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Spectroscopic Properties of Orthometalated Platinum(II) Bipyridine Complexes Containing Various Ethynylaryl Groups

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Abstract: Neutral orthometalated platinum(II) complexes of the deprotonated 6-phenyl-2,2′-bipyridine ligand (bearing a trialkoxygallate, tolyl, ethynyltrialkoxygallate, or ethynyltolyl substituent) and a σ-bonded Cl, ethynyltolyl, or ethynyltrialkoxygallate coligand have been prepared by a stepwise procedure based on copper-promoted cross-coupling reactions. The X-ray structure of the [2-(*p*-tolyl)ethynyl][4-{2-(*p*-tolyl)-ethynyl}-6-phenyl-2,2′-bipyridyl)]platinum(II) complex revealed a coplanar arrangement of all residues bound to platinum, although the tolylethynyl groups exhibit position-dependent bending in the solid state. The complexes exhibit charge-transfer absorption in the visible region. All except two of the complexes also exhibit charge-transfer emission, typically from an excited state that has a submicrosecond lifetime at room temperature in deoxygenated dichloromethane solution. In accordance with the presence of a carbometalated polypyridine ligand, the emitting state is assumed to have a mixture of metal-to-ligand charge-transfer (MLCT) and intraligand charge-transfer (ILCT) character. However, spectral comparisons and electrochemical data suggest that the emissive state also exhibits interligand charge-transfer (LLCT) character when an electron-rich ethynylaryl group is bound to platinum. In keeping with altered orbital parentage in the latter systems, the emission occurs at longer wavelength. The excited-state lifetime is also shorter, evidently due to vibronic interactions. The decay is so efficient when an ethynyltrialkoxygallate group binds to platinum that there is no detectable emission in fluid solution, although the complexes do emit in a frozen glass. The excited states are subject to associative (exciplex) quenching by Lewis bases, but the admixture of ILCT and/or LLCT character diminishes efficiency, except for relatively strong bases like dimethyl sulfoxide and dimethylformamide.

Keywords: charge transfer · luminescence · platinum · redox chemistry · tridentate ligands

Introduction

Square-planar d^8 platinum(II) complexes have been shown to display intriguing spectroscopic and luminescence properties,[1,2] which are affected by unusual metal–metal and π–π stacking interactions of the surrounding ligands in the solid, liquid-crystalline, or gel state.[3,4] Solvent-induced aggregation and marked solvatochromism have been observed as well.[5] Early studies on d^8 platinum(II) complexes of the type [Pt(diimine)L$_2$] (L = halide, nitrile, thiolate, isocyanide, and acetylide) revealed low-energy absorptions arising from metal-to-ligand charge-transfer (MLCT) electronic transitions.[6,7] However, the development of these complexes was limited by their nonemissive or short-lived excited states in solution at room temperature. The lack of emission is due to the presence of low-lying d–d excited states, which provide facile nonradiative deactivation pathways aided by molecular distortion.[1,8] One successful strategy used to construct long-lived and emissive terpyridyl platinum(II) complexes involves utilizing substituted terpyridine ligands with low-lying LUMOs and/or ancillary acetylide ligands with large electron-donating abilities to raise the HOMO of the metal center, which lowers the MLCT excited-state energy.[9] As a result, the energy gap between the MLCT and d–d states in-

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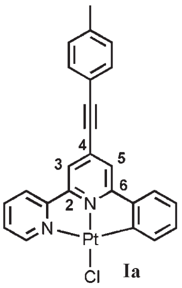
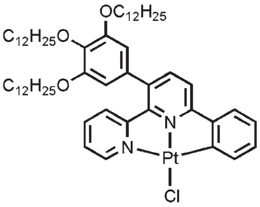
creases favorably.[10] Theoretical investigations confirm that substituents on the ancillary ligand can play a major role in tailoring the optical properties of such complexes.[10c] This trend was confirmed in many platinum(II) σ-alkynyl complexes displaying high quantum yield and long-lived photoluminescence from MLCT excited states.[11] Recently, such a strategy has proven to also be suitable in bipyridine-based Pt^{II} acetylide complexes, in which the available π orbitals on the ligand can be fully conjugated with the d_{xy} orbitals of the metal.[12] The interest in the photophysical properties arises because platinum(II) complexes are effective as DNA intercalators[13] as molecular probes for biological macromolecules,[14] in medicinal chemistry,[15] and in electroluminescent devices.[16] More recently, uses in singlet-oxygen production,[17] photocatalytic hydrogen generation,[18,19] vapochromism,[20] luminescence-based probes for cation sensing,[21] and sensitization of lanthanide emission have provided additional motivation for study.[22]


Ia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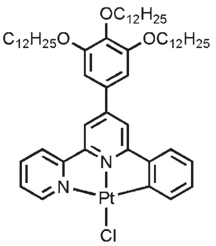
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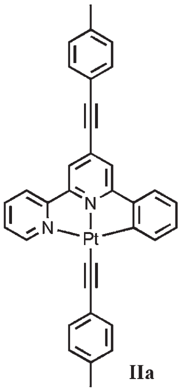
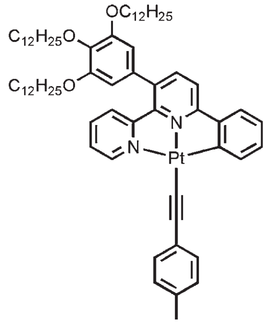

IIa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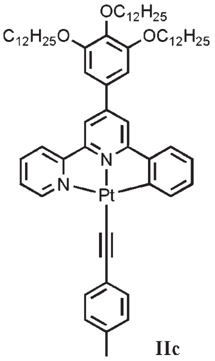
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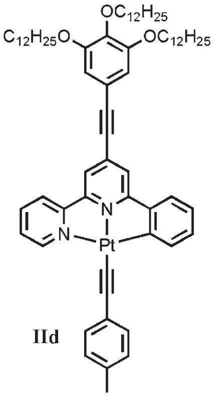
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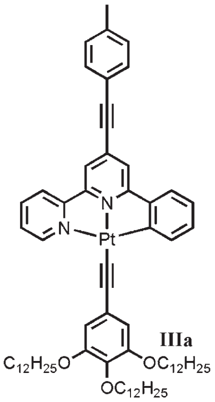
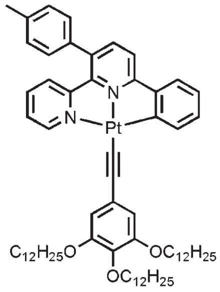
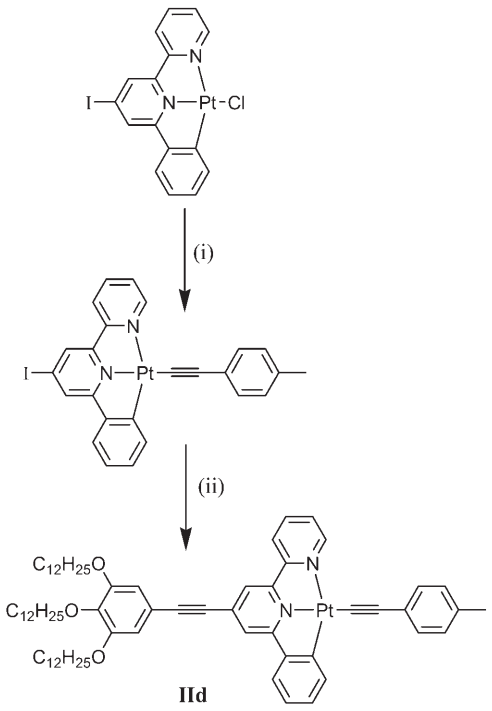

IIIa


IIIb

Electronic tuning of Pt^{II} complexes is possible because the properties of the core chelate (bipyridine, terpyridine, phenylbipyridine, thiophene–bipyridine, furan–bipyridine, etc.) are readily modified by incorporation of electron-donating or electron-withdrawing residues.[23–25] The ancillary coligand can also be advantageously replaced by σ-alkynyl residues, which can also bear substituents. Cationic or neutral complexes are obtainable with phenanthroline or bipyridine templates.[26,27] Orthometalated phenyl-bipyridine ligands also yield neutral complexes in conjunction with a σ-bonded acetylide ligand. A systematic study of the positional dependence of substituent effects is worthwhile and has not been realized to date. Our present study on the series of neutral complexes **I–III** including some in which gallate fragments (3,4,5-dodecaalkoxyphenyl) are present at the 3- or 4-position of the phenylbipyridine ligand or on the coligand. Comparisons with the chloro-substituted Pt complexes revealed that the presence of an ancillary σ-alkynylated ligand does not always positively influence the emission lifetime and quantum yield.

Results

Synthesis: The platinum chloro complexes **Ia** to **Ic** were prepared by heating the corresponding ligands with K_2PtCl_4 in a suitable solvent until disappearance of the ligand was observed by thin-layer chromatography. Cross-linking of *p*-tolylacetylene produced complexes **IIa–IIc** from the corresponding chloro complexes **Ia–Ic** under mild anaerobic conditions in the presence of CuI and triethylamine (to quench the nascent acid). Similar conditions were used to prepare complexes **IIIa** and **IIIb** from the chloro precursors and 3,4,5-tris(dodecyloxy)-5-ethynylbenzene. Direct reaction of the free ligand 4-{2-[3,4,5-tris(dodecyloxy)phenyl]ethynyl}-6-phenyl-2,2′-bipyridine with K_2PtCl_4 failed to give **IId**, likely due to degradation of the ligand. Synthesis was possible by first combining the 4-iodo-6-phenyl-2,2′-bipyridine ligand with K_2PtCl_4 in acetonitrile/water and then replacing the chloro coligand with *p*-tolylacetylene in the presence of catalytic amounts of CuI (Scheme 1).



Scheme 1. i) 4-Ethynyltoluene, CuI (10 mol %), DMF/NET$_3$, RT, 69 %; ii) 4-ethynylgallate, piperidine, [Pd(PPh$_3$)$_4$] (10 mol %), RT, 47 %.

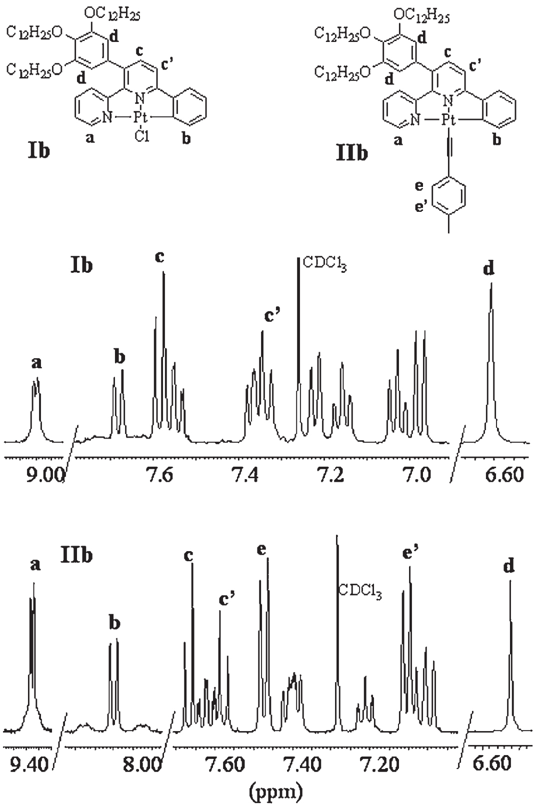


Figure 1. ^{1}H NMR (400 MHz, CDCl$_3$) spectra of complex **Ib** (top) and **IIb** (bottom). For the sake of clarity only the aromatic protons are shown.

Subsequent cross-coupling with 3,4,5-tris(dodecyloxy)-5-ethynylbenzene was achieved under mild conditions with piperidine as both solvent and base, and [Pd(PPh$_3$)$_4$] as catalyst. There was no sign of any scrambling of the ethynylaryl motifs during the last step. The complexes obtained are all thermally and photochemically stable and were characterized by classical spectroscopic methods and elemental analysis. Typical ^{1}H NMR spectra are shown in Figure 1. The most deshielded signal (a) is attributed to the proton in the position α to the nitrogen atom of the external pyridine ring. The second signal at low field (b) corresponds to the proton located next to the carbon–platinum σ bond. The observation of characteristic ^{195}Pt satellites for these two signals testifies to coupling with the platinum atom. The protons in *para* (c) and *meta* (c′) positions of the central pyridine ring form an AB quartet with J_{AB} coupling constant depending on the ligand substituents. Interestingly, when the chloro coligand is replaced by a tolyl acetylide group, proton signals (a) and (b) are shifted downfield from 9.00 to 9.30 ppm and 7.68 to 8.02 ppm respectively. A second AB quartet (ee′, $J_{AB}=8.3$ Hz, $\vartheta_0\delta=34.9$ Hz) is representative of the newly bound tolyl residue.

X-ray structure: The crystal structure reveals a distorted square-planar geometry around the metal center in complex **IIa** with a quasiplanar tridentate ligand.[28] The Pt−C bond lengths (1.963 and 1.976 Å) are not unusual, and the Pt−N bond lengths *trans* to the phenyl group (2.131 and 2.106 Å) are markedly longer than the Pt−N bond to the central nitrogen atom (1.941–1.966 Å). C≡C bond lengths linked to the metal center are shorter (1.151 and 1.185 Å) than the other C≡C bond lengths (1.235 and 1.180 Å). The Pt−C≡C bond lengths lie in the range 1.987–2.039 Å. Complex **IIa** crystallizes as head-to-tail dimers (Figure 2), stacked in an offset manner (involving half the tridentate ligand) through π–π interactions (the closest approach of 3.54 Å is between the centroids of the (*Cg4* = N2, C12–C16) and (*Cg2′* = Pt′ N1′ C11′ C12′ N2′) rings. Furthermore, the dihedral angles between any rings of the two platform ligands do not exceed 3.31°. The two crystallographically independent molecules (A and A′) display differences in the tilt angles of the two ethynyltolyl rings with respect to the quasiplanar Pt core, and pronounced bending of the substituents *Cg7* and *Cg7′* out of the metal–ligand planes by 20 and 12°, respectively, provides the most obvious distinction between the **A** and **A′** forms found in the crystal. The tilt-angle difference between **A** and **A′** is significantly greater for the ethynyltolyl group bound to the metal (89.1 vs. 32.1°) than for that bound to the ligand (53.3 vs. 33.9°). The ligand conformation reflects intermolecular C−H···π interactions that sandwich ring (*Cg7* = C28–33) between C20′ of ring (*Cg6′* = C19′–22′) and C15 of ring (*Cg4*) in position ($1+x$, y, z) according to interactions of type I and type III geometries,[29] respectively. The C20′−H20′···*Cg4* distance and angle are 2.888 Å and 172.8°, and the C15−H15···*Cg7* distance and angle are 2.982 Å and 136.5°. The *Cg6′* ring is also stabilized by weak π–π stacking

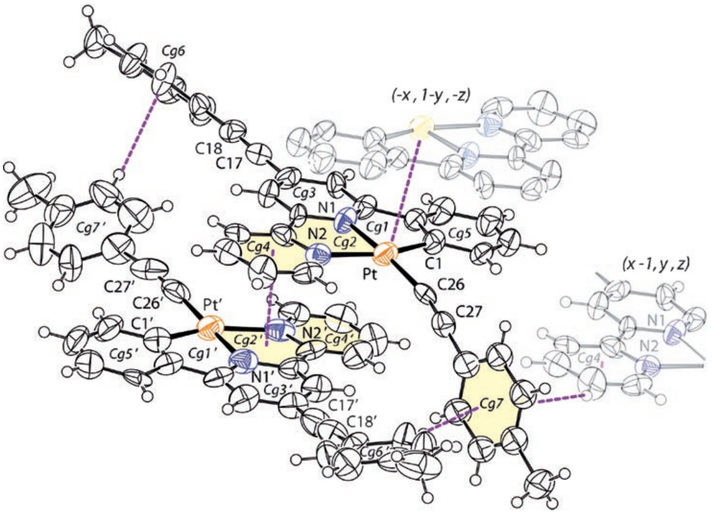


Figure 2. ORTEP view of compound **IIa** (50% probability displacement ellipsoids). Selected distances [Å] and angles [°]: Pt−N2 2.131, Pt−N1 1.976, Pt−C1 1.988, Pt−C26 2.039, C26−C27 1.151, C17−C18 1.235, N2-Pt-N1 79.33, N2-Pt-C1 160.11, N1-Pt-C26 174.76, Pt′−N2′ 2.16, Pt′−N1′ 1.963, Pt′−C1′ 1.970, Pt′−C26′ 1.997, C26′−C27′ 1.185, C17′−C18′ 1.180; N2′-Pt′-N1′ 79.59, N2′-Pt′-C1′ 158.84, N1′-Pt′-C26′ 177.40.

on its symmetry-related counterpart in position $8-x$, $1-y$, $-1-z$. At the opposite end of the dimer, the type III interaction involves ring *Cg6* facing C32′ with a C32′−H32′···*Cg6* distance of 2.892 Å and an angle of 134.0°.

The elongated conformers extend in the crystal along the [101] direction and are piled up along the *b* axis upside down through propagation of π–π interactions and C−H···π interactions in directions normal to *b*. Adjacent conformers of the same type are either offset by a 180° rotation around the 3.34 Å Pt−Pt axis running along *b* (for **A** conformers) or in π–π stacking interactions [for **A′** conformers, the shortest distance being 3.51 Å between *Cg1′* (Pt′, N1′, C1′, C6′-7′) and *Cg5′* (C1′–C6′)]. Nevertheless, all metal platforms lie on the (151) plane with average interplanar distances of about 3.3 Å, such that metal platform and tolyl sheets alternate along the normal to the *b* axis (Figure 3a and b).

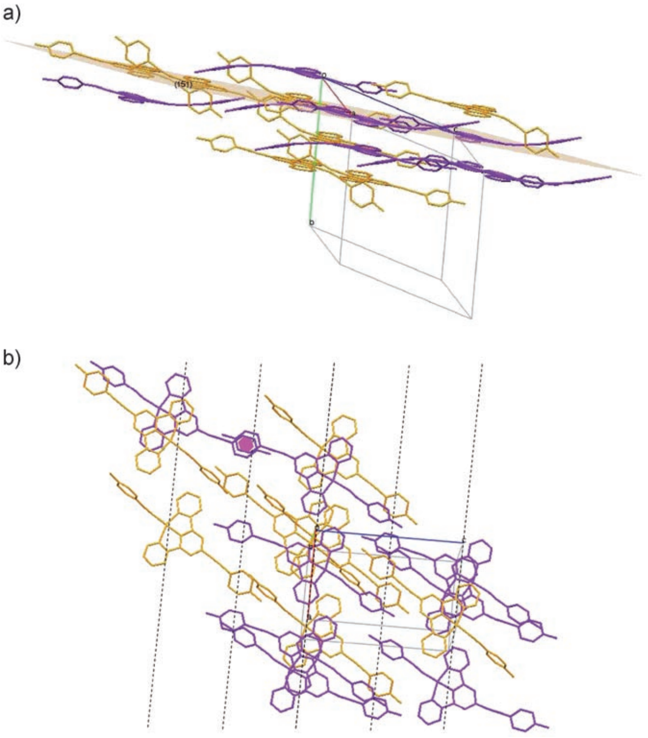


Figure 3. Views of the crystal packing of **IIa** down the *a* and *b* axes. Dashed lines are guidelines for sheets.

Table 1. Electrochemical data for the new *ortho*-metalated Pt^{II} complexes.[a]

	E^0 [V]	E^0 [V] (ΔE_p [mV])
Ia	–[b]	−1.29 (60)
Ib	–[b]	−1.36 (70)
Ic	–[b]	−1.36 (70)
IIa	+1.02 (irr.)	−1.29 (70)
IIb	+1.05 (irr.)	−1.37 (70)
IIc	+1.09 (irr.), +1.45 (irr.)	−1.37 (70)
IId	+1.02 (irr.), +1.30 (irr.)	−1.28 (70)
IIIa	+0.88 (irr.), +1.49 (irr.)	−1.29 (70)
IIIb	+0.90 (irr.), +1.49 (irr.)	−1.40 (70)

[a] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solution containing 0.1 M $[Bu_4N]PF_6$ at a solute concentration of about 1.5 mM and 20 °C. Potentials were standardized versus ferrocene (Fc) as an internal reference and converted to the SCE scale by assuming that $E_{1/2}(Fc/Fc^+) = +0.38$ V ($\Delta E_p = 60$ mV) versus SCE. Error in half-wave potentials is ±15 mV. For irreversible (irr.) processes the peak potentials E_{ap} are quoted. [b] Ill-defined processes.

Electrochemistry: Electrochemical data (Table 1) were measured in dichloromethane with tetrabutylammonium hexafluorophosphate as supporting electrolyte. All complexes show at least one reversible couple in the cathodic region and usually one or two irreversible waves in the anodic region. Comparison of the CVs of **Ia**–**IIIa** is informative. All three complexes exhibit a single reversible reduction at −1.29 V, independent of the coligand (Cl, ethynyltolyl, or ethynylgallate), in each instance attributable to reduction of the N^N^C ligand, influenced by complexation to Pt^{II}. Analogous results are found for Pt^{II} terpyridine complexes,[30,31] such as *tert*-butylterpyridine complexes, which in fact tend to display two reversible reduction processes.[32] In keeping with ligand reduction, introduction of an electron-donating gallate substituent on the periphery of the N^N^C ligand makes the reduction potential more cathodic by about 70 mV, regardless of whether the position of substitution is C2 or C3 (compare **Ib** with **IIb** and **Ic** with **IIc** in Table 1). Here, too, variation of the coligand has no effect. On the other hand, insertion of an ethynyl spacer between the N^N^C ligand and the gallate group shifts the reduction potential back into the range observed for ethynyltoluene-substituted derivatives.

Except for the systems with chloride as coligand, the complexes all display irreversible anodic waves as well. The first oxidation wave usually corresponds to removal of an electron from the HOMO and formally involves oxidation of

Pt^{II} to Pt^{III}.[33,34] In line with this view oxidation occurs at virtually the same potential [(+1.05±0.04) V vs. SCE] for all four complexes in series **II**. However, the fact that the first oxidation potential is about 15 mV more positive than those of the complexes in series **III** possibly signals more participation of the coligand in the HOMO. Most of the complexes containing a gallate group exhibit a second oxidation process (Table 1), likely assignable to gallate-centered process. Comparison between the oxidation of complex **IIc** and its metal-free ligand clearly allow the conclusion that the oxidation occurring at about +1.45 V is localized on the gallate residue (Figure 4). No such process is found in complex **IIa** or the corresponding metal-free ligand.

Room-temperature spectra: Representative absorption spectra of the platinum complexes in Figure 5 reveal at least two classes of electronic transitions. As is typical of platinum(II) polypyridine complexes,[14b,35] a network of relatively intense intraligand π–π* excitations appears in the UV region, at wavelengths below about 400 nm. Weaker bands ($\varepsilon \lesssim 10000\,\mathrm{M^{-1}cm^{-1}}$) with charge-transfer (CT) orbital parentage occur in the 400–550 nm window. The CT band system of complex **Ia** is similar to that of $[Pt(trpy)Cl]^+$ and related systems in exhibiting poorly resolved structure.[35,36] As illustrated in Figure 5, complexes with an ethynylaryl coligand, such as **IIc**, exhibit a broadened CT absorption that extends farther toward longer wavelengths. Complex **IIa**, which has an ethynyltolyl coligand and an ethynylaryl substituent at the 4-position of the N^N^C ligand, exhibits an even broader CT absorption.

The coordination environment also has a marked influence on the room-temperature emission properties, and this is especially true for the coligand. In particular, complexes **IIIa** and **IIIb**, which have an ethynylgallyl coligand, are unique among the series in that they do not exhibit detectable emission in fluid solution. In keeping with the absorption energies, complexes with a chloro coligand emit at shorter wavelengths than those in series **II**. Figure 6 depicts the emission spectra of the same complexes as in Figure 5. The room-temperature spectra are broad and featureless except when chloro is the coligand, and there is evidence of vibronic structure. The emission efficiencies are on the order of 2–4 % and tend to be higher for the complexes in series **I** (Table 2). Complex **Ia** exhibits the brightest emission signal. Substituents on the tridentate ligand also have an impact. In particular, the emission wavelength and quantum yield are higher when the aryl substituent of the N^N^C ligand is linked through an ethynyl spacer at the C4 position. In the absence of an ethynyl spacer, the emission yield tends to be higher when the aryl substituent is connected at the C4 as opposed to the C3 position of the N^N^C platform. There is, however, no obvious trend in the emission maxima of the aryl-substituted complexes.

The emission lifetime also tends to be longer when the aryl substituent is at the C4 position. When an ethynyl spacer is present, the lifetime is even

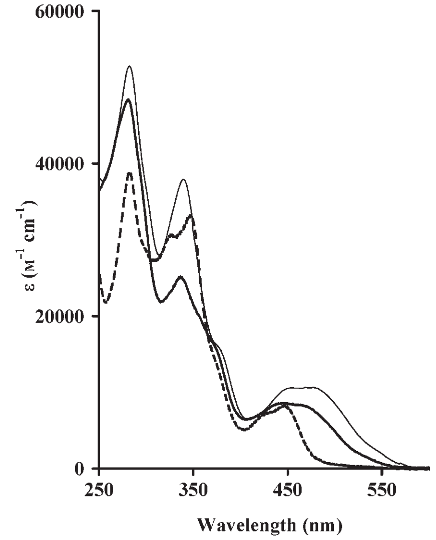


Figure 5. Absorption spectra of **Ia** (dashed), **IIa** (thin), and **IIc** (thick) in dichloromethane at room temperature.

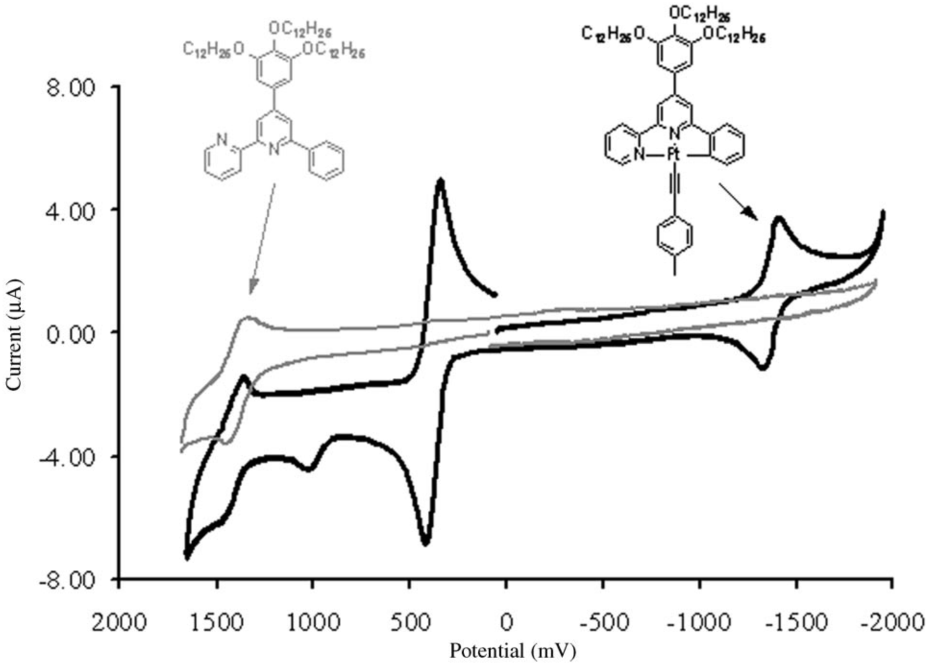


Figure 4. Cyclic voltammetry of complex **IIc** (thick line) and **L** (gray line) in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at room temperature, scan rate 200 mV s⁻¹.

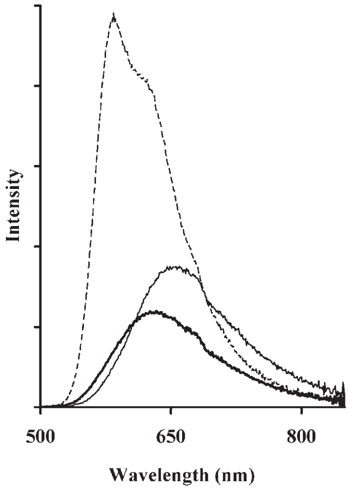


Figure 6. Corrected emission spectra of complexes **Ia** (dashed), **IIa** (thin), and **IIc** (thick) in deoxygenated dichloromethane at room temperature. The relative areas under the curves are in proportion to the quantum yields.

Table 2. Emission data corrected for instrument response.

Complex	Emission at 298 K[a]			Emission at 77 K[b]
	λ_{max} [nm]	τ [ns][c]	Φ[c]	λ_{max} [nm]
Ia[d]	584	1150	0.060	545, 589, 635br
Ib	583	310	0.020	528, 565, 615sh
Ic	569	530	0.049	525, 563, 610sh
IIa	639	379	0.018	533, 600sh
IIb	609	167	0.018	534, 574, 630sh
IIc	617	297	0.025	538, 560sh
IId	639	426	0.023	563, 600sh
IIIa	–[e]	–	–	543, 583, 630sh
IIIb	–[e]	–	–	535, 573, 620sh

[a] In deoxygenated dichloromethane solution. [b] In dichloromethane/chloroform (1/1). [c] Estimated error of 10%. [d] Fluid-solution data extrapolated to infinite dilution. [e] No measurable signal.

longer despite the fact that emission occurs at a longer wavelength (Table 2). All else the same, however, the complexes in series **I** exhibit the longest excited-state lifetimes. The lifetime of complex **Ia** is unique in that it is concentration dependent, and the value reported in Table 2 pertains to infinite dilution. Within experimental error, the other complexes do not show self-quenching, but the effect may simply be harder to detect when the excited-state lifetime is shorter.

Frozen-solution emission: The spectra observed from frozen solutions in chloroform/dichloromethane (1/1) at 77 K exhibit enhanced vibronic structure, except for the complexes of series **II** that have an ethynyltolyl coligand; see Figure 7 for representative spectra. As is frequently the case with related polypyridine complexes,[37] the emission appears at a shorter wavelength when the system is in a frozen matrix. In addition, the energy differences between emission maxima narrow, but the systems with a chloro coligand still emit at shorter wavelengths, while the 4-substituted complexes emit at longer wavelengths. One of the most striking effects is that the complexes of series **III** also exhibit emission in a frozen matrix. See Figure 7 for the emission spectrum of **IIIb**. One other finding is that some complexes are apparently prone to aggregation in frozen solution. The inset in Figure 7 shows the emission from a concentrated and a more dilute solution of complex **IIc**. The emission from the aggregated form occurs at a longer wavelength and in this particular case shows more vibronic structure.

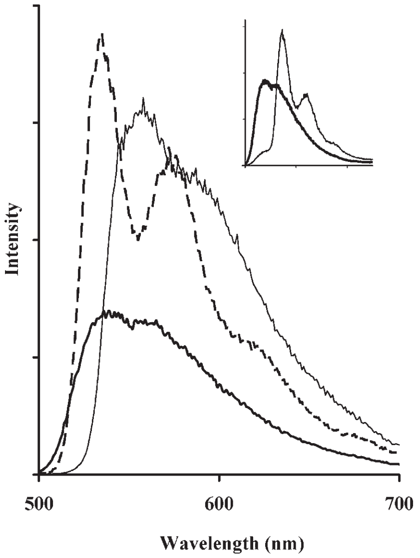


Figure 7. Corrected emission spectra of complexes **IIIb** (dashed), **IIa** (thin), and **IIc** (thick) in a dichloromethane/chloroform (1/1) glass at 77 K. The areas under the curves are arbitrary. The inset shows the emission spectrum of **IIc** in dilute (thick) and more concentrated solution (thin).

Quenching studies: Because the excited states of platinum(II) polypyridine complexes are often subject to quenching by Lewis bases, quenching studies were carried out, and Table 3 summarizes the results obtained for complexes **Ia** and **IIa**. The rate constants come from fits of the lifetime data depicted in Figure 8. Because quenching is inefficient except for relatively strongly donating Lewis bases, the results reported pertain to DMF and DMSO, which have donor numbers of 24.0 and 29.8, respectively.[38] When the Stern–Volmer plot shows evidence of upward curvature, the analysis allows for first- and second-order dependence on the concentration of Lewis base. Comparisons based on the

Table 3. Quenching rate constants measured in dichloromethane at room temperature.

Quencher	k_q [M^{-2}s^{-1}] (k_q [M^{-2}s^{-1}])[a]		Donor number[b]
	Ia	**IIa**	
DMF	1.1×10^7 (2.4×10^7)	9.2×10^5	24.0
DMSO	4.4×10^8	7.5×10^7 (7.3×10^7)	29.8

[a] Third-order rate constant extracted from curved Stern–Volmer plots. [b] Ref. [38].

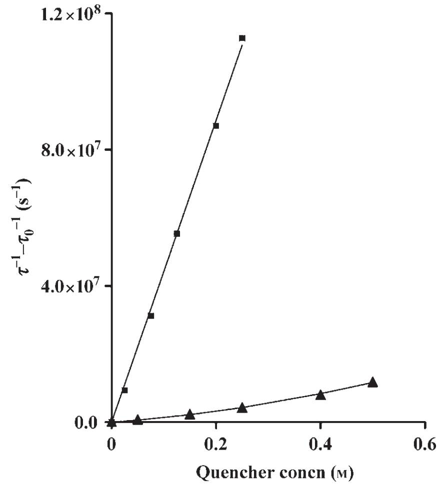


Figure 8. Quenching rates from the excited state lifetime of **Ia** as a function of the concentration of Lewis base at room temperature in dichloromethane. The quenchers are DMSO (■) and DMF (▼). The symbols τ and τ_0 designate the excited-state lifetime, at the same concentration of platinum, in the presence and absence of quencher, respectively.

rate constant for the term that is first-order in base (quencher) are more informative, because the second-order term is not always evident. The results reveal that the quenching efficiency of complex **Ia** is approximately an order of magnitude greater than that of **IIa**. Also, in line with the donor strengths, DMSO is a more potent quencher than DMF.

Discussion

CT absorption: The absorption maxima of the CT absorption bands of the complexes in series **I** appear at about 50 nm longer wavelength than the CT bands of [Pt(trpy)Cl]$^+$. Because the metal center formally becomes Pt^{III} in the excited state, the presence of the electron-rich carbometalated ligand accounts in large part for the reduction in energy required for excitation. In addition, theory suggests that excitation of a carbometalated system entails a degree of intraligand charge transfer (ILCT).[39,40] Thus, within the N^N^C ligand, some degree of charge transfer probably occurs from the π system of the phenyl moiety to that of the adjoining bipyridine group.

At least two other effects are evident in the visible spectra. One is that the CT absorption extends to significantly longer wavelengths for all complexes in series **II** and **III**. According to theoretical work on related systems,[10c,12a,41,42] the extra excitation at the longer wavelength end of the spectrum has ligand-to-ligand charge transfer (LLCT) character. Interligand CT excitation is possible when an orbital of the coligand, in this case an electron-rich ethynylaryl group, mixes into the HOMO. The electrochemical data in Table 1 suggest, in fact, that is the case. In the case of complexes **IIa**, **IId**, or **IIIa**, the CT absorption extends to even longer wavelengths due to the presence of the ethynyl spacer at the C4 position of the N^N^C ligand. In general, coupling to the empty π system of a substituent stabilizes the LUMO and lowers the energy of a CT transition. Although the other complexes in series **II** and **III** also have conjugating substituents at the C3 or C4 position, steric forces keep an aryl substituent from being in the plane of the polypyridine ligand and limit the magnitude of the shift that occurs.[8,43,44]

Photoluminescence: The photoluminescence properties summarized in Table 2 show interesting trends. All else the same in fluid solution, the emission yield is higher and the excited-state lifetime is longer if the complex has a chloro coligand as opposed to an ethynyltolyl coligand. Exactly the opposite trend occurs with simple terpyridine analogues. Thus, [Pt(trpy)Cl]$^+$ is virtually nonemissive in fluid solution,[35] whereas [Pt(trpy)(C≡CC$_6$H$_5$)]$^+$ emits with a microsecond excited-state lifetime in room-temperature dichloromethane solution.[9] Figure 9 schematically summarizes the key factors at work. Deactivation of photoexcited [Pt(trpy)Cl]$^+$ apparently occurs via a thermally accessible d–d excited state,[14b,35] or possibly a vibronic state characteristic of trpy complexes.[45] Either way, the nonradiative pathway becomes less accessible when a strong-field acetylide donor replaces the chloro coligand.[9] Replacing trpy with the carbometalated 6-phenyl-2,2′-bipyridine ligand has a similar effect, and [Pt(N^N^C)Cl] systems are also luminescent in solution.[46] Thus, the d–d excited states are apt to be thermally inaccessible in all three series under investigation. Direct, nonradiative decay to the ground state must, therefore, regulate the lifetime, and the process appears to be intrinsically more efficient for the excited states that exhibit LLCT character.

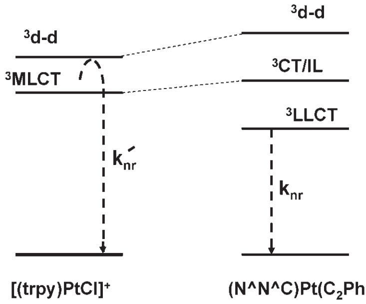
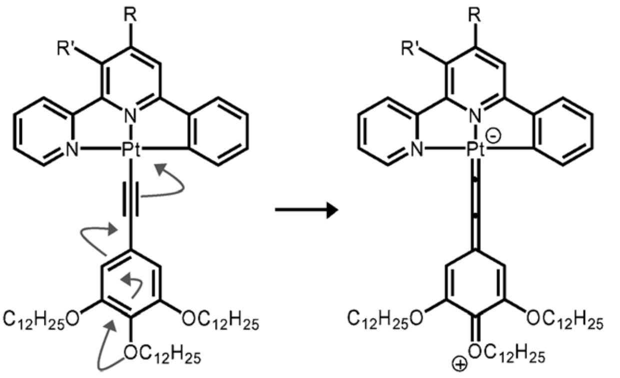


Figure 9. Excited-state energy-level schemes for [Pt(trpy)Cl]$^+$ and [Pt(N^N^C)(CCPh)]. Thermally assisted nonradiative decay via a ^{3}d–d excited state is efficient in the chloro complex, whereas direct nonradiative decay of the ^{3}LLCT state occurs in the ethynyl derivative.

The effect may be even more exaggerated in complexes **IIIa** and **IIIb**, both of which are nonemissive in fluid solution. As suggested by Scheme 2, the electron-rich gallate groups are capable of enhancing the LLCT charge separation. The electronic reorganization depicted in Scheme 2 implicitly involves changes in hybridization at various carbon centers and suggests that structural relaxation will occur in the excited state. All else the same, geometry changes in an



Scheme 2. Possible electron-donating scheme in 3,4,5-dodecaalkoxyphenylethynyl platinum complexes.

excited state facilitate curve crossing and radiationless decay to the ground-state surface. This model could explain the fact that complexes **IIIa** and **IIIb** become emissive in a frozen glass, because embedding the complex in a rigid matrix would inhibit the structural changes that promote radiationless decay. Others have also found that radiationless decay is efficient in platinum(II) terpyridine complexes with electron-rich ethynyl coligands.[47,48] In particular, the system studied by Han et al. has an $-C{\equiv}C(4\text{-}NR_2C_6H_4)$ coligand, and the complex is nonemissive in solution except in the presence of a strong acid, which curtails the electron-donating ability of the coligand by virtue of protonating the electron pair on the aniline nitrogen atom.[48] A referee suggested another possible explanation for the onset of emission from complexes **IIIa** and **IIIB** in a rigid glass, namely, that the energy ordering and/or orbital parentage of the low-lying excited states may be different in frozen solution due to changes in solvation.

Quenching phenomena: Another process of interest is formation of excited-state complexes, or exciplexes, by Lewis bases, as this can be an important quenching mechanism for platinum polypyridine complexes.[2a,36] In their ground electronic states, Pt^{II} complexes are almost always four-coordinate, and the ligands form sigma bonds with the $d_{x^2-y^2}$ orbital and define a more or less square-planar coordination geometry. However, higher energy configurations (i.e., d–d or MLCT excited states) can support a higher coordination number, so that association of a Lewis base becomes feasible after photoexcitation. Coupling to the added degrees of freedom induces quenching, and the rate constants increase with increasing donor strength of the base. However, they rarely approach the diffusion limit.[14b,49] For the complexes involved in this study, the quenching rates are relatively low, and studies have only been feasible with the strong donors DMF and DMSO. In fact, the rates are slow enough for the rate law to include a term that is second order in base concentration, consistent with, if not indicative of, pre-association of the quencher in the ground state. At least two factors limit the rate of exciplex quenching. One is the barrier to a change in coordination geometry that stems from the strength of coordinative covalent bonds to platinum. Simple theory suggests that the barrier to adding a fifth ligand scales with the ligand field parameter D_q, which is large for third-row transition metal ions.[49,50] The other mitigating factor is that the susceptibility to quenching varies with the orbital parentage of the excited state. For example, for a given base the rate of quenching is at least an order of magnitude faster for the photoexcited state of $[Pt(trpy)SCN]^+$ when compared with $[Pt(4'\text{-}NMe_2\text{-}T)Cl]^+$, where 4′-NMe_2-T designates 4′-(N,N-dimethylamino)-2,2′:6′,2′′-terpyridine.[49] The $[Pt(trpy)SCN]^+$ system is reactive because the excited state has mainly ^{3}MLCT character, so that the "hole" induced by excitation is localized largely on the metal center. In the case of the 4′-NMe_2-T complex the reactive excited state has substantial ^{3}ILCT character, and the platinum center is much less electrophilic in the photoexcited state.[31] Other systems in which the emissive excited state has substantial intraligand character are also less susceptible to quenching by Lewis bases[14b,51] Due to the presence of the carbometalated N^N^C ligand, the excited states of the complexes in series **I** and **II** all have substantial ^{3}ILCT character, and hence it is not surprising that the magnitudes of the quenching constants compiled in Table 3 are relatively modest. Quenching by Lewis bases is less efficient for the complexes in series **II** because the photoexcited states have an admixture of ^{3}LLCT character as well.

The other type of quenching worth noting occurs with complex **Ia**, which exhibits a concentration-dependent lifetime in solution. The effect is not without precedent, because Connick et al. found that neutral complexes of platinum are prone to self-quenching.[52] Che and co-workers found this to be the case with platinum complexed to a N^N^C ligand system as well.[46] For complexes with a carbometalated NCN ligand, Williams and co-workers reported that the observation of excimer emission is also possible.[53]

Conclusion

We have reported three new series of ternary platinum(II) complexes bearing electronically active substituents on the phenylbipyridine ligand and/or the coligand. All complexes are redox active and exhibit a reversible reduction wave and, with the exception of the PtCl complexes, one or more irreversible oxidation waves. Interestingly, the complex with the highest luminescence quantum yield (6%) in solution has a chloro coligand. Complexes with an electron-rich ethynylgallate coligand are nonemissive, but complexes with the same group grafted to the C4 position of the phenylbipyridine ligand emit normally. In general the emitting states exhibit ^{3}ILCT character, but LLCT character is also evident when an ethynylaryl coligand is present. The LLCT character enhances radiationless decay rates, especially in systems with an ethynylgallate coligand. Excited states with intra- and/or interligand orbital parentage tend to be less susceptible to exciplex quenching by Lewis bases. Future plans include extending the dimensionality by incorporating electron-withdrawing metal-containing groups in place of the ethynylaryl moieties.

Experimental Section

General methods: 200.1 (^{1}H), 300.1(^{1}H), 400 (^{1}H), 50.3 (^{13}C), 75.46 (^{13}C) and 100.3 MHz (^{13}C) NMR spectra were recorded at room temperature with the residual proton resonances of deuterated solvents as internal references. Fast-atom bombardment mass spectra were obtained by using a ZAB-HF-VB-analytical apparatus in positive mode with *m*-nitrobenzyl alcohol (*m*-NBA) as matrix. FTIR spectra were recorded on the neat liquids or as thin films, prepared by evaporating a drop of dichloromethane solution to dryness on KBr pellets. Chromatographic purification was conducted on standardized aluminum oxide 90 or silica gel Si 60 (40–63 μm). TLC was performed on aluminum oxide or silica gel plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio.

Materials: K_2PtCl_4, 4-ethynyltoluene, CuI, NEt_3, and piperidine were used as purchased. 4-(2-*p*-Tolylethynyl)-6-phenyl-2,2′-bipyridine, 3-[3,4,5-tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine, 4-[3,4,5-tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine, 3-(*p*-tolyl)-6-phenyl-2,2′-bipyridine, 3-(*p*-tolyl)-6-phenyl-2,2′-bipyridine)chloroplatinum,[54] and 3,4,5-tris(dodecyloxy)-5-ethynylbenzene[55] were prepared and purified according to literature procedures. The solvents, dichloromethane and chloroform, as well as the quenchers, dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF), came from Mallinckrodt. Exciton, Inc. supplied the laser dyes. G. Frederick Smith Chemical Company and/or Mallinckrodt were also the vendors for $[Ru(2,2'\text{-bipyridine})_3]Cl_2$ and acetonitrile.

[4-(2-*p*-Tolylethynyl)-6-phenyl-2,2′-bipyridine]chloroplatinum (Ia): 4-(2-*p*-Tolylethynyl)-6-phenyl-2,2′-bipyridine (100 mg, 0.29 mmol) and K_2PtCl_4 (122 mg, 0.29 mmol) were dissolved in of acetonitrile/water/chloroform (40 mL, 8/2/1) in a closed Schlenk tube and heated to 110 °C for 5 days. The solvents were evaporated; the residue was treated with water and extracted with dichloromethane. The residue was crystallized from dichloromethane/diethyl ether to give **Ia** (77 mg; 46 %) as yellow crystals. ^{1}H NMR ($(CD_3)_2SO$), 400 MHz): $\delta=8.96$ (dd with ^{195}Pt satellites, 1 H, $^{3}J=5.3$ Hz, $^{4}J=0.9$ Hz), 8.02 (td, 1 H, $^{3}J=7.9$, $^{4}J=1.6$), 7.86 (d, 1 H, $^{3}J=7.8$ Hz), 7.68 (dd with ^{195}Pt satellites, 1 H, $^{3}J=7.9$ Hz, $^{4}J=1.0$ Hz), 7.59–7.56 (m, 1 H), 7.51–7.47 (m, 3 H), 7.36 (d, 1 H, $^{4}J=1.0$ Hz), 7.28–7.23 (m, 3 H), 7.19 (td, 1 H, $^{3}J=7.4$ Hz, $^{4}J=1.3$ Hz), 7.06 (td, 1 H, $^{3}J=7.4$ Hz, $^{4}J=1.1$ Hz), 2.42 ppm (s, 3 H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz): $\delta=165.2$, 156.3, 154.4, 148.2, 146.4, 142.5, 140.6, 140.3, 134.3, 133.4, 131.8, 130.6, 129.7, 128.5, 125.2, 124.2, 124.1, 121.3, 120.9, 118.0, 97.1, 86.9, 21.3 ppm; UV/Vis (CH_2Cl_2): λ (ε)$=446$ (8200), 421 (sh, 6200), 346 (33 000), 325 (30 800), 282 nm (38 500 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}=2213$ (w, C=C), 1608 (m), 1534 (m), 1413 (m), 783 cm^{-1} (m); FAB^{+} MS: *m/z* (nature of the peak, relative intensity): 577.1, 576.1, 575.2, ($[M+H]^{+}$, 100, 95, 65); elemental analysis (%) calcd for $C_{25}H_{17}ClN_2Pt$: C 52.13, H 2.98, N 4.86; found: C 52.07, H 2.79, N 4.72.

{3-[3,4,5-Tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine)}chloroplatinum (Ib): 3-[3,4,5-Tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine (282 mg, 0.33 mmol) and K_2PtCl_4 (136 mg, 0.33 mmol) were charged into a Schlenk flask with THF (30 mL) and H_2O (7 mL). The biphasic mixture was heated to 65 °C for 18 h. The THF was removed by rotary evaporation and the residue was extracted with dichloromethane, washed with water and saturated brine, and filtered over hygroscopic cotton wool. The solvent was removed by rotary evaporation and the product purified by reprecipitation from dichloromethane/methanol to give **Ib** (305 mg; 85 %) as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=9.00$ (d, 1 H, $^{3}J=4.5$ Hz), 7.68 (d with ^{195}Pt satellites, 1 H, $^{3}J=7.0$ Hz), 7.59–7.53 (m, 2 H), 7.38–7.32 (m, 2 H), 7.22 (d, 1 H, $^{3}J=8.0$ Hz), 7.16 (t, 1 H, $^{3}J=7.5$ Hz), 7.03 (t, 1 H, $^{3}J=7.5$ Hz), 6.98 (d, 1 H, $^{3}J=8.5$ Hz), 6.60 (s, 2 H), 4.06 (t, 2 H, $^{3}J=6.5$ Hz), 3.97 (td, 4 H, $^{3}J=6.3$ Hz, $^{4}J=2.2$ Hz), 1.83–1.76 (m, 6 H), 1.58–1.25 (m, 54 H), 0.91–0.86 ppm (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=165.9$, 157.8, 154.4, 152.0, 148.6, 146.8, 143.4, 141.3, 138.6, 138.2, 136.0, 135.1, 132.2, 131.1, 126.9, 126.7, 124.4, 124.0, 117.7, 106.6, 73.8, 69.5, 32.1, 32.0, 30.6, 30.0, 29.9, 29.8, 29.6, 29.5, 26.3, 26.2, 22.9, 22.8, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε)$=437$ (1900), 367 (9300), 328 (15 000), 298 (sh, 21 500), 276 (27 900), 267 (sh, 26 700 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}=3045$ (w), 2915 (s), 2848 (s), 1576 (m), 1465 (s), 1430 (m), 1364 (m), 1336 (m), 1228 (s), 1088 (s), 1018 (m), 837 (m), 742 cm^{-1} (s); FAB^{+} MS: *m/z* (nature of the peak, relative intensity): 1056.1, 1055.1, 1054.1 ($[M-Cl]^{+}$, 100, 100, 60); elemental analysis (%) calcd for $C_{58}H_{87}ClN_2O_3Pt$: C 63.86, H 8.04, N 2.57; found: C 63.57, H 7.62, N 2.27.

{4-[3,4,5-Tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine}chloroplatinum (Ic) was prepared by the same procedure as for **Ib** from 4-[3,4,5-tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine (153 mg, 0.18 mmol), K_2PtCl_4 (82 mg, 0.20 mmol), THF (10 mL), and H_2O (5 mL); quick chromatography on silica gel with dichloromethane as eluent gave **Ic** (175 mg; 89 %) after reprecipitation from dichloromethane/methanol. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.50$–8.49 (m, 1 H), 7.79–7.68 (m, 2 H), 7.43–7.37 (m, 2 H), 7.12–7.11 (m, 3 H), 6.95–6.91 (m, 4 H), 4.15 (t, 4 H, $^{3}J=6.2$ Hz), 4.07 (t, 2 H, $^{3}J=6.4$ Hz), 1.91–1.79 (m, 6 H), 1.56–1.53 (m, 6 H), 1.30–1.26 (m, 48 H), 0.91–0.86 ppm (m, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta=165.4$, 157.2, 154.1, 153.9, 151.1, 148.1, 146.6, 142.6, 140.1, 138.6, 135.0, 133.0, 130.5, 126.6, 123.9, 123.6, 123.0, 117.4, 116.3, 106.3, 73.8, 69.9, 32.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 22.9, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε)$=437$ (6700), 420 (6500), 363 (sh, 16 700), 332 (22 400), 296 (sh, 25 800), 278 (36 200), 269 (sh, 32 200), 241 nm (sh, 30 900 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}=2919$ (s), 2850 (s), 1605 (m), 1583 (m), 1467 (m), 1243 (m), 1115 (s), 720 cm^{-1} (s); EI-MS: *m/z* (nature of the peak, relative intensity): 1090.5, 1089.5, 188.5 ($[M]$, 100, 100, 60); elemental analysis (%) calcd for $C_{58}H_{87}ClN_2O_3Pt$: C 63.86, H 8.04, N 2.57; found: C 63.59, H 7.53, N 2.39.

General procedure for copper-promoted coupling reaction: The chloroplatinum complex and the ethynyl derivate were dissolved in the appropriate solvent (CH_2Cl_2, DMF, or CH_2Cl_2/DMF). Triethylamine was added and the mixture was degassed by bubbling argon for 30 min. Then copper(I) iodide was added and the reaction mixture was stirred in the dark at room temperature for 1–3 days. The residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water and then with saturated brine and filtered over hygroscopic cotton wool. The solvent was removed by rotary evaporation and the residue was purified by column chromatography.

(2-*p*-Tolylethynyl)[4-(2-*p*-tolylethynyl)-6-phenyl-2,2′-bipyridine]platinum (IIa) was prepared by the general procedure from **Ia** (110 mg, 0.19 mmol), *p*-tolylacetylene (100 μL, 0.79 mmol), CuI (4 mg, 0.02 mmol), DMF (10 mL), and triethylamine (2 mL). Chromatography on aluminum oxide with dichloromethane/petroleum ether (75/25) as eluent gave **IIa** (100 mg; 82 %) as dark red crystals after recrystallization from dichloromethane/cyclohexane. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=9.03$ (dd, 1 H, $^{3}J=5.5$ Hz, $^{4}J=1.0$ Hz), 7.94–7.89 (m, 2 H), 7.79 (d, 1 H, $^{3}J=8.0$ Hz), 7.50–7.40 (m, 7 H), 7.29–7.26 (m, 1 H), 7.22 (d, 2 H, $^{3}J=8.0$ Hz), 7.14 (td, 1 H, $^{3}J=7.4$ Hz, $^{4}J=1.3$ Hz), 7.08 (d, 2 H, $^{3}J=8.0$ Hz), 7.02 (td, 1 H, $^{3}J=7.5$ Hz, $^{4}J=1.5$ Hz), 2.42 (s, 3 H), 2.35 ppm (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=165.0$, 157.8, 154.4, 151.6, 146.4, 142.7, 140.3, 138.7, 138.6, 134.8, 134.1, 132.2, 131.8, 131.5, 129.5, 128.8, 127.6, 126.1, 124.6, 123.7, 123.0, 120.2, 120.0, 118.8, 106.9, 104.6, 97.3, 86.9, 21.9, 21.5 ppm; UV/Vis (CH_2Cl_2): λ (ε)$=478$ (10 600), 454 (10 500), 374 (sh, 15 900), 339 (37 200), 282 (51 800), 249 nm (37 000 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}=3050$ (w), 2209 (w, C=C), 2088 (m, C=C), 1596 (m), 1500 (m), 1400 (m), 1237 (m), 1018 (w), 862 (m), 814 (s), 778 cm^{-1} (s); FAB^{+} MS: *m/z* (nature of the peak, relative intensity): 657.1, 656.1, 655.1 ($[M+H]^{+}$, 85, 100, 70), 540.0 ($[M-(C{=}CTol)]^{+}$, 35); elemental analysis (%) calcd for $C_{34}H_{24}N_2Pt$: C 62.28, H 3.69, N 4.27; found: C 61.92, H 3.44, N 3.89.

2-(*p*-Tolylethynyl){3-[3,4,5-tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine}platinum (IIb) was prepared by the general procedure from **Ib** (81 mg, 0.074 mmol), *p*-tolylacetylene (100 μl, 0.77 mmol), CuI (2 mg, 0.01 mmol), dichloromethane (10 mL), and triethylamine (2 mL); chromatography on silica gel with dichloromethane/petroleum ether (65/35) as eluent gave **IIb** (60 mg; 69 %) as an orange solid after reprecipitation from dichloromethane/methanol. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=9.30$ (dd, 1 H, $^{3}J=5.3$ Hz, $^{4}J=1.2$ Hz), 8.03 (dd with ^{195}Pt satellites, 1 H, $^{3}J=7.5$ Hz, $^{4}J=1.0$ Hz), 7.60 (AB system, 2 H, $J_{AB}=8.3$ Hz, $\vartheta_0\delta=34.9$ Hz), 7.59 (td, 1H, ^3J = 7.9 Hz, ^4J = 1.5 Hz), 7.45 (d, 2H, ^3J = 8.0 Hz), 7.40–7.36 (m, 2H), 7.19 (td, 1H, ^3J = 7.4 Hz, ^4J = 1.3 Hz), 7.09–7.01 (m, 4H), 6.54 (s, 2H), 4.05 (t, 2H, ^3J = 6.5 Hz), 3.94–3.90 (m, 4H), 2.34 (s, 3H), 1.84–1.74 (m, 6H), 1.46–1.25 (m, 48H), 0.90–0.86 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.0, 158.4, 154.4, 152.0, 151.9, 146.9, 143.1, 141.5, 138.7, 138.6, 137.8, 135.8, 134.8, 132.4, 131.8, 131.6, 128.7, 127.1, 126.8, 125.9, 124.5, 123.8, 117.7, 106.6, 106.5, 103.5, 73.8, 69.4, 32.1, 32.0, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.8, 21.5, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 461 (5300), 370 (12800), 335 (sh, 16600), 279 nm (44800 $M^{-1}cm^{-1}$), IR (KBr): $\tilde{\nu}$ = 3044 (w), 2920 (s), 2852 (s), 2099 (m, C≡C), 1583 (m), 1507 (m), 1462 (m), 1430 (m), 1340 (m), 1240 (s), 1111 (s), 821 (m), 751 (m), 718 cm^{-1} (m); FAB$^+$ MS: *m/z* (nature of the peak, relative intensity): 1172.0, 1171.0, 1170.0 ($[M+H]^+$, 100, 100, 55); elemental analysis (%) calcd for $C_{67}H_{94}N_2O_3Pt$: C 68.75, H 8.09, N 2.39; found: C 68.49, H 7.72, N 2.17.

(2-*p*-Tolylethynyl){4-[3,4,5-tris(dodecyloxy)phenyl]-6-phenyl-2,2′-bipyridine}platinum (IIc) was prepared by the general procedure from **Ic** (60 mg, 0.055 mmol), *p*-tolylacetylene (100 µl, 0.77 mmol), CuI (1 mg, 5.10^{-3} mmol), dichloromethane (8 mL), and triethylamine (2 mL). Chromatography on silica gel with dichloromethane/petroleum ether (50/50 to 1/0) as eluent gave **IIc** (45 mg; 70%) as an orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.91 (d with ^{195}Pt satellites, 1H, ^3J = 4.9 Hz), 7.96–7.90 (m, 2H), 7.80–7.78 (m with ^{195}Pt satellites, 1H), 7.57 (d, 1H, ^4J = 0.8 Hz), 7.34–7.25 (m, 3H), 7.24 (AB system, 4H, J_{AB} = 8.0 Hz, $\vartheta_0\delta$ = 125.3 Hz), 7.00–6.95 (m, 2H), 6.80 (s, 2H), 4.05–3.99 (m, 6H), 2.35 (s, 3H), 1.83–1.76 (m, 6H), 1.54–1.46 (m, 6H), 1.41–1.23 (m, 54H), 0.91–0.86 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.0, 158.3, 154.5, 153.9, 151.6, 151.4, 147.0, 142.5, 140.2, 138.7, 138.3, 134.7, 133.3, 131.6, 131.1, 128.8, 127.2, 126.2, 124.2, 123.4, 123.0, 116.5, 116.2, 106.2, 106.0, 105.2, 73.8, 69.7, 32.1, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 22.8, 21.5, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 465 (8300), 443 (8700), 366 (sh, 17300), 337 (24900), 296 (sh, 35700), 281 (47800), 269 (sh, 43100); IR (KBr): $\tilde{\nu}$ = 2921 (s), 2852 (s), 2098 (m, C≡C), 1606 (m), 1504 (m), 1464 (m), 1313 (m), 1114 (s), 816 (m), 722 cm^{-1} (m); EI-MS: *m/z* (nature of the peak, relative intensity): 1171.2, 1170.0, 1169.1 ($[M]$, 90, 100, 60); elemental analysis (%) calcd for $C_{67}H_{94}N_2O_3Pt$: C 68.75, H 8.09, N 2.39; found: C 68.67, H 7.67, N 2.11.

(2-*p*-Tolylethynyl){4-{2-[3,4,5-tris(dodecyloxy)phenyl]ethynyl}-6-phenyl-2,2′-bipyridine}platinum (IId): (2-*p*-Tolylethynyl)(4-iodo-6-phenyl-2,2′-bipyridine)platinum (75 mg, 0.11 mmol) and 3,4,5-tris(dodecyloxy)-5-ethynylbenzene (98 mg, 0.15 mmol) were charged into a Schlenk tube with piperidine (15 mL). The mixture was degassed by bubbling argon for 30 min, and then $[Pd(PPh_3)_4]$ (15 mg, 0.013 mmol) was introduced and the reaction mixture stirred at room temperature for 18 h. The solvent was evaporated and the residue purified by column chromatography on silica gel with dichloromethane/petroleum ether (70/30). The product was reprecipitated from dichloromethane/methanol to give **IId** (62 mg; 47%) as a red solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.88 (d, 1H, ^3J = 5.1 Hz), 7.85 (dd with ^{195}Pt satellites, 1H, ^3J = 7.3 Hz, ^4J = 0.9 Hz), 7.79–7.69 (m, 2H), 7.45–7.41 (m, 3H), 7.31–7.23 (m, 2H), 7.14 (d, 1H, ^3J = 7.7 Hz), 7.08–7.04 (m, 3H), 6.90 (td, 1H, ^3J = 7.5 Hz, ^4J = 1.1 Hz), 6.69 (s, 2H), 4.05–3.95 (m, 6H), 2.34 (s, 3H), 1.87–1.74 (m, 6H), 1.51–1.28 (m, 54H), 0.89 ppm (t, 9H, ^3J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.7, 157.6, 154.3, 153.3, 151.2, 146.4, 142.7, 140.5, 138.5, 138.4, 134.8, 133.8, 131.8, 131.3, 128.8, 127.3, 126.1, 124.6, 123.6, 123.2, 120.1, 119.9, 116.1, 110.8, 106.8, 104.9, 97.7, 86.4, 73.8, 69.4, 32.1, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 21.5, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 478 (10900), 455 (10700), 361 (28100), 346 (28400), 283 nm (55100 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3042 (w), 2919 (s), 2851 (s), 2207 (m, C≡C), 2102 (m, C≡C), 1601 (m), 1572 (m), 1504 (m), 1466 (m), 1364 (m), 1235 (s), 1116 (s), 1020 (m), 816 (m), 777 (m), 723 cm^{-1} (m); FAB$^+$ MS: *m/z* (nature of the peak, relative intensity): 1196.0, 1195.0, 1194.0 ($[M+H]^+$, 100, 95, 55), 1080.0 ($[M-(C{\equiv}CTol)]^+$, 30); elemental analysis (%) calcd for $C_{69}H_{94}N_2O_3Pt$: C 69.38, H 7.93, N 2.35; found: C 69.19, H 7.78, N 2.07.

{2-[3,4,5-Tris(dodecyloxy)phenyl]ethynyl}[4-(2-*p*-tolylethynyl)-6-phenyl-2,2′-bipyridine]platinum (IIIa) was prepared by the general procedure from **Ia** (77 mg, 0.13 mmol), 3,4,5-tris(dodecyloxy)-5-ethynylbenzene (95 mg, 0.145 mmol), CuI (2.5 mg, 0.013 mmol), dichloromethane (10 mL), and triethylamine (2 mL). Chromatography on silica gel with dichloromethane/petroleum ether (50/50 to 1/0) as eluent gave **IIIa** (85 mg; 55%) as a red solid after reprecipitation from dichloromethane/acetonitrile. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.08 (dd with ^{195}Pt satellites, 1H, ^3J = 5.2 Hz, ^4J = 0.9 Hz), 7.96–7.81 (m, 3H), 7.50–7.42 (m, 5H), 7.29 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.2 Hz), 7.21 (d, 2H, ^3J = 7.9 Hz), 7.14 (td, 1H, ^3J = 7.4 Hz, ^4J = 1.3 Hz), 7.01 (td, 1H, ^3J = 7.5 Hz, ^4J = 1.1 Hz), 6.78 (s, 2H), 4.01–3.94 (m, 6H), 2.41 (s, 3H), 1.84–1.72 (m, 6H), 1.51–1.26 (m, 54H), 0.91–0.85 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.2, 157.7, 154.3, 152.8, 151.8, 146.4, 142.5, 140.4, 138.7, 138.6, 137.1, 134.2, 132.2, 131.6, 129.5, 127.6, 124.6, 123.8, 123.7, 123.0, 120.3, 119.9, 118.7, 110.7, 107.3, 103.9, 97.5, 86.8, 73.7, 69.2, 32.1, 32.0, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 21.8, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 483 (sh, 8600), 452 (9700), 374 (sh, 15000), 342 (37200), 283 nm (55900 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 2923 (s), 2852 (s), 2214 (w, C≡C), 2094 (w, C≡C), 1600 (m), 1466 (m), 1230 (m), 1114 cm^{-1} (m); FAB$^+$ MS: *m/z* (nature of the peak, relative intensity): 1196.0, 1195.0, 1194.0 ($[M+H]^+$, 100, 95, 50); elemental analysis (%) calcd for $C_{69}H_{94}N_2O_3Pt$: C 69.38, H 7.93, N 2.35; found: C 69.19, H 7.62, N 2.17.

{2-[3,4,5-Tris(dodecyloxy)phenyl]ethynyl}[3-(*p*-tolyl)-6-phenyl-2,2′-bipyridine]platinum (IIIb) was prepared by the general procedure from **Ib** (170 mg, 0.30 mmol), 3,4,5-tris(dodecyloxy)-5-ethynylbenzene (265 mg, 0.40 mmol), CuI (8 mg, 0.04 mmol), DMF (22 mL), dichloromethane (16 mL), and triethylamine (6 mL). Chromatography on silica gel with dichloromethane/petroleum ether (30/70 to 1/0) as eluent gave **IIIb** (122 mg, 35%) as a red solid after reprecipitation from dichloromethane/methanol. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.25 (dd with ^{195}Pt satellites, 1H, ^3J = 5.3 Hz, ^4J = 1.3 Hz), 7.98 (d with ^{195}Pt satellites, 1H, ^3J = 7.0 Hz), 7.58–7.51 (m, 3H), 7.37–7.28 (m, 6H), 7.16 (td, 1H, ^3J = 7.4 Hz, ^4J = 1.3 Hz), 7.05–6.99 (m, 2H), 6.78 (s, 2H), 4.00–3.93 (m, 6H), 2.47 (s, 3H), 1.83–1.72 (m, 6H), 1.50–1.43 (m, 6H), 1.36–1.26 (m, 48H), 0.90–0.86 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.9, 158.6, 152.7, 152.0, 151.9, 146.9, 143.0, 142.0, 139.4, 138.7, 137.7, 137.0, 135.7, 134.7, 131.5, 130.5, 128.6, 127.0, 126.6, 124.6, 123.8, 123.7, 117.9, 110.6, 106.7, 103.7, 73.6, 69.2, 32.1, 32.0, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 21.5, 14.3 ppm; UV/Vis (CH_2Cl_2): λ (ε) = 469 (4300), 446 (4400), 370 (11300), 339 (14000), 290 nm (42300 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 2918 (s), 2850 (m), 2092 (m, C≡C), 1586 (m), 1464 (m), 1224 (m), 1113 (s), 746 cm^{-1} (s); FAB$^+$ MS: *m/z* (nature of the peak, relative intensity): 1172.0, 1171.1, 1170.2 ($[M+H]^+$, 100, 100, 50); elemental analysis (%) calcd for $C_{67}H_{94}N_2O_3Pt$: C 68.75, H 8.09, N 2.39; found: C 68.59, H 7.71, N 2.17.

Spectroscopic methods: Room-temperature absorption, luminescence, and excitation spectra were recorded in dichloromethane. For the luminescence spectra, the slit setting was 5 nm, and an appropriate long-pass filter prevented stray excitation light reaching the detector. For the excitation spectra, the slit setting was usually 10 nm. The method of Parker and Rees[56] provided estimates of the emission yields with [Ru(2,2′-bipyridine)$_3$]$^{2+}$ in acetonitrile as the standard (Φ = 0.062).[57] The correction factors for the emission intensities came from the manufacturer.

The frozen-glass emission spectra were collected in dichloromethane/chloroform (1/1) at the temperature of liquid nitrogen with the aid of an immersion Dewar. Simple dilution counteracted the tendency of some complexes to aggregate in the frozen solution. For glassy samples, luminescence spectra were collected by using a 400 nm notch filter on the excitation side and a 475 nm long-pass filter on the emission side. The slit setting was 10 nm.

For lifetime measurements and quantum yield determination, the samples were deoxygenated by means of a series of freeze–pump–thaw cycles. The excitation wavelength was 460 nm, and a combination of 555 and 585 nm long-pass filters served to isolate the emission signal. A previously described method for extracting lifetimes was used.[58] For the quenching measurements the sample was in contact with air. When the excited-state lifetime depended on the platinum concentration, it was necessary to determine the lifetime without quencher at each platinum concentration. A least-squares method yielded estimates of the quenching constants from a variation of the Stern–Volmer equation,[59] which in some instances included a term that was second-order in quencher.

Instrumentation: The absorption spectrometer was a Varian Cary 100 Bio instrument, and the spectrofluorimeter was a Varian Cary Eclipse. See previous work for a description of the nitrogen-pumped dye laser and associated equipment used for lifetime determinations.[60]

X-ray diffraction: Compound **IIa**: $C_{34}H_{24}N_2Pt$, $M_r = 655.64$, crystal size $0.30 \times 0.19 \times 0.05$ mm, triclinic, space group $P1-$. $a = 9.701(1)$, $b = 16.628(2)$, $c = 17.579(2)$ Å, $\alpha = 67.085(3)$, $\beta = 89.414(2)$, $\gamma = 80.768(2)°$. $V = 2573.8(5)$ Å^3, $Z = 4$, $Z' = 2$, $\rho_{calcd} = 1.692\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 5.496\ mm^{-1}$, $F(000) = 1280.0$, $T = 293$ K, $-10 \leq h \leq 6$, $-17 \leq k \leq 17$, $-17 \leq l \leq 18$, collected/unique reflections: 7032/3082; $R(\text{int}) = 0.0407$; method: full-matrix least-squares refinement on F^2; data/restraints/parameters: 5865/296/632, GOF on F^2 1.015; final R indexes ($I > 2\sigma(I)$): $R1 = 0.0668$, $wR2 = 0.1537$; for all data: $R1 = 0.1092$, $wR2 = 0.1814$. Largest difference peak and hole: $+2.98$ and -1.02 e Å^{-3}.

Electrochemical measurements: Cyclic voltammetry was performed with a conventional three-electrode system by using a voltammetric analyzer equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter electrode. Ferrocene was used as internal standard and was calibrated against a saturated calomel electrode (SCE) reference separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electroactive substrate in deoxygenated and anhydrous dichloromethane containing doubly recrystallized tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible within about 10 mV.

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[1] V. H. Houldin, V. M. Miskowski, *Coord. Chem. Rev.*, **1991**, *111*, 145.
[2] a) C. W. Chan, L. K. Cheng, C. M. Che, *Coord. Chem. Rev.* **1994**, *132*, 87; b) W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger, R. Eisenberg, *Coord. Chem. Rev.* **1998**, *171*, 125.
[3] F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita, J. P. Bucher, *Angew. Chem.* **2007**, *119*, 2713; *Angew. Chem. Int. Ed.* **2007**, *46*, 2659.
[4] a) A. Y.-Y. Tam, K. M.-C. Wong, G. Wang, V. W.-W. Yam, *Chem. Commun.* **2007**, 2028; b) R. Büchner, J. S. Field, R. J. Haines, L. P. Ledwaba, R. McGuire, Jr., D. R. McMillin, O. Q. Munro, *Inorg. Chim. Acta* **2007**, *360*, 1633.
[5] V. W.-W. Yam, K. M.-C. Wong, N. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 6506.
[6] M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115.
[7] a) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447; b) J. E. McGarrah, Y.-J. Kim, M. Hissler, R. Eisenberg, *Inorg. Chem.* **2001**, *40*, 4510; c) J. E. McGarrah, R. Eisenberg, *Inorg. Chem.* **2003**, *42*, 4355; d) K. M.-C. Wong, W.-S. Tang, X.-X. Lu, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2005**, *44*, 1492; e) Q.-Z. Yang, L.-Z. Wu, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, *Inorg. Chem.* **2002**, *41*, 5633; f) Q.-Z. Yang, Q.-X. Tong, L.-Z. Wu, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, *Eur. J. Inorg. Chem.* **2004**, 1948.
[8] 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.* **2001**, *40*, 2193.
[9] V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, K.-K. Cheung, *Organometallics* **2001**, *20*, 4476.
[10] a) J. E. Rogers, T. M. Copper, P. A. Fleitz, D. J. Glass, D. G. McLean, *J. Phys. Chem. A* **2002**, *106*, 10108; b) L. A. Emmert, W. Choi, J. A. Marshall, J. Yang, L. A. Meyer, J. A. Brozik, *J. Phys. Chem. A* **2003**, *107*, 11340; c) X.-J. Liu, J.-K. Feng, J. Meng, Q.-J. Pan, A.-M. Ren, X. Zhou, H.-X. Zhang, *Eur. J. Inorg. Chem.* **2005**, 1856.
[11] Q.-Z. Yang, L.-Z. Wu, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, *Inorg. Chem.* **2002**, *41*, 5653.
[12] a) F. Hua, S. Kinayyigit, J. R. Cable, F. N. Castellano, *Inorg. Chem.* **2005**, *44*, 471; b) F. Hua, S. Kinayyigit, A. A. Rachford, E. A. Shikhova, S. Goeb, J. R. Cable, C. J. Adams, K. Kirschbaum, A. A. Pinkerton, F. N. Castellano, *Inorg. Chem.* **2007**, *46*, 8771.
[13] G. Arena, L. M. Scolaro, R. F. Pasternack, R. Romeo, *Inorg. Chem.* **1995**, *34*, 2994.
[14] a) E. M. A. Ratilla, H. M. Brothers, N. M. Kostic, *J. Am. Chem. Soc.* **1987**, *109*, 4592; b) D. R. McMillin, J. J. Moore, *Coord. Chem. Rev.* **2002**, *229*, 113.
[15] D.-L. Ma, T. Y.-T. Shum, F. Zhang, C.-M. Che, M. Yang, *Chem. Commun.* **2005**, 4765.
[16] S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung, N. Zhu, *Chem. Eur. J.* **2001**, *7*, 4180.
[17] Y. Yang, D. Zhang, L.-Z. Wu, B. Chen, L.-P. Zhang, C.-H. Tung, *J. Org. Chem.* **2004**, *69*, 4788.
[18] P. Du, J. Schneider, P. Jarosz, R. Eisenberg, *J. Am. Chem. Soc.* **2006**, *128*, 7726.
[19] R. Narayana-Prabhu, R. H. Schmehl, *Inorg. Chem.* **2006**, *45*, 4319.
[20] W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, Z. He, K.-Y. Wong, *Chem. Eur. J.* **2003**, *9*, 6155.
[21] K. M.-C. Wong, W.-S. Tang, B. W.-K. Chu, N. Zhu, V. W.-W. Yam, *Organometallics* **2004**, *23*, 3459.
[22] R. Ziessel, S. Diring, P. Kadjane, L. Charbonnière, P. Retailleau, C. Philouze, *Chem. Asian J.* **2007**, *2*, 975, and references therein.
[23] a) W. Lei, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu, S.-T. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 4958; b) W. Lu, M. C. W. Chan, N. Zhu, C.-M. Che, C. Li, Z. Hui, *J. Am. Chem. Soc.* **2004**, *126*, 7639.
[24] R. Ziessel, S. Diring, P. Retailleau, *Dalton Trans.* **2006**, 3285.
[25] R. Ziessel, S. Diring, *Tetrahedron Lett.* **2006**, *47*, 4687.
[26] F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro, N. Rajapakse, *Coord. Chem. Rev.* **2006**, *250*, 1819.
[27] S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard, J. A. G. Williams, *Inorg. Chem.* **2005**, *44*, 9690.
[28] W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, N. Y. Zhu, S. T. Lee, C. M. Che, *Chem. Commun.* **2002**, 206.
[29] J. F. Malone, C. M. Murray, M. H. Charlton, R. Docherty, A. J. Lavery, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 3429.
[30] M. G. Hill, J. A. Bailey, V. M. Miskowski, H. B. Gray, *Inorg. Chem.* **1996**, *35*, 4585.
[31] D. K. Crites, C. T. Cunningham, D. R. McMillin, *Inorg. Chim. Acta* **1998**, *273*, 346.
[32] E. Shikkova, E. O. Danilov, S. Kinayyigit, I. E. Pomestchenko, A. D. Tregubov, F. Camerel, P. Retailleau, R. Ziessel, F. N. Castellano, *Inorg. Chem.* **2007**, *46*, 3038–3048.
[33] C. B. Blanton, Z. Murtaza, R. J. Shaver, D. P. Rillema, *Inorg. Chem.* **1992**, *31*, 3230.
[34] A. von Zelewsky, G. Gremaud, *Helv. Chim. Acta* **1988**, *71*, 1108.
[35] T. K. Aldridge, E. M. Stacy, D. R. McMillin, *Inorg. Chem.* **1994**, *33*, 722.
[36] J. A. G. Williams, *Top. Curr. Chem.* **2007**, *281*, 205.
[37] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, New York, **1992**, 128–130.
[38] V. Gutmann, *Chimia* **1977**, *31*, 1.
[39] K. Pierloot, A. Ceulemans, M. Merchan, L. Serrano-Andres, *J. Phys. Chem. A* **2000**, *104*, 4374.
[40] H. Yersin, D. Donges, W. Humbs, J. Strasser, R. Sitters, M. Glasbeek, *Inorg. Chem.* **2002**, *41*, 4915.
[41] X. Zhou, H.-X. Zhang, Q.-J. Pan, B.-H. Xia, A.-C. Tang, *J. Phys. Chem. A* **2005**, *109*, 8809.
[42] X. Zhou, Q.-J. Pan, B.-H. Xia, M.-X. Li, H.-X. Zhang, A.-C. Tung, *J. Phys. Chem. A* **2007**, *111*, 5465.
[43] C. C. Phifer, D. R. McMillin, *Inorg. Chem.* **1986**, *25*, 1329.
[44] N. H. Damrauer, T. R. Boussie, M. Devenney, J. K. McCusker, *J. Am. Chem. Soc.* **1997**, *119*, 8253.

[45] Y.-Z. Hu, M. H. Wilson, R. Zong, C. Bonnefous, D. R. McMillin, R. P. Thummel, *Dalton Trans.* **2005**, 354.

[46] T. C. Cheung, K. K. Cheung, S. M. Peng, C. M. Che, *J. Chem. Soc. Dalton Trans.* **1996**, 1645.

[47] X. Han, L.-Z. Wu, G. Si, J. Pan, Q.-Z. Yang, L.-P. Zhang, C.-H. Tung, *Chem. Eur. J.* **2007**, *13*, 1231.

[48] Y. Fan, Y.-M. Zhu, F.-R. Dai, L.-Y. Zhang, Z.-N. Chen, *Dalton Trans.* **2007**, 3885.

[49] D. K. C. Tears, D. R. McMillin, *Coord. Chem. Rev.* **2001**, *211*, 195.

[50] W. L. Jolly, *Modern Inorganic Chemistry*, 2nd. ed., McGraw-Hill, New York, **1991**, 482.

[51] M. H. Wilson, L. P. Ledwaba, J. S. Field, D. R. McMillin, *Dalton Trans.* **2005**, 2754.

[52] W. B. Connick, D. Geiger, R. Eisenberg, *Inorg. Chem.* **1999**, *38*, 3264.

[53] M. Cocchi, D. Virgili, V. Fattori, J. A. G. Williams, J. Kalinowski, *Appl. Phys. Lett.* **2007**, *90*, 023506/1.

[54] a) S. Diring, P. Retailleau, R. Ziessel, *Synlett* **2007**, 3027; b) S. Diring, P. Retailleau, R. Ziessel, *Tetrahedron Lett.* **2007**, *48*, 8069; c) S. Diring, P. Retailleau, R. Ziessel, *J. Org. Chem.* 2007, 72, 10181.

[55] J. Wu, M. D. Watson, L. Zhang, Z. Wang, K. Mullen, *J. Am. Chem. Soc.* **2004**, *126*, 177.

[56] C. A. Parker, W. T. Rees, *Analyst* **1960**, *85*, 587.

[57] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1983**, *105*, 5583.

[58] F. Liu, K. L. Cunningham, W. Uphues, G. W. Fink, J. Schmolt, D. R. McMillin, *Inorg. Chem.* **1995**, *34*, 2015.

[59] N. J. Turro, *Modern Molecular Photochemistry*; Benjamin/Cummings, Menlo Park, **1978**, 247.

[60] K. L. Cunningham, C. R. Hecker, D. R. McMillin, *Inorg. Chim. Acta* **1996**, *242*, 143.

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