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14. ABSTRACT The primary focus of this program was to synthesize π -conjugated oligomers that feature high cross section two-photon absorbing (TPA) chromophores combined with transition metal centers. The TPA chromophores imbue the oligomers with high cross sections for two-photon absorption, whereas the metal centers provide for efficient production of long-lifetime, strongly absorbing triplet excited states. Because of the strong absorption of the triplet excited states, the materials display reverse saturable absorption (RSA). The second generation organometallic materials provide efficient, broad wavelength and broad temporal response non-linear absorption via a dual mode TPA/RSA mechanism.					
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Final Report

Grant : "Second Generation Organometallic Materials for Non-Linear Optical Application"

Funding Period : Feb. 15, 2006 – Feb. 14, 2009

PI: Kirk S. Schanze, Department of Chemistry, University of Florida

I. Project Objectives, Significance and Overview

During the past several years in an AFOSR sponsored project our group has carried out a research program that has investigated the photophysics and non-linear absorption properties of π -conjugated platinum-acetylide oligomers and polymers (Figure 1). The photophysical properties of these materials are dominated by long-lived, strongly absorbing triplet excited states. Due to the strong triplet excited state absorption, Pt-acetylides display non-linear absorption via the reverse saturable absorption (RSA) mechanism. As a result, this class of organometallic compounds has considerable potential for optical limiting applications.¹⁻³ Our research program on Pt-acetylides has been carried out in close coordination with the Agile Limiters group at the Air Force Research Laboratory (AFRL/MLPJ).



Figure 1. Structure of platinum-acetylide materials.

Work carried out during the 2006 – 2009 period focused on the development of second generation organometallic chromophore systems for application as non-linear absorption materials. The specific aim for this program was to explore organometallic materials that exhibit strong non-linear absorption properties in the visible and near-IR region. The strategy is to incorporate high σ_2' two-photon absorption (TPA) chromophores into structures that contain heavy metal centers that will act to produce high yields of triplet excited states rapidly following excitation. As shown in Figure 2, these materials exhibit non-linear absorption by two mechanisms. Specifically, TPA chromophores imbue the materials with the ability to efficiently absorb photons in the near-infrared region. Following intersystem crossing, which is promoted by the heavy metal centers, long-lifetime triplet excited states are generated. Due to the strong absorption of the triplet state, these materials also feature reverse saturable absorption, which gives rise to the possibility for efficient optical limiting via a dual mode TPA/RSA mechanism.

In the following sections, accomplishments which have resulted from work carried out in this project are summarized.

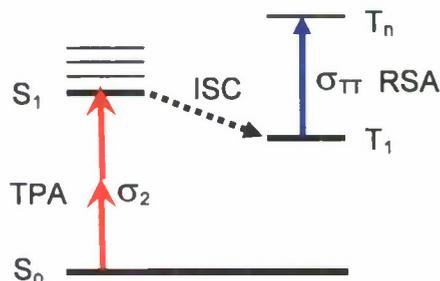


Figure 2. Jablonski diagram for a chromophore that exhibits TPA and RSA.

II. Summary of Accomplishments

II.A. Organometallic Chromophores for Dual Mode Non-Linear Absorption: Tuning the Triplet-Triplet Absorption. A central objective of the work carried out during most recent period has been to study organometallic chromophores that display non-linear absorption resulting from a dual mode mechanism involving two-photon absorption and excited state absorption (TPA and RSA, refer to Figure 2). In work that was recently published,⁴ we successfully demonstrated that platinum acetylides that contain high cross-section TPA chromophores of the type donor- π -donor (D- π -D) produce high yields of triplet excited states rapidly following excitation to give rise to enhanced nonlinear absorption via the dual-mode TPA/RSA mechanism.

As an extension of this work, we recently set out to explore the relationship between the non-linear response of this family of complexes and their triplet-triplet absorption properties. In order to achieve this objective, we synthesized a series of complexes that contain large cross section TPA chromophores combined with various central π -conjugated (arylene) segments. As shown by the cartoon in Figure 3 these multifunctional complexes feature two TPA chromophores linked via Pt units to a central arylene moiety that serves as a “triplet chromophore”. The chemical structures of the series of complexes that have been studied are also shown in Figure 3. Each of these complexes contains two TPA chromophores that are based on the diphenylaminofluorene (DPAF) moiety (D- π type), linked to the core arylene segment via Pt-acetylide linkages. The core arylene units -Ar- are systematically varied to alter the triplet-triplet absorption properties of the complexes. The concept for utilizing a variety of central Ar groups comes from our previous observation that in Pt-acetylide dimers of the type [Ar'-Pt(PBu₃)₂-C \equiv C-Ar-C \equiv C-Pt(PBu₃)₂-Ar'], the lowest triplet excited state is localized on the central arylene unit (Ar).⁴ Because of this effect, the triplet-triplet absorption of the long-lived excited state is for the most part determined by the structure of this central arylene chromophore.

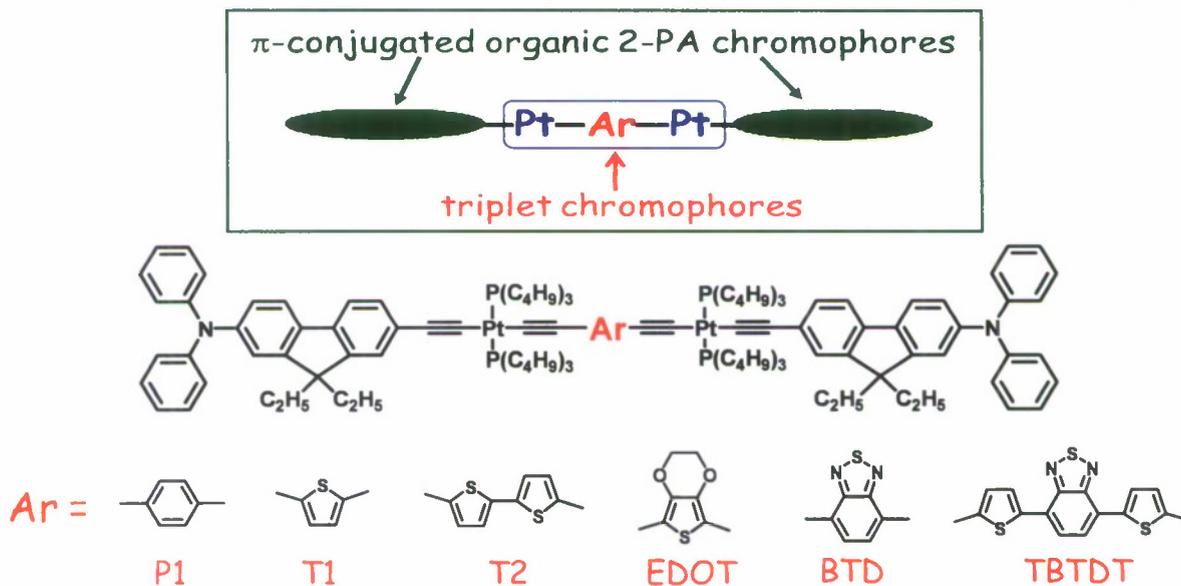


Figure 3. Molecular structure of Pt-2-Ar series, where Ar = P1, T1, T2, EDOT, BTD and TBTDT.

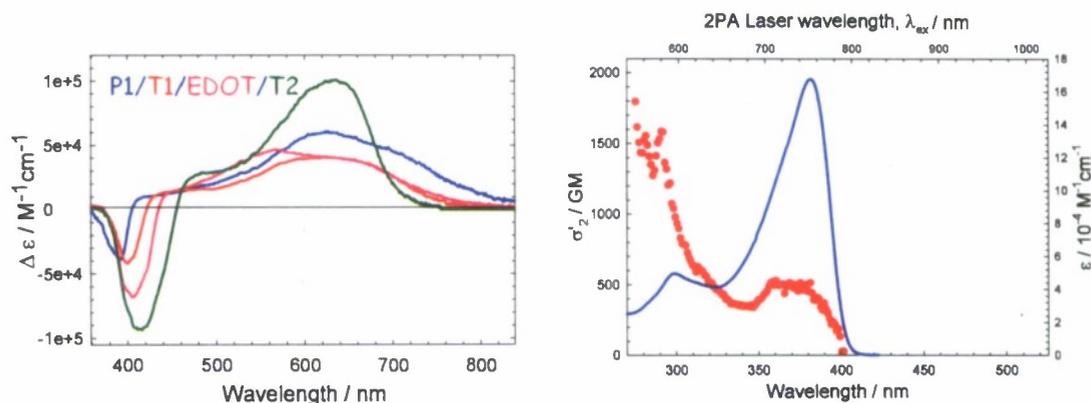


Figure 4. (a) Triplet-triplet absorption spectra for Pt-2-Ar complexes (Ar = P1, T1, EDOT, T2). Note that the molar absorptivity of the T2 complex is largest for the series. (b) Comparison of two-photon absorption spectrum (red symbols) with one photon absorption (blue line) for Pt-2-P1.

Six different Ar groups including π -conjugated electronic systems such as phenyl (**P1**) and oligothiophene (**T1**, **T2**) and heterocyclic donor/acceptors (**EDOT**, **BTD**, **TBTDT**) were used. All of these Ar groups are reported to have different triplet state energies and exhibit large triplet-triplet absorption cross sections (σ_{TT}) in the visible and near-infrared regions. Since the triplet state energies of these Ar chromophores are less than 2.5 eV,⁵ the lowest energy triplet is localized on the core chromophores rather than on the DPAF units. However, since the Pt-acetylide dimers in Figure 3 all share the common DPAF TPA chromophore, they are expected to show similar intrinsic σ_2' values. In addition, because of the different central Ar chromophores, the triplet-triplet absorption will vary, giving rise to different non-linear absorption properties with respect to long (i.e., nanosecond) laser pulses.

The series of six Pt-2-Ar complexes was subjected to a detailed photophysical investigation which included quantitative measurement of the complexes' absorption, photoluminescence, intersystem crossing and triplet-triplet absorption spectra. In addition, in collaboration with Prof. Alex Rebane at Montana State University, the wavelength-dependent two-photon absorption cross section (σ_2') for two of the complexes was determined. All of this data was then correlated with the effective non-linear absorption response of the complexes in the near-infrared region (600 – 800 nm). Here we only summarize the most significant findings of this work; a manuscript that gives a complete report is submitted for publication.

Four of the Pt-2-Ar complexes (Ar = **P1**, **T1**, **EDOT** and **T2**) absorb in the blue of the visible region (400 – 450 nm) and the absorption red-shifts as the conjugation length or donor strength of the core arylene unit increases. Pt-2-BTD and Pt-2-TBTDT are different in that they absorb at significantly longer wavelength (500 – 600 nm), presumably due to charge-transfer transitions arising from the **BTD** and **TBTDT** chromophores. The intersystem crossing efficiencies of all of the complexes were determined under one-photon excitation, and in each case the efficiencies are very high (> 90%). Transient absorption studies reveal that the complexes feature strong triplet-triplet absorption which extends throughout the visible region (for example, see Figure 4a). By using the relative actinometry method,⁶ the molar absorptivity of the triplet excited states for the complexes were determined. The peak molar absorptivity values for the series vary from $4 \times 10^4 - 1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, with the Pt-2-T2 complex exhibiting the largest triplet-triplet absorptivity. Working in collaboration with Prof. Alex Rebane of

Montana State University, we determined the wavelength dependence of the effective two-photon absorption cross section for several of the complexes, and typical results are shown in Figure 4b. In particular, the complexes display relatively large effective TPA cross sections, with $\sigma_2' > 1000 \text{ GM}$ occurring for $\lambda \sim 600$.

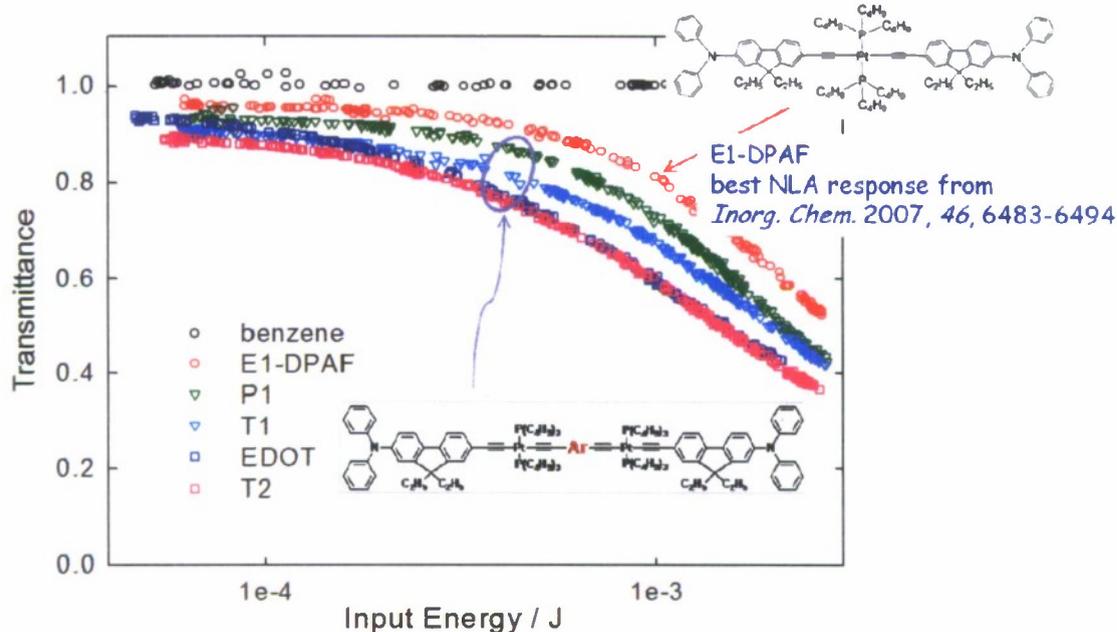


Figure 5. Comparison of non-linear absorption of series of **Pt-2-Ar** complexes compared to E1-DPAF, which was characterized in a published study (ref. 32). Non-linear absorption measured at 600 nm using 5 ns pulses from a Nd:YAG-pumped OPO.

During the past several years a non-linear absorption test apparatus was assembled at the University of Florida, and this instrument has been used to characterize the relative non-linear absorption response of the **Pt-2-Ar** series.⁷ Figure 5 shows a comparison of the non-linear absorption of four **Pt-2-Ar** complexes (**Ar** = **P1**, **T1**, **EDOT** and **T2**) and **E1-DPAF** (see figure for structure) measured at 600 nm. Each of the complexes displays strong non-linear absorption. Several important features emerge from inspection of this data. First, the non-linear response of the **Pt-2-Ar** complexes is larger compared to that of **E1-DPAF**, which suggests that the incorporation of the Pt-Ar-Pt “triplet chromophore” into the structure improves the non-linear response due to the triplet-triplet absorption. Second, the response of the **Pt-2-T2** complex is the largest among the series, and this complex is the one that exhibits the largest triplet-triplet molar absorptivity.

II.B. Organometallic Dendrimers: Cooperative Non-Linear Absorption Chromophore Response. A second major line of investigation that we have pursued involves the study of organometallic dendrimer structures. These systems were developed based on earlier work on all-organic TPA chromophores which showed that branched or dendritic π -conjugated systems consisting of donor- π -donor (D- π -D) segments display a synergistic or cooperative interaction that leads to enhanced two photon absorptivity relative to the individual TPA units.⁸⁻¹⁰ The structures that were the focus of the work are shown in Figure 6. In particular, two different dendrimers were prepared (**Pt4-C4** and **Pt4-C8**), each containing four

“arms” consisting of platinum-acetylide units connected to two triaryl amine donor units. The core of the dendrimers contains a phenylene ethynylene segment capped on either end with triaryl amines. The two dendrimers differ in the nature of the phosphine ligands used on the

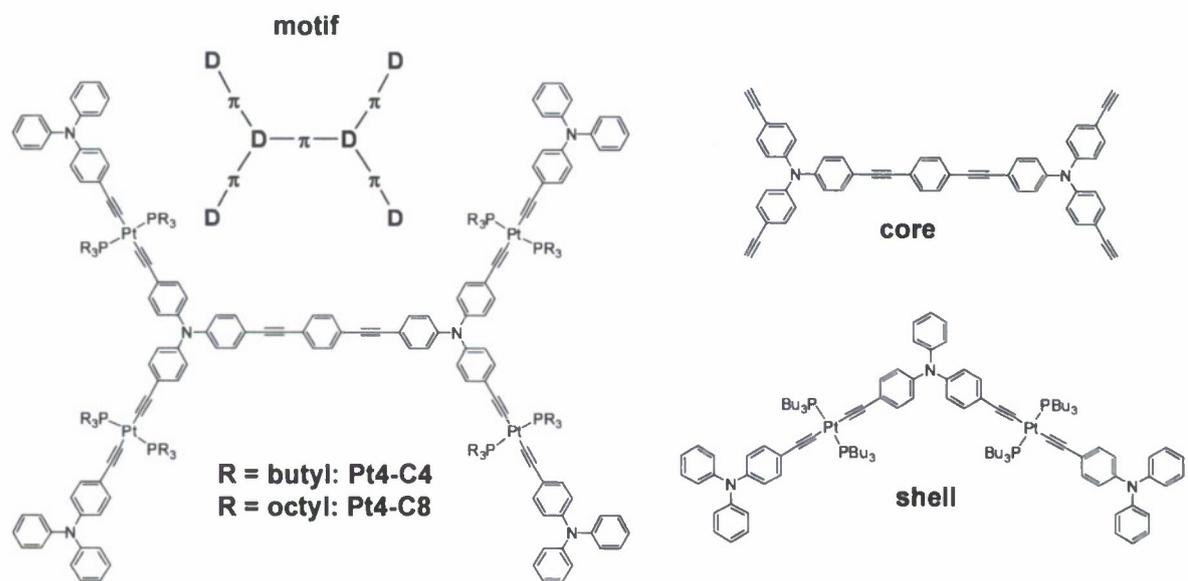


Figure 6. Structures of dendrimer platinum-acetylide complexes and chromophore sub-unit structures.

platinum centers. In **Pt4-C4** the tributyl phosphine ligand was used, whereas in **Pt4-C8** the trioctyl phosphine ligand was used. The optical properties of two dendrimers are essentially the same; however, the difference in phosphine ligands imbues the two systems with different materials properties. Specifically, at ambient temperature (~25 °C) **Pt4-C4** is a waxy solid whereas **Pt4-C8** is a viscous liquid. Both of the oligomers were prepared on a scale of ~1 g, and samples were transferred to the AFRL group for optical testing. In order to help understand the properties of the dendrimer, studies were also carried out on the core chromophore and the platinum acetylide shell (**core** and **shell** structures in Figure 6).

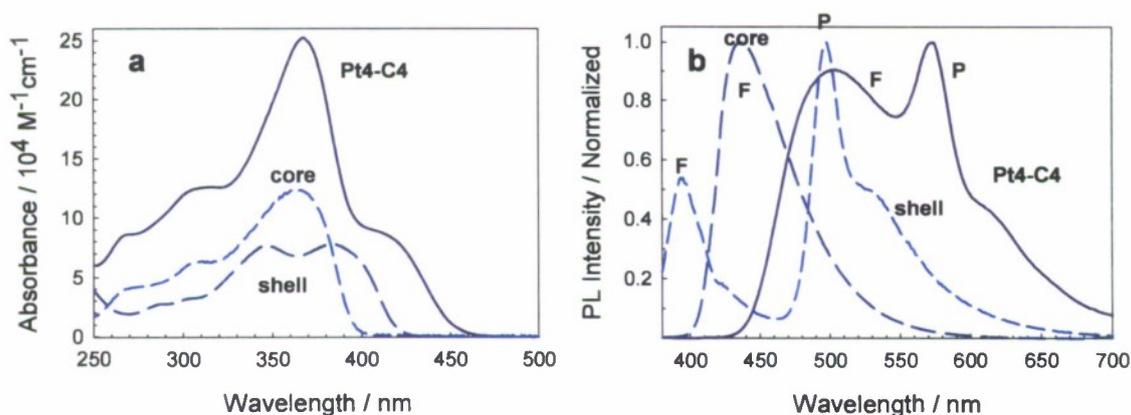


Figure 7. Absorption (a) and photoluminescence (b) spectra of **Pt4-C4**, **core** and **shell** in THF solution. In figure (b) F = fluorescence and P = phosphorescence.

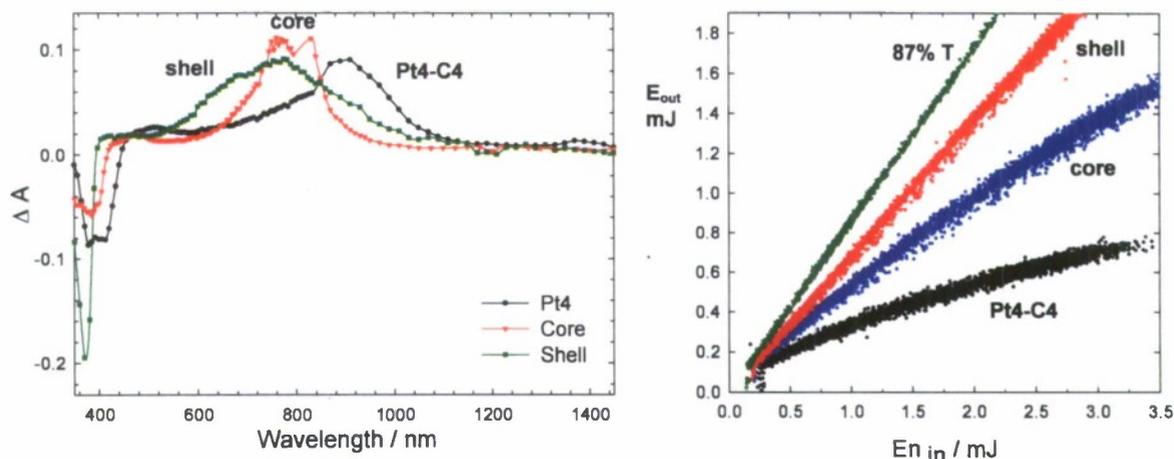


Figure 8. (a) Nanosecond transient absorption spectra of **shell**, **core** and **Pt4-C4** in THF following 355 nm excitation. (b) Non-linear transmittance of 20 mM solutions of **shell**, **core** and **Pt4-C4**. Experiments carried out using 5 ns, 800 nm pulses.

The absorption and photoluminescence spectra of **Pt4-C4** and the **core** and **shell** models are compared in Figure 7. This data clearly illustrates two important points. First, the absorption and fluorescence of the **Pt4-C4** dendrimer is not the simple sum of the **core** and **shell** components—the absorption and fluorescence bands are all red-shifted in the dendrimer relative to their positions in the component structures. Second, while the dendrimer does display fluorescence, there is also a pronounced phosphorescence band ($\lambda_{\text{max}} \sim 580$ nm) which indicates that the platinum-acetylide units serve to enhance the triplet yield in the system. Transient absorption shows that **Pt4-C4** displays a broad and intense triplet-triplet absorption with ($\lambda_{\text{max}} \sim 900$ nm, Figure 8). The triplet-triplet absorption band is red-shifted compared to its position in the **core** and **shell** units, again suggesting that there is a synergistic interaction among the chromophore segments in the branched dendrimer structure.

In order to assess the TPA properties of **Pt4-C4** and **Pt4-C8**, Rachel Jakubiak at AFRL carried out z-scan measurements using 100 fs, 800 nm excitation. Both materials display significant two photon absorptivity, with $\sigma_2' = 80$ GM and 60 GM for **Pt4-C4** and **Pt4-C8**, respectively. Finally, non-linear absorption measurements were carried out in our labs, using 5 ns, 800 nm pulses from an OPO for excitation and the results are illustrated in Figure 8. The results show that **Pt4-C4** displays substantial non-linear absorption and the response of the dendrimer is significantly larger compared to that of either the **core** or **shell** chromophore sub-units. Although this result is qualitative, it clearly shows that the dendrimer exhibits enhanced non-linear response compared to the chromophore sub-units, leading to the conclusion that there is a synergistic interaction in the structure that enhances its non-linear response.

II.C. Comparative Study of Metal-Organic Complexes with Two-Photon Chromophore-Ligand. In a third line of investigation, Dr. John Peak carried out a study in which he correlated the photophysics and non-linear absorption properties of the homologous series of three metal complexes which contained the donor- π -donor type bipyridine ligand (**TPA-Ru**, **TPA-Re** and **TPA-Ir**, Figure 9).⁷ A very similar ligand system was reported earlier as a Ni(II) complex, and in that study it was shown that the ligand exhibits strong two-photon absorption with σ_2' in excess of 100 GM.¹¹ The objective of our study was to correlate the non-linear absorption with the properties of the long lived triplet excited states produced by photoexcitation of the series of complexes. On the basis of earlier studies, we anticipated that the nature of the excited state would vary from metal-to-ligand charge transfer (MLCT) to ligand-centered triplet π,π^* .¹² In particular, we expected that for $M = Ru$, the excited state would be largely MLCT, whereas for $M = Ir$ the excited state would be ligand-centered triplet π,π^* . The absorption, photoluminescence and transient absorption properties of the three complexes were investigated. The absorption and photoluminescence of the complexes are qualitatively similar, with each system exhibiting a strongly allowed absorption in the visible region ($\lambda \sim 480$ nm) and phosphorescence in the red ($\lambda \sim 700$ nm). While the phosphorescence of the complexes is similar, there are differences in band-shape, lifetime and quantum yield that support the assignment of the long-lived excited state to MLCT for **TPA-Ru** and triplet π,π^* for **TPA-Re** and **TPA-Ir**.⁷ Each of the complexes features a strong transient absorption due to the long lived excited state, and the maximum is in the near infrared with $\lambda_{max} \sim 1000$ nm. The transient absorption is slightly blue-shifted for **TPA-Ru**, consistent with the MLCT assignment.

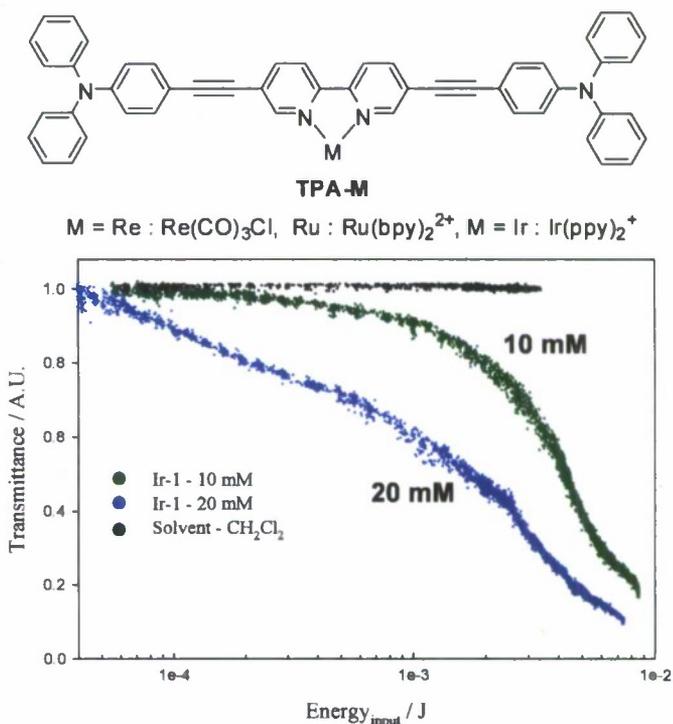


Figure 9. Top: Structures of TPA-M complexes. Bottom: Nonlinear transmission for 10 and 20 mM, CH_2Cl_2 solutions of **TPA-Ir** at 1064 nm.

An extensive series of non-linear absorption experiments was conducted using the three complexes. It was found that each system exhibited efficient non-linear absorption at 1064 nm, and the response of the complexes was benchmarked relative to that of solutions of C60, which previously has been reported to exhibit non-linear absorption at 1064 nm.¹³ While all three of the metal complexes exhibited non-linear absorption, **TPA-Ir** was the most effective, mainly due to the fact that this complex exhibited excellent solubility. In particular, it was possible to make solutions with concentrations in excess of 20 mM with **TPA-Ir**, whereas for **TPA-Ru** and **TPA-Re** solutions with concentrations higher than 1 mM exhibited considerable light scattering due to incomplete dissolution. As shown in Figure 9, the non-linear response of **TPA-Ir** solutions of 10 mM and 20 mM concentration is outstanding, with the more concentrated solution exhibiting an

onset of non-linear absorption for input energies $< 50 \mu\text{J}$. Since this complex does not display any one-photon absorption beyond 600 nm, it is evident that the non-linear response arises due to the dual mode mechanism involving TPA centered on the D- π -D bipyridine ligand coupled with ESA from to the long-lived triplet π, π^* excited state.

II.D. Platinum-Acetylide Organogelators. Gelators are small molecules that when dissolved at moderate concentration in a solvent lead to an increase in the viscosity of the system.¹⁴ Gelation is the result of the formation of molecular aggregates that form fibers that often lead to an interpenetrating network that modifies the rheological properties of the solution. Although gelators can have a variety of different molecular structures, a common format for molecular gelators is structures that have a rigid-rod core capped on either end with alkyl or alkyloxy chains. For example, in recent work Stupp and co-workers studied a series of oligo(phenylene vinylene) (OPV) gelators.¹⁵ These OPVs were asymmetrically functionalized, with an oligo(ethylene glycol) chain on one end and an alkyl chain on the other, and they gelate a variety of organic solvents and water.

In ongoing work we have synthesized and characterized the solution and photophysical properties of a platinum-acetylide gelator, Figure 10. This complex was designed by analogy to Stupp's work on the OPVs; the structure consists of a rigid rod platinum-acetylide phenylene ethynylene core capped on one end with an oligo(ethylene glycol) chain and on the other end with a dodecyl chain. This structure gels organic solvents and water when dissolved at concentrations above 10 mM, see Figure 10. The gelled solutions retain the optical properties characteristic of the platinum-acetylide chromophore, i.e., they absorb in the near-UV and emit phosphorescence in the mid-visible region. The fact that there is interaction between the organometallic chromophores in the aggregates is signaled by the observation of a red-shift in the near-UV absorption. This red-shift is believed to arise due to the formation of H-aggregates. Although non-linear absorption experiments have not yet been performed on these systems, the

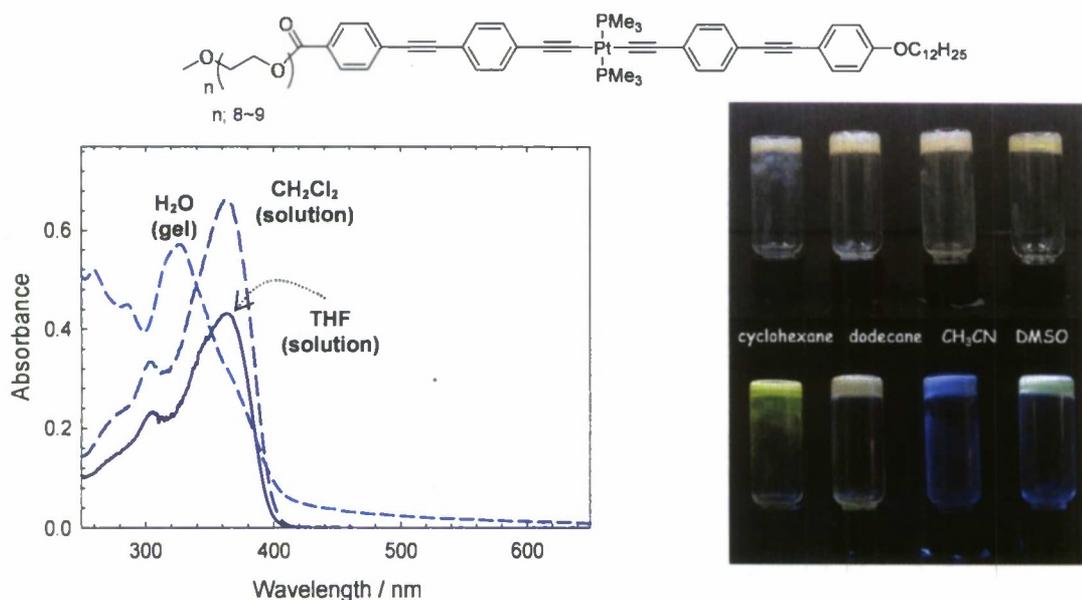


Figure 10. Top: Molecular structure of platinum-acetylide gelator. Left: UV-visible absorption of solutions (gels) of the top. Right: photographs of gels produced from 10 mM solutions of the complex in various solvents. Upper photograph is taken under visible light and lower taken under UV illumination, and it illustrates the photoluminescence.

fact that the linear optical properties of the chromophores are preserved in the gels suggests that they will exhibit non-linear absorption characteristic of the platinum acetylide complexes.

II.E. Development of a z-Scan Apparatus to Quantify NLA Response. In the past we have carried out qualitative non-linear absorption measurements to characterize the response of the organometallic materials being developed in the program. These experiments are difficult to accomplish and do not provide the ability to quantitatively compare the NLA response of the different chromophores. Thus, in order to provide the means to better quantify the NLA response of the new materials, we have established an open aperture nanosecond z-scan system, Figure 11.¹⁶ The z-scan system utilizes the third harmonic output of a Continuum Surelite II Nd:YAG laser coupled to a Continuum Surelite OPO Plus for excitation in the 400 – 700 and 800 – 1100 nm regions.

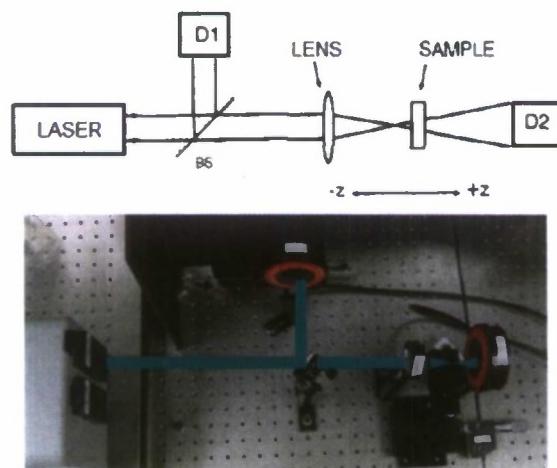


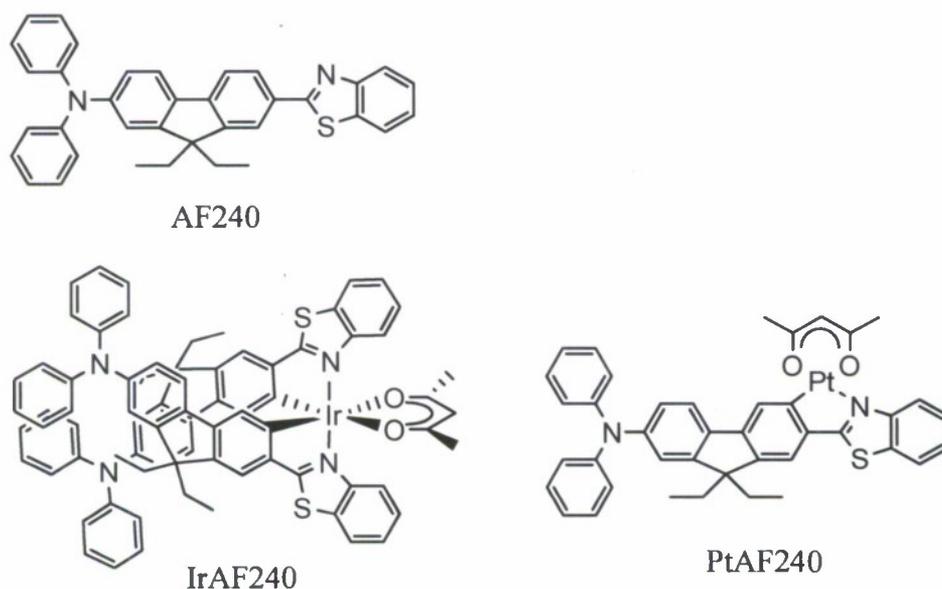
Figure 11. Schematic diagram (top) and photograph (bottom) of z-scan apparatus. The green line in the photograph illustrates the laser beam path

This z-scan system has the advantage of moving the short path length (1 mm) sample along the optical axis through a tight focal plane. The laser flux increases along the focal plane; this is analogous to manually increasing the laser energy, but is achieved without manipulation of the laser settings. A one-directional translation stage positioned directly behind a 50.8 mm focal length plano-convex lens moves the sample through the focal plane. A beam splitter (BS) divides the single beam prior to the focusing lens so that the transmittance of the sample through the focus can be measured as a ratio of detector 2 (D2) over detector 1 (D1). If the sample displays non-linear absorption, the transmittance will change with respect to the position along the optical axis. The energy of the laser light is detected with Ophir pyroelectric heads (2 μJ – 10 mJ) and an Ophir Laserstar energy monitor; the data are collected using StarCom32 software.

The previously studied platinum acetylide, T2, which exhibits strong non-linear absorption at 600 nm, was used to characterize the response of the z-scan system. Benzene or THF are used as solvents for the measurements since they show linear response even at high laser energies. Sample concentrations as low as 0.5 mM and laser energies from approximately 100 μJ – 1.5 mJ have been successful at monitoring non-linear absorption response. Excitation wavelengths are accessible with this system from 420 – 720 nm. To utilize the 2PA pathway

however, we use excitation wavelengths that are one-photon absorption silent, typically from 500 – 700 nm.

II.F. New Iridium and Platinum Orthometallated Complexes as TPA/ESA Chromophores. Ir(III) and Pt(II) complexes with 2-phenylbenzothiazole (bt) have been synthesized by Thompson¹⁷ and Chen's groups.¹⁸ The resulting Irbt and Ptbt complexes exhibit efficient phosphorescence and their colors are tunable by modifying the ligand. These complexes have been utilized as active materials in organic light emitting diodes, oxygen sensors, bioanalytical devices, and photocatalytic water splitting.¹⁹ Using the same framework, we have synthesized new iridium and platinum complexes bearing an efficient two-photon absorbing π -conjugated chromophore, AF240 (Scheme 1).²⁰ AF240 has a bt moiety and will react with iridium or platinum salts in the same mode as the bt ligand. The resulting IrAF240 and PtAF240 complexes (Scheme 1) elicit large TPA/ESA dual-mode nonlinear absorption (NLA) due to spin-orbit coupling effect induced by the heavy atom effect of Pt and Ir metal center.



Scheme 1. Structures of AF240 ligand, IrAF240 and PtAF240.

IrAF240 was synthesized via a modification of Thompson's method.¹⁷ AF240 was reacted with iridium chloride hydrate to give chloride-bridged iridium dimer, which was further reacted with acetylacetonate to give a more soluble and more efficiently emissive monomeric IrAF240. PtAF240 was synthesized in the same manner using potassium tetrachloroplatinate.¹⁸ The octahedral structure of IrAF240, with *trans* Ir-N bonds and the square planar structure of PtAF240, were confirmed by ¹H and ¹³C NMR (¹³C chemical shifts were measured by indirect detection, in a gHMQC spectrum), HMBC, NOESY and HR ESIMS.

The photophysical properties of IrAF240 and PtAF240 under one-photon excitation conditions were characterized (Figure 12). As anticipated, both complexes exhibit strong

absorption in the similar range similar as Ptbt and Irbt. Ground state absorption is assigned to metal to ligand charge transfer (MLCT) and $\pi-\pi^*$ transitions (Figure 12a). The absence of fluorescence in the photoluminescence spectrum suggests the quantum efficiency of intersystem crossing is both compounds (Figure 1c). The transient absorption spectra of PtAF240 and IrAF240 cover broad near-IR region and extinction coefficients for the T-T absorption are relatively large for both complexes (Figure 12b, d).

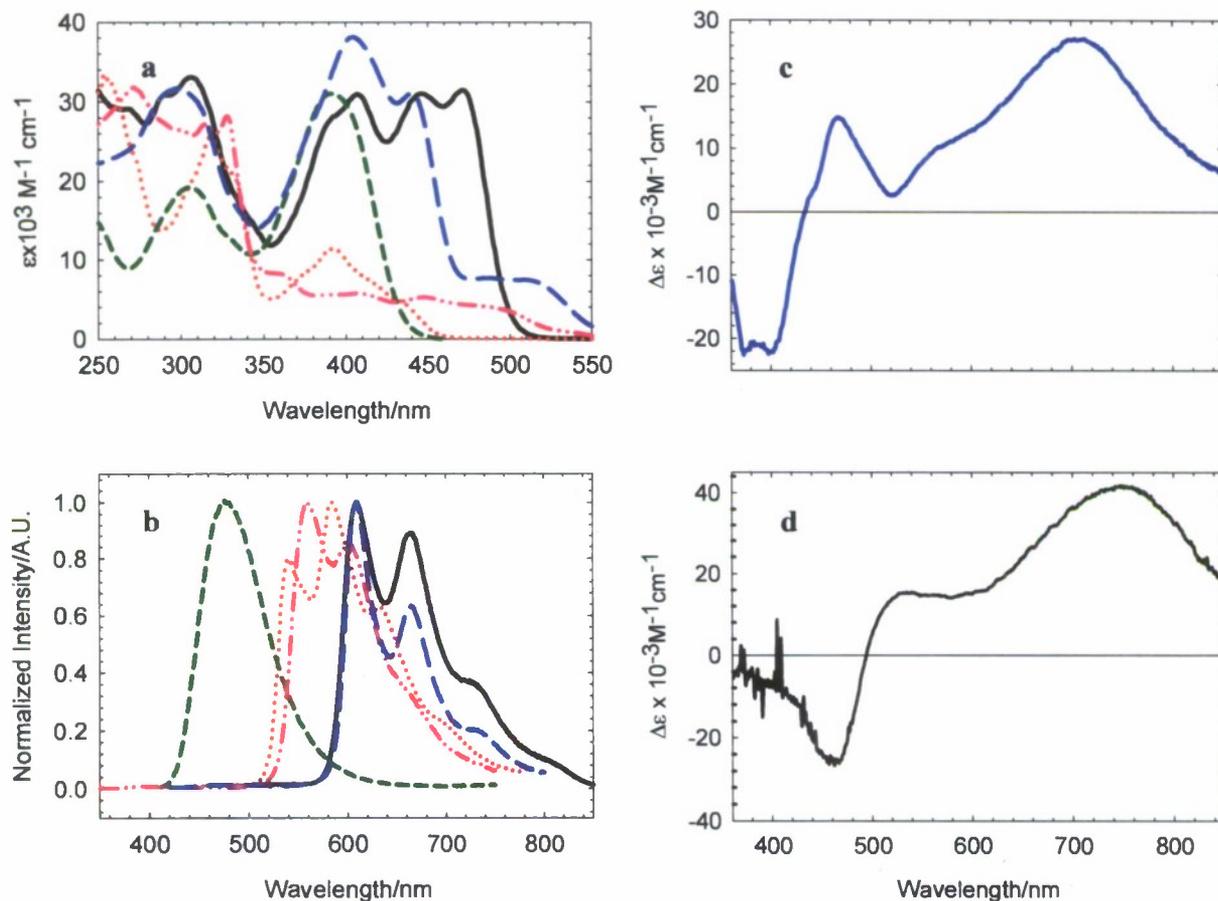


Figure 12. a) Ground state absorption of AF240 (green dash), Irbt(purple dash-dot), IrAF240 (blue long dash), Ptbt (red dot), and PtAF240 (black solid) are shown in the upper panel. b) (Room temperature) emission spectra in argon-purged THF upon excitation at λ_{max} are shown in the lower panel. c) Transient absorption spectrum of IrAF240 in argon-purged THF excited at 355nm. d) Transient absorption spectrum of PtAF240 in argon-purged THF excited at 355nm.

The NLA responses of AF240, Irbt, IrAF240, Ptbt, and PtAF240 were measured by open aperture Z-scan method,²¹ Figure 12. E1-DPAF⁴ and T2 were developed at AFRL as benchmarks for NLA in the near-IR region. The samples were excited at 628 nm where one-photon absorption is essentially zero. Under the conditions used, Ptbt, Irbt and AF240 show no nonlinear response; Ptbt and Irbt do not contain a TPA chromophore while AF240 cannot efficiently populate the triplet excited state being probed. IrAF240 shows larger TPA response but PtAF240 shows less TPA response than E1-DPAF. One of the most plausible explanation for IrAF240's significantly more NLA responses in comparison to PtAF240 is that the presence of an extra TPA chromophore in IrAF240. This suggests that the possible synergistic effect of two

chromophores may enhance the NLA responses much more than the sum of individual chromophores. Octahedral IrAF240 provides better accessibility to the TPA chromophores for photons than the square planar PtAF240.

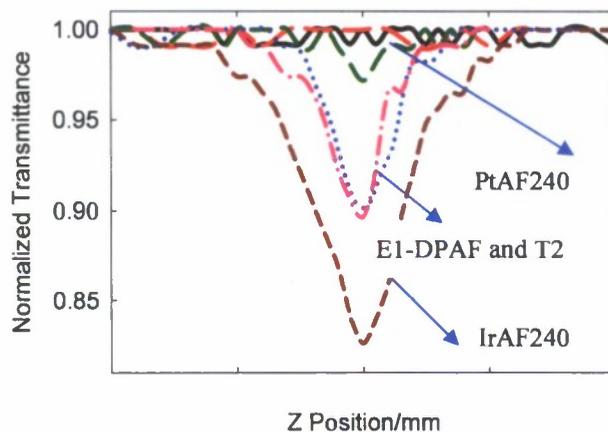
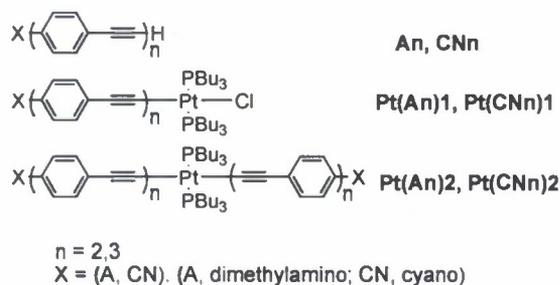


Figure 13. Nonlinear absorption detection, 1 mM in THF, excitation at 628 nm (Power measured at 240-280 $\mu\text{J}/\text{pulse}$). AF240 (black, solid), Ptbt (black, solid) Irbt (red, long dash), IrAF240 (brown, long dash), PtAF240 (green, long dash), E1-DPAF (blue, dash-dot), and T2 (purple, dot) in the upper panel.

To summarize, two-dimensional (PtAF240) and three-dimensional (IrAF240) nonlinear responsive organometallic complexes were synthesized and their photophysical properties were investigated. TPA/ESA dual mechanism is operating in these novel systems with synergistic effect observed in 3D IrAF240.

II.G. Understanding and Controlling the Triplet-Triplet (T-T) Absorption. Platinum acetylide oligomers (PAO) display well-behaved NLA responses operating in TPA/ESA mechanism. The wavelength and strength (cross-section) of the T-T absorption are key parameters in determining the efficiency of NLA in TPA/ESA mechanism. In order to investigate the effects of conjugation length and the type of electron donor/acceptor on triplet-triplet absorption, a series of PAOs were synthesized varying different lengths. The outer most phenyl rings were functionalized with either a dimethylamino (donor) or cyano (acceptor) group on the 4-position (Scheme 2). The increase of the conjugation length is expected to red-shift the wavelength of T-T absorption, while the effects of electron donor and acceptor are unpredictable.



Scheme 2. Shown are the structures of ligands and PAOs.

Compared to that of Pt(A2)2, UV-Vis absorption spectrum of Pt(A3)2 shows a red shift and enhancement in extinction coefficients (Figure 14a), and phosphorescence peak of Pt(A3)2 shows a red shift of 26 nm. This observation agrees with previous studies on PAOs that singlet and triplet excited states are more delocalized in the three-ring PAO than two-ring system. Compared to monosubstituted Pt(A2)1, disubstituted Pt(A2)2 absorbs at a slightly longer wavelength, but phosphoresces at the same wavelength (Figure 14b). This result can be attributed to the fact that singlet is delocalized through the Pt center, while triplet is more localized on the ligand.²² Pt(A2)2 and Pt(CN2)2 have the same absorption and phosphorescence

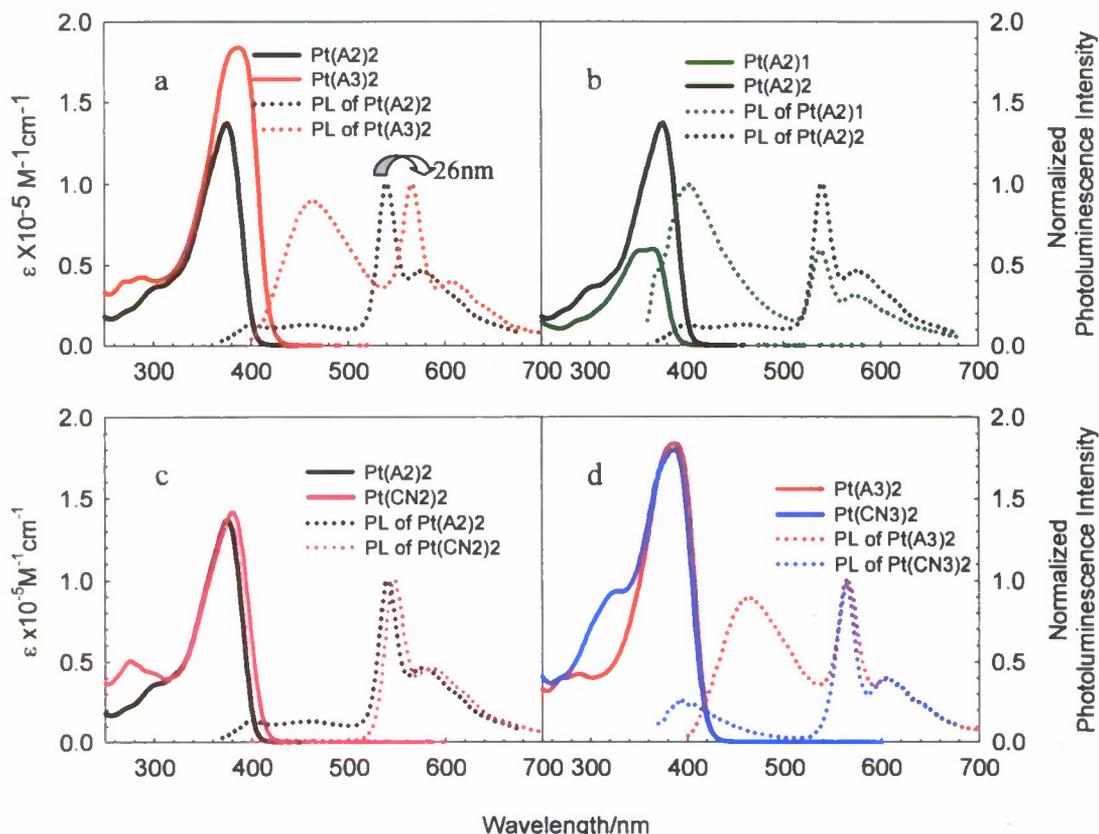


Figure 14. Ground state absorption and photoluminescence of platinum acetylides in argon-purged DCM are shown. a) Pt(A2)2 (black), Pt(A3)2 (red); b) Pt(A2)1 (green), Pt(A2)2 (black); c) Pt(A2)2 (black), Pt(CN2)2 (purple); d) Pt(A3)2 (red), Pt(CN3)2 (blue).

peak, which suggests that electron donor or acceptor do not change the HOMO and LUMO gap of PAOs, nor do they change the energies of triplet excited states (Figure 14c). The lack of electron donor or acceptor effect is also observed in Pt(A3)2 and Pt(CN3)2 (Figure 14d). The T-T absorption spectra of these PAOs are shown in Figure 15. Increasing the conjugation length from Pt(A2)1 to Pt(A3)1 leads to a significant red shift and increase in absorption strength for the T-T absorption (Figure 15a). Conjugation through the platinum center does not lead to any change in the wavelength of T-T absorption, but it does appear to increase the intensity of the transition (Figure 15c). This result suggests that an organometallic species with two chromophores would exhibit greater NLA response, since NLA response increases with strength of the T-T absorption. Both Figure 15b and 15d show the effect of changing the substituent on the organic chromophore from EDG (dimethylamino) to EWG (cyano) on the T-T absorption. In each case, a change from EDG \rightarrow EWG leads to a significant red-shift in the λ_{max} of the T-T absorption.

In summary, the strength of T-T absorption can be enhanced by increasing the conjugation length and/or the number of chromophores. Electron donor/acceptor substituents do not increase the transient absorption strength, however they provide a way of tuning T-T absorption wavelengths.

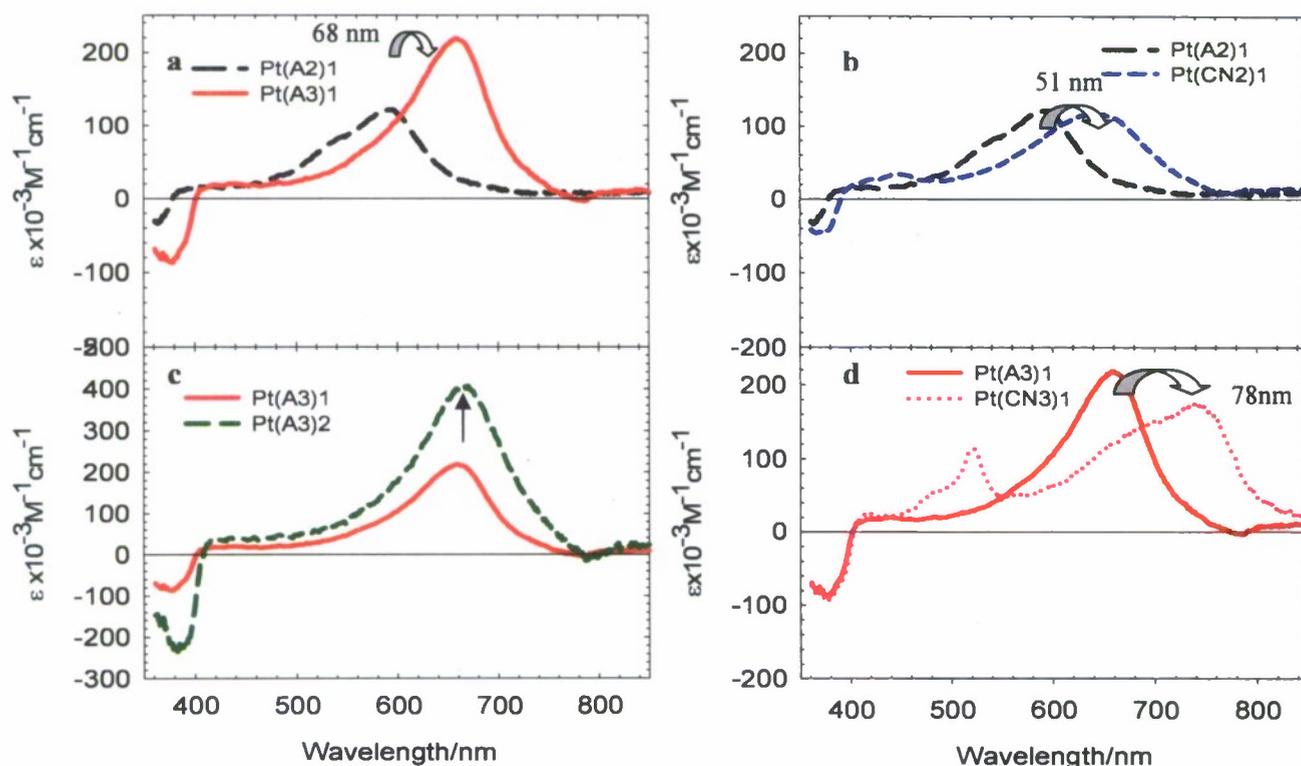


Figure 15. Transient absorption spectra of PAOs in argon-purged THF are shown. A sample with optical density of 0.8 at 355nm was excited using the third harmonic Nd/YAG laser. a) Pt(A2)1 (black), Pt(A3)1 (red); b) Pt(A2)1 (black), Pt(CN2)1 (blue); c) Pt(A3)1 (red), Pt(A3)2 (green); d) Pt(A3)1 (red), Pt(CN3)1 (pink).

References

1. Evidence for Broadband Optical Limiting in a Pt : Ethynyl Compound, Staromlynska, J.; McKay, T. J.; Bolger, J. A.; Davy, J. R. *J. Opt. Soc. Am. B-Opt. Phys.* **1998**, *15*, 1731-1736.
2. Linear and Nonlinear Optical Properties of Platinum-Ethynyl, McKay, T. J.; Bolger, J. A.; Staromlynska, J.; Davy, J. R. *J. Chem. Phys.* **1998**, *108*, 5537-5541.
3. Cross Sections for Excited-State Absorption in a Pt:Ethynyl Complex, McKay, T. J.; Staromlynska, J.; Davy, J. R.; Bolger, J. A. *J. Opt. Soc. Am. B* **2001**, *18*, 358-362.
4. Platinum acetylide two-photon chromophores, Rogers, J. E.; Slagle, J. E.; Krein, D. M.; Burke, A. R.; Hall, B. C.; Fratini, A.; McLean, D. G.; Fleitz, P. A.; Cooper, T. M.; Drobizhev, M.; Makarov, N. S.; Rebane, A.; Kim, K. Y.; Farley, R.; Schanze, K. S. *Inorg. Chem.* **2007**, *46*, 6483-6494.
5. Triplet States in a series of Pt-containing ethynylenes, Wilson, J. S.; Kohler, A.; Friend, R. H.; Al-Suti, M. K.; Al-Mandhary, M. R. A.; Khan, M. S.; Raithby, P. R. *J. Chem. Phys.* **2000**, *113*, 7627-7634.
6. Triplet-Triplet Absorption-Spectra of Organic-Molecules in Condensed Phases, Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1-250.
7. Dual Mechanism Nonlinear Response of Selected Metal-Organic Chromophores, Peak, J. D., Ph.D. Dissertation, University of Florida, Gainesville, 2007,
8. Cooperative enhancement of two-photon absorption in multi-branched structures, Chung, S. J.; Kim, K. S.; Lin, T. H.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741-10745.
9. Dendrimer Molecules with Record Large Two-Photon Absorption Cross Section, Drobizhev, M.; Karotki, A.; Rebane, A.; Spangler, C. W. *Opt. Lett.* **2001**, *26*, 1081-1083.
10. Synthesis of Triphenylamine-Cored Dendritic Two-Photon Absorbing Chromophores, Wei, P.; Bi, X.; Wu, Z.; Xu, Z. *Org. Lett.* **2005**, *7*, 3199-3202.
11. Novel Two-Photon-Absorbing, 1,10-Phenanthroline-Containing pi-Conjugated Chromophores and their Nickel(II) Chelated Complexes with Quenched Emissions, Zheng, Q. D.; He, G. S.; Prasad, P. N. *J. Mater. Chem.* **2005**, *15*, 579-587.
12. Photoluminescence and Electroluminescence of d⁶ Metal-Organic Conjugated Oligomers: Correlation of Photophysics and Device Performance, Cunningham, G. B.; Li, Y. T.; Liu, S. X.; Schanze, K. S. *J. Phys. Chem. B* **2003**, *107*, 12569-12572.
13. Nonlinear optical characteristics of C-60 and C-70 films and solutions, Ganeev, R. A.; Ryasnyansky, A. I.; Kodirov, M. K.; Usmanov, T. *Optics Communications* **2000**, *185*, 473-478.
14. Low Molecular Mass Gelators of Organic Liquids and the Properties of Their Gels, Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133-3160.
15. Self-Assembly and Luminescence of Oligo(*p*-phenylene vinylene) Amphiphiles., Hulvat, J. F.; Sofos, M.; Tajima, K.; Stupp, S. I. *J. Am. Chem. Soc.* **2005**, *127*, 366-372.

16. Sensitive measurement of optical nonlinearities using a single beam, Sheikbahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Vanstryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760-769.
17. Synthesis and characterization of phosphorescent cyclometalated iridium complexes, Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorganic Chemistry* **2001**, *40*, 1704-1711.
18. Highly efficient orange-emitting OLEDs based on phosphorescent platinum(II) complexes, Laskar, I. R.; Hsu, S. F.; Chen, T. M. *Polyhedron* **2005**, *24*, 881-888.
19. Synthetically tailored excited states: Phosphorescent, cyclometalated iridium(III) complexes and their applications, Lowry, M. S.; Bernhard, S. *Chemistry-a European Journal* **2006**, *12*, 7970-7977.
20. Diphenylaminofluorene-based two-photon-absorbing chromophores with various pi-electron acceptors, Kannan, R.; He, G. S.; Yuan, L. X.; Xu, F. M.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L. S. *Chem. Mater.* **2001**, *13*, 1896-1904.
21. Sensitive measurement of optical nonlinearities using a single beam, Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760-9.
22. Photophysics of monodisperse platinum-acetylide oligomers: Delocalization in the singlet and triplet excited states, Liu, Y.; Jiang, S. J.; Glusac, K.; Powell, D. H.; Anderson, D. F.; Schanze, K. S. *Journal of the American Chemical Society* **2002**, *124*, 12412-12413.

Publications Resulting From This Work

1. An Ir(III) Complex That Exhibits Dual Mechanism Non-Linear Absorption, Kim, K.-Y.; Farley, R. T.; Schanze, K. S. *J. Phys. Chem. B* **2006**, *110*, 17302-17304..
2. Platinum Acetylde Two-Photon Chromophores, Rogers, J. E.; Slagle, J. E.; Krein, D. M.; Burke, A. R.; Hall, B. C.; Fratini, A.; McLean, D. G.; Cooper, T. M.; Drobizhev, M.; Makarov, N. S.; Rebane, A.; Kim, K.-Y.; Farley, R.; Schanze, K. S., *Inorg. Chem.* **2007**, *46*, 6483-6494.
3. Platinum Acetylde Nonlinear Absorbing Chromophores: Tuning the Triplet-Triplet Absorption, Kim, K.-Y.; Shelton, A. H.; Drobizhev, M.; Makarov, N.; Rebane, A.; Schanze, K. S., submitted.
4. Ortho-metallated Ir(III) and Pt(II) Chromophores for non-Linear Absorption, Liao, C.; Shelton, A. H.; Schanze, K. S., submitted.
5. Photophysics of Platinum and Iridium Organometallic Materials: From Molecular Wires to Nonlinear Optics, Richard Farley, Ph.D. Dissertation, University of Florida, 2007 (<http://www.chem.ufl.edu/~kschanze/Dissertations/farley.pdf>)
6. Dual Mechanism Nonlinear Response of Selected Metal Organic Chromophores, John D. Peak, Ph.D. Dissertation, University of Florida, 2007. (<http://www.chem.ufl.edu/~kschanze/Dissertations/peak.pdf>)

Cumulative List of Personnel Contributing to Project : 2006 - 2009

Principal Investigator

Kirk S. Schanze

Postdocs

Kye-Young Kim: 2006 – 2008

Chen Liao: 2008 - 2009

Graduate Students

Richard Farley: 2006

John Peak: 2006 – 2007 (Active Duty Air Force Lt. Colonel)

Abigail Shelton: 2007 - 2009