Terpyridine-platinum(II) acetylide complexes bearing pendent coordination units†

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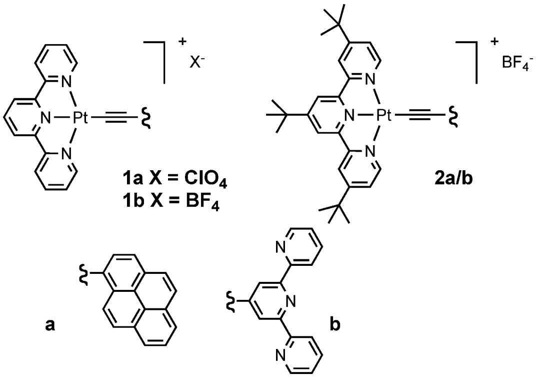
Platinum(II) complexes bearing various alkyne–pyrene, alkyne–4′-terpyridine and alkyne–dibutoxyphenylacetylide–terpyridine units were constructed in a step-by-step procedure based on copper-promoted cross-coupling reactions with preconstructed modules; formation of bis(ligand) complexes of Fe(II) and Zn(II) by binding of the pendent terpyridine units provided heterotrinuclear derivatives, all of which exhibit highly structured absorption features in solution and display a rich electrochemistry due to the presence of various redox active modules.

Currently there is great interest in the development of square-planar d^8-complexes of Pt(II) containing aromatic α,α′-diimine ligands, mainly due to their interesting spectroscopic and luminescence behavior.[1–5] Complexes which possess functional groups have proved to be particularly effective as DNA intercalators[6] and molecular probes for biological macromolecules.[7] Paramount in the design of luminescent molecules, polymers and devices is the need to incorporate transition metals such as Pt(II) into the backbone in order to relax the spin selection rules for phosphorescence through spin–orbit coupling.[8] This has proven to be important in the design of light emitting diodes,[9] non-linear optical materials[10] and conductance switches.[11]

Monomeric oligopyridine platinum(II) complexes display remarkably rich luminescence properties arising from the ligand (so-called intra-ligand, IL, emission), from metal-to-ligand-charge-transfer (MLCT) or in some cases from ligand field (LF) states.[12] Platinum(II) terpyridine complexes have been shown to display especially intriguing spectroscopic and luminescence properties depending on the metal–metal interactions and π–π stacking of the surrounding ligands.[13] In particular, solvent induced aggregation and marked solvato-chromism have been found[14] and the grafting of pyrenyl fragments to terpyridine has provided exceptionally long excited state lifetimes (*e.g.* 64 μs).[15]

Lately, there has been a considerable surge of interest in developing platinum(II) σ-alkynyl complexes, as the π-orbitals on the ligand can be fully conjugated with the d_{xy} orbitals of the metal. This creates favourable structural and electronic conditions for fast electron/hole or exciton migration, a *sine qua non* condition for efficient electron/hole recombination and the regeneration of the ground state through luminescence.[16,17] Remarkably high quantum yields (48%) and microsecond triplet excited state lifetimes have been measured in Pt(II)–bipyridine–bis-silylacetylide complexes.[18] However, very few Pt(II)–terpyridine complexes bearing an acetylide connected to uncomplexed polypyridine fragments or large chromophoric centres have been described.

Herein, we detail the synthesis of terpyridine-based, functionalized-alkyne platinum(II) complexes and report some preliminary optical and electrochemical measurements. For **1a** and **1b**, we chose unsubstituted [(terpy)Pt(Cl)]$^+$ (terpy = 2,2′:6′,6″-terpyridine) as the starting material. CuI-catalysed cross-coupling with 1-ethynylpyrene and 4′-ethynyl-terpy afforded the desired complexes in good yields. To solve solubility problems arising with this first set of complexes, we introduced *tert*-butyl substituents onto the terpy ligands to produce complexes **2a** and **2b** under similar conditions (Scheme 1).



Scheme 1

Alternatively, the solubility problem was circumvented by using a 1,4-dialkoxyphenyl substituted alkyne fragment as a spacer between the platinum and the uncomplexed terpy units (Scheme 2). The synthesis of complex **7** was accomplished in eight steps commencing with 1,4-hydroquinone. Alkylation followed by bromination provided a good yield of **3**, which was readily converted to its dipropargylic alcohol derivative. The key step is the mono-deprotection of one of the propargylic functions by means of NaOH under anhydrous benzene. With compound **4** in hand, cross coupling with 4′-[{(trifluoromethyl)sulfonyl}oxy]-2,2′:6′,2″-terpyridine and deprotection of the resulting alkyne gave the target ligand **5**. Compound **5** flanked by two butoxy solubilizing groups can be cross-coupled with unsubstituted or substituted (terpy)platinum chloro-salts in the presence of catalytic amounts of CuI, leading respectively to complexes **6** and **7** (Scheme 2).

The functionalisation of the pendent terpy units in **6** and **7** is not such as to obstruct their complexation and reaction of **7** with $Fe(ClO_4)_2{\cdot}6H_2O$ or $Zn(OTf)_2{\cdot}4H_2O$ afforded the heterotrinuclear

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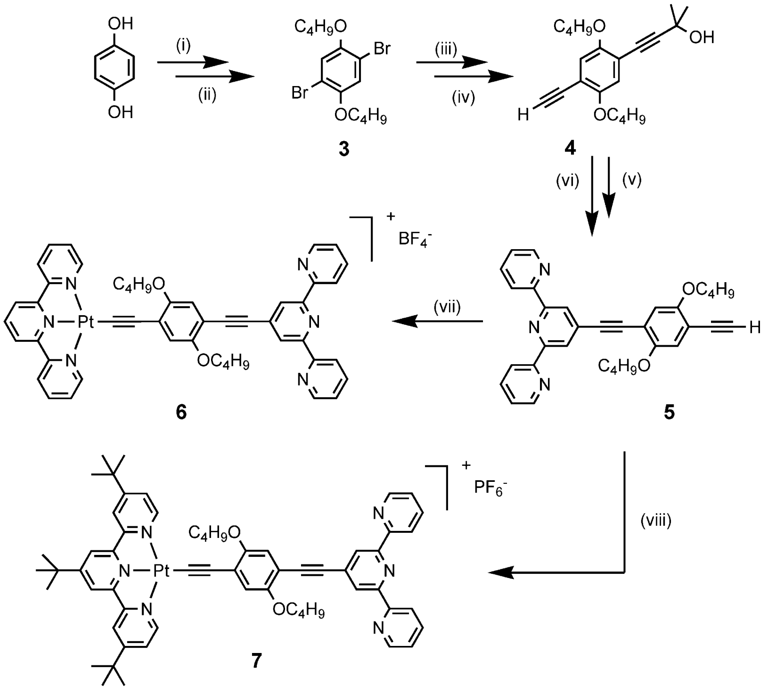
† Electronic supplementary information (ESI) available: Table S1 for π–π interactions; Fig. S1 for the packing. See DOI: 10.1039/b603603a

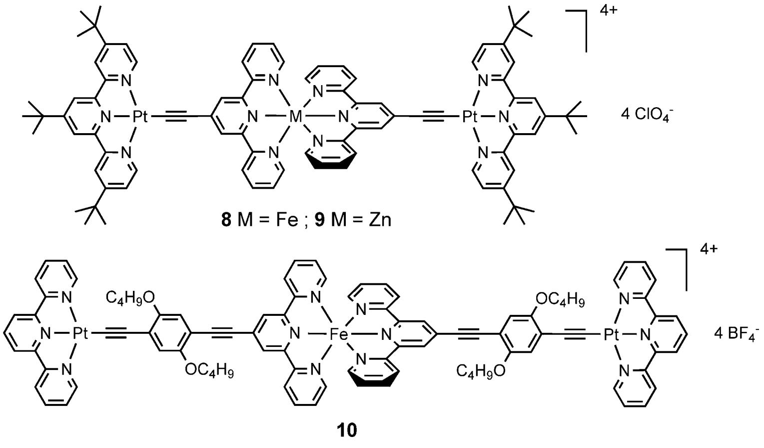


Scheme 2 (i) C_4H_9Br, NaOH, DMF, 150 °C, 18 h, 75%; (ii) Br_2, CCl_4, reflux, 70 h, 80%; (iii) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_4$ (12 mol%), $nPrNH_2$, 65 °C, 70 h, 86%; (iv) NaOH, C_6H_6, 70 °C, 14 h, 45%; (v) terpy-OTf, $Pd(PPh_3)_4$ (6 mol%), $^iPr_2NH$, Tol, 70 °C, 24 h, 62%; (vi) NaOH, Tol, 120 °C, 18 h, 86%; (vii) $[(terpy)PtCl]BF_4$, CuI (10 mol%), TEA, DMF, $NaBF_4$, rt, 70 h, 38%; (viii) $[(tertBu)_3\text{-}terpy)PtCl]BF_4$, CuI (10 mol%), TEA, DMF, $NaPF_6$, rt, 70 h, 43%.

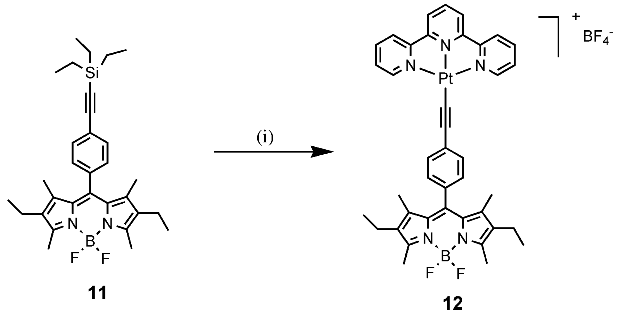
complexes **8** and **9**, while complex **10** resulted from the reaction of **6** with Fe(II) salts (Scheme 3).

Having achieved such syntheses, we then evaluated the possibility of cross-coupling additional luminophores to the platinum(II)–terpy centre. It turns out that the deprotected form of the boraindacene **11** only slowly reacts with $[(terpy)PtCl]^+$ in the presence of CuI in DMF at rt and has a strong tendency to give an oxidative homocoupling reaction leading to butadiene-bridged bis-indacene compounds. Catalysis of this homocoupling by both Pd and Cu salts has been observed previously.[19] After several failures to achieve coupling to the Pt complex, success was achieved simply by deprotecting compound **11** with anhydrous potassium carbonate in DMF in the presence of the $[(terpy)PtCl]^+$ complex (Scheme 4). Copper catalysis appears not to be essential to reach the target and it is surmised that the chloro ligand is readily substituted by the deprotonated alkyne. Although the use of a biphasic mixture (benzene/water) in the presence of a phase transfer catalyst has previously been found useful for the preparation of sophisticated tritopic ligands,[20] this does not appear to be of any benefit here.

For all complexes, the IR spectra exhibit an intense $\nu_{PtC\equiv C}$ stretching vibration around 2100 cm^{-1}. A second $\nu_{C\equiv C}$ absorption is observed around 2200 cm^{-1} whenever a C≡C unit is present to link different organic fragments (such as in **6**, **7** and **10**).



Scheme 3



Scheme 4 (i) Anhydrous K_2CO_3 excess, DMF, [(terpy)PtCl]BF_4, rt, 1 day.

X-Ray structure of complex 7

The coordination geometry around platinum is essentially square planar but with the central Pt–N2 distance (1.959(5) Å) slightly shorter than those to the two outer nitrogen atoms (Pt–N1 2.016(5) Å and Pt–N3 2.013(5) Å) and the $N_{central}$–Pt–N_{outer} bond angles <90°, as expected from the restrictions of the terpy ligand structure (Fig. 1).‡ The Pt–C16 distance of 1.965(7) Å compares well with values reported in the literature,[21] and the C≡C bond length of 1.203(9) Å is comparable to those in related Pt(II) acetylide complexes. An important feature of the crystal structure is the *quasi*-planarity of the molecule (Fig. 1b) with insignificant dihedral angles between ϕ_B and ϕ_{Pt} (2.87°), ϕ_B and ϕ_T (3.53°), ϕ_{Pt} and ϕ_T (1.52°) (ϕ_B denotes the average plane of the central benzene, ϕ_{Pt} the one containing the Pt and ϕ_T the one containing the uncomplexed terpy). Analysis of the crystal packing of **7** suggests pronounced intermolecular interactions between the complexes by revealing π–π stacking distances around 3.6 Å between the different ring moieties of a molecule in general position *x*, *y*, *z* and four neighbouring complexes (Table S1 for π–π interactions† and Fig. 1c for the packing).

In DMF solution at 298 K, all the complexes show intense multiple absorption peaks in the range 250–600 nm (Fig. 2). On the basis of earlier studies of related compounds,[15,18] the high-energy structured absorption bands are ascribed to π–π* transitions of the terpy units and of the phenylalkynyl moiety. In cases **1a** and **2a**, the intense additional absorption centred at 370 nm is due to absorption of the pyrene moieties. These well defined transitions are not observed when unbound terpy is substituted for pyrene, as in complexes **1b** and **2b** (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). This band is found near 400 nm in the terpy-substituted alkyne complexes **1b** and **2b**, whereas in the pyrene derivatives **1a** and **2a** it appears at 492 and 474 nm respectively. This bathochromic shift is probably induced by the increase of electronic density imported by the pyrene and the 18 nm shift found in **2a** compared to **1a** is due to the donor properties of the *tert*-butyl fragments. Interestingly, by complexing the free terpy sites in complexes **2b** and **7** with iron(II) a new intense FeLCT band located around 580–590 nm is seen (Fig. 2b), while the PtLCT band is shifted to the blue by *ca*. 40 nm. In the Zn/Pt_2 complex **9**, no additional MLCT band was observed but the hypsochromic shift of the PtLCT band (*ca*. 40 nm) is retained (Table 1). For complex **12**, the strong absorption at 524 nm is due to the $S_0 \rightarrow S_1$ transition of the indacene fragment[19] and that at 402 nm is assigned as PtLCT

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

Complex	Yield (%)	$\nu_{C\equiv C}{}^a$/cm^{-1}	ES-MS^b	$\lambda_{max}{}^c$/nm (ε/M^{-1}cm^{-1})
1a	90	2103	$653.1^{]1+}$	492 (5800)
1b	82	2101	$684.1^{]1+}$	408 (5600)
2a	92	2099	$821.4^{]1+}$	474 (7300)
2b	74	2122	$852.4^{]1+}$	403 (8450)
6	38	2201/2111	$928.3^{]1+}$	478 (9550)
7	43	2197/2106	$1096.4^{]1+}$	466 (13 000)
8	87	2099	$440.3^{]4+}$ $620.2^{]3+}$	584 (29 700) 425 (sh, 9800) 375 (21 300)
10	65	2194/2106	$478.3^{]4+}$	590 (49 000) 425 (40 000) 375 (49 000)
12	96	2111	$831.3^{]1+}$	524 (70 300) 402 (sh, 12 000)

[a] One drop of CH_2Cl_2 containing the sample was evaporated on a KBr disk. [b] Nature of the cluster determined by electrospray mass spectroscopy in methanol/acetonitrile at V_c = 110 V, except for analysis of compound **10**, where V_c = 200 V. The molecular peaks correspond either to $[M - BF_4]^+$, $[M - PF_6]^+$ or to $[M - ClO_4]^+$. For compounds **8**, **9** and **10** the 3+ peaks correspond to $[M - 3ClO_4]^{3+}$ and the 4+ peaks to $[M - 4ClO_4]^{4+}$. All isotopic profiles correspond to the expected sequence. [c] Averaged value determined from at least two different solutions of non-degassed DMF.

Complex **2b** showed two quasi reversible couples at −0.97 and −1.48 V *vs*. ferrocene (+0.38 V) in CH_2Cl_2 and $^nBuNPF_6$ as supporting electrolyte. The first reduction must arise from a terpy-based reduction and the second reduction is tentatively assigned to a metal-centered reduction (Fig. 3).[22] However, we could not exclude based on our experimental evidence that the second reduction is also localized on the complexed *tert*-butyl-terpy. The potential difference of about 500 mV would be acceptable for electron pairing into the same orbital as previously hypothetized in more complex architectures.[23,24] In the trinuclear Fe/Pt_2 complex **8**, similar terpy-Pt and Pt centered reduction waves are found at −0.96 and −1.54 V (two electron exchange process) and two additional single electron reversible processes are found at −1.27 and −1.40 V (Fig. 3b). These are probably due to successive reductions of the two terpy units coordinated to iron. In addition, a reversible one electron oxidation corresponding to an Fe(II)/(III) couple is observed at +1.09 V. No such process is observed in complex **2b**. However, addition of anhydrous iron salts to a solution of **2b** results in the instantaneous formation of the deep-violet Fe/Pt_2 complex and the emergence of new redox waves identical to those found for the isolated complex **8**.

In summary, a series of terpyridine–platinum(II) acetylide complexes bearing various appended moieties (pyrene, 4′-terpy, dibutoxyphenylacetylide–terpy) has been successfully synthesized using a rational protocol. High solubility has been ensured by the use of *tert*-butyl substituents on the terpy–Pt center and/or by linear butyl chains grafted on the central phenoxy moiety. An X-ray molecular structure determination revealed a coplanar arrangement of the terpy–Pt/ethynylphenoxy/ethynylterpy entities favourable for conjugation of the different modules. The nature of the acetylide residues has a strong influence on the absorption

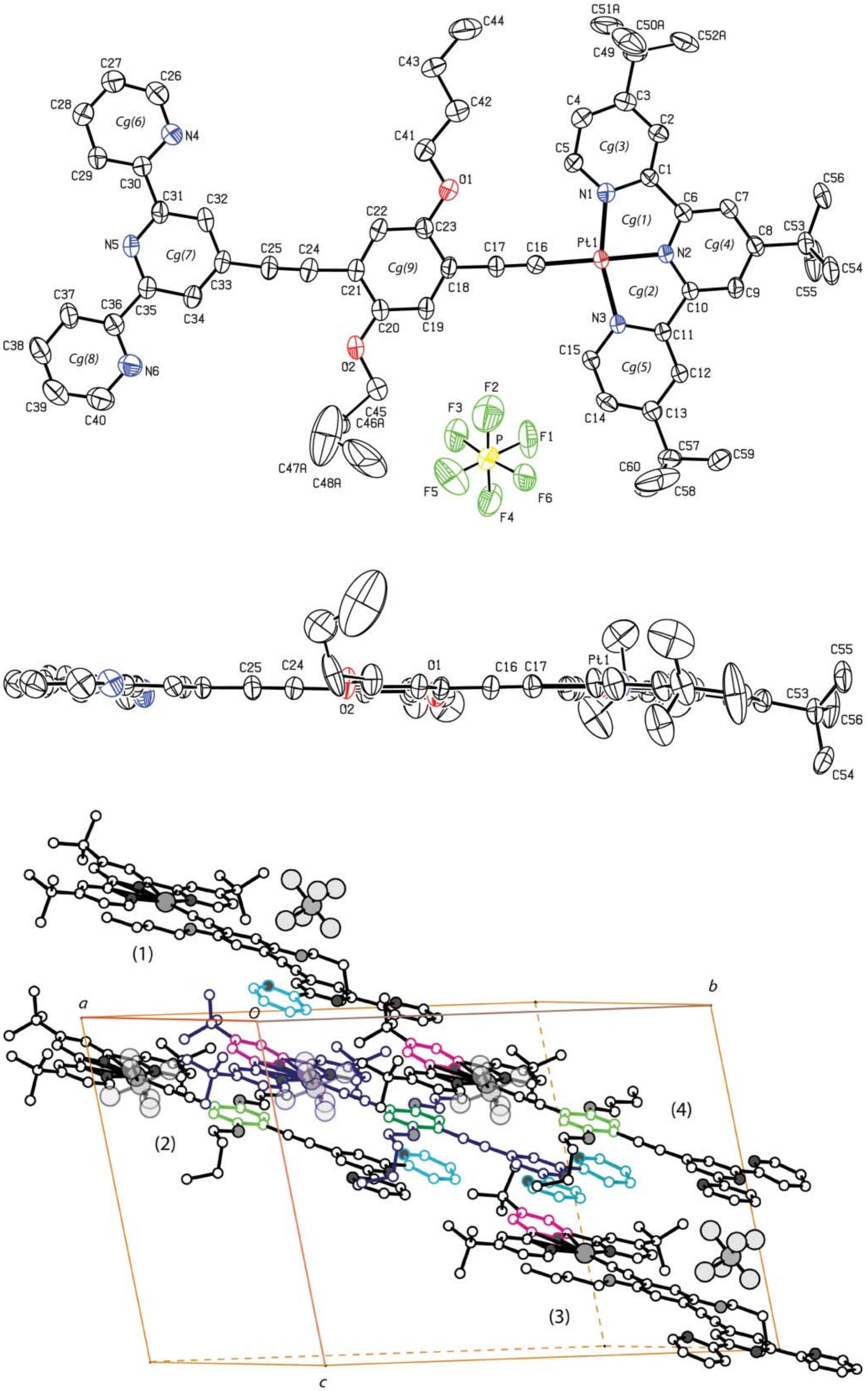


Fig. 1 TOP: ORTEP view of complex **7** with atom labelling. Probability displacement ellipsoids are shown at 50% level. Selected distances and angles: C24–C25 1.195(10) Å, N3–Pt–N2 80.46(19)°, N2–Pt–N1 80.7(2)°, N3–Pt–N1 161.1(2)°, N2–Pt–C16 178.2(2)°. Middle: view along the Pt–pyridine N5 axis. Bottom: crystal packing.

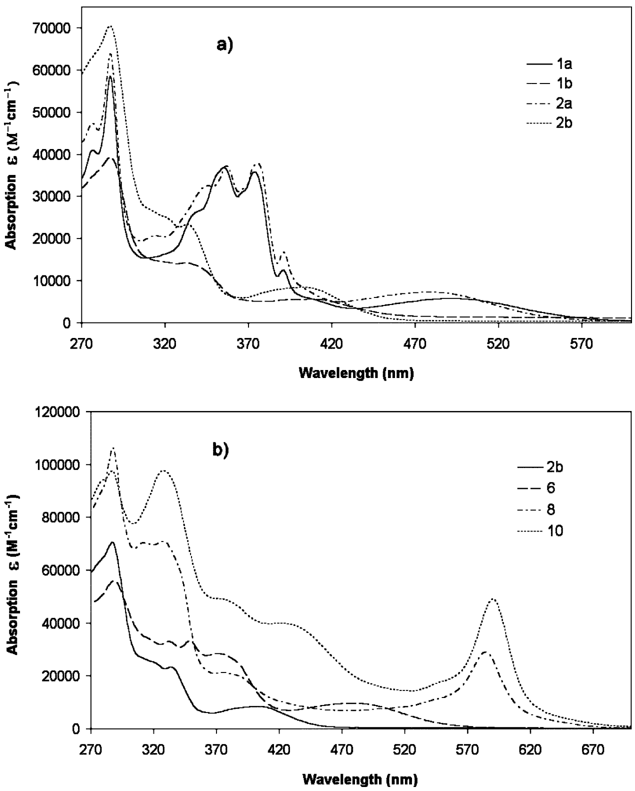


Fig. 2 Overlay of absorption spectra recorded for various complexes in dimethylformamide solution.

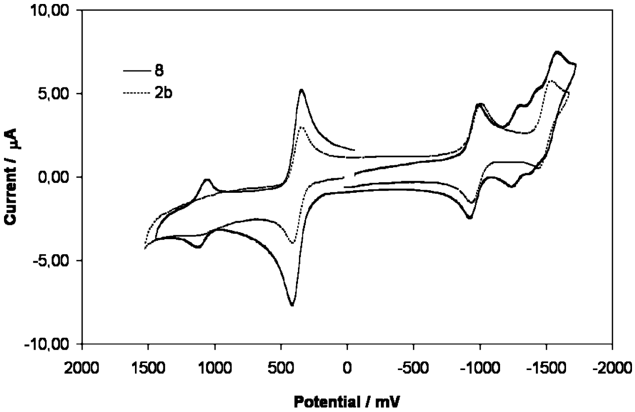


Fig. 3 Cyclic voltammetry of complexes **8** and **2b** in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate at rt, scan rate 200 mV s^{-1}.

of the ^{3}MLCT state with a strong bathochromic shift observed for the electron-rich pyrenyl modules. This trend is confirmed with the dibutoxyphenyl fragments. Preliminary electrochemical studies showed two reversible redox processes (ligand and Pt based) for the key complex **2b**. Complexation of the pendent terpy unit with iron(II) enabled the successive reduction of each terpy coordinated to iron in addition to the one bound to Pt. In-depth characterization of the photophysical properties of these new complexes is currently in progress.

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Notes and references

‡ X-Ray crystal data for **7** at 293 K ($C_{60}H_{60}N_6O_2PtF_6P$, $Mr = 1237.2$): monoclinic, space group $P2_1/c$, $a = 10.8334(3)$, $b = 33.5765(9)$, $c = 16.8022(5)$ Å, $\beta = 104.462(1)°$, $V = 5918.1(3)$ Å^3, $Z = 4$, $\mu = 2.462$ mm^{-1}, reflections measured: 16893, unique: 9663, $R(\text{int}) = 0.035$, final $R1(F) = 0.047$, $wR2(F^2) = 0.1055$ for 784 parameters, 25 restraints and 7013 reflections with $I > 2\sigma(I)$ and $1.74 < \theta < 24.4°$ (corresponding R values based on all 9658 reflections are 0.0763 and 0.1166, respectively). Largest difference peak and hole are 1.071 and −0.696. CCDC reference number 600978. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603603a

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