An insight into fluorescent transition metal complexes

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Review

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The emission from a transition metal complex is usually produced from triplet excited states. Due to strong spin-orbit coupling (SOC), fast conversion of singlet to triplet excited states via intersystem crossing (ISC) is facilitated. Hence, in transition metal complexes, emission from singlet excited states is not favoured. Despite this, a number of examples of transition metal complexes that fluoresce with high intensity have been found and some of them were even comprehensively studied. In general, three common photophysical characteristics are used for the identification of fluorescent emission from a transition metal complex, these are: emission lifetimes on the nanosecond scale; a small Stokes shift; and intense emission under aerated conditions. For most of the complexes reviewed here, singlet emission is the result of ligand-based fluorescence, which is the dominant emission process due to poor metal-ligand interactions thus lead to a small metal contribution in the excited states, and a competitive fluorescence rate constant when compared to ISC rate constant. On top of pure fluorescence from metal complexes was being concerned, another two types of fluorescent emissions were also reviewed namely delayed fluorescence and fluorescence-phosphorescence dual emissions. Both emissions also have their respective unique characteristics and being discussed in this perspective.

Introduction

The complexes of ruthenium(II) tris(bipyridine), $[Ru(bpy)_3]^{2+}$, and iridium(III) tri(phenyl pyridine), $[Ir(ppy)_3]$, have been extensively studied and being used as the model for luminescent transition metal complexes.[1-7] In general, the singlet excited states of most metal complexes are known to have extremely short lifetimes, i.e. about 100 fs for $[Ir(ppy)_3]$[8,9] and 15±10 fs for $[Ru(bpy)_3]^{2+}$,[10] because the metal centre plays a role in the conversion of singlet excited states to triplet excited states with extremely fast ISC rate (10^{12} s^{-1}). For this reason, the fluorescence from these metal complexes is very difficult to observe, and the fluorescent quantum yields are very small, i.e. the fluorescence quantum yield for $[Ru(bpy)_3]^{2+}$ was found to be 9 x 10^{-5}.[11]

However, several metal complexes have been reported in 2000s with intense fluorescence in nanosecond scale lifetimes. This has raised questions regarding the heavy atom effect, which is influenced by the metal centre in a complex. In this perspective, we not only report information on the fluorescent characteristics in transition metal complexes, but also describe the results of photophysical studies that have been conducted. In addition, metal-ligand interactions are discussed. We focus on the complexes, where fluorescence has been found by comprehensive experimental studies and we aim to emphasize that fluorescent emission from transition metal complexes is actually possible. Nevertheless, there are many known fluorescent metal complexes which are not discussed here. The main reason for this is because the papers do not include any detailed investigations into the fluorescence.[12-17]

d^6 –d^{10} octahedral complexes

Rhodium

The photophysical properties of rhodium complexes were extensively studied in the 1980s and 1990s. The photophysical behaviour of $[Rh(bpy)_3]^{3+}$ is very different from that of $[Ru(bpy)_3]^{2+}$. The various high intensity bands below 350 nm in the absorption spectrum of $[Rh(bpy)_3]^{3+}$ are generally assigned to the ^1LC $\pi \rightarrow \pi^*$ transitions in the bpy ligands, and no MLCT transition bands were observed in the spectrum.[18] At room temperature, $[Rh(bpy)_3]^{3+}$ is non-emissive in fluid solution. The emission from $[Rh(bpy)_3]^{3+}$ at 448 nm with a lifetime of 2.2 ms is only observed at low temperature (77 K) in a rigid glass.[19]

In 2001, a remarkable fluorescent rhodium containing metallacycle complex namely 2,5-bis(ditolylethynyl) rhodacyclopentadienes was reported by Marder, Rourke et al.[20]

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At that time, the group only briefly reported the photophysical properties of this complex. Until recently, the group reported a comprehensive photophysical properties studies concerning this type of metallacycle rhodium fluorescent complexes (**Fig. 1**). The λ_{max} absorption wavelengths are within the range of 453-517 nm while the λ_{max} of emissions are in the region of 496-590 nm. The nano-second scale lifetimes (0.45-1.21 ns) and the small Stokes shifts (1870-2390 cm^{-1}) indicated that the metallacycle rhodium complexes (called as rhodacycle) exhibit fluorescent emissions with the quantum yields of 0.01-0.18.[21] The group carried out singlet oxygen sensitization experiments and found that the quantum yields for singlet oxygen formation (0.45-0.61) was close to those of ISC.

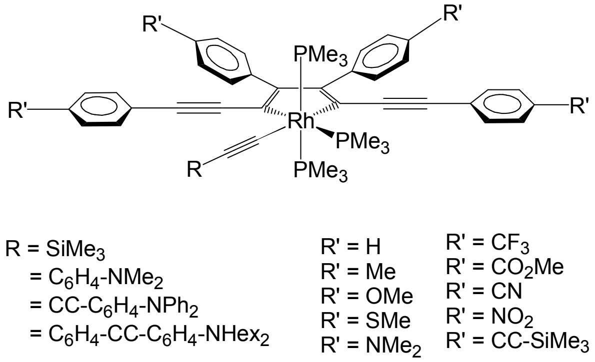
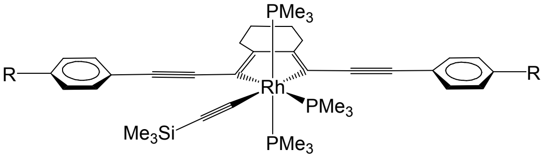


Fig. 1 Structure of 2,5-bis(ditolylethynyl)rhodacyclopentadienes.

The slow ISC (10^8 s^{-1}) leads to a longer emission from the S_1 states and this contradicts to the common understanding of luminescent organometallics whereby heavy atom such as rhodium (SOC constant of Rh, ξ: 1200 cm^{-1}) shall facilitate fast ISC (10^{12} s^{-1}). Although the experiment did show the presence of T_1 state, the authors presumed that it must be low in energy and underwent fast decay as they could not detect any phosphorescence.[21]

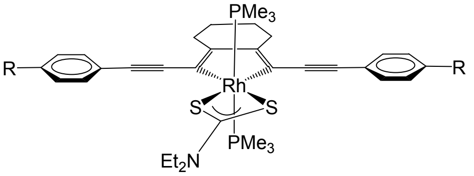
In fact, in 2010, the group has reported another type of rhodacycle complexes (**Fig. 2**) which are structurally similar to the complexes shown in **Fig. 1**.[22] Both series of the rhodacycle complexes emitted highly intensive (Φ_f = 0.07–0.69) and long lived (τ_f = 0.4–3.0 ns) fluorescence despite the fact that carbon atoms are directly bound to the rhodium centre.

The ground and excited states of rhodacycle complex (**1a**) were studied by using picoseconds time-resolved IR (TRIR) vibrational spectroscopy, which confirmed that the triplet excited states were formed in 1.6±0.6 ns but did not emit as phosphorescence. Interestingly, the ISC rate constant for this complex (k_{ISC} = 5 x 10^8 s^{-1}) is unexpectedly slower than other luminescent metallacycle complexes such as [Ir(ppy)$_3$]. The slow k_{ISC} is competitive with the fluorescence constant (k_f = 2.75 x 10^8 s^{-1}). The group introduced a strong electron donating ligand, thiocarbamate, to the rhodacycle complexes (complexes **2a-c**) with the aim to destabilise the filled *d*-orbitals of rhodium. However, the emission from this complex was still from the singlet excited states and the Stokes shifts was only ~2000 cm^{-1}.[22]



1

R = H (**a**), SMe (**b**), CO_2Me (**c**), $BMes_2$ (**d**)



2

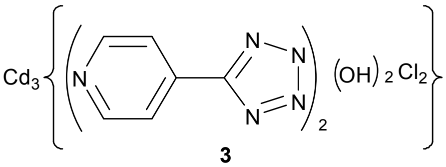
R = H (**a**), SMe (**b**), CO_2Me (**c**)

Fig. 2 Structure of rhodacycle complexes **1** and **2**.

Cadmium

Despite cadmium being a Group XII *d*-block transition metal, the complexation studies of cadmium have attracted considerable attention from inorganic chemists. From the literature, we found that three types of cadmium complexes exhibit fluorescent emission (their photophysical properties are described below). In the original papers, detailed photophysical studies were not reported.

A cadmium(II) coordination polymer complex **3** (**Fig. 3**), [Cd_3(4-PTZ)$_2$(OH)$_2$$Cl_2$], where 4-PTZ = 5-(4-pyridyl)tetrazolate, was observed to emit fluorescence.[23] Complex **3** shows a strong emission at 390 nm with the lifetime of ~1.5 ns and the quantum yield of ~0.31. The emission was claimed to have originated from a LLCT transition. Apart from fluorescence, complex **3** was also found to exhibit relatively weak phosphorescent emission at 470 nm with a lifetime of ~2.0 s and a quantum yield of ~0.15. The authors stated that they were unclear about the exact mechanism for the phosphorescence, but it may be due to the Cd–OH–Cl group which formed 2D network that acts as sheets to link the 4-PTZ ligands into pillared-layered structure.[23]



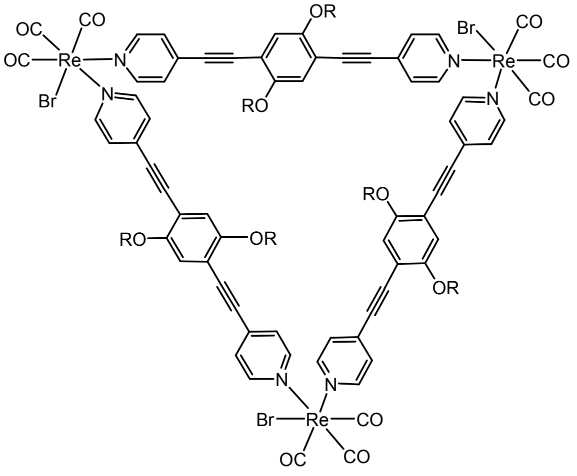
3

Fig. 3 Structure of [Cd_3(4-PTZ)$_2$(OH)$_2$$Cl_2$], **3**.

In 2011, Zha et al.[24] reported two cadmium(II) complexes, [Cd_2(pqc)$_4$(phen)$_2$(H_2O)$_2$]·$2H_2O$ (complex **4**) and [Cd_2(pqc)$_4$(bpy)(H_2O)$_2$]·$2H_2O$ (complex **5**), (pqc = 2-phenylquinoline-4-carboxylates, phen = phenanthroline), that exhibit intense fluorescence centred at 400 and 380 nm, respectively, even in the solid state. According to the authors, the strong emission at 400 nm of complex **4** may originate from the ligand-to-ligand charge transfer (LLCT) transition of the pqc and phen similar to the emission at 380 nm of complex **5**, which was also due to the LLCT transition of pqc and bpy. Further investigation into the luminescent properties of these two complexes was still underway at the time of publication.

Rhenium

In 2000, Sun et al. reported a series of self-assembly macrocyclic compounds that have *fac*-[Re(CO)$_3$X] (X = Cl or Br) as corner pieces with linear bipyridyl bridging ligands. Two of these macrocyclic complexes, namely triangles [BrRe(CO)$_3$(μ-BPDB)]$_3$ where BPDB = 1,4-bis(4'-pyridylethynyl)-2,5-dihexyloxybenzene (complex **6**) and [BrRe(CO)$_3$(μ-BPDDB)]$_3$ where BPDDB = 1,4-bis(4'-pyridylethynyl)-2,5-didodecyloxybenzene (complex **7**) (**Fig. 4**) exhibited luminescence emission which was believed to be from the $^1\pi\rightarrow\pi^*$ state.[25]



R = C_6H_{13} (**6**), $C_{12}H_{25}$ (**7**)

Fig. 4 The structure of [BrRe(CO)$_3$(μ-BPDB)]$_3$, **6**, and [BrRe(CO)$_3$(μ-BPDDB)]$_3$, **7**.

The photophysical data showed that the emission maxima of complex **6** in 1,2-dichloroethene were at 499 and 476 nm with the fluorescence quantum yield, Φ_f = 0.032 and a lifetime of 0.36 ns; whereas the Φ_f of complex **7** was 0.012 and its lifetime was 0.37 ns at the emission maxima 512 and 470 nm. Both emissions were from the ligand based $^1\pi\rightarrow\pi^*$ transition. This can be explained from the fact that the fast radiative decay rate ($k_r \sim 10^8$ s^{-1}) was able to compete with the ISC process. Nonetheless, a very weak emission was observed at 602 nm with a lifetime of 163 µs at 77 K, which was assigned as the ^{3}MLCT transition.[25]

Another fluorescent rhenium(I) octahedral complex was reported by Czerwieniec et al. in 2001. The group has studied the [Re(I)(tricarbonyl)(8-quinolinato)] complexes in monomeric and dimeric form. The monomeric complex, [Re(CO)$_3$(OX)(pyr)] exhibited phosphorescence, but this emission was not observed in the dimeric analogue, [Re$_2$(CO)$_6$(OX)$_2$], indeed, it displayed fluorescence.[26] The fluorescent quantum efficiency of the two emission bands at 16500 and 17500 cm^{-1} did not change in the oxygen saturation probe, hence, the authors concluded that the excited state would most probably be ligand localized.[26]

Ligand-based fluorescence can also be seen in rhenium complex synthesized by Aly et al. (2002). The complex [(OTC)Re(CO)$_3$Cl] (**Fig. 5**) exhibited intraligand fluorescence at λ_{max} = 570 nm with a quantum yield of 2x10^{-3} upon excitation at 390 nm.[27] This emission was claimed as fluorescence due to the overlapping of the absorption and emission band. Indeed, the authors claimed that the intersystem crossing due to heavy atom effect from rhenium is only transmitted efficiently to the π-acceptor ligands. Since the phenolate ligand that they used in [(OTC)Re(CO)$_3$Cl] complex is not a π-acceptor, as a result, the intraligand emission was concluded as fluorescence. In addition, the authors also mentioned that the fluorescence quantum yield was enhanced in the complex compared to the ligand due to the removal of a phenolic proton in the ligand. Upon deprotonation of the phenolic proton, the charge transfer donor strength was increased. However, the phosphorescence cannot be completely ruled out because it is probably less dominant over the strong fluorescence.[27]

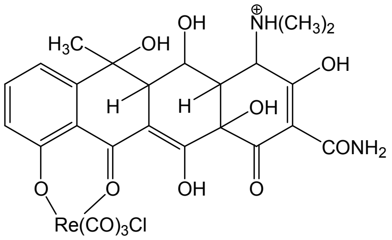


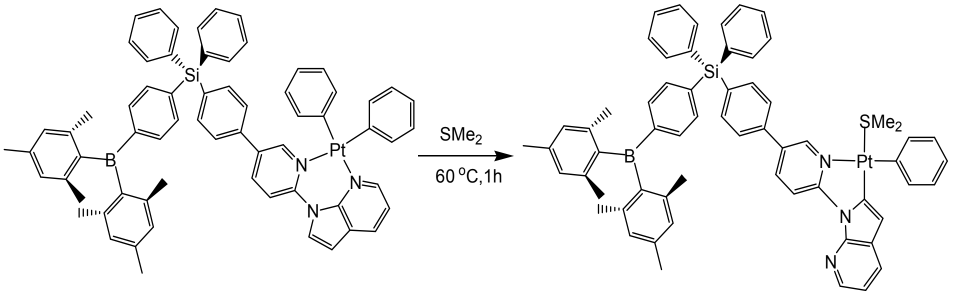
Fig. 5 The structure of rhenium complex (OTC)Re(CO)$_3$Cl, **8**.

$d^8 - d^{10}$ square planar complexes

Platinum

Not only octahedral complexes exhibit fluorescent emission, indeed, examples of fluorescence from complexes with square planar and linear geometries are also known. Platinum square planar complexes have been well studied concerning their applications, for example, the anti-cancer activities of *cis*- and *trans*-[PtCl$_2$(NH$_3$)$_2$] and also the photophysical properties of platinum terpyridyl complexes.[29a] Platinum is well known to have a large SOC constant (ξ = 4000 cm^{-1}), several reports of fluorescent platinum complexes have been found and further studies on their photophysical properties were well described in the relevant papers.

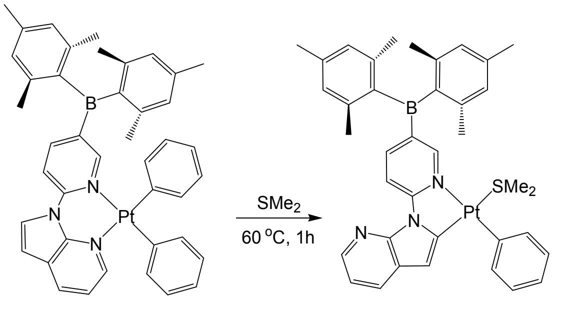
Hudson et al. (2009) reported an impressive triarylboron–platinum(II) complex which displayed unusual white singlet-triplet dual emissions at 77 K. The Pt(II) complex, [Pt(N,N-Si-BNPA)Ph$_2$] (**9**) has an unstable six-membered non-planar N,N-chelate ring, and underwent an intramolecular "roll-over" C–H activation to form a more stable five-membered N,C-chelate complex, [Pt(N,C-Si-BNPA)(SMe$_2$)Ph] (**10**) (**Fig. 6**).[29b]



9 **10**

Fig. 6 Transformation of [Pt(*N*,*N*-Si-BNPA)Ph$_2$], **9** to [Pt(*N*,*C*-Si-BNPA)(SMe$_2$)Ph],**10**.

For complex **9**, the emission spectrum showed a singlet emission peak at λ_{max} = 399 nm with a shoulder band at ~362 nm and a very weak triplet emission peak centred at 494 nm. On the other hand, the more stable complex **10** has a similar singlet peak at λ_{max} = 392 nm (with a shoulder at ~348 nm) and also a strong green phosphorescence at 495 nm. Indeed, the emissions at 392 and 399 nm in both complexes **9** and **10** were believed to be the fluorescence originated from the Si-BNPA ligand (λ_{max} = 405 nm, ϕ = 0.12) which is due to the transition of mesityl→boron charge-transfer. The phosphorescence of both complexes **9** and **10** originated from NPA-centered $^3\pi\rightarrow\pi^*$ transition. The phosphorescence intensity increased when the temperature decreased due to elimination of quenching process at low temperature. On the other hand, the excitation profile at 77 K showed that both fluorescence and phosphorescence emissions were identical, which proved that the dual emission is from the same molecule.[29b]



11 **12**

Fig. 7 Transformation of [Pt(*N*,*N*-BNPA)Ph$_2$], **11** to [Pt(*N*,*C*-BNPA)(SMe$_2$)Ph], **12**.

The unusual singlet-triplet dual emissions required further studies in order to understand the mechanistic details. The study concluded two main findings: firstly, the heavy atom effect of platinum(II) facilitates ISC to produce phosphorescence. Hence, the dual emission is visible at ambient temperature. Secondly, the chelate mode (*N*,*N*-, *N*,*C*-) does have an impact on the intensity of the singlet and triplet emission peaks.[29b] It is noteworthy that after removal of the tetraphenyl silicate moiety, the platinum complexes **11** and **12** (**Fig. 7**) only showed a respective single phosphorescent emission at 543 and 535 nm with the lifetime of 25 and 12 μs.[29b]

Later in 2010, Lentijo and co-workers reported a series platinum(II) complexes with the perylene (Per) and perylene monoimide (PMI) ligands (**Fig. 8**). The complexes showed intense fluorescent emissions with the quantum yields of 0.30–0.80 and lifetimes of 1.9–5.0 ns in solution at room temperature. In general, the Stokes shifts of these platinum(II) complexes were less than 1000 cm^{-1}, which can be assigned to an intra-ligand $\pi\rightarrow\pi^*$ singlet transition.[30]

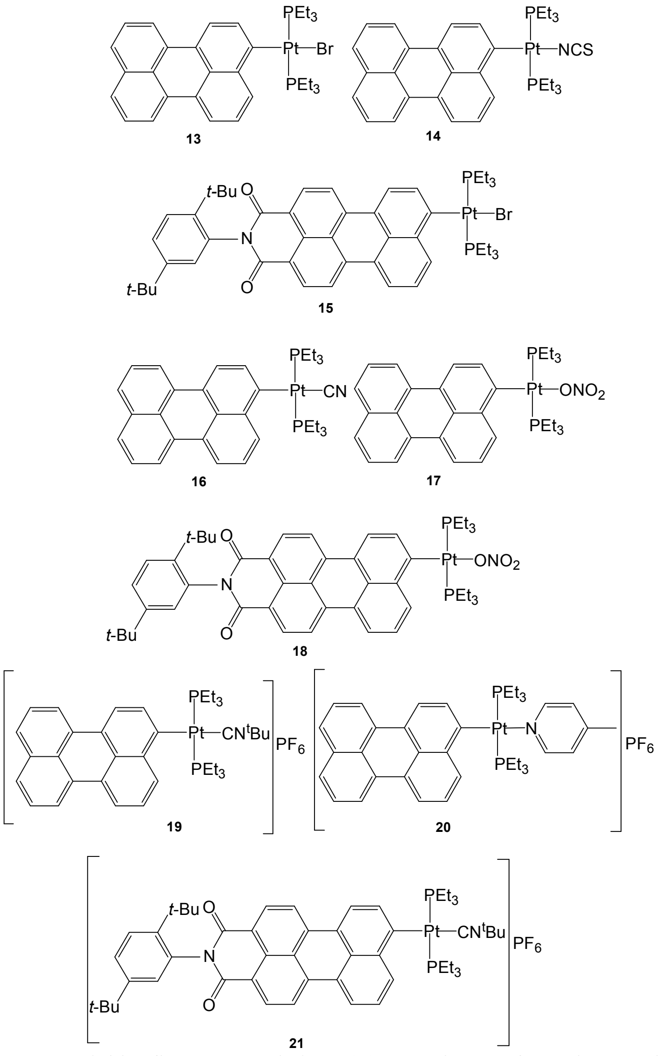
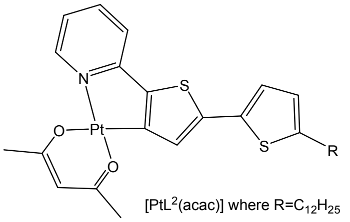


Fig. 8 Highly fluorescent platinum(II) complexes of perylene and perylene monoimide.

Again, the authors also confirmed the emissions originated from singlet excited states based on the unchanged luminescent properties in the presence of oxygen and also the nanosecond scale lifetime. In addition, the emission spectrum of complex **13** at low temperature also showed an identical spectrum with the one in room temperature, which indicated that there was no phosphorescence observed. It is believed that the poor interaction of filled d_π orbitals from platinum with the empty frontier π*-orbitals from Per or PMI ligands is the reason for the low heavy atom effect from platinum. Indeed, the interaction between the Pt—C bond is transmitted mainly *via* a σ interaction of the $5d_z$ orbitals of Pt with the aryl group of the ligands.[30]

Kozhevnikov et al. (2011) have synthesized two [PtL^n(acac)](**Fig. 9**) (n = 2 or 3), where 2 = 5-(2-pyridyl)-5'-dodecyl-2,2'-bithiophene; and 3 = 5-(2-pyridyl)-5''-dodecyl-2,2':5'2''-terthiophene. The luminescent properties of both [PtL^2(acac)] and [PtL^3(acac)] complexes were compared the known luminescence behavior of [PtL^1(acac)], where 1 = 2-(2-thienyl)pyridine. It was found that the [PtL^1(acac)] displayed intense phosphorescence,[31] while [PtL^2(acac)] and [PtL^3(acac)] showed weak phosphorescence but also exhibited fluorescence.[32] The emission at $\lambda_{\max}$ of 495 nm (τ <0.5 ns) in complex [PtL^2(acac)] and 525 nm in [PtL^3(acac)] were assigned as fluorescence. Another emission band at $\lambda_{\max}$ of 706 and 775 nm (τ = 2.3 μs) in [PtL^2(acac)] and 735 nm in [PtL^3(acac)] were attributed to phosphorescence. The lifetime of [PtL^3(acac)] cannot be recorded because of poor emission due to the extended π-conjugated structure in [PtL^3(acac)]. The authors claimed that the low participation of the metal d orbitals in the HOMO of [PtL^2(acac)] and [PtL^3(acac)] reduced the influence of SOC, which decreased the rate of ISC ($k_{\mathrm{ISC}} \approx k_{\mathrm{f}}$ in this case), as a result, dual emission was observed. It is noteworthy that the addition of one thiophene ring can increase the conjugation of the structure and also the $S_1 - T_1$ energy gap, which will in turn reduce the rate of the ISC too.[32]


[PtL^2(acac)] where R=$C_{12}H_{25}$

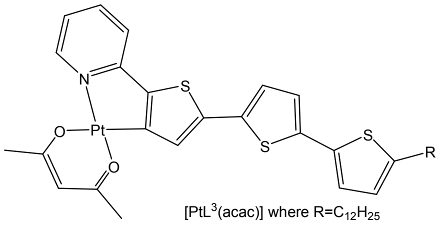
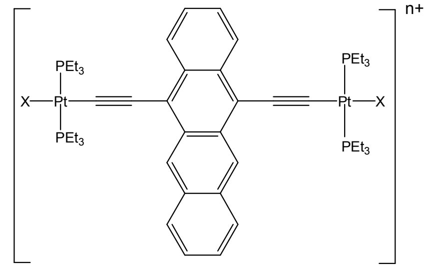

[PtL^3(acac)] where R=$C_{12}H_{25}$

Fig. 9 The structure of [PtL^2(acac)] and [PtL^3(acac)].

The findings from Kozhevnikov et al. (2011)[32] were parallel with the study of the dual emissive Pt(II) metallacycle complexes, Pt-1 and Pt-2 (the structures are quite similar to [PtL^n(acac)] in **Fig.9**) reported by Liu et al. in the same year. The fluorescence of Pt-1 emitted at 502 nm with a quantum yield of 0.95% and a lifetime of 0.06 ns at the absorption of 459 nm whereas the phosphorescence centred at 753 nm with the lifetime of 1.53 μs and quantum yield of 0.22%. Meanwhile, Pt-2 showed the fluorescence emission at 521 nm with a lifetime of 0.14 ns at the absorption of 474 nm. On the other hand, the phosphorescence of Pt-2 at 692 nm has a quantum yield and lifetime of 0.57% and 3.75 μs, respectively.[33] The well separation of fluorescent and phosphorescent emissions in both complexes was due to the large energy gap splitting in between singlet and triplet (singlet-triplet splitting: Pt-1 = 5279 cm^{-1}; Pt-2 = 4743 cm^{-1}). These emission bands were characterized as singlet and triplet emissions based on their respective luminescence lifetimes, the emission spectra at 77 K and oxygen sensitivity experiment. In agreement to the statements from Kozhevnikov et al. (2011),[32] increasing the ligand size resulted in the decrease of SOC influence from metal centre and ISC rate. This is one of the factors which can lead the transition metal complexes exhibit dual emissions.[32,33]

In 2012, another dual emissions platinum complex was found. Durrell et al. synthesized a diplatinum(II,II) complex called per(difluoroboro)tetrakis(pyrophosphito) diplatinate(II), [Pt(pop-BF$_2$)]$^{4-}$, which displayed both intense fluorescent and phosphorescent emissions in its spectrum. The fluorescent emission centred at 393 nm with a lifetime of 1.6 ns and quantum yield of 2.7×10^{-1}. The Stokes shift of singlet emission is 1760 cm^{-1}; whereas for the triplet emission, the Stokes shift is 2460 cm^{-1} with the emission at 512 nm and the lifetime of 8.4 μs.[34] Compared to the parent complex, [Pt(pop)]$^{4-}$, the ISC pathway of [Pt(pop-BF$_2$)]$^{4-}$ is much more slower because the perfluoroboration of the complex increased the rigidity of the covalent BF$_2$ linkages and therefore increased the energy of LMCT states. In addition, the electron-withdrawing power of BF$_2$ also enhanced the effect. This could increase the barrier of $^1A_{2u} - {}^3E_u$, as a result, the SOC effect was reduced and slowed down the ISC. Other than that, the slow ISC was also due to the increase in the singlet-triplet energy splitting from 1190 to 2230 cm^{-1}, which allowed dual emission to be observed.[34]

A recent paper reported by Nguyen et al. found the singlet emission from their dinuclear platinum complexes with the 5,12-diethynyltetracene ligand (complex **22, Fig. 10**).[35] The fluorescent platinum(II) complexes have their emissions located in the range of 561-608 nm with a quantum yield of 0.13-0.97. Based on the small Stokes shift (290-800 cm^{-1}) and their short lifetimes (2.0-9.3 ns), the emissions were assigned to singlet excited states. The authors believed that this is due to the low ISC rate caused by large extent of ligand π conjugation and the long-lived S_1 excited state. In addition, the ligand, tetracene, is known as an alternant hydrocarbon which has a large energy gap between S_1 and T_1 (10800 cm^{-1}) thereby creating a Franck–Condon barrier for the intersystem crossing.[35]



X = neutral, π-accepting ligands or X = anionic, π-donating ligands

Fig. 10 Dinuclear platinum complexes with 5,12-diethynyltetracene ligand, **22**.

Palladium

Apart from platinum complexes, two palladium complexes (**Fig. 11**) have also been found by Weissman and co-workers in 2007 to exhibit unexpectedly strong fluorescence.[36] Both palladium(II) complexes **23** and **24** exhibited similar emission spectra with an intense luminescence at 584 nm. The complex **23** was determined to have a quantum yield of 0.65 in dichloromethane and a lifetime of 7.5 ns, whereas for complex **24**, the quantum yield was 0.22 with a lifetime of 2.8 ns. These emissions were believed to be fluorescence because of the small Stokes shift and nanosecond scale lifetimes. In addition, the absorption and emission properties of both complexes were identical even though the experiments were performed in the open air.[36] Femtosecond and nanosecond transient absorption experiments were conducted and confirmed that both organopalladium complexes were highly fluorescent. In fact, the two palladium complexes also have triplet excited states with yields of 0.06 and 0.2 for complexes **23** and **24**, respectively.

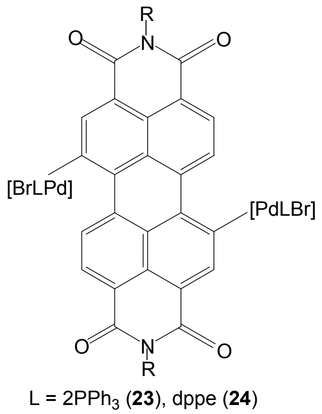


Fig. 11 Fluorescent palladium complexes of perylene diimide ligands.

TD-DFT calculations were performed in order to gain an insight into the palladium-induced heavy-atom effect. It was found that the HOMO and LUMO of the complexes were mainly localized on the ligand, perylene tetracarboxylic acid diimides (PDIs). Thus, the σ-bond is dominant between the palladium and the ligand, whereas the π-interaction between metal and ligand is very weak, which resulted a diminution of the heavy-atom effect. The intersystem crossing in complex **24** is more efficient than complex **23** as it has a smaller fluorescence quantum yield and higher phosphorescence yield compared to complex **23**. It was believed that the palladium d_{z^2} orbital in complex **24** has more participation in the HOMO than the one in complex **23**.[36]

d^{10} tetrahedral complexes

Copper

Cu(I) complexes have been focused as the potential material for organic light emitting diodes (OLEDs) due to the ability to exhibit delayed fluorescence in the luminescence process which can lead to relatively short radiative decay times and increase the OLED performance. The early examples of Cu(I) tetrahedral complexes that exhibit prompt fluorescence were reported about a decade ago, and in recent papers, there are many Cu(I) complexes exhibiting thermally activated delayed fluorescence (TADF) phenomenon at ambient temperature.

In 2003, Abedin-Siddique et al.[37] reported three fluorescent copper(I) bis(diimine) complexes (**Fig. 12**) namely [Cu(dmphen)$_2$]$^+$ where dmphen = 2,9-dimethyl-1,10-phenanthroline (**25**), [Cu(dbphen)$_2$]$^+$ where dbphen = 2,9-dibutyl-1,10-phenantroline (**26**) and [Cu(dmbpy)$_2$]$^+$ where dmbpy = 6,6'-dimethyl-2,2'-bipyridine (**27**) all with similar photophysical properties. The fluorescent lifetimes of these three copper(I) bis(diimine) complexes are in the range of 13-16 ps and these short-lived emissions were assigned as the prompt fluorescence from ^{1}MLCT. For complex **25**, the structure of the lowest ^{1}MLCT in this complex was flattened due to the Jahn-Teller effect in $3d^9$ electronic configuration and the distortion caused a large energy splitting (6.9 x 10^3 cm^{-1}) between orbitals HOMO and HOMO–1. As a result, the ISC process between the metal-centred HOMO and HOMO–1 were energetically unfavourable. The quantum yields of the fluorescence were very low which were about 2.1-3.0 x 10^{-5}. These fluorescent quantum yields were one-seventh that of the steady state emission quantum yield which is about 10^{-4}.[38]

Apart from complex **25**, complexes **26** and **27** also showed similar photophysical properties with quantum yields of 3.0 x 10^{-5} and 2.1 x 10^{-5} respectively, emission at 400 nm, and their fluorescence lifetimes were in the range of 15-16 ps.

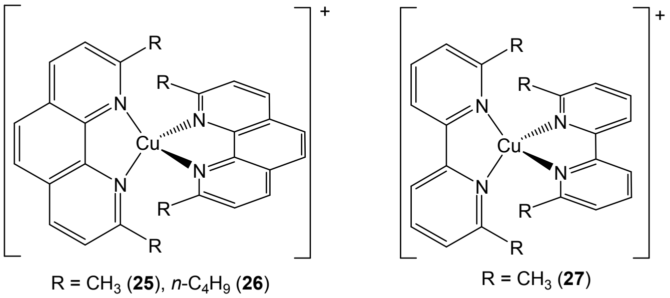


Fig. 12 Structure of [Cu(dmphen)$_2$]$^+$, (**25**), [Cu(dbphen)$_2$]$^+$ (**26**) and [Cu(dmbpy)$_2$]$^+$ (**27**).

Meanwhile, in 2010, Deaton et al. reported that its Cu(I) complex [Cu(PNP-^{t}Bu)]$_2$, with a quantum yield of 0.57, a decay time and radiative decay rate of 11.5 µs and 7.24×10^6 s^{-1}, respectively, exhibited delayed fluorescence.[39] The small Stokes shift of ~2070 cm^{-1} would be too small for a triplet emission, indicating that it probably comes from the lowest excited singlet state during thermal repopulation by the T$_1$ state, and this is possible with the singlet-triplet splitting gap [$\Delta E=(S_1 - T_1)$] of about 740 cm^{-1}. The authors also made the singlet state assignment based on the fact that the extinction coefficients are in the normal range for singlet MLCT transitions (5601 M^{-1} cm^{-1} at 433 nm and 4203 M^{-1} cm^{-1} at 463 nm) and it would be too high if it is for triplet absorptions.[39]

In the following year, Yersin et al. proposed that their distorted Cu(I) complex, [Cu(pop)(pz$_2$Bph$_2$)] emitted fluorescence at ambient temperature with a high quantum yield of up to 90%.[40] It was pointed out that this complex also has a small gap (800-1300 cm^{-1}) between its singlet and triplet state whereby this increases the radiationless decay rate (energy gap law) and causes the emission decay time to be significantly short (13 µs) at 300 K. This decay time is shorter than the one from pure triplet emission, but it is longer than the prompt fluorescence (120 ns). Hence, the emission at ambient temperature is convincingly a fluorescence originating from thermal activation of the lowest singlet state.[40]

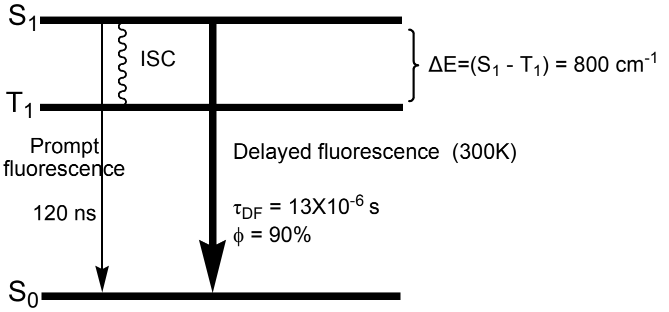


Fig. 13 Emission behaviour diagram of $[Cu(pop)(pz_2Bph_2)]$

Herein, we review another three examples of Cu(I) TADF emitters reported in 2013. Again, Yersin et al. presented a rigid $[Cu(dmp)(phanephos)]^+$ complex with high quantum yield (ϕ = 0.8), fast decay rate (k_r(DF) = 6 x 10^4 s^{-1}) and a short decay time (14 μs) with λ_{max} = 530 nm at T = 300 K.[41] The assignment of the emission as TADF was based upon small singlet-triplet splitting (1000 cm^{-1}) and a higher decay rate due to the presence of S_1 singlet state. However, it should be noted that phosphorescence with a lifetime of 240 μs occurred at 20-120 K while spontaneous fluorescence was not observed.[41] Similarly, Igawa et al. (2013) synthesized a series of emissive Cu(I) complexes, where part of the emissions were believed to be TADF. As mentioned in the examples above, it can be deduced that the TADF would probably occur if the singlet-triplet splitting gap is small enough (~1000 cm^{-1}). In this case, $\Delta E=(S_1 - T_1)$ is 167 cm^{-1} and at 293 K, emission at 545 nm has a lifetime of 3.8 μs (shorter than the phosphorescence at 77 K).[42] In addition to that, Zink et al. (2013) also found TADF at the ambient-temperature from dinuclear copper(I) halide complexes bearing with P^N ligands. At T = 300 K, emission at 539 nm with a quantum yield of 0.8 bears with a radiative decay rate of k_r(DF) = 1.2×10^5 s^{-1} and a decay time of 6.5 μs. The increase by more than a factor of 4 for the radiative rate is attributed to thermally activated decay channel via $S_1 \rightarrow S_0$ emission.[43]

Zinc

The fluorescence of zinc complexes was widely reported in many papers,[12-14] and even some of them already been used in the cell imaging and fluorescence probe application.[44] However, most of these papers do not enclose a comprehensive study of their fluorescence properties. Among them, we particularly choose the one reported by Kunkely and Vogler (2007) due to more information about the fluorescence study in their complexes. In their report, the complexes of Ni^{2+}, Zn^{2+}, Gd^{3+} and Th^{4+} with alizarin complexone (AC) ligand showed weak intraligand luminescence (**Fig. 14**). The Zn^{2+} complex shows one band at 630 nm and this luminescence remained even in ethanol glasses at 77 K.[28] The emission was classified as fluorescence due to the overlapping of the absorption and emission band. Excited state proton transfer (ESPT) was resulted when light absorption led to a charge transfer (CT) from the hydroxy to the quinone carbonyl groups. The fluorescence and ESPT were fast enough to compete with ISC despite the presence of heavy atom such as Zn^{2+}, Gd^{3+} and Th^{4+}. Due to this reason, the authors concluded that AC complexes are not phosphorescent even at low temperature.[28]

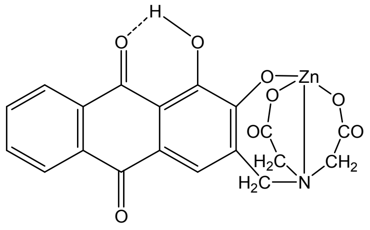


Fig. 14 Structure of Zn(II) complex reported by Kunkely and Vogler (2007).

Platinum

In 2004, Abedin-Siddique and co-workers reported their work on a tetrahedral $[Pt(0)(binap)_2]$ complex (**Fig. 15**), where binap = 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl. At that time, this platinum complex was considered as the first example that produced the high quantum yields of both prompt and delayed fluorescence.[45] The lifetime of the prompt fluorescence was 3.2 ps with the quantum yield of 1.6 x 10^{-4}, which was a thousand times smaller than the total emission quantum yield (Φ = 0.12). In fact, the authors also found that another main emission centred at the wavenumber of 13100 cm^{-1} with a lifetime of 1.2 μs in toluene at ambient temperature. The prompt fluorescence radiative rate constant in toluene was 4.9 x 10^7 s^{-1}, which was higher than the normal radiative rate constants for ^{3}MLCT (<10^6 s^{-1}). For example: 4.6 x 10^5 s^{-1} for $[Ru(bpy)_3]^{2+}$,[46] 2.5 x 10^5 s^{-1} for $[Re(bpy)(CO)(py)]^+$,[47] 1 x 10^5 s^{-1} for $[Os(bpy)_3]^{2+}$,[48] and 2 x 10^5 s^{-1} for $[Ir(ppy)_3]$.[49] Interestingly, the authors claimed that the long-lived emission with a lifetime of 1.2 μs was not related to the triplet excited state. In fact, it was assigned to delayed fluorescence. The reason for this is because it was found that the quantum yield decreased when the temperature decreased, contrary to the typical phosphorescence process. The researchers explained that the ^{1}MLCT and ^{3}MLCT states are very close in energy (1200 cm^{-1}), therefore the ^{3}MLCT state can return back to the ^{1}MLCT and fluoresce at ambient temperature. At low temperatures, the delayed-fluorescence was then replaced by phosphorescence with a lifetime of 1.2 μs. Importantly, the authors also pointed out that the ISC rate is dependent on the effectiveness of the SOC instead of the value of the SOC constant of the heavy atom.[45]

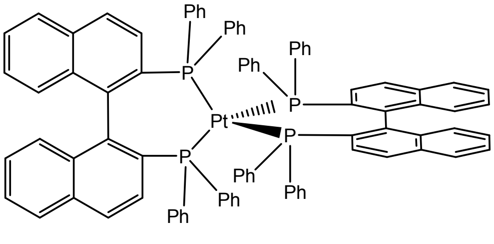


Fig. 15 Structure of $[Pt(0)(binap)_2]$.

MLCT fluorescence in $[Pt(binap)_2]$ showed a fairly large Stokes shift, 5.7 x 10^3 cm^{-1} as a MLCT transition of d^{10} metal compounds involved a change in the electron configuration to d^9, accompanied by structural changes due to the Jahn–Teller effect. The structural distortion due to the Jahn–Teller effect lowers the overall energy of the molecule, hence, a longer wavelength and larger Stokes shift are observed.

$d^8 - d^{10}$ linear complexes

Gold

Lu et al. (2003) reported the gold(I) complex **29** (**Fig. 16**) that exhibited strong fluorescent emissions at 413 and 428 nm with a quantum yield of 0.22 and a lifetime of <50 ns. In addition, this fluorescent emission was also confirmed from a small Stokes shift (1040 cm^{-1}). No phosphorescence was observed even at 77 K, and the group believed that its T_1 state must be very close in energy to the ground state, which leads to a very low Φ_p value.[50]

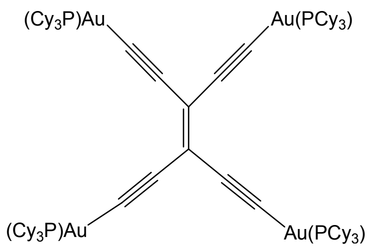


Fig. 16 The structure of gold(I) complex **29**, $[TEE][Au(PCy_3)]_4$.

In 2005, Espinet and co-workers managed to report a liquid crystalline tetrafluorophenyl gold(I) isocyanide complex which displayed strong photoluminescence in the mesophase, solution and solid state. Indeed, examples of liquid crystals that display intrinsic luminescence in the mesophase are rare. Moreover, the metallomesogens which have been reported to display photoluminescence in the solution and solid state are just limited to a few lanthanide and palladium complexes.[51]

Gold(I) complex **30** (**Fig. 17**) exhibited three broad emissions at 384, 490 and 524 nm in the solid state. The emission at 384 nm was due to the intraligand π→π* transition with a lifetime shorter than 10 μs. The authors claimed that this emission was due to a singlet excited state emission because of its short lifetime value and the relatively small Stokes shift (3028 cm^{-1}) compared to those of the triplet excited state (>4000 cm^{-1}).

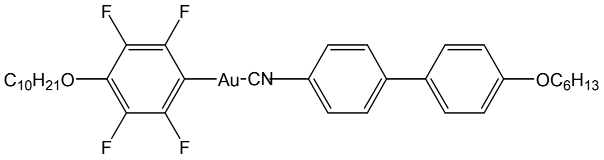


Fig. 17 Structure of gold(I) complex **30**, $[Au(C_6F_4OC_{10}H_{21})(C{\equiv}NC_6H_4C_6H_4OC_6H_{13})]$.

In 2010, Kuchison and co-workers reported gold(I) complexes with a terthiophene ligand (**Fig. 18**) that emit fluorescence. Gold(I) complexes **31** and **32** are emissive at room temperature in dichloromethane solution while the complex **33** is non-emissive. The lifetimes of the emissions from both complexes were less than 50 ps, which is attributed to the terthiophene derivative.[52-53] Gold(I) complex **31** has emission at 425 and 479 nm with a small quantum yield of 0.016, meanwhile, the quantum yield of complex **32** was twice that of complex **31** with emission at 447 and 475 nm. The generally low quantum yield is most likely to be due to the heavy atom effect.[54] Although complex **33** does not emit at room temperature, interestingly it is emissive at low temperature, 85 K. Nonetheless, the intensity of its emission decreases with increasing temperature. The authors mentioned that the emission (ligand-based) is fluorescence instead of phosphorescence based on the following three observations namely a small Stokes shifts, short emission lifetime and the identical emission spectra to that of the terthiophene ligand even at low temperature.[55]

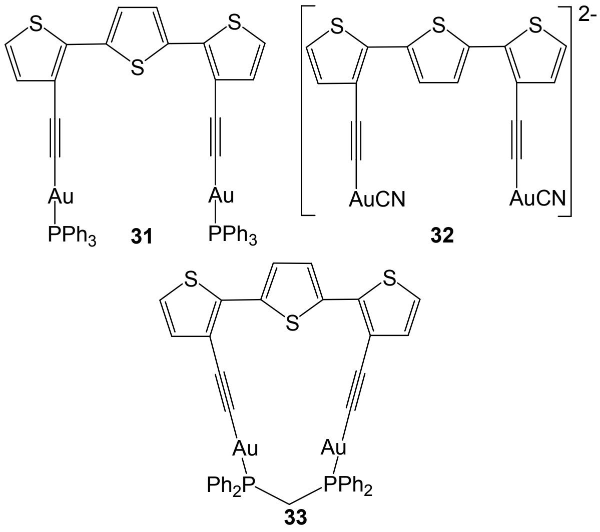


Fig. 18 The structure of gold(I) complexes with terthiophene ligand.

Conclusions

This paper has reviewed the fluorescent processes in transition metal complexes and its photophysical properties. In many cases, the photophysical properties of these complexes have been extensively studied especially using low temperature and singlet oxygen sensitization experiments, and of course, DFT calculations. Indeed, intensive fluorescence from a transition metal complex is a possible process. This is due to the fact that the fluorescence rate is competitive to the ISC process,[21,25] and a lack of π interaction between metal and ligand, causes a minimum metal centre contribution in the photophysical processes.[30,36] Due to these reasons, most of the fluorescence in the transition metal complexes is from the ligand-based fluorescence which can be seen from the examples of two cadmium complexes **4** and **5**,[24] two rhenium complexes **6** and **7**,[25] the platinum complexes[29,30] and gold complexes.[51,55]

Thermal activated delayed fluorescence (TADF) has been observed in the cases of $[Pt(binap)_2]$[45] and copper(I) complexes[37,39-43] The emission is actually due to the thermal population back from the triplet excited state to the singlet excited state. Indeed, the metal centre plays its role as the heavy atom, but the triplet and singlet excited states are too close to each other in energy (small singlet-triplet splitting), and therefore a thermal population process becomes more favourable. Importantly, the emission lifetime of delayed fluorescence is in the microsecond timescale, which may cause confusion to the researchers if no further photophysical experiments are conducted.

Meanwhile, another interesting luminescence was observed called fluorescence-phosphorescence dual emissions, which have been found in cadmium(II) polymer complex[23] and several platinum(II) complexes.[29b,32-24] The structural perturbations in the complex, such as the addition of a ring system, e.g. thiophene, or introducing a large ligand, can lead to an increase in the singlet-triplet splitting and hence, decrease the ISC rate. In addition to that, structural perturbations would also indirectly lower the metal participation in the frontier orbitals and diminish the SOC effect.

Given the vast examples of fluorescent complexes shown above, common perspective that phosphorescence should be observed due to the heavy atom effect exerted by the late transition metals is no longer definite. We intend to emphasize that metal participation in the frontier orbital is the main factor that determines the types of emission from a metal complex. This could be resulted from the interaction of metal centre with their ligand. However, so far none of the papers report in detail about the indicator that can represent the interaction between the metal and ligand. During the reviewing process, we only found two brief discussions about the bond length between metal and ligands in relation to the metal and ligand interaction. Juris et al. (1988) has stated that the bond length of Ru–N for $[Ru(bpy)_3]^{2+}$ (205.6 pm) is relatively shorter than that of $[Ru(NH_3)_6]^{2+}$ (210.4 pm) due to the backbonding from Ru to the π^* orbitals of bpy ligands.[5] In addition, Lentijo (2010) also mentioned that the Pt–C bond length for complex **13** is mainly due to the σ-interaction between Pt and ligand.[30]

Further insight into the photophysical properties especially fluorescence in transition metal complexes is indeed very important for different applications in respective field. For example, the efficiency of current organic light emitting diode (OLED) devices can be increased if TADF is present. The emission from the triplet state with long emission decay time will affect the performance of the device due to saturation effects. Indeed, TADF creates a platform for singlet harvesting effect with high radiative rates and short decay time, which is preferred in OLED illumination devices as it minimized the efficiency roll-off of the OLED.[40]

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An insight into fluorescent transition metal complexes

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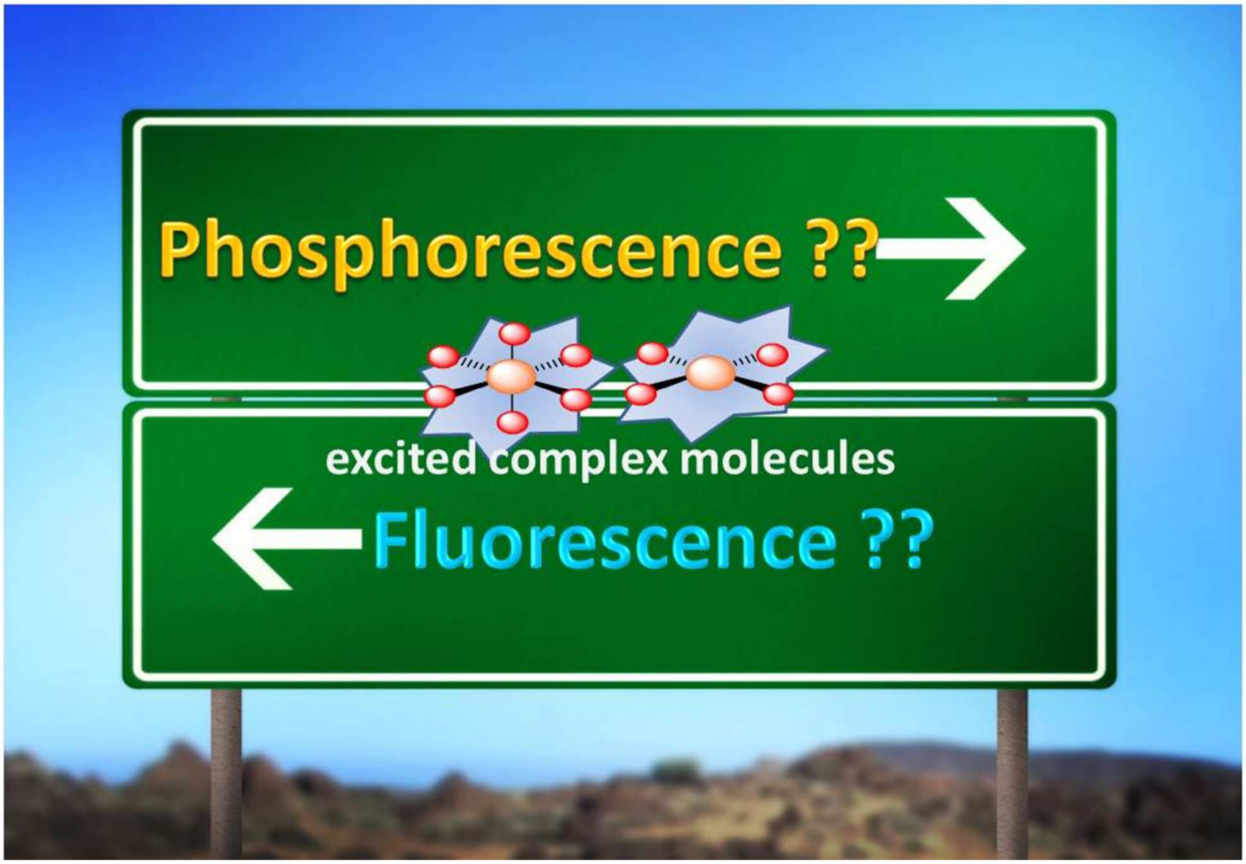

The emission from a transition metal complex is usually produced from triplet excited states. Due to strong spin-orbit coupling (SOC), fast conversion of singlet to triplet excited states via intersystem crossing (ISC) is facilitated. Hence, in transition metal complexes, emission from singlet excited states is not favoured. Despite this, a number of examples of transition metal complexes that fluoresce with high intensity have been found and some of them were even comprehensively studied. In general, three common photophysical characteristics are used for the identification of fluorescent emission from a transition metal complex, these are: emission lifetimes on the nanosecond scale; a small Stokes shift; and intense emission under aerated conditions. For most of the complexes reviewed here, singlet emission is the result of ligand-based fluorescence, which is the dominant emission process due to poor metal-ligand interactions thus lead to a small metal contribution in the excited states, and a competitive fluorescence rate constant when compared to ISC rate constant. On top of pure fluorescence from metal complexes was being concerned, another two types of fluorescent emissions were also reviewed namely delayed fluorescence and fluorescence-phosphorescence dual emissions. Both emissions also have their respective unique characteristics and being discussed in this perspective.