent disclosures. (If none, report None.)**

US Patent 6953570 (2006) "Porphyrins with enhanced multi-photon absorption cross-sections for photodynamic therapy," was issued to E. Nickel, Ch. Spangler, A. Rebane. This technology is currently considered for next stage of R&D funding by a group of venture capital investors (Pacific Horizon/Rasiris Inc., Seattle, WA).

#### **8. Honors/Awards:**



**(a) Honors and awards received during the grant/contract period.**

**(b) Lifetime achievement honors prior to this effort:**

1993 International Commission for Optics Prize

1996 Leopold Ruzicka Prize of the Swiss Federal Institute of Technology

1999 Charles and Nora Wiley Award of the Montana State University.

2004 Montana State University Cox Award