

## Review

## Photophysical properties and applications of coordination complexes incorporating pyrene



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## ABSTRACT

Pyrene is a well-known aromatic hydrocarbon with unique photophysical properties that have been extensively studied. Coordination of pyrene and pyrene-containing ligands to metal centres gives rise to diverse photophysical behaviour that cannot be observed in pyrene alone. This review summarizes the photophysics of pyrene-containing coordination complexes, and examples of applications where these complexes are useful are discussed.

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## 1. Introduction and scope

Pyrene has become one of the most widely studied organic molecules in the field of photochemistry and photophysics. Its

unique properties have inspired research in many scientific fields and as a result, pyrene has become the fluorophore of choice in both fundamental and applied photochemical research [1]. There have been numerous studies on the photophysical properties of pyrene, including its electronic spectrum and state assignments [2–4], kinetic details of excimer formation [5,6], formation and kinetics of excited states [7,8], photoionization [9,10], delayed luminescence [11] and the sensitivity of its excitation spectrum to environmental

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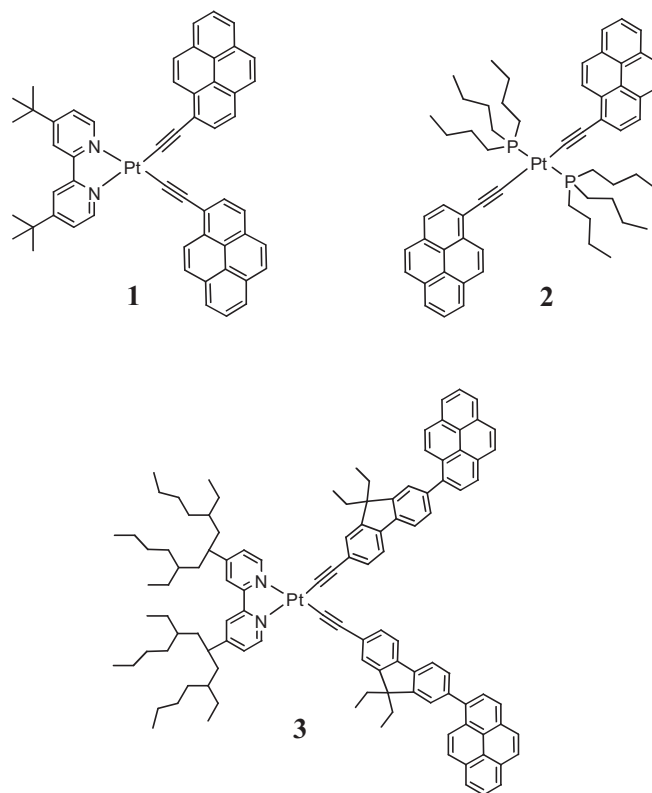
changes [12]. Pyrene monomer emission typically occurs between 370 and 420 nm and is a characteristic violet colour. Pyrene is one of few polycyclic aromatic hydrocarbons that show vibronic structure in its monomer fluorescence spectrum in solution [12]. The relative intensities of the vibronic bands in the emission spectrum are dictated by the relative positions of the potential energy surfaces of the excited singlet states relative to the ground state singlet and by the Franck–Condon principle [12]. Like many fluorophores, pyrene fluorescence becomes quenched as the molar concentration of the solution is increased. This concentration dependent quenching is accompanied by the appearance of broad, structureless excimer fluorescence which typically occurs around 480 nm [6]. The term excimer was first introduced by Stevens and Hutton to describe an excited dimer which is associated in an electronic excited state and dissociated in the ground state [13]. The formation of a pyrene excimer requires the encounter of an electronically excited pyrene with a second pyrene in a ground electronic state. Consequently, the two pyrenes must be sufficiently far apart when light is absorbed, so that excitation is localized on only one of them. The observation of excimer emission therefore indicates that diffusive encounter between pyrenes has occurred [14]. Pyrene phosphorescence is much less commonly observed than fluorescence, due to the spin forbidden nature of the triplet transition. Special conditions such as cooling to 77 K in rigid media or adding a heavy atom to induce spin–orbit coupling are often required to observe pyrene phosphorescence [15].

This review will discuss how coordination of pyrene-containing ligands to metal centres affects and expands upon the rich photo-physiology of pyrene.

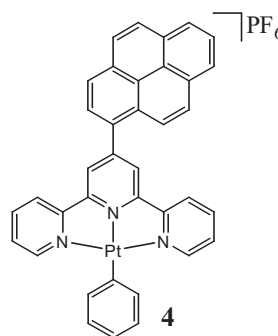
## 2. Photophysical properties of pyrene-containing coordination complexes

### 2.1. Complexes displaying ${}^3\pi-\pi^*$ ( ${}^3\text{IL}$ ) emission from a pyrene chromophore

There have been numerous studies on coordination complexes with excited state behaviour which is dictated by a triplet metal-to-ligand charge transfer ( ${}^3\text{MLCT}$ ) state. Emission from a  ${}^3\pi-\pi^*$  state of a coordinating ligand is rare because these states typically lie much higher in energy than the corresponding  ${}^3\text{MLCT}$  states. Complexes can be designed, however, such that the  ${}^3\pi-\pi^*$  state lies lower in energy than the  ${}^3\text{MLCT}$  state. In these instances, with the help of the internal heavy atom effect,  ${}^3\pi-\pi^*$  emission can be observed. This concept has been demonstrated a few times using pyrene as the low-lying  ${}^3\pi-\pi^*$  emitter. Castellano et al. reported a square planar, Pt(II) diimine bis(pyrenylacetylide) complex (**1**) that displays long-lived ( $48.5 \mu\text{s}$ )  ${}^3\pi-\pi^*$  ( ${}^3\text{IL}$ ) pyrene-based emission at room temperature in solution [16]. In this example, direct excitation into the MLCT excited state leads to the rapid formation of the triplet intraligand ( ${}^3\text{IL}$ ) state ( $\tau_{\text{isc}} = 240 \pm 40 \text{ fs}$ ). The formation of the  ${}^3\text{IL}$  state in **1** occurs significantly faster than intersystem crossing to the  ${}^3\text{IL}$  state in a model complex (**2**) which is lacking an MLCT excited state. This suggests that the presence of the MLCT state enables fast triplet sensitization [17]. Room temperature pyrene  ${}^3\pi-\pi^*$  emission is also observed in a related example, where the pyrene group is separated from the acetylide linker via a fluorene bridge (**3**) [18].



McMillin et al. studied a series of  $\text{Pt}(\text{trpy})\text{Ph}^+$  complexes ( $\text{trpy} = 2,2':6',2''\text{-terpyridine}$ ) with electron-rich groups at the 4' position of the trpy ligand [19]. In general,  $\text{Pt}(\text{trpy})\text{Ph}^+$  complexes are not emissive in solution due to non-radiative decay from a sigma-bond-to-ligand charge transfer ( ${}^3\text{SBLCT}$ ) state. Electron-rich groups on the 4' position of the trpy ligand alter the lowest-lying excited state in these complexes and promote emission by introducing intraligand charge-transfer (ILCT) character. Attaching pyrene at the 4' position (**4**) had the most significant effect on the orbital parentage of the emitting state. Unlike the other complexes in the series, **4** did not give rise to ILCT character, but instead the emission spectrum was dominated by pyrene  ${}^3\pi-\pi^*$  emission with a lifetime of  $45 \mu\text{s}$ .



Ziessel et al. synthesized a series of Ru(II) complexes with bipyridine and terpyridine ligands containing multiple acetylide bridged pyrene moieties (**5–9**) [20]. In all cases the emission spectrum is dominated by pyrene  ${}^3\pi-\pi^*$  emission at room temperature in

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