Experimental and Theoretical Investigation for Level of Conjugation in Carbazole-based Precursors and their Mono-, Di- and Polynuclear Pt(II) Complexes

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Experimental and Theoretical Investigation for Level of Conjugation in Carbazole-based Precursors and their Mono-, Di- and Polynuclear Pt(II) Complexes†

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ABSTRACT
A series of trimethylsilyl-protected mono-alkynes (Me₃SiC≡C−R) and bis-alkynes (Me₃SiC≡C−R−C≡CMe₃) incorporating carbazole spacer groups (R = carbazole-2-yl, carbazole-3-yl, carbazole-2,7-diyl, N-(2-ethylhexyl)carbazole-2,7-diyl, carbazole-3,6-diyl, N-(2-ethylhexyl)carbazole-3,6-diyl), together with the corresponding terminal mono-alkynes (H−C≡C−R) and bis-alkynes (H−C≡C−R−C≡C−H), have been synthesized and characterized. The CuI-catalyzed dehydrohalogenation reaction between trans-[(Ph)(Et₃P)₂PtCl], trans-[(Et₃P)₂PtCl₂] and trans-[(P₅Bu₅)₂PtCl₂] and the terminal alkynes in iPr₂NH/CH₂Cl₂ affords a series of Pt(II) mono- and di-yynes, while the dehydrohalogenation polycondensation reactions with trans-[(P₅Bu₅)₂PtCl₂] under similar reaction conditions yields four Pt(II) poly-yynes of the form trans-[(P₅Bu₅)₂Pt−C≡C−R−C≡C−]ₙ. The acetylide-functionalized carbazole ligands and the mono-, di- and poly-nuclear Pt(II) σ-acetylide complexes have been characterized spectroscopically, with a subset analysed using single-crystal X-ray diffraction. The Pt(II) mono-, di- and poly-yynes incorporating the carbazole spacers are soluble in common organic solvents, and solution absorption spectra show a consistent red-shift between the 2- and 2,7- as well as 3- and 3,6-carbazole complexes. Computational modelling is used to explain the observed spectral shifts, which are related to the enhanced electronic delocalization in the latter systems. These results also indicate that the inclusion of carbazole-2,7-diyl units into rigid-rod organometallic polymers should enhance electronic transport along the chains.

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INTRODUCTION

The last few decades have seen huge research effort in the pursuit of developing novel materials with enhanced optoelectronic properties. Metal-organic frameworks (MOFs), especially conjugated organometallic compounds, have attracted considerable attention due to their potential applications in the modern materials industry (e.g. photovoltaic cells, field-effect transistors, light-emitting diodes and non-linear optics). One of the most promising systems is the rigid-rod type Pt(II) poly-ynes, \( \text{trans-}[-\text{Pt}(\text{P}^{\text{Bu}}_{\text{3}})_{2}-\text{C}≡\text{C}−\text{R}−\text{C}≡\text{C}−]_{\text{n}}, \) where R is one of a number of aromatic, hetero-aromatic or mixed-heterocycle spacer groups. A particularly attractive feature of the Pt(II) poly-ynes is the ability to fine-tune their opto-electronic properties by variation of the spacer groups. Whereas the spacer plays an important role in determining the physico-chemical properties of the materials, the Pt(II) ion plays a crucial role in controlling the photo-physical properties. It is well known that triplet (T\(_1\)) states play an important role in the opto-electronic processes of conjugated polymers, and the incorporation of Pt(II) into the polymer backbone populates the T\(_1\) excited states by intersystem crossing, allowing for light emission from the decay of these states. Synthetic flexibility and compatibility with different conjugated spacers thus together allow fine control over the photo-physical properties.

Among the more electron-rich of the reported spacers used in Pt(II) poly-ynes is the carbazole unit (Chart 1). This moiety provides a rigid planar biphenyl unit within the polymer backbone, and facile functionalization via the N atom, offering the prospects of both improving polymer processability and of mediating potential inter-chain interactions in polymer films. There is also considerable interest in the solid-state structures of the polymeric materials due to evidence of interchain interactions which influence their opto-electronic properties. In this context, an analysis of intermolecular interactions in the crystal structures of the ligand precursors and of suitable model complexes may lead to a better understanding of the interactions in the polymers. Mono- and di-yne compounds are viewed as building blocks for the high molecular-weight poly-ynes, and valuable information on their properties (e.g. electronic structure and optical absorption) can be obtained by studying these model systems. Mono- and di-yne compounds are also often more easily crystallised than the corresponding poly-ynes, allowing for a detailed structural analysis, and, thus, an assessment of structure-property relationships.
Several carbazole-based chromophores have been prepared, and their photophysical properties investigated in order to explore their potential applications in organic electroluminescent devices. Several recent reports have also studied the incorporation of carbazole-based auxiliaries into conjugated MOFs. In this work, we report the synthesis and characterization of a set of acetylide-functionalized carbazole ligands and their mono-, di-, and poly-nuclear Pt(II) σ-acetylide complexes. The crystal structures of two acetylide ligand precursors, together with those of a mono-nuclear and di-nuclear Pt(II) σ-acetylide complexes are also reported. The optoelectronic properties are characterized, compared to those of related organometallic complexes and polymers, and investigated through computational modelling.

**RESULTS AND DISCUSSION**

**Synthesis**

Alkylation of 2,7- and 3,6-dibromo carbazoles using NaH in anhydrous DMF was performed in high yields by following the reported literature method. However, the subsequent removal of DMF was found to be a tedious and time-consuming process, which also resulted in significant loss of the final products. Yang et al. alkylated phenothiazine ($p$Ka ~ 23) using potassium tert-butoxide (KO'Bu) as the base and THF as the solvent. Since carbazole has a $p$Ka of ~ 20, we successfully applied Yang’s method to alkylate carbazoles. No reaction occurred upon stirring at room temperature for 6-8 hrs, but refluxing the reaction mixture overnight gave the desired products in quantitative yield (Scheme 1). After completion of the reaction, removal of the solvent in vacuo, followed by purification using column chromatography, gave the products in very high yield, making the modified alkylation method more convenient than existing literature method.
The mono- and bis-ethynyl carbazole derivatives were synthesised by a sequence of coupling and proto-desilylation reactions (Scheme 2). A total of six trimethylsilyl-protected alkynyl ligand precursors were prepared through a scheme adapted from published procedures involving a Pd\[^{0}\]/Cu\[^{1}\]-catalyzed cross-coupling reaction of the monobromo or dibromocarbazoles with trimethylsilylethylene in an \[^{t}\]Pr\(_2\)NH/THF solvent\[^{4c,8b,11,14}\]: 2-trimethylsilylethylnylcarbazole (1-TMS), 3-trimethylsilylethylnylcarbazole (2-TMS), 2,7-bis(trimethylsilylethylene)carbazole (3a-TMS), 2,7-bis(trimethylsilylethylene)-N-(2-ethylhexyl)carbazole (3b-TMS), 3,6-bis(trimethylsilylethylene)carbazole (4a-TMS), and 3,6-bis(trimethylsilylethylene)-N-(2-ethylhexyl)carbazole (4b-TMS). Wong et al. reported that alkylation at the carbazole N atom should precede the cross-coupling reaction with trimethylsilylethylene,\[^{11a}\] presumably due to the instability of the N-H group in \[^{t}\]Pr\(_2\)NH. However, we were able successfully to introduce trimethylsilylethylene groups onto the non-alkylated 2,7- and 3,6-carbazoles by conducting the cross-coupling reactions in a mixture of \[^{t}\]Pr\(_2\)NH and THF.

Conversion of the protected ligand precursors into their terminal alkynes was accomplished by smooth removal of the trimethylsilyl group(s) with dilute aqueous KOH in MeOH/THF, yielding 2-ethynylcarbazole (L1), 3-ethynylcarbazole (L2), 2,7-bis(ethynyl)carbazole (L3a), 2,7-bis(ethynyl)-N-(2-ethylhexyl)carbazole (L3b), 3,6-bis(ethynyl)carbazole (L4a), and 3,6-bis(ethynyl)-N-(2-ethylhexyl)carbazole (L4b). The products were purified by silica-gel column chromatography and isolated as off-white to light-yellow solids or viscous liquids in 88 – 99 % yields. The trimethylsilyl-protected mono- and bis-alkynes were stable to air and light and were characterized by infrared (IR) spectroscopy, nuclear-magnetic resonance (NMR; \(^{1}\)H and \(^{13}\)C), electron-impact/electrospray ionisation mass spectrometry (EI-MS/ESI-MS), and elemental analyses. The mono- and bis-terminal alkynes were found to be somewhat less stable, and hence were freshly prepared before reaction with the Pt(II) bis-phosphine dihalide complexes.
Scheme 2 Syntheses of mono- and bis-acetylide-functionalized carbazole ligands.

The reaction of the terminal mono-alkynes L1 and L2 with one equivalent of trans-[(Ph)(Et3P)2PtCl] in tPr2NH/CH2Cl2 in the presence of CuI at room temperature readily afforded the mono-nuclear Pt(II) mono-ynes M1 and M4, respectively. Treating L1 and L2 with 0.5 equivalent of trans-[(Et3P)2PtCl2] and trans-[(PnBu3)2PtCl2] yielded the corresponding mono-nuclear Pt(II) di-ynes M2 and M5, and M3 and M6, respectively (Scheme 3 and Scheme 4). On the other hand, the reaction of trans-[(Ph)(Et3P)2PtCl] with the terminal di-alkynes L3 and L4 (1:2 equivalent) under similar conditions gave the di-nuclear Pt(II) di-ynes M7-M10 (Scheme 5 and Scheme 6). The CuI-catalyzed dehydrohalogenation polycondensation reaction between trans-[(PnBu3)2PtCl2] and the terminal di-alkynes L3 and L4 (1:1 equivalent) under similar reaction conditions readily afforded the poly-ynes P1-P4 (Scheme 5 and Scheme 6). It is worth noting that ethynylation with Pt(II) chloride complexes proceeded smoothly in basic medium despite the presence of acidic NH protons. We attribute this to the stabilization of carbazole NH protons through H-bonding with solvent as well as other carbazole moiety. The involvement of carbazole NH protons in H-bond possibly prompted the terminal
acetylenic protons for preferential dehydro-halogenation reaction. Purification of the Pt(II) mono- and diynes (M1-M10) was performed using silica column chromatography, while the Pt(II) polyynes (P1-P4) were purified by chromatography on alumina. The synthesis of the Pt(II) mono-nuclear di-yne M6, dinculear di-ynes M7-M9 and poly-ynes P1-P3 were reported previously.11e,f

Scheme 3 Synthesis of the mono-nuclear Pt(II) mono- and di-ynes M1-M3, incorporating carbazole-2-yl moiety.
Scheme 4 Synthesis of the mono-nuclear Pt(II) mono- and diynes M4-M6, incorporating carbazole-3-yl moiety.

(i) 1.0 equiv. trans-[Ph(PEt₃)₂PtCl₂], Cul, iPr₂NH, DCM
(ii) 0.5 equiv. trans-[PEt₃₃₂PtCl₂], Cul, iPr₂NH, DCM
(iii) 0.5 equiv. trans-[PBu₃₃₂PtCl₂], Cul, iPr₂NH, DCM

Scheme 5 Synthesis of the di-nuclear Pt(II) diynes M7 and M8 and the corresponding poly-yynes P1 and P2.

(i) 2.0 equiv. trans-[Ph(PEt₃)₂PtCl₂], Cul, iPr₂NH, DCM
(ii) 1.0 equiv. trans-[PBu₃₃₂PtCl₂], Cul, iPr₂NH, DCM
Scheme 6 Synthesis of the Pt(II) diynes M9 and M10 and the corresponding polyynes P3 and P4.

Spectroscopic characterization

Preliminary characterization of the acetylide-functionalized carbazole ligands and their Pt(II) mono-, di- and polyynes was carried out using IR spectroscopy and $^1$H, $^{13}$C and $^{31}$P NMR. The IR spectra of the Pt(II) mono-, di- and poly-yne compounds provided clear evidence for the presence of the C≡C bond from its characteristic absorption at around ~ 2095 cm$^{-1}$.$^{4d,e,8b,11,16}$ The single, sharp $\nu_{C≡C}$ absorptions indicate a trans-configuration of the alkynyl bridging ligands around the bis(trialkynylphosphine) Pt(II) moieties. The Pt(II) mono-, di- and polyynes display lower $\nu_{C≡C}$ values than those of the terminal alkynes (L1-L4) which is attributed to metal-to-alkynyl ligand back bonding. The $\nu_{C≡C}$ values for the terminal alkynes (L1-L4; 2104–2108 cm$^{-1}$) were found to be lower than those of the trimethylsilyl-protected alkynes (1-TMS-4-TMS; 2148 – 2152 cm$^{-1}$); the fact that terminal alkynes (HC≡C─R) have lower $\nu_{C≡C}$ frequencies than their protected counterparts RC≡C─R (typically around 50 cm$^{-1}$) is well known, and thus expected.$^{17}$

The $^1$H and $^{13}$C NMR spectra of all the compounds contained peaks corresponding to the expected alkyl, aryl and alkynyl fragments. The peak area ratios in the $^1$H NMR spectra were found to agree with the feed mole ratio of the precursors for the mono-, di- and poly-yynes. The IR and $^{31}$P{ $^1$H}-NMR spectral features are similar to those observed in other previously-reported Pt(II) mono-, di- and poly-yynes,$^{18}$ and indicate an all-trans configuration and hence a rigid-rod like structure. The mass-spectrometry results confirm
the molecular masses expected for the acetylide ligands and the mono- and di-nuclear platinum-acetylide complexes.

Gel-permeation chromatography (GPC), calibrated against a polystyrene standard, gave weight-average molecular weights for the polyynes P1-P4 in the range of 17,900 – 40,500 g/mol, corresponding to degrees of polymerizations (DPs) between 22 and 43. The polydispersity index (PDI) was found to vary between 1.6 and 1.9. These molecular weights should, however, be viewed with caution, due to the difficulties associated with characterizing rigid-rod polymers using GPC. This technique does not give absolute values of the molecular weights, but rather provides a measure of hydrodynamic volume, and rod-like polymers in solution show very different hydrodynamic properties to more flexible polymers. Therefore, calibration of the GPC with a polystyrene standard is likely to artificially increase the measured molecular weights to some extent. However, the lack of discernible resonances corresponding to end groups in the NMR spectra does indicate high degree of polymerization in these polyynes.

**Optical-absorption spectroscopy**

The TMS-protected carbazole ligands, the ten Pt(II) complexes and the four polymers were found to be readily soluble in common organic solvents, and we therefore measured the room-temperature absorption spectra of all 20 compounds in dilute CH$_2$Cl$_2$ solution. Table 1 summarises absorption spectral data of the compounds.

Room-temperature absorption spectra of the 2- and 3-trimethylsilylacetylide carbazole ligands (1-TMS and 2-TMS) and corresponding mono-nuclear Pt(II) complexes (M1-M3 and M4-M6, respectively) are shown in Figure 1.
Figure 1 Solution absorption spectra (CH$_2$Cl$_2$) of the 2- and 3- trimethylsilylacetylide carbazole ligands 1-TMS (a) and 2-TMS (b), together with those of the corresponding mono-nuclear Pt(II) complexes M1-M3 (c, e, g) and M4-M6 (d, f, h).

The spectrum of 1-TMS displays a pair of strong absorption bands at 258 and 315 nm, which overlap to form an asymmetric peak, and two weaker shoulder features at ~340 and 350 nm. In contrast, M1 displays an intense, narrow absorption band at 350 nm, with higher-energy shoulders at 330 and 310 nm. The spectra of M2 and M3 are similar in form, with both displaying broad, asymmetric peaks with maxima around 360 nm; this shape might be likened to the spectrum of M1, but with the lower-energy transitions broadened and slightly red shifted. The spectrum of M2 displays a noticeable shift in the absorption edge with respect to M1 and M3, although the low-energy absorptions in all three complexes are significantly enhanced with respect to 1-TMS. This points towards extended delocalisation in the complexes, across the Pt(II) centre and between the
aromatic ligands; the red shift seen in the absorption edge of M2 and M3 compared to M1 may be explained by the higher degree of electronic delocalization possible over the two carbazole ligands in these complexes, versus the single carbazole ligand and phenyl ring in M1.

In contrast, the spectrum of 2-TMS has a sharp maximum and shoulder feature at ~280 and 290 nm, respectively, with some fine structure at longer wavelengths including two comparatively much weaker peaks around 335 and 350 nm. The considerable blue shift compared to the 2-carbazole acetylide analogue is mirrored in the spectra of the Pt(II) complexes M4-M6. As with M1-M3, complexation leads to an enhancement of the lower-energy absorption features, with the spectrum of M4 displaying sharper features than those of M5 and M6. The first absorption band in the spectrum of M4 occurs around 370 nm, but is considerably weaker than the clear peak ~ 325 nm. As for M2 and M3, the spectra of M5 and M6 consist of broad low-energy absorption peaks, but with the maxima blue shifted to at 340-350 nm. However, the absorption edge of both 3-carbazole complexes is noticeably broader than that of the 2-carbazole analogues.

We also recorded and compared room-temperature absorption spectra of the 2,7- and 3,6-functionalised TMS-protected carbazole ligands (3a/3b-TMS and 4a/4b-TMS, respectively) and the corresponding di-nuclear Pt(II) complexes (M7-M10) and polymers (P1-P4) (Figure 2).

Comparing Figure 2 a/b and c/d, the changes to the spectra on alkylating the N atom are subtle, but noticeable. The first absorption maximum of 3a-TMS occurs at ~325 nm, with shoulder features at 335-340 and approx. 350 nm, while the maximum of 3b-TMS was measured at 335 nm, and the shoulder features at ~360 and 380 nm. The spectrum of the alkylated 2,7-acetylide carbazole also has sharper features than the H form, particularly in the low-energy part of the spectrum, although this difference is not apparent for the 3,6-functionalised carbazoles. 4a-TMS has an absorption maximum at ~290 nm, a shoulder around 300 nm, and a weaker absorption at approx. 340 nm, whereas in the alkylated 4b-TMS the maximum and shoulders occur at 295-300 and 310/320 nm, with a pair of smaller peaks at 350 and 365 nm. For both the 2,7- and 3,6-carbazole systems, alklylation thus leads to a slight enhancement of the long-wavelength part of the absorption spectrum. The spectroscopy suggests that alklylation induces a small red shift in the absorption, although this is secondary to the significant blue shift observed between the 2,7- and 3,6- substitution patterns; the latter is analogous to the blue shift between the 2- and 3-functionalised carbazoles evident in Figure 1, and can be understood
qualitatively as a loss in electronic delocalisation in the 3,6-substituted ligand (Figure 3), which possesses a so-called “break junction” in the molecular structure. As per the figure, complete delocalisation across 3,6-diyl spacer is not possible without generating pentavalent carbon centres (Figure 3, middle), which is not possible. Another possibility of delocalisation is involving the lone pair on the nitrogen atom, leading to the generation of charged centers. Overall, delocalisation was favoured in the case of 2,7-isomers, while it is less in 3,6-diyl-isomers.

![Figure 2](image_url) Solution absorption spectra (CH$_2$Cl$_2$) of the 2,7- and 3,6-functionalized TMS-protected carbazole ligands 3a/3b-TMS (a, b) and 4a/4b-TMS (c, d), and the corresponding dinucelar Pt(II) complexes M7-M10 (e-h) and polymers P1-P4 (i-l).

Table 1 Optical absorption data for protected ligands and Pt(II) complexes incorporating carbazole spacers. Absorption spectra were taken in CH$_2$Cl$_2$ at room temperature. ($\varepsilon$ x 10$^5$ M$^{-1}$cm$^{-1}$, $\lambda_{max}$ / nm).

<table>
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<th>$\lambda_{max}$</th>
<th>$\varepsilon_1$</th>
<th>$\lambda_{2max}$</th>
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<th>$\lambda_{3max}$</th>
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<td>350</td>
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**Figure 3** Schematic illustration of the electronic delocalization across the carbazole-2,7-diyl and carbazole-3,6-diyl spacers. Adapted with permission from reference 11f.

The photophysical properties of M7-M9 and P1-P3 in the solid-state have been previously reported,11f and we observed no significant differences in the band shapes and absorption maxima in thin films and solution, save for some very small shifts in band positions, which can be attributed to the differences in environment.

As for the mono-nuclear complexes, incorporation of the ligands into di-nuclear Pt(II) complexes lead to a red shift in the absorption edge. In contrast, however, the clear trend of an enhancement of the low-energy absorption is less clear cut for M7-M10. There is a sharp increase in intensity of the absorption edge of M8, whereas there seems to be a reduction in the intensity of the long-wavelength part of the spectrum of M7, although this is relative to the bright band at ~250 nm, and not on an absolute scale. With
reference to the spectra of the protected carbazole ligands, the spectra of M9 and M10 appear to show a broadening of the sharp features in the spectra of 4a- and 4b-TMS, respectively, in addition to the apparent red shift in the feature positions. Compared to the di-nuclear complexes M7-M10, the polymers P1-P4 show a further red shift in the absorption, consistent with the extended electronic delocalization, together with a general broadening of the spectral features. The polymers also show a relative increase in long-wavelength absorption, which is particularly noticeable in the cases of P2 and P4.

To summarise, from the spectroscopic characterization, we extract four general observations:

1. The 3- and 3,6-substituted carbazoles and their complexes display a blue shifted absorption compared to the 2- and 2,7-substituted analogues, which may be attributed to a reduction in electronic delocalisation in the former ligands due to the presence of a break junction;
2. Incorporation of the carbazole spacers into Pt(II) complexes generally leads to an enhancement of the absorption in the longer-wavelength part of the profile;
3. Functionalisation of the carbazole N atom can in principle allow the absorption profile to be tuned; and
4. The polymers show a further red shift and a broadening of the absorption profiles with respect to the model di-nuclear complexes.

Extended conjugation across the metal centres in these complexes is consistent with previous results on related systems,10a,11a,14,19 and the red shifts in the spectra of the complexes and polymers compared to those of the protected ligands, suggestive of electronic excitations between highly-delocalised states, is consistent with observations made from other Pt(II) polyynes incorporating carbocyclic and heterocyclic spacers.3a,14,16a

Crystal structures

In order to complement the spectroscopic characterization of the polymer precursors, we attempted to grow single crystals suitable for X-ray diffraction of several of the key precursors and intermediates in the synthesis. We were able to obtain suitable single crystals of the 2,7- and 3,6-carbazole trimethylsilyl-acetylide ligands (3a-TMS, 4a-TMS) and of the mono- and di-nuclear Pt(II) σ-acetylide compounds M3 and M7, and so crystallographic studies were carried out on these systems. The structures of 3a-
TMS, 4a-TMS and the model compounds M3 and M7 are shown in Figure 4-8, and key crystallographic parameters are summarised in Table 2.

Molecules of 4a-TMS (Figure 4), which lack N functionalization, but have the 3,6-alkynyl substitution pattern, aggregate through a hydrogen bond between the N-H group and the mid-point of the C(15)≡C(16) bond of a neighbouring molecule [N-H…midpoint distance 2.392 Å, N-H-midpoint angle 162.90 °]. However, this has no significant impact on the length of the alkyne bond [1.208(5) Å] in comparison to that of the non-hydrogen bonded group [C(5)≡C(6); 1.202(4) Å]. In contrast, the structure of 3a-TMS (Figure 5) which has the alkylnyl groups at the 2,7 positions, has too much steric crowding around the N-H to allow for this interaction. All the intramolecular bond lengths and angles for both 3a-TMS and 4a-TMS lie within the expected ranges.

The molecular structure of the mono-nuclear Pt(II) di-yne M3 is illustrated in Figure 6. The molecule occupies a crystallographic centre of symmetry, which is coincident with the central platinum atom. This metal exhibits the trans-square planar geometry suggested by the spectroscopic characterization, which is consistent with that found in related platinum poly-yne molecules.4e,8b The platinum–alkynyl σ-interaction has a Pt(1)–C(3) distance of 2.002(2) Å, which is within the expected range. The ethynylene unit is almost linear [∠Pt(1)–C(3)–C(4) 175.7(2) °, ∠C(3)–C(4)–C(5) 172.3(3) °] and the C(3)–C(4) bond is similar, at 1.210(3) Å, to that observed in the precursor 3a-TMS. The carbazolyl unit is essentially planar (maximum deviation from the C(5)-N(17) unit of -0.038 Å for C(5); RMSD 0.019 Å), and the bond parameters are not significantly different to those observed in 3a-TMS, the di-yne M7 (Figure 7) and to those in other, related, reported carbazole structures.11a,11e The carbazolyl ring plane makes an angle of 81.88° with the square planar Pt unit (Pt(1), P(2), C(3), P(2i), C(3i); the “i” atoms are related to those in the asymmetric unit by the symmetry operation (-x, -y, -z).

M7 crystallises as a methanol solvate [PhPt(P(PEt$_3$)$_2$)$_2$C≡CC≡C(P(PEt$_3$)$_2$PtPh)].MeOH, with one molecule each of the complex and solvent in the asymmetric unit (Figure 7). The methanolic oxygen atom acts as a hydrogen-bond acceptor20 to the carbazole N-H group [H(1)...O(1) 2.02 Ǻ, N(1)...O(1) 2.869(10) Ǻ, ∠N(1)-H(1)...O(1) 161.9 °]. The methanolic hydrogen atom acts as a hydrogen-bond donor to the C≡C C(19)-C(20) on an adjacent molecule (Figure 8), though again this has no significant influence on the length of the C≡C bond [1.212(12) Ǻ] which, as in the structure of 4a-TMS, is not significantly
different from the length of the other alkyne bond [C(33)=C(34); 1.208(13) Å]. The two Pt(II) centres adopt the expected square planar geometry, as observed in a wide variety of diplatinum diyne complexes with a range of central spacer groups. The dihedral angle between the two platinum-containing planes is 35.5°. The terminal phenyl rings on each platinum are planar and essentially perpendicular to the Pt-coordination planes; the angle between the planes containing the atoms Pt(1)P(1)P(2)C(13)C(19) and C(13)-C(18) ring is 84.5 °, and that between the planes containing the atoms Pt(2)P(3)P(4)C(34)C(35) and C(35)-C(40) is 90.0 °. The acetylenic units show only slight deviations from linearity, with ∠Pt(1)-C(19)-C(20) 175.3(8)°, ∠Pt(2)-C(34)-C(33) 171.6(12)°, ∠C(19)-C(20)-C(21) 177.1(10)° and ∠C(31)-C(33)-C(34) 171.0(13)°. The central carbazole group is essentially planar, with angles of 2.2 ° and 1.3 ° between the C(21)-C(26) and N(1)C(24)C(25)C(27)C(28) planes, and between the N(1)C(24)C(25)C(27)C(28) and C(24)C(27)C(29)C(30)C(31)C(32) planes, respectively. The interplanar angle between Pt(1)P(1)P(2)C(13)C(19) and C(21)-C(26) is 45.7 °, and that between the Pt(2)P(3)P(4)C(34)C(35) and C(24)C(27)C(29)C(30)C(31)C(32) planes is 82.9 °.

The Pt-P distances average 2.286 Å, and the Pt-C(≡C) bond lengths average 2.01 Å, which is slightly shorter than the average Pt-C(Ph) bond length of 2.03 Å. These values are consistent with the geometries of related diplatinum diynes. The two acetylenic C≡C bond lengths average 1.21 Å, which is, again, within the expected range. The bond parameters within the carbazole spacer group do not show any significant deviations from those reported in 3-(trimethylsilyl)carbazole, and are consistent with those in the mono-nuclear platinum complex trans-bis(carbazol-3-ylethynyl)bis-tri-n-butylphosphine)-platinum(II). Across all four structures, the C10-C11, C11-C12 and C12-C13 bond distances in the heterocycle (numbering as in Chart 1), and the bond lengths in the C-C≡C groups, are the same to within experimental error. Thus, the proposed enhanced delocalisation within the carbazole-2,7-diyl derivatives compared to the 3,6-substituted analogues (Figure 3) appears to have no discernible effect on the bond lengths. The data are also consistent with previously-reported structures of Pt, Au and Hg complexes of carbazole-3,6-diyls.
Figure 4 Structure of 4a-TMS showing the atom-numbering scheme; thermal ellipsoids are set at 40 % probability.

Figure 5 Structure of 3a-TMS showing the atom-numbering scheme; thermal ellipsoids are set at 40 % probability.

Figure 6 Structure of M3 showing the atom-numbering scheme; thermal ellipsoids are set at 40 % probability. Selected geometric data (distances in Å, angles in °): Pt(1)-C(3) 2.002(2), Pt(1)-P(2) 2.3200(6), C(3)-C(4) 1.210(3), ∠Pt(1)-C(3)-C(4) 175.7(2), ∠C(3)-Pt(1)-P(2) 91.61(7).
**Figure 7** Structure of M7 showing the atom-numbering scheme and the interaction with the methanol solvent molecule. Only one orientation of the disordered component of the structure (labelled Ca) is shown for clarity; C(3a) and C(11) are obscured by C(6a) and C(12), respectively. Thermal ellipsoids are set to 40% probability. Selected geometric data (distances in Å, angles in °):

- Pt(1)-P(1) 2.294(3), Pt(1)-P(2) 2.277(3), Pt(2)-P(3) 2.282(3), Pt(2)-P(4) 2.291(3), Pt(1)-C(13) 2.064(9), Pt(1)-C(19) 2.007(9), Pt(2)-C(35) 2.072(3), Pt(1)-C(34) 2.013(9), C(19)-C(20) 1.212(12), C(33)-C(34) 1.208(13), ∠Pt(1)-C(19)-C(20) 175.3(8), ∠Pt(2)-C(34)-C(33) 171.6(12), ∠C(19)-C(20)-C(21) 177.1(10), ∠C(31)-C(33)-C(34) 171.0(13).

**Figure 8** The association of the M7 di-yne molecules through solvent-mediated hydrogen bonding. Selected geometric data (distances in Å, angles in °):

- N-H(1)...O(1) 2.02, ∠N-H(1)...O(1) 161.7, O-H...midpoint C(19')-C(20') 2.31, ∠O-H...midpoint C(19')-C(20') 157.0.
Table 2 Crystallographic data for 3a-TMS, 4a-TMS, M3 and M7.

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**Computational modelling**

To complement the optical spectroscopy, and in particular to understand the origin of the spectral changes observed between the carbazole ligands with different substitution patterns and the Pt(II) complexes, we performed gas-phase molecular quantum-chemical calculations on 1-TMS, 2-TMS, M3 and M6. The four models were optimised at the hybrid density-functional theory (DFT) level of theory, and the minima were verified by computing vibrational frequencies. We then performed time-dependent DFT (TD-DFT) calculations on these optimised models to investigate the optical properties and to
characterise the electronic excitations. The computational methodology is described in detail in the Experimental section.

**Figure 9** shows the simulated absorption spectra of the four complexes, together with isosurface plots of the frontier highest-occupied and lowest-unoccupied molecular orbitals (HOMOs/LUMOs). The simulated spectra compare reasonably well with the corresponding solution spectra in **Figure 1**, and in particular mirror the key trends observed from these measurements, *viz.* the red shift and stronger absorption of the 2-substituted carbazoles and their Pt(II) complexes compared to the 3-substituted analogues, and also of both Pt(II) complexes compared to the TMS-protected ligands.

Aside from some small shifts in the positions of absorption bands, a notable discrepancy between the simulated and experimentally-recorded spectra is the presence of additional fine structure (e.g. shoulders) in the latter. Two possible reasons for this are that (1) a constant peak broadening was assumed when generating the simulated spectra (see Experimental), whereas in general each state may have a different line width, and (2) low-energy singlet excitations with small oscillator strengths, of which there are several in the M3 and M6 Pt(II) complexes, could be enhanced relative to the brighter transitions at finite temperature by geometric distortions induced through thermal vibration. Furthermore, as evident in **Figure 9**, all four complexes possess low-lying triplet excitations; these are formally spin forbidden, but in principle could also contribute to small features in the spectra.

To interpret the spectroscopic activity of the four complexes, we chose to analyse the “brightest” low-energy transition in each, i.e. the excitations with the highest oscillator strengths, $f$, among the transitions with excitation wavelengths above 300 nm. **Table 3** lists the excitation energies/wavelengths, oscillator strengths, and an assignment of each state in terms of contributions from individual orbital transitions; the calculated HOMO-LUMO gap is also given for reference.

In **1-TMS**, there are two predicted transitions with $\lambda > 300$ nm. The brightest of these, at 302 nm, can be assigned as a HOMO-LUMO excitation, although there is a considerably weaker transition between the HOMO-1 and LUMO orbitals at 321 nm ($f = 0.032$). Mirroring the blue shift observed experimentally, **2-TMS** has a single, comparatively weak calculated transition above 300 nm ($\lambda = 314$ nm, $f = 0.024$), which can be assigned to the HOMO $\rightarrow$ LUMO absorption with a small contribution from the HOMO-1 $\rightarrow$ LUMO+1 excitation. From inspection of the frontier orbitals, it is apparent that both the HOMO and LUMO in **1-TMS** are more delocalised than the corresponding
orbitals in 2-TMS, which could account for the smaller energy gap and longer excitation wavelengths of 1-TMS.

![Simulated gas-phase absorption spectra of 1-TMS (a), 2-TMS (b), M3 (c) and M6 (d) from time-dependent density-functional theory (TD-DFT) using adiabatic B3LYP. Each plot shows the simulated absorption profile obtained from the spin-allowed (singlet) states (blue), with the spin-forbidden (triplet) states marked by red lines/gold stars. Isosurface plots of the highest-occupied and lowest-unoccupied molecular orbitals (HOMOs/LUMOs) for each system are shown to the right of the simulated spectra. These plots were prepared using the VESTA software.]

Figure 9
Table 3 HOMO-LUMO gaps ($E_{\text{H-L}}$) and energies, wavelengths, oscillator strengths and assignments of the “brightest” low-energy transitions ($\lambda > 300$ nm) in gas-phase 1-TMS, 2-TMS, M3 and M6, obtained from time-dependent density-functional theory (TD-DFT) using adiabatic B3LYP. The assignments are based on the percentage of the sum of the squared coefficients (given in brackets), and only the major components of the overall transition are listed.

<table>
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<tr>
<th>Model</th>
<th>$E_{\text{H-L}}$ / eV</th>
<th>$E$ / eV</th>
<th>$\lambda$ / nm</th>
<th>$f$</th>
<th>Assignment</th>
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<td>2-TMS</td>
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<td>0.024</td>
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<td>HOMO-1 → LUMO+1 (10.5 %)</td>
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<td>M3</td>
<td>4.085</td>
<td>3.720</td>
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<td>1.471</td>
<td>HOMO → LUMO (92.9 %)</td>
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<td>HOMO → LUMO+3 (17.5 %)</td>
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</table>

As can be seen clearly from the data in Table 3, incorporation of the carbazole ligands into Pt(II) complexes leads to a red shift in the absorption energies and a substantial enhancement of the oscillator strengths, which once again mirrors the observations made from the spectroscopy. The very strong low-energy absorption at 333 nm in M3 is due to the HOMO-LUMO transition, and from inspection of the orbitals the red shift can be explained by delocalisation of the HOMO orbitals in the two carbazole ligands across the metal centre. A similar pattern is observed in M6, for which the composite HOMO → LUMO and HOMO-1 → LUMO-1 transition in 2-TMS undergoes a red shift and an increase in oscillator strength ($\lambda = 343$ nm, $f = 0.054$). However, in this complex, there is also a considerably brighter transition at 320 nm, corresponding to a redistribution of electron density from the HOMO to the LUMO+2 and LUMO+3 orbitals, and it is this excitation which makes the largest contribution to the long-wavelength tail feature in the simulated spectrum. The oscillator strength of this transition, however, is still an order of magnitude smaller than the HOMO-LUMO transition in M3.

In summary, the computational modelling presented here confirms the key inferences drawn from the optical spectroscopy, and confirms (1) that the frontier orbitals in the 2-substituted carbazole ligands are more delocalised than those in the 3-substituted analogues, and (2) that the red shift and enhancement of the absorption in the Pt(II) complexes can be explained by delocalisation of the ligand HOMO orbitals across the Pt centres.
CONCLUSION

We have synthesized and characterized a series of acetylide-functionalized carbazole ligands and Pt(II) mono-, di- and poly-ynes incorporating 2-, 3-, 3,6- and 2,7-carbazole spacer groups. We have reported crystal structures of several of these precursors and model compounds, providing insight into possible intermolecular interactions in the polymeric systems, viz. hydrogen bonding between the carbazole N-H and alkyne groups on neighbouring molecules, which may be mediated by included solvent molecules. This study has also shed valuable light on the relationship between molecular and electronic structure in this family of systems, in particular showing that there is a significantly higher degree of electronic delocalisation within the complexes and polymers with the 2- and 2,7-functionalised ligands compared to those with the 3- and 3,6-substituted ones, which leads to a marked red shift in the absorption spectra. Incorporation of the carbazole ligands into Pt(II) complexes produces a further red shift and an enhancement of the low-energy absorption profile, which can be explained by electronic delocalisation between ligands across the Pt(II) centres. These hypotheses have been confirmed both spectroscopically and using computational modelling. Organometallic rigid-rod polymers based on carbazole-2,7-diyl units are expected to display enhanced electron transport within the chains, whereas polymers based on the carbazole-3,6-diyl analogue are expected to show poorer transport properties. The systematic study carried out in this work should assist in the future rational design of conjugated Pt(II) poly-ynes with improved optoelectronic properties for a range of technological applications.

EXPERIMENTAL SECTION

General procedures
All reactions were performed under a dry Ar atmosphere using the standard Schlenk technique. Solvents were pre-dried and distilled before use according to standard procedures. All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and used as received. The compounds 3a, trans-[(Ph)(PEt$_3$)$_2$PtCl]; and trans-[(P$_{n}$Bu$_3$)$_2$PtCl] were prepared according to literature procedures. NMR spectra were recorded in CDCl$_3$ using Bruker WM-250 and AM-400 spectrometers, and a Bruker Avance III HD 700 MHz spectrometer equipped with 5 mm TCI H/C/N cryoprobe. The
1H and 13C{1H} NMR spectra were referenced to solvent resonances, and the 31P{1H} NMR spectra were referenced to external trimethylphosphite or 85 % H3PO4. IR spectra were recorded either in CH2Cl2 solutions in a NaCl cell using a Perkin-Elmer 1710 FT-IR spectrometer or directly on the sample as attenuated total reflectance (ATR) on Diamond using Cary 630 FT-IR spectrometer. UV/Vis spectra were recorded with Shimadzu UV-2450 spectrometer. Mass spectra were acquired using a Kratos MS 890 spectrometer using electron-impact (EI) and electrospray-ionization (ESI) techniques. Microanalyses were carried out at the University Chemical Laboratory, University of Cambridge. Preparative thin-layer chromatography was carried out on commercial Merck plates with a 0.25 mm layer of silica. Column chromatography was performed using either Kieselgel 60 silica gel (230-400 mesh) or Brockman Grade II-III alumina.

**Caution:** All chemicals used in the current work are sensitive to skin, eyes and respiratory system. Therefore, all reactions were performed in well-ventilated fume hood. Inhalation of silica/alumina and low boiling solvents like dichloromethane and hexane may cause injuries to internal organ. Safety glasses, gloves, masks and lab coats were worn during the experiments.

**Ligand synthesis**

**2,7-Dibromo-N-(2-ethylhexyl)carbazole, 3b**

A mixture of 2,7-carbazole 3a (1.00 g, 3.08 mmol) and potassium tert-butoxide (KO'Bu) (0.415 g, 3.70 mmol) in dry THF (80 mL) was placed in a two-necked flask and stirred at room temperature for 20 minutes under an Ar atmosphere. 2-ethylhexyl bromide (0.640 mL, 3.70 mmol) was added to the reaction mixture, which was then refluxed overnight. After removing the solvent, the crude product was purified using a silica-gel column eluted with hexane, yielding a white solid (1.32 g, 97.8 %). 1H NMR (700 MHz, CDCl3, ppm) δ 7.89 (d, J = 8.2 Hz, 2H, H-4, 5), 7.34 (dd, J = 8.2, 1.2 Hz, 2H, H-3, 6), 7.26 (s, 2H, H-1,8), 4.07 (d, J = 8.0 Hz, 2H, N-CH2), 2.02 (hept, J = 6.7 Hz, 1H, alkyl CH), 1.45 – 1.22 (m, 8H, alkyl CH2), 0.89 (ddt, J = 31.4, 24.3, 12.3 Hz, 6H, alkyl CH3). 13C NMR (176 MHz, CDCl3, ppm) δ 141.86, 122.53, 121.43, 121.25, 119.66, 112.31 (aromatic), 47.70 (N-CH2), 41.06 (alkyl CH), 31.90, 29.72, 28.56, 24.34 (alkyl CH2),14.08, 10.91 (alkyl CH3). ESI-MS: m/z 437.21 (M+). Anal. Calc. for C20H23Br2N: C, 54.94; H, 5.30, observed: C, 55.01; H, 5.32 %.
3,6-Dibromo-N-(2-ethylhexyl)carbazole, 4b

The same procedure as used to synthesize 3b using 3,6-dibromocarbazole 4a was followed. The product was obtained as a colourless viscous liquid (96.2 %). $^1$H NMR (700 MHz, CDCl$_3$, ppm) $\delta$ 7.90 (s, 2H, H-4, 5), 7.39 (dd, $J = 8.7, 1.8$ Hz, 2H, H-1, 8), 7.06 (d, $J = 8.7$ Hz, 2H, H-2, 7), 3.92 – 3.82 (m, 2H, N-CH$_2$), 1.87 – 1.77 (m, 1H, alkyl CH), 1.26 – 1.06 (m, 8H, alkyl CH$_2$), 0.81 – 0.67 (m, 6H, alkyl CH$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm) $\delta$ 162.56, 139.61, 129.09, 123.61, 123.33, 112.20, 110.87 (aromatic), 47.55 (N-CH$_2$), 39.41 (alkyl CH), 32.15, 30.88, 28.64, 24.25 (alkyl CH$_2$), 13.73, 10.66 (alkyl CH$_3$). ESI-MS: $m/z$ 437.15 ($M^+$). Anal. Calc. for C$_{20}$H$_{23}$Br$_2$N: C, 54.94; H, 5.30; observed: C, 55.02; H, 5.31 %.

2-(Trimethylsilyl)-9H-carbazole, 1-TMS

To a solution of 2-bromocarbazole 1 (1.00 g, 4.06 mmol) in iPr$_2$NH/THF (70 mL, 1:4 v/v) under an Ar atmosphere were added catalytic amounts of CuI (10 mg), Pd(OAc)$_2$ (10 mg) and PPh$_3$ (52 mg). The solution was stirred for 30 min at room temperature, and then trimethylsilylithyne (0.87 mL, 6.09 mmol) was added under vigorous stirring. The reaction mixture was then refluxed overnight. The completion of the reaction was confirmed by silica TLC and IR spectroscopy. After being cooled to room temperature, the mixture was filtered and concentrated in vacuo. The impure residue was redisolved in CH$_2$Cl$_2$ and purified by silica column chromatography using a hexane/CH$_2$Cl$_2$ (1: 1 v/v) eluent to yield a pale yellow solid (0.85 g, 79 %, m.p. 218 ºC). IR (ATR, diamond): $\nu$ / cm$^{-1}$ 3402 (N-H), 2151 (–C≡C–). $^1$H NMR (700 MHz, CDCl$_3$, ppm): $\delta$, 8.04 (d, $J = 8.1$ Hz, 2H, H-4, 5), 7.99 (d, $J = 8.0$ Hz, 1H, H-8), 7.55 (s, 1H, H-1), 7.43 (m, 2H, H-6, 7), 7.35 (d, $J = 8.0$ Hz, 1H, H-3), 5.76 (s, 1H, NH), 0.28 (s, 9H, SiMe$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm): $\delta$ 140.24, 139.03, 132.27, 126.55, 123.76, 123.10, 120.71, 120.25, 120.14, 119.94, 114.32, 110.85 (aromatic) 106.39, 93.70 (–C≡C–), 0.22 (SiMe$_3$). ESI-MS: $m/z$ 261.9 ($M^+$). Anal. Calc. for C$_{17}$H$_{17}$NSi C, 77.52; H, 6.51, observed: C, 77.55; H, 6.53 %.

3-(Trimethylsilyl)-9H-carbazole, 2-TMS

A similar procedures to that used for the synthesis of 1-TMS was adopted using 3-bromocarbazole 2. The compound was obtained as a white solid (0.79 g, 73 %, m.p. 189 ºC). IR (ATR, diamond): $\nu$ / cm$^{-1}$ 3392 (N-H), 2148 (–C≡C–). $^1$H NMR (700 MHz,
CDCl₃, ppm): δ 8.22 (s, 1H, H-4), 8.11 (br s, 1H, NH), 8.04 (d, J = 7.8 Hz, 1H, H-5), 7.53 (d, J = 8.3 Hz, 1H, H-8), 7.48 – 7.39 (m, 3H, H-2, 6, 7), 7.33 (d, J = 8.3 Hz, 1H, H-1), 0.29 (s, 9H, SiMe₃).¹³C NMR (176 MHz, CDCl₃, ppm): δ 139.89, 139.35, 129.97, 126.47, 124.67, 123.36, 123.05, 120.62, 120.11, 114.00, 110.88, 110.60 (aromatic), 106.65, 91.91 (–C≡C–), 0.31 (SiMe₃). ESI-MS: m/z 261.9 (M⁺). Anal. Calc. for C₁₇H₁₇NSiC, 77.52; H, 6.51, observed: 77.60; H, 6.50 %.

2,7-Bis(trimethylsilylethynyl)carbazole, 3a-TMS

A similar procedures to that used for the synthesis of 1-TMS was adopted using 3,6-dibromocarbazole 3 (1.20 g, 3.69 mmol), CuI (7 mg), Pd(OAc)₂ (8 mg), PPh₃ (48 mg), and trimethylsilylethyne (1.30 mL, 9.22 mmol). The product was isolated as a pale brown solid (1.2 g, 90 %), m.p. 184.7 – 185.2 ºC). IR (CH₂Cl₂): ν / cm⁻¹ 3401 (N-H), 2150 (–C≡C–).¹H NMR (700 MHz, CDCl₃, ppm): δ 8.06 (br s, 1H, NH), 7.95 (d, J = 8.1 Hz, 2H, H-4, 5), 7.58 (s, 2H, H-1, 8), 7.54 (d, J = 8.3 Hz, 2H, H-3, 6), 0.28 (s, 18H, SiMe₃).¹³C NMR (176 MHz, CDCl₃, ppm): δ 140.81, 139.51, 124.10, 123.92, 123.10, 122.95, 121.67, 120.57, 120.31, 120.09, 114.29, 113.80 (aromatic), 105.99, 95.04 (–C≡C–), 0.03 (SiMe₃). ESI-MS: m/z 359.6 (M⁺). Anal. Calc. for C₂₂H₂₅Si₂N: C, 73.50; H, 7.01, observed: C, 73.66; H, 7.08 %.

3,6-Bis(trimethylsilylethynyl)carbazole, 4a-TMS

A similar procedure to that adopted for the synthesis of 1-TMS was adopted using 3,6-dibromocarbazole 4a afforded a pale yellow solid (60.1 %). IR (CH₂Cl₂): ν / cm⁻¹ 3394 (N-H), 2149 (–C≡C–).¹H NMR (700 MHz, CDCl₃): δ 8.32 (br s, 1H, NH), 8.18 (s, 2H, H-4, 5), 7.54 (dd, J = 8.3, 1.1 Hz, 2H, H-1, 8), 7.33 (d, J = 8.3 Hz, 2H, H-2, 7), 0.29 (s, 18H, SiMe₃).¹³C NMR (176 MHz, CDCl₃) δ 139.61, 130.40, 124.84, 122.96, 121.75, 121.67, 120.57, 120.31, 120.09, 114.29, 113.80 (aromatic), 105.99, 95.04 (–C≡C–), 0.33 (SiMe₃). ESI-MS: m/z 359.5 (M⁺). Anal. Calc. for C₂₂H₂₅Si₂N: C, 73.50; H, 7.01, observed: C, 73.74; H, 7.02 %.

2,7-Bis(trimethylsilylethynyl)-N-(2-ethylhexyl)carbazole, 3b-TMS

A similar procedure to that followed in the synthesis of 1-TMS was adopted using 3b afforded a pale yellow solid (71 %). IR (CH₂Cl₂): ν / cm⁻¹ 2151 (–C≡C–).¹H NMR (700 MHz, CDCl₃, ppm): δ 7.96 (d, J = 8.0 Hz, 2H, H-4, 5), 7.47 (s, 2H, H-1, 8), 7.33 (dd, J =
8.0, 1.0 Hz, 2H, H-3, 6), 4.12 (ddd, $J = 36.3, 14.8, 7.6$ Hz, 2H, N-CH$_2$), 2.12 – 2.01 (m, 1H, alkyl CH), 1.44 – 1.22 (m, 8H, alkyl CH$_2$), 0.92 – 0.82 (m, 6H, alkyl CH$_3$), 0.33 – 0.24 (m, 18H, SiMe$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$): $\delta$ 140.97, 123.18, 122.54, 120.22, 120.19, 112.64 (aromatic), 106.35, 93.75 ($-C=C-$), 47.51 (N-CH$_2$), 39.09 (alkyl CH), 30.70, 28.49, 24.37, 23.00 (alkyl CH$_2$), 14.00, 10.92 (alkyl CH$_3$), 0.03, 0.01 (SiMe$_3$). ESI-MS: $m/z$ 472.0 ($M^+$). Anal. Calc. for C$_{30}$H$_{41}$Si$_2$N: C, 76.39; H, 8.76, observed: C, 76.45; H, 8.75 %.

3,6-Bis(trimethylsilyl ethynyl)-N-(2-ethylhexyl)carbazole, 4b-TMS

A similar procedure to that used in the synthesis of 1-TMS were followed using 4b afforded a pale yellow viscous liquid (80 %). IR (CH$_2$Cl$_2$): $\nu$ / cm$^{-1}$ 2152 ($-C≡C-$). $^1$H NMR (700 MHz, CDCl$_3$, ppm): $\delta$ 8.19 (s, 2H, H-4, 5), 7.56 (dd, $J = 8.4, 1.5$ Hz, 2H, H-1, 8), 7.28 (dd, $J = 8.3, 3.8$ Hz, 2H, H-2, 7), 4.12 (d, $J = 7.6$ Hz, 2H, N-CH$_2$), 2.00 (hep, $J = 6.8$ Hz, 1H, alkyl CH), 1.39 – 1.14 (m, 8H, alkyl CH$_2$), 0.89 (t, $J = 7.4$ Hz, 3H, alkyl CH$_3$), 0.82 (t, $J = 7.2$ Hz, 3H, alkyl CH$_3$), 0.31 – 0.14 (m, 18H, SiMe$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm): $\delta$ 141.05, 129.85, 124.79, 122.70, 113.82, 109.24 (aromatic), 106.50, 92.29 ($-C=C-$), 47.66 (N-CH$_2$), 39.32 (alkyl CH), 30.60, 28.87, 24.17, 23.06 (alkyl CH$_2$), 14.13, 10.91 (alkyl CH$_3$), 0.28, 0.28, 0.25, 0.19, 0.16, 0.12 (SiMe$_3$). ESI-MS: $m/z$ 472.0 ($M^+$). Anal. Calc. for C$_{30}$H$_{41}$Si$_2$N: C, 76.39; H, 8.76, observed: C, 76.45; H, 8.75 %.

2-(Ethynyl)-9H-carbazole, L1

1-TMS (0.600 g, 2.28 mmol) was proto-desilylated in THF/methanol (20 mL, 4:1, v/v) using aqueous KOH (0.19 g, 3.45 mmol). The reaction mixture was stirred at room temperature for 1 h, during which time TLC and IR revealed that all the protected compound had been converted to the terminal alkyne ligand. The solvent was then removed and the residue dissolved in CH$_2$Cl$_2$ and purified by column chromatography on silica using hexane/CH$_2$Cl$_2$ (1:1, v/v) as eluent, to give the product as a pale brown solid (0.391 g, 89.8 %). IR (ATR, diamond): $\nu$ / cm$^{-1}$ 2104 ($-C≡C-$), 3276 ($-C≡C-$). $^1$H NMR (250 MHz, CDCl$_3$, ppm): $\delta$ 9.11 (s, 1H, NH), 7.56 (s, 1H, H-1), 7.54 (d, $J = 7.9$ Hz, 1H, H-8), 7.51 (d, $J = 8.1$ Hz, 1H, H-4), 7.40 (d, $J = 7.9$ Hz, 1H, H-5), 7.16 (d, $J = 7.4$ Hz, 1H, H-3), 7.08 – 7.00 (m, 2H, H-6, 7), 3.06 (s, 1H, C=C-H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 135.52, 133.43, 131.14, 126.05, 125.63, 124.10, 123.22, 121.98, 120.15, 118.52,
114.31, 112.53 (aromatic), 105.9, 82.4 (–C≡C–). ESI-MS m/z 191.99 (M*). Anal. Calc. for C_{14}H_{9}N: C, 87.93; H, 4.74, observed: C, 88.01; H, 4.73 %.

3-(Ethynyl)-9H-carbazole, L2
A similar procedure to the one followed for the synthesis of L1 was adopted using 2-TMS afforded a pale yellow solid (87.6 %). IR (ATR, diamond): ν / cm\(^{-1}\) 2108 (–C≡C–), 3300 (C≡C–H). \(^1\)H NMR (250 MHz, CDCl\(_3\), ppm): δ 9.93 (s, 1H, NH), 7.70 (d, J = 7.7 Hz, 1H, H-1), 7.55 (d, J = 7.8 Hz, 1H, H-8), 7.50 (d, J = 8.0 Hz, 1H, H-4), 7.40 (d, J = 8.2 Hz, 1H, H-5), 7.24 (d, J = 7.7 Hz, 1H, H-2), 7.08 (t, J = 7.2 Hz, 1H, H-7), 7.00 (t, J = 7.4 Hz, 1H, H-6), 3.06 (s, 1H, C≡C–H). \(^{13}\)C NMR (100.6 MHz, CDCl\(_3\), ppm): δ 138.43, 134.25, 132.15, 127.46, 125.11, 123.26, 123.01, 122.36, 120.06, 116.10, 113.46 (aromatic), 107.3, 105.9 (–C≡C–). ESI-MS: m/z 192.2 (M*). Anal. Calc. for C_{14}H_{9}N: C, 87.98; H, 4.72 %.

2,7-Bis(ethynyl)carbazole, L3a
A similar procedure to that used to synthesize L1 was adopted using 3a-TMS afforded a pale yellow viscous liquid (93.0 %). IR (CH\(_2\)Cl\(_2\)): ν / cm\(^{-1}\) 2105 (–C≡C–), 3302 (C≡C–H). \(^1\)H NMR (700 MHz, CDCl\(_3\), ppm) δ 8.12 (br s, 1H), 7.88 (d, J = 8.3 Hz, 2H, H-4, 5), 7.58 (s, 2H, H-1, 8), 7.36 (d, J = 8.2 Hz, 2H, H-3, 6), 3.14 (s, 2H, C≡C–H), 2.06 (m, 1H, alkyl-CH), 1.44 – 1.22 (m, 8H, alkyl CH\(_2\)), 0.94 – 0.83 (m, 6H, alkyl CH\(_3\)). \(^{13}\)C NMR (176 MHz, CDCl\(_3\), ppm) δ 140.15, 138.81, 125.39, 123.90, 122.93, 121.78, 120.23, 119.50, 114.57, 113.68, 110.62, 109.26 (aromatic), 86.75, 84.29 (–C≡C–). ESI-MS: m/z 216.1 (M*). Anal. Calc. for C_{16}H_{9}N: C, 89.28; H, 4.19, observed: C, 89.70; H, 4.26 %.

2,7-Bis(ethynyl)-N-(2-ethylhexyl)carbazole, L3b
A similar procedure to that followed to synthesize L1 was adopted using 3b-TMS afforded the product as a pale yellow viscous liquid (98.7 %). IR (CH\(_2\)Cl\(_2\)): ν / cm\(^{-1}\) 2105 (–C≡C–), 3298 (C≡C–H). \(^1\)H NMR (700 MHz, CDCl\(_3\), ppm) δ 8.00 (d, J = 8.0 Hz, 2H, H-4, 5), 7.53 (s, 2H, H-1, 8), 7.37 (d, J = 8.0 Hz, 2H, H-3, 6), 4.13 (qd, J = 14.8, 7.7 Hz, 2H, N-CH\(_2\)), 3.16 (s, 2H, C≡C–H), 2.06 (m, 1H, alkyl-CH), 1.44 – 1.22 (m, 8H, alkyl CH\(_2\)), 0.94 – 0.83 (m, 6H, alkyl CH\(_3\)). \(^{13}\)C NMR (176 MHz, CDCl\(_3\), ppm) δ 141.03, 123.24, 122.81, 120.49, 119.33, 113.06 (aromatic), 84.90 (–C≡C–), 47.64 (N-CH\(_2\)), 39.26 (alkyl CH), 30.87, 28.64, 24.37, 23.06 (alkyl CH\(_2\)), 14.02, 10.92 (alkyl CH\(_3\)). ESI-MS:
Anal. Calc. for C_{24}H_{25}N: C, 88.03; H, 7.70, observed: C, 88.14; H, 7.65 %.

3,6-Bis(ethynyl)carbazole, L4a

A similar procedure as was used to synthesize L1 was followed using 4a-TMS afforded the product as a colorless microcrystalline solid (98.3 %). IR (CH\textsubscript{2}Cl\textsubscript{2}): ν / cm\textsuperscript{-1} 2105 (–C≡C–), 3302 (C≡C–H). \textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, ppm) δ 8.20 (s, 1H, NH), 8.13 (s, 2H, H-1, 8), 7.36 (d, J = 8.3 Hz, 2H, H-2, 7), 3.07 (s, 2H, CC–H). \textsuperscript{13}C NMR (176 MHz, CDCl\textsubscript{3}, ppm) δ 139.73, 138.55, 130.41, 129.27, 124.89, 124.00, 123.25, 122.40, 113.57, 112.96, 112.22, 110.88 (aromatic), 84.40, 84.04 (–C≡C–). ESI-MS: m/z 216.3 (M\textsuperscript{+}). Anal. Calc. for C_{16}H_{9}N: C, 89.28; H, 4.19, observed: C, 89.48; H, 4.21 %.

3,6-Bis(ethynyl)-N-(2-ethylhexyl)carbazole, L4b

A similar procedure to that used in the synthesis of L1 was followed using 4b-TMS afforded the product as a yellow viscous liquid (90.0 %). IR (CH\textsubscript{2}Cl\textsubscript{2}): ν / cm\textsuperscript{-1} 2104 (–C≡C–), 3299 (C≡C–H). \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}, ppm): δ 7.99 (d, J = 7.6 Hz, 2H, H-4, 5), 7.51 (s, 2H, H-1, 8), 7.36 (dd, J = 13.8, 7.3 Hz, 2H, H-3, 6), 4.10 – 4.12 (m, 2H, N-CH\textsubscript{2}), 3.15 (s, 2H, C≡C–H), 2.05 – 2.08 (m, 1H, alkyl CH), 1.25 – 1.29 (m, 8H, alkyl CH\textsubscript{2}), 0.87 – 0.88 (m, 6H, alkyl CH\textsubscript{3}). \textsuperscript{13}C NMR (100.6 MHz, CDCl\textsubscript{3}, ppm): δ 142.53, 137.63, 132.49, 130.10, 123.22, 122.83, 120.95, 120.02, 119.46, 117.46, 113.01, 112.31 (aromatic), 106.56, 89.91 (–C≡C–), 48.10 (N-CH\textsubscript{2}), 40.32 (CH), 30.95, 28.62, 24.41, 22.94 (alkyl CH\textsubscript{2}), 14.97, 11.24 (alkyl CH\textsubscript{3}). ESI-MS: m/z 327.97 (M\textsuperscript{+}). Anal. Calc. for C_{24}H_{25}N: C, 88.03; H, 7.70, observed: C, 88.14; H, 7.65 %.

Synthesis of Pt(II) mono-, di- and poly-ynes

\textit{Trans-[R-C≡C-(PEt}_{3})_{2}Pt-Ph} (R = Carbazole-2-yl), M1

To a stirred mixture of L1 (0.100 g, 0.522 mmol) and \textit{trans-[Ph(PEt}_{3})_{2}PtCl} (0.284 g, 0.522 mmol) in \textsuperscript{3}Pr\textsubscript{2}NH (20 mL) and CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added CuI (1 mg). The solution was stirred at room temperature under Ar over a period of 18 h, after which all volatile components were removed under vacuum. The crude product was taken up in CH\textsubscript{2}Cl\textsubscript{2} and passed through a silica column with hexane/CH\textsubscript{2}Cl\textsubscript{2} (1:1, v/v) as eluent. The product was obtained as a pale brown solid (0.300 g, 82.6 %, m.p. 170.2 °C). IR (ATR, diamond): ν /
cm$^{-1}$ 3230.9 (N-H), 2079 (−C≡C−). $^1$H NMR (700 MHz, CDCl₃, ppm): $\delta$, 7.99 (d, $J$ = 7.7 Hz, 1H, -5), 7.92 (s, 1H, H-1), 7.88 (d, $J$ = 8.0 Hz, 1H, H-4), 7.40 − 7.31 (m, 3H, H-8 and H$_{ortho}$ of Ph), 7.20 (dd, $J$ = 13.8, 7.3 Hz, 1H, H-3), 6.97 (t, $J$ = 7.1 Hz, 1H, H$_{para}$ of Ph), 6.90 (dt, $J$ = 24.4, 7.1 Hz, 2H, H$_{meta}$ of Ph), 6.81 (t, $J$ = 7.1 Hz, 2H, H-6, 7), 5.29 (br s, 1H, NH), 1.92 − 1.33 (m, 12H, PCH$_2$), 1.14 − 0.94 (m, 18H, alkyl CH$_3$). $^{13}$C NMR (176 MHz, CDCl₃, ppm): $\delta$ 139.90, 139.87, 139.37, 136.94, 128.02, 127.45, 127.20, 125.24, 123.84, 123.48, 122.04, 121.36, 120.74, 120.08, 119.78, 119.46, 113.17, 113.09 (aromatic), 111.26, 110.49 (−C≡C−), 15.43 − 13.56 (PCH$_2$), 8.27 − 7.86 (alkyl CH$_3$). $^{31}$P{$^1$H}NMR (122 MHz, DMSO-d$_6$, ppm): $\delta$ 11.46, $^1J_{Pt-P}$ = 2631.5 Hz. ESI-MS: $m/z$ 696.9 (M$^+$$\ast$). Anal. Calc. for C$_{34}$H$_{43}$NP$_2$Pt: C, 63.72; H, 7.20, observed: C, 63.80; H, 7.22 %.

**Trans-[R-C≡C-(PET$_3$)$_2$Pt-C≡C-R] (R = Carbazole-2-yl), M2**

A similar procedure as was used in the synthesis of M1 was followed using L1 (0.100 g, 0.522 mmol) and trans-[Pt(PET$_3$)$_2$Cl$_2$] (0.132 g, 0.261 mmol) and CuI (1 mg). The monomer was obtained as a pale brown solid (0.326 g, 77.3 %, m.p. 280.4 °C). IR (ATR, diamond): $\nu$/cm$^{-1}$ 3395 (N-H), 2092 (−C≡C−). $^1$H NMR (700 MHz, CDCl$_3$, ppm): 8.00 (d, $J$ = 7.5 Hz, 2H, H-5, 5'), 7.95 (s, 2H, H-1, 1'), 7.90 (d, $J$ = 7.7 Hz, 2H, H-4, 4'), 7.43 (dd, $J$ = 14.6, 8.1 Hz, 2H, H-8, 8'), 7.20 (t, $J$ = 7.4 Hz, 4H, H-6, 6', 7', 7'), 7.14 (d, $J$ = 8.0 Hz, 2H, H-3, 3'), 5.28 (s, 2H, NH, NH'), 1.31 − 1.25 (m, 12H, PCH$_2$), 1.16-1.08 (m, 18H, alkyl CH$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm): $\delta$ 139.94, 139.75, 136.13, 134.25, 129.84, 127.66, 125.56, 125.42, 123.71, 123.36, 120.74, 120.19, 120.16, 119.90, 119.86, 119.54, 112.67 (aromatic), 110.56, 110.54 (−C≡C−), 18.35 − 14.72 (PCH$_2$), 8.60 − 8.13 (alkyl CH$_3$). $^{31}$P{$^1$H}NMR (122 MHz, CDCl$_3$, ppm): $\delta$ 11.98, $^1J_{Pt-P}$ = 2769.4 Hz. ESI-MS: $m/z$ 810.3 (M$^+$$\ast$). Anal. Calc. for C$_{40}$H$_{46}$N$_2$P$_2$Pt: C, 59.18; H, 5.71, observed: C, 59.23; H, 5.73 %.

**Trans-[R-C≡C-(Bu$_3$P)$_2$Pt-C≡C-R] (R = Carbazole-2-yl), M3**

A similar procedure as was used in the synthesis of M1 was followed using L1 (0.100 g, 0.522 mmol), trans-[(PBu$_3$)$_2$PtCl$_2$] (0.175 g, 0.261 mmol) and CuI (1 mg). The product was obtained as biege powder (0.224 g, 87.5 %, m.p. 242.6 °C). IR (ATR, diamond): $\nu$/cm$^{-1}$ 3383 (N-H), 2084 (−C≡C−). $^1$H NMR (700 MHz, CDCl$_3$, ppm): $\delta$, 8.00 (d, $J$ = 7.7 Hz, 2H, H-4, 4'), 7.94 (s, 2H, H-1, 1'), 7.89 (d, $J$ = 8.0 Hz, 2H, H-5, 5'), 7.39 (d, $J$ = 7.9
Hz, 2H, H-8, 8’), 7.35 (dd, J = 15.1, 7.2 Hz, 2H, H-3, 3’), 7.19 (t, J = 8.1 Hz 4H, 6, 6’,7, 7’), 5.29 (br s, 2H, NH, NH’), 1.72 – 1.42 (m, 36H, alkyl CH2), 0.94 (m, 18H, alkyl CH3).

$^{13}$C NMR (176 MHz, CDCl3, ppm): δ 139.80, 139.76, 126.88, 125.33, 123.77, 123.42, 120.88, 120.09, 119.76, 119.81, 112.80, 110.50 (aromatic), 110.08, 108.19, 108.11, 108.03 (–C≡C–), 26.56 – 24.01 (alkyl CH2), 14.01 – 13.86 (alkyl CH3).

$^{31}$P{$^{1}$H} NMR (122 MHz, CDCl3, ppm): δ 4.04, $^{1}J_{Pt-P}$ = 2368.0 Hz. ESI-MS: m/z 980.3 (M$^{+}$). Anal. Calc. for C$_{52}$H$_{70}$N$_{2}$P$_{2}$Pt: C, 63.72; H, 7.20, observed: C, 63.90; H, 7.21 %.

Trans-[R-C≡C-(PEt$_{3}$)$_{2}$Pt-Ph] (R = Carbazole-3-yl), M4
A similar procedure to that used to synthesize M1 was followed using L2 afforded a pale brown solid (76.6 %, m.p. 154.1 ºC). IR (ATR, diamond): ν / cm$^{-1}$ 3406 (N-H), 2085 (–C≡C–).

$^{1}$H NMR (700 MHz, CDCl3, ppm): δ 8.04 (d, J = 7.7 Hz, 1H, H-5), 8.00 (s, 1H, H-4), 7.97 (s, 1H, NH), 7.41 – 7.37 (m, 2H, H$_{ortho}$ of Ph), 7.20 (dd, J = 9.1, 4.5 Hz, 2H, H-1, 8), 6.97 (t, J = 7.1 Hz, 3H, H$_{para}$, H$_{meta}$ of Ph), 6.93 (d, J = 6.0 Hz, 1H, H-2), 6.81 (t, J = 7.0 Hz, 2H, H-7, 6), 1.40 (m, 12H, PCH$_{2}$), 0.90 (m, 18H, alkyl CH$_{3}$).

$^{13}$C NMR (176 MHz, CDCl3, ppm): δ 115.68, 139.93, 139.44, 137.38, 129.61, 128.00, 127.65, 127.38, 125.95, 125.72, 124.74, 123.39, 122.44, 121.25, 120.93, 120.46, 119.55, 119.33 (aromatic), 110.71, 110.65, 110.20, 109.31 (–C≡C–), 15.43-13.45 (PCH$_{2}$), 8.28 – 7.85 (alkyl CH$_{3}$).

$^{31}$P{$^{1}$H} NMR (122 MHz, CDCl3, ppm): δ 10.73, $^{1}J_{Pt-P}$ = 2653.5 Hz. ESI-MS: m/z 698.0 (M$^{+}$). Anal. Calc. for C$_{34}$H$_{43}$NP$_{2}$Pt: C, 63.72; H, 7.20, observed: 63.81; H, 7.22 %.

Trans-[R-C≡C-(PEt$_{3}$)$_{2}$Pt-C≡C-R] (R = Carbazole-3-yl), M5
A similar procedure to the synthesis of M2 using L2 afforded a pale yellow solid (69.2 %, m.p. 209 ºC). IR (ATR, diamond): ν / cm$^{-1}$ 3387 (N-H), 2096 (–C≡C–).

$^{1}$H NMR (700 MHz, CDCl3, ppm): δ 8.03 (s, 2H, H-4, 4’), 7.81 (d, J = 7.6 Hz, 2H, H-5, 5’), 7.56 – 7.51 (m, 4H, H-1, 1’,8, 8’), 7.37 (d, J = 7.9 Hz, 2H, H-2, 2’), 7.16 – 7.11 (m, 4H, H-6, 6’,7, 7’), 5.22 (s, 2H, NH, NH’), 1.25 – 1.11 (m, 12H, PCH$_{2}$), 0.83 – 0.73 (m, 18H, alkyl CH$_{3}$).

$^{13}$C NMR (176 MHz, CDCl3, ppm): δ 139.96, 137.72, 137.57, 136.23, 134.52, 134.38, 134.33, 134.29, 134.25, 134.04, 130.30, 130.05, 129.84, 129.54, 129.39, 127.89, 127.82, 127.66, 125.97, 125.83, 123.43, 123.28, 122.54, 120.47, 119.57, 119.45 (aromatic), 110.70, 110.68, 110.35, 110.26 (–C≡C–), 14.75 – 14.65 (PCH$_{2}$), 8.64 – 8.26 (alkyl CH$_{3}$).
$^{31}$P{$^1$H}NMR (122 MHz, CDCl$_3$, ppm): $\delta$ 11.89, $^1$J$_{Pt-P}$ = 2104.1 Hz. ESI-MS: $m/z$ 810.0 ($M^+$). Anal. Calc. for C$_{40}$H$_{46}$N$_2$P$_2$Pt: C, 59.18; H, 5.71, observed: C, 59.21; H, 5.70 %.

**Trans-[R-C≡C-(Bu$_3$P)$_2$Pt-C≡C-R] (R = Carbazole-3-yl), M6**

A similar synthesis to that used to prepare M3 was followed using L2 afforded a pale brown solid (81.6 %, m.p. 187.3 °C). IR (ATR, diamond): $\nu$ / cm$^{-1}$ 3397 (N-H), 2097 (C=C), 1412, 1374, 1328, 1299, 1263, 1227, 1219, 1193, 1165, 1098, 1086, 1048, 1035, 1025 (C=C-), 2687 – 2414 (alkyl CH$_2$), 1485 – 1324 (alkyl CH$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm): $\delta$ 139.95, 137.48, 137.43, 129.48, 129.35, 125.77, 123.38, 122.46, 120.34, 119.44, 110.70, 110.19, 109.35 (aromatic), 104.88, 104.86, 104.78, 104.70 (C=C–).

$^{31}$P{$^1$H}NMR (122 MHz, CDCl$_3$, ppm): $\delta$ 3.37, $^1$J$_{Pt-P}$ = 2380.2 Hz. ESI-MS: $m/z$ 979.4 ($M^+$). Anal. Calc. for C$_{52}$H$_{70}$N$_2$P$_2$Pt: C, 63.72; H, 7.20, C, observed: 63.90; H, 7.21 %.

**Trans-[(Ph)(Et$_3$P)$_2$Pt-C≡C-R≡C-Pt(Et$_3$)$_2$Ph] (R = Carbazole-2,7-diyl), M7**

The compound was prepared as previously reported.$^{11f}$ $^1$H NMR (250 MHz, CDCl$_3$, ppm): $\delta$ 7.80 (d, $J = 7.9$ Hz, 4H, H$_{ortho}$ of Ph), 7.42 (d, $J = 7.9$ Hz, 4H, H-$4$, 5), 7.32 (s, 2H, H-$1$, 8), 7.20 (dd, $J = 13.9$, 7.4 Hz, 2H, H-$3$, 6), 6.98 (t, $J = 7.4$ Hz, 4H, H$_{meta}$ of Ph), 6.82 (t, $J = 7.3$ Hz, 2H, H$_{para}$ of Ph), 5.20 (br s, 1H, NH), 1.80 – 1.61 (m, 24H, PCH$_2$), 1.07 – 0.98 (m, 36H, alkyl CH$_3$). FAB-MS: $m/z$ 1230.2 ($M^+$).

**Trans-[(Ph)(Et$_3$P)$_2$Pt-C≡C-R≡C-Pt(Et$_3$)$_2$Ph] (R = N-(2-ethylhexylcarbazole-2,7-diyl), M8**

The compound was prepared as previously reported.$^{11f}$ $^1$H NMR (250 MHz, CDCl$_3$, ppm): $\delta$ 7.81 (d, $J = 7.7$ Hz, 2H, H-$4$, 5), 7.35 (d, $J = 7.9$ Hz, 4H, H$_{ortho}$ of Ph), 7.25 (s, 2H, H-$1$, 8), 7.14 (dd, $J = 13.2$, 7.0 Hz, 2H, H-$3$, 6), 6.97 (t, $J = 7.6$ Hz, 4H, H$_{meta}$ of Ph), 6.88 (t, $J = 8.0$ Hz, 2H, H$_{para}$ of Ph), 4.05 – 4.06 (m, 2H, NCH$_2$), 1.81 – 1.78 (m, 24H, PCH$_2$), 1.62 – 1.57 (m, 1H, alkyl CH), 1.43 – 1.38 (m, 8H, alkyl CH$_2$), 1.20 – 1.14 (m, 36H, alkyl CH$_3$), 0.88 (t, $J = 7.8$ Hz, 6H, alkyl CH$_3$). FAB-MS: $m/z$ 1342.3 ($M^+$).

**Trans-[(Ph)(Et$_3$P)$_2$Pt-C≡C-R≡C-Pt(Et$_3$)$_2$Ph] (R = Carbazol-3,6-diyl), M9**
The compound was prepared as previously reported.\textsuperscript{11f} \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}, ppm): \( \delta 7.53\) (d, \( J = 7.9\) Hz, 2H, H-4, 5), 7.41 (d, \( J = 8.0\) Hz, 2H, H-2, 7), 7.32(dd, \( J = 14.0, 7.4\) Hz, 4H, H\textsubscript{ortho} of Ph), 7.26 (d, \( J = 8.0\) Hz, 2H, H-1, 8), 6.96 (t, \( J = 7.9\) Hz, 4H, H\textsubscript{meta} of Ph), 6.80 (t, \( J = 7.9\) Hz, 2H, H\textsubscript{para} of Ph), 9.55 (s, 1H, NH), 1.82 – 1.75 (m, 24H, PCH\textsubscript{2}), 0.86 (t, \( J = 7.2\) Hz, 36H, CH\textsubscript{3}). FAB-mass spectrum: \( m/z 1230.1 (M^+). \)

\textit{Trans-[\(\text{Ph} \text{Et}_3\text{P})_2\text{Pt-}\text{C}==\text{C}-R\text{-C}==\text{C}-\text{Pt(PEt}_3\text{)}_2\text{Ph}] (R = N-(2-ethylhexylcarbazole-3,6-diyl), M10}

To a stirred mixture of \textit{L4b} (0.150 g, 0.461 mmol) and \textit{trans-[Pt(PEt}_3\text{)\textsubscript{2}PhCl]} (0.543 g, 1.00 mmol) in \textit{iPr}_2\text{NH} (20 mL) and CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added CuI (1 mg). The solution was stirred at room temperature under Ar over a period of 18 h, after which all volatile components were removed under reduced pressure. The crude product was taken up in CH\textsubscript{2}Cl\textsubscript{2} and purified using silica column chromatography with hexane/CH\textsubscript{2}Cl\textsubscript{2} (1:1, v/v) as the eluent. The product was obtained as a brown solid (0.480 g, 77.5%). IR (CH\textsubscript{2}Cl\textsubscript{2}): \( \nu / \text{cm}^{-1} 2090 (–C≡C–). \)

\textsuperscript{1}H NMR (700 MHz, CDCl\textsubscript{3}, ppm) \( \delta 8.08\) (s, 1H, H-4), 7.88 (s, 1H, H-5), 7.48 (dd, \( J = 8.7, 1.9\) Hz, 1H, H-1), 7.40 (ddd, \( J = 21.9, 8.5, 1.7\) Hz, 1H, H-8), 7.29 (d, \( J = 7.0\) Hz, 2H, H-2, 7), 7.17 – 7.13 (m, 4H, H\textsubscript{ortho} of Ph), 6.90 (t, \( J = 7.4\) Hz, 4H, H\textsubscript{meta} of Ph), 6.74 (dd, \( J = 14.1, 6.9\) Hz, 2H, H\textsubscript{para} of Ph), 3.60 – 3.56 (m, 2H, NCH\textsubscript{2}), 1.99 – 1.88 (m, 1H, alkyl CH), 1.77 – 1.65 (m, 24H, PCH\textsubscript{2}), 1.34 – 1.10 (m, 8H, alkyl CH\textsubscript{2}), 1.10 – 0.91 (m, 36H, alkyl CH\textsubscript{3}), 0.85 – 0.69 (m, 6H, alkyl CH\textsubscript{3}). \textsuperscript{13}C NMR (176 MHz, CDCl\textsubscript{3}, ppm) \( \delta 138.77, 138.28, 137.95, 128.91, 127.98, 126.89, 126.25, 123.42, 122.41, 122.21, 121.96, 121.35, 120.63, 120.13, 110.92\) (aromatic), 110.20, 109.67, 109.29, 107.73 (–C≡C–), 52.42, 46.66, 46.52, 38.35, 38.32, 29.97, 29.94, 28.70, 27.81, 27.74, 23.34, 22.03, 21.99, 21.70 (alkyl CH\textsubscript{2}), 14.23, 14.14, 14.04, 13.13, 13.03, 12.99, 9.88, 9.86, 7.09, 6.82 (alkyl CH\textsubscript{2}).\textsuperscript{31}P{\textsuperscript{1}H}-NMR (101.3 MHz, CDCl\textsubscript{3}): \( \delta -131.8, \) \( J_{\text{Pt-P}} = 2637\) Hz. FAB-MS: \( m/z 1342.1 (M^+). \) Anal. Calc. for C\textsubscript{60}H\textsubscript{93}P\textsubscript{4}Pt\textsubscript{2}N: C, 53.69; H, 6.98, observed: C, 53.72; H, 6.91 %.

\textit{Trans-[(Bu}_3\text{P})_2\text{Pt-C}==\text{C}-R\text{-C}==\text{C}-\text{Pt(PEt}_3\text{)}_2\text{Ph}] (R = Carbazole-2,7-diyl), P1}

The compound was prepared according to the previously-reported procedure.\textsuperscript{11f} \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}, ppm): \( \delta 7.81\) (dd, \( J = 7.2, 2.2\) Hz, 2H, H-4, 5), 7.27 (s, 2H, H-1, 8), 7.15 (d, \( J = 7.0\) Hz, 2H, H-3, 6), 5.65 (s, 1H, NH), 2.18 – 2.10 (m, 12H, PCH\textsubscript{2}), 1.58 – 1.30 (m, 24H, alkyl CH\textsubscript{2}), 1.08 – 0.87 (m, 18H, alkyl CH\textsubscript{3}). GPC (THF): \( M_n = 25,500\) g/mol\textsuperscript{-1} (\( n = 31\)), \( M_w = 40,500\) g/mol\textsuperscript{-1}, PDI = 1.6.
**Trans- [-(Bu$_3$P)$_2$Pt-C≡C-R-C≡C]-n (R = N-(2-ethylhexylcarbazole-2,7-diyl)), P2**

The compound was prepared according to the previously-reported procedure.$^{11f}$ $^1$H NMR (250 MHz, CDCl$_3$, ppm): δ 7.83 (d, $J = 6.9$ Hz, 2H, H-4), 7.21 (s, 2H, H-1, 8), 6.99 (d, $J = 7.1$ Hz, 2H, H-3, 6), 4.04 – 4.01 (m, 2H, NCH$_2$), 2.66 – 2.57 (m, 1H, alkyl CH), 2.22 (m, 12H, PCH$_2$), 1.58 – 1.46 (m, 32H, alkyl CH$_2$), 1.12 – 0.90 (m, 24H, alkyl CH$_3$). GPC (THF): $\bar{M}_n = 40,000$ gmol$^{-1}$ ($n = 43$), $\bar{M}_w = 72,000$ gmol$^{-1}$, PDI = 1.8.

**Trans- [-(Bu$_3$P)$_2$Pt -C≡C-R-C≡C]-n (R = Carbazol-3,6-diyl), P3**

The compound was prepared following the previously-reported procedure.$^{11f}$ $^1$H NMR (250 MHz, CDCl$_3$, ppm): δ 7.50 (d, $J = 7.7$ Hz, 2H, H-4, 5), 7.41 (dd, $J = 13.9$, 7.4 Hz, 2H, H-1, 8), 7.25 (d, $J = 8.2$ Hz, 2H, H-2, 7), 5.57 (s, 1H, NH), 2.20 – 2.01 (m, 12H, PCH$_2$), 1.67 – 1.01 (m, 24H, alkyl CH$_2$), 0.93 (t, $J = 7.9$ Hz, 18H, alkyl CH$_3$). GPC (THF): $\bar{M}_n = 17,900$ gmol$^{-1}$ ($n = 22$), $\bar{M}_w = 30,500$ gmol$^{-1}$, PDI = 1.7.

**Trans- [-(Bu$_3$P)$_2$Pt-C≡C-R-C≡C]-n (R = N-(2-ethylhexylcarbazole-3,6-diyl)), P4**

The poly-yne was synthesised by mixing L4b (0.100 g, 0.305 mmol), trans-[Pt(PBu$_3$)$_2$Cl$_2$] (0.205 g, 0.305 mmol) and CuI (1 mg) in $^1$Pr$_2$NH/CH$_2$Cl$_2$ (50 mL, 1:1, v/v). After stirring at room temperature overnight under Ar, the solvent was evaporated under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and filtered through a short alumina column, using hexane/CH$_2$Cl$_2$ (1:1, v/v) as eluent, to remove ionic impurities and catalyst residues. After removal of the solvent, the crude product was purified twice by precipitation in CH$_2$Cl$_2$ from MeOH. Subsequent washing with hexane and drying in vacuo gave a brown solid (0.226 g, 80.1 %). IR (CH$_2$Cl$_2$): ν / cm$^{-1}$ 2097 (–C≡C–). $^1$H NMR (700 MHz, CDCl$_3$, ppm) δ 7.94 (s, 2H, H-4, 5), 7.38 (d, $J = 8.2$ Hz, 2H, H-1, 8), 7.18 (d, $J = 8.3$ Hz, 2H, H-2, 7), 4.14 – 4.02 (m, 2H, NCH$_2$), 3.29 (m, 1H, alkyl CH), 2.21 (t, $J = 21.4$ Hz, 10H, PCH$_2$), 2.09 – 1.99 (m, 2H, PCH$_2$), 1.75 – 1.11 (m, 32H, alkyl CH$_2$), 0.99 – 0.75 (m, 24H, alkyl CH$_3$). $^{13}$C NMR (176 MHz, CDCl$_3$, ppm) δ 138.07, 127.93, 123.10, 121.53, 121.22, 118.51 (aromatic), 108.27, 107.34 (–C≡C–), 46.27 (NCH$_2$), 38.35 (alkyl CH), 29.94, 28.70, 27.74, 25.44, 25.34, 25.12, 23.52, 23.49, 23.45, 23.34, 23.09, 22.99, 22.89, 22.05 (alkyl CH$_2$), 13.02, 12.92, 12.86, 9.90 (alkyl CH$_3$). $^{31}$P{$^1$H}-NMR (101.3 MHz, CDCl$_3$): δ –137.55, $^1$J$_{Pt,P}$ = 233 Hz. Anal. Calc. for [C$_{48}$H$_{77}$P$_2$PtN]$_n$:  

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C, 62.31; H, 8.39, observed: C, 62.20; H, 8.36 %. GPC (THF): $\bar{M}_n = 36,000 \text{ gmol}^{-1} \ (n = 39)$, $\bar{M}_w = 70,000 \text{ gmol}^{-1}$, PDI = 1.9

X-ray crystallography
The crystals of 3a-TMSA, 4a-TMSA, M3 and M7 were mounted in inert oil on glass fibres. Data were measured using Mo-Kα radiation ($\lambda = 0.71073 \text{ Å}$) with a Bruker Kappa CCD diffractometer or a Agilent Gemini A-Ultra diffractometer (for M3) both equipped with an Oxford Cryostream low-temperature attachment. Structures were solved by direct methods (SHELXS-86) and subjected to full-matrix least-squares refinement on $F^2$ (SHELXL-97). In both M3 and M7, there was extensive disorder in the alkyl groups of the phosphine ligands, and in M7 two orientations of one of the terminal phenyl groups were also observed. These features were modelled over two or three sites using partial occupancies, summed to unity, and additional constraints were placed on the bond parameters to maintain reasonable bond lengths and angles. In M7 the two partially-occupied phenyl-ring positions were restrained using the FLAT command. Except for some of the disordered carbon atoms in the alkyl chains of the phosphine ligands, all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model and, again, partial occupancies were included as appropriate. Refinement continued until convergence was reached, and in the final cycles of refinement a weighting scheme was introduced that afforded a relatively flat analysis of variance.

Molecular-weight measurements
Molar masses were determined by gel-permeation chromatography (GPC), using two PL Gel 30 cm, 5 micron mixed C columns at 30 C, running in THF at 1 cm$^3$ min$^{-1}$ with a Roth Mocel 200 high-precision pump. A DAWN DSP (Wyatt Technology) multi-angle laser-light scattering (MALLS) apparatus with 18 detectors and an auxiliary Viscotek model 200 differential refractometer/viscometer detector was used to calculate the molecular weights (the overall technique is referred to as GPC-LS).

Computational modelling
Molecular quantum-chemical calculations were carried out using the density-functional theory (DFT) formalism, as implemented in the NWChem code. The B3LYP hybrid functional was used in conjunction with Pople split-valence basis sets of 6-31g and 6-
31g** quality for the H and non-H atoms, respectively, and the LANL2DZ pseudopotential\textsuperscript{33} and corresponding double-zeta basis set were used to describe Pt. The convergence tolerances for the optimisation of the electronic wavefunctions were set to 10\textsuperscript{-6}, 10\textsuperscript{-5} and 5 \times 10\textsuperscript{-4} a.u. on the total energy, density and gradients, respectively. The geometries of the four initial models were optimised until the maximum and root-mean-square (RMS) gradients on the ions were less than 4.5 \times 10\textsuperscript{-4} and 3 \times 10\textsuperscript{-4} a.u., respectively, and the maximum RMS Cartesian steps in the last iteration fell below 1.8 \times 10\textsuperscript{-3} and 1.2 \times 10\textsuperscript{-3} a.u. The minima were then verified by computing the vibrational frequencies using analytical gradients; during these calculations, the tolerances on the energy, density and gradients during the electronic minimisation were tightened to 10\textsuperscript{-8}, 10\textsuperscript{-6} and 10\textsuperscript{-5} a.u., respectively. Finally, time-dependent DFT (TD-DFT) calculations were carried out on the optimised models using adiabatic B3LYP. The 50 lowest-lying singlet (spin-allowed) and triplet (spin-forbidden) electronic excitations were computed, and the former were used to generate a simulated UV/vis absorption spectrum according to the equation:

\[
\varepsilon(\nu) = \sum_i 1.3062974 \times 10^8 \frac{f_i}{\sigma} \exp\left(-\left[\frac{\nu - \nu_i}{\sigma}\right]^2\right)
\]

where the energies, \(\nu\), are in wavenumbers (cm\textsuperscript{-1}), \(\varepsilon\) is the molar extinction coefficient in L mol\textsuperscript{-1} cm\textsuperscript{-1}, \(f_i\) are the (dimensionless) oscillator strengths, \(\nu_i\) are the band positions and \(\sigma\) is a uniform bandwidth used to broaden the peaks, here set to 0.2 eV.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI:

Crystallographic information file (CIF)

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Notes
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The computational modelling was carried out using the UK Archer facility, accessed through the UK Materials Chemistry Consortium, which is funded by the EPSRC (grant no. EP/L000202). Some modelling was also performed using the Balena HPC system at the University of Bath, which is maintained by Bath University Computing Services.

REFERENCES


Table of Content Synopsis
A series of Pt(II) mono-, di- and poly-ynes incorporating carbazole spacers were synthesized. X-ray crystal structure of two protected ligand precursors and two model Pt(II) di-yne complexes are reported. Both experimental and computational studies indicate an enhanced conjugation in 2- and 2,7-carbazole based complexes compared to the 3- and 3,6-carbazole analogues.