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Luminescent digold ethynyl thienothiophene and dithienothiophene complexes; their synthesis and structural characterisation

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A series of protected and terminal dialkynes with extended π-conjugation through the fused oligothienyl linker unit in the backbone, 2,5-bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene **1a**, 5,5′-bis(trimethylsilylethynyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene **1b**, 2,5-bis(ethynyl)thieno[3,2-*b*]thiophene **2a**, 5,5′-bis(ethynyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene **2b**, has been synthesized and characterised. The digold alkynyl complexes $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ **3a** and $[(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)]$ **3b** have then been prepared by the reaction of two equivalents of Ph_3PAuCl and a methanolic KOH solution of **1a** and **1b**, respectively. The complexes have been characterised spectroscopically. The crystal structures show that the gold centres adopt a linear two-coordinate geometry appropriate for Au(I) complexes. Within the crystals adjacent molecules are linked by Au · · · S intermolecular interactions in the range 3.48–3.89 Å, but there are no short Au · · · Au contacts. The absence of Au · · · Au interactions in solution is confirmed by UV/visible absorption and emission spectroscopy, the spectra being dominated by ligand-centred π–π* interactions.

Introduction

Oligomers and polymers containing thiophene rings have attracted considerable attention as new functional materials for use in molecular devices because of their near-metallic conductivity.[1] Among the thiophene derivatives, fused ring systems such as thienothiopene and dithienothiophene have emerged as excellent building blocks in the synthesis of a variety of opto-electronic materials. The self-rigidification of these materials due to the fused ring system and the delocalised π-systems that extend over the fused ring units give them novel opto-electronic properties.[2] Thus, dithienothiophene derivatives have been used in photo- and electro-luminescent devices, two-photon absorption and excited fluorescence, non-linear optical chromophores, and photochromic materials.[3] While these materials have exhibited considerable potential in applications such as LEDs, LEPs and photoswitches,[4] there are a number of ways in which the electronic properties of these materials can be optimised further. The solubility of oligomeric thienophenes and dithienothiophenes in organic solvents is limited and, more importantly, in the organic systems it is only possible to excite into the excited singlet states of the materials using optical methods, which limits the luminescent efficiency to 25% (because there are three excited triplet states for each singlet state).[5] The inclusion of transition metal-containing units into the purely organic materials can help to overcome these problems. For example, the inclusion of metal–phosphine units, where the phosphines are long chain alkyl phosphines, such as *n*-butyl phosphine, improve the solubility of the materials in a range of organic solvents.[6] Secondly, heavy transition metals have, among their properties, high levels of spin–orbit coupling, one of the consequences of which is that quantum mechanical selection rules are modified, and spin crossover into the excited triplet states becomes possible, improving the luminescent efficiency of the materials.[7] Further, the presence of the metals may afford additional luminescent properties to the materials as well as those resulting purely from the ligands.[8] We have exploited these advantages in our investigations of the physical and electronic properties of the platinum-containing diyne dimers and poly-yne polymers of the types illustrated in Fig. 1.[9] In these complexes and polymers the electronic properties of the materials can be tuned by altering the nature of the aromatic or heteroaromatic spacer group, X. The more electron withdrawing the spacer group is the lower is the band gap between the S_0 ground state and the first singlet excited state, S_1. In all the systems studied the S_1 level is *ca.* 0.7 eV above the first triplet excited state, T_1.[10]

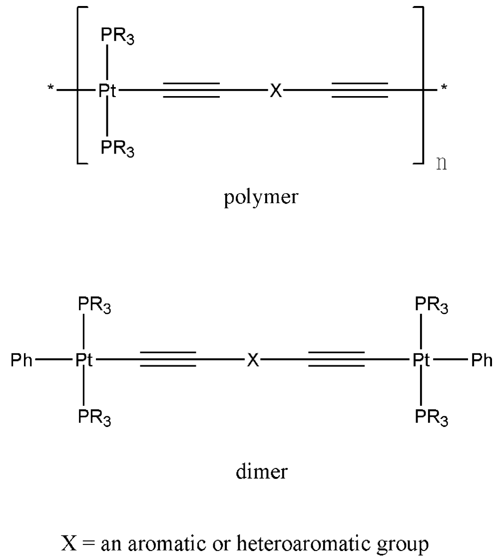

Fig. 1 Platinum-containing "rigid rod" dimers and poly-yne polymers.

Of particular interest are our studies on platinum[11] and gold poly-yne complexes and oligomers[12] that contain one, two or three thiophene rings (Fig. 2), and their relationship to the purely organic polythiophene oligomers and polymers.[3] As the

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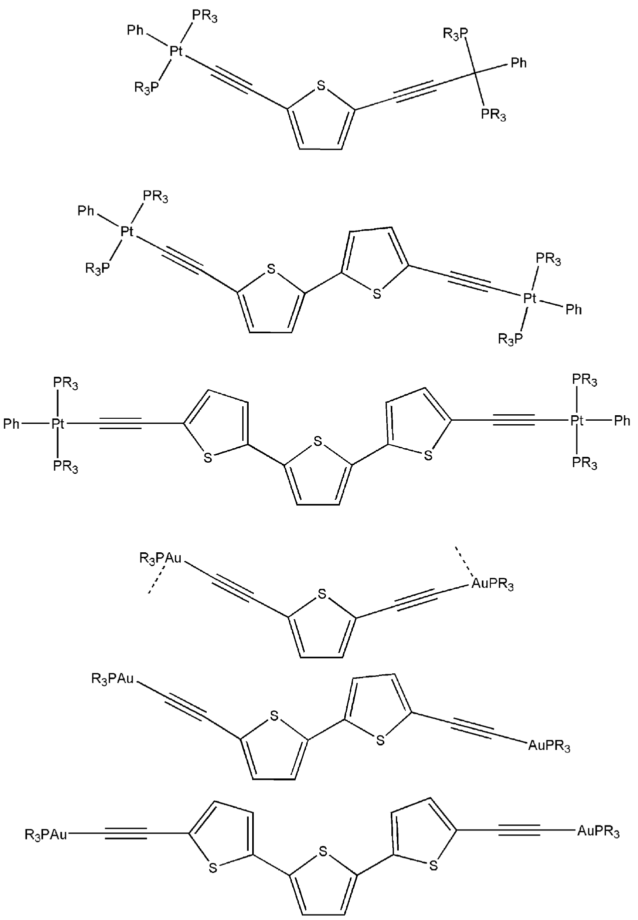


Fig. 2 Platinum or gold-containing polythiophine poly-yne complexes.

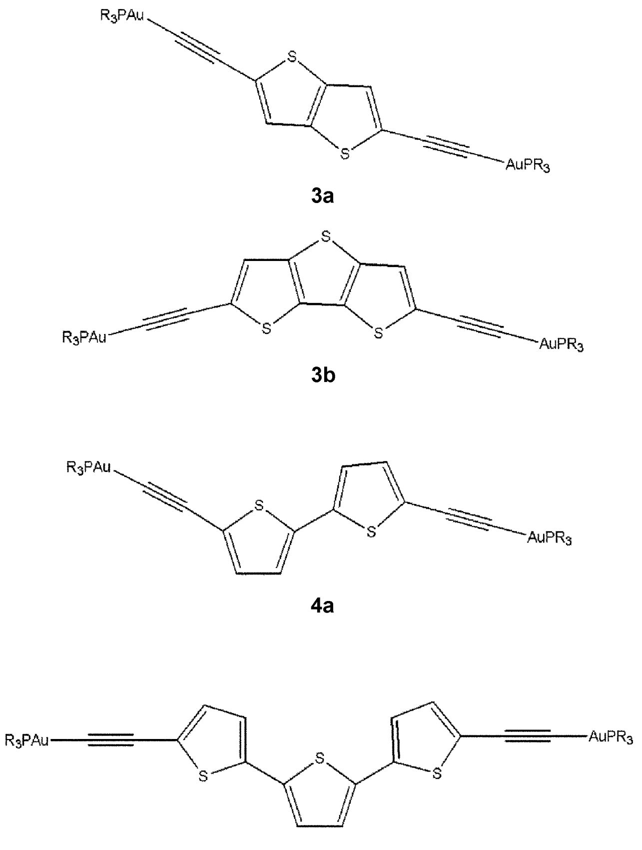


Fig. 3

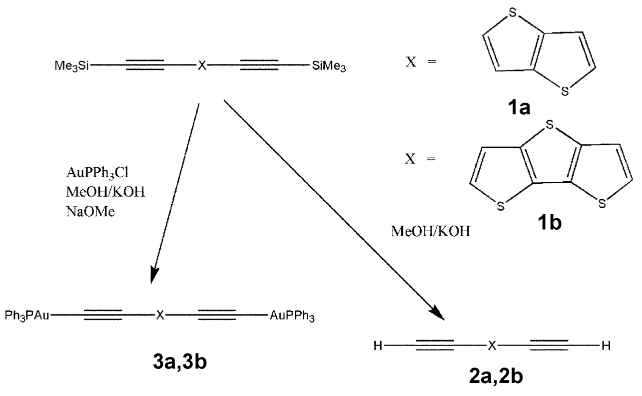
number of thiophene rings in the system increases, the optical band gap is reduced, as is the intersystem crossing from the singlet to triplet excited state.[10] We have recently extended our studies to the related platinum-containing thienothiophene and dithienothiophene dimers and polymers, and compared the results to the studies on the non-fused poly-thiophene platinum poly-ynes.[13] We find that the band gap is related to the conjugation length through the polythiophene, and whether the thiophene is fused or not is of secondary importance.

We now describe a related series of systematic studies on gold-containing ethynyl thienothiophene and dithienothiophene complexes, $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ **3a** and $[(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)]$ **3b**. Here, we report their synthesis, characterisation and solution luminescent properties, and compare the results with those found for the related dithiophene **4a** and terthiophene gold complexes **4b** (Fig. 3).[12]

Results and discussion

Synthesis and spectroscopic characterisation

The trimethylsilyl-protected diynes **1a** and **1b** were prepared as described previously by the palladium(II)/copper(I)-catalysed cross-coupling reaction of trimethylsilylethyne with 2,5-dibromothieno[3,2-*b*]thiophene and 5,5′-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene in ^{i}Pr$_2$NH–THF.[14–16] The protected alkynes are indefinitely stable towards light and air at ambient temperature and were fully characterised by IR, NMR (^{1}H and ^{13}C) spectroscopy, EI mass spectrometry, as well as by satisfactory elemental analyses. The desilylation reaction to produce the deprotected diynes **2a**[17] and **2b** was achieved by treating **1a** and **1b** with methanolic KOH (Scheme 1). The products were purified by silica gel column chromatography and characterised spectroscopically. The diterminal alkynes **2a** and **2b** are somewhat unstable; storage at ambient temperature and under aerobic conditions led to the formation of dark insoluble material that was presumed to be a polymerisation product. Because of this instability the digold complexes **3a** and **3b** were obtained in good yield by adding two equivalents of triphenylphosphine gold chloride directly to solutions of **1a** and **1b** in methanolic KOH, respectively (Scheme 1). Additional methoxide ions, as the sodium or potassium salt, were added to each reaction, as the methoxide acts both as a base and as a halide abstractor. The products were purified by passing them through a short alumina column using THF as eluent, and recrystallised from a dichloromethane–hexane mixture.



Scheme 1

The initial characterisation of **3a** and **3b** as $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ and $[(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)]$, respectively, was carried out spectroscopically (see Experimental section). The IR spectrum of each of the two complexes exhibited a single absorption at 2105 cm^{-1}(**3a**) and 2104 cm^{-1} (**3b**) that can be assigned to $\nu(C{\equiv}C)$ stretches, and are typical of the values found in other gold–alkynyl complexes.[12] While this IR fingerprint is useful for confirming the presence of the acetylenic unit in the complexes, there is little change in its position over a wide range of metals or X groups attached to the acetylene and, therefore, it does not provide information as to the electronic properties of the coordinating groups. The ^1H and ^{13}C NMR confirm the presence of the phosphine ligands and of the thienothiophene and dithienothiophene groups in **3a** and **3b**, respectively. In the ^{13}C NMR spectrum two signals at δ 96.67 and 96.85 for **3a**, and a broad signal at δ 96.84 for **3b**, can be assigned to the alkynylic carbons. The ^{31}P NMR spectra of **3a** and **3b** show only one signal at δ 42.77 for **3a**, and at δ 42.75 **3b**, which indicates that the two phosphorus nuclei in each complex are equivalent. LSIMS mass spectra exhibit the molecular ions for the complexes at m/z 1105 (**3a**) and 1161 (**3b**).

X-Ray structure determinations

Single crystals suitable for X-ray analyses were grown from layering dichloromethane and hexane solutions, although crystals of **3a** were so small and weakly diffracting that the data was collected using synchrotron X-ray radiation, on Station 9.8, at the CCLRC Daresbury Laboratory. The structures were determined in order to establish the molecular conformations of the two complexes and to investigate the possibility of polymer formation through Au ⋯ Au interactions in the solid state. Previously, it has been found that many gold–alkynyl complexes do form oligomers or polymers through $d^{10} \cdots d^{10}$ Au ⋯ Au interactions, and that these interactions contribute to the luminescent properties of these materials.[8,12] Recently, it has been suggested that the formation of intermolecular Au ⋯ Au interactions in digold alkynyl complexes, or the absence of them, may be influenced by the separation between the Au atoms in the molecular dimers.[12,18]

The molecular structure of $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ **3a** is shown in Fig. 4 while selected bond parameters are listed in Table 1. As expected for Au(I) complexes, the two gold centres adopt the linear two-coordinate geometry with an average (C≡)C–Au–P angle of 176.3(5)°, and the alkynylic units also adopt a linear geometry with an average C≡C–Au angle of 173.1(12)°. The average Au–P (2.278(4) Å) and Au–C(≡C) (1.98(2) Å) are similar to those observed in a range of alkynyl–gold phosphine complexes.[11,12] The average C≡C bond length of 1.22(2) Å is also close to the idealised value. The bond parameters within the thienothiophene ligand not deviate significantly from those observed in the free trimethylsilyl protected diethynyl compound[15] and from those in related metal complexes.[19] The thienothiophene group is essentially planar with a maximum deviation of 0.02 Å for C(4) from the least-squares plane through the C_6S_2 unit.

From the structural viewpoint, the intermolecular interactions within the crystal are the most interesting. A packing diagram for **3a** is shown in Fig. 5, and what is immediately apparent is that there are no intermolecular Au ⋯ Au contacts under 4 Å. In fact, in **3a** the shortest intermolecular Au ⋯ Au distance is 7.177 Å while the intramolecular Au(1) ⋯ Au(2) separation along the molecular chain is 13.733 Å. The shortest intermolecular contacts involving gold atoms are with the thiophene sulfur atoms: Au(1) ⋯ S(1a) 3.484 Å and Au(2) ⋯ S(2b) 3.520 Å, and through this weak interaction molecular sheets in the (110) plane are formed. The Au ⋯ S distances can be compared with the value of 3.841 Å found in $[(Ph_3P)Au(C{\equiv}C)(C_4H_2S)(C_4H_3S)]$. There are no other short intermolecular contacts within the crystal structure.

Table 1 Bond lengths (Å) and angles (°) for **3a**

Au(1)–C(1)	1.979(19)	C(3)–S(1)	1.763(17)
Au(1)–P(1)	2.271(4)	C(5)–S(2)	1.729(14)
Au(2)–C(10)	1.992(14)	C(6)–S(1)	1.721(15)
Au(2)–P(2)	2.279(4)	S(2)–C(8)	1.768(17)
C(1)–C(2)	1.23(3)	C(8)–C(9)	1.43(2)
C(2)–C(3)	1.42(2)	C(9)–C(10)	1.18(2)
C(1)–Au(1)–P(1)	176.4(5)	C(10)–C(9)–C(8)	172.0(16)
C(10)–Au(2)–P(2)	174.7(4)	C(9)–C(10)–Au(2)	174.3(12)
C(2)–C(1)–Au(1)	173.1(13)	C(6)–S(1)–C(3)	89.9(8)
C(1)–C(2)–C(3)	176.2(19)	C(5)–S(2)–C(8)	92.1(7)

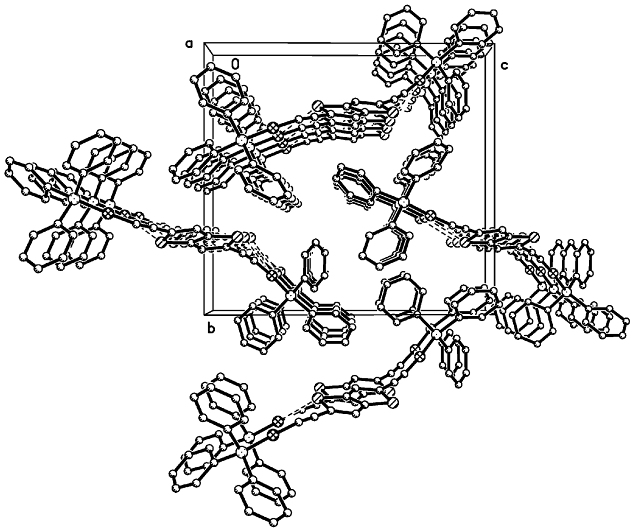


Fig. 5 The packing diagram of $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ **3a** viewed down the {100} direction.

The molecular structure of $[(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)]$ **3b** (Fig. 6) and its molecular parameters (Table 2) are generally similar to those of **3a** but with the fused three-ring dithienothiophene ring replacing the two-ring thienothiophene linker group. The two gold centres are again linear two coordinate, and the average Au–P (2.273(4) Å) and Au–C(≡C) (2.05(2) Å) distances are similar to those in **3a** and within the range found in related alkynyl gold phosphine complexes.[11,12] The average C≡C distance of 1.20(1) Å is not significantly different from that in **3a** either. The bond parameters within the dithienothiophene unit are similar to those in the trimethylsilyl-substituted diethynyl precursor compound,[16] and from those

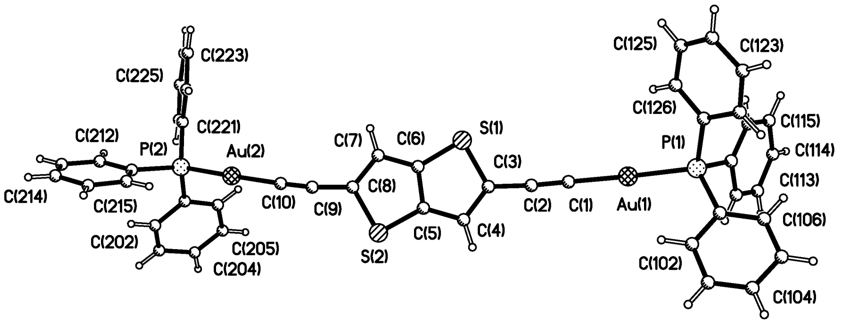


Fig. 4 The molecular structure of $[(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)]$ **3a** showing the atom numbering scheme adopted.

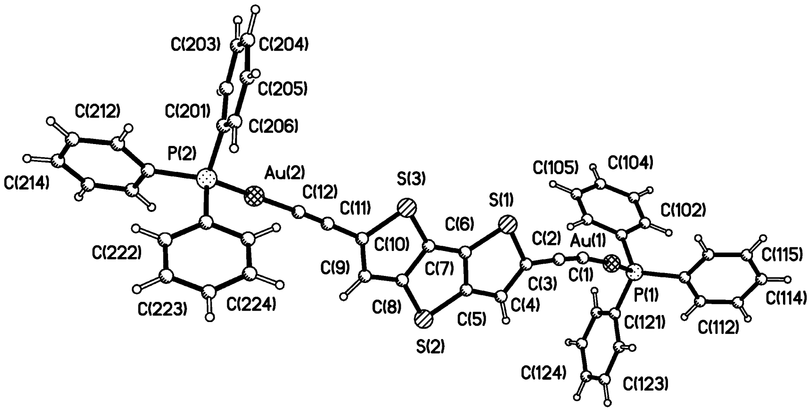


Fig. 6 The molecular structure of [(Ph$_3$P)Au(C≡C)(C$_8$H$_2$S$_3$)(C≡C)Au(PPh$_3$)] **3b** showing the atom numbering scheme adopted.

Table 2 Bond lengths (Å) and angles (°) for **3b**

Au(1)–C(1)	2.010(6)	S(1)–C(6)	1.733(6)
Au(1)–P(1)	2.2758(16)	C(5)–S(2)	1.733(6)
Au(2)–C(12)	2.000(6)	S(2)–C(8)	1.737(6)
Au(2)–P(2)	2.2700(16)	C(7)–S(3)	1.716(6)
C(1)–C(2)	1.206(9)	S(3)–C(10)	1.761(6)
C(2)–C(3)	1.409(8)	C(10)–C(11)	1.436(9)
C(3)–S(1)	1.760(6)	C(11)–C(12)	1.187(9)
C(1)–Au(1)–P(1)	171.65(18)	C(11)–C(12)–Au(2)	169.6(6)
C(12)–Au(2)–P(2)	174.01(19)	C(6)–S(1)–C(3)	91.8(3)
C(2)–C(1)–Au(1)	165.9(6)	C(5)–S(2)–C(8)	90.6(3)
C(1)–C(2)–C(3)	170.1(6)	C(7)–S(3)–C(10)	91.5(3)
C(12)–C(11)–C(10)	178.1(7)		

in related compounds.[20] The whole dithienothiophene unit is essentially planar with a maximum deviation of 0.025 Å for S(3) from the least squares plane through all the atoms.

There is a significant difference between **3a** and **3b** in terms of the intermolecular packing as can be seen in Fig. 7. In **3b** only the central sulfur atom of the dithienothiophene unit is involved in Au···S interactions. This sulfur atom displays contact distances of 3.820 Å with Au(1) related by the symmetry operation $-x$, $-y-1$, $-z$, and 3.892 Å with Au(1) related by the symmetry operation $x-1$, y, z. These Au···S distances are comparable to those in [(Ph$_3$P)Au(C≡C)(C$_4$H$_2$S)(C$_4$H$_3$S)], but significantly longer than those found in **3a**. This arrangement of contacts gives AuS$_2$Au diamonds linking three adjacent molecules through the structure (Fig. 6). As in **3a** there are no short Au···Au intermolecular contacts, the shortest being 5.483 Å, between Au(2) and the Au(2) atom related by the symmetry operation $-2-x$, $-1-y$, $1-z$. This intermolecular distance may be compared to the intermolecular Au···Au distance of 7.177 Å in **3a**. This intramolecular Au(1)···Au(2) distance in **3a**, along the molecular chain, is of 15.365(1) Å which, as expected from the dimensions of the spacer group, is longer than in **3a** (13.733 Å).

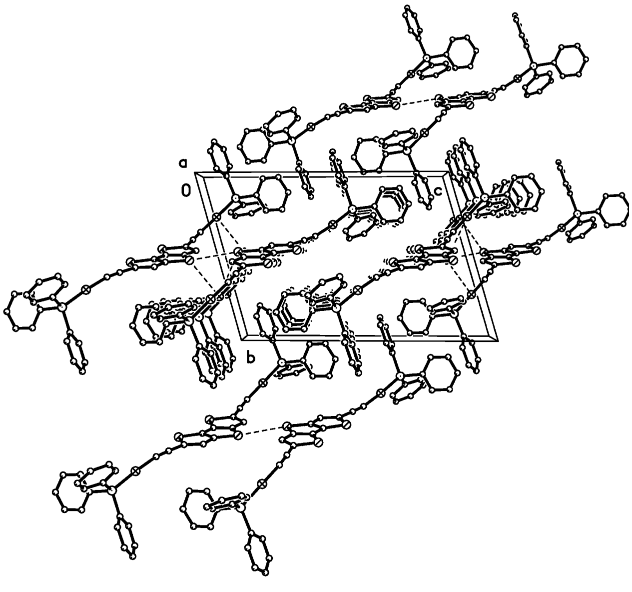


Fig. 7 The packing diagram of [(Ph$_3$P)Au(C≡C)(C$_8$H$_2$S$_3$)(C≡C)-Au(PPh$_3$)] **3b** viewed down the {100} direction showing the intermolecular interactions.

Absorption and emission spectra

The absorption and emission spectral data for **3a** and **3b** is presented in Table 3 as is the data for the terminal diethynyl ligands HC≡C(C$_6$H$_2$S$_2$)C≡CH **2a** and HC≡C(C$_8$H$_2$S$_3$)C≡CH **2b**. The data was recorded at room temperature in dichloromethane solution.

Both the digold complexes and the organic precursors exhibit absorptions in the range 300–400 nm, and the general shape of the absorption spectra for the complexes is similar to that of the free ligands, but shifted to longer wavelengths. This strong dependence of the absorption spectra on the alkynyls suggests that the absorptions are ligand-centred, but the red-shift upon coordination of the gold phosphine units is consistent with there being an increase in conjugation length over the molecule. In related systems it has been suggested that there is some mixing of the ligand π–π* transitions with a σ(Au–C) contribution in the HOMO and possibly some Au 6p$_\pi$ contribution in the LUMO.[21] This may also be the case here. However, the red shift observed between the free ligand and the complex could be explained, alternatively, in terms of the existence of a higher lying, ligand centred HOMO caused by the inductive effect of the Au–C≡C bond, and is thus unrelated to the conjugation length of the spacer group, but this ambiguity cannot be resolved with the available data.

The value of the red-shift upon complexation to the Au centre decreases as the size of the central spacer group increases: *ca.* 52 nm for **3a** *vs.* **2a** compared to *ca.* 30 nm for **3b** *vs.* **2b**. This is understandable as the percentage contribution

Table 3 Absorption and emission data for the free ligands [H(C≡C)-(C$_6$H$_2$S$_2$)(C≡C)H] **2a**, [H(C≡C)(C$_8$H$_2$S$_3$)(C≡C)H] **2b**, and the complexes [(Ph$_3$P)Au(C≡C)(C$_6$H$_2$S$_2$)(C≡C)Au(PPh$_3$)] **3a** and [(Ph$_3$P)Au-(C≡C)(C$_8$H$_2$S$_3$)(C≡C)Au(PPh$_3$)] **3b** at room temperature, in CH$_2$Cl$_2$

	Absorption. λ/nm (ε/10^4 dm^3 mol^{-1} cm^{-1})	Emission (λ/nm) excited at λ_{max}
2a	304 (sh, 3.0), 317 (3.6), 332 (3.5)	355, 380 (sh)
2b	327 (2.8), 342 (3.9), 359 (3.9)	370 (sh), 387
3a	356 (6.6), 376 (8.2)	390, 406
3b	357 (sh, 4.3), 376 (7.8), 397 (8.9)	411, 431

of the gold-centred orbitals in the HOMO and LUMO decrease as the conjugation length in the spacer group increases. The absorption maxima can also be compared to those observed in [$(Ph_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PPh_3)$] **4a** and [$(Ph_3P)Au(C{\equiv}C)(C_4H_2S)_3(C{\equiv}C)Au(PPh_3)$] **4b**,[12] which showed transitions at 373, 391 and 415 nm and 401, 421 and 451 nm, respectively. There is a general shift to shorter wavelength in the fused systems, and the most informative comparison is between the absorption maxima for **3b** and **4a** since both these systems have the same number of "formal" conjugated double bonds. On average the absorptions in **3b** are shifted by *ca.* 15 nm to shorter wavelength compared to those for **4a** consistent with higher energy transitions in the fused ring system.

The emission behaviour of **2a** and **3a** and **2b** and **3b** in solution, at room temperature, mirrors their absorption behaviour, in that the emission maxima are a function of the spacer group. The excitation spectra have similar profiles to the absorption spectra, suggesting that the emission arises from the lowest-energy absorption band. The variation in the excitation wavelength has little influence on the emission spectrum, indicating a single emissive state or multiple states that are in equilibrium. The Stokes shifts for **3a** and **3b** of *ca.* 30 and 52 nm, respectively, are relatively small and are consistent with the lowest emission state being a singlet. Related Au(I) complexes have also been reported as having lowest emission states with lifetimes in the order of nanoseconds.[22,23] Also, the observed Stokes shifts here are somewhat smaller than those reported for the related non-fused polythiophene complexes [$(Ph_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PPh_3)$] **4a** and [$(Ph_3P)Au(C{\equiv}C)(C_4H_2S)_3(C{\equiv}C)Au(PPh_3)$] **4b**,[12] which may reflect the fact that the rigid fused thiophene ring systems allow limited geometric rearrangements in the excited state.

The absence of Au···Au interactions in the solid state, as confirmed by the crystal structure analyses, and, therefore, presumably in solution is entirely consistent with the observed solution absorption and emission spectra where ligand π–π* transitions dominate.

Comparison of structural and emission data with that in other digold alkynyl complexes

The inter- and intramolecular Au···Au separations, together with phosphine cone angles,[24] the volume occupied by the C≡C–X–C≡C spacer groups, and the significant peaks in the emission spectra for **3a** and **3b** are compared with equivalent data for other known digold alkynyl complexes in Table 4. It is interesting to note that in the structures of the simple digold alkynyl complexes that have been reported, where the alkynyls are linked by a spacer group that consists of a single aromatic ring, and in which the central unit is close to linear, molecules are linked by Au···Au interactions in the range 3.122–3.235 Å. However, as the spacer groups and, therefore, the intramolecular Au···Au separations increase in length the Au···Au contacts are replaced by other types of intermolecular interactions such as Au···S contacts or π–π stacking. In Table 4 the structures are listed in order of increasing intramolecular Au···Au separation, which can be used as a measure of the length of the linker group. Although the number of structural examples in Table 4 is limited, and only tentative suggestions can be made, it appears that bonding Au···Au intermolecular interactions occur only in systems where the intermolecular Au···Au distances are short (*ca.* 3.2 Å), and where the phosphine groups or the spacer groups are not bulky. For instance, it appears that when PCy_3 groups (cone angle 170°) are present intermolecular Au···Au bonding does not occur regardless of the size of the spacer group present. For example, there is no Au···Au bonding interaction in $(Cy_3P)Au–C{\equiv}C–C{\equiv}C–Au(PCy_3)$[25] although the intramolecular Au···Au separation, at 7.785 Å, and the volume of the spacer group, at 53.1 $Å^3$, are the shortest and smallest, respectively, in Table 4. Not surprisingly, there is an approximate correlation between the length of and the volume occupied by the spacer groups. However, there are no discernable trends in the lengths of the intermolecular Au···Au interactions. It is apparent, however, from Table 4 that for the complexes with Au···Au bonding interactions, where both solid-state and solution state emission data is available, there is a significant red shift in the emission position in the solid state compared to the solution. This is consistent with a contribution from the Au···Au bond to the emission process in the solid state, and indicates that short Au···Au contacts do not occur in solution. For the systems with the longer spacer groups, where there are no Au···Au interactions in the solid state, there is little difference between the solid state and solution emission spectra.

In a more detailed comparison, it is found that the complex [$(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)$] **3b** has a similar intramolecular Au···Au separation (15.365(1) Å) to those in the related non-fused dithiophene systems [$(Ph_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PPh_3)$] **4a** (15.382(1) Å) and [$(Cy_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PCy_3)$] (15.376(1) Å).[12] The shortest intermolecular Au···Au separation in **3a** is *ca.* 1.5 Å shorter than in **4a** and *ca.* 2.0 Å shorter than in [$(Cy_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PCy_3)$]. These differences may reflect differences in crystal packing in the three structures. Both **4a** and [$(Cy_3P)Au(C{\equiv}C)(C_4H_2S)_2(C{\equiv}C)Au(PCy_3)$] have solvent molecules present in the lattice that are involved in hydrogen bonding, and do not exhibit any Au···S interactions, whereas **3b** is free of solvent in the crystal and the central sulfur atom of the dithieno[3,2-*b*:2′,3′-*d*]thiophene ring is involved in Au···S non-covalent interactions (*vide supra*).

Conclusions

The thienothiophene and dithienothiophene alkynyl digold derivatives [$(Ph_3P)Au(C{\equiv}C)(C_6H_2S_2)(C{\equiv}C)Au(PPh_3)$] **3a** and [$(Ph_3P)Au(C{\equiv}C)(C_8H_2S_3)(C{\equiv}C)Au(PPh_3)$] **3b** can be prepared readily from the trimethylsilyl-protected dialkynyl derivatives, in methanolic KOH, by the reaction with two equivalents of $(Ph_3P)AuCl$. The crystal structures of **3a** and **3b** show that, in both cases, adjacent molecules are linked by Au···S interactions, and that Au···Au interactions, that are common in related systems where the spacer groups between the two alkynyl groups are shorter in length, are absent. The UV/visible absorption and emission spectra are both dominated by ligand-centred π–π* transitions, and there is only a small mixing contribution from the gold centres, consistent with the small observable red-shift of the signals when the spectra for the metal complexes are compared to those from the free ligand.

Experimental

General

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled, dried and degassed before use by standard procedures.[30] Infrared spectra were recorded using a NaCl cell on a PERKIN ELMER PARAGON 1000 FT-IR spectrometer. UV/vis spectra were recorded on Perkin-Elmer Lambda-12 spectrometer and Cary 100 Bio UV-visible spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker28 DRX-400/500 spectrometers. Chemical shifts in ppm are relative to the residue solvent resonance (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were recorded on KRATOS CONCEPT/MSI CONCEPT IH/MICROMASS PLATFORM-LC mass spectrometers. Elementary analyses were performed at Department of Chemistry, University of Cambridge. Solution emission spectra were recorded at 293 K on AMINCO Bowman Series 2 Luminescence Spectrometer. $Au(PPh_3)Cl$,[31] thieno[3,2-*b*]thiophene[32] and dithieno[3,2-*b*:2′,3′-*d*]thiophene[32] were prepared by a literature methods.

Table 4 Intra- and intermolecular Au · · · Au contacts in digold poly-yne complexes with a variety of different linker groups

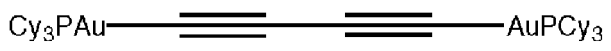
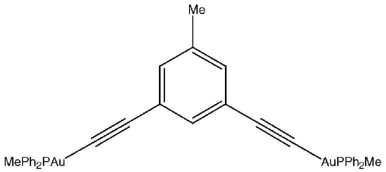
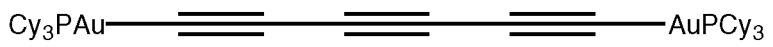
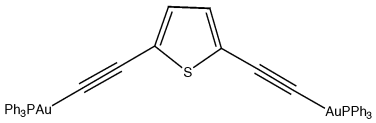
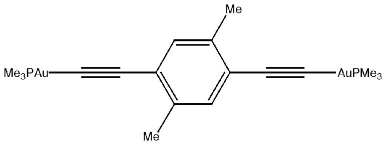
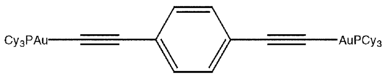
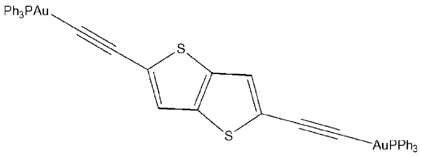
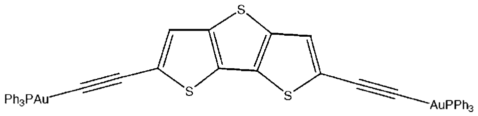
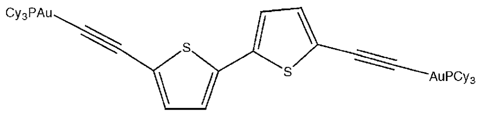
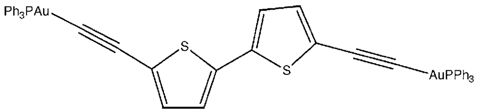
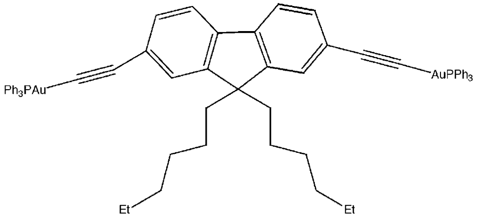
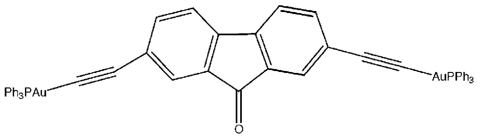
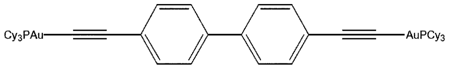
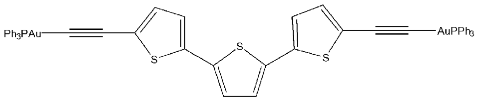
Compound	Intramolecular Au · · · Au distance(s)/Å	Shortest intermolecular Au · · · Au distance/Å	Phosphine cone angle[24]/°	Atomic volume of the diacetylenic spacer group, X/Å^3	Emission (λ/nm) at 290 K in CH_2Cl_2	Ref.
	7.785	5.596	170	53.1	417, 457, 506, 566, 643	25
	10.188,[a] 10.431	3.122, 3.147	130	129.8	440, 550[b]	26
	10.305	5.250	170	75.2	498, 557, 632, 726	27
	11.516,[a] 11.542	3.292, 3.235	145	111.9	374, 390	12
	12.051,[a] 12.721	3.136	118	142.5	415, 540[b]	21
	12.070	5.648	170	116.4	488, 517, 527, 547, 560, 580	28
	13.733	7.177	145	147.6	390, 406	This work
	15.365	5.483	145	182.3	411, 431	This work

Table 4 (*Contd.*)

Compound	Intramolecular Au · · · Au distance(s)/Å	Shortest intermolecular Au · · · Au distance/Å	Phosphine cone angle[24]/°	Atomic volume of the diacetylenic spacer group, X/Å^3	Emission (λ/nm) at 290 K in CH_2Cl_2	Ref.
	15.376	7.532	170	162.7	430, 453, 495	12
	15.382	6.878	145	170.8	432, 455, 495	12
	15.899	4.298	145	366.2	567[b]	29
	15.971	7.359	145	193.5	575, 589[b]	29
	16.354	5.331	170	180.5	361, 376, 391, 536, 574, 605	28
	19.294	6.750	145	226.8	472, 499, 545	12

[a] The structure contains two molecules in the asymmetric unit. [b] Spectrum recorded in the solid state.

Syntheses

2,5-Dibromothieno[3,2-*b*]thiophene[33]**.** A solution of NBS (21.34 g, 0.12 mol) in DMF (150 mL) was added to a stirred and ice-cooled solution of thieno[3,2-*b*]thiophene (8.35 g, 59.58 mmol) in DMF (70 mL). After the mixture was stirred for 3 h under ice cooling, crushed ice was added and the resulting mixture was extracted with $CH_2Cl_{2.}$ The extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to alumina column chromatography. ^{1}H NMR ((δ, 500 MHz, $CDCl_3$)): 7.62 (s, 2H, thienothiophene). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): 124.48, 126.53, (*ipso*-C), 138.67 (*ipso*-C), (thienothiophene). EIMS (*m*/*z*): 298 (Calc. M_r = 298.03 for $C_6H_2Br_2S_2$).

5,5′-Dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene. Dithieno[3,2-*b*:2′,3′-*d*]thiophene was prepared according to a literature preparation.[34] 0.98 g (5.0 mmol) dithieno[3,2-*b*:2′,3′-*d*]thiophene in DMF (20 cm^3) was reacted with 2 g (11.2 mmol) NBS at room temperature overnight. The light yellow suspension was treated with water and filtered off. After silica column chromatography with hexane, 1.7 g (88%) pale greenish fine needle crystals was obtained. ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 7.27 (s, 2H, H of thiophenes). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): 112.32 (*ipso*-C), 123.17, 130.82 (*ipso*-C), 139.05 (*ipso*-C) (aromatic C of thiophenes). EI (*m*/*z*): 353.8 (Calc. M_r = 354.092 for $C_8H_2Br_2S_3$).

2,5-Bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (1a). To a solution of 2,5-dibromothieno[3,2-*b*]thiophene (2.0 g, 6.71 mmol) in ^{i}Pr$_2$NH–THF (70 cm^3, 1 : 1 v/v) under nitrogen was added a catalytic mixture of CuI (20 mg), Pd(OAc)$_2$ (20 mg) and PPh_3 (60 mg). The solution was stirred for 20 min. at 50 °C and then trimethylsilylethyne (1.64 g, 16.7 mmol) was added. The reaction mixture was left with stirring for 20 h at 75 °C. 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 removed under reduced pressure. The residue was subjected to silica column chromatography using hexane to afford **1a** as a colourless solid in 85% yield (1.78 g). IR (CH_2Cl_2): ν/cm^{-1} 2141 (–C≡C–). ^{1}H NMR (δ, 250 MHz, $CDCl_3$): 0.26 (s, 18H, $SiMe_3$), 7.26 (s, 2H, fused bithienyl). ^{13}C NMR (δ, 100 MHz, $CDCl_3$): 0.04 (s, $SiMe_3$), 97.68, 101.68 (C≡C), 124.60, 126.71, 138.75 (fused bithienyl). EI MS: *m*/*z*: 332 (M^+). Calc. for $C_{16}H_{20}Si_2S_2$: C, 57.80; H, 6.06. Found C, 57.68; H, 6.01%.

2,5-Bis(ethynyl)thieno[3,2*b*]thiophene (2a). The bis-trimethylsilylethynyl derivative **1a** (1.0 g, 3.01 mmol) was proto-desilylated in THF–methanol (50 cm^3, 4 : 1 v/v) using aqueous KOH (0.38 g, 6.86 mmol in 1 cm^3 H_2O). The reaction mixture was stirred at room temperature for 2 h, solvent removed and the crude product was purified by silica column chromatography using hexane. **2a** was isolated as a yellow solid in 95% yield (0.54 g). This material slowly darkened upon standing at atmospheric and reduced pressure. IR (CH_2Cl_2): ν/cm^{-1} 2105 (–C≡C–), 3297 (C≡C–H). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 3.50 (s, 2H, C≡CH), 7.25 (s, 2H, thienothiophene). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): 79.81, 82.56 (C≡C), 123.88, 133.92 (*ipso*-C), 138.06 (*ipso*-C), (thienothiophene). EIMS (*m*/*z*): 188 (Calc. M_r = 188.26).

5,5′-Bis(trimethylsilylenthynyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene (1b). This compound was synthesised by the same method as for **1a** using 1.56 g (4.4 mmol) 5,5′-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene. The product was purified by alumina column chromatography with hexane and subsequent recrystallisation from methanol. Yield: 0.91 g (52%) light yellow crystalline solid. IR (CH_2Cl_2): ν/cm^{-1} 2141 (–C≡C–). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 0.26 (s, 18H, H of TMS), 7.37 (s, 2H, H of thiophenes). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): −0.25 (s, $SiMe_3$); 97.54, 101.14 (–C≡C–); 124.13(*ipso*-C), 125.82, 131.15 (*ipso*-C), 141.58 (*ipso*-C) (aromatic C of thiophenes). LSIMS (*m*/*z*): 388.03 (Calc. M_r = 388.71). Anal. Calc. for $C_{18}H_{20}S_3Si_2$: C, 55.62; H, 5.19. Found: C, 55.85; H, 5.29%.

5,5′-Bis(ethynyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene (2b). Compound **1b** was proto-desilylated as in **1a** and the crude product was worked up, as before, to yield a red solid. Silica column chromatography with CH_2Cl_2–hexane (1 : 1 v/v) gave a red solid identified as **2b** in 76% yield. The purified diterminal alkyne was used immediately to prepare the Pt(II) di-ynes and poly-ynes or, if necessary, was stored as dilute solution in pentane at 0 °C. Decomposition of the pentane solution was apparent by an orange color after storage of more than a few days at room temperature. IR (CH_2Cl_2): ν/cm^{-1} 2101 (–C≡C–), 3298 (C≡C–H). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 3.50 (s, 2H, C≡CH), 7.31 (s, 2H, dithienothiophene). ^{13}C NMR (δ, 100.6 MHz, $CDCl_3$): 79.50, 80.16 (C≡C), 120.73 (*ipso*-C), 126.76, 131.17 (*ipso*-C), 141.61 (*ipso*-C) (dithienothiophene). EIMS (*m*/*z*): 244. (Calc. M_r = 244.34).

[(Ph_3P)Au(–C≡C–$C_6H_2S_2$–C≡C–)Au(PPh_3)] (3a). To a freshly prepared sample of alkyne, 43 mg (0.13 mmol) 2,5-bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (**1a**), obtained from the reaction of trimethylsilyl-protected alkyne with KOH/CH_3OH) in CH_2Cl_2 (30 cm^3), was added gold(I) phosphine chloride 125 mg (0.25 mmol), followed by CH_3OH/$NaOCH_3$ (20 cm^3, containing 20–30 mg Na). The mixture was stirred under N_2 at room temperature overnight and then filtered through cellulose. The filtrate was evaporated to dryness under reduced pressure. CH_2Cl_2 was added to the residue. The resulting suspension was stirred for about 15 min and filtered off. The filtrate was reduced in volume and loaded on a short alumina column, and then eluted with mixed solvents of THF (or ethyl acetate)–hexane. Solvents were removed *in vacuo* to yield a yellow power. Pure product was obtained either by layering concentrated CH_2Cl_2 solution with hexane, or by ether vapour diffusion into the concentrated CH_2Cl_2 solution. Yield: 109 mg (72%) yellow crystalline solid. IR (CH_2Cl_2): ν/cm^{-1} 2105vw (–C≡C–). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 7.17 (s, 2H, H of thiophene), 7.42–7.56 (m, 30H, H of PPh_3). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): 96.67, 96.85 (–C≡C–); 123.16, 127.61 (*ipso*-C), 137.60 (*ipso*-C) (aromatic C of thiophenes); 129.08, 129.17, 129.37 (*ipso*-C), 129.82 (*ipso*-C), 131.55, 134.21, 134.32 (C of PPh_3). ^{31}P{^{1}H} NMR (δ, 400 MHz, $CDCl_3$): 42.77. LSIMS (*m*/*z*): 1105 (Calc. M_r = 1104.764). Anal. Calc. for $Au_2C_{46}H_{32}P_2S_2$: C, 50.01; H, 2.92. Found: C, 49.48; H, 3.00%.

[(Ph_3P)Au(–C≡C–$C_8H_2S_3$–C≡C–)Au(PPh_3)] (3b). The complex **3b** was synthesised using the same general procedure as for **3a** using 50 mg (0.13 mmol) 5,5′-bis(trimethylsilylenthynyl)-dithieno[3,2-*b*:2′,3′-*d*]thiophene (**1b**) and 130 mg (0.26 mmol) Au(PPh_3)Cl. Yield: 42 mg (28%) brownish crystalline solid. IR (CH_2Cl_2): ν/cm^{-1} 2104vw (–C≡C–). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 7.29 (s, 2H, H of thiophene), 7.43–7.56 (m, 30H, H of PPh_3). ^{13}C NMR (δ, 500 MHz, $CDCl_3$): 96.84 (br, –C≡C–); 124.37, 125.60 (*ipso*-C), 130.14 (*ipso*-C), 140.77 (*ipso*-C) (aromatic C of thiophenes); 129.10, 129.19, 129.34 (*ipso*-C), 129.78 (*ipso*-C), 131.57, 131.58, 134.21, 134.32 (C of PPh_3). ^{31}P{^{1}H} NMR (δ, 400 MHz, $CDCl_3$): 42.75. LSIMS (*m*/*z*): 1161 (Calc. M_r = 1160.846). Anal. Calc. for $Au_2C_{48}H_{32}P_2S_3$: C, 49.66; H, 2.78. Found: C, 48.86; H, 2.88%.

X-Ray crystallography

For crystal data, see Table 5.

Data collection and reduction. The crystals of **3a** and **3b** were mounted in inert oil on a glass fibre. Data were measured using Mo-Kα radiation (λ = 0.71073 Å) with a Nonius Kappa area detector (**3b**), or a Bruker AXS SMART CCD area detector on Station 9.8 of the CLRC Daresbury Laboratory (**3a**), both fitted with an Oxford Cryostream low-temperature attachment.

Table 5 Crystallographic data for $[(Ph_3P)Au(C\equiv C)(C_6H_2S_2)(C\equiv C)Au(PPh_3)]$ **3a** and $[(Ph_3P)Au(C\equiv C)(C_8H_2S_3)(C\equiv C)Au(PPh_3)]$ **3b**

	3a	**3b**
Empirical formula	$C_{46}H_{32}Au_2P_2S_2$	$C_{48}H_{32}Au_2P_2S_3$
M_r	1104.71	1160.79
T/K	150(2)	180(2)
λ/Å	0.68870	0.71070
Crystal system	Monoclinic	Triclinic
Space group	Pc	$P\bar{1}$
Unit cell dimensions:		
a/Å	7.1766(17)	8.9500(2)
b/Å	15.917(4)	12.8200(2)
c/Å	17.041(4)	18.6550(4)
α/°	90	73.760(1)
β/°	92.13(2)	84.726(1)
γ/°	90	85.198(1)
V/Å^3	1945.2(7)	2042.58(7)
Z	2	2
D_c/Mg m^{-3}	1.886	1.887
μ/mm^{-1}	7.756	7.440
F(000)	1056	1112
Crystal size/mm	0.08 × 0.08 × 0.04	0.15 × 0.15 × 0.02
θ Range for data collection/°	3.66–25.49	1.14–27.50
Index ranges, hkl	−4 to 7, −3 to 19, −20 to 17	−11 to 11, −16 to 16, −24 to 24
Reflections collected	3875	49223
Independent reflections (R_{int})	3865 (0.0295)	9354 (0.0966)
Absorption correction	Semi-empirical	Semi-empirical
Max., min. transmission	0.7467, 0.5758	0.8654, 0.4016
Data/restraints/parameters	3865/20/469	9354/0/496
Goodness-of-fit on F^2	1.042	1.043
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0428$, $wR2 = 0.1091$	$R1 = 0.0460$, $wR2 = 0.1168$
R Indices (all data)	$R1 = 0.0439$, $wR2 = 0.1103$	$R1 = 0.0653$, $wR2 = 0.1327$
Absolute structure parameter	0.003(11)	—
Largest diff. peak, hole/e Å^{-3}	1.302, −0.956	2.713, −3.307

Structure solution and refinement. Structures were solved by direct methods (SHELXS-86)[35] and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).[36] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model.

CCDC reference numbers 252933 and 252934.

See http://www.rsc.org/suppdata/dt/b4/b415965a/ for crystallographic data in CIF or other electronic format.

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