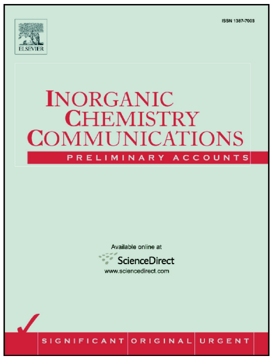

Synthesis and photophysical properties of cyclometalated 4′-phenyl-2,2′:6′,2″-terpyridyl Pt(II) chloride complexes with different aryl substituents

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Synthesis and photophysical properties of cyclometalated 4'-phenyl-2,2':6',2″-terpyridyl Pt(II) chloride complexes with different aryl substituents

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Abstract: A series of 4'-phenyl-2,2':6',2″-terpyridyl Pt(II) chloride complexes bearing different aryl substituents (**1a**–**1f**) was designed and synthesized. The photophysical properties of these complexes have been systematically investigated. All complexes exhibit strong $^1\pi,\pi^*$ absorption bands in the UV region; and broad, structureless metal-to-ligand charge transfer (^{1}MLCT) absorption bands in the visible region. When excited at the charge-transfer absorption band, the complexes exhibit room temperature luminescence (λ_{em} = 555-614 nm) in CH_3CN. The emissions of complexes **1c**–**1f** with electron-donating or extended π-conjugation substituents are assigned to the ^{3}MLCT states. Meanwhile, the emitting state of **1a** and **1b** exhibits a significant intraligand $^3\pi,\pi^*$ character. Complexes **1a**–**1d** exhibit moderate triplet transient absorptions from visible to NIR region, where reverse saturable absorption (RSA) occurs. Their photophysical properties have been investigated with the aim to provide a basis for elucidating the structure-property correlations and developing new nonlinear optical materials.

Keywords: Pt(II) complexes; Nonlinear optical ; Photophysical property; Electrochemistry; Transient absorption

Nonlinear optical materials for protection of optical sensors against lasers have been studied for decades [1,2]. To date, the widely investigated nonlinear optical materials are metallophthalocyanines [3], organic dendrimers [4,5], bis(styryl)benzene derivatives [6] and metalloporphyrins [7]. Besides these, cyclometalated Pt(II) complexes have attracted great interest in recent years due to their intriguing spectroscopic properties as well as potential applications in the fields of optoelectronic devices [8-12], photocatalysis [13-15], chemosensors [16,17] and nonlinear optics [18-22]. Their rich photophysical properties and applications are intrinsically based on the presence of multiple charge transfer excited states, such as metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), intraligand charge transfer (ILCT), in addition to the ligand localized π,π* transitions. These features lead to long-lived triplet excited states, broadband excited-state absorption (ESA) in the visible to the near-IR region. More importantly, their photophysical properties can be readily tuned by modifying the ligand structures, which offers researchers the opportunity to design new functional optical materials.

Among these cyclometalated Pt(II) complexes, 2,2':6',2″-terpyridyl Pt(II) complexes are particularly intriguing by virtue of their relatively intense emission, broadband nonlinear absorption and the ease of structural modification on terpyridine ligand and acetylide ligand. Yam group [11] and Wu group [23] revealed that variations in the auxiliary substituents on acetylide ligand drastically shifted the emission energy of Pt(II) terpyridyl complexes. McMillin group attached both π-donating groups and π-accepting groups on the 4′-position of the terpyridyl ligand, which significantly increased the excited-state lifetime of the Pt(II) complexes, indicating that the large conjugating aryl substituents could tune or even change their emitting state [24]. The research conducted by Sun group also demonstrated that changing the strength of the electron-donor on terpyridyl ligand could significantly change the excited-state absorption characteristics of the Pt(II) complexes, and thus strongly impact their optical limiting performances [25].

The reported works suggest that terpyridyl Pt(II) complexes and their derivatives could be promising candidates for efficient optical limiting materials. To the best of our knowledge, studies on the optical properties and structure-property correlation of 2,2':6',2″-terpyridyl Pt(II) complexes with different aryl substituents on terpyridyl motif are still limited. Understanding how the nature of these aryl substituents influences the photophysics of Pt(II) complexes is essential for the rational design of novel optical materials.

In this work, a series of 4'-phenyl-2,2':6',2″-terpyridyl Pt(II) chloride complexes terminally capped with different aryl substituents on terpyridyl ligand were designed and synthesized (Chart 1). Compared to the reference complex **1a** bearing phenyl group, 2,4-difluoro groups were chosen as electron-withdrawing substituents, 4-methoxyl, 3-carbazolyl and 4-diphenylamio groups were chosen as electron-donating substituents. Meanwhile, fluorenyl group were chosen as expanded π-electron system to replace phenyl group in order to study the effect of extended π-conjugation on the photophysics. The photophysical properties of these Pt(II) complexes were systematically investigated with the aim of understanding the structure-property correlations and developing new nonlinear absorbing materials.

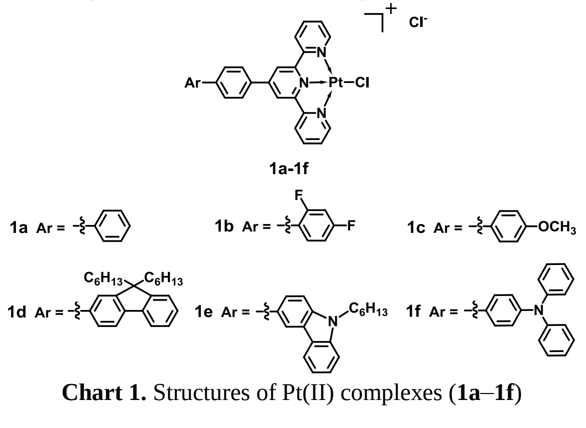

Chart 1. Structures of Pt(II) complexes (**1a**–**1f**)

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