

Synthesis and photophysical properties of luminescent platinum(II) complexes with terdentate polypyridine ligands: [Pt(bpqb)X] and [Pt(tbbpppy)X](PF₆) (bpqb-H=1,3-bis(4'-phenyl-2'-quinoliny) benzene; tbbpppy = 4-tert-butyl-1,3-bis(4'-phenyl-2'-quinoliny) pyridine; X=Cl, C≡CC₆H₅, C≡CC₆H₄NMe₂, C≡CC₆H₄NO₂)

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Abstract

A series of square planar platinum(II) complexes, [Pt(bpqb)X] (X=Cl (1), C≡CC₆H₅ (2), C≡CC₆H₄NMe₂-4 (3), C≡CC₆H₄NO₂-4 (4)), [Pt(tbbpppy)X](PF₆) (X=Cl (5), C≡CC₆H₅ (6), C≡CC₆H₄NMe₂-4 (7), C≡CC₆H₄NO₂-4 (8)), bearing terdentate polypyridine ligands have been prepared. Their electronic absorption spectra and emission characteristics at room temperature have been investigated. These complexes display room temperature photoluminescence. The emission energies are sensitive to the nature of the acetylide ligands with different substituents on the phenyl ring. An emission origin of a dπ(Pt) → π*(bpqb or tbbpppy)³MLCT excited state, with some mixing of a π(C≡CR) → π*(bpqb or tbbpppy)³LLCT state, is assigned. All the complexes display two quasi-reversible reduction couples and one irreversible oxidation wave in the cyclic voltammograms. The reactivity of [Pt(bpqb)Cl] with π-acceptor ligands and the X-ray crystal structures of tbbpppy, **1**, and [Pt(bpqb)(PEt₃)₂Cl] (**9**) are also described.

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Keywords: Room temperature luminescence; Platinum(II) acetylide; N[^]C[^]N; N[^]N[^]N

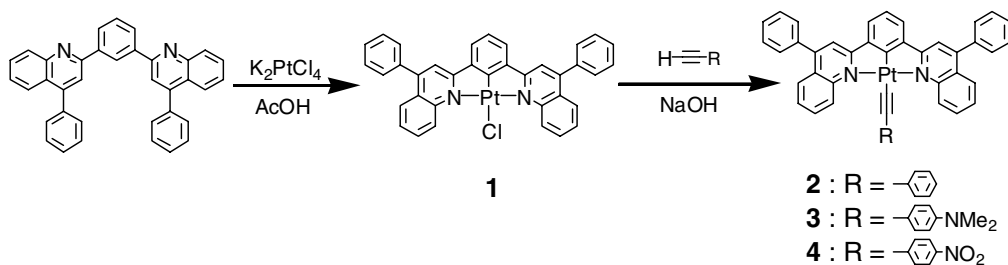
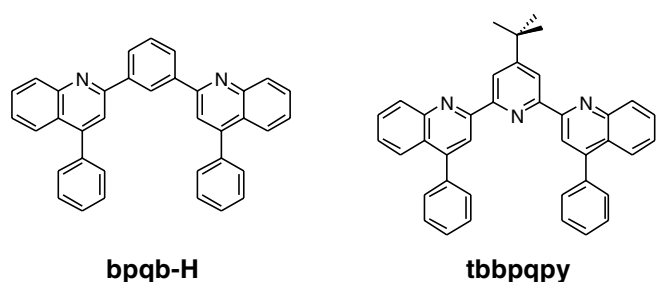
1. Introduction

Square-planar platinum(II) complexes with terdentate monoanionic or terdentate neutral ligands with pyridine units have attracted much attention in recent years, due to their unique photophysical properties [1] and their biological activities [2]. These complexes are known to display a strong tendency towards the formation of high ordered extended linear chains [3] or oligomeric structures [4], leading to the interesting luminescence proper-

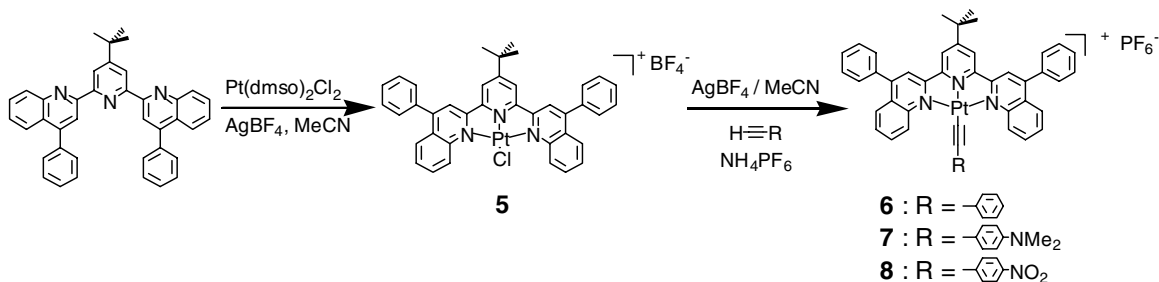
ties. Even though these complexes are luminescent in the solid state and in low-temperature glasses, many Pt(II) complexes with terpyridine ligands are scarcely emissive at room temperature due to efficient non-radiative decay processes [5]. On the other hand, the square-planar Pt(II) complexes offer possible reactivity such as axial interactions, leading to self-quenching [6] and photochemical reactivity [7]. These render such Pt(II) complexes emissive in solution at room temperature. To obtain emissive platinum(II) terpyridyl complexes with long-lived excited states and high quantum yield, much effort has been performed. An approach to the achievement of such goals involves utilizing substituted tpy ligands with a low-lying LUMO and/or a high-lying

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HOMO. The tuning of the electronic absorption and emission properties was shown to be achieved through a change in the ancillary ligands [8]. It is well-known that suitable substituents in the 4-position of the terpyridine ligand [9] and aryl substituents of the phenylacetylene ligand [10] can extend emission lifetime and increase quantum yield. Another approach is to increase strength of the ligand field. Platinum(II) complexes with cyclometalated ligands fall into this category [11] since the strong ligand field of the cyclometalated carbon raises the energy of the d–d states, diminishing their deactivating effect. Such a strategy has led to Pt(II) complexes which are emissive in solution at room temperature. In order to obtain room temperature luminescence from square-planar platinum(II) complexes, we have synthesized a series of terdentate polypyridine ligands [12] (bpqb-H and tbbpppy) exhibiting an extended conjugation and π -activating units such as quinolinyl unit and their platinum(II) complexes. Herein are reported the synthesis, electronic absorption and luminescence of a series of square-planar platinum(II) complexes.



Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Synthesis

[1,3-Bis(4'-phenyl-2'-quinolinyl)benzene] (bpqb-H) and [4-*tert*-butyl-1,3-bis(4-phenyl-2-quinolinyl)pyridine] (tbbpppy) were synthesized by modification of literature procedures using an excess of diphenyl phosphate in toluene [12]. The structures of bpqb-H and tbbpppy were established by single crystal X-ray analysis. The synthetic route for the terdentate platinum(II) complexes is summarized in Scheme 1. Bpqb-H has two nitrogen donor atoms able to coordinate to a metal center. The activation of the proton on the carbon atom at the C2 of benzene ring (see supporting information) would allow the ligand to chelate to a platinum center as terdentate chelate ligand. Pt(II) metal ion is well documented for its ability to undergo ortho-metalation by cleaving a C–H bond [13]. As expected, treating the ligand, bpqb-H, with K_2PtCl_4 in CH_3COOH at $110 \sim 120^\circ C$ afforded the complex $[Pt(bpqb)Cl]$ (**1**) in 75% yield. The synthesis of terdentate platinum(II) acetylide complexes **2–4** followed the procedures described for analogous compounds. Reaction of **1** with $H-C\equiv C-R$ in methanol in the presence of sodium hydroxide afforded **2–4**. The synthetic procedure for the formation of platinum(II) terpyridyl complexes is outlined in Scheme 2. The starting material $[Pt(tbbpppy)Cl]BF_4$ (**5**) was readily synthesized by reacting $Pt(dmsO)_2Cl_2$, instead of $Pt(PhCN)_2Cl_2$, with the corresponding ligand, tbbpppy, in refluxing acetonitrile using a procedure similar to that reported by McMillin et al. [14]. The synthesis of platinum(II) terpyridyl acetylide complexes **6–8** is conveniently prepared in two steps from **5**: **5** reacted with an excess of

acetonitrile in the presence of AgBF_4 to give $[\text{Pt}(\text{tbbpqpy})\text{-(MeCN)}](\text{BF}_4)_2$. Reaction of $[\text{Pt}(\text{tbbpqpy})(\text{MeCN})](\text{BF}_4)_2$ with $\text{HC}\equiv\text{CR}$ in methanol in the presence of sodium hydroxide, followed by metathesis reaction using NH_4PF_6 , afforded **6–8** as dark red crystals. The identities of all the complexes **1–8** were confirmed by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, satisfactory elemental analysis, and mass spectroscopy. The crystal structure of $[\text{Pt}(\text{bpqb})\text{Cl}]$ (**1**) has also been determined. All of the complexes are soluble in organic solvents (CH_2Cl_2 , CH_3CN , THF) and very stable both as solids and in solution.

2.2. Crystal structure determination

Molecular structure of tbbpqpy is shown in Fig. 1. The crystallographic data and processing parameters are given in Table 1. All of the atoms in the terpyridyl lie approximately in the same plane. The dihedral angle between the terpyridyl units and the phenyl group is 51.49° . The two quinoline units are located in the opposite direction to the central pyridyl unit. The perspective drawing of the complex **1** is shown in Fig. 2. The coordination geometry about platinum is approximately square planar with the bond distances of the platinum to nitrogen atoms slightly longer than those to the other terpyridine complexes. A feature of interest is the bent of Cl atom from the planar Pt(II) geometry ($\text{C}(21)\text{--Pt--Cl}$ $156.20(10)^\circ$). The Pt–C(21) bond distance [$1.908(3)\text{ \AA}$] lies in the range observed for

Table 1
Crystal and structure refinement data for tbbpqpy, **1**, and **9**

Parameter	tbbpqpy	1	9
Empirical formula	$\text{C}_{39}\text{H}_{31}\text{N}_3$	$\text{C}_{36}\text{H}_{23}\text{ClN}_2\text{Pt}$	$\text{C}_{48}\text{H}_{53}\text{ClN}_2\text{P}_2\text{Pt}$
Formula weight	541.67	714.10	950.40
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/C$	$Pbcn$
<i>a</i> (Å)	9.267(2)	11.308(12)	32.229(11)
<i>b</i> (Å)	12.187(3)	14.4446(15)	15.056(5)
<i>c</i> (Å)	15.198(4)	16.2404(17)	19.404(6)
α (°)	110.033(5)	90	90
β (°)	94.556(5)	94.565(2)	90
γ (°)	111.046(4)	90	90
<i>V</i> (Å ³)	1464.2(6)	2644.3(5)	9416(5)
<i>Z</i> value	2	4	8
<i>D</i> _{calc} (g/cm ³)	1.229	1.794	1.341
<i>F</i> (000)	572	1392	3840
μ (Mo K α) (mm ⁻¹)	0.072	5.437	3.137
2θ range (°)	3.94–56.66	3.62–56.72	2.52–57.52
Number of reflections measured	20058	19182	64252
Number of observed reflections	7226	6574	11905
<i>R</i>	0.0702	0.0241	0.0417
<i>R</i> _w	0.1952	0.0470	0.1238
Goodness of fit	1.068	1.048	1.180

other Pt complexes with related N[^]C[^]N terdentate ligands [15]. The Pt–N(1) and Pt–N(2) bond distances [$2.075(3)$ and $2.060(3)\text{ \AA}$] are slightly longer than those observed in

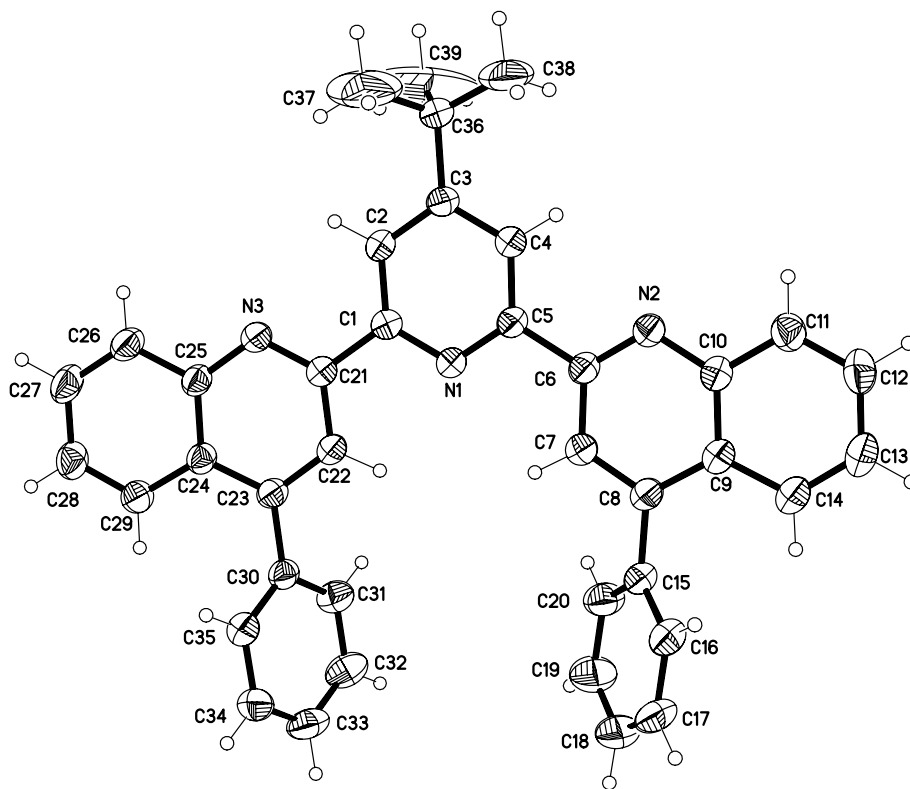


Fig. 1. Molecular Structure of tbbpqpy with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (°): N(1)–C(5) 1.337(3), N(1)–C(1) 1.344(3), C(5)–C(6) 1.491(3), N(2)–C(6) 1.318(3), N(1)–C(5)–C(6) 115.21(17), C(5)–C(6)–N(2), 117.80(18).

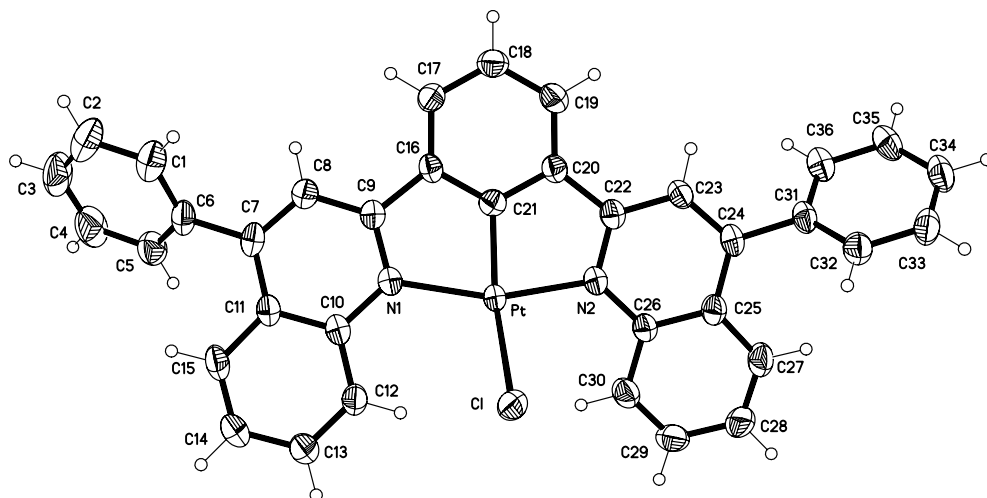


Fig. 2. Molecular structure of $[\text{Pt}(\text{bpqb})\text{Cl}]$ (**1**), with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (\AA) and angles ($^\circ$): Pt–C(21) 1.908(3), Pt–N(1) 2.075(3), Pt–N(2) 2.060(3), Pt–Cl 2.4343(9), N(1)–Pt–C(21) 80.03(12), N(2)–Pt–C(21) 80.10(12), N(1)–Pt–N(2) 159.11(11), N(1)–Pt–Cl 104.63(8), N(2)–Pt–Cl 96.16(8), C(21)–Pt–Cl 156.20(10).

related complexes [16]. The angles $[\text{N}(1)\text{--Pt--C}(21)$, 80.03(12) $^\circ$; $\text{N}(2)\text{--Pt--C}(2)$, 80.10(12) $^\circ$; $\text{N}(1)\text{--Pt--N}(2)$, 159.11(11) $^\circ$] deviate from the idealized values of 90 $^\circ$ and 180 $^\circ$ as a consequence of chelate ring strain. The Pt–Cl bond distance is 2.4343(9) \AA , which compares well with that of the similar cycloplatination complex [17].

2.3. Electronic absorption spectra

Fig. 3 shows the electronic absorption spectra of platinum complexes **1–4** in dichloromethane solutions at the concentration of 1.0×10^{-5} mol/L. The absorption obeys Beer's law when the concentration is lower than 1.0×10^{-4} mol/L, suggesting the lack of any significant occurrence of complex aggregation. The absorption band

maxima and the extinction coefficients are presented in Table 2. All of the spectra show intense absorption bands at 260 ~ 370 nm with extinction coefficients (ϵ) on the order of $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and less intense bands at 425 ~ 445 nm with ϵ on the order of $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. With reference to previous spectroscopic work on platinum(II) terpyridyl complexes [18], the absorption bands at $\lambda < 370$ nm are assigned to the intraligand (IL) transition of quinolinyl benzene ligand and acetylide ligands. The low energy bands at 425 ~ 445 nm are tentatively assigned to the $d\pi(\text{Pt}) \rightarrow \pi^*(\text{bpqb})$ MLCT transition, while the broad MLCT absorption band of **3** at 426 nm is assigned to MLCT and $\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*$ (bpqb) ligand-to-ligand charge-transfer (LLCT) transition, probably mixed with some MLCT contribution. The relatively

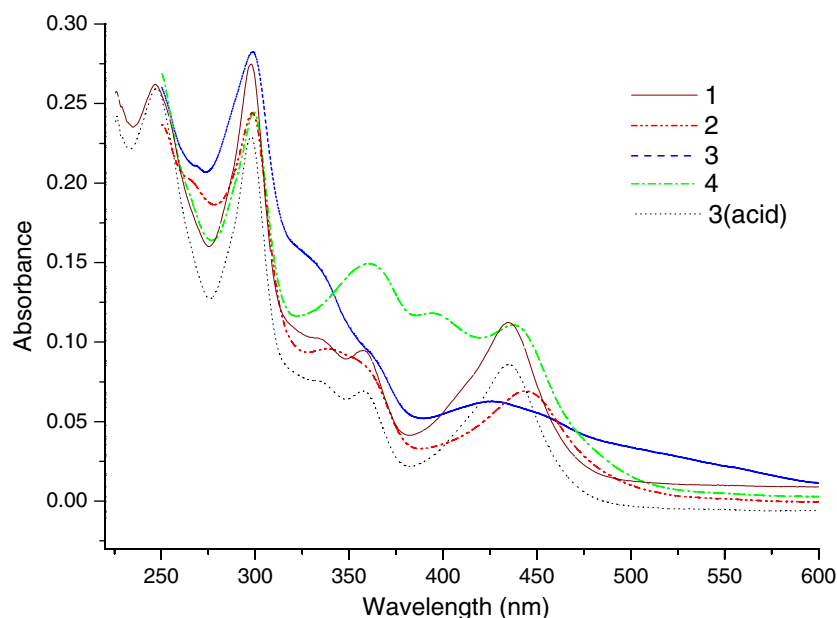


Fig. 3. Absorption spectra of complexes **1–4** measured in CH_2Cl_2 solution. Absorption spectrum taken upon addition of HCl to **3** (···).

Table 2
Photophysical properties of complexes **1–8** in CH₂Cl₂ at 298 K

Complex	λ_{ab} (nm) (ϵ (dm ³ mol ⁻¹ cm ⁻¹))	$\lambda_{\text{em}}^{\text{a}}$	$\tau_{\mu\text{s}}^{\text{b}}$	$\Phi_{\text{em}}^{\text{c}}$
1	297 (27394), 333 (9660), 353 (8852), 434 (10654)	603	2.8	0.14
2	265 sh (22104), 299 (26588), 338 (10472), 444 (7578)	610	3.6	0.21
3	299 (28279), 331 sh (15416), 360 (9895), 426 (6801)	616	4.2	0.28
4	299 (17796), 361 (10807), 395 (8509), 438 (7964)	604	3.2	0.18
5	250 (28047), 314 sh (10200), 324 sh (9877), 370 sh (3442)	Nonemissive		
6	258 (26746), 284 sh (23325), 305 sh (17580), 340 sh (15189), 374 (11344), 391 (13430), 475 (1647)	664	1.2	0.08
7	262 (27995), 288 (26344), 325 sh (21344), 374 (16196), 390 (15614), 475 (3436)	686	2.4	0.11
8	276 (22812), 289 (23339), 334 (17475), 373 (14917), 392 (15278), 463 (3303)	633	0.9	0.06

^a Room temperature emission band maximum in CH₂Cl₂ solution.

^b Emission decay lifetime at room temperature in degassed H₂Cl₂ solution.

^c Measured using quinine sulfate in 1.5 N H₂SO₄ ($\Phi = 0.446$).

low energy of the LLCT absorption may be attributable to the good electron-donating ability of the amino moiety. This phenomenon is consistent with the notion that the HOMO is predominantly acetylide-ligand-based, while the bpqb-ligand-based LUMO remains the same. An electron-rich group would render the HOMO more electron-rich and hence raise the HOMO, leading to lower energy absorption [19]. For complex **3**, the LLCT transition can be viewed as an intramolecular charge-transfer transition from the amino group on the aryl alkynyl to the π -accepting bpqb ligand through the metal center, considering the observation that the LLCT band disappears upon protonation of **3** (see Fig. 3). In the case of **4**, a distinct, solvent-sensitive band maximizes at 440 nm (CH₂Cl₂, 437 nm, 7960 M⁻¹ cm⁻¹; CH₃CN, 419 nm, 8660 M⁻¹ cm⁻¹; C₂H₅OH, 414 nm, 9280 M⁻¹ cm⁻¹). The bathochromic shift with decreasing solvent polarity indicates additional support for the assignment to the MLCT band. Fig. 4 depicts the absorption spectra of complexes **5–8**. Note that there are also very weak absorptions at longer wave-

length. According to previously reported spectroscopic studies on platinum(II) terpyridyl alkynyl complexes and the observed absorption trend [20], the low-energy absorption band in the visible region is assigned to a metal-to-ligand charge-transfer (MLCT) [$d\pi(\text{Pt}) \rightarrow \pi^*$ (tbbpppy)] transition, with some mixing of an alkynyl-to-tbbpppy ligand-to-ligand charge-transfer (LLCT) transition. Complex **8**, with the most electron-withdrawing nitro group on the acetylide, shows an absorption band at 463 nm, which is at the highest energy among the complexes (**6–8**). This observation is consistent with an MLCT assignment of the low-energy absorption band with some mixing of LLCT character, since electron-rich substituents on the phenyl ring of the acetylide ligand would render the platinum metal center more electron-rich and hence raise the $d\pi(\text{Pt})$ orbital energy, leading to a lower energy MLCT absorption. The MLCT and LLCT transitions for compounds **1–4** occur at higher energies compared with those of compounds **6–8** because the former compounds have higher π^* levels.

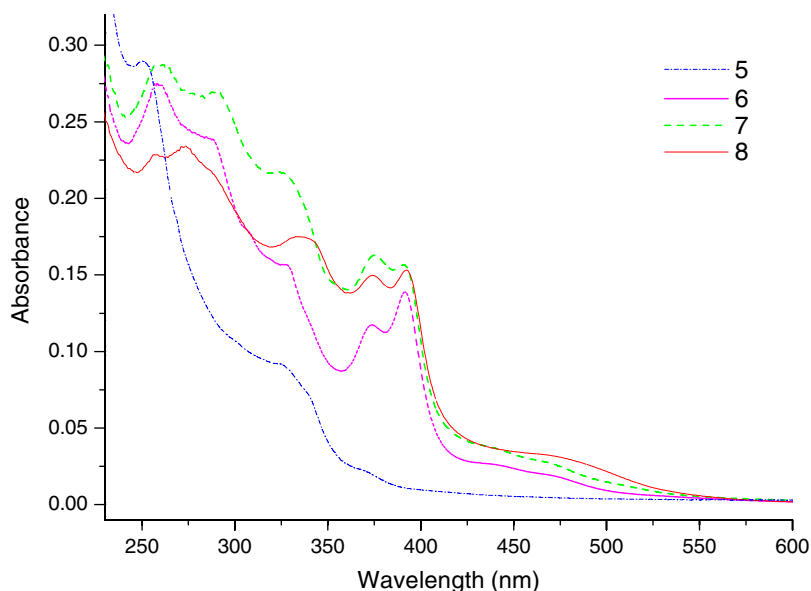


Fig. 4. Absorption spectra of complexes **5–8** measured in CH₂Cl₂ solution.

2.4. Photoluminescence

Complexes **1–4**, **6–8** show emission properties in solution at room temperature, while complex **5** is nonemissive. The emission data of complexes **1–4**, **6–8** are shown in Table 2. Representative excitation and emission spectra of **4** and **8** are illustrated in Fig. 5. Upon excitation at $\lambda > 420$ nm, the complexes exhibit intense luminescence at about 603–664 nm. The emissions of complexes **1–4** with the N[^]C[^]N ligand occurred at higher energies than the complexes **6–8** with the N[^]N[^]N ligand due to the higher π^* level of the former. The large Stokes shift and lifetime in the microsecond range of the photoluminescence of the complexes suggest that the emission originates from a triplet parentage. The emission spectrum of **4** in the solid state at 77 K shows an emission at 576 nm, while at room temperature in CH₂Cl₂ an emission band at 604 nm is observed. With reference to the previous spectroscopic studies on other platinum(II) terpyridyl complexes [21], the origin of the luminescence is tentatively assigned as derived from states of ³MLCT [$d\pi(\text{Pt}) \rightarrow \pi^*(\text{bpqb}$ or $\text{tbbppy})$] character, with some mixing of a $\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{bpqb}$ or $\text{tbbppy})$ ³LLCT character. The excitation spectra of **4** and **8** (Fig. 5) show excitation bands at 442 nm (for **4**) and ~ 500 nm (for **8**), which closely resemble that of the low-energy MLCT bands in their electronic absorption spectra, further supportive of a ³MLCT band mixed with some of ³LLCT character. Complex **3**, which bears the electron-rich amino group, shows the lowest emission energy, while complexes **4** and **8**, with the electron-poor nitro group, shows the highest emission energy, which is consistent with the observations by Eisenberg [1d], Yam [22], and

others [23] on the aromatic diimine, terpyridyl, and cyclometalated platinum(II) acetylide complexes. The relatively long lifetimes and high emission quantum yields of complexes **1–4** may be attributed to the stronger ligand field exerted by the bpqb chelate, which serves to further raise the energy of the d–d excited state, resulting in cutting off this pathway of nonradiative deactivation. Similar result has been observed in [PtL²Cl] [HL² = methyl-3,5-di(2-pyridyl)benzoate] [11c].

2.5. Electrochemistry

The electrochemical data for complexes **1–8** are summarized in Table 3. All the complexes exhibit two quasi-reversible couples at ca. -0.80 and -1.49 V vs. SCE. The insensitivity of the potentials toward the acetylide ligands demonstrates that the two reduction couples are assigned

Table 3
Electrochemical data for complex **1–8**^a

Complex	Oxidation E_{pa} (V) vs. SCE ^b	Reduction $E_{1/2}$ (V) vs. SCE ^c
1	+0.93	-0.94, -1.44
2	+0.98	-0.91, -1.41
3	+0.96	-0.95, -1.49
4	+1.23	-0.90, -1.38
5	+0.96	-0.84, -1.32
6	+1.08	-0.85, -1.36
7	+0.98	-0.82, -1.38
8	+1.28	-0.80, -1.35

^a In dichloromethane solution with 0.1 M ⁿBu₄NClO₄ as supporting electrolyte at room temperature; scan rate 100 mV s⁻¹.

^b E_{pa} refers to the anodic potential for the irreversible oxidation waves.

^c $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potential, respectively.

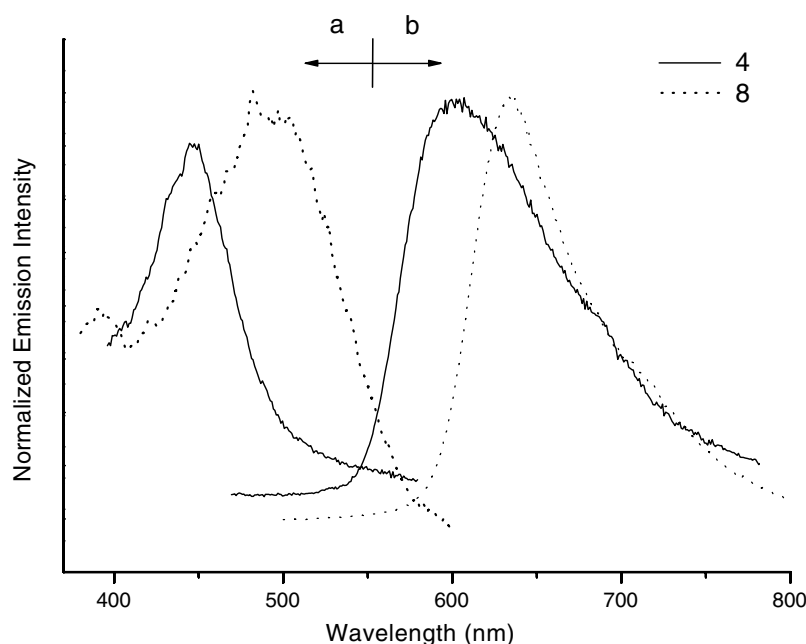


Fig. 5. Excitation (a) and emission (b) spectra of **4** (—) and **8** (···) in dichloromethane at 298 K.

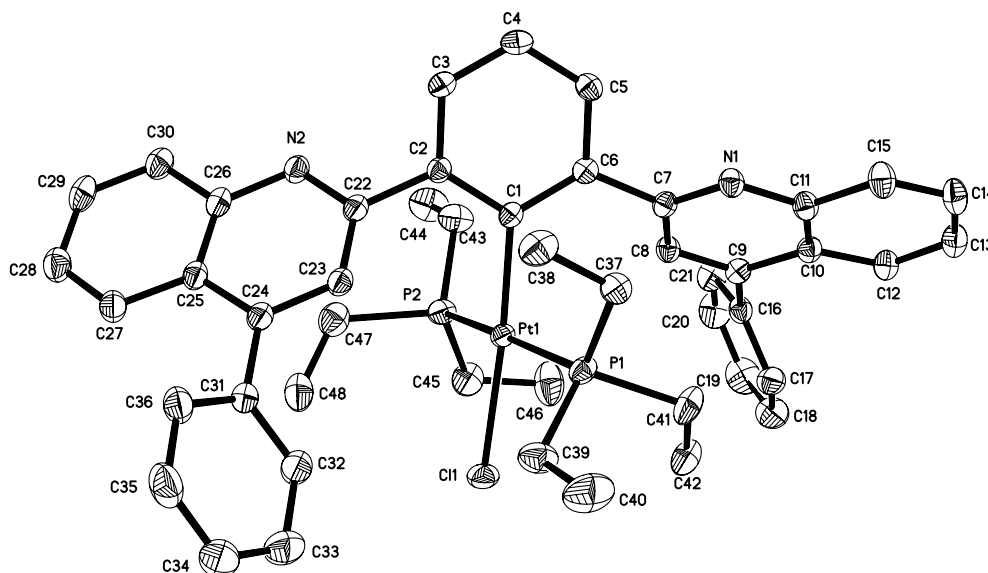
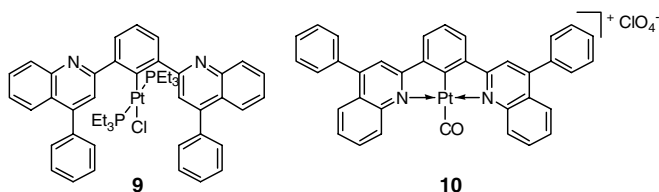


Fig. 6. ORTEP drawing of $[\text{Pt}(\text{bpqb})(\text{PEt}_3)_2\text{Cl}]$ (**9**), with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Pt(1)–C(1) 2.033(6), Pt(1)–Cl(1) 2.4091(17), Pt(1)–P(1) 2.3242(17), Pt(1)–P(2) 2.3304(18), C(1)–Pt(1)–Cl(1) 174.73(15), P(1)–Pt(1)–P(2) 172.77(6), P(1)–Pt(1)–C(1) 91.23(15), P(2)–Pt(1)–C(1) 92.68(15), P(1)–Pt(1)–Cl(1) 88.20(6), P(2)–Pt(1)–Cl(1) 88.46(6).

as the two successive reductions of the terdentate ligand with some mixing of the Pt(II) metal character. Similar assignments have also been reported for other related platinum(II)-terpyridyl system [24]. Irreversible anodic waves were observed at ca. +0.93 to +1.28 V vs. SCE. With reference to previous studies on other platinum(II) complexes [25], metal-centered oxidation from Pt(II) to Pt(III) is tentatively assigned. The oxidations of **4** and **8** occur at more positive potential than the others. The observation could be attributed to the presence of the electron-withdrawing nitro group on the phenylacetylide ligand, resulting in lowering the energy of the $d\pi(\text{Pt})$ orbital. Thus, complexes **4** and **8** are most difficult to be oxidized among the complexes studied.

2.6. Reactivity of **1** with π -acceptor ligands

Attempts were made to react two π -acceptor ligands with **1**. Thus, reaction of a dichloromethane solution of **1** and triethylphosphine in a 1:1 molar ratio, followed by the addition of excess LiClO_4 , afforded unexpectedly neutral diphosphine substituted Pt(II) complex **9**. Cationic derivative **10** can be obtained by abstraction of the halide ion of compound **1** with LiClO_4 under CO stream.



To provide structural information for one of the new compounds prepared, a single crystal X-ray diffraction study of **9** was undertaken. The molecular structure of **9** is shown in Fig. 6. A summary of cell constants and data collection parameters is included in Table 1. The X-ray crystal structure of **9** confirmed the presence of two phosphine substituted product. The P1–Pt–P2 bond angle is a slightly bent ($177.77(6)^\circ$) due to the strain of two phenyl groups. The ^1H , ^{13}C , and ^{31}P NMR spectra, mass spectra, and elemental analyses of compounds **9**–**10** were consistent with the proposed structures for **9**–**10**. The ^{31}P NMR spectrum of **9** displays a single resonance at -2.6 ppm with ^{135}Pt satellites. The $J_{\text{P-Pt}}$ coupling constant of 2728 Hz is typical for a *trans* geometry about the platinum atom [26]. The mass spectrum of **9** shows an intense peak at m/z 950 corresponding to the $[\text{M}]^+$ ion. In the ^{13}C NMR spectrum of **10**, the carbonyl carbon shows a resonance at 205.1 ppm. The IR spectrum of **10** exhibits one strong $\nu(\text{C}\equiv\text{O})$ absorption band at 1996 cm^{-1} .

3. Conclusion

A new class of square planar platinum(II) complexes (**1**–**8**) containing terdentate polypyridine ligands have been prepared, and their absorption spectra and luminescence properties have been investigated. The emission energies in dichloromethane at room temperature were found to depend on the nature of the acetylide ligands with different substituents on the phenyl ring. An emission origin of a $d\pi(\text{Pt}) \rightarrow \pi^*(\text{bpqb}$ or $\text{tbbpppy})$ $^3\text{MLCT}$ excited state, with some mixing of a $\pi(\text{C}\equiv\text{CR}) \rightarrow \pi^*$ (bpqb or $\text{tbbpppy})$ $^3\text{LLCT}$ state, is tentatively assigned. The relatively long lifetimes and high emission quantum yields of **1**–**4** com-

pared with other Pt(II) terpyridyl acetylide complexes may be due to the stronger ligand field exerted by the N[∧]C[∧]N chelate, which serves to further raise the energy of the d–d excited state, resulting in cutting off this pathway of nonradiative deactivation. These compounds may utilize potential applications such as molecular sensors and electroluminescence.

4. Experimental

All experiments were performed under a nitrogen atmosphere in a vacuum atmosphere drybox or by standard Schlenk technique. THF, toluene, ether, and hexane were distilled from sodium benzophenone. Methylene chloride, CHCl₃, MeOH, MeCN and EtOH were distilled under nitrogen from P₂O₅. The ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. IR spectra were recorded on a Biorad FTS-165 spectrometer. ESI-MS spectra were recorded on a Micromass QTOF2 mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. 2,6-Diacetyl pyridine, pivalic acid, 2-amino-benzophenone, K₂PtCl₄, phenylacetylene, sodium peroxodisulfate, and diphenyl phosphate were purchased from Aldrich Chemical Co. 4-Ethynyl-*N,N*-dimethylaniline [27], and 4-ethynyl-nitrobenzene [27] were synthesized according to the literature methods. [1,3-Bis(4'-phenyl-2'-quinolinyl)benzene] (bpqb-H) and [4-*tert*-butyl-2,6-bis(4'-phenyl-2'-quinolinyl)pyridine] (tbbpppy) were synthesized by modification of the literature method [12].

4.1. Synthesis of [Pt(bpqb)Cl] (1)

Bpqb-H (0.30 g, 0.62 mmol) and K₂PtCl₄ (0.25 g, 0.62 mmol) were added to acetic acid (10 ml). The mixture was heated at 100 ~ 120 °C and refluxed for 72 h under N₂. After the reaction mixture was cooled to ambient temperature, the yellow solid was collected by filtration and washed with 5 ml of CH₃OH, and diethyl ether. Recrystallization of the product from DMSO and diethyl ether yielded yellow crystals of **1** in a 75% yield. m.p. > 350 °C. ¹H NMR (CDCl₃): δ 10.03 (d, 2H, *J* = 8.7 Hz), 7.98–7.82 (m, 4H), 7.75 (s, 2H), 7.66–7.56 (m, 14H), 7.26(t, 1H, *J* = 7.8 Hz). ¹³C{¹H} NMR (CDCl₃): δ 166.6, 152.4, 149.3, 142.7, 140.5, 137.5, 130.7, 129.8, 129.4, 128.9, 127.6, 126.1, 125.3, 122.7, 117.7, 115.4. FAB-MS: *m/z* 714 [M⁺]. Anal. Calc. for C₃₆H₂₃ClN₂Pt: C, 60.55; H, 3.25. Found: C, 60.28; H, 3.16%.

4.2. Synthesis of [Pt(bpqb)(CCC₆H₅)] (2)

A mixture of phenylacetylene (0.015 ml, 0.15 mmol) and sodium hydroxide (6 mg, 0.15 mmol) in methanol was stirred at room temperature for 30 min. [Pt(bpqb)Cl] (100 mg, 0.14 mmol) was added to the reaction mixture and stirred

for 12 h at room temperature. The mixture was filtered. The pure orange-red product **2** was obtained by diffusion of diethyl ether into an acetonitrile solution of the product in 67% yield (73 mg). m.p. > 350 °C. ¹H NMR (CDCl₃): δ 10.70 (d, 2H, *J* = 8.7 Hz), 7.97–7.88 (m, 6H), 7.85 (s, 2H), 7.75 (d, 2H, *J* = 6.9 Hz), 7.74–7.52 (m, 11H), 7.40 (d, 2H, *J* = 7.2 Hz), 7.30 (t, 2H, *J* = 8.7 Hz), 7.12 (t, 1H, *J* = 7.8 Hz). ¹³C{¹H} NMR (CDCl₃): δ 168.6, 161.4, 156.5, 156.2, 149.7, 148.2, 144.4, 141.6, 137.2, 135.8, 131.1, 130.6, 129.6, 129.1, 127.1, 125.4, 123.6, 105.9, 104.4, 101.1, 100.1, 97.0, 38.0. FAB-MS: *m/z* 779 [M⁺]. IR (KBr pellet, cm⁻¹): 2084 ν(C≡C). Anal. Calc. for C₄₄H₂₈N₂Pt: C, 67.77; H, 3.62. Found: C, 67.48; H, 3.44%.

4.3. Synthesis of [Pt(bpqb)(CCC₆H₄NMe₂-4)] (3)

Complex **3** was synthesized by a procedure similar to that of **2** except that (4-*N,N*-dimethylaminophenyl)acetylene (20 mg, 0.15 mmol) was used in place of phenylacetylene to give red product. Yield: 63%. m.p. > 350 °C. ¹H NMR (CDCl₃): 10.78 (d, 2H, *J* = 8.4 Hz), 7.93 (t, 2H, *J* = 7.2 Hz), 7.84 (d, 2H, *J* = 7.8 Hz), 7.77 (s, 2H), 7.70 (d, 2H, *J* = 7.5 Hz), 7.65–7.51 (m, 12H), 7.30 (d, 2H, *J* = 8.8 Hz), 7.23 (t, 1H, *J* = 7.2 Hz), 6.65 (d, 2H, *J* = 8.8 Hz), 2.94 (s, 6H). ¹³C{¹H} NMR (CDCl₃): δ 181.1, 169.8, 156.7, 152.0, 149.9, 148.3, 145.0, 137.9, 132.9, 132.0, 130.8, 130.2, 129.5, 128.9, 127.4, 126.1, 125.8, 124.1, 123.5, 118.0, 116.9, 113.3, 111.6, 39.9. IR (KBr Pellet, cm⁻¹): 2078 ν(C≡C). FAB-MS: *m/z* 822 [M⁺]. Anal. Calc. for C₄₆H₃₃N₃Pt: C, 67.14; H, 4.04. Found: C, 66.74; H, 3.91%.

4.4. Synthesis of [Pt(bpqb)(CCC₆H₄NO₂-4)] (4)

Complex **4** was synthesized by a procedure similar to that of **2** except that (4-nitrophenyl)acetylene (20 mg, 0.15 mmol) was used in place of phenylacetylene. Yield: 58%. ¹H NMR (CDCl₃): δ 10.45 (d, 2H, *J* = 7.5 Hz), 8.12 (d, 2H, *J* = 7.2 Hz), 7.92–7.85 (m, 4H), 7.82 (s, 2H), 7.75 (d, 2H, *J* = 8.1 Hz), 7.67–7.55 (m, 12H), 7.42 (d, 2H, *J* = 8.8 Hz), 7.31 (t, 1H, *J* = 7.2 Hz). ¹³C{¹H} NMR (CDCl₃): δ 167.4, 160.6, 156.6, 156.4, 149.7, 148.2, 146.8, 142.4, 135.9, 135.6, 131.1, 130.6, 130.1, 128.2, 127.4, 125.6, 125.1, 120.6, 106.8, 105.6, 103.6, 100.8, 98.6, 38.1. IR (KBr pellet, cm⁻¹): 2067 ν(C≡C). FAB-MS: *m/z* 824 [M⁺]. Anal. Calc. for C₄₄H₂₇N₃O₂Pt: C, 64.07; H, 3.30. Found: C, 64.28; H, 3.48%.

4.5. Synthesis of [Pt(tbbpppy)Cl]BF₄ (5)

To a stirred suspension of Pt(dmsO)₂Cl₂ (0.17 g, 0.42 mmol) in MeCN (15 ml) was added AgBF₄ (0.089 g, 0.46 mmol). The mixture was refluxed for 15 h. After filtration, tbbpppy (0.10 g, 0.44 mmol) was added to the reaction mixture and refluxed for 15 h. After filtration to remove additional AgCl, the filtrate was evaporated to dryness under reduced pressure to give an orange-red solid.

The product was extracted with hot MeCN. Recrystallization from diffusion of diethyl ether into an acetonitrile solution yielded orange crystals. Yield: 78%. ^1H NMR (CDCl_3): δ 9.51 (d, 2H, $J = 8.8$ Hz), 8.31 (s, 2H), 8.23 (s, 2H), 7.87 (t, 4H, $J = 7.8$ Hz), 7.70 (m, 2H), 7.65 (d, 2H, $J = 7.8$ Hz), 7.59 (m, 4H), 7.49 (m, 4H), 1.55 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 168.4, 160.8, 156.7, 156.4, 149.8, 136.0, 133.5, 131.7, 131.1, 130.6, 130.2, 129.9, 129.5, 127.8, 125.3, 121.6, 38.2, 14.6. FAB-MS: m/z 714 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{39}\text{H}_{31}\text{BClF}_4\text{N}_3\text{Pt}$: C, 54.53; H, 3.64. Found: C, 54.28; H, 3.48%.

4.6. Synthesis of $[\text{Pt}(\text{tbbpqpy})(\text{MeCN})](\text{BF}_4)_2$

A mixture of $[\text{Pt}(\text{tbbpqpy})\text{Cl}]\text{BF}_4$ (0.10 g, 0.117 mmol) and AgBF_4 (0.05 g, 0.257 mmol) in acetonitrile was refluxed for 4 h. After the reaction mixture was cooled to ambient temperature, the solution was filtered. The red product was obtained by diffusion of diethyl ether into an acetonitrile solution of the product in a quantitative yield. ^1H NMR (CDCl_3): δ 8.78 (d, 2H, $J = 8.8$ Hz), 8.42 (s, 2H), 8.30 (s, 2H), 8.12 (t, 2H, $J = 7.8$ Hz), 8.08 (d, 2H, $J = 8.1$ Hz), 7.79–7.65 (m, 12H), 2.16 (s, 3H), 1.57 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.0, 158.7, 157.6, 156.9, 148.0, 135.2, 134.6, 132.1, 130.8, 130.0, 129.2, 128.0, 127.0, 124.1, 122.4, 120.4, 119.1, 69.0, 30.2, 2.5. FAB-MS: m/z 951 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{41}\text{H}_{34}\text{B}_2\text{F}_8\text{N}_4\text{Pt}$: C, 51.76; H, 3.60. Found: C, 51.57; H, 3.45%.

4.7. Synthesis of $[\text{Pt}(\text{tbbpqpy})(\text{CCC}_6\text{H}_5)]\text{PF}_6$ (6)

A mixture of phenylacetylene (0.013 ml, 0.115 mmol) and sodium hydroxide (5 mg, 0.138 mmol) in methanol was stirred at room temperature for 30 min. $[\text{Pt}(\text{tbbpqpy})(\text{MeCN})](\text{BF}_4)_2$ (0.10 g, 0.105 mmol) was added to the reaction mixture and stirred for 12 h at room temperature. The mixture was filtered and a saturated solution of ammonium hexafluorophosphate in methanol was added. The mixture was evaporated under reduced pressure and washed with methanol. Subsequent recrystallization by diffusion of diethyl ether into an acetonitrile solution of the product gave as dark red solid. Yield: 36%. ^1H NMR (CD_3CN): δ 10.02 (d, 2H, $J = 9.0$ Hz), 8.30 (s, 2H), 8.10 (s, 2H), 7.78 (d, 2H, $J = 8.7$ Hz), 7.69–7.59 (m, 11H), 7.42 (d, 2H, $J = 6.6$ Hz), 7.31 (m, 4H), 7.17 (d, 2H, $J = 6.6$ Hz), 1.40 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 168.6, 161.4, 156.5, 156.3, 149.7, 141.2, 139.4, 135.8, 133.2, 132.2, 131.1, 130.2, 129.6, 127.1, 105.9, 104.2, 101.1, 100.1, 97.0, 95.2, 93.2, 38.0, 12.6. IR (KBr pellet, cm^{-1}): 2117 $\nu(\text{C}\equiv\text{C})$. FAB-MS: m/z 982 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{47}\text{H}_{36}\text{F}_6\text{N}_3\text{PPt}$: C, 57.44; H, 3.69. Found: C, 57.61; H, 3.86%.

4.8. Synthesis of $[\text{Pt}(\text{tbbpqpy})(\text{CCC}_6\text{H}_4\text{NMe}_2)]\text{PF}_6$ (7)

This compound was prepared using the same procedure as that described for **6**. Yield: 38%. ^1H NMR (CD_3CN): δ 9.88 (d, 2H, $J = 9.0$ Hz), 8.03 (s, 2H), 7.80 (s, 2H), 7.66–

7.59 (m, 4H), 7.52 (t, 4H, $J = 7.4$ Hz), 7.44 (t, 2H, $J = 7.5$ Hz), 7.31–7.25 (m, 6H), 6.73 (d, 2H, $J = 8.4$ Hz), 6.51 (d, 2H, $J = 8.7$ Hz), 2.93 (s, 6H), 1.35 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 161.2, 158.3, 157.2, 156.1, 155.7, 152.6, 149.7, 147.4, 146.1, 142.3, 135.5, 132.1, 131.2, 130.3, 129.7, 129.3, 128.2, 127.3, 122.8, 119.3, 112.8, 111.2, 37.9, 37.2, 15.0. IR (KBr pellet, cm^{-1}): 2112 $\nu(\text{C}\equiv\text{C})$. FAB-MS: m/z 1052 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{49}\text{H}_{41}\text{F}_6\text{N}_4\text{PPt}$: C, 57.37; H, 4.03. Found: C, 57.11; H, 3.91%.

4.9. Synthesis of $[\text{Pt}(\text{tbbpqpy})(\text{CCC}_6\text{H}_4\text{NO}_2)]\text{PF}_6$ (8)

This compound was prepared using the same procedure as that described for **6**. Yield: 31%. ^1H NMR (CD_3CN): δ 9.48 (d, 2H, $J = 8.7$ Hz), 8.29 (s, 2H), 8.21 (s, 2H), 7.89–7.72 (m, 14H), 7.52–7.43 (m, 6H), 1.53 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 160.6, 158.1, 156.6, 156.4, 155.2, 149.7, 139.4, 135.9, 133.5, 131.8, 131.0, 130.6, 130.1, 128.2, 127.4, 125.2, 124.6, 122.2, 104.3, 101.6, 98.3, 95.8, 38.1, 12.8. IR (KBr pellet, cm^{-1}): 2113 $\nu(\text{C}\equiv\text{C})$. FAB-MS: m/z 1028 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{47}\text{H}_{35}\text{F}_6\text{N}_4\text{O}_2\text{PPt}$: C, 54.92; H, 3.43. Found: C, 54.71; H, 3.31%.

4.10. Synthesis of $[\text{Pt}(\text{bpqb})(\text{PEt}_3)_2\text{Cl}]\text{PF}_6$ (9)

To a stirred solution of **1** (0.20 g, 0.28 mmol) in CH_2Cl_2 (30 ml) was added PEt_3 (0.3 mmol, 1.0 M in THF). The mixture was stirred for 2 h and excess LiClO_4 was added to the solution. After the mixture was stirred for 3 h, a dark red solution was filtered. Recrystallization by diffusion of diethyl ether into a dichloromethane solution afforded reddish crystals in 37% yield. ^1H NMR (CDCl_3): δ 8.69 (s, 2H), 8.26 (d, 2H, $J = 8.4$ Hz), 7.90 (d, 2H, $J = 8.4$ Hz), 7.74 (t, 2H, $J = 7.5$ Hz), 7.70 (d, 2H, $J = 8.1$ Hz), 7.62 (d, 4H, $J = 7.5$ Hz), 7.53–7.44 (m, 8H), 7.32 (t, 1H, $J = 7.5$ Hz), 1.36 (m, 12H), 0.51 (m, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 164.5, 148.6, 147.3, 146.4, 138.4, 135.5, 131.2, 130.2, 130.0, 129.8, 129.5, 129.1, 128.7, 128.4, 127.8, 124.8, 122.8, 15.3, 7.5. ^{31}P NMR (CDCl_3): δ -2.6 ($J_{\text{P-Pt}} = 2728$ Hz). FAB-MS: m/z 950 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{48}\text{H}_{53}\text{ClN}_2\text{P}_2\text{Pt}$: C, 60.66; H, 5.62. Found: C, 60.24; H, 5.47%.

4.11. Synthesis of $[\text{Pt}(\text{bpqb})(\text{CO})]\text{ClO}_4$ (10)

Carbon monoxide was bubbled to a stirred suspension of **1** (0.05 g, 0.11 mmol). After 2 h, excess LiClO_4 was added to the solution. After the mixture was stirred for 2 h, a dark red solution was filtered. Recrystallization by diffusion of diethyl ether into a dichloromethane solution afforded reddish crystals in 43% yield. ^1H NMR (CD_3CN): δ 8.56 (d, 2H, $J = 9.0$ Hz), 7.78 (d, 2H, $J = 8.7$ Hz), 7.72 (d, 2H, $J = 7.8$ Hz), 7.62–7.41 (m, 16H), 7.28 (t, 1H, $J = 7.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 205.1, 166.4, 156.7, 152.3, 149.0, 147.4, 145.9, 142.3, 137.3, 135.1, 130.8, 129.7, 129.1, 128.2, 127.4, 126.4, 123.9, 121.0. IR

(KBr pellet, cm^{-1}): 1996 $\nu(\text{C}\equiv\text{O})$, 1077 $\nu(\text{ClO}_4)$. FAB-MS: m/z 806 $[\text{M}^+]$. Anal. Calc. for $\text{C}_{37}\text{H}_{23}\text{ClN}_2\text{P}_2\text{Pt}$: C, 55.06; H, 3.00. Found: C, 55.33; H, 2.97%.

4.12. Photophysical measurement

The electronic absorption spectra were measured on a Hewlett–Packard 8452A diode array spectrophotometer. The room temperature emission and excitation spectra were measured in dichloromethane solutions on a SPEX Fluorolog-3 fluorescence spectrophotometer. The excitation wavelength was 425 nm. For solution emission and excitation spectral studies, the solutions were purged with argon for 15 min before measurement. The room temperature emission lifetimes were performed with a laser system. The samples were excited by the third-harmonic output (355 nm) of a Quantel Brilliant Nd:YAG laser. The emission quantum yields were determined by the optical dilute method reported by Demas and Crosby [28]. A degassed aqueous solution of quinine sulfate in 1.5 N H_2SO_4 solution ($\Phi_{\text{em}} = 0.446$, excited at 425 nm) was used as the reference.

4.13. X-ray crystallography

Suitable crystals of **1**, **tbbpppy** and **9** were grown by DMSO/ether and CH_2Cl_2 /ether, respectively. All X-ray intensity data of compounds **tbbpppy**, **1** and **9** were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The collected data were processed for integration; an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities (SADABS). Structure were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using SHELXL97 [29]. All non-hydrogen atoms in compounds **tbbpppy**, **1** and **9** were refined anisotropically. All hydrogen atoms were included in the calculated positions.

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Appendix A. Supplementary material

CCDC 278638, 278639 and 278640 contains the supplementary crystallographic data for **1**, **9** and **tbbpppy**. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] (a) H. Yersin, W. Humbs, J. Strasser, *Coord. Chem. Rev.* 159 (1997) 325; (b) B.C. Tzeng, W.F. Fu, C.-M. Che, H.Y. Chao, K.K. Cheung, S.M. Peng, *J. Chem. Soc., Dalton Trans.* (1999) 1017; (c) C.L. Choi, Y.F. Cheng, C. Yip, D.L. Phillips, V.W.W. Yam, *Organometallics* 19 (2000) 3192; (d) M. Hissler, W.B. Connick, D.K. Geiger, J.E. McGarrah, D. Lipa, R.J. Lachicotte, R. Eisenberg, *Inorg. Chem.* 39 (2000) 447.
- [2] (a) S.J. Lippard, *Acc. Chem. Res.* 11 (1978) 211; (b) M. Howe-Grant, S.J. Lippard, *Biochemistry* 18 (1979) 5762; (c) G. Arena, L.M. Scolaro, R.F. Pasternack, R. Romeo, *Inorg. Chem.* 34 (1995) 2994.
- [3] (a) V.H. Houlding, V.M. Miskowski, *Coord. Chem. Rev.* 111 (1991) 145; (b) C. Yu, K.M.-C. Wong, K.H.-Y. Chan, V.W.W. Yam, *Angew. Chem., Int. Ed.* 44 (2005) 791.
- [4] (a) J.A. Bailey, M.G. Hill, R.E. Marsh, V.M. Miskowski, W.P. Schaefer, H.B. Gray, *Inorg. Chem.* 34 (1995) 4591; (b) H.-K. Yip, L.-K. Cheng, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Dalton Trans.* (1993) 2933.
- [5] (a) D.G. Nocera, *Acc. Chem. Res.* 28 (1995) 209; (b) S.D. Cummings, R. Eisenberg, *Inorg. Chem.* 34 (1995) 2007; (c) G. Rosace, G. Giuffrida, M. Saitta, G. Guglielmo, S. Campagna, S. Lanza, *Inorg. Chem.* 35 (1996) 6816.
- [6] (a) W.B. Connick, H.B. Gray, *J. Am. Chem. Soc.* 119 (1997) 11620; (b) C.N. Pettijohn, E.B. Jochnowitz, B. Chuong, J.K. Nagle, A. Vogler, *Coord. Chem. Rev.* 171 (1998) 85.
- [7] L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri, V. Balzani, *J. Am. Chem. Soc.* 108 (1986) 6084.
- [8] (a) J.F. Michalec, S.A. Bejune, D.G. Cuttell, G.C. Summerton, J.A. Gertenbach, J.S. Field, R.J. Haines, D.R. McMillin, *Inorg. Chem.* 40 (2001) 2193; (b) V.W.W. Yam, K.M.-C. Wong, N. Zhu, *J. Am. Chem. Soc.* 124 (2002) 6506.
- [9] (a) G. Arena, G. Calogero, S. Campagna, L.M. Scolaro, V. Ricevuto, R. Romeo, *Inorg. Chem.* 37 (1998) 2763; (b) T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, N. Tamai, T. Kawai, M. Irie, H. Nishihara, *Inorg. Chem.* 41 (2002) 7143.
- [10] Q.-Z. Yang, L.-Z. Wu, L.-P. Zhang, C.-H. Tung, *Inorg. Chem.* 41 (2002) 5653.
- [11] (a) J. Brooks, Y. Babayan, S. Lamansky, P.I. Djurovich, I. Tsyba, R. Bau, M.E. Thompson, *Inorg. Chem.* 41 (2002) 3055; (b) H. Yersin, D. Donges, W. Humbs, J. Strasser, R. Sitters, M. Glasbeek, *Inorg. Chem.* 41 (2002) 4915; (c) J.A. Williams, A. Beeby, E.S. Davides, J.A. Weinstein, C. Wilson, *Inorg. Chem.* 42 (2003) 8609; (d) W. Sotoyama, T. Satoh, N. Sawatari, H. Inoue, *App. Phys. Lett.* 86 (2005); (e) K. Okamoto, T. Kanbara, T. Yamamoto, A. Wada, *Organometallics* 25 (2006) 4026.
- [12] A. Mamo, *J. Heterocycl. Chem.* 37 (2000) 1225.
- [13] (a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kakitani, M. Sonoda, N. Chatani, *Pure Appl. Chem.* 66 (1994) 1527; (b) A.D. Ryabov, *Chem. Rev.* 90 (1990) 403; (c) S. Fernández, J. Forniés, B. Gil, J. Gómez, E. Lalinde, *J. Chem. Soc., Dalton Trans.* (2003) 822.
- [14] R. Buchner, J. Field, R.J. Haines, C.T. Cunningham, D.R. McMillin, *Inorg. Chem.* 36 (1997) 3952.
- [15] J. Terheijden, G. van Koten, J.A.M. van Beek, *Organometallics* 6 (1987) 89.
- [16] (a) T.K. Aldridge, E.M. Stacy, D.R. McMillin, *Inorg. Chem.* 33 (1994) 722; (b) D.J. Cárdenas, A.M. Echavarren, M.C.R. de Arellano, *Organometallics* 18 (1999) 3337.

- [17] (a) D. Song, Q. Wu, A. Hook, I. Kozin, S. Wang, *Organometallics* 20 (2001) 4683;
(b) Y.-Z. Hu, M.H. Wilson, R. Zong, C. Bonnefous, D.R. McMillin, R.P. Thummel, *J. Chem. Soc., Dalton Trans.* (2005) 354.
- [18] (a) R. Buchner, C.T. Cunningham, J.S. Field, R. Haines, D.R. McMillin, G.C. Summerton, *J. Chem. Soc., Dalton Trans.* (1999) 711;
(b) S.W. Lai, M.C.W. Chan, K.K. Cheung, C.-M. Che, *Inorg. Chem.* 38 (1999) 4262.
- [19] (a) K.M.-C. Wong, W.-S. Tang, B.W.-K. Chu, N. Zhu, V.W.W. Yam, *Organometallics* 23 (2004) 3459;
(b) F. Guo, W. Sun, Y. Liu, K. Schanze, *Inorg. Chem.* 44 (2005) 4055.
- [20] (a) V.W.W. Yam, R.P.L. Tang, K.M.C. Wong, C.C. Ko, K.K. Cheung, *Inorg. Chem.* 40 (2001) 571;
(b) K.M.-C. Wong, W.-S. Tang, X.-X. Lu, N. Zhu, V.W.W. Yam, *Inorg. Chem.* 44 (2005) 1492.
- [21] V.W.W. Yam, K.M.-C. Wong, N. Zhu, *Angew. Chem., Int. Ed.* 42 (2003) 1400.
- [22] V.W.W. Yam, R.P.-L. Tang, K.M.-C. Wong, K.K. Cheung, *Organometallics* 20 (2001) 4476.
- [23] C.E. Whittle, J.A. Weinstein, M.W. George, K.S. Schanze, *Inorg. Chem.* 40 (2001) 4053.
- [24] (a) M.G. Hill, J.A. Bailey, V.M. Miskowski, H.B. Gray, *Inorg. Chem.* 35 (1996) 4585;
(b) D.K. Crites, C.T. Cunningham, D.R. McMillin, *Inorg. Chim. Acta* 273 (1998) 346.
- [25] C.B. Blanton, Z. Murtaza, R.J. Shaver, D.P. Rillema, *Inorg. Chem.* 31 (1992) 3230.
- [26] (a) W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca, P. Rigo, *Angew. Chem., Int. Ed.* 42 (2003) 105;
(b) C. Loeber, D. Matt, P. Briard, D. Grandjean, *J. Chem. Soc., Dalton Trans.* (1996) 513.
- [27] A. Elangovan, Y.-H. Wang, T.-I. Ho, *Org. Lett.* 5 (2003) 1841.
- [28] J.N. Demas, G.A. Grosby, *J. Phys. Chem.* 75 (1971) 991.
- [29] G.M. Sheldrick, *SHELXS97* and *SHELXL97*, University of Goettingen, Germany, 1997.