SYNTHESIS AND OPTICAL CHARACTERIZATION OF OPTICAL POWER LIMITING PLATINUM(II) ACETYLIDES

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Title
Synthesis and optical characterization of optical power limiting platinum(II) acetylides

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Abstract
Interactions between light and a molecule can result in reversible or irreversible changes in properties of both the light and the molecule. Of the many known interactions, nonlinear absorption is a process in which an intense light signal, for instance from a laser, can be moderated. This can be manifested either in a marked lowering of the light’s intensity or in reductions in fluctuations of its intensity. Such an effect is often termed ‘optical power limiting’ (OPL).

High power lasers can be very dangerous since their high intensity can damage or destroy eyes and optical sensors. However, there are currently no adequate protective measures against lasers that cover the entire visible region and there is an increasing demand for new or improved OPL materials. Some of the most promising optical power limiting materials are substances that combine nonlinear optical properties with high transparency in normal light, but after activation by a laser beam, their light transmittance falls extremely rapidly via so-called self-activating mechanisms. The platinum(II) acetylides comprise one class of compounds with such properties.

In this study, various OPL Pt(II) acetylides were synthesized and their nonlinear optical properties were characterized. The emphasis of the work was on preparation of the compounds, but in order to design organoplatinum chromophores for OPL, attempts were also made to obtain insight into the mechanisms of nonlinear absorption.

The work was divided into two main parts. In the first the goal was to find compounds that are good optical limiters in solution. The possibility of isolating the chromophore site by dendron shielding and the effects of incorporating a thiophene ring into the organic molecular system were also explored. In addition, a new route for synthesizing these compounds was developed. The second part was focused on incorporating the most interesting compounds into solid materials. The preparation and characterization of Pt(II) acetylides with molecular groups for covalent attachment to a silica matrix via the solution gel approach is described.

Keywords
Platinum acetylides, nonlinear absorption, optical power limiting, Sonogashira coupling, solution gels, thiophene,
TO JENNY
Contents

1. LIST OF PAPERS.................................................................1

2. LIST OF ABBREVIATIONS.................................................2

3. INTRODUCTION..............................................................3

   3.1. GENERAL.........................................................3
   3.1.1. Nonlinear Optics......................................4
   3.1.2. Optical Power limiting........................4
   3.2. NLO CHROMOPHORES FOR OPL................7
      3.2.1. Pt(II) acetylides...............................8
   3.3. BACKGROUND OF SYNTHESIS.....................10
      3.3.1. Sonogashira coupling........................10
      3.3.2. Synthesis of Pt(II) Acetylides...........11

4. AIMS OF THE PRESENT STUDIES...............................15

5. SYNTHESIS AND OPTICAL CHARACTERIZATION OF THIOPHENE
   CONTAINING Pt(II) ACETYLIDES (PAPERS I-III).................17

   5.1. BACKGROUND.....................................................17
   5.2. SYNTHESIS....................................................18
   5.3. STRUCTURAL AND OPTICAL CHARACTERIZATION........21
      5.3.1. Structure of arylalkynyl Pt(II) compounds
              from X-ray diffraction and quantum chemistry
              methods.............................................21
      5.3.2. Optical Characterization......................23
   5.4. CONCLUSION...................................................27

6. SYNTHESIS AND OPTICAL CHARACTERIZATION OF DENDRON
   DECORATED PLATINUM(II) ACETYLIDES (PAPER III)..............29

   6.1. BACKGROUND.....................................................29
   6.2. SYNTHESIS....................................................30
   6.3. OPTICAL CHARACTERIZATION........................32
   6.4. CONCLUSION...................................................35

7. ONE-POT SYNTHESIS OF TRANS MONO- OR DIARYLALKYNYL
   SUBSTITUTED Pt(II) COMPOUNDS (PAPER IV).....................37

   7.1. BACKGROUND.....................................................37
   7.2. RESULTS AND DISCUSSION............................37
   7.3. CONCLUSION...................................................39

8. SOLID MATERIAL (PAPER V)............................................41

   8.1. BACKGROUND.....................................................41
   8.2. SYNTHESIS....................................................42
   8.3. SOL GEL PREPARATION.................................45
   8.4. OPTICAL CHARACTERIZATION......................46
   8.5. CONCLUSION...................................................47

9. CONCLUDING REMARKS..............................................49
10. POPULÄRVETENSkapLIG SAMMANFATTNING.......................... 51
11. ACKNOWLEDGEMENT ................................................................. 53
12. REFERENCES .................................................................................. 55
1. List of Papers

This thesis is based on the following papers, which will be referred to in the text by their roman numerals I-V.


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2. List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>Bis-MPA</td>
<td>2,2-Bis-hydroxymethyl-propionic acid</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethylamine</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>ESA</td>
<td>Excited state absorption</td>
</tr>
<tr>
<td>ICTES</td>
<td>3-Isocyanatopropyl triethoxysilane</td>
</tr>
<tr>
<td>LASER</td>
<td>Light Amplification by Stimulated Emission of Radiation</td>
</tr>
<tr>
<td>LO</td>
<td>Linear optical</td>
</tr>
<tr>
<td>MTEOS</td>
<td>Methyltriethoxysilane</td>
</tr>
<tr>
<td>NLO</td>
<td>Nonlinear optical</td>
</tr>
<tr>
<td>OPL</td>
<td>Optical power limiting</td>
</tr>
<tr>
<td>RSA</td>
<td>Reversed saturable absorption</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>TBDPS</td>
<td>\textit{tert}-butyldiphenylsilyl</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyl</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>TPA</td>
<td>Two-photon absorption</td>
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<td>UN</td>
<td>United Nations</td>
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3. Introduction

3.1. General

Ever since the advent of the laser in 1960 laser equipment has been increasingly widely used. Lasers can be found in common products such as CD/DVD players and laser pointers, in surgical and industrial equipment, and in military devices such as range finders and target designators. Since very high-power lasers can be manufactured, they can be dangerous instruments to work with. Therefore suitable protection should always be used to prevent severe eye damage when handling a high power laser. The human eye is the only organ in which visible light can deeply penetrate. When the light is focused in the eye, the lens increases the irradiance between the cornea and retina by a factor substantially higher than 10,000-fold. In moderately intense light, such as direct sunlight, the reaction time of an eye blink is sufficiently rapid to protect the eye, but with light of higher intensity the retina can be damaged before the blink reflex is activated.

A serious consequence of this is that dangerous weapons have been developed in order to dazzle (continuous-wave lasers) or blind (pulsed lasers) optical sensors including the human eye. In 1995, a UN Convention (Protocol IV) banned antipersonnel laser weapons that permanently blind their targets, but weapons designed to dazzle were considered legitimate. Furthermore, use of banned types of weapons has been reported at several occasions.

There are currently no adequate means of protecting eyes against lasers that cover a wide spectral range in the visible region, which is essential for practical applications in which the object may be exposed to an unknown laser source. The major problem to overcome in developing appropriate protective systems is that they should allow high transmission (>70 %) of low-intensity light, and thus clear sight, in the visible region. A possible approach to solve this problem is to create a protective system that is activated by the laser itself. This can be done by external devices such as electro-optical sensors that detect the laser and trigger a protective mechanism. However, such devices are unlikely to switch sufficiently rapidly to provide protection against a laser pulse with a duration of only a few nanoseconds or less. Another approach is to use a so-called self-activating material such as a nonlinear optical (NLO) material. These materials can have high transmittance in low-intensity light, but their transmittance rapidly falls when exposed to light of high irradiance. It may be difficult to find a
single material that functions well at all relevant wavelengths and for various pulse lengths, so a combination of different systems is probably required, including that the laser beam is focused in the protecting material by an external device.

3.1.1. Nonlinear Optics

In the last decade nonlinear optical materials have been used in increasingly wide ranges of applications such as optical limiters, optical data storage, frequency doubling, photonic circuitry and optical switches. Nonlinear optical phenomena occur when an appropriate medium is subjected to a strong electrical field, such as an intense laser pulse, and its responses to the strong oscillating field result in nonlinear polarization. By designing suitable molecules the nonlinear response may be manipulated in diverse ways, in order to increase or decrease the amplitude or change the frequency of the light. One of the major advantages of such media is that they can respond much more rapidly than electronic systems since photons travel many orders of magnitude faster than electrons.

3.1.2. Optical Power limiting

To protect an optical sensor from high-intensity light, its intensity or energy must be reduced to a non-harmful level before it reaches the sensor. For the human eye the fluency of a nanosecond (ns) laser pulse must be reduced to ≤0.5 µJ/cm². To achieve this goal one can use nonlinear optical materials to protect the sensor. An optical limiting (OPL) material has high transmittance in low-intensity light (normal light) and low transmittance in high-irradiance light, in contrast with a linear optical (LO) material which has a constant transmittance regardless of the power of the incoming light. Hence, at low irradiance, the NLO material acts as a LO material in which the intensity ratio of the input and the output energy are the same, but in a specific energy range its transmittance rapidly declines. If the material is sufficiently efficient the output energy will then remain constant, regardless of the power of the input energy. This constant-energy level is called the clamping level. A schematic diagram of this linear and nonlinear behavior is shown in Figure 3.1.
A number of NLO mechanisms can be involved in OPL responses, such as nonlinear refraction, optically induced scattering, two-photon absorption (TPA) or multi-photon absorption, and excited state absorption (ESA). However, for the OPL materials synthesized and characterized in the work underlying this thesis, the OPL mechanisms involved are thought to be largely two-photon absorption and excited state absorption. Thus, the introduction will focus on these mechanisms.

When a molecule absorbs electromagnetic radiation, the excitation and subsequent return to the ground state can occur by several pathways. In Figure 3.2, a few of these excitation and relaxation processes are represented by an energy diagram called a Jablonski diagram.

**Figure 3.1** Schematic energy diagram showing the difference between a linear and nonlinear optical material.

**Figure 3.2** Jablonski diagram of selected excitation and relaxation processes.
An electron can have two different spins; denoted \( \alpha \) and \( \beta \). When a molecule with an even number of electrons is in its electronic ground state, all of its electrons are normally paired with antiparallel (\( \alpha \beta \)) spins. Such a ground state is denoted a singlet state (\( S_0 \)). If the molecule is subjected to light, it can undergo a transition to an excited state. The excited states can either be singlets (\( S_{1,a} \)) or triplets (\( T_{1,a} \)), and in the latter type there are two more electrons of parallel spin than of antiparallel spin. Further, the two unpaired electrons occupy different molecular orbitals. An excitation can be roughly described as an event in which one of the electrons absorbs a photon and is ‘transferred’ to a higher energy level, and the energy difference between the two states matches the energy of the photon.

The direct transition between the ground state (\( S_0 \)) and the first triplet absorption level (\( T_1 \)) is a spin-forbidden pathway. Therefore, in order to change the spin states an unpaired electron must change spin, which often occurs through intersystem crossing from the first singlet excited state (\( S_1 \)). This process is a radiation-less transition between different spin states and is more likely to happen if there is a heavy atom in the molecule that provides a pathway between the spin states via so-called spin-orbit coupling, also known as the heavy atom effect.

Excitation of an electron from the ground state to a singlet excited state (\( S_{1,a} \)) by a single photon is called one-photon absorption, and is typically the basis of linear absorption. A molecule designed to offer eye protection in the visible spectrum (400-800 nm) should absorb linearly below 400 nm (and its maximum-absorption wavelength, \( \lambda_{\text{max}} \), should be below this wavelength) to allow high transmission in normal intensity light. Another possibility is that the electron may be excited by two or more photons simultaneously, that is, by two- or multi-photon absorption. If the molecule is excited from the ground state by high intensity light, two photons with different or identical frequencies can excite the electron to, for instance, the first singlet excited state (\( S_1 \)) via a virtual state. TPA is an instantaneous process and can be seen as the initial NLO effect in OPL. Even if the molecule does not absorb linearly in the visible region, two photons with wavelengths in this region can be absorbed since the sum of the energy of both photons can cause TPA.

If a photon is absorbed in such a way as to elevate the molecule to an excited state, the molecule can be excited by a new photon to higher states. This is called excited state absorption (ESA). The probability for ESA is, of course, higher when there are many molecules in the initially excited state and there is a high radiant flux. If more absorption occurs from the exited state than from the ground state, the process is called reverse saturable absorption (RSA). This NLO effect is very important for OPL since more photons will be absorbed and further transformed to heat.

Several mechanisms are involved in the relaxation from the excited state to the ground state. Internal conversion is the radiation-less transition between different electronic states of the same spin, usually given off as heat to the surroundings. Another radiation-less process is vibrational relaxation,
which is the return from a higher to the lowest vibration level of the excited state. In this process the molecule gives up energy to the surroundings via vibrations and rotations through collisions. The timescale for these radiationless relaxation processes is typically $10^{-13} - 10^{-11}$ s.

The two radiative relaxation processes are fluorescence and phosphorescence. Fluorescence occurs between states of the same spin (e.g. $S_1 \rightarrow S_0$) and phosphorescence occurs between different spin states (e.g. $T_1 \rightarrow S_0$). The decay timescale (measured) for these processes is typically between $10^{-12}$-$10^{-6}$ for fluorescence and $10^{-6}$-$10^{1}$ s for phosphorescence.

In OPL, it is important for the lifetimes of the excited states to be sufficiently long for efficient ESA to occur. Spectroscopic characterization of these radiative pathways can give important clues about the photo-physical mechanisms involved.

In summary, a good NLO molecule for OPL should have high transmittance in the visible region in low intensity light. Ideally, it should also have suitable TPA-accessible state(s) in the visible region to provide broadband protection and to activate the NLO response. In addition, the molecule should also have RSA properties, in order to decrease the energy by converting it to heat.

### 3.2. NLO Chromophores for OPL

A number of classes of molecules have been tested for OPL, including porphyrins, fullerences, phthalocyanines, metallo polyynes, platinum acetylides and dialkynyl thiophenes.

A comparison of these compounds reveals that many of them have conjugated systems constructed from aromatic or heteroatomic ring units and some of them also contain metals. These observations suggest that good features to incorporate in a designed OPL molecule may include a large conjugated system and a metal to increase the NLO effect. However, since increasing the conjugated system often results in decreased transmittance in the visible region it is essential to find a compound that has a good balance between the degree of conjugation of the $\pi$-system and its transmission at these wavelengths. One way in such a balance could be achieved may be to connect unsaturated rings in the conjugated systems with ethynyl instead of ethenyl bridges, and thus obtain somewhat ‘less conjugated’ $\pi$-systems.

Another way may be to select an appropriate metal. Platinum compounds generally cause less absorbance than Pd, Ni or Ru in the visible region, which makes Pt suitable for OPL compounds. In the work underlying this thesis, the focus was on the synthesis and NLO characterization of diarylalkynyl Pt
In introduction (II) compounds, so a more detailed discussion of this class of compounds is presented in Section 3.2.1.

### 3.2.1. Pt(II) acetylides

The compounds investigated in this thesis are square planar *trans*-diarylalkynes bis-tributylphosphine platinum(II) molecules. One example of such compounds is the platinum (II) acetylide (I) displayed in Figure 3.3. The OPL and NLO properties of this compound have been intensively studied by McKay and Staromlynska et al., and it is well-known to have broad-banded OPL ability. The compound shows strong singlet absorption at 355 nm, weak triplet absorption at 520 nm, and strong ESA from the $T_1$ state in the region of 400-700 nm. At wavelengths shorter than 500 nm, its major excitation mechanism is singlet absorption from $S_0 \rightarrow S_1$ followed by fast intersystem crossing to the $T_1$ state. In the region of 513-532 nm the excitation mechanisms involve the spin-forbidden $S_0 \rightarrow T_1$ transition. At wavelengths longer than 560 nm, the $S_0 \rightarrow S_1$ transition is dominated by TPA.

![Figure 3.3](image)

**Figure 3.3** Structure of di(4-(phenylethynyl)phenylethynyl)bis(tributylphosphine) platinum (II). Lower: Crystal structure from Cambridge Crystallographic Data Centre (structure no. br787). Hydrogens omitted for clarity.

The structure of the aryalkynyl Pt(II) compound is composed of two aryalkynyl ligands, containing aromatic units connected by ethynyl bridges, and two tributyl phosphine ligands coordinating the platinum atom in a square planar structure. The bond between the sp hybridized Carbon and the platinum atom is often described as a σ type overlap composed of the $C_{sp}$ hybrid orbital and a Pt hybrid constructed from the 6s, 5d$_{x^2−y^2}$ and 5d$_{z^2}$ atomic
Introduction

orbitals. To illustrate this, the orbital configuration of the platinum atom is shown in Figure 3.4.

![Orbital configuration of the platinum atom.](image)

If the arylalkynyl ligands have a *trans* configuration they can mutually interact through the metal, creating a long conjugated system. This is believed to occur through $\pi$-back bonding resulting from the overlap between the alkyne $\pi^*$ and Pt $d_{xy}$ orbitals, and the $\pi^*_z$ and Pt $d_{xz}$ orbitals (Figure 3.5). Because of this $\pi$-back bonding, the platinum atom contributes to the $\pi$-conjugated system which could enhance the compound's NLO properties. As mentioned earlier, the heavy Pt atom has the ability to provide the intersystem crossing ($S_0 \rightarrow T_1$) pathway that can result in strong ESA from the $T_1$ state, which in turn gives arylalkynyl Pt(II) compounds interesting OPL properties.

![Orbitals involved in $\pi$-backbonding in (a) the X-Y plane and (b) the Z-X plane](image)
3.3. Background of Synthesis

3.3.1. Sonogashira coupling

For an organic chemist, reactions that can form carbon-carbon bonds are very important. One such reaction is Sonogashira cross-coupling (Figure 3.6), in which terminal alkynes are coupled with aryl or vinyl halides using copper-palladium as catalysts. Before this reaction was discovered, the only published method for coupling alkynes and iodoarenes was the Stephens-Castro reaction,\textsuperscript{35, 36} involving reactions between the preformed Cu-acetylide and the iodoarene in pyridine at high temperature.

\[
\begin{align*}
R & \quad X-Ar \quad \text{Pd(II), CuI} \quad \text{Base} \quad \text{R} & \quad \rightarrow & \quad \text{Ar}
\end{align*}
\]

\textbf{Figure 3.6} Example of a Sonogashira carbon-carbon bond formation reaction

This reaction had several drawbacks related to the preparation and safe handling of the Cu-acetylide, and was performed under quite harsh conditions. The Sonogashira reaction was first published by Sonogashira et al. in October 1975,\textsuperscript{37} but a few months earlier Cassar\textsuperscript{38} and Heck\textsuperscript{39} had independently reported the same cross-coupling using similar catalysts in the absence of the Cu species. By using CuI as co-catalyst for the alkyne, instead of alkoxide (Cassar) or amine (Heck) bases, a larger range of substrates could be coupled under milder conditions. Nevertheless, the work of Cassar and Heck was significant because they prompted research into so-called “copper-free Sonogashira coupling”, which can be used for copper-sensitive substrates.

The exact mechanism of the reaction is not entirely known, especially with respect to the role of the copper catalyst. However the reaction certainly follows the normal oxidative addition and reductive elimination steps that are common to all palladium-catalyzed carbon-carbon cross-couplings.
Figure 3.7 Proposed catalytic cycle for the Sonogashira reaction

Figure 3.7 shows the commonly proposed catalytic cycle for the Sonogashira reaction. The reaction is believed to start from a Pd(0) species, generated from the Pd(II) precatalyst, which undergoes oxidative addition with the aryl halide. The next step is believed to occur through transmetallation of a Cu-acetylide complex which generates a trans-aryl-alkynyl Pd(II) complex. The trans isomer of the Pd complex will equilibrate to the cis isomer which collapses by reductive elimination. This results in the desired product and regenerates the Pd(0) catalyst.

3.3.2. Synthesis of Pt(II) Acetylides

The α-alkynyl complexes of transition metals can be prepared from a dehydrohalogenation reaction between the metal halide and an alkynyl compound using copper halide as catalyst. The copper catalyzed reaction was discovered by Sonogashira and Hagihara et al.\textsuperscript{40} and was previously prepared from the anionic acetylide\textsuperscript{34, 41} and the corresponding metal halide or direct dehydrohalogenation of the metal with electron-withdrawing acetylides using diethylamine.\textsuperscript{41} In the work underlying this thesis, the copper-catalyzed dehydrohalogenation reaction was utilized for preparing trans-diarylalkynyl bis(tri-\textit{n}-butylphosphine) platinum(II) compounds. These compounds are often prepared via initial synthesis of the \textit{cis}- or trans-\textit{PtCl}_2(\textit{PR}_3)_2 precursor,
Introduction

usually obtained by treating PtCl₂, K₂PtCl₄ or some other platinum chloride with ≥ 2 eq of the phosphorus ligand. A general trend for these isomers is that heat generally favors the trans isomer, and if free phosphine is added, a rapid isomerization will begin, catalyzed by the free phosphine ligand. The equilibrium position will be dependent on the ligands, solvent and temperature.

Figure 3.8 shows an overview of different synthetic approaches for the preparation of the alkynyl substituted Pt(II) compounds, starting from the cis- or trans- PtCl₂(PR₃)₂ precursor.

If the cis- or trans-PtCl₂(PR₃)₂ complex is treated with ≥ 2 eq of the alkyne in the presence of CuI and an amine, the corresponding cis- or trans-diarylalkynyl Pt(II) compound can be prepared. The cis isomer readily converts to the trans isomer in the presence of CuI, so low temperatures and controlled reaction times are essential for preparing the cis isomer in good yield. Asymmetrical trans diarylalkynyl Pt(II) compounds can be prepared in good yields from the trans mono-arylalkynyl Pt(II) compound and the alkyne using CuI as catalyst. A trans mono-arylalkynyl Pt(II) compound can be prepared in several ways. Adding 1 eq of alkyne to the trans-PtCl₂(PR₃)₂ complex using CuI gives a mixture of mono- and di-arylalkynyl Pt(II) complexes. The yield of the mono compound can be increased if the reaction is performed at low temperature with excess of the PtCl₂(PR₃)₂ precursor, but the reaction will still give the disubstituted compound. However, if the reaction mixture is refluxed in a solution of amines, the disubstituted compound converts to the mono complex via a reaction with trans-PtCl₂(PR₃)₂ and Cu(I). This reaction can also be performed to convert the disubstituted compound to the mono compound or used for depolymerization of metal-poly-yne polymers. The drawbacks of these reactions is their long reaction times, up to weeks, and they may not be suitable for unstable alkynes.
The mono species can be more selectively prepared by refluxing \textit{cis}-PtCl$_2$(PR$_3$)$_2$ and the alkyne with amine in the absence of CuI.\textsuperscript{48, 57} This procedure rarely gives the disubstituted compound and the reaction time is hours instead of weeks. According to Liu et al., the yield of this reaction can be as high as 88\%.\textsuperscript{57} A problem associated with this reaction is that the \textit{cis}-PtCl$_2$(PR$_3$)$_2$ complex has a tendency to isomerize under heat to the \textit{trans} isomer, which is quite unreactive without CuI as catalyst. Experiments have been performed to increase the yield of this reaction by adding extra phosphine to the reaction in order to regenerate the \textit{cis} isomer, but this only inhibited the reaction.
4. Aims of the present studies

The studies underlying this thesis were contributions to two much larger, consecutive research programs initiated by the Swedish Defence Material Administration (FMV). The aim of the first program, named “Photonics in Defense Applications”, was to identify compounds with good nonlinear optical (OPL) properties in solution. The main aim of the second program, named “Swedish Defense Nano Technology Program”, which will continue until September 2007, is to incorporate good NLO compounds into solid-state materials.

The goals of this doctoral project were to synthesize novel compounds with OPL properties in solution, to gain knowledge about how to design molecules with improved NLO properties, and subsequently synthesize OPL compounds that can be efficiently incorporated into solid-state glass materials.

More specific objectives were to:

- Synthesize and characterize optical properties of thiophenyl-containing trans-diarylalkynyl bis-tributylphosphine platinum(II) compounds, and compare their nonlinear effects with those of phenylenyl-containing Pt(II) compounds.

- Increase the length of thiophenyl-containing ligands of trans-diarylalkynyl bis-tributylphosphine platinum(II) compounds and further investigate the effects of the thiophene ring unit in the structure.

- Investigate the possibility of isolating a Pt(II) chromophore from oxygen quenching using dendritic shielding, and thereby increase the lifetime of the triplet state.

- Improve the synthesis of Pt(II) acetylides.

- Synthesize trans-diarylalkynyl bis-tributylphosphine platinum(II) compounds with a silica scaffold for preparing solution gels (SOL-GELS).
5. Synthesis and Optical Characterization of Thiophene Containing Pt(II) acetylides (Papers I-II)

5.1. Background

The aim of this study was to investigate the possibility to enhance the nonlinear optical properties with a thiophene unit present in the π-conjugated system for the Pt(II) acetylides, and by this increase OPL ability. Other studies have shown that the thiophene ring can be more effective than phenylene and common nitrogen- and/or oxygen-containing rings in increasing the third-order nonlinear properties in a π-systems, and large TPA cross-sections have been measured for sulfur-containing ring systems at for instance 602\(^5\) and 810\(^5\) nm. It has also been shown that oligothiophenes have fast triplet state formation populated via a TPA-excited singlet state.\(^6\)\(^6\)-\(^6\)\(^3\)

In the first project (Paper I), the synthesis of two Pt(II) compounds, with thiophenyl/thiophenylene and phenylene in the two-ring aryalkynyl ligand, is described (Figure 5.1). One has the thiophene close to the Pt atom (2a) and the other has the thiophene at the end of the ligands (2b). For comparison, the Pt(II) compounds 1 and 1b-c, with only phenyl/phenylene rings were also prepared (Figure 5.1).

![Figure 5.1](image)

**Figure 5.1** Structure of Pt(II) compound 2a-b, 1 and 1b-c with ligands composed of two arylethynyl units.
In the second project (Paper II), compounds with three arylethynyl groups were prepared in order to gain more knowledge about Pt(II) acetylides with thiophene rings in the ligands. The thiophylene/thiophenyl group was placed in three different positions in the alkyne (Figure 5.2). In an attempt to increase the solubility and the nonlinear optical properties from that of compound 3c, compound 3d with two methoxy groups on each phenylene ring was synthesized. For comparison, compound 3e with only phenyl/phenylene rings was also prepared (Figure 5.2).

![Figure 5.2 Structure of the Pt(II) compounds 3a-e with three arylethynyl units in the ligands.](image)

### 5.2. Synthesis

The syntheses of the trans-di-arylalkynyl Pt(II) compounds were accomplished by initial preparation of the PtCl₂(PBu₃)₂ precursor and the arylalkynes. Using the dehydrohalogenation reaction developed by Sonogashira and Hagiwara et al., which utilizes CuI as catalyst, the arylalkynyl ligand could be coupled to the platinum complex in good yields.

The synthesis of the arylalkynyl ligands were performed using a Sonogashira coupling/deprotection strategy, as outlined in Schemes 5.1-5.4. The Sonogashira reactions were performed with PdCl₂(PPh₃)₂ and CuI as catalysts in a solution of TEA and THF. The catalytic loadings were between 0.5-2.5 mol-% of the Pd(II) catalyst and 1-5 mol-% of CuI. The protecting group chosen for the alkynes was the 2-propanol-2-yl group. This protecting group can be removed in several ways; via a base-catalyzed elimination of acetone (retro Favorsky reaction), by treating the compound with NaOH, \(^{54-66}\) KOH, \(^{67}\) or other strong base such as NaH. These reactions were usually
performed in refluxing toluene. In order to speed up the reaction time, the formed acetone was typically distilled off.\textsuperscript{66} To remove this protecting group, harsher environment is required than for the removal of TMS or TIPS, but the product in each reaction step will either be more polar or aprotic than the starting material which simplifies the purification. Because of the low vapor pressure of compound 7, it was synthesized according to a description by Mal’kina et al.\textsuperscript{57} Compound 6 was mixed with paraffin oil and KOH, whereafter the solution of 7 and acetone could be distilled under reduced pressure, to remove the acetone and give compound 7 in good yield.

**Scheme 5.1** Synthesis of the two-arylethynyl-unit ligands with a thiophene ring.

\textbf{a}) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}, CuI, PPh\textsubscript{3}, TEA and THF; \textbf{b}) KOH, paraffin oil, distillation; \textbf{c}) KOH, toluene, reflux; \textbf{d}) NaH, toluene; Yield in brackets.

\[ 13 + 9 \rightarrow 17 (88\%) \]

\[ 16 + 9 \rightarrow 19 (70\%) \]

\[ 21 \rightarrow 22 (86\%) \]

\[ 25 \rightarrow 24 (60\%) \]

**Scheme 5.2** Synthesis of the three-arylethynyl-unit ligands with a thiophene ring.

\textbf{a}) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}, CuI, PPh\textsubscript{3}, TEA and THF; \textbf{b}) KOH, toluene, reflux; Yield in brackets.
Synthesis and Optical Characterization of Thiophene Containing Pt(II) acetylides

Scheme 5.3 Synthesis of the methoxysubstituted arylalkyne. a) I₂, NaOtl, AcOH, H₂SO₄, H₂O, reflux.; b) PdCl₂(PPh₃)₃, Cul, PPh₃, TEA and THF; c) KOH, toluene, reflux; Yield in brackets.

The trans-PtCl₂(PBu₃)₂ precursor was synthesized from PtCl₂ or K₂PtCl₆. The Pt(II) source was treated with 2 eq of PBu₃ in water, and 2 eq of Na₂SO₃ was added when K₂PtCl₆ was used. A mixture of trans and cis PtCl₂(PBu₃)₂ was obtained after heating the reaction at 80°C overnight. The isomers could be separated by re-crystallization from 50:1 heptane:EtOAc for the cis isomer and EtOH for the trans isomer, or by flash chromatography. To increase the yield of the trans isomer, the cis isomer was heated to melting for ca 20 min which afforded full isomerization to the trans isomer. The combined yield of the trans isomer was approximate 60%.
Using the reaction setup developed by Hagihara et al., with CuI in presence of PBu₃ as catalyst and diethylamine as solvent, compounds 2a and 2b were synthesized in 91 % (after 3 days at room temperature) and 17 % yield (after 3 h in room temperature), respectively. After changing solvent to TEA and THF (1:1 ratio) and heating the reaction at 60°C for 6 min in the presence of CuI, compounds 1a-b, 2a and 3a-e were obtained in good yield with much shorter reaction time (Scheme 5.5).

5.3. Structural and Optical Characterization

5.3.1. Structure of arylalkynyl Pt(II) compounds from X-ray diffraction and quantum chemistry methods

To investigate the structures of compounds 2a-b, the crystal structures were determined from single crystal X-ray diffraction data at 100 K. The single crystals of both compounds were obtained by re-crystallization from heptane. The X-ray analyses reveal that both compounds have crystal unit cells with two symmetry-independent molecules of similar geometry. For compound 2a the P-Pt bonds are aligned along the plane containing the two thiophene rings, but for 2b the P-Pt bonds lie approximate 50° out of the plane containing the inner phenylene rings. The crystal structure of compound 1, obtained by Bruce et al., shows that this structure is similar to that of 2b, having the Pt-P bonds aligned 62° out of the aromatic-ring plane. The X-ray structures of 1, 2a-b also show that the C-Pt-P bond angles deviate 3-4° from
right angle, which appears to be common in crystal structures of Pt(II) acetylides.\textsuperscript{69}

To fully characterize the geometries for compounds 1, 2a and 2b, computer calculations were performed at the density functional theory (DFT) level. The geometry optimizations were performed with the B3LYP functional and the LANL2DZ basis set. To shorten the computational time the PBU\textsubscript{3} ligands were replaced with PME\textsubscript{3} groups. The compounds are thus denoted 1', 2a' and 2b'. The optimization of 2a' was performed starting from three different geometries. One optimization started from the x-ray structure. The energy minimum, confirmed by frequency calculations, was found to have similar conformation as the X-ray structure. The second optimization started from a geometry with the Pt-P bonds approximately perpendicular to the thiophene plane, and with the thiophene rings oriented to have the two S atoms in opposite direction, i.e. an anti conformation. The calculation resulted in a dihedral angle of approximate 77° between the Pt-P bonds and the plane of the thiophenylene. However, this conformation was a saddle point, with an energy of only 0.2 kcal/mol higher than that of the true energy minimum. To form the third starting structure, one thiophenylene in the geometry optimum found by the first calculation was turned 180° to give a syn conformation of the ligands. A new transition state was found with the energy of 0.05 kcal/mol higher than that of the true energy minimum. The optimization of 1' and 2b' were performed starting from two different geometries, the x-ray structure and the conformation having the Pt-P bonds in the plane of the aromatic rings. Both calculations resulted in the same conformation with Pt-P bonds perpendicular to the plane of the aromatic rings. These results show that the B3BLYP/ LANL2DZ model seems to perform well in describing the ground state for compounds 1, 2a-b, and that one should pay attention to the orientation of Pt-P bonds relative the plane of the aromatic rings and the possibility of several coexisting conformations.

The calculations also showed that the two conformations with Pt-P bonds parallel with or perpendicular to the plane of the aromatic rings, have similar electron distributions in the highest occupied molecular orbital (HOMO), but different distribution of the lowest unoccupied orbital. For 2a', LUMO has a significant orbital coefficient at the Pt nucleus, but for 1' and 2b' the corresponding coefficients were zero. DFT calculations of electronic excitations showed that the longest wavelength absorption of the different compounds is predominantly described by a HOMO→LUMO transition, which was suggested to be a reason for the shorter decay times of fluorescence and phosphorescence of 2a compared to 1 and 2b, see further discussion below.
5.3.2. Optical Characterization

The UV-Vis spectra of compounds 1, 2a and 2b are displayed in Figure 5.3. Each spectrum shows two distinct peaks, one smaller and one larger. The latter appears at 353 nm, 378 nm, and 362 nm for 1, 2a and 2b, respectively. When the thiophene is incorporated into the structure, the absorption band is red shifted, and the shift is slightly larger when the thiophenyl unit is close to the Pt atom.

![UV-Vis spectra of compounds 1, 2a and 2b.](image)

*Figure 5.3 UV-Vis spectra of compounds 1, 2a and 2b. (Not same concentration in the samples).*

The same trend can be seen for compounds 3a-c and 3e, displayed in Figure 5.4. It is also noticed that the band is shifted further to the red when the length of the ligand is increased from two to three arylethynyl units.
The OPL measurements of compounds 2a and 2b were performed at three different wavelengths: 532 nm, 550 nm and 610 nm. For comparison compound 51a (Chapter 6) was included in study. Values of the transmitted laser energy ($E_{\text{out}}$) at an input energy ($E_{\text{in}}$) of 150 µJ are displayed in Table 5.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{out}}$ (µJ) at $E_{\text{in}}$=150 µJ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>532 nm</td>
</tr>
<tr>
<td>2a</td>
<td>5.0</td>
</tr>
<tr>
<td>2b</td>
<td>7.6</td>
</tr>
<tr>
<td>51a</td>
<td>5.2</td>
</tr>
</tbody>
</table>

The clamping levels for compounds 3a-e and 2 are displayed in Table 5.2. For comparison, these measurements were performed for samples in THF with the same concentration as above. The measurements were conducted at three different occasions (A, B and C) with new samples each time. Since the optical bench setup was not perfectly identical at the different times, the data are not fully consistent. However, similar trends can be seen for the three occasions.
Table 5.2 Optical power limiting data of 2a-b and 3a-e in THF.

<table>
<thead>
<tr>
<th>Compound</th>
<th>532 nm (µJ)</th>
<th>600 nm (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>3a</td>
<td>4.7</td>
<td>3.3</td>
</tr>
<tr>
<td>3b</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>6.5</td>
<td>3.4</td>
</tr>
<tr>
<td>3d</td>
<td>4.1</td>
<td>2.5</td>
</tr>
<tr>
<td>3e</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The OPL data indicate that the thiophenylethylnyl unit does not increase the OPL ability at 532 or 600 nm compared to the phenylethylnyl unit. Lower clamping levels are obtained when the ligand lengths are increased, from two to three arylethylnyl units.

The emission spectra of compounds 3a-e are displayed in Figure 5.5. In resemblance to the absorption spectra, the emission peaks are more red-shifted when the thiophene ring is closer to the platinum atom.

![Emission spectra of 3a-e in THF. The two inserts show magnified phosphorescence bands for 3b and 3e.](image-url)
The compounds show very weak phosphorescence in air saturated samples. The largest peaks are observed for compounds 3e and 3b at 555 nm and 630 nm, respectively.

To increase the phosphorescence, the samples were purged with argon to remove the oxygen in the samples. In the emission spectra of the air-saturated samples, compounds 3e and 3b had the largest peaks. For the argon-purged samples, the peak for 3b was only slightly increased while the other samples showed significantly increased phosphorescence peaks (Figure 5.6).

![Emission spectra of argon-purged 10 µM THF samples of 3a-e.](https://example.com/emission_spectra)

**Figure 5.6.** Emission spectra of argon-purged 10 µM THF samples of 3a-e.

However, the $\tau_{\text{phos}}$ values are the same for these two compounds (Table 5.3). Therefore, the $T_1$ state appears to be more efficiently populated for compound 3e than for compound 3b. This means that 3b has more efficient pathways for non-radiative relaxation previous to reaching the $T_1$ state.

The fluorescence quantum yields ($Q_{\text{fl}}$) for compounds 2a-b, 3a-e and 1 are summarized in Table 5.3. Although the quantum yields are low for all compounds, the values are higher for compounds containing three arylethynyl units than compounds containing two. This should relate to a faster intersystem crossing for compounds 2a-b and 1 compared to 3a-e.
### Table 5.3 Fluorescence and phosphorescence emission data for compounds 1, 2a-b, 3a-e

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{fl}$ (nm)</th>
<th>$Q_{fl}$</th>
<th>$\tau_{fl}$ (ps)</th>
<th>$\lambda_{phos}$ (nm)</th>
<th>$\tau_{phos}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>410$^b$</td>
<td>0.002</td>
<td>330$^b$</td>
<td>520$^b$</td>
<td>500$^b$</td>
</tr>
<tr>
<td>2a</td>
<td>420</td>
<td>0.0045</td>
<td>$&lt; 2$ (94 %), $~450$ (6 %)</td>
<td>610</td>
<td>190</td>
</tr>
<tr>
<td>2b</td>
<td>392</td>
<td>0.0007</td>
<td>3 (100 %)</td>
<td>550</td>
<td>330</td>
</tr>
<tr>
<td>3a</td>
<td>440</td>
<td>0.026</td>
<td>9 (99 %), 200 (1%)</td>
<td>630</td>
<td>-</td>
</tr>
<tr>
<td>3b</td>
<td>424</td>
<td>0.034</td>
<td>30 (90 %), 400 (10 %)</td>
<td>630</td>
<td>- 50000</td>
</tr>
<tr>
<td>3c</td>
<td>412</td>
<td>0.020</td>
<td>90 (40 %), 300 (60 %)</td>
<td>566, 604</td>
<td>-</td>
</tr>
<tr>
<td>3d</td>
<td>446</td>
<td>0.054</td>
<td>15 (94 %), 700 (6 %)</td>
<td>625</td>
<td>-</td>
</tr>
<tr>
<td>3e</td>
<td>406$^c$</td>
<td>0.012$^c$</td>
<td>13 (95 %), 200 (5 %)</td>
<td>555, 592, 525, 250</td>
<td>50000$^d$</td>
</tr>
</tbody>
</table>

$^a$ Conc. 10 µM (THF). Excitation at 380 nm for 2a-b; 390 nm for 3a-e. $^b$In ref. 24: CH$_2$Cl$_2$ solution, at 300K. $^c$In ref. 70: $\lambda_{fl} = 396$ nm (3.13 eV), $Q_{fl} = 0.0168$. $^d$In ref. 71; $\lambda_{phos} = 555$ nm in benzene solution; $\tau_{phos} = 86$ µs for a sample degassed by three freeze-pump-thaw cycles.

### 5.4. Conclusion

Incorporating a thiophenylethynyl instead of a phenylethynyl unit into the π-conjugated system for the Pt(II) acetylides does not increase the OPL property at 532 or 600 nm. However, compounds containing three arylethynyl units show lower clamping levels than those containing two.

Both the X-ray structure and DFT calculation show that the platinum(II) acetylides can have different ground state conformations with respect to the orientations of the Pt-P bonds and the plane of the aromatic rings. These conformations can play an important role for the photophysical mechanisms and should be investigated further.

6.1. Background

A dendrimer is a highly branched structure, built up from layers of repeating units around the central core. Each layer of repeating units is called generation, see Figure 6.1. The dendrimers can be constructed from two different approaches, the divergent\textsuperscript{72, 73} or the convergent\textsuperscript{74}. In the divergent approach the synthesis starts from the core and the generation increases by connecting the monomers to the end groups. In the convergent approach the synthesis starts from the end groups and grows toward the core by connecting the focal point to the monomer and finally to the core.

Since the possibility to vary the molecular structure and the number of generations, different molecular properties can easily be fine tuned. Such properties can be size, solubility\textsuperscript{75, 76} and physico-chemical properties\textsuperscript{77}. Another possibility is to create a microenvironment inside.\textsuperscript{78} That means that
the dendrimer structure shields the covalently bonded core or a coordinated molecule from the surrounding by so called site isolation.

If the lifetime of the excited state is long, the probability for ESA to occur is higher. When a molecule exists in the excited state, oxygen or other molecules can accelerate the relaxation to the ground state. If the quenching of the excited state can be decreased the excited state absorption during a certain time should increase which should relate to an increase in the OPL effect. In order to decrease the oxygen or molecular quenching, the molecule can be isolated by dendrimeric shielding.79

In this project, the idea was to decorate the Pt(II) acetylide 1 with dendrimeric substituents in hope of shielding the core (π-system) by site isolation (Figure 6.2). The polyester dendrimer based on 2,2-bis-(hydroxymethyl)propionic acid (bis-MPA) was chosen because it has good stability and high transparency in the entire visible region and should not itself effect the NLO measurement.80

![Figure 6.2 A dendron decorated platinum(II) molecule](image)

### 6.2. Synthesis

The synthesis was performed in a similar manner as for the Pt compounds with thiophene rings. First, the hydroxymethyl-substituted alkyne 44 was synthesized, using Sonogashira couplings and alkaline (KOH) cleavage of the protecting groups (Scheme 6.1). The dendrimer was grown on the alkyne using stepwise synthesis in a divergent approach. Hence, the first-generation dendrimer 46 was synthesized by reaction between the alcohol 44, the anhydride 45 and DMAP in a solution of pyridine and dichloromethane.81, 82
In order to obtain the second-generation dendrimer 48, the alkyne 46 was first deprotected using DOWEX resin (proton source) in MeOH solution and then coupled again with the anhydride 45 (Scheme 6.2). By repeating the same procedure, the higher generation dendrimers (third generation, 49, and fourth generation, 50) were obtained.

**Scheme 6.1** Synthesis of hydroxymethyl-substituted arylalkynes. a) PdCl$_2$(PPh$_3$)$_2$, CuI, PPh$_3$, pyridine, TEA, 120 °C; b) KOH, THF, Dean-Stark, 80 °C; Yield in brackets.

**Scheme 6.2** Synthesis of dendron decorated alkynes. a) DMAP, pyridine, DCM, rt; b) DOWEX resin, MeOH, THF, 50 °C; Yield in brackets.

Using the improved platinum coupling reaction described in Section 5.2, the dendron decorated Pt(II) acetylides, up to 4th generation, could be obtained in excellent yields (Scheme 6.3).
Synthesis and Optical Characterization of Dendron Decorated Pt(II) Acetylides

![Image](image_url)

Scheme 6.3 Synthesis of dendron decorated Pt(II) acetylides. a) CuI, TEA, THF, 60 °C.

6.3. Optical Characterization

The UV-Vis spectra of compounds 51a-d are displayed in Figure 6.3. The spectra are very similar and have two main peaks; one larger at 357 nm and one smaller peak at 304 nm for all compounds. The extinction coefficients ($\varepsilon$) at 357 nm were all in the same order of magnitude ($1.02 \times 10^5$ M$^{-1}$cm$^{-1}$). This shows that the compounds have an almost identical linear absorption and that the size of the dendrimer does not effect the transmission in the visible region.

![Figure 6.3](image_url)

Figure 6.3 UV-Vis spectrum of dendron decorated Pt(II) acetylides 51a-d. (Not same concentration in the samples).
The OPL measurements were done at three different wavelengths: 532, 580, and 630 nm. As a comparison, the non-decorated Pt(II) acetylide 1 was included in this study. All measurements were performed on 30 mM solutions in THF and measured with the same optical bench setup. The overall transmission at these wavelengths was >92% for all samples.

The results from the OPL measurements are listed in Table 6.1. The table shows a general trend; that a higher-generation dendrimer has a lower clamping level compared to a lower-generation compound, at all three wavelengths. This might be due to the fact that the higher generations are more efficient at shielding the chromophoric system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Clamping at 532 nm (µJ)</th>
<th>Clamping at 580 nm (µJ)</th>
<th>Clamping at 630 nm (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0</td>
<td>9.5</td>
<td>18.4</td>
</tr>
<tr>
<td>51a</td>
<td>7.6</td>
<td>7.5</td>
<td>12.7</td>
</tr>
<tr>
<td>51b</td>
<td>7.1</td>
<td>7.2</td>
<td>11.9</td>
</tr>
<tr>
<td>51c</td>
<td>6.3</td>
<td>6.3</td>
<td>10.2</td>
</tr>
<tr>
<td>51d</td>
<td>6.6</td>
<td>6.2</td>
<td>9.9</td>
</tr>
</tbody>
</table>

To understand more about the reasons for the increased clamping levels for higher generations, Z-scan measurements were performed with 50 mM THF solutions of compounds 51b and 1. In this type of measurement, the sample is moved along the laser-beam propagation direction and displays a variation in transmission as it moves through the focus of the beam.83, 84 The experiment provides the TPA cross section at the specific wavelength of the Z-scan. The measurements were performed at two different pulse repetition frequencies (100 kHz and 76 MHz) at 725 nm. At frequencies below 100 kHz the time between the laser pulses are long in comparison with the lifetime of excited states, and the response originates mostly from TPA with minor or negligible contribution from ESA. For narrower laser pulses (76 MHz) the response has some contribution from ESA (triplet absorption). When the Z-scan was performed at 100 kHz, a slight difference in the NLO absorption could be seen between the two compounds (Figure 6.4). When the measurement was performed at 76 MHz a large difference in the NLO absorption occurred (Figure 6.5). This shows that the ESA is much larger for the dendron decorated compound 51b compared to the uncoated compound 1 which could explain the slightly increased NLO absorption for 51b in the first Z-scan measurement. The TPA cross section was determined from the Z-scan analyses to approximate 10 GM (Göppert-Mayer; 1GM = 10^{-50} cm^4/(photon molecule)) at low pulse repetition rate for all the compounds.
To further confirm the increased ESA for the dendron decorated Pt(II) acetylides 1 and 51a-d, emission measurements of 10 µM samples in THF were performed. These studies showed that the emission spectra have similar shapes (Figure 6.6), and that the undecorated 1 is slightly blue shifted (4 nm) compared to the others. Compounds 51b and 1 show somewhat higher emission intensity, which is believed to originate from concentration errors due to variations in the preparation of the samples. The two strong bands at 395 and 422 nm are fluorescence from the S1 state and the two weak bands at approximately 525 and 555 nm are related to phosphorescence emission (T1-S0).24

Figure 6.4 Z-scan at 100 kHz. Ti:Sapphire Mira 180-200 fs pulses at 725 nm, 8 nJ/pulse, 50 mM samples. Black square 51b, gray triangle 1.

Figure 6.5 Z-scan at 76 MHz. Ti:Sapphire Mira 180-200 fs pulses at 725 nm, 1.9 nJ/pulse, 50 mM samples. Black square 51b, gray triangle 1.

Figure 6.6 Luminescence spectra of ca. 10 µM samples in THF, using excitation at 375 nm.
The decay time of the $T_1$-$S_0$ emission at approximately 525 nm were measured for 1, 51a-d after excitation at 360 nm with the femtosecond (fs) laser at a frequency of 50 kHz. With low concentration samples (2 µM), no significant difference between the compounds was found. The time spans were between 0.22 µs for 1 and 0.29 µs for 51d. When the concentration was increased to 100 µM, a remarkable difference was noticed compared to the low concentration samples. The decay time of the phosphorescence emission increased several orders of magnitude for compounds 51b (0.092 ms), 51c (0.137 ms) and 51d (0.196 ms). A subsequent study on these compounds was performed by Lindgren et al., which showed that the primary effect of the dendrimers, at least for the higher sample concentrations, was to prevent dissolved oxygen to quench the triplet state.

6.4. Conclusion

The dendron decorated Pt(II) acetylides up to 4th generation were successfully prepared in good yields. It was shown that the OPL properties increase with increased generation of the dendrimer, without affecting the transmission in visible region. In addition, it was shown that the dendron decorated compounds have lower clamping levels compared to the uncoated compound 1. According to the Z-scan measurements, the ESA is significantly improved with the dendritic substituents. This is likely to be caused by a protection of the chromophore from bi-molecular and oxygen quenching due to site isolation by the dendritic scaffolds. However, since the decay time of the phosphorescence only increases for high-concentration samples, it is believed that the origin of the increased ESA relates to molecular assemblies which shield the core by site isolation.
7. One-Pot Synthesis of trans Mono- or Diarylalkynyl Substituted Pt(II) Compounds (Paper IV)

7.1. Background

The main idea behind this study was that the isolation of the PtCl₂(PR₃)₂ precursor may not be needed prior to the synthesis of the Pt(II) acetylides. If the platinum intermediate could instead be formed in situ, the synthetic work should be more efficient because of fewer reaction steps and reduced time-consuming product isolation.

7.2. Results and discussion

The reaction setup for the one-pot synthesis of the diarylalkynyl Pt(II) complex in this study was adopted from the usual preparation of the organo-Pt compound except that the PtCl₂(PR₃)₂ precursor was replaced with PtCl₂ and PR₃. After mixing the PtCl₂ oligomer and the alkyne with THF/TEA 1:1 in microwave vial, 2 eq of the phosphine or phosphite was added. When a clear solution appeared, CuI was added and the reaction was run at 60 °C for 6 min using microwave irradiation. After purification of the resulting mixture the diarylalkynyl compound was collected in ca 60 % yield or higher (Scheme 7.1).

\[
\begin{align*}
\text{R-} & \text{–C≡C–PtCl}_2 \quad \xrightarrow{a)} \quad \text{R-} & \text{–C≡C–Pt(PR}_3\text{)}_2 \quad \text{–R} \\
52\text{a} & \quad \text{R=}\text{MeO} \quad \text{R=}\text{PBu}_3 \quad 60\% \\
52\text{b} & \quad \text{R=}\text{NO}_2 \quad \text{R=}\text{PPh}_3 \quad 59\% \\
52\text{c} & \quad \text{R=}\text{NO}_2 \quad \text{R=}\text{PBu}_3 \quad 60\% \\
52\text{d} & \quad \text{R=}\text{CC-Ph} \quad \text{R=}\text{P(OBu)}_3 \quad 63\% \\
1 & \quad \text{R=}\text{CC-Ph} \quad \text{R=}\text{PBu}_3 \quad 76\%
\end{align*}
\]

Scheme 7.1 One pot synthesis of diarylalkynyl substituted Pt(II) compounds 1, 52a-d.

a) 2 eq PR₃, 2 eq CuI; yield in %.

CHCl₃ was used instead of THF as solvent because of the low solubility of the PPh₃ ligand.
Since the disubstituted Pt(II) acetylides could be prepared in a one-pot reaction, it was believed that the mono-arylalkynyl Pt(II) compounds could be obtained in a similar way. As described in Section 3.3.2, the mono-substituted Pt(II) acetylides can be prepared selectively from a reaction between the cis-PtCl₂(PR₃)₂ complex and the alkyne, in presence of base but without CuI. The first attempt of the reaction was performed in similar conditions as described by D’Amato et al., except for that PCl₂ and 2 eq PBu₃ were used instead of cis-PtCl₂(PBu₃)₂ and the reaction was heated with microwave irradiation. When the reaction was carried out at 130 °C for 15 min in CHCl₃:TEA 48:1, compound 53a was isolated in 25 % yield. Changing the solvent to TEA:THF 1:1 gave the same result. The major product in these reactions was the trans-PtCl₂(PBu₃)₂ complex, which does not undergo the desired reaction. In order to increase the yield, the temperature was raised to 160 °C and the reaction was allowed to proceed for 1 h in two solvent mixtures (CHCl₃:TEA 48:1 and TEA:THF 1:1). When the reaction was performed in the chloroform solution, 53a was isolated in 42 % yield. The alkyne was fully consumed as determined from the 'H-NMR spectrum of the crude product. However, when the solvent mixture TEA:THF was used, the yield was similar but only half of the amount of alkyne had reacted. From these reactions, it seemed that CHCl₃ is a less good solvent. Although our previous experiments had shown that the addition of PBu₃ to the reaction slows down or inhibits the reaction, it was anticipated that cis-PtCl₂(PBu₃)₂ could be recovered from the trans isomer by increasing the amount of the PBu₃ at higher reaction temperature (160 °C).

When the reaction was run with 4 eq of PBu₃ using THF:TEA as solvents at 160 °C for 1 h, almost all of the trans-PtCl₂(PBu₃)₂ was consumed. After purification, compound 53a was obtained in 73 % yield. In accord with this latter reaction procedure, compounds 53b-c were synthesized in good yields after purification (Scheme 7.2).

![Scheme 7.2](image)

**Scheme 7.2** One-pot synthesis of the mono-arylalkynyl compounds 53a-c. a) 4eq PR₃, TEA, THF, 160 °C for 1h using microwave irradiation.
7.3. Conclusion

The mono- or diarylalkynyl Pt(II) compounds can be prepared in a one-pot reaction in good yields, compared to the usual synthesis calculated over two steps. The preparation of the mono-arylalkynyl Pt complex demands rather high temperature for completion, and if unstable or sensitive ligands are used in the synthesis this route may not be suitable. However, these reactions are good complements to the regular synthetic procedures since the reaction times are short and the yields are fairly good.
8. Solid Material (Paper V)

8.1. Background

The purpose of this study was to prepare inorganic (silica) glass containing the platinum(II) acetylide. For practical applications, it is preferable to have solid materials compared to solution-based optical limiters. The main disadvantage using solid materials is if damage occurs in the glass it will be irreversible, but for a solution based filter the damage can self-heal. Therefore the material needs to have high damage threshold. Organic-inorganic silica hybrid materials are expected to be good choices for OPL, since such materials can have excellent optical properties, good thermal mechanical properties and high damage threshold.86, 87 These organic-inorganic hybrid materials can be prepared using the solution gel route (Figure 8.1).

\[
\text{Si(OMe)}_4 \\
\text{Acidic hydrolysis} \\
\text{SOL} \\
\text{Chromophore} \\
\text{Chromophore-ICTES} \\
\text{Class I Gel} \\
\text{Class II Gel} \\
\text{Drying} \\
\text{Class I Glass} \\
\text{Class II Glass}
\]

Figure 8.1 Steps in the preparation of class-I and -II glasses.

The optically active chromophore can either be dissolved in the silica matrix (class I glass) or covalently attached to the glass network (class II). To
obtain a glass with high concentration of the chromophore, the interaction between the inorganic and the organic matrix should be strong. Hence, the class II material is preferred.

In this study, the goal was to prepare class II materials of compound 1, 3c, 3d and a modified version of compound 1 having two methoxy groups on the phenylene ring close to Pt, see Figure 8.2. In order to covalently attach the chromophores to the silica matrix, the compounds were synthesized with Si(OEt)$_3$ groups in the alkyne ligands (Figure 8.3).

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**8.2. Synthesis**

The attachment of a trialkoxysilyl group can be achieved by functionalizing the chromophore with an amine or hydroxyl group, which can react with 3-isocyanatopropyl triethoxysilane (ICTES) through carbamate formation. In order to prepare the Pt(II) ICTES-acetylides, the desired arylalkyne ligands were synthesized with hydroxymethyl (-CH$_2$-OH) functionality at the end of
the ligands. The synthesis of ligand 44 was performed similar to the previously described procedure (Section 6.2). Another approach was tried for the methoxy-substituted ligand 56. Because of the hydroxyl substituent, the synthesis of such a ligand can be performed in one pot reaction (Scheme 8.1). The byproducts will either be significantly more polar or aprotic compared to the target molecule, which makes the purification by flash chromatography simple.

**Scheme 8.1** Synthesis of alkyne 56. Yield in brackets

The hydroxyl substituted Pt(II) acetylides 57 and 58 were obtained using the coupling reaction described in Section 5.2 (Scheme 8.2). In the subsequent step, 57 or 58 was allowed to react with ICTES in THF, using TEA as catalyst. The mixture was refluxed at approximately 104 °C in a Smith Process Vial (2.0-5.0 ml filling volume), sealed with a Teflon septum and an aluminum crimp top. The reaction was monitored by H-NMR, and compounds 1-ICTES or 54-ICTES were obtained after 1-2 days. The compounds were too unstable for purification using flash chromatography over silica or alumina. When silica was used for purification, the compounds seemed to covalently attach to the silica gel. Instead, the compounds could be purified by triturating with hexane.

**Scheme 8.2** Synthesis of compounds 1-ICTES and 54-ICTES. a) PtCl₂(PBu₃)₂, Cul; Yield in brackets.
In order to synthesize thiophene-containing alkynes with hydroxymethyl groups, the hydroxyl group was protected using tert-butyl-chloro-diphenyl-silane. Without the TBDPS protecting group, the reaction yields for the deprotection of the acetylides were low because of the presence of two hydroxyl groups in basic media. The synthesis of compound 3c-ICTES and 3d-ICTES are outlined in Scheme 8.3.

Scheme 8.3 Synthesis of compounds 3c-ICTES and 3d-ICTES. a) NaBH₄, MeOH; b) TBDPSCI, imidazole and DMF; c) PdCl₂(PPh₃)₂, CuI, PPh₃, TEA and THF; d) KOH and toluene; e) PtCl₂(PPh₃)₂, CuI, TEA and THF; f) TBAF; g) ICTES, TEA and THF; Yield in brackets.
8.3. Sol gel preparation

In order to prepare the class II materials, two different procedures were developed by our co-workers, see Figure 8.4. Both procedures start with the hydrolysis of the silicon precursor (MTEOS or TEOS), where compound is dissolved in ethanol, and treated with HCl (aq) (pH =2.5). In one method, the Si(OR)$_3$ groups of the chromophore are co-hydrolysed in the sol. In this case, the aging process (full hydrolysis and condensation) takes 2-3 weeks prior to the drying of the gel. In the other method, the chromophore and the alkoxy silane are hydrolyzed separately in THF and alcohol, and then mixed together. The aging process takes approximately 5 days prior to complete drying in the mold. After the class II material is obtained, the glass can be cut to an appropriate size and polished.

![Diagram of sol-gel procedures](image)

Figure 8.4 Two sol-gel procedures.

Utilizing the sol-gel routes described above, solid materials of compound 1-ICTES was successfully prepared. A glass containing the methoxy-
substituted compound 54-ICTES was also prepared. Unfortunately this latter glass could not be polished due to its softness. However, new attempts to prepare the material are under progress. The glass preparations of the thiophene-containing compounds were not fully successful either. Compound 3c-ICTES gave precipitation during the sol-gel process, and the solid material containing the 3d-ICTES chromophore became markedly colored during its preparation. According to these results, the sol-gel routes described above may not be the best protocol for preparation of the thiophene-containing glasses.

### 8.4. Optical characterization

The solid materials of 1-ICTES, with three different concentrations (120, 90, and 40 mM) of the chromophore, were cut and polished to an approximate thickness of 2.2, 1.4 and 0.8 mm respectively. Figure 8.5 shows the linear transmission spectrum of the glass containing 90 mM of the chromophore. From this spectrum, it is apparent that the material has some absorption in the whole visible region, but the absorption is most intense between 400 and 600 nm.

![Figure 8.5](image-url)  
**Figure 8.5** Transmission spectrum of a 90 mM (black line) hybrid material of compound 1-ICTES. Linear transmission of a pure silica matrix (white line).
The OPL measurements were done at four different wavelengths; 480, 532, 580 and 630 nm. The clamping levels are displayed in Table 8.1. As expected, the lowest transmittance was found for the highest concentration, 120 mM (Figure 8.6).

**Table 8.1** Clamping levels for the glass material of 1-ICTES.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>480 nm (µJ)</th>
<th>532 nm (µJ)</th>
<th>580 nm (µJ)</th>
<th>630 nm (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 mM</td>
<td>0.2</td>
<td>3</td>
<td>4.5</td>
<td>7</td>
</tr>
<tr>
<td>90 mM</td>
<td>1</td>
<td>3.5</td>
<td>4.5</td>
<td>8</td>
</tr>
<tr>
<td>40 mM</td>
<td>5.5</td>
<td>3</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>

**Figure 8.6** OPL of silica glass from 1-ICTES (120 mM)

### 8.5. Conclusion

Utilizing the sol-gel process, grafted hybrid materials containing the Pt(II) acetylides 1-, 3d-, and 54-ICTES have been prepared. After cutting and polishing, the silica glasses with the chromophore 1-ICTES, have been obtained with good optical quality. The measurements have shown that linear
and nonlinear transmittance properties of the dye are maintained in the matrix and that low clamping values can be obtained.
9. Concluding Remarks

This thesis describes the synthesis and nonlinear optical characterization of platinum(II) acetylides for an optical power limiting application. The main conclusions of the thesis are summarized below.

- The OPL property increases from a shorter to a longer compound, that is, when the size of the arylalkynyl ligands is increased from two to three units. The OPL property does not increase at 532 or 600 nm when a thiophene ring instead of a phenylene ring is present in the π-conjugated system of the ligand.

- Dendrimers of the acetonide protected bis-MPA were covalently attached to the chromophore. The dendritic substituents largely influence the photophysical properties of the platinum(II) acetylides by increasing the lifetime of the triplet state without affecting the linear transmission. The effect of the dendritic substituents increases with increased size/generation of dendrimer and also with increased concentration of the compound in the sample. This leads to the conclusion that the dendrimeric shielding is an effect of molecular aggregates.

- A new synthetic route has been developed for synthesis of mono- or di-arylalkynyl substituted Pt(II) compounds. This synthetic route is performed in a one-pot fashion.

- Solid materials containing Pt(II) acetylides covalently attached to a silica matrix have been prepared. For this, the chromophores were synthesized with Si(OEt)_3 groups at the end of the arylalkynyl ligands. The materials show high damage threshold and good OPL properties.
10. Populärvetenskaplig Sammanfattning

Interaktionen mellan ljus och en molekyl kan resultera i att egenskaperna för både ljuset och molekylen ändras. En av många kända effekter är optisk begränsning, dvs att intensiteten hos ljuset (ljusflödet) dämpas proportionellt mer vid höga än vid låga ljusintensiteter.


En grupp av icke-linjärt optiska föreningar som är intressanta för optisk begränsning är platina(II) acetylde. Vi har i detta arbete syntetiserat och studerat föreningar från denna grupp för icke-linjär optik med tillämpning som Laserskydd. Första delen av projektet har varit att hitta bra kandidater för optisk begränsning i lösning. Sedan har projektet utvecklats till att tillverka fasta glasmaterial med den aktiva substansen inbunden i materialet.
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