



## Review

The triplet state in Pt-acetylide oligomers, polymers and copolymers<sup>☆</sup>Eric E. Silverman, Thomas Cardolaccia, Xiaoming Zhao, Kye-Young Kim,  
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## Abstract

Platinum acetylide oligomers and polymers are  $\pi$ -conjugated materials that display luminescence from the triplet exciton. This property makes platinum acetylides useful for exploring the properties of the triplet state in  $\pi$ -conjugated systems. In the present review we describe the excited state properties of a series of Pt-acetylide oligomers and polymers with an emphasis placed on understanding structure–property relationships for the triplet state in  $\pi$ -conjugated systems.

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## 1. Introduction

Conjugated materials have been the focus of considerable research during the past several decades [1]. This field has been stimulated by the large number of potential applications for conjugated materials in electronic and electro-optical devices [2]. Although most of the work in this field has focused on conjugated materials that are comprised of organic build-

ing blocks, there has been increasing interest in the properties of organometallic conjugated materials [3]. This interest derives from the fact that incorporation of heavy metals into an organic conjugated framework can elicit large effects on the electronic and optical properties of the materials. In many cases the effects are predictable and tunable, allowing one to use structure to control the properties of a desired material [4–7].

Organometallic materials are of particular interest in applications that require light emission, for example as the active materials in light emitting diodes (LEDs) [4,8–11] and optical oxygen sensors [12,13]. The propensity of heavy transition metals such as Ir and Pt to mix singlet and triplet excited states via spin-orbit coupling leads to molecule-based

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materials, which feature high phosphorescence yields and relatively long emission lifetimes. These properties are particularly useful in LEDs and oxygen sensing. In particular, in LEDs, the ability to harvest light emission from both singlet and triplet excitons leads to devices that operate with high quantum efficiency [8,9].

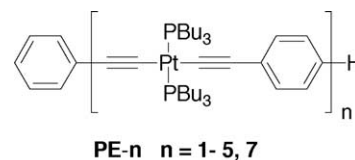
Another application which has received interest is non-linear absorption and reverse saturable absorption [14]. In particular, in a recent study it was shown that a Pt-acetylide oligomer is an effective optical limiter for nanosecond pulses of visible light [15,16]. Optical limiting is believed to arise via reverse saturable absorption due to the triplet state. This observation has stimulated interest in investigation of the factors that control the yield and absorption of the triplet excited state in Pt-acetylide materials [17,18].

Our group has carried out a number of investigations which seek to develop structure–property relationships for the optical properties of Pt-acetylide materials [19–21]. In the course of this work we have prepared and characterized the optical properties of a variety of Pt-acetylide based oligomers and polymers, with particular emphasis being placed on understanding how structure controls the properties of the triplet excited state. In the present review we provide an overview of some of the recent work that we have carried out in this area.

## 2. Monodisperse platinum-acetylide oligomers

Excited-state structure and electronic delocalization in Pt-acetylide based  $\pi$ -conjugated polymers have been investigated considerably [22–27]. While these studies have provided much insight into the optical and photophysical properties of these materials, there are several inherent difficulties in using polymers for careful photophysical studies. First, synthetic polymers are by nature polydisperse – any given polymer sample includes a variety of chain lengths. In addition, polymer chains may have defects in their backbones that are not easily detected by normal structural characterization techniques, but which may influence the photophysical properties of the polymer.

Our group has been interested in using conjugated oligomers as models for large conjugated polymer systems [20,28–32]. The oligomer-based approach allows systematic

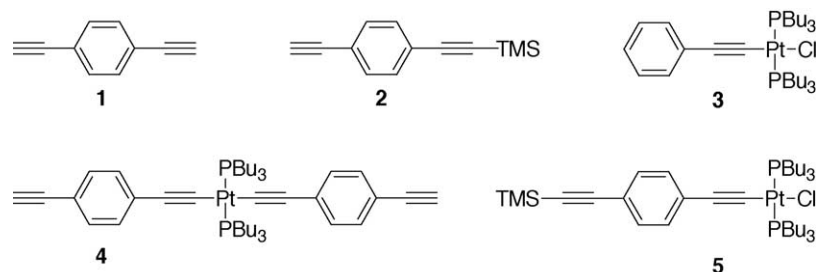


Scheme 1. Structure of PAOs.

investigation of the changes in optical properties that accompany an increase in conjugation length. Despite its utility in providing an understanding of the relationship between structure and optical properties, until now very few studies have focused on structurally well-defined Pt-acetylide oligomers [33]. Recently, we completed a systematic photophysical study of a series of mono-disperse Pt-acetylide oligomers [34]. This investigation was carried out with the objective of providing insight concerning electronic delocalization in Pt-acetylide polymers. The series of Pt-acetylide oligomers (PAOs) that were the focus of this work are shown in Scheme 1 [20].

Schemes 2 and 3 illustrate the overall synthetic route used to prepare the PAOs. Aryl acetylide building blocks such as **1** and **2** were obtained by Pd(0)-mediated Sonogashira coupling reactions. Trimethylsilyl protected terminal acetylene groups allowed the selective coupling of one side of the molecule with platinum containing building blocks. Oligomers PE-1 to PE-7 were prepared in good yields by the sequential Hagihara coupling of aryl acetylides with *bis*(tributylphosphine)platinum(II) chloride. The reactions were carried out in the presence of an amine base (typically diethylamine) at or slightly above room temperature. Without the presence of catalyst, the major product of these reactions is the mono-substituted platinum acetylide complex, whereas the *bis*-acetylide complex is typically obtained in the presence of a catalytic amount of CuI.

The PAOs were structurally characterized by spectroscopic analyses including  $^{31}\text{P}$  NMR.  $^{31}\text{P}$  NMR spectra allow us to confirm that the oligomers have the all-*trans* geometry (with respect to the Pt center). Moreover, it is possible to distinguish the phosphines on the terminal and internal Pt units, and therefore by integrating the peaks in the  $^{31}\text{P}$  NMR spectrum it is possible to confirm that the ratio of internal to terminal units is consistent with the length of the each oligomer. The length of each oligomer was also confirmed



Scheme 2. Pt-acetylide building blocks.

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