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Design and preparation of neutral substituted fluorene- and carbazole-based platinum(II)–acetylide complexes

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Various combinations of mono- or diethynyl-substituted fluorene or carbazole building blocks were connected *via* a σ-bonded ethynyl linkage to *ortho*-metallated Pt(II) fragments, giving rise to phosphorescent mono- and dinuclear complexes for which the solubility and extent of delocalization could be tuned by the chemistry on the acidic methylene position of the fluorene.

Much attention has been focused recently on alkyne-substituted molecular frameworks because they not only provide useful models for intramolecular information transfer but also have potential applications in materials science, including polymer chemistry.[1] Acetylide anions derived from terminal alkynes are particularly useful for extending electronic conjugation[2] as well as for tethering chromophores to transition metals,[3] boron centres[4] and larger organic edifices.[5] In these regards, the chemistry of alkynyl–platinum(II) and –gold(I) has received much recent attention.[6,7]

The preference of d^8 Pt(II) to form square-planar species, along with the linearity and pronounced electron density of C≡C bonds make the "Pt–C≡C–" moiety, in particular, an attractive and promising candidate for the design of luminescent complexes with applications in fluid solution, thin films and the solid state. It has been shown recently that some of these complexes show liquid-crystalline and nonlinear optical properties,[8] electroluminescence,[9] and singlet oxygen photosensitization,[10] and can be used in photocatalytic hydrogen production,[11] cation sensing,[12] and conductance switches.[13] The square-planar coordination geometry of Pt(II) in its complexes of large aza-aromatic ligands makes such complexes effective DNA intercalators and useful molecular probes for biological macromolecules.[14] Many alkynyl–platinum complexes exhibit intriguing luminescent properties and polyimine (phenanthroline, bipyridine, terpyridine and phenyl bipyridine)–Pt(II) complexes incorporating σ-alkynyl ligands, in particular, are well-known for their rich photochemistry, forming a class of luminophores that may find application in advanced electronic and light converting devices.[9] In view of the fact that fluorene and carbazole frameworks are easily transformable and often used in OLEDs and polymeric materials,[15] but are yet to be found as systematically introduced components of coordination complexes, the linking of these building blocks to square-planar species seemed to us to offer intriguing possibilities for extension of this chemistry.

Thus, as a part of our research program on the construction of extended π-electronic systems, we attempted the development of an efficient method for the synthesis of novel mono- and binuclear Pt(II) complexes with electron-rich fluorene and carbazole moieties. Ligands of this type are known, as are Pt(II) complexes and polymers containing these species,[16] although the introduction of neutral Pt(II) complexes of *ortho*-metallated and tridentate ligands in conjunction with fluorene and carbazole units has not been reported before to the best of our knowledge. The key building blocks (Chart 1) were prepared according to adapted literature procedures, usually comprising four-synthetic steps involving: (i) bromination of the substrates; (ii) alkylation of the methylene (fluorene) and nitrogen (carbazole) centres; (iii) alkynylation by Sonogashira coupling; and (iv) deprotection.[15,17]

The mono- and dibromo starting materials were prepared from fluorene and carbazole using stoichiometric amounts of *N*-bromosuccinimide in $CHCl_3$ at rt. Alkylation of 2-bromofluorene and 2,7-dibromofluorene was achieved using CH_3I, C_4H_9Br or $C_{12}H_{25}Br$ in a mixture of DMSO–H_2O–NaOH, with $[Et_3BzN]Cl$ as phase transfer catalyst (for **1a** and **4a**), or with NaH in anhydrous DMF for **2a** and **3a**. Methylation of 3-bromocarbazole and 3,6-dibromocarbazole is also very efficient using NaH and CH_3I in anhydrous DMF at rt. The best conditions for the synthesis of the ethynyl derivatives **1b** to **6b** requires $HC{\equiv}CSiMe_3$, $[Pd(PPh_3)_4]$ (5 mol% per Br), CuI (10 mol% per Br), and piperidine as solvent at 80 °C. Removal of the TMS group may be achieved using excess K_2CO_3 in CH_3OH–CH_2Cl_2 at rt.

To test the efficiency of cross-coupling of the monoethynyl compounds **1c–3c** and **5c**, we targeted a neutral [Pt(C^N^N)Cl] precursor prepared according to a known procedure (C^N^N designates the deprotonated 6-phenyl-

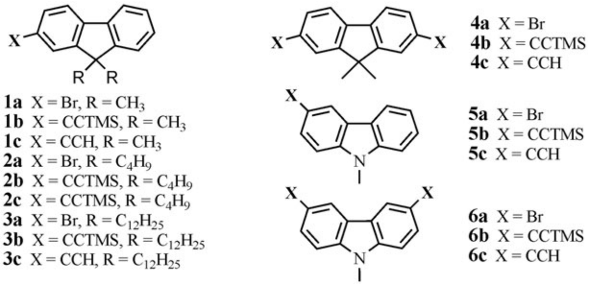

Chart 1

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

Compound	Isolated yield (%)	$\nu_{C\equiv C}$/cm^{-1a}	λ_{max}/nm (ε/M^{-1} cm^{-1})^{b}	λ_{em}/nm^{c}
7	95	2090	446 (6300)	634
8	82	2091	449 (7000)	614
9	80	2092	465 (6700)	612
10	76	2097	480 (5300)	522
11	60	2089	444 (7600)	616
12	67	2093	475 (10 000)	651
13	38	2081	478 (5700)	543
14	46	2093	484 (9900)	544
15	51	2113	445 (5700)	605
17	60	2095	468 (7700)	586

[a] One drop of CH_2Cl_2 containing the sample was evaporated on a KBr disk. [b] Averaged value determined from at least two different solutions of non-degassed CH_2Cl_2 solution. [c] Phosphorescence peak measured in non-degassed CH_2Cl_2 solution with an excitation wavelength corresponding to the maximum of absorption.

2,2′-bipyridine ligand).[18] Cross-coupling with ethynyl-fluorene and ethynyl-carbazole is effective (Table 1) in the presence of catalytic amounts of CuI (8 mol%) in CH_2Cl_2 and triethylamine (acid quencher) when conducted under strictly anaerobic conditions (Chart 2).

Interestingly, mixing 2,7-diethynyl-9,9-dimethylfluorene **4c** or 3,6-diethynyl-9-methylcarbazole **6c** with [Pt(C^N^N)Cl] under similar conditions provides the neutral mononuclear complexes **11** and **13** and no significant amounts of the disubstituted analogues. After some experimentation with the reaction mixture composition, the temperature and reaction time, we succeeded in isolating the desired dinuclear Pt(II) complexes **12** and **14** (Chart 3) in modest yields. We believe that grafting the first metal to the diethynyl derivative deactivates the remaining ethynyl group, rendering its binding more difficult.

The molecular structures of **7** and **10** were confirmed by X-ray crystallography (Fig. 1). In both cases the Pt(C^N^N)-acetylide fragment is square-planar whereas the dimethylfluorene fragment is titled out of the plane by 76° (for **7**), and the methylcarbazole by 60° (for **10**). This implies that π-orbitals of the fluorene and carbazole are not engaged in favourable overlap with the Pt core in the solid. Furthermore, the Pt–C, C≡C and C–aryl bond lengths are consistent with weak Pt–alkynyl back-bonding. As would be expected for an *ortho*-metallated ligand, the Pt–C bonds (Pt–C1 2.069 and 1.988 Å for **7** and **10**) lie in the expected range. Furthermore, the central Pt–N bond is shorter than the peripheral one (Pt–N1 1.984 and 2.042; Pt–N2 1.993 and 2.119 Å for **7** and **10**). For compound **7**, there is evidence of π–π stacking involving aromatic ring plane separations ∼3.4 Å. We contend that the conjugation based on σ–π interaction between the Pt(II) and arylacetylide moieties confers high stability and rigidity to this system.

To test the efficiency of the copper-catalyzed cross-coupling with a more polar alkyne substrate, we decided to prepare a poly(ethylene glycol)-substituted fluorene derivative by substitution of the methylene protons under phase transfer conditions with [2-(2-{2-(2-bromoethoxy)ethoxy}ethoxy)-ethoxy]methyl.[19] Despite the strong polarity of the substituted derivative, cross-coupling with $HC\equiv CSiMe_3$ was straightforward using [$Pd(PPh_3)_4$] (5 mol% per Br) and CuI (10 mol% per Br), in hot piperidine. After removal of the TMS group with K_2CO_3 in CH_3OH–CH_2Cl_2, the resulting terminal alkyne was linked to the neutral [Pt(C^N^N)Cl] precursor, leading to the stable complex **15** (Chart 4).

The proton and carbon NMR spectra clearly show that the aromatic protons of the fluorene and C^C^N ligand are well-defined with 16 different multiplets and peaks for a strongly deshielded single proton at 8.99 ppm (Fig. 2), likely attributed to the proton b (see Chart 4). Interestingly, the protons (a) in

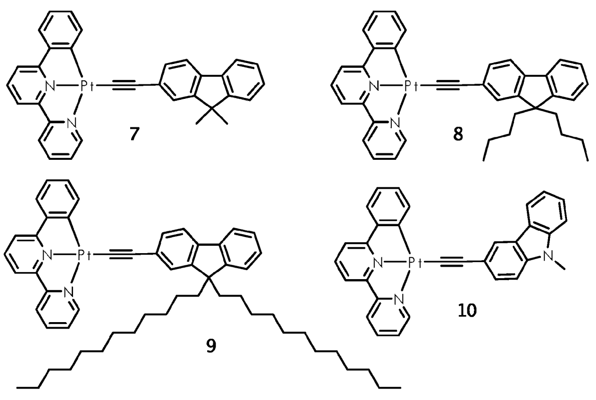

Chart 2

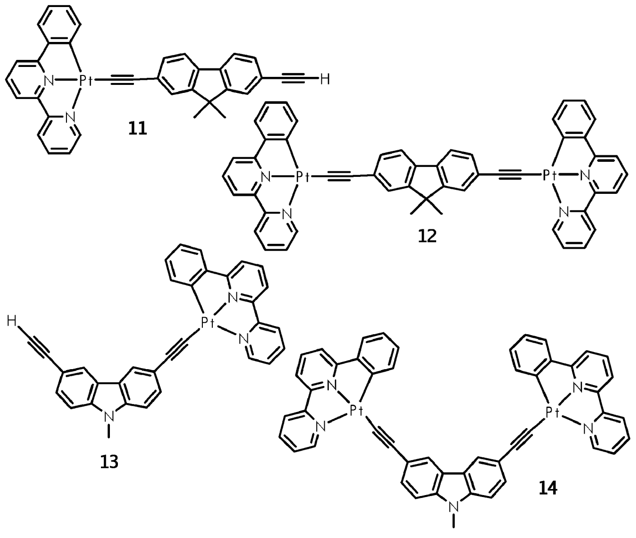

Chart 3

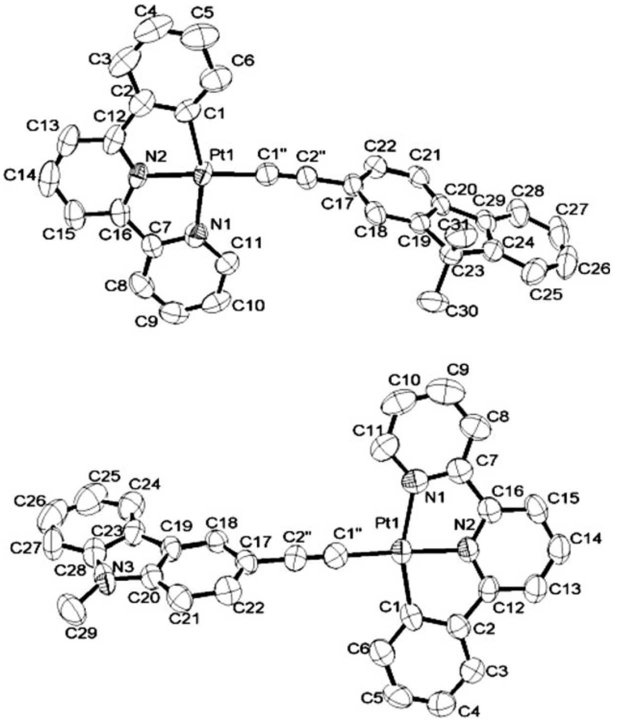

Fig. 1 ORTEP view of compound **7** (a) and **10** (b) (50% probability displacement ellipsoids), with all hydrogen atoms removed for the sake of clarity.

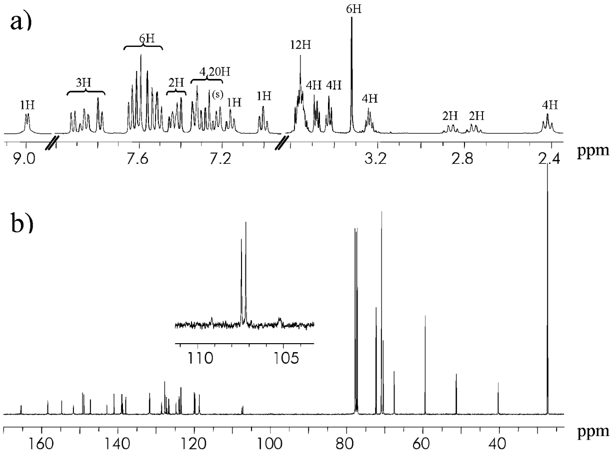

Fig. 2 (a) Expanded proton NMR spectrum of **15** in $CDCl_3$ (s), integration 0.2, at 400.13 MHz. (b) Carbon NMR spectrum of **15** in $CDCl_3$ at 100.61 MHz. Inset is the expanded ethynyl region.

close proximity to the fluorene and oxygen atoms are diastereotopic, leading to an AA′X pattern integrating for 2H around 2.8 ppm. The carbon NMR spectrum is in keeping with the molecular structure, with two characteristic ethynyl carbon resonances at 107.5 and 107.2 ppm (Fig. 2b).

Subsequently, we applied this synthetic protocol to the preparation of more highly conjugated systems. The synthesis of complex **17** was achieved in a three-step procedure involving: (i) deprotonation of 2-(trimethylsilylacetylene)fluorene with LDA at −78 °C in THF followed by reaction with benzophenone; (ii) removal of the TMS protecting group with a base under polar conditions; and (iii) cross-coupling with CuI as catalyst (Chart 5).

The electronic absorption spectra of all complexes in CH_2Cl_2 solution at 298 K show intense multiple absorption peaks in the range 250–600 nm (Fig. 3a). On the basis of earlier studies of related compounds,[20] the high-energy, structured absorption bands are ascribed to π–π* transitions of the C^N^N fluorene– and carbazole–alkynyl moieties. 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-C^N^N ligand-to-ligand charge transfer character (LLCT).[21] This band is found around 445 nm in the mononuclear fluorene complexes, **7** and **11**, whereas in the mononuclear carbazole derivatives, **10** and **13**, it appears around 479 nm (Table 1). For the dinuclear complexes **12** and **14**, these broad bands are split and one band is clearly shifted to the red and tails beyond 550 nm. This bathochromic shift is probably induced by the increase of electronic delocalization imported by the second Pt centre and could be assigned to the contribution of the alkynyl–fluorene/–carbazole to C^N^N ligand-to-ligand charge transfer. Excitation of the fluorene complexes in fluid solution at 450 nm results in red phosphorescence at 634 nm (ϕ = 1%, τ = 39 ± 2 ns), 616 nm (ϕ = 0.1%, τ = 55 ± 5 ns), and 651 nm (ϕ = 0.2%, τ = 1.5 ± 0.5 ns), respectively for **7**, **11** and **12** (Fig. 3b). The weakness of the fluorescence of the carbazole derivatives is possibly a consequence of intramolecular electron transfer involving the tertiary amine of the carbazole subunit. As anticipated from previous data obtained with *ortho*-metallated ligands, the increase in charge density is responsible for the decrease in excited state lifetimes due to the occurrence of non-radiative deactivation pathways.

In summary, a series of *ortho*-metallated platinum(II) acetylide complexes bearing various appended moieties (fluorene and carbazole) has been synthesized successfully, using a rational protocol. High solubility in apolar or polar solvents has been ensured by the use of alkyl substituents or a

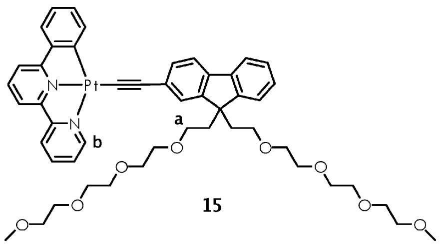

Chart 4

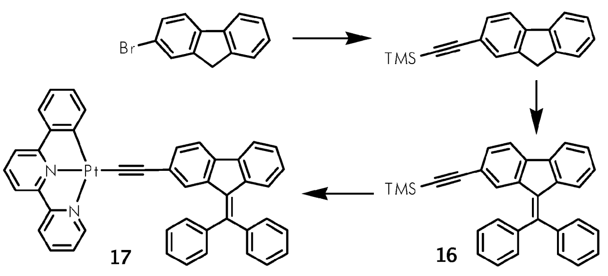

Chart 5

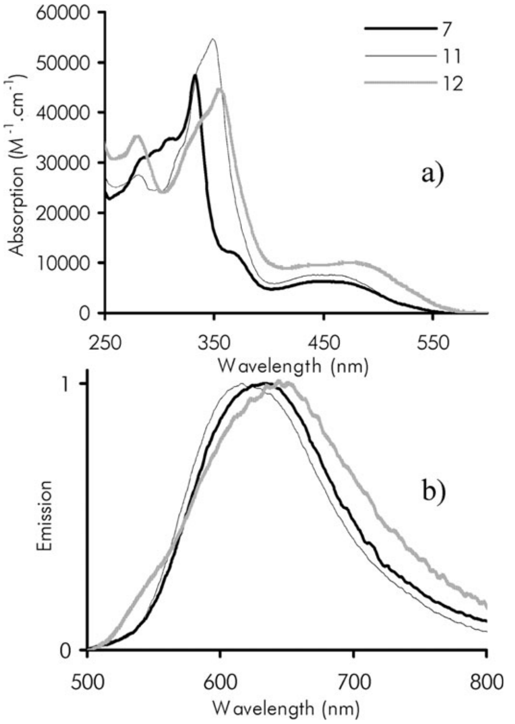

Fig. 3 (a) Overlay of absorption spectra recorded for the fluorene series in dichloromethane solution at rt. (b) Phosphorescence spectra measured at rt, in dichloromethane in air, with an excitation wavelength of 446 nm for **7**, 444 nm for **11** and 475 nm for complex **12**.

poly(ethylene glycol) chain grafted on the central fluorene moiety. Additional reaction on this central fluorene position allows the construction of a diphenylvinyl group, which further extends the electron delocalization. X-Ray molecular structures have revealed a non-coplanar arrangement of the fluorene and carbazole entities with respect to the square-planar platinum core. For the dinuclear complexes, the absorption of the ^{3}MLCT state exhibits a bathochromic shift, which is more pronounced for the carbazole bridging unit. This trend is confirmed with the diphenylvinyl fragment. In-depth characterization of the photophysical and redox properties of these new complexes is currently in progress.

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Experimental

Representative synthesis: compound 15

A mixture of (6′-phenyl-2,2′-bipyridine)chloroplatinum (C^N^N)PtCl (0.090 g, 0.16 mmol) and 2-ethynyl-9,9-[2-(2-{2-(2-ethoxy)ethoxy}ethoxy)ethoxy]fluorene (0.090 g, 0.19 mmol) in dichloromethane (15 ml) and triethylamine (3 ml) was degassed by bubbling argon for 30 min. Then CuI powder (8 mol% per Pt) was added as a solid and the solution was stirred for 18 h at rt. The reaction mixture was then evaporated to dryness under reduced pressure and the crude oil purified by column chromatography (Al_2O_3, CH_2Cl_2–MeOH (1%) as eluant) and recrystallized in a mixture dichloromethane–methanol–cyclohexane to give **15** as a red waxy solid (0.080 g, yield: 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.99 (d, 1H, ^3J = 5.0 Hz), 7.93–7.78 (7 line m, 3H), 7.65–7.49 (8 line m, 6H), 7.45–7.40 (4 line m, 2H), 7.34–7.21 (8 line m, 4H), 7.15 (t, 1H, ^3J = 7.5 Hz), 7.00 (t, 1H, ^3J = 7.5 Hz), 3.54–3.52 (11 line m, 12H), 3.49–3.46 (4 line m, 4H), 3.42 (t, 4H, ^3J = 5.0 Hz), 3.32 (s, 6H), 3.25–3.22 (4 line m, 4H), 2.28–2.83 (5 line m, 2H), 2.79–2.73 (5 line m, 2H), 2.42 (t, 4H, ^3J = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): 165.4, 158.3, 154.7, 151.6, 149.3, 148.9, 147.2, 142.9, 141.0, 139.0, 138.9, 138.8, 137.9, 131.7, 128.5, 127.7, 127.2, 126.6, 124.7, 123.9, 123.4, 119.9, 119.8, 118.6, 107.4, 107.1, 70.9, 70.9, 70.8, 70.4, 67.5, 59.4, 51.3, 40.2, 27.3; UV-Vis (CH_2Cl_2) λ nm (ε, M^{-1} cm^{-1}) = 445 (5700), 366 (12 900), 333 (41 700), 313 (35 000), 282 (33 200), 229 (39 800); IR (KBr): ν = 3069 (w), 2924 (s), 2854 (s), 2113 (w, $\nu_{C\equiv C}$), 1729 (m), 1603 (m), 1452 (s), 1398 (w), 1291 (m), 1257 (m), 1043 (s), 1036 (s), 844 (w), 770 (m), 741 (m), 522 (w); ESI-MS m/z (nature of peak, relative intensity): 997.2, 996.2, 995.2 ($[M + H]^+$, 90, 100, 65), 451.2, 450.2, 449.1 ($[M - \text{fluo}(C_9H_{19}O_4)_2{-}{\equiv}{-}]^+$, 35); anal. Calcd for $C_{49}H_{56}N_2O_8Pt$: C, 59.09; H, 5.67; N, 2.81. Found: C, 58.72; H, 5.42; N, 2.57%.

X-Ray crystallography

Crystal data for 7. $C_{33}H_{24}N_2Pt$, M = 643.63, monoclinic, space group $P2_1/c$, a = 7.2707(6) Å, b = 12.3313(10) Å, c = 28.699(2) Å, β = 96.684(2)°, V = 2555.6(3) Å^3, Z = 4, λ = 0.71073 Å, D_c = 1.673 g cm^{-3}, μ = 5.515 mm^{-1}, F(000) = 1256, T = 100(2) K. 31 394 measured reflections with 1.43° < θ < 31.00°, 8052 unique R_{int} = 0.0423, and 7626 reflections with [$I > 2\sigma(I)$], 327 variable parameters R_1 = 0.0399 and wR_2 = 0.1001 refined on F^2. CCDC reference number 644875. For crystallographic data in CIF format see DOI: 10.1039/b702374j

Crystal data for 10. $C_{31}H_{21}N_3Pt$, M = 630.60, orthorhombic, space group $P2_12_12_1$, a = 7.301(5) Å, b = 12.688(5) Å, c = 25.728(5) Å, V = 2383.3(19) Å^3, Z = 4, λ = 0.71069 Å, D_c = 1.757 g cm^{-3}, μ = 5.913 mm^{-1}, F(000) = 1224, T = 293(2) K. 14 854 measured reflections with 1.58° < θ < 25.43°, 4276 unique R_{int} = 0.0425, and 3759 reflections with [$I > 2\sigma(I)$], 317 variable parameters R_1 = 0.0306 and wR_2 = 0.0760 refined on F^2. CCDC reference number 644876. For crystallographic data in CIF format see DOI: 10.1039/b702374j

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