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Tetrahedron Letters 47 (2006) 4687–4692

Tetrahedron Letters

Step-controlled synthesis of platinum(II) acetylide frameworks from conjugated polyaromatic modules

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Received 20 March 2006; revised 18 April 2006; accepted 26 April 2006

Abstract—A simple synthetic route for the efficient preparation of mono- and dinuclear platinum(II) derivatives containing σ-bonded ethynyl aryl groups is described. A dinuclear complex pointing its two Pt–Cl dipoles in opposite directions is prepared either by complexation of a back-to-back terpyridine ligand with platinum salts or by cross-coupling [(4′-ethynylterpyridine)PtCl] with dibromodidodecylphenyl derivatives. FT-IR, UV–vis absorption and cyclic voltammetry are used as spectroscopic tools to characterize these new complexes.

The design and synthesis of luminescent molecular materials is one of the most attractive challenges at the frontier of fundamental research, applications such as light emitting devices and energy management. Extended π-systems have received particular attention due to their multiple potential applications as advanced electronic and photonic materials.[1] The development of such sophisticated systems still suffers from time-consuming empirical processes because structure–property relationships are often not predictable in material science. The rapid construction of highly luminescent architectures remains an open avenue.[2] Paramount in such a design is the need to incorporate transition metals (e.g., Ru(II), Os(II), Re(I), Pt(II), etc.), into the backbone in order to favour phosphorescence due to spin–orbit coupling with heavy metals.[3,4]

Recently, there has been increasing interest in the properties of d^8-platinum(II) complexes such as [Pt(diimine)L_2] [L = halide, nitrile, thiolate, isocyanide and acetylide].[5] Terpyridine platinum(II) complexes and analogues are among the best luminescent labels, widely used as DNA intercalators[6] and biological probes.[7] Their spectroscopic properties and low-energy absorptions also arise from MLCT transitions. However, the development of this first generation of complexes was limited by their non-emissive or short-lived metal-to-ligand-charge-transfer electronic transitions (MLCT) in solution at room temperature.[8] This lack of emission originates from low-lying d–d excited states, which provide facile non-radiative deactivation pathways by molecular distortion. One successful strategy used to construct long-lived and emissive terpyridyl-platinum(II) complexes involves utilizing substituted terpyridines ligands with low-lying LUMOs and/or ancillary acetylide ligands with large electron-donating abilities to raise the HOMO of the metal centre, resulting in a reduction of the MLCT excited state energy.[9] As a result, the energy gap between the MLCT and the d–d states increases favourably. This trend is confirmed in many platinum(II) acetylide complexes and high quantum yield and long life-time photoluminescence likely due to Pt → diimine MLCT.[10] Recently, such a strategy has proven to also be suitable in bipyridine based Pt(II)–acetylide complexes.[11] Theoretical investigations confirm that the substituent effects on the terpyridyl-platinum(II) acetylide ligand play a major role in the tailoring of the optical properties of such complexes.[12]

Herein we describe our synthetic efforts to develop an efficient procedure for the rapid construction of soluble mononuclear and dinuclear platinum(II) complexes bearing alkyne substituted polyaromatic fragments, some of which contain uncomplexed terpyridine, bipyridine and bipyrimidine units. The strategy consists in

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doi:10.1016/j.tetlet.2006.04.131

producing in a single step the alkyne substituted Pt(II) complex from the alkyne grafted organic fragments. By following this method, we succeeded in rapidly making complexes with extended π-systems (Chart 1), by cross-coupling [(*tert*-terpy)PtCl](BF_4), *tert*-terpy accounts for 4,4′,4″-*tert*-butyl-2,2′:6′,2″-terpyridine, with several highly luminescent materials (1-ethy-ethynylperylene,[13] 2-ethynyl-9,9′-dibutylfluorene,[14] 1-ethynylpyrene[15]) in DMF under anaerobic conditions and mediated by catalytic amounts of CuI (3 mol %). In our hands the use of large amounts of copper (>10 mol %) resulted in intractable mixture of polar complexes.

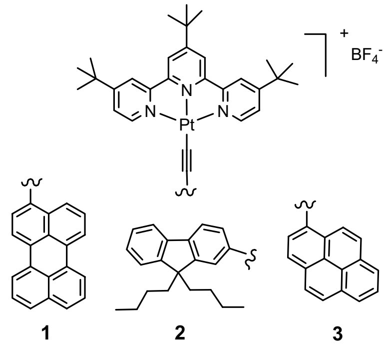
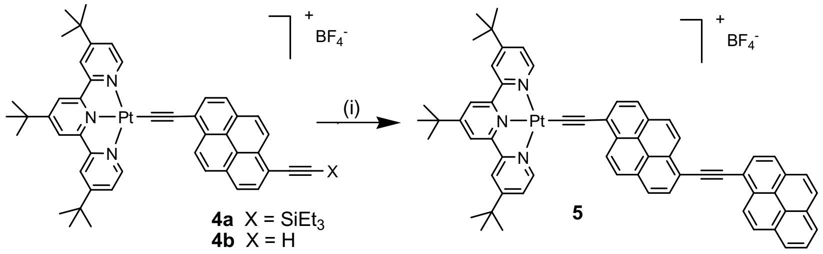


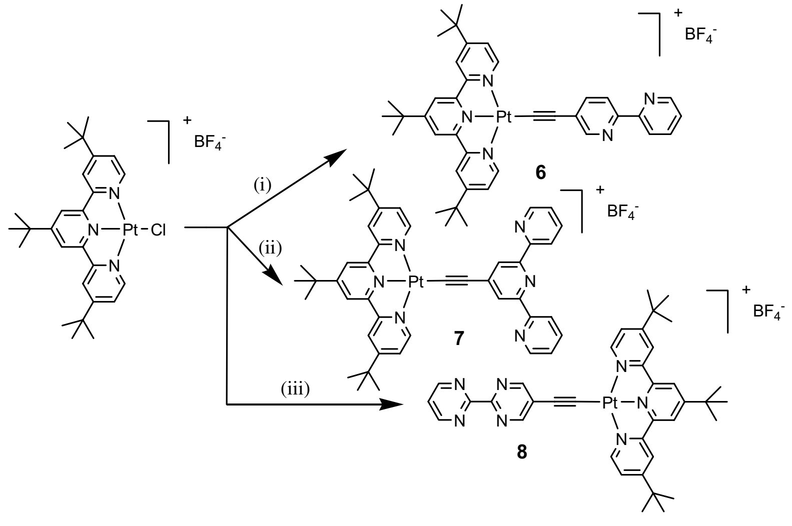
Chart 1.

Similarly, complex **4a** was readily prepared in good yield from 1-ethynyl-6-triethylsilylacetylenpyrene. Deprotection of the silyl group with KF in protic conditions produces **4b** which has been cross-coupled with 1-bromopyrene in the presence of low valent palladium(0). The formation of complex **5** (Scheme 1) is confirmed by ES–MS which exhibit a molecular peak at 1045.5 $[M-BF_4]^+$. This reaction is very sensitive to the reaction conditions and the presence of the Pt–terpy subunit does not tolerate strong bases and temperature above 60 °C.

The proof-of-principle of our strategy is illustrated in Scheme 2 and Chart 2. Various mononuclear (**6**, **7**,[16]**8**) and dinuclear complexes (**9b** and **10b**) bearing empty coordination sites were prepared either using 1 equiv of the mono- or 0.5 equiv of the diethynyl building blocks, with respect to the Pt precursor. However, the scope of this reaction suffered severely from low reactivity when the preparation of dinuclear complexes was envisaged. The low yield (20%) obtained under stoichiometric conditions was increased to 35% by using a two-fold excess of the platinum(II) starting material. During the preparation of complexes **9b** and **10b**, formation of the mononuclear complexes **9a** and **10a** are clearly evidenced by TLC and could ultimately be isolated in modest yields (25%). This is an interesting situation because hybrid complexes bearing various donor–acceptor spacing units could be envisaged for



Scheme 1. Reagents and conditions: (i) 1-bromopyrene, $[Pd(PPh_3)_4]$ (6 mol %), $^iPrNH_2$, 60 °C, 4 h.



Scheme 2. Reagents and conditions: (i) 5-ethynyl-2,2′-bipyridine, CuI (3 mol %); (ii) 4-ethynyl-2,2′:6′,2″-terpyridine, CuI (3 mol %); (iii) 3-ethynyl-2,2′-bipyrimidine, CuI (10 mol %). All cases in DMF, TEA.

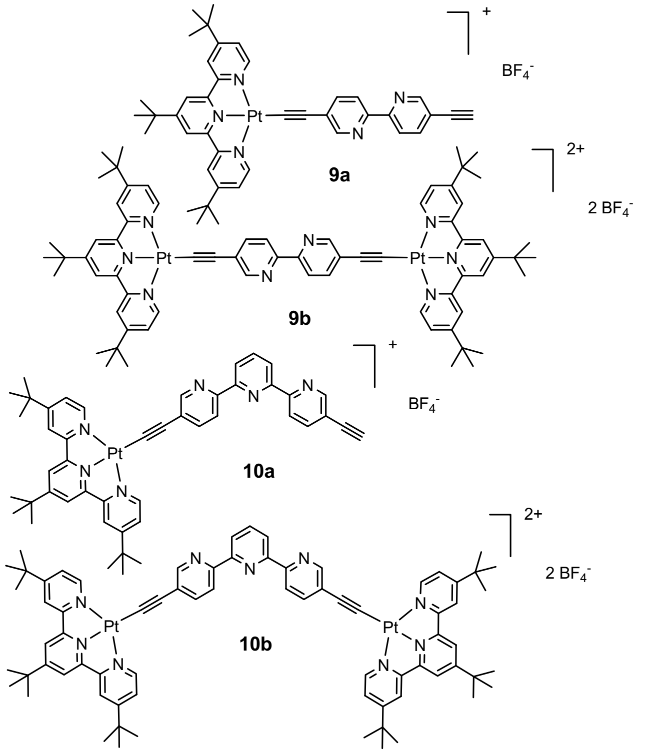


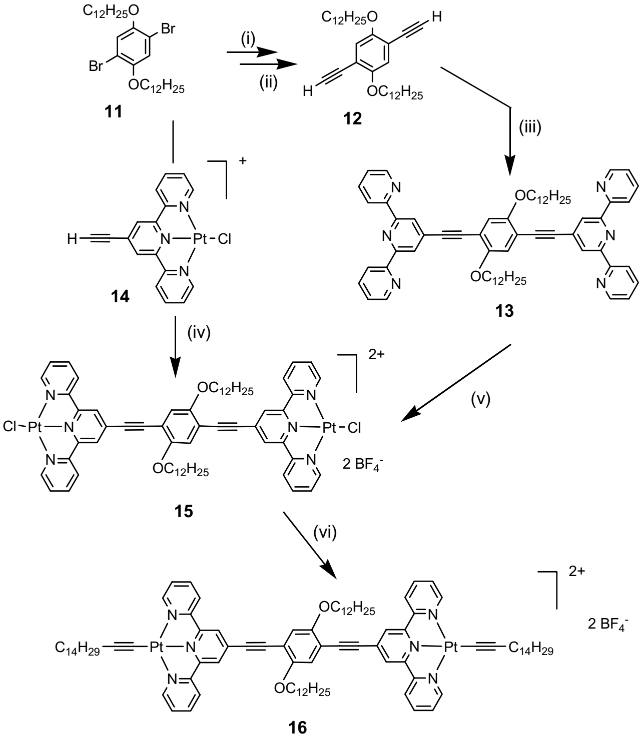
Chart 2.

specific applications in light emitting diodes. Indeed the use of 2 equiv of 5,5′-diethynyl-2,2′-bipyridine or 2 equiv of 5,5″-diethynyl-2,2′:6′,2″-terpyridine versus 1 equiv of [(*tert*-terpy)PtCl](BF_4) produces the mononuclear complexes with acceptable yields (≈75%).

Another way to extend the dimentionality of the dinuclear complexes and to inverse the directionality of the MLCT transition (along the main axis in complex **15** versus the periphery in complexes **9b** and **10b**) is to engineer back-to-back terpyridine ligands and complexes (Scheme 3).

The desired solubility is imported by the use of building block **11** carrying two dodecyloxy paraffin chains. Double cross-coupling of **12** with [{(4′-trifluoromethyl)sulfonyl}oxy]-2,2′:6′,2″-terpyridine and catalytic amounts of palladium(0) afforded the ditopic ligand **13** in 85% yield.

A perspective view of ligand **13** determined by X-ray diffraction is shown in Figure 1. As surmised from the NMR studies, all three nitrogen atoms of a single terpy moiety lie in a transoidal position that minimizes electrostatic interactions between the neighbouring lone pairs, a situation frequently found in oligopyridine ligands. The crystal structure confirmed the flat arrangement of the terpy fragments (around a 1° tilt) and the complete planarity of all the ditopic ligand in the solid state. A slight distorsion between the flat terpy and the diphenoxyphenyl is evidenced by a weak dihedral angle of 4–5°. A striking result revealed by the crystal packing is the organization of the molecules in layers [$\bar{1}$ 1 1] with a graphite like-network and an average inter-layer distance of 3.4 Å (Fig. 1).



Scheme 3. Reagents and conditions: (i) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_4$ (12 mol %), $^{n}PrNH_2$, 65 °C, 48 h, 88%; (ii) NaOH, C_6H_6, 70 °C, 14 h, 75%; (iii) terpy–OTf, $Pd(PPh_3)_4$ (6 mol %), $^{i}Pr_2NH$, toluene, 70 °C, 24 h, 85%; (iv) complex **14**, CuI (6 mol %), TEA, DMF, rt, 48 h, 87%; (v) K_2PtCl_4, CH_3CN, H_2O, CH_2Cl_2, 60 °C CuI (6 mol %), 23 h, 64%; (vi) $C_{14}H_{29}C{\equiv}CH$, CuI (6 mol %), TEA, DMF, rt, 24 h, 80%.

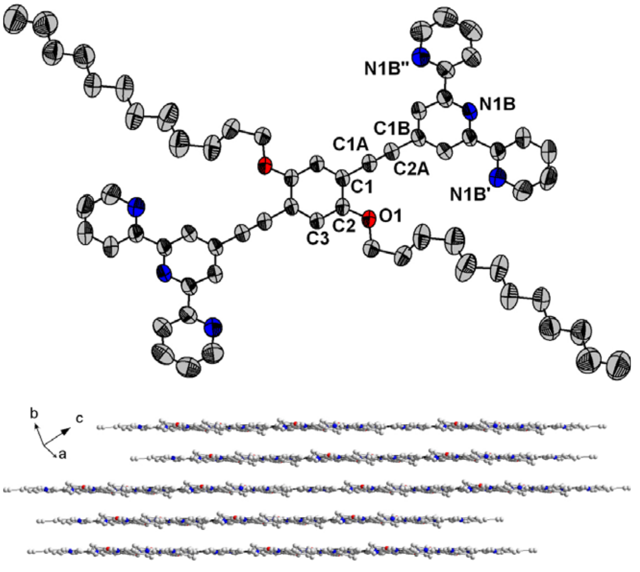


Figure 1. Top: ORTEP view of ligand **13** with atom labelling. Probability displacement ellipsoids are shown at 50% level. Selected distances and angles: C1A–C2A 1.186(10), C2–O1 1.361(8), C1–C1A 1.438(12), C2A–C1B 1.439(13) Å; C1–C1A–C2A 177.6(3)° and C1A–C2A–C1B 176.2(4)°. Bottom: crystal packing showing the planar organization of the molecules.

Complexation of **13** with K_2PtCl_4 in $CH_3CN/CH_2Cl_2/H_2O$ provides the insoluble complex **15** in 64% isolated yield. Interestingly, this dinuclear complex was also prepared from complex **14**[17] by a double cross-coupling of the dibromo derivative **11** with low valent palladium(0). This chemistry on the complex is very efficient under the described conditions (87%). Complex **14** ($\delta_{C\equiv CH}$ = 3.17 ppm in DMSO-d_6) was originally prepared in 77% yield from 4′-ethynyl-2,2′:6′,2″-terpyridine and $[Pt(DMSO)_2Cl_2]$[18] in THF at 80 °C.

In DMF solution at 298 K, all the complexes show intense multiple absorption peaks in the range 250–500 nm (Fig. 2). On the basis of earlier studies of related compounds,[11,19] the high-energy structured absorption bands are ascribed to π–π* transitions of the terpy units and of the ethynylaryl moiety. In cases **1** and **3**, the intense additional absorption centred, respectively, at 463 and 400 nm is due to absorption of the perylene and pyrene fragments. As expected such low energy transitions are not present in the fluorene derivative **2** (Fig. 2a). The low energy absorption band in the visible region is assigned to a platinum-to-ligand charge transfer transition (MLCT) probably mixed with an alkynyl-to-terpyridine ligand-to-ligand charge transfer character (LLCT).[19] This band is found near 470 nm in the fluorene and pyrene complexes **2** and **3**, whereas in the perylene derivatives **1** it appears above 500 nm. This bathochromic shift is induced by the increase of electronic density imported by the perylene moiety. Notice that when a chloride is coordinated in place of an ethynylaryl (compd **14**) the MLCT is much weaker and shifted to higher energies. Importing a second pyrene residue in **5** with respect to complexes **4a** and **4b** resulted in the increase of the absorptivity and a decrease of the transition energy. Interestingly by grafting a second alkyne–terpy–Pt unit on complex **6** leading to **9b** the absorption of the MLCT is not shifted but a non-linear increase of the absorption coefficient is observed (Fig. 2b). Finally, connecting two hexadecyne units in place of the chloro ligands in complex **15** also resulted in a bathochromic shift and an increase of the absorption coefficient in complex **16** (Table 1).

Complexes **2** and **4a** showed two quasi reversible couples at −1.02 (ΔE_p = 60 mV) and −1.51/56 V (ΔE_p = 60 mV) versus ferroccene (+0.38 V) in CH_2Cl_2 and $^nBuNPF_6$. The first reduction must arise from the

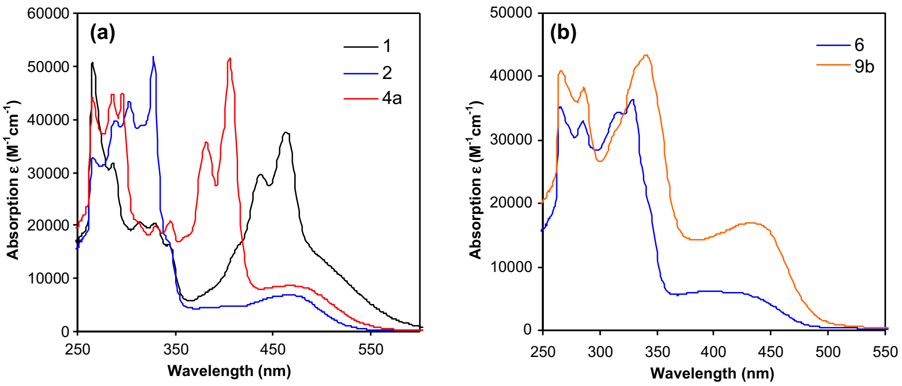


Figure 2. Overlay of absorption spectra recorded for various complexes in dimethylformamide solution.

Table 1. Selected data for the novel Pt(II) complexes

Complex	Isolated yield (%)	$\nu_{C\equiv C}$[a] (cm^{-1})	ES-MS (nature of the cluster)[b]	λ_{max} (nm), ε (M^{-1} cm^{-1})[c]
1	73	2095	$871.4^{]+}$	507 (sh; 12,500); 463 (37,600); 437 (29,600)
2	85	2110	$897.5^{]+}$	466 (6800)
3	92	2099	$821.4^{]+}$	474 (7300)
4a	69	2155/2098	$959.5^{]+}$	470 (8600); 406 (51,500)
4b	92	2139/2100	$845.4^{]+}$	486 (12,500); 408 (56,200)
5	62	2206/2102	$1045.5^{]+}$	494 (13,200); 410 (99,300)
6	67	2115	$775.4^{]+}$	420 (6000)
7	88	2122	$852.4^{]+}$	403 (8450)
8	76	2119	$777.4^{]+}$	428 (7900)
9b	35[d]	2117	$1481.7^{]+}$; $697.4^{]2+}$	424 (16,700)
10b	36[d]	2192	$1558.7^{]+}$; $735.5^{]2+}$	465 (17,200)
14	77	2112	$487.2^{]+}$	405 (3300)
15	64	2203	$708.5^{]2+}$	439 (9200)
16	80	2202/2071	$895.1^{]2+}$	450 (19,400)

[a] One drop of CH_2Cl_2 containing the sample was evaporated on a KBr disk.

[b] Electro-spray mass spectroscopy in methanol/acetonitrile at V_c = 110 V. The molecular peaks correspond to $[M-BF_4]^+$, for complexes **9b**, **10b**, **15** and **16**, $[M-Cl]^+$, for complexes **14**, the 2+ peak correspond to $[M-2BF_4]^{2+}$. All isotopic profiles correspond to the expected sequence.

[c] Averaged value determined from at least two different solutions of non-degassed DMF solution.

[d] The corresponding mononuclear complexes have been obtained as side-products with an average yield of 25%.

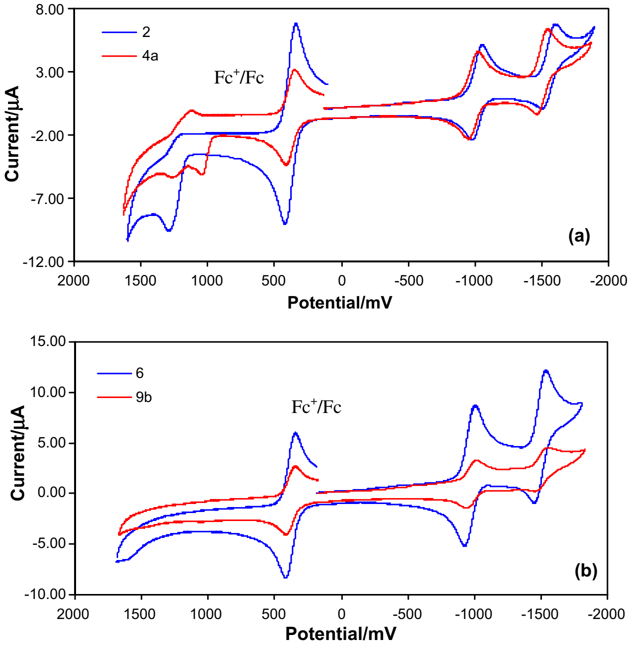


Figure 3. Cyclic voltammetry in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at rt, scan rate 200 mV s^{-1}. Ferrocene was used as internal reference +0.38 V versus SCE.

terpy-based reduction and the second reduction is tentatively assigned to a metal-centred reduction whereas the irreversible oxidation are likely assigned to fluorine and pyrene based oxidation (Fig. 3a).[20] In the bipyridine complexes **6** and **9b**, no such oxidation could be detected within the given oxidation window but two reversible reductions are also found at -0.99 ($\Delta E_p = 60$ mV) and -1.50 V ($\Delta E_p = 60$ mV) in both complexes (Fig. 3b).

In summary, a series of mononuclear terpyridine–platinum(II) acetylide complexes bearing various appended moieties (perylene, fluorene, pyrene, bipyridine, bipyrimidine, terpyridine) and dinuclear complexes bridged by a bipyridine, terpyridine or a back-to-back bis-terpyridine ligand has been successfully synthesized using a rational protocol. High solubility has been ensured by the use of *tert*-butyl substituents on the terpy–Pt centre or by linear dodecyloxy chains grafted at the central phenoxy moiety. The nature of the acetylide residues has a strong influence on the absorption of the ^{3}MLCT state with a strong bathochromic shift observed for the electron-rich perylene module. This trend is confirmed by increasing the number of pyrene nucleus. Preliminary electrochemical studies showed two reversible redox processes (ligand and Pt based) for the key complexes **2**, **6** and **9b**. Further work is directed towards the complexation of the empty terpyridine and bipyridine sites by luminescent transition metal salts in order to study energy or electron transfer processes.

Acknowledgements

The Ministère de la Recherche et des Nouvelles Technologies is gratefully acknowledged for financial support of this work in the form of an Allocation de Recherche for S.D.

References and notes

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402; Martin, R. E.; Diederich, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 1350; Segure, J. L.; Martin, N. *J. Mater. Chem.* **2000**, *10*, 2403.
2. Ziessel, R. *Synthesis* **1999**, 1839.
3. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Beser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
4. Chan, C. W.; Cheng, L. K.; Che, C. M. *Coord. Chem. Rev.* **1994**, *132*, 87; Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125.
5. Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115.
6. Arena, G.; Monsu Scolaro, L.; Pasternack, R. F.; Romeo, R. *Inorg. Chem.* **1995**, *34*, 2994.
7. Ratilla, E. M. A.; Brothers, H. M.; Kostic, N. M. *J. Am. Chem. Soc.* **1987**, *109*, 4592.
8. Michalec, J. F.; Bejune, S. A.; Cuttell, D. G.; Summerton, G. C.; Gertenbach, J. A.; Field, J. S.; Haines, R. J.; McMillin, D. R. *Inorg. Chem.* **2001**, *40*, 2193.
9. Yam, V. W. W.; Tang, R. P. L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 4476.
10. Yang, Q. Z.; Wu, L. Z.; Zhang, L. P.; Tung, C. H. *Inorg. Chem.* **2002**, *41*, 5653.
11. Ha, F.; Kinayyigit, S.; Cable, J. R.; Castellano, F. N. *Inorg. Chem.* **2005**, *44*, 471.
12. Liu, X.-J.; Feng, J.-K.; Meng, J.; Pan, Q.-J.; Ren, A.-M.; Zhou, X.; Zhang, H.-X. *Eur. J. Inorg. Chem.* **2005**, 1856.
13. Inouye, M.; Hyodo, Y.; Nakazumi, H. *J. Org. Chem.* **1999**, *64*, 2704.
14. Prepared by an adapted procedure from Thomas, K. R. J.; Lin, J. T.; Lin, Y.-Y.; Tsai, C.; Sun, S.-S. *Organometallics* **2001**, *20*, 2262.
15. Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Chem. Commun.* **1999**, 735; Hissler, M.; Harriman, A.; Khatyr, A.; Ziessel, R. *Chem. Eur. J.* **1999**, *11*, 3366.
16. Compound **7.** The preparation began with the dissolution of $[(^t\mathrm{Bu}_3\text{–terpy})\mathrm{PtCl}](\mathrm{Cl})$ (0.163 g, 0.244 mmol) in a mixture of DMF (3 mL) and triethylamine (1 mL), followed by the addition of 4-ethynyl-2,2′:6′,6″-terpyridine (0.063 g, 0.244 mmol). The solution was degassed vigorously by bubbling argon through the solution. The addition of CuI (0.001 g, 0.005 mmol) to the yellow solution resulted in the instantaneous colour change to red. After stirring at rt for one night, the deep-red solution is concentrated to roughly 1 mL and filtrated over Celite and dropped into an aqueous solution (10 mL) containing $\mathrm{NaBF_4}$ (1.200 g). The complex was recovered by filtration over paper, washed with water (3 × 100 mL) and the red solid dried under high vacuum. Purification was insured by column chromatography using alumina as solid support and a gradient of methanol (0–1%) in dichloromethane as mobile phase. Ultimate recrystallization by slow evaporation of dichloromethane from a dichloromethane/hexane solution afforded complex **7** (0.202 g, 88%). ^{1}H (200.1 MHz) NMR δ 9.12 (d, $^3J = 6.0$ Hz, 2H), 8.97 (s, 2H), 8.96 (s, 2H), 8.89 (d, $^3J = 8.0$ Hz, 4H), 8.69 (dm, $^3J = 4.8$ Hz, 1H), 8.61 (d, $^3J = 8.0$ Hz, 1H), 8.47 (s, 2H), 7.87 (td, $^3J = 8.0$ Hz, $^4J = 1.9$ Hz, 1H), 7.60 (7 lines m, 2H), 7.34 (8 lines m, 1H), 1.65 (s, 9H), 1.52 ppm (s, 18H). ^{13}C{^{1}H} (100.6 MHz) δ 169.3, 169.1, 168.3, 167.7, 162.5,

158.9, 158.5, 156.1, 155.2, 154.2, 153.9, 150.9, 149.1, 125.2, 124.5, 124.3, 123.9, 123.5, 122.9, 122.6, 121.4, 30.8, 30.4, 37.9, 36.6 ppm. UV–vis (DMF): λ nm (ε, M^{-1} cm^{-1}) = 403 (8500), 334 (23,300), 323 (24,400), 287 (70,600); FT-IR (KBr): $\nu = 3338$ (m), 2960 (m), 2122 (m, $\nu_{C\equiv C}$), 1614 (s), 1582 (s), 1563 (s), 1466 (s), 1392 (m), 1261 (m), 880 (m), 792 (m). ES–MS *m*/*z* 852.4 (100%, $[M-BF_4]^+$) in CH_2Cl_2. Anal. Calcd for $C_{44}H_{45}N_6PtBF_4$ (Mr = 939.75): C, 56.24; H, 4.83; N, 8.94. Found: C, 55.75; H, 4.62; N, 8.63.

17. Compound **14**. 4-ethynyl-2,6-di(pyridin-2-yl)pyridine (40 mg, 0.15 mmol) was dissolved in THF (10 ml). *cis*-$[PtCl_2(dmso)_2]$ (100 mg, 0.24 mmol) was added and the mixture heated up to 60 °C for 18 h. The yellow precipitate was filtered off and washed with THF than acetonitrile to afford 60 mg (77%) of **14**. ^{1}H NMR (DMSO-d_6 300.1 MHz): δ 8.91 (d, 2 H, $^3J = 5.5$ Hz), 8.82 (s, 2H), 8.70 (d, 2H, $^3J = 7.3$ Hz), 8.53 (dd, 2H, $^3J = 7.9$ Hz, $^4J = 1.5$ Hz), 7.97 (dd, 2H, $^3J = 5.7$ Hz, $^4J = 1.3$ Hz), 3.17 (s, 1H); ^{13}C {^{1}H} NMR (DMSO-d_6 100.1 MHz): 157.6, 154.4, 151.0, 142.6, 134.8, 129.4, 126.6, 126.1, 91.9, 80.2; UV–vis (DMF): λ nm (ε, M^{-1} cm^{-1}) = 405 (3300), 387 (3100), 360 (5500), 337 (9900), 320 (9700), 287 (19400); FT-IR (KBr): $\nu = 3252$ (m), 3049 (m), 2911 (m), 2112 (m, $\nu_{C\equiv C}$), 1605 (s), 1475 (s), 1417 (s), 1132 (s), 1019 (s), 785 (s); ES-MS *m*/*z*: 487.2 (100%, $[M-Cl]^+$) in DMSO. Anal. Calcd for $C_{17}H_{11}Cl_2N_3Pt$ (Mr = 523.27): C, 39.02; H, 2.12; N, 8.03. Found: C, 38.72; H, 1.69; N, 7.76.
18. Price, J. H.; Birk, J. P.; Wayland, B. B. *Inorg. Chem.* **1978**, *17*, 2245.
19. Michalec, J. F.; Bejune, S. A.; Cuttell, D. G.; Summerton, G. C.; Gertenbach, J. A.; Field, J. S.; Haines, R. J.; McMillin, D. R. *Inorg. Chem.* **2001**, *40*, 2193.
20. Hill, M. G.; Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 4585.