Unprecedented formation of an acetamidate-bridged dinuclear platinum(II) terpyridyl complex—correlation of luminescence properties with the crystal forms and dimerization studies in solution†

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An unprecedented acetamidate-bridged dinuclear platinum(II) terpyridyl complex has been isolated in two crystal forms, a red form and a dark form, with different luminescence properties; electronic absorption, emission and ^{1}H NMR studies revealed the presence of a dimerization process in the solution state.

Square-planar platinum(II) polypyridyl complexes have attracted considerable attention due to their rich spectroscopic properties and their potential applications in materials and biomedical sciences.[1–6] The platinum(II) terpyridyl system is one of the most extensively studied classes and most of them exhibit interesting electronic absorption and luminescence behaviours that are associated with the occurrence of metal···metal interaction and/or π–π stacking interactions.[2,3,4b,5a–d] Some dinuclear platinum(II) terpyridyl complexes with the bridging ligand holding the two platinum(II)–terpyridyl planes in close proximity have been studied.[3] Compared to the mononuclear complexes, a new electronic absorption band together with an emission band at lower-energy region were observed in such dinuclear systems, which were ascribed to the presence of Pt···Pt and π–π stacking interactions that led to the formation of these metal–metal-to-ligand charge-transfer (MMLCT) bands and excited states.[1b–f,2a–e,3b,c,5b–d] Herein, we report the unprecedented formation of an acetamidate-bridged dinuclear platinum(II) terpyridyl complex, [{Pt(trpy)}$_2$(μ-η^1:η^1-NHC(=O)Me)](OTf)$_3$ (**1**), from a common precursor complex, [Pt(trpy)(CH$_3$CN)](OTf)$_2$. Its identity and structure have also been confirmed by X-ray crystallography,‡ various spectroscopic techniques and elemental analysis.

Complex **1** was obtained by suspending a solid sample of [Pt(trpy)(CH$_3$CN)](OTf)$_2$ in analytical grade acetone for 3–4 days in air, during which the solid slowly dissolved to give a dark brown solution. Upon slow evaporation of the solvent, dark crystals of **1** were obtained in 80% yield. Dissolution of **1** in hot acetone gave a saturated solution, from which crystals of the red form of **1** (**1**-red) appeared, while crystals of the dark form of **1** (**1**-dark) were obtained from the slow evaporation of a dilute acetone solution of **1**. It is interesting to note that crystals of **1**-red would convert to the dark form of **1** (**1**-dark) upon exposure to air for a while after their removal from the mother liquor. The absence of a methyl

signal in the ^{1}H NMR spectrum of the product prepared from [Pt(trpy)(CD$_3$CN)]$^{2+}$ as the starting material indicated that the acetamidate bridge was derived from the coordinated acetonitrile. Independent reaction of the precursor complex, [Pt(trpy)(CH$_3$-CN)]$^{2+}$ with a small amount of weak base, Et$_3$N, also afforded the same dinuclear complex **1**, suggesting that the formation of **1** was initiated by the hydrolysis of coordinated acetonitrile with trace amounts of base or water in acetone solution.[7]

Fig. 1 (left) shows the crystal structure of the complex cation of **1**-red, in which the two platinum(II)-terpyridyl ([Pt(trpy)]) moieties are linked by the acetamidate bridge to form a molecular clip-like structure. Each platinum(II) atom is in a distorted square-planar geometry and the deviation of the *trans*-N–Pt–N bond angle from 180° [N(1)–Pt(1)–N(3) 161.5(3)° and N(4)–Pt(2)–N(6) 162.8(3)°] is due to the restricted bite angle of terpyridine, commonly observed in related platinum(II) terpyridyl complexes.[2,3,4b,d,5] The bond distances of Pt(1)–N(7) [2.053(6) Å] and Pt(2)–O(1) [2.022(6) Å] are comparable to those found in the related platinum(II)-amidate complexes.[8b,d] The two [Pt(trpy)] coordination planes are essentially parallel and eclipsed to each other, as revealed by the interplanar angle of 7.08° and the torsion angles of N(2)–Pt(1)–Pt(2)–N(5), N(1)–Pt(1)–Pt(2)–N(4), N(3)–Pt(1)–Pt(2)–N(6) and N(7)–Pt(1)–Pt(2)–O(1) [5.49, 9.57, 8.37 and 2.36°, respectively]. The interplanar distance is 3.48 Å, calculated from the average distances of the atoms on the two least-squares planes. This, together with the observation of short Pt···Pt distance [Pt(1)–Pt(2) 3.119 Å] suggested the presence of intramolecular Pt···Pt and π–π interactions.

Crystal packing diagram of **1**-red shows that the complex cations of **1** are arranged in a head-to-tail configuration with
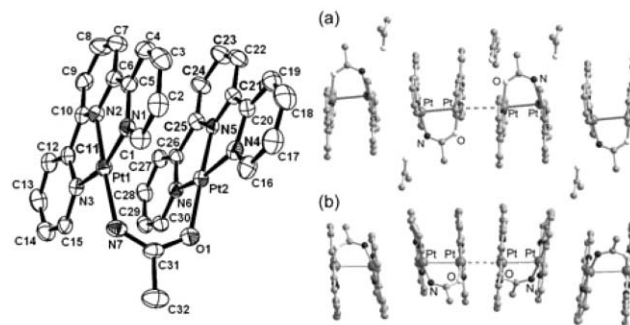
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Fig. 1 (Left) Perspective drawing of the complex cation of **1**-red with atomic numbering scheme. Hydrogen atoms are omitted for clarity. (Right) Crystal packing showing the dimer-of-dimer structure of **1**-red (a) and **1**-dark (b).

respect to each other [N(5)–Pt(2)–Pt(2*)–N(5*) torsion angle, 180°] and are extended along the *a* axis to form a one-dimensional infinite chain with alternating intermolecular Pt(2)–Pt(2*) and Pt(1)–Pt(1*) separations of 3.682 and 4.449 Å, respectively [Fig. 1 (right a)]. For the **1**-dark crystal form, the molecular structure of the complex cation is essentially identical to that of the **1**-red form but the intramolecular Pt⋯Pt contact is comparatively shorter [Pt(1)–Pt(2) 3.063 Å]. It is noteworthy that the complex cations of **1** were found to exist in a tetranuclear dimer-of-dimer structure, in which the platinum(II) atom forms a weak intermolecular Pt⋯Pt bonding interaction with another platinum(II) atom of the adjacent cationic molecule [Pt(2)–Pt(2*) 3.255 Å] and intermolecular π–π stacking is also anticipated with the N(5)–Pt(2)–Pt(2*)–N(5*) torsion angle of 102.11°, while the Pt(1)–Pt(1*) separation of 4.913 Å is too long for any Pt⋯Pt bonding interactions to exist [Fig. 1 (right b)]. Their crystal packings revealed that each formula unit contained 1.5 acetone solvent molecules in the **1**-red form but no solvent molecule was located in the **1**-dark form. The conversion between the two forms from **1**-red to **1**-dark was presumably due to the loss of acetone solvent of crystallization upon standing in air. Noticeably, the darkening of the crystal colour was in line with the decrease in both the intra- and inter-molecular Pt⋯Pt and π–π separations.

Dissolution of both **1**-red and **1**-dark crystals in acetonitrile at room temperature gave identical UV-vis absorption spectra that showed a low-energy absorption band at about 426–478 nm at concentrations below 2×10^{-5} M. With reference to the previous spectroscopic works on the related dinuclear platinum(II) terpyridyl system,[2a,3c,e] the low-energy absorption band is assigned to the dσ*(Pt$_2$) → π*(trpy) metal–metal-to-ligand charge transfer (MMLCT) transition. The absence of such low-energy absorption shoulder in the previous spectroscopic studies of the mononuclear [Pt(trpy)Cl]⁺,[2a,c–e] in which the dπ(Pt) → π*(trpy) metal-to-ligand charge transfer (MLCT) absorption band appeared at about 400 nm, supported the involvement of the Pt⋯Pt interaction and/or π–π stacking in such low-energy electronic transitions.

Upon excitation at $\lambda > 400$ nm, **1** exhibited intense luminescence in both crystal forms at room temperature and at 77 K. The solid-state emission spectrum of **1**-red crystals at room temperature showed a featureless emission band at 690 nm, which is tentatively assigned to be derived from the ³MMLCT excited state (Fig. 2a).
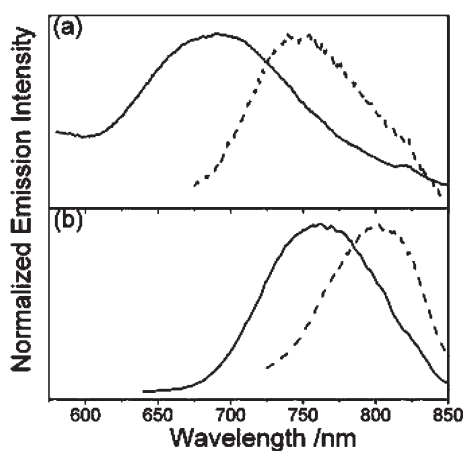

Fig. 2 Uncorrected solid state emission spectra of **1**-red (——) and **1**-dark (– – –) at 298 K (a) and 77 K (b).

Other related dinuclear complexes, such as [{Pt(trpy)}$_2$-(μ-L)]³⁺,[2a,3b,e] and the red-form of [Pt(trpy)Cl](ClO$_4$),[2c] have also been reported to display solid-state emission bands at 700–710 nm at ambient temperature. Similar assignments of a ³MMLCT character have also been made for these complexes in view of the observation of their discrete dimeric structures with short Pt⋯Pt contacts and the shift of the emission energy to the red relative to their monomeric counterparts. Even lower emission energy was observed in the solid-state emission spectrum of **1**-dark at 750 nm at room temperature (Fig. 2a). Since both intermolecular Pt⋯Pt and π–π stacking interactions are present in the crystal form of **1**-dark as revealed in the crystal packing, the 750 nm emission band is attributed to a ³MMLCT excited state of the dimer-of-dimer, which resulted in a shift of the emission band to lower energy relative to that of the **1**-red crystal form that arose from the shorter Pt⋯Pt and π–π separation and hence a greater extent of Pt⋯Pt and π–π interactions. When the temperature was lowered to 77 K, the ³MMLCT emission bands of both **1**-red (762 nm) and **1**-dark (805 nm) in the solid state showed a red shift in emission energy, which could be ascribed to the further shortening of the Pt⋯Pt separation and hence an increased Pt⋯Pt interaction as a result of the lattice contraction upon cooling.

The emission spectrum of **1** in acetonitrile solution at room temperature displayed a structureless emission band at about 600 nm, irrespective of which crystal forms were used. It is likely that the 600 nm emission originates from a ³MMLCT excited state of the dinuclear species with a slight extension of the intramolecular Pt⋯Pt separation in the solution state relative to that in the solid-state, leading to a shift of the MMLCT emission energy to the blue. A related complex, [{Pt(trpy)}$_2$(μ-guanidine)](ClO$_4$)$_3$, was also reported to exhibit an emission band at 620 nm in room-temperature acetonitrile solution and an assignment of a dσ*(Pt$_2$) → π*(trpy) ³MMLCT excited state for this emission origin has similarly been made.[2a,3c,e]

In view of the possible existence of **1** in the solid state as a dimer-of-dimer, the UV-vis absorption spectra of **1** in acetonitrile have been recorded at different concentrations, ranging from 4.5×10^{-5} to 7.5×10^{-3} M. In dilute sample solutions (4.5×10^{-5}–2.0×10^{-4} M), the extinction coefficients of the low-energy absorption region (430–550 nm) were found to be independent of concentration, while an increase in the apparent extinction coefficient in this region was observed for concentrated solutions (4×10^{-4}–7.5×10^{-3} M) (Fig. 3 left). A plot of the absorbance at 458 or 478 nm *vs.* concentration gave a nonlinear relationship that deviates from Beer's law, suggesting that an equilibrium probably exists in solution. This, together with the straight line plot of $[\mathbf{1}]/(A_{480})^{1/2}$ *vs.* $(A_{480})^{1/2}$ (Fig. 3 left insert),[2c,4b] suggested the occurrence of a ground state dimerization process involving a monomer–dimer equilibrium at concentrations $> 4 \times 10^{-4}$ M. Similar to the dimer-of-dimer molecular arrangement revealed in the solid-state crystal packing, some of the cationic dinuclear complexes of **1** may also exist in pairs in concentrated solutions resulting from such monomer–dimer equilibrium. The absorption shoulder at $\lambda > 430$ nm probably originates from a metal–metal-to-ligand charge-transfer (MMLCT) transition arising from such a dimer-of-dimer arrangement. Although the related mononuclear platinum(II) polypyridyl complexes have been shown to undergo solution-state dimerization processes at high concentrations,[2c,4b,5d] to the best of our knowledge, the present study represents the first
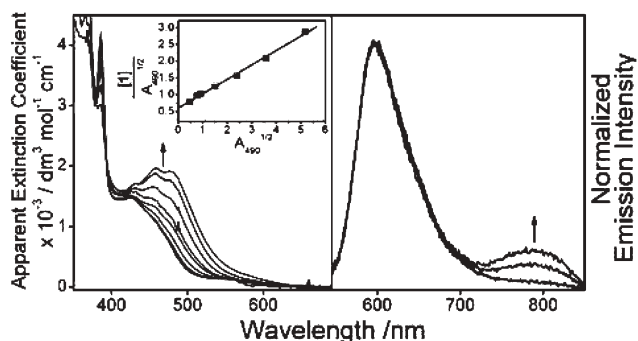
Fig. 3 (Left) Electronic absorption spectra (apparent extinction coefficient) of **1** at different concentrations (4.6×10^{-5}–7.5×10^{-3} M; from bottom to top) in acetonitrile at 298 K. Inset shows the dimerization plot for a monomer–dimer equilibrium. (Right) Uncorrected emission spectra of **1** at different concentrations (1×10^{-4}, 1×10^{-3}, 2×10^{-3} M; from bottom to top) in acetonitrile at 298 K.

of its kind in the observation of a dimer-of-dimer structure in dinuclear platinum(II) polypyridine systems in the solution state. The dimerization constant (K_d) and extinction coefficient of the dimer (ε_d) were estimated to be 605 M^{-1} and 4655 M^{-1}cm^{-1}, respectively, which are comparable to those values reported for the related [Pt(trpy)Cl]$^{+}$.[2c]

In the corresponding studies of the emission properties, a new emission band was formed with emission maximum at around 790 nm in acetonitrile solution at concentrations higher than 1×10^{-3} M (Fig. 3 right), in accordance with the observation of a dimerization process. Based on the UV-vis absorption studies, this new emission origin was suggested to be derived from the ^{3}MMLCT excited state resulting from the dimer-of-dimer species with a larger extent of Pt$\cdots$Pt and π–π interactions. The occurrence of the dimerization process was further supported by concentration-dependent and variable-temperature ^{1}H NMR spectroscopic studies, in which an additional set of terpyridyl signals were observed at more upfield positions in the concentrated or low-temperature samples (Figure S1 and S2 in the ESI).† Similar upfield shifts were evident of π–π stacking interactions found in the aggregate formation of platinum(II) terpyridyl system.[4b,e] A dimerization constant of 565 M^{-1} estimated from concentration-dependent ^{1}H NMR spectroscopic technique is in good agreement with that obtained by the UV-vis absorption studies.

Notes and references

‡ Crystal data of **1**-red (CCDC 297545): $C_{35}H_{26}F_9N_7O_{10}Pt_2S_3$·1.5$C_3H_6O$, $M = 1449.11$, triclinic, $a = 13.743(3)$, $b = 13.814(3)$, $c = 13.969(3)$ Å, $\alpha = 105.61(3)$, $\beta = 106.55(3)$, $\gamma = 98.27(3)°$, $U = 2377.5(9)$ Å^3, $T = 301$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 6.111 mm^{-1}, 17972 reflections measured, 8328 unique ($R_{int} = 0.0376$) which were used in all calculations. The final R was 0.0390 [$I > 2\sigma(I)$]. **1**-dark (CCDC 297546): $C_{35}H_{26}F_9N_7O_{10}Pt_2S_3$, $M = 1361.99$, monoclinic, $a = 34.308(7)$, $b = 13.701(3)$, $c = 24.105(5)$ Å, $\beta = 129.42(3)°$, $U = 8753(3)$ Å^3, $T = 253$ K, space group $C2/c$, $Z = 8$, μ(Mo-Kα) = 6.630 mm^{-1}, 16747 reflections measured, 4913 unique ($R_{int} = 0.0733$) which were used in all calculations. The final R was 0.0736 [$I > 2\sigma(I)$]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606352g

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