

Synthesis, Characterization, Absorption Spectra, and Luminescence Properties of Organometallic Platinum(II) Terpyridine Complexes

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A series of new organometallic platinum(II) complexes containing terdentate polypyridine ligands has been prepared and characterized. Their absorption spectra in 4:1 (v/v) MeOH/EtOH fluid solution at room temperature and luminescence in the same matrix at 77 K have been investigated. The new species are [Pt(terpy)Ph]Cl (**3**, terpy = 2,2':6',2''-terpyridine, Ph = phenyl), [Pt(Ph-terpy)Cl]Cl (**4**, Ph-terpy = 4'-phenyl-2,2':6',2''-terpyridine), [Pt(Ph-terpy)Me]Cl (**5**), and [Pt(Ph-terpy)Ph]Cl (**6**). The results have been compared with those for [Pt(terpy)Cl]Cl (**1**) and [Pt(terpy)Me]Cl (**2**). NMR data evidence that all the complexes but **3** and **6** oligomerize in solution leading to stacked species. The absorption spectra are dominated by moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region and by intense ligand-centered (LC) bands in the UV region. All the compounds are luminescent in a 4:1 (v/v) MeOH/EtOH rigid matrix at 77 K, exhibiting a structured emission within the range 460–600 nm. This feature is assigned to formally ³LC excited states which receive substantial contribution from closely lying ³MLCT levels. Complexes **1**, **2**, **4**, and **5** also exhibit a relatively narrow and unstructured luminescence band within the range 680–800 nm, which dominates the luminescence spectrum on increasing concentration and exciting at longer wavelengths. The band is assigned to a dσ*(metal) → π*(polypyridine) (³MMLCT) state, originating from metal–metal interactions occurring in head-to-tail dimers (or polymers). A third broad band is shown by **1** and **4** under all concentration conditions and by **2** and **5** only in concentrated solutions and is attributed to excimeric species originating from π–π interactions due to stacking between polypyridine ligands.

Introduction

Luminescent polypyridine transition metal complexes are extensively investigated because of their outstanding photo-physical and redox properties,¹ which make these species play a key role in the development of supramolecular systems for solar energy conversion,² information treatment,³ and sensor technology.⁴ Most of the studies concern d⁶ transition metal complexes (e.g., Ru(II) and Os(II) species), but in recent times d⁸ transition metal complexes (in particular, Pt(II)–polypyridine

complexes) have attracted increasing attention.^{5–12} Actually, for particular purposes, luminescent square-planar d⁸ metal

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complexes seem to exhibit some advantages over luminescent octahedral d^6 metal complexes because of their geometry. For example, they are well-suited (i) to interact with DNA by intercalation^{13–16} as well as with other biomolecules¹⁷ and (ii) to lead to luminescent metallomesogenes.¹⁸ When properly designed, square-planar complexes oligomerize in solution^{5d,7,8,10c,d,13e,19} leading to supramolecular architectures whose photophysical properties can be used to evidence ligand–ligand (π – π) and metal–metal interactions.

Here we report the synthesis, characterization, absorption spectra, and luminescence properties of a series of new organometallic Pt(II)–polypyridine complexes. The complexes are [Pt(terpy)Ph]Cl (3, terpy = 2,2':6',2''-terpyridine, Ph = phenyl), [Pt(Ph-terpy)Cl]Cl (4, Ph-terpy = 4'-phenyl-2,2':6',2''-terpyridine), [Pt(Ph-terpy)Me]Cl (5, Me = methyl), and [Pt(Ph-terpy)-Ph]Cl (6). For comparative purposes, we have also studied the already known complexes [Pt(terpy)Cl]Cl (1) and [Pt(terpy)-Me]Cl (2). Structural formulas of these compounds are given in Figure 1.

Experimental Section

Materials and Methods. K_2PtCl_4 was obtained from Strem Chemical Co. and was separated from metallic Pt and K_2PtCl_6 by dissolution in water and filtering. The 2,2':6',2''-terpyridine (terpy) ligand and tetramethyltin were received from Aldrich, and their purity was checked by 1H NMR. Dimethyl sulfoxide was purified by liquid chromatography on alumina under argon and stored over molecular sieves. The solvents used were purified and dried by standard techniques. All the other reagents were of the highest commercial grade

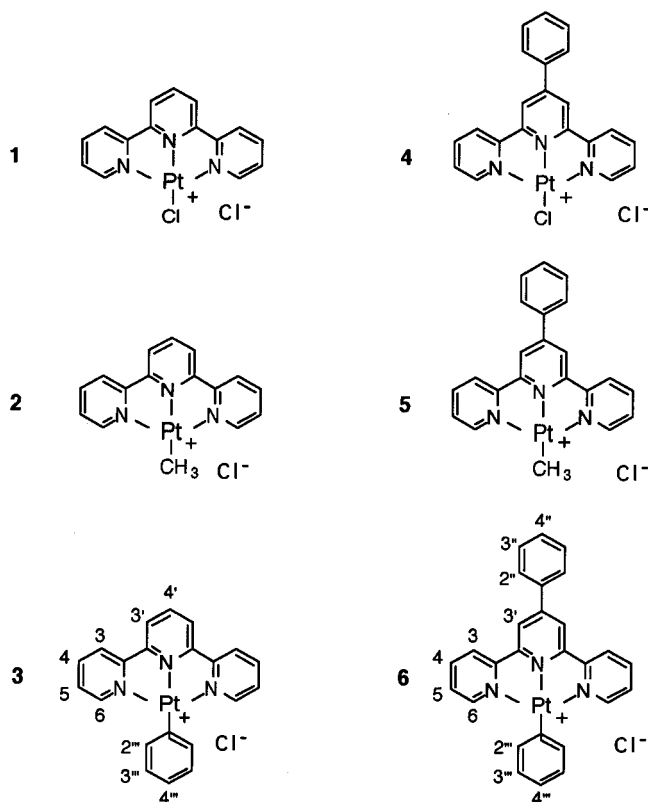


Figure 1. Structural formulas of the complexes.

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available and were used as received or were purified by distillation or recrystallization where necessary.

One- and two-dimensional correlated (COSY) 1H NMR and ^{13}C spectra were recorded on a Bruker ARX-300 spectrometer equipped with a broad-band probe operating at 300.13 and 75.5 MHz, respectively. Chemical shifts are reported in parts per million (δ) from TMS as internal reference. ^{13}C NMR chemical shifts were taken with reference to the solvent peak and are reported in parts per million versus TMS. The temperature within the probe was checked by the methanol or ethylene glycol method.²⁰ Absorption spectra were recorded on a Cary 219 spectrophotometer. A Perkin-Elmer LS-5B spectrofluorimeter equipped with a Hamamatsu R928 phototube was used to obtain luminescence spectra. Emission maxima are uncorrected for photomultiplier response. Luminescence lifetimes were measured with an Edinburgh FL900 single photon counting apparatus using a nitrogen discharge as a pulsed-light source (pulse width: 3 ns). The emission decay traces were deconvoluted for the instrumental flash lamp by the Marquardt algorithm. For each measurement, at least five determinations were carried out. Experimental errors are as follows: absorption and emission maxima, ± 2 nm; emission lifetimes, 10%.

Synthesis of the Compounds. 4'-Phenyl-2,2':6',2''-terpyridine (Ph-terpy). The ligand was prepared according to the literature.²¹ 1H NMR ($CDCl_3$, $T = 303$ K): δ 8.76 (s, 2H); 8.73 (d, $^3J_{HH} = 4.4$; 2H); 8.66 (d, $^3J_{HH} = 7.9$ Hz; 2H); 7.91 (d, $^3J_{HH} = 6.8$ Hz, 2H); 7.84 (ddd, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.6$ Hz; 2H); 7.48 (m, 3H); 7.31 (ddd, $^3J_{HH} = 5.9$ Hz, $^4J_{HH} = 1.6$ Hz; 2H). ^{13}C NMR ($CDCl_3$, $T = 303$ K): δ 156.2 (2C, C₂); 155.8 (2C, C₂); 150.1 (1C, C₄); 149.0 (2C, C₆); 138.4 (1C, C_{1'}); 136.7 (2C, C₅); 128.9 (1C, C_{4'}); 128.8 (2C, C_{3''}); 127.2 (2C, C_{2'}); 123.6 (2C, C₄); 121.2 (2C, C₃); 118.8 (2C, C_{3''}).

The precursor complexes *cis*-[Pt(Me₂SO)₂Cl₂],²² *trans*-[Pt(Me₂SO)₂(CH₃)Cl],²³ and [Pt(Me₂SO)₂(Ph)Cl],²³ and the complex [Pt(terpy)(CH₃)Cl] (2)¹⁶ were prepared according to published methods. They were crystallized several times, and their purity was checked by 1H NMR.

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[Pt(terpy)Cl]Cl (1). This complex was prepared according to the method of Morgan and Burstall²⁴ as modified by Howe-Grant and Lippard.²⁵ ¹H NMR (0.002 M in methanol-*d*₄): δ 9.11 (dd, ³J_{HH} = 5.5 Hz, ⁴J_{HH} = 1.1 Hz; ³J_{PH} = 36.0 Hz; 2H); 8.50 (m, 7H), 7.89 (ddd, ³J_{HH} = 6.4 Hz, ⁴J_{HH} = 1.6 Hz; 2H). ¹³C NMR (methanol-*d*₄, *T* = 308 K): δ 160.1, 156.2 (4C, C₂ + C_{2'}), 152.6 (2C, ²J_{PC} = 21 Hz, C₆), 143.8 (2C, C₄), 143.2 (1C, C_{4'}), 130.1 (2C, ³J_{PC} = 30 Hz, C₅), 126.8 (2C, ³J_{PC} = 31 Hz, C₃), 125.6 (2C, ³J_{PC} = 30 Hz, C_{3'}).

[Pt(terpy)(Ph)]Cl (3). 2,2':6',2''-Terpyridine (70 mg, 0.3 mmol) was allowed to react with [Pt(Me₂SO)₂(Ph)Cl] (139 mg, 0.3 mmol) in 20 mL of methanol with stirring. After 20 min, the yellowish solution was concentrated under vacuum, diethyl ether was added, and the mixture was cooled. The red precipitate was collected, washed with diethyl ether, and dried under vacuum (120 mg; yield 75%). Anal. Calcd for C₂₁H₁₆N₃ClPt: H, 2.98; C, 46.64; N, 7.77; Cl, 6.56. Found: H, 3.02; C, 46.70; N, 7.65; Cl, 6.47. ¹H NMR (0.002 M in methanol-*d*₄, *T* = 308 K): δ 8.50 (m, 7H); 8.36 (ddd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.5 Hz; 2H); 7.70 (ddd, ³J_{HH} = 6.8 Hz, ⁴J_{HH} = 1.2 Hz; 2H); 7.55 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, ³J_{PH} = 33.3 Hz; 2H); 7.24 (t, ³J_{HH} = 7.5 Hz; 2H); 7.11 (t, ³J_{HH} = 7.5 Hz; 1H). ¹³C NMR (methanol-*d*₄, *T* = 308 K): δ 160.8 (2C), 154.6 (2C, ²J_{PC} = 38 Hz, C₆), 150.7 (1C, C_{1''}), 142.7 (1C, C_{4'}), 142.5 (2C, C₄), 137.8 (2C, C_{3''}), 129.9 (2C, ³J_{PC} = 47 Hz, C₅), 129.3 (2C, ²J_{PC} = 52 Hz, C_{2''}), 126.6 (2C, ³J_{PC} = 31 Hz, C₃), 125.6 (1C, C_{4''}), 124.7 (2C, ³J_{PC} = 14 Hz, C_{3'}).

[Pt(Ph-terpy)Cl]Cl (4). A methanol solution (30 mL) of Ph-terpy (48 mg, 0.155 mmol) was added dropwise to a stirred methanol (100 mL) suspension of *cis*-[Pt(Me₂SO)₂Cl₂] (65 mg, 0.155 mmol). After 2 h, the yellowish solution was concentrated under vacuum, diethyl ether was added, and the mixture was cooled. The pale-yellow precipitate was collected, washed with diethyl ether, and dried under vacuum (64 mg; yield 72%). Anal. Calcd for C₂₁H₁₅N₃Cl₂Pt: H, 2.63; C, 43.86; N, 7.30; Cl, 12.33. Found: H, 2.65; C, 43.69; N, 7.16; Cl, 12.21. ¹H NMR (0.002 M in methanol-*d*₄, *T* = 308 K): δ 9.10 (ddd, ³J_{HH} = 5.7 Hz, ⁴J_{HH} = 1.2 Hz, ⁴J_{PH} = 34.0 Hz; 2H); 8.76 (s, 2H); 8.64 (dd, ³J_{HH} = 7.9 Hz; 2H); 8.43 (ddd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.4 Hz; 2H); 8.08 (m, 2H); 7.88 (ddd, ³J_{HH} = 6.6 Hz, ⁴J_{HH} = 1.4 Hz; 2H); 7.66 (m, 3H). ¹³C NMR (methanol-*d*₄, *T* = 308 K): δ 160.2, 156.4, 156.0, 137.0 (6C, C₂ + C_{2'} + C_{4'} + C_{1''}), 152.9 (2C, ³J_{PC} = 24 Hz, C₆), 143.6 (2C, C₄), 132.6 (1C, C_{4''}), 130.8, 128.9 (4C, C_{2''} + C_{3''}), 130.0 (2C, ³J_{PC} = 33 Hz, C₅), 126.8 (2C, ³J_{PC} = 33 Hz, C₃), 122.8 (2C, ³J_{PC} = 32 Hz, C_{3'}).

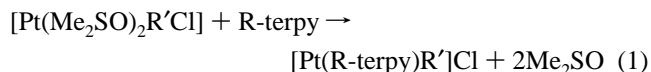
[Pt(Ph-terpy)Me]Cl (5). 4'-Phenyl-2,2':6',2''-terpyridine (77 mg, 0.249 mmol) was allowed to react with *trans*-[Pt(Me₂SO)₂(CH₃)Cl] (100 mg, 0.249 mmol) in 50 mL of methanol with stirring. After 20 min, the yellowish solution was concentrated under vacuum, diethyl ether was added, and the mixture was cooled. The orange precipitate was collected, washed with diethyl ether, and dried under vacuum (127 mg; yield 92%). Anal. Calcd for C₂₂H₁₈N₃ClPt: H, 3.27; C, 47.62; N, 7.57; Cl, 6.39. Found: H, 3.20; C, 47.51; N, 7.42; Cl, 6.32. ¹H NMR (0.002 M in methanol-*d*₄, *T* = 308 K): δ 8.88 (dd, ³J_{HH} = 5.6 Hz, ⁴J_{HH} = 1.2 Hz, ³J_{PH} = 52.0 Hz; 2H); 8.69 (s, 2H); 8.56 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{PH} = 18.0 Hz; 2H); 8.36 (ddd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.6 Hz; 2H); 8.00 (m, 2H); 7.76 (ddd, ³J_{HH} = 6.2 Hz, ⁴J_{HH} = 1.4 Hz; 2H); 7.63 (m, 3H), 1.15 (s, ²J_{PH} = 73.5; 3H). ¹³C NMR (methanol-*d*₄, *T* = 308 K): δ 161.4, 154.5, 153.9, 137.7 (6C, C₂ + C_{2'} + C_{4'} + C_{1''}), 152.5 (2C, ²J_{PC} = 33 Hz, C₆), 142.2 (2C, C₄), 132.1 (1C, C_{4''}), 130.8, 128.7 (4C, C_{2''} + C_{3''}), 129.8 (2C, ³J_{PC} = 42 Hz, C₅), 126.7 (2C, ³J_{PC} = 31 Hz, C₃), 122.3 (2C, ³J_{PC} = 12 Hz, C_{3'}), -5.2 (1C, CH₃).

[Pt(Ph-terpy)(Ph)]Cl (6). This complex was prepared following the same procedure reported for **3** (yield 72%). Anal. Calcd for C₂₇H₂₀N₃ClPt: H, 3.27; C, 52.57; N, 6.81; Cl, 5.75. Found: H, 3.20; C, 52.63; N, 6.89; Cl, 5.60. ¹H NMR (0.002 M in methanol-*d*₄, *T* = 308 K): δ 8.82 (s, 2H); 8.65 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.3 Hz; 2H); 8.48 (ddd, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.3 Hz, ³J_{PH} = 53.0 Hz; 2H); 8.38

(ddd, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.3 Hz; 2H); 8.06 (m, 2H); 7.69 (ddd, ³J_{HH} = 6.7 Hz, ⁴J_{HH} = 1.3 Hz; 2H); 7.64 (m, 3H); 7.57 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.3 Hz, ³J_{PH} = 33.3 Hz; 2H); 7.24 (t, ³J_{HH} = 7.5 Hz; 2H); 7.11 (t, ³J_{HH} = 7.5 Hz; 1H). ¹³C NMR (methanol-*d*₄, *T* = 308 K): δ 160.8, 155.5, 154.7, 137.5 (6C, C₂ + C_{2'} + C_{4'} + C_{1''}), 154.5 (2C, ²J_{PC} = 38 Hz, C₆), 150.8 (1C, C_{1''}), 142.4 (2C, C₄), 137.9 (2C, C_{3''}), 132.2 (1C, C_{4''}), 130.8, 128.9 (4C, C_{2''} + C_{3''}), 129.9 (2C, ³J_{PC} = 47 Hz, C₅), 129.3 (2C, ³J_{PC} = 52 Hz, C_{2''}), 126.8 (2C, ³J_{PC} = 31 Hz, C₃), 125.6 (1C, C_{4''}), 122.3 (2C, C_{3'}).

Results

The chloride salts of these cationic square-planar platinum(II) complex ions were easily synthesized according to the following general reaction:



The simultaneous presence in the starting complexes of two sulfoxides²⁶ and in the organometallic compounds of a high trans-activating σ -donor carbon group²⁷ makes the substitution by the terdentate ligand very facile. The course of the reaction can be monitored by conventional spectrophotometry in the near-UV/vis region.

All the complexes were obtained as solids and were fully characterized through their elemental analyses and NMR spectra. The ¹H NMR spectra in methanol-*d*₄ were assigned following the numeration pattern reported in Figure 1 and according to previously published results on analogous complexes.^{13e,16} The assignment was achieved by standard 1D and 2D techniques and was facilitated by the presence of large coupling constants associated with the isotopically abundant ¹⁹⁵Pt (33%, *I* = 1/2). The values of the coupling constants ²J_{PH} = 74 Hz, for the methyl group in complexes **2** and **5**, is in the range of values reported in the literature for a methyl group trans to pyridine.²⁸ The H₆ protons originate a doublet coupled with H₅ with satellite peaks due to ¹⁹⁵Pt coupling. The values of this coupling constant lie near 52 and 35 Hz for the organometallic and the coordination complexes, respectively. A collection of ¹H NMR data for the various complexes is reported in Table I. A comparison of the chemical shift values of the H₆ protons for the couples of complexes **2–3** and **5–6** reveals an upfield shift of about 0.4 ppm, which could be attributed to the anisotropy of the metal-coordinated phenyl ring with respect to a methyl substituent.

The peaks in the spectra for all the complexes, except **3** and **6**, are concentration and temperature dependent. When the concentration increases the peaks move upfield, while the effect of the temperature goes in the reverse direction (data not shown). These effects are related to the occurrence of extensive stacking of the complex in solution.²⁹ As expected, this phenomenon is smaller in dilute solution, at high temperatures, and in non-aqueous solvents.^{13e,16} The determination of the dimerization equilibrium constants was prevented by solubility problems.

¹³C NMR spectra of complexes were assigned on the basis of the ligand carbon spectra, the presence of coupling constants

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Table 1. ¹H NMR Data for R-terpy and [Pt(R-terpy)R']Cl Complexes^a

no.	complex	H ₆	H ₅	H ₄	H ₃	H _{3'}	H _{4'}	H _{2''}	H _{3''}	H _{4''}	H _{2'''}	H _{3'''}	H _{4'''}	Me
	terpy ^b	8.70	7.45	7.98	8.58	8.42	8.06							
1	[Pt(terpy)Cl]Cl	9.11 (36.0) ^c	7.89	8.50	8.50	8.50	8.50							
2	[Pt(terpy)Me]Cl ^e	8.98 (52.2)	7.32	8.39	8.48	8.48	8.45							1.23 (73.7) ^d
3	[Pt(terpy)(Ph)]Cl	8.50	7.70	8.36	8.52	8.50	8.50				7.55 (33.3) ^c	7.24	7.11	
	Ph-terpy ^b	8.73	7.84	7.31	8.66	8.76		7.91	7.48	7.48				
4	[Pt(Ph-terpy)Cl]Cl	9.10 (34.0)	7.88	8.43	8.64	8.76		8.08	7.66	7.66				
5	[Pt(Ph-terpy)Me]Cl	8.88 (52.0)	7.76	8.36	8.56	8.69		8.00	7.63	7.63				1.15 (73.5)
6	[Pt(Ph-terpy)(Ph)]Cl	8.48 (53.0)	7.69	8.38	8.65	8.82		8.06	7.64	7.64	7.57 (33.3)	7.24	7.11	

^a At 308 K in methanol-*d*₄ as solvent (0.002 M). Spectra were recorded at 300.13 MHz, and chemical shifts are given in parts per million from TMS as external standard. ^b In CDCl₃. ^c ³J_{PH} in hertz. ^d ²J_{PH} in hertz. ^e In methanol-*d*₄ at 298 K (0.001 M).

with ¹⁹⁵Pt, and the knowledge of the *trans*-influence effect on the their size.²⁸

All the studied complexes are stable in the most common solvents, as shown by the constancy of their absorption spectra within a week.

The absorption spectra of the complexes follow Beer's law in the concentration range investigated (1 × 10⁻⁵ to 3 × 10⁻⁴ M). They are dominated by moderately intense bands in the visible region (ε in the 10³–10⁴ M⁻¹ cm⁻¹ range) and by intense bands in the UV region (ε in the 10⁴–10⁵ M⁻¹ cm⁻¹ range). In general, Ph-terpy complexes have the lowest energy absorption band at slightly lower energy than that of the terpy-containing compounds. The same bands move to lower energy along the series Cl, Me, Ph of ancillary ligands, for both Ph-terpy and terpy compounds.

All the compounds are luminescent in a 4:1 (v/v) MeOH/EtOH rigid matrix at 77 K. Compounds **3** and **6** exhibit only a structured luminescence around 470 and 520 nm, respectively (lifetime in the range 10⁻⁵–10⁻⁴ s), while all the other compounds exhibit multiple luminescence features, each one of them characterized by a different lifetime. For these latter complexes, the luminescence at the highest energy is structured with a vibrational progression of ~1300 cm⁻¹ and is quite similar to the luminescence bands of **3** and **6**. A second emission, unstructured, occurs in the range 670–800 nm. An additional third broad, unstructured and intermediate in energy, luminescence band is also clearly exhibited by **1** and **4** within the entire concentration range used (> 1 × 10⁻⁵ M). A similar band is also shown by **2** and **5** as a lower intensity component of the luminescence spectra in highly concentrated solutions (> 1 × 10⁻³ M). The relative intensities of the luminescence bands depend on excitation wavelength and complex concentration in all cases. In general, the bands at lower energies increase their relative intensities with respect to the higher energy one on increasing concentration and for longer excitation wavelengths. Various attempts to obtain reliable excitation spectra for the complexes at 77 K failed because of technical problems, including the high concentrations needed to evidence the intermediate energy bands in complexes **2** and **5**.

The absorption and luminescence data of all the compounds are gathered in Tables 2 and 3, respectively. The absorption spectra of the complexes are shown in Figure 2. Figure 3 reports

Table 2. Selected Absorption Data for [Pt(R-terpy)R']Cl Complexes^a

no.	complex	λ _{max} , nm (ε, 10 ³ M ⁻¹ cm ⁻¹)
1	[Pt(terpy)Cl]Cl	284 (23.0); 334 (13.4); 404 (1.6) ^b
2	[Pt(terpy)Me]Cl	274 (15.9); 314 (10.1); 434 (1.3) ^b
3	[Pt(terpy)Ph]Cl	272 (24.4); 318 (11.6); 424 (2.0)
4	[Pt(Ph-terpy)Cl]Cl	284 (36.6); 334 (23.5); 410 (7.6)
5	[Pt(Ph-terpy)Me]Cl	278 (39.9); 342 (13.5); 430 (4.3)
6	[Pt(Ph-terpy)Ph]Cl	276 (31.5); 336 (17.2); 426 (4.2)

^a In 4:1 MeOH/EtOH as solvent. [Complex] = 2 × 10⁻⁵ M. The uncertainty on the lowest energy maxima is ±4 nm due to the broadness of the bands. ^b Shoulder.

Table 3. Luminescence Properties of the Complexes and Free Polypyridine Ligands at 77 K in 4:1 (v/v) MeOH/EtOH (Excitation Wavelength = 337 nm Unless Otherwise Stated)

no.	complex	λ _{max} , nm	τ, μs
	terpy	430 ^a	1300 ^a
1	[Pt(terpy)Cl]Cl	470	15.0
		670 ^c	3.1
		730 ^b	2.0
2	[Pt(terpy)Me]Cl	470	<i>d</i>
		600 ^c	7.0
		730	1.0
3	[Pt(terpy)Ph]Cl	470	4.0
		Ph-terpy	> 1 × 10 ⁶
4	[Pt(Ph-terpy)Cl]Cl	515	15
		650 ^c	3.7
		690 ^b	2.6
5	[Pt(Ph-terpy)Me]Cl	500	16
		700 ^c	<i>d</i>
		780	1.0
6	[Pt(Ph-terpy)Ph]Cl	520	10.0

^a In a butyronitrile rigid matrix. ^b The excitation wavelength is 540 nm. ^c The uncertainty on the reported maxima is ±10 nm, due to the broadness of the band and the low intensity. ^d Emission too weak to measure lifetime.

the luminescence spectra of **2**, **3**, **5**, and **6**. The luminescence spectra of **4** at different excitation wavelengths are displayed in Figure 4. Finally, the luminescence spectra of **4**, on changing concentration, are given as Supporting Information (Figure S11).

Discussion

Synthesis and NMR Spectra. Reaction 1 offers an easy synthetic route to cationic complexes of the type [Pt(R-terpy)-R']Cl. The starting complexes [PtR'Cl(Me₂SO)₂] (R' = Me or Ph) can be considered versatile synthons to access organometallic species containing the Pt-R' moiety.³⁰ The terpyridine ligands act as terdentate, and no evidence of fluxionality³¹ has been detected for the investigated complexes. In a previous study,¹⁶ we showed that complex **2** exhibits a considerable tendency to stack in aqueous solution, forming dimers or more

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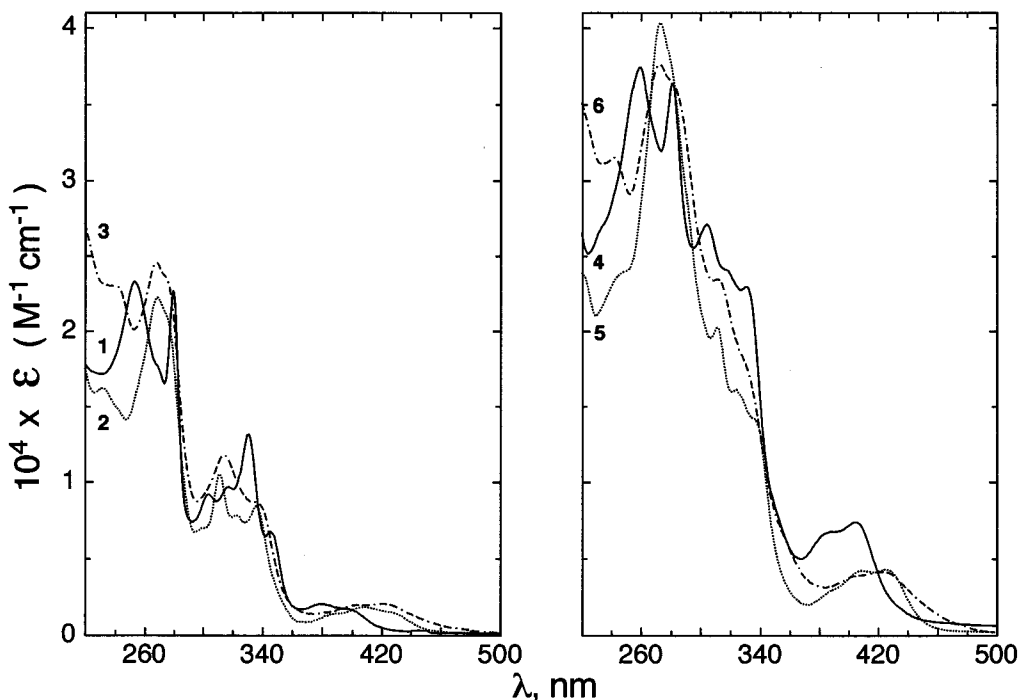


Figure 2. Absorption spectra of the studied complexes in 4:1 (v/v) MeOH/EtOH fluid solution at 298 K.

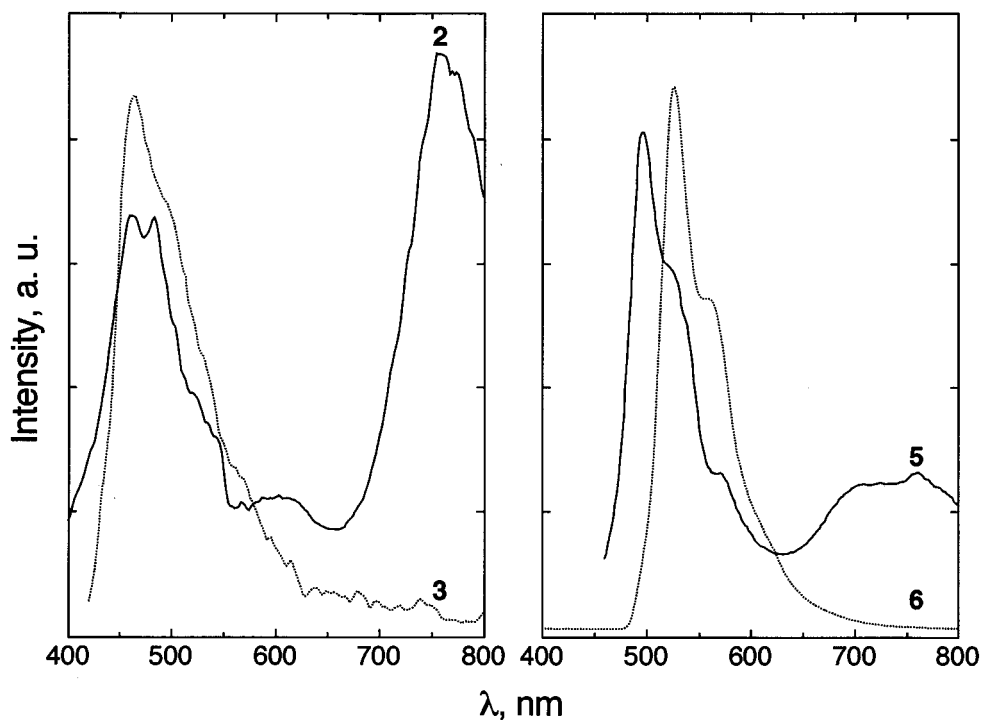


Figure 3. Normalized luminescence spectra of 2, 3, 5, and 6 in 4:1 (v/v) MeOH/EtOH rigid matrix at 77 K. The excitation wavelength is 380 nm.

extended aggregates, according to the experimental conditions. Light-scattering measurements have clearly pointed out that, on going from aqueous to alcoholic solutions, aggregation is fostered.³² Accordingly, the equilibrium for the investigated complexes in methanol is expected to move forward the

formation of the dimer or higher aggregated species. Further evidence for aggregation comes from the ¹H NMR data. On increasing the concentration or on lowering the temperature, some resonances experience an upfield shift. The shift to lower frequencies of the signals in the NMR spectra is a well-documented phenomenon due to the ring effect of different interacting aromatic moieties.²⁹ The temperature dependence indicates again that the π -stacking interactions between two terpyridyl moieties are weakened on increasing the temperature.

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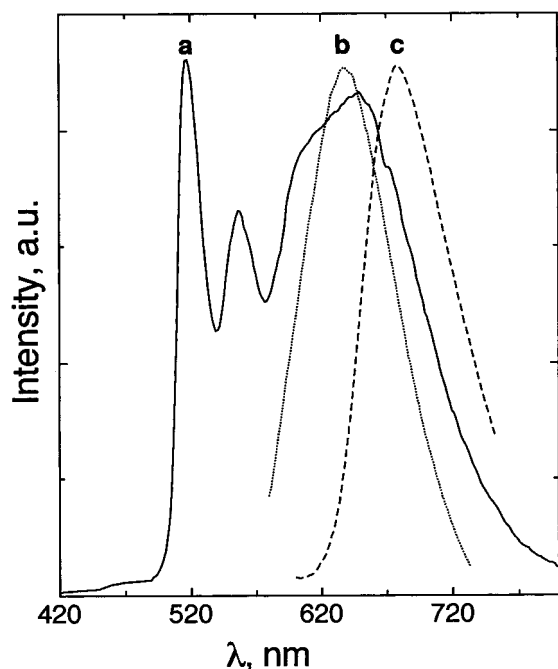


Figure 4. Normalized luminescence spectra of **4** in 4:1 (v/v) MeOH/EtOH rigid matrix at 77 K. The excitation wavelength is 350 nm (a), 460 nm (b), and 540 nm (c). The concentration is 1×10^{-4} M in all cases.

This finding is in line with the fact that platinum complexes containing 2,2'-bipyridyl,³³ purine bases, and acridine-based dyes³⁴ exhibit negative values for the enthalpy of stacking formation.

These observations apply to all the complexes, except **3** and **6**. As these latter complexes contain a phenyl ring directly coordinated to the metal center, it is possible that it prevents the dimerization process. Even through the rotation of this group is still allowed, molecular models show that it is difficult for the phenyl group to become coplanar with the coordination plane. The observation of an upfield shift (-0.4 ppm) of the H₆ protons on the terpyridine ligand could be attributed to the shielding effect of the phenyl ring current and supports this hypothesis.

Absorption Spectra. The moderately intense visible absorption of complexes **1–6** can be assigned to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions involving a d π platinum orbital as the donor orbital and π^* terpyridine orbitals as acceptor ones. Such an assignment is based on the absence of visible bands in the absorption spectra of the free ligands (which excludes ligand-centered assignment) and on the molar absorptivity (Table 2) of the compounds (which excludes metal-centered, MC, and ligand-to-metal charge transfer, LMCT, assignments). Furthermore, similar MLCT bands are peculiar to Pt(II)–polypyridine compounds.^{5d,10,11}

It is of interest to compare the energies of the MLCT bands within the series of complexes (Table 2). Within experimental error, the energy of the MLCT band in the homologous series (**1**, **2**, **3** and **4**, **5**, **6**) seems to decrease in the order Cl > Ph \approx Me, as a consequence of changes in the σ -donor electron ability of the fourth coordinated ligand. Electron donation increases

on passing from chloride to phenyl and methyl groups, the removal of an electron from d π metal orbital(s) becomes easier, the oxidation potential of the metal decreases, and the corresponding bands move to lower energies.

As far as the UV bands are concerned, they can be safely attributed to LC transitions due to the polypyridine ligands. Detailed assignment of such bands, however, is prevented by band overlapping.

The absorption spectra of the complexes do not change appreciably in the concentration range investigated (1×10^{-5} to 3×10^{-4} M). This observation suggests that there is no significant change in the distribution of the species within such a range. However, on increasing concentration above 1×10^{-3} M, low-intensity absorption features appear in the red portion of the spectra of **1**, **2**, **4**, and **5**, which probably are due to the increased concentration of the oligomeric structures, as suggested by NMR analysis. The study of the absorption properties of the highly concentrated solutions of these compounds is outside the aim of this paper.

Luminescence Properties. Luminescence of platinum(II)–polypyridine complexes in fluid solution at room temperature has been reported.^{6,9–11} However, in many cases⁶ room-temperature luminescence is reduced due to the presence of low-lying MC excited states, which can be easily populated by thermal activation, and provide fast deactivation pathways via molecular distortion.^{5–12} The situation is quite different in a rigid matrix at 77 K. Under these conditions the thermally activated deactivation processes are blocked and luminescence from MLCT and/or LC levels can be easily obtained.^{5–12} Besides MLCT and LC excited states, d $\sigma^* \rightarrow \pi^*$ (polypyridine) (hereafter, MMLCT) charge-transfer excited states have to be taken into account for the complexes under study. These excited states originate from metal–metal interactions usually occurring in head-to-tail dimers (or polymers) and have been demonstrated to be responsible for the emission of a number of metal–metal-bonded systems,^{5,7,10,19} including complex **1** in single crystals.^{5d,10c} The NMR analysis strongly suggests that head-to-tail dimerization occurs also for all the compounds studied here, except **3** and **6**, so that MMLCT excited states are indeed expected in our systems. Furthermore, when face-to-face approach is not hampered by steric factors, even excimer formation within dimers (or oligomers) can be obtained by π – π stacking interactions for complexes carrying large aromatic frameworks, and the possibility of excimeric emission has to be taken into account.^{5d,8,10d}

For the sake of simplicity, we will start the discussion of the photophysical properties of the studied compounds from **3** and **6**. We assign the luminescence exhibited by both of the complexes (Figure 3) to metal-perturbed ³LC excited states, on the basis of the following considerations: (i) the vibrational progression corresponds to the C=C and C=N stretching modes, the dominant high-frequency acceptor modes of CT and LC levels involving polypyridine-type ligands; (ii) a pure ³MLCT assignment can be ruled out by comparing the luminescence of **3** and **6** with the higher energy emission of **1** and **4** (Table 3, Figure 4). If pure ³MLCT states were responsible for the emission, in fact, the emission energies of **3** and **6** should be quite different from those of **1** and **4**, respectively, as dictated by the different nature of the fourth coordinated ligand.

The difference in emission energy between **3** and **6** stems from the difference in energy between the triplet π – π^* level in terpy and Ph-terpy, as evidenced by the luminescence spectra at 77 K of the free ligands (430 and 470 nm for terpy and Ph-terpy, respectively, see Table 3). The luminescence lifetimes

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of the two complexes, anyway, are much shorter than luminescence lifetimes of a “pure” ^3LC Pt emitter.^{35,36} This seems to indicate that $^3\text{MLCT}$ excited states could partially mix with the ^3LC level and contribute to the luminescence lifetime decay. Actually, it is known that higher level MLCT states can influence decay dynamics of luminescent metal-perturbed ^3LC excited states in metal-terpyridine compounds.³⁷

A mixed ^3LC – $^3\text{MLCT}$ assignment could also be proposed for the high-energy emission of all the other compounds **1**, **2**, **4**, and **5** (Table 3). The high-energy emissions of such compounds exhibit spectral characteristics similar to those of **3** (**1** and **2**) or **6** (**4** and **5**). The values of the excited-state lifetimes do not appear to differ significantly along the series of examined compounds.³⁸ The slight differences observed can be related to a different extent of mixing between MLCT and LC levels, in agreement with the results of Aldridge et al.,¹¹ concerning the luminescence properties of dilute $[\text{Pt}(\text{terpy})\text{X}]^+$ compounds ($\text{X} = \text{NCS}, \text{OH}, \text{OCH}_3$), which emphasize the delicate energetic balance of multiple states in this class of compounds.

The lowest energy emission exhibited by complexes **1**, **2**, **4**, and **5** (Table 3, Figures 3 and 4) can be safely assigned to triplet charge-transfer ($^3\text{MMLCT}$) excited states. Such an assignment is based on the unstructured, narrow shape of the luminescence bands (Figures 3 and 4) and on similar emissions of $\text{Pt}(\text{II})$ -terpyridine complexes reported by various authors,^{5,7,10} including the luminescence of **1** in the solid state^{10c} and in glasses.^{5d} The enhanced lower energy/higher energy emission intensity ratio, on increasing complex concentration (Figure S11), further supports the $^3\text{MMLCT}$ assignment. As stated above, NMR data suggest that concentration-dependent oligomerization occurs in **1**, **2**, **4**, and **5**, so confirming photophysical results. Emission within the range 690–800 nm, therefore, originates from excitation of oligomerized species, differently from emission within the range 460–560 nm, which originates from excitation of the “isolated” monomers. The introduction of a Pt–C bond in the complexes under investigation, while it does have an enormous impact on their self-aggregation,^{16,32} does not alter the luminescence properties, which are essentially similar to those reported by Che and co-workers for similar non-organometallic terpyridine complexes.^{10c}

The third emission found for **1** at about 670 nm (Table 3) already has been reported^{5d} in a different matrix and has been attributed to excimeric species originating from π – π interactions between the partially stacked terpy ligands. Our findings confirm the reported statement. A practically identical behavior is exhibited by **4** (Figure 4, Table 3), so that the above discussion also applies to this latter complex. In our matrix the excimeric emission obscures the $^3\text{MMLCT}$ emissions of both **1** and **4** when the complexes are illuminated with light of a wavelength shorter than 480 nm (Figure 4). In fact, $^3\text{MMLCT}$ emission becomes dominant at excitation wavelengths longer than 500 nm. It can be noted that the room-temperature absorption spectra of **1** and **4** do not show any absorption feature above 500 nm at the concentration studied (Figure 2). However, they exhibit a strong absorption in the range 480–600 nm in a rigid matrix at 77 K. This large rigidochromic effect is clearly evidenced by the red color of the frozen matrixes.

In contrast, the excimeric emission evidenced by **2** and **5** is only a low-intensity component of the more intense $^3\text{MMLCT}$

emission (Figure 3), in relatively concentrated solutions (where the contribution of “isolated” molecules to the global luminescence output is reduced). This could be explained on assuming different luminescent quantum yields for excimeric and $^3\text{MMLCT}$ emissions in the various complexes. However, an alternative hypothesis can be taken into account. Excimer formation depends strongly on the possibility of the individual monomers to assume a suitable conformation within the oligomeric assembly. Competition between stacked oligomers having different geometries can occur in solution, as suggested for other platinum-polypyridine systems,^{5d} so that a similar pattern is expected for the investigated complexes. In particular, some oligomers could assume the usual solid-state head-to-tail configuration,^{10c,d} which is mainly stabilized by metal–metal interactions, while some oligomers could assume different conformations, essentially stabilized by π – π interactions. It has been proposed that π – π stacking would take advantage of reduced electronic density on the aromatic frameworks.³⁹ Substitution of a strongly electron withdrawing ligand, such as chloride (**1** and **4**), with the electron donor methyl ligand (**2** and **5**) leads to an increased electron density at the metal and on the polypyridine ligands. This is expected to reduce π – π interactions and to favor stacking dominated by head-to-tail oligomers. Therefore excimeric emission in **2** and **5** is strongly reduced compared to that in **1** and **4**.

The dependence of the stacking arrangement on the nature of the ancillary ligands would represent an interesting example of how self-assembly can be driven toward different routes by suitable design of the building blocks. In this respect square-planar organometallic compounds appear to be particularly suitable because of the fine-tuning of their structural and electronic properties, and they deserve further investigation.

Conclusions

A series of new organometallic cationic platinum(II) complexes containing terdentate polypyridine ligands (**1**–**6**) have been prepared and characterized, and their absorption spectra in 4:1 (v/v) MeOH/EtOH fluid solution and luminescence properties in the same matrix at 77 K have been investigated. NMR experiments demonstrate that all the complexes but **3** and **6** oligomerize in solution to form stacked structures. While **3** and **6** exhibit only one luminescence feature originating from “isolated” molecules, all the other complexes exhibit multiple emission, including luminescence originating from oligomerized species.

The photophysical properties of the monomeric species depend on a delicate energetic balance between excited states, while the luminescence of the oligomers is interpreted by considering the presence of $^3\text{MMLCT}$ levels and excimeric species. Furthermore, these properties can be exploited as a useful tool for evaluating the steric and electronic stabilization effects of the ancillary ligands on the structure of the oligomeric arrays.

Acknowledgment. We wish to thank the CNR and MURST for financial support.

Supporting Information Available: Figure S11 displaying the concentration dependence of the luminescence spectra for complex **4** (1 page). Ordering information is given on any current masthead page.

IC9704896

(35) The luminescence lifetime of $[\text{Pt}(\text{ppy})_2(\text{CH}_2\text{Cl})\text{Cl}]$, a “*bona fide*” ^3LC emitter, is 300 μs .³⁶

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(38) For complex **2**, the lifetime of the highest energy emission was too weak to be measured. This is probably due to the fact that **2** is already strongly oligomerized, even at low concentration, as demonstrated by NMR analysis.³²

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