

Synthesis, characterisation and optical spectroscopy of diynes and poly-yne containing derivatised fluorenes in the backbone

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A series of trimethylsilyl-protected and terminal mono- and bis-alkynes based on 9,9-dioctylfluorene, 2-(trimethylsilylethynyl)-9,9-dioctylfluorene **1a**, 2-ethynyl-9,9-dioctylfluorene **1b**, 2,7-bis(trimethylsilylethynyl)-9,9-dioctylfluorene **2a**, 2,7-bis(ethynyl)-9,9-dioctylfluorene **2b**, have been synthesised. Reaction of *trans*-[(PⁿBu₃)₂PtCl₂] with 2 equivalents of the terminal ethyne **1b** yields the mononuclear platinum(II) diyne **3**, reaction of *trans*-[(Ph)(Et₃P)₂PtCl] with 0.5 equivalents of the dimeric ethyne **2b** gives the dinuclear platinum(II) diyne **4** while 1 : 1 reaction between *trans*-[(PⁿBu₃)₂PtCl₂] and **2b** gives the platinum(II) poly-yne **5**. Treatment of 2,5-dioctyloxy-1,4-diiodobenzene with **1b** in 1 : 2 stoichiometry produces the organic di-yne **6** while 1 : 1 reaction between 2,5-dioctyloxy-1,4-diiodobenzene and **2b**, 2,7-bis(ethynyl)fluorene or 2,7-bis(ethynyl)fluorene-9-one produces the organic co-poly-yne **7–9**. All the new materials have been characterised by analytical and spectroscopic methods and the single crystal X-ray structures of **2a** and **3** have been determined. The diynes and poly-yne are soluble in organic solvents and are readily cast into thin films. Optical spectroscopic measurements reveal that the attachment of octyl side-chains on the fluorenyl spacer reduces inter-chain interaction in the poly-yne while a fluorenyl spacer creates a donor–acceptor interaction along the rigid backbone of the organometallic poly-yne and organic co-poly-yne.

Introduction

In recent years there has been a considerable interest in the optoelectronic properties of conjugated polymers.^{1,2} Many potential applications such as nonlinear optics, electroluminescence, optical information storage, *etc.*, using conjugated polymers have been proposed.³ Among the variety of conjugated polymers that are now studied, poly(arylene ethynylene) type polymers (PAEs) and metal poly-yne polymers have been the focus of much research with regard to the development of optoelectronic devices.⁴ Of particular interest are a series of PAEs that have been employed in successful liquid crystal display and photocell technology.^{5,6} Platinum acetylide-based π -conjugated polymers have provided model systems to explain the electronic properties of conjugated organic polymers⁷ used in light emitting diodes (LEDs),⁸ lasers,⁹ photocells,¹⁰ and field-effect transistors (FETs).¹¹ The inclusion of heavy transition metals such as platinum in the polymer backbone introduces sufficient spin–orbit coupling to allow light emission from the triplet excited state of the conjugated ligand.^{12–14} For commercial exploitation of these materials and for direct application-oriented synthesis, a thorough understanding of the structure–property relationship is necessary such that suitable modification of the chemical structure may fine-tune the optoelectronic properties of the polymers.

Recently we reported a series of platinum(II) poly-yne where the bridging alkynyl units are separated by a variety of carbocyclic and heterocyclic spacers (*e.g.*, oligothieryl, oligopyridyl, thienyl-pyridine, phenylene, *etc.*).^{13,15–17} The platinum centre is electron rich compared to the conjugated ligands and the metal-phosphine fragment acts as an electron donor within the polymer.^{12,18,19} In a comparative series of studies we have shown that when the 2,5-dioctyloxy-1,4-phenylene unit replaces the platinum-phosphine group it acts as a donor and readily couples to acceptor units *via* alkynyl bridges.²⁰ In contrast, fluorenes are widely used as electron acceptors in charge transfer complexes²¹ and electron transport materials.²² π -Conjugated polymers with

donor–acceptor architectures are currently of interest because the intra-molecular charge transfer can facilitate ready manipulation of the electronic structure (HOMO–LUMO levels), leading to small band gap semi-conducting polymers²³ or materials with enhanced third-order nonlinear optical properties.²⁴ The donor–acceptor interaction in fluorene-based platinum(II) poly-yne and organic co-poly-yne may impart interesting materials properties to such polymeric systems. The fluorene structural moiety provides a rigidly planar biphenyl unit within the polymer backbone and facile functionalisation at C-9, the latter offering the prospect of improving both polymer processability and mediating potential inter-chain interactions in films.²⁵ There is also considerable interest in the solid-state structures of the polymeric materials because of evidence for inter-chain interactions that influence their optoelectronic properties. In this context an analysis of intermolecular interactions in the crystal structures of the ligand precursors and of model complexes may lead to a better understanding of the interactions in the polymers.²⁶ With these ideas in mind we have been interested in the chemistry and photophysics of new platinum(II) poly-yne incorporating fluorene-based auxiliaries. A few recent reports have concerned the incorporation of fluorene-based auxiliaries into conjugated poly-yne frameworks.²⁷

In this paper, we report the synthesis and characterisation of mono- and bis-(ethynyl)-9,9-dioctylfluorene derivatives **1a,b**, and **2a,b**, and the incorporation of **2b** into the new rigid-rod platinum(II) poly-yne **5** (Chart 1). In order to evaluate the role of the platinum(II) centres and to undertake a systematic study of the optoelectronic properties of the poly-yne, a series of

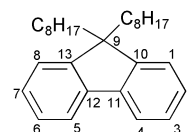
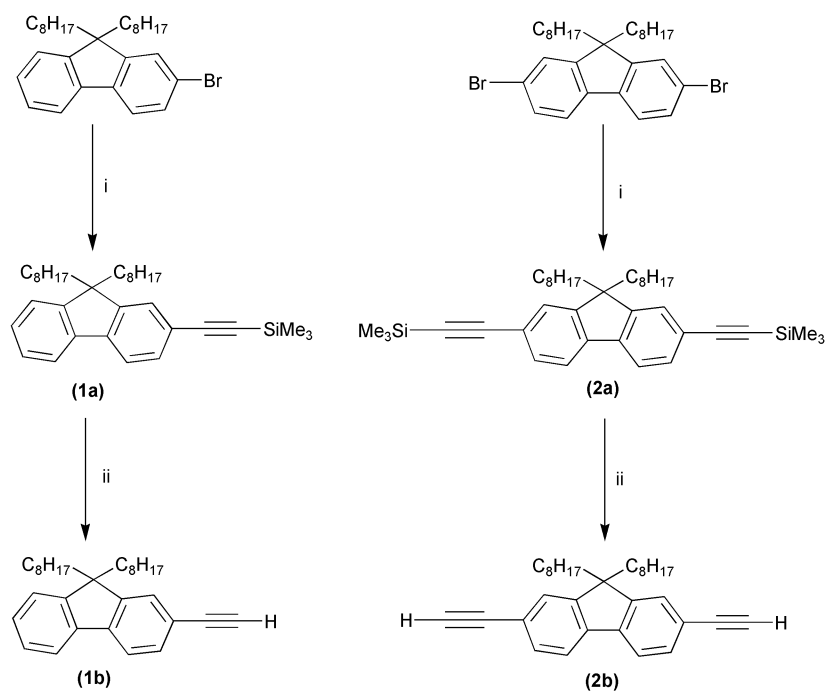


Chart 1 The numbering scheme for 9,9-dioctylfluorene.



Scheme 1 i $\text{Me}_3\text{SiC}\equiv\text{CH}$, CuI , $\text{Pd}(\text{OAc})_2$, PPh_3 , ${}^i\text{Pr}_2\text{NH}$, THF; ii KOH , MeOH , THF.

organic co-poly-ynes **7–9** that contain derivatised fluorene groups in the backbone have also been synthesised. In addition, the synthesis and characterisation of the model diyne compounds **3**, **4** and **6** is reported. Diynes can be considered as building blocks for the high molecular weight polymers and valuable information concerning their molecular and electronic properties can be obtained through the studies of these model compounds. Recently, attention has also been directed towards linear π -conjugated dimers and oligomers, taken not only as model compounds, but also as efficient molecular wires in electronic applications.²⁸ Diynes are often more crystalline than the corresponding poly-ynes, allowing for a detailed structural analysis and, thus, an assessment of the structure–electronic property relationship.²⁹ The structural characterisation of a fluorene-based ligand precursor **2a** and of a mononuclear platinum(II) σ -acetylide complex **3** are reported. The optoelectronic properties of the new materials are described and compared with related organometallic and organic polymers.

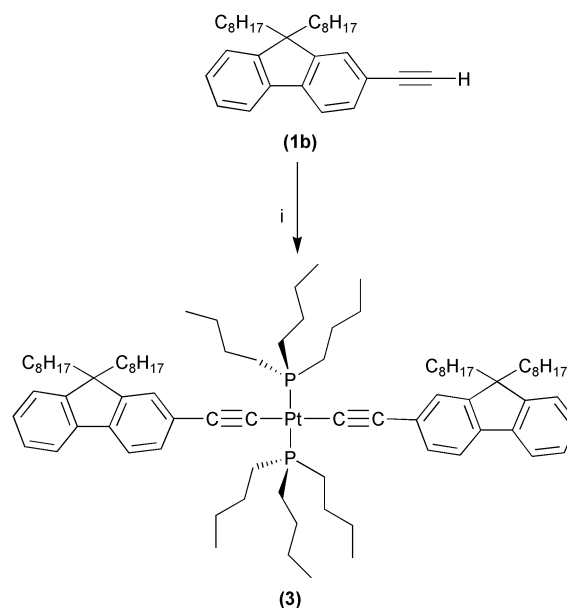
Results and discussion

Syntheses

The key starting materials for the alkynyl ligand precursors, 2-bromo-9,9-dioctylfluorene and 2,7-dibromo-9,9-dioctylfluorene were prepared by adaptation of literature procedures involving alkylation of 2-bromofluorene and 2,7-dibromofluorene with 1-bromooctane in a two-phase system using tetra(*n*-butyl)ammonium bromide as the phase-transfer catalyst.^{30,31} The trimethylsilyl-protected alkynyl ligand precursors, 2-(trimethylsilylethynyl)-9,9-dioctylfluorene **1a** and 2,7-bis(trimethylsilylethynyl)-9,9-dioctylfluorene **2a** were prepared by improved procedures involving a palladium(II)/copper(I)-catalysed cross-coupling reaction of 2-bromo-9,9-dioctylfluorene and 2,7-dibromo-9,9-dioctylfluorene with trimethylsilylacetylene in diisopropylamine/THF as illustrated in Scheme 1.³² The protected alkynes are indefinitely stable towards light and air at ambient temperature and were fully characterised by IR, NMR (${}^1\text{H}$ and ${}^{13}\text{C}$) spectroscopy, EI mass spectrometry, as well as by satisfactory elemental analyses and single crystal X-ray structure determination for **2a**. Conversion of the protected ligands into their terminal mono- and bis-alkynes, 2-ethynyl-9,9-dioctylfluorene **1b** and 2,7-bis(ethynyl)-

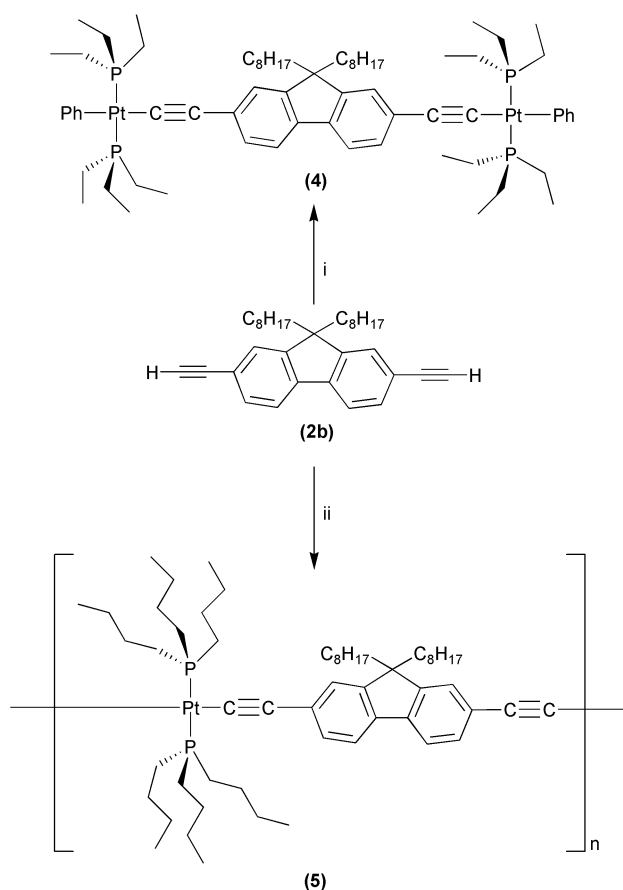
9,9-dioctylfluorene **2b** was accomplished by cleavage of the trimethylsilyl protecting group with dilute aqueous KOH in MeOH – THF (Scheme 1). The products were purified by silica gel column chromatography and isolated as off-white to light yellow solids or colourless liquids in yields of 75–85%. The new terminal mono- and bis-alkynes are stable in air and light and were characterised by IR, NMR (${}^1\text{H}$ and ${}^{13}\text{C}$) spectroscopy, EI mass spectrometry as well as by satisfactory elemental analyses.

The complex $\text{trans}-[(\text{P}^n\text{Bu}_3)_2\text{PtCl}_2]$ was reacted with two equivalents of **1b** in ${}^i\text{Pr}_2\text{NH}$ – THF , in the presence of CuI at room temperature to afford the mononuclear platinum(II) diyne complex **3** (Scheme 2).



Scheme 2 i $\text{trans}-[\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2]$, CuI , ${}^i\text{Pr}_2\text{NH}$, CH_2Cl_2 .

The reaction of $\text{trans}-[(\text{Ph})(\text{Et}_3\text{P})_2\text{PtCl}]$ with **2b** (2 : 1 stoichiometry) gave the dinuclear platinum(II) diyne **4** while the dehydrohalogenation polycondensation reaction between $\text{trans}-[(\text{P}^n\text{Bu}_3)_2\text{PtCl}_2]$ and **2b** (1 : 1 stoichiometry) under similar conditions readily afforded the platinum(II) poly-yne **5** (Scheme 3).

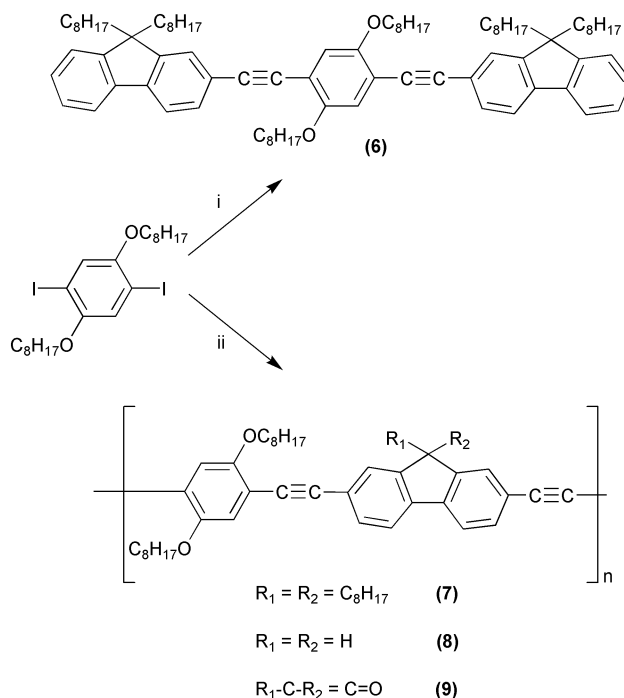


Scheme 3 i) $2[\text{Pt}(\text{PEt}_3)_2(\text{Ph})\text{Cl}]$, CuI , ${}^i\text{Pr}_2\text{NH}$, CH_2Cl_2 ; ii) $\text{trans-}[\text{Pt}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2]$, CuI , ${}^i\text{Pr}_2\text{NH}$, CH_2Cl_2 .

The synthesis of platinum(II) fluorene-poly-yne **11** and platinum(II) fluorenone-poly-yne **12** has been reported previously.^{27a} Reaction of 2,5-dioctyloxy-1,4-diiodobenzene with **1b** (1 : 2 stoichiometry) in ${}^i\text{Pr}_2\text{NH}$ -THF gave the organic diyne **6** while the reaction between 2,5-dioctyloxy-1,4-diiodobenzene and **2b**, bis(ethynyl)fluorene or bis(ethynyl)fluorenone (1 : 1 stoichiometry) produced the organic co-poly-ynes **7–9** (Scheme 4). The poly-ynes were obtained in yields over 90%, pointing to a very high conversion. The model diyne compounds **3**, **4** and **6** were synthesised to control the reaction conversion and to facilitate spectroscopic and photophysical characterisation of the poly-ynes. Standard palladium-catalyzed acetylene coupling (Sonogashira–Hagihara) methodologies were employed in the synthesis of the organic diynes and poly-ynes.^{32c} The reaction conditions typically used involved stirring a mixture of the diiodo- and diethynyl-fluorene precursors and catalyst in diisopropylamine–THF (1 : 4, v/v) for 20 h at a temperature of 70 to 80 °C. The solvent mixture was degassed by passing argon through the solution for 1 h prior to the start of the reaction, with the aim of excluding the Cu(I)-catalyzed oxidative coupling of terminal bis-alkynes³³ which may compete with the desired cross-coupling or polycondensation reaction. The polymers remained in solution during the reaction, with the help of the octyloxy and octyl side-groups. They were isolated by precipitation into methanol. Purification of diynes **3**, **4**, **6** and organic poly-ynes **7–9** was accomplished by silica column chromatography while the platinum(II) poly-yne **5** was purified by chromatography on an alumina column.

Spectroscopic characterisation

Systematic characterisation of the diynes and poly-ynes was achieved by spectroscopic methods (IR, ${}^1\text{H}$, ${}^{13}\text{C}$ and ${}^{31}\text{P}$ NMR). The IR spectra of the organic diyne **6** and poly-ynes **7–9** provided clear evidence for the presence of the $\text{C}\equiv\text{C}$ bond, detected



Scheme 4 i) **21b**, CuI , $\text{Pd}(\text{OAc})_2$, PPh_3 , ${}^i\text{Pr}_2\text{NH}$, THF; ii) **2b**/bis(ethynyl)fluorene/fluorenone, CuI , $\text{Pd}(\text{PPh}_3)_4$, ${}^i\text{Pr}_2\text{NH}$, THF.

by its typical absorptions at 2210 and 2202 cm^{-1} . Following the cross-coupling polycondensation reaction, the $\nu_{\text{C}\equiv\text{C}}$ band of the terminal alkynes **1b** and **2b** at 2107–2110 cm^{-1} is shifted to a higher frequency by about 100 cm^{-1} , consistent with the known trend that disubstituted alkynes $\text{R-C}\equiv\text{C-R}'$ display a $\nu_{\text{C}\equiv\text{C}}$ band at a frequency higher than that of monosubstituted alkynes $\text{RC}\equiv\text{C-H}$.³⁴ The IR spectra of the mononuclear platinum(II) diyne **3**, dinuclear platinum(II) **4** and platinum(II) poly-yne **5** display a single sharp $\nu_{\text{C}\equiv\text{C}}$ absorption at around 2095 cm^{-1} consistent with a *trans*-configuration of the ethynyl ligands around the platinum(II) centre. The platinum(II) diynes and poly-yne display lower $\nu_{\text{C}\equiv\text{C}}$ values than those of the organic diyne and poly-ynes by about 110 cm^{-1} , which is attributed to a metal-to-alkynyl ligand charge transfer process.³⁵ The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of all the compounds exhibit the expected signals for the systems including appropriate resonances for the backbone ethynylene carbons. The peak area ratios in the ${}^1\text{H}$ NMR spectra agree with the feed mole ratio of the precursors for the diynes and poly-ynes. The single resonance in the ${}^{31}\text{P}$ NMR spectra of the platinum(II) diynes and poly-yne confirms the *trans* arrangement of the phosphine ligands. From the ${}^{31}\text{P}$ - $\{{}^1\text{H}\}$ NMR spectral data, it is clearly seen that the ${}^1J_{\text{P-C}}$ coupling constants for the diynes **3**, **4** are larger than those of the poly-yne **5** by about 300 Hz. The spectral features of the diyne and poly-yne **3–5** are similar to other platinum(II) diynes and poly-ynes previously reported,^{13,15–17,19} and confirm the all-*trans* configuration of the complexes.

The mass spectrometric results confirm the molecular assignments for the organic ligands and the platinum(II) diynes. Gel permeation chromatography (GPC), using a polystyrene (PS) calibration shows that the number-average molecular weights of the poly-ynes are in the range of 9500–43500 g mol^{-1} , corresponding to degrees of polymerisation between 17 and 42. The polydispersity (PDI) varied between 1.6 and 1.9. The narrow polydispersity (PDI < 2) in molecular weights is consistent with the proposed linear structure³⁶ from the condensation polymerisation. The molecular weights should be treated with caution in view of the difficulties associated with utilising GPC for rigid-rod polymers. GPC does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. Rod-like polymers in solution possess very different hydrodynamic properties to those of flexible

polymers. Therefore, calibration of the GPC with PS standards is likely to inflate the values of the molecular weights of the poly-yne to some extent. However, the lack of discernable resonances that could be attributed to end groups in the NMR spectra provides support for the view that there is high degree of polymerisation in these poly-yne.

Optical spectroscopy

The thin film absorption and emission spectra of the mononuclear platinum(II) diyne **3**, the dinuclear platinum(II) diyne **4** and the platinum(II) poly-yne **5** are compared in Fig. 1(a). In

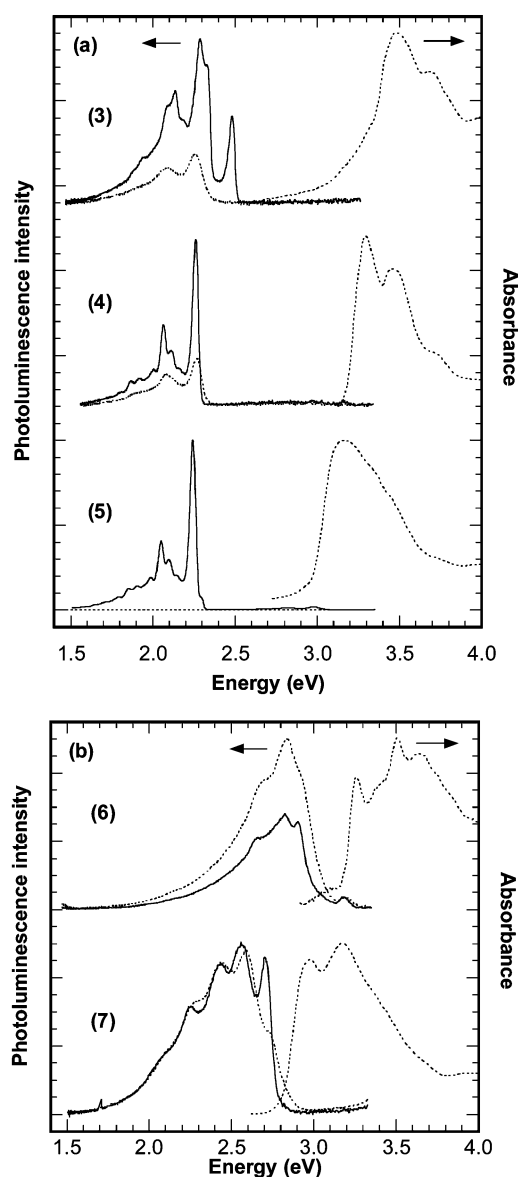


Fig. 1 Absorption spectra at 290 K (dotted line) and emission spectra at 290 K (dotted line) and at 10 K (solid line) taken from thin films. (a) platinum(II) diynes **3** and **4** and platinum(II) poly-yne **5** as indicated in the figure. (b) Organic diyne **6** and organic co-poly-yne **7** as indicated in the figure.

similar compounds^{14–21} the transitions giving rise to the first absorption band have a strong π - π^* character due to mixing particularly between the platinum 6p orbitals and the π^* orbitals of the ligand.

In Fig. 1(a), the peak of the first absorption band shifts by about 0.3 eV to the red from **3** to **5** which indicates an increase in conjugation. This suggests that the singlet excited state S_1 can extend through the platinum(II) site.

The low-temperature emission spectra of platinum(II) diynes and poly-yne typically show two emission bands, a fluorescence band just below the absorption band and a phosphorescence band about 0.7 eV lower.^{14–21} However, for the 9,9-dioctylfluorene spacer used here, fluorescence can be seen in the platinum(II)-poly-yne **5** at about 3.0 eV but not in the platinum(II) diynes **3** and **4**. The low-temperature phosphorescence spectra are dominated by a strong, narrow peak around 2.2–2.3 eV. For the mononuclear diyne **3**, there is an additional peak at 2.5 eV that disappears above 75 K. The fact that this peak has a different temperature dependence from the remainder of the band, coupled with the fact that it is not present in the dinuclear platinum(II) diyne **4** and the platinum(II) poly-yne **5**, suggest that it may have a different electronic origin that could be related to the relative orientations of rings along the chains. Recent research on poly-9,9-dioctylfluorene (PF8) **10** shown in Chart 2 has identified two electronic singlet S_1 states separated by about 0.1 eV,²⁵ which are assigned to two different phases of the homo-polymer. Further research will be needed to clarify whether in the mononuclear diyne **3** two separate triplet states are also caused by particular thin film morphologies.

Apart from this peak and the loss of vibronic structure, the room-temperature spectra are similar. In contrast to the diynes **3** and **4**, the phosphorescence of the poly-yne **5** is about three orders of magnitude lower at 290 K than at 10 K. This increase in non-radiative decay with temperature can be attributed to thermally activated diffusion of triplet excitons along the polymer chain, which can lead to triplet-triplet annihilation or an increased sampling of dissociation sites or non-radiative sites.

In Fig. 1(b), the absorption and emission spectra of the organic diyne **6** and the organic poly-yne **7** are compared. The 0–0 peak of the absorption spectrum shifts by about 0.3 eV to the red from the diyne **6** to the poly-yne **7**, which is the same shift as that observed for the platinum compounds and further supports the fact that the platinum compounds are well-conjugated even through the metal site. Because there is no metal-induced spin-orbit coupling in these organic analogues, only fluorescence can be seen. The 0–0 emission peak at 2.90 eV in the 10 K spectrum of the diyne **6** shifts to 2.71 eV in the poly-yne **7**. As for the analogous mononuclear platinum(II) diyne **3** a high energy emission peak in the organic diyne **6** is observed at 3.2 eV. Taking the red-shift between diyne and poly-yne into account, this feature would be expected to appear at about 2.9–3.0 eV in the poly-yne, yet as in platinum(II) poly-yne **5**, there is no such emission at that energy.

In order to make a systematic study of the optoelectronic properties of the poly-yne the materials to be investigated have been extended to form the set shown in Chart 2 including the related compounds **10**, **11** and **12**. This set allows a comparison to be made between the platinum(II) poly-yne and the organic co-poly-yne, in addition to a study the effect of substitution at C-9.

The absorption and room temperature photoluminescence (PL) spectra of the organic and platinum(II) poly-yne are shown in Fig. 2. The related homo-polymer **10** is included in Fig. 2 (a and b) to facilitate a comparison with the platinum(II) poly-yne. The platinum(II) poly-yne **5** and **11** both show two emission bands, one centred around 2.95 eV and one centred around 2.2 eV. At room temperature, the lower-energy band is more pronounced for **11** than for **5**. The positions of the high-energy emission band and of the first absorption band are slightly blue-shifted (by 0.05 eV) with respect to the organic polymer **10**. The vibronic peaks in emission shifts, so that the 0–0 peak is now the main peak rather than a shoulder as in **10**. This is typical for platinum(II)-poly-yne.¹⁹ The absorption and emission of the platinum(II) fluorenone poly-yne **12** are shifted by 0.7 eV with respect to **10**. As for the organic analogue **9**, the emission is unstructured at room temperature. The first absorption band centred at 2.5 eV is of much lower intensity

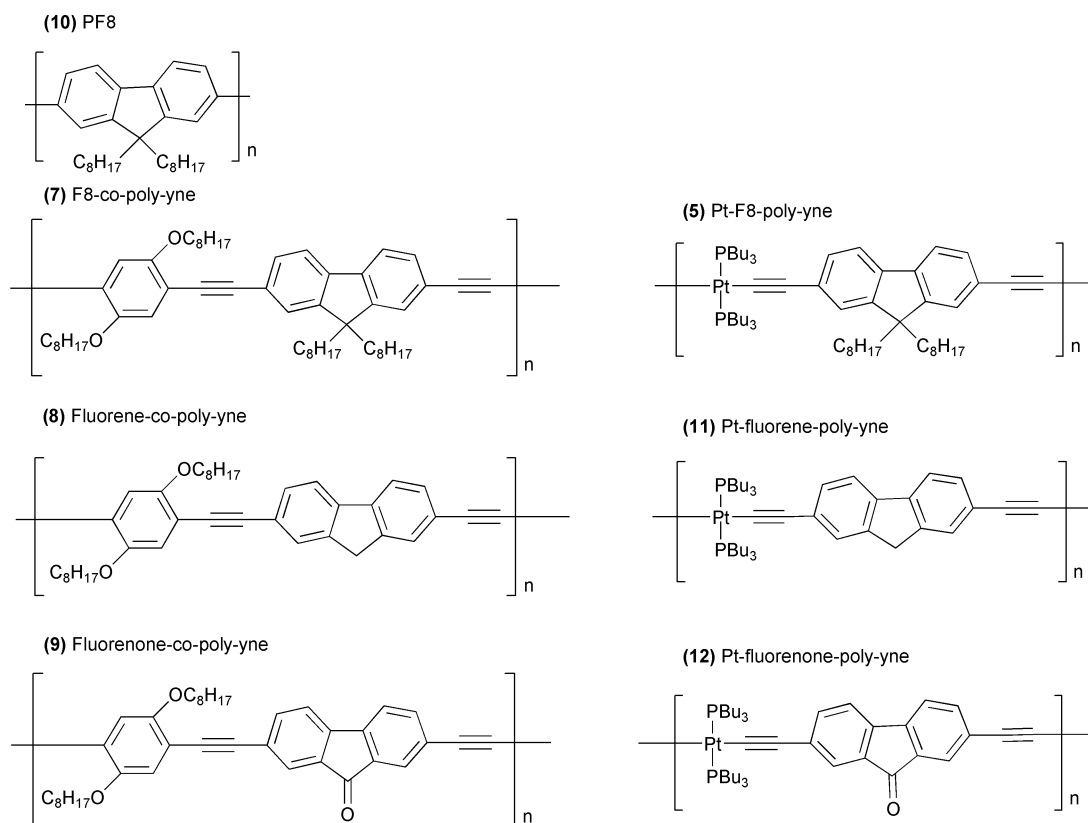


Chart 2 The chemical structures and compound numbers of the platinum(II) and analogous organic poly-ynes.

than the second absorption band centred at 3.2 eV. The photoluminescence quantum yields measured at room temperature for these four polymers are: **10** ($60 \pm 20\%$) (as before); **5** ($0.6 \pm 0.2\%$); **11** ($0.4 \pm 0.2\%$); **12** ($0.4 \pm 0.2\%$).

The absorption and PL spectra of the organic co-polymers are shown in Fig. 2(b). When moving from the homopolymer **10** to the copolymer **7** a small red-shift of 0.15 eV in the onset of absorption and photoluminescence and an increased vibronic structure in the first absorption band is observed. Omitting the alkyl side-chains at C-9 as for fluorenyl co-poly-yne **8** leads to an increased red-shift of 0.5 eV of absorption and emission with respect to **10** and to a loss of vibronic structure in emission. The emission from the fluorene-9-onyl co-poly-yne **9** obtained by derivatisation at C-9 of the fluorene ring is similarly unstructured and further red-shifted with respect to **10** (by 0.7 eV) and it has a pronounced low-energy shoulder in the absorption. The thin film PL quantum yield efficiencies measured at room temperature for these four polymers are: **10** ($60 \pm 20\%$); **7** ($30 \pm 10\%$); **8** ($3 \pm 1\%$); **9** ($3 \pm 1\%$).

It is instructive to consider the temperature dependence of PL for the seven polymers studied. For **10**, the intensity of the first vibronic peak increases with decreasing temperature. This is accompanied by an overall red-shift of the emission. These same trends are also observed for the co-poly-yne **7**. The other two co-poly-ynes, **8** and **9**, show hardly any change in emission with temperature except for a slight red-shift at low temperature. For the platinum(II) poly-ynes **5** and **11** the intensity of the low-energy band increases by almost three orders of magnitude with decreasing temperature, and the intensity of the high-energy band increases by up to one order of magnitude as shown in Figs. 2 (c) and (d). The lower-energy emission also shows a well-resolved vibronic structure at low temperature. For **5**, the relative weights of the vibronic bands remain constant with temperature, only the resolution improves, while for **11**, the spectral shape of the emission changes between the spectra at 300 and 200 K and compared to

those in the range 100–10 K. The emission of the platinum(II) fluorenone poly-yne **12** shows only a slight red-shift and an increased structure at lower temperature.

Previous studies^{14,19} have shown that the inclusion of a heavy transition metal, such as platinum, into the backbone of an organic poly-yne increases spin–orbit coupling so that triplet state emission (phosphorescence) can be observed. The T_1 triplet state is typically found to be 0.7 ± 0.1 eV below the S_1 singlet state. Comparison of the organic co-poly-ynes **7** and **8** with the platinum(II) poly-ynes **5** and **11** (Fig. 2) shows that this is also the case here. The low energy emission in **5** and **11** has a strong temperature dependence and a high degree of vibronic structure at low temperature, and is 0.7 eV below the S_1 singlet emission (fluorescence) for both polymers. Thus by comparison with other similar polymers this emission is assigned to the T_1 triplet state (phosphorescence). The strong spin–orbit coupling induced by the platinum atoms causes strong inter-system crossing from the S_1 state to the T_1 state. Since the non-radiative decay rate from the T_1 triplet state is equal or larger than the radiative decay rate¹⁴ the PL quantum efficiencies of the platinum(II) poly-ynes are reduced from those observed for the organic polymers.

By comparing polymer **7** with **8**, and **5** with **11**, the effect of side-chains on the emission and absorption spectra can be studied, since the main backbone, which determines the intrachain properties of the polymers, is the same in each of these pairs. The loss of vibronic structure even at low temperature in **8** compared to **7** [Fig. 2(b)] along with the reduction of PL quantum yield by a factor of 10 and the associated red-shift all point to a strong inter-chain interaction. We therefore attribute the emission in **8** to inter-chain excited states such as excimers or aggregates.

Similarly, the vibronic structure at 300 and 200 K for **11** [Fig. 2(d)] is different from that in **5** [Fig. 2(c)], which could indicate inter-chain interactions. Such interactions will be weaker here than in **8** as the butyl side-chains on the Pt atoms help to decrease aggregation effects.

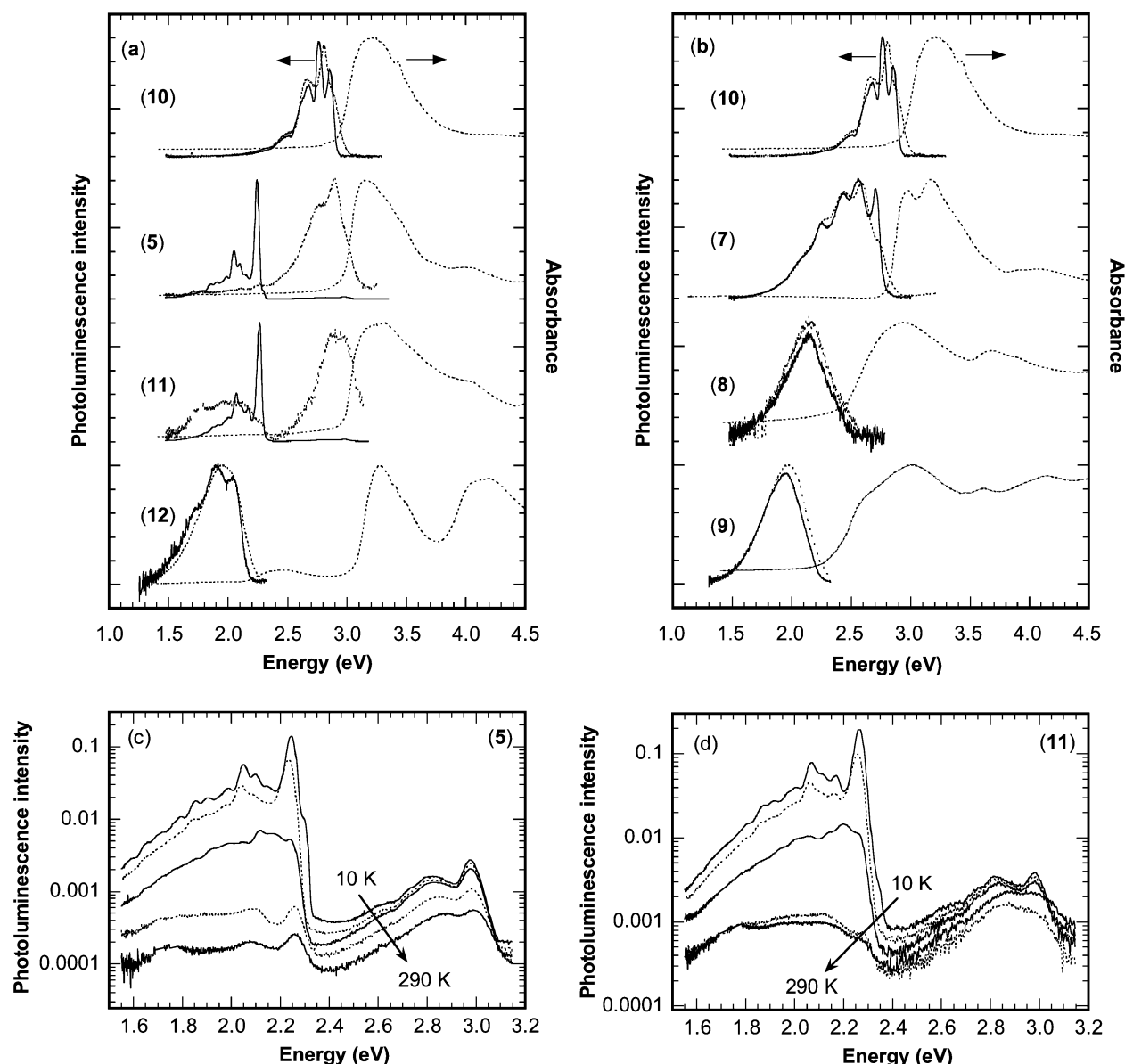


Fig. 2 Absorption spectra at 290 K (dotted line) and emission spectra at 290 K (dotted line) and at 10 K (solid line) taken from thin films for (a) platinum(II) poly-ynes **5**, **11**, **12** and (b) organic co-poly-ynes **7**, **8**, **9**. The spectra for **10** are included in both panels for comparison. All spectra show the correct relative emission intensities except in the case of compounds **5** (and **11**) which are normalised to unity at the emission peak. The emission spectra with the correct relative emission intensities at 290, 200, 100, 50 and 10 K for compounds **5** and **11** are shown in (c) and (d), respectively, on a logarithmic scale.

For both the organic co-poly-ynes and the platinum(II) poly-ynes, the inclusion of a fluorenyl unit in the backbone causes a significant red-shift in the absorption and emission spectra from the fluorene-containing polymers [compare **10** with **9** in Fig. 2(b); **10** with **12** in Fig. 2(a)]. This points to a strong donor–acceptor interaction between the electron-donating Pt fragment and the electron-accepting fluorenone spacer. The low intensity of the first absorption band is consistent with the charge-transfer nature of this transition.¹⁹

Crystal structure determinations of **2a** and **3**

In order to underpin the spectroscopic characterisations of the polymer precursors attempts were made to grow single crystals suitable for X-ray diffraction studies on a number of the key molecules along the reaction route to polymer formation. These attempts were successful for compounds **2a** and **3**, and single-crystal X-ray analyses were undertaken.

The molecular structure of 2,7-bis(trimethylsilylethynyl)-9,9-dioctylfluorene **2a** is illustrated in Fig. 3, which includes the atomic numbering scheme. As expected from the spectroscopic

studies the molecular geometry of the backbone is very similar to that of the unsubstituted compound 2,7-bis(trimethylsilylethynyl)fluorene.^{27a} Selected bond parameters are presented in Table 1. The central fluorenyl unit is essentially planar, with the linear Me₃SiC≡C groups occupying the 2 and 7 positions. The geometry about the Si atoms is distorted tetrahedral, and the two carbon–carbon triple bonds have an average C–C distance of *ca.* 1.21 Å, typical for that found in terminal acetylides.³⁷ In **2a** the two octyl groups lie on opposite sides of the plane of the fluorenyl unit, and while one chain extends perpendicular to the central backbone the other chain bends around to lie close to the SiMe₃ group centred on Si(2). Both the chains and the trimethylsilyl groups are subject to considerable positional disorder and the structure was modelled using two sites for the silicon atoms and the majority of the carbon atoms in the chains, with the occupancies summing to unity. It is this disorder that is responsible for the relatively high residual *R* factor at the end of the structure refinement process; however, the overall molecular conformation has been established unambiguously.

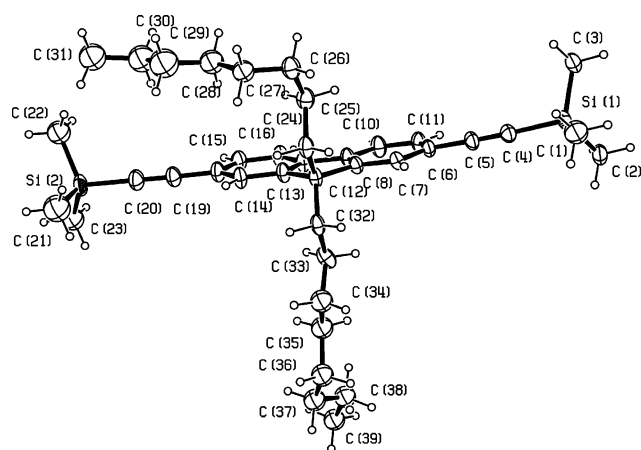


Fig. 3 The molecular structure of **2a** showing the atom numbering scheme. Only one orientation of the disordered chains is shown for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for compound **2a**

Si(1)–C(1)	1.877(8)	Si(1)–C(2)	1.853(4)
Si(1)–C(3)	1.857(4)	Si(1)–C(4)	1.831(4)
C(4)–C(5)	1.208(5)	C(5)–C(6)	1.452(5)
C(6)–C(7)	1.395(5)	C(7)–C(8)	1.382(5)
C(8)–C(9)	1.400(5)	C(6)–C(11)	1.382(5)
C(8)–C(12)	1.527(5)	C(9)–C(10)	1.380(5)
C(9)–C(18)	1.463(5)	C(10)–C(11)	1.386(5)
C(12)–C(24)	1.535(5)	C(12)–C(13)	1.534(5)
C(12)–C(32)	1.549(5)	C(13)–C(18)	1.385(5)
C(13)–C(14)	1.385(5)	C(14)–C(15)	1.411(5)
C(15)–C(16)	1.394(5)	C(15)–C(19)	1.441(5)
C(16)–C(17)	1.382(5)	C(17)–C(18)	1.400(5)
C(19)–C(20)	1.205(5)	Si(2)–C(20)	1.822(4)
Si(2)–C(21)	1.826(7)	Si(2)–C(22)	1.874(7)
Si(2)–C(23)	1.856(6)		
Si(1)–C(4)–C(5)	177.8(3)	C(4)–C(5)–C(6)	178.3(4)
C(8)–C(12)–C(13)	100.1(3)	C(8)–C(12)–C(24)	112.4(3)
C(8)–C(12)–C(32)	111.0(3)	C(24)–C(12)–C(32)	109.3(3)
C(15)–C(19)–C(20)	178.4(4)	C(19)–C(20)–Si(2)	177.6(4)

An analysis of the intermolecular contacts within the crystal lattice of **2a** shows no strong intermolecular interactions. The shortest contacts involve the C(4)–C(5) triple bond and a hydrogen atom, H(1F), from a methyl group on an adjacent molecule. The C(4)···H(1F) and C(5)···H(1F) distances are 2.85 and 2.98 Å, respectively. From the packing diagrams there is little indication of the long alkyl chains interdigitating between adjacent molecules.

The molecular structure of the mononuclear platinum(II) diene **3** is illustrated in Fig. 4 that includes the atom numbering scheme adopted. Selected bond lengths and angles are listed in Table 2. The molecule sits on a crystallographic centre of symmetry that is coincident with the platinum atom, Pt(1). This metal exhibits the expected *trans* square planar geometry, as is found in related platinum poly-yne molecules.^{17,38} The Pt(1)–P(1) distance of 2.2987(12) Å lies at the longer end of the expected range for platinum–phosphine interactions and reflects the steric bulk of the *n*-butyl substituents.³⁸ The platinum–alkynyl σ -interaction is also within the normal range, with the Pt(1)–C(1) distance of 2.007(4) Å. The ethynylene unit is linear [Pt(1)–C(1)–C(2), 176.9(4) and C(1)–C(2)–C(13), 178.8(5)°] and the C(1)–C(2) bond is of a similar length, at 1.202(6) Å, to that found in the precursor compound **2a**. Similarly, the fluorenyl unit is essentially planar and the bond parameters do not show significant differences to those observed in **2a** and in the unsubstituted compound, 2,7-bis(trimethylsilylethynyl)fluorene.^{27a} The conformation of the octyl chain substituents at C-9 of the central ring of the fluorene are also similar to that observed for **2a**. The two chains lie on

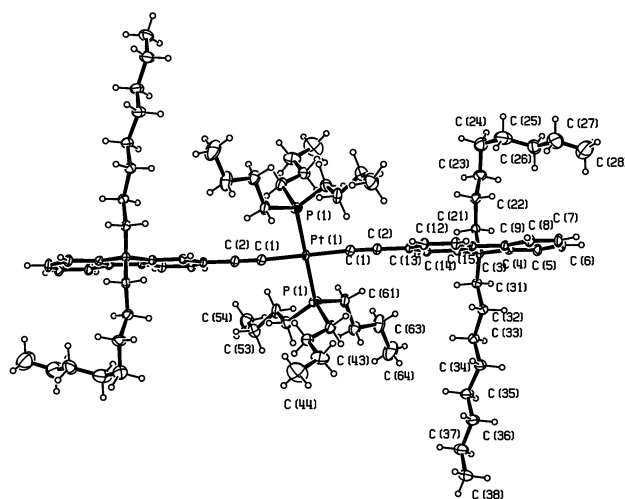


Fig. 4 The molecular structure of **3** showing the atom numbering scheme.

Table 2 Selected bond lengths (Å) and angles (°) for compound **3**

Pt(1)–C(1)	2.007(4)	Pt(1)–P(1)	2.2987(12)
C(1)–C(2)	1.202(6)	C(2)–C(13)	1.440(5)
C(3)–C(4)	1.531(5)	C(3)–C(31)	1.541(6)
C(3)–C(15)	1.523(5)	C(4)–C(5)	1.389(6)
C(5)–C(6)	1.399(6)	C(4)–C(9)	1.398(6)
C(7)–C(8)	1.387(6)	C(8)–C(9)	1.397(6)
C(9)–C(10)	1.472(5)	C(10)–C(11)	1.382(5)
C(10)–C(15)	1.403(5)	C(11)–C(12)	1.389(6)
C(12)–C(13)	1.409(6)	C(13)–C(14)	1.408(6)
C(14)–C(15)	1.387(5)		
C(1)–Pt(1)–C(13a)	180.0	C(1)–Pt(1)–P(1)	86.79(13)
C(1a)–Pt(1)–P(1)	93.21(13)	P(1)–Pt(1)–P(13a)	180.0
Pt(1)–C(1)–C(2)	176.9(4)	C(1)–C(2)–C(13)	178.8(5)
C(4)–C(3)–C(15)	101.0(3)	C(4)–C(3)–C(21)	110.6(3)
C(15)–C(3)–C(21)	111.8(3)		

Symmetry transformation used to generate equivalent atoms: 3a $-x - 1, -y + 1, -z + 1$.

opposite sides of the fluorenyl plane, but while the chain C(32)–C(38) extends perpendicular to the ring plane, the second chain C(21)–C(28), shows a significant bend at C(24) and the carbon atoms C(24)–C(28) lie almost parallel to the six-membered ring C(4)–C(9). While the atoms in the octyl chains and in the *n*-butyl groups show relatively high displacement parameters the disorder is not as severe as in **2a** and the structure was refined without resorting to a disordered model.

As in **2a** there are no short intermolecular interactions when the intermolecular contacts in the crystal lattice of **3** are analysed. In addition, the bulky *n*-butyl phosphines shield the acetylenic C–C triple bonds from hydrogen-bond contacts.

Conclusion

We have shown that the soluble π -conjugated platinum(II)-poly-yne **5**, organic poly-ynes **7–9** and their low molecular weight model diene compounds **3, 4, 6** containing derivatised fluorenes in the backbone can be prepared by polycondensation and cross-coupling reactions. The poly-ynes are easily processable from organic solvents and exhibit good film-forming properties. Fluorescence and phosphorescence spectra of the poly-ynes **5, 7, 8, 9, 11** and **12** have been assigned. The inclusion of side-chains has been shown to prevent aggregation. A strong red-shift has been achieved when a fluorenone spacer was introduced into the poly-yne unit.

Experimental

General procedures

All reactions were performed under a dry argon atmosphere using standard Schlenk or glove box techniques. Solvents were pre-dried and distilled before use by standard procedures.³⁹ All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and used as received. The compounds *trans*-[(Ph)(PEt₃)₂PtCl]₂,⁴⁰ *trans*-[(PⁿBu₃)₂PtCl₂]₂⁴¹ and 1,4-diiodo-2,5-bis(octyloxy)benzene⁴² were prepared *via* literature procedures. PF8 **10** was synthesised at the Cambridge Display Technology (CDT) *via* a Suzuki coupling reaction.⁴³ The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in CDCl₃. The ¹H and ¹³C{¹H} NMR spectra were referenced to solvent resonances and ³¹P{¹H} NMR spectra were referenced to external trimethylphosphite. IR spectra were recorded as CH₂Cl₂ solutions, in a NaCl cell, on a Perkin-Elmer 1710 FT-IR spectrometer, mass spectra on a Kratos MS 890 spectrometer by the electron impact (EI) and fast atom bombardment (FAB) techniques. Microanalyses were performed in the University Chemical Laboratory, University of Cambridge. Preparative TLC was carried out on commercial Merck plates with a 0.25 mm layer of silica. Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II-III).

Molecular weight measurements

Molar masses were determined by the GPC method⁴⁴ using two PL Gel 30 cm, 5 micron mixed C columns at 30 °C running in THF at 1 cm³ min⁻¹ with a Roth Mocol 200 high precision pump. A DAWN DSP (Wyatt Technology) Multi-Angle Laser Light Scattering (MALLS) apparatus with 18 detectors and auxiliary Viscotek model 200 differential refractometer/viscometer detectors was used to calculate the molecular weights (referred to as GPC LS).

Optical characterisation

All polymers dissolved readily in dichloromethane with gentle heating to 40 °C in a closed vial. Films for use in absorption and PL measurements were made by spin-coating onto a disc of Spectrosil B at 1500 revs/minute using a conventional photoresist spin-coater, resulting in typical film thicknesses of 150 nm as measured on a Dektak profilometer. Absorption spectra were taken using a Hewlett-Packard UV-VIS spectrometer, over the range 190–1100 nm. PL spectra were taken by exciting the sample with the UV lines of an argon ion continuous wave (cw) laser (334, 335 and 365 nm) operating at a typical power of a few mW. The samples were held in a continuous-flow helium cryostat, with temperature control provided by an Oxford-Intelligent temperature controller-4 (ITC-4). The emitted light was collected by an optical fibre and measured using an Oriol Spectrograph and a cooled CCD array. The emission was corrected for the spectral response of the detection system. For low luminescence intensities, second order scatter of the excitation lines occurring around 1.7 eV becomes noticeable and was subtracted from the data. PL quantum yields for excitation with the UV lines of the argon ion laser were calculated using the integrating sphere technique.⁴⁵

X-Ray crystallography

Data for compounds **2a** and **3** were collected on an Enraf Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling apparatus. Semi-empirical absorption corrections based on interframe scaling were applied. The structures were solved by direct methods (for **2a**) and heavy atom methods (for **3**) and subsequent Fourier difference syntheses (SHELX 86)⁴⁶ and refined by full-matrix least-squares on *F*² (SHELXL 97).⁴⁷ Hydrogen atoms were placed in

Table 3 Crystallographic data for compounds **2a** and **3**

Compound	2a	3
Molecular formula	C ₃₉ H ₅₈ Si ₂	C ₈₆ H ₁₃₆ P ₂ Pt
<i>M</i>	583.03	1426.98
Crystal system	Triclinic	Monoclinic
<i>a</i> /Å	10.1696(2)	9.1636(3)
<i>b</i> /Å	14.1102(2)	26.4658(18)
<i>c</i> /Å	14.4029(3)	16.5754(12)
<i>α</i> /°	68.2370(10)	90
<i>β</i> /°	89.3960(10)	95.231(4)
<i>γ</i> /°	83.8980(10)	90
<i>U</i> /Å ³	1907.63(6)	4003.2(4)
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> ₂ / <i>c</i>
<i>Z</i>	2	2
<i>D</i> _c /Mg m ⁻³	1.015	1.184
μ /mm ⁻¹	0.116	1.833
Temperature/K	150(2)	170(2)
Data collection range/ θ	2.93 < θ < 27.5	3.78 < θ < 27.47
Reflections measured	46744	27296
Independent reflections	8639 (<i>R</i> _{int} = 0.074)	9117 (<i>R</i> _{int} = 0.041)
Parameters, restraints	323, 19	408, 0
<i>wR</i> 2 (all data) ^a	0.3348	0.109
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] ^b	0.0976	0.0457

^a Data in common: Graphite-monochromated Mo-K α radiation, λ = 0.71073 Å. ^b *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, *wR*2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, *w* = $1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, *P* = $(F_o^2 + 2F_c^2)/3$, where *x* and *y* are constants adjusted by the program. Goodness-of-fit = $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

geometrically-idealised positions and refined using a riding model. In the structure of **2a** the octyl chains and the trimethylsilyl groups exhibited severe positional disorder, and where second positions could be found for the disordered atoms these were refined as a pair, with the occupancies summed to unity, and assigned isotropic displacement parameters. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. Crystal data and refinement details are summarised in Table 3.

CCDC reference numbers 193884 and 193885.

See <http://www.rsc.org/suppdata/dt/b2/b208963g/> for crystallographic data in CIF or other electronic format.

Ligand synthesis

2-Bromo-9,9-dioctylfluorene 1. 2-Bromofluorene (10.0 g, 41.0 mmol) was reacted with 1-bromooctane (18.2 g, 94.3 mmol) in a two-phase system composed of 90 mL of toluene and 90 mL of 50 wt% aqueous NaOH using tetra(*n*-butyl)ammonium bromide as the phase transfer catalyst at 60 °C for 4 h. After diluting the reaction mixture with ethyl acetate, the organic layer was washed with water several times to remove excess NaOH. The organic layer was separated and dried with anhydrous MgSO₄. The solvent mixture was pumped off and the residue was subjected to silica column chromatography using hexane as the eluent. A colourless oil was obtained (16.4 g, 85% yield) which was identified as the title compound. ¹H NMR (250 MHz, CDCl₃): δ 7.53 (d, 1H, H-5), 7.46 (d, 1H, H-4), 7.44 (m, 2H, H_{1,8}), 7.35 (m, 3H, H_{3,6,7}), 1.91 (m, 4H), 1.26–1.05 (m, 20H), 0.81 (t, 6H), 0.52 (m, 4H). ¹³C NMR (100.6 MHz, CDCl₃): δ 152.44 (C₁₀), 150.5 (C₁₃), 141.6 (C₁₂), 140.3 (C₁₁), 131.1–119.97 (C_{1 to 8}), 55.1 (C₉), 40.3, 33.9–22.5 (CH₂), 14.0 (CH₃). EI-mass spectrum: *m/z* 469.6 (*M*⁺). Calc. for C₂₉H₄₁Br: C, 74.18; H, 8.80. Found: C, 74.22; H, 8.89%.

2-Trimethylsilylethynyl-9,9-dioctylfluorene 1a. To a solution of 2-bromo-9,9-dioctylfluorene (2 g, 4.25 mmol) in 70 mL of diisopropylamine–THF (1 : 1, v/v) under argon was added a catalytic mixture of CuI (10 mg), Pd(OAc)₂ (10 mg) and PPh₃ (30 mg). The solution was stirred for 20 min at 50 °C and then trimethylsilylethyne (0.62 g, 6.4 mmol) was added and the mixture stirred for another 20 min. The reaction temperature was then raised to 75 °C and left at reflux with stirring for 20 h.

The completion of the reaction was determined by silica TLC and IR spectroscopy. The solution was allowed to cool down to room temperature, filtered and the solvent mixture was removed. The residue was subjected to silica column chromatography using hexane-CH₂Cl₂ (1 : 1) as eluant to afford **1a** as a colourless liquid in 87% yield (1.80 g). IR (CH₂Cl₂): ν/cm^{-1} 2152 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 7.65 (dd, 1H, H₅), 7.60 (d, 1H, H₄), 7.43 (m, 2H, H_{1,8}), 7.30 (m, 3H, H_{3,6,7}), 2.15–1.01 (m, 24H, CH₂ × 12), 0.83 (t, 6H, CH₃ × 2), 0.52 (m, 4H), 0.27 (s, 9H, SiMe₃). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.0 (C₁₀), 150.5 (C₁₃), 141.6 (C₁₂), 140.3 (C₁₁), 131.1–119.97 (C_{1 to 8}), 106.3 (C≡C), 93.7 (C≡C), 55.1 (C₉), 40.3, 33.9–22.5 (CH₂), 14.0 (CH₃), 0.049 (SiMe₃). EI-mass spectrum: m/z 486.8 (*M*⁺). Calc. for C₃₄H₅₀Si: C, 83.88; H, 10.35. Found: C, 84.02; H, 10.29%.

2-Ethynyl-9,9-dioctylfluorene 1b. 2-Trimethylsilylethynyl-9,9-dioctylfluorene (**1a**) (2.0 g, 4.10 mmol) was protodesilylated in THF-methanol (50 cm³, 4 : 1, v/v) using aqueous KOH (0.5 g, 8.9 mmol in 1 cm³ water). The reaction mixture was stirred at room temperature for 2 h during which period IR and TLC revealed that all protected compound had been converted to the terminal alkyne ligand. The solvent was then removed and the residue was dissolved in CH₂Cl₂ and subjected to column chromatography on silica using hexane-CH₂Cl₂ (1 : 1, v/v) as eluant to afford a light yellow viscous liquid identified as **1b** (1.29 g, 76%). IR (CH₂Cl₂): ν/cm^{-1} 2107 (C≡C-), 3299 (C≡C-H). ¹H NMR (250 MHz, CDCl₃): δ 7.66 (dd, 1H, H₅), 7.63 (d, 1H, H₄), 7.45 (m, 2H, H_{1,8}), 7.34 (m, 3H, H_{3,6,7}), 3.12 (s, 1H, C≡C-H), 2.18–1.04 (m, 24H), 0.85 (t, 6H), 0.54 (m, 4H). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.2 (C₁₀), 150.7 (C₁₃), 141.7 (C₁₂), 140.5 (C₁₁), 130.4–120.37 (C_{1 to 8}), 85.8 (C≡C), 76.7 (C≡C), 55.1 (C₉), 40.3, 34.6–22.9 (CH₂), 14.4 (CH₃). EI-mass spectrum: m/z 414.6 (*M*⁺). Calc. for C₃₁H₄₂: C, 89.79; H, 10.21. Found: C, 89.82; H, 10.11%.

2,7-Dibromo-9,9-dioctylfluorene 2. 2,7-Dibromofluorene (3.24 g, 10.00 mmol) was reacted with 1-bromooctane (8.23 g, 42.60 mmol) in 25 mL of toluene and 25 mL of 50 wt% aqueous NaOH using tetra(*n*-butyl)ammonium bromide as the phase transfer catalyst at 80 °C for 4 h. The reaction was maintained at 90 °C for a further 20 h period. A yellowish-green solution was obtained in the organic phase after cooling to room temperature. After diluting the reaction mixture with ethyl acetate, the organic layer was washed with water several times to remove excess NaOH. The organic layer was separated and dried over anhydrous MgSO₄. The solvent mixture was stripped off. The residue was dissolved in CH₂Cl₂ and subjected to column chromatography on silica using hexane as eluent to afford a white solid. Recrystallisation from ethanol afforded analytically pure sample as colourless crystals (4.11 g, 75% yield). Mp: 46–47 °C. ¹H NMR (CDCl₃, 250 MHz): δ 7.53 (d, 2H, *J* = 7.7 Hz), 7.46 (d, 2H, *J* = 1.8 Hz), 7.44 (d, 2H, *J* = 1.1 Hz), 1.91 (m, 4H, *J* = 3.7 Hz), 1.26–1.05 (m, 20 H), 0.83 (t, 6H, *J* = 3.6 Hz), 0.58 (m, 4H, *J* = 3.5 Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ 152.44, 138.94, 130.04, 126.07, 121.38, 120.96, 55.56, 40.02, 31.63, 29.78, 29.04, 29.01, 23.51, 22.47, 13.94. EI-mass spectrum: m/z 548 (*M*⁺). Anal. calc. for C₂₉H₄₀Br₂: C, 63.49; H, 7.35. Found: C, 63.95; H, 7.30%.

2,7-Bis(trimethylsilylethynyl)-9,9-dioctylfluorene 2a. 2,7-Dibromo-9,9-dioctylfluorene (2 g, 3.65 mmol), trimethylsilylethyne (0.89 g, 9.1 mmol) and ^tPr₂NH-THF (70 mL, 1 : 1) were mixed with catalytic amounts of CuI (8 mg), Pd(OAc)₂ (9 mg) and PPh₃ (25 mg) at room temperature. The temperature was then slowly increased and the reaction mixture was refluxed for 16 h. The solvent was stripped off under reduced pressure. The residue was passed through a short column of silica gel using toluene as the eluent. Evaporation of the solvent led to a brown oil, which crystallised upon standing. Double recrystallisation from ethanol gave 1.53 g (yield: 72%) of **2a** as white crystals. Mp: 89.3–89.9 °C. IR (CH₂Cl₂): ν/cm^{-1} 2149 (C≡C-).

¹H NMR (250 MHz, CDCl₃): δ 7.58 (dd, 2H, H_{4,5}), 7.44 (dd, 2H, H_{3,6}), 7.41 (brs, 2H, H_{1,8}), 1.92 (m, 4H), 1.21–1.01 (m, 20H), 0.83 (t, 6H), 0.53 (m, 4H), 0.18 (s, 18H, SiMe₃ × 2). ¹³C NMR (100.6 MHz, CDCl₃): δ 150.91 (C-10,13), 140.83 (C-11,12), 131.20 (C_{1,8}), 126.19, 121.76, 119.79 (C_{2 to 7}), 106.07 (C≡C), 94.21 (C≡C), 55.21 (C-9), 40.30, 31.75–22.56 (CH₂), 14.04 (CH₃), 0.17 (SiMe₃). EI-mass spectrum: m/z 582.8 (*M*⁺). Calc. for C₃₉H₅₈Si₂: C, 80.36; H, 10.03. Found: C, 80.27; H, 10.08%.

2,7-Bis(ethynyl)-9,9-dioctylfluorene 2b. Methanol (45 mL and aqueous potassium hydroxide (4 mL, 20%) were added at room temperature to a stirred solution of **2a** (2.54 g, 4.36 mmol) in THF (80 mL). The reaction mixture was left at room temperature for 10 h. The solvent mixture was stripped off to obtain a viscous liquid, which was then purified by silica gel column chromatography using hexane as the eluent followed by recrystallisation in ethanol to give 1.55 g (yield: 82%) of **2b** as light yellow microcrystals. Mp: 36.0–36.5 °C. IR (CH₂Cl₂): ν/cm^{-1} 2107 (C≡C-), 3299 (C≡C-H). ¹H NMR (250 MHz, CDCl₃): δ 7.61 (dd, 2H, H_{4,5}), 7.46 (dd, 2H, H_{3,6}), 7.44 (brs, 2H, H_{1,8}), 3.14 (s, 2H, C≡C-H), 1.94 (m, 4H), 1.26–1.04 (m, 20H), 0.89 (t, 6H), 0.56 (m, 4H). ¹³C NMR (100.6 MHz, CDCl₃): δ 151.03 (C_{10,13}), 140.97 (C_{11,12}), 131.21 (C_{1,8}), 126.53, 120.82, 119.93 (C_{2 to 7}), 84.50 (C≡C), 76.98 (C≡C), 55.18 (C₉), 40.17, 31.73–22.54 (CH₂), 14.02 (CH₃). EI-mass spectrum: m/z 438.67 (*M*⁺). Calc. for C₃₃H₄₂: C, 90.34; H, 9.65. Found: C, 90.21; H, 9.59%.

Platinum(II) diyne and poly-yne preparations

Trans-[(Bu₃P)₂Pt-(C≡C-R)₂] (R = 9,9-dioctylfluorene-2-yl) 3. To a stirred solution *trans*-[(PBu₃)₂PtCl₂] (0.335 g, 0.5 mmol) and (**1b**) (0.41 g, 1.0 mmol) in CH₂Cl₂-Pr₂NH (50 cm³, 1 : 1 v/v) under nitrogen was added a catalytic amount (~5 mg) of CuI. The yellow solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and passed through a silica column eluting with hexane-CH₂Cl₂ (1 : 1, v/v). Removal of the solvents *in vacuo* gave the title complex as a bright yellow solid in 70% yield (0.49 g). IR (CH₂Cl₂): ν/cm^{-1} 2095. ¹H NMR (250 MHz, CDCl₃): δ 7.60 (dd, 2H), 7.52 (d, 2H), 7.30–7.20 (m, 10H), 2.25–1.00 (m, 84H), 0.94 (t, 12H), 0.81 (t, 18H, PCH₃), 0.65 (m, 8H). ¹³C NMR (100 MHz, CDCl₃): δ 150.69 (C₁₀), 150.25 (C₁₃), 141.24 (C₁₂), 138.09 (C₁₁), 129.53–119.07 (C_{1 to 8}), 107.97 (C≡C), 54.73 (C₉), 40.55, 33.99–22.56 (CH₂), 14.04 (CH₃), 13.83 (CH₃). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ -138.07 (¹J_{Pt-P} = 2633 Hz). FAB-mass spectrum: m/z 1427.038 (*M*⁺). Calc. for C₈₆H₁₃₆P₂Pt: C, 72.38; H, 9.60. Found: C, 72.44; H, 9.58%.

Trans-[(Ph)(Et₃P)₂Pt-C≡C-R-C≡C-Pt(PEt₃)₂(Ph)] (R = 9,9-dioctylfluorene-2,7-diyl) 4. This compound was synthesised by adopting a similar procedure as in **3** using **2b** (0.22 g, 0.50 mmol) and *trans*-[(PEt₃)₂(Ph)PtCl] (0.543 g, 1.0 mmol). The product was purified on preparative TLC plates with hexane-CH₂Cl₂ (30 : 70, v/v) as eluant giving compound **4** as a red viscous liquid in an isolated yield of 65% (0.47 g). IR (CH₂Cl₂): ν/cm^{-1} 2095 (C≡C-). ¹H NMR (250 MHz, CDCl₃): δ 7.53 (d, 2H, H-4,5), 7.41 (d, 2H, H-3,6), 7.32 (m, 4H, H_{ortho} of Ph), 7.26 (m, 2H, H-1,8), 6.96 (t, 4H, H_{meta} of Ph), 6.80 (t, 2H, H_{para} of Ph), 1.82–1.75 (m, 28H, CH₂), 1.25–1.05 (m, 24H, PCH₂), 0.86 (t, 6H, CH₃), 0.82 (t, 36H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 156.43 (C_{10,13}), 150.41 (C_{11,12}), 139.20–118.69 (C_{1 to 8} and Ph Cs), 112.73, 111.56 (C≡C), 54.42 (C₉), 40.43–14.95 (CH₂ in C₈H₁₇ and Et₃P), 14.07 (CH₃ in C₈H₁₇), 8.04 (CH₃ in Et₃P). ³¹P{¹H} NMR (101.3 MHz, CDCl₃): δ -131.17 (¹J_{Pt-P} = 2643 Hz). FAB-mass spectrum: m/z 1453.63 (*M*⁺). Calc. for C₆₉H₁₁₀P₄Pt₂: C, 57.00; H, 7.62. Found: C, 56.96; H, 7.58%.

Trans-[(Bu₃P)₂Pt-C≡C-R-C≡C-], (R = 9,9-dioctylfluorene-2,7-diyl) 5. CuI (5 mg) was added to a mixture of *trans*-[Pt-

($\text{PBu}^n_3\text{Cl}_2$) (0.670 g, 1.0 mmol) and **2b** (0.438 g, 1.0 mmol) in $\text{Pr}_2\text{NH}-\text{CH}_2\text{Cl}_2$ (50 cm^3 , 1 : 1 v/v). The solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and passed through a short alumina column. After removal of the solvent by a rotary evaporator, an off-white film was obtained readily which was then washed with methanol to give the polymer **7** in 85% isolated yield (0.88 g). Further purification can be accomplished by precipitating the polymer solution in dichloromethane from methanol. IR (CH_2Cl_2): ν/cm^{-1} 2095 ($-\text{C}\equiv\text{C}-$). ^1H NMR (250 MHz, CDCl_3): δ 7.53 (d, 2H, $\text{H}_{4,5}$), 7.41 (s, 2H, $\text{H}_{1,8}$), 7.25 (d, 2H, $\text{H}_{3,6}$), 2.20–2.01 (m, 12H, PCH_2), 1.67–1.01 (m, 52H, CH_2), 0.93 (t, 18H), 0.82 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.28 ($\text{C}_{10,13}$), 137.89 ($\text{C}_{11,12}$), 129.56–118.76 ($\text{C}_{1\text{ to }8}$), 112.23, 111.16 ($\text{C}\equiv\text{C}$), 54.50 (C_9), 40.79–22.56 (CH_2), 14.05–13.83 (CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3): δ -138.03 ($^1J_{\text{P}-\text{P}} = 2363$ Hz). Calc. for ($\text{C}_{57}\text{H}_{94}\text{P}_2$) $_n$: C, 65.92; H, 9.31. Found: C, 65.77; H, 9.34%. GPC (THF): $M_n = 43550$ g mol^{-1} ($n = 42$), $M_w = 82745$ g mol^{-1} , PDI = 1.9.

Organic diyne and poly-yne preparations

$[\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2-\text{C}\equiv\text{C}-\text{R}^1]$ ($\text{R}^1 = 9,9$ -dioctylfluoren-2-yl; $\text{R}^2 = 2,5$ -dioctyloxybenzene-1,4-diyyl) **6**. To a mixture of **1b** (0.207 g, 0.5 mmol), 1,4-diiodo-2,5-dioctyloxybenzene (0.138 g, 0.25 mmol), CuI (5 mg), Pd(OAc) $_2$ (5 mg) and PPh_3 (15 mg) in a Schlenk flask, Pr_2NH (10 cm^3) and THF (30 cm^3) were added under nitrogen. The resulting mixture was refluxed with stirring for 20 h. Analysis by TLC and IR revealed that the reaction was complete. It was then filtered warm to remove the inorganic compounds. The filtrate was poured into an excess of methanol, and a bright yellow solid precipitated after cooling. The precipitate was collected and dissolved in CH_2Cl_2 (20 cm^3). Reprecipitation (twice) of the CH_2Cl_2 solution into methanol followed by silica column chromatography with hexane–dichloromethane (4 : 1, v/v) gave a yellow solid in 65% yield (0.19 g). IR (CH_2Cl_2): ν/cm^{-1} 2210 ($-\text{C}\equiv\text{C}-$). ^1H NMR (250 MHz, CDCl_3): δ 7.69–7.64 (m, 4H), 7.52–7.50 (m, 4H), 7.36 (m, 6H), 7.08 (t, 2H), 3.94 (t, 4H), 1.97–1.04 (m, 72H), 0.84 (t, 18H), 0.61 (m, 8H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 154.15 ($\text{C}_{2,5}$ benzene), 150.77 ($\text{C}_{10,13}$), 141.44 (C_{12}), 138.09 (C_{11}), 131.47–117.51 (other aryl carbons), 112.89, 111.16 ($\text{C}\equiv\text{C}$), 55.13 (C_9), 40.31, 31.76–22.57 (CH_2), 14.04 (CH_3). EI-mass spectrum: m/z 1157.768 (M^+). Calc. for $\text{C}_{84}\text{H}_{118}\text{O}_2$: C, 89.45; H, 10.54. Found: C, 89.57; H, 10.48%.

$[\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2-\text{C}\equiv\text{C}-]$ ($\text{R}^1 = 9,9$ -dioctylfluoren-2,7-diyyl; $\text{R}^2 = 2,5$ -dioctyloxybenzene-1,4-diyyl) **7**. A dried three-necked flask, equipped with condenser and magnetic stirring bar was charged with CuI (5 mg) and Pd(Ph_3P) $_4$ (20 mg), **2b** (0.219 g, 0.5 mmol) and 1,4-diiodo-2,5-dioctyloxybenzene (0.277 g, 0.5 mmol). The flask was evacuated and filled with nitrogen. Pr_2NH (20 cm^3) and THF (20 cm^3) were then added *via* syringe. The reaction mixture was stirred at 75 °C for 20 h. After the reaction mixture cooled to rt, the salt precipitate was removed by filtration and the solvents were pumped off. The residue was dissolved in CH_2Cl_2 and the solution was passed through a silica gel chromatographic column eluting with CH_2Cl_2 . The solvent was removed, and the resulting material was dissolved in CH_2Cl_2 (80 cm^3). The solution was added dropwise into methanol (250 cm^3) with vigorous stirring. The precipitate was collected and dried under vacuum. Yield: 0.32 g (85%). IR (CH_2Cl_2): ν/cm^{-1} 2202 ($-\text{C}\equiv\text{C}-$). ^1H NMR (250 MHz, CDCl_3): δ 7.72 (m, 2H), 7.50 (m, 4H), 7.01 (t, 2H), 3.94 (t, 4H), 2.01–1.05 (m, 48H), 0.85 (t, 12H), 0.60 (m, 4H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 153.95 ($\text{C}_{2,5}$ benzene), 150.86, 149.27, 141.39, 131.40, 126.71, 120.51–117.80, (other aryl carbons), 113.06, 112.43 ($\text{C}\equiv\text{C}$), 55.00 (C_9), 40.43, 31.58–22.36 (CH_2), 13.81 (CH_3). Calc. for ($\text{C}_{55}\text{H}_{76}\text{O}_2$) $_n$: C, 89.61; H, 10.39. Found: C, 89.76; H, 10.38%.

GPC (THF): $M_n = 19200$ g mol^{-1} ($n = 25$), $M_w = 32650$ g mol^{-1} , PDI = 1.7.

Poly-yne **8** and **9** were synthesised in an analogous manner.

$[\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2-\text{C}\equiv\text{C}-]$ ($\text{R}^1 =$ fluoren-2,7-diyyl; $\text{R}^2 = 2,5$ -dioctyloxybenzene-1,4-diyyl) **8**. Off-white solid (67% yield). IR (CH_2Cl_2): ν/cm^{-1} 2203 ($-\text{C}\equiv\text{C}-$). ^1H NMR (250 MHz, CDCl_3): δ 7.72 (m, 2H), 7.50 (m, 4H), 7.01–6.95 (m, 2H), 3.94 (m, 4H), 3.78 (s, 2H, CH_2), 1.82 (m, 4H), 1.53–1.27 (m, 20H), 0.85 (t, 6H). ^{13}C NMR (100.6 MHz, CDCl_3): δ 153.55 ($\text{C}_{2,5}$ benzene), 150.77, 149.34, 141.48, 131.50, 120.45–117.60, (other aryl carbons), 113.06, 112.43 ($\text{C}\equiv\text{C}$), 54.65 (C_9), 40.21, 31.46–22.25 (CH_2), 13.74 (CH_3). Calc. for ($\text{C}_{39}\text{H}_{44}\text{O}_2$) $_n$: C, 85.98; H, 8.14. Found: C, 85.74; H, 8.16%. GPC (THF): $M_n = 12000$ g mol^{-1} ($n = 22$), $M_w = 19150$ g mol^{-1} , PDI = 1.6.

$[\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2-\text{C}\equiv\text{C}-]$ ($\text{R}^1 =$ fluoren-9-on-2,7-diyyl; $\text{R}^2 = 2,5$ -dioctyloxybenzene-1,4-diyyl) **9**. Red solid (84% yield). IR (CH_2Cl_2): ν/cm^{-1} 2202 ($-\text{C}\equiv\text{C}-$), 1715 ($\text{C}=\text{O}$). ^1H NMR (250 MHz, CDCl_3): δ 7.49 (m, 2H), 7.30 (m, 4H), 7.01–6.94 (m, 2H), 3.91 (m, 4H), 1.80 (m, 4H), 1.51–1.23 (m, 20H), 0.82 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.20 ($\text{C}=\text{O}$), 153.35 ($\text{C}_{2,5}$ benzene), 143.34, 138.28, 134.28, 128.41, 124.23, 120.45 (other aryl carbons), 103.65, 96.56 ($\text{C}\equiv\text{C}$), 31.80–22.64 (CH_2), 14.06 (CH_3). Calc. for ($\text{C}_{39}\text{H}_{42}\text{O}_3$) $_n$: C, 83.83; H, 7.58. Found: C, 84.02; H, 7.49%. GPC (THF): $M_n = 9500$ g mol^{-1} ($n = 17$), $M_w = 17100$ g mol^{-1} , PDI = 1.8.

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