Synthesis and characterization of platinum(II) diynes and polyynes incorporating ethylenedioxythiophene (EDOT) spacers in the backbone


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A series of trimethylsilyl-protected di-alkynes incorporating 3,4-ethylenedioxythiophene (EDOT) linker groups Me3Si-C=C-R=C=SiMe3 (R = ethylenedioxythiophene-3,4-diyl 1a, 2,2'-bis-3,4-ethylenedioxythiophene-5,5'-diyl 2a, 2,2',5,2''-ter-3,4-ethylenedioxythiophene-5,5''-diyl 3a) and the corresponding terminal di-alkynes, H-C=C-R=C-H 1b-2b has been synthesized and characterized and the single crystal X-ray structure of 1a has been determined. Cul-catalyzed dehydrohalogenation reaction between trans-[{(Ph)EtPt}2PtCl] and the terminal di-alkynes 1b-2b in Pr3NH/CH2Cl2 (2:1 mole ratio) gives the Pt(II) di-ynes trans-[(Et2P)2(pt-C=C-R=C-C=C-Pt(Ph)(Et2P)] 1M-2M while the dehydrohalogenation polycondensation reaction between trans-[(Bu3P)2PtCl2] and 1b-2b (1:1 mole ratio) under similar reaction conditions affords the Pt(II) polyynes trans-[(Pt(Bu3P)2-C-R-C=C-)]n 1P-2P. The di-ynes and polyynes have been characterized spectroscopically and, for 1M and 2M, by single-crystal X-ray which confirms the “rigid rod” di-yne backbone. The materials possess excellent thermal stability, are soluble in common organic solvents and readily cast into thin films. Optical absorption spectroscopic measurements reveal that the EDOT spacers create stronger donor-acceptor interactions between the platinum(II) centres and conjugated ligands along the rigid backbone of the organometallic polymers compared to the related non-fused and fused oligothiophene spacers.

Introduction

Conjugated polymers are used as light emitting diodes (LEDs), lasers, photocells, sensors, piezo- and pyroelectric materials, and are being investigated for use as optical data storage devices, as optical switches and signal processing devices as well as having nonlinear optical (NLO) applications. Within the domain of conjugated polymers two classes of material have sparked special interest. The first class of materials is the polythiophenes because of their applications as organic semiconductor for transistor applications and photovoltaic cells. The second class of materials comprises the “rigid-rod” platinum poly-ylene polymers of general formula trans-[(Bu3P)2Pt-C=C-R-C=C-]n, where R is a conjugated spacer group. Metallopolymer derived from platinum(II) alkynyl structural units have been studied widely as π conjugated materials featuring high quantum efficiency for inter-system crossing to produce the triplet excited state following direct excitation, providing considerable insight concerning the electronic structure, delocalization, and dynamics of the triplet exciton. We have combined the polythiophenes with the platinum(II) polyynes by incorporating a broad range of oligothiophene spacers into platinum(II) polyynes and investigated the electronic structure of the singlet (S1) and triplet (T1) excited states in fused and non-fused oligo thiophenes. The energies of the optical transitions for the S1 and T1 states shift to higher energies when going from the non-fused to the fused systems. The shift in electronic energies to higher values in fused system compared to non-fused system with the same number of thiophene rings is attributed to the level of conjugation within the oligothiophene spacers. The greater the number of conjugated double bonds, the lower is the energy gap. Apart from the non-fused and fused thiophene ring systems, 3,4-ethylenedioxythiophene (EDOT) also occupies a prominent position as the functional component for conjugated polymers due, among other things, to the strong electron donor effect of the ethylenedioxy group, the self-rigidification of the structure by non-covalent intermolecular interactions as well as quinoidization of the conjugated system. The past decade has witnessed some spectacular development in EDOT-based organic polymers and copolymers but the organometallic chemistry based on the EDOT system remains relatively unexplored. To the best of our knowledge, there has been no report of EDOT-containing metal alkynyl complexes and polymers except two recent reports on the use of EDOT-benzothiazazole hybrid spacer in platinum(II) polyynes. This background prompted us to undertake the synthesis of platinum(II) polyynes incorporating EDOT spacers in the backbone, the motivation for their synthesis is to extend the range of organometallic polymers and establish in what way the incorporation of EDOT spacers affects the physico-chemical properties of the new materials. Recently, attention
has also been directed toward \(\pi\)-conjugated dimers and oligomers, taken not only as model compounds for the high molecular weight polymers, but also as efficient molecular wires in electronic device applications.\(^{16}\) They are more crystalline than the corresponding polymers, allowing for a detailed structural analysis and, thus, an assessment of the structure-electronic property relationship.\(^{17}\) There is also considerable interest in the solid-state structures of the polymeric materials because of evidence for inter-chain interactions that influence their electronic properties. In this context an analysis of intermolecular interactions in the crystal structures of the dialkynyl ligands and of the model di-yne complexes may lead to a better understanding of the interactions in the poly-ynes.\(^{18}\) The structural analysis of a ligand precursor 1a and of two model dinuclear platinum(II) di-yne complexes, 1M and 2M, are reported in this paper. Spectroscopic, thermal and opto-electronic properties of the new platinum(II) di-ynes and poly-ynes, 1M-2M and 1P-2P, are also presented and compared with those of related organometallic complexes and polymers.

**Results and discussion**

**Synthesis**

The key starting materials for the dialkynyl ligand precursors, 2,5-diiodo-3,4-ethylenedioxythiophene, 5,5’-diiodo-2,2’-bis-3,4-ethylenedioxythiophene and 5,5”-diiodo-2,2’,5’,2”-ter-3,4-ethylenedioxythiophene were prepared in high yields by adaptation of a literature procedure involving iodination of EDOT/bis-EDOT/tris-EDOT with iodine monochloride-pyridine complex.\(^{15}\) The bis-ethynyl ligands were synthesized by a sequence of cross-coupling and protodesilylation reactions. The protected dialkynyl ligand precursors, 2,5-bis(trimethylsilylthethyl)-3,4-ethylenedioxythiophene 1a, 5,5’-bis(trimethylsilylthethyl)-

2,2’-bis-3,4-ethylenedioxythiophene 2a and 5,5’-bis(trimethylsilylthethyl)-2,2’,5’,2”-ter-3,4-ethylenedioxythiophene 3a were prepared by palladium(II)/copper(I)-catalyzed cross-coupling reaction of 3,4-ethylenedioxythiophene with the respective diiodo-EDOT, in \(\text{Pr}_2\text{NH}-\text{THF}\) as illustrated in Scheme 1.\(^{19}\) The protected dialkynes are indefinitely stable towards light and air at ambient temperature and were fully characterised by IR, \(^1\)H NMR and \(^13\)C NMR, \(^1\)H and \(^13\)C spectroscopy, EI mass spectrometry, as well as by satisfactory elemental analyses. Conversion of the protected dialkynes 1a-2a into the diterminal alkynes, 2,5-bis(ethynyl)-3,4-ethylenedioxythiophene 1b, and 5,5’-bis(ethynyl)-2,2’-bis-3,4-ethylenedioxythiophene 2b, was accomplished by cleavage of the trimethylsilyl groups with dilute aqueous KOH in MeOH-THF (Scheme 1). The products were purified by silica gel column chromatography and isolated as orange to red solids in 78–85\% yields. The diterminal alkynes 1b and 2b are somewhat unstable; storage over a long period of time at ambient temperature and under aerobic conditions leads to the formation of dark insoluble material that was presumed to be polymerization products. Hence, 1b and 2b were prepared freshly before reaction with the platinum(II) phosphine complexes. The diterminal alkyne 3b rapidly decomposed as formed during the cleavage reaction and therefore could not be isolated for reaction with the platinum(II) phosphine complexes.

The dehydrohalogenation reactions between trans-\([\text{Ph}(\text{Et})_2\text{P})_2\text{PtCl}_2\] and the diterminal alkynes 1b - 2b in a 2:1 stoichiometry, in \(\text{Pr}_2\text{NH}-\text{CH}_2\text{Cl}_2\), in the presence of Cul at room temperature gave the dinuclear platinum(II) di-ynes 1M-2M while the polycondensation reactions between trans-\([\text{P}^\text{Bu}_3\text{Cl}_2\) and 1b - 2b, in a 1:1 ratio, under similar reaction conditions, readily afforded the platinum(II) poly-ynes 1P and 2P (Scheme 2). The poly-ynes were obtained in yields of 85-90\%, pointing to a very high conversion.

![Scheme 1](image-url)
Purification of the platinum(II) diynes was accomplished by column chromatography or preparative TLC on silica while the polyynes were purified by chromatography on an alumina column.

**Spectroscopic characterization**

Preliminary, systematic characterization of the organic ligand precursors as well as the platinum(II) diynes and polyynes was achieved by spectroscopic methods. The IR spectra of the platinum(II) diynes and polyynes show a single, sharp νC≡C absorption at around 2085 cm⁻¹ consistent with a trans-configuration of the ethynyleneic units around the platinum(II) centre, and the observed value is similar to that found in a range of related materials. The νC≡C values for the terminal diynes 1b-2b (2107 cm⁻¹) are much lower than those of the trimethylsilyl-protected dialkynes 1a-2a (2140-2150 cm⁻¹). The fact that terminal ethynes (HC≡C-R) have lower νC≡C frequencies than their protected counterparts RC≡C-R (by about 40 cm⁻¹ in this case) is well established. Furthermore, the platinum (II) diynes and polyynes display lower νC≡C values than those in the corresponding protected or terminal dialkynes. This may be attributed to either metal-yne π-backbonding or the Mδ⁺-Cδ⁻ polarity. NMR analyses indicate a rigid structure for the platinum(II) diynes and polyynes. In all cases, ¹H NMR resonances arising from the protons of the aromatic ring systems were clearly observed. In addition, two distinct ¹³C NMR peaks for the individual ethynyleneic carbons in the diynes and polyynes were observed, in accord with their formulations, and they are shifted downfield with respect to the signals in the diterminal alkynes. The resonances due to the ethyl and butyl groups were clearly identified. The single resonance in the ³¹P NMR spectra of the platinum(II) diynes and polyynes confirms the trans arrangement of the phosphine ligands. The ¹J_{Pt-P} values range from 2628 to 2645 Hz for the diynes and 2363-2377 Hz for the polyynes; the spectral features are quite similar to other platinum(II) diynes and polyynes reported previously and confirm the all-trans configuration of the compounds.

The mass spectrometric results confirm the molecular...
assignments for the organic precursors and the platinum(II) diynes. Gel permeation chromatography (GPC), using a polystyrene (PS) standard shows that the number-average molecular weights (Mn) of the polyynes are in the range of 40,000 – 52,000 g/mol, corresponding to degrees of polymerization of between 66 and 44 repeat units. The value of polydispersity index (PDI) varies between 1.4 and 1.7. The narrow polydispersity (PDI < 2) in the molecular weights is consistent with the extended linear structure. GPC data indicate that the number of repeat unit per chain for the EDOT-containing poly-yne is higher than that for the bis(EDOT)-based poly-yne. The reduction in chain length with increasing size of the spacer group may reflect a reduction in solubility of the larger species. The molecular weight values should be viewed with caution in view of the difficulties associated with utilizing GPC for rigid-rod type 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 flexible polymers. Therefore, calibration of the GPC with PS standards could inflate the values of the molecular weights of the polyynes 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 a high degree of polymerization has been achieved in these organometallic polycondensation reactions.

Crystal structure analysis

Single crystals of compounds 1a, 1M and 2M were obtained, and the crystal and molecular structures of these materials were determined in order to confirm the spectroscopic assignments, and investigate the intermolecular interactions in the solid state, with a view to correlating the structure/property relationships in these systems.

The molecular structure of 2,5-bis(trimethylsilyl)thiophene 1a is shown in Fig. 1 along with selected bond parameters. The molecules show the expected linear geometry (average Si-C=C, 171.8(3)°, and average C=C-C, 177.3(4)° along the two acetylene groups on either side of the ethylenedioxythiophene group). The two C=C bonds have an average length of 1.209(4) Å, consistent with values found in a range of bis-trimethylsilylthynyl derivatives. For the trimethylsilyl groups the (Me)C-Si-C(Me) (average 110.63°) are slightly larger than the (≡C)-Si-C(Me) angles (average 108.27°), and the geometry around Si is distorted tetrahedral. The 

The acetylinic units show a significant deviation from linearity with C(5)C(6) the (Me)C-Si-C(Me) angles (average 110.63°) are slightly larger than the (≡C)-Si-C(Me) angles (average 108.27°), and the geometry around Si is distorted tetrahedral. The 

The two S-C bond lengths are not significantly different at 1.736(3) Å, and the four C-O distances average 1.404(5) Å. The thiophene ring is essentially planar with a maximum deviation from the ring plane of 0.014 Å for C(4). The ethylenedioxy unit has a total puckering parameter of 0.490(4) Å, with q1 of 0.384(3), q2 of 0.304(3) and q3 of -0.86(4)°, consistent with a distorted half-chair conformation. All these parameters are not significantly different from those reported in several structures that contain EDTG ring systems.

The 1a molecules are packed into double-stranded columns along the (1 0 0) direction. The two strands of these columns are connected by two weak C-H...O hydrogen bonds. One, between the ethylenedioxy oxygen acceptor atom, O(1), and an ethylenedioxy hydrogen donor, H(1a), on a molecule related by the symmetry operation 2-x, -y, 1-z O(1)...H(1a), 2.68 (3) Å; C(1)-H(1), 0.86(3) Å; O(1)...H(1a)-C(1), 141 (2)°. This interaction forms a cooperative pair of hydrogen bonds across a crystallographic centre of symmetry. The second hydrogen bond involves the other ethylenedioxy oxygen atom, O(2), and a methyl hydrogen atom, H(10b), on a molecule related by the symmetry operation 1-x, -y, 1-z. Here the hydrogen bond parameters are O(2)...H(10b), 2.45(5) Å, C(10)-H(10b), 1.00(5) Å and O(2)...H(10b)-C(10) 149(4)°.

In the crystal structure of [(Ph)(PEt3)2Pt-C=C-(EDOT)-C=C-Pt(PEt3)2Ph] 1M the asymmetric unit contains one unique dimetallic fragment the structure of which is shown in Fig. 2 which also contains a selection of relevant bond parameters. The structure is closely related to the previously reported “rigid rod” diplatinum di-ynyl complexes with the general formula trans-[(Ph)(R)2Pt-C=C-X-C=C-Pt(PR3)2Ph], where R = Et or t-Bu and X = C6H6, (C6H2S) and related derivatives. The two PtC2P2 units are planar and the bond parameters associated with the platinum(II) centres are similar to previously reported values. The dihedral angle between the Pt(1)Pt(2)C(2)C(4)C(9) and the thiophene ring plane, C(3)C(4)C(5)C(6)S(1), is 40.9° while that between the thiophene ring and Pt(2)Pt(3)Pt(4)C(16)C(17) is 63.8° in such an orientation that the resultant dihedral angle between the two Pt square planes is 90.7°. The acetylenic units show small deviations from linearity with C(5)-C(7)-C(8), 171.4(10)°, Pt(1)-C(8)-C(7), 176.1(8)°, C(6)-C(15)-C(16), 170.5(10)°, and Pt(2)-C(16)-C(15), 178.9(9)°. The bond parameters within the central EDTG ring are similar to those found in the structure of 1a and, again, the thiophene ring shows slight deviations from planarity with the maximum
There is a crystallographic centre of symmetry at the midpoint of the C(6)-C(6a) bond that links the two EDOT groups. The structure of the dimetallic molecule is shown in Fig. 3 which also contains a selection of relevant bond parameters. As with 1M, the structure closely resembles that of a range of previously reported diplatinum di-yn complexes with various aromatic and heteroaromatic linker groups. The unique Pt(II) centre adopts the expected square planar geometry and the Pt1C1C9P1P2 plane makes a dihedral angle of 46.2° with the plane of the unique thiophene ring (C3C4C5C6S1); a value within 6° of that found in 1M. The two thiophene rings in the bi(3,4-ethylenedioxythiophene) spacer group are necessarily coplanar by crystallographic symmetry. The intramolecular S(1)...O(1a) distance is 2.938(3) Å, which is significantly shorter than the sum of the van der Waals distances and has previously been taken as being indicative of a strong intramolecular interaction. Unlike the structures of 1a and 1M, the ethylenedioxy ring displays disorder with two orientations of the C(7) and C(8) atoms. However, the ring conformation can still be described as a half-chair. The bond parameters within the unique EDOT fragment closely resemble those in 1a, 1M and in a series of bi(3,4-ethylenedioxythiophene)-containing compounds. The “rigid-rod” nature of the complex is again confirmed by the near linear acetylene unit; C(2)-C(1)-Pt(1), 176.0(3)°; C(1)-C(2)-C(3), 177.9(3)°.

**Fig. 2** The molecular structure of [(Ph)(PEt3)Pt-(C-C)-(EDOT)-C=C-(PEt3)Pt(Ph)] 1M with displacement ellipsoids drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)-C(8), 2.023(8); Pt(1)-C(9), 2.061(9); Pt(1)-P(1), 2.289(2); Pt(1)-P(2), 2.286(3); Pt(2)-C(16), 2.032(10); Pt(2)-C(17), 2.062(9); Pt(2)-P(3), 2.279(3); Pt(2)-P(4), 2.287(3); C(7)-C(8), 1.194(11); C(15)-C(16), 1.201(12); C(1)-O(1), 1.399(12); C(1)-C(2), 1.419(17); C(2)-O(2), 1.545(14); C(3)-O(1), 1.364(11); C(3)-C(5), 1.387(12); C(3)-C(4), 1.415(11); C(4)-O(2), 1.367(10); C(4)-C(6), 1.380(13); C(5)-C(7), 1.424(11); C(5)-S(1), 1.732(9); C(6)-S(1), 1.742(8); C(8)-Pt(1)-C(9), 178.14(4); C(8)-Pt(1)-P(2), 88.13(1); C(9)-Pt(1)-P(2), 91.20(3); C(8)-Pt(1)-P(1), 92.73(3); C(9)-Pt(1)-P(1), 87.93(3); P(2)-Pt(1)-P(1), 178.82(11); C(16)-Pt(2)-C(17), 179.6(4); C(16)-Pt(2)-P(3), 91.48(3); C(17)-Pt(2)-P(3), 88.93(3); C(16)-Pt(2)-P(4), 86.93(3); C(17)-Pt(2)-P(4), 92.83(3); P(3)-Pt(2)-P(4), 178.04(12).

with a total puckering parameter of 0.407(6) Å, q2 of 0.333(4), q3 of 0.233(4) and $\phi_3$ of 53.3(6)°.

An analysis of the intermolecular interactions in the crystal structure of 1M shows no abnormally short intermolecular interactions. The shortest potential C-H...O hydrogen bond with a C-H...O angle greater than 140° is between one of the methyl hydrogen atoms and a ring oxygen atom in a molecule related by the symmetry operation $x,y,0.5$; the hydrogen bond parameters are C(38)...O(2) 3.65(1) Å, H(38a)...O(2) 2.91 Å and C(38)-H(38a)...O(2) 142°.

As with 1M the complex [(Ph)(PEt3)Pt-C=C-(EDOT)-(EDOT)-C=C-Pt(PEt3)Pt(Ph)] 2M crystallises in space group C2/c but, in this case, the asymmetric unit contains only half the dimeric unit and there is a crystallographic centre of symmetry at the mid-point of the C(6)-C(6a) bond that links the two EDOT groups. The molecular packing of 2M shows no abnormally short intermolecular interactions. The only significant short intermolecular interactions. The only significant short intermolecular interactions. The only significant short intermolecular interactions. The only significant short intermolecular interactions.
Table 1 Thermal analysis results for decomposition temperatures: all temperatures in °C. Uncertainties are approximately ± 8°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_{decomp} (onset) °C</th>
<th>T_{decomp} (peak) °C</th>
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<tr>
<td>1M</td>
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<td>426</td>
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<td>398</td>
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<td>418</td>
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<td>2P</td>
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<td>422</td>
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Table 2 Optical gap of 1M-2M, 1P-2P and other related compounds

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<tr>
<td>Pt-thienothiophene poly-yne</td>
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</table>

Fig. 4 Optical absorption spectra of Pt(II) di-ynes and poly-ynes (1 = 1M, 2 = 1P, 3 = 2M and 4 = 2P) taken at room temperature.

Conclusions

In summary, the present work has demonstrated that it is possible to synthesize acetylide-functionalized heterocyclic ligands based on EDOT spacer groups and incorporate them into platinum(II) di-ynes and poly-ynes, by CuI catalysed dehydrohalogenation and polycondensation reaction respectively. Dinuclear platinum(II) complexes as well as polymeric materials with molar masses in the range of 40,000 – 52,000 g mol⁻¹ containing EDOT and bis-EDOT spacer groups have been characterised by spectroscopic methods. Attempts have been made to evaluate how the EDOT linker units would influence the structural, thermal and optical properties of the dimeric and polymeric organoplatinum(II) compounds. The results of optical absorption measurements reveal that the electron-rich EDOT spacers create stronger donor-acceptor interactions between
the platinum(II) centres and conjugated ligands compared to the non-fused and fused oligothiophene counterparts. The EDOT spacer groups also have a significant effect on the thermal stability of the dimeric as well as polymeric platinum(II) complexes. The improved properties of the new materials have stimulated a study of organometallic polymers containing a variety of hybrid spacer groups based on EDOT systems and further investigation of other properties (such as redox and photovoltaic properties) of these π-conjugated organometallic systems and their organic analogues are in progress.

**Experimental**

**General procedures**

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk or glove box techniques. Solvents were pre-dried and distilled before use by standard procedures. All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and used as received. The compounds trans-[Ph(PET$_3$)$_2$]Cl$_2$, trans-[(P$^3$Bu$_3$)$_2$]Cl$_2$, 2,2'-bis-EDOT and 2,2',5',2''-ter-EDOT were prepared by adaptation of literature procedures. The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in CDCl$_3$. The $^1$H and $^{13}$C($^1$H) NMR spectra were referenced to solvent resonances and $^{31}$P($^1$H)NMR spectra were referenced to external trimethylphosphite. IR spectra were recorded as CH$_3$Cl$_2$ 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 Department of Chemistry, University of Bath. 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 GPC method 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 auxiliary Viscotek model 200 differential refractometer/viscometer detectors was used to calculate the molecular weights (referred to as GPC LS).

**Optical spectroscopy**

The dimeric and polymeric platinum(II) complexes were dissolved in dichloromethane. Thin films were prepared on quartz substrates using a conventional photoresist spin-coater. Typical film thicknesses were 100-150 nm as measured on a Dektak profilometer. The optical absorption spectra were measured with a Hewlett-Packard ultraviolet-visible (UV-VIS) spectrometer. Measurements of photoluminescence (PL) were made with the sample in a continuous-flow helium cryostat. The temperature was controlled with an Oxford-Intelligent temperature controller and was measured adjacent to the sample with a calibrated silicon diode. For PL measurements, excitation was provided from a continuous wave (cw) argon ion laser. The UV lines (334-365 nm) of this laser were used for the compounds with benzene and naphthalene spacers and 488 nm was used for the compounds with the anthracene spacer. Typical intensities used were a few mW mm$^{-2}$. The emission spectra were recorded using a spectrograph with an optical fibre input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspec IV).

**Thermal analysis**

Thermal analysis (differential thermal analysis, DTA, and thermogravimetry, TG) was performed simultaneously in a Stanton-Redcroft model STA-780 Simultaneous Thermal Analyser under flowing N$_2$. Sample masses were ~1 mg packed with ~1 mg Al$_2$O$_3$ in open Inconel crucibles. The reference crucible contained Al$_2$O$_3$. Samples were heated at 10 °C/min to 485 °C. The thermocouple readings were calibrated using a series of DTA standard materials: KNO$_3$, In, Sn, Ag$_2$SO$_4$, and K$_2$SO$_4$ as well as Pb and Al as secondary standards, using the same heating rates as the samples.

**X-ray Crystallography**

Data for 1a and 1M were collected on a Bruker Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling apparatus, and using graphite monochromater Mo-K$_\alpha$ radiation. Data for 2M was collected on Station 9.8 at the SRS Daresbury synchrotron facility using a Bruker APEX II diffractometer, also equipped with an Oxford Cryosystems crystal cooling device. In all cases semi-empirical absorption corrections based on interframe scaling were applied. The structures were solved using direct methods (SIR92) and from subsequent Fourier difference syntheses. The structures were refined by full-matrix least-squares on $F^2$ (SHELXL 97). For 1a the hydrogen atoms were located in the electron density difference map and were allowed to refine freely. For 1M and 2M the hydrogen atoms were placed in geometrically-idealised positions and refined using a riding model. In 1M some of the ethyl groups displayed a tendency to disorder, but the best refinement model was obtained by using single sites with the carbon atoms assigned isotropic displacement parameters. In 2M the C(7) and C(8) atoms in the EDOT ligand showed positional disorder over two sites. The pairs of atoms were refined with the occupancies summed to unity. The refinements were continued until convergence was reached, and in the final cycles of refinement weighting schemes were introduced which produced relatively flat analyses of variance. Crystal data and refinement details are summarised in Table 3. CCDC reference numbers 000000 and 000000. See http://www.rsc.org/suppdata/dt/xx/xx/xxxxxxx/ for crystallographic data in CIF or other electronic format.

**Ligand Synthesis**

The ligand precursors were synthesized by following a general procedure outlined below for 1a and 1b.
Table 3 Crystal data and refinement parameters for 1a, 1M and 2M

<table>
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<th>Compound reference</th>
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<th>1M</th>
<th>2M</th>
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2.5-Diido-3,4-ethylendioxythiophene 1

A solution of 3,4-ethylendioxythiophene (2.8 g, 20.0 mmol) and iodine monochloride-pyridine complex (11.5 g, 45.0 mmol) in dichloromethane (75 mL) was stirred at room temperature for 1 h during which time a precipitate of pyridinium salt was produced. The precipitate was removed by filtration and the filtrate was removed under reduced pressure. The solid residue was rinsed with a mixture of water/methanol (1:1) and it was recrystallized twice from propanone. The product was obtained as greenish-white crystals (7.4 g, 93%).¹HNMR (400 MHz, CDCl₃): δ = 4.24 ppm (s, 4H, H₂2), 64.84 (C₂2), 143.84 (C₃4), and EI-MS: m/z 393.7 (M⁺).

2.5-Bis(trimethylsilylethyl)-3,4-ethylendioxythiophene 1a

To a deoxygenated solution of 1 (1.50g, 3.80 mmol) in THF (50 mL, 1:1 (v/v)) under N₂ was added a catalytic mixture of Cul (12 mg), Pd(OAc)₂ (11 mg) and PPh₃ (65 mg). The solution was stirred for 10 minutes at room temperature and then trimethylsilylthiophene (0.93 g, 9.5 mmol) was added. The reaction temperature was then raised to 40 °C and the reaction mixture was left with stirring for 2 h. The reaction mixture was then allowed to cool down to room temperature, filtered and the solvent mixture was removed. The desired compound 1a was isolated as a light-yellow solid (1.1 g, 85% yield). IR(CHCl₃): ν/cm⁻¹ 2141 (-C≡C-).¹HNMR (250 MHz, CDCl₃): δ = 0.20 (s, 18H, H₃4), 4.24 ppm (s, 4H, H₂2).¹C NMR (100.6 MHz, CDCl₃): δ = 54.08 (CH₂), 64.84 (C₂2), 143.84 (C₃4), and EI-MS: m/z 393.7 (M⁺).

2.2′-Bis-(3,4-ethylendioxythiophene) 2

3,4-Ethendioxythiophene 1 (5.00g, 0.036 mol) in 170 mL THF was cooled to -78 °C under N₂. BuLi (1.6M, 0.036 mol) was then added dropwise and the solution was stirred for 45 minutes. After that CuCl₂ (4.7 g, 0.036 mol) was added and the reaction mixture was left to stir at 40 °C for 2 h. The solution was allowed to cool down to room temperature and the reaction was washed with water, solvent was removed and the solid residue was purified by silica column chromatography eluting with chloroform. The title compound was isolated as a white crystalline solid (6.73 g, 68% yield).¹HNMR (250 MHz, CDCl₃): δ = 4.27 (s, 8H, H₂2).¹C NMR (100.6 MHz, CDCl₃): δ = 64.5 (CH₂), 95.2 (C₂2), 99.07, 106.23 (C=C), 144.4 (C₃4) and EI-MS: m/z 190.3 (M⁺). Calc. for C₁₀H₈O₃S: C, 63.14; H, 3.18; Found: C, 63.20; H, 3.00 %.

2,5-Diido-2,2′-bis-(3,4-ethylendioxythiophene) 2

Similar method to the synthesis of 1 was applied but using 2,2′-bis-(3,4-ethylendioxythiophene) instead. The title compound was isolated as a dark-green crystalline solid in 85% yield.¹HNMR (250 MHz, CDCl₃): δ = 4.27 (s, 8H, H₂2).
 Similar procedure to the synthesis of 1a was applied using 2
(1.50g, 2.8 mmol). 2a was isolated as a pale yellow solid (1.1 g, 83% yield). IR(CHCl₃): v /cm⁻¹ 2135 (-C≡C-). ¹H NMR
(250 MHz, CDCl₃); δ 4.22 ppm (s, 8H, HEDOT), 0.17 ppm (s, 18H, HME). ¹³C NMR (100.6 MHz, CDCl₃); δ 139.0 (C(3,4), 85.2 (C(2,5)) and 65.1 (CH₂), 106.23, 92.07 (C(=C), 0.17 (SiMe₃)). EI-MS: m/z 534.1 (M⁺). Calc. for C₁₂H₂₆Si₂O₂S₂: C, 56.68; H, 1.51; Found: C, 56.07; H, 1.48 %.

Similar procedure to the synthesis of 1b was applied using 2a (0.668 g, 1.41 mmol). 2b was isolated as a colorless microcrystalline solid (0.37g, 80% yield). IR(CHCl₃): v /cm⁻¹ 2107 (-C≡C-), 3298 (-C≡C-H). ¹H NMR (250 MHz, CDCl₃); δ 4.42 ppm (s, 8H, HEDOT), 3.3 ppm (s, 2H, H terminal). ¹³C NMR (100.6 MHz, CDCl₃); δ 138.6 (C(3,4)), 85.2 (C(2,5)) and 64.5 (CH₂), 106.23, 92.07 (C(=C)). EI-MS: m/z 330.5 (M⁺). Calc. for C₁₂H₁₀Si₂O₂S₂: C, 58.17; H, 3.05; Found: C, 58.30; H, 3.20 %.

2,2′,5′,2''-Ter-3,4-ethylenedioxythiophene
A solution of 3-4-ethylenedioxythiophene (1.33 g, 9.37 mmol) in 50 mL THF under nitrogen was cooled to -78 °C via a cooling bath. To the stirred pre-cooled solution, (3.7 mL, 9.25 mmol) of ᵗBuLi was added via syringe. After 45 minutes the reaction mixture was allowed to warm to 0°C, then MgBr₂Et₂O (2.50 g, 9.66 mmol) was added in one portion. After 45 minutes, NiCl₂dppe (0.10 g, 0.187mmol) was added followed by 2.5-diiodo-EDOT 1 (1.40 g, 3.56 mmol). The mixture was allowed to warm slowly to room temperature. The product was precipitated in water/pentane mixture and the title compound was isolated as a medium brown solid (2.6 g, 65.5%). ¹H NMR (250 MHz, CDCl₃); δ = 4.27 ppm (s, 4H, H-4,5); ¹³C NMR (100.6 MHz, CDCl₃); δ = 139.8 (C(3,4), 85.5 (C(2,5)) and 64.9 (CH₂). EI-MS: m/z 325 (M⁺).

5,5''-Diodo-2,2',5',2''-Ter-3,4-ethylenedioxythiophene
Similar method to the synthesis of 1 was applied using 2,2',5',2''-ter-3,4-ethylenedioxythiophene. Dark-green crystalline solid (83% yield). ¹H NMR (250 MHz, CDCl₃); δ = 4.30 ppm (br, 12H, HEDOT). ¹³C NMR (100.6 MHz, CDCl₃); δ = 140.3, 139.20, 131.10, 128.64, 124.63, 124.02, 92.07, 85.2, 64.5. EI-MS: m/z 674.1 (M⁺). Calc. for C₁₃H₁₂Si₂O₂S₂: C, 32.06; H, 1.79; Found: C, 32.11; H, 1.83 %.

5,5''-Bis(trimethylsilylenyl)-2,2',5',2''-Ter-3,4-ethylenedioxythiophene, 3a
Similar procedure to the synthesis of 1a was applied using 3 (1.50g, 2.23 mmol) instead. Pale yellow solid (1.1 g, 83% yield). IR(CHCl₃): v /cm⁻¹ 2135 (-C≡C-). ¹H NMR (250 MHz, CDCl₃); δ = 4.28 ppm (s, 12H, HEDOT), 0.16 ppm (s, 18H, HME). ¹³C NMR (100.6 MHz, CDCl₃); δ = 139.0 (C(3,4), 85.0 (C(2,5)) and 66.7 (CH₂), 105.0, 91.0 (C=C), 0.22 (SiMe₃)). EI-MS: m/z 614.9 (M⁺). Calc. for C₂₃H₃₈Si₂O₂S₃: C, 54.68; H, 4.93; Found: C, 55.07; H, 5.05 %.

5,5''-Bis(ethenylc)-2,2',5',2''-Ter-3,4-ethylenedioxythiophene, 3b
Similar procedure to that of 1b was applied using 3a (0.867 g, 1.51 mmol), KOH (0.25 g, 4.4 mmol) in THF/methanol (30 mL, 5:1,v/v). The product decomposed to a black solid during work-up and isolation.

Synthesis of Pt(II) diynes

Trans-[Pt(Et₃P)₂Pt-C≡C-R-C≡C-Pt(Et₃P)₂Pt] [R=3,4-ethylenedioxythiophene-2,5-diyli] 1M
1b (0.0448 g, 0.2338 mmol) and trans-[Pt(Et₃P)₂PtCl₂] (0.2816 g, 0.5187 mmol) were dissolved in CH₂Cl₂/Pr₂NH (50 mL, 1:1, v/v) under nitrogen. A catalytic amount of Cul (~5 mg) was added and the solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure and the residue was dissolved in CH₂Cl₂, passed through a silica column eluting with hexane/CH₂Cl₂ (1:1, v/v). Removal of the solvents under reduced pressure gave the title compound as a pale yellow solid (0.21 g, 75%). IR(CHCl₃): v /cm⁻¹ 2080 (C≡C). ¹H NMR (250 MHz,CDCl₃); δ = 7.21 ppm (d, 4H, H ortho of Ph), 6.89 ppm (dd, 4H, H meta of Ph), 6.75 ppm (dd, 2H, H para of Ph), 4.20 ppm (s, 4H, HEDOT), 1.65 ppm (q, 24H, H CH₂CH₂), 1.00 ppm (t, 36H, H P(CH₂)₃). ¹³C NMR (100.6 MHz, CDCl₃); δ = 156.74, 139.19, 138.41, 128.76, 127.14, 122.47, 122.29 (Arom.) 107.95, 105.86 (C=C), 15.02, 7.99 (Et). ³¹P [¹H] NMR (100 MHz, CDCl₃); δ = -138.07 δ [⁴⁷P]P=266 Hz FAB-MS: m/z 1205 (M⁺). Calc. for C₆H₁₂Pt₂O₂P₂: C, 45.84; H, 6.19.

Trans-[Pt(Et₃P)₂Pt-C≡C-R-C≡C-Pt(Et₃P)₂Pt] [R=2,2'-bis-3,4-ethylenedioxythiophene-5,5'-diyl] 2M
Similar procedure to the synthesis of 1M was applied using 2b (0.090 g, 0.272 mmol), trans-[Pt(Et₃P)₂PtCl₂] (0.50 g, 0.92 mmol) in Pr₂NH/CH₂Cl₂ (50 mL, 1:1, v/v) and Cul (5 mg). 1M was isolated as a pale yellow solid (0.30 g, 58% yield). IR (CHCl₃): v /cm⁻¹ 2135 (-C≡C-). ¹H NMR (250 MHz, CDCl₃); δ = 7.25 ppm (d, 4H, H ortho of Ph), 6.90 ppm (dd, 4H, H meta of Ph), 6.70 ppm (dd, 2H, H para of Ph), 4.20 ppm (s, 8H, HEDOT), 1.65 ppm (q, 12H, H P(CH₂)₂), 1.00 ppm (t, 36H, H P(CH₂)₃). ¹³C NMR (100 MHz, CDCl₃); δ = 140.4, 139.14, 137.7, 131.6 (C=C), 30.1 (PCH₂), 8.45 (CH₂). ³¹P [¹H] NMR (100 MHz, CDCl₃); δ = -138.27 δ [⁴⁷P]P=2640 Hz FAB-MS: m/z 1345.6(M⁺). Calc. for C₆H₁₂Pt₂O₂P₂: C, 46.42; H, 5.84. Found: C, 46.60; H, 5.90 %.

Synthesis of Pt(II) polyynes

Trans-[Pt(PBu₃)₂Pt-C≡C-R-C≡C-Pt(PBu₃)₂Pt] [R = 3,4-ethylenedioxythiophene-2,5-diyli] 1P
To a solution of trans-[Pt(PBu₃)₂Cl₂] (0.1904 g, 0.28 mmol) and 1b (0.0540 g, 0.28 mmol) in Pr₂NH/CH₂Cl₂ (25 mL, 1:1, v/v) was added Cul (5mg). The mixture was stirred at room temperature for 18 h, after which all volatile compounds was removed under reduced pressure. The residue was
dissolved in CH₂Cl₂ and passed through a short alumina column. Removal of the solvent under vacuum gave the title compound as a bright yellow solid (0.17 g, 70%). Further purification was accomplished by precipitating the polymer solution from CH₂Cl₂ into methanol. IR(CH₂Cl₂): ν/cm⁻¹ 2088. ¹H NMR (250 MHz, CDCl₃): δ 4.18 (s, 4H, HEDOT), 2.17 (m, 12H, H₃CCH₂), 2.20 (br, 12H, H₂CCH₂), 1.52 (sextet, 12H, H₂CCH₂), 0.90 (t, 18H, H₃CCH₂). ¹³C¹H₃ NMR (100 MHz, CDCl₃): δ 139.19, 138.41, 128.76 (Arom.), 121.62 (C=C), 26.05-24.26, 13.83 (alkyl).

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]; See DOI: 10.1039/b000000x
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.


Graphical Abstract

Synthesis and characterization of platinum(II) di-ynes and poly-ynes incorporating ethylenedioxythiophene (EDOT) spacers in the backbone


Two new rigid-rod organometallic polymers $\text{trans-}[\text{Pt}(\text{P}^3\text{Bu}_3)_2\text{-C=R-C}=\text{C-}]_n$ and their phenyl-terminated di-yne analogues $\text{trans-}[\text{Et}_3\text{P}_2(\text{Ph})\text{Pt-C=R-C=Pt(Ph)}(\text{Et}_3\text{P})_2]$, incorporating EDOT linker groups (R = ethylenedioxythiophene-3,4-diyl and 2,2'-bis-3,4-ethylenedioxythiophene-5,5'-diyl), have been prepared and their optical absorption properties established.