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Review

Luminescence platinum(II) terpyridyl complexes—From fundamental studies to sensory functions

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Contents

Abstract

Different types of luminescent platinum(II) terpyridyl complexes, $[Pt(trpy)X]^{+/2+}$ (X = anionic or neutral ligand), have been designed, synthesized and characterized. Their electronic absorption and luminescence behaviour has been investigated. Through systematic variation of the ligands, their electronic absorption properties and emission origin have also been elucidated. By the judicious design and choice of the ancillary ligand $X^{0/-}$, some of these complexes could be employed as potential chemosensors as well as biomolecule labeling agents.

Keywords: Platinum(II); Luminescence; Terpyridine; Chemosensor

1. Introduction

Square planar platinum(II) complexes with coordinate-unsaturation have received a great deal of interest due to their capability to exhibit metal···metal interactions. One of the widely studied complexes is the dinuclear platinum(II) complex, $[Pt_2(POP)_4]^{4-}$, which exhibits rich luminescence and photochemistry associated with the presence of Pt···Pt interaction as a result of the close separation between the two anions of 2.925 Å [1]. Since the first report on the preparation and characterization of the so-called Magnus' salt, $[Pt(NH_3)_4][PtCl_4]$, in 1828, extensive optical investigations of such complexes have been made due to the surprising green colour associated with the presence of the Pt···Pt interaction, when compared to the colourless $[Pt(NH_3)_4]^{2+}$ and the pink $[PtCl_4]^{2-}$ ions [2]. Recently, numerous double salts of platinum(II)–platinum(II), $[Pt(CNR)_4][Pt(CN)_4]$, have been shown to exhibit interesting vapochromic and vapoluminescence behaviour, which is presumably attributed to the change of Pt···Pt interaction upon sorption of guest vapor [3–5]. The platinum(II) polypyridyl system has also aroused a growing interest in the past few decades owing to its rich photoluminescence and polymorphism

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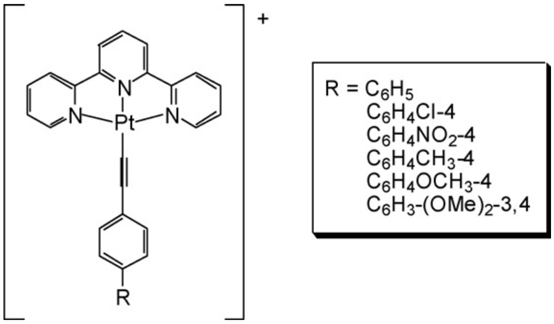
behaviour [6–24], with some of the intriguing spectroscopic features ascribed to the occurrence of Pt···Pt and/or π–π interactions. For instance, two crystal forms of $[Pt(bpy)Cl_2]$, the red form and the yellow form, have been isolated with identical chemical behaviour and they can be inter-converted into each other. The variation in such optical properties was attributed to the different Pt···Pt separation of 3.45 and 4.44 Å, respectively, in the red and yellow form as revealed by X-ray crystallography [6–8].

The platinum(II) terpyridyl system, $[Pt(trpy)X]^{+/2+}$ (trpy = 2,2′:6′,2″-terpyridine; X = anionic or neutral ligand), is another representative class of the platinum(II) polypyridyl system. The synthesis of the chloroplatinum(II) terpyridyl complex, $[Pt(trpy)Cl]Cl{\cdot}2H_2O$, was first reported by Morgan and Burstall [25]. Apart from the subsequent structural and mechanistic investigation [26,27], the complex was found to bind calf thymus DNA through an intercalative interaction involving the planar terpyridyl moiety and the formation of covalent bond with the bases, as reported by Lippard and co-workers [28,29]. Later on, the same group and others reported a variety of the related thiolate analogues, $[Pt(trpy)(SR)]^+$, as well as other mononuclear and dinuclear platinum(II) terpyridyl complexes that exhibit metallointercalation and cytotoxicity behaviour [28–35]. The potential of these complexes as antitumor drugs has also been explored.

The chloroplatinum(II) terpyridyl complex, $[Pt(trpy)Cl]^+$, was reported to exhibit very strong luminescence in the solid state and in low-temperature glass [17,18]. Moreover, the solid-state colours and luminescence energies were dependent on the nature of the counter anions, including PF_6^-, ClO_4^-, Cl^- and $CF_3SO_3^-$, which was attributed to the variations of stacking arrangement that gave rise to different Pt···Pt and π–π interactions [18]. Although, a low-lying triplet [dπ(Pt) → π*(trpy)] metal-to-ligand charge-transfer (^{3}MLCT) excited state is anticipated to show luminescence, no detectable emission was observed in its solution state at room temperature due to the quenching of the ^{3}MLCT state by the thermally accessible ^{3}d–d excited state via non-radiative decay [9]. The introduction of various substituents on the 4′-position of the terpyridine ligand on $[Pt(4'\text{-R-trpy})Cl]^+$ greatly enhances their luminescence properties by rendering the ^{3}MLCT excited state lower-lying than the non-emissive ^{3}d–d excited state or through the incorporation of intra-ligand character into the excited state [17,22–24].

In this review, we describe efforts that mainly focus on the studies of numerous platinum(II) terpyridyl complexes, $[Pt(trpy)X]^{+/2+}$, with various anionic or neutral ancillary ligand X, including alkynyl, thiolato and phosphino groups, prepared by this laboratory. Through the systematic variation of different substituents on the ligand $X^{-/0}$ or functionalization of such ligands, a fundamental understanding of the origin of their photophysical properties has been elucidated. Some of the complexes have also been shown to serve as chemosensors as well as biomolecule labeling agents.

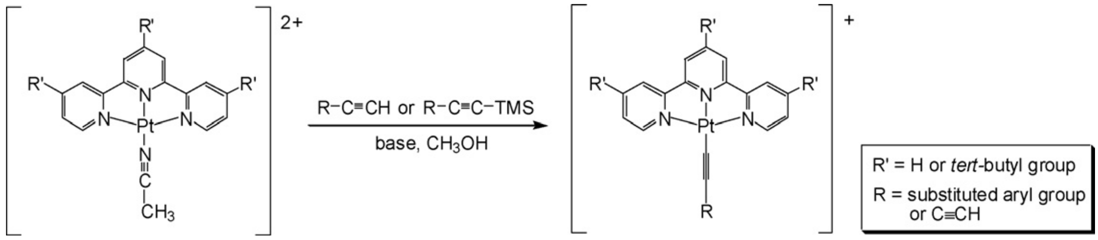


Scheme 1.

2. Mononuclear platinum(II) terpyridyl alkynyl complexes

2.1. Syntheses and characterization

Subsequent to the first report on the synthesis and preliminary photophysical studies of platinum(II) diimine bisalkynyl complexes, $[Pt(N{\wedge}N)(C{\equiv}CR)_2]$ (N∧N = diimine ligand) by Che and co-workers [12], numerous studies on their chemical, photophysical and electroluminescence properties by different research groups have appeared [14,36–42]. Despite numerous reports on the photophysical studies of the platinum(II) terpyridyl system [15–24], related work on the platinum(II) terpyridyl alkynyl system did not appear until 2001 when we reported the first successful synthesis of a series of platinum(II) terpyridyl alkynyl complexes, $[Pt(trpy)(C{\equiv}CR)]^+$ [43] (Scheme 1), which represents a continuation of our efforts on transition metal alkynyl complexes [44–50]. Later on, several laboratories showed their research interests in this novel class of complexes [51–57]. The preparation of such class of complexes was achieved by the reaction of the acetonitrile-coordinated precursor complex, $[Pt(N{\wedge}N{\wedge}N)(MeCN)]^{2+}$, with various organic alkynes under basic condition (Scheme 2). Triethylamine or sodium hydroxide was employed to deprotonate the acetylenic proton of the terminal alkynes, which



Scheme 2.

subsequently replaced the labile acetonitrile ligand to form the corresponding platinum(II) alkynyl complexes. Alternatively, potassium fluoride could also be used in the reaction of the precursor complex, $[Pt(N\wedge N\wedge N)(MeCN)]^{2+}$, with the respective trimethylsilyl-protected alkynes, R-C≡C-TMS, for the deprotection and deprotonation by a one-pot reaction under reflux condition in methanolic solution [58,59]. This latter pathway is advantageous in that it can extend the versatility and flexibility of the synthetic methodology by employing the trimethylsilyl-protected alkynes without the need to isolate the deprotected alkyne, which is usually less stable upon prolonged storage. The ^1H NMR spectra of these complexes characteristically showed platinum satellites in the 6- and 6″-proton signals of the terpyridyl ring with $J_{H–Pt}$ coupling constants of ca. 40–45 Hz, which are also observed in other related platinum(II) tridentate ligand system [60,61]. A weak to moderate band at 2110–2125 cm^{-1}, typical of the ν(C≡C) stretching frequency, was observed in their IR spectra. The crystal structures of some of the complexes have been determined by X-ray crystallography. Such platinum(II) terpyridyl alkynyl complexes adopt a distorted square-planar geometry due to the steric demand of the terpyridyl ligand with the fourth coordinating site occupied by the alkynyl moiety. All the bond lengths and bond angles are within the normal range and are comparable to those found in the related platinum(II) terpyridyl and platinum(II) alkynyl systems. Similar to the other platinum(II) polypyridyl complexes, e.g. $[Pt(bpy)X_2]$ and $[Pt(N\wedge N\wedge N)Cl]^+$, short Pt···Pt and π–π separations have been revealed by their crystal packing in some cases, suggesting the presence of appreciable Pt···Pt and π–π interactions [43,62]. Polymorphism behaviour has also been observed in different crystal forms of $[Pt(trpy)(C≡C–C≡CH]^+$ [62].

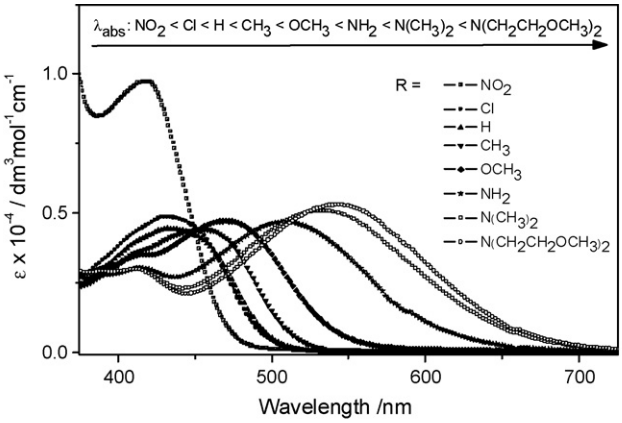


Fig. 1. Electronic absorption spectra of $[Pt(trpy)(C≡C\text{-}C_6H_4\text{-}R\text{-}4)]^+$ with various substituents R in acetonitrile at room temperature.

2.2. *Electronic absorption and emission spectroscopy*

The electronic absorption spectra of the platinum(II) terpyridyl complexes with various substituted phenylethynyl groups, $[Pt(trpy)(C≡CC_6H_4–4–R)]^+$ (R = H, Cl, NO$_2$, CH$_3$, OCH$_3$, NH$_2$, NMe$_2$, N(CH$_2$CH$_2$OCH3)$_2$), in acetonitrile solution exhibited intense absorption bands at 286–350 nm and less intense bands at 412–546 nm. With reference to previous spectroscopic work on platinum(II) terpyridine complexes [20–24], the high-energy intense absorption bands are assigned to intraligand (IL) transitions of the terpyridine and alkynyl ligands. Apart from the absorption band or shoulder at ca. 412–414 nm, additional low-energy absorptions are observed in the range of 432–546 nm. Such low-energy absorption bands are usually shifted more to the red and become more well-resolved in the complexes with electron-donating substituents on the phenylethynyl ligand, i.e. R = CH$_3$, OCH$_3$, NH$_2$, NMe$_2$, N(CH$_2$CH$_2$OCH$_3$)$_2$. Their electronic absorption spectra in the low-energy absorption region are shown in Fig. 1. According to the previous spectroscopic studies on related platinum(II) terpyridyl systems, $[Pt(trpy)X]^+$ (X = Cl, Br, SCN, N$_3$, NH$_3$, PPh$_2$R, NC$_5$H$_4$C≡CR), where no significant shifts in the energy of the low-energy [dπ(Pt) → π*(trpy)] MLCT absorption band at ca. 400 nm were observed [17,63], the bands at 412–414 nm are accordingly assigned as a [dπ(Pt) → π*(trpy)] metal-to-ligand charge transfer (MLCT) transitions. On the other hand, the low-energy absorption bands at 432–546 nm are assigned to a [π(C≡C) → π*(trpy)] ligand-to-ligand charge-transfer (LLCT) transition, with mixing of some MLCT contribution, on the basis of the observation that there was a dramatic red shift of the low-energy absorption band for the complexes $[Pt(trpy)X]^+$ when X = I and SR, and such low-energy absorption was tentatively assigned as LLCT transition [64,65]. As a result of the possible extensive mixing between metal and/or ligand localized orbitals in these complexes, a transition of predominantly LLCT character mixed with some MLCT contribution has accordingly been assigned to these lowest energy absorption bands. In general, the stronger the electron-donating ability of the alkynyl ligand is, the lower will be the energy of the lowest energy absorption. The dependence of the absorption energy on the nature of the alkynyl ligands is in the order R = NO$_2$ > Cl > H > CH$_3$ > OCH$_3$ > NH$_2$ > N(CH$_3$)$_2$ > N(CH$_2$CH$_2$OCH$_3$)$_2$, which is in line with the assignment of a transition of predominantly LLCT character with some mixing of a MLCT character. The sensitive dependence of the absorption energy on the R substituents of the alkynyl ligands has also been demonstrated from the plot of the energy of this low-energy absorption band versus the Hammett σ^+ value, in which a slope of about 2200 cm^{-1}/σ^+ was obtained, indicating the substantial involvement of the alkynyl ligand in the transition (Fig. 2). Due to its better solubility in acetonitrile solution, the BF$_4$-salt of $[Pt(trpy)(C≡C\text{-}C_6H_5)]^+$ was subjected to a concentration-dependent electronic absorption spectroscopic study [66]. Different concentrations of $[Pt(trpy)(C≡C\text{-}C_6H_5)]BF_4$ in acetonitrile were prepared, ranging from 5×10^{-3} to 5×10^{-5} M, and the electronic absorption spectra of each concentration were recorded (Fig. 3). The observation of growth of an absorption tail beyond 500 nm for concentrated sample solutions, together with the non-linear plot of absorbance against concentration that deviated from Beer's law (Fig. 3, inset), suggested that ground state complex aggregation occurs in acetonitrile solution at concentrations $>10^{-3}$ M. The electronic absorption at $\lambda > 500$ nm is assigned as a metal–metal-to-ligand charge-transfer (MMLCT) transition, resulting from the presence of intermolecular Pt···Pt

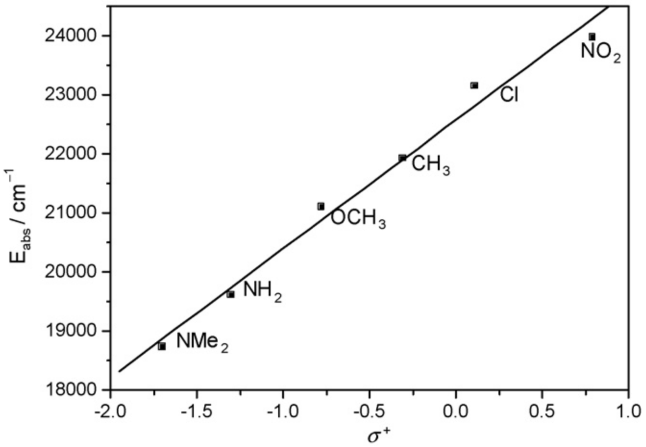


Fig. 2. Plot of the energy of the lowest energy absorption band vs. the Hammett σ^+ value for $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}R\text{-}4)]^+$ (R = OCH_3, CH_3, Cl, NO_2, NH_2 and NMe_2) (■) and its linear least-squares fit (—). Reproduced with permission from ref. [58].

contacts and π–π interactions in solutions of such high concentrations. Similar results have been reported in the concentration studies of other related platinum(II) terpyridyl systems [18,30].

Unlike the chloro-counterpart, $[Pt(trpy)Cl]^+$, which is non-emissive in the solution state at ambient temperature, most of the platinum(II) terpyridyl alkynyl complexes were found to exhibit luminescence at 560–665 nm in acetonitrile solution at 298 K. The large Stokes shifts and observed lifetimes in the microsecond range for their emissions are suggestive of an origin of triplet parentage. With reference to the previous spectroscopic studies of other related platinum(II) terpyridyl complexes, together with consideration of the strong electron-donating properties of the alkynyl ligand, an emission origin of a $[d\pi(Pt) \rightarrow \pi^*(trpy)]$ ^{3}MLCT excited state, with some mixing of a $[\pi(C{\equiv}CR) \rightarrow \pi^*(trpy)]$ ^{3}LLCT state, is assigned. Similar to the electronic absorption studies, the emission energies of the complexes in solution were found to depend on the nature of the substituents on the phenyl ring of the alkynyl ligands (Fig. 4). The observation of the emission band of $[Pt(trpy)(C{\equiv}CC_6H_4\text{-}NO_2\text{-}4)]^+$ at highest energy than the others is in line with a ^{3}MLCT excited state origin assignment, since the presence of the electron-deficient nitro group on the alkynyl unit would render the dπ(Pt) orbital lower-lying in energy, leading to a higher energy MLCT emission. The complexes with stronger electron-donating substituents, such as methoxy and amino groups, on the phenyl ring of the alkynyl ligand were non-emissive in acetonitrile solution at 298 K [43,58,59]. The non-emissive behaviour of these complexes may be ascribed to the quenching of the emissive state by photoinduced electron transfer (PET), in which the electron is transferred from the electron-rich methoxy or amino group to the platinum terpyridyl unit to quench the emissive ^{3}MLCT excited state. The quenching of the ^{3}MLCT excited state could also be rationalized by the presence of an energetically accessible or lower-lying non-emissive ^{3}LLCT excited state, as a result of a relatively higher-lying π(C≡CR) orbital due to the presence of the electron-donating methoxy or amino substituent. The concentration-dependent emission properties of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_5)]BF_4$ in acetonitrile were also investigated within the concentration range 10^{-6} to 10^{-3} M. At concentrations higher than 10^{-3} M, a new emission band appeared with λ_{em} beyond 850 nm and the corresponding excitation spectra for this new band exhibited a tail at about 650 nm. According to the electronic absorption studies showing a growth of an absorption tail beyond 500 nm at similar conditions, this new emission band was assigned to be derived from the ^{3}MMLCT excited state due to the Pt···Pt contacts and π–π interactions resulting from aggregate formation.

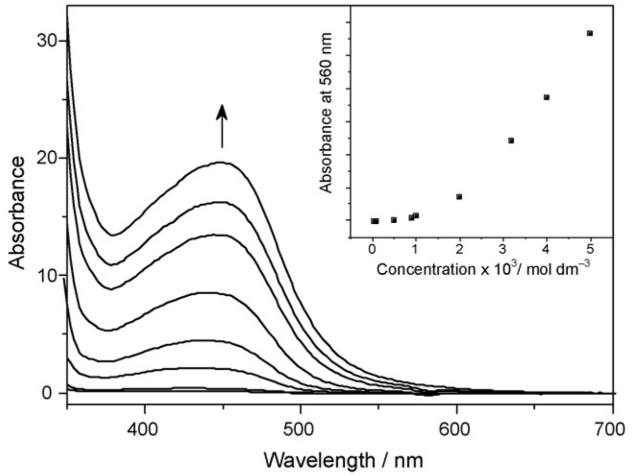


Fig. 3. UV–vis absorption spectroscopic changes of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_5)]BF_4$ as the concentration is increased from 5×10^{-3} to 5×10^{-5} M. *Inset*: Plot of absorbance at 560 nm as a function of concentration. Reproduced with permission from ref. [66].

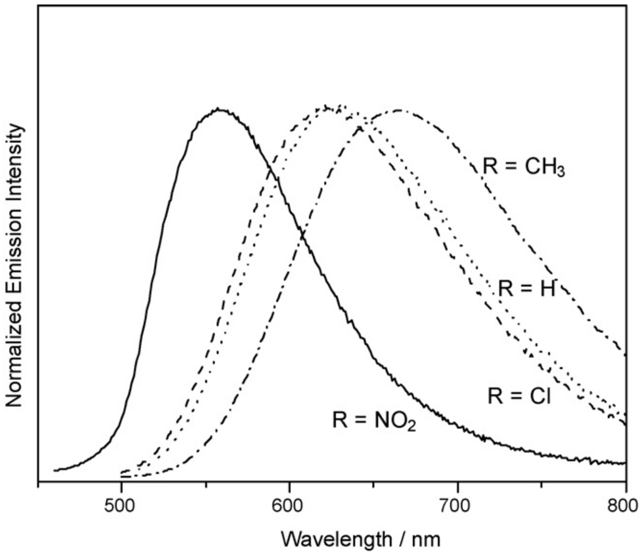
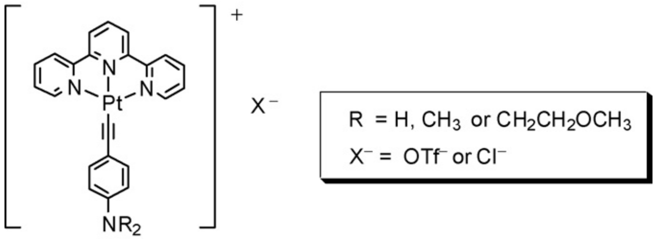


Fig. 4. Normalized solution emission spectra of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}R\text{-}4)]^+$ [R = H (···), Cl (– –), CH_3 (– · –) and NO_2 (—)] in acetonitrile at 298 K. Reproduced with permission from ref. [43].



$R = H, CH_3$ or $CH_2CH_2OCH_3$
$X^- = OTf^-$ or Cl^-

Scheme 3.

3. Platinum(II) terpyridyl complexes with functionalized ancillary ligand

3.1. Amino-substituted phenylethynyl ligand

Organic pH sensors have been well known for a long time and the corresponding inorganic pH sensors based on the use of transition metal complexes has attracted growing interest for the past decade. Among the systems studied, most exhibit a luminescence response at various acid concentrations, with limited examples showing drastic electronic absorption spectroscopic changes. In light of the strong dependence of the spectroscopic and photophysical properties of the platinum(II) terpyridyl alkynyl complexes on the nature of the substituents on the phenylethynyl ligand, a series of platinum(II) terpyridyl alkynyl complexes, $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NR_2\text{-}4]X$ [$R = N(CH_2CH_2OCH_3)_2$, $N(CH_3)_2$, NH_2; X = trifluoromethanesulfonate (OTf^-) or chloride (Cl^-)], with various amino-substituted alkynyl ligands as well as with different counter anions were designed and synthesized for the exploitation of their potential as colorimetric and luminescent inorganic-based pH sensors [58] (Scheme 3). The synthetic methodology is the same as described in Section 2.1 and the complexes with chloride anion were prepared, from the metathesis reaction with lithium chloride, for the spectroscopic studies in aqueous solution.

As mentioned in Section 2.2, the electronic absorption spectra of the complexes with the OTf^- anion exhibited a low-energy absorption band at about 510–546 nm in acetonitrile, assignable to the $[\pi(C{\equiv}C) \rightarrow \pi^*(trpy)]$ LLCT transition mixed with $[d\pi(Pt) \rightarrow \pi^*(trpy)]$ MLCT character. This LLCT/MLCT absorption band of the complex with the $N(CH_2CH_2OCH_3)_2$ group was the lowest in energy, compared to the others with $N(CH_3)_2$ and NH_2 substituents, since this strong electron-donating group would raise the energy of the $\pi(C{\equiv}C)$ orbital to the largest extent. This low-energy absorption is responsible for the characteristic purple colour of these solutions. For those complexes with chloride anion, a similar low-energy absorption band at 488–520 nm was also observed in their electronic absorption spectra in aqueous solution. A negative solvatochromism was observed for this low-energy LLCT absorption band, where a blue shift was observed in aqueous solution when compared to that in acetonitrile. Similar behaviour has also been reported in other platinum(II) polypyridyl systems [23,40,42,64]. All these complexes were found to be non-emissive in fluid solution or in the solid state, ascribed to the quenching process by the lower-lying non-emissive ^{3}LLCT state as well as by reductive electron transfer due to the presence of the amino functional group.

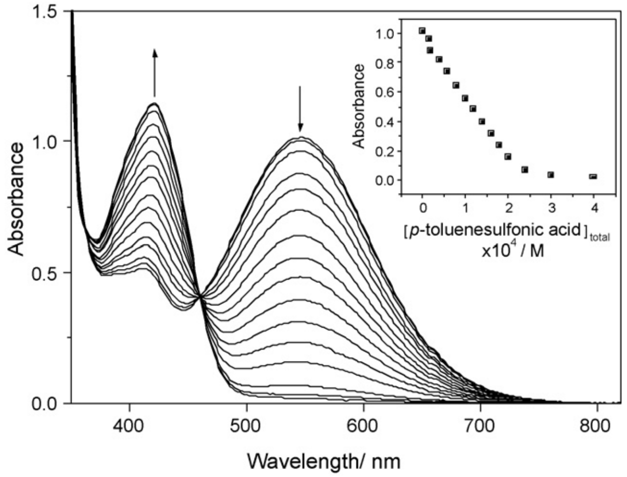


Fig. 5. UV–vis absorption changes of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}N(CH_2CH_2OCH_3)_2\text{-}4]OTf$ (concentration = 1.96×10^{-4} M) in acetonitrile (0.05 M $^nBu_4NPF_6$) with increasing *p*-toluenesulfonic acid content. *Inset*: Plot of absorbance at 546 nm against the total concentration of *p*-toluenesulfonic acid content. Reproduced with permission from ref [58].

All these complexes showed dramatic colour changes and emission enhancement upon the addition of acid, both in organic and in aqueous media. In acetonitrile solution, the complexes with the OTf^- anion exhibit a drastic colour change from purple through orange to yellow upon addition of *p*-toluenesulfonic acid. Such colour changes could be inferred from the corresponding electronic absorption studies, in which the low-energy LLCT absorption bands drop in absorbance with a concomitant growth in the higher energy MLCT absorption band, leading to a blue shift in the absorption energy. A well-defined isosbestic point was observed at various concentrations of *p*-toluenesulfonic acid, suggestive of a clean conversion of the complexes to their protonated species. The electronic absorption spectroscopic changes of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}N(CH_2CH_2OCH_3)_2\text{-}4]$ OTf in acetonitrile with increasing *p*-toluenesulfonic acid content are shown in Fig. 5. Repeated cycles of such reversible colour changes were demonstrated upon alternate addition of *p*-toluenesulfonic acid and triethylamine into the complex solutions. Protonation of the amino substituents results in significant drops of their electron-donating abilities, accounting for the dramatic colour changes since the low-energy LLCT absorption bands are very sensitive to the nature of the substituents on the alkynyl ligand. In addition to the electronic absorption spectroscopic changes, a remarkable luminescence enhancement at about 580 nm was also observed upon addition of *p*-toluenesulfonic acid to the corresponding complex solutions. Based on the assignment made for the luminescence origin of the mononuclear platinum(II) terpyridyl alkynyl system described in Section 2.2, such luminescence is similarly assigned as derived from excited states of a $[d\pi(Pt) \rightarrow \pi^*(trpy)]$ ^{3}MLCT/$[\pi(C{\equiv}C) \rightarrow \pi^*(trpy)]$ ^{3}LLCT origin. Fig. 6 shows the luminescence spectroscopic traces of $[Pt(trpy)(C{\equiv}C\text{-}C_6H_4\text{-}N(CH_2CH_2OCH_3)_2\text{-}4]$ OTf in acetoni-

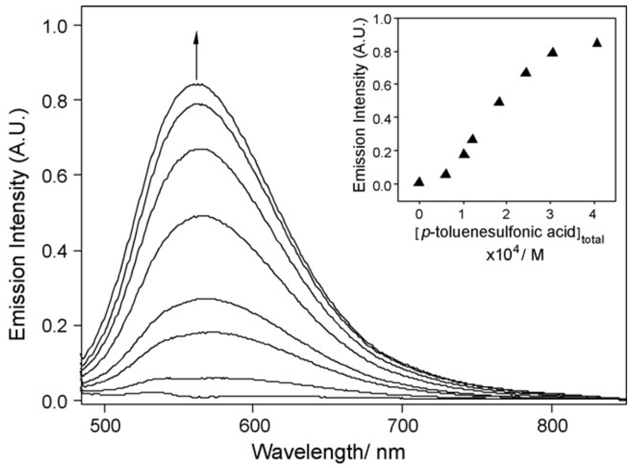


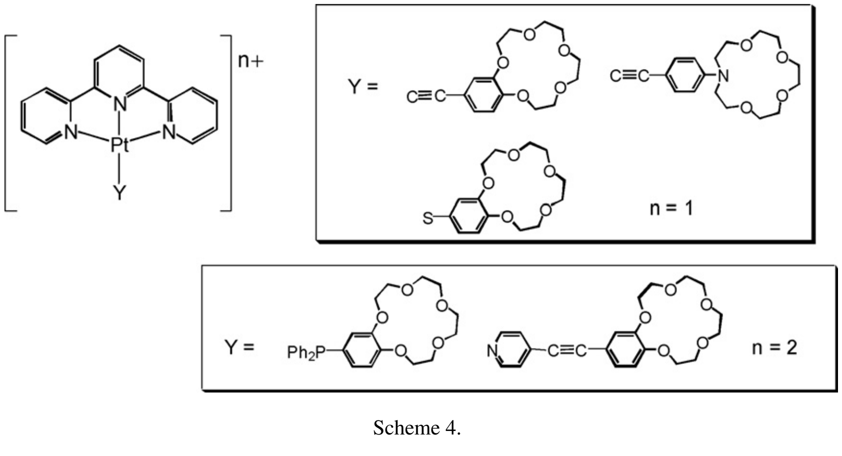
Fig. 6. Emission spectroscopic traces of [Pt(trpy)(C≡C-C_6H_4-N(CH_2CH_2 OCH_3)$_2$-4]OTf (concentration = 1.77 × 10^{-4} M) in acetonitrile with increasing *p*-toluenesulfonic acid content. *Inset*: Plot of relative emission intensity at 563 run against the concentration of *p*-toluenesulfonic acid. Reproduced with permission from ref. [58].

trile with increasing *p*-toluenesulfonic acid content. According to the explanation for the non-emissive behaviour of the unprotonated species, the switching on or revival of luminescence, upon protonation of the amino group, is attributed to the blocking of quenching pathway resulting from the blue shift of the ^{3}LLCT excited state as well as the elimination of the reductive electron transfer ability of the amino substituents. On the other hand, the corresponding electronic absorption spectroscopic studies of the complexes with chloride salt were employed for the determination of the pK_a in aqueous buffer solutions. The pK_a values of [Pt(trpy)(C≡C-C_6H_4-N($CH_2CH_2OCH_3$)$_2$-4]Cl, [Pt(trpy)(C≡C-C_6H_4-N(CH_3)$_2$-4]Cl and [Pt(trpy)(C≡C-C_6H_4-NH_2-4]Cl, were found to be 3.55, 2.29 and 3.22, respectively. A similar blue shift in the electronic absorption spectra as well as luminescence enhancement, were also observed upon decreasing the pH values of the buffer solution. These observations demonstrate the abilities of these complexes to function as colorimetric and luminescence pH sensors with dramatic colour changes and luminescence enhancement upon introduction of acid.

3.2. Crown ether-containing phosphine, thiolate and alkynyl ligand

The host–guest chemistry of crown ethers and other related inclusion compounds has been of growing interest in view of the search for new molecular sensors and probes. Although, the molecular recognition of crown ether compounds with organic fluorophoric units has been extensively studied based on fluorescence signaling, the utilization of transition metal complexes as luminescent metal ion sensors was relatively less explored, with only some examples of ruthenium polypyridyl-containing crown ether complexes as luminescent sensors [67–71]. Despite a number of spectroscopic studies on the platinum(II) terpyridyl systems being known, the utilization of such systems in molecular recognition and chemosensing work is rare, in particular, those related to the crown ether-containing platinum(II) systems and their ion-binding properties. Recently, a number of platinum(II) terpyridyl complexes containing crown ether pendants as chemosensing functionality have been designed and synthesized and their ion-binding behaviour studied. Such complexes can be classified into two main categories, with one series coordinated with anionic ligands, $[Pt(trpy)Y]^+$ [43,58,65] (Y = C≡C-B15C5, C≡C-PA15C5 and S-B15C5), while another series with neutral P- and N-donor crown ether pendants, $[Pt(trpy)Y]^{2+}$ [63] (Y = Ph_2PB15C5 and pyC≡CB15C5) (B15C5 = benzo-15-crown-5; PA15C5 = *N*-phenylaza-15-crown-5) (Scheme 4).

The electronic absorption spectra of [Pt(trpy)(C≡C-B15C5)]$^+$ and [Pt(trpy)(C≡C-PA15C5)]$^+$ showed a low-energy absorption band at about 480 and 546 nm in acetonitrile, respectively. Such absorption bands are comparable to those observed in the analogous crown-free complexes with electron-donating alkoxy- and amino-substituted alkynyl groups and are assigned as the MLCT/LLCT and LLCT transitions, respectively. [Pt(trpy)(S-B15C5)]$^+$ displayed a low-energy absorption band at 572 nm in acetonitrile, assignable to a [pπ(S-B15C5) → π*(trpy)] LLCT transition. All these three complexes have been found to be non-emissive both in fluid solution and in the solid state at room temperature. For the second series of crown ether-containing platinum(II) terpyridyl complexes with phosphino and pyridyl ligands, their



Scheme 4.

lowest-energy absorption bands occur at a relatively high-energy region of 370–390 nm, attributed to [d$\pi \rightarrow \pi^*$(trpy)] MLCT transition. Only [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ shows a high-energy emission at 440 nm in acetonitrile at 298 K, assignable to the metal-perturbed ligand centered phosphorescence, while its room-temperature solid-state luminescence is located at 580 nm and is tentatively assigned as originating from a [dπ(Pt) $\rightarrow \pi^*$(trpy)] ^{3}MLCT state. Both [Pt(trpy)(Ph$_2$PB15C5)]$^{2+}$ and [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ in low-temperature glass show a vibronic-structured band at 460–472 nm with progressional spacings of about 1300 cm^{-1}, typical of the skeletal vibrational frequency of the terpyridine ligand and are therefore assigned as the metal-perturbed IL phosphorescence of terpyridine.

The cation-binding properties of such crown ether-containing platinum(II) terpyridyl complexes have been studied by electronic absorption and luminescence spectrophotometries, as well as ^{1}H NMR spectroscopy in some cases. In general, a blue shift of the low-energy absorption band was observed upon addition of various metal cations, such as Na$^+$, Li$^+$, Mg^{2+}, Ca^{2+}, Cd^{2+} and Zn^{2+}, to the complex solutions. Fig. 7 shows the electronic absorption spectroscopic traces upon addition of sodium cations to a dimethylformamide solution of [Pt(trpy)(C≡C-B15C5)]$^+$, in which a well-defined isosbestic point was observed. No such spectroscopic changes were observed in the control experiment with the use of the crown-free control complex, confirming that the spectroscopic changes could not be due to ionic effects and required the presence of the crown moiety for the ion-binding. The observed blue shift in the low-energy MLCT/LLCT absorption band upon ion-binding is likely to be a result of the complexation of metal ions to the crown ether moiety, which would decrease the electron-donating ability of the alkynyl ligand, leading to the lowering of the dπ(Pt) orbital energy. For binding of Na$^+$ with [Pt(trpy)(C≡C-B15C5)]$^+$, the log K_s values of 1.40 and 3.76 were obtained in dimethylformamide and acetonitrile solutions, respectively. The smaller stability constant obtained in dimethylformamide is ascribed to the better solvation or stabilization of the sodium cations in the highly polar solvents, leading to the smaller binding affinity. The log K_S values of Li$^+$, Mg^{2+}, Ca^{2+} and Cd^{2+} are 4.09, 4.82, 5.74 and 2.05, respectively, for [Pt(trpy)(C≡C-B15C5)]$^+$ by the determination method of electronic absorption spectrophotometry in acetonitrile solution. Similarly, changes in the electronic absorption spectra of [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ were also observed upon addition of metal cations. Less dramatic blue shifts of the LLCT absorption band were observed for the monovalent metal ions like Li$^+$ and Na$^+$, while the LLCT absorption band at 546 nm was found to diminish together with a growth of MLCT absorption band at 410 nm in the cases of the divalent Mg^{2+}, Ca^{2+}, Cd^{2+} and Zn^{2+} addition. The different spectroscopic changes for mono- and divalent metal ion complexation with [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ are ascribed to the changes in the charge density of the metal cations. A more dramatic electronic absorption spectroscopic change would be envisaged upon coordination of the higher charge density divalent metal cations, which would lead to a stronger interaction with the azacrown moiety (Fig. 8). In the corresponding luminescence studies of their ion-binding behaviour upon excitation at the isosbestic wavelength, only [Pt(trpy)(C≡C-B15C5)]$^+$ exhibited intense luminescence with luminescence enhancement of more than 31- and 8-fold at 634 and 625 nm in acetonitrile upon addition of Ca^{2+} and Mg^{2+} ions, respectively. The luminescence spectroscopic traces of [Pt(trpy)(C≡C-B15C5)]$^+$ in acetonitrile upon addition of Mg(ClO$_4$)$_2$ are shown in Fig. 9. The log K_s values of Li$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, Cd^{2+} and Zn^{2+} are 2.55, 2.11, 3.76, 3.67, 3.08 and 1.60, respectively, for [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ in acetonitrile solution. The higher stability constant for the binding of Cd^{2+} in [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ when compared with [Pt(trpy)(C≡C-B15C5)]$^+$ demonstrated that the nitrogen atom in the azacrown ether moiety would enhance the binding of the softer Cd^{2+} cations based on the hard–soft acid–base principle. For the complex

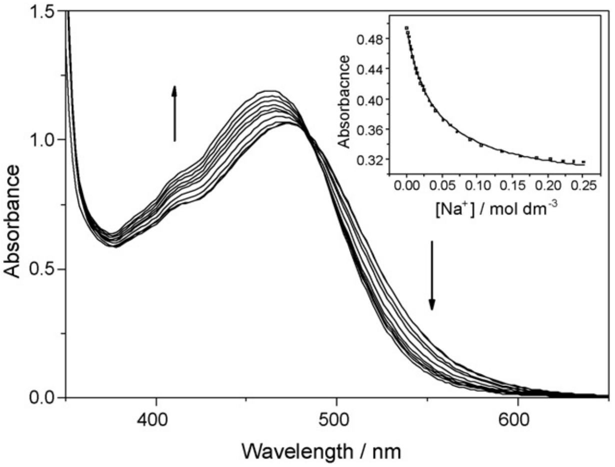


Fig. 7. Electronic absorption spectroscopic traces of [Pt(trpy)(C≡C-B15C5)]$^+$ (2.6 × 10^{-4} M) in dimethylformamide (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of NaClO$_4$. The insert shows a plot of absorbance vs. [Na$^+$] monitored at λ = 530 nm (■) and its theoretical fit (—). Reproduced with permission from ref [43].

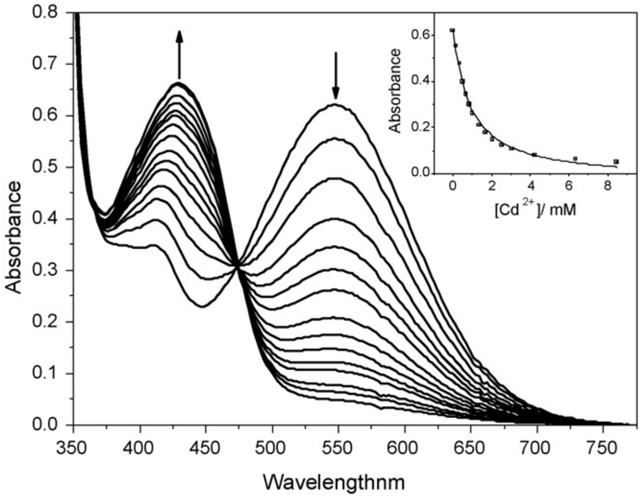


Fig. 8. UV–vis absorption spectroscopic changes of [Pt(trpy)(C≡C-PA15C5)]$^{2+}$ (concentration = 1.3 × 10^{-4} M) in acetonitrile upon addition of Cd(ClO$_4$)$_2$. The insert shows a plot of absorbance vs. [Cd^{2+}] monitored at λ = 550 nm (■) and its theoretical fit (–). Reproduced with permission from ref. [59].

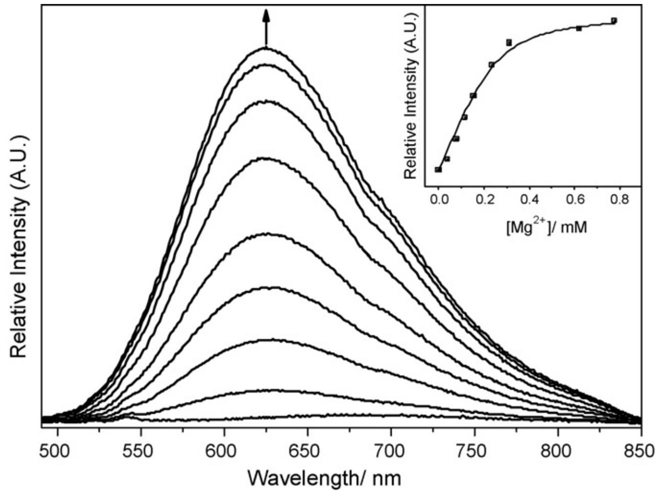


Fig. 9. Luminescence spectroscopic traces of [Pt(trpy)(C≡C-B15C5)]$^+$ (concentration = 2.5×10^{-4} M) in acetonitrile upon addition of Mg(ClO$_4$)$_2$. The insert shows a plot of relative emission intensity at 625 nm against [Mg^{2+}] (■) and its theoretical fit (–). Reproduced with permission from ref. [59].

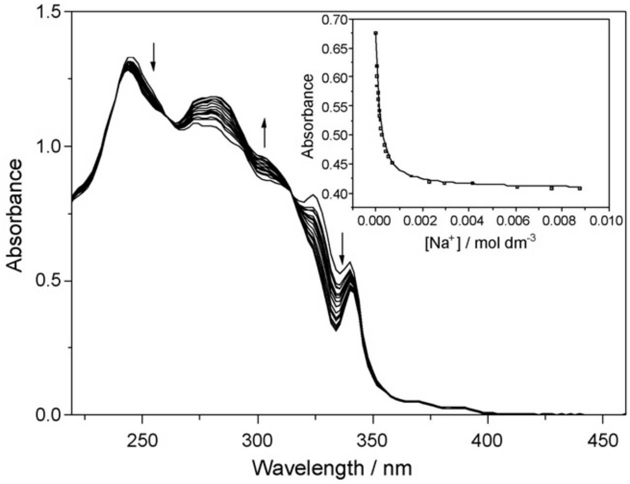
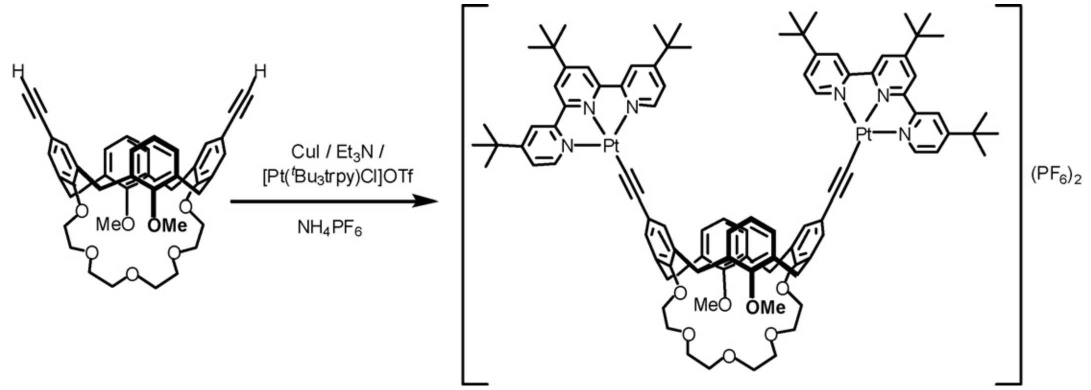


Fig. 10. Electronic absorption spectroscopic traces of [Pt(trpy)(pyC≡CB15C5)]$^{2+}$ (2.5×10^{-5} M) in CH$_3$CN (0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of NaClO$_4$. The insert shows a plot of absorbance against [Na$^+$] monitored at λ = 320 nm (■) and its theoretical fit (—). Reproduced with permission from ref. [63].

[Pt(trpy)(S-B15C5)]$^+$, its electronic absorption spectra exhibited a blue shift of the LLCT absorption band with well-defined isosbestic points upon addition of Na$^+$ cations in acetonitrile solution and a stability constant (log K_s) of 4.01 was obtained. For K$^+$, the lack of well-defined isosbestic points in the electronic spectroscopic change suggested that both complexes with stoichiometries of 2:1 ([Pt(trpy)(S-B15C5)]$^+$:K$^+$) and 1:1 were formed. The corresponding log K_{11} and log K_{21} values of 3.30 and 2.93, respectively, were obtained. In the ion-binding studies of the dicationic complexes, [Pt(trpy)(Ph$_2$PB15C5)]$^{2+}$ and [Pt(trpy)(pyC≡CB15C5)]$^{2+}$, only little observable electronic absorption spectroscopic change was observed upon addition of alkali and alkaline earth metal cations into the solution of [Pt(trpy)(pyC≡CB15C5)]$^{2+}$. Fig. 10 depicts the electronic absorption spectroscopic traces of [Pt(trpy)(pyC≡CB15C5)]$^{2+}$ in acetonitrile upon addition of NaClO$_4$. Such spectrochemical recognition of guest metal ions is confirmed by the absence of spectroscopic changes in the electronic absorption spectra of the respective crown ether-free control complex. Similar to the other complexes with the cavity size of benzo-15-crown-5, [Pt(trpy)(pyC≡CB15C5)]$^{2+}$ showed a 1:1 binding mode for Na$^+$ and a mixture of 1:1 and 2:1 binding for K$^+$ ions, with the log K_s value for Na$^+$ of 3.85, while the log K_{11} and log K_{21} for K$^+$ are 3.40 and 3.44, respectively, in acetonitrile.

3.3. Calix[4]crown-5 alkynyl ligand

There has been a growing interest in the study of calixarenes and calixcrowns because of their unique molecular structures with tunable molecular shapes and conformations, their ease of undergoing chemical transformations, and their well-known supramolecular host–guest chemistry. As an extension of the studies of the utilization of crown ether-containing platinum(II) terpyridyl alkynyl complexes as colorimetric and luminescence probes, the design, synthesis, photophysical and ion-binding properties of a related dinuclear calix[4]crown containing platinum(II) terpyridyl complex, [{Pt(^{t}Bu$_3$trpy)}$_2$L](PF$_6$)$_2$ (L = 5,17-diethynyl-25,27-dimethoxycalix[4]crown-5) have been reported. This complex was synthesized by the reaction of [Pt(^{t}Bu$_3$trpy)Cl]OTf and H$_2$L under Sonogashira conditions, followed by a metathesis reaction withNH$_4$PF$_6$ (Scheme 5) [72].



Scheme 5.

The complex $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ showed a similar electronic absorption spectrum as other platinum(II) terpyridyl alkynyl complexes in acetonitrile, in which the high-energy absorption bands at about 264 nm and 312–338 nm are attributed to the intraligand (IL) transitions of calixcrown ligand and alkynyl/*tert*-butyl-terpyridyl moieties, respectively, while the low-energy absorption band at 408–466 nm is assigned as a $[d\pi(Pt) \rightarrow \pi^*(^tBu_3trpy)]$ MLCT transition, with some mixing of a $[\pi(C{\equiv}C) \rightarrow \pi^*(^tBu_3trpy)]$ LLCT character. The complex was found to be weakly emissive in acetonitrile solution at 738 nm upon excitation at $\lambda > 400$ nm and such luminescence is assigned as derived from the predominantly $[d\pi(Pt) \rightarrow \pi^*(^tBu_3trpy)]$ ^{3}MLCT excited state, mixed with some $[\pi(C{\equiv}C) \rightarrow \pi^*(^tBu_3trpy)]$ ^{3}LLCT character. Since the calix[4]crown moiety could be considered as an electron-rich alkoxy-substituted phenylethynyl ligand, the weakly emissive behaviour can similarly be attributed to the reductive electron transfer quenching by photoinduced electron transfer (PET), similar to other platinum(II) terpyridyl complexes with electron-donating substituted alkynyl ligand [43,58,59].

The ion-binding properties of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ towards Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+} have been studied. A blue shift in energy of the low-energy absorption band, together with well-defined isosbestic points, was observed upon addition of Li^+, Na^+ and K^+ cations into the complex solution in acetonitrile. Fig. 11 shows the electronic absorption spectroscopic traces of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ in acetonitrile upon addition of K^+ at room temperature. With Li^+, Na^+ and K^+, $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ was shown to Exhibit 1:1 complexation and the respective $\log K_s$ values of 1.11, 2.73 and 5.21 were obtained. Very low or negligible complexation towards Ca^{2+} and Mg^{2+} was suggested since there were no observable electronic absorption spectroscopic changes upon addition of these two types of cations. Similar to the electronic absorption spectroscopy, upon inclusion of Li^+, Na^+ and K^+ cations, there are also changes in the luminescence response of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$, which shows a remarkable luminescence enhancement as well as a blue shift in luminescence energy at about 635–685 nm. Fig. 12 shows the emission titration curve of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ with K^+ ions in acetonitrile. Upon cation inclusion, the $d\pi(Pt)$ orbital energy is lowered as a result of the reduced electron-donating ability of the diethynyl-calixcrown moiety which could account for the blue shift in luminescence energy as well as the blocking of reductive PET quenching pathway. Besides, the increase in rigidity of the complex molecule upon formation of inclusion complex would also slow down the non-radiative decay pathways. Electronic absorption and luminescence spectrophotometries gave comparable $\log K_s$ values for $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ with various cations. The K^+/Na^+ and K^+/Li^+ selectivity ratios of 2.5×10^2 and 1.4×10^4, respectively, suggest that $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ binds K^+ ions preferentially over Na^+ and Li^+. Compared to the crown ether-containing platinum(II) terpyridyl alkynyl complexes, an improved selectivity of such calixcrown analogue towards cation is ascribed to the preorganized conformation of the calixcrown with high rigidity over the crown ether unit.

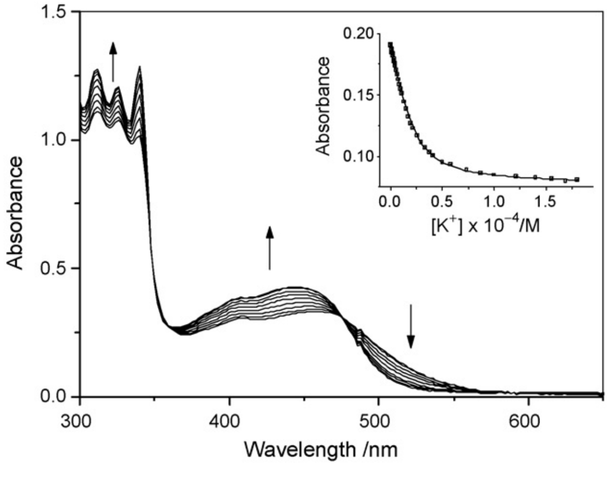


Fig. 11. Electronic absorption spectroscopic traces of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ upon addition of various concentrations of KPF_6 in acetonitrile (0.1 M $^nBu_4PF_6$) at room temperature. *Inset*: A plot of absorbance at 502 nm (■) as a function of the concentration of K^+ ions with theoretical fits. Reproduced with permission from ref. [72].

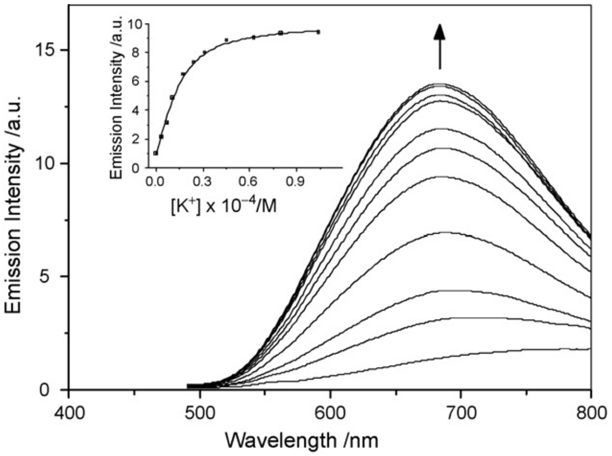


Fig. 12. Corrected emission spectroscopic changes of $[\{Pt(^tBu_3trpy)\}_2L](PF_6)_2$ upon addition of KPF_6 in acetonitrile (0.1 M $^tBu_4NPF_6$). *Inset*: A plot of emission intensity upon excitation at 475 nm (■) as a function of the concentration of K^+ with theoretical fits. Reproduced with permission from ref. [72].

3.4. *Isothiocyanate- and iodoacetamide-substituted pheynylethynyl ligand*

There has been much interest in the search for luminescent transition metal complex systems to serve as biomolecular probes due to their phosphorescence nature with long-lived excited states that can improve the immunoassay performance. Although, the photophysical properties as well as the biological activities of square planar platinum(II) polypyridyl system have been extensively studied, the utilization of this class of platinum(II) complexes as luminescent labeling reagents for biomolecules is very rare, compared with other luminescent transition metal complexes of Ru(II), Re(I), Os(II), Rh(III) and Ir(III) [73–78]. Through the modification of $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NH_2\text{-}4)]^+$, two platinum(II) terpyridyl alkynyl complexes, $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NCS\text{-}4)]^+$ and $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}$

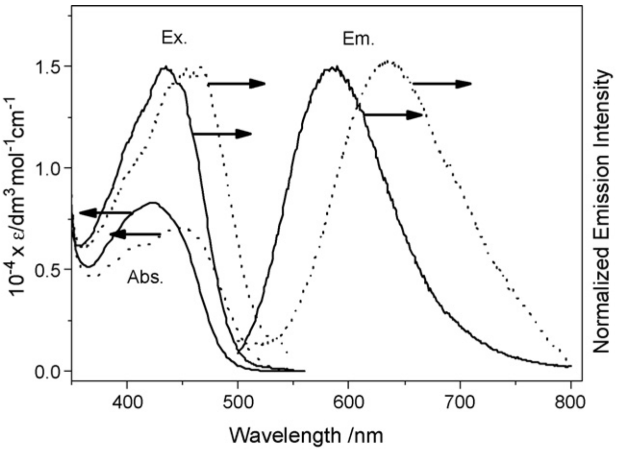


Fig. 13. Electronic absorption (Abs.), excitation (Ex.) and emission (Em.) spectra of $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NCS\text{-}4)]^+$ (—) and $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NHCOCH_2I\text{-}4)]^+$ (· · ·) in acetonitrile at room temperature.

$C_6H_4\text{-}NHCOCH_2I\text{-}4)]^+$, with isothiocyanate and iodoacetamide substituents have been synthesized for luminescence biolabeling based on their ready reaction with the primary amine and sulfhydryl group, respectively, of the biomolecules [79].

The electronic absorption, emission and excitation spectra of the complexes in acetonitrile solution at room temperature are depicted in Fig. 13. Similar to other related systems described earlier, the low-energy absorption bands of $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NCS\text{-}4)]^+$ and $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NHCOCH_2I\text{-}4)]^+$ at 400–488 nm are assigned as a $[d\pi(Pt) \rightarrow \pi^*(^tBu_3trpy)]$ MLCT transition, mixed with a $[\pi(C{\equiv}C) \rightarrow \pi^*(^tBu_3trpy)]$ LLCT transition. Similarly, the intense emission bands at 586–708 nm upon photoexcitation are attributed to the excited states of ^{3}MLCT/^{3}LLCT origin. Human serum albumin (HSA) has been labeled with these biolabels to afford the corresponding bioconjugates (Scheme 6). Similar to their parent labels, both bioconjugates are highly coloured and exhibit luminescence in the visible region upon photoexcitation. The bioconjugate resulting from the isothiocyanate complex is found to emit with a different luminescence colour when compared to its parent label (Fig. 14), while the bioconjugate derived from the iodoacetamide complex is found to emit with a higher luminescence intensity.

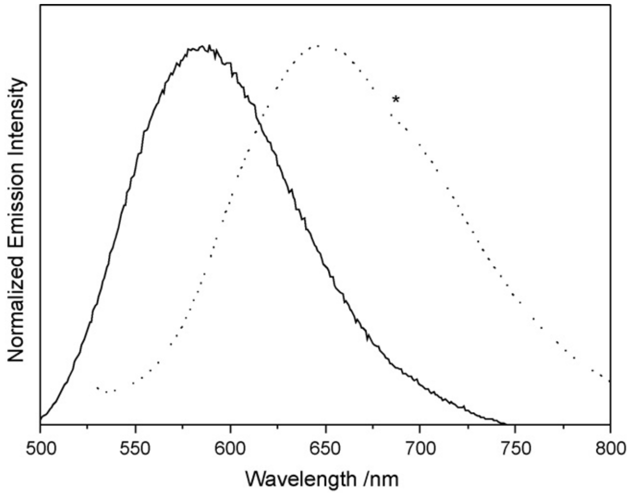
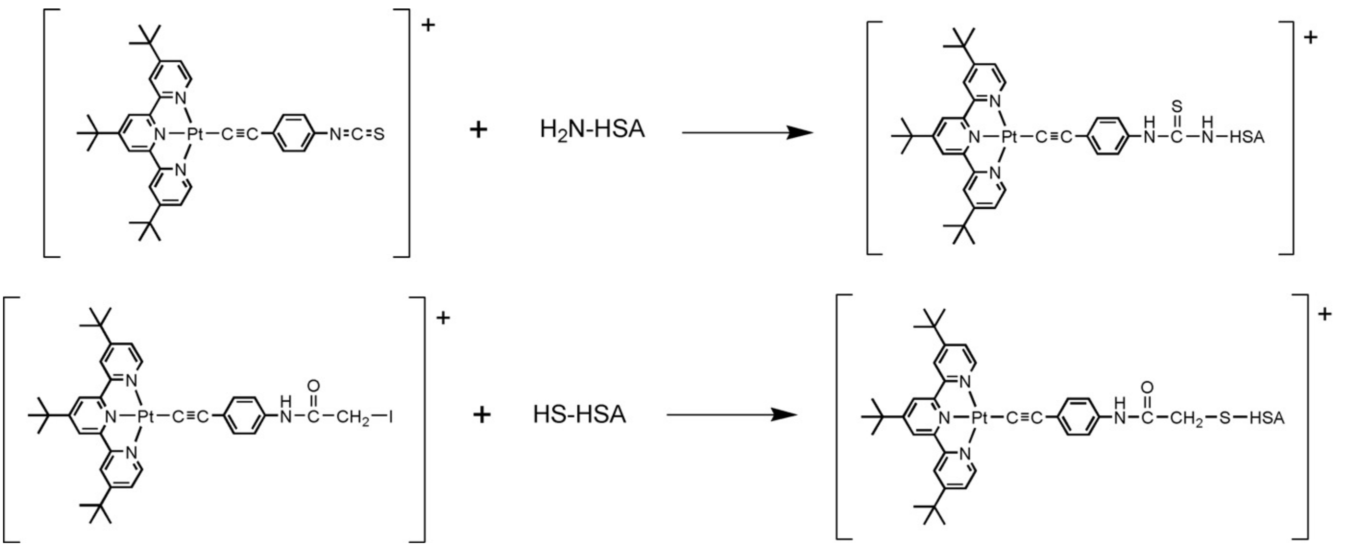


Fig. 14. Emission spectra of $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NCS\text{-}4)]^+$ (—) in acetonitrile at room temperature and $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}NHCSNH\text{-}HSA)]^+$(· · ·) in 50 mM Tris–Cl (pH 7.4) buffer solution at 298 K. The asterisk denotes the instrumental artifact.

4. Concluding remarks

This review summarizes the design, syntheses and photophysical studies of selected platinum(II) terpyridyl complexes of alkynyl, thiolato, phosphino and pyridyl ligands. The fundamental photophysical behaviour of a series of platinum(II) terpyridyl alkynyl complexes, $[Pt(^tBu_3trpy)(C{\equiv}C\text{-}C_6H_4\text{-}R)]^+$, have been discussed. In acetonitrile, the low-energy absorption shoulder observed at 412–414 nm is assigned as a $[d\pi(Pt) \rightarrow \pi^*(^tBu_3trpy)]$ MLCT transition, while the lowest energy absorption band in the range of 432–546 nm is attributed to a $[\pi(C{\equiv}C) \rightarrow \pi^*(^tBu_3trpy)]$ LLCT transi-



Scheme 6.

tion, with mixing of a MLCT character. In contrast to the chloro-counterpart, $[Pt(trpy)Cl]^+$, which is non-emissive in the solution state at ambient temperature, most of the platinum(II) terpyridyl alkynyl complexes were found to exhibit luminescence at 560–665 nm in acetonitrile solution at 298 K. The luminescence origin is suggested to be derived from the excited state of $[d\pi(Pt) \rightarrow \pi^*({}^t\mathrm{Bu_3trpy})]$ ^{3}MLCT, mixed with a $[\pi(C{\equiv}C) \rightarrow \pi^*({}^t\mathrm{Bu_3trpy})]$ ^{3}LLCT character. Some of them, including the thiolate, phosphino and pyridyl analogues, were modified with various functionalities, such as amino, crown ether and calixcrown to exhibit pH and metal cation sensing abilities. In the presence of the various stimuli, their electronic absorption and luminescence spectra were found to show changes to give the respective colorimetric and luminescence sensors. On the other hand, some of these platinum(II) complexes could also function as luminescent labeling reagents for biomolecules to afford the luminescent bioconjugates.

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